LIMS (Laboratory Information Management System) for Light Stable Isotopes

User Manual

September 27, 2017
LIMS for Light Stable Isotopes version 9.202 and later

Foreword

The routine measurement of stable isotope ratios of light elements (hydrogen, carbon, nitrogen, oxygen, silicon, sulfur, chlorine, and others) of solid, liquid, and gaseous samples by mass spectrometry is a common and cost-effective analytical tool in anthropology, atmospheric sciences, biology, chemistry, environmental sciences, food and drug authentication, forensic applications, geochemistry, geology, oceanography, and paleoclimatology around the world. For analysis of liquid water samples for stable hydrogen and oxygen isotopic composition by laser absorption spectrometry (LAS), the reader is referred to the Microsoft Access program LIMS for Lasers 2015, which can be found at http://isotopes.usgs.gov/research/topics/lims.html or http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html#lims . As of version 9.201 of LIMS for Light Stable Isotopes, LAS data files can no longer be imported and LAS instrument-sample-list templates can no longer be created. Users should use LIMS for Lasers 2015.

The adoption of isotope-ratio mass spectrometry into routine laboratory operations is demanding, owing to substantive offline data manipulation required by the instrument operator. Other day-to-day challenges include client sample-project management, storage and tracking of instrument measurement data files, derivation and application of algorithms to correct for blank and linear and non-linear instrumental drift over the course of analysis sequences. Many mass spectrometer users developed complex Excel data processing spreadsheets that can be difficult for new users to adopt. Further, the use of spreadsheets presents a challenge to maintaining and reporting long-term QA/QC and laboratory audits.

The latest Microsoft Access-based Laboratory Information Management System (LIMS) for Light Stable Isotopes is presented herein. It simplifies and automates these difficult processes, and it eliminates the need for most offline data manipulation. LIMS manages clients and their project data, and it enables users to generate instrument-sample-list templates for isotope-ratio mass spectrometers and laser absorption spectrometers, which otherwise requires extensive typographical data input. Analytical output files from mass spectrometers are imported by LIMS for processing. Sample blank and instrumental drift can be corrected for. Mass-spectrometric results can be normalized to isotope-delta scales using isotopic reference materials interspersed among samples. QA/QC can be evaluated with graphical plots. These automated processing features reduce mistakes and operator errors. In short, LIMS greatly eases the adoption of isotope-ratio mass spectrometry into new and current laboratories by introducing productivity efficiencies and improved reliability through consistent approaches. In this document the terms reference and standard are used interchangeably.

This document describes how to implement LIMS for Light Stable Isotopes in an isotope laboratory. To facilitate use of LIMS for Light Stable Isotopes by users, this document contains download links to the latest software repository. The figures in this document were obtained

using Microsoft Office Professional Plus 2010. Forms in Office 2007, 2013, and 2016 may be rendered slightly differently.

A variety of files are provided as examples and as tutorial materials in folders named Section 4, Section 7, Appendix B, etc.

Note: For European and other international users, the Windows Regional Settings in the computer Control Panel may have either a point or a comma as the decimal separator. LIMS should function properly with either choice, but the figures in this document were created with a point as the decimal separator.

Acknowledgments

Since Penny Higgins (University of Rochester, Rochester, NY, USA) prepared her very useful LIMS Implementation Guide and her Tutorial for LIMS for Light Stable Isotopes in 2009, neither a manual nor training class for LIMS for Light Stable Isotopes has existed. This user manual has been prepared with substantial text preparation and editing by U.S. Geological Survey staff including Jacqueline Benefield, Miranda Marvel, Lauren Reid, and Yesha Shrestha. Helpful discussion and(or) mass spectrometric files have been provided by Wendy Abdi (University of Ottawa, Ottawa, Ontario, Canada), Laura Arppe (University of Helsinki, Helsinki, Finland), Victor Evrard (University of Basel, Basel, Switzerland), Francisco Fernandoy (Andrés Bello National University, Santiago, Chile), Bastian Hambach (University of Southampton, United Kingdom), Janet Hannon (U.S. Geological Survey), Benjamin Harlow (Washington State University, Pullman, WA, USA), Jean-François Hélie (University of Québec at Montréal, Montréal, Canada), Sven Kaehler (Rhodes University, Grahamstown, South Africa), Geoff Koehler (National Hydrology Research Centre, Saskatoon, Saskatchewan, Canada), Magda Mandic (Thermo Fisher Scientific, Bremen, Germany), Paul Middlestead (University of Ottawa, Ottawa, Ontario, Canada), Stanley Mroczkowski (U.S. Geological Survey), Andrew Park (Sercon Limited, Crewe, Cheshire, United Kingdom), Haiping Qi (U.S. Geological Survey), Sam Poynter (University of Melbourne, Burnley, Victoria, Australia), Alison Pye (Memorial University of Newfoundland, St. John's, Newfoundland, Canada), Michael Sudnik (Elementar, Stockport, United Kingdom), and Leonard I. Wassenaar (International Atomic Energy Agency, Vienna, Austria).

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1 Introduction to LIMS for Light Stable Isotopes

LIMS for Light Stable Isotopes (LIMS hereafter) is a Laboratory Information Management System (LIMS) for light element stable isotope-ratio mass spectrometers (IRMSs). LIMS provides a convenient Windows environment to manage clients, projects, samples, and mass spectrometric data. It is provided at no cost by the U.S. Geological Survey. Key features include:

- Full client, project, and sample management, invoicing, and reporting system
- Automated instrumental drift correction
- Instrumental blank correction capability
- Automated normalization of data to VSMOW-SLAP, VPDB, and other isotope scales
- Track My Lab QA/QC for instrument and laboratory assessment
- Excel sample submission templates for laboratory clients (customers)

User Benefits of LIMS include:

- Increased laboratory productivity by eliminating complex spreadsheets
- Improved long-term performance through standardized approaches
- Reduction of laboratory error in client and data management
- Track My Lab QA/QC for instrument and laboratory assessment
- Excel sample submission templates for laboratory clients

LIMS is built upon Microsoft Access, and it works in a client server configuration. The laboratory client data, samples, and mass-spectrometric results are stored in a backend database. Users access their data from one or more LIMS frontends. Laboratories having laser absorption spectrometers as well as IRMSs use the same backend database. The frontend database for LAS instrumentation is LIMS for Lasers 2015, which can be found at http://isotopes.usgs.gov/research/topics/lims.html or http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html#lims .

LIMS for Light Stable Isotopes was developed [1] and is maintained by T. B. Coplen at the U.S. Geological Survey (USGS) in Reston, Virginia, USA. See http://isotopes.usgs.gov/research/topics/lims.html

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

2 LIMS for Light Stable Isotopes at a Glance

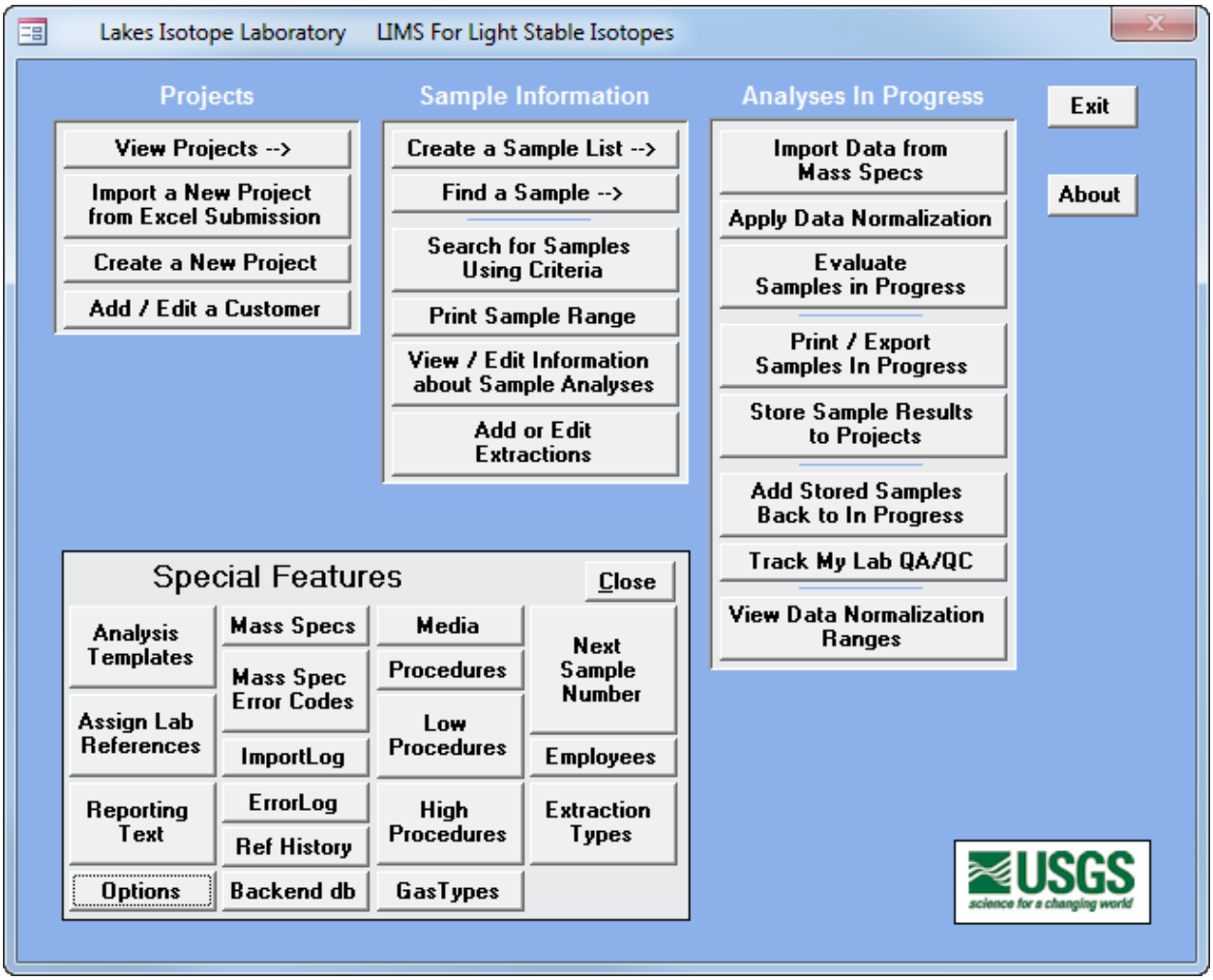


Fig. 2.1. The main page of LIMS for Light Stable Isotopes with the Special Features window open.

The main page of LIMS (Fig. 2.1) is divided into several sections:

Projects

- View projects, print reports, and export data to Excel
- Import an Excel client sample submission file to create a new LIMS project
- Create a new LIMS project by entering information manually
- Add new clients (customers)

Special Features

- Design or edit sample analysis templates
- Add or edit laboratory reference materials
- Add or edit client reporting text for media
- Customize the database for the laboratory
- Add or edit mass spectrometers
- Add or edit mass spectrometer error codes
- View or delete the log of analysis import errors
- View or delete the log of LIMS software errors
- View values of isotopic reference samples as changed in database over time
- Set backup database location and implement daily backups
- Add or edit sample media
- Add or edit analytical procedures
- Add or edit link between media and procedures
- Add or edit the GasTypes parameter used by Thermo Scientific/Thermoquest/Finnigan ISODAT
- Edit numerical values of next LIMS Our Lab IDs (sample number)
- Add or edit employees
- Add or edit offline analytical extraction type

Sample Information

- Create sample-list files that can be imported into mass spectrometers
- Find a sample from the LIMS Our Lab ID
- Search for samples in the database with user-specified criteria
- For specified samples print sample information including mean values
- View and edit mass spectrometric results
- Search, view, and edit extractions

Analyses in Progress

- Import mass spectrometric results
- Determine and apply blank corrections, drift corrections, and normalize results to isotope scales
- View and edit isotope results
- Print or save selected isotope results to Excel files
- Store final accepted results for reporting
- Un-store final results to enable re-evaluation of sample analyses
- Evaluate results and track laboratory QA/QC
- View and print equations used for normalization

3 Computer and Software Requirements

3.1 Computer Requirements

A Microsoft Windows laptop or desktop computer having a USB port or a connection to the mass spectrometer is needed. Windows XP, Windows 7, Windows 8, and Windows 10 operating systems (either 32 bit or 64 bit) are satisfactory. More RAM is better and a faster processor is better to handle Microsoft Access queries.

LIMS should not be installed on the computer used for mass spectrometer data acquisition and control because it may interfere with data acquisition.

A backup USB external drive or a second internal drive (used by the USGS in Reston, VA) is strongly recommended for making Sunday—Saturday daily backups. Because a laboratory's data is so important, it is recommended that weekly backups of the LIMS database are stored offsite.

3.2 Software Requirements

3.2.1 LIMS Software Components

LIMS is built upon Microsoft Access, and it works in a client server configuration. The laboratory client data, samples, and mass-spectrometric results are stored in tables in a backend Microsoft Access relational database. Tables needed to enable LIMS to perform include the following, which are listed by their general names and are discussed in this manual.

Table of Mass Spectrometers	Table of Samples to be Analyzed
Table of Isotopes	Table of Samples in Progress
Table of [Analytical] Procedures	Table of Analysis Headings
Table of Media	Table of Analysis Results
Table of Low Procedure Codes	Table of References
Table of High Procedure Codes	Table of Reporting Text
Table of Customers	Table of Countries
Table of Projects (including invoices)	Table of States (Provinces)
Table of Samples	Table of Extractions
Table of Sample List Templates	Table of Employees

LIMS software is composed of three components:

- The LIMS version 9 frontend (9.201 or later). LIMS operates as a client server software application. The frontend database contains the forms, reports, queries, and code needed to perform operations on your data in the backend database. The backend database

contains the client data, sample data, mass-spectrometric results, and laser absorption spectrometric results (if the laboratory has a laser absorption spectrometer). The backend database contains the 20 tables specified in Section 3.2.1. In this manner, as software bugs are identified, users can replace the frontend database.

- A new LIMS backend database (or an existing one for current LIMS users, including LIMS for Lasers 2015 users). Users following this manual will set up their first backend database (for the Lakes Isotope Laboratory) in Section 4.8.
- An Excel client sample submission file

The latest software can be downloaded at no cost from the USGS website at http://isotopes.usgs.gov/research/topics/lims.html or obtained from tbcoplen@usgs.gov.

It is simplest if the LIMS frontend and the LIMS backend are stored in different folders. A typical arrangement of folders is shown in Figure 3.1 in which a Frontend and a Backend folder are located in a folder named LIMS. A third folder named Daily Backup should be created. This folder can hold the backups of the backend database, which are created when a user exits LIMS. The Daily Backup folder will contain as many as seven copies of the backend database, labelled with the days of the week, Monday, Tuesday, etc. Each time LIMS is closed, the daily backup file is replaced with the latest version of the backend database. In this manner, a backup of the backend database from the previous workday will be available when it is needed.

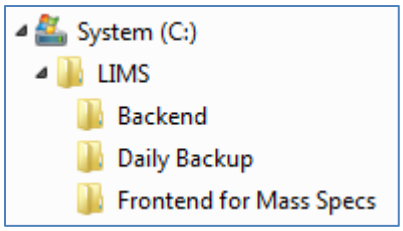


Fig. 3.1. Common folder arrangement for LIMS.

In the situation in which a laboratory has both IRMSs and isotope-water laser absorption spectrometers (*e.g.* Fig. 25.3), the laboratory will need to use both LIMS for Light Stable Isotopes and LIMS for Lasers 2015. Figure 3.2 shows a possible arrangement of folders.

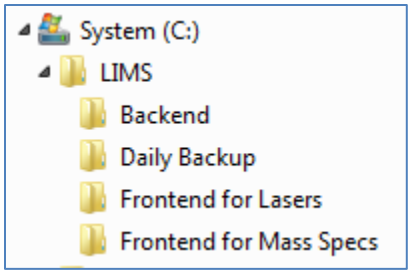


Fig. 3.2. Possible folder arrangement for a laboratory having both mass spectrometers and laser absorption spectrometers. LIMS for Lasers 2015 would be found in the Frontend for Lasers folder. The backend folder contains the Access backend database file containing the client data, sample data, mass-spectrometric results, and laser absorption spectrometric results.

3.2.2 Microsoft Office

LIMS requires Microsoft Office 2007, 2010, 2013, or 2016 with Access. Commonly Office with Access is called Microsoft Office Professional. Later versions of Office are available as 32-bit or 64-bit applications. LIMS will only work with 32-bit Office. Therefore, ensure that your IT specialist installs 32-bit Office and not 64-bit Office. Note that 32-bit Office can be installed on 64-bit Windows. The figures in this manual were created with Office 2010 Professional Plus. Forms might be rendered slightly differently in other versions of Microsoft Office.

LIMS requires adding trusted locations in Microsoft Access for the location of the frontend and the backend database. You may require Administrator rights to change these settings. Some IT policies do not allow the Windows Desktop to be set as a trusted location in case a user desires to use it for this purpose. If you obtain macro errors, set Access to enable all macros.

Assume that the location of the frontend is "C:\LIMS\Frontend for Mass Specs" (as shown in Fig. 3.1). This location needs to be added to Trusted Locations in Access. The process is similar in Office 2007, 2010, 2013, and 2016. The process for Office 2010 is presented here:

1. Open Access.
2. Select the "File" tab if not already open.
3. Click "Options," which will open the Access Options Window shown in Figure 3.3.
4. Select "Trust Center" and click "Trust Center Settings…" to open the Trust Center window (Fig. 3.4).
5. Select "Trusted Locations" and a window similar to that of Figure 3.5 should appear.
6. Click "Add new location…" and add the location "C:\LIMS\Frontend for Mass Specs" or browse to the desired folder and add it.

7. Click the "Subfolders of this location are also trusted" check box, if desired. This is usually a good idea in case one wants to move the frontend database to a subfolder and run it from there. Click "OK" is needed.
8. Click the "Add new location…" button again and navigate to the desired backend folder and add it.
9. Click "OK," and the new location should be shown under User Locations.
10. Click "OK" and "OK" to return to the File tab. This completes addition of a Trusted Location in Access for the LIMS frontend and backend.

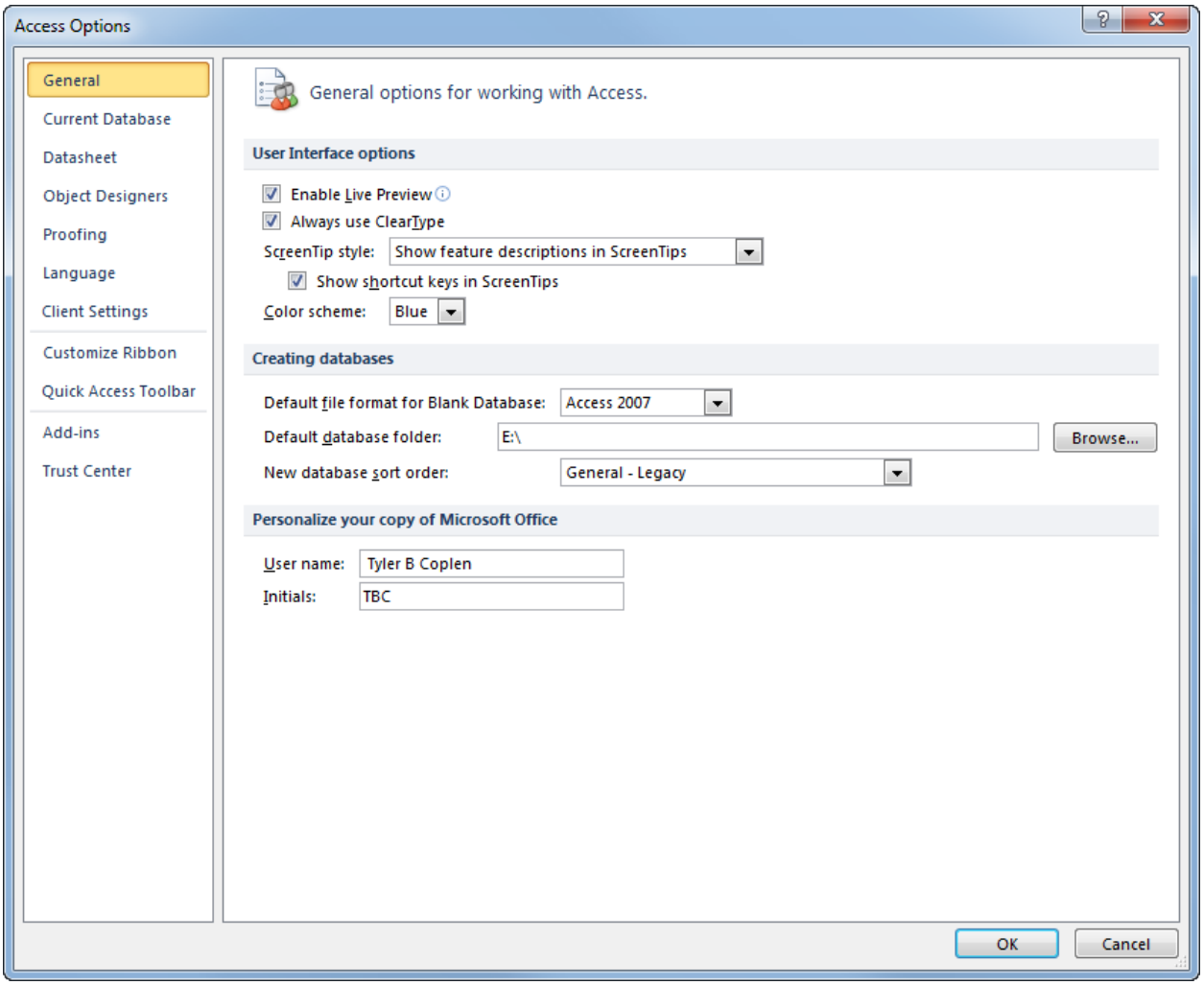


Fig. 3.3. Access Options window in Office 2010.

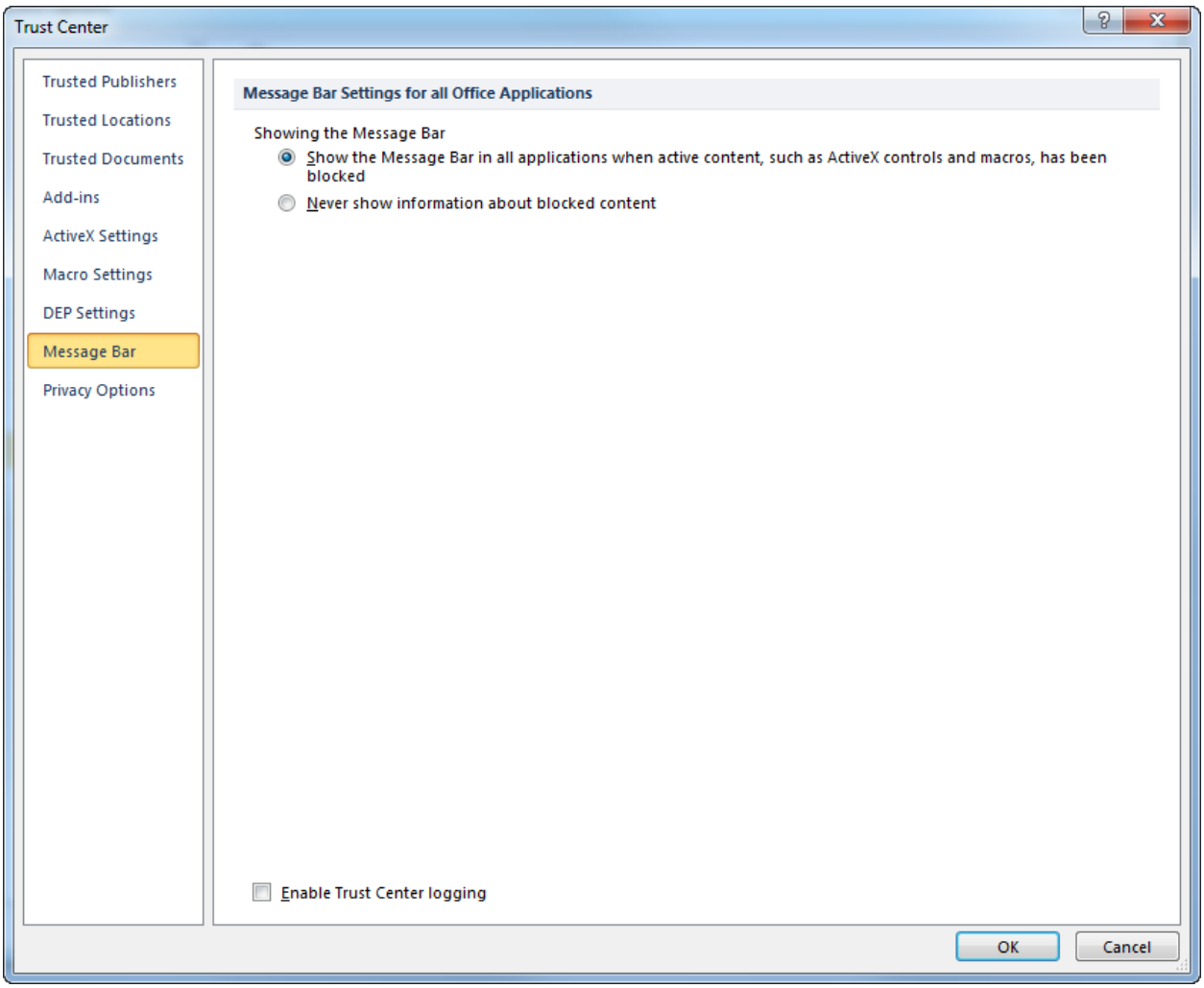


Fig. 3.4. Trust Center window in Office 2010.

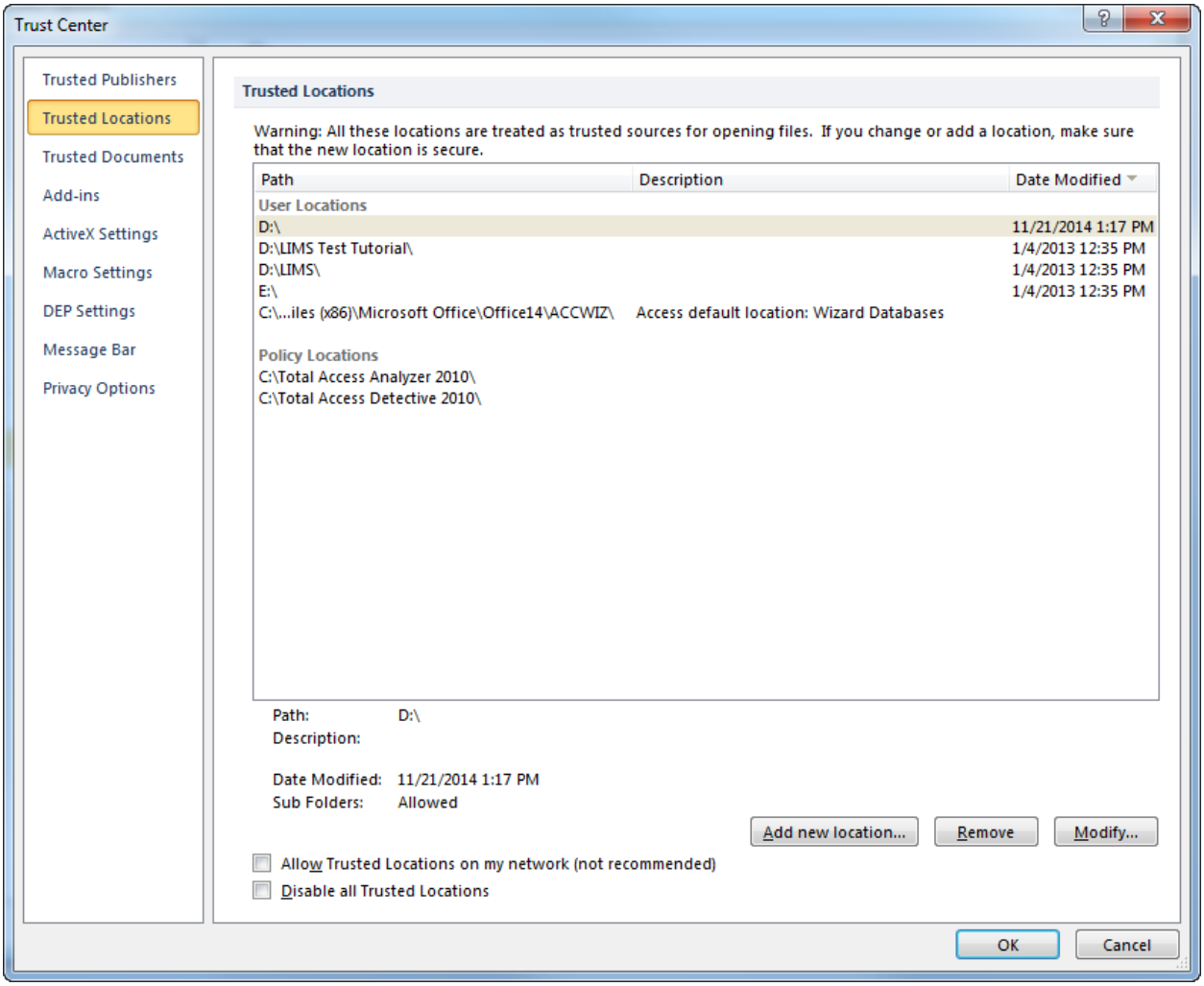


Fig. 3.5. Trusted Locations in the Trust Center window in Office 2010.

4 Getting Started with LIMS

4.1 Setting up LIMS in a New Laboratory

To set up LIMS in a new laboratory, follow the steps below:

1. Create LIMS folders on your laboratory computer as described in Section 3.2.1 and shown in Figures 3.1 or 3.2. Do not use a computer that is used for data acquisition and control of an IRMS. These folders are for the LIMS frontend database (user interface), backend database, and daily backups. The LIMS folder for the backend should be located on a dedicated computer or on a reliable (and preferably fast) networked drive. It is best if the LIMS frontend and backend are on the same computer to prevent LIMS from operating too slowly.
2. Ensure that Microsoft Office 2007, 2010, 2013, or Office 2016 (32-bit only) (including Access) is installed with the latest service pack, and make sure that the folder containing the LIMS frontend and backend are Trusted Locations (see Section 3.2.2).
3. In the files that accompany this manual, a LIMS frontend database file named "LIMS9.202.zip" (or similar) is located in a folder named "Section 4." Extract the LIMS frontend file and move it to "C:\LIMS\Frontend for Mass Specs" or the folder created for the frontend. Downloading the latest frontend database for a new laboratory from http://isotopes.usgs.gov/research/topics/lims.html is recommended once the information in this manual has been mastered.
4. In the files that accompany this manual, a backend database file for a new laboratory named "LIMS_Backend_DB_20170505.accdb" (or similar) is located in a folder named "Backend DB for a new lab." Extract this file and move it to "C\LIMS\Backend" or the folder created for the backend database. Downloading the latest backend database for a new laboratory from http://isotopes.usgs.gov/research/topics/lims.html is recommended once the information in this manual has been mastered.
5. Consider renaming the LIMS backend database to one that is descriptive of your laboratory, such as "My Laboratory LIMS Backend.accdb."
6. Open the frontend database file ("LIMS9.202.accdb" or similar).
    a. When opening a newly extracted version of LIMS, the dialog box in Figure 4.1 that LIMS cannot find the backend database should appear; if so, continue with step 7. However, LIMS may not be compiled; if so, LIMS will display a "not compiled" message (Fig. 4.2). If this occurs, click "OK," and LIMS should recompile (taking a few minutes) and will close. The user should be able to reopen LIMS successfully. If the "not compiled" message persists, please contact tbcoplen@usgs.gov.
    b. If a warning, such as shown in Figures 4.3 or 4.4, appears, Trusted Locations were not set up properly—see Section 3.2.2 and set up the Trusted Locations.

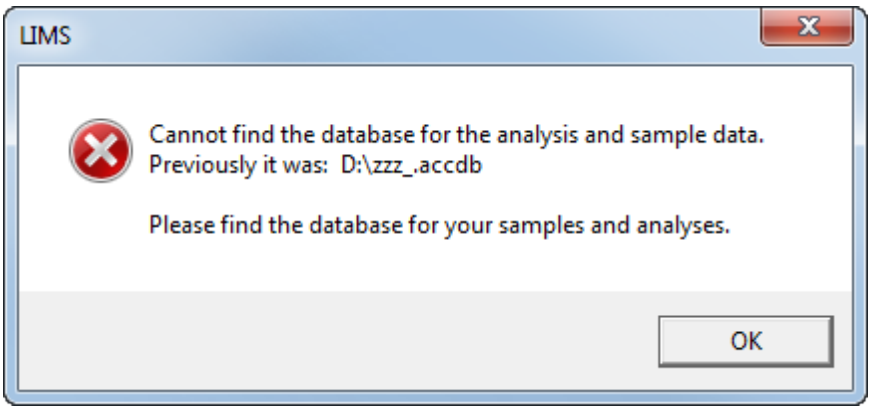


Fig. 4.1. Cannot find the backend database message. This appears in normal program flow.

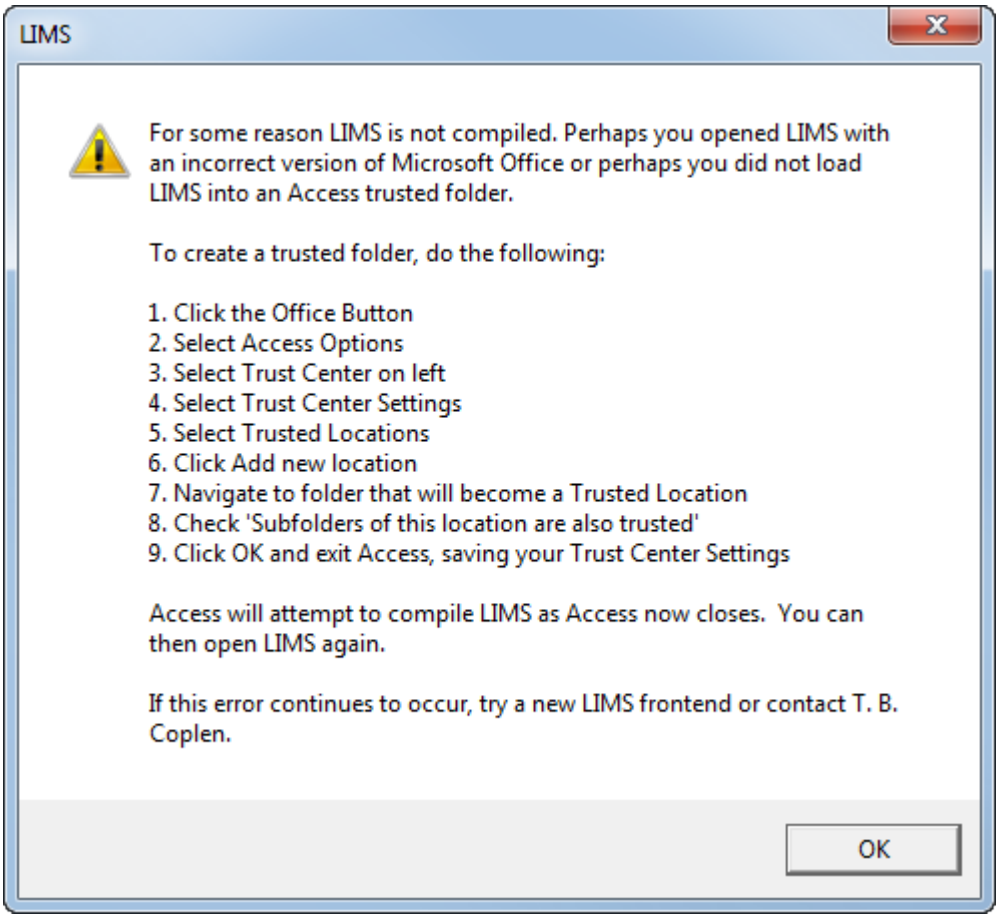


Fig. 4.2. Not compiled warning. If observed, click "OK," wait for LIMS to recompile and automatically close. One should be able to reopen LIMS successfully—the message in Figure 4.1 indicates success, for example.

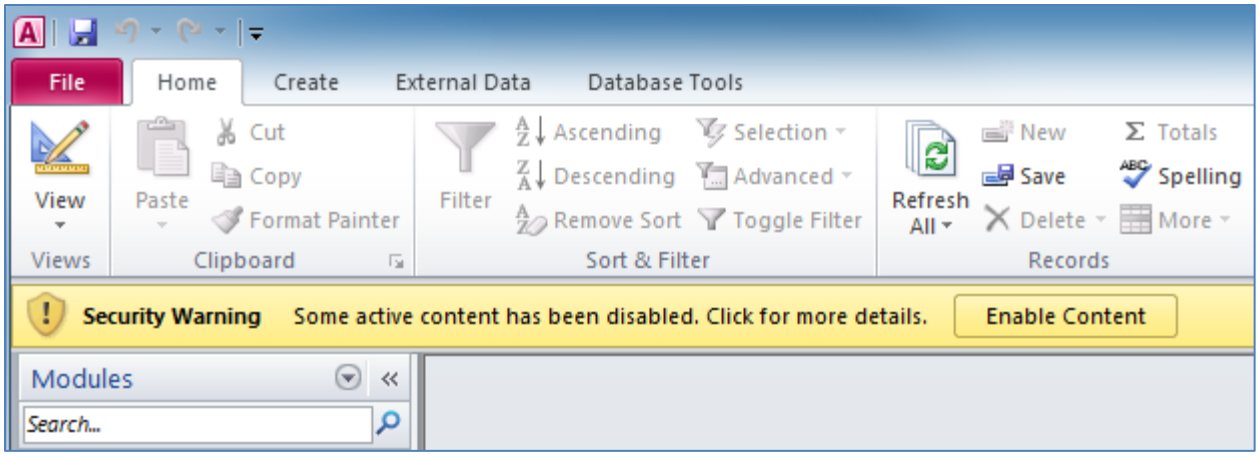


Fig. 4.3. Trusted Location warning.

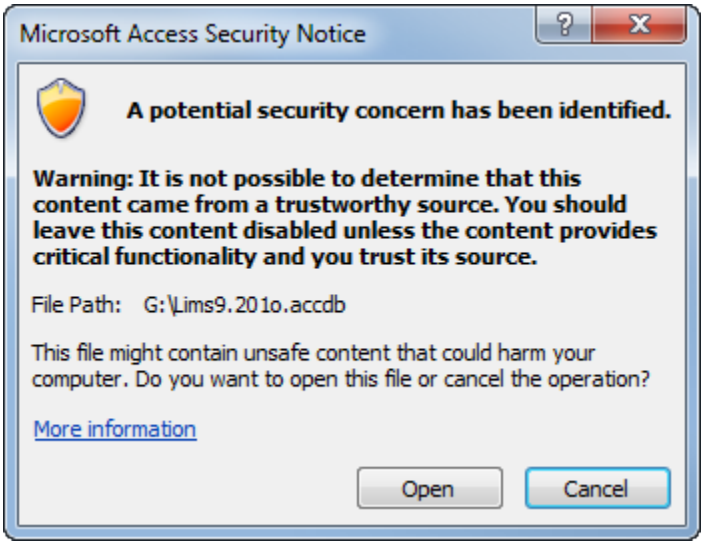


Fig. 4.4. Security warning indicating that Trusted Locations were not properly set up.

7. Click “OK” and use the Windows file dialog box to select the backend database file that you created in Step 4. LIMS will indicate that it needs to close.
8. Click “OK” and LIMS will close.
9. Reopen LIMS and it will display the paper-size message shown in Figure 4.5.
10. Click “OK” and LIMS will prompt that it needs to update settings and close.
11. Click “OK” and LIMS will close.
12. Reopen LIMS and a message will appear that indicates that a mass spectrometer needs to be installed (Fig. 4.6).
13. Click “OK” and LIMS will display Figure 4.7 about daily backups.
14. Click “OK” and the LIMS main page (Fig. 4.8) will be displayed.

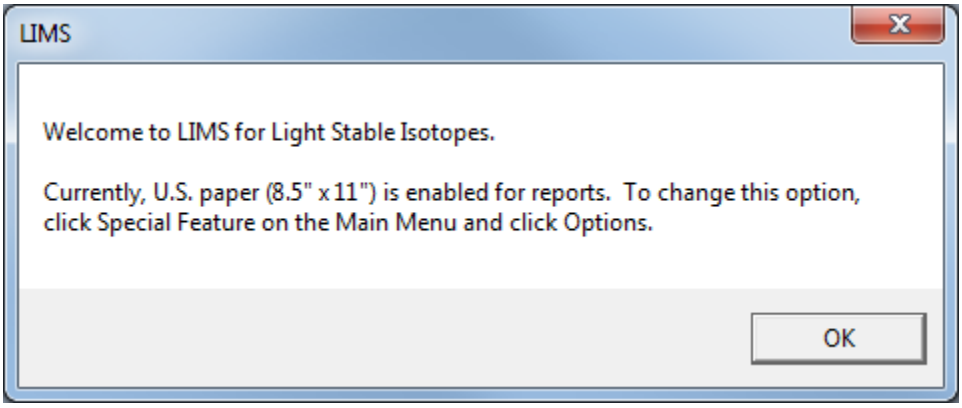


Fig. 4.5. Setup paper-size message.

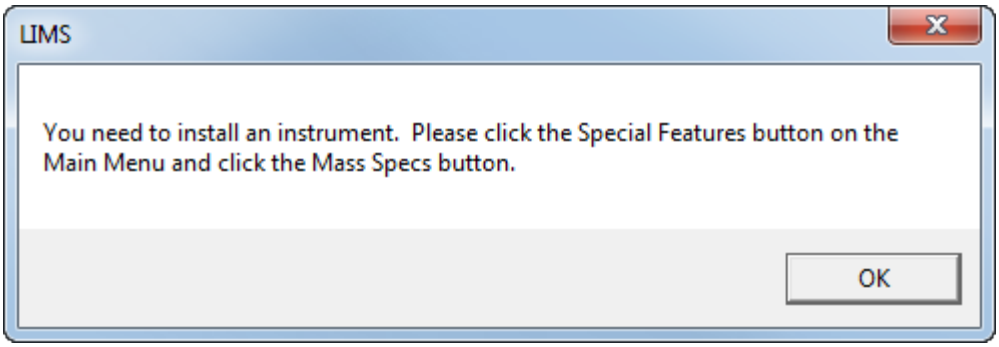


Fig. 4.6. Install instrument reminder message.

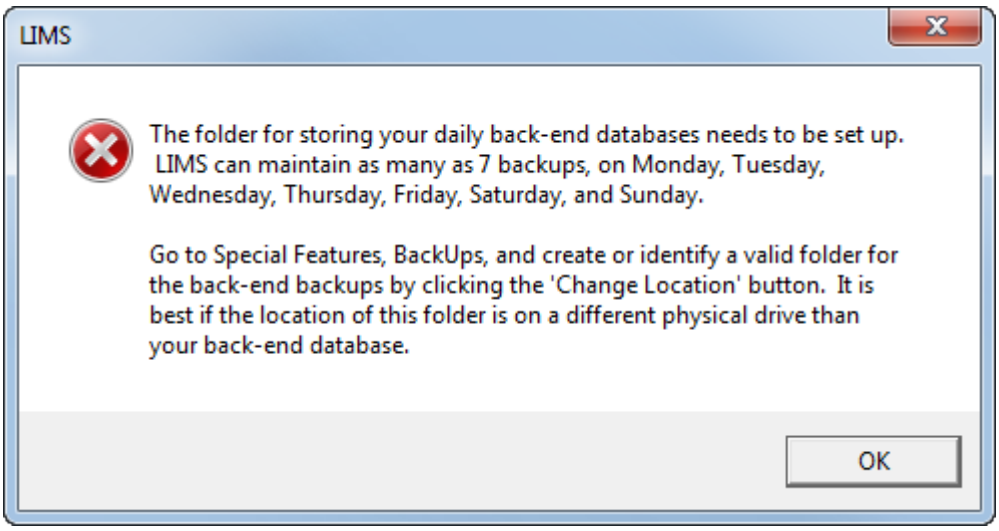


Fig. 4.7. Reminder message concerning daily backups.

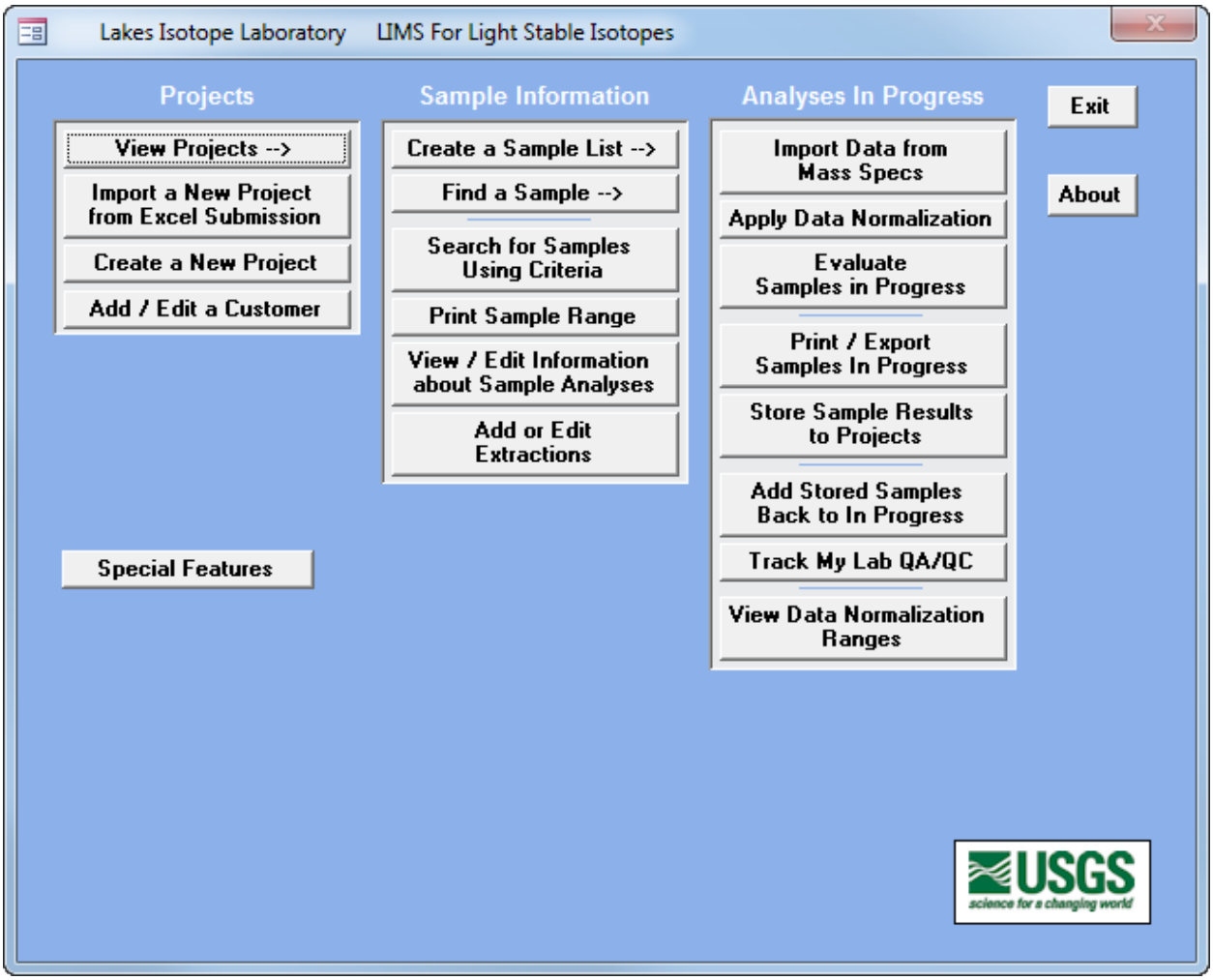


Fig. 4.8. LIMS main page with the Special Features Window closed in an example database.

15. Click "Special Features" on the LIMS main page (Fig. 4.8) to open the Special Features window (Fig. 4.9).
16. Click "Backend db" to open the BackEnd and FrontEnd Databases form (Fig. 4.10).
17. Click "Change Location" to locate the folder for the Monday to Sunday backups, for example C:\LIMS\Daily Backups (see Fig. 3.1). Navigate to the Daily Backups folder and click "Select."
18. Click "Close" to return to the main page.
19. It is recommended that you register LIMS for Light Stable Isotopes by emailing tbcoplen@usgs.gov. Registration ensures you will be informed of updates to LIMS. Similarly, suggestions for improvements to LIMS, reporting of bugs, and improvements to the user manual would be appreciated.

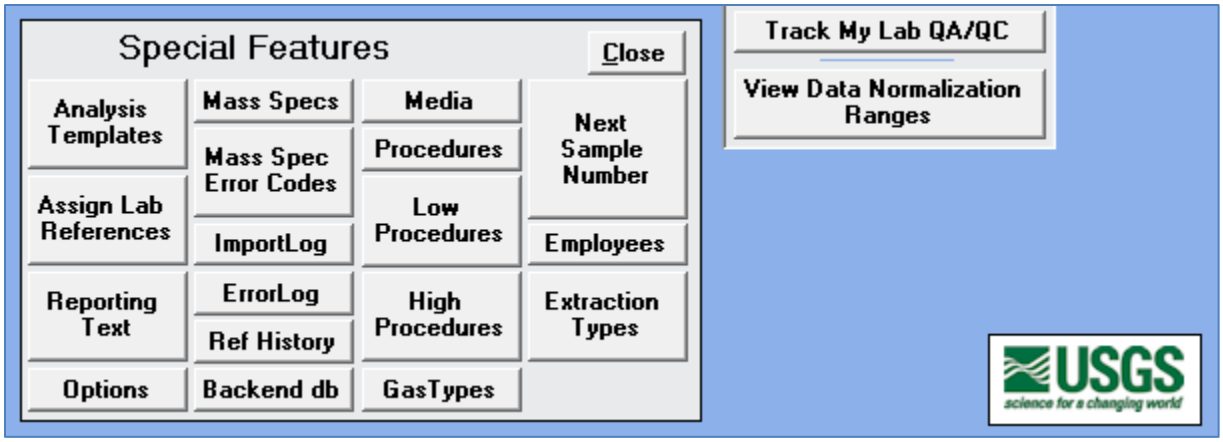


Fig. 4.9. Special Features Window.

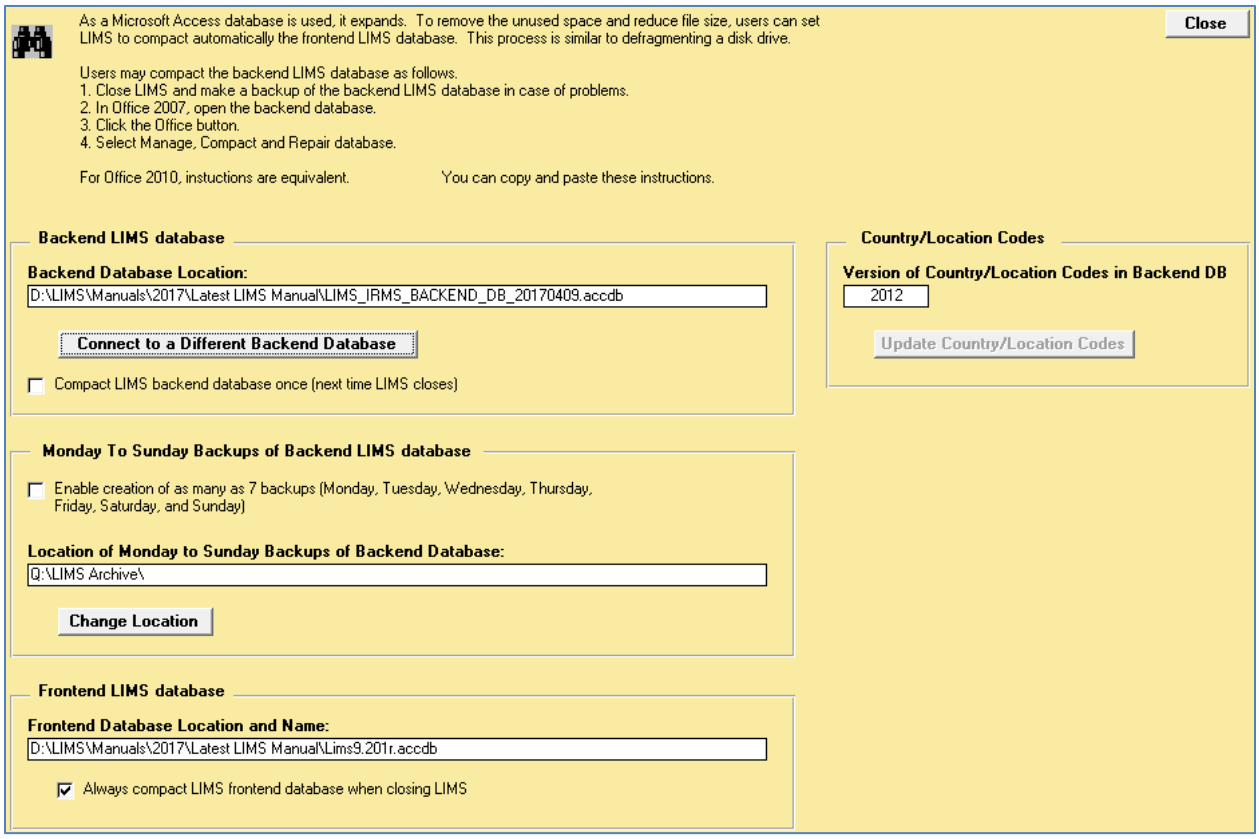


Fig. 4.10. BackEnd and FrontEnd Databases form.

4.2 Checking the LIMS Version

LIMS for Light Stable Isotopes software is continually improved. Updates are posted at https://isotopes.usgs.gov/research/topics/lims.html. To determine which version of LIMS one is using, click "About" on the main page. An example of the dialog box is shown in Figure 4.11.

To update the LIMS frontend, follow steps 3 and 7 in Section 4.1. If you created a Windows desktop "shortcut" to the frontend interface folder, be sure to update the shortcut to the newer version.

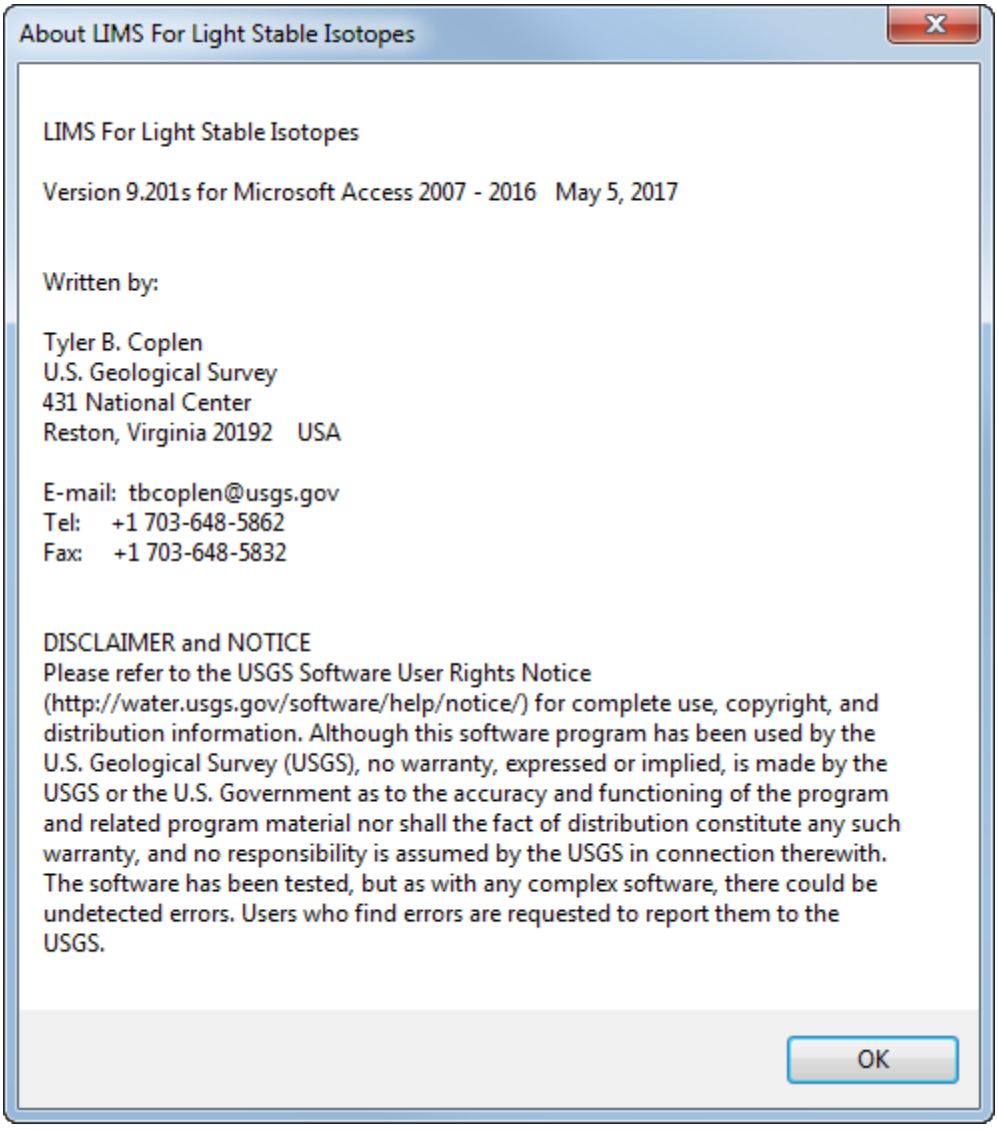


Fig. 4.11. Example of About LIMS for Light Stable Isotopes dialog box.

4.3 Customizing Your Laboratory Settings

Prior to adding a mass spectrometer to LIMS, one should create laboratory customizations (location, laboratory name, paper size, printers, etc.). This customization will be stored in a file in the LIMS frontend directory, and it is named "LM9PREFS", "LM9PREFS.ACCDB", or "LM9PREFS.MDB", depending upon whether Windows is set to display file suffixes.

This "Preferences" file must reside in the same directory as the LIMS frontend database. If this file is deleted when a new LIMS frontend is installed, all customizations may be lost and LIMS might revert to default values. However, if you move a working frontend LIMS file to a new folder and fail to move the preferences file, LIMS will automatically create another copy of the preferences file that contains the custom settings of the laboratory.

> To protect against mistaken entries and deletions in daily use, most forms in LIMS require the user to purposely click the **"Edit"** button at the top of the screen before any changes can be made. This may be confusing at first – but remember it is for your data protection! Think "**Click Edit**" and it will become a routine habit.

To edit the laboratory settings, click "Special Features" on the LIMS main page, and select "Options." The LIMS Options form (Fig. 4.12) will open. This form is divided into three sections: General Preferences, Alternative Field Names for Samples Form, and Form Colors. Each of the General Preferences is discussed below in Table 4.1. At minimum users should enter the organization name, select the paper size for reports, and select the print destination (either "Default Printer" or "Any Installed Printer"). Many of these preferences provide helpful features to laboratories.

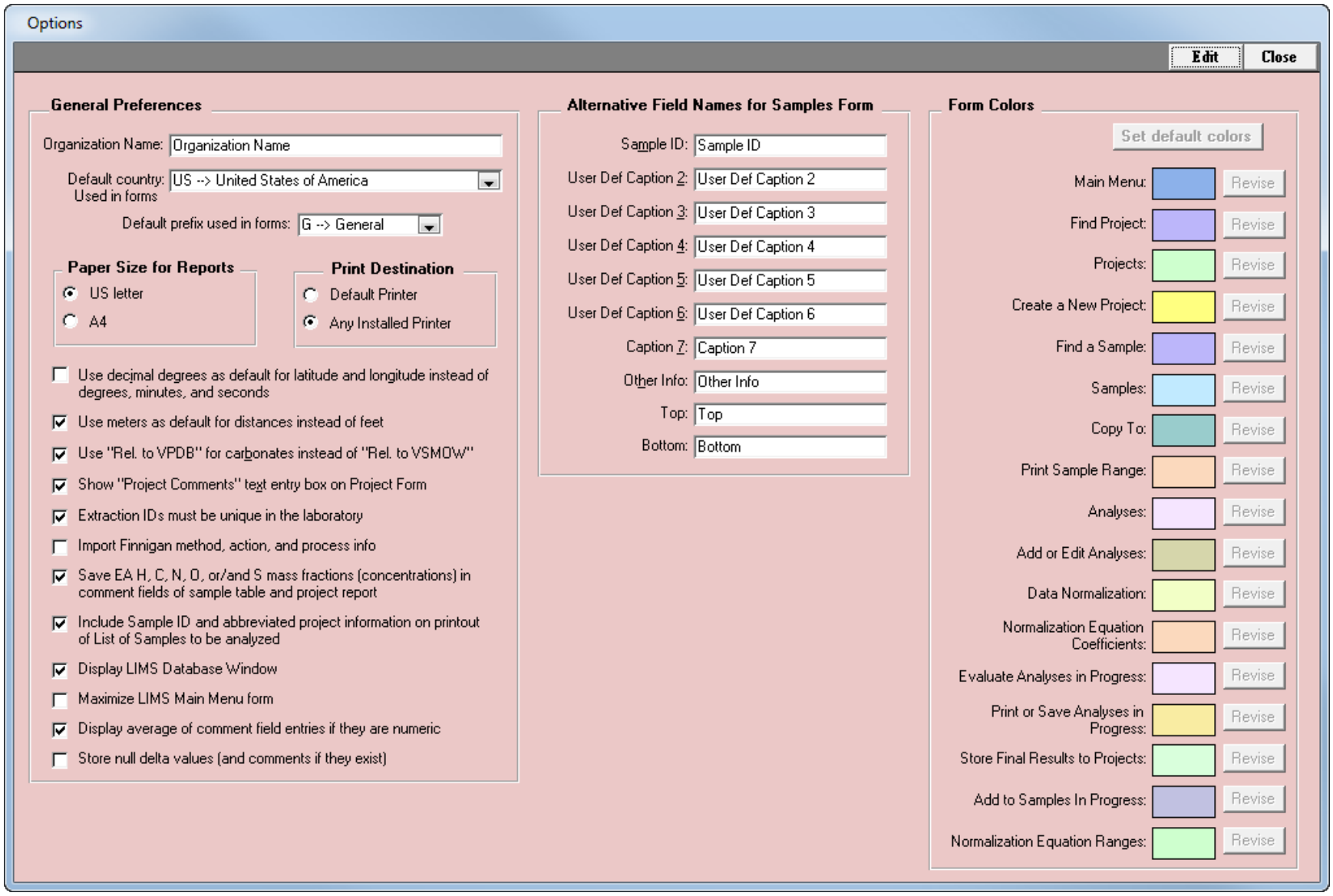


Fig. 4.12. The LIMS Options form.

Table 4.1. General Preferences on the Options form

Item	Comments
Organization name	Name of organization.
Default country used in forms	The 2012 default LIMS table consists of 248 country names and country codes.
Paper Size for Reports	Either U.S. letter or A4.
Print Destination	Either Default Printer or Any Installed Printer. Choosing Any Installed Printer will bring up the Windows Print Dialog box enabling a user to select a printer. If Adobe Acrobat is installed, creating a pdf file is one of the choices, which is convenient for many users.
Use decimal degrees as default for latitude and longitude instead of degrees, minutes, and seconds	Gives user the choice of displaying, for example, 30° 30' 00" or 30.50000°.
Use meters as default for distances instead of feet	Select meters or feet as the units for Top and Bottom alternative field names.
Use “Rel. to VPDB” for carbonates instead of “Rel. to VSMOW”	Display choice for laboratories analysing carbonates for oxygen isotopic composition.
Show “Project Comments” text entry box on Project Form	Display choice for Project Form (see Fig. 7.24)
Extraction IDs must be unique in the laboratory	Option to provide information about the preparation of each sample or each aliquot of each sample. Also termed the Aliquot ID. Accessed by clicking “Add or Edit Extractions” on the LIMS main page (Fig. 4.8). See Sections 11 , 19.2, 24.3, and 26.
Import Finnigan method, action, and process info	Import information in the method, action, and process info columns of an ISODAT file.
Save EA H, C, N, O, or/and S mass fractions (concentrations) in comment fields of sample table and project report	Used by laboratories to provide mass fractions along with stable isotope results of EA (elemental analysis) analyses on the LIMS project report form. See Section 24.6.

Include Sample ID and abbreviated project information on printout of List of Samples to be analyzed	Display option. See Figure 33.26.
Display LIMS Database Window	Display option for those debugging LIMS Visual Basic code. Normally check box is not enabled.
Maximize LIMS Main Menu form	Some users prefer to maximize the LIMS main page form so that it spans the full display.
Display average of comment field entries if they are numeric	Some users import numerical information in the Comment field, for example EA mass fractions (concentrations). Replicate measurements of the same sample will provide numerical values that can be averaged (Section 25.3) and exported to an Excel file (Section 26).
Store null delta values (and comments if they exist)	Enable check box to store concentrations of samples whose isotope-delta values cannot be determined and are null.

The use of Alternative Field Names in the center of the form is discussed in Section 7.5.1.

The background form colors of many of the forms in LIMS can be customized using the controls on the right side of the Options form (Fig. 4.12). Click "Edit," make the desired color change, and click "Save" when finished editing. Click "Close" to return to the LIMS main page.

4.4 Connecting to a Different Backend Database

To connect to another backend database:

1. Click "Special Features" on the main page, and the Special Features window will open (Fig. 2.1).
2. Click "Backend db" and the BackEnd and FrontEnd Databases form will open (Fig. 4.10).
3. Click "Connect to a Different Backend Database" and LIMS will display a dialog box to make a backend of the frontend database before proceeding (Fig. 4.13).
4. Make a backup of the frontend database, click "Yes," and navigate to the new backend database.
5. Click "Select" and a dialog box should indicate that LIMS has successfully linked to the new backend database (Fig. 4.14).

6. Click “OK” and LIMS will prompt whether you want to keep the same Preferences file (Fig. 4.15).
7. Click “Yes” because the preferences that are in use are fully satisfactory and LIMS will prompt with a dialog box that it needs to close (Fig. 4.16). LIMS needs to close to carryout housekeeping activities.
8. Click “OK” and Microsoft Access will close.
9. Reopen the LIMS frontend and the LIMS main page should be displayed (Fig. 4.8).

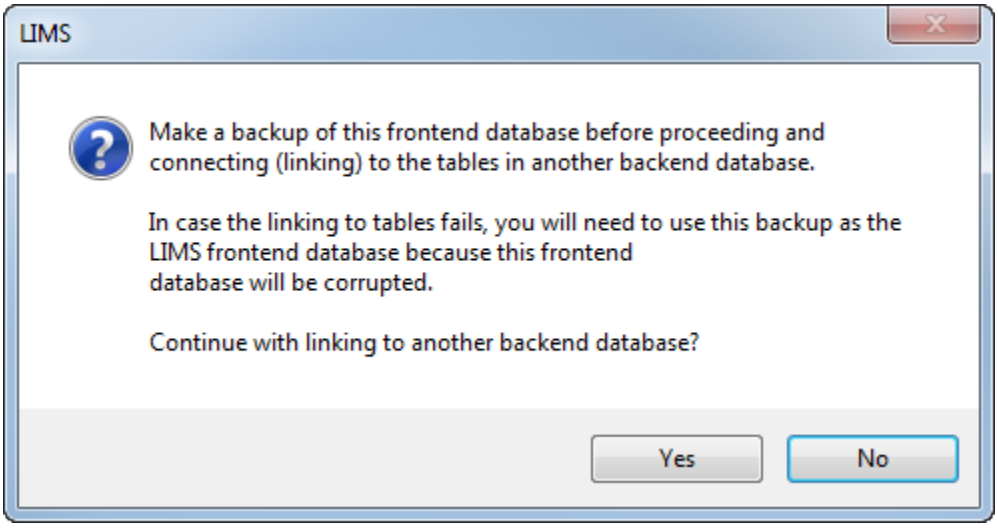


Fig. 4.13. Prompt to make a backup of the LIMS frontend database.

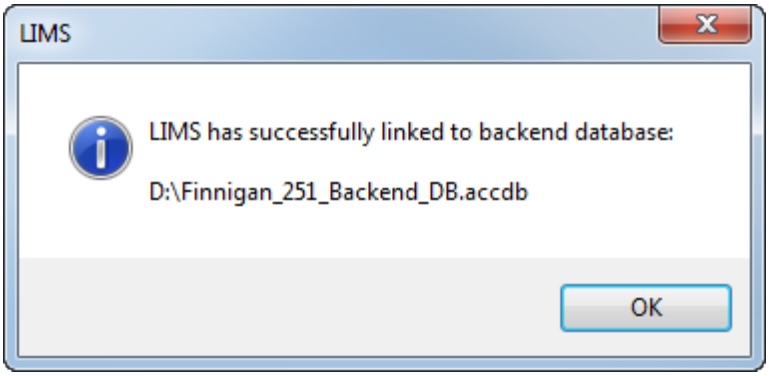


Fig. 4.14. Dialog box indicating success in linking to the specified database.

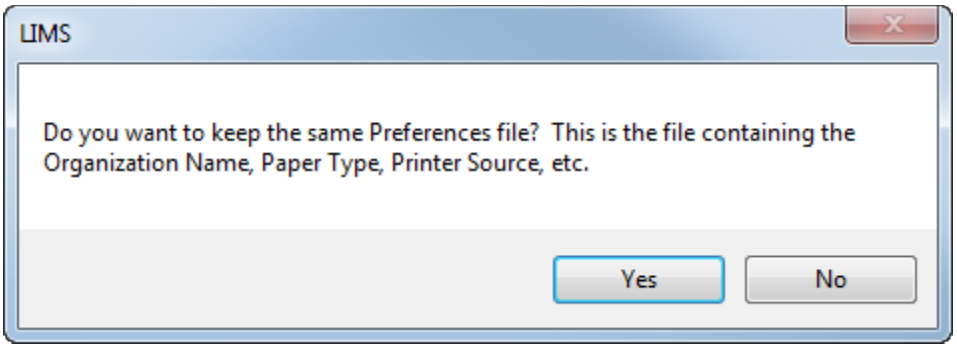


Fig. 4.15. LIMS dialog box prompt to keep the same LIMS Preferences file.

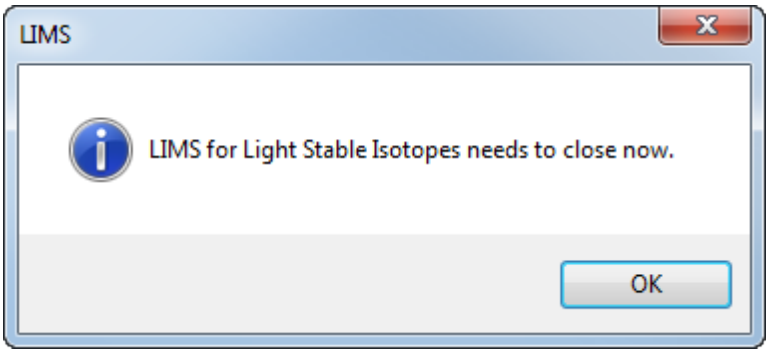


Fig. 4.16. Dialog box indicating that LIMS need to close.

The backend database should be compacted at least once a month. If LIMS is running slower than normal, try compacting the backend database to see if performance improves.

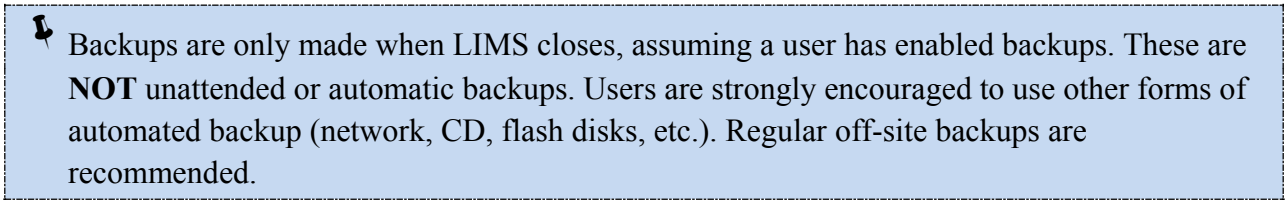
The option in Figure 4.10 to "Compact LIMS backend database once (next time LIMS closes)" forces a file compression, and LIMS will notify the user that the backend database is being compacted as LIMS closes.

4.5 Setting or Changing the Location of Backups of the Backend Database

To set or change the location of the Monday—Sunday backups of the backend database:

1. Click "Special Features" on the main page, and the Special Features window will open (Fig. 2.1).
2. Click "Backend db" and the BackEnd and FrontEnd Databases form will open (Fig. 4.10).

3. Enable the check box labelled "Enable creation of as many as 7 backups (Monday, Tuesday, Wednesday, Thursday, Friday, Saturday, and Sunday)." This allows for a week of back-up protection.
4. Click "Change Location" and navigate to the target folder that will contain the backups of the backend LIMS database. Click "Select."
5. Click "Close" to return to the LIMS main page.


Backups are only made when LIMS closes, assuming a user has enabled backups. These are **NOT** unattended or automatic backups. Users are strongly encouraged to use other forms of automated backup (network, CD, flash disks, etc.). Regular off-site backups are recommended.

4.6 Compacting the Frontend Database as it Closes

Many users prefer to have the frontend Access database compact as it closes. To set or edit this capability:

1. Click "Special Features" on the main page, and the Special Features window will open (Fig. 2.1).
2. Click "Backend db" and the BackEnd and FrontEnd Databases form will open (Fig. 4.10).
3. Ensure that the check box labelled "Always compact LIMS frontend database when closing LIMS" is checked.
4. Click "Close" to return to the LIMS main page.

4.7 Updating Country/Location Codes in a Backend Database

The Country/Location codes were last updated in LIMS in 2012, and in a new database they are identified as 2012 (Fig. 4.17) on the BackEnd and FrontEnd Databases form. These 2012 codes are identical to those on the Countries-Locations worksheet of the "LIMS for Light Stable Isotopes Default Sample Submission.xlsx" file (see Fig. 7.12 and Section 7.5.1). South Sudan is found in the 2012 codes, whereas it is missing from the 1996, 2002, and 2008 Country/Location codes.

If a user has a database with 1996, 2002, or 2008 Country/Location codes, it may be updated to 2012 codes with the following steps:

1. Click "Special Features" on the main page, and the Special Features window will open (Fig. 2.1).

2. Click “Backend db” and the BackEnd and FrontEnd Databases form will open (Fig. 4.10).
3. Click “Update Country/Location Codes,” and LIMS will update the codes in the backend database. In case countries or locations cannot be resolved by LIMS, LIMS will notify the user and may create an Excel file of samples needing location resolution. An example would be any samples identified as having been collected in Yugoslavia.
4. Click “Close” to return to the LIMS main page.
5. Click “Exit” to close LIMS.

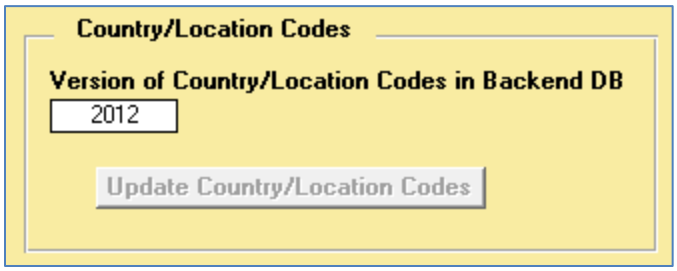


Fig. 4.17. Country/Location Codes version in LIMS.

If Country/Location codes are updated and if LIMS Sample Submission files are being provided to laboratory clients (see Section 7.5.1), be sure to update the “Countries-Locations” worksheet of the Sample Submission Excel file with 2012 codes.

4.8 Setting up the Lakes Isotope Laboratory LIMS Example for this Manual

Examples in the remainder of this manual will use an example backend database for the Lakes Isotope Laboratory whose laboratory supervisor is Herkimer Goodperson. To set up this new laboratory:

1. Create a new folder. It can be within a LIMS folder or elsewhere.
2. Identify the folder as an Access Trusted Location (Section 3.2.2).
3. Copy the zip file “Lakes_LIMS_Example.zip,” which is located in a folder named “Section 4” that accompanies this manual, into this new folder and extract the files from it, keeping them in the same folder.
4. Transfer into this folder a fresh copy of the LIMS frontend, which is named “Lims9.202.zip” (or similar) and is located in a folder named “Section 4” that accompanies this manual. Extract this frontend database from the zip file and keep in the same folder—it will be named “Lims9.202.accdb” or similar.

5. Double-click the new frontend (Lims9.202.accdb or similar) to open it. It should open with the message that LIMS cannot find the backend database (Fig. 4.1).
6. Click “OK” and navigate to “Lakes_Backend_DB.accdb.”
7. LIMS will display a message that it needs to close.
8. Click “OK.”
9. Reopen this frontend database and LIMS should display the welcome message in Figure 4.18.
10. Click “Yes” and LIMS will prompt that it needs to update settings and close.
11. Click “OK” and LIMS will perform cleanup activities upon closing.
12. Reopen this frontend database and LIMS should open with the main page (Fig. 4.8).
13. Click “Special Features” and click “Options.”
14. Set the paper size to A4 if needed, and set the print destination to “Any Installed Printer” if there is more than one printer available. A pdf creator might be one of the printers.
15. Click “Close” to close the Options form.
16. Click “Exit” and this completes installation of the Lakes Isotope Laboratory LIMS database for use throughout this manual.
17. If desired, create a Windows shortcut to the LIMS frontend (“Lims9.202.accdb” or similar) and name it Lake Isotope Laboratory. One can right-click on the frontend and select “Create shortcut.” Then move the shortcut created to the Windows Desktop.

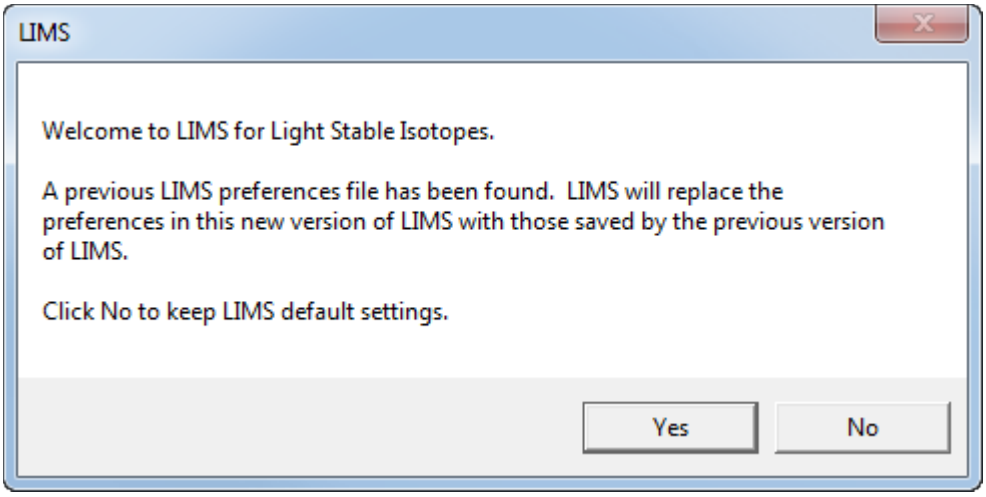


Fig. 4.18. LIMS welcome message.

5 Customers in LIMS

A customer (client) is the person responsible for the submission of samples to the laboratory and the person to whom the results will be reported. A customer may include laboratory and technical staff. LIMS keeps track of all laboratory customers and their mailing addresses, email addresses, and other pertinent information.

A customer list can be populated with a list of regular clients, or customers may be added over time. Ensure that a customer exists in LIMS before attempting to create new projects. Pay close attention to name spelling to avoid duplicating the same customer (*e.g.* Bill Smith, William Smith). In this section, the Lake Isotope Laboratory LIMS database created in Section 4.8 will be used. To open the Customer form:

1. Open the LIMS frontend database created in Section 4.8.
2. On the LIMS main page, click "Add / Edit a Customer" and the Customers form opens (Fig. 5.1).

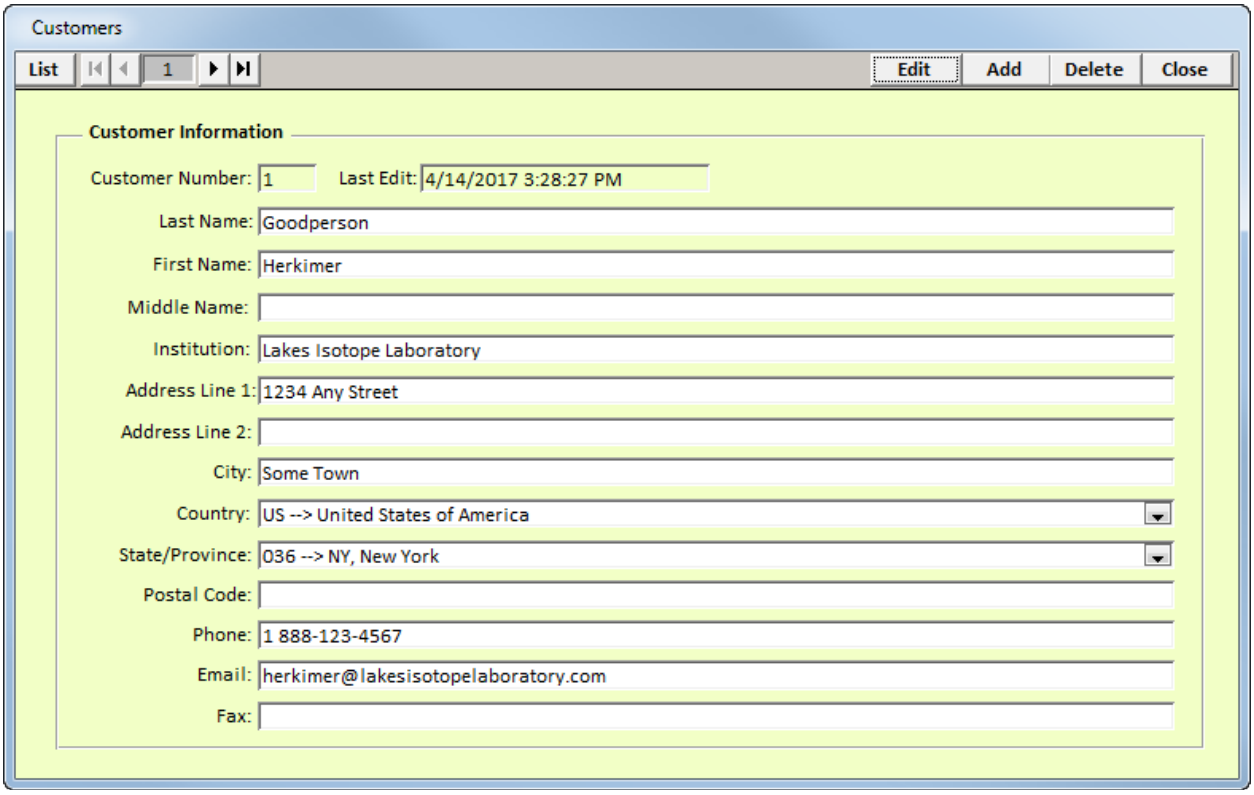


Fig. 5.1. The Customers form in the Lakes Isotope Laboratory LIMS database.

If this were a backend database for a new laboratory, the last name of the record shown would be "MyLastName," and it is envisioned that this record will be edited and changed to the laboratory owner, the laboratory supervisor, or the key person providing samples to the laboratory. Other fields, such as "First Name" and address would be updated accordingly.

To add a new customer:

1. Click "Add."
2. Enter "Snodgrass" in the "Last Name" field.
3. Enter "Cyrus" in the "First Name" field.
4. Click "Save."
5. Click "Close" to return to the main page.

Last name and first name are required. All other contact and address information are optional. Since training for LIMS for Lasers 2015 began at the International Atomic Energy Agency (IAEA) in Vienna, it was realized that the allotted character lengths for last name, first name, and middle initial were too small, and these have been increased to 50, 16, and 9 characters, respectively. When LIMS opens an older backend LIMS database, it will automatically increase the size of these fields in the table of customers.

It may never be necessary, but to remove a customer, click the "Delete" button. LIMS will check the database to ensure that no samples have been logged in for the customer prior to deletion. If samples exist for the customer, the customer cannot be deleted until the sample submitter of all sample projects have been reassigned to another customer (Section 7.6).

At a minimum, the last name and first name are required. All other customer fields are optional. Customer information can be updated at a later time by choosing the client name from the "List" menu and then clicking "Edit." The Customer entries "Reference" and "Test" are default entries that can be used for performing laboratory tests or for analyzing calibration materials.

The Customers form is a good example of the controls used for navigation on many of the forms in LIMS. The four navigation controls, shown in Figure 5.2, enable users to move to the first record, move to the next record, move to the previous record, and move to the last record. Clicking the "List" button in the upper left corner of a form causes LIMS to display a list of records, such as shown in Figure 5.3. The record number, "3" in Figure 5.2, is shown between the next record and previous record controls.

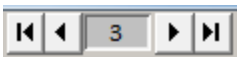


Fig. 5.2. Navigation controls on many LIMS forms. These controls enable the user to easily move to the first record, move to the next record, move to the previous record, and move to the last record.

Fig. 5.3. Example of list of records in the table of customers. The dropdown control is displayed by clicking "List."

6 Media, Isotope, and Procedure Codes

6.1 Media and Isotope Codes

Media are the different types of materials or compounds analyzed in the laboratory. When customers submit samples to a laboratory to be analyzed, they will specify the media or the media code for their samples, and they will indicate which isotope deltas should be measured. Common isotope deltas include the SI (International System of Units in English) quantities $\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$. Note that LIMS uses $\delta^{2}H$ instead of δD to be in accord with the International Union of Pure and Applied Chemistry (IUPAC). [2]

The backend LIMS database for a new laboratory contains common media analyzed in isotope laboratories. These can be found under the Special Features panel of the LIMS main menu. Selected media codes are shown in Table 6.1. If media descriptions need to be edited or new media codes need to be added, instructions are provided in Appendix A. If needed, users can create media codes for materials analyzed for tritium (^{3}H), ^{3}He, ^{4}He, ^{81}Br, CFC-11, CFC-12, CFC-113, and others (see Appendix A).

Table 6.1. Selected media and isotope codes in LIMS

Media code	Prefix	Media	Isotope deltas	Isotope code	
				Low	High
1	W	water	$\delta^{2}H$ and $\delta^{18}O$	2	8
2	C	calcite	$\delta^{13}C$ and $\delta^{18}O$	3	8
4	C	dissolved inorganic carbon (DIC)	$\delta^{13}C$	3	
5	G	gaseous carbon dioxide	$\delta^{13}C$ and $\delta^{18}O$	3	8
6	G	gaseous hydrogen	$\delta^{2}H$	2	
8	R	gaseous carbon dioxide reference	$\delta^{13}C$ and $\delta^{18}O$	3	8
10	R	gaseous hydrogen reference	$\delta^{2}H$	2	
12	R	gaseous nitrogen reference	$\delta^{15}N$	5	
19	G	hydrogen- and oxygen-bearing material	$\delta^{2}H$ and $\delta^{18}O$	2	8
25	G	organic carbon	$\delta^{13}C$	3	
26	G	carbon- and nitrogen-bearing material	$\delta^{13}C$ and $\delta^{15}N$	3	5
55	N	water (dissolved nitrate)	$\delta^{15}N$ and $\delta^{18}O$	5	8
64	S	water (dissolved sulfate)	$\delta^{34}S$ and $\delta^{18}O$	6	8
66	S	sulfide mineral	$\delta^{34}S$	6	

Each medium may be assigned and analyzed for one or two isotope deltas (or isotope or CFC values). Dissolved inorganic carbon (DIC), organic carbon, and sulfide minerals are examples of media that are analyzed for one isotope delta. Calcite, dissolved nitrate, and carbon- and nitrogen-bearing materials are examples of media that can be analyzed for two isotope deltas (Table 6.1). The isotope of the element with the lower atomic number is termed the Low Isotope in LIMS and that of the element with the higher atomic number is termed the High Isotope in LIMS, and these are listed for the selected media in the last two columns of Table 6.1. The codes of available isotopes, isotope ratios, and other quantities in LIMS are shown in Table 6.2.

Table 6.2. Isotope codes in LIMS

[*x*, atom fraction, commonly incorrectly termed atom percent.[2]]

Isotope code	Isotope or other quantity	Isotope code	Isotope or other quantity
1	specialized use	15	^{3}H
2	$\delta^{2}H$ or $x(^{2}H)$	16	^{3}He
3	$\delta^{13}C$ or $x(^{13}C)$	17	^{4}He
4	$\delta^{33}S$ or $x(^{33}S)$	18	^{38}Ar
5	$\delta^{15}N$ or $x(^{15}N)$	20	^{40}Ar
6	$\delta^{34}S$ or $x(^{34}S)$	21	^{21}Ne
7	$\delta^{17}O$ or $x(^{17}O)$	22	^{22}Ne
8	$\delta^{18}O$ or $x(^{18}O)$	23	$\delta^{81}Br$
9	$\delta^{36}S$ or $x(^{36}S)$	24	^{86}Kr
10	$\delta^{7}Li$	25	UDI1 (user definable isotope 1)
11	$\delta^{11}B$	26	UDI2 (user definable isotope 2)
12	$\delta^{30}Si$ or $x(^{30}Si)$	27	CFC-11
13	$\delta^{37}Cl$ or $x(^{37}Cl)$	28	CFC-12
14	^{14}C	29	CFC-113

If a sample needs to be analyzed for three or more isotope deltas, it must be logged into LIMS at least twice with different media codes. For example, wood specimens to be analyzed for $\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$ values could be logged in using media codes 19 and 26 (Table 6.1).

Each media code has a unique single-letter Prefix, one of seven sample Prefixes used in LIMS, and these are shown in Table 6.3. The idea behind the use of sample prefixes is that samples entering the laboratory for isotopic analysis commonly are stored in different areas, depending

upon the isotope deltas to be measured. For example, samples submitted for $\delta^{13}C$ and $\delta^{15}N$ analysis by elemental analyzer (EA) combustion commonly are submitted in 96-hold plastic trays, whereas liquid water samples commonly are submitted in bottles containing 10 to 60 mL of water. The water samples would typically be stored in their own cabinets separated from the storage are of the $\delta^{13}C$ and $\delta^{15}N$ samples. The sample Prefix guides the laboratory staff to the location where such samples are stored.

Table 6.3 Sample Prefixes

Prefix	Description
C	Carbonate samples submitted for $\delta^{13}C$ and $\delta^{18}O$ analysis
G	General samples
J	Unused; available for user-defined media
N	Samples submitted primarily for $\delta^{15}N$ analysis
R	Reference samples
S	Samples submitted primarily for $\delta^{34}S$ analysis
W	Water samples submitted for $\delta^{2}H$ and $\delta^{18}O$ analysis

6.2 The Our Lab ID

When samples arrive in the laboratory, the customer has distinguished each one by giving it a unique Sample ID. When logged into LIMS by laboratory personnel, each sample is assigned a unique Our Lab ID, consisting of the single letter sample prefix depending on the media (Tables 6.1 and 6.3) followed by an integer sample number, separated by a hyphen (for example, W-1001 for a water sample). The Our Lab ID is the identifier used by laboratory staff and by LIMS to uniquely identify a client's sample.

The Our Lab ID to be used for each of the seven Prefixes in logging in the next sample is found by clicking "Special Features" on the main page and clicking "Next Sample Number," which opens the Next Our Lab ID form (Fig. 6.1). The Our Lab ID of the next sample for any of the seven Prefixes can be changed with this form, and its use is discussed in Section 7.4.

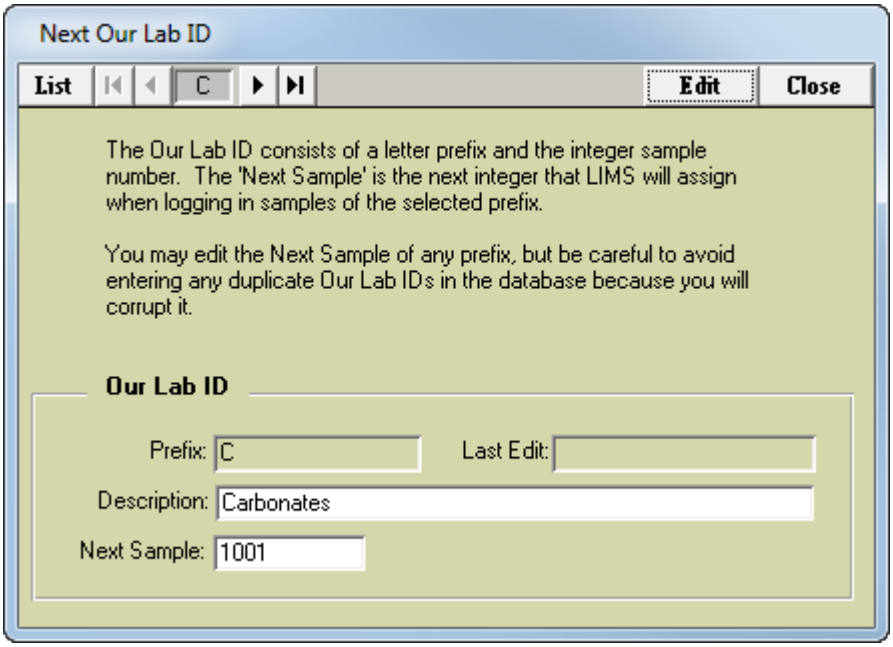


Fig. 6.1. The Next Our Lab ID form.

6.3 Media with Isotopic Abundances in Atom Fractions (in Percent)

Some IRMSs have the capability of reporting isotopic abundances as atom fractions, sometimes incorrectly termed atom percent.[2] LIMS can import, normalize, store, report, and export ten isotopes (^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{36}S, ^{30}Si, and ^{37}Cl) as atom fractions. The low isotope or the high isotope in media can either be an isotope-delta value (column 4 of Table 6.1) or an atom fraction value (Table 6.2). To designate that an isotope of a medium should be treated and expressed as an atom fraction, the description of that medium must contain the "x(2H)", "x(13C)", "x(15N)", "x(17O)", "x(18O)", "x(33S)", "x(34S)", "x(36S)", "x(^{30}Si)", and "x(37Cl)", respectively, to designate atom fraction of the isotope ^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{36}S, ^{30}Si, or ^{37}Cl. For example, 155 is a default medium included in the backend database for tracer studies for a new isotope laboratory (Fig. 6.2). The "Medium Description" is "13C & x(15N) 15N enriched." The character string "x(15N)" enables nitrogen-15 to be imported, normalized, stored, reported, and exported as the atom fraction x(^{15}N) for isotope-tracer studies. See Appendix B for an example of importing a file containing samples having medium 155.

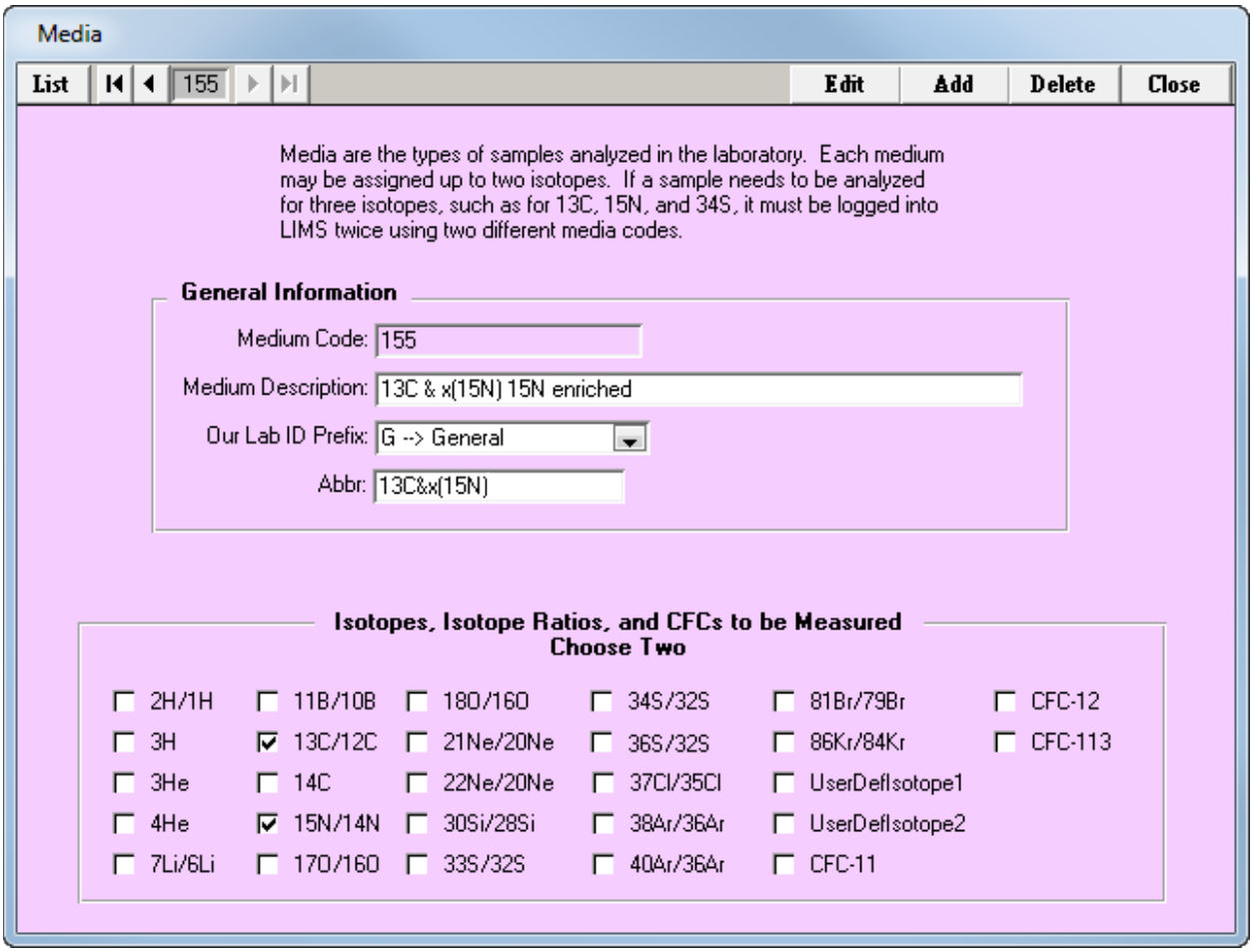


Fig. 6.2. Medium 155 in the LIMS backend database for a new laboratory. The description "13C & x(15N) 15N enriched" enables ^{13}C to be imported, normalized, stored, reported, and exported as the isotope delta value $\delta^{13}C$ and ^{15}N to be imported, normalized, stored, reported, and exported as the atom fraction $x(^{15}N)$, such as for isotope-tracer studies. The atom fraction of nitrogen-15 is enabled by inclusion of the character string "x(15N)" in the "Medium Description."

6.4 Procedure Codes

Procedure codes are numerical values assigned to analytical methods by which samples are converted into gases (or equilibrated with gases) and introduced into the mass spectrometer for analysis. Procedure codes are grouped by isotope to be analyzed (Fig. 6.3). For example, procedure codes 200–299 are designated for performing δ^2H analyses, all of which have isotope code 2 (Table 6.1). Procedure codes 300–399 are designated for performing δ^{13}C analyses, all of which have isotope code 3. Dividing the procedure code by 100 and taking the integer yields the isotope code. Many pre-assigned procedure codes are provided in the backend database for a new laboratory, and a few selected codes are shown in Table 6.4. New codes can be added (see Appendix C). Although most procedure codes identify a specific analytical method, those with values between 100 and 199 indicate a quantity being measured, not an analytical method. For example, procedure codes 187–191 are hydrogen, carbon, nitrogen, sulfur, and oxygen mass fractions (concentrations), respectively. Determining mass fractions in LIMS is discussed in Section 24.6.

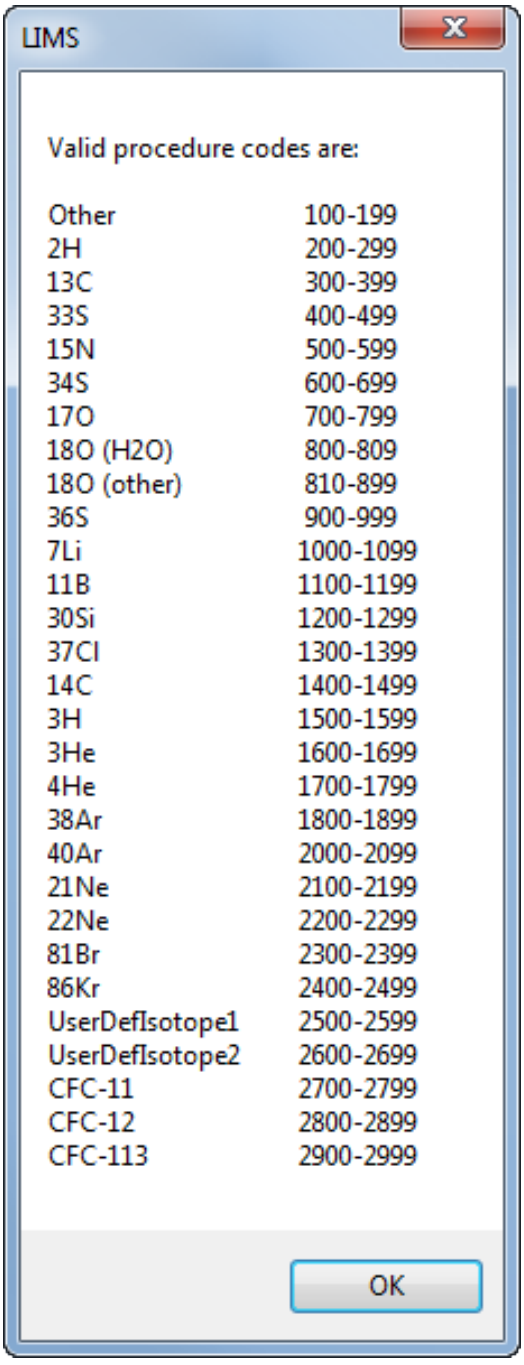


Fig. 6.3. Ranges of procedure codes for each isotope in LIMS

LIMS needs to keep track of whether a specific procedure code correlates to the low isotope or the high isotope of a medium. For example, a procedure code for a δ^{15}N measurement of dissolved nitrate in water (medium 55 in Table 6.1) would be identified as a low procedure code because the low isotope code of this medium is 5—the high isotope code is 8. But a δ^{15}N measurement of a carbon- and nitrogen-bearing material would be designated a high procedure code. Table 6.5 summarizes low and high procedure codes for three media from Table 6.1. Low and high procedure codes are discussed in more detail in Appendix D.

Table 6.4. Selected procedure codes and isotope deltas in LIMS

Procedure code	LIMS Description	Isotope delta
241	Pyrolysis converted to H2, CF, delta H-2	$\delta^{2}H$
356	CF, EA, Delta 13C	$\delta^{13}C$
584	CF, EA, Delta 15N	$\delta^{15}N$
587	CF, Denitrifier Method, P. aureofaciens, N-15	$\delta^{15}N$
889	CF, Denitrifier Method, P. aureofaciens, O-18	$\delta^{18}O$
891	Pyrolysis, converted to CO, CF, delta O-18	$\delta^{18}O$

Table 6.5. Selected media and isotope codes in LIMS

Media code	Prefix	Media	Isotope deltas	Procedure code	
				Low	High
19	C	hydrogen- and oxygen-bearing material	$\delta^{2}H$ and $\delta^{18}O$	241	891
26	G	carbon- and nitrogen-bearing material	$\delta^{13}C$ and $\delta^{15}N$	336	584
55	N	water (dissolved nitrate)	$\delta^{15}N$ and $\delta^{18}O$	587	889

7 Projects and Sample Submission

7.1 Projects

Projects are defined in LIMS as one or more samples of the same medium submitted by a client for one or two specified isotopic analyses. These samples may be from the same location, study area, investigation, etc. Projects are identified by submission date, last name of sample submitter, range of Our Lab IDs, and medium. The range of Our Lab IDs uniquely identifies a project.

7.2 Finding Projects

LIMS has a flexible form that enables users to search for projects using one or more criteria. In this section, the Lake Isotope Laboratory LIMS database created in Section 4.8 will be used. On the LIMS main page click "View Projects -->" and the Find Project form opens (Fig. 7.1). The Find Project form displays a number of attributes for each project in its lower panel, including:

- Project submission date.
- Last name of the sample submitter.
- Range of Our Lab IDs.
- Medium.
- Purpose.
- Location.
- Date results were reported to sample submitter.

Note that projects are sorted by default by increasing submission date. To sort by any of the other six columns, click the  icon at the top of the desired sort column.

The default backend database for a new laboratory has several projects for internationally distributed isotopic reference materials (*e.g.* VSMOW2, SLAP2) and several projects for local measurement standards (*e.g.* your own laboratory isotopic reference materials); the assigned customer for these project is "Reference" (see Figs. 5.3 and 7.1). In this document the terms reference and standard are used interchangeably. Projects identified with the submitter "Test" (see Fig. 7.1) are default projects containing samples typically used as dummy samples, for conditioning instrumentation, or for testing instrumentation. These default projects should not be deleted. Your laboratory references can be added to the default projects by editing them.

The Find Project form is a very flexible utility that enables users to search for one or more projects based on one or more criteria including:

1. Last name of the client.
2. Sample Prefix, which is "C", "G", "J", "N", "R", "S", or "W".

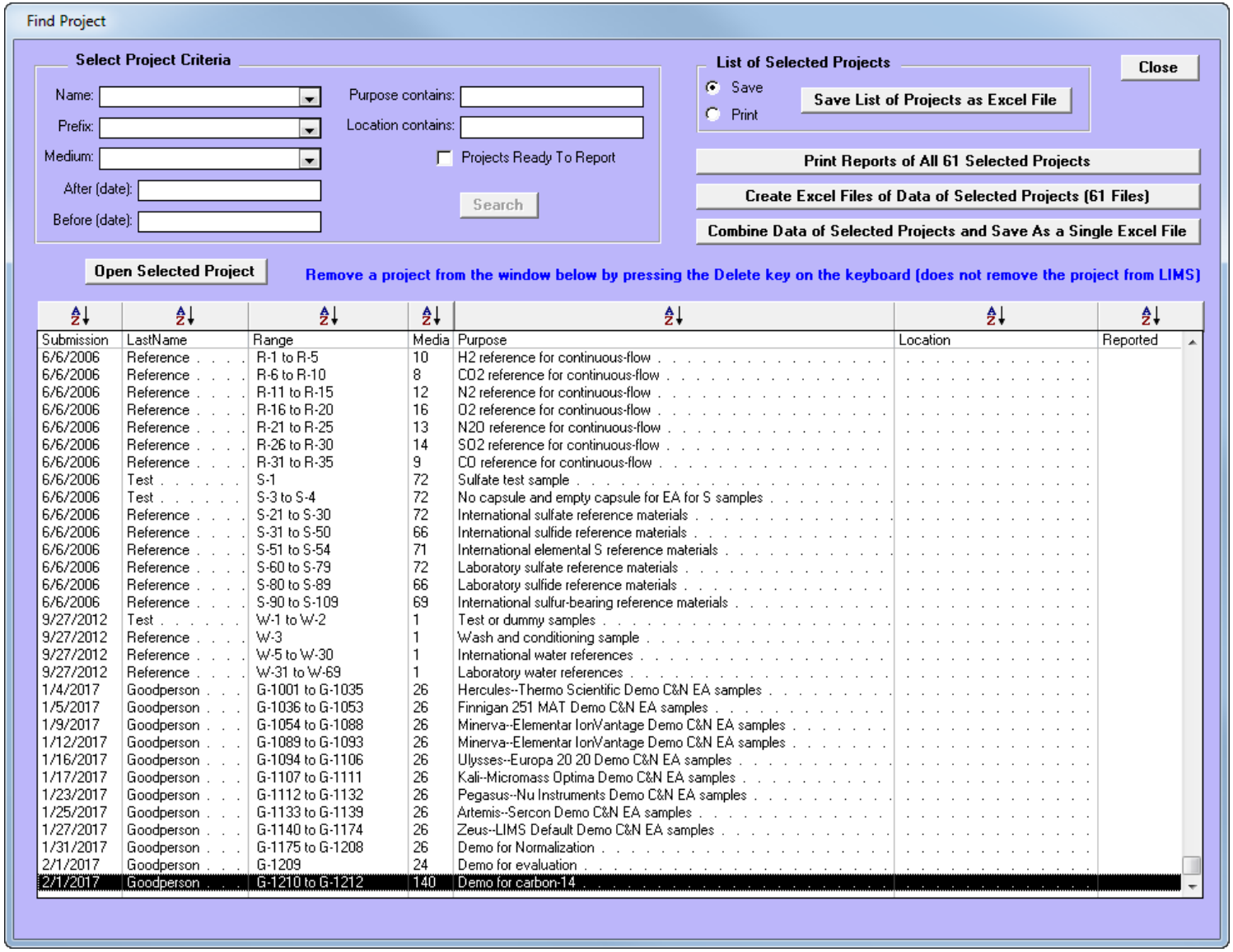


Fig. 7.1. The Find Project form.

3. An entry from the dropdown control for the medium.
4. Before a date-time, after a date-time, or between two date-time values.
5. One or more characters in the "Purpose contains" text box.
6. One or more characters in the "Location contains" text box.

As an example, search for all "G" projects that are international isotopic reference materials:

1. For "Prefix" select "G --> General."
2. Enter "International" in the "Purpose contains" text box.
3. Click "Search," and LIMS queries the database and displays five projects (Fig. 7.2).

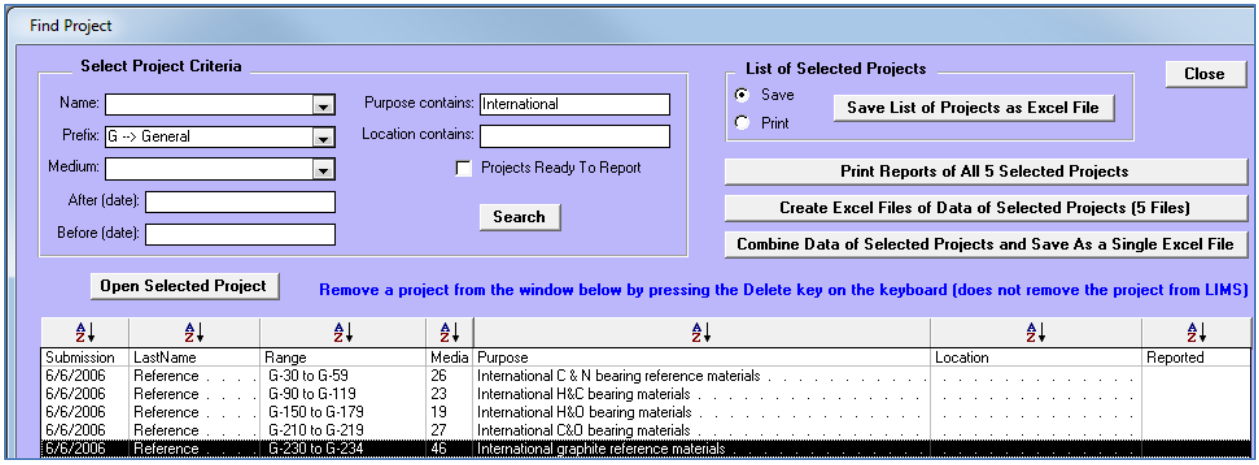


Fig. 7.2. Query of projects in which the purpose contains "International" and the Prefix is "G."

Controls on the upper right portion of the form provide added capabilities and enable users to:

- Print these five projects as they are shown in the form (Fig. 7.3).
- Save these five projects to an Excel file with seven columns: submission date, last name, range of Our Lab IDs, media code, purpose, location, and date results were reported to client.
- Print a LIMS project report of each project. For example, a portion of the first page of the first project in the list, "G-30 to G-59" is shown in Figure 7.4.
- Create an Excel file of each of the five projects shown—five files total.
- Create a combined Excel file in which the data in the five projects has been appended into a single file.

To display a specific project, either double-click on the project or highlight it and click "Open Selected Project," which opens the Project form. The Project form is discussed in Section 7.6.

List Of Projects 2/3/2017 5:30:18 PM

Submission:	Last Name:	Range:	Purpose:	Location:	Date Reported:
6/6/2006	Reference	G-30 to G-59	International C & N bearing reference materials		
6/6/2006	Reference	G-90 to G-119	International H&C bearing materials		
6/6/2006	Reference	G-150 to G-179	International H&O bearing materials		
6/6/2006	Reference	G-210 to G-219	International C&O bearing materials		
6/6/2006	Reference	G-230 to G-234	International graphite reference materials		

Fig. 7.3. List of Projects Report for "G" samples having "International" in the Purpose.

Submission: 6/6/2006 Reference G-30 to G-59 2/3/2017

Medium: 26 --> G [C & N] C- and N-bearing material
Purpose: International C & N bearing reference materials

Location:

Sample ID:	Collection Date	Our Lab ID	$\delta^{13}C_{VPDB}$, in ‰ Value	$\delta^{13}C_{VPDB}$, in ‰ Comment	$\delta^{15}N_{AIR}$, in ‰ Value	$\delta^{15}N_{AIR}$, in ‰ Comment
IAEA-600 caffeine		G-30				
USGS61 caffeine		G-31				
USGS62 caffeine		G-32				
USGS63 caffeine		G-33				
USGS64 glycine		G-34				
USGS65 glycine		G-35				
USGS66 glycine		G-36				
USGS73 L-valine		G-37				
USGS74 L-valine		G-38				
USGS75 L-valine		G-39				
USGS40, L-Glutamic Acid		G-40				
USGS41, L-Glutamic Acid		G-41				
USGS42 Tibetan Hair		G-42				
USGS43 Indian Hair		G-43				
USGS41a, L-Glutamic Acid		G-44				
USGS54 Canadian lodgepole pine		G-45				
USGS55 Mexican ziricote		G-46				
USGS56 South African red ivorywood		G-47				
ref19		G-48				
ref20		G-49				

Fig. 7.4. Top portion of a project report of project 6/6/2006 Reference G-30 to G-59. G-48 to G-59 are unassigned and are available for future internationally distributed carbon- and nitrogen-bearing isotopic reference materials.

The Find Project form in LIMS (Fig. 7.1) can be an exceedingly useful tool for retrieving specific projects submitted by an investigator over a long period. For example, for a client that submits numerous sample projects from different topics and areas over a long time period, one could assign a specific character string or code to a client's projects as a retrieval key. For example, including the string "W_SEA_4" in either the project or location fields for work in West Seattle enables one to retrieve selectively all of a client's projects from phase 4 of a multiple-year study in West Seattle. The client might have submitted numerous projects from the Seattle area, and the specific character strings can make data retrieval easier.

7.3 Manually Creating a New Project

New projects can be created in either of two ways:

- Manually entering customers and their sample information (Section 7.3)
- Automatically importing customer sample information from an Excel sample submission file (Section 7.5).

The second option may be preferable because the file contains all the information supplied by the customer and accompanies the samples arriving at the laboratory. Importing information from an Excel file provided by the client ensures no typographic errors are made by laboratory staff.

Manual project creation and entry of samples is illustrated with an example. Cyrus Snodgrass, a client added in Section 5, submitted nine water samples from Dunedin, New Zealand for a water resources evaluation project. The sample bottles arriving in the laboratory are labelled "1" through "9."

1. On the LIMS main page, click "Create a New Project."
2. Click "Submission Date" and enter 3/3/2017. One can use the calendar icon to select a date.
3. Choose "Snodgrass, Cyrus" from the "Customer" pull down menu.
4. Choose "01 --> W [Water] water (H & O)" as the "Medium."
5. Enter "Water resources evaluation project" in "Project Purpose or Title" field.
6. For "Location" enter "Dunedin."
7. Choose "NZ --> New Zealand" for the "Country."
8. Select "111 --> , Otago" for the "State/Province."
9. In the "Sample ID" field, enter the sample IDs (1 to 9), one sample per line.
10. An "Account No" field is available if needed. Do not use it now.
11. The form should appear as shown in Figure 7.5.
12. Click "Save," and a dialog box (Fig. 7.6) notifies the user that a project with samples ranging from W-1001 to W-1009 is to be created.
13. Click "OK" to create the project, which will be added to the LIMS backend database.

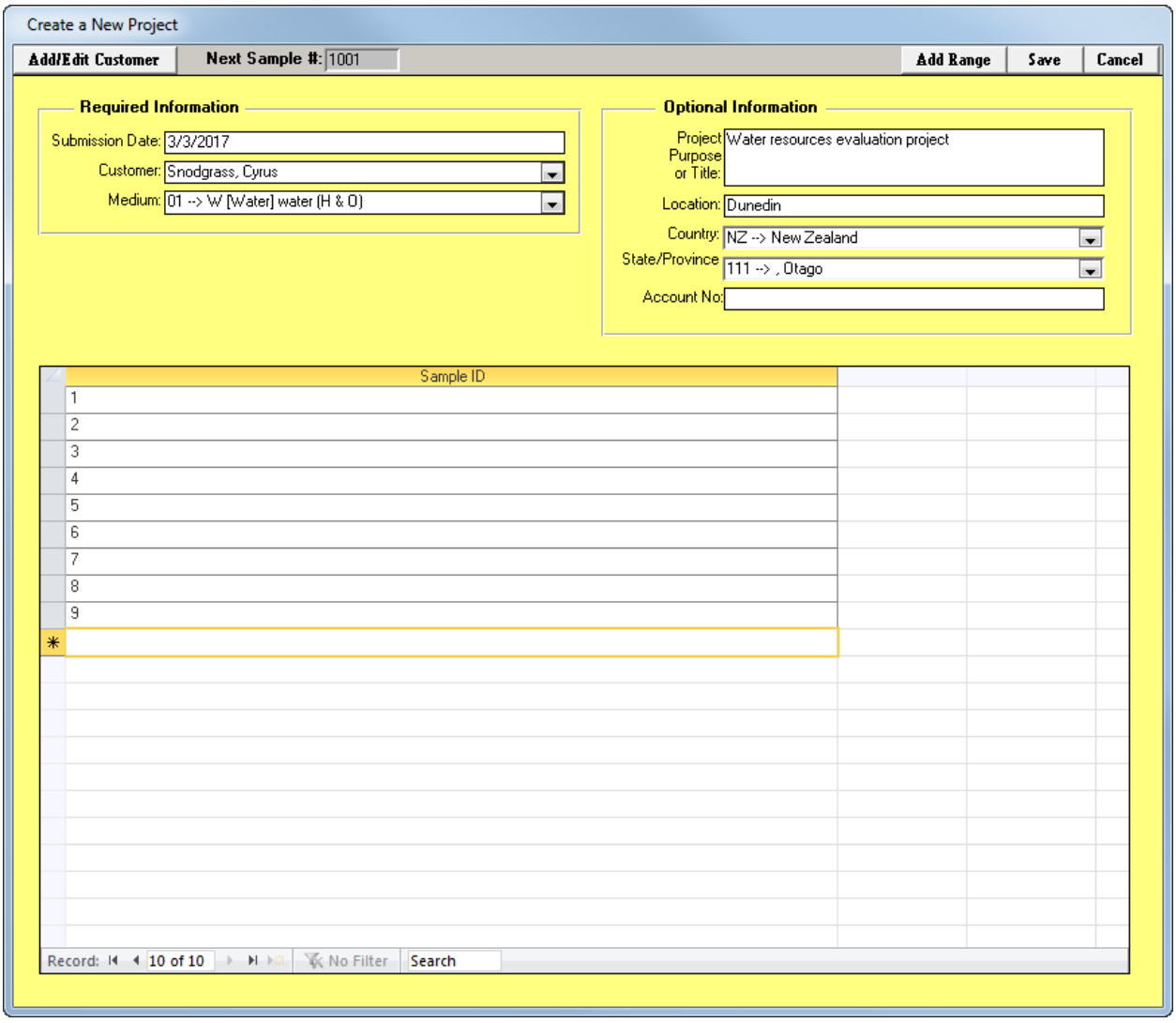


Fig. 7.5. Create a New Project form.

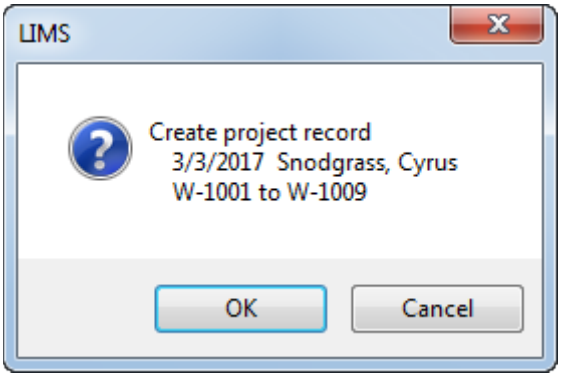


Fig. 7.6. LIMS prompt to create a new project.

The minimum information required to create a new project manually is Submission Date, Customer, Medium, and at least one Sample ID. Optional information can be entered or edited at a later time as shown in Section 7.6. Note that Sample IDs must be unique; any duplicates should be renamed uniquely, *e.g.* Sample1, Sample1a, Sample1b, etc.

To facilitate entry of a series of Sample IDs with incremental numbering, LIMS provides a time-saving "Add Range" action. This control is located on the top right of the Create a New Sample page (Fig. 7.5). Clicking the "Add Range" control opens the entry box shown in Figure 7.7.

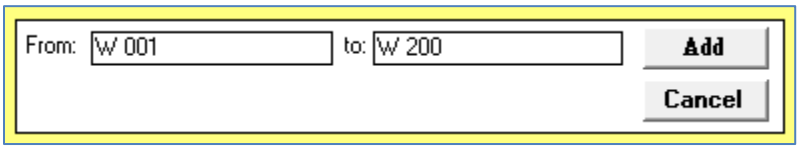


Fig. 7.7. Add Range entry box.

The format of the "From" and "to" fields requires that both entries have the same nonnumeric prefix if applicable.

Correct Range Entry Format

Example: From: W 001 To: W 200
Action: Automatically adds 200 samples of consecutively numbered samples

Example From: W 4.011 To: W 4.210
Action: Automatically adds 200 consecutively numbered samples

Example From: W200 To: W1
Action: Automatically adds 200 consecutively numbered samples, in decreasing value

Incorrect Range Entry Format (Results in a Range Error)

Example: From: Test1 To: Testsample200 (non-numeric prefix different)

7.4 Specifying the Next Our Lab IDs of Samples in a New Project

Clicking the "Next Sample Number" button in the Special Features panel of the main page opens the Next Our Lab ID form. This form is used to assign the next Our Lab ID for any of the seven Prefixes (Table 6.2). While this option is rarely needed (*e.g.* to fix errors), it is useful for adding

laboratory measurement standards and keeping them constrained within a specific Our Lab ID range. Generally, it is preferable and easier to remember standards having low Our Lab IDs.

As an example, suppose we want to add five dolomite laboratory standards. First, one needs to see if dolomite already exists as a medium. Click “Special Features,” click “Media,” and click “List.” The List dropdown displays dolomite as media code 03 with Prefix “C” (Fig. 7.8). Therefore, one does not need to add dolomite to the Media table. Click “Close” to close the Media form.

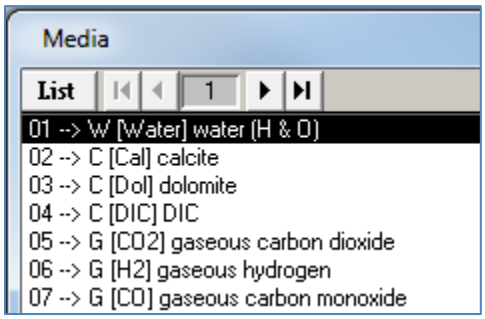


Fig. 7.8. Media displayed by clicking “List” on the Media form.

For reference samples it is convenient to create an interval with low Our Lab IDs. On the main page, click “View Projects -->.” To identify existing projects with Prefix “C,” select Prefix “C” and click “Search.” LIMS shows seven projects (Fig. 7.9). The fourth column, Media, indicates that there are no projects in the database with medium 3 (dolomite). There is an interval from C-29 to C-50 that is not used. Therefore, we want to add five dolomite samples beginning with C-29. Click “Close” to return to the main page.

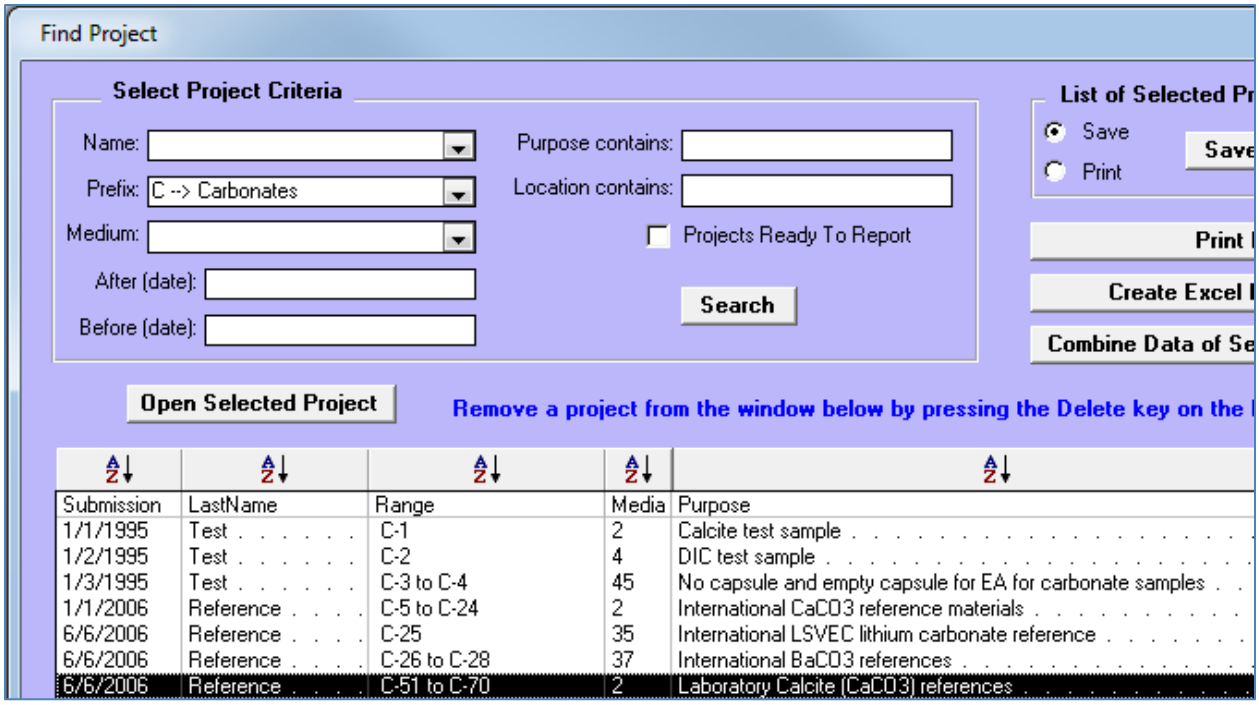


Fig. 7.9. Projects in the database having a Prefix of "C."

To add the five new Our Lab IDs for Prefix "C" beginning at C-29:

1. In the Special Features Window, click "Next Sample Number."
2. Prefix "C" is displayed; therefore, record the value of the "Next Sample" so that it can be re-entered. It is "1001."
3. Click "Edit."
4. Replace "1001" with "29."
5. Click "Save" and click "Close."
6. Click "Create a New Project."
7. Enter 2/2/2017 for the submission date.
8. Enter "Reference" for the customer.
9. Enter 03 for the medium.
10. Enter "Laboratory dolomite isotopic references" for the project purpose.
11. Enter "Dolomite 1", "Dolomite 2", "Dolomite 3", "Dolomite 4", and "Dolomite 5" for the Sample IDs. You can use the "Add Range" button if desired.
12. Click "Save" and LIMS prompts with the message in Figure 7.10 that the project having samples with Our Lab IDs from C-29 to C-33 are ready to be created.
13. Click "OK."
14. Click "Next Sample Number" in the Special Features Window.
15. Click "Edit" and change the "Next Sample" back to the value recorded in step 2, namely "1001." This ensures you do not attempt to overlap with any pre-existing

Our Lab IDs.

16. Click “Save” and click “Close.”

To confirm that the project has been added, click “View Projects -->,” select Prefix “C,” and click “Search.” Figure 7.11 displays eight projects and the last project is the one just added.

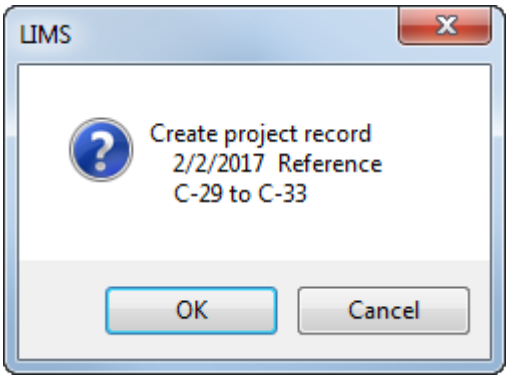


Fig. 7.10. LIMS prompt that a project with five Reference samples has been created.

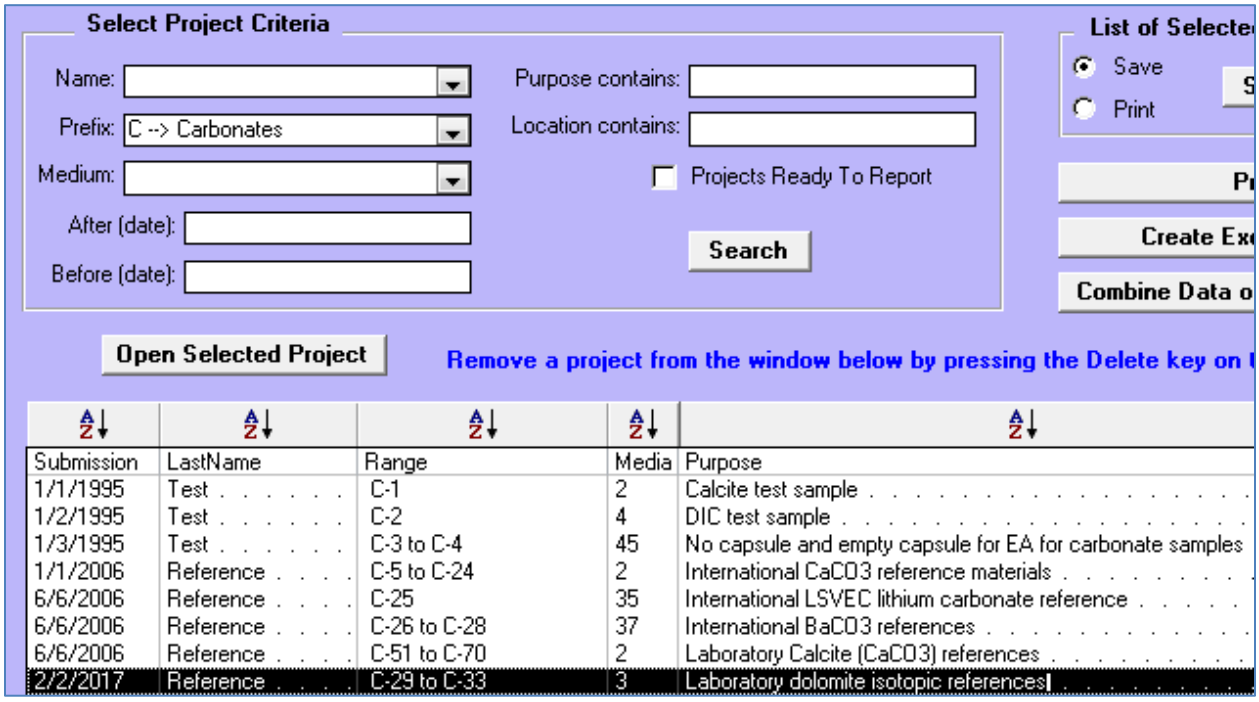


Fig. 7.11. Find Project form with project 2/2/2017 Reference C-29 to C-33 added.

7.5 Importing a Project Using a LIMS Sample Submission File

7.5.1 Creating a LIMS Sample Submission File

When manually creating a new project (Section 7.3), a user only has the ability to enter the Sample ID, the country, and the state/province of each sample. LIMS has the capability to store as many as 19 data fields for samples (Table 7.1). For example, Sample ID, aquifer, conductivity, pH, latitude, longitude, elevation, and collection date/time might be useful in an isotope hydrology laboratory (see column 3 of Table 7.1 for example field names that might be used in an isotope hydrology laboratory). In a biology laboratory performing EA analyses, Sample ID, tray number, tray position, sample weight, and sample type might be useful. LIMS enables users to customize 10 of these 19 field names (see the second column of Table 7.1). The only required field is "Sample ID" and the other 18 fields need not be used—they can be ignored. For added flexibility, the default name "Sample ID" can be changed, such as to "Field ID," which is used in some laboratories. For samples collected over a time interval, such as precipitation samples, both collection date-time and ending collection date-time fields are available.

To minimize typographic errors and laboratory staff effort, it is beneficial to have clients provide in an Excel file all the information required by a laboratory for each sample submitted. LIMS provides a default Excel sample submission file, named "LIMS_for_Light_Stable_Isotopes_Default_Sample_Submission.xlsx," which can be found in the files accompanying this manual in the folder named "Section 7." It is intended that this default file be modified by the laboratory as needed to provide the required information for the project and for each sample. Some laboratories may require geographic information, such as latitude, longitude, state/province, and country. For other laboratories, geographic information is not needed. Some laboratories concentrate on EA sample preparation of carbon-, nitrogen-, and (or) sulfur-bearing samples, followed by isotopic analysis of carbon dioxide, nitrogen, and (or) sulfur dioxide. Such samples may be provided in trays so that tray position number is important. The LIMS sample submission file is flexible and can accommodate these and many other customized uses.

The LIMS default sample submission file has five worksheets (Fig. 7.12):

- Headings (Fig. 7.12)
- Media
- Countries-Locations
- States-Provinces
- Temp

Table 7.1. Names and properties of data fields of a sample in LIMS

[Def, defined; Lat., latitude; Long., longitude; Lat. Long. Acc., latitude and longitude accuracy; Coll., collection' Double, a floating point number in Microsoft Access expressed with eight bytes.]

Default name of field in LIMS	Can default name be changed in LIMS?	Example field name in an isotope hydrology laboratory	Can field be omitted in a Sample Submission file?	Field size in LIMS
Sample ID	Yes	Sample ID	No	70 characters
User Def Caption 2	Yes	Aquifer	Yes	40 characters
User Def Caption 3	Yes	River/Lake	Yes	20 characters
User Def Caption 4	Yes	Conductivity	Yes	20 characters
User Def Caption 5	Yes	Temperature	Yes	20 characters
User Def Caption 6	Yes	pH	Yes	30 characters
Caption 7	Yes	Alkalinity	Yes	26 characters
Other Info	Yes	Other Info	Yes	255 characters
Top	Yes	Top	Yes	Double
Bottom	Yes	Bottom	Yes	Double
Elevation	No	Elevation	Yes	Double
Length Unit	No	Length Unit	Yes[1]	1 character
Degrees Lat.	No	Degrees Lat.	Yes	Double
Degrees Lon.	No	Degrees Lon.	Yes	Double
Lat. Long. Acc.	No	Lat. Long. Acc.	Yes	1 character
Country Code	No	Country Code	Yes	2 characters
State/Province	No	State/Province	Yes	Integer
Collection Date/Time	No	Collection Date/Time	Yes	Date/Time
End Coll. Date/Time	No	End Coll. Date/Time	Yes	Date/Time

[1] The "Length Unit" field, which is either meters or feet, should not be omitted if "Top", "Bottom", or "Elevation" is used on the Sample Submission file.

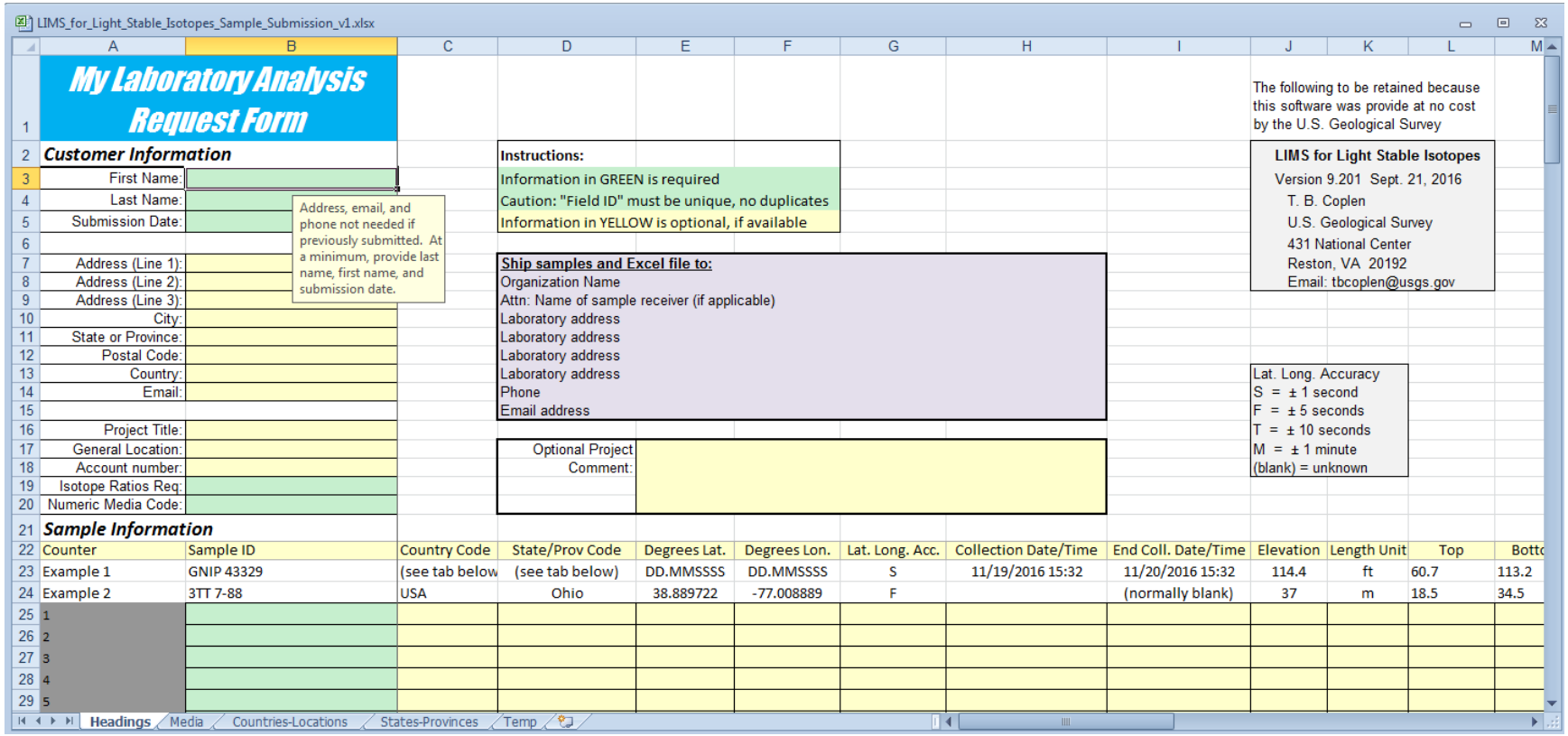


Fig. 7.12. Headings worksheet of "LIMS_for_Light_Stable_Isotopes_Default_Sample_Submission.xlsx." This Excel file can be customized for use by clients to provide information on their samples submitted to the laboratory.

The LIMS for Light Stable Isotopes permission insignia must be retained on Excel sample submission files for legal purposes because this software is provided by the U.S. Geological Survey at no cost. The spreadsheet will not import properly without it.

The “Headings” worksheet (Fig. 7.12) contains the information provided by a customer about their samples and the sample project. Although the “Media” worksheet is not required, it should be retained and modified to provide laboratory clients with the specific LIMS media codes that can be analyzed by the laboratory. The “Countries-Locations” worksheet lists countries and their codes for use in LIMS, and this worksheet can be deleted if geographic information is not collected and stored in LIMS. The “States-Provinces” worksheet lists the state or province names and codes for use in LIMS, and this worksheet can be deleted if geographic information is not collected and stored. The Temp worksheet can be used by customers as needed.

To customize the default sample submission file, a laboratory should make the following changes to the sample submission file shown in Figure 7.12 and found in the Section 7 folder of the files accompanying this manual:

1. Open file with Excel.
2. Select the Excel “Review” tab.
3. Click the “Unprotect Sheet” icon to unprotect the worksheet because it is locked (with no password). If Excel requests a password, click “OK.”
4. In cell A1 enter the organization name (and logo if desired).
5. Range D7:H15 may be edited to identify the shipping address of the isotope laboratory and laboratory personnel contact information.
6. The range B22:T22 contains the 19 names of LIMS sample data fields shown in the first column of Table 7.1. Decide which names should be retained, which omitted, and which changed (see the second column of Table 7.1 to identify names that can be changed).
7. For each field name to be omitted (deleted), delete the information in its column between rows 22 and 174. Any or all field names, except “Counter” and “Sample ID,” can be omitted (removed).
8. For each field name to be changed (maximum of 10 as noted in Table 7.1), replace the existing name with the new name. In the same column, update the example information in rows 23 and 24 to give your clients hints on providing the desired data.
9. If any field names were deleted in step 7, populate the range between rows 22 and 174 by moving any data fields from the right to the empty range. For example, if “Caption 7” was the only field name omitted in step 7, move “Other Info” (range T22:T174 to S22:S174). **Do not move only the top few cells in the range. Move all cells between rows 22 and 174 because each range has its own validation.** For example, the validation for cells T25:T174 is limited to a maximum of 26 characters because the last column of Table 7.1 shows that the field “Caption 7” is limited to 26 characters.
10. This worksheet contains space for 150 samples, and customers enter their Sample IDs into cells B25:B174. If space for more samples is needed, the worksheet can be extended as long as the integers in the column A counter are incremented.

11. Note that the order of field names in the worksheet does not matter, and users can customize the worksheet to meet their needs.
12. If desired, the information in the range A7:B18 can be deleted or changed. Additional rows can be added—LIMS will identify the field names no matter what row they are in.
13. The "LIMS for Light Stable Isotopes" insignia in range J2:L8 can be moved, but it must be retained; otherwise the data on the worksheet will not be imported by LIMS.
14. If geographic information is not required nor desired from customers, rows 22 to 174 of columns C, D, E, F, and G can be deleted, and the worksheets "Countries-Locations" and "States-Provinces" also can be removed.
15. If latitude and longitude have been omitted, the legend for latitude-longitude accuracy in the range J13:K14 can be removed.
16. The revised field names on the Excel file must match exactly the "Alternative Field Names for Samples Form" on the LIMS Options form (Figs. 4.11 and 7.13). On the LIMS main page, click "Special Features."
17. Click "Options."
18. Click "Edit."
19. Edit the "Alternative Field Names" (see Fig. 7.13). If a laboratory does not use some of the alternative field names (*e.g.* "Caption 7"), those alternative field names should be deleted from the Options form so that these text boxes are blank.
20. Switch to the "Media" worksheet and delete all the media that the laboratory does not analyze.
21. After creating new media (see Appendix A), add them to the "Media" worksheet.
22. Click "Save" and click "Close."

⚠ **Caution:** Frequent modifications to the headings in the sample submission file is strongly discouraged to prevent import errors.

There is considerable flexibility in modifying the LIMS sample submission files. Before customizing the default file, users may want to examine the following example sample submission files, which may be found in the Section 7 folder accompanying this manual:

1. "WSU_sample_submission_for_bulk_samples.xlsx" (Fig. 7.14).
2. "WSU_sample_submission_for_preweighed_samples.xlsx" (Fig. 7.15).
3. "Memorial_Univ_Newfoundland_Example_Sample_Submission.xlsx" (Fig. 7.16).
4. "Univ_Ottawa_sample_submission.xlsx" (Fig. 7.17).

These examples display many of the possibilities available for modifying the default sample submission file.

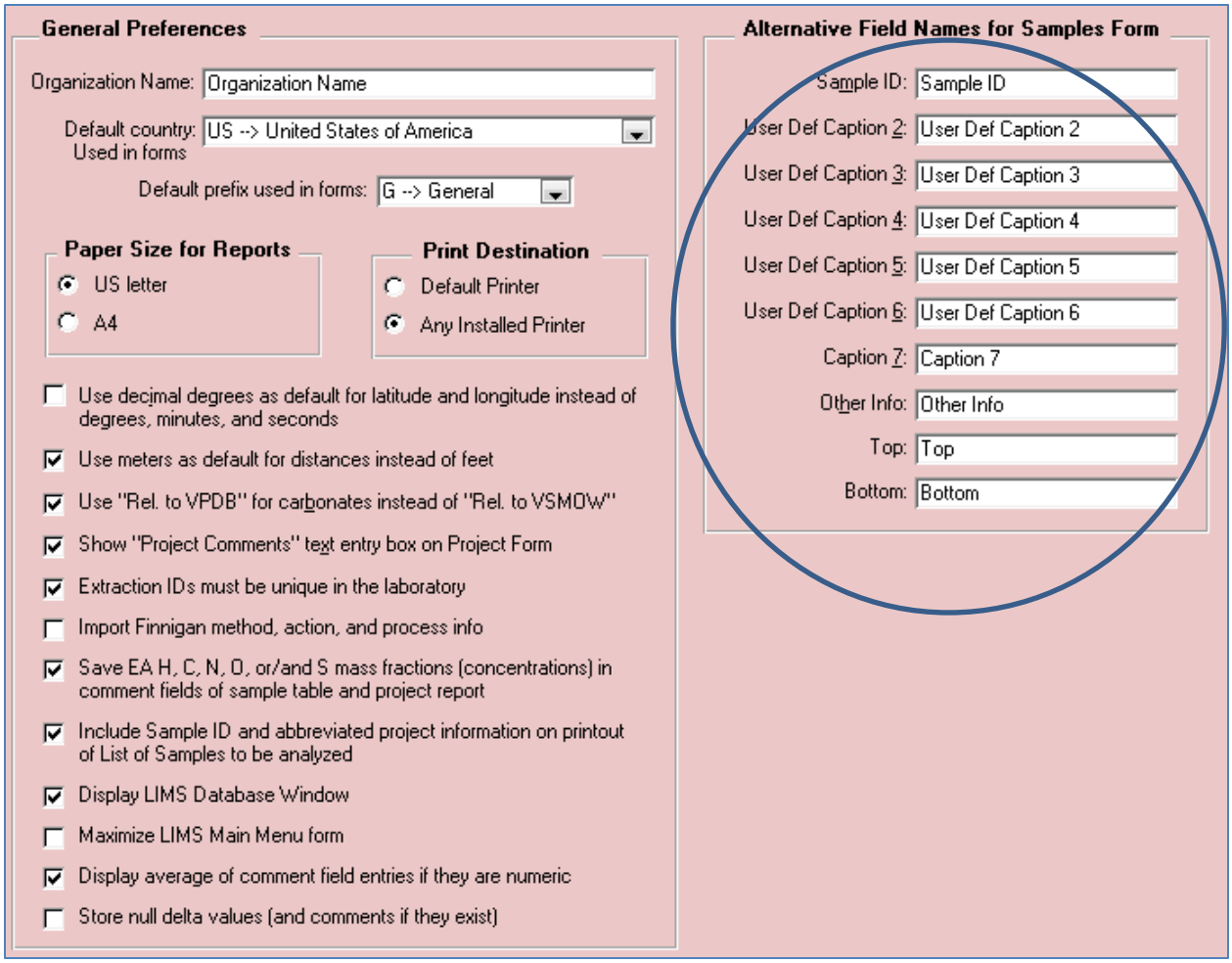


Fig. 7.13. Options page highlighting the 10 alternative field names that are customizable.

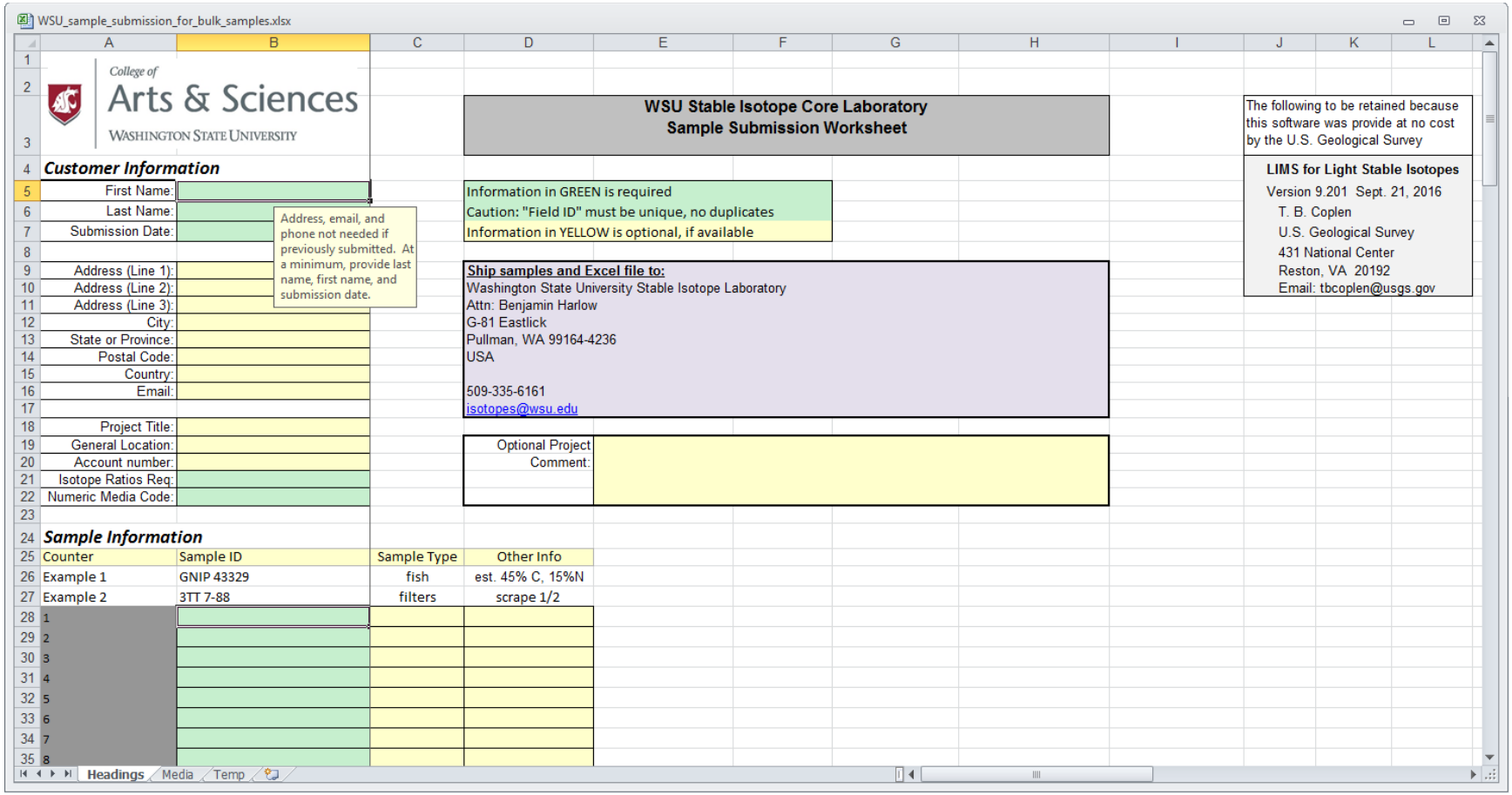


Fig. 7.14. Headings worksheet for bulk samples of the Washington State University Stable Isotope Core Laboratory. This Excel file is named "WSU_sample_submission_for_bulk_samples.xlsx" and is found in the folder named "Sample Submission Examples." This file was kindly provided by Benjamin Harlow (Washington State University, Pullman, WA, USA).

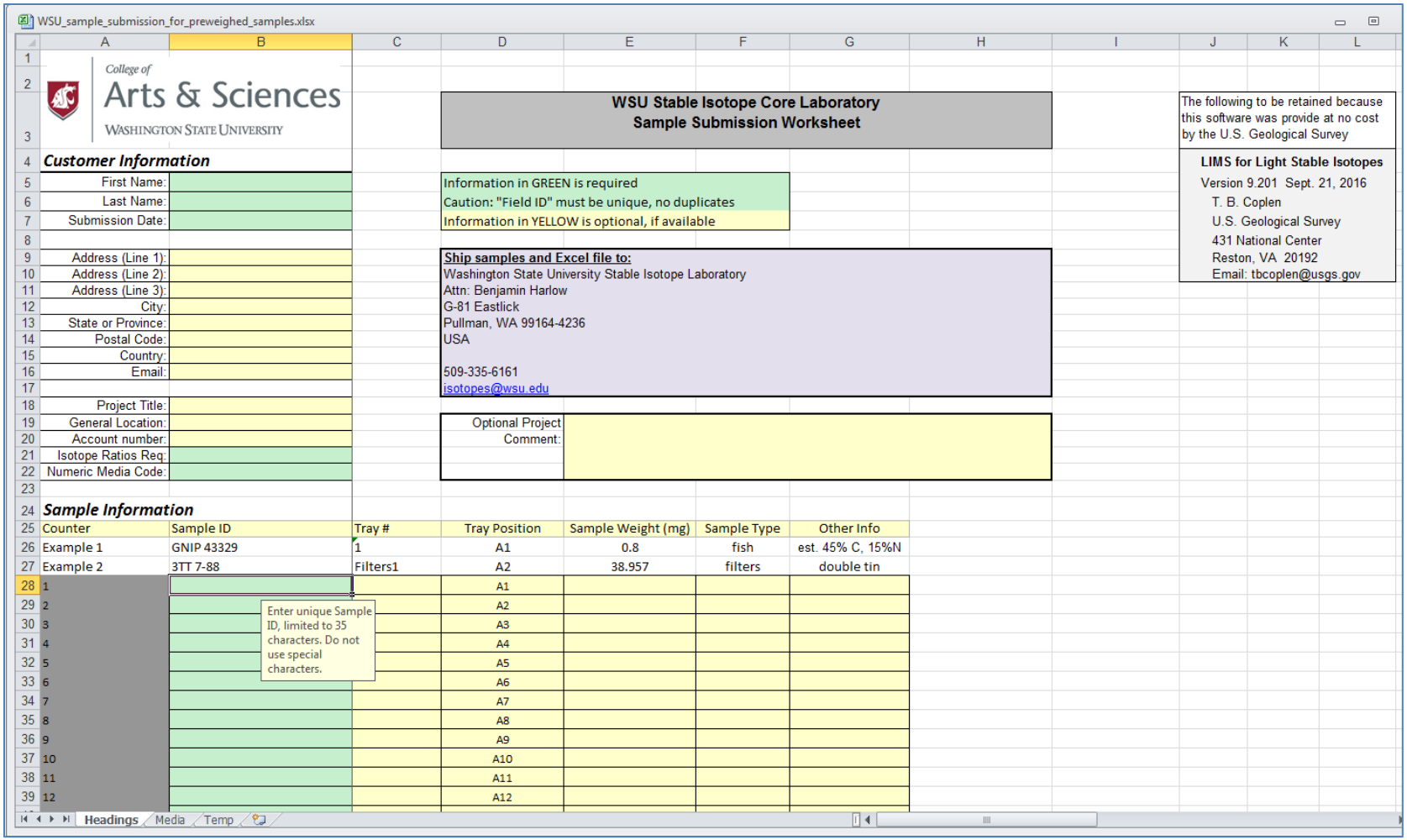
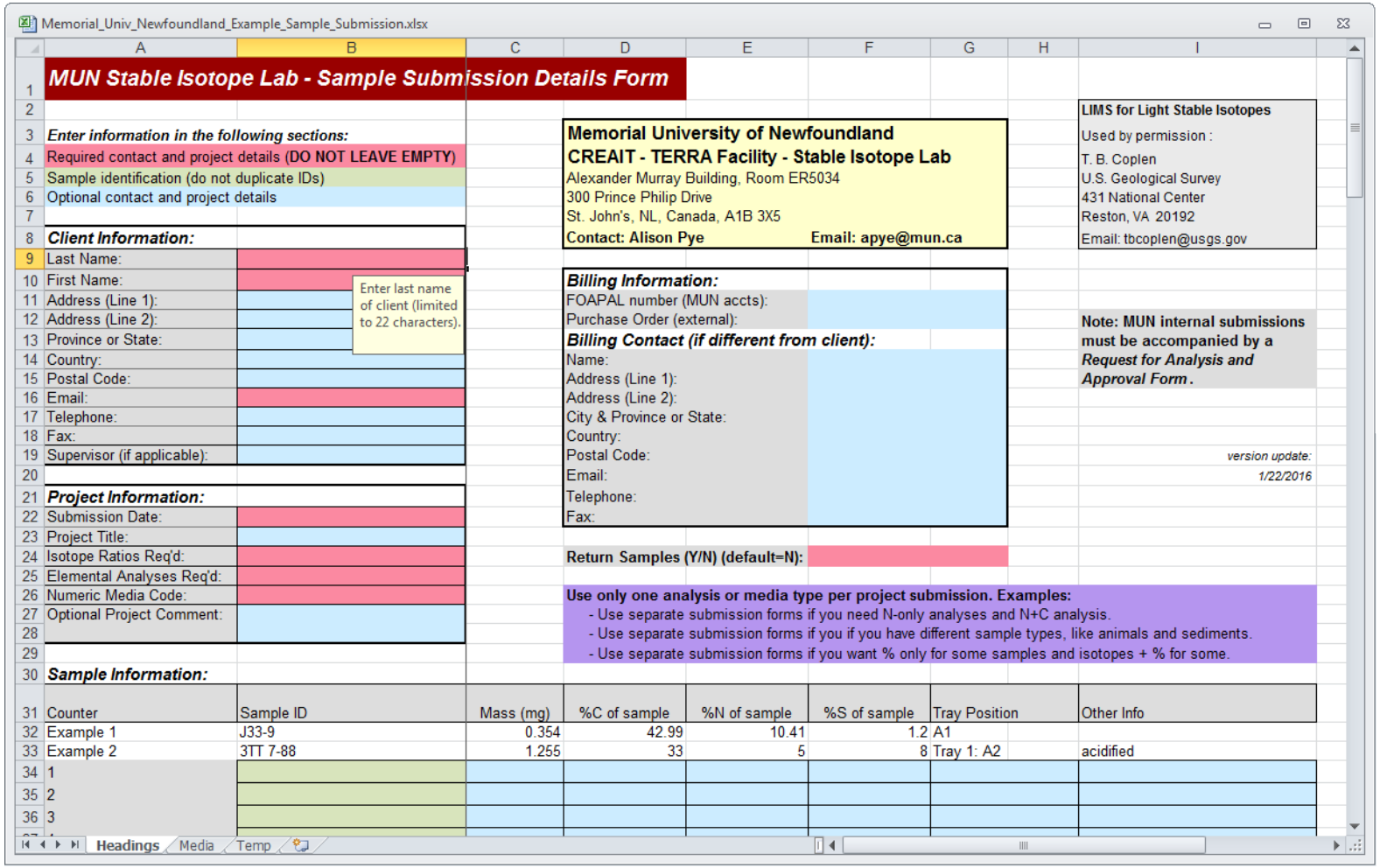


Fig. 7.15. Headings worksheet for preweighed samples of the Washington State University Stable Isotope Core Laboratory. This Excel file is named "WSU_sample_submission_for_preweighed_samples.xlsx" and is found in the folder named "Sample Submission Examples." This file was kindly provided by Benjamin Harlow (Washington State University, Pullman, WA, USA).



Memorial_Univ_Newfoundland_Example_Sample_Submission.xlsx

MUN Stable Isotope Lab - Sample Submission Details Form

Enter information in the following sections:
Required contact and project details (DO NOT LEAVE EMPTY)
Sample identification (do not duplicate IDs)
Optional contact and project details

Memorial University of Newfoundland
CREAIT - TERRA Facility - Stable Isotope Lab
Alexander Murray Building, Room ER5034
300 Prince Philip Drive
St. John's, NL, Canada, A1B 3X5
Contact: Alison Pye **Email: apye@mun.ca**

LIMS for Light Stable Isotopes
Used by permission :
T. B. Coplen
U.S. Geological Survey
431 National Center
Reston, VA 20192
Email: tbcoplen@usgs.gov

Client Information:
Last Name:
First Name:
Address (Line 1):
Address (Line 2):
Province or State:
Country:
Postal Code:
Email:
Telephone:
Fax:
Supervisor (if applicable):

Enter last name of client (limited to 22 characters).

Billing Information:
FOAPAL number (MUN accts):
Purchase Order (external):
Billing Contact (if different from client):
Name:
Address (Line 1):
Address (Line 2):
City & Province or State:
Country:
Postal Code:
Email:
Telephone:
Fax:

Note: MUN internal submissions must be accompanied by a *Request for Analysis and Approval Form*.

version update:
1/22/2016

Project Information:
Submission Date:
Project Title:
Isotope Ratios Req'd:
Elemental Analyses Req'd:
Numeric Media Code:
Optional Project Comment:

Return Samples (Y/N) (default=N):

Use only one analysis or media type per project submission. Examples:
- Use separate submission forms if you need N-only analyses and N+C analysis.
- Use separate submission forms if you if you have different sample types, like animals and sediments.
- Use separate submission forms if you want % only for some samples and isotopes + % for some.

Sample Information:

Counter	Sample ID	Mass (mg)	%C of sample	%N of sample	%S of sample	Tray Position	Other Info
Example 1	J33-9	0.354	42.99	10.41	1.2	A1	
Example 2	3TT 7-88	1.255	33	5	8	Tray 1: A2	acidified
1							
2							
3							

Headings | Media | Temp

Fig. 7.16. Headings worksheet of the Memorial University of Newfoundland. The Excel file is named "Memorial_Univ_Newfoundland_Example_Sample_Submission.xlsx" and is found in the folder named "Sample Submission Examples." This file was kindly provided by Alison Pye (Memorial University of Newfoundland, St. John's, Newfoundland, Canada).

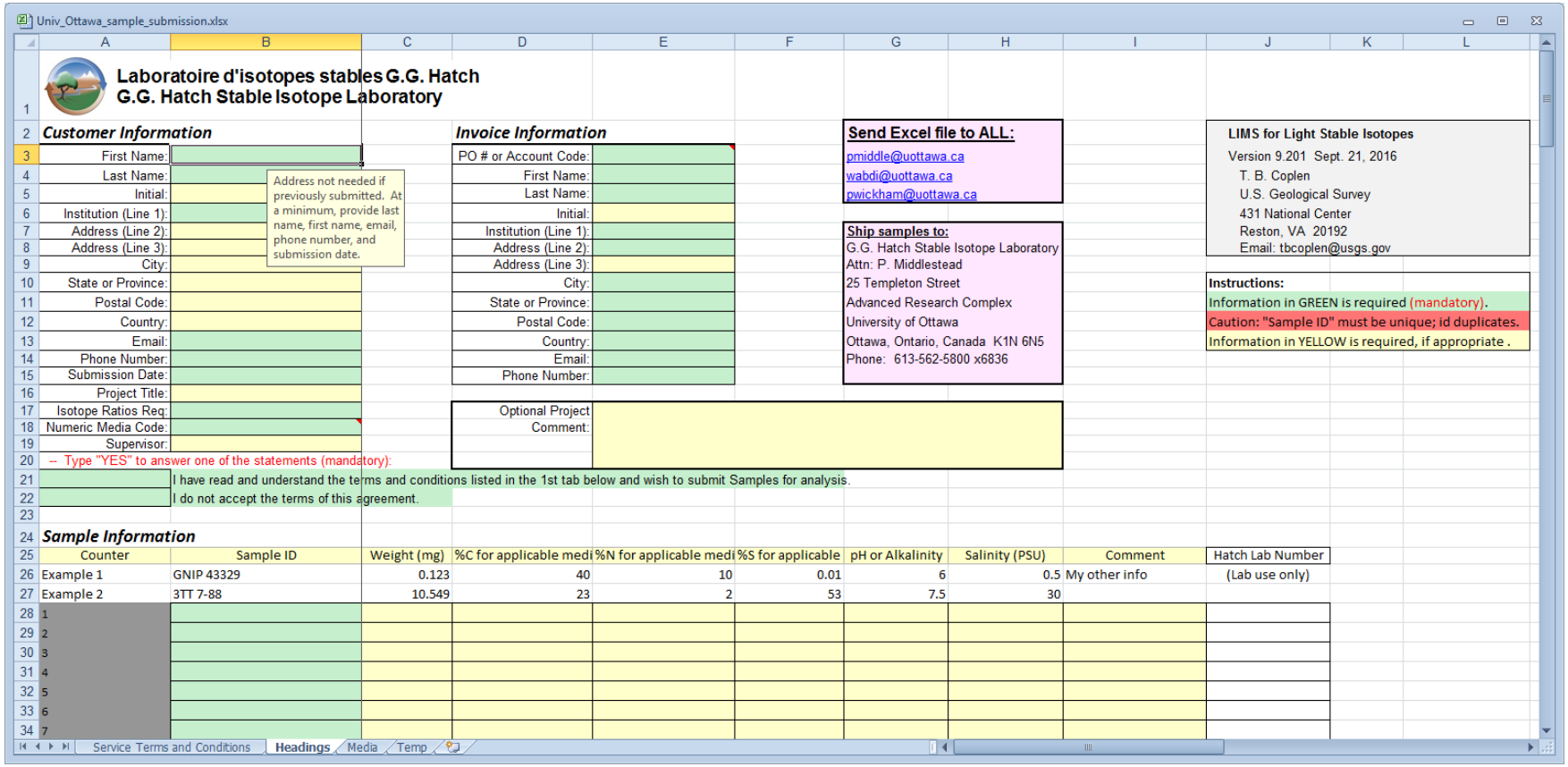


Fig. 7.17. Headings worksheet of the G. G. Hatch Stable Isotope Laboratory. The Excel file is named "Univ_Ottawa_sample_submission.xlsx" and is found in the folder named "Sample Submission Examples." This file was kindly provided by Wendy Abdi and Paul Middlestead (University of Ottawa, Ottawa, Ontario, Canada).

7.5.2 Sample Submission Template Protection

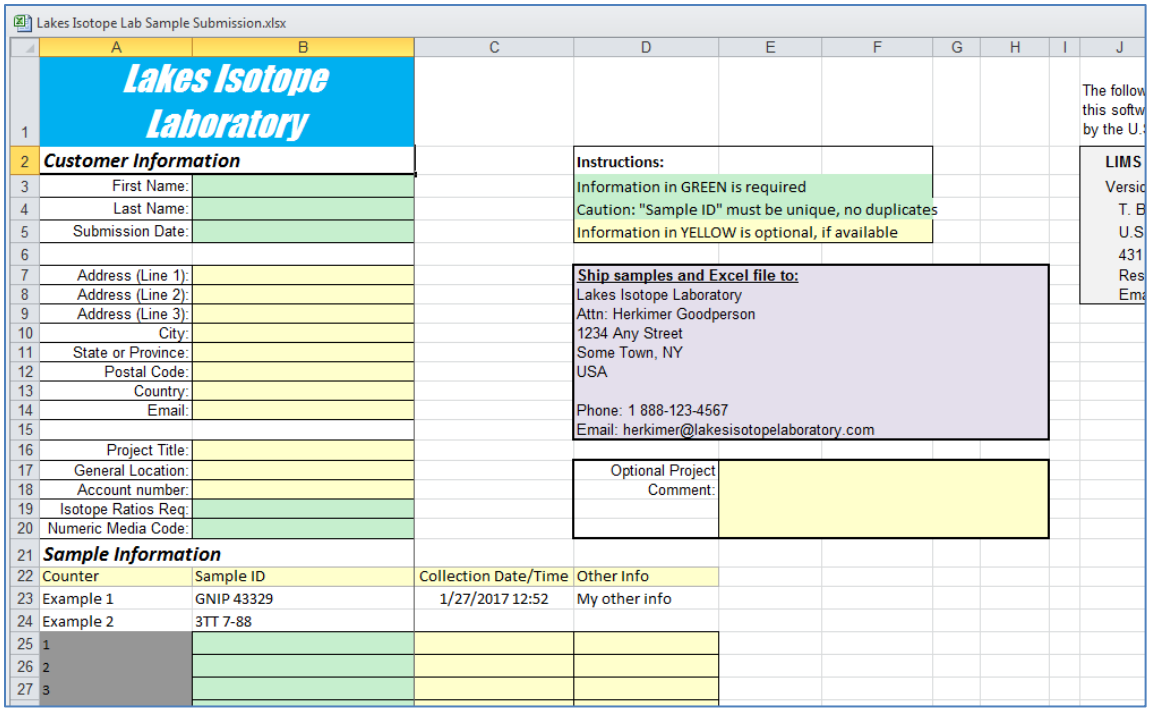
Experience has shown that distributed Excel sample submission files are invariably tampered with by customers (*e.g.* customers may delete or add columns, paste incorrect cell formats, paste to a new spreadsheet, etc.), all of which cause a LIMS import failure. For this reason, the "Headings" worksheet should be "protected" to allow clients to enter data only in those fields required by the laboratory. While Excel cell protection is not foolproof, your laboratory should also provide explicit instruction on its use. To help protect the Sample Submission Excel file of your laboratory:

1. In Excel, Click on the "Review" Tab.
2. Click on "Protect Sheet" and enter a password.
3. Save the file and distribute to customers.
4. Now clients can add their project and sample information to the project and sample data fields required by LIMS. All other fields should be locked to prevent editing, unless the password is entered.

7.5.3 Populating an Excel Sample Submission File

Consider an example in which the Lake Isotope Laboratory has created an Excel sample submission file named "Lakes Isotope lab Sample Submission.xlsx" following the instructions in Sections 7.51 and 7.52 (see Fig. 7.19). In the files that accompany this manual, this Excel file can be extracted from a file named "Lakes_LIMS_Example.zip" that is provided in a folder named "Section 4" in files that accompany this manual. Assume Cyrus Snodgrass has downloaded the sample submission file from the Web site of the Lakes Isotope Laboratory. To create a submission file for three samples for carbon- and nitrogen-isotope analysis, Cyrus Snodgrass carries out the following steps:

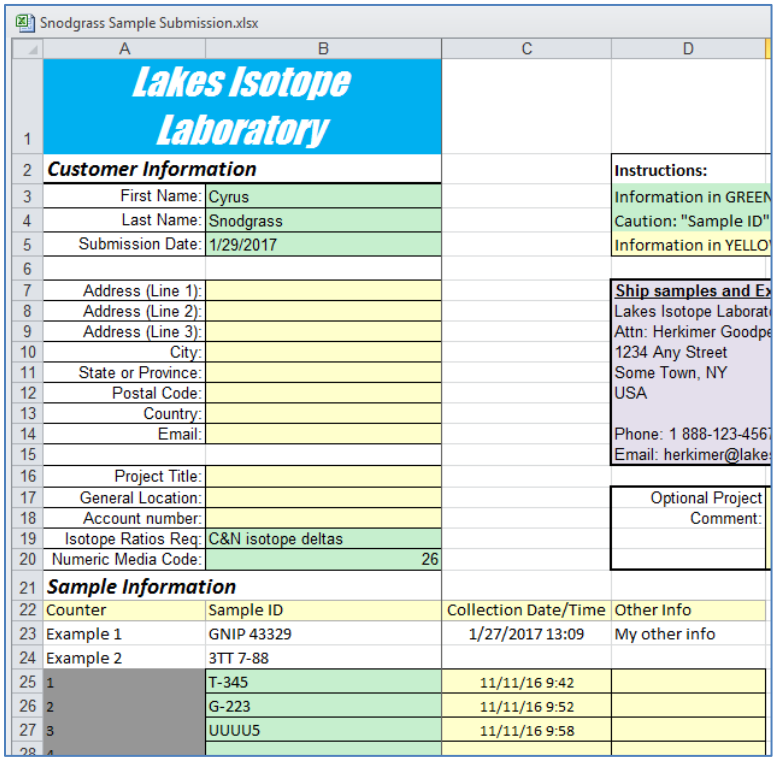
1. Open "Lakes Isotope lab Sample Submission.xlsx" with Excel.
2. Save the file with a new filename: "Snodgrass Sample Submission.xlsx."
3. In column B, populate cells with green background, entering the first name, last name, submission date, and the isotope ratios required as shown in Figure 7.19.
4. To find the numeric media code, open the "Media" worksheet (Fig. 7.20).
5. Note that the medium for carbon- and nitrogen-bearing materials is 26.
6. Return to the "Headings" worksheet and enter 26 in cell B20 for the media code.
7. Enter Sample IDs in B25 to B27 as shown in Figure 7.19.
8. Enter dates in cells C25 to C27 as shown in Figure 7.19.
9. If desired one could enter a project title, a general location, an account number, an optional project comment, etc.
10. Save and close Excel. The file is now ready for importing.



Lakes Isotope Lab Sample Submission.xlsx

	A	B	C	D
1	Lakes Isotope Laboratory			
2	*Customer Information*			Instructions:
3	First Name:			Information in GREEN is required
4	Last Name:			Caution: "Sample ID" must be unique, no duplicates
5	Submission Date:			Information in YELLOW is optional, if available
6				
7	Address (Line 1):			Ship samples and Excel file to:
8	Address (Line 2):			Lakes Isotope Laboratory
9	Address (Line 3):			Attn: Herkimer Goodperson
10	City:			1234 Any Street
11	State or Province:			Some Town, NY
12	Postal Code:			USA
13	Country:			
14	Email:			Phone: 1 888-123-4567
15				Email: herkimer@lakesisotopelaboratory.com
16	Project Title:			
17	General Location:			Optional Project Comment:
18	Account number:			
19	Isotope Ratios Req:			
20	Numeric Media Code:			
21	*Sample Information*			
22	Counter	Sample ID	Collection Date/Time	Other Info
23	Example 1	GNIP 43329	1/27/2017 12:52	My other info
24	Example 2	3TT 7-88		
25	1			
26	2			
27	3			

Fig. 7.18. Lakes Isotope Laboratory Excel sample submission file.



Snodgrass Sample Submission.xlsx

	A	B	C	D
1	Lakes Isotope Laboratory			
2	*Customer Information*			Instructions:
3	First Name:	Cyrus		Information in GREEN
4	Last Name:	Snodgrass		Caution: "Sample ID"
5	Submission Date:	1/29/2017		Information in YELLO
6				
7	Address (Line 1):			Ship samples and Ex
8	Address (Line 2):			Lakes Isotope Laborat
9	Address (Line 3):			Attn: Herkimer Goodpe
10	City:			1234 Any Street
11	State or Province:			Some Town, NY
12	Postal Code:			USA
13	Country:			
14	Email:			Phone: 1 888-123-456
15				Email: herkimer@lake
16	Project Title:			
17	General Location:			Optional Project Comment:
18	Account number:			
19	Isotope Ratios Req:	C&N isotope deltas		
20	Numeric Media Code:	26		
21	*Sample Information*			
22	Counter	Sample ID	Collection Date/Time	Other Info
23	Example 1	GNIP 43329	1/27/2017 13:09	My other info
24	Example 2	3TT 7-88		
25	1	T-345	11/11/16 9:42	
26	2	G-223	11/11/16 9:52	
27	3	UUUU5	11/11/16 9:58	

Fig. 7.19. Snodgrass' Excel sample submission file.

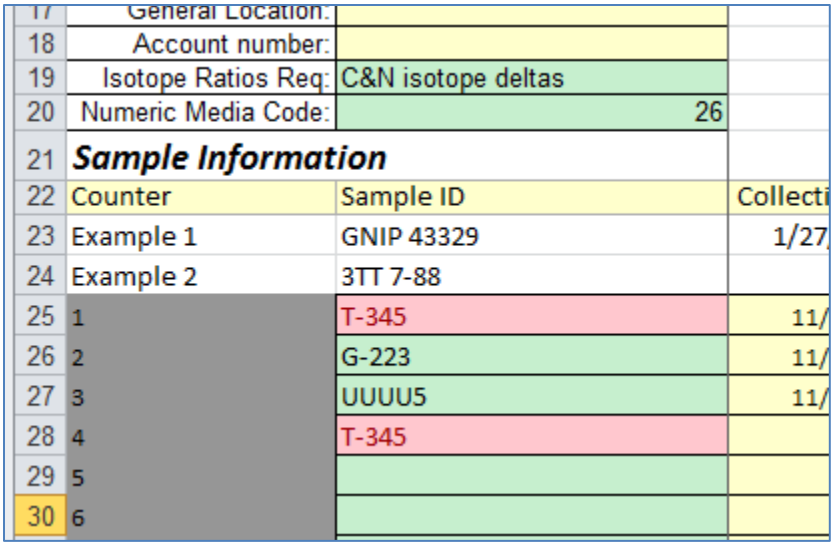
Snodgrass Sample Submission.xlsx

	A	B	C
1	Media Code	Prefix	Media
2	1	W	water (H & O)
3	2	C	calcite
4	3	C	dolomite
5	4	C	DIC
6	5	G	gaseous carbon dioxide
7	6	G	gaseous hydrogen
8	7	G	gaseous carbon monoxide
9	8	R	gaseous carbon dioxide reference
10	9	G	gaseous carbon monoxide reference
11	10	R	gaseous hydrogen reference
12	12	R	gaseous nitrogen reference
13	13	R	gaseous nitrous oxide reference
14	14	R	gaseous sulfur dioxide reference
15	16	R	gaseous oxygen reference
16	19	G	H- and O-bearing material
17	20	G	methane (H & C)
18	21	G	coal (H & C)
19	22	G	oil (H & C)
20	23	G	cellulose (H & C)
21	24	G	other H-bearing material
22	25	G	organic C
23	26	G	C- and N-bearing material
24	27	G	C- and O-bearing material
25	28	G	C- and S-bearing material
26	29	G	C- and Cl-bearing material
27	30	G	other C-bearing material
28	31	C	aragonite
29	35	C	lithium carbonate
30	37	C	barium carbonate
31	41	C	lead carbonate
32	45	C	other carbonate
33	46	G	graphite
34	50	N	pure nitrogen gas
35	52	N	N-bearing solid (salts, rock, etc)
36	55	N	water (dissolved nitrate)
37	58	N	other N- & O-bearing materials
38	59	N	other N-bearing material

Headings | Media | Temp

Fig. 7.20. "Media" worksheet of the sample submission file.

Each Sample ID must be unique in LIMS. If the customer enters duplicate Sample IDs, the background of the duplicates turns to red. The only required column headings are columns A (Counter) and B (Sample ID).



17	General Location:		
18	Account number:		
19	Isotope Ratios Req:	C&N isotope deltas	
20	Numeric Media Code:	26	
21	***Sample Information***		
22	Counter	Sample ID	Collecti
23	Example 1	GNIP 43329	1/27
24	Example 2	3TT 7-88	
25	1	T-345	11/
26	2	G-223	11/
27	3	UUUU5	11/
28	4	T-345	
29	5		
30	6		

Fig. 7.21. The backgrounds of duplicate Sample IDs turn red.

This Excel submission file will alert users when they enter in a duplicate sample ID by highlighting the cells in red, as shown in Fig. 7.21.

7.5.4 Creating a New Project by Importing an Excel Sample Submission File

Consider that the Lakes Isotope Laboratory has received the sample submission file shown in Figure 7.19 from Cyrus Snodgrass, and it needs to be imported into LIMS. To Import the Excel file and create a new project:

1. Open LIMS if not already open and the main menu of the Lakes Isotope Laboratory should appear as in Figure 4.8.
2. On the LIMS main page, click "Import a New Project from Excel Submission" under the "Projects" heading.
3. In the Windows filename dialog box, navigate to the Excel sample submission file to be imported ("Snodgrass Sample Submission.xlsx"), which should be in the same folder as the Lakes backend database, and click "Select." LIMS should import the spreadsheet and notify the user that there are three samples in the project (Fig. 7.22).
4. Click "OK" and LIMS will display a confirmation dialog box (Fig. 7.23) that indicates the Our Lab IDs of the samples to be imported. Click "OK."
5. Click "OK" to complete the import of Cyrus Snodgrass' sample and create a new project having three samples with Our Lab IDs of G-1213, G-1214, and G-1215.

Before importing an Excel file, ensure the customer has been added to the customer list and double check that their first and last names are spelled exactly the same in the customer list and the Sample Submission Excel file.

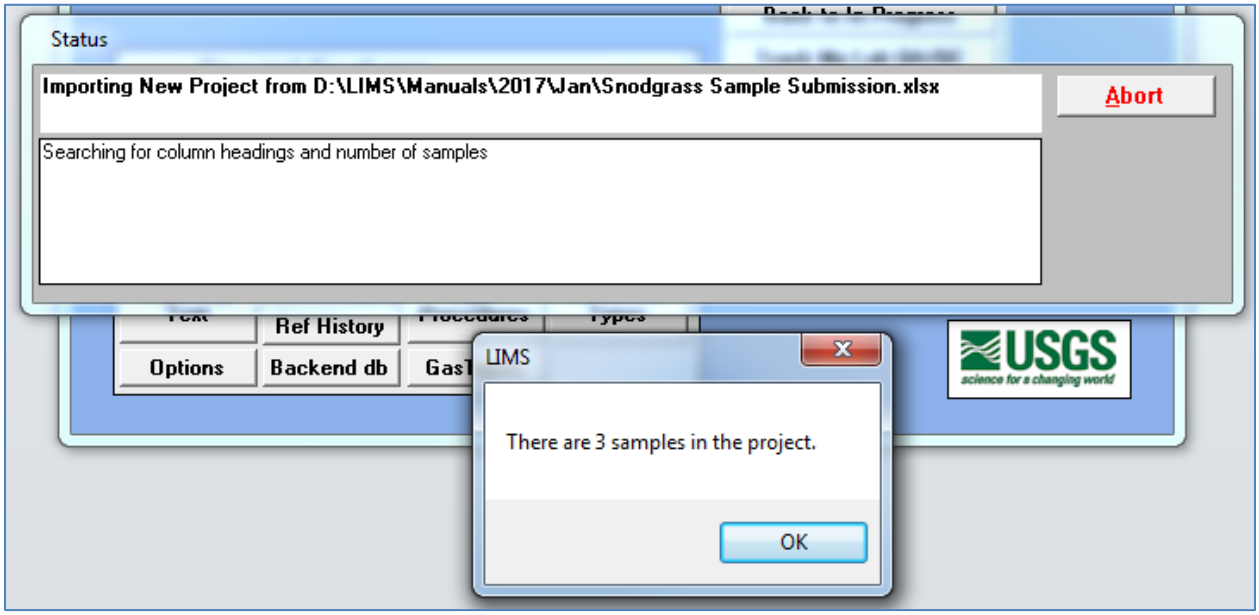


Fig. 7.22. LIMS prompt to confirm the number of samples to be imported.

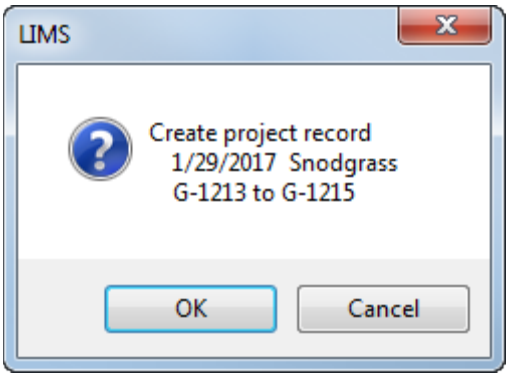


Fig. 7.23. Confirmation dialog box indicating the Our Lab IDs of samples to be imported.

The imported project can be viewed by clicking "View Projects -->" on the LIMS main page and double-clicking the project with Our Lab IDs "G-1213 to G-1215" (see Fig. 7.24), which opens the Project form (see Section 7.6 for discussion of the Project form).

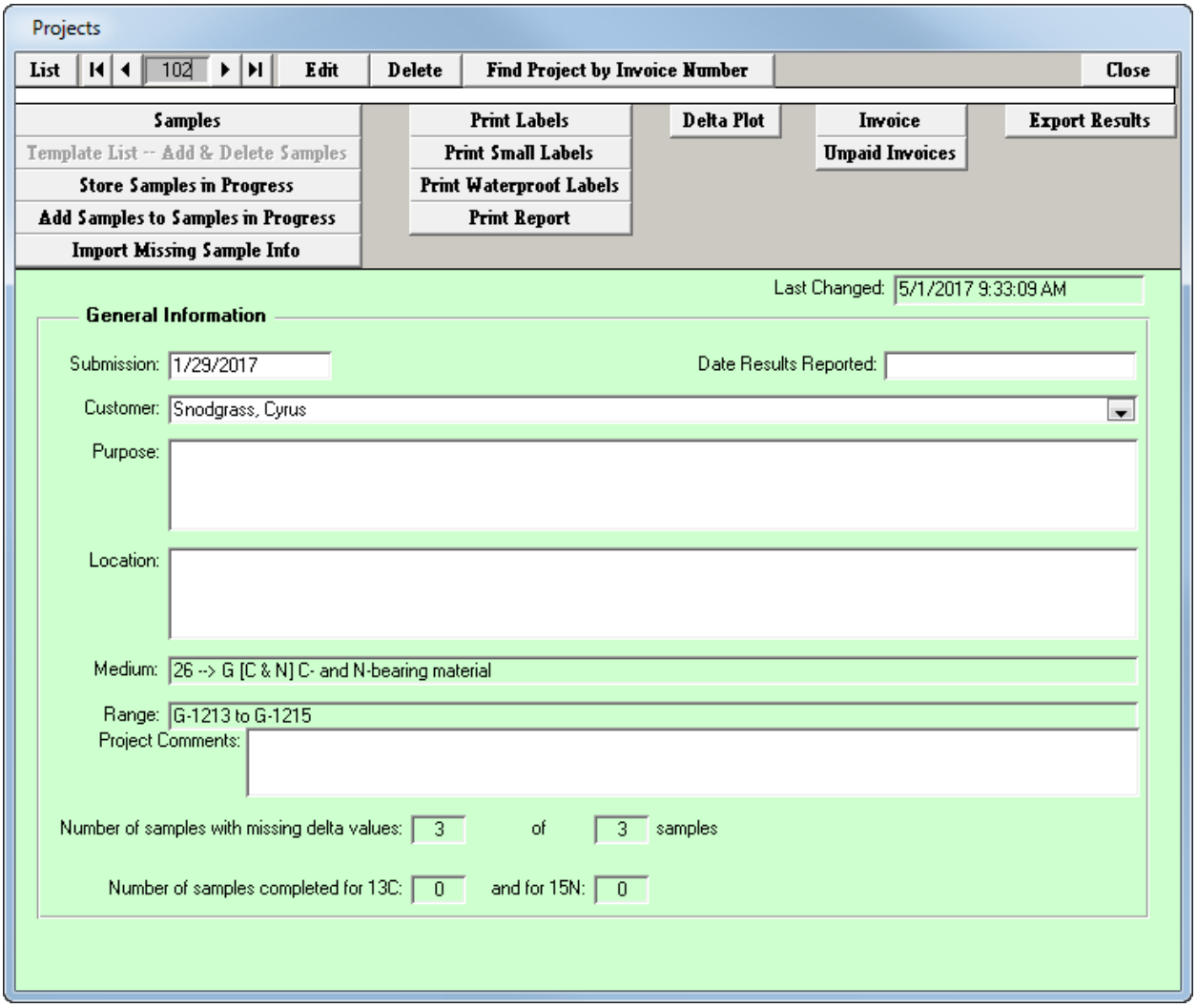


Fig. 7.24. The Projects form resulting from import of Cyrus Snodgrass' file.

If a user attempts to import a Sample Submission Excel file into a fresh LIMS IRMS backend database for a new laboratory, LIMS will prompt the user that a mass spectrometer needs to be installed before the Excel file can be imported. This is intentional and is an example of the validation provided throughout LIMS. One should not be able to import samples for carbon and nitrogen isotopic analysis unless the laboratory has an IRMS that is capable of performing these measurements.

7.5.5 Tips for a Successful Excel Sample Submission File

Below are some tips for the successful use of Excel sample submission forms.

In the Laboratory

- Download the default Excel sample submission file and add/edit your required data (contact information, address, add laboratory logos, etc.).
- Ensure any changed alternative field names in the Excel file **exactly** match those in the LIMS "Options" form.
- Ensure that all the media on the "Media" worksheet can be accepted by the laboratory.
- Protect your distributable Excel sample submission file with a password.
- Test your new Excel sample submission file with dummy data to ensure that imports work correctly.
- **Do not** combine different customer samples into a single project—this will be confusing.
- **Do not** change the name of the "Headings" worksheet—this will cause an import error in LIMS.

For the Customer

- Download the protected Excel sample submission file from the Web site of the laboratory.
- It is recommended that customers keep a copy of the original Excel sample submission file for future samples.
- Customers should complete their information and "Save As" using an appropriately descriptive filename.
- The Excel sample submission file should be sent to the isotope laboratory by email, and a paper copy of the Excel file should accompany the samples.
- The minimum items required are: Last name, First name, Submission Date, Media code, and Sample IDs.
- **Do not** change the name of the "Headings" worksheet—this will cause an import error in LIMS.

7.6 The Projects Form

7.6.1 Finding, Editing, and Deleting Projects

Attributes of a LIMS project include:

- Project submission date.
- Last names of sample submitter.
- Range of Our Lab IDs.

- Medium.
- Purpose.
- Location.
- Date results were reported to sample submitter.

These data are viewed and edited with the Project form (Fig. 7.24), which is opened by double-clicking the desired project in the lower panel of the Find Project form (Fig. 7.1) or selecting the project and clicking "Open Selected Project" (Fig. 7.1). In addition to the attributes above, the Projects form also displays:

- A "Project Comments" field.
- The number of samples with missing isotope-delta values or atom fraction values, depending upon the medium.
- The number of sample completed for the low isotope-delta value (see Section 6.1 and Table 6.1 for discussion of the low isotope).
- The number of samples completed for the high isotope-delta value if the medium has two isotopes (see Section 6.1 and Table 6.1 for discussion of the high isotope).

The top row of the Projects form has buttons to navigate to, edit, and delete a project. Specifically: Other buttons and their action include the following:

- The four navigation buttons (see Figs. 5.2 and 5.3) enable users to navigate through the project records.
- Clicking the "List" button causes LIMS to display as many and 40 projects.
- The "Edit" button enables users to edit the submission date, customer, purpose, location, and project comments. The medium cannot be edited. If the medium needs to be changed, the project will need to be deleted and re-imported with the new media code. If one needs the Our Lab IDs to be the same, it may be necessary to change the next Our Lab ID prior to importing (see Section 7.4).
- The "Delete" button enables a user to delete the project as long as no analyses of any sample in the project exist, commonly used to delete the most recent project logged into LIMS.
- The "Find Project by Invoice Number" button enables a user to search for a project by invoice number. Invoices are discussed in Section 7.6.6.

7.6.2 Samples

The "Samples" button lies immediately below the navigation buttons on the Projects form (Fig. 7.24). Clicking the "Samples" button opens the Sample form for the project 2/7/2017—Snodgrass G-1213 to G-1215 (Fig. 7.25). The first sample in the project (G-1213) is displayed by default. The Samples form is discussed in depth in Section 8.3.

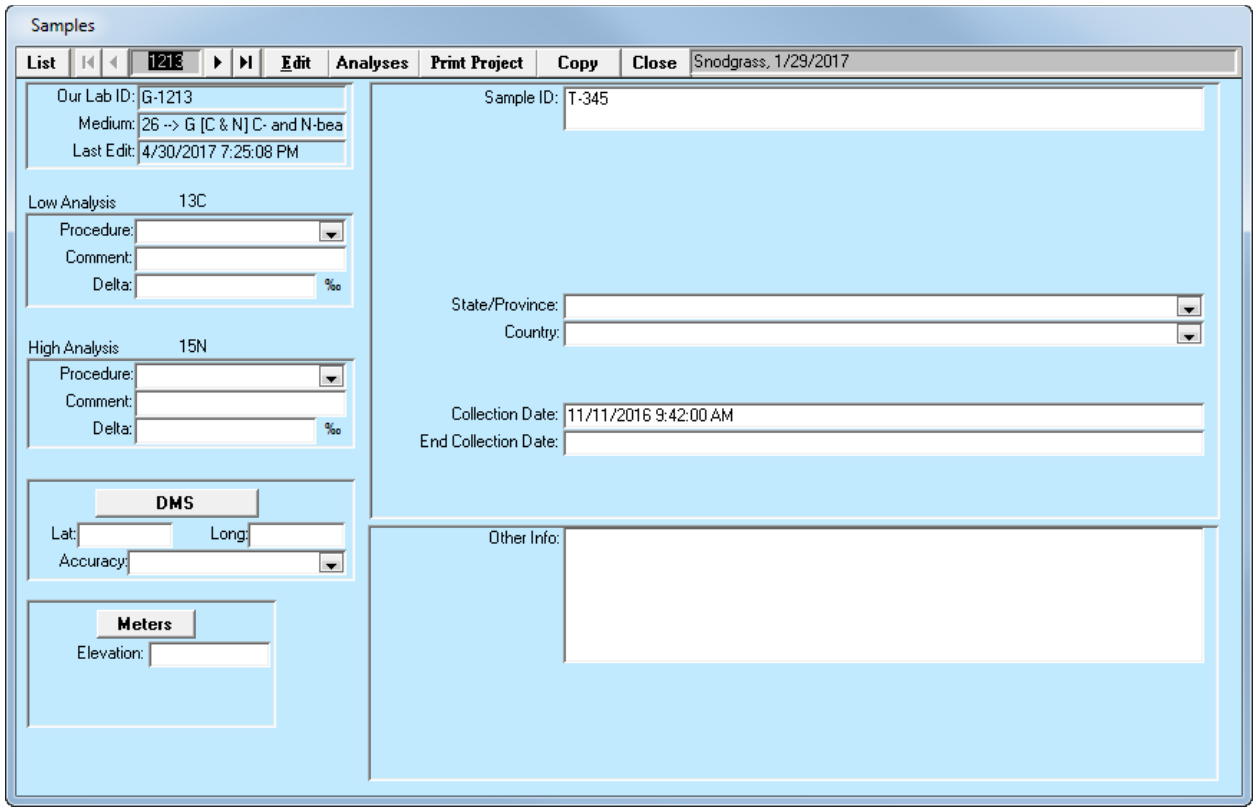


Fig. 7.25. The Samples form for the project 2/7/2017—Snodgrass G-1213 to G-1215.

7.6.3 Shortcut Buttons and Adding and Deleting Samples from Sample Analysis Lists

The Projects form has more than 20 buttons to carry out actions. Many of these buttons are shortcuts for actions that can be achieved by clicking other buttons on the LIMS main page, and they are found in the first column of the Project form. These buttons and their actions are discussed below:

- The "Samples" button opens the Samples form, which is discussed in Section 8.3.
- One of the useful features of LIMS is to create sample lists for instruments. These lists can be used to populate the so-called sequence table of a mass spectrometer. The "Template List – Add & Delete Samples" button enables the user to add or remove samples of this project from the sample analysis template queues used for creating sample lists for mass spectrometers. This feature is discussed in Section 33.5.2.
- The "Store Samples in Progress" button is a shortcut for this project to activate the "Store Final Results to Projects" button on the main page (Fig. 2.1). This button enables a user to "Store" final results of samples of this project for final reporting. This action is carried out after the analyst has normalized all results of samples and controls that were measured, and the analyst is satisfied that their results are acceptable within their

evaluation criteria. Once all samples in a project have been analyzed, LIMS notifies the user that project results are ready to be reported with a "Project Ready to Report" message highlighted in yellow (Fig. 7.26). Storing analytical results is discussed in more detail in Section 28.

- Sometimes results of isotopic analyses need to be re-evaluated after they have been stored. The "Add Samples to Samples in Progress" button is a shortcut for this project to activate the "Add Stored Samples Back to in Progress" on the main page (Fig. 2.1) that enables re-evaluation of analyses of samples. The use of this button is discussed in Section 29.
- The "Import Missing Sample Info" button is useful when a customer provides minimal sample information during sample submission and latter provides additional information. For example, latitudes, longitudes, and well depths may not be available until weeks after sample submission. This new data may be added to the project and its samples using this import feature. Because the last name, first name, date, medium, and Sample IDs of the file with new information must match exactly what already exists in LIMS, it is best to add new information to the original Excel file used to create the project.

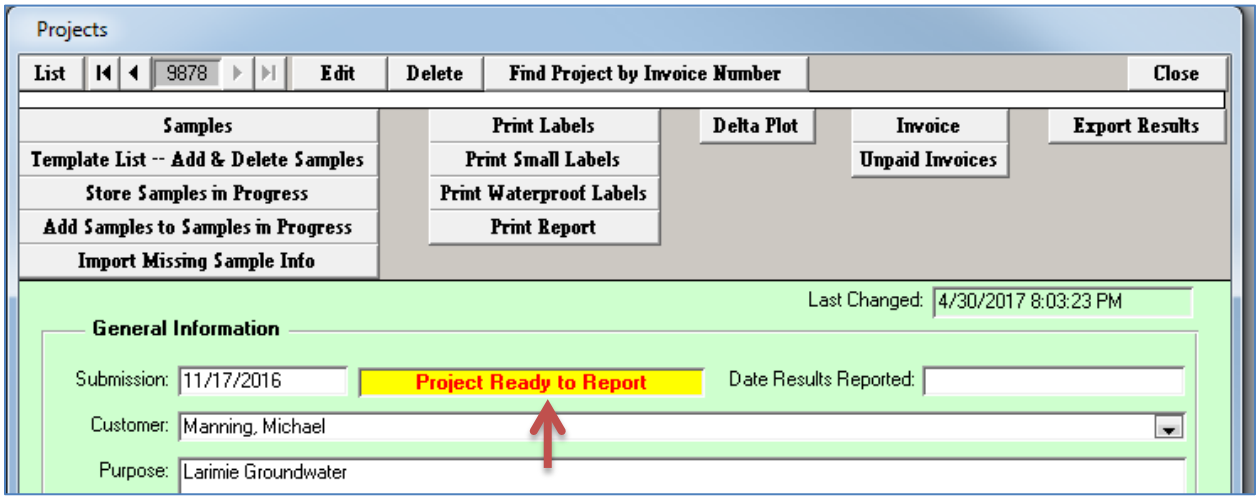


Fig. 7.26. Project Ready to Report message.

Consider that additional project and sample information has been received from Cyrus Snodgrass as shown in Figure 7.27. After importing the Excel file with new data ("Snodgrass Sample Submission with New Info.xlsx"), the Projects form appears as shown in Figure 7.28.

6	Project Title:	Becker evaluation IIB		
7	General Location:	Ravenhill landfill		Optional Project Comment:
8	Account number:			
9	Isotope Ratios Req:	C&N isotope deltas		
10	Numeric Media Code:	26		
11	***Sample Information***			
12	Counter	Sample ID	Collection Date/Time	Other Info
13	Example 1	GNIP 43329	2/10/2017 8:01	My other info
14	Example 2	3TT 7-88		
15	1	T-345	11/11/16 9:42	High H2S
16	2	G-223	11/11/16 9:52	Not filtered
17	3	UUUU5	11/11/16 9:58	Very brown

Fig. 7.27. Snodgrass' Excel sample submission file with new information in red.

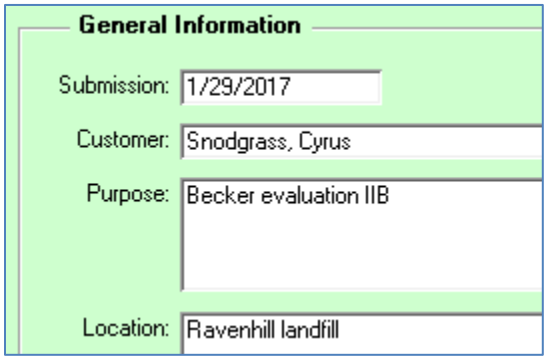


Fig. 7.28. Project form showing new purpose and location provided by Cyrus Snodgrass.

7.6.4 Printing Labels for Samples and Printing a Project Report

The buttons on the second column of the Project form (Fig. 7.24) are used to print adhesive labels (Avery or equivalent) for samples and to print a project report. Table 7.2 shows Avery and NALGENE order numbers. The "Print Waterproof Labels" button will not appear on the Project form if the A4 paper size is selected on the Options form (Fig. 4.12).

Table 7.2. Sample labels in LIMS for U.S. letter and A4 paper sizes

Button name	U.S. letter paper	A4 size paper
Print Labels	Avery 5260 or equivalent (30 labels per sheet)	Avery L7160 or equivalent (21 labels per sheet)
Print Small Labels	Avery 5267 or equivalent (80 labels per sheet)	Avery L7656 or equivalent (84 labels per sheet)
Print Waterproof Labels	NALGENE® PolyPaper labels	Currently not available

To print a label, click "Print Labels" and LIMS prompts whether labels should be printed for every sample in the project (Fig. 7.29). Selecting "Yes" prints labels for all samples, and selecting "No" enables the user to print labels for the desired range of samples in the project. The succeeding LIMS prompt enables users to print one or more labels for each sample.

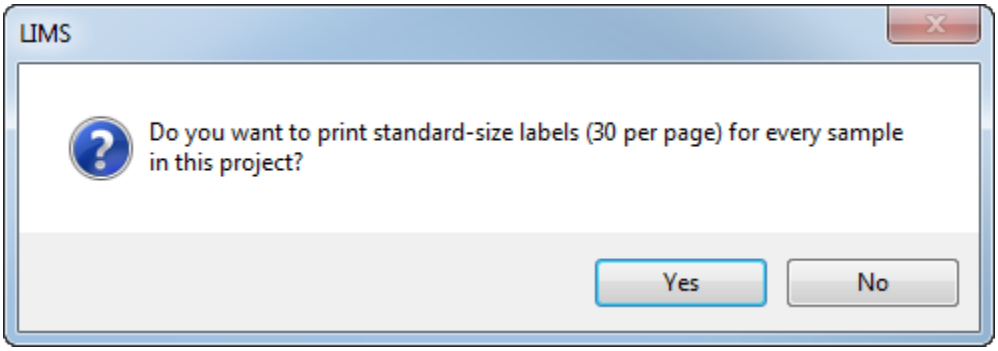


Fig. 7.29. LIMS label-size prompt.

The "Print Report" button prints a project report an example of which is shown in Figure 7.4. If pdf creator software is installed, an electronic report can be selected and created.

7.6.5 Creating Isotope-Delta Plots for Data Evaluation

Before reporting final results of a "W" project, one should examine the results using the "Delta Plot" feature. Clicking the "Delta Plot" button produces a δ^2H versus δ^{18}O cross plot from the Project samples (Fig. 7.30). Be aware the data axes will scale according to the isotope-delta values of the samples. This plot provides a quick means of visualizing the correlation between the two isotope deltas arising from the "global meteoric water line" (GMWL) relationship. The GMWL of Rozanski et al. [3] is used in LIMS and is shown as a turquoise line (Fig. 7.30).

Outliers that fall away from the GMWL may be suspect or they may be acceptable. Non-linear relationships on this plot may result from (1) added isotopic tracers distorting the correlation, (2) natural evaporation, (3) analysis of landfill samples (δ^2H values can plot substantially above the GMWL), or (4) axis scaling artefacts when there is little to no isotopic variation in the project samples. This plot can be of help in identifying samples that were inadvertently switched on an analytical run because two samples may lie far from and on opposite sides of the GWML line.

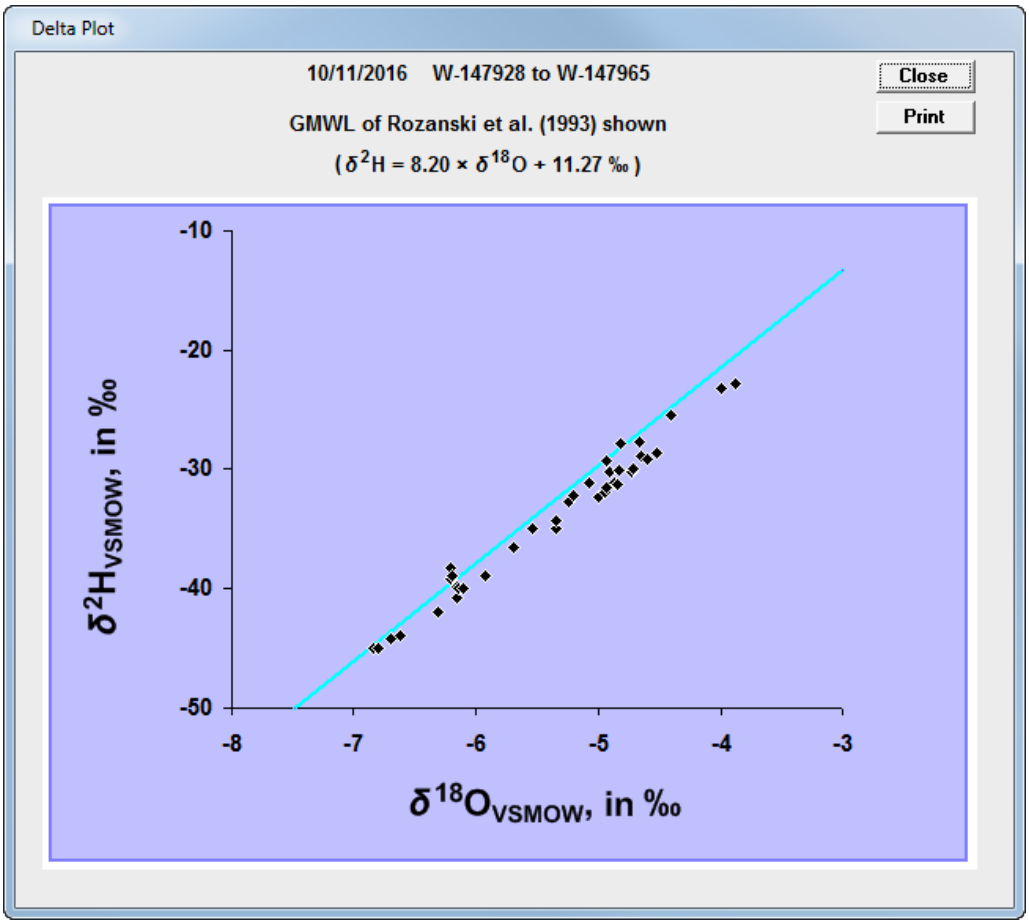


Fig. 7.30. Example isotope-delta plot.

7.6.6 Invoices

LIMS has the capability to create invoices for projects that need to be billed. For example, to create an invoice for the nine water samples submitted by Cyrus Snodgrass in Section 7.5.4:

1. Click "View Projects -->" on the LIMS main page.
2. Select the project Snodgrass W-1001 to W-1009 and open the Projects form by double-clicking this project or clicking "Open Selected Project."

3. Click “Invoice” to open the Invoice Generation form (Fig. 7.31).
4. Click “Edit” and LIMS will prompt to provide “Sold To” information (Fig. 7.32).
5. Click “OK” and LIMS will populate the “Sold To” panel with name and address information from the Customers table (see Section 5). Because we did not previously enter an address for Cyrus Snodgrass, we need to do so here.
6. Enter “123 My Street” in the Addr2 text box (Fig. 7.33).
7. Enter “My City” in the Addr3 text box.
8. Enter “”My State 12345” in the Addr4 text box.
9. The “Sold By” information needs to be updated. For the institution name in the Addr1 text box in the “Sold By” panel, enter “Lakes Isotope Laboratory” (Fig. 7.33).
10. Enter “123 Lakeside Avenue” for Addr2; enter “Big Lake” for Addr3; enter “Virginia 20999” for Addr4; enter “USA” for Addr5.
11. LIMS will provide an “Invoice Number.” The invoice number can be edited as desired, but invoice numbers need to be unique in LIMS.
12. Edit the invoice date to that desired—“2/11/2017” is used in this example.
13. For the account number or purchase order number, enter “TR-123.”
14. Enter a “Price per Sample” amount of 25.50. The Windows Regional Settings will provide the currency symbol ($ in this example).
15. Enter a “Surcharge Amount” of 3.00 because the samples were not provided in the required sample bottles and they needed to be transferred to new bottles in this example.
16. Enter a “Surcharge Comment” that the correct bottles were not provided and the samples needed to be transferred.
17. Click “Save” and the updated form is shown in Figure 7.33 with a cost of $232.50.
18. Click “Print” to print the invoice and an invoice similar to that in Figure 7.34 is printed. A useful feature in many laboratories is to install pdf creation software on the computer so that pdf files can be created (see comment for “Print Destination” in Table 4.1).
19. Click “Close” to return to the Project form, which now appears as shown in Figure 7.35.
20. The final steps are to mail the invoice, click “Edit” on the Project form, set the “Billed” control in the lower left of the form (Fig. 7.36) to “Y” for yes, “N” for no, or “N/A” for not applicable, and click “Save.”

The invoice report can be customized by adding the logo of the university or laboratory if desired by editing either the Access report named “Invoice Report” or “Invoice Report (A4)” in the frontend database using Microsoft Access. After editing, the “not compiled” message (Fig. 4.2) may appear. Clicking “OK” will cause LIMS to close. LIMS can be reopened and should open normally. Once an invoice is created, it cannot be deleted.

If a new LIMS frontend database is installed, to retain their customized invoice report users can:

1. Rename the frontend database and save in an archive folder.
2. Download and install a new LIMS frontend database (Section 4.1).

3. Open the new LIMS frontend and delete the reports “Invoice Report” and “Invoice Report (A4).” It is helpful if the “Display LIMS Database Window” check box on the Options form (Table 4.1 and Figure 4.12) is enabled.
4. Click the Access “External Data” tab, select the Access icon, navigate to the renamed database in step 1, and import the reports “Invoice Report” and “Invoice Report (A4).”
5. Close the frontend database.
6. Upon opening the frontend database with Access, the “not compiled” message (Fig. 4.2) will likely appear. Clicking “OK” will cause LIMS to close. LIMS can be reopened and should open normally with the customized invoice report.

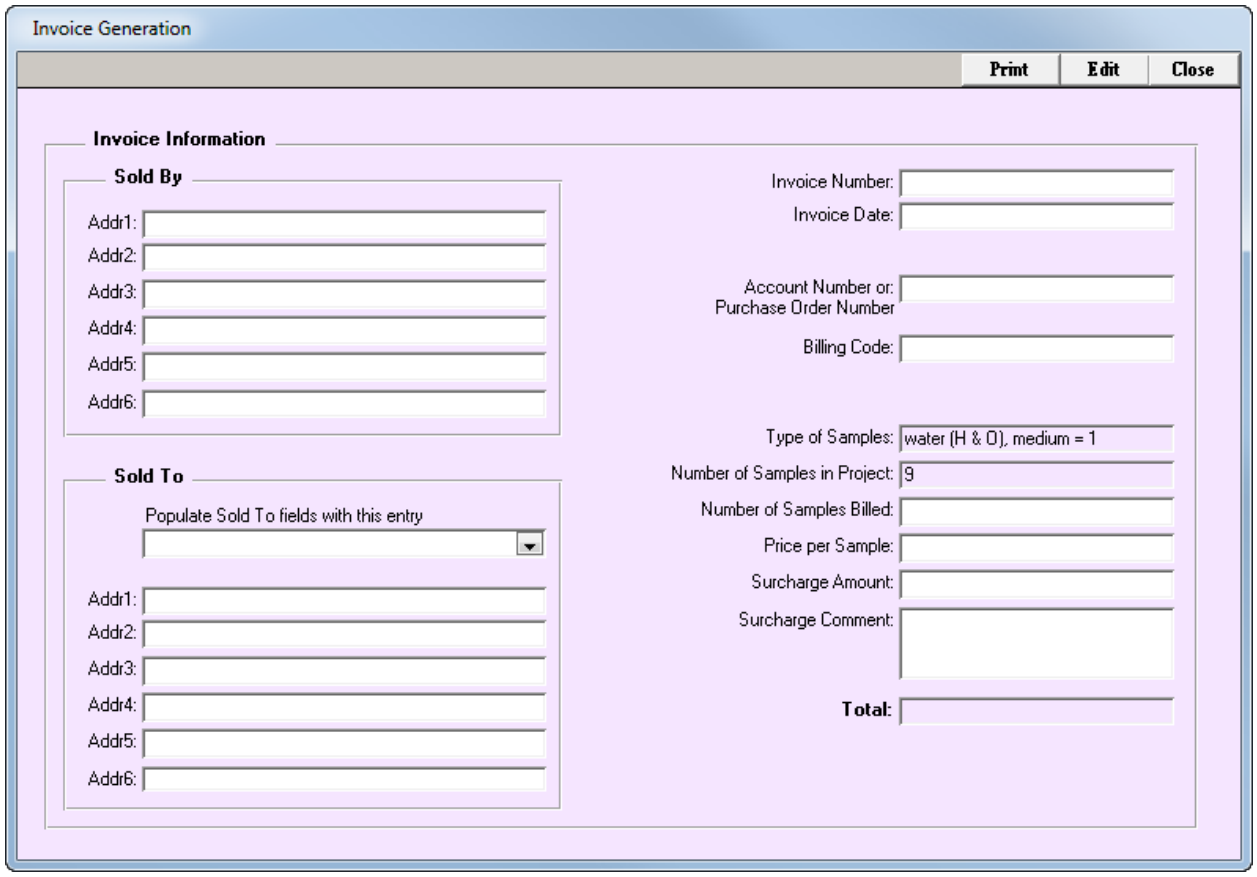


Fig. 7.31. The Invoice Generation form.

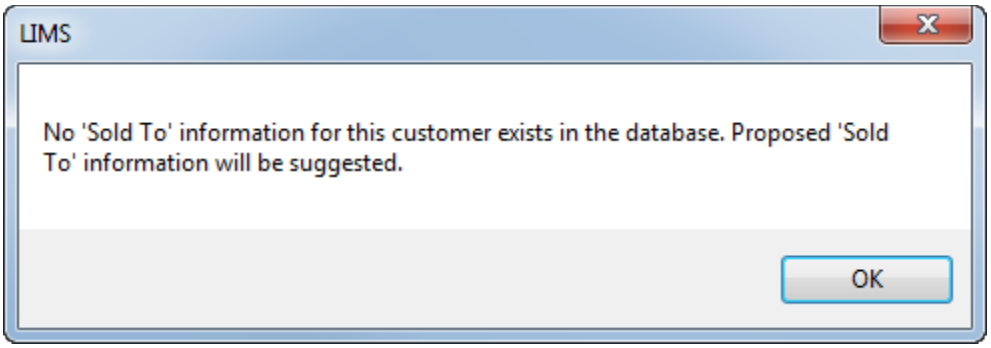


Fig. 7.32. LIMS prompt to populate the Invoice Generation form.

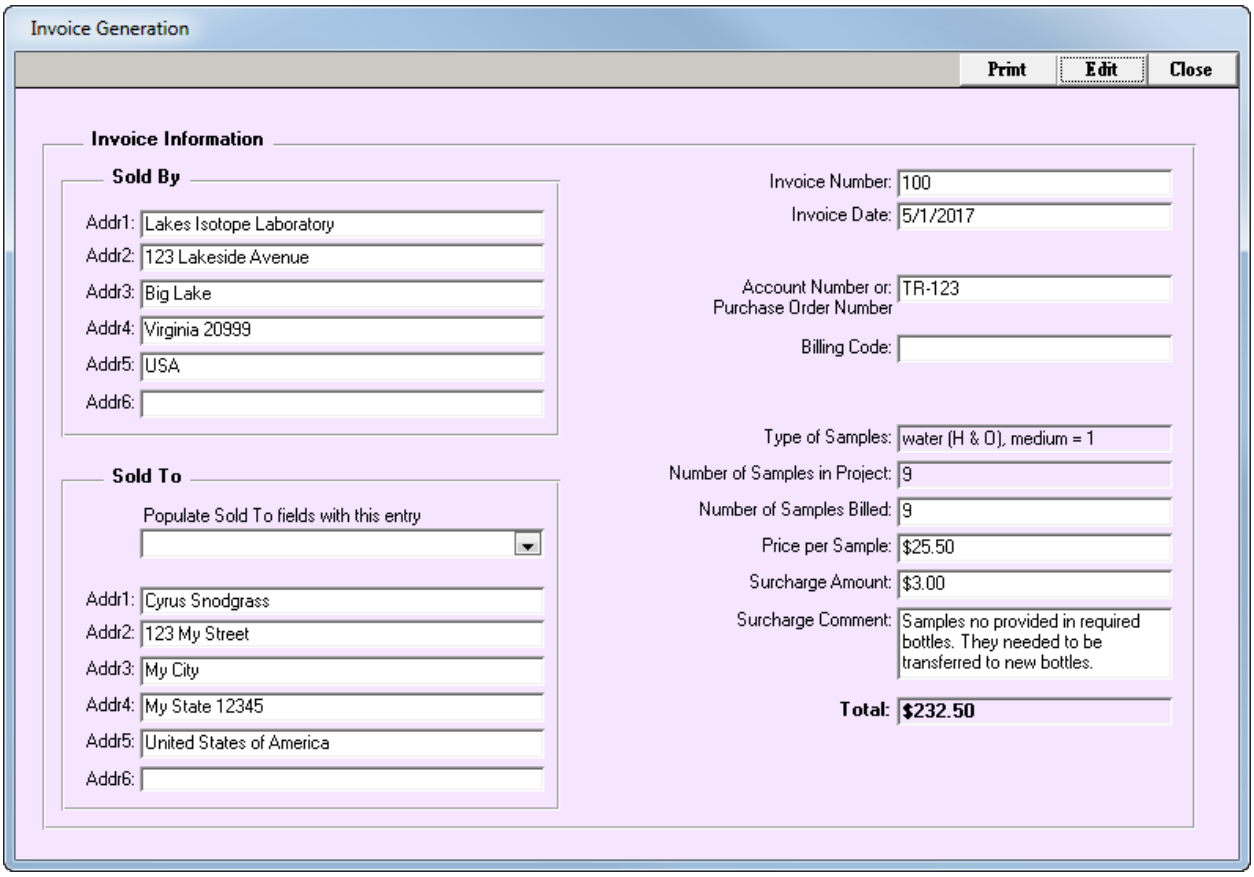


Fig. 7.33. The Invoice Generation form populated for Cyrus Snodgrass' nine water samples.

Invoice

Isotopic Analyses Performed By

Lakes Isotope Laboratory
123 Lakeside Avenue
Big Lake
Virginia 20999
USA

Invoice Number 100

Invoice Date 5/1/2017

Sold To:

Cyrus Snodgrass
123 My Street
My City
My State 12345
United States of America

Account Number or Purchase Order Number TR-123

Billing Code

Sample Description:

Customer	Snodgrass, Cyrus
Submission Date	3/3/2017
Sample Type	water (H & O), medium = 1
Purpose	Water resources evaluation project
Location	Dunedin
Results Reported	
Sample Range	W-1001 thru W-1009

Total Number of Samples	9	
Number Samples Billed	9	
Price Per Sample	$25.50	
Surcharge	$3.00	Samples no provided in required bottles. They needed to be transferred to new bottles.

Total **$232.50**

Fig. 7.34. Invoice for Cyrus Snodgrass' nine water samples.

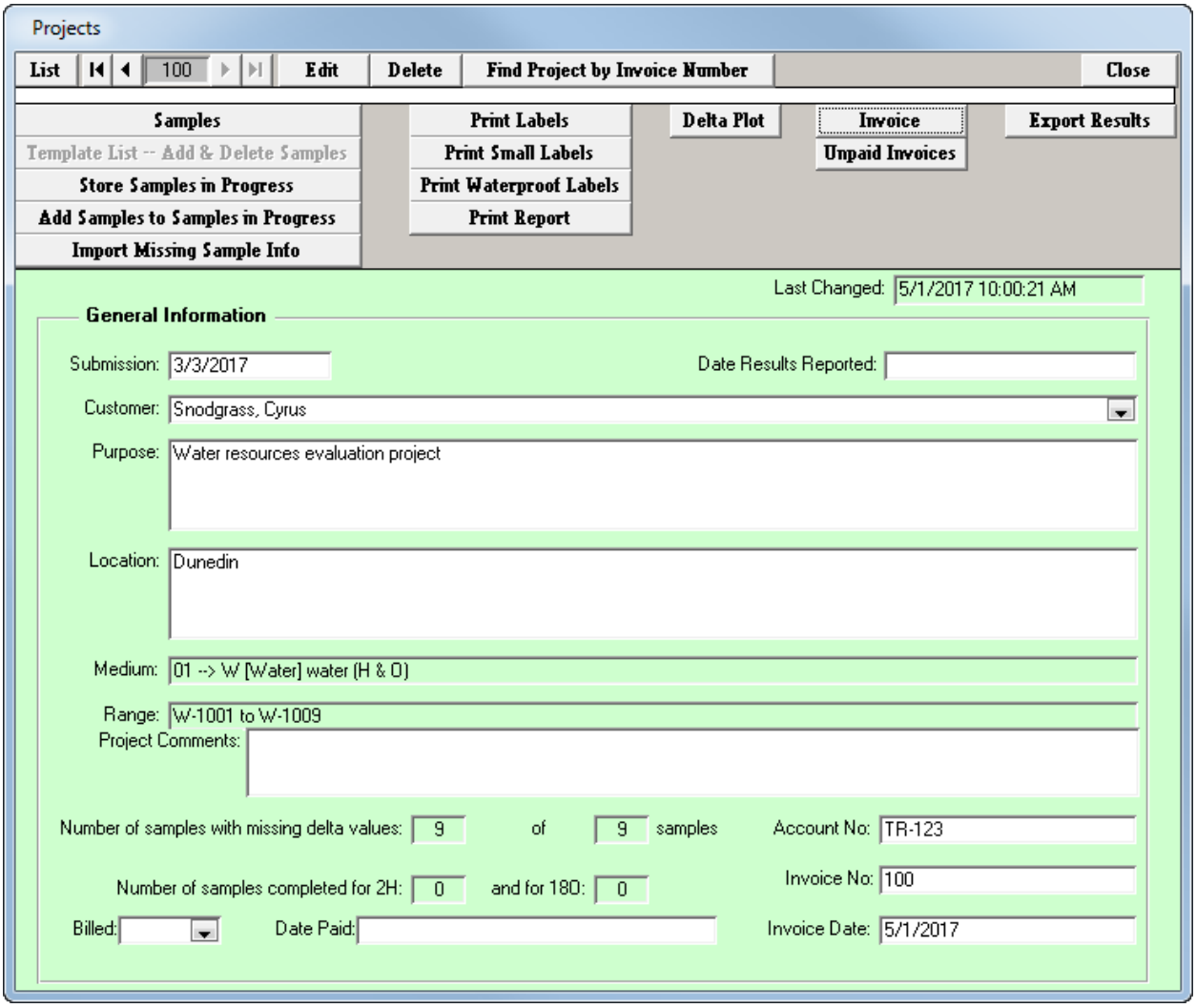


Fig. 7.35. Projects form after creation of an invoice.

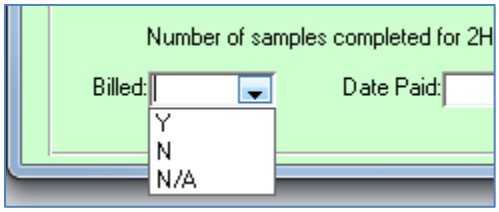


Fig. 7.36. Billed control on the Projects form.

The "Unpaid Invoices" button is useful for identifying invoices that have not been paid, and clicking this button creates an Excel file of unpaid invoices. In order for this feature to work

correctly, users need to populate the “Billed” control as either “Y”, “N”, or “N/A”, and they need to enter the received date in the “Date Paid” text box conscientiously (Figs. 7.35 and 7.36).

7.6.7 Exporting Results of a Project

Clicking the “Export Results” button enables a user to export an ASCII text file and (or) an Excel file of the project and sample data.

8 Samples, Sample Information, and Finding a Sample

8.1 Introduction

The center column of the main page (Figs. 2.1 and 4.7) contains buttons that execute sample actions, such as finding a sample or printing a range of samples. The "Create a Sample List -->" button enables users to populate a new sample list (sometimes called a sequence table) once the standardized template has been created (see Section 33.5.1). Searching for samples using several criteria is discussed in Section 9. Printing or exporting a range of samples is discussed in Section 10. Viewing and editing analyses of samples is discussed in Section 27. Information on use of extractions is presented in Sections 11 , 19.2, 24.3, and 26.

8.2 The Find a Sample Form

As discussed in Section 7.6.2, the "Samples" button lies immediately below the navigation buttons on the Projects form (Fig. 7.24). Clicking the "Samples" button opens the Samples form, an example of which is shown in Figure 7.25. An alternative method of finding a specific sample is to click "Find a Sample -->" on the main page, which opens the Find a Sample form (Fig. 8.1). Enter the Our Lab ID "W-1001" to open the same Samples form as shown in Figure 7.25. To open the Samples form and display a specific Our Lab ID, it is quicker to use the "Find a Sample -->" button on the main page as shown in Figure 8.2.

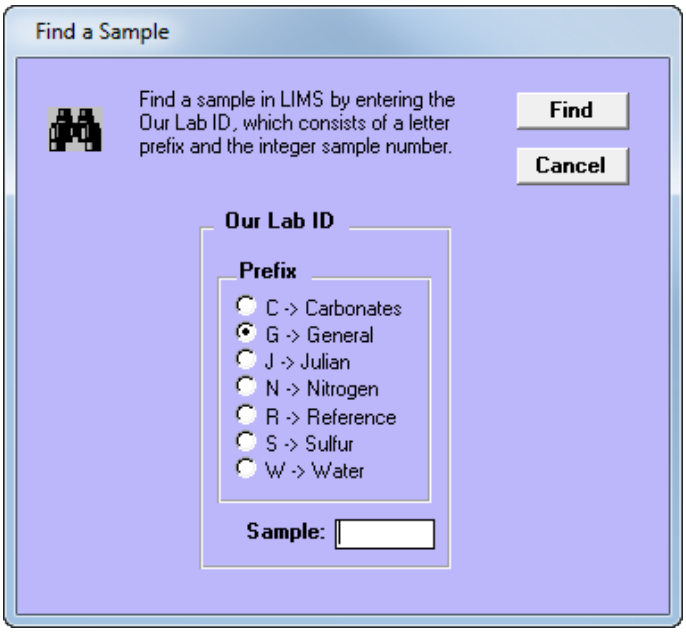


Fig. 8.1. Find a Sample form.

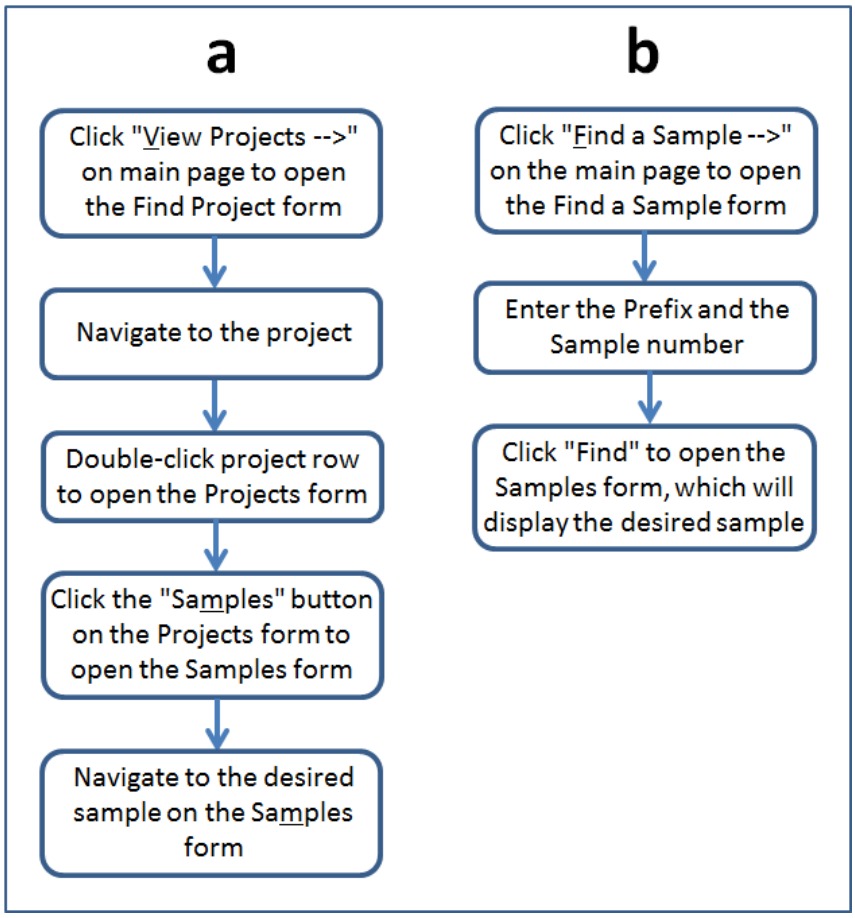


Fig. 8.2. Two ways to open the Samples form to display a specific sample. Strategy **b** takes fewer steps than strategy **a**.

8.3 The Samples Form

An example of the Samples form is shown in Figure 8.3. Specific comments about the controls (buttons, drop downs, and text boxes) include the following:

- As in many other forms in LIMS, users navigate through the samples using the navigation buttons in the left corner of the form (Fig. 5.2).
- Clicking the “List” button displays as many as 42 samples at a time (Fig. 8.4).
- The “Edit” button enables a user to update all properties of the sample except for the Our Lab ID and the medium. Labels for 10 text boxes are user definable (see Section 7.5.1 and Table 7.1).
- The “Analyses” button opens the Analyses form. This form can display each of the analyses of a sample. An example from a compound specific isotopic analysis discussed in Section 32 is shown in Figure 8.5.
- The “Print Project” button prints a project report similar to that shown in Figure 7.4.

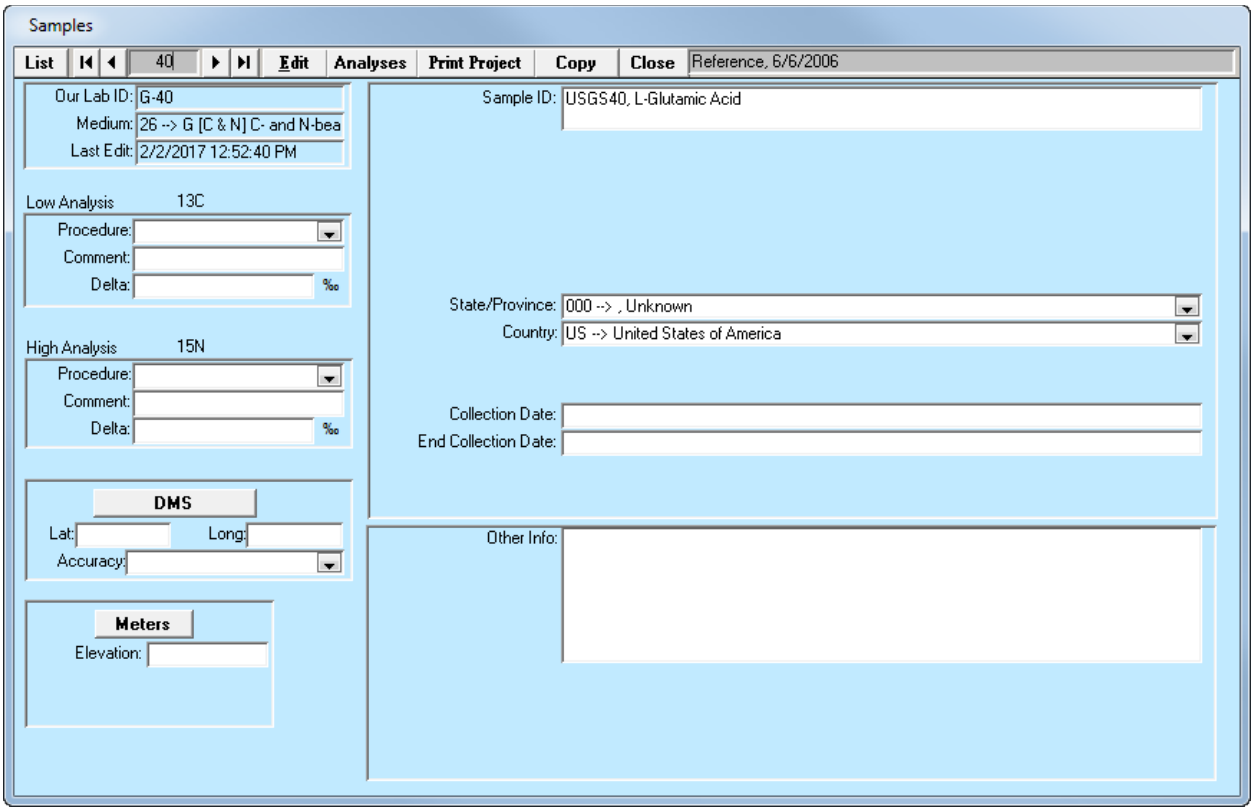


Fig. 8.3. Samples form for Our Lab ID G-40 in a database for a new laboratory.

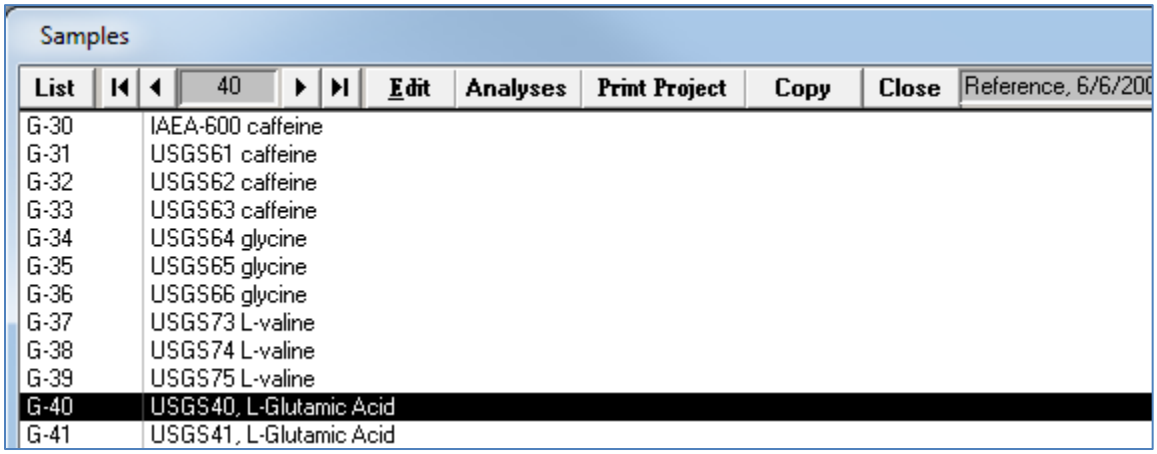


Fig. 8.4. Samples in a project displayed by clicking the “List” button.

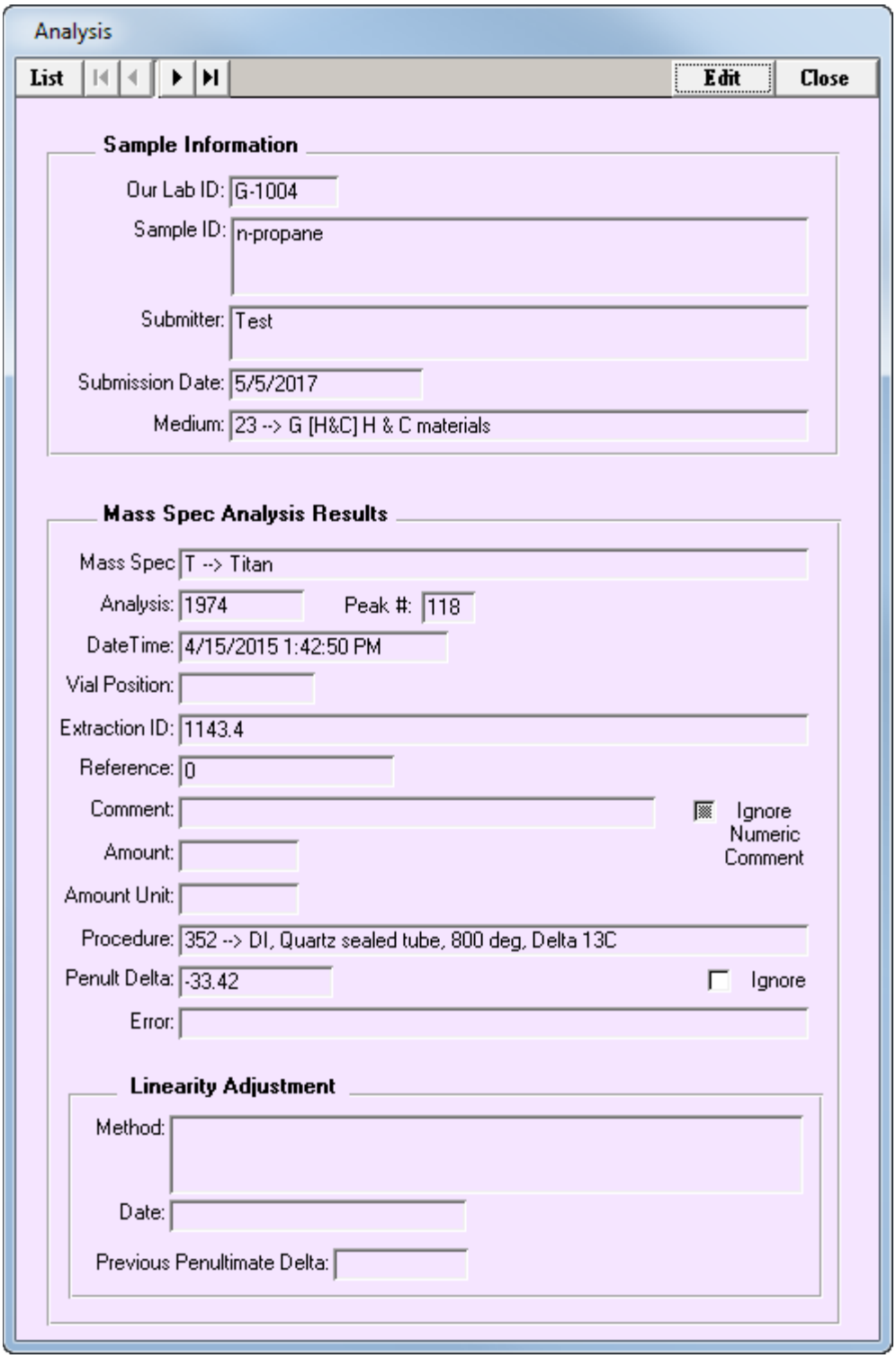


Fig. 8.5. Example of the Analysis form. The Analysis form can also display procedures below 200, such as continuous-flow area, which is procedure 185.

- Sometimes it is useful to copy information from one Our Lab ID to that of another. For example, two samples may have been collected from the same wells—one for stable hydrogen and oxygen isotopic analysis ("W" Prefix) and the other for nitrogen and oxygen isotopic analysis of dissolved nitrate ("N" Prefix). The "Copy" button enables the user to copy the information for each of the "W" samples to each of the respective "N" samples one-by-one. Clicking the "Copy" button displays the form and dialog box shown in Figure 8.6 with yellow background in controls whose information is to be copied. Clicking "OK" opens the Copy To form (Fig. 8.7) in which the user designates the Our Lab ID that is to receive the information from the controls with yellow backgrounds. Clicking "Copy" copies the data in the highlighted cells to the designated Our Lab ID. After copying, it may be desirable to edit the Sample ID of the designated Our Lab ID.

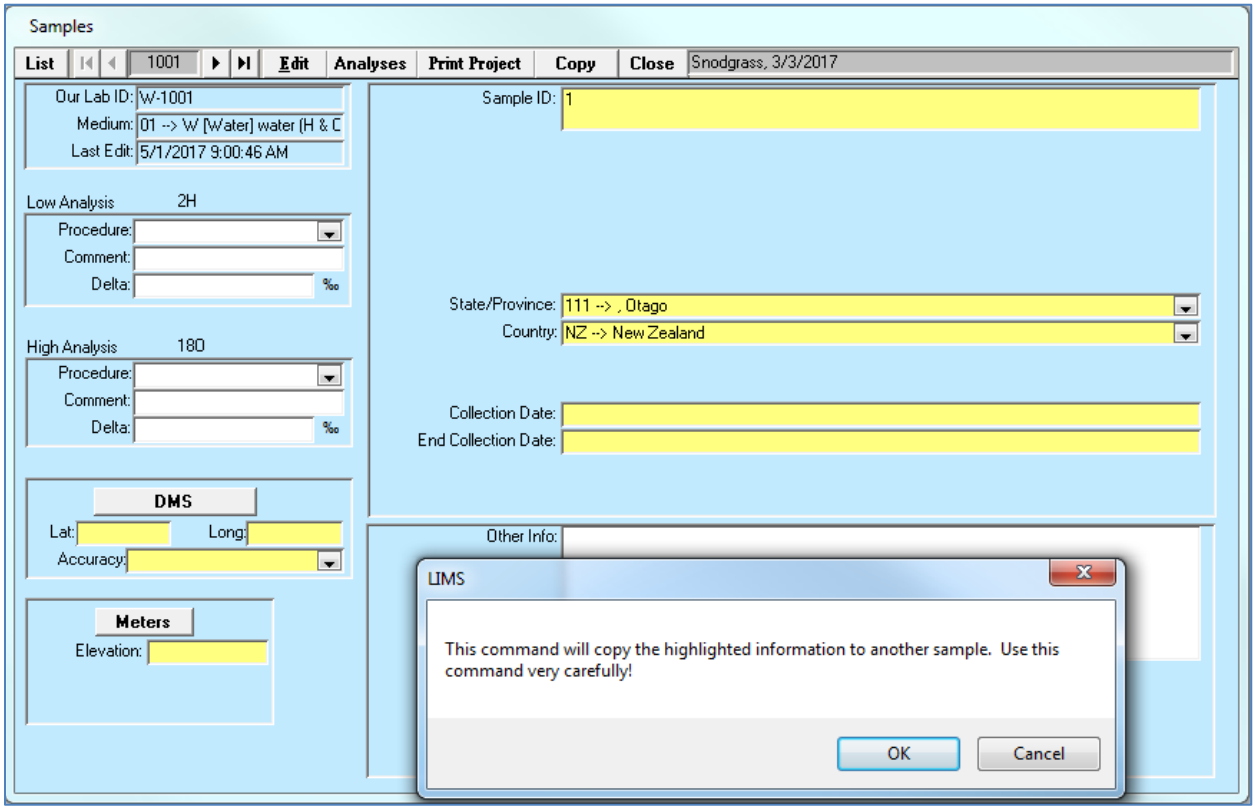


Fig. 8.6. Example of dialog box resulting from clicking the "Copy" button. Note the controls with yellow backgrounds whose values will be copied to the Our Lab ID designated in the Copy To form that opens when "OK" is clicked.

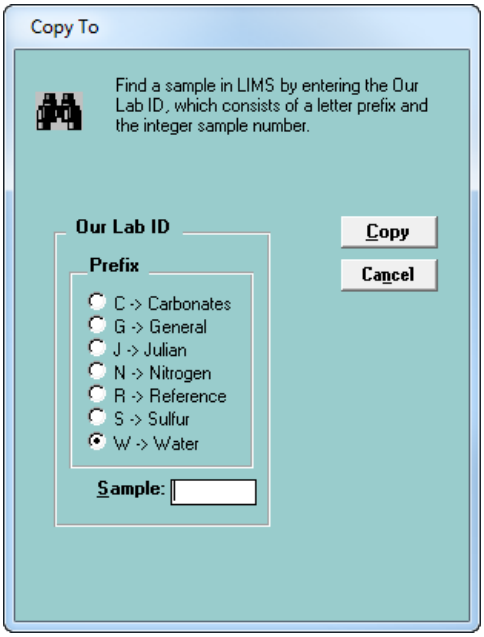


Fig. 8.7. Copy To form.

- The "Low Analysis" and "High Analysis" panels contain controls for the low and high procedures (see Section 6.4), low and high isotope-delta values, and low and high comments. These fields are empty because this sample has not been analysed. Figures 24.36, 28.4, and B.23 display examples of the use of these fields.
- The "DMS" button enables a user to toggle back and forth between decimal format and degree-minute-second format for latitude and longitude if they exist.
- The "Meters" button enables one to toggle back and forth between meters and feet.
- The "State/Province", "Country", "Collection Date", "Ending Collection Date", and "Other Info" controls are discussed in Section 7.51 and Table 7.1.

9 Searching for Samples Using Criteria

Clicking “Search for Samples Using Criteria” on the main page opens the Find a Sample or Group of Samples form, which enables a user to search for one or all samples in the database that meet specified search criteria using text field wildcards or Boolean criteria based on delta values or dates. For example, one can quickly locate all data or samples from a specific region or date, regardless of the client, provided the sought information was supplied with the sample submission information. These search results can be saved to an Excel file. For example, searching a database for water samples with a collection date ≥ 2/15/2015 and ≤ 2/20/2015 might yield the records shown in Figure 9.1.

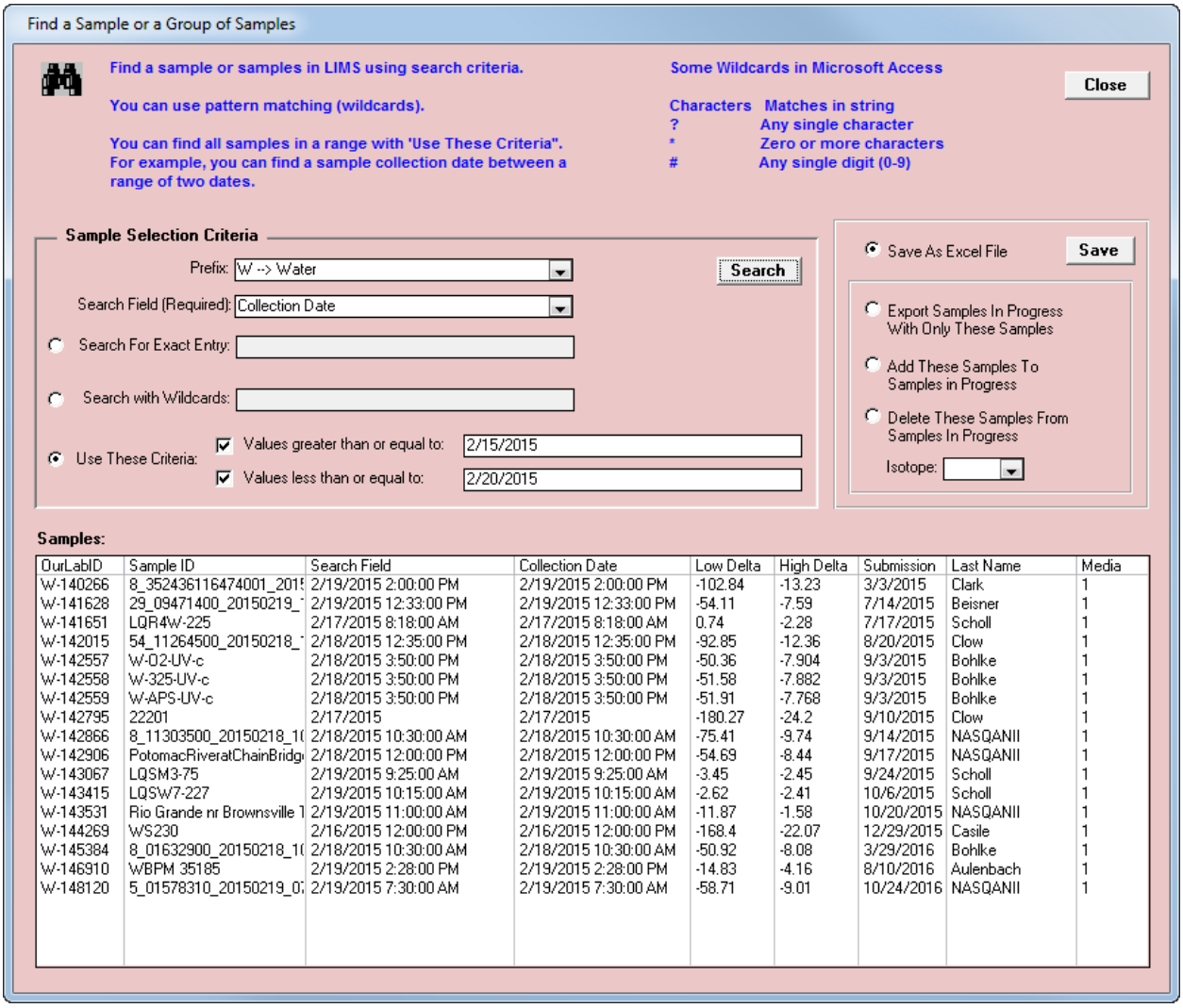


Fig. 9.1. Example of a records query using the Find a sample or a Group of Samples form.

One can use pattern matching (wildcards) in the Find a Sample or a Group of Samples form. Some wildcards available in Microsoft Access include:

- ? Any single character
- * Zero or more characters
- # Any single digit (0–9)

Entering "B?###" finds the following records:

B-421
B-822
BM135

Entering "CA#*" finds the following records:

Ca3-199
Ca7
Ca6-97.5

Clicking "Save" creates an Excel file having nine columns (Our Lab ID, Sample ID, Search Field, Collection Date, Low Delta, High Delta, Submission [date], Last Name, and Media).

It is possible to add the selected samples to the Samples in Progress queue, delete them from the Samples in Progress queue, or export any samples that are also in the Samples in Progress queue. See Sections 25 and 26 for a discussion of the Samples in Progress queue.

10 Printing a Range of Samples

One of the helpful reports in LIMS is the Print Sample Range Report. This report is enabled by clicking “Print Sample Range” on the main page, which opens the Print Sample Range form (Fig. 10.1). Entering W-1001 to W-1002 prints the report shown in Figure 10.2.

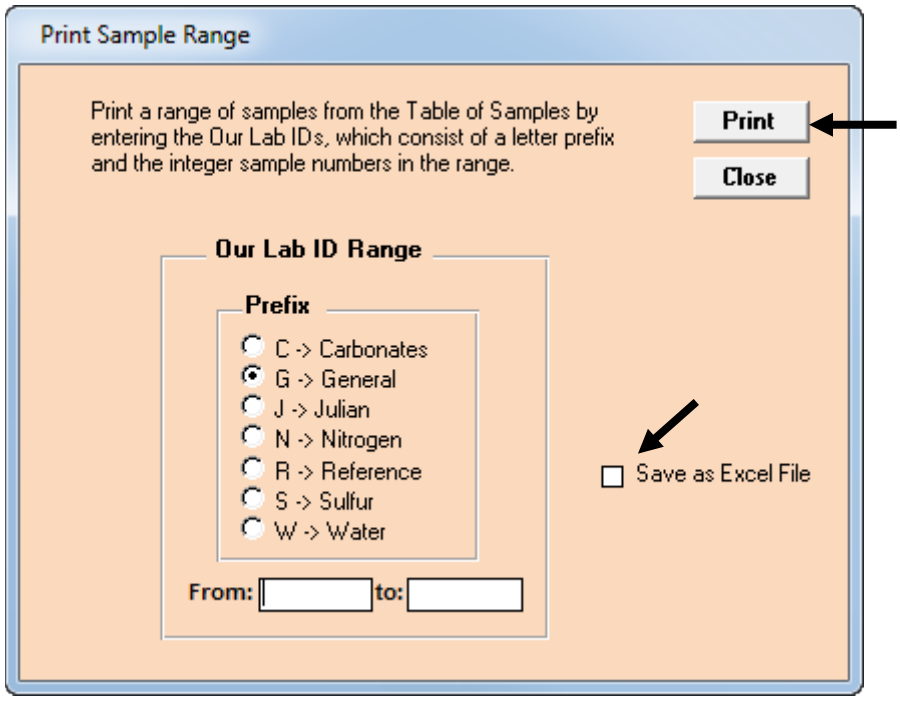


Fig. 10.1. The Print Sample Range form.

⚠ **Helpful Hint:** Even though there are boxes for both “From” and “to,” if one wants to print just one sample, one only needs to enter in the Our Lab ID into the “From” box and click the Enter key three times to print the sample. LIMS will automatically fill in the blank “to” field.

An Excel file of samples in the range can be created by enabling the “Save as Excel File” check box. The Excel file may have 25 to 30 columns, depending upon the number of user definable fields retained for alternative field names on the Options form (Fig. 4.12 and Section 7.5.1).

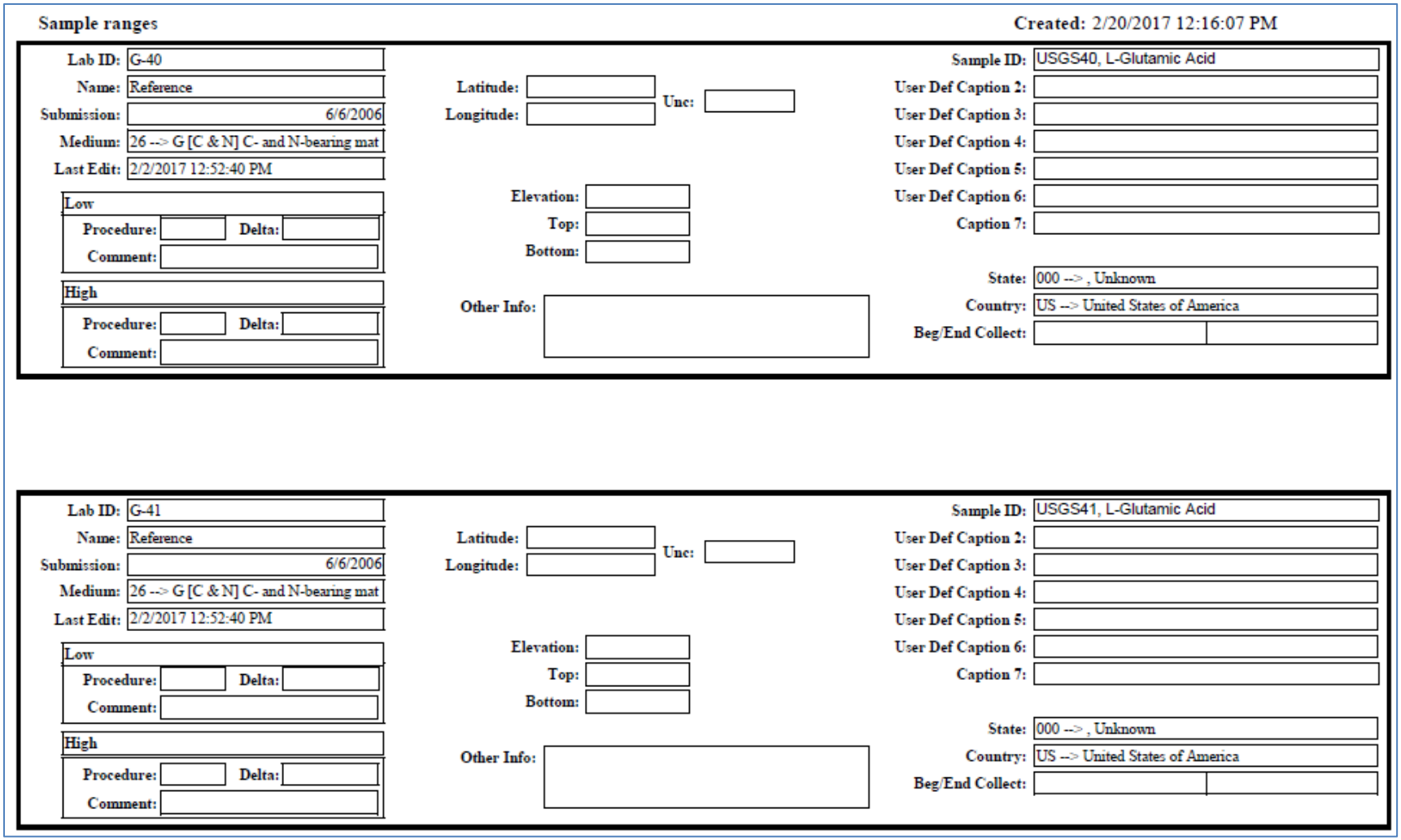


Fig. 10.2. The Sample Range report for G-40 to G-41 in a database for a new laboratory.

11 The Add or Edit Extractions Form for Documenting Sample Preparations

Some laboratories keep detailed records on the sample preparation of each aliquot of each sample. Clicking “Add or Edit Extractions” on the main page opens the Extraction Information form, which is used for this purpose (Fig. 11.1). Each Extraction ID must be unique. Prior to using the Extraction Information form, a user should populate the LIMS employees table by clicking “Special Features” and “Employees,” which will open the Employees form (Fig. 11.2). Additionally, users need to add extraction types to LIMS. This is accomplished by clicking “Special Features” and “Extraction Types,” which will open the Extraction Types form (Fig. 11.3). Extractions are added by clicking “Add,” entering a code and description, and clicking “Save.” The Extraction ID typically will be part of the data provided to a mass spectrometer sequence table (or sample analysis table) (see Section 19.2) so that an individual isotopic analysis will include the extraction ID as part of its information. In LIMS versions 7 and 8, this field was termed the Aliquot ID. [1]

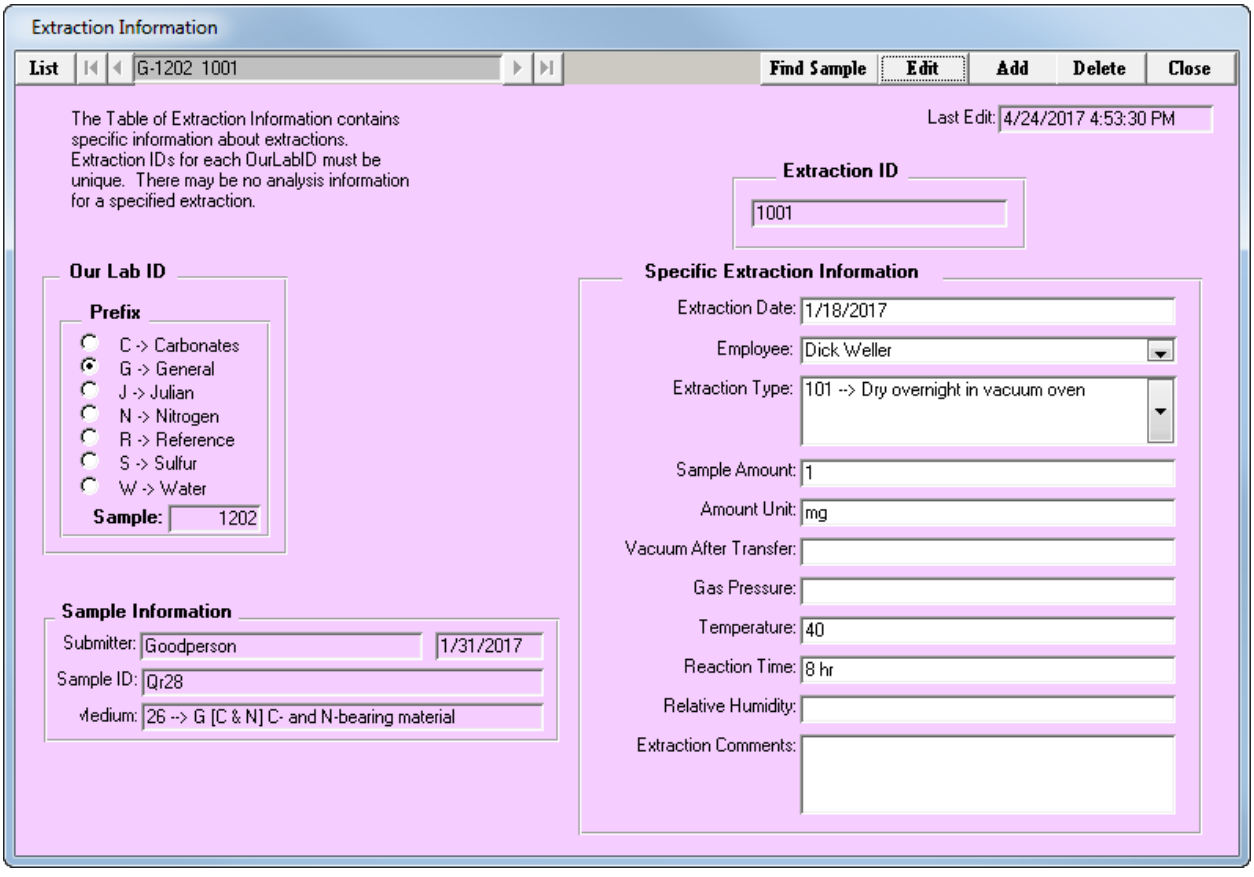


Fig. 11.1. The Extraction Information form.

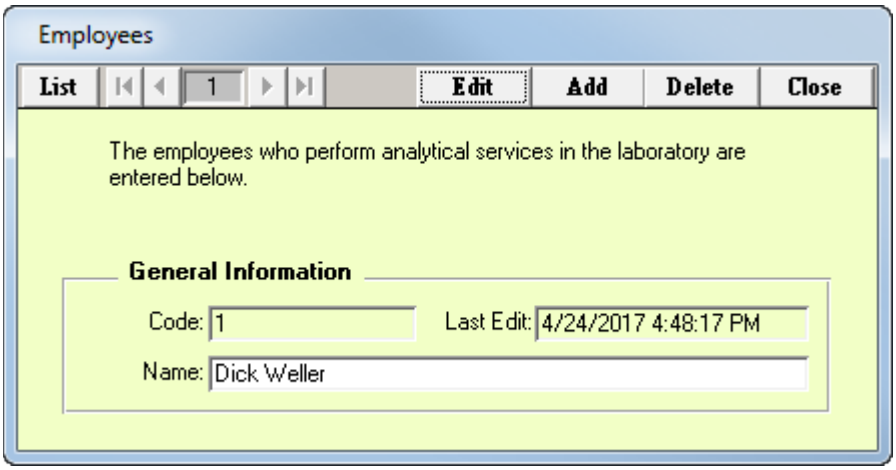


Fig. 11.2. The Employees form.

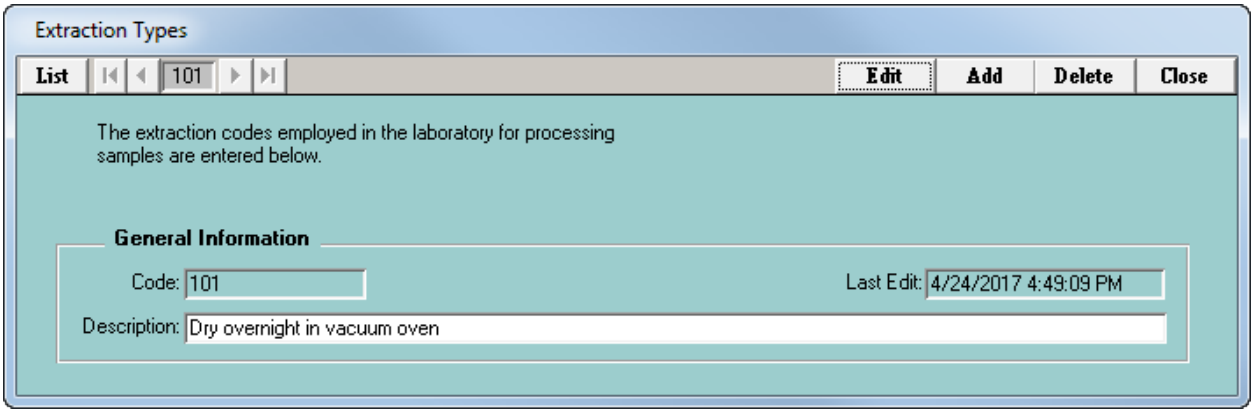


Fig. 11.3. The Extraction Types form.

12 Isotope-measurement References

12.1 The Reference Samples Form

The default backend database for a new laboratory contains several projects for internationally distributed isotopic reference materials (*e.g.* VSMOW2, SLAP2, etc.) and several projects for local measurement standards (*e.g.* your own laboratory isotopic reference materials) (see Section 7.2). The assigned customer for these project is "Reference" (see Figs. 5.3 and 7.1). In this document the terms reference and standard are used interchangeably. LIMS maintains a "Table of References" whose isotope-delta values are used to normalize sample results to international isotope-delta scales. [4, 5] Values in the "Table of References" are viewed, added to, and edited with the Reference Samples form. To open the Reference Samples form:

1. On the LIMS main page click "Special Features."
2. Click "Assign Lab References" to display the Reference Samples form (Fig. 12.1).

The top of the Reference Samples form has the LIMS standard navigation buttons and buttons for editing, adding, and deleting records from the Table of References. The isotope code of each record is shown in the "Isotope" panel (Fig. 12.2), and the value must be one of those in Table 6.2. The "Reference Information" panel contains the following fields:

- The "Our Lab ID" consists of the sample prefix and the integer sample number (Section 6.2). In Figure 12.1, G-90 is the internationally distributed isotopic reference material NBS 22 oil.
- The "Sample ID" (see Table 7.1); in Figure 12.1 it is NBS 22 oil.
- The "Medium" displays the code and description of the medium (see Section 6.1); for this example it is "23 --> G [H&C] H & C materials."
- The "Final Delta" is the delta value assigned to the sample for the specified isotope. The δ^2H value of NBS 22 oil is –117.2 ‰. [6] The delta values selected for the backend database for a new laboratory are those found in Schimmelmann and others. [6] If a value is not found in Schimmelmann and others, then the value recommended by Brand and others [7] is used. The Samples form (Fig. 8.3) need not have delta values; the delta value fields are normally empty.
- Mass fraction of element (H, N, etc.) for EA analyses is used by LIMS to determine elemental mass fractions of samples (see Section 24.6). For example, USGS40 L-glutamic acid is used commonly to determine the mass fraction of carbon in samples. The mass fraction of carbon in USGS40 (G-40) is 40.8 percent (Fig. 12.2).

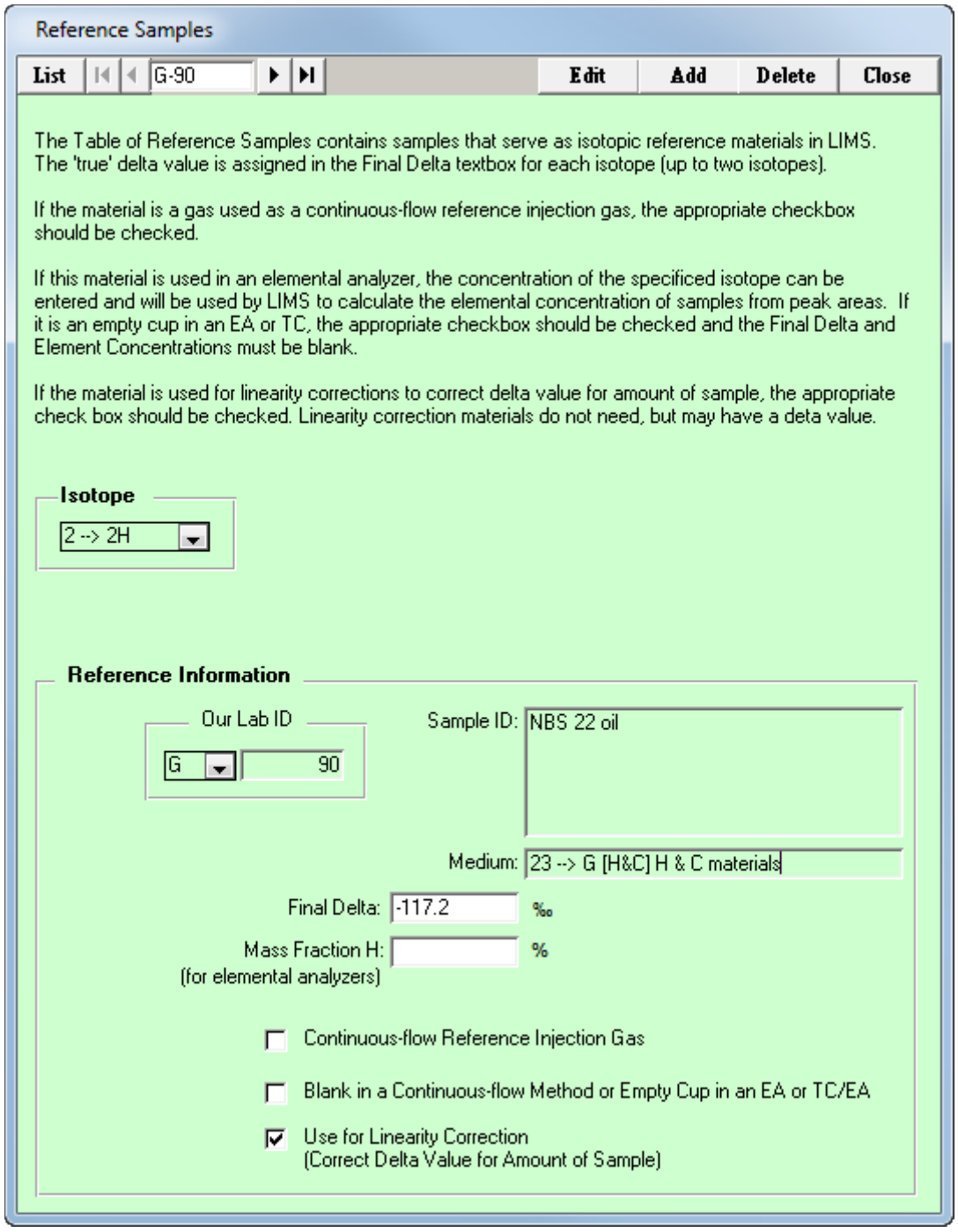


Fig. 12.1. Reference Samples form.

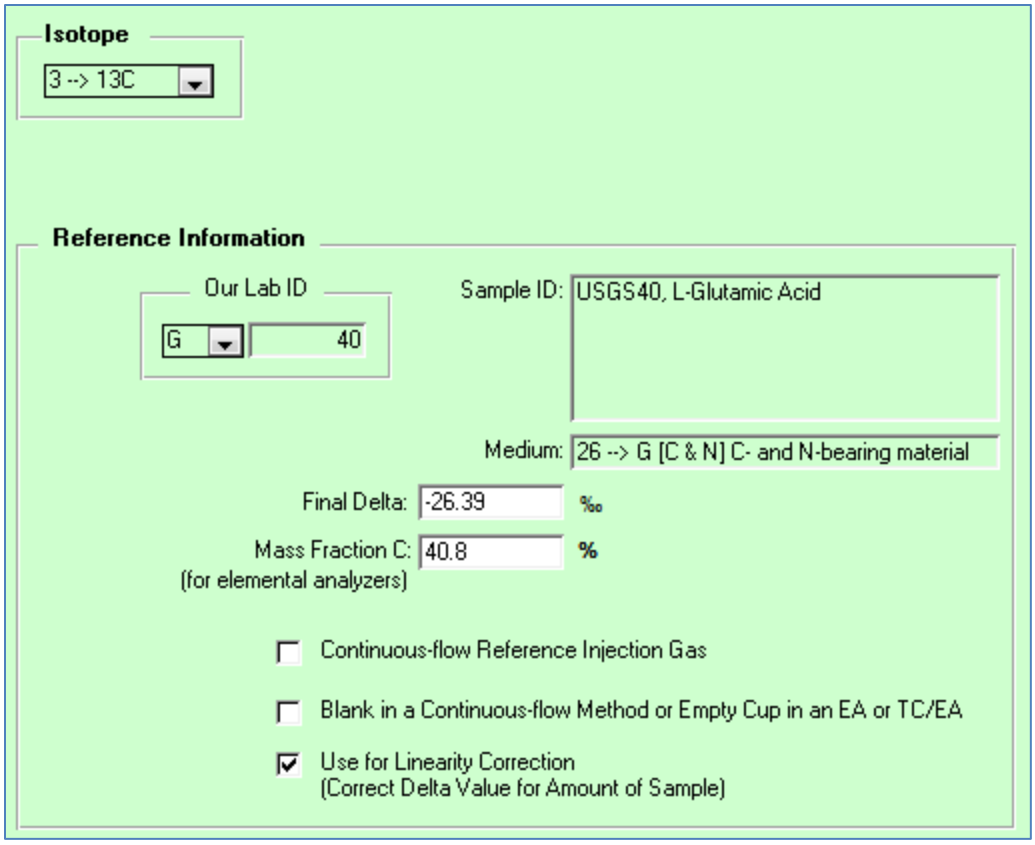


Fig. 12.2. Section of the Reference Samples form showing the mass fraction of carbon of USGS40 (G-40) assigned as 40.8 %.

- A "Continuous-flow Reference Injection Gas" is identified by checking the top check box. Figure 12.3 shows that R-6 is designated as a $\delta^{13}C$ reference injection gas with an assigned value of zero. The user may want to update this value after measuring the $\delta^{13}C$ of R-6 in their own laboratories.
- A sample used as a blank or empty cup in an EA method is identified by checking the middle check box. Figure 12.4 shows that G-4 is designated as an empty cup in a $\delta^{13}C$ EA analysis. It can be used for blank correction as exemplified in Section 24.5.
- Designating that a sample should be used for a so-called linearity correction (correct a delta value for amount of sample) during importing of mass spectrometric data is enabled by checking the bottom check box; for example, see Figure 12.2 showing that G-40 (USGS40) can be used for adjusting isotope-delta values during importing of mass spectrometer data. The "Final Delta" entry can be blank for a sample used for linearity corrections.

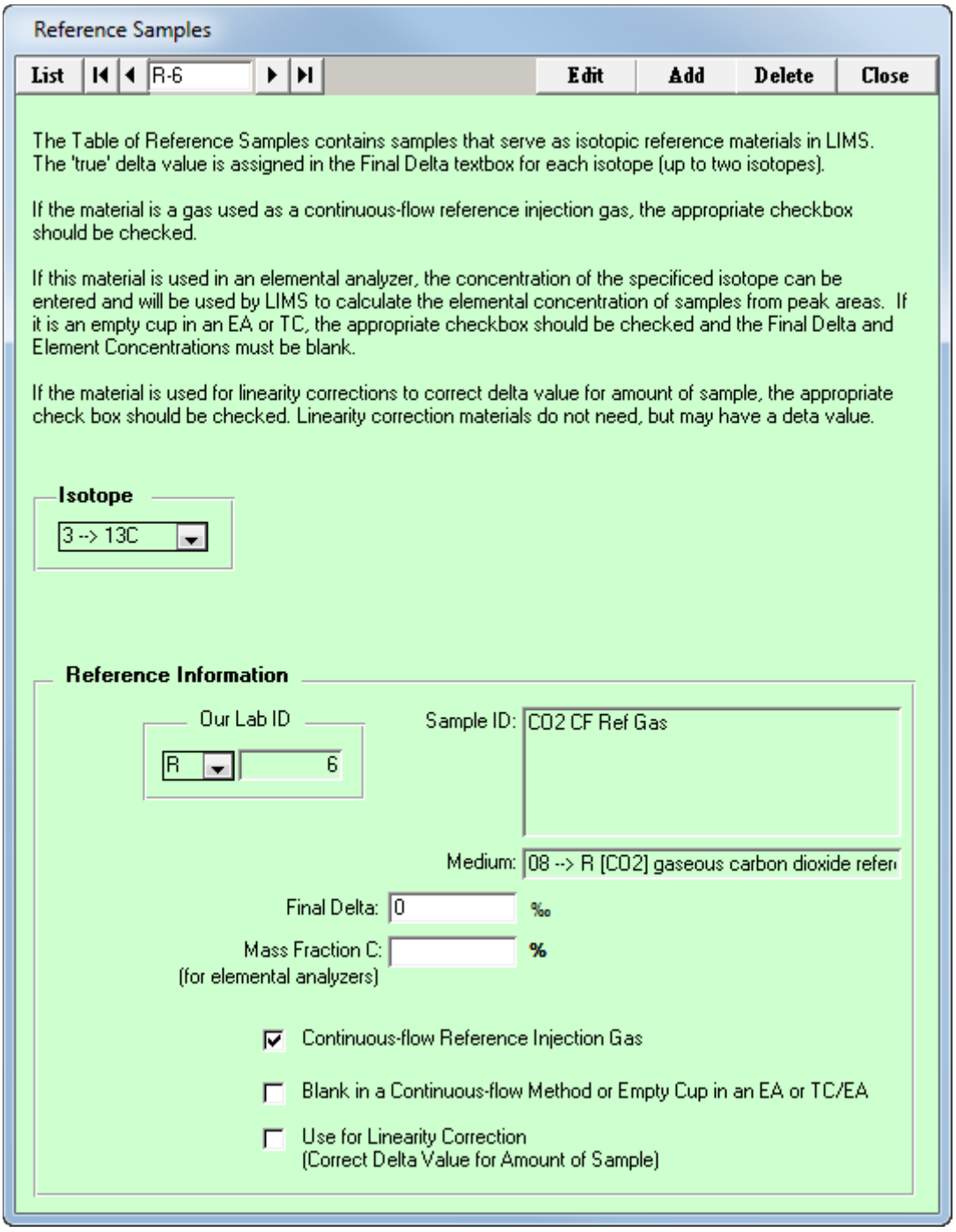


Fig. 12.3. Reference Samples form showing R-6 CO_2 designated as a continuous-flow reference injection gas. Its $\delta^{13}C$ value is zero, and users may want to update this value depending upon the measured value in their own laboratories.

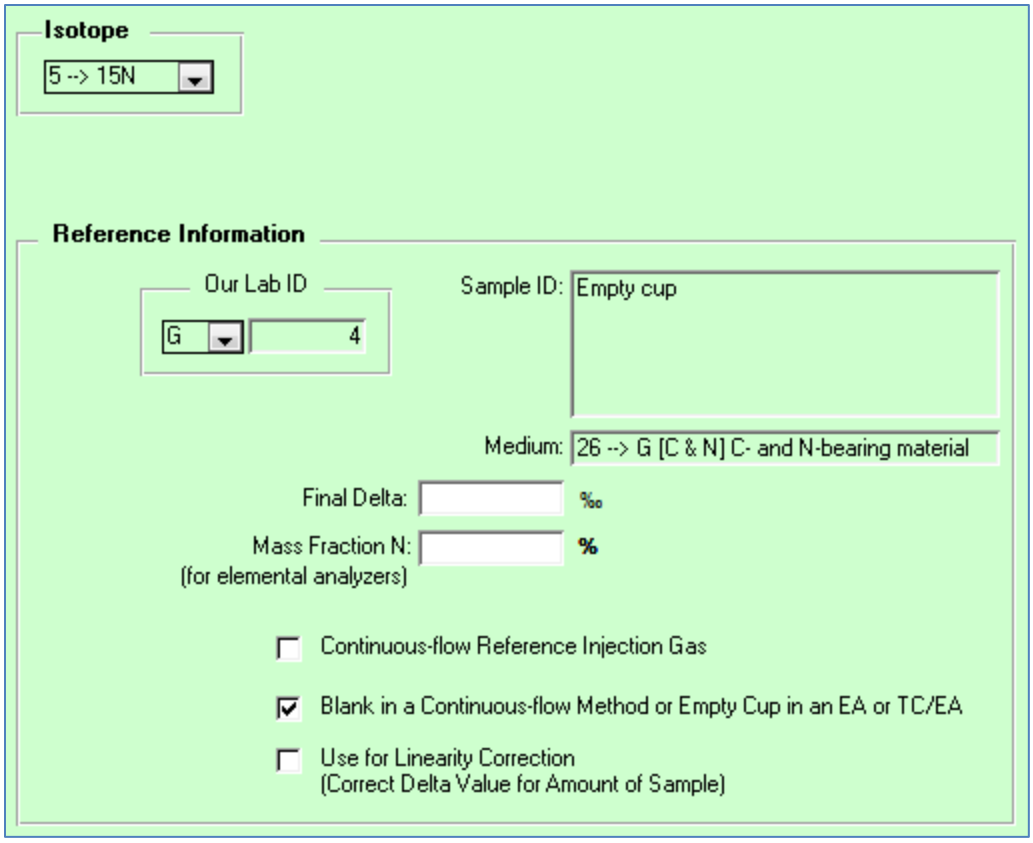


Fig. 12.4. Section of the Reference Samples form showing G-4 designated as an empty cup in a $\delta^{13}C$ EA analysis.

In a backend database for a new laboratory, the "Table of References," which underlies the Reference Samples form, contains several different types of references, including the possibility of samples from:

- Fifteen projects of internationally distributed isotopic reference materials, each with unique media codes (Fig. 12.5).
- Eleven projects for local laboratory measurement references, each with unique media codes (Fig. 12.6).
- Seven projects for H_2, CO_2, N_2, O_2, N_2O, SO_2, and CO continuous-flow reference injection gases (Fig. 12.7).
- Four projects containing samples that represent an empty cup or an empty capsule of an EA analysis (Fig. 12.8). These samples enable LIMS to make blank corrections for EA analyses.
- Ten projects that contain samples for testing analytical methods (Fig. 12.9).

Submission	LastName	Range	Media	Purpose
1/1/2006	Reference	C-5 to C-24	2	International CaCO3 reference materials
6/6/2006	Reference	C-25	35	International LSVEC lithium carbonate reference
6/6/2006	Reference	C-26 to C-28	37	International BaCO3 refernces
6/6/2006	Reference	G-30 to G-59	26	International C & N bearing reference materials
6/6/2006	Reference	G-90 to G-119	23	International H&C bearing materials
6/6/2006	Reference	G-150 to G-179	19	International H&O bearing materials
6/6/2006	Reference	G-210 to G-219	27	International C&O bearing materials
6/6/2006	Reference	G-230 to G-234	46	International graphite reference materials
6/6/2006	Reference	N-23 to N-31	52	International (NH4)2SO4 reference materials
6/6/2006	Reference	N-32 to N-50	55	International nitrate reference materials
6/6/2006	Reference	S-21 to S-30	72	International sulfate reference materials
6/6/2006	Reference	S-31 to S-50	66	International sulfide reference materials
6/6/2006	Reference	S-51 to S-54	71	International elemental S references
6/6/2006	Reference	S-90 to S-109	69	International sulfur-bearing reference materials
9/27/2012	Reference	W-5 to W-30	1	International water references

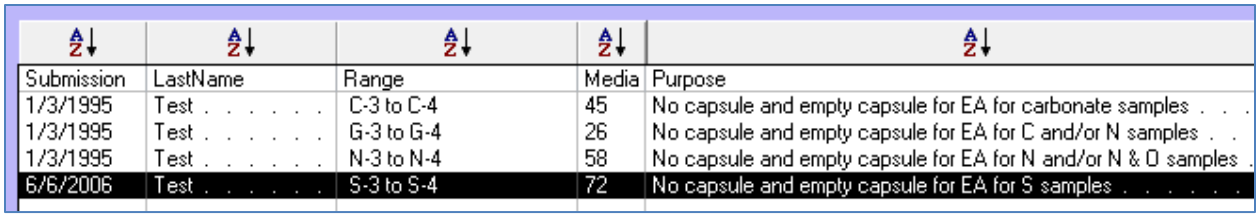
Fig. 12.5. Projects of internationally distributed isotopic reference materials in a backend database for a new laboratory.

Submission	LastName	Range	Media	Purpose
6/6/2006	Reference	C-51 to C-70	2	Laboratory calcite (CaCO3) references
6/6/2006	Reference	G-60 to G-89	26	Laboratory C&N reference materials
6/6/2006	Reference	G-120 to G-149	23	Laboratory H&C references
6/6/2006	Reference	G-180 to G-209	19	Laboratory H&O bearing materials
6/6/2006	Reference	G-220 to G-229	19	Laboratory C&O bearing materials
6/6/2006	Reference	G-235 to G-239	46	Laboratory graphite reference materials
6/6/2006	Reference	N-61 to N-80	52	Laboratory (NH4)2SO4 reference materials
6/6/2006	Reference	N-81 to N-100	55	Laboratory nitrate reference materials
6/6/2006	Reference	S-60 to S-79	72	Laboratory sulfate reference materials
6/6/2006	Reference	S-80 to S-89	66	Laboratory sulfide reference materials
9/27/2012	Reference	W-31 to W-69	1	Laborabory water references

Fig. 12.6. Projects of local laboratory measurement references in a backend database for a new laboratory.

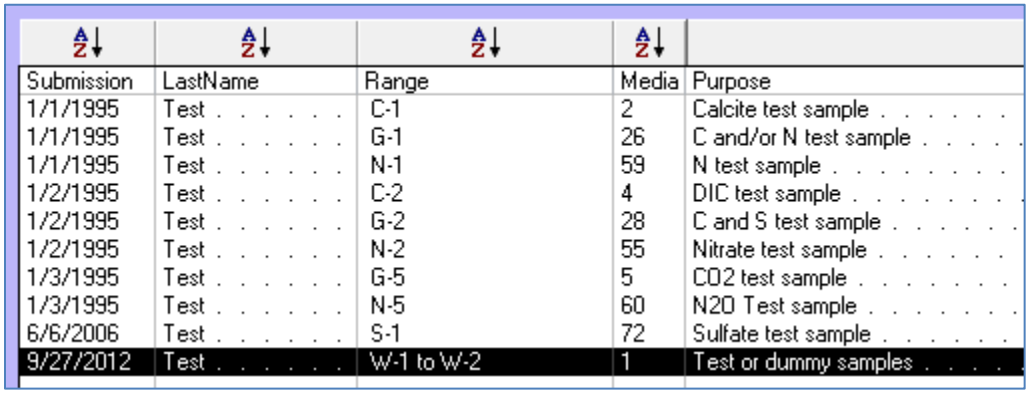
Submission	LastName	Range	Media	Purpose
6/6/2006	Reference	R-1 to R-5	10	H2 reference for continuous-flow
6/6/2006	Reference	R-6 to R-10	8	CO2 reference for continuous-flow
6/6/2006	Reference	R-11 to R-15	12	N2 reference for continuous-flow
6/6/2006	Reference	R-16 to R-20	16	O2 reference for continuous-flow
6/6/2006	Reference	R-21 to R-25	13	N2O reference for continuous-flow
6/6/2006	Reference	R-26 to R-30	14	SO2 reference for continuous-flow
6/6/2006	Reference	R-31 to R-35	9	CO reference for continuous-flow

Fig. 12.7. Projects containing samples of continuous-flow reference injection gases.



Submission	LastName	Range	Media	Purpose
1/3/1995	Test	C-3 to C-4	45	No capsule and empty capsule for EA for carbonate samples
1/3/1995	Test	G-3 to G-4	26	No capsule and empty capsule for EA for C and/or N samples
1/3/1995	Test	N-3 to N-4	58	No capsule and empty capsule for EA for N and/or N & O samples
6/6/2006	Test	S-3 to S-4	72	No capsule and empty capsule for EA for S samples

Fig. 12.8. Projects containing samples that represent an empty cup or an empty capsule of an EA analysis. These samples enable LIMS to make blank corrections.



Submission	LastName	Range	Media	Purpose
1/1/1995	Test	C-1	2	Calcite test sample
1/1/1995	Test	G-1	26	C and/or N test sample
1/1/1995	Test	N-1	59	N test sample
1/2/1995	Test	C-2	4	DIC test sample
1/2/1995	Test	G-2	28	C and S test sample
1/2/1995	Test	N-2	55	Nitrate test sample
1/3/1995	Test	G-5	5	CO2 test sample
1/3/1995	Test	N-5	60	N2O Test sample
6/6/2006	Test	S-1	72	Sulfate test sample
9/27/2012	Test	W-1 to W-2	1	Test or dummy samples

Fig. 12.9. Projects containing samples that can be used for testing of analytical methods.

12.2 Adding Daily-Use, Local Laboratory References

Daily-use, local laboratory measurement references (or in-house standards) are used to normalize measured isotopic results of samples to isotope-delta scales, such as the VSMOW-SLAP scales for δ^2H and δ^{18}O measurements.[2] It is the responsibility of the laboratory to obtain and use appropriate local measurement standards, and ensure they are carefully calibrated against international measurement scales. The backend database for a new laboratory is provided with 11 projects containing samples for this use (Fig. 12.6).

Consider an example in which a laboratory has prepared an L-glutamic acid reference material having δ^{13}C and δ^{15}N values of –3.02 ‰ and +4.14 ‰, respectively. The steps to add this material to the backend database for a new laboratory are:

1. On the LIMS main page click “View Projects -->.”
2. Select “Reference” for the name of the project submitter and click “Search.”
3. Note that the purpose of project with samples G-60 to G-89 is “Laboratory C&N reference materials,” which is what we need.
4. Open this project by double-clicking on it (Fig. 12.10)

5. Click “Samples” to display the first sample in this project, G-60, whose Sample ID is “ref1.”
6. Click “Edit.”
7. Replace “ref1” with “Lab L-glutamic acid A.”
8. Click “Save”, “Close”, “Close”, and “Close” to return to the main page. Note that no delta values were entered on the Sample form. They need to be entered using the Reference Samples form.

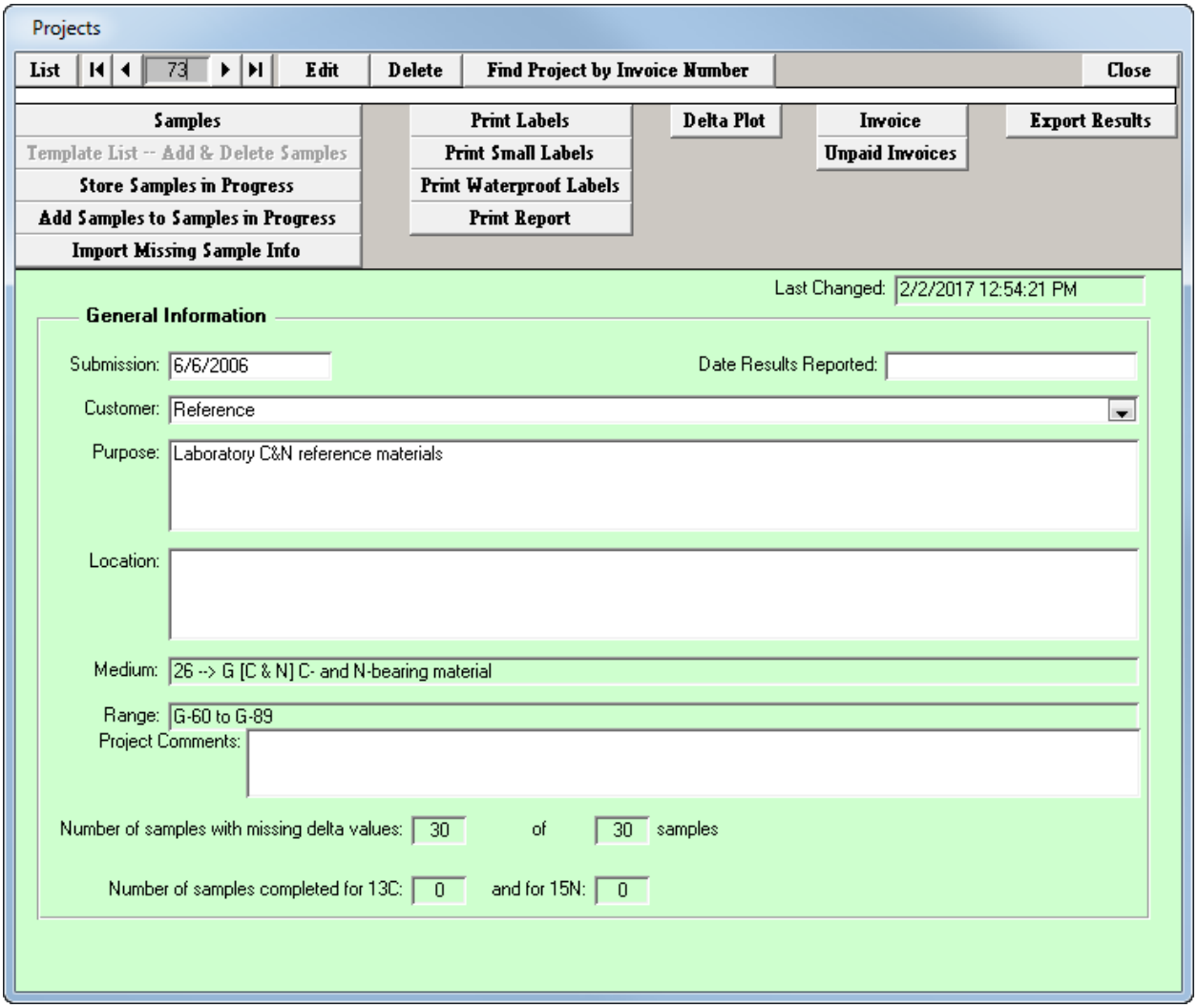


Fig. 12.10. Reference project for samples G-60 to G-89.

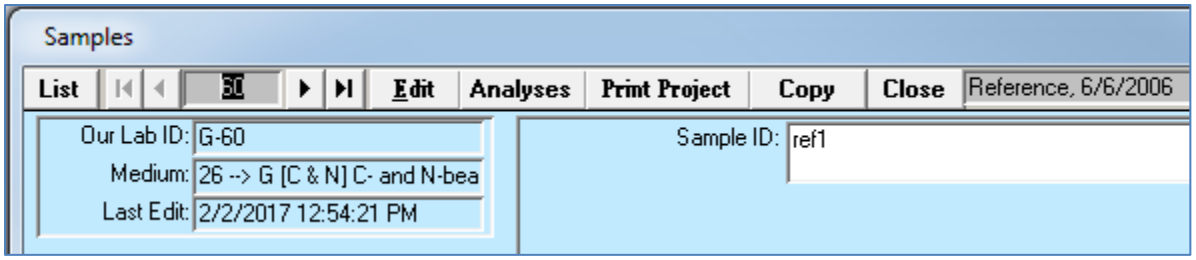


Fig. 12.11. Samples form showing G-60.

9. Click "Special Features" and click "Assign Lab References."
10. Click "Add."
11. Select "3 --> 13C" for the "Isotope."
12. Enter "G" and "60" for the "Our Lab ID."
13. Enter "–3.02" for the "Final Delta."
14. Enter "40.8" for the "Mass Fraction C" field, which is the same as for USGS40 (G-40).
15. Click the "Use for Linearity Correction" check box in case one might want to use this feature in LIMS.
16. Click "Save." The Reference Samples form should appear as shown in Figure 12.12.
17. Repeat steps 10 through 16, entering the δ^{15}N value of +4.14 ‰ and a mass fraction of nitrogen of 9.52 percent with an "Isotope" of "5 --> 15N."

⚠ IMPORTANT NOTE ABOUT MEASUREMENT STANDARD VALUES

Edited laboratory measurement standard values only affect **future results and samples that have not yet been normalized and stored.**
Previously normalized and stored results are not changed retroactively, and they retain all of the normalization parameters and the assigned isotope-standard values that were used at the time of their normalization processing. Prior data normalizations are therefore protected.

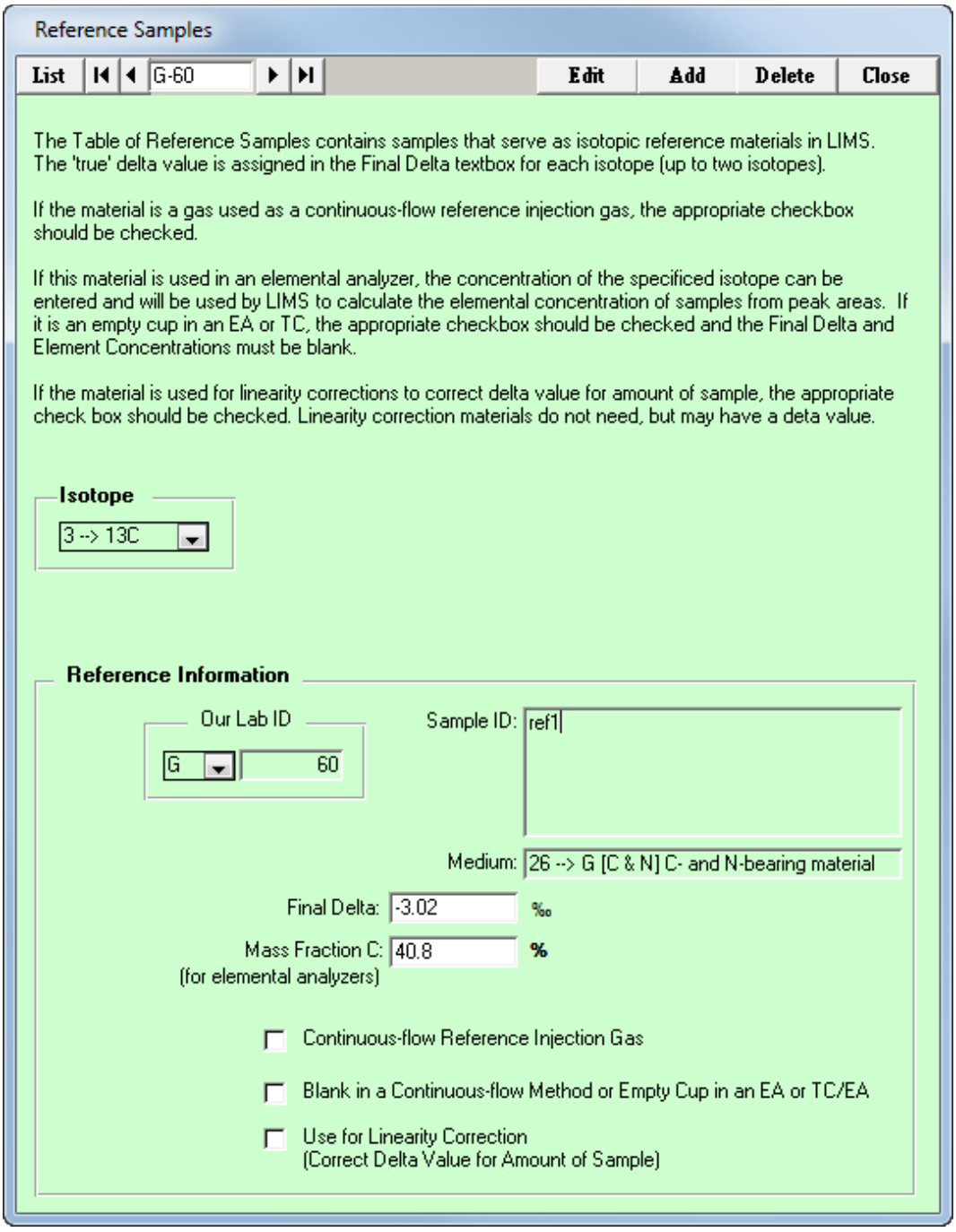


Fig. 12.12. Reference Samples form after entry of δ^{13}C value of G-60.

12.3 Adding Control Standards

A control standard is a reference material that is analyzed regularly and interspersed among samples and references to monitor the laboratory's quality assurance over time, such as with the

"Track My Lab QA/QC" feature in LIMS. A control standard is designated by assigning the high delta a value of "–999 ‰." The value of –999 serves as a flag in LIMS to denote that the delta value of this material is null. Because the control is null, LIMS will not use it in for normalization when it is included in analysis runs, and one is able to monitor its analytical results. If a medium has only a low delta value, it is assigned –999. Figure 12.13 is an example of an L-glutamic control standard with Our Lab ID of G-61.

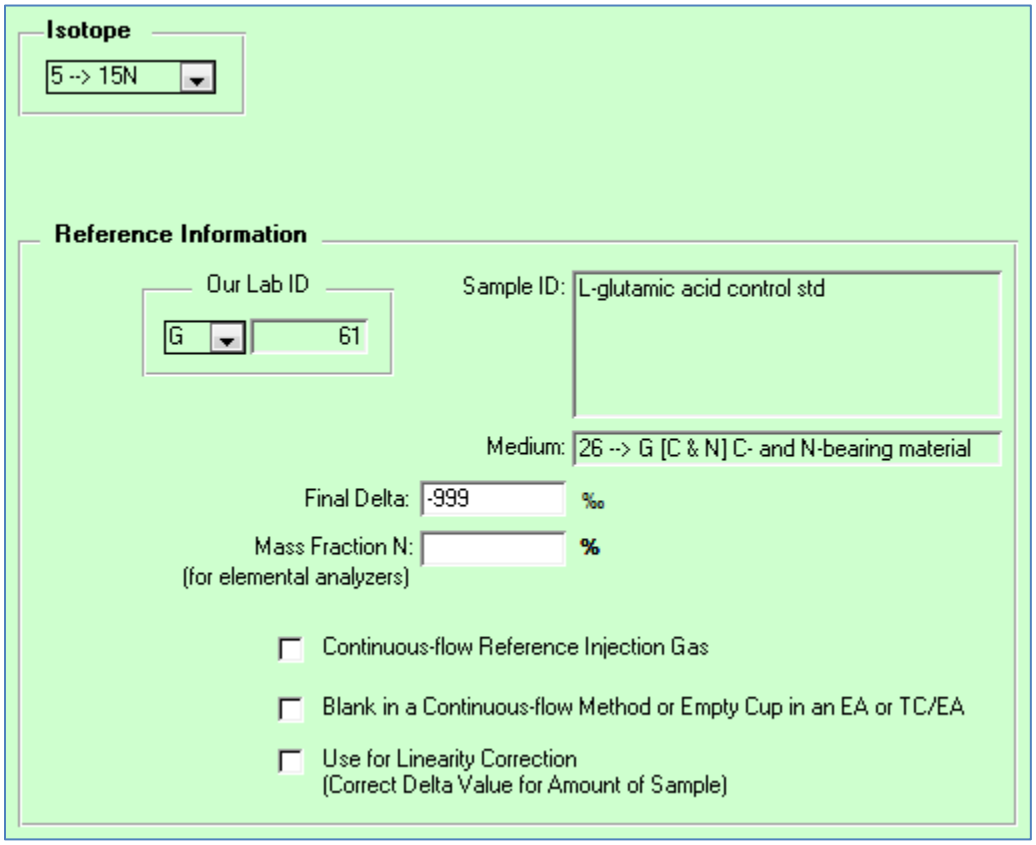


Fig. 12.13. Example of an L-glutamic control standard.

12.4 The Reference History Utility

As measurement techniques improve, isotope-delta values of internationally distributed isotopic reference materials can change, and users should update these values in their LIMS databases to stay current. If delta values of normalization references are changed, users need to keep in mind that delta values of identical samples analyzed prior to and after updates were implemented may not be comparable. Thus, a long-term, time-series evaluation of a control sample using the "Track My Lab QA/QC" feature in LIMS (Section 30), may show an offset at the time an isotope-delta value of a normalization reference was changed. Therefore, it is important to

maintain a list of edits to the "Table of References" that includes the date-time values of any changes to values of materials used for isotope-delta normalizations. This capability is performed by the "Ref History" button in Special Features (Fig. 12.14). Clicking "Ref History" opens the dialog box in Figure 12.15.

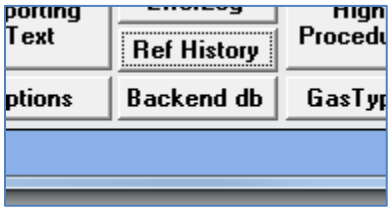


Fig. 12.14. The "Ref History" button in the Special Features panel.

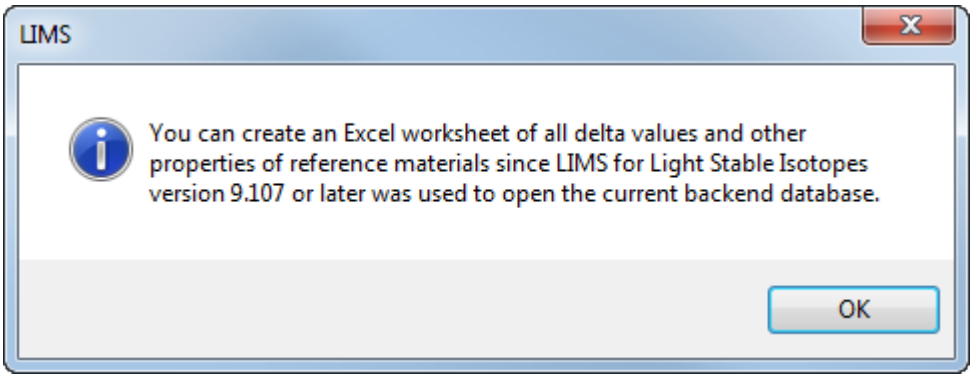


Fig. 12.15. Reference history message.

Clicking "OK" enables a user to create an Excel file named "Lab_Reference_History.xlsx." This file will contain a row for any changes made by users in the "Table of References." The file contains the eight columns:

- Isotope
- Element concentration (mass fraction)
- Use for Linearity Correction?
- OurLabID
- CF Std?
- Date-time of Row
- Delta Value
- Empty cup?

13 The Mass Spec Form

13.1 General Comments

A mass spectrometer is identified throughout LIMS by a single uppercase letter assigned to each instrument, such as T, and these codes are unique. Once analyses have been imported, this mass spectrometer code cannot be changed and the mass spectrometer cannot be deleted. Therefore, select these codes thoughtfully. It is best to avoid use of any of the sample prefixes, namely C, G, J, N, R, S, or W. Additionally, users may want to avoid I and O to eliminate confusion with 1 and 0. Additionally, the letter E is already used in LIMS, so that leaves 16 choices. Most laboratories will have far fewer than 16 mass spectrometers.

This section will use the Lake Isotope Laboratory LIMS database created in Section 4.8. Open the Mass Spec form by clicking "Special Features" and "Mass Specs" (or "Instruments" if a laser absorption spectrometer is installed in the laboratory and LIMS for Lasers 2015 also is in use). The mass spectrometer Diana ("D") is displayed (Fig. 13.1). Its use is discussed below.

The upper left panel of the Mass Spec form (Fig. 13.1) contains general information, properties, and preferences. Specific comments include:

- The "Code" field is a single letter as discussed above.
- If possible, it is best to keep the "Short Name" of the mass spectrometer relatively short; between 4 and 12 characters is best.
- The "Vendor serial number" is informational and can be omitted with no loss in LIMS performance.
- The "Analysis import format" is mass spectrometer dependent and is discussed below.
- The "Sample export format" is discussed below.
- The "Prefix of most common sample analyzed" is not required, but it makes LIMS more user friendly. In an isotope hydrology laboratory this might be "W," and in a biology laboratory it might be "G."
- The "Check for missing mass spec analyses when starting program" check box is enabled if it is important that all analyses be imported into LIMS. If analyses will not be imported, such as for on-off tests, then one can leave this check box unchecked.
- The "Require port numbers to be integers between 0 and 99" check box applies to dual-inlet off-line peripherals, and is not applicable to a laboratory using only continuous-flow IRMS (CF-IRMS).
- The "Require reference gas name to be integer between 1 and 366" check box is only applicable in some laboratories have a dual-inlet IRMS (DI-IRMS) and is not applicable to a laboratory using only a CF-IRMS.

- The check box labelled “Store unexpected procedures, such as 13C during an 18O analysis of water by equilibration with CO2” is an option for consideration. In most cases, the storage of these data is not needed.

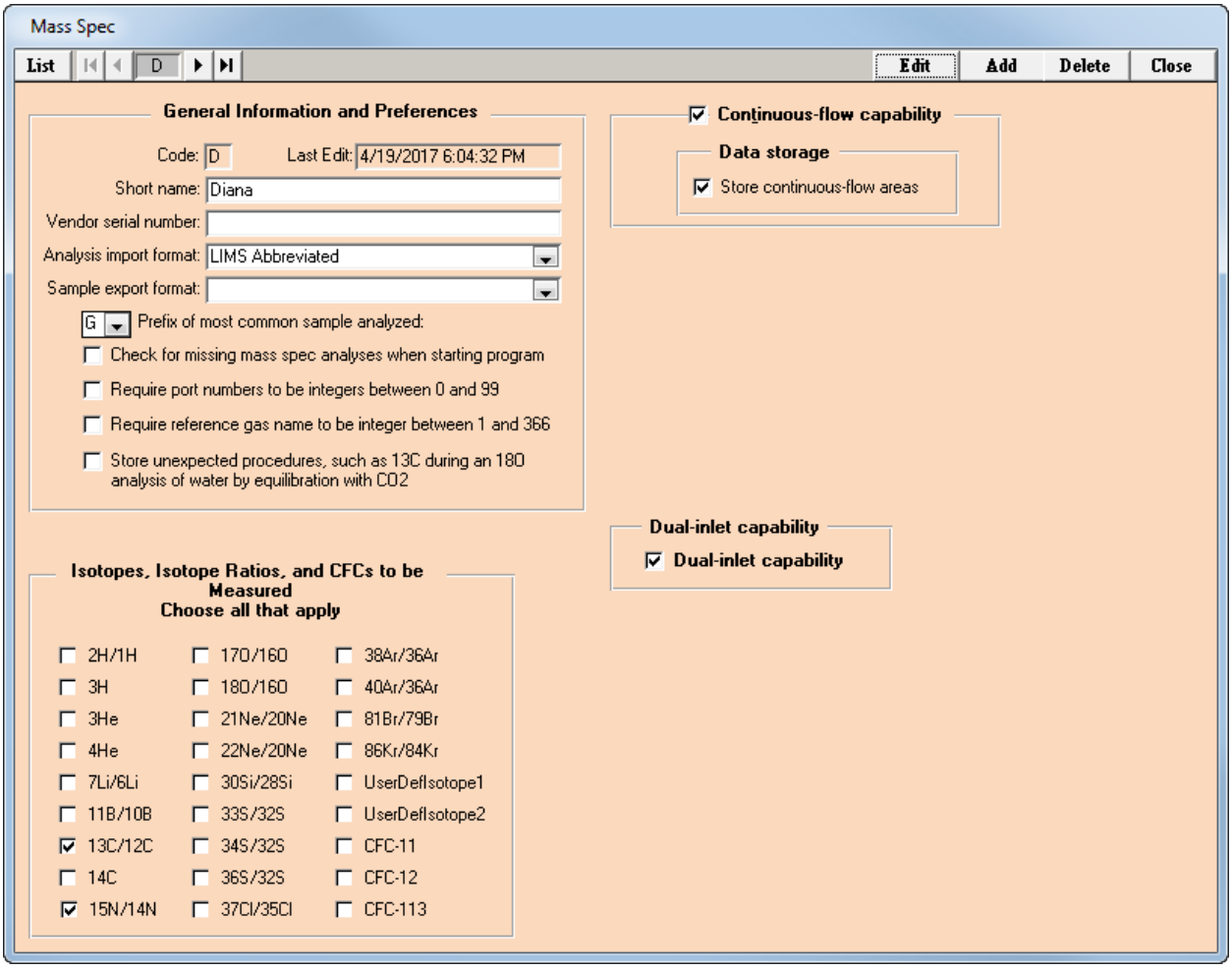


Fig. 13.1. Mass Spec form.

The lower left panel contains isotopes, isotope ratios and CFCs that can be analyzed with an instrument. There are two user definable isotopes, UserDefIsotope1 and UserDefIsotope2, that can be used for isotopes not listed in this panel. For example, a user might want to use LIMS to store and report δ^{65}Cu results and either UserDefIsotope1 or UserDefIsotope2 could be used for this purpose.

The upper right panel is used to provide details of a CF-IRMS. Normally the “Store continuous-flow areas” check box will be checked so that these areas are imported and can be used for

determining elemental mass fractions (concentrations) if desired. If the "Analysis import format" field is set to "Thermoquest Finnigan ISODAT NT," the user will have the possibility to have LIMS check the minimum and/or maximum amplitude of electrometer outputs. LIMS can provide an error code upon importing an analysis indicating that the peak amplitude is too low (very small sample or bad sample conversion) or the amplitude is too high, indicating that an electrometer may be saturated. The "CF Ref Inj Gases" are needed if the "Analysis import format" field is set to "Thermoquest Finnigan ISODAT NT." The user has the opportunity to import and store information for each of the reference injection peak analyses. Commonly, these data are not stored; nevertheless, LIMS needs the entries of the "CF Ref Inj Gases" in case they are stored.

The lower right panel is used to provide details of a DI-IRMS. The data in most of these fields apply to ISODAT used on a Finnigan 251 IRMS.

Very occasionally one may realize that the mean isotope-delta value calculated from several mass spectrometer analyses is in error and needs to be adjusted. If the user has knowledge of what the true value of the sample should be, *e.g.* the weighted average of two "close" delta values, the Ethereal mass spectrometer shown in Figure 13.2 can be used to add this isotope-delta value to the table of analyses in LIMS. This is discussed in Section 25.4).

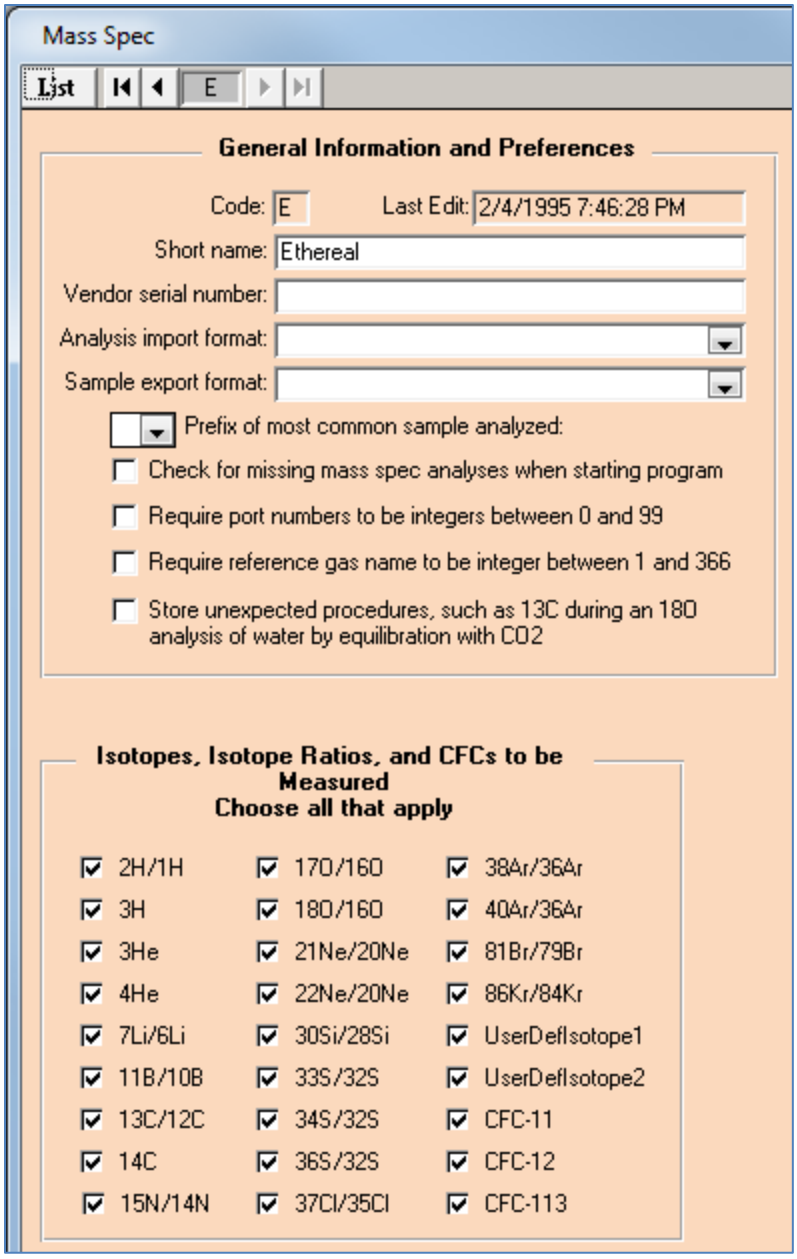


Fig. 13.2. The Ethereal mass spectrometer.

13.2 Analysis Import Formats

From the "Analysis import format" control, one is able to select the import format of the mass spectrometer, which will depend upon the manufacturer of the mass spectrometer. Import formats in this control and specific comments are presented in Table 13.1. Most users will either select the "LIMS Abbreviated" format or the "Thermoquest Finnigan ISODAT NT" format.

Table 13.1. Analysis import formats in LIMS

Name	Comments
LIMS Abbreviated	A very flexible import format that uses an Excel file. It is discussed in Section 17.
LIMS Default	This format uses a Microsoft Access file and has been updated since it use and description in versions 7 and 8 of LIMS [1] with the addition of importing amount and amount unit columns. It is discussed in Section 18.
Europa 20 20 CF	These files are now imported using the LIMS Abbreviated format (see Section 17). See importing example in Section 22.3.
Europa Scientific	These files are now imported using the LIMS Abbreviated format (see Section 17). See importing example in Section 22.3.
Los Gatos Research	These csv files must be imported using LIMS for Lasers 2015, which can be linked to the LIMS backend database of the laboratory.
Micromass	This is a csv file format and is now imported using the LIMS Abbreviated format (see Section 17). See importing example in Section 22.4.
Micromass MassLynx	These files along with IonVantage files can be imported. See importing example in Section 21.
Micromass OS/2 v. 1.67 CF	These files are now imported using the LIMS Abbreviated format (see Section 17). See importing example in Section 22.4.
Nu	These files are now imported using the LIMS Abbreviated format (see Section 17). See importing example in Section 22.5.
Picarro	These csv files must be imported using LIMS for Lasers 2015, which can be linked to the LIMS backend database of the laboratory.
SerCon Callisto	These files are now imported using the LIMS Abbreviated format (see Section 17). See importing example in Section 22.6.
Thermoquest Finnigan ISODAT	These files can be converted to Excel and imported. See importing example in Section 20.
Thermoquest Finnigan ISODAT NT	This may be the most common import format used with LIMS. Select it for Delta, Delta Plus, Delta XL, Delta V Plus, and similar mass spectrometers. See importing example in Section 19.
<Multiple>	No longer needed. Retained for future expansion. Should not be used for any Thermo Scientific, Thermoquest, or Finnigan instruments.

<None>	If an instrument cannot generate a data output file for some reason, it is suggested that the LIMS Abbreviated format be use (see Section 17).

13.3 Sample Export Formats

The "Sample export format" dropdown enables a user to select the format of the file created by LIMS when a user clicks "Create a Sample List -->" on the LIMS main page (Section 33.5.2), and they are presented in Table 13.2. Commonly, an Excel file of samples to be analyzed in a run is created, and they can be copied and pasted into the so-called sequence table of the mass spectrometer data acquisition and control software. The most commonly used sample export format is "LIMS EA + TC/EA."

Table 13.2. Sample export formats in LIMS

Name	Comments
LIMS Default	Creates a Microsoft Excel (xls) file (Section 33.4.2). [1]
LIMS Default for old ISODAT	Creates a Microsoft Excel (xls) file (Section 33.4.5).
Analytical Precision	No longer available. [1]
Europa Scientific	No longer available. [1]
IonVantage 1.1	Creates a Microsoft Access 2.0 file with a suffix of spl (Section 33.4.4).
LIMS EA + TC/EA	Creates an Excel file enabling user to cut and paste to the ISODAT sequence table (Section 33.4.3).
Los Gatos Research	This version of LIMS will not export CSV files. These files need to be created using LIMS for Lasers 2015, which can be linked to the LIMS backend database of the laboratory.
MassLynx 4.0	Creates a Microsoft Access 2.0 file with a suffix of spl (Section 33.4.4).
Micromass MassLynx 3.6	Creates a Microsoft Access 2.0 file with a suffix of spl (Section 33.4.4).
Picarro	This version of LIMS will not export csv files. These files need to be created using LIMS for Lasers 2015, which can be linked to the LIMS backend database of the laboratory.
<Multiple>	Commonly selected for Thermo Scientific, Thermoquest, or Finnigan Delta mass spectrometers so that user can select the "LIMS EA + TC/EA" format and another export format.
<None>	Equivalent to leaving this field blank.

14 Adding a Thermo Scientific/Thermoquest/Finnigan Mass Spectrometer having an ISODAT NT or Later Data System

14.1 Steps in LIMS

In the following example, a Thermo Scientific DELTA V PLUS IRMS having both continuous-flow and dual-inlet capabilities for $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ measurements will be created in LIMS. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8.Users can modify these instructions to set up Delta, Delta^{plus}, Delta XL, 252, 253, and other similar IRMSs. Before continuing, readers should be fully familiar with Section 13.

1. On the LIMS main page click "Special Features."
2. Click "Mass Specs" (or "Instruments" if a Picarro or Los Gatos Research laser absorption spectrometer is installed).
3. Click "Add" and LIMS displays the message shown in Figure 14.1.
4. Click "OK."
5. Enter "H" for the "Code" for this example.
6. Enter "Hercules" for the "Short name" for this example.

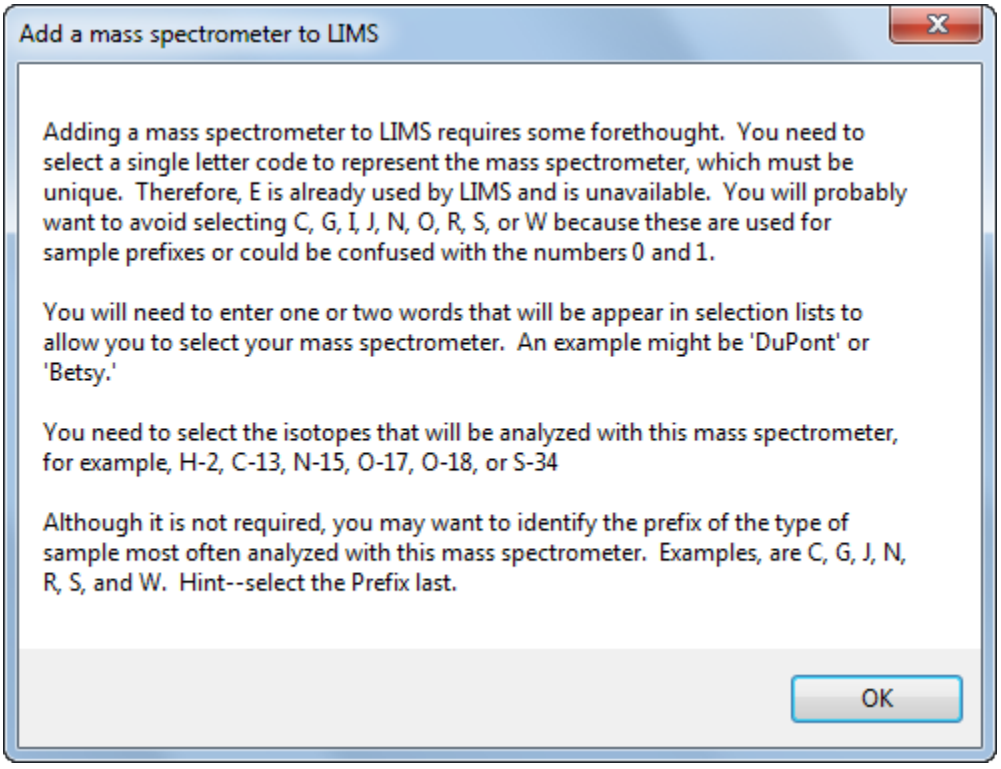


Fig. 14.1. Tips for installing a new mass spectrometer.

7. Select “Thermoquest Finnigan ISODAT NT” for the “Analysis import format.”
8. Select “LIMS EA + TC/EA” for the “Sample export format.”
9. In the lower left panel, enable check boxes for “13C/12C”, “15N/14N”, “18O/16O”, and “34S/32S.”
10. In the upper left panel, select “G” for the “Prefix of the most common sample analyzed.”
11. In the upper right panel, enable the “Continuous-flow capability” check box.
12. Enable the “Store continuous-flow areas” check box.
13. Enable the “Check peak amplitudes” check box.
14. Select “<0.5 V Amplitude” for the “Min amplitude” so that users will be alerted by LIMS when the amplitude of any peak is less than 0.5 V. Should the desired value not be listed, users can add additional values (see Appendix D).
15. Select “>40 V Amplitude” for “Max amplitude” to alert users that an electrometer may have saturated or may be close to saturating because a Thermo Scientific DELTA V PLUS has 50-V electrometers. For a Delta Plus and a Delta XL, a more reasonable value would be “>10 V Amplitude” because the electrometer outputs are less than 15 V. Should the desired value not be listed, users can add additional values (see Appendix D).
16. For the “CF Ref Inj Gases” CO field enter “R-31,” which is the first CO reference injection gas shown in Figure 12.7. LIMS will prompt the user for the $\delta^{13}C$ value of R-31 (Fig. 14.2) and the $\delta^{18}O$ value of R-31.
17. Add “R-6”, “R-11”, “R-21”, “R-26”, and “R-16”, respectively, for “CO2”, “N2”, “N2O”, “SO2”, and “O2” continuous-flow reference injection gases.
18. Enable the “Dual-inlet capability” check box as Hercules has a dual-inlet.
19. Click “Save” to create the mass spectrometer in LIMS (Fig. 14.3).

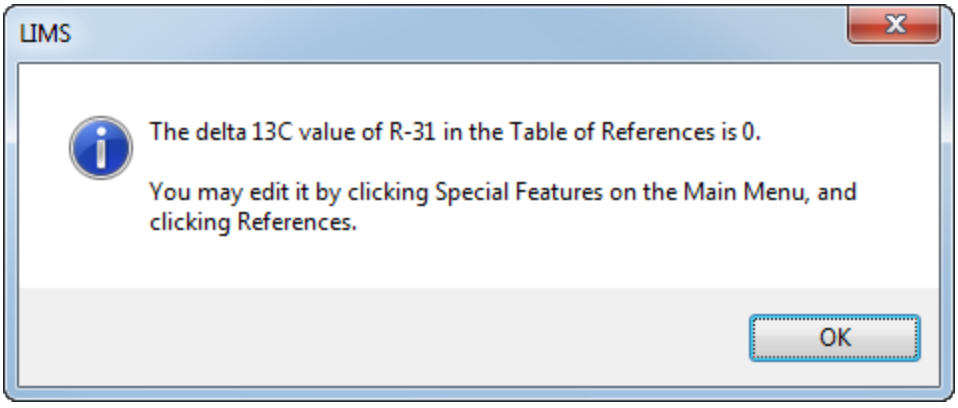


Fig. 14.2. Example of LIMS prompt when adding a continuous-flow reference injection gas.

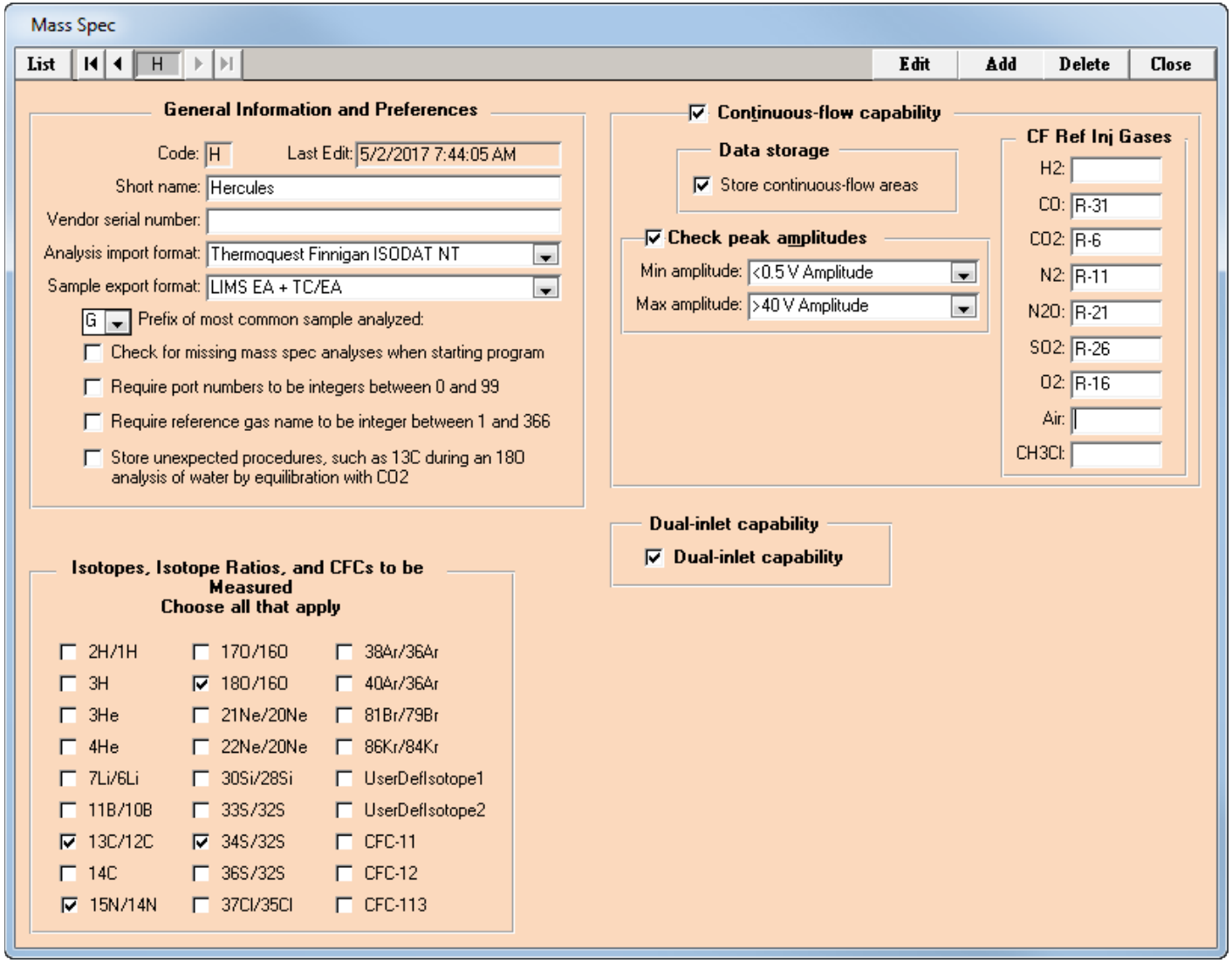


Fig. 14.3. Example of a mass spectrometer created in LIMS having an analysis import format of "Thermoquest Finnigan ISODAT NT" and having both continuous-flow and dual-inlet capability.

A mass spectrometer can only be deleted if it has no analyses, that is if no analyses have been imported or have been created manually using the "Add or Edit Analyses" by clicking "View / Edit Information about Samples Analyses" on the LIMS main page (Section 27).

Some users may analyze "Air" in continuous-flow mode. In such a case, a continuous-flow nitrogen- and oxygen-bearing gaseous reference material, presumably with prefix R, needs to be created (see Section 12) and entered into the "CF Ref Inj Gases" field labelled "Air."

For some mass spectrometers all isotopic analyses will be imported. In the event that one or more analyses are not imported, LIMS can alert the user that analyses are missing if the "Check for missing mass spec analyses when starting program" check box is enabled. The purposes of the other check boxes and fields in the Mass Spec form are presented in Section 13.

⚠ Remember that once data from a mass spectrometer has been imported into LIMS, that instrument cannot be deleted!

14.2 Steps in ISODAT

In the following example, a Delta^{plus} XP IRMS is set up for LIMS by assigning "X" as the LIMS mass spectrometer code. Using ISODAT (version NT 1.50 or later):

1. Close all ISODAT windows that are open.
2. ISODAT is running in the background, even when all windows are closed. Right-click the ISODAT icon in the taskbar in the lower right corner of the screen and select "Shut Down" (Fig. 14.4) to fully close ISODAT.
3. When prompted to confirm the shutdown of ISODAT, click "Yes."
4. Open the ISODAT Configurator program.
5. Once the application opens, select the "Options" tab and select "Global Settings" (Fig. 14.5), and a form will open (Fig. 14.6) with which one can edit the prefix of mass spectrometer analyses, the "Start at No" value for analyses, color display preferences, and the number of digits displayed when presenting results.
6. To edit the prefix of mass spectrometer analyses enter an upper case letter followed by a hyphen in the "Prefix" field. For this example, enter "X-" as shown in Figure 14.6. This entry should be identical to the mass spectrometer ID in LIMS and must be unique in LIMS. It is suggested that C, G, J, N, R, S, and W be avoided as they are used for sample prefixes of the LIMS Our Lab ID. Additionally, it is suggested that I and O be avoided to avoid confusion with 0 and 1.
7. Click "OK" to save the entry.

Importing Thermo Scientific DELTA V PLUS analyses is the next step and is discussed in Section 19.

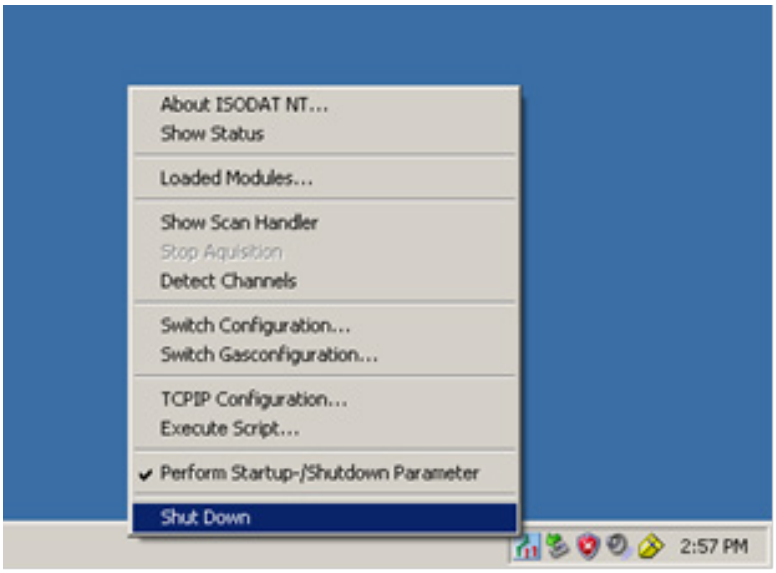


Fig. 14.4. Menu shown after right-clicking the ISODAT icon in the taskbar.

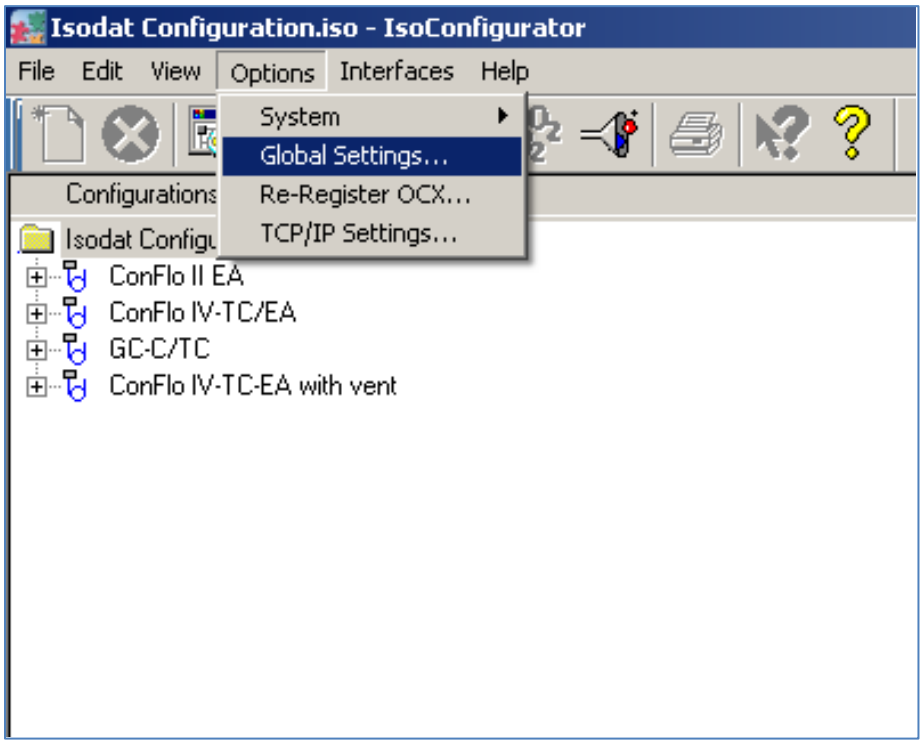


Fig. 14.5. Toolbar of the ISODAT Configurator.

⚠ If a hard drive or a computer is replaced, remember to set the “Prefix” and the “Start at No” as soon as ISODAT is installed. It is critical that the value of the “Start at No” be greater than any value in LIMS because all analyses of a mass spectrometer must be unique in LIMS.

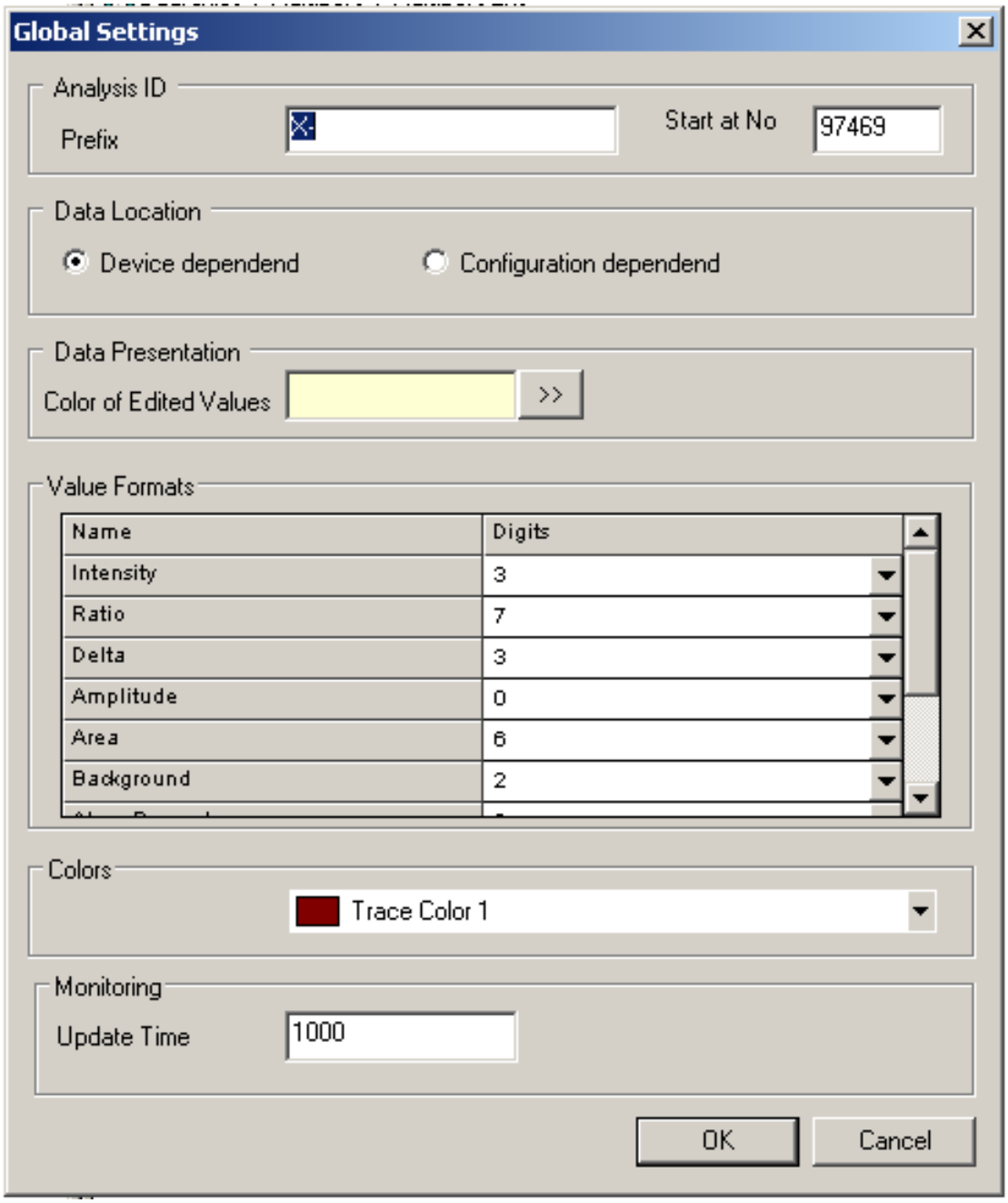
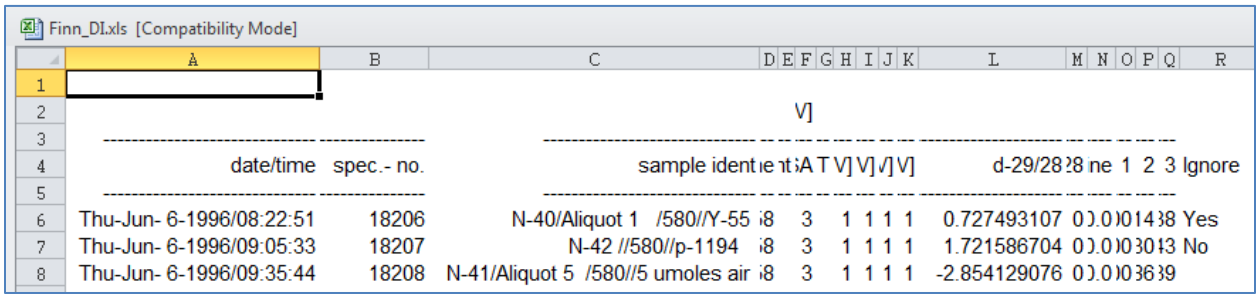


Fig. 14.6. Global Setting form of the ISODAT Configurator.

15 Adding a Finnigan MAT Mass Spectrometer

15.1 Adding a Dual-inlet Finnigan MAT 251

The ISODAT data acquisition and control system of a MAT 251 saves isotope-data files as Microsoft Works wks files. Because Microsoft Office 2007 and later versions do not import wks files, these wks files need to be saved as Excel files so that they can be imported by LIMS. Figure 15.1 displays an example of a dual-inlet file from a MAT 251 that has been saved as an Excel file.



Finn_DI.xls [Compatibility Mode]

	A	B	C	D E F G H I J K	L	M N O P Q	R
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2				V]			
3	----------	----------	----------	-- -- -- -- -- -- --	----------	-- -- -- -- --	
4	date/time	spec.- no.	sample identıe ıt ;A T V] V] √] V]		d-29/28 ?8 ne 1 2 3		Ignore
5	----------	----------	----------	-- -- -- -- -- -- --	----------	-- -- -- -- --	
6	Thu-Jun- 6-1996/08:22:51	18206	N-40/Aliquot 1 /580//Y-55 ;8	3 1 1 1 1	0.727493107	0).0)0 1 4 }8	Yes
7	Thu-Jun- 6-1996/09:05:33	18207	N-42 //580//p-1194 ;8	3 1 1 1 1	1.721586704	0).0)0 3 0 13	No
8	Thu-Jun- 6-1996/09:35:44	18208	N-41/Aliquot 5 /580//5 umoles air ;8	3 1 1 1 1	-2.854129076	0).0)0 3 6 39	

Fig. 15.1. Example Excel file created from a MAT 251 dual-inlet wks exported file.

In the following example, a MAT 251 DI-IRMS for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$ measurements will be created in LIMS. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13.

1. On the LIMS main page click "Special Features."
2. Click "Mass Specs" (or "Instruments" if a Picarro or Los Gatos Research laser absorption spectrometer is installed).
3. Click "Add" and LIMS displays the message shown in Figure 15.2.
4. Click "OK."
5. Enter "F" for the "Code" for this example.
6. Enter "Finnigan 251" for the "Short name" for this example.
7. Select "Thermoquest Finnigan ISODAT" for the "Analysis import format."
8. In the lower left panel, enable check boxes for "13C/12C", "15N/14N", and "18O/16O."
9. In the upper left panel, select "G" for the "Prefix of the most common sample analyzed."
10. Enable the "Dual-inlet capability" check box.
11. Click "Set Thermoquest Finnigan ISODAT Default Column Headings," which will populate prompt to replace the existing headings. Click "OK" and the "Column

Heading" will be updated.

12. Confirm that the analysis heading for each isotope-delta value is correct, that is, agrees with values in heading of files to be imported. These column names are best guesses and may need to be changed. For example, for δ^{15}N imports, confirm that the value "d-29/28" is the column heading in each dual-inlet δ^{15}N file to be imported. For example, this entry occurs as cell L4 in Figure 15.1. If "d-29/28" is not correct, it is suggested that the correct text entry in the cell identifying δ^{15}N results be copied and pasted.
13. Click "Save" to create the mass spectrometer in LIMS (Fig. 15.3).

Previous versions of LIMS, such as LIMS 9.101 (July 31, 2013) were able to import the major ion beam values, interfering masses, and ion gauge values. These capabilities were seldom used, and have been eliminated from this new version of LIMS. Should these importing capabilities be needed, one only needs to retain LIMS 9.101 and run it in parallel with this later version of LIMS in the same manner as one can connect both LIMS for Light Stable Isotopes and LIMS for Lasers 2015 to the same backend database.

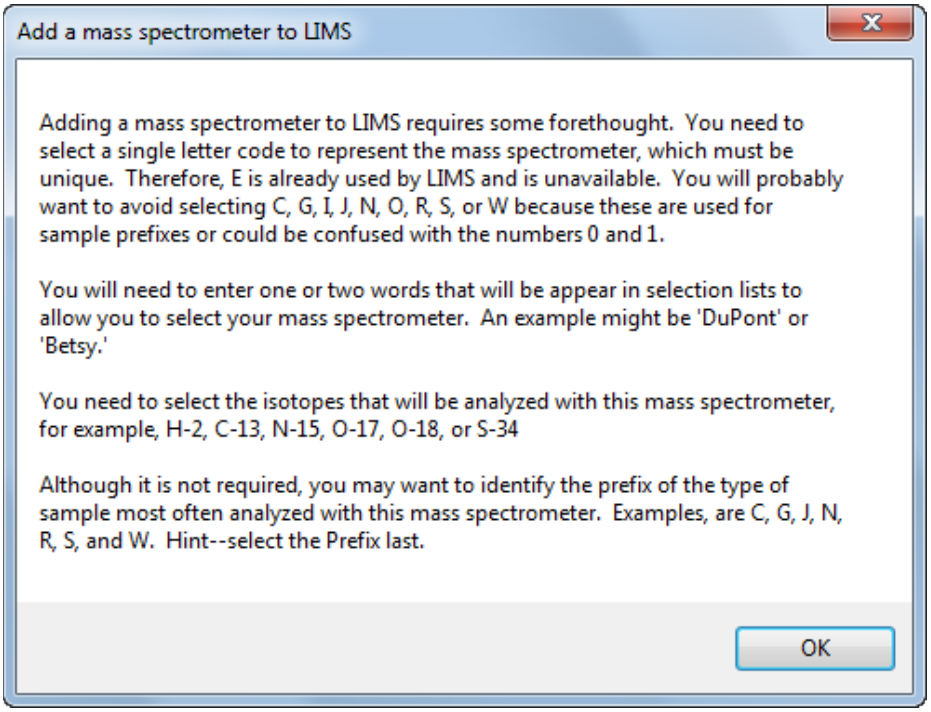


Fig. 15.2. Tips for installing a new mass spectrometer.

Finnigan mass spectrometer files that require the LIMS ISODAT import format can be identified by the fact that they have no mass spectrometer prefix in the analysis number column and "spec.- no." or "Spec.-no." appears in the analysis number column.

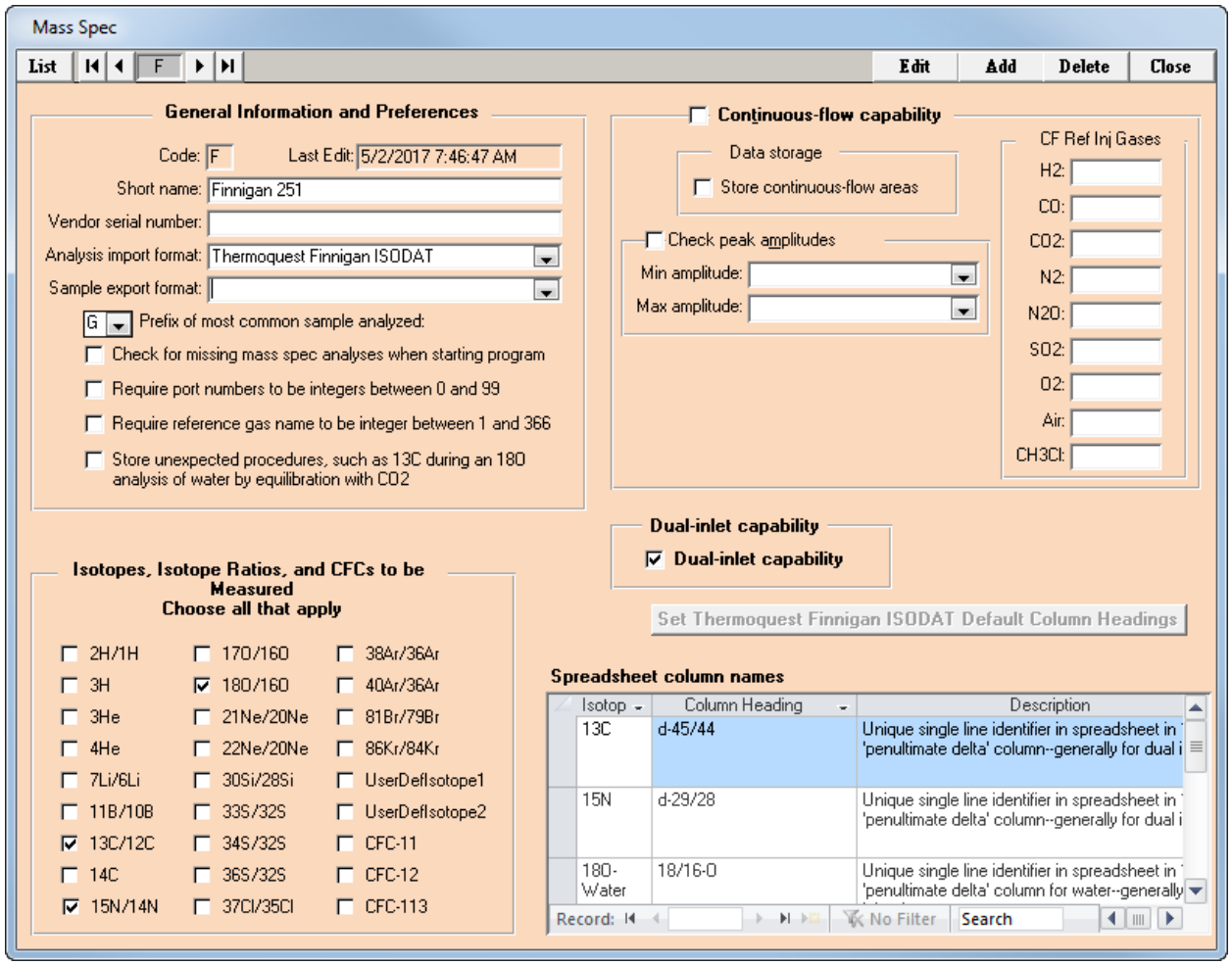


Fig. 15.3. Example of a MAT 251 DI-IRMS created in LIMS.

> If a user needs to replace a computer or hard disk, the Spec No must be set during installation to the next unique integer analysis number.

15.2 Adding Continuous-flow Capability

Some Finnigan MAT IRMSs have continuous-flow capability, enabling them to connect to EAs or gas chromatograph combustion (GCC) peripherals. To add continuous-flow capability to the IRMS shown in figure 15.3, perform the following steps:

1. Click “Edit.”
2. Enable the “Continuous-flow capability” check box.
3. Enable the “Store continuous-flow areas” check box.

4. Because the IRMS has $\delta^{13}C$, $\delta^{15}N$, and $\delta^{18}O$ capabilities, one can expect that at a minimum CO_2 and N_2 continuous-flow reference injections gases will be needed. Enter "R-6" for the "CO2" reference injection gas and enter "R-11" for the "N2" reference injection gas. LIMS will display messages such as shown in Figure 14.2.
5. Click "Save" to add continuous-flow capability to the Finnigan 251 IRMS in LIMS (Fig. 14.3).

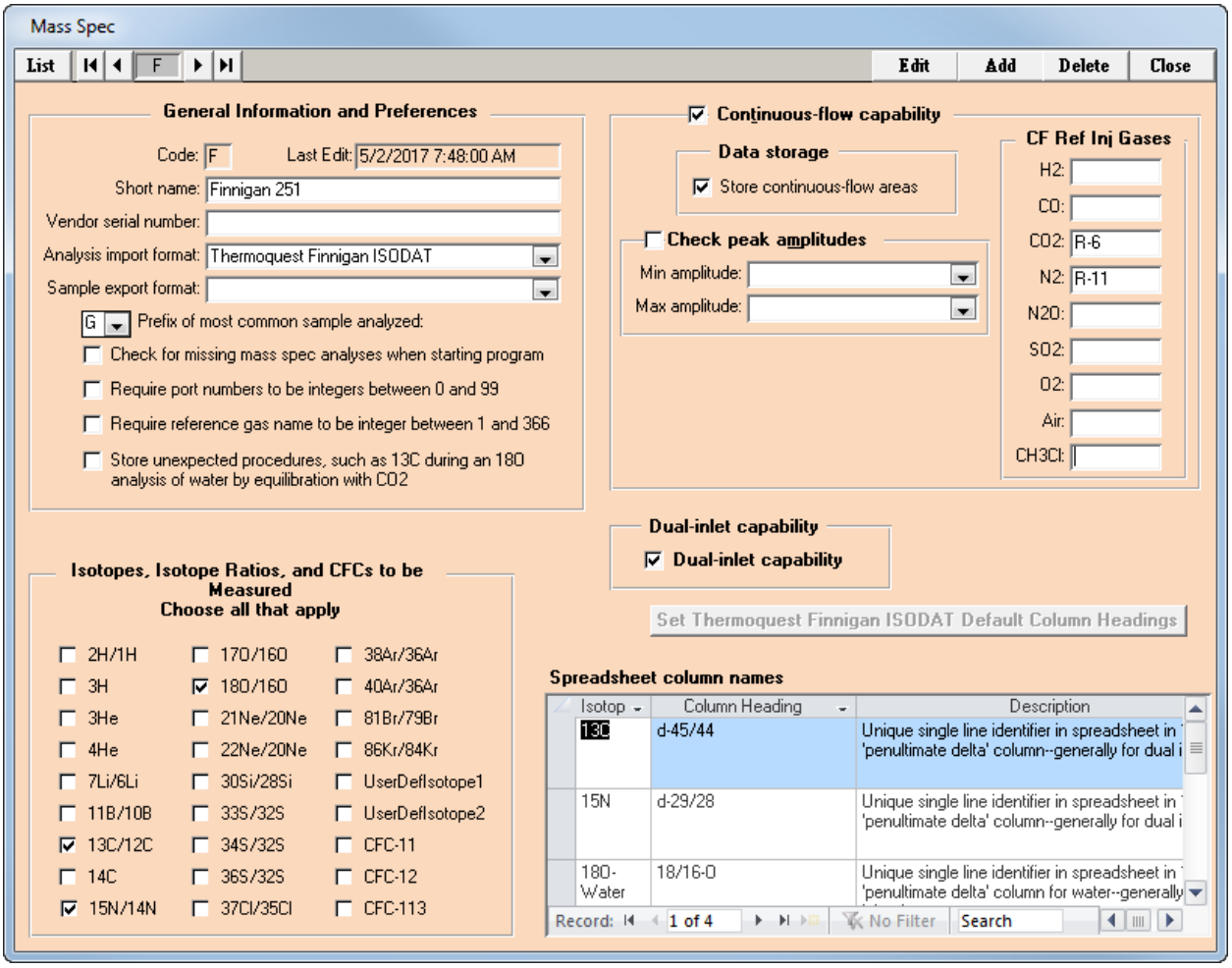


Fig. 15.4. Example of a MAT 251 having continuous-flow and dual-inlet capability.

This completes the installation of a Finnigan MAT IRMS. Importing Finnigan analyses is the next step and is discussed in Section 20.

16 Adding an Elementar/GV Instruments/Micromass Mass Spectrometer having an IonVantage or MassLynx Data Acquisition and Control System

16.1 Steps in LIMS

The IonVantage 4x, MassLynx 3.6, and MassLynx 4.0 data acquisition and control systems of Elementar, GV Instruments, and Micromass UK Limited are fully compatible with LIMS.[8] In the following example, an IRMS having an IonVantage data acquisition and control system and both continuous-flow and dual-inlet capabilities for $\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ measurements will be created in LIMS. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13.

1. On the LIMS main page click "Special Features."
2. Click "Mass Specs" (or "Instruments" if a Picarro or Los Gatos Research laser absorption spectrometer is installed).
3. Click "Add" and LIMS displays the message shown in Figure 14.1.
4. Click "OK."
5. Enter "M" for the "Code" for this example.
6. Enter "Minerva" for the "Short name" for this example.
7. Select "Micromass MassLynx" for the "Analysis import format."
8. Select "IonVantage 1.1" for the "Sample export format." If a user had an IRMS having either a "MassLynx 3.6" or "MassLynx 4.0" data acquisition and control system, "MassLynx 3.6" or "MassLynx 4.0" would be selected to create sample files with the correct file format.
9. In the lower left panel, enable check boxes for "2H/1H", "13C/12C", "15N/14N", "18O/16O", and "34S/32S".
10. In the upper left panel, select "G" for the "Prefix of the most common sample analyzed."
11. In the upper right panel, enable the "Continuous-flow capability" check box.
12. Enable the "Store continuous-flow areas" check box.
13. For the CO "CF Ref Inj Gases" enter "R-31," which is the first CO reference injection gas shown in Figure 12.7. LIMS will prompt the user of the $\delta^{13}C$ value of R-31 (Fig. 14.2) and the $\delta^{18}O$ value of R-31.
14. Add "R-1", "R-6", "R-11", "R-21", "R-26", and "R-16", respectively, for "H2", "CO2", "N2", "N2O", "SO2", and "O2" continuous-flow reference injection gases.
15. Enable the "Dual-inlet capability" check box.
16. Click "Save" to create the mass spectrometer in LIMS (Fig. 16.1).

For some mass spectrometers all isotopic analyses will be imported. In the event that one or more analyses are not imported, LIMS can alert the user that analyses are missing if the "Check for missing mass spec analyses when starting program" check box is enabled. The purposes of the other check boxes and fields in the Mass Spec form are presented in Section 13.

⚠ Remember that once data from a mass spectrometer has been imported into LIMS, that instrument cannot be deleted!

16.2 Steps in IonVantage or MassLynx 3.6 or 4.0

The IonVantage and MassLynx data acquisition and control systems are unique in that they can transfer isotopic results to a LIMS backend database in real time. Instructions for setting up IonVantage and MassLynx 3.6 or 4.0 for LIMS are found in section 4 of the "MassLynx 3.6i LIMS interface handbook,"[8] created by Tim Brockwell (Micromass UK Ltd.) with assistance from Len Wassenaar (when at Environment Canada, Saskatoon, Saskatchewan, Canada). Setting up the LIMS interface is discussed in Section 5.3 of this handbook. This highly-detailed handbook is provided as a file named "MassLynx-LIMS interface manual-SCN1022ib5.pdf" in a folder named "Section 16" that accompanies this manual. If there are difficulties with the installation, please contact tbcoplen@usgs.gov for suggestions on resolution of issues.

This completes installation of an IRMS with $\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ measurement capability and with an IonVantage data acquisition and control system. Importing IonVantage analyses is the next step and is discussed in Section 21.

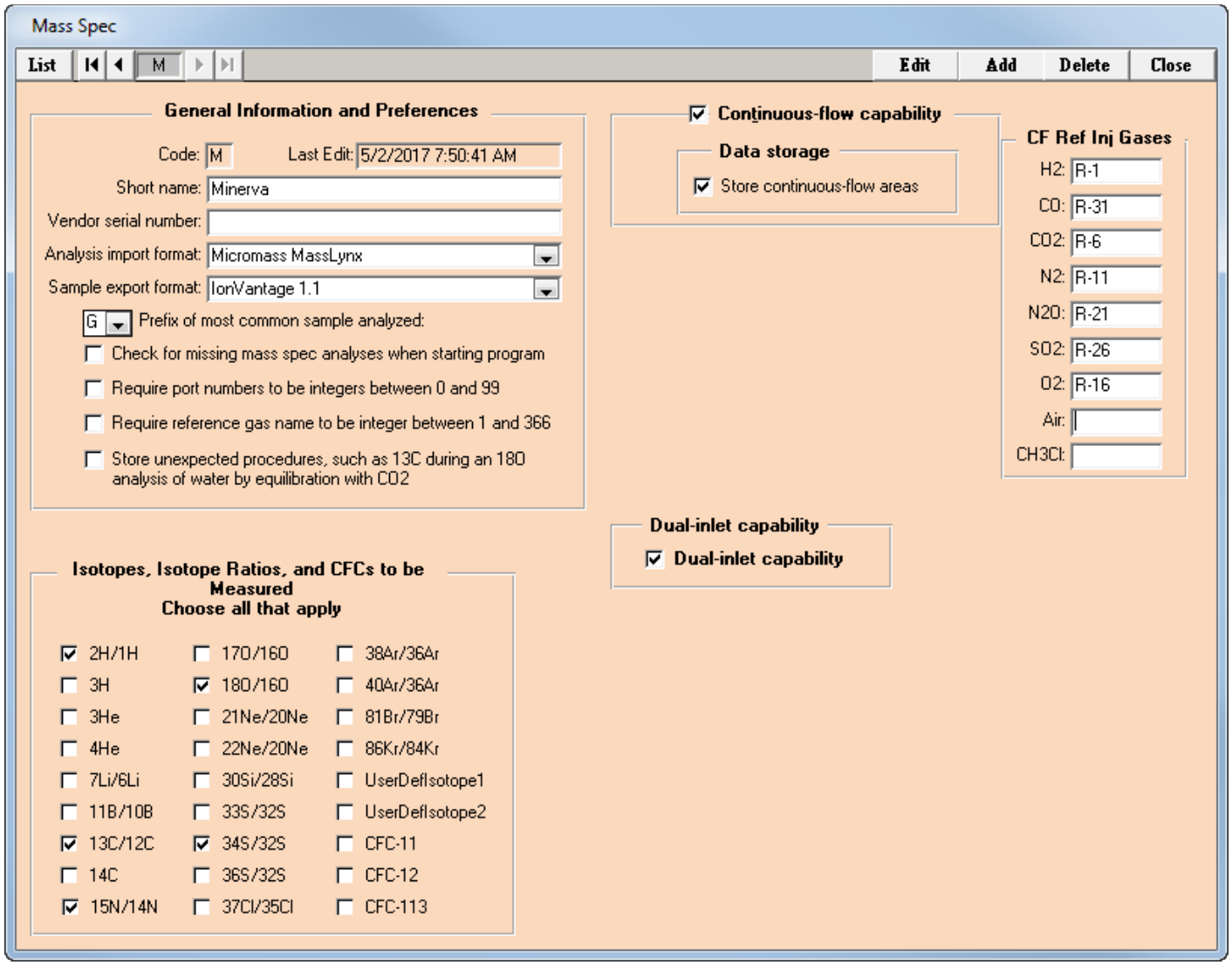


Fig. 16.1. Example of a mass spectrometer created in LIMS having an IonVantage data system and having both continuous-flow and dual-inlet capability.

17 Adding a Mass Spectrometer having the "LIMS Abbreviated" Import Format

17.1 The LIMS Abbreviated Import Format

The LIMS Abbreviated import format is the most flexible of all formats for importing measurement results into LIMS. Isotope-measurement results (or results from other instruments) are imported using an Excel file. The first row of the Excel file contains unique column headings to identify data in each column. Rows two and greater contain the measured results to be imported (Table 17.1). An Excel file can have as few as three data columns or more than a dozen columns, depending upon the user's needs. An example of an Excel file having the minimum number of data columns (three) is shown in Figure 17.1.

An Excel file can contain optional columns as shown in Table 17.2. The user should pay attention to the comments for each column heading in the right column of Table 17.2 because all column headings cannot be used in every Excel file. For example, if "Procedure" appears, only one delta-value column is allowed. "Area" should not be used if there are two delta-value columns; instead, for each area columns, of which there can be two, use "Area All C", "Area All N", etc., as appropriate for the isotope deltas being imported.

Table 17.1. Required data columns for the LIMS Abbreviated import format
[Column headings must be spelled exactly as shown and are case sensitive.]

Column heading	Isotope code	Description and comments
Line		Commonly 1, 2, 3, etc. Should be an integer.
OurLabID		This is the ID LIMS assigns to samples upon login. Note no spaces.
A delta or other value, which can be any one of the following:		
Delta H-2	2	$\delta^{2}H$
Delta C-13	3	$\delta^{13}C$
Delta S-33	4	$\delta^{33}S$
Delta N-15	5	$\delta^{15}N$
Delta S-34	6	$\delta^{34}S$

Delta O-17	7	$\delta^{17}O$
Delta O-18	8	$\delta^{18}O$
Delta S-36	9	$\delta^{36}S$
Delta Li-7	10	$\delta^{7}Li$
Delta B-11	11	$\delta^{11}B$
Delta Si-30	12	$\delta^{30}Si$
Delta Cl-37	13	$\delta^{37}Cl$
C-14	14	^{14}C
H-3	15	^{3}H
He-3	16	^{3}He
He-4	17	^{4}He
Ar-38	18	^{38}Ar
Ar-40	20	^{40}Ar
Ne-21	21	^{21}Ne
Ne-22	22	^{22}Ne
Br-81	23	$\delta^{81}Br$
Kr-86	24	^{86}Kr
UserDefIso-1	25	UDI1 (user definable isotope 1)
UserDefIso-2	26	UDI2 (user definable isotope 2)
CFC-11	27	CFC-11
CFC-12	28	CFC-12
CFC-113	29	CFC-113

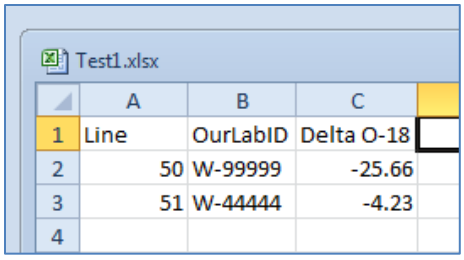


Fig. 17.1. Example Excel file having three columns that can be imported with the LIMS Abbreviated import format.

Table 17.2. Optional data columns for the LIMS Abbreviated import format

[Column headings must be spelled exactly as shown and are case sensitive. CF, continuous-flow.]

Column heading	Comment
A delta or other value, which can be any of the following that does not repeat another column heading: Delta H-2 Delta C-13 Delta S-33 Delta N-15 Delta S-34 Delta O-17 Delta O-18 Delta S-36 Delta Li-7 Delta B-11 Delta Si-30 Delta Cl-37 C-14 H-3 He-3 He-4 Ar-38 Ar-40 Ne-21 Ne-22 Br-81 Kr-86 UserDefIso-1 UserDefIso-2 CFC-11 CFC-12 CFC-113	
Mass Spec	Single-character mass spectrometer prefix.
Analysis	This is an integer that typically increases by one for each analysis number.
Peak	This is the peak number of a continuous-flow (CF) analysis. An integer, 1, 2, 3, etc. For dual-inlet analyses, it is always 1 if present.
	Integer procedures code in LIMS. If there is a

Procedure	second delta value column, this column must be omitted because LIMS cannot correlate it to the appropriate delta value.
Date-Time Analyzed	Date or date-time of the analysis in Microsoft Office format.
Port	Port, manifold, or tray location ID. Maximum of 6 characters.
Extraction ID	One of two analysis comments available to users. Typically 20 characters maximum. Can be used with Extractions (Sections 11 , 19.2, 24.3, and 26).
Comment	The second of two analysis comments available to users. Typically 32 characters maximum.
Amount	Mass of sample. Numeric value, i.e. 0.214.
Amount Unit	Four character maximum; i.e., mg.
MS Error	See list of integer LIMS mass spectrometer error codes Appendix D).
Ignore	True of false, –1 or 0, respectively. If –1 or True, LIMS imports analysis, but does not use it in calculations.
Area	Area of a CF peak. Area is used when there is only one delta value in the file.
An area of a CF peak of the first delta value, which can be any of the following: Area All H Area All C Area All N Area All O Area All S Area All Si Area All Cl	Number such as 344. If this column is present, the column “Area” should not be used.
An area of a CF peak of the second delta value, if present, which can be any of the following: Area All H Area All C Area All N Area All O Area All S Area All Si	Number such as 455. If this column is present, the column “Area” should not be used. This column should only exist if there is a second delta value column.

Area All Cl	
Component	Component in a compound specific GC combustion analysis.
Rt	Retention time.

17.2 Adding an Elementar Mass Spectrometer having an IonOS Data System

The LIMS Abbreviated Import format can be used to import Elementar IonOS files once they have been modified and saved as Excel files (see Section 22.2). This example shows how to add an IRMS having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability that can import a continuous-flow Elementar IonOS files. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13**.**

1. On the main page of LIMS click "Special Features."
2. Click "Mass Specs" and the Mass Spec form will open.
3. Click "Add" and LIMS will display an informational message (Fig. 15.2).
4. Click "OK."
5. Enter "V" for the "Code" for this example.
6. Enter "Vulcan" for the "Short name" for this example.
7. Select "LIMS Abbreviated" for the "Analysis import format" and LIMS will display the informational message in Figure 17.2.
8. Click "OK."
9. Enable the "13C/12C", "15N/14N", and "34S/32S" check boxes.
10. Select "G" for the "Prefix of the most common sample analyzed."
11. Enable the "Continuous-flow capability" check box.
12. Enable the "Store continuous-flow areas."
13. Click "Save" and the Vulcan IRMS for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ importing of continuous-flow Elementar IonOS files will be created (Fig. 17.3).
14. Click "Close."

This completes the installation of a Elementar IRMS having an IonOS data system and an EA having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability. Importing Elementar IonOS data files is the next step and is discussed in Section 22.2.

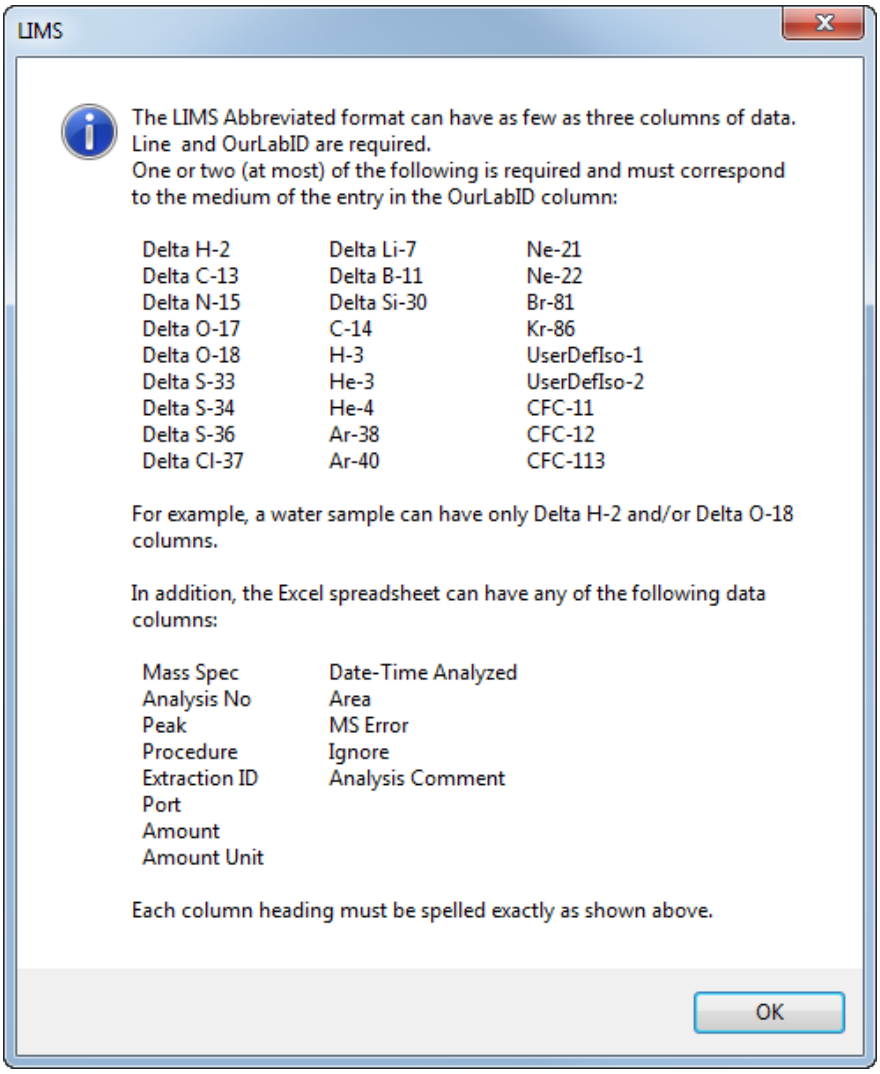


Fig. 17.2. Tips for creating an instrument having the LIMS Abbreviated import format.

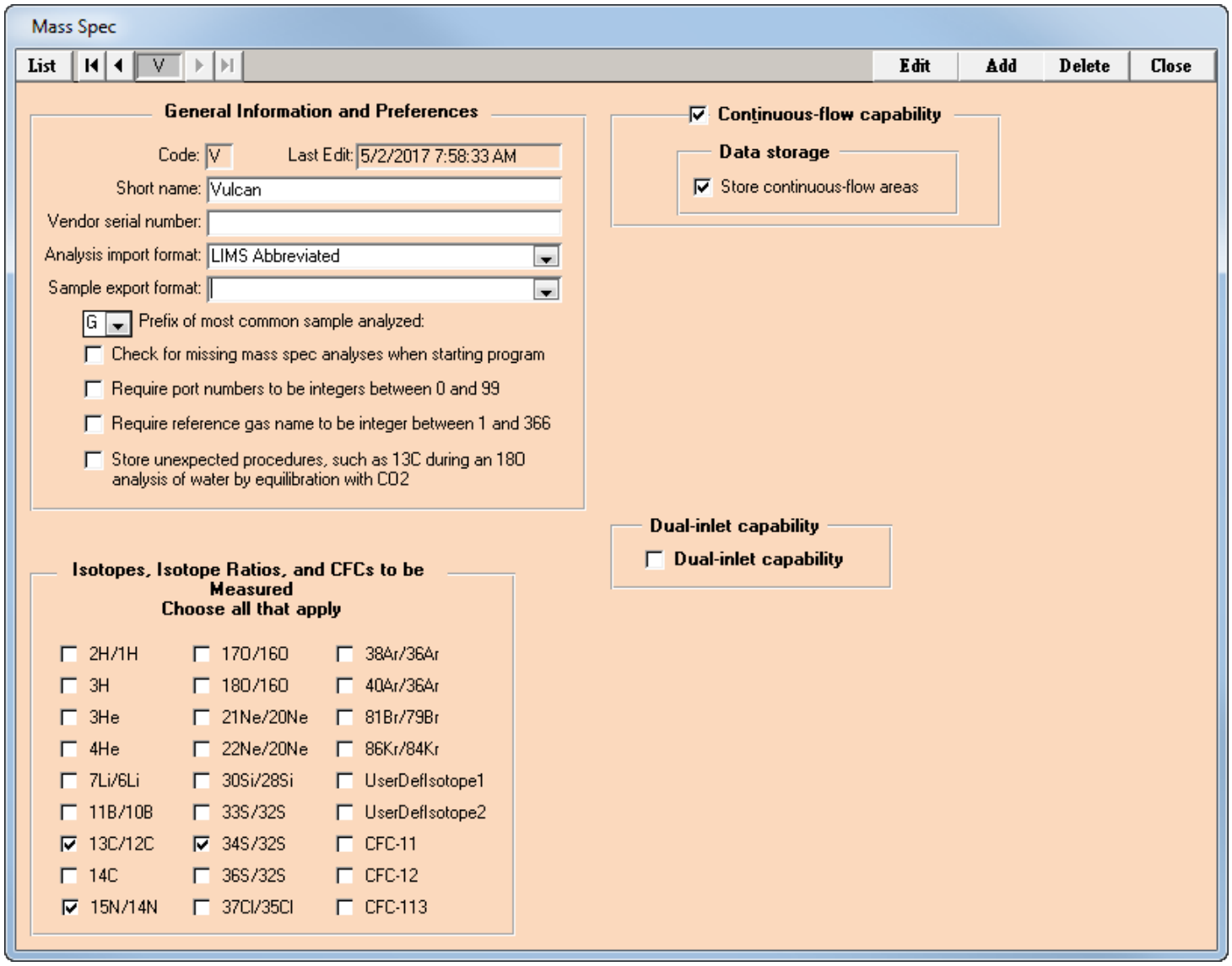


Fig. 17.3. Elementar IRMS having an IonOS data system for importing $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ data.

17.3 Adding an Europa or Europa 20 20 Mass Spectrometer

The LIMS Abbreviated Import format can be used to import Europa and Europa 20 20 data files after they have been modified and saved as Excel files (see Section 22.3). Europa and Europa 20 20 data files are tab separated text files, commonly with the suffix txt or prn. If the suffix of a file is "prn", "prn" can be replaced by "txt" so that the file can be opened with Excel, modified as needed, and saved as either an Excel xls or xlsx file. This example shows how to add an IRMS having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability that can import Europa and Europa 20 20 data from an instrument having an EA. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13.

1. On the main page of LIMS click "Special Features."
2. Click "Mass Specs" and the Mass Spec form will open.
3. Click "Add" and LIMS will display an informational message (Fig. 15.2).
4. Click "OK."
5. Enter "U" for the "Code" for this example.
6. Enter "Ulysses" for the "Short name" for this example.
7. Select "LIMS Abbreviated" for the "Analysis import format" and LIMS will display the informational message in Figure 17.2.
8. Click "OK."
9. Enable the "13C/12C", "15N/14N", and "34S/32S" check boxes.
10. Select "G" for the "Prefix of the most common sample analyzed."
11. Enable the "Continuous-flow capability" check box.
12. Enable the "Store continuous-flow areas."
13. Click "Save" and the Ulysses IRMS for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ importing of Europa and Europa data will be created (Fig. 17.4).
14. Click "Close."

This completes the installation of a Europa IRMS with EA having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability. Importing Europa and Europa 20 20 data is the next step and is discussed in Section 22.3.

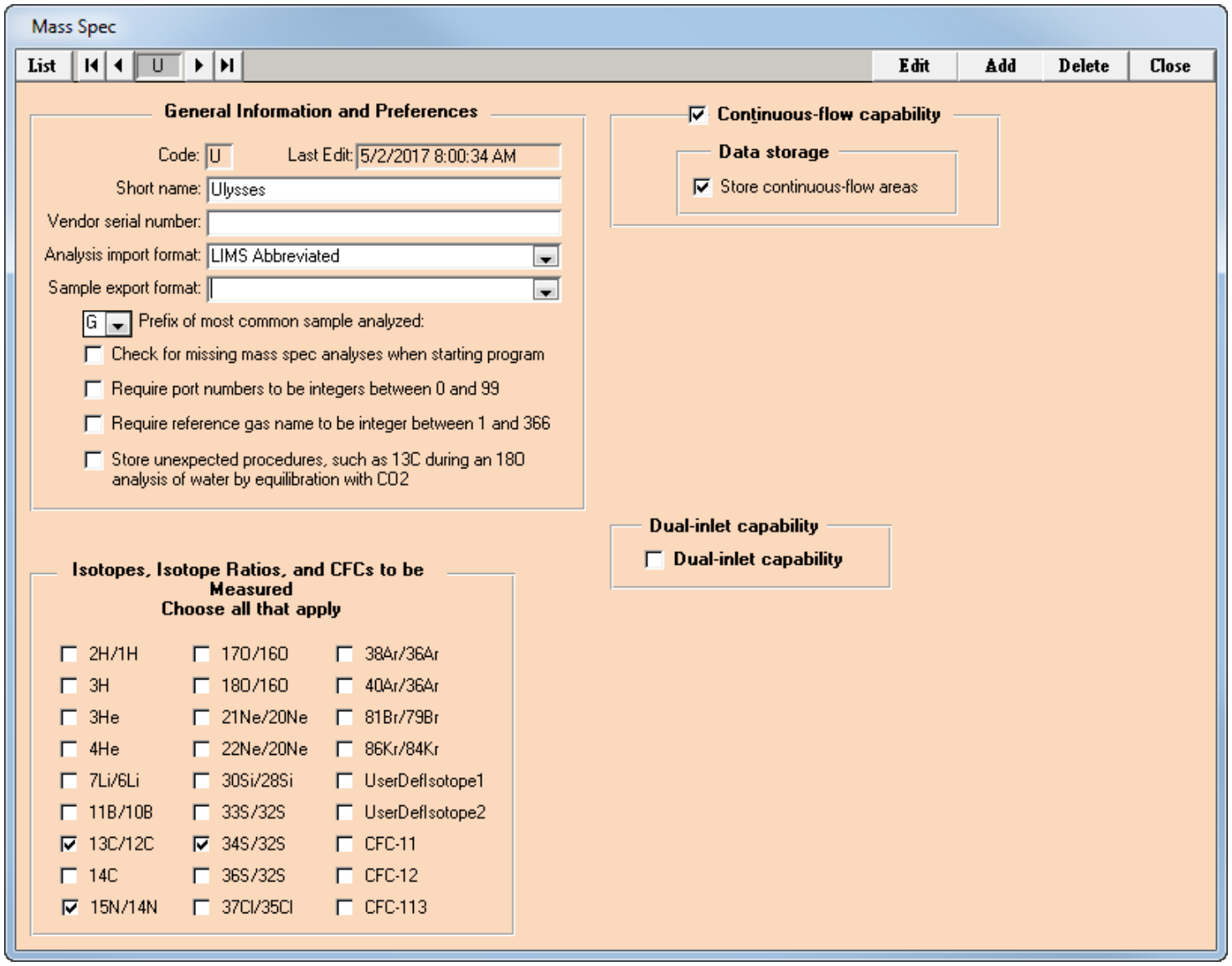


Fig. 17.4. Europa IRMS with the LIMS Abbreviated import format for importing $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ data generated using an EA.

17.4 Adding a Micromass Optima Mass Spectrometer

The LIMS Abbreviated Import format can be used to import Micromass Optima "Micromass OS/2 v.1.67 CF" and "Micromass" data files after modification and saving as Excel files (see Section 22.4). These Optima data files are csv text files with commas as text qualifiers. This example shows how to add an IRMS having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability that can import Optima data from an instrument having an EA. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13.

1. On the main page of LIMS click "Special Features."
2. Click "Mass Specs" and the Mass Spec form will open.
3. Click "Add" and LIMS will display an informational message (Fig. 15.2).
4. Click "OK."
5. Enter "K" for the "Code" for this example.
6. Enter "Kali" for the "Short name" for this example.
7. Select "LIMS Abbreviated" for the "Analysis import format" and LIMS will display the informational message in Figure 17.2.
8. Click "OK."
9. Enable the "13C/12C", "15N/14N", and "34S/32S" check boxes.
10. Select "G" for the "Prefix of the most common sample analyzed."
11. Enable the "Continuous-flow capability" check box.
12. Enable the "Store continuous-flow areas."
13. Click "Save" and the IRMS for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ importing of Optima data will be created (Fig. 17.5).
14. Click "Close."

This completes the installation of a Optima IRMS with EA having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability. Importing Optima data is the next step and is discussed in Section 22.4.

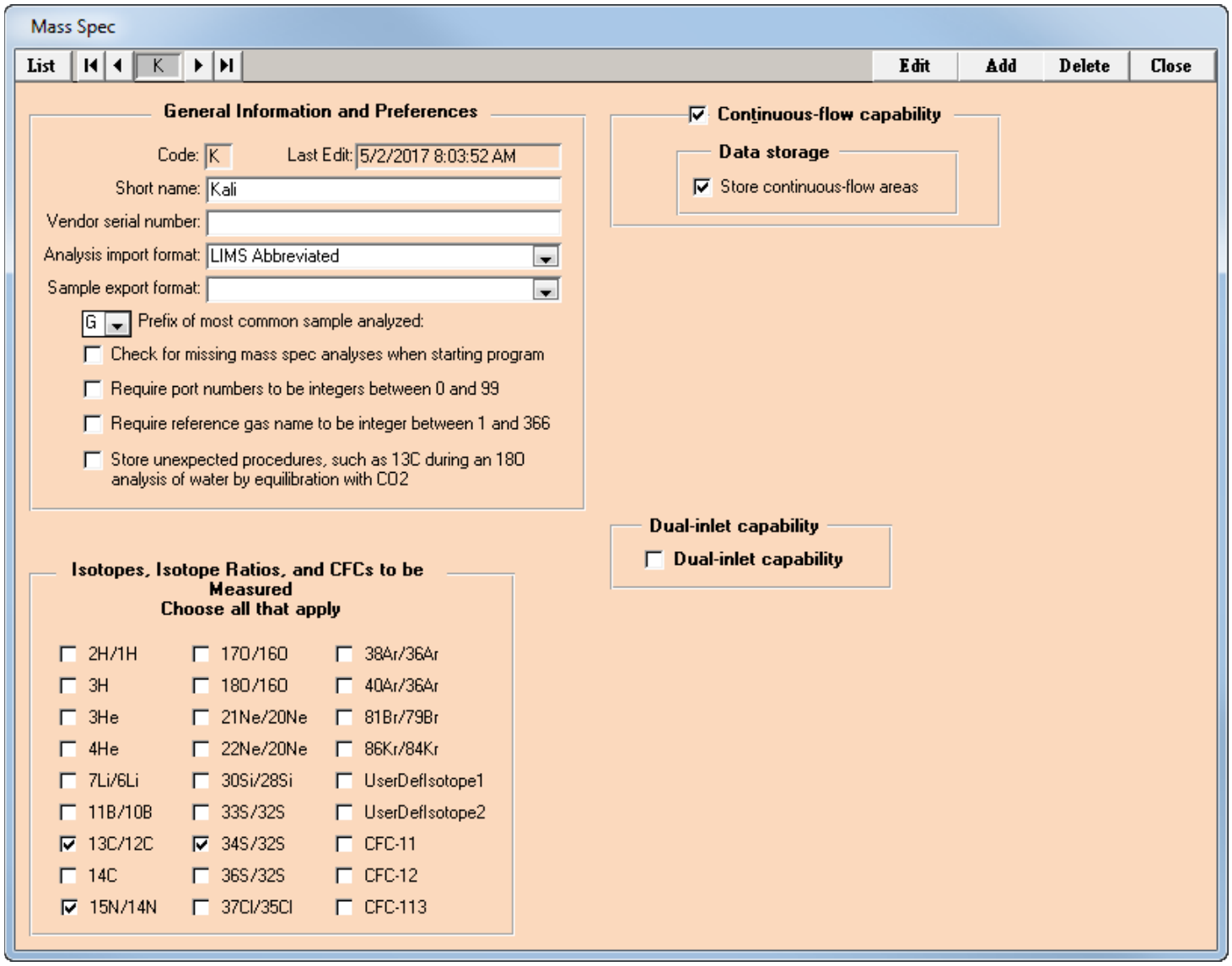


Fig. 17.5. Optima IRMS with the LIMS Abbreviated import format for importing $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ data generated using an EA.

17.5 Adding a Nu Instruments Mass Spectrometer

The LIMS Abbreviated Import format can be used to import data files after their modification from a Nu Instruments IRMS, such as the Perspective. Nu Instruments data files are comma separated variable (csv) files. This example shows how to add an IRMS having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability that can import Nu Instruments data from an IRMS having an EA. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13.

1. On the main page of LIMS click "Special Features."
2. Click "Mass Specs" and the Mass Spec form will open.
3. Click "Add" and LIMS will display an informational message (Fig. 15.2).
4. Click "OK."
5. Enter "P" for the "Code" for this example.
6. Enter "Pegasus" for the "Short name" for this example.
7. Select "LIMS Abbreviated" for the "Analysis import format" and LIMS will display the informational message in Figure 17.2.
8. Click "OK."
9. Enable the "13C/12C", "15N/14N", and "34S/32S" check boxes.
10. Select "G" for the "Prefix of the most common sample analyzed."
11. Enable the "Continuous-flow capability" check box.
12. Enable the "Store continuous-flow areas."
13. Click "Save" and the IRMS for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ importing of Nu Instruments data will be created (Fig. 17.6).
14. Click "Close."

This completes the installation of a Nu Instruments IRMS with EA having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability. Importing Nu Instruments data is the next step and is discussed in Section 22.5.

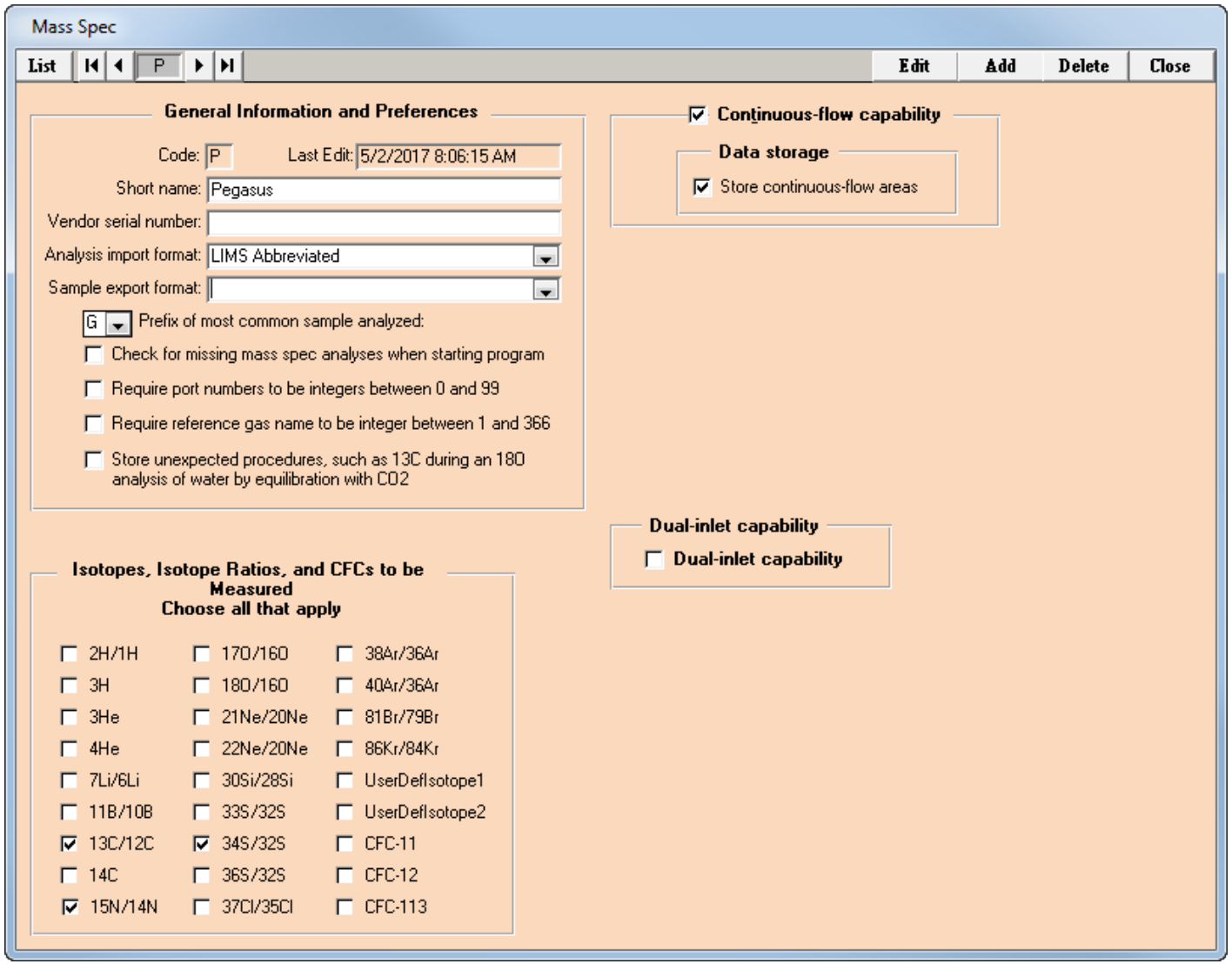


Fig. 17.6. Nu Instruments IRMS with the LIMS Abbreviated import format for importing $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ data generated using an EA.

17.6 Adding a Sercon Mass Spectrometer

The LIMS Abbreviated Import format can be used to import Sercon data files after they have been modified and saved as Excel files (see Section 22.6). Sercon data files commonly are tab separated text files having the suffix prn. Because the latest versions of Excel do not recognize files with the prn suffix, the suffix can be changed to txt or the file can be opened with an older version of Excel (2007 and earlier). This example shows how to add an IRMS having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ capability that can import Sercon data from an instrument having an EA. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13.

1. On the main page of LIMS click "Special Features."
2. Click "Mass Specs" and the Mass Spec form will open.
3. Click "Add" and LIMS will display an informational message (Fig. 15.2).
4. Click "OK."
5. Enter "A" for the "Code" for this example.
6. Enter "Artemis" for the "Short name" for this example.
7. Select "LIMS Abbreviated" for the "Analysis import format" and LIMS will display the informational message in Figure 17.2.
8. Click "OK."
9. Enable the "13C/12C", "15N/14N", and "34S/32S" check boxes.
10. Select "G" for the "Prefix of the most common sample analyzed."
11. Enable the "Continuous-flow capability" check box.
12. Enable the "Store continuous-flow areas" check box.
13. Click "Save" and the IRMS for $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ importing of Sercon data will be created (Fig. 17.7).
14. Click "Close."

This completes the installation of a Europa IRMS with an EA having $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ measurement capability. Importing Sercon data files is the next step and is discussed in Section 22.6.

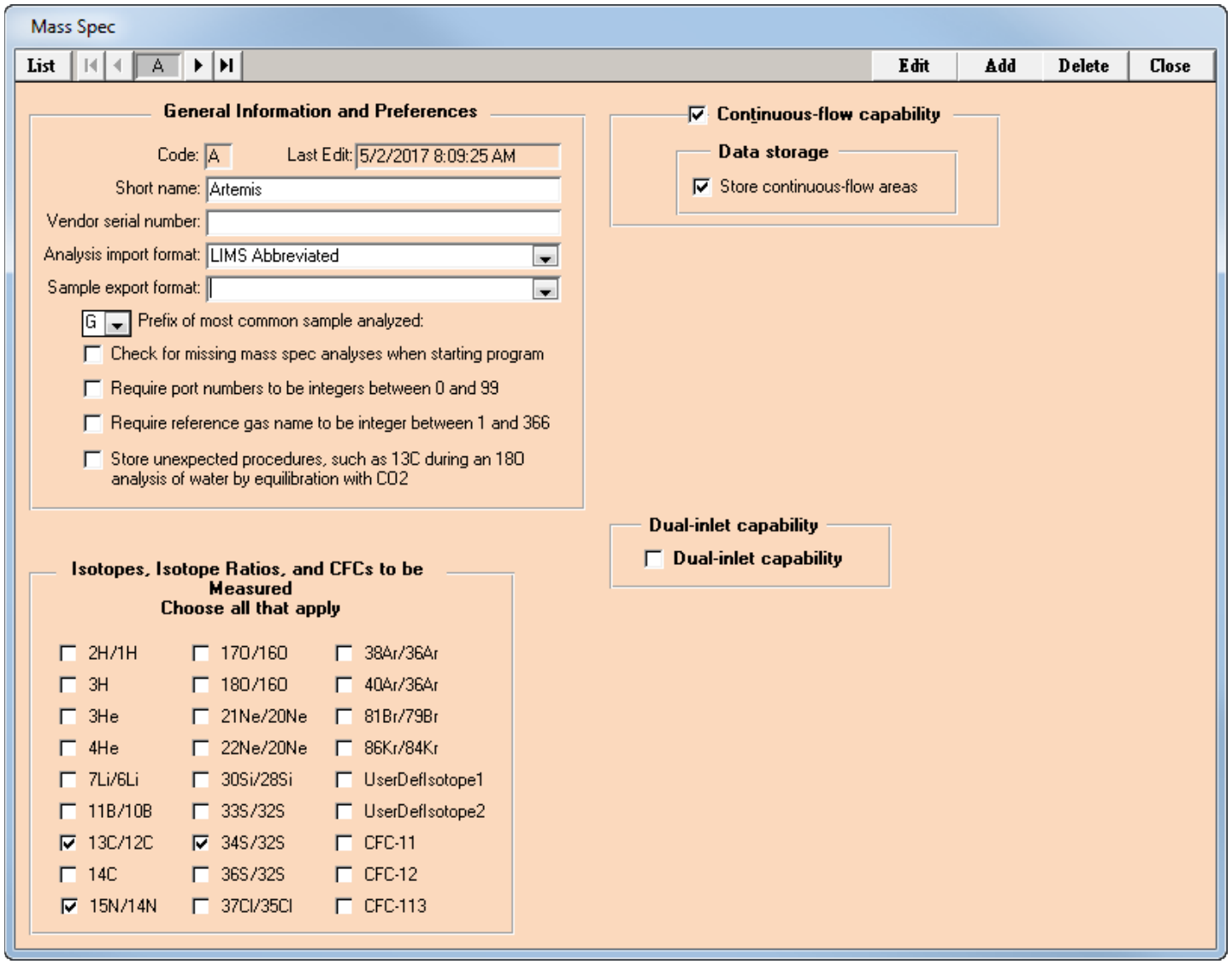


Fig. 17.7. Sercon IRMS with the LIMS Abbreviated import format for importing $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ data generated using an EA.

17.7 Adding a Carbon-14 Scintillation Counter

This example shows the flexibility of the LIMS Abbreviated import format for importing data from instruments other than light-element IRMSs. In this example, a carbon-14 counter uses the simplest LIMS Abbreviated import consisting of an Excel file having only three columns ("Line", "OurLabID", and "C-14"). This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. To add a carbon-14 counter:

1. On the main page of LIMS click "Special Features."
2. Click "Media" to investigate whether a medium for carbon-14 exists in the database.
3. Click "List" and scroll through the existing media to determine if a carbon-14 medium exists and to identify an unused code for a carbon-14 medium. Note that code 140 is available in a newly-opened backend database for a new laboratory.
4. Assuming the user is using a fresh backend database for a new laboratory in which no carbon-14 media exist, click "Add" and LIMS displays the message shown in Figure 17.8.
5. Click "OK."
6. Enter "140" for the "Medium Code" for this example.
7. Enter "14C-bearing material" for the "Medium Description."
8. Enter "14C" for the "Abbr."
9. Enable the "14C" check box.
10. Select "G --> General" for the "Our Lab ID Prefix" for this example.
11. Click "Save" and LIMS prompts the user with the message in Figure 17.9 to add this medium to the laboratory's Excel sample submission file used by clients (see Section 7.5).
12. Click "OK" and LIMS displays the new carbon-14 medium (Fig. 17.10).
13. Click "Close" to close the form.
14. Click "Procedures" to add a new procedure code for carbon-14 analyses, and LIMS displays the ranges of procedure codes for each medium (Fig. 6.3).
15. Note that "14C" procedures must lay in the interval 1400 to 1499.
16. Click "OK" and the Procedure Codes form opens.
17. Click "Add" to add a new procedure code.
18. Enter "1400" for the "Code" for this example, and LIMS prompts that a procedure code for "14C" is being entered.
19. Enter "14C prep and analysis" in the Description field for this example. The "Amount of Sample" field is for information only and is not required by LIMS. Leave it blank.
20. Click "Save" and LIMS shows the newly-created procedure (Fig. 17.11). Click "Close."
21. To link the new medium to the new procedure click "Low Procedures" and the Low Procedure Codes form opens.
22. Click "Add" and select "140 --> G [14C] 14C-bearing material" for the "Medium."

23. Select “1400 --> 14C prep and analysis” for the “Low Procedure” code.
24. Although not strictly needed, set the “Default” entry to “*” to identify to LIMS that this default code of 1400 should be used by LIMS for medium 140 in case additional carbon-14 procedures are added.
25. Click “Save” and LIMS displays the linkage of the new carbon-14 medium and procedure (Fig. 17.12).
26. Click “Close.”

If a user needs a medium with two isotopes with carbon-14 as the isotope with the higher isotope number (see Tables 6.2 or 17.1), the user would link the carbon-14 medium and procedure using the “High Procedure Codes” form (see Appendix C).

Once the medium, procedure code, and linkage between the medium and procedure code has been established, the “mass spectrometer” can be created:

1. Click “Mass Specs” and the Mass Spec form will open.
2. Click “Add” and LIMS will display an informational message (Fig. 15.2).
3. Click “OK.”
4. Enter “B” for the “Code” for this example.
5. Enter “Beta” for the “Short name” for this example.
6. Select “LIMS Abbreviated” for the “Analysis import format” and LIMS will display the informational message in Figure 17.2.
7. Click “OK.”
8. Enable the “14C” check box.
9. Select “G” for the “Prefix of the most common sample analyzed.”
10. Click “Save” and the carbon-14 “Mass Spec” will be created (Fig. 17.13).
11. Click “Close.”

This completes the installation of a carbon-14 scintillation counter. Importing carbon-14 data is the next step and is discussed in Section 22.7.

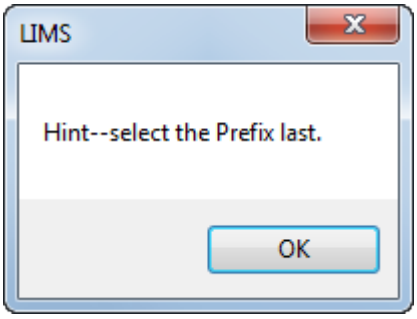


Fig. 17.8. LIMS prompt to enter the Prefix of the Our Lab ID last.

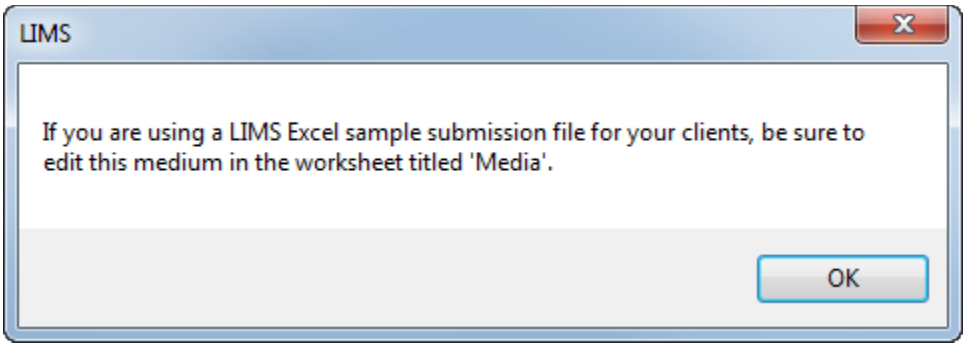


Fig. 17.9. LIMS prompt to add medium to laboratory's sample submission file.

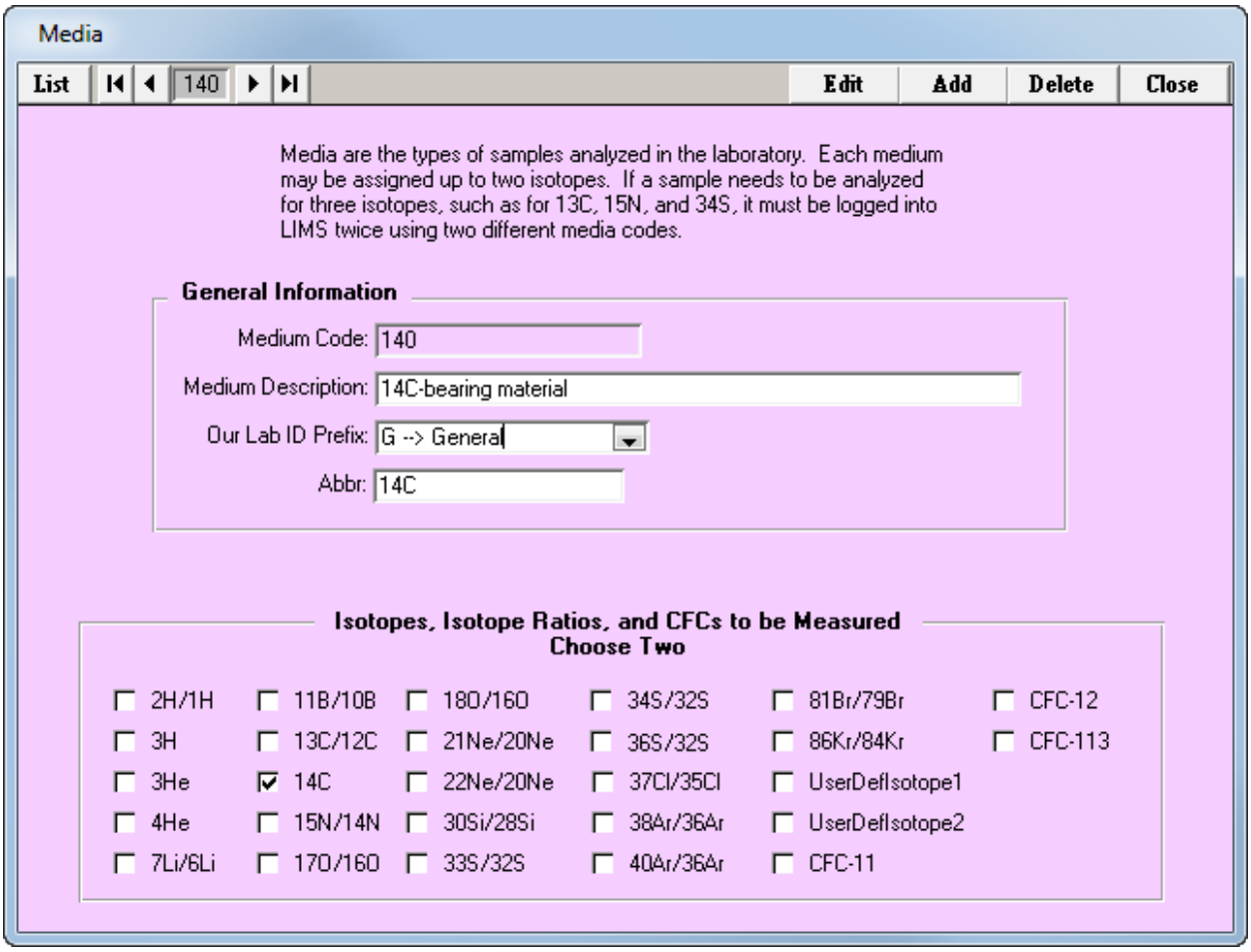


Fig. 17.10. Newly-created carbon-14 medium.

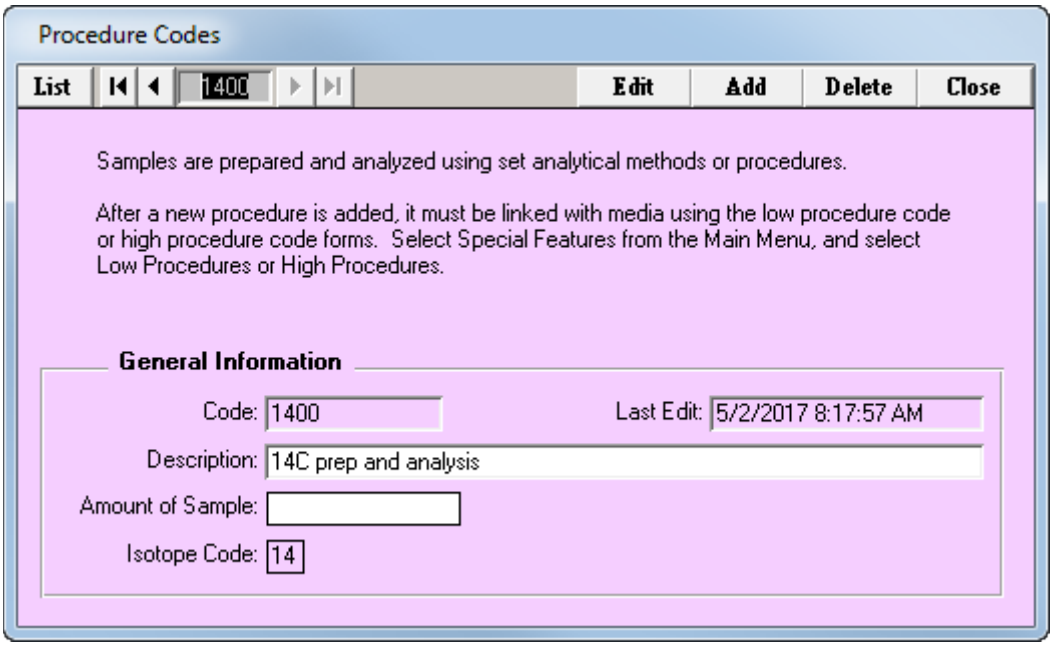


Fig. 17.11. Newly-created carbon-14 procedure.

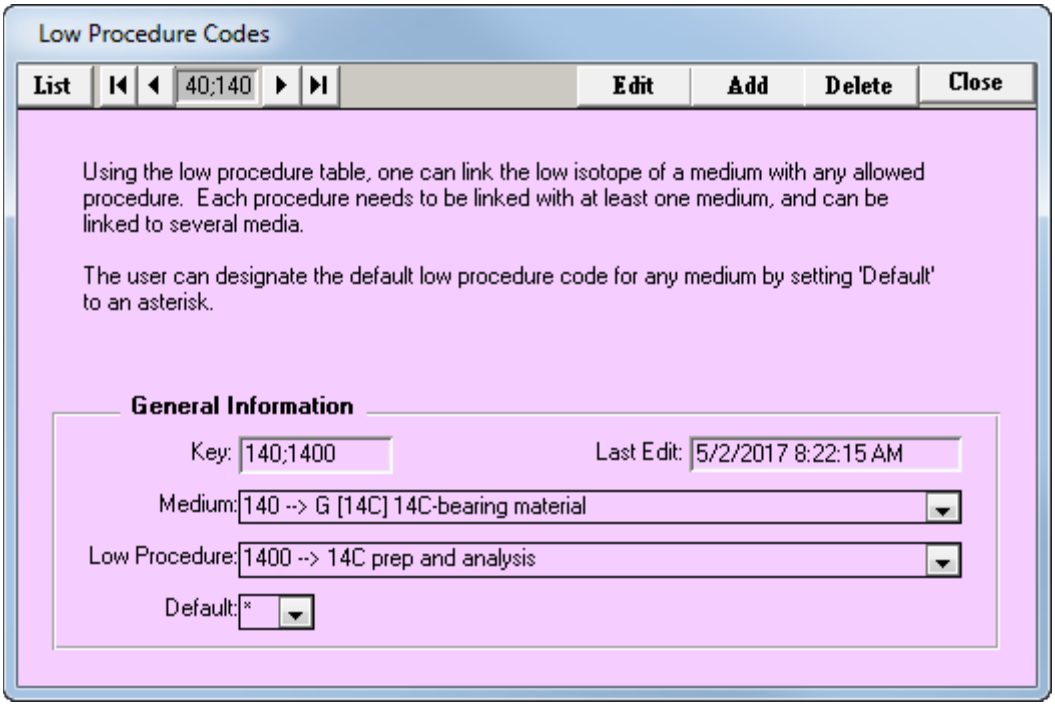


Fig. 17.12. Low Procedure Codes form showing the linkage between the new carbon-14 medium and procedure.

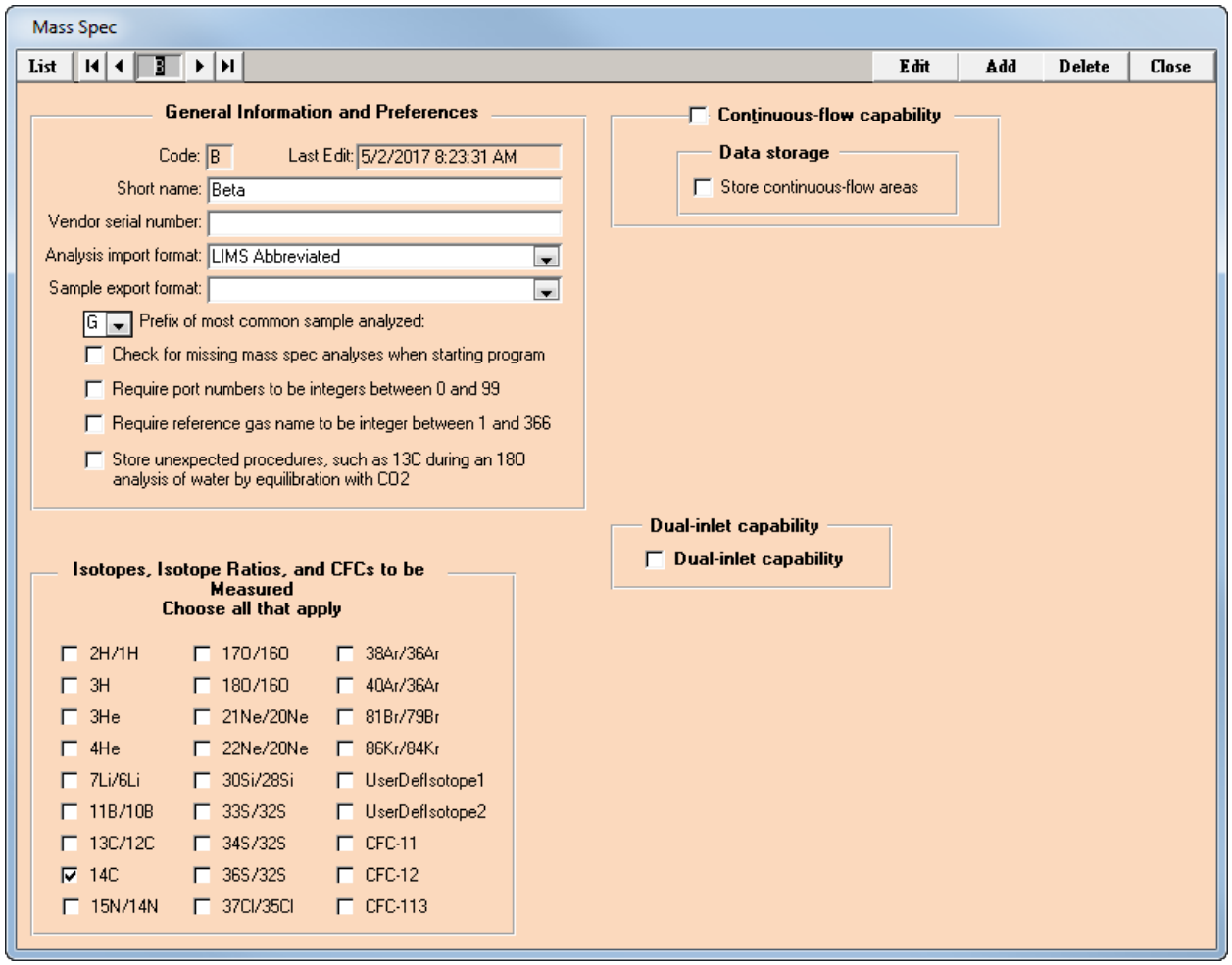


Fig. 17.13. Carbon-14 “Mass Spec” using the LIMS Abbreviated import format.

18 Adding a Mass Spectrometer having the "LIMS Default" Import Format

The LIMS Default import format is a Microsoft Access file (either mdb or accdb) having one table named "tbl_IsotopicResults," which has fields shown in Figure 18.1, which are described in Table 18.1. Table 18.1 is provided to enable IRMS manufacturers to create data files that can be imported easily by LIMS users. In the following example, an IRMS having both continuous-flow and dual-inlet capabilities for $\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ measurements will be created in LIMS. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database set up in Section 4.8. Before continuing, readers should be fully familiar with Section 13.

1. On the LIMS main page click "View Projects -->."
2. Click "Mass Specs" (or "Instruments" if a Picarro or Los Gatos Research laser absorption spectrometer is installed).
3. Click "Add" and LIMS displays the message shown in Figure 14.1.
4. Click "OK."
5. Enter "Z" for the "Code" for this example.
6. Enter "Zeus--LIMS Default" for the "Short name" for this example.
7. Select "LIMS Default" for the "Analysis import format" and LIMS will display the informational message in Figure 18.2.

tbl_IsotopicResults

Field Name	Data Type
rstr_MassSpec	Text
str_VendorMSID	Text
lng_Analysis	Number
lng_PeakNumber	Number
rstr_Prefix	Text
rlng_Sample	Number
str_AliquotID	Text
str_Port	Text
str_Std	Text
dat_Analyzed	Date/Time
str_Comment	Text
dbl_Amount	Number
str_AmountUnit	Text
int_Procedure	Number
dbl_PenultimateDelta	Number
rint_Error	Number
ysn_Ignore	Yes/No

Fig. 18.1. Fields in the table "tbl_IsotopicResults" of the Microsoft Access file of the LIMS Default import format.

Table 18.1. Fields in the table "tbl_IsotopicResults" of a Microsoft Access file having the LIMS Default import format.

Field	Description
rstr_MassSpec	Single letter mass spectrometer code or ID.
str_VendorMSID	Mass spectrometer serial number or vendor ID number. Does not need to be supplied if rstr_MassSpec is supplied.
lng_Analysis	Analysis number. Unique interfere that should be generated by the mass spectrometer and printed on analysis report.
lng_PeakNumber	Peak number. Acceptable values are 1 to 999. Default value for dual-inlet IRMS analyses is 1.
rstr_Prefix	Single letter sample prefix: C, G, J, N, R, S, or W. Together with rlng_Sample forms the Our Lab ID.
rlng_Sample	Integer with sample number. Together with sample prefix, this forms the Our Lab ID, *e.g.* W-12344.
str_AliquotID	Aliquot identification. Also identified as Extraction ID.
str_Port	Name or identifier of the sample port or tray ID on the preparation unit, manifold, carousel, etc.
str_Std	Name or identifier of the working standard if a dual-inlet file; if a continuous-flow file, "0" signifies a sample peak and "1" signifies a continuous-flow reference injection peak.
dat_Analyzed	Date and time sample analysis of this peak is begun. Generally increments for each peak.
str_Comment	Comment
dbl_Amount	Amount of sample
str_AmountUnit	Unit of amount
int_Procedure	Procedure code used to analyze sample
dbl_PenultimateDelta	Penultimate delta value
rint_Error	Error code. Default value is 0.
ysn_Ignore	Default value is No. Mass spectrometer can set this field to Yes if it can determine that isotopic analysis is unsatisfactory and should not be included in LIMS calculations of the final delta value.

8. Click “OK.”
9. Select “LIMS Default” for the “Sample export format.”
10. In the lower left panel, enable check boxes for “2H/1H”, “13C/12C”, “15N/14N”, “18O/16O”, and “34S/32S”.
11. In the upper left panel, select “G” for the “Prefix of the most common sample analyzed.”
12. Enable the check box “Check for missing mass spec analyses when starting program” because in this example we want LIMS to alert us of any missing analyses—LIMS will check for missing analyses when LIMS is started (opened).
13. In the upper right panel, enable the “Continuous-flow capability” check box.
14. Enable the “Store continuous-flow areas” check box.
15. For the CO “CF Ref Inj Gases” enter “R-31,” which is the first CO reference injection gas shown in Figure 12.7. LIMS will prompt the user of the $\delta^{13}C$ value of R-31 (Fig. 14.2) and the $\delta^{18}O$ value of R-31.
16. Add “R-1”, “R-6”, “R-11”, “R-21”, “R-26”, and “R-16”, respectively, for “H2”, “CO2”, “N2”, “N2O”, “SO2”, and “O2” continuous-flow reference injection gases.
17. Enable the “Dual-inlet capability” check box.
18. Click “Save” to create the mass spectrometer in LIMS (Fig. 18.3).

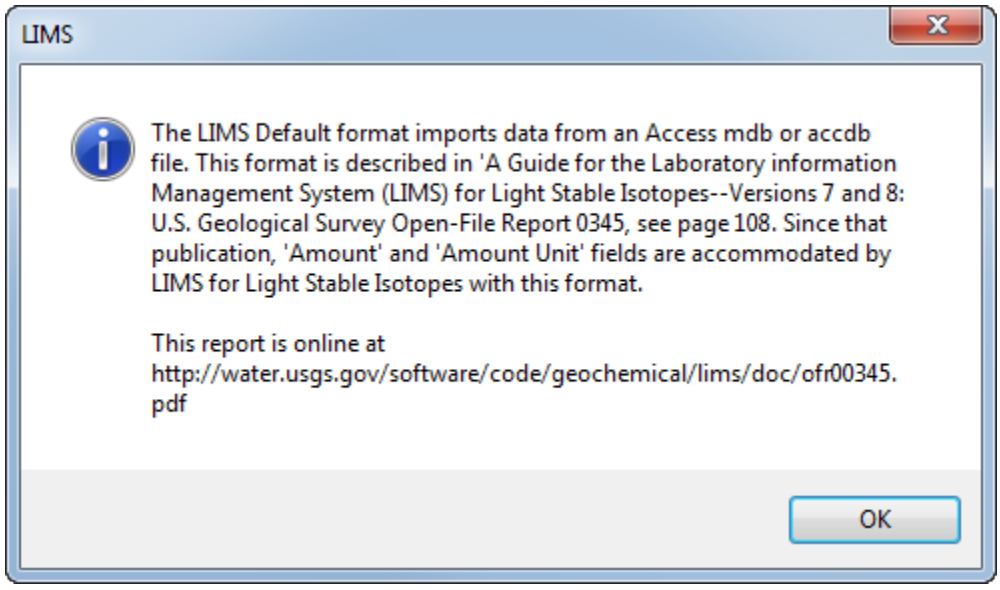


Fig. 18.2. LIMS Default import format informational message.

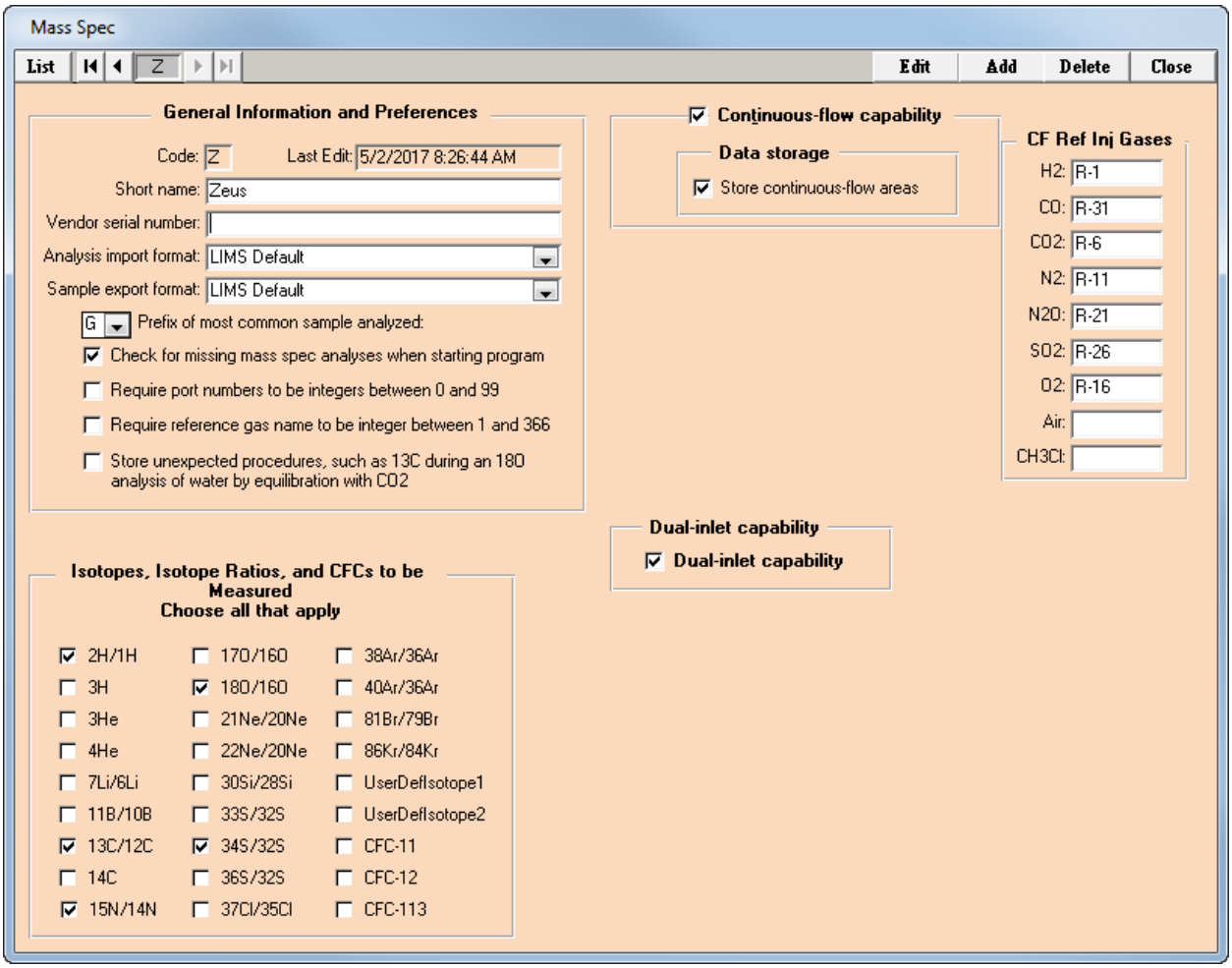


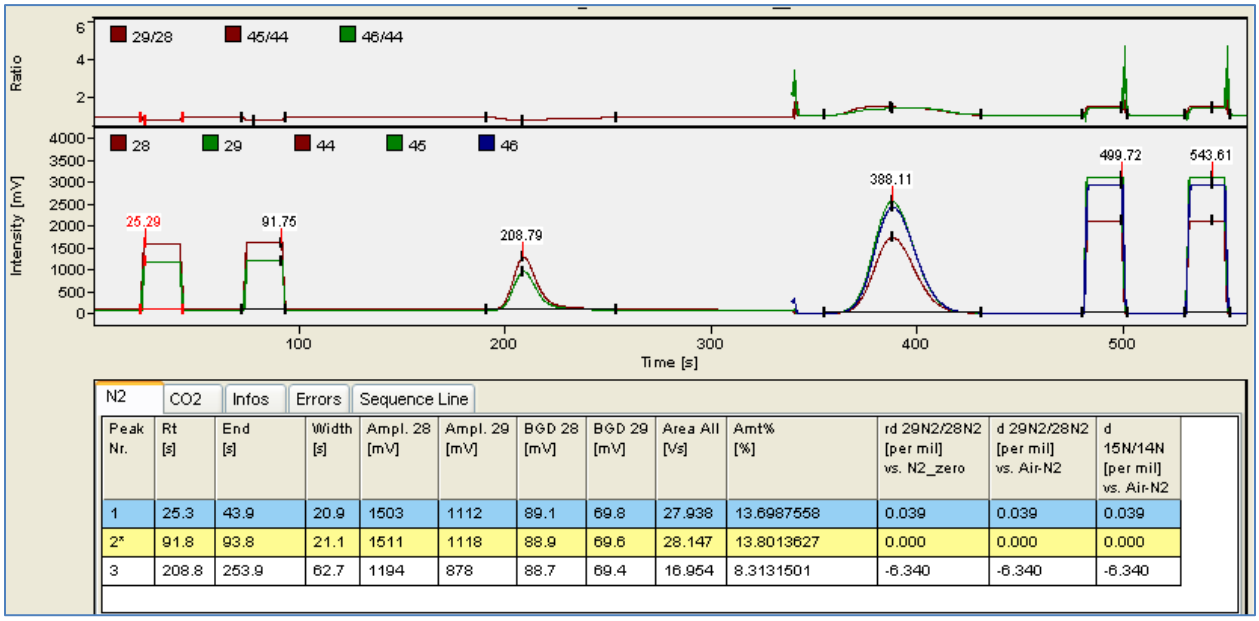
Fig. 18.3. IRMS with the LIMS Default import format for importing δ^{2}H, δ^{13}C, δ^{15}N, δ^{18}O, and δ^{34}S data.

This completes installation of an IRMS with δ^{2}H, δ^{13}C, δ^{15}N, δ^{18}O, and δ^{34}S measurement capability and with a LIMS Default import format. Importing IRMS analyses is the next step and is discussed in Section 23.

19 Importing Data from a Thermo Scientific/Thermoquest/Finnigan Mass Spectrometer having ISODAT NT or Later Data System

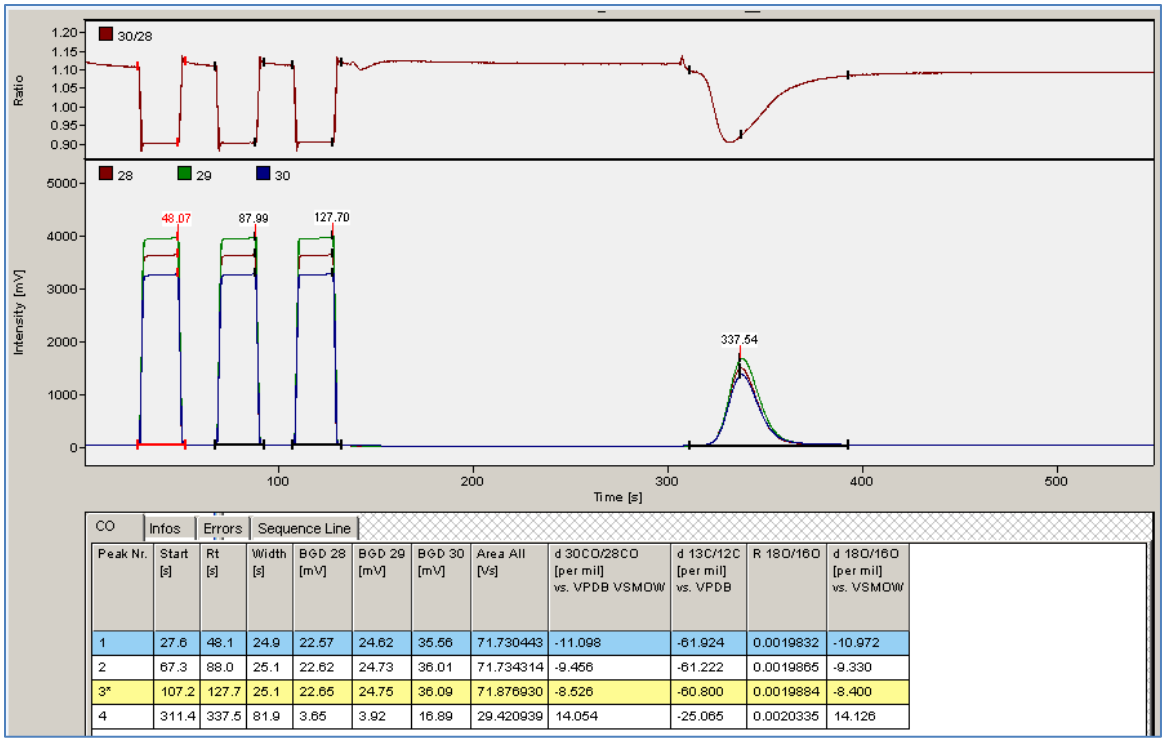
19.1 General Comments

Users will perform isotopic analyses of samples on their Thermo Scientific, Thermoquest, or Finnigan IRMS, which commonly is connected to a peripheral, such as an EA, a thermal-conversion EA (TC/EA), or/and a GasBench. An EA uses high temperature combustion to convert a sample to N_2, CO_2, and SO_2 for subsequent $\delta^{15}N$ and (or) $\delta^{13}C$ and (or) $\delta^{34}S$ analysis by an IRMS. A TC/EA uses high temperature pyrolysis to convert a sample to H_2 and CO for δH^2 and/or δO^{18} analysis by an IRMS. Several examples are given in Section 19. Figure 19.1 is an example of an ISODAT 2.5 carbon- and nitrogen-isotope analysis from an IRMS having an EA. Figure 19.2 is an example of an ISODAT 2.5 oxygen-isotope analysis from an IRMS having a TC/EA. Figures 19.1 and 19.2 have a number of features in common. They both have columns for peak number, retention time, area, and isotope-delta value. One of the continuous-flow reference injection data rows is identified by an asterisk (*) following the peak number entry. For example, in Figure 19.1 this is shown as "2*" and in Figure 19.2 as "3*."



Peak Nr.	Rt [s]	End [s]	Width [s]	Ampl. 28 [mV]	Ampl. 29 [mV]	BGD 28 [mV]	BGD 29 [mV]	Area All [Vs]	Amt% [%]	rd 29N2/28N2 [per mil] vs. N2_zero	d 29N2/28N2 [per mil] vs. Air-N2	d 15N/14N [per mil] vs. Air-N2
1	25.3	43.9	20.9	1503	1112	89.1	69.8	27.938	13.6987558	0.039	0.039	0.039
2*	91.8	93.8	21.1	1511	1118	88.9	69.6	28.147	13.8013627	0.000	0.000	0.000
3	208.8	253.9	62.7	1194	878	88.7	69.4	16.954	8.3131501	-6.340	-6.340	-6.340

Fig. 19.1. Example ISODAT 2.5 $\delta^{13}C$ and $\delta^{15}N$ analysis of an IRMS having an EA. The first two peaks are N_2 continuous-flow reference injections peaks. The third and fourth peaks are the N_2 and CO_2 peaks, respectively, of the sample. The last two peaks are CO_2 continuous-flow reference injections peaks.



Peak Nr.	Start [s]	Rt [s]	Width [s]	BGD 28 [mV]	BGD 29 [mV]	BGD 30 [mV]	Area All [Vs]	d 30CO/28CO [per mil] vs. VPDB VSMOW	d 13C/12C [per mil] vs. VPDB	R 18O/16O	d 18O/16O [per mil] vs. VSMOW
1	27.6	48.1	24.9	22.57	24.62	35.56	71.730443	-11.098	-61.924	0.0019832	-10.972
2	67.3	88.0	25.1	22.62	24.73	36.01	71.734314	-9.456	-61.222	0.0019865	-9.330
3*	107.2	127.7	25.1	22.65	24.75	36.09	71.876930	-8.526	-60.800	0.0019884	-8.400
4	311.4	337.5	81.9	3.65	3.92	16.89	29.420939	14.054	-25.065	0.0020335	14.126

Fig. 19.2. Example ISODAT 2.5 $\delta^{18}O$ analysis of an IRMS having a TC/EA. The first three peaks are CO continuous-flow reference injections peaks. The last peak is the CO peak of the sample.

Users need to export their measurement results to an Excel file, and the Excel file data is imported into LIMS for blank correction, normalization to isotope-delta scales, and reporting to clients. If continuous-flow data are imported and masses are available, users can determine element mass fractions (concentrations) with LIMS. To import continuous-flow results into LIMS, the Excel file must contain the eight data columns listed in Table 19.1. To import dual-inlet result, the Excel file only needs the six data columns listed in Table 19.2. Table 19.3 lists a few of the many fields that can be imported by LIMS. Retention time and component are important for compound specific GC combustion analyses, and importing these files is discussed in Section 32.

The gas configuration (Tables 19.1 and 19.2) is required for both continuous-flow and dual-inlet analyses. The backend database for a new laboratory contains the gas configurations (Gas Types) AIR, CO, CO_2, H_2,H_2O, N_2, N_2O, NO, O_2, SF_6, SiF_4, SO, and SO_2. If a new gas configuration is needed, it can be added by clicking Special Features on the main page, clicking Gas Types, and entering the new gas configuration.

Table 19.1. Required fields in an Excel file of continuous-flow data for importing into LIMS.

Field	Description
Analysis	Single letter mass spectrometer code and an integer, *e.g.* H-12445.
Identifier 1 (or Identifier 2)	Contains the Our Lab ID at a minimum, *e.g.* G-1013.
Gas configuration	For example, CO2, N2, SO2, etc.
Is CF reference?	Typically 1 for true indicating that a row is a measurement of a continuous-flow reference injection gas, and 0 for false indicating that it is not.
Peak number	An integer between 1 and 999.
Date-time	Date-time of analysis; *e.g.* "2009/03/06 10:27:45."
Area All	Sum of continuous-flow areas (volt seconds).
Isotope-delta value	For example, –5.238

Table 19.2. Required fields in an Excel file of dual-inlet data for importing into LIMS.

Field	Description
Analysis	Single letter mass spectrometer code and an integer, *e.g.* H-12445.
Identifier 1 (or Identifier 2)	Contains the Our Lab ID at a minimum, *e.g.* G-1013.
Gas configuration	For example, CO2 or N2.
Date-time	Date-time of analysis; *e.g.* "2009/03/06 10:27:45."
Dual-inlet reference name	For example, "R-8 Tank O2."
Isotope-delta value	For example, –5.238

Table 19.3. Selected optional fields in an Excel ISODAT file that can be imported into LIMS.

Field	Description
Line	Sequence line number
Amount	Amount of sample
Amount unit	For example, mg.
Port	Name or identifier of the sample port or tray ID on the preparation unit, manifold, carousel, etc.
Std	Name or identifier of the working standard.
Comment	Comment limited to 32 characters in LIMS.
Rt	Retention time
Component	The component in a GC combustion analysis or compound-specific GC combustion analysis.
Maximum amplitude of peak	For example, “Amp 28” or “Amp 29” column headings.

19.2 Special Uses of ISODAT’s “Identifier 1” and “Identifier 2” Fields

LIMS is able to concatenate as many as five information items in either the ISODAT “Identifier 1” or “Identifier 2” data columns, and this format can also be used in Micromass and other csv files. In this manner, LIMS can create a sample list having low and high procedure codes and pass this information to ISODAT through ISODAT’s sequence table. Subsequently, ISODAT will pass this information back to LIMS with isotope-delta results. In this manner, LIMS isotope-delta values and procedure codes used for their determination are automatically imported into LIMS with no additional data entry. Five items can be concatenated in either of the fields “Identifier 1” or “Identifier 2” (Table 19.4). When all five items are provided, they are delimited with forward slashes as:

Our Lab ID / Extraction ID / Low Procedure Code / High Procedure Code / Comment

The minimum information needed by LIMS to import an analysis is the Our Lab ID. For importing analysis data LIMS will use default procedure codes for the medium if not provided. The following are examples for valid entries for either Identifier 1 or Identifier 2:

C-1/My test #34/312/820/Temp = 41 C
C-1 / My test #34 / 312 / 820 / Temp = 41 C
C-1

C-1 //// Temp = 41 C
C-1 / My test #34 /// Temp = 41 C
C-1/My test #34
C-1 // 312 / 820
C-1 // 820

The Extraction ID is also known as the Aliquot ID. The Extraction ID can be an ID in the Extraction table in LIMS to provide information on the sample preparation of a sample or of an aliquot of a sample (see Sections 11 , 19.2, 24.3, and 26). Note that if a comment is provided as a unique column (Table 19.3), then it should not be provided as the last item of the concatenation (Table 19.4).

Table 19.4. Data that can be concatenated in ISODAT's "Identifier 1" or "Identifier 2" fields.

Item	Example
Our Lab ID	G-33541
Extraction ID (Aliquot ID)	A2b
Low procedure code	352
High procedure code	580
Comment	Temp = 41 C

19.3 Creating an Export Template with ISODAT

Once samples have been analyzed by the IRMS, they need to be exported with the columns that are optional or that LIMS requires (Section 19.1). An ISODAT export template needs to be created as follows:

1. Open ISODAT.
2. Open Workspace (Fig. 19.3) to review isotope results.
3. Click the "New" icon and select "Data Export."
4. To create the fields (columns in the Excel file) one needs to drag parameters from the "Available Columns" pane in the center of Figure 19.4 to the "Columns to export" pane on the right side of Figure 19.4. To narrow search results, only select one "Data Type" check box at a time. The most important "Data Types" will be "Sequence Line", "Gas Configuration", "Result Peak", "Element Ratio", and "Environment"; however, other data types may be of interest depending upon the analytical method.
5. For a continuous-flow analysis, drag the eight parameters listed in Table 19.1 to the "Columns to export" pane; for a dual-inlet analysis, drag the six parameter listed in Table 19.2 to the "Columns to export" pane.

6. Drag other desired optional parameters to the “Columns to export” pane, an example of which is shown for the gas configuration CO_2 in Figure 19.5.
7. Once one is satisfied with the parameters in the export template, save it with a descriptive name (Fig. 19.6). Pay attention to the warning at the end of this section.

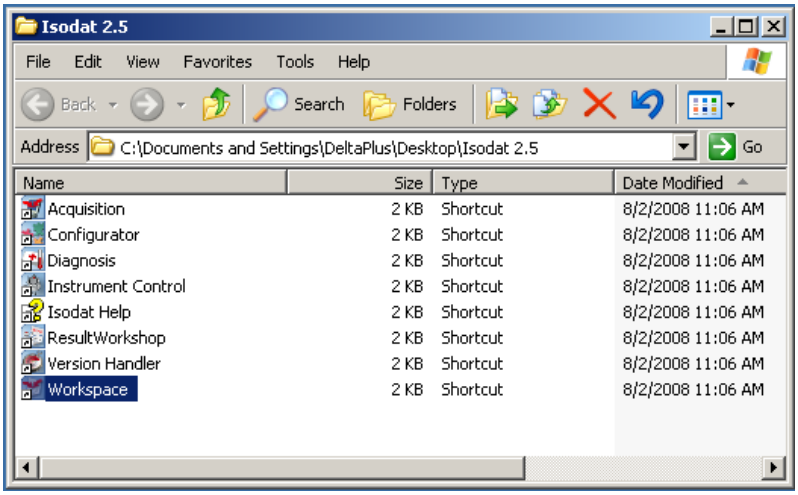


Fig. 19.3. Workspace in ISODAT 2.5.

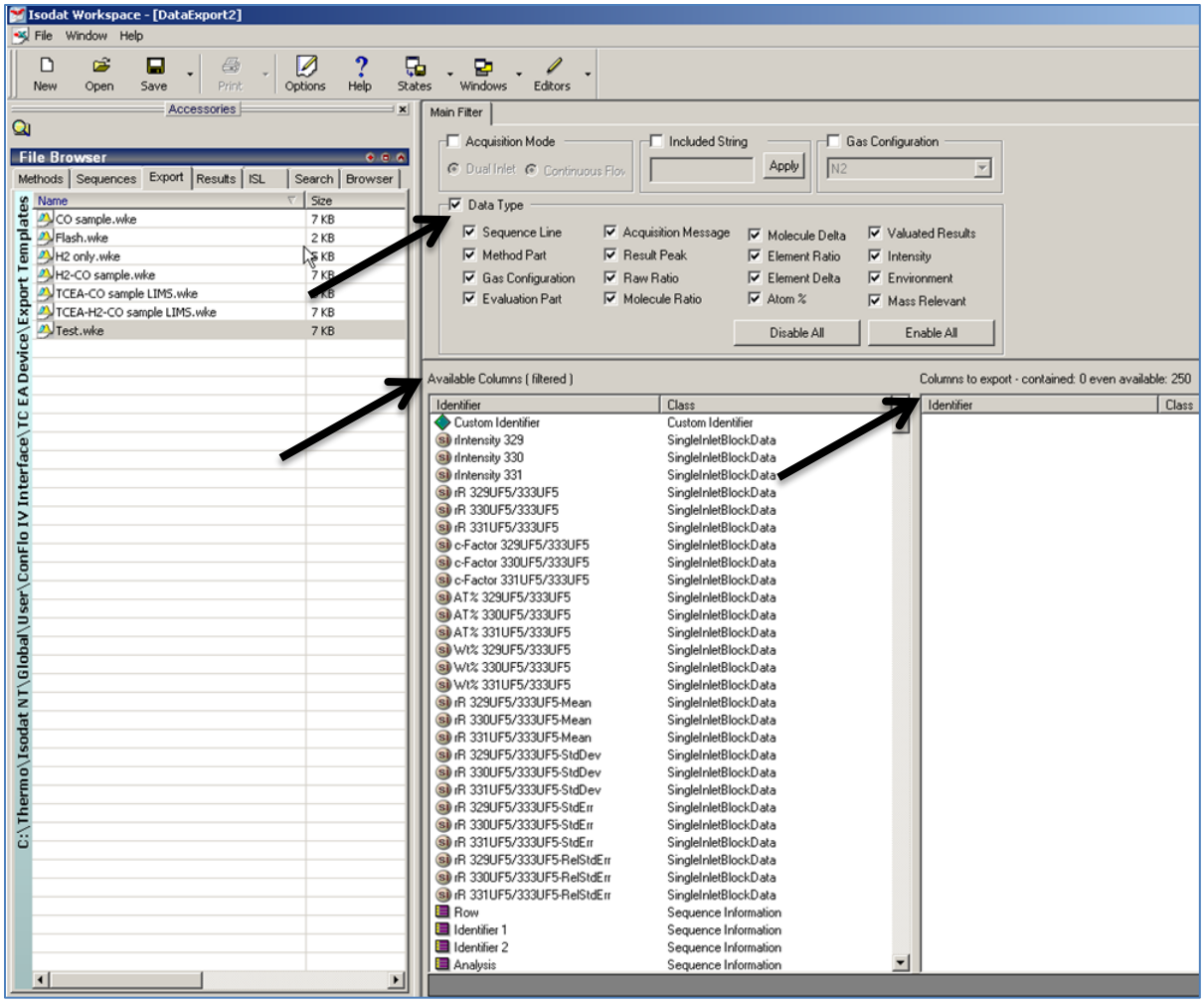


Fig. 19.4. Example data export form in ISODAT.

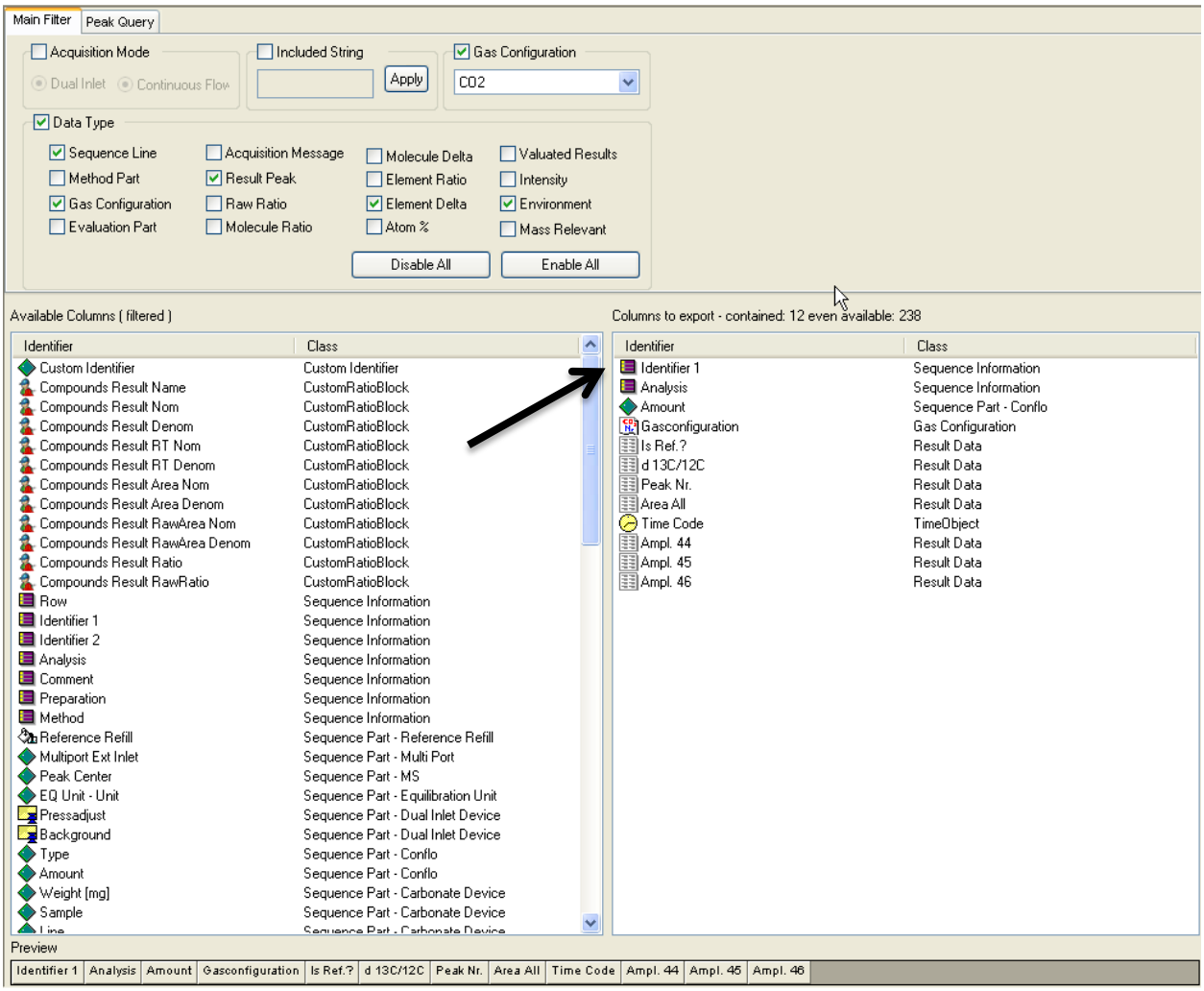


Fig. 19.5. Example data export form in ISODAT with the “Columns to export” pane populated.

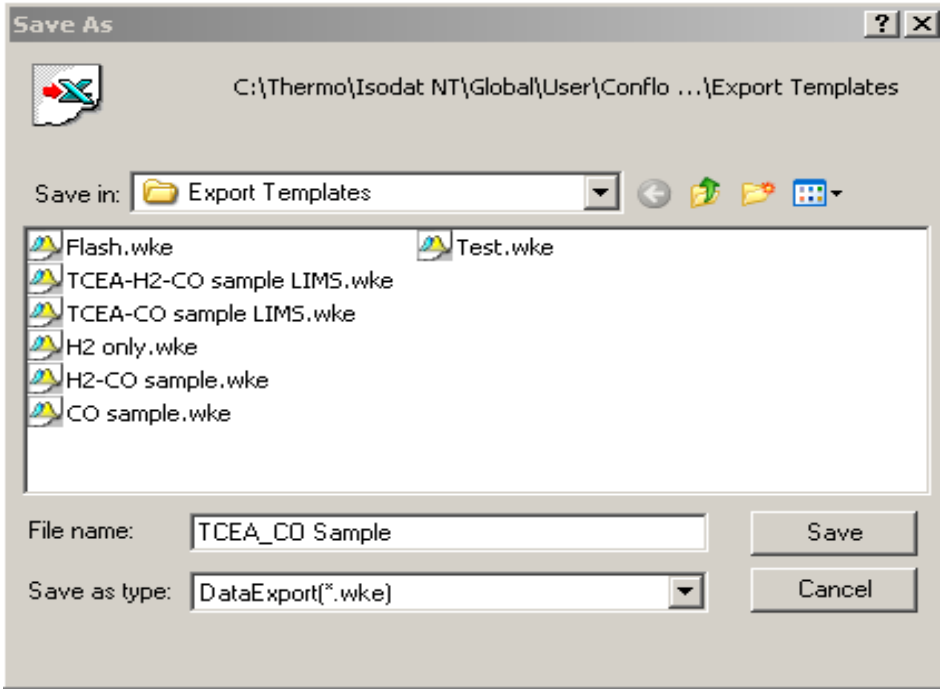


Fig. 19.6. Example data export form in ISODAT with the "Columns to export" pane.

One of the parameters in the left pane in Figure 19.5 is "Weight (mg)." LIMS does not recognize this column name in an Excel file; instead, "Amount" should be used as indicated in Table 19.3.

⚠ **Caution:** Watch out for the 11 characters that are deadly to some versions of ISODAT. Specifically, do not use any of these characters in ISODAT folder file names because the sample will be analyzed, BUT THE RESULTS WILL NOT BE SAVED TO THE HARD DRIVE. Also, DO NOT USE THEM IN ISODAT COMMENTS OR LIMS EXTRACTION IDs. These 11 deadly characters are:

! " ' * : < > ? \ | /

19.4 Exporting Results from ISODAT

To export isotope results:

1. In the ISODAT Workspace application, click on the Results tab.
2. Click on the folder of the results to be exported.
3. Highlight and press the Shift key to select all of the results to be exported.
4. Right click and select "Re-Process" (Fig. 19.7).

5. Unclick the “Use Method” box and click the “Add” button indicated in Figure 19.8.
6. Select the export template previously created in Section 19.3 and the export file will be created in Excel format and saved to the hard drive.
7. To find the Excel file right click on the results files selected in step 3.
8. Click Launch Explorer and scroll to the file created in step 6.
9. Save the Excel file to a memory stick or another desired location.

If the Excel file generated is for a dual-inlet instrument, it is ready for importing into LIMS. For a continuous-flow IRMS the “Is Ref?” column needs to be included.

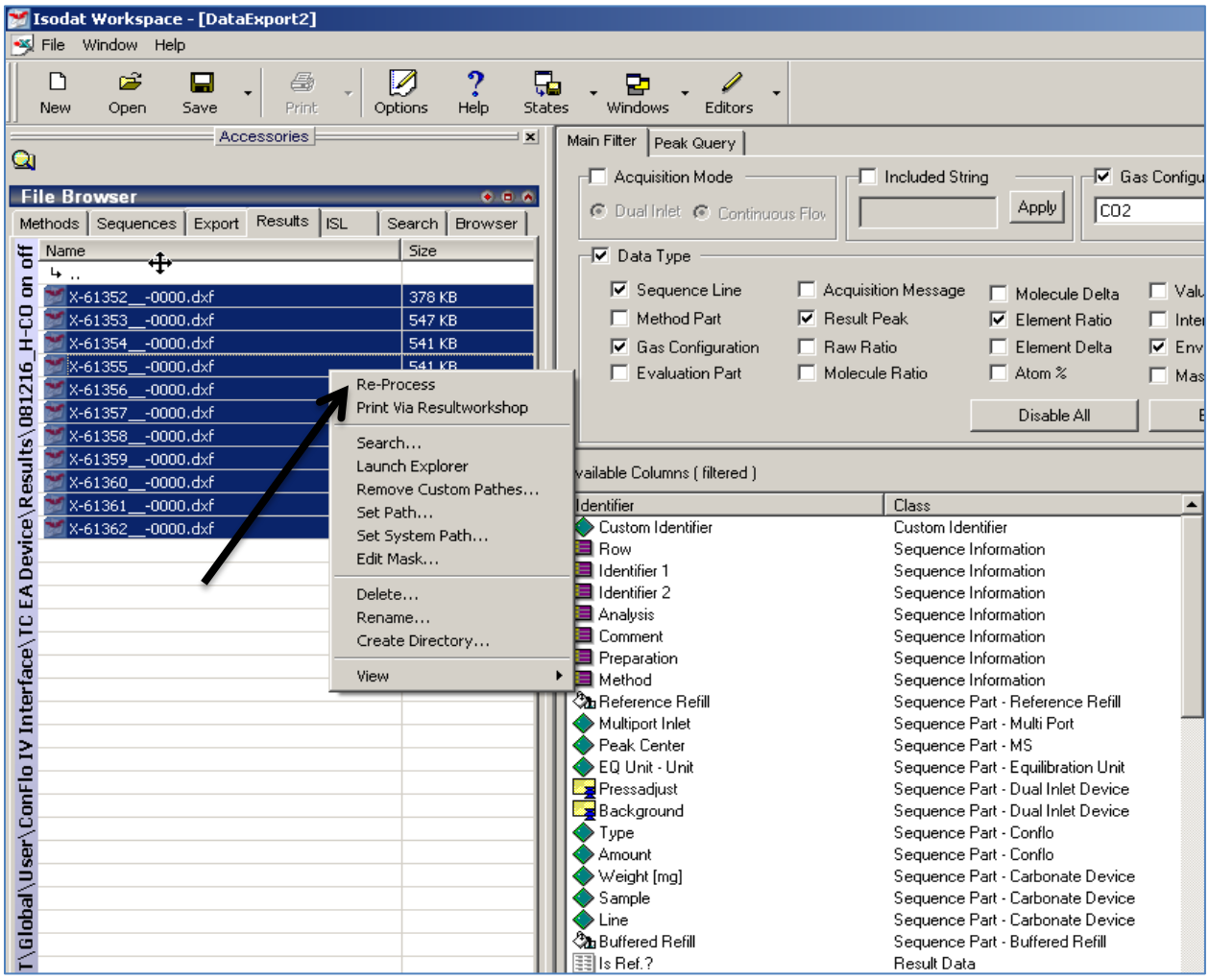


Fig. 19.7. Selecting results to be exported.

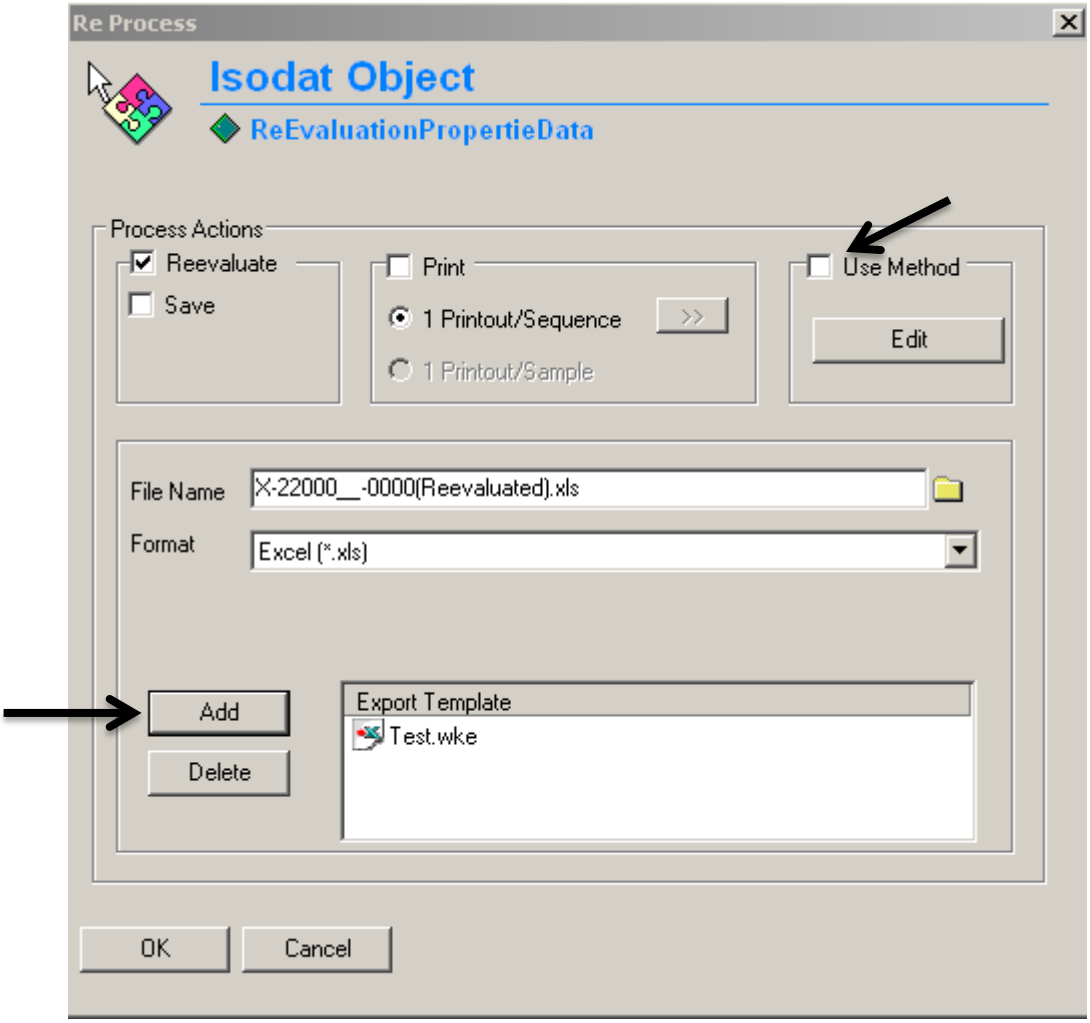


Fig. 19.8. Re-evaluation form.

19.5 Modifying Continuous-flow Excel Files for LIMS Importing

The EA method shown in Figure 19.1 has six peaks—two N_2 reference injection peaks followed by a sample N_2 peak, a sample CO_2 peak, and two CO_2 reference injection peaks. A section of the corresponding Excel file is shown in Figure 19.9. In ISODAT-generated continuous-flow Excel files column I, "Is Ref _," should identify all of the reference injection gas entries with a value of 1 and sample peaks with a value of 0. However, if there are two or more reference injection peaks ISODAT does not do this correctly. For example, in Figure 19.9 the "Is Ref _" entries for peaks 1 and 5 are incorrectly designated as sample peaks because the "Is Ref _" values are 0. The same problem occurs in TC/EA and other ISODAT Excel files. There are two relatively simple solutions: (1) remove all rows having reference injection data from the Excel file, or (2) make sure that the entries in the "Is Ref _" column for all reference injections are 1. Figure 19.10 shows strategy (2) applied to the Excel file data shown in Figure 19.9. The two

entries in red font have been changed to reflect that they represent reference injection peaks. Figure 19.11 shows a portion of the original and updated data files for a TC/EA analysis. Depending upon the version of ISODAT in use, the "Is Ref _" column heading may be written as "Is Ref.?." Because many laboratories see no need to retain rows of reference injection data in their LIMS backend database, they might select option (1) outlined above and delete all data rows with peak numbers that do not correspond to sample data (e.g all rows except 3 and 4 in the EA analyses shown in Figures 19.9 and 19.10, and for Figure 19.11 all rows except row 4). The choice between (1) deleting reference injection data or (2) correcting the values in column I is up to each isotope laboratory.

H	I	J
Gasconfiguration	Is Ref _	Peak Nr
N2	0	1
N2	1	2
N2	0	3
CO2	0	4
CO2	0	5
CO2	1	6

Fig. 19.9. Excel file of $\delta^{13}C$ and $\delta^{15}N$ analysis of an IRMS having an EA. See Figure 19.1. Peaks 3 and 4 are the sample.

H	I	J
Gasconfiguration	Is Ref _	Peak Nr
N2	1	1
N2	1	2
N2	0	3
CO2	0	4
CO2	1	5
CO2	1	6

Fig. 19.10. Excel file of $\delta^{13}C$ and $\delta^{15}N$ analysis of an IRMS having an EA after modification. Updated entries in red font.

F	G	H
Peak Nr	Is Ref _	Gasconfiguration
1	0	CO
2	1	CO
3	0	CO
4	0	CO

F	G	H
Peak Nr	Is Ref _	Gasconfiguration
1	1	CO
2	1	CO
3	1	CO
4	0	CO

Fig. 19.11. Before and after update of a TC/EA analysis, such as that shown in Figure 19.1. Updated entry in red font.

19.6 Importing Results into LIMS

19.6.1 Importing Continuous-flow Results

Once the rows of reference injection gas data have been deleted or correctly identified in the Excel file (See Section 19.5), the file is ready to import into LIMS. This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had the Thermo Scientific DELTA V PLUS IRMS "Hercules" added to it in Section 14. In the event the "Lakes_Backend_DB.accdb" backend database with Hercules is not available, a backend database for use in this section can be extracted from a file named "Thermo_Hercules_Backend_DB.zip" that is provided in a folder named "Section 19" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this example, $\delta^{13}C$ and $\delta^{15}N$ results from an EA will be imported. The file to be imported is named "Hercules_C&N.xls" and is found in a folder named "Section 19" that accompanies this manual. If this file is opened with Excel, it can be seen that all of the rows of continuous-flow reference injection data have been removed. Only peak numbers 3 and 4 are found in the fourth column. To import these analyses:

1. On the LIMS main page click "Import Data from Mass Specs" and the Analysis Import Format form (Fig. 19.12 or similar) will open.
2. Select "H --> Hercules" the Thermo Scientific IRMS.
3. Click "Import."
4. Navigate to "Hercules_C&N.xls."
5. Click "Select" and the Import Criteria for Mass Spectrometer form will open (Fig. 19.13). The "Columns Headings" panel in the upper left of this form contains columns for (1) the "Gas Type," which identifies the ISODAT Gas configuration, (2) the "Isotope" that was measured, (3) the "Column Headings," which identify the column in the Excel file that contains the isotope-delta values, (4) the "CF Ref Gas" column, and (5) check boxes to identify isotopes to be imported, to perform area adjust,

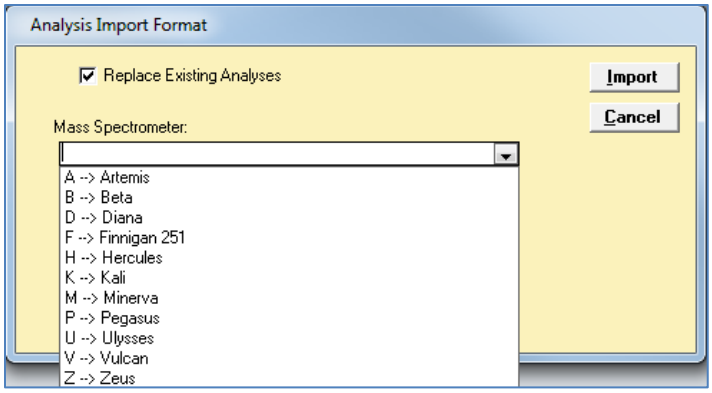


Fig. 19.12. Analysis Import Format form.

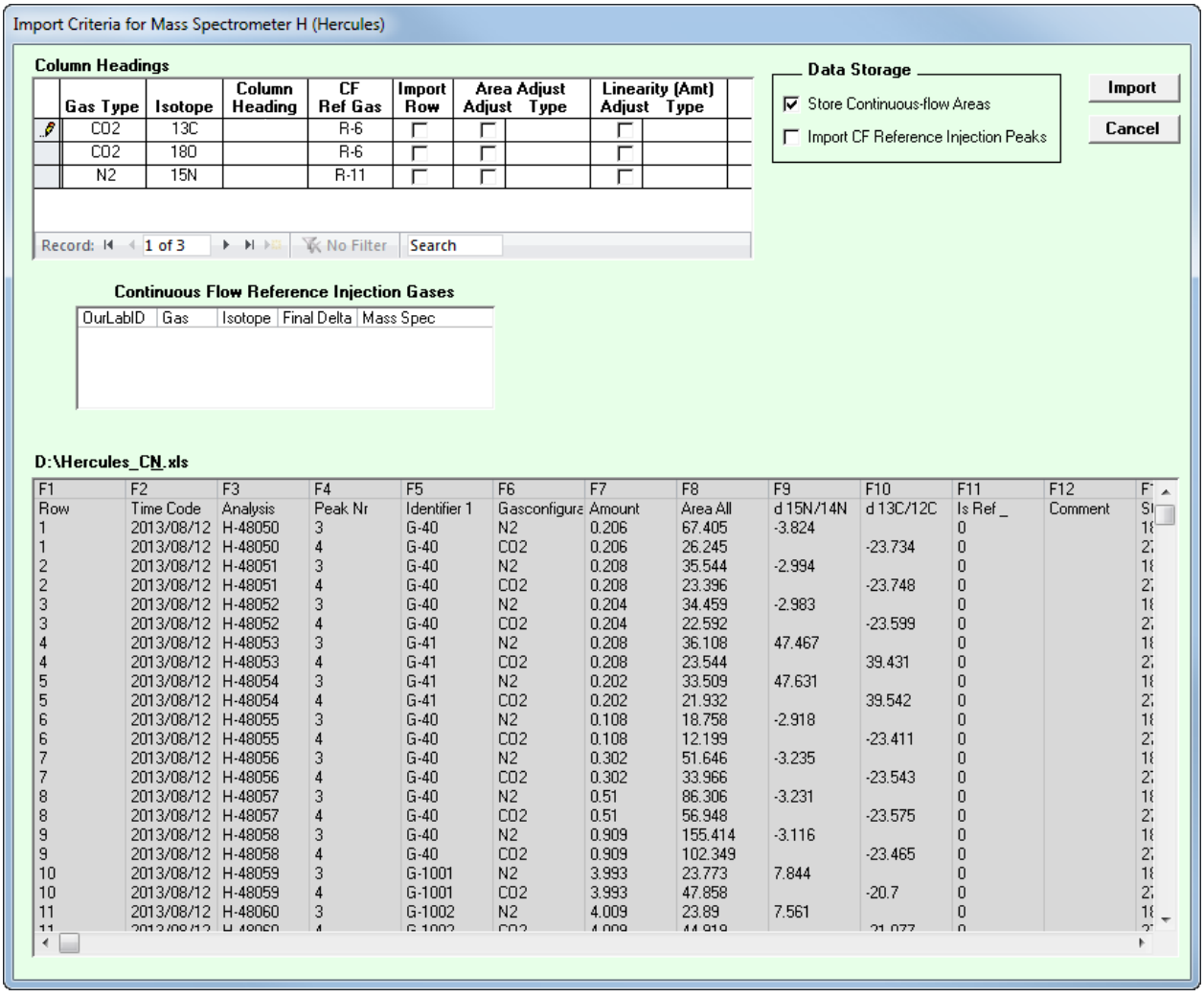


Fig. 19.13. Import Criteria for Mass Spectrometer form for a Thermo Scientific IRMS.

and to perform linearity adjust. The "Data Storage" panel in the upper right has check boxes that enable the importing of continuous-flow areas and (or) continuous-flow reference injection data. The lower panel displays a preview of the Excel form being imported. EA $\delta^{13}C$ and $\delta^{15}N$ results are found in columns "F10" and "F9," respectively.

6. To import $\delta^{13}C$ results, enter "F10" in the "Column Heading" column next to "13C" and enable the "Import Row" check box in the same row (Fig. 19.14).
7. To import $\delta^{15}N$ results, enter "F9" in the "Column Heading" column next to "15N" and enable the "Import Row" check box in the same row.
8. There can be an increase (or decrease) in peak area over time for the same mass of the same reference with an EA or TC/EA. LIMS can adjust for an increase (or decrease) in peak area of all peak of the same gas type based on values of the ratios of the peak areas and masses of a selected reference over time. This normalization should improve elemental mass fraction (element concentration) determinations. To perform this evaluation for CO_2 areas, click the "Area Adjust" check box in the row having "13C" in the "Isotope" column and LIMS will display the Area Adjust form (Fig. 19.15). The Area Adjust form (Fig. 19.15) shows a plot of analysis number versus CO_2 area of the reference G-40 divided by the mass of G-40. The user can select a choice of regressions (linear, quadratic, logarithmic, or power) to fit their data. The *R* squared value of the fit is shown. By clicking "Import Adjusted Areas" all of the CO_2 areas in the imported file will be adjusted (normalized) using the algorithm in the "Trend line." In figure 19.15, the first analysis (H-48050) shows an anomalously high value for the ratio Area / Amount. The first sample in any run may be anomalous and is routinely ignored in many laboratories.
9. Click the check box in the row H-48050 to ignore the data point for H-48050 and the plot will be updated immediately (Fig. 19.16).
10. The linear plot has an *R* squared value of 0.79 and appears reasonable. Therefore, click "Import Adjusted Areas" and LIMS will notify the user that all peak areas will be updated with the linear regression. If a user changes their mind, the file can be reimported.

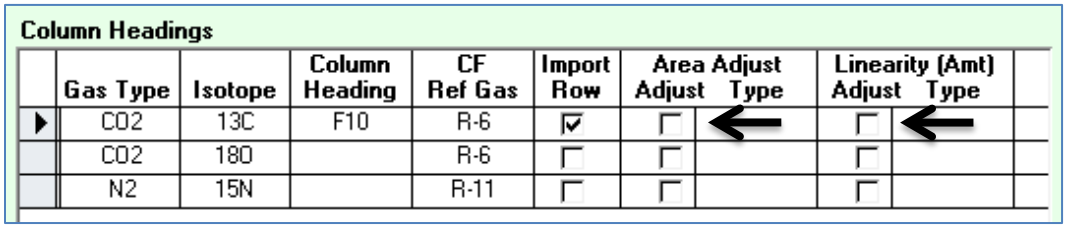


Fig. 19.14. Entering the column heading for $\delta^{13}C$ data import.

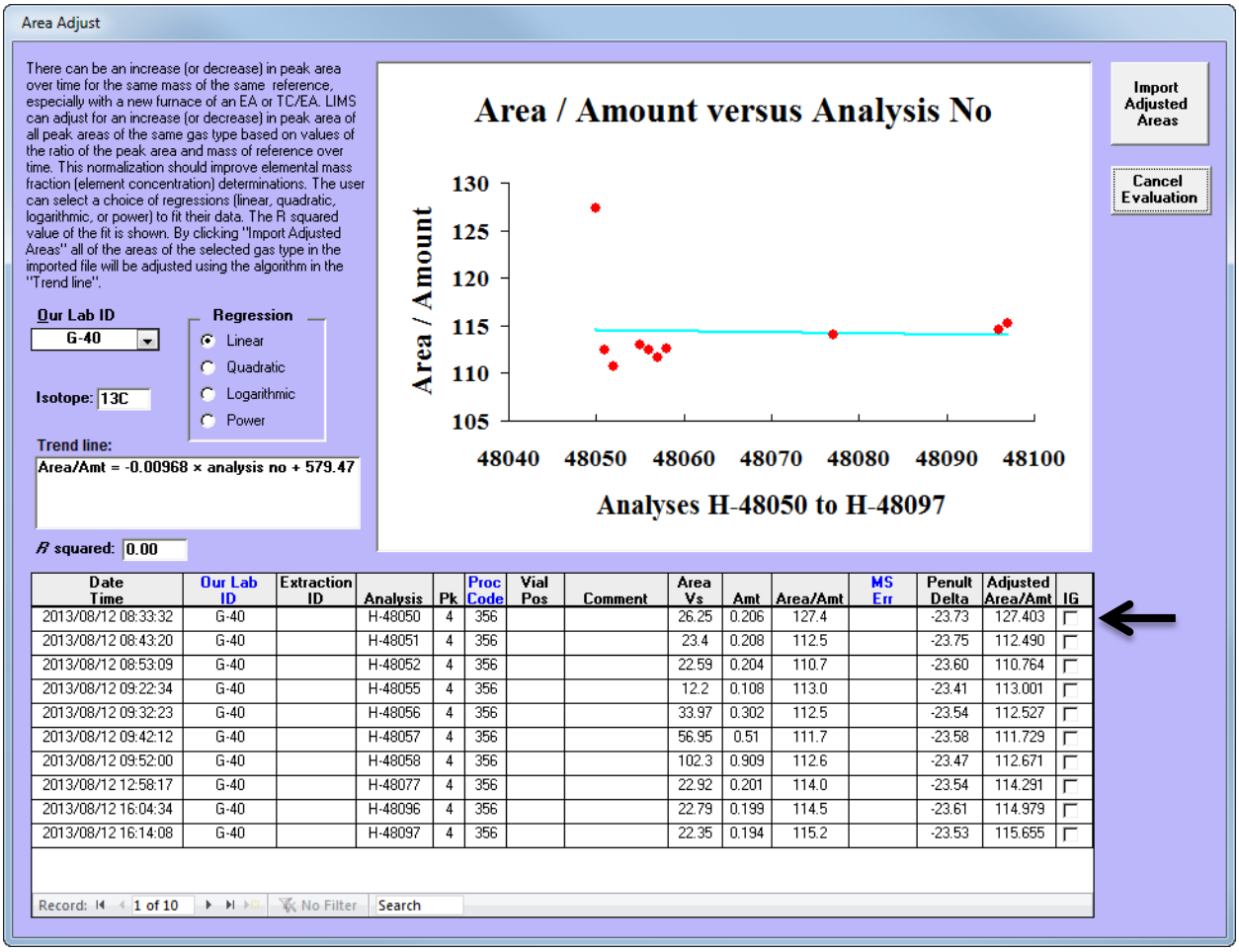


Fig. 19.15. The Area Adjust form showing analysis number versus CO_2 area / amount of standard.

11. Click “OK.”
12. To evaluate the so-called “Linearity” from a plot of peak area versus $\delta^{13}C$ values of G-40, click the “Linearity (Amt)” check box for the row having the isotope “13C,” and LIMS displays the Adjustment for Variation in Delta Value with Variation in Amount of Sample form (Fig. 19.18).
13. Over the peak area interval of 11 to 102 Vs, the $\delta^{13}C$ value of G-40 (USGS40) remains relatively constant with an *R* squared value of 0.07. There is no justification to apply a linearity adjustment. Therefore, click “Cancel Evaluation,” and the updated Column Headings in the upper left panel of the Import Criteria for Mass Spectrometer form are shown in Figure 19.19.
14. Perform the same steps for the Gas Type “N2,” and enable the Import Row check box having “N2.”
15. Click the Area Adjust check box for “N2,” and the Area Adjust form open.

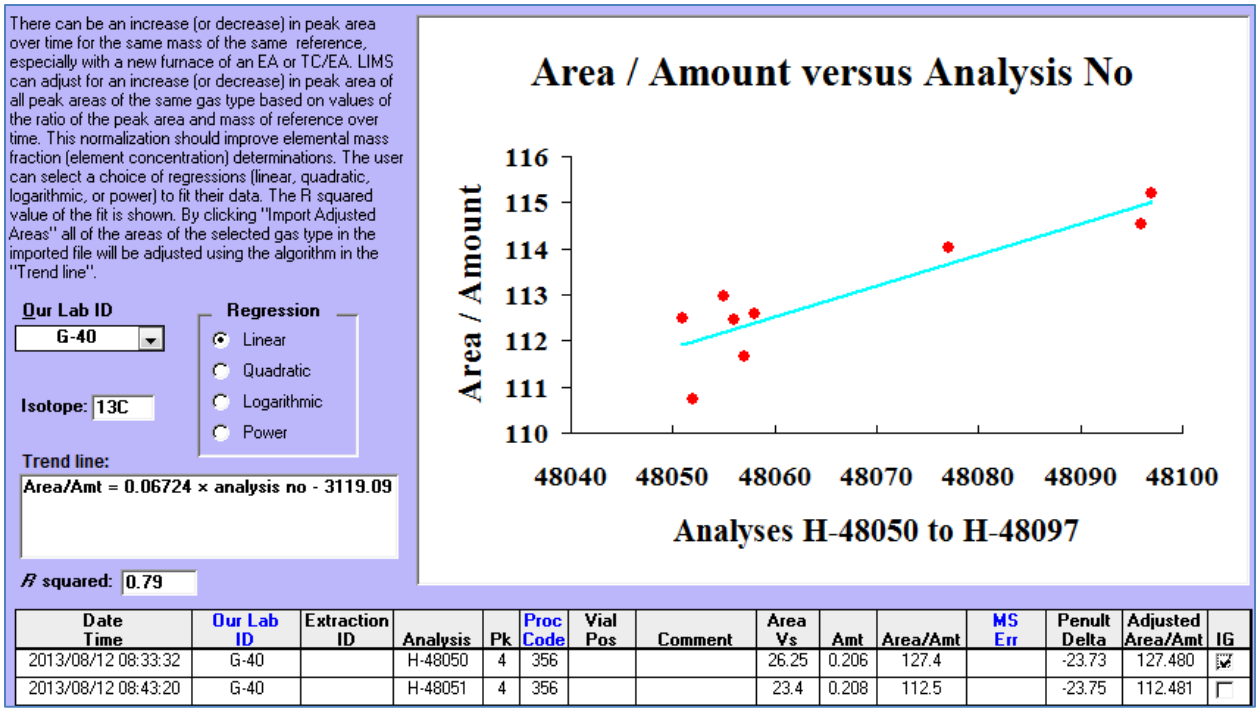


Fig. 19.16. Updated Area Adjust form after ignoring analysis H-48050.

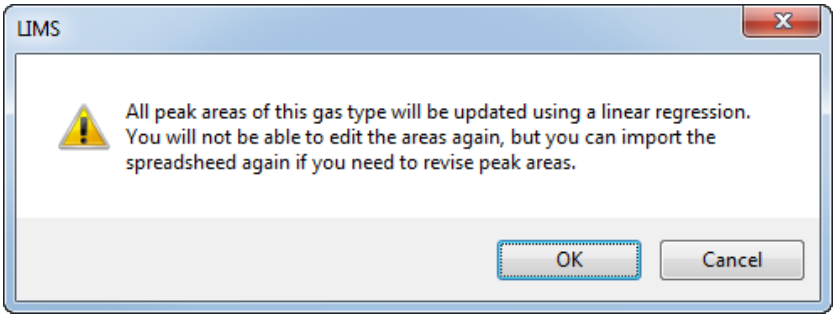


Fig. 19.17. LIMS notification that peak areas will be updated.

16. Ignore analysis “H-48050” as done above by clicking the “IG” check box for this analysis.
17. The *R* squared value is 0.16 so that there is no justification to apply an adjustment. Click “Cancel Evaluation.”

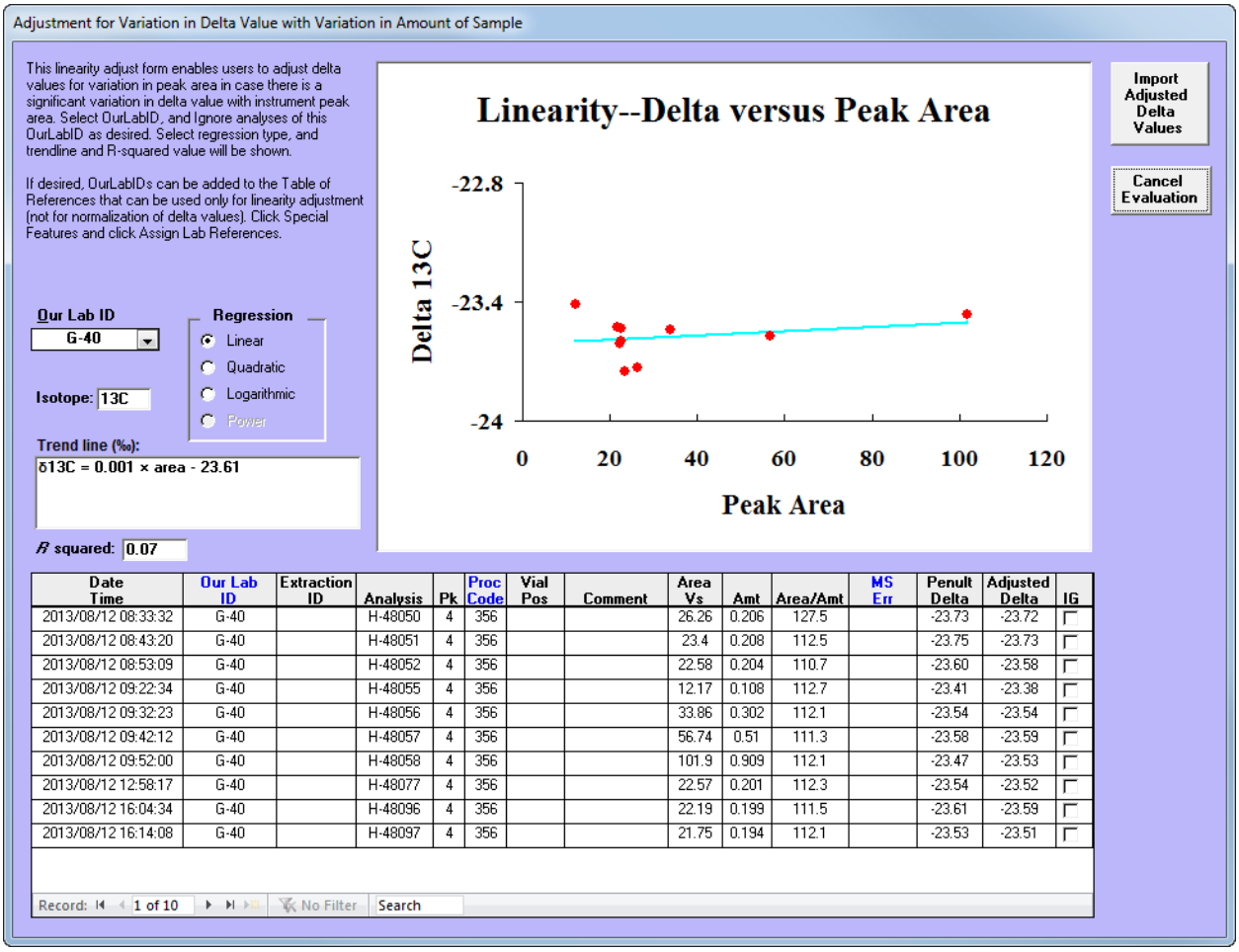


Fig. 19.18. The Adjustment for Variation in Delta Value with Variation in Amount of Sample (linearity adjustment) form.

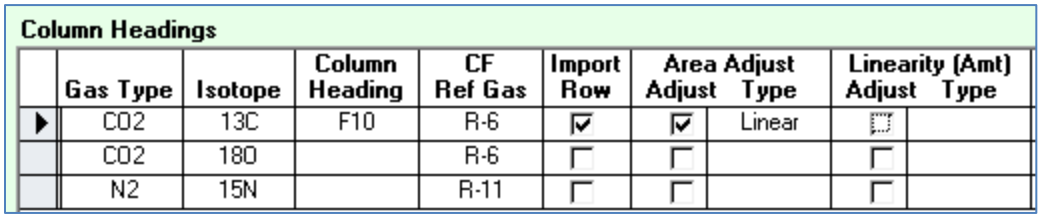


Fig. 19.19. Updated Column Headings in the Import Criteria of Mass Spectrometer form.

18. Evaluate the need for a linearity adjustment by clicking the "Linearity (Amt)" check box for the isotope "15N," and LIMS prompts the user with the message shown in Figure 19.20 to perform the Area Adjust first. Because in the step above, there was no justification to perform an Area Adjust owing to the low *R* squared value, click "No," and

LIMS will display the Adjustment for Variation in Delta Value with Variation in Amount of Sample form.

19. Note that the *R* squared value is low (0.08). Even clicking the "IG" check box for H-48050 only increases the *R* squared value to 0.19. Therefore, click "Cancel Evaluation" and the updated upper portion of the Import Criteria for Mass Spectrometer form is shown in Figure 19.21. The "Store Continuous-flow Areas" check box is enabled, which is correct, so it can be retained as is. The "Import CF Reference Injection Peaks" check box is not checked, which is correct, especially because there are no continuous-flow reference injection peak data in the Excel file to import—they were all deleted.
20. These data are ready to import. Click "Import" and LIMS displays the informational message in Figure 19.22.
21. Click "OK" and LIMS imports the analyses and displays a summary message (Fig. 19.23). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking "Special Features" then "ImportLog."
22. Click "OK" and this completes the importing of the Excel file "Hercules_C&N.xls"

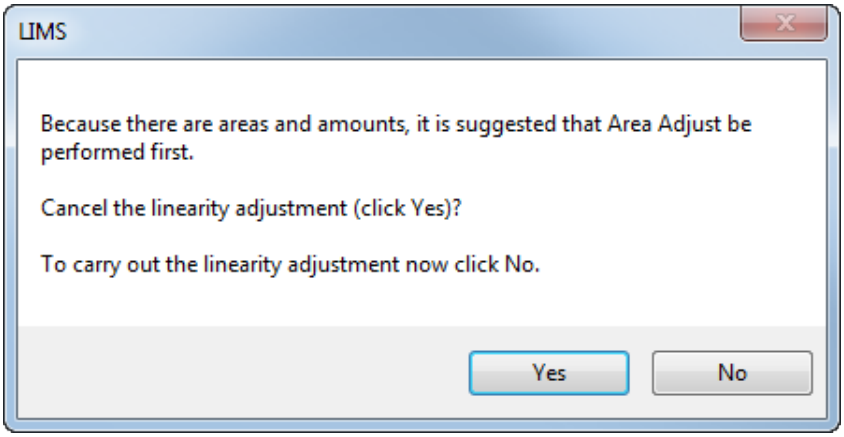


Fig. 19.20. LIMS prompt to perform Area Adjust first.

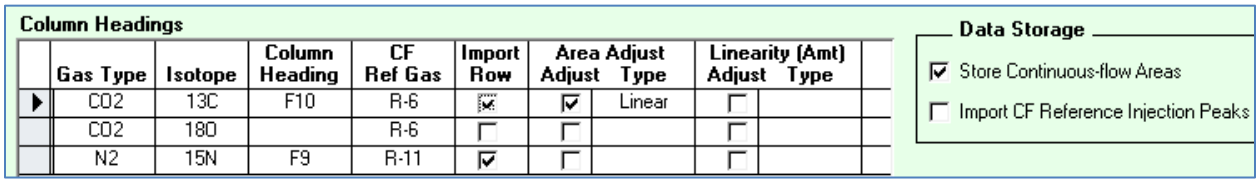


Fig. 19.21. Updated Import Criteria of Mass Spectrometer form.

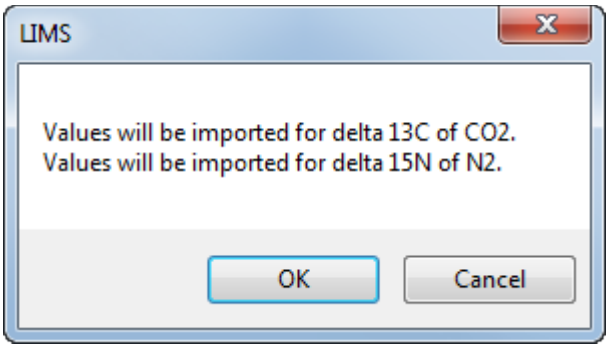


Fig. 19.22. LIMS information import prompt.

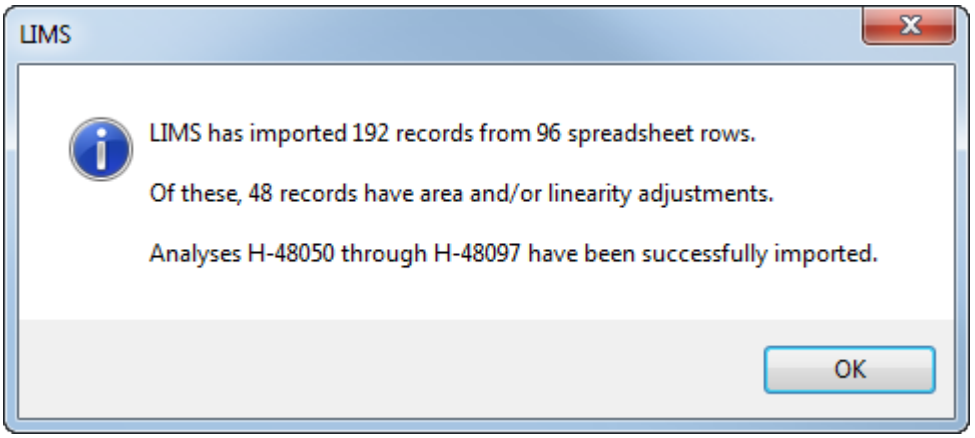


Fig. 19.23. LIMS continuous-flow import summary.

Normalization of the $\delta^{13}C$ and $\delta^{15}N$ results with determination of element mass fractions (element concentrations) is the next step, which is discussed in Section 24.

19.6.2 Importing Dual-inlet Results

Importing dual-inlet results is similar to that of importing continuous-flow results. Because dual-inlet results do not have continuous-flow areas, there are three fewer column headings. For example, a portion of the Import Criteria for Mass Spectrometer form for dual-inlet CO_2 analyses (*e.g.* "Dual-inlet_CO2.xls" in the folder named "Section 19") is shown in Figure 19.24. One only needs to identify the column headings (F5 for $\delta^{13}C$ and F6 for $\delta^{18}O$) and select which isotope-delta values to import (both). Importing the results generates a dialog box similar to that of Figure 19.22 and a summary dialog box (Fig. 19.25).

Normalization of the isotope-delta values is the next step and is discussed in Section 24.

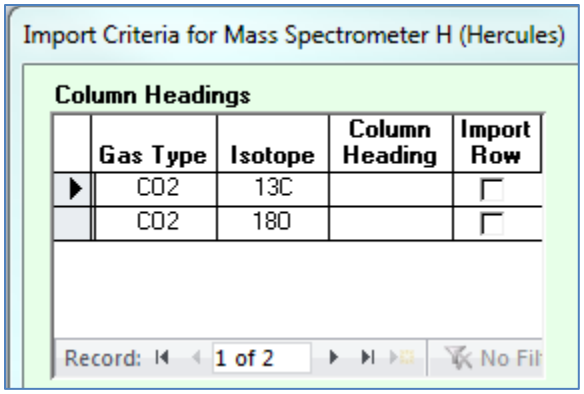


Fig. 19.24. Column Headings pane for of the Import Criteria of Mass Spectrometer form for Thermo Scientific dual-inlet CO_2 analyses.

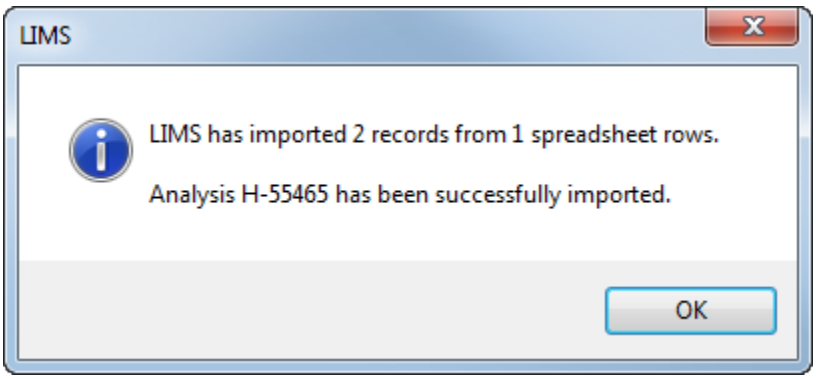


Fig. 19.25. Summary dialog box for example dual-inlet analysis.

20 Importing Data from a Finnigan MAT 251 Mass Spectrometer

20.1 General Comments

Importing Finnigan MAT 251 results is very similar to that of importing analyses from a Thermo Scientific or Thermoquest IRMS (see Section 19.1 and Tables 19.1, 19.2, and 19.3, which are all applicable to Finnigan MAT imports). Users should be familiar with Section 19.2 on special uses of ISODAT's "Identifier 1" and "Identifier 2" fields. This LIMS concatenation format was originally created for Finnigan MAT instruments.

The ISODAT data acquisition and control system of a Finnigan MAT 251 saves isotope-data files as Microsoft Works wks files. Because Microsoft Office 2007 and later versions do not import wks files, these wks files need to be saved as Excel files so that they can be imported by LIMS.

Finnigan mass spectrometer files that require the LIMS ISODAT import format can be identified by the fact that they have no mass spectrometer prefix in the analysis number column and "spec.- no." or "Spec.-no." appears in the analysis number column.

20.2 Importing Continuous-flow Results

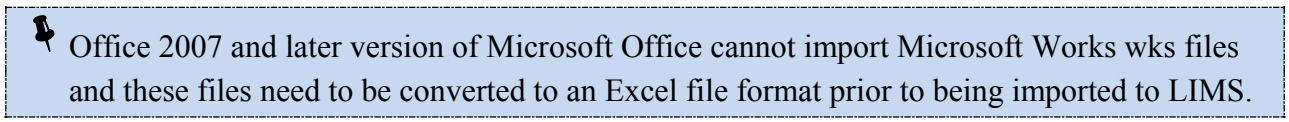
This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had the "Finnigan 251" IRMS added to it in Section 15. In the event the "Lakes_Backend_DB.accdb" backend database with the Finnigan 251 is not available, a backend database for use in this section can be extracted from a file named "Finnigan_251_Backend_DB.zip" that is provided in a folder named "Section 20" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this example, the continuous-flow file named "ISODAT_FinEA.xls," which is found in the folder named Section 20 in the files that accompany this manual, will be imported using the Finnigan MAT 251 added to LIMS in Section 15.

1. On the main page click "Import Data from Mass Specs" and the Analysis Import Format form will open.
2. Select "F --> Finnigan 251."
3. Click "Import" and LIMS will display the reminder to identify all row of continuous-flow reference injection gas with an asterisk (Fig. 20.1).

4. Open “ISODAT_FinEA.xls” with Excel and confirm that all of the reference injection peaks have been identified by an asterisk (*)—see column N of the file. Close Excel.
5. Click “Yes” and navigate to the Excel file.
6. Click “Select” and the Import Criteria for Mass Spectrometer will open, and it is similar to that shown in Figure 19.13. The “Columns Headings” panel in the upper left of this form contains columns for (1) the “Gas Type,” which identifies the ISODAT Gas configuration, (2) the “Isotope” that was measured, (3) the “Column Headings,” which identify the column in the Excel file that contains the isotope-delta values, (4) the “CF Ref Gas” column, and (5) check boxes to identify isotopes to be imported, to perform area adjust, and to perform linearity adjust. The “Data Storage” panel in the upper right has check boxes that enable the importing of continuous-flow areas and (or) continuous-flow reference injection data. The lower panel displays a preview of the Excel form being imported. EA $\delta^{13}C$ and $\delta^{15}N$ results are found in columns “F10” and “F9,” respectively.
7. Enter “F27” for the “Column Heading” row having “13C” as the “Isotope” and “F26” for the “Column Heading” row having “15N” as the “Isotope.”
8. Enable the “Import Row” check boxes for “13C” and “15N”, and the top section of the Import Criteria for Mass Spectrometer form should appear as shown in Figure 20.2.
9. There are too few analyses of references to perform an “Area Adjust” evaluation or a “Linearity (Amt)” evaluation. The “Store Continuous-flow Areas” check box is already enabled, so retain this setting. The “Import CF Reference Injection Peaks” check box is not enabled. Because there is little benefit in importing continuous-flow reference injection data, retain this setting. To import these results, click “Import” and LIMS displays an isotope information message (Fig. 19.22).
10. Click “OK” and LIMS imports the results and provides a summary message (Fig. 20.3). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking “Special Features” then “ImportLog.”
11. Click “OK” and this completes the importing of the Excel file “ISODAT_FinEA.xls.”

Normalization of the $\delta^{13}C$ and $\delta^{15}N$ results with determination of element mass fractions (element concentrations) is the next step and is discussed in Section 24.



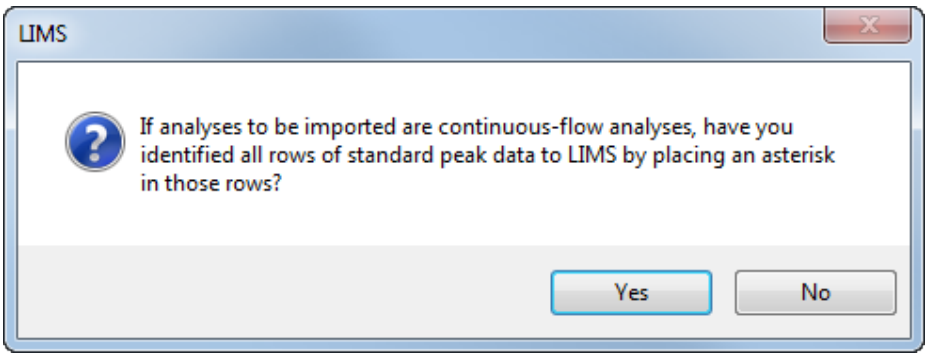


Fig. 20.1. LIMS reminder to identify all rows of continuous-flow reference injection gases with an asterisk.

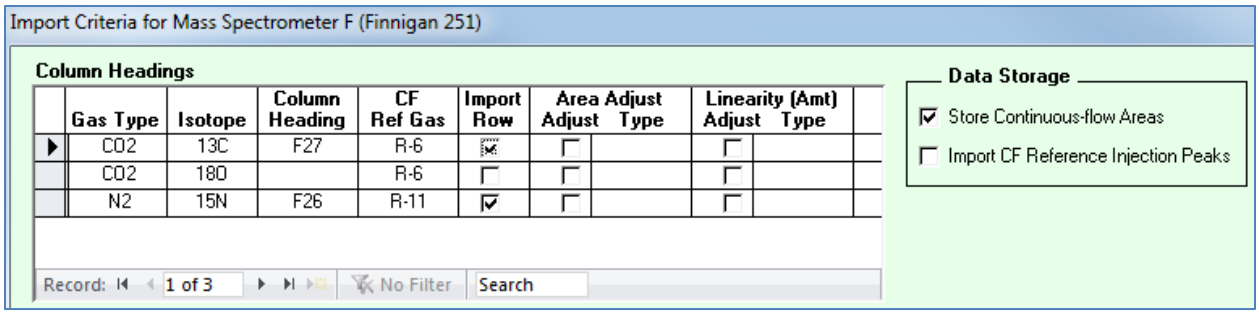


Fig. 20.2. Upper portion of the Import Criteria for Mass Spectrometer form.

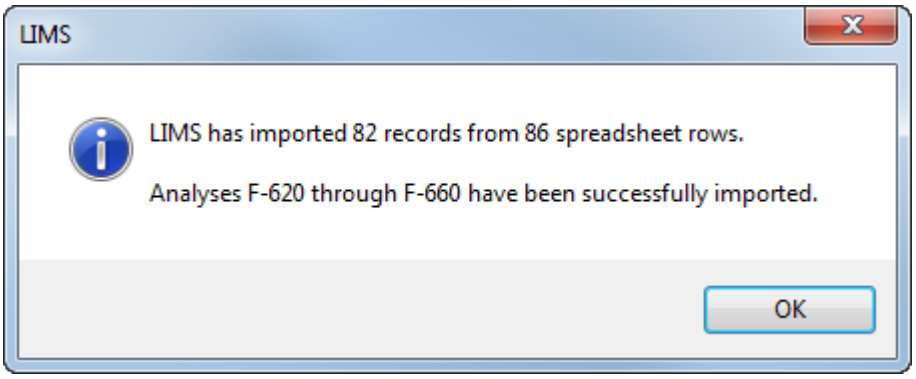


Fig. 20.3. LIMS continuous-flow import summary.

20.3 Importing Dual-inlet Results

Importing dual-inlet results is similar to that of importing continuous-flow results except that the column headings for isotopes of interest must have previously been entered into the lower right pane of the Mass Spec form (Fig. 15.3). Referring to the Excel file ("MAT_CO2_DI.xls"), the

$\delta^{13}C$ values are found in a column having a heading of "d-45/44," and the $\delta^{18}O$ values are found in a column having a heading of "18/16-O." To import these data:

1. On the main page click "Import Data from Mass Specs" and the Analysis Import Format form will open (Fig. 19.12 or similar).
2. Select "F --> Finnigan 251."
3. Click "Import" and LIMS will display the information prompt in Figure 20.1.
4. Click "Yes" and navigate to the file "MAT_CO2_DI.xls."
5. Click "Select" and the Import Criteria for Mass Spectrometer will open, and it is similar to that shown in Figure 19.13. Because dual-inlet results do not have continuous-flow areas, there are three fewer column headings. For example, a portion of the Import Criteria for Mass Spectrometer form for dual-inlet CO_2 analyses is shown in Figure 20.4. One only needs to select which isotope-delta values are to be imported.
6. Enable the "Import Row" check boxes for "13C" and for "18O."
7. Click "Import" and LIMS displays an isotope information message (Fig. 20.5).
8. Click "OK" and LIMS imports the results and provides a summary message (Fig. 20.6). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking "Special Features" then "ImportLog."
9. Click "OK" and this completes importing of the Excel file "MAT_CO2_DI.xls."

Normalization of the isotope-delta values is the next step and is discussed in Section 24.

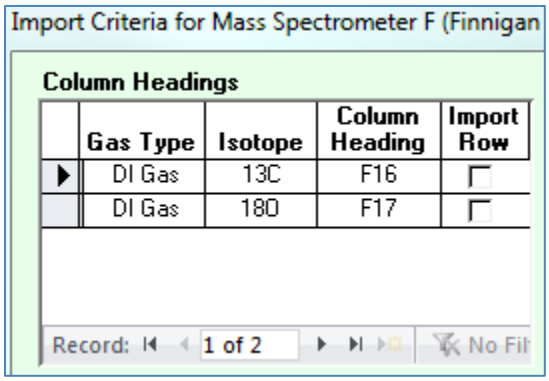


Fig. 20.4. Column Headings pane for of the Import Criteria of Mass Spectrometer form for dual-inlet CO_2 analyses.

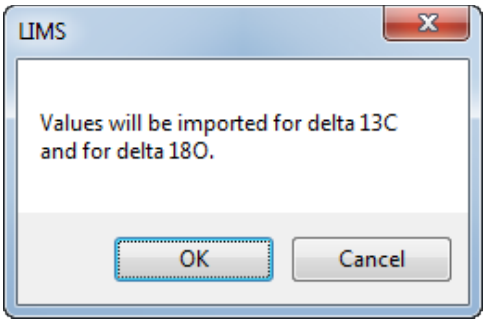


Fig. 20.5. LIMS information import prompt.

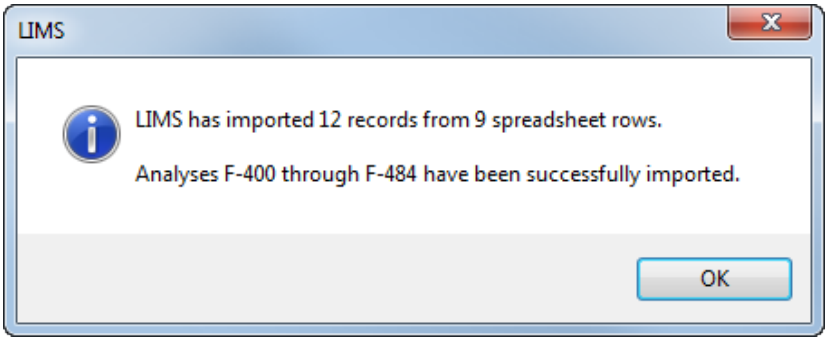


Fig. 20.6. LIMS dual-inlet import summary.

21 Importing Data from an Elementar/GV Instruments/Micromass Mass Spectrometer having an IonVantage or MassLynx Data System

21.1 General Comments

The IonVantage 4x, MassLynx 3.6, and MassLynx 4.0 data acquisition and control systems of Elementar, GV Instruments, and Micromass UK Limited can both:

- Transfer isotopic results to a LIMS backend database in real time, which is termed "Remote logging" in section 5.3.1 of the "MassLynx 3.6i LIMS interface handbook,"[8] which is provided as a pdf file in a folder named "Section 16" that accompanies this manual.
- Transfer isotopic results to a local database file, which is termed "Local logging" in section 5.3.1 of the interface handbook. The local database file can be exported to a flash drive and can be imported manually into LIMS.

The examples in this section demonstrate the use of "Local logging," which has the advantage that users can make linearity corrections (corrections for change in isotope-delta value with variation in amount of sample) as shown in Figure 19.18.

21.2 Importing Continuous-flow Results

This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had the "Minerva" IRMS added to it in Section 16. In the event the "Lakes_Backend_DB.accdb" backend database with Minerva is not available, a backend database for use in this section can be extracted from a file named "IonVantage_Minerva_Backend_DB.zip" that is provided in a folder named "Section 21" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this example, a file named "Minerva_CF_IonVantage_Analyses.mdb," which is found in the folder "Section 21" in the files that accompany this manual, was created using "local logging" with an IRMS having an IonVantage data acquisition and control system (added to LIMS in Section 16). To import this file:

1. On the main page click "Import Data from Mass Specs" and the Analysis Import Format form will open (Fig. 19.12 or similar).
2. Select "M --> Minerva" the IRMS with an IonVantage data system.
3. Click "Import."
4. Navigate to "Section 21" and select "Minerva_CF_IonVantage_Analyses.mdb" and, depending upon the location of the file, a Microsoft Access Security Notice may appear

(Fig. 21.1). If it does appear, click “Open,” and a second security notice may appear because LIMS is attempting to access two tables in this file. If so, click “Open.” The Import Criteria for Mass Spectrometer form should open (Fig. 21.2). The upper left pane of this form contains the “Isotope” and rows for check boxes for importing, area adjust, and linearity adjust. The upper right panel has check boxes to enable importing of continuous-flow areas and importing of continuous-flow reference injection data. The lower panel displays data in the Microsoft Access file being imported.

5. There can be an increase (or decrease) in peak area over time for the same mass of the same reference with an EA or TC/EA. LIMS can adjust for an increase (or decrease) in peak area of all peak of the same gas type based on values of the ratios of the peak areas and masses of a selected reference over time. This normalization should improve elemental mass fraction (element concentration) determinations. To perform this evaluation, click the “Area Adjust” check box in the row having “13C” in the “Isotope” column and LIMS will display the Area Adjust form (Fig. 21.3).
6. The Area Adjust form (Fig. 21.3) shows a plot of analysis number versus CO2 area of the reference G-40 divided by the mass of G-40. The user can select a choice of regressions (linear, quadratic, logarithmic, or power) to fit their data. The *R* squared value of the fit is shown. By clicking “Import Adjusted Areas” all of the CO2 areas in the imported file will be adjusted (normalized) using the algorithm in the “Trend line.” In figure 21.3, the first analysis (M-48050) shows an anomalously high value for the ratio Area / Amount. The first sample in any run may be anomalous and is routinely ignored in many laboratories. To ignore the data point for M-48050, click the check box in the row for analysis M-48050 and the plot will be updated immediately (Fig. 21.4).

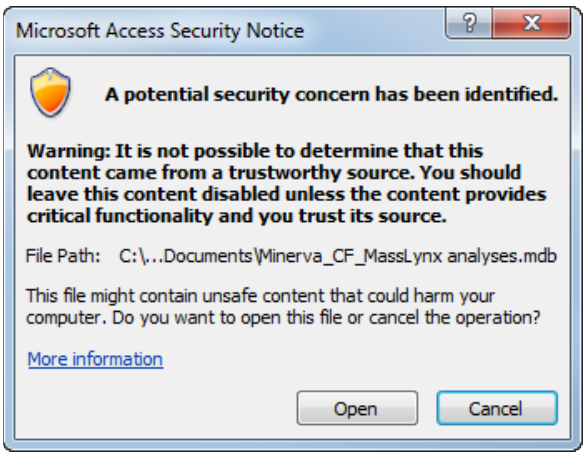


Fig. 21.1. Microsoft Access Security Notice.

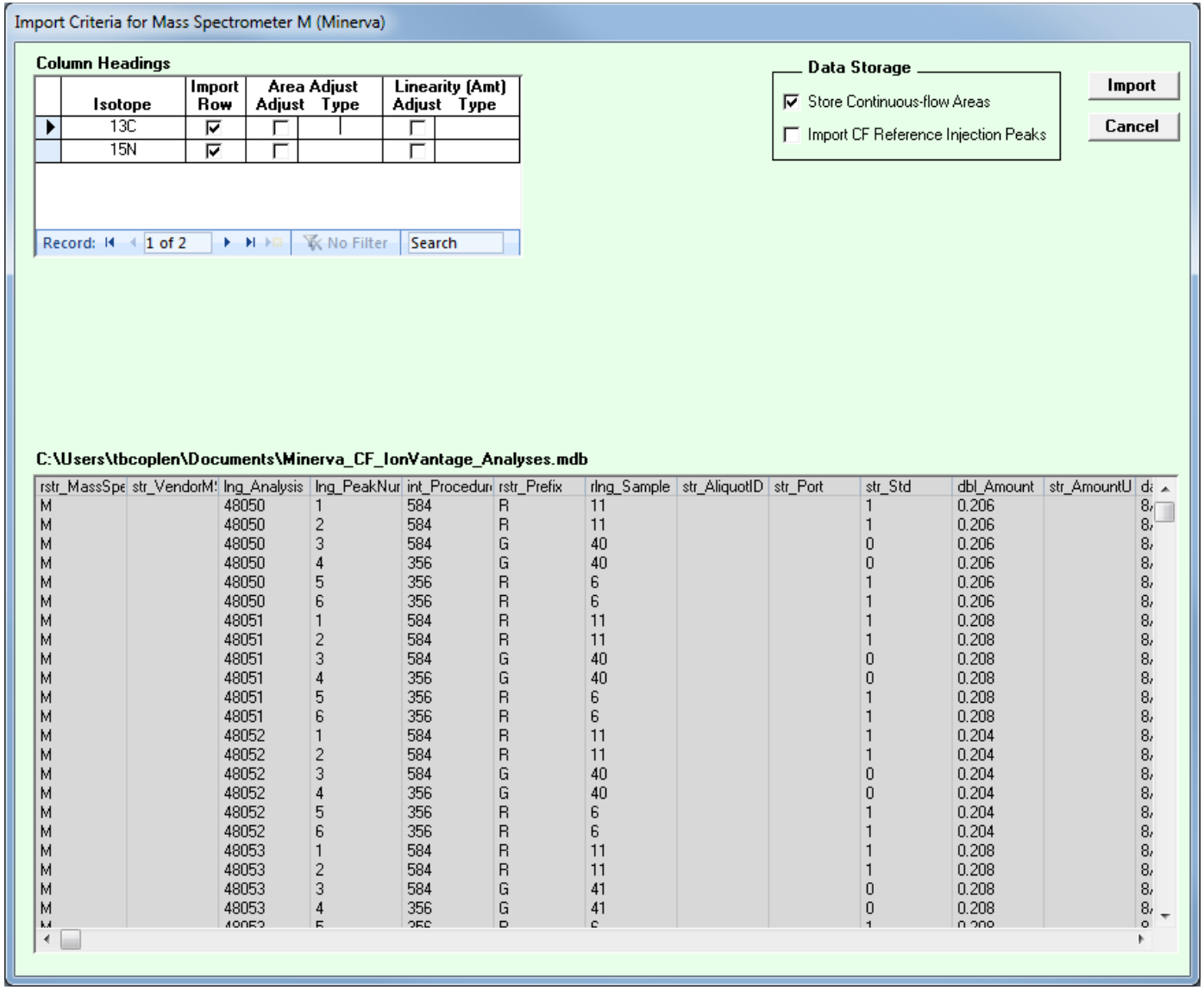


Fig. 21.2. The Import Criteria for Mass Spectrometer form.

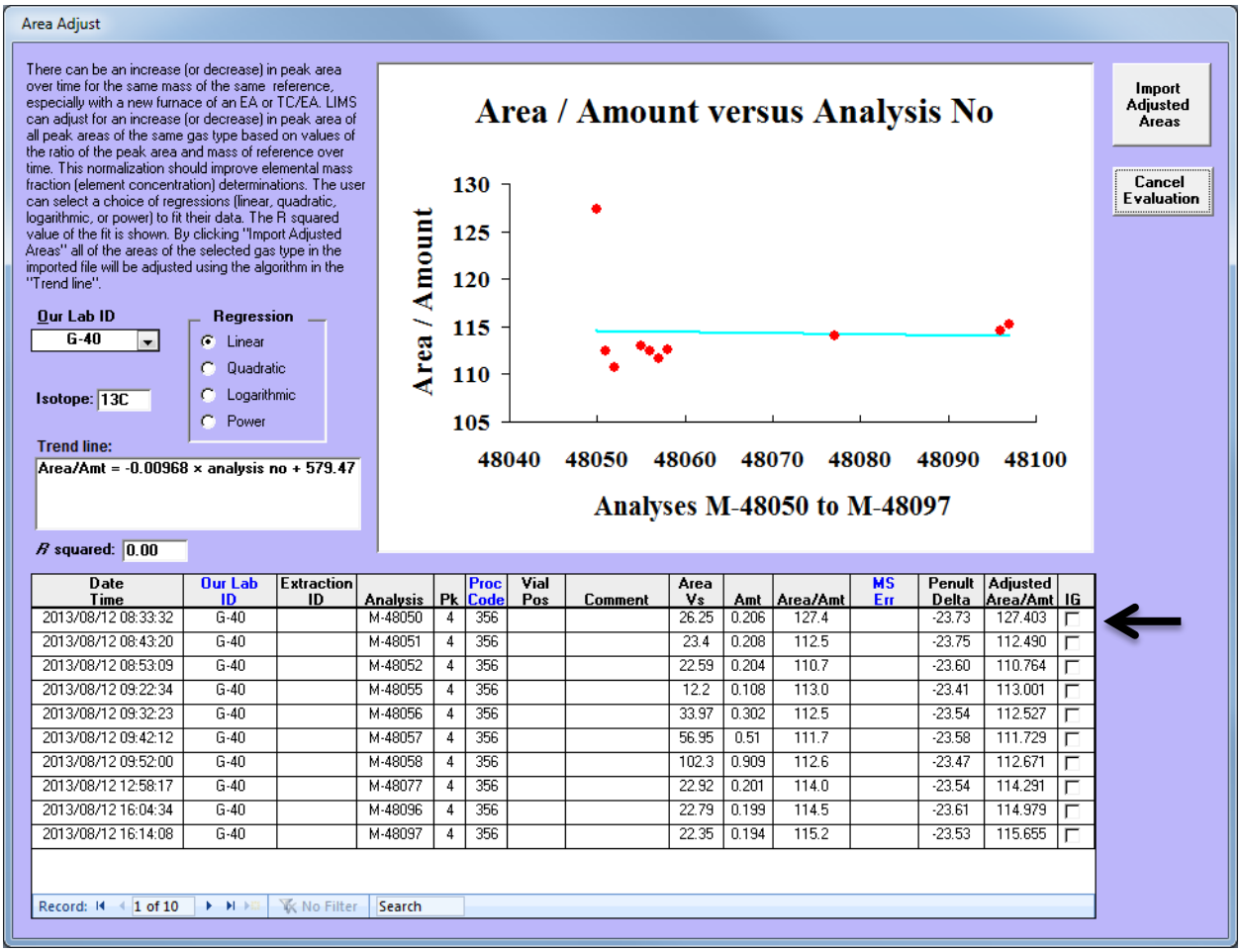
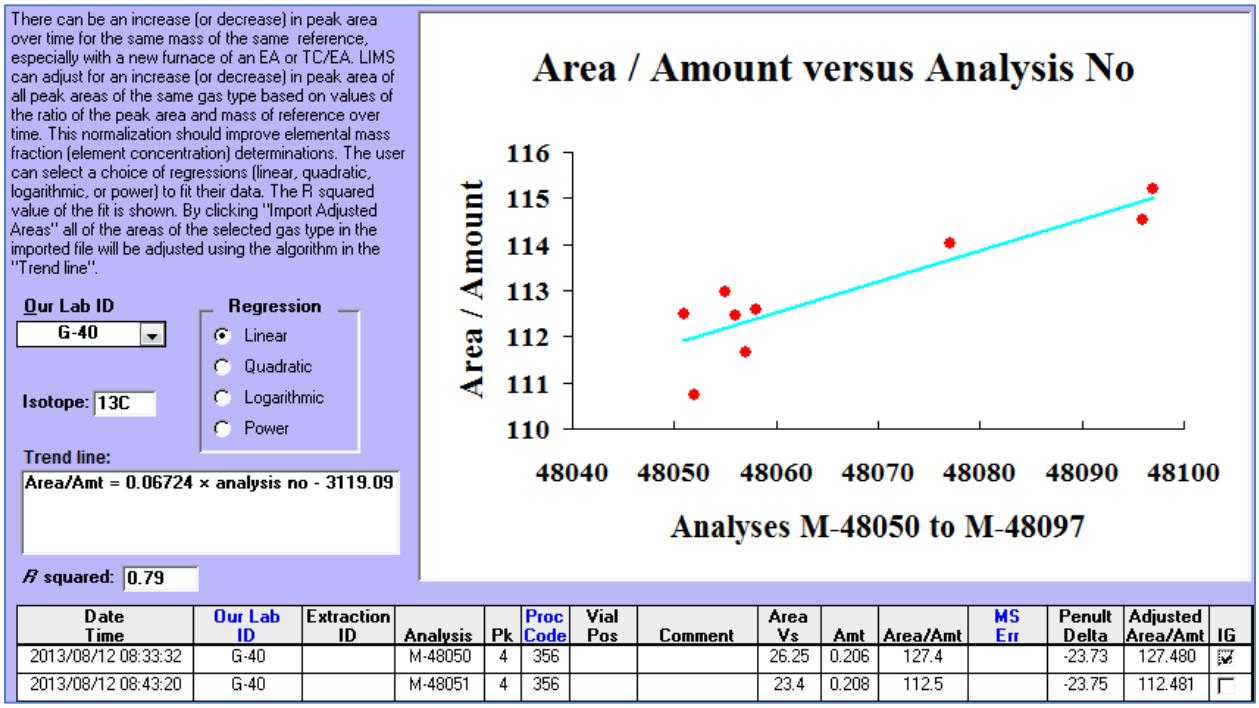


Fig. 21.3. The Area Adjust form showing analysis number versus CO_2 area / amount of standard.

7. The linear plot has an *R* squared value of 0.79 and appears reasonable. Therefore, click "Import Adjusted Areas" and LIMS will notify the user that all peak areas will be updated with the linear regression. If a user changes their mind, the file can be reimported.
8. Click "OK."
9. To evaluate the so-called "Linearity" from a plot of peak area versus $\delta^{13}C$ values of G-40, click the "Linearity (Amt)" check box for the row having the isotope "13C," and LIMS displays the Adjustment for Variation in Delta Value with Variation in Amount of Sample form (Fig. 21.5).
10. Over the peak area interval of 11 to 102 Vs, the $\delta^{13}C$ value of G-40 (USGS40) remains relatively constant with an *R* squared value of 0.07. There is no justification to apply a linearity adjustment. Therefore, click "Cancel Evaluation."



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Area Vs	Amt	Area/Amt	MS Err	Penult Delta	Adjusted Area/Amt	IG
2013/08/12 08:33:32	G-40		M-48050	4	356			26.25	0.206	127.4		-23.73	127.480	☑
2013/08/12 08:43:20	G-40		M-48051	4	356			23.4	0.208	112.5		-23.75	112.481	☐

Fig. 21.4. Updated Area Adjust form after ignoring analysis M-48050.

11. Perform the same steps for the Isotope "15N" and enable the "Import Row" check box for "15N."
12. Click the Area Adjust check box for "15N" and the Area Adjust form open.
13. Ignore analysis "M-48050" as done above by clicking the "IG" check box for this analysis.
14. The *R* squared value is 0.16 so that there is no justification to apply an adjustment. Click "Cancel Evaluation."
15. Evaluate the need for a linearity adjustment by clicking the "Linearity (Amt)" check box for the isotope "15N" and LIMS prompts the user with the message shown in Figure 21.6 to perform the Area Adjust first. Because in the step above, there was no justification to perform an Area Adjust owing to the low *R* squared value, click "No," and LIMS will display the Adjustment for Variation in Delta Value with Variation in Amount of Sample form.
16. Note that the *R* squared value is low (0.07). Therefore, click "Cancel Evaluation" and the updated upper portion of the Import Criteria for Mass Spectrometer form is shown in Figure 21.7.

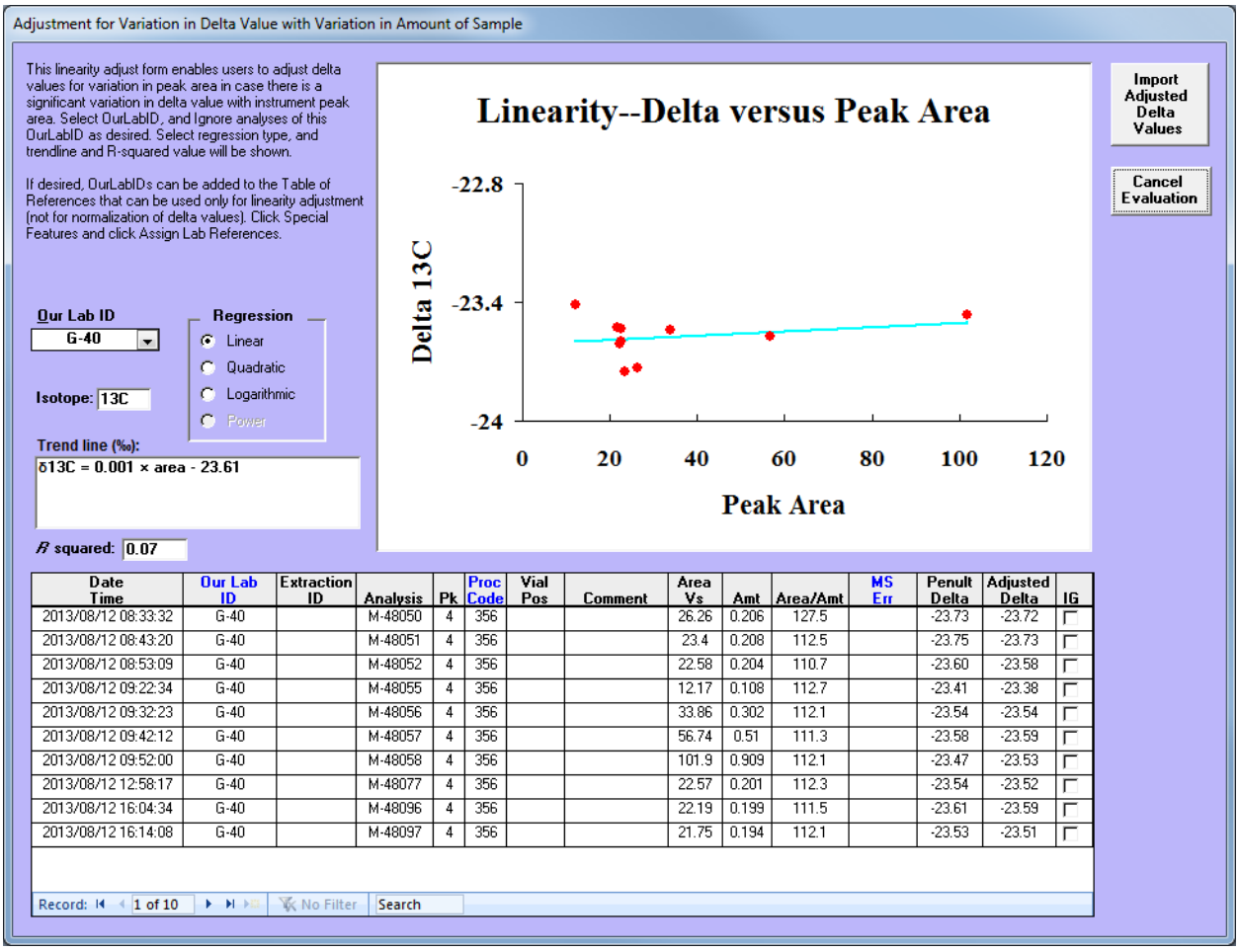


Fig. 21.5. The Adjustment for Variation in Delta Value with Variation in Amount of Sample (linearity adjustment) form.

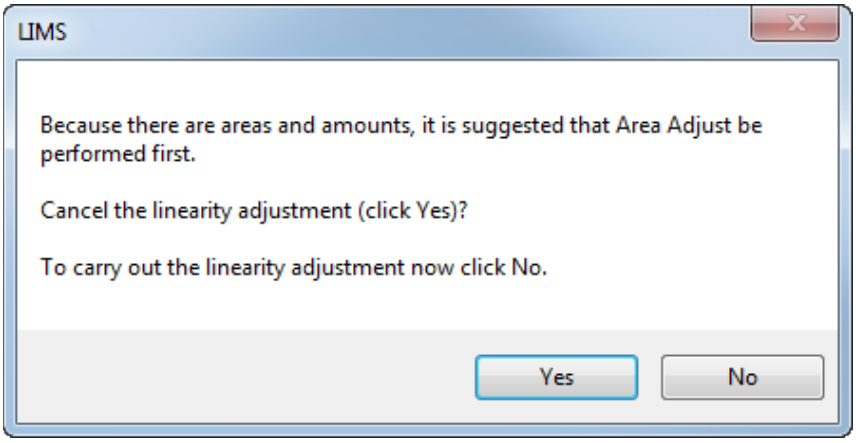


Fig. 21.6. LIMS prompt to perform Area Adjust first.

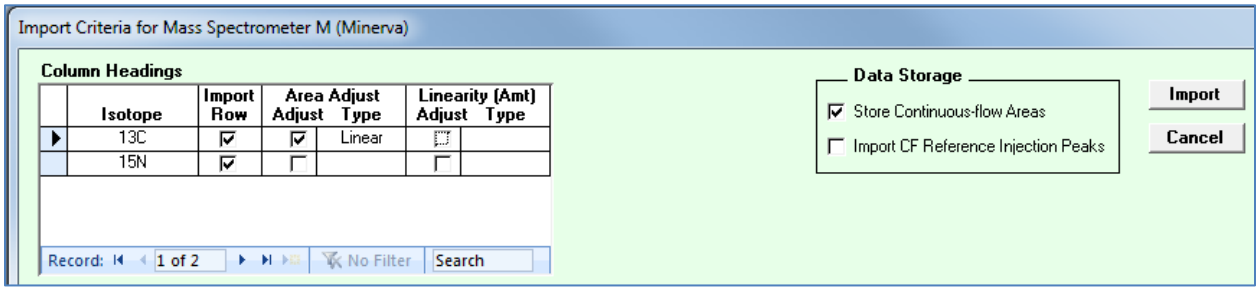


Fig. 21.7. Updated Import Criteria of Mass Spectrometer form.

17. The "Store Continuous-flow Areas" check box is enabled, which is correct, so it can be retained as is. The "Import CF Reference Injection Peaks" check box is not checked, but can be checked if the user prefers to import continuous-flow reference injection peak data. Normally, CF Reference Injection Peak data are not imported.
18. These data are ready to import. Click "Import" and LIMS displays the informational message in Figure 21.8.
19. Click "OK;" LIMS imports the results and provides a summary message (Fig. 21.9). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking "Special Features" then "ImportLog."
20. Click "OK" and this completes importing of the file "Minerva_CF_IonVantage_Analyses.mdb."

Normalization of the $\delta^{13}C$ and $\delta^{15}N$ results and determinations of element mass fractions (element concentrations) is the next step, and they are discussed in Section 24.

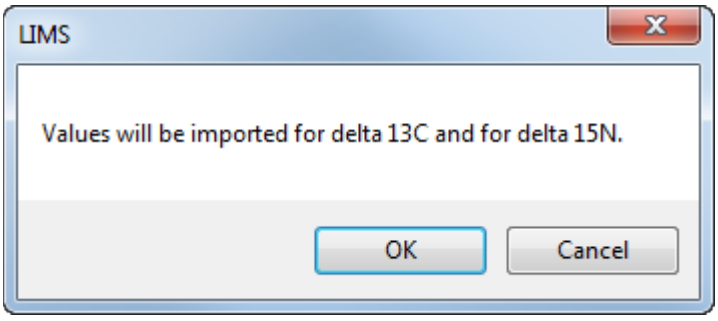


Fig. 21.8. LIMS information import prompt.

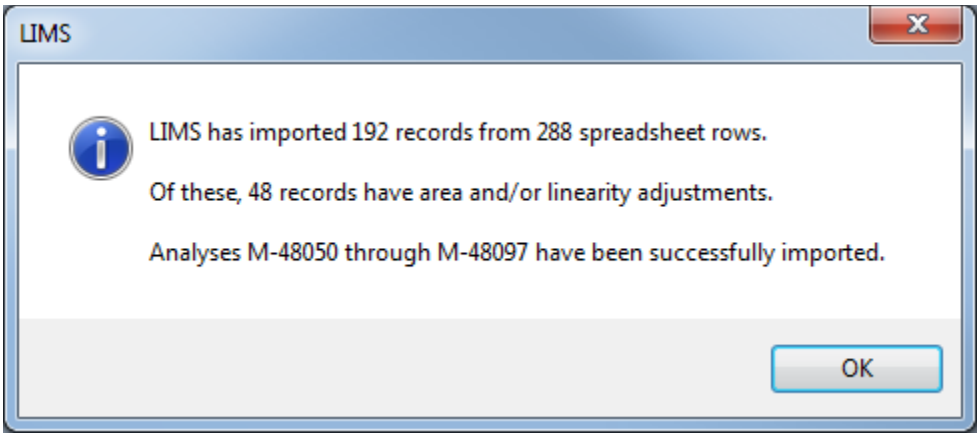


Fig. 21.9. LIMS continuous-flow import summary.

21.3 Importing Dual-inlet Results

Importing dual-inlet results is straight forward. In the following example, an Access file named "Minerva_DI_IonVantage_Analyses.mdb," which is found in the folder "Section 21" in the files that accompany this manual, was created using "local logging" with an IRMS having an IonVantage data acquisition and control system (added to LIMS in Section 16). To import this file:

1. On the main page click "Import Data from Mass Specs" and the Analysis Import Format form will open (Fig. 19.12 or similar).
2. Select "M --> Minerva" the Elementar IonVantage IRMS.
3. Click "Import."
4. Navigate to "Section 21" and select "Minerva_CF_IonVantage_Analyses.mdb" and, depending upon the location of the file, a Microsoft Access Security Notice may appear (Fig. 21.1). If it does appear, click "Open," and a second security notice may appear because LIMS is attempting to access two tables in this file. If so, click "Open."
5. LIMS will import the file provide the summary message shown in Figure 21.10.
6. Click "OK" and this completes importing of the dual-inlet file.

Normalization of these dual inlet results is the next step and is discussed in Section 24.

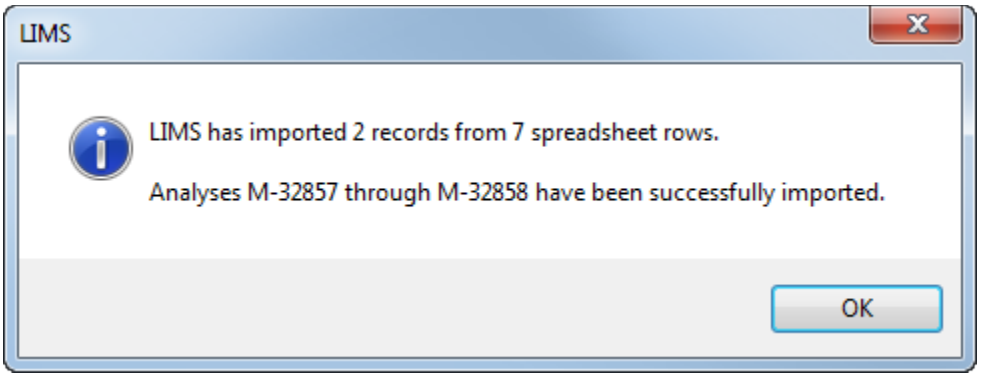


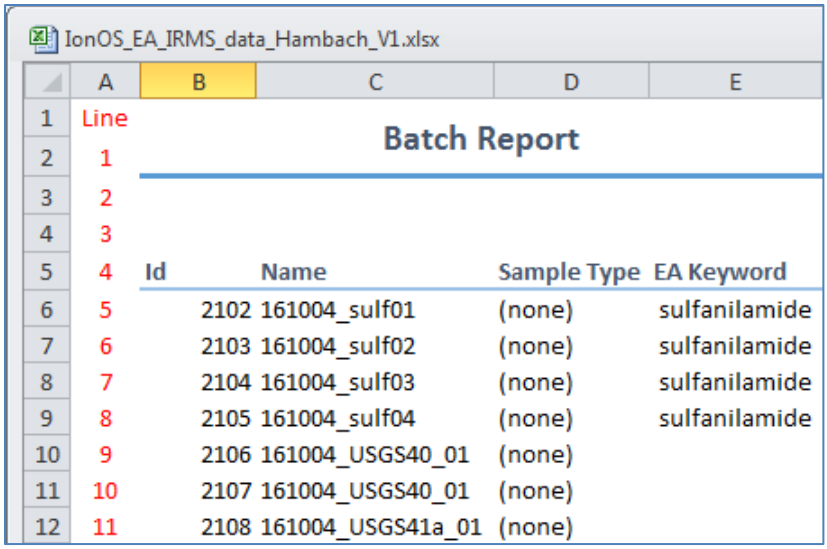
Fig. 21.10. LIMS dual-inlet import summary for the IonVantage IRMS.

22 Importing Data from a Mass Spectrometer having the "LIMS Abbreviated" Import Format

22.1 General Comments

The LIMS Abbreviated import format (Section 17.1) uses an Excel file and is the most flexible of all formats for importing measurement results into LIMS. The first row of the Excel file contains unique column headings to identify data in each column. Rows two and greater contain the results to be imported. Before proceeding, the reader should be fully familiar with the information in Section 17.1. The strategy outlined below for a variety of mass spectrometer data files can be reduced to the following steps:

1. If not already an Excel file, open the data file with Excel and save it as an Excel file (either xls or xlsx).
2. If there is no "Line" column, create one and add increasing integers one or greater, *e.g.* 1, 2, 3, etc. (Fig. 22.1)
3. For each column of data to be imported, identify the data in the column in row one using the unique LIMS Abbreviated column headings listed in Tables 17.1 and 17.2.
4. Add columns for information that is missing. For example, a "Comment" column, an "Extraction ID" column, an "Amount Unit" column, and an "Ignore" column might be of use. The Ignore column enables one to import and label suspect data in LIMS; such data will not be used in calculations.
5. All other data columns, if they exist, will have data that do not need to be imported into LIMS; make their column headings blank.
6. Remove all other worksheets in the Excel workbook, or copy this worksheet into a new Excel workbook having only one worksheet.
7. Save the Excel file that is now ready to be imported into LIMS.
8. To save time on future imports, make an Excel template of the top row. Then, copy new data into this file.



IonOS_EA_IRMS_data_Hambach_V1.xlsx

	A	B	C	D	E
1	Line	Batch Report			
2	1				
3	2				
4	3				
5	4	Id	Name	Sample Type	EA Keyword
6	5	2102	161004_sulf01	(none)	sulfanilamide
7	6	2103	161004_sulf02	(none)	sulfanilamide
8	7	2104	161004_sulf03	(none)	sulfanilamide
9	8	2105	161004_sulf04	(none)	sulfanilamide
10	9	2106	161004_USGS40_01	(none)	
11	10	2107	161004_USGS40_01	(none)	
12	11	2108	161004_USGS41a_01	(none)	

Fig. 22.1. An Elementar IonOS file to which a column with the heading of "Line" has been added. Increasing integers are entered in rows two and greater.

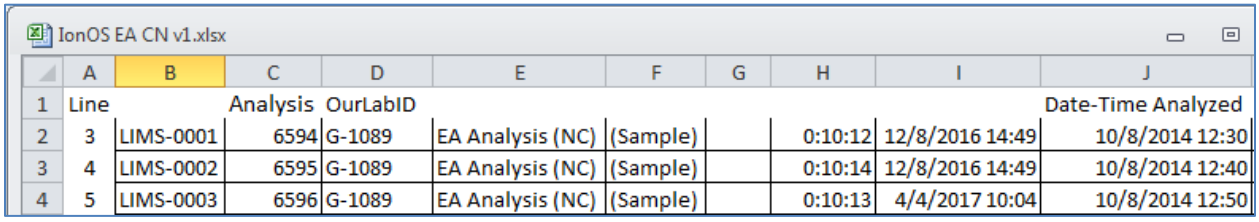
22.2 Importing IonOS Data Files from an Elementar Mass Spectrometer

This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had an Elementar mass spectrometer named "Vulcan" with an IonOS data system added to it in Section 17.2. In the event the "Lakes_Backend_DB.accdb" backend database with "Vulcan" is not available, a backend database for use in this section can be extracted from a file named "IonOS_Vulcan_Backend_DB.zip" that is provided in a folder named "Section 22.2" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this section, an Elementar IonOS data file having $\delta^{13}C$ and $\delta^{15}N$ results generated by Vulcan will be imported into LIMS. Before proceeding, the reader should be fully familiar with the information in Section 17.1. The original file "IonOS EA CN v0.xlsx" is located in the folder named "22.2 IonOS" that accompanies this manual. The reader will create a file named "IonOS EA CN v1.xlsx" and this file is provided in folder "22.2 IonOS" for reference. To create a file that LIMS can import:

1. Save the file with a new name. The name "IonOS EA CN v1.xlsx" is used in this example.
2. Insert a row at the top of the worksheet so that LIMS column heading can be added.
3. Insert a column that will become column A.
4. Enter "Line" in cell A1.
5. Enter 1 through 48 in the Excel range A2:A49.

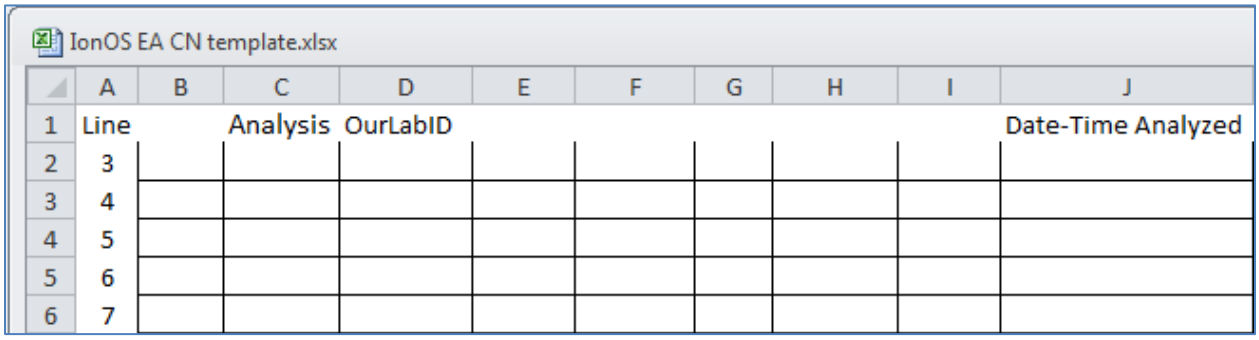
6. Enter “Analysis” in cell C1.
7. Enter “OurLabID” (with no spaces) in cell D1.
8. Enter “Date-Time Analyzed” in cell J1.
9. Enter “Amount” in cell P1.
10. Enter “Area All N” in cell X1.
11. Enter “Delta N-15” in cell AE1.
12. Enter “Area All C” in cell AI1.
13. Enter “Delta C-13” in cell AS1.
14. Delete rows 2 and 3.
15. Save and close the worksheet, a portion of which should appear as shown in Figure 22.2.
16. To save time on future imports, make an Excel template of the column headings and the first column. To create this Excel template, one can delete all the information in the Excel range B2:AW47 in the file just created. This template is named “IonOS EA CN template.xlsx” and is found in the folder named “22.2 IonOS.” A portion of it appears in Figure 22.3.



IonOS EA CN v1.xlsx

	A	B	C	D	E	F	G	H	I	J
1	Line		Analysis	OurLabID						Date-Time Analyzed
2	3	LIMS-0001	6594	G-1089	EA Analysis (NC)	(Sample)		0:10:12	12/8/2016 14:49	10/8/2014 12:30
3	4	LIMS-0002	6595	G-1089	EA Analysis (NC)	(Sample)		0:10:14	12/8/2016 14:49	10/8/2014 12:40
4	5	LIMS-0003	6596	G-1089	EA Analysis (NC)	(Sample)		0:10:13	4/4/2017 10:04	10/8/2014 12:50

Fig. 22.2. A portion of an Elementar IonOS file, which has been modified for importing using the LIMS Abbreviated import format.



IonOS EA CN template.xlsx

	A	B	C	D	E	F	G	H	I	J
1	Line		Analysis	OurLabID						Date-Time Analyzed
2	3									
3	4									
4	5									
5	6									
6	7									

Fig. 22.3. A portion of an Elementar IonOS Excel template file.

To import the file:

1. On the LIMS main page click “Import Data from Mass Specs” and the Analysis Import Format form (Fig. 19.12 or similar) will open.
2. Select “V --> Vulcan” the Elementar IonOS IRMS and click “Import.”
3. Navigate to the file created, “IonOS EA CN V1.xlsx” in this example, click “Select,” and LIMS will display the message in Figure 22.4.
4. Click “OK” and the Import Criteria for Mass Spectrometer form will open (Fig. 22.5).
5. The upper left pane of this form contains the “Isotope” and rows for check boxes for importing, area adjust, and linearity adjust. The upper right panel has a check box to enable importing of continuous-flow areas. The lower panel displays the Excel form being imported.
6. There can be an increase (or decrease) in peak area over time for the same mass of the same reference with an EA or TC/EA. LIMS can adjust for an increase (or decrease) in peak area of all peak of the same gas type based on values of the ratios of the peak areas and masses of a selected reference over time. This normalization should improve elemental mass fraction (element concentration) determinations. To perform this evaluation for CO_2 areas, click the “Area Adjust” checkbox in the row having “13C” in the “Isotope” column and LIMS will display the Area Adjust form (Fig. 22.6). The Area Adjust form (Fig. 22.6) shows a plot of analysis number versus CO_2 area of the reference G-30 divided by the mass of G-30. The user can select a choice of regressions (linear, quadratic, logarithmic, or power) to fit their data. The *R* squared value of the fit is shown. Analyses can be ignored by clicking the check boxes in the “IG” column in the panel in the lower section of the form. One can select another standard for the “Our Lab ID” control. For example, selecting G-41, the *R* squared value increases to 0.72 (Fig. 22.7). By clicking “Import Adjusted Areas” all of the CO_2 areas in the imported file will be adjusted (normalized) using the algorithm in the “Trend line.”

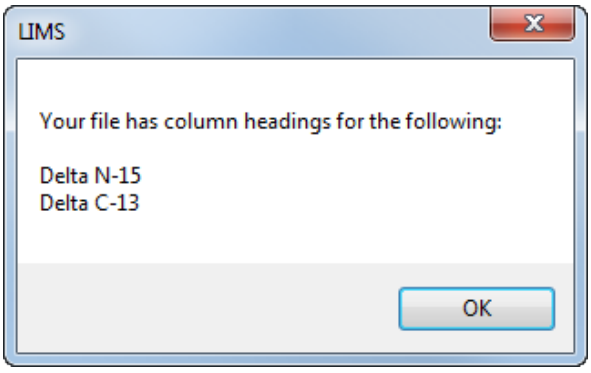


Fig. 22.4. Isotope-import message.

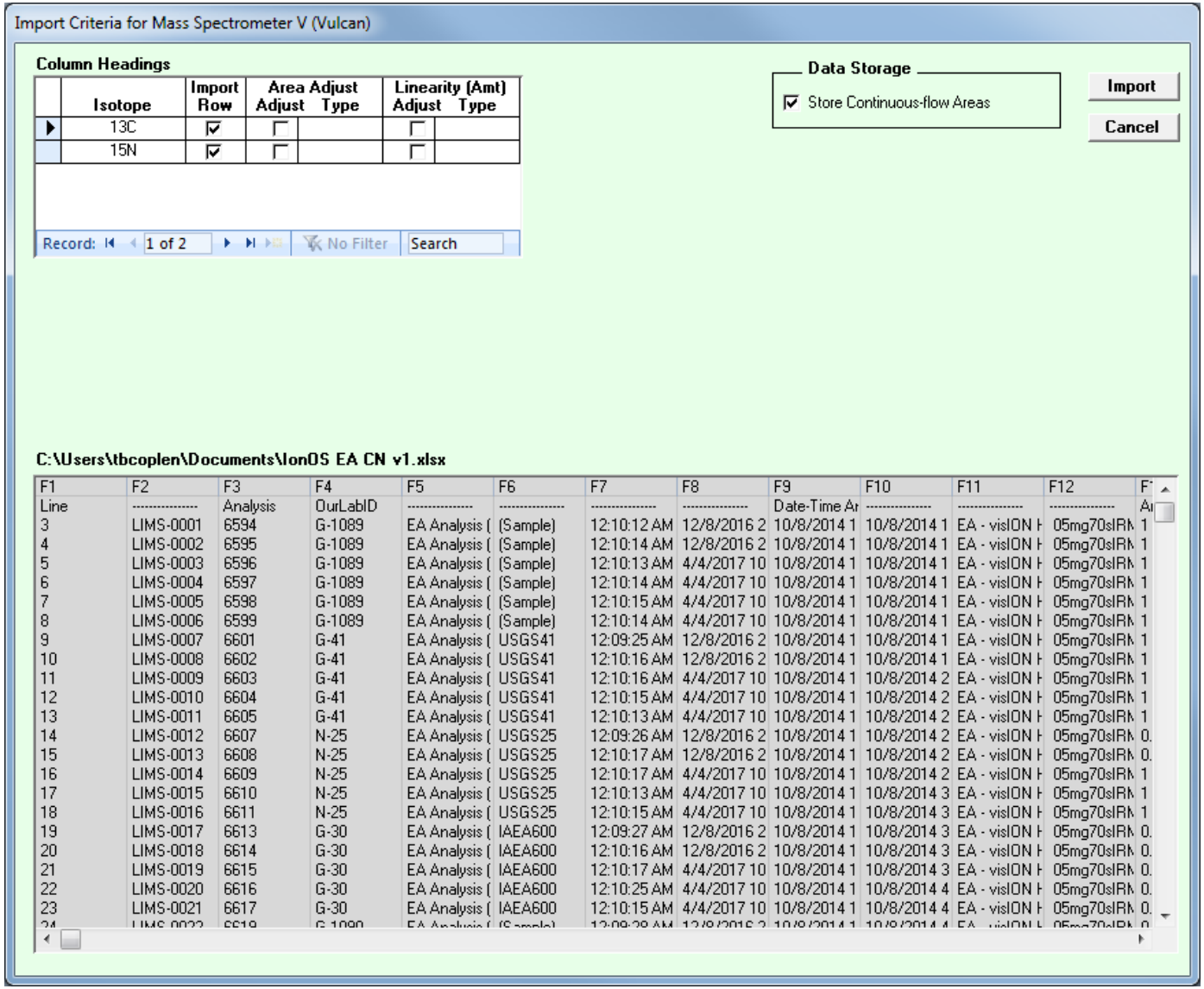


Fig. 22.5. Import Criteria for Mass Spectrometer form for Elemental IRMS with IonOS data system.

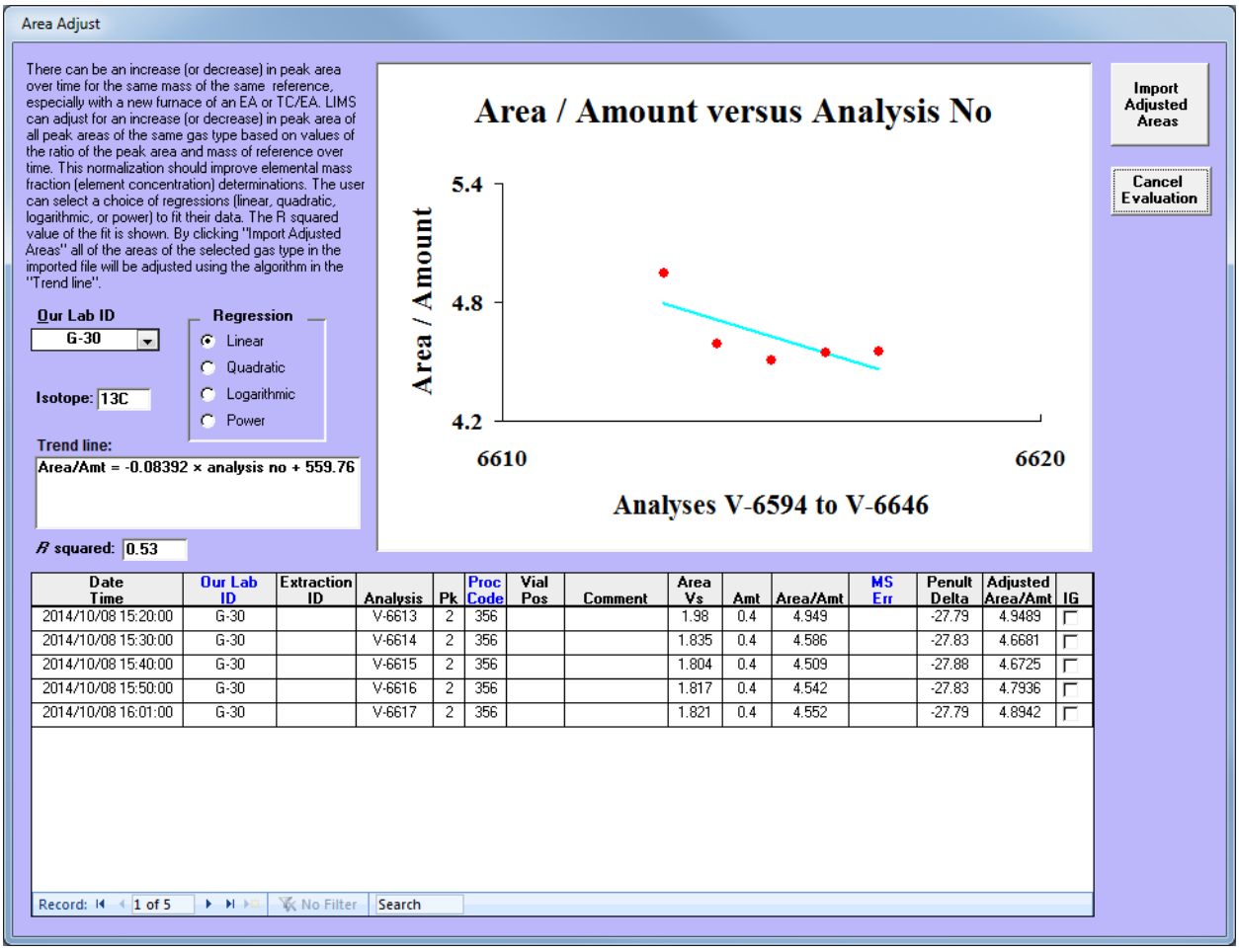


Fig. 22.6. The Area Adjust form showing analysis number versus CO_2 area / amount of standard.

7. Because the *R* squared value with G-41 is 0.72, click "Import Adjusted Areas" and LIMS will notify user that all peak areas of specified gas type will be updated using the selected regression (Fig. 22.8). If the user changes their mind at a later date, the Excel file can be re-imported.
8. Click "OK."
9. Click the "Linearity (Amt)" check box and the Adjustment for Variation in Delta Value with Variation in Amount of Sample form opens (similar to Fig. 19.18). The variation in peak area is very small; therefore, performing a linearity adjust is not merited.
10. Click "Cancel Evaluation."
11. Click the "Area Adjust" check box for "15N," select G-41, click "Import Adjusted Areas," and click "OK" to the LIMS prompt (Fig. 22.8).
12. Click the "Linearity (Amt)" check box for "15N" and confirm that a linearity adjustment is not merited; "Cancel Evaluation."

13. Click “Import” and LIMS displays an isotope-import message (Fig. 22.9).
14. Click “OK” and LIMS displays the summary message (Fig. 22.10). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking “Special Features” then “ImportLog.”
15. Click “OK” to complete the import of IonOS data from “Vulcan.”

Normalization of these $\delta^{13}C$ and $\delta^{15}N$ results with determination of element mass fractions (element concentrations) is the next step and is discussed in Section 24.

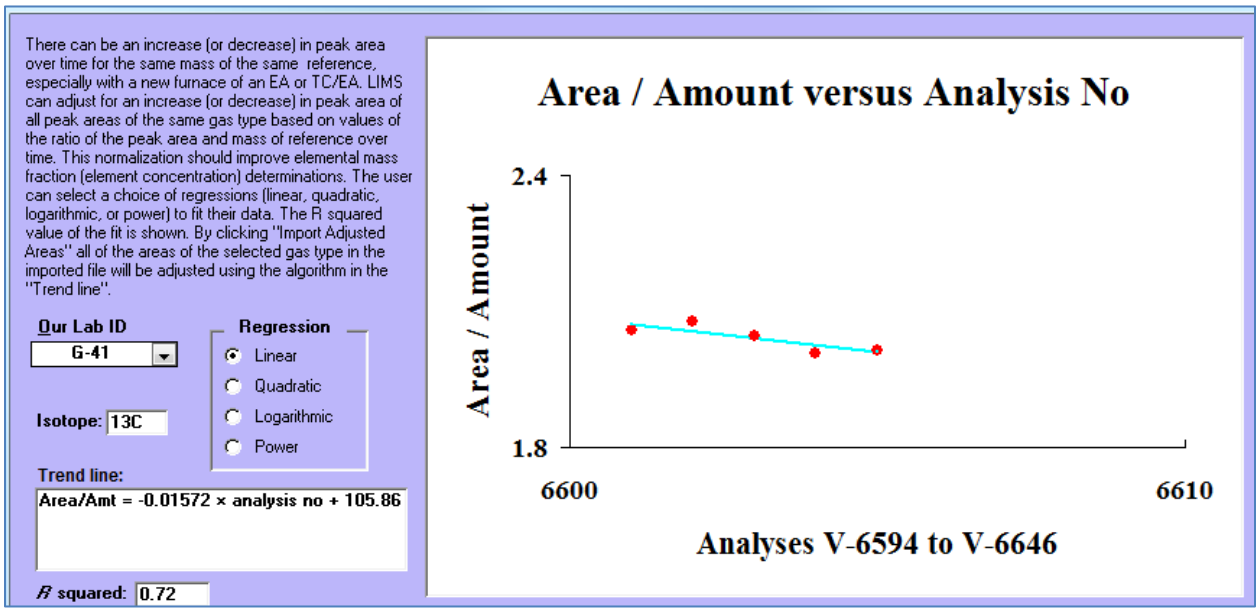


Fig. 22.7. The Area Adjust form for G-41.

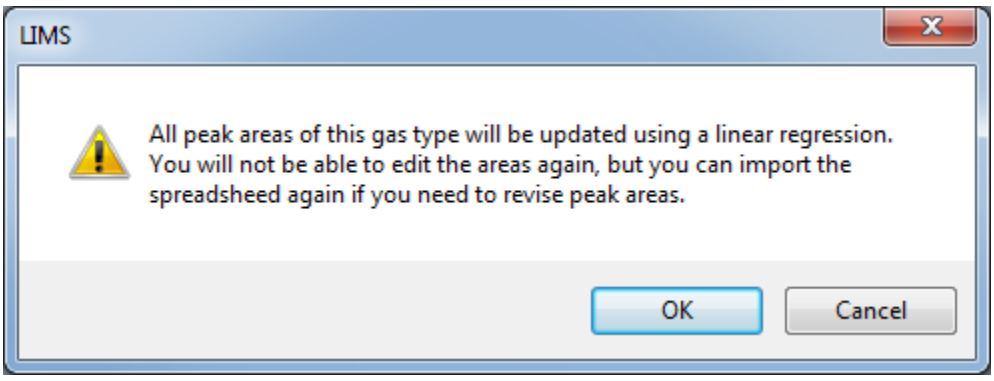


Fig. 22.8. Message that that all peak areas will be updated.

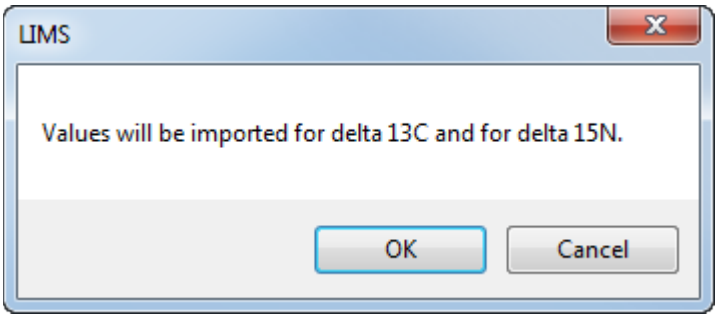


Fig. 22.9. Isotope-import message.

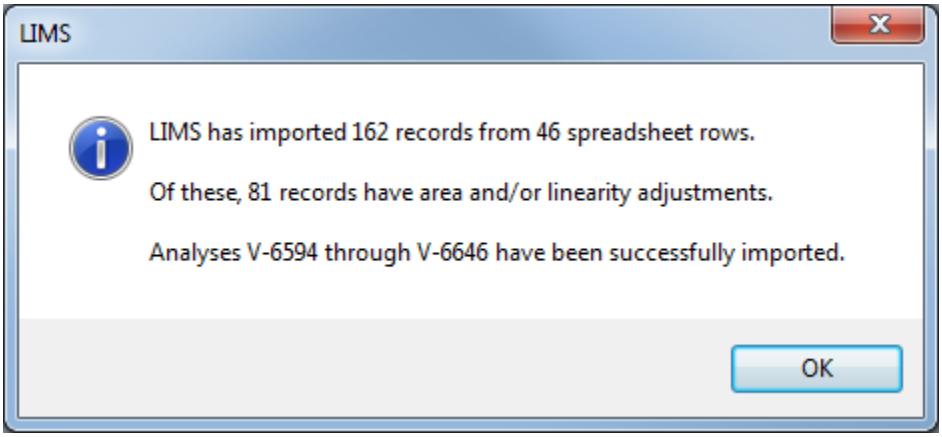


Fig. 22.10. LIMS IonOS Abbreviated Import summary.

22.3 Importing Data Files from Europa and Europa 20 20 Mass Spectrometers

This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had a Europa mass spectrometer named "Ulysses" added to it in Section 17.3. In the event the "Lakes_Backend_DB.accdb" backend database with "Ulysses" is not available, a backend database for use in this section can be extracted from a file named "Europa_Ulysses_Backend_DB.zip" that is provided in a folder named "Section 22.3" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this section a Europa 20 20 data file having will be imported into LIMS. Before proceeding, the reader should be fully familiar with the information in Section 17.1. Europa and Europa 20 20 data files are tab separated text files, typically with the suffix txt or prn. If the suffix of a file is "prn", "prn" can be replaced by "txt" so that the file can be opened with recent versions of Excel, modified as needed, and saved as either an Excel xls or xlsx file. The example file "Europa 20 20 C&N v0.TXT" is located in the folder named "22.3 Europa & Europa 20 20"

that accompanies this manual. The reader will create a file named “Europa 20 20 C&N v1.xlsx” and this file is provided in folder “22.3 Europa & Europa 20 20” for reference. In case Excel is not set up as a default program to open txt files automatically, to create a file that LIMS can import:

1. Open Excel.
2. From the “File” tab select “Open.”
3. For the filter in the lower right of the Windows Open dialog box, select text files.
4. Navigate to the file “Europa 20 20 C&N v0.TXT.”
5. Click “Open” and the Excel text Import Wizard should open (Fig. 22.11).
6. Ensure that the “Delimited” option is selected, click “Next >,” and Excel should show step 2 of the wizard.
7. Ensure that “Tab” is selected as the delimiter and that “{none}” is selected as the “Text qualifier” (Fig. 22.12).
8. Click “Next >” and step 3 of the Excel import wizard will enable one to set the date format. Because there are no dates, click “Finish,” and Excel will display the text file (Fig. 22.13). To avoid having to use the Text Import Wizard, assign Excel as one of the programs that can open txt files. Right click on a txt file, select “Open With,” select “Choose default program,” and browse for and select Excel.
9. Save the file with a new name. The name “Europa 20 20 C&N v1.xlsx” is used in this example and this file is provided in the folder named “22.3 Europa & Europa 20 20.”
10. Enter “Line” in cell B1 and delete “Reprocessed” in cell A1.
11. Enter “OurLabID” (with no spaces) in cell C1 and enter “Amount” in cell D1.
12. Enter “Area All N” in cell E1 and enter “Delta N-15” in cell G1.
13. Enter “Area All C” in cell J1 and enter “Delta C-13” in cell L1.
14. Delete Excel rows 25 to 44 to eliminate duplicate analyses data.
15. Delete Excel row 2 to 4 and save the file, which is now ready to import (Fig. 22.14).
16. To save time on future imports, make an Excel template of the column headings and the first and second columns. To create this Excel template, one can delete all the information in the Excel range C2:N21 in the file just created. This template is named “Europa 20 20 C&N Template.xlsx” and is found in the folder named “22.3 Europa & Europa 20 20.” It appears in Figure 22.15. If more than 20 lines are needed, extend the line numbers as needed.

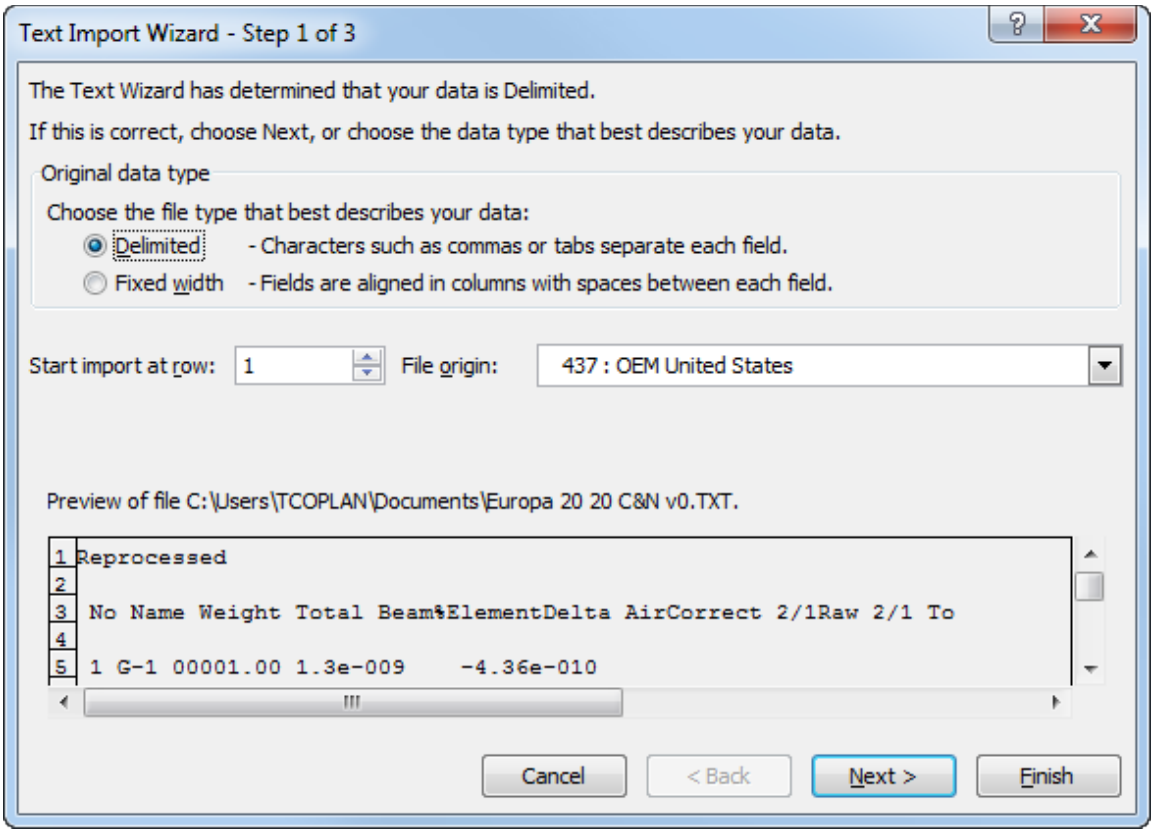


Fig. 22.11. Step 1 of the Excel Text Import Wizard.

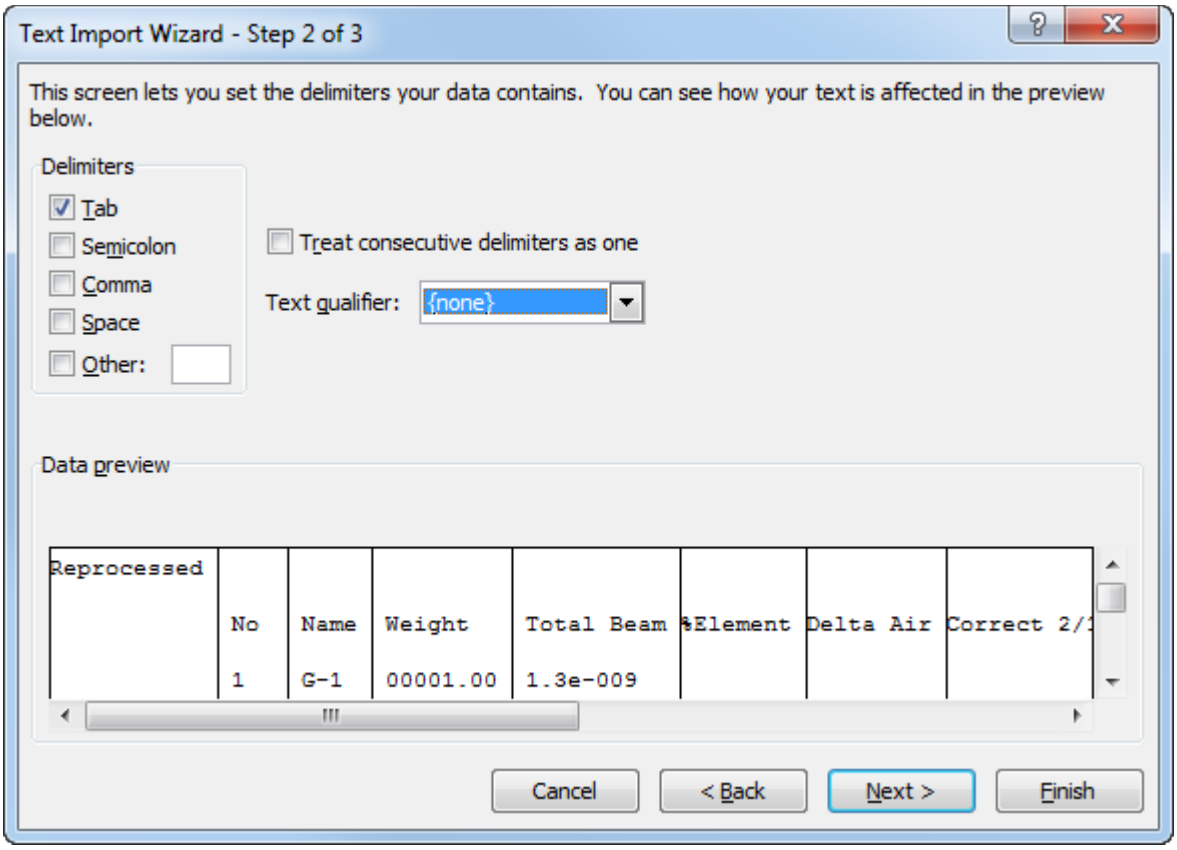
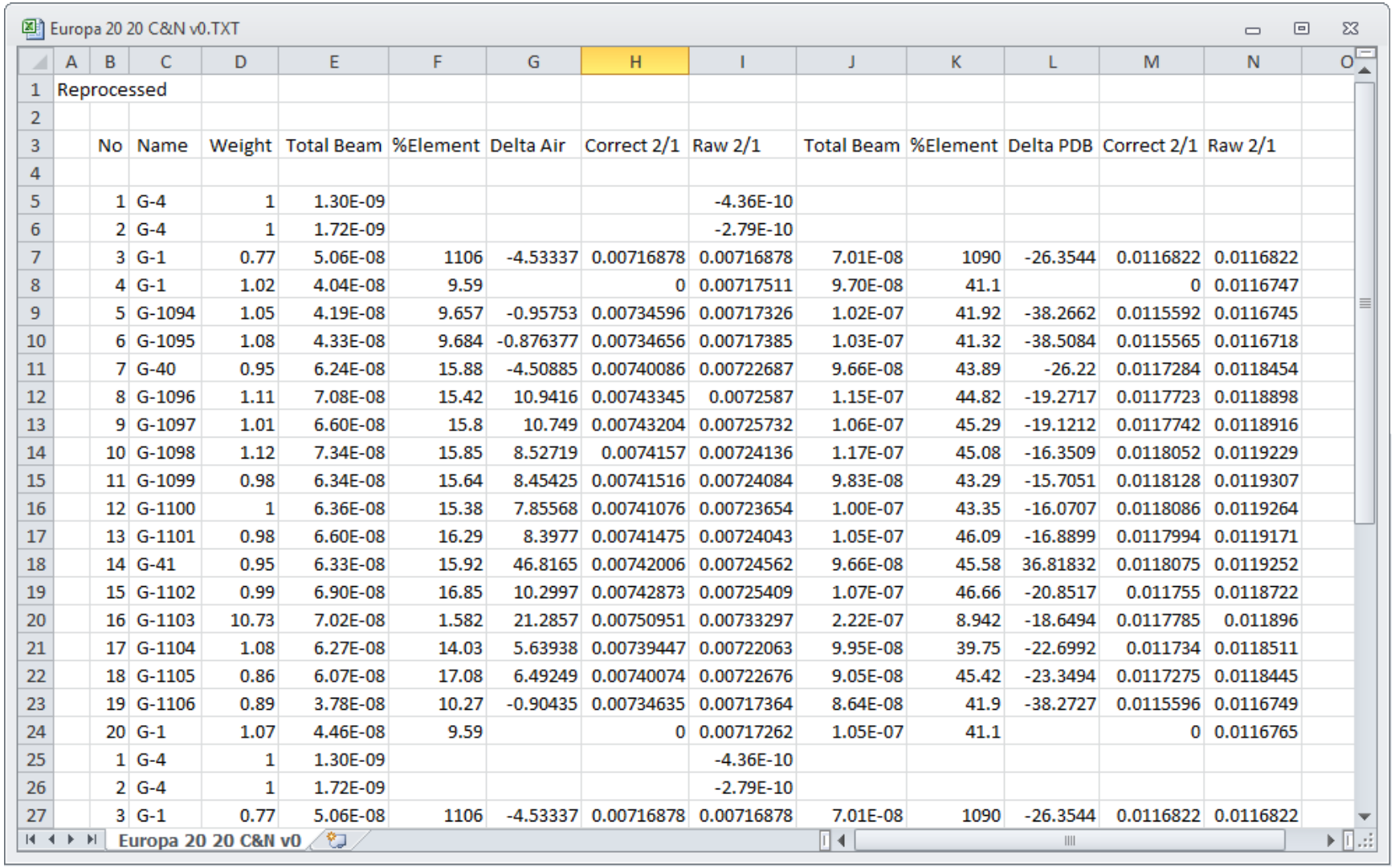


Fig. 22.12. Step 2 of the Excel Text Import Wizard. The "Text qualifier" needs to be set to "{none}."

If desired, additional columns can be added to the Excel file to be imported (Figs. 22.14 and 22.15), which might include "Mass Spec", "Analysis", "Date-Time Analyzed", "Port", "Extraction ID", "Comment", or (and) "Ignore".



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	Reprocessed														
2															
3		No	Name	Weight	Total Beam	%Element	Delta Air	Correct 2/1	Raw 2/1	Total Beam	%Element	Delta PDB	Correct 2/1	Raw 2/1	
4															
5		1	G-4	1	1.30E-09				-4.36E-10						
6		2	G-4	1	1.72E-09				-2.79E-10						
7		3	G-1	0.77	5.06E-08	1106	-4.53337	0.00716878	0.00716878	7.01E-08	1090	-26.3544	0.0116822	0.0116822	
8		4	G-1	1.02	4.04E-08	9.59		0	0.00717511	9.70E-08	41.1		0	0.0116747	
9		5	G-1094	1.05	4.19E-08	9.657	-0.95753	0.00734596	0.00717326	1.02E-07	41.92	-38.2662	0.0115592	0.0116745	
10		6	G-1095	1.08	4.33E-08	9.684	-0.876377	0.00734656	0.00717385	1.03E-07	41.32	-38.5084	0.0115565	0.0116718	
11		7	G-40	0.95	6.24E-08	15.88	-4.50885	0.00740086	0.00722687	9.66E-08	43.89	-26.22	0.0117284	0.0118454	
12		8	G-1096	1.11	7.08E-08	15.42	10.9416	0.00743345	0.0072587	1.15E-07	44.82	-19.2717	0.0117723	0.0118898	
13		9	G-1097	1.01	6.60E-08	15.8	10.749	0.00743204	0.00725732	1.06E-07	45.29	-19.1212	0.0117742	0.0118916	
14		10	G-1098	1.12	7.34E-08	15.85	8.52719	0.0074157	0.00724136	1.17E-07	45.08	-16.3509	0.0118052	0.0119229	
15		11	G-1099	0.98	6.34E-08	15.64	8.45425	0.00741516	0.00724084	9.83E-08	43.29	-15.7051	0.0118128	0.0119307	
16		12	G-1100	1	6.36E-08	15.38	7.85568	0.00741076	0.00723654	1.00E-07	43.35	-16.0707	0.0118086	0.0119264	
17		13	G-1101	0.98	6.60E-08	16.29	8.3977	0.00741475	0.00724043	1.05E-07	46.09	-16.8899	0.0117994	0.0119171	
18		14	G-41	0.95	6.33E-08	15.92	46.8165	0.00742006	0.00724562	9.66E-08	45.58	36.81832	0.0118075	0.0119252	
19		15	G-1102	0.99	6.90E-08	16.85	10.2997	0.00742873	0.00725409	1.07E-07	46.66	-20.8517	0.011755	0.0118722	
20		16	G-1103	10.73	7.02E-08	1.582	21.2857	0.00750951	0.00733297	2.22E-07	8.942	-18.6494	0.0117785	0.011896	
21		17	G-1104	1.08	6.27E-08	14.03	5.63938	0.00739447	0.00722063	9.95E-08	39.75	-22.6992	0.011734	0.0118511	
22		18	G-1105	0.86	6.07E-08	17.08	6.49249	0.00740074	0.00722676	9.05E-08	45.42	-23.3494	0.0117275	0.0118445	
23		19	G-1106	0.89	3.78E-08	10.27	-0.90435	0.00734635	0.00717364	8.64E-08	41.9	-38.2727	0.0115596	0.0116749	
24		20	G-1	1.07	4.46E-08	9.59		0	0.00717262	1.05E-07	41.1		0	0.0116765	
25		1	G-4	1	1.30E-09				-4.36E-10						
26		2	G-4	1	1.72E-09				-2.79E-10						
27		3	G-1	0.77	5.06E-08	1106	-4.53337	0.00716878	0.00716878	7.01E-08	1090	-26.3544	0.0116822	0.0116822	

Fig. 22.13. Europa 20 20 text file opened with Excel.

Europa 20 20 C&N v1.xlsx

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1		Line	OurLabID	Amount	Area All N		Delta N-15			Area All C		Delta C-13		
2		1	G-4	1	1.30E-09				-4.36E-10					
3		2	G-4	1	1.72E-09				-2.79E-10					
4		3	G-1	0.77	5.06E-08	1106	-4.53337	0.007169	0.00716878	7.01E-08	1090	-26.3544	0.0116822	0.0116822
5		4	G-1	1.02	4.04E-08	9.59		0	0.00717511	9.70E-08	41.1		0	0.0116747
6		5	G-1094	1.05	4.19E-08	9.657	-0.95753	0.007346	0.00717326	1.02E-07	41.92	-38.2662	0.0115592	0.0116745
7		6	G-1095	1.08	4.33E-08	9.684	-0.876377	0.007347	0.00717385	1.03E-07	41.32	-38.5084	0.0115565	0.0116718
8		7	G-40	0.95	6.24E-08	15.88	-4.50885	0.007401	0.00722687	9.66E-08	43.89	-26.22	0.0117284	0.0118454
9		8	G-1096	1.11	7.08E-08	15.42	10.9416	0.007433	0.0072587	1.15E-07	44.82	-19.2717	0.0117723	0.0118898
10		9	G-1097	1.01	6.60E-08	15.8	10.749	0.007432	0.00725732	1.06E-07	45.29	-19.1212	0.0117742	0.0118916
11		10	G-1098	1.12	7.34E-08	15.85	8.52719	0.007416	0.00724136	1.17E-07	45.08	-16.3509	0.0118052	0.0119229
12		11	G-1099	0.98	6.34E-08	15.64	8.45425	0.007415	0.00724084	9.83E-08	43.29	-15.7051	0.0118128	0.0119307
13		12	G-1100	1	6.36E-08	15.38	7.85568	0.007411	0.00723654	1.00E-07	43.35	-16.0707	0.0118086	0.0119264
14		13	G-1101	0.98	6.60E-08	16.29	8.3977	0.007415	0.00724043	1.05E-07	46.09	-16.8899	0.0117994	0.0119171
15		14	G-41	0.95	6.33E-08	15.92	46.8165	0.00742	0.00724562	9.66E-08	45.58	36.81832	0.0118075	0.0119252
16		15	G-1102	0.99	6.90E-08	16.85	10.2997	0.007429	0.00725409	1.07E-07	46.66	-20.8517	0.011755	0.0118722
17		16	G-1103	10.73	7.02E-08	1.582	21.2857	0.00751	0.00733297	2.22E-07	8.942	-18.6494	0.0117785	0.011896
18		17	G-1104	1.08	6.27E-08	14.03	5.63938	0.007394	0.00722063	9.95E-08	39.75	-22.6992	0.011734	0.0118511
19		18	G-1105	0.86	6.07E-08	17.08	6.49249	0.007401	0.00722676	9.05E-08	45.42	-23.3494	0.0117275	0.0118445
20		19	G-1106	0.89	3.78E-08	10.27	-0.90435	0.007346	0.00717364	8.64E-08	41.9	-38.2727	0.0115596	0.0116749
21		20	G-1	1.07	4.46E-08	9.59		0	0.00717262	1.05E-07	41.1		0	0.0116765

Europa 20 20 C&N v2

Fig. 22.14. Europa 20 20 Excel file after modification for importing using the LIMS Abbreviated import format.

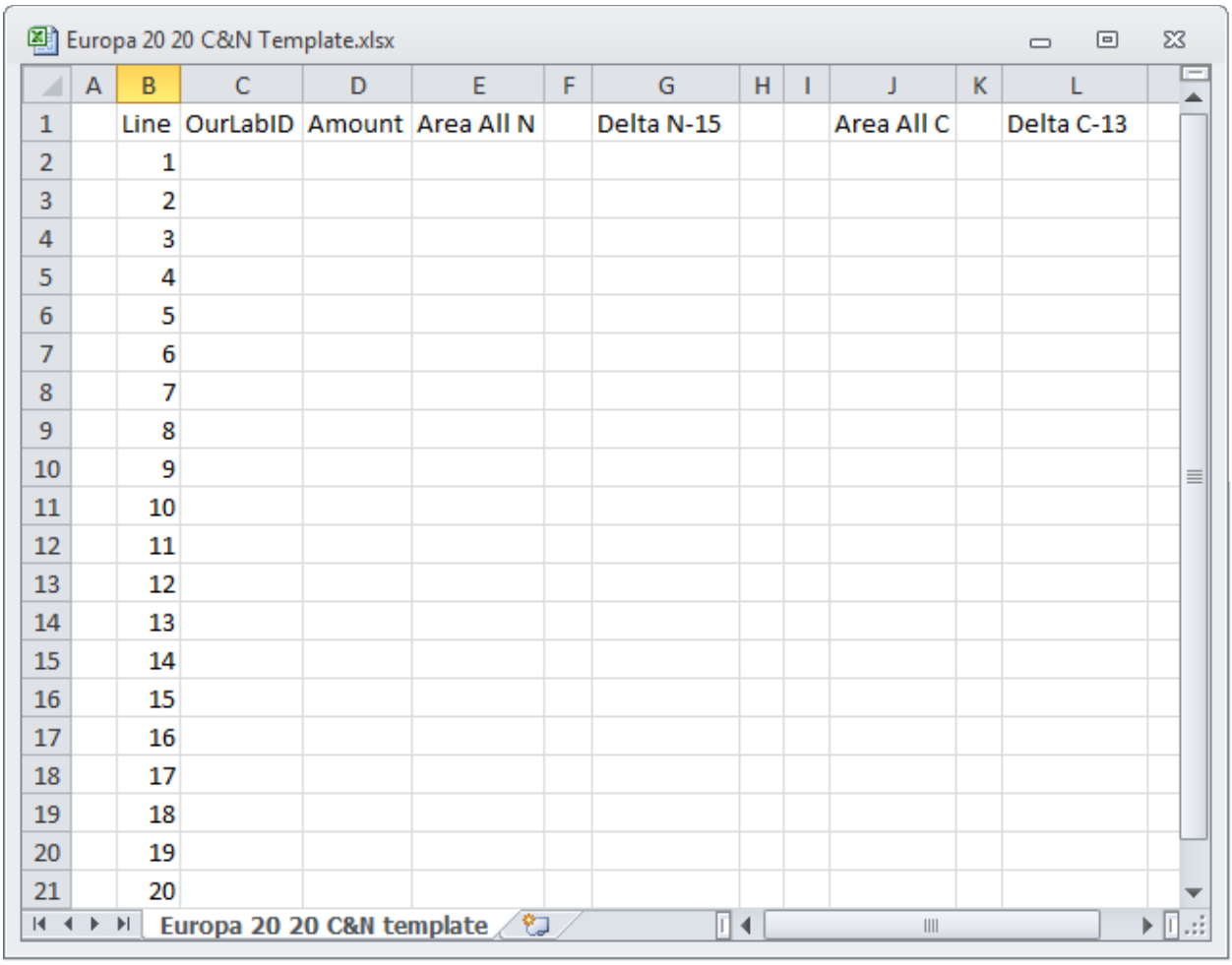


Fig. 22.15. Europa 20 20 template for C&N data importing using the LIMS Abbreviated import format. Extend line numbers as needed for all rows to be imported.

To import the Europa 20 20 file:

1. On the LIMS main page click “Import Data from Mass Specs” and the Analysis Import Format form (Fig. 19.12 or similar) will open.
2. Select “U --> Ulysses” the IRMS with a Europa 20 20 data system.
3. Click “Import.”
4. Navigate to the file created, “Europa 20 20 C&N v1.xlsx,” click “Select,” and LIMS will prompt for a date (Fig. 22.16).
5. Click “OK” and LIMS will identify the delta values to be imported (Fig. 22.17).
6. Click “OK” and LIMS will open the Import Criteria for Mass Spectrometer form (Fig. 22.18).

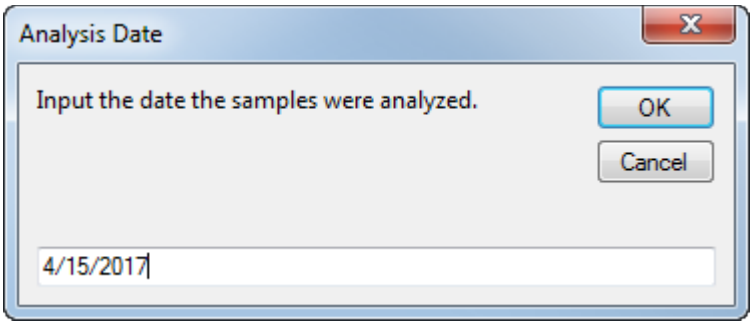


Fig. 22.16. LIMS date prompt.

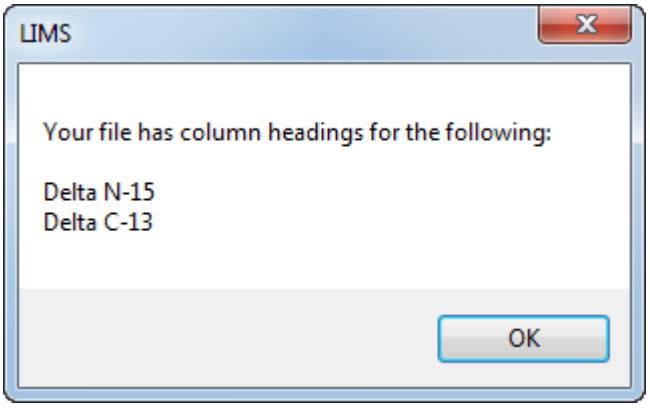
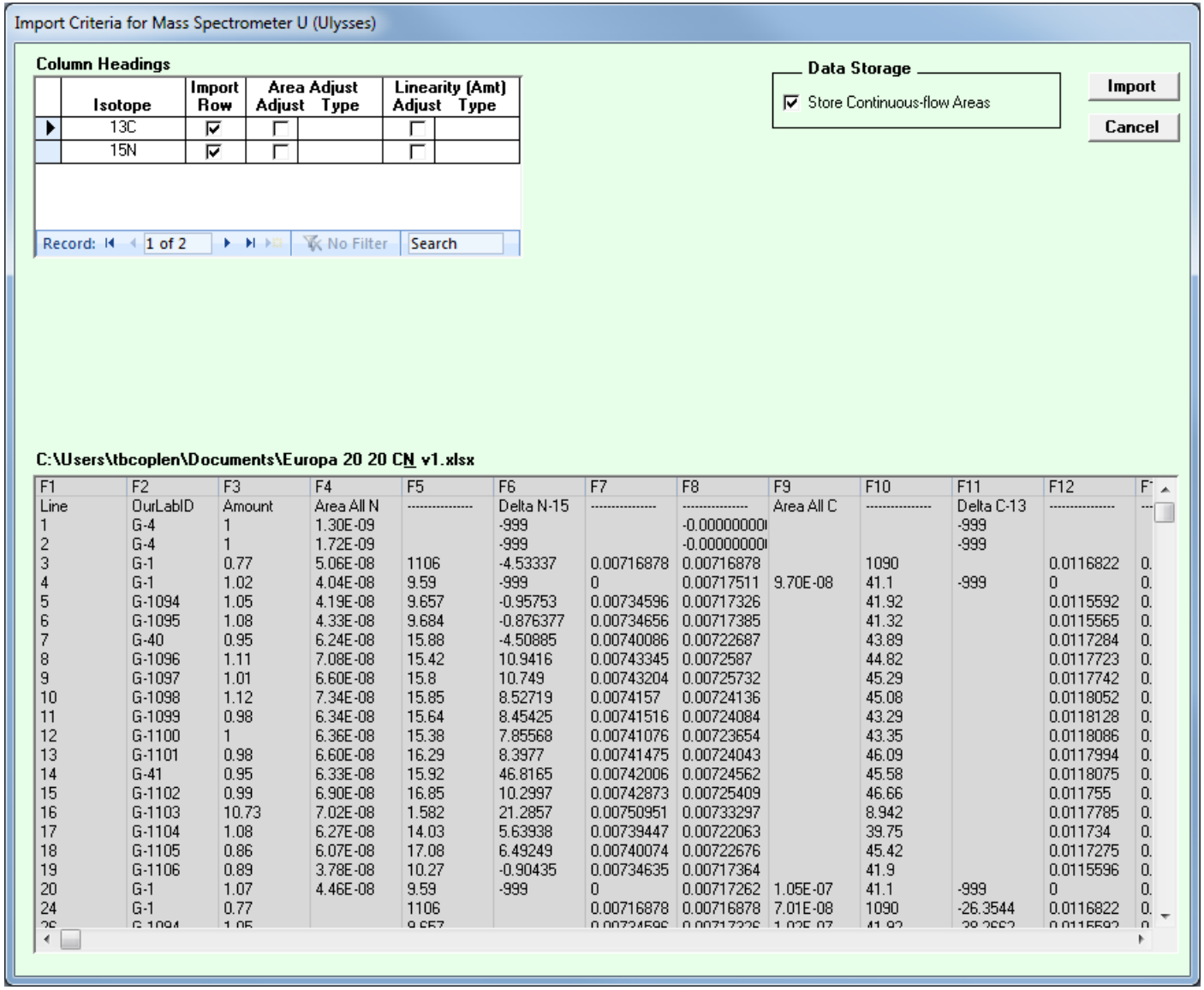


Fig. 22.17. Delta values to be imported.

⚠ Users need to remember that Europa and Europa 20 20 files do not have an analysis number. Therefore, if they are imported more than once, analyses will be replicated in LIMS. One way to avoid this conundrum is to add an "Analysis" column to each Excel file and populate with regularly increasing integers.



F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F
Line	OurLablD	Amount	Area All N	----------	Delta N-15	----------	----------	Area All C	----------	Delta C-13	----------	---
1	G-4	1	1.30E-09		-999		-0.000000001			-999		
2	G-4	1	1.72E-09		-999		-0.000000001			-999		
3	G-1	0.77	5.06E-08	1106	-4.53337	0.00716878	0.00716878		1090		0.0116822	0.
4	G-1	1.02	4.04E-08	9.59	-999	0	0.00717511	9.70E-08	41.1	-999	0	0.
5	G-1094	1.05	4.19E-08	9.657	-0.95753	0.00734596	0.00717326		41.92		0.0115592	0.
6	G-1095	1.08	4.33E-08	9.684	-0.876377	0.00734656	0.00717385		41.32		0.0115565	0.
7	G-40	0.95	6.24E-08	15.88	-4.50885	0.00740086	0.00722687		43.89		0.0117284	0.
8	G-1096	1.11	7.08E-08	15.42	10.9416	0.00743345	0.0072587		44.82		0.0117723	0.
9	G-1097	1.01	6.60E-08	15.8	10.749	0.00743204	0.00725732		45.29		0.0117742	0.
10	G-1098	1.12	7.34E-08	15.85	8.52719	0.0074157	0.00724136		45.08		0.0118052	0.
11	G-1099	0.98	6.34E-08	15.64	8.45425	0.00741516	0.00724084		43.29		0.0118128	0.
12	G-1100	1	6.36E-08	15.38	7.85568	0.00741076	0.00723654		43.35		0.0118086	0.
13	G-1101	0.98	6.60E-08	16.29	8.3977	0.00741475	0.00724043		46.09		0.0117994	0.
14	G-41	0.95	6.33E-08	15.92	46.8165	0.00742006	0.00724562		45.58		0.0118075	0.
15	G-1102	0.99	6.90E-08	16.85	10.2997	0.00742873	0.00725409		46.66		0.011755	0.
16	G-1103	10.73	7.02E-08	1.582	21.2857	0.00750951	0.00733297		8.942		0.0117785	0.
17	G-1104	1.08	6.27E-08	14.03	5.63938	0.00739447	0.00722063		39.75		0.011734	0.
18	G-1105	0.86	6.07E-08	17.08	6.49249	0.00740074	0.00722676		45.42		0.0117275	0.
19	G-1106	0.89	3.78E-08	10.27	-0.90435	0.00734635	0.00717364		41.9		0.0115596	0.
20	G-1	1.07	4.46E-08	9.59	-999	0	0.00717262	1.05E-07	41.1	-999	0	0.
24	G-1	0.77		1106		0.00716878	0.00716878	7.01E-08	1090	-26.3544	0.0116822	0.
26	G-1094	1.05		9.657		0.00734596	0.00717326	1.03E-07	41.92	-38.2662	0.0115592	0.

Fig. 22.18. The Import Criteria for Mass Spectrometer form for Europa 20 20 samples.

7. Clicking the “Area Adjust” or “Linearity (Amt)” check boxes indicates that there are not sufficient references to perform these regressions.
8. Click “OK” and the Area Adjust form opens.
9. Click “Cancel Evaluation” and the Area Adjust form closes.
10. Click “Import” and LIMS displays the dialog box shown in Figure 22.19. Had there been sufficient references in the run, then the user could have performed regressions as discussed in Section 22.2 (see also Figs. 21.4 and 21.5).
11. Click “OK” and LIMS displays the summary message shown in Figure 22.20. If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking “Special Features” then “ImportLog.”
12. This completes importing of Europa 20 20 δ^{13}C and δ^{15}N results from an EA.

Normalization of these δ^{13}C and δ^{15}N results with determination of element mass fractions (element concentrations) is the next step and is discussed in Section 24.

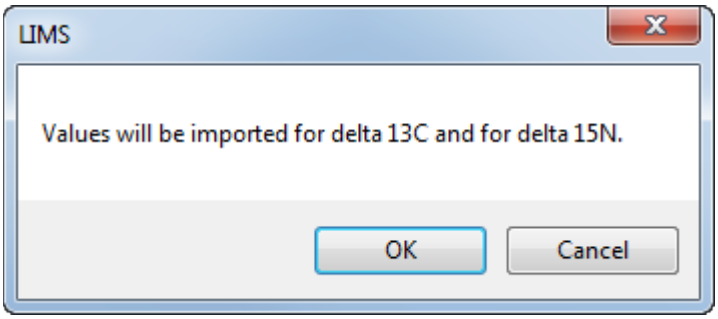


Fig. 22.19. Delta values to be imported.

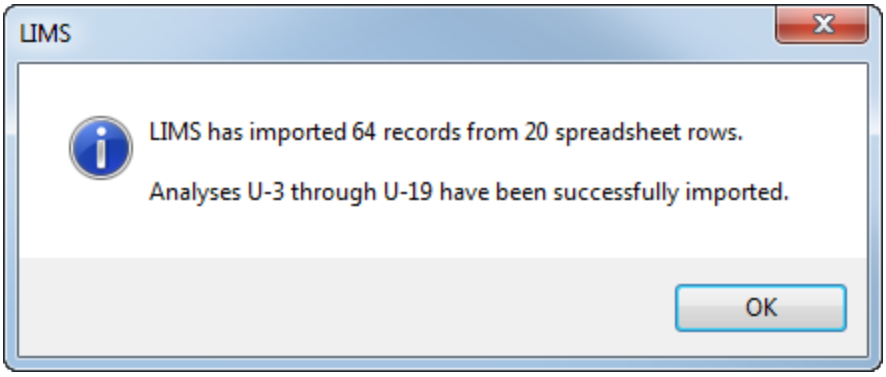


Fig. 22.20. LIMS summary message for importing samples having the Europa 20 20 format.

22.4 Importing Data Files from a Micromass Optima Mass Spectrometer

This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had a Micromass Optima mass spectrometer named "Kali" added to it in Section 17.4. In the event the "Lakes_Backend_DB.accdb" backend database with "Kali" is not available, a backend database for use in this section can be extracted from a file named "Micromass_Optima_Kali_Backend_DB.zip" that is provided in a folder named "Section 22.4" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this section a Micromass Optima data file having $\delta^{13}C$ and $\delta^{15}N$ results will be imported into LIMS. Before proceeding, the reader should be fully familiar with the information in Section 17.1. These files typically are csv files with commas as text qualifiers. Excel should open them automatically, but if not, one can assign Excel as one of the programs that can open csv files. Right click on a csv file, select "Open With," select "Choose default program," and browse for and select Excel.

The example Micromass Optima file "C&N Optima CF v0.csv" is located in the folder named "22.4 Micromass Optima" that accompanies this manual. The reader will create a file named "C&N Optima CF v1.xlsx" and this file is provided in folder "22.4 Micromass Optima" for reference. To create an Excel file that LIMS can import:

1. Open the example Microsoft Optima csv file "C&N Optima CF v0.csv" with Excel (Fig. 22.21).
2. Save the file with a new name and file type. The name "C&N Optima CF v1.xlsx" is used in this example and this file is provided in the folder named "22.4 Micromass Optima."
3. Enter "Line" in cell A1.
4. Enter "OurLabID" in cell B1.
5. Enter "Amount" in cell C1.
6. Enter "Delta C-13" in cell G1.
7. Enter "Delta N-15" in cell H1.
8. Delete rows 2 through 21, save the file, and close the file, which is now ready to import (Fig. 22.22).

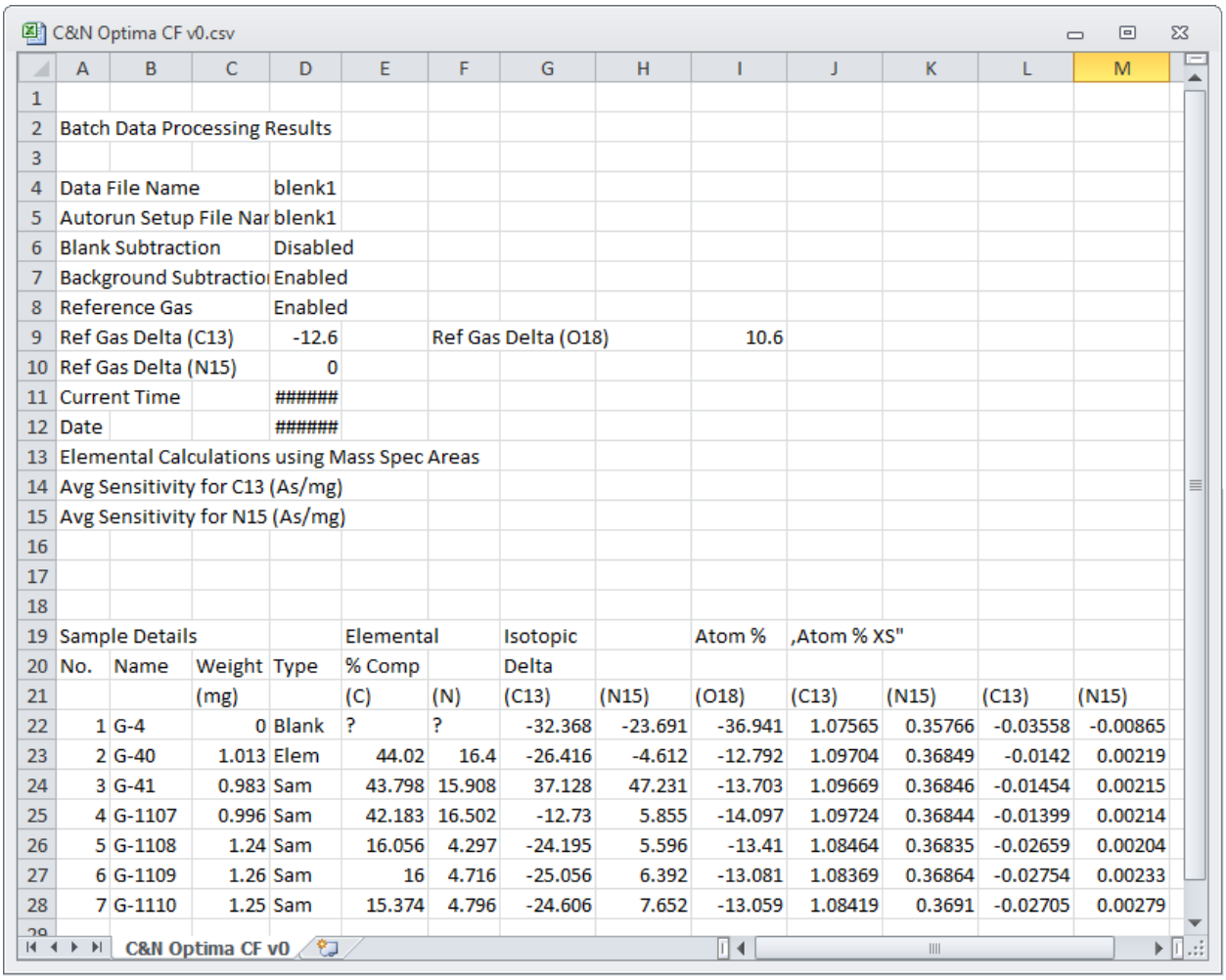
If desired, additional columns can be added to the Excel file to be imported (Figs. 22.22), which might include "Mass Spec", "Analysis", "Date-Time Analyzed", "Port", "Extraction ID", "Comment", or (and) "Ignore".

To import the Europa 20 20 file:

1. On the LIMS main page click “Import Data from Mass Specs” and the Analysis Import Format form (Fig. 19.12 or similar) will open.
2. Select “K --> Kali” the Micromass Optima IRMS and click “Import.”
3. Navigate to the file created, “C&N Optima CF v1.xlsx,” click “Select,” and LIMS will prompt for a date (Fig. 22.16).
4. Click “OK” and LIMS will identify the delta values to be imported (Fig. 22.17).
5. Click “OK” and LIMS will import the results and display a summary form (Fig. 22.18). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking “Special Features” then “ImportLog.”
6. Click “OK” and this completes importing of the Micromass Optima $\delta^{13}C$ and $\delta^{15}N$ results from an EA.
7. To save time on future imports, make an Excel template of the column headings and the first column. To create this Excel template, one can delete all the information in the Excel range B2:M8 in the file just created. This template is named “C&N Optima CF template.xlsx” and is found in the folder named “22.4 Micromass Optima.” It appears in Figure 22.24. If more than 7 lines are needed, extend the line numbers as needed.

Note that LIMS did not open the Import Criteria for Mass Spectrometer form during importing of the example Micromass Optima csv file. This is because the file did not contain continuous-flow areas. Have continuous-flow areas been found on the spreadsheet, LIMS would have opened the Import Criteria for Mass Spectrometer form, enabling linearity adjustment.

Normalization of these $\delta^{13}C$ and $\delta^{15}N$ results is the next step and is discussed in Section 24. Because continuous-flow areas were not imported, LIMS will be unable to determine element mass fractions (element concentrations). Element mass fractions appear on the spreadsheet and they could be imported by using the “Extraction ID” and “Comment” column headings.

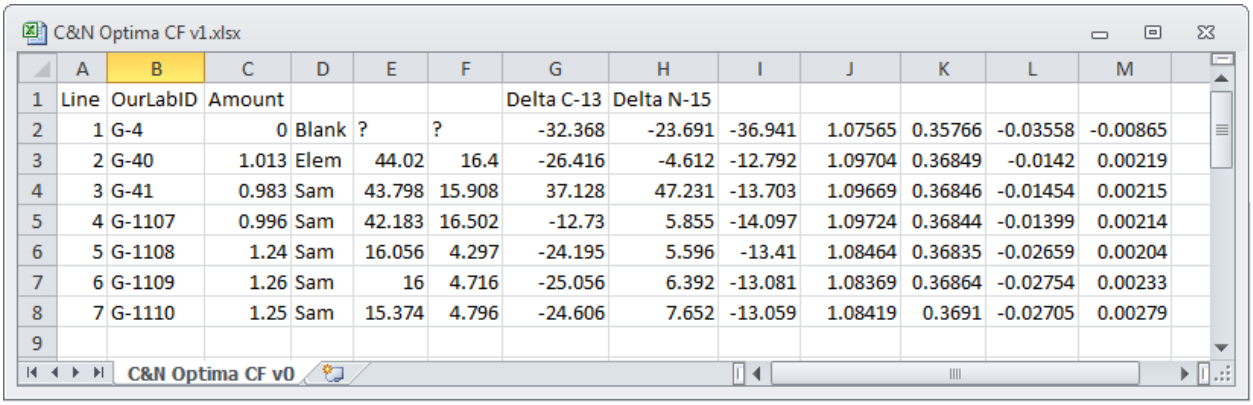


C&N Optima CF v0.csv

	A	B	C	D	E	F	G	H	I	J	K	L	M
1													
2	Batch Data Processing Results												
3													
4	Data File Name			blenk1									
5	Autorun Setup File Nar			blenk1									
6	Blank Subtraction			Disabled									
7	Background Subtractio			Enabled									
8	Reference Gas			Enabled									
9	Ref Gas Delta (C13)			-12.6		Ref Gas Delta (O18)			10.6				
10	Ref Gas Delta (N15)			0									
11	Current Time			######									
12	Date			######									
13	Elemental Calculations using Mass Spec Areas												
14	Avg Sensitivity for C13 (As/mg)												
15	Avg Sensitivity for N15 (As/mg)												
16													
17													
18													
19	Sample Details				Elemental		Isotopic		Atom %	,Atom % XS"			
20	No.	Name	Weight	Type	% Comp		Delta						
21			(mg)		(C)	(N)	(C13)	(N15)	(O18)	(C13)	(N15)	(C13)	(N15)
22	1	G-4	0	Blank	?	?	-32.368	-23.691	-36.941	1.07565	0.35766	-0.03558	-0.00865
23	2	G-40	1.013	Elem	44.02	16.4	-26.416	-4.612	-12.792	1.09704	0.36849	-0.0142	0.00219
24	3	G-41	0.983	Sam	43.798	15.908	37.128	47.231	-13.703	1.09669	0.36846	-0.01454	0.00215
25	4	G-1107	0.996	Sam	42.183	16.502	-12.73	5.855	-14.097	1.09724	0.36844	-0.01399	0.00214
26	5	G-1108	1.24	Sam	16.056	4.297	-24.195	5.596	-13.41	1.08464	0.36835	-0.02659	0.00204
27	6	G-1109	1.26	Sam	16	4.716	-25.056	6.392	-13.081	1.08369	0.36864	-0.02754	0.00233
28	7	G-1110	1.25	Sam	15.374	4.796	-24.606	7.652	-13.059	1.08419	0.3691	-0.02705	0.00279

C&N Optima CF v0

Fig. 22.21. Example Microsoft Optima csv file opened with Excel.



C&N Optima CF v1.xlsx

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Line	OurLabID	Amount				Delta C-13	Delta N-15					
2	1	G-4	0	Blank	?	?	-32.368	-23.691	-36.941	1.07565	0.35766	-0.03558	-0.00865
3	2	G-40	1.013	Elem	44.02	16.4	-26.416	-4.612	-12.792	1.09704	0.36849	-0.0142	0.00219
4	3	G-41	0.983	Sam	43.798	15.908	37.128	47.231	-13.703	1.09669	0.36846	-0.01454	0.00215
5	4	G-1107	0.996	Sam	42.183	16.502	-12.73	5.855	-14.097	1.09724	0.36844	-0.01399	0.00214
6	5	G-1108	1.24	Sam	16.056	4.297	-24.195	5.596	-13.41	1.08464	0.36835	-0.02659	0.00204
7	6	G-1109	1.26	Sam	16	4.716	-25.056	6.392	-13.081	1.08369	0.36864	-0.02754	0.00233
8	7	G-1110	1.25	Sam	15.374	4.796	-24.606	7.652	-13.059	1.08419	0.3691	-0.02705	0.00279
9													

C&N Optima CF v0

Fig. 22.22. Example Microsoft Optima csv file after modification for importing using the LIMS Abbreviated import format.

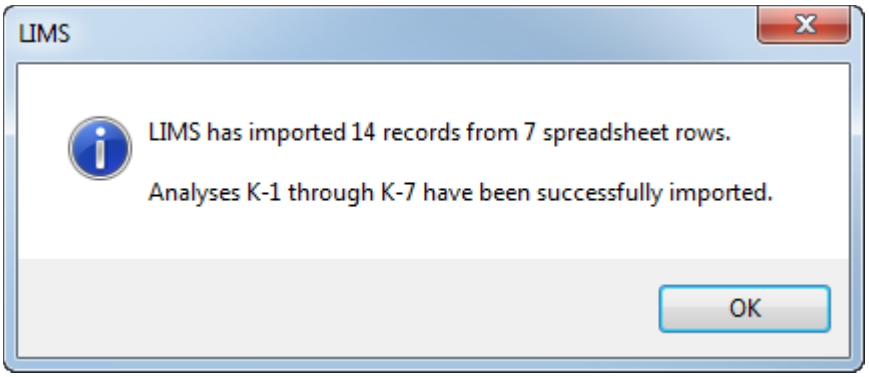


Fig. 22.23. LIMS summary message for importing samples having the Micromass Optima csv format.

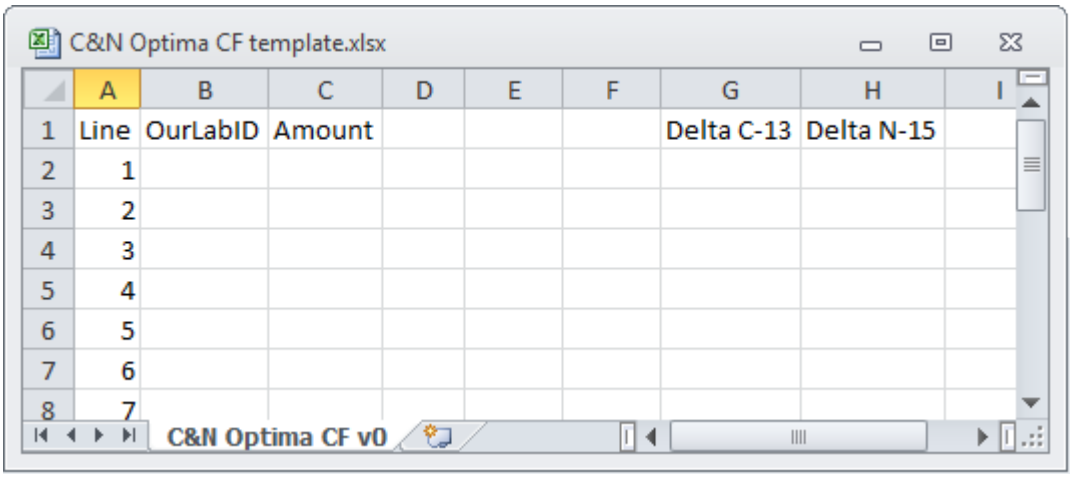


Fig. 22.24. Example Microsoft Optima template for C&N data importing using the LIMS Abbreviated import format. Extend line numbers as needed for all rows to be imported.

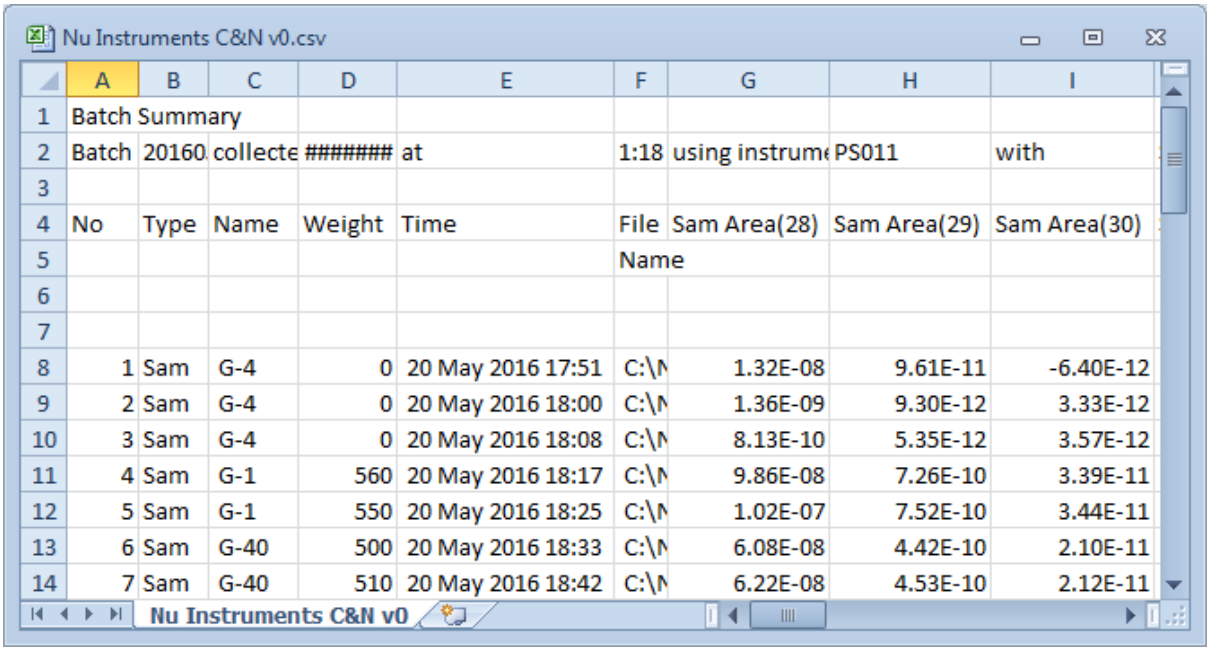
22.5 Importing Data Files from a Nu Instruments Mass Spectrometer

This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had a Nu Instruments mass spectrometer named "Pegasus" added to it in Section 17.5. In the event the "Lakes_Backend_DB.accdb" backend database with "Pegasus" is not available, a backend database for use in this section can be extracted from a file named "Nu_Instruments_Pegasus_Backend_DB.zip" that is provided in a folder named "Section 22.5" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this section a data file from a Perspective mass spectrometer from Nu Instruments having $\delta^{13}C$ and $\delta^{15}N$ results will be imported into LIMS. Before proceeding, the reader should be fully familiar with the information in Section 17.1. A Nu Instruments file is a csv file without commas as text qualifiers. Excel should open these files automatically, but if not, one can assign Excel as one of the programs that can open csv files. Right click on a csv file, select "Open With," select "Choose default program," and browse for and select Excel.

The example Nu Instruments csv file "Nu Instruments C&N v0.csv" is located in the folder named "22.5 Nu Instruments" that accompanies this manual. The reader will create a file named "Nu Instruments C&N v1.xlsx" and this file is provided in folder "22.5 Nu Instruments" for reference. To create an Excel file that LIMS can import:

1. Open the example Nu Instruments csv file "Nu Instruments C&N v0.csv" with Excel. A portion of this file is shown in Figure 22.25.
2. Save the file with a new name and file type. The name "Nu Instruments C&N v1.xlsx" is used in this example and this file is provided in the folder named "22.5 Nu Instruments."
3. Replace "Batch Summary" in cell A1 by "Line."
4. Enter "OurLabID" in cell C1.



	A	B	C	D	E	F	G	H	I
1	Batch Summary								
2	Batch	20160	collecte	#######	at	1:18	using instrume	PS011	with
3									
4	No	Type	Name	Weight	Time	File	Sam Area(28)	Sam Area(29)	Sam Area(30)
5						Name			
6									
7									
8	1	Sam	G-4	0	20 May 2016 17:51	C:\N	1.32E-08	9.61E-11	-6.40E-12
9	2	Sam	G-4	0	20 May 2016 18:00	C:\N	1.36E-09	9.30E-12	3.33E-12
10	3	Sam	G-4	0	20 May 2016 18:08	C:\N	8.13E-10	5.35E-12	3.57E-12
11	4	Sam	G-1	560	20 May 2016 18:17	C:\N	9.86E-08	7.26E-10	3.39E-11
12	5	Sam	G-1	550	20 May 2016 18:25	C:\N	1.02E-07	7.52E-10	3.44E-11
13	6	Sam	G-40	500	20 May 2016 18:33	C:\N	6.08E-08	4.42E-10	2.10E-11
14	7	Sam	G-40	510	20 May 2016 18:42	C:\N	6.22E-08	4.53E-10	2.12E-11

Fig. 22.25. Section of a Nu Instruments csv file opened with Excel. File kindly provided by Francisco Fernandoy (Andrés Bello National University, Santiago, Chile).

5. Enter “Amount” in cell D1.
6. Enter “Date-Time Analyzed” in cell E1.
7. Enter “Area All N” in cell G1, which is the area of the m/z 28 peak. It would be better if this were an “Area All” type peak containing the sum of the areas of the *m*/*z* 28, 29, and 30 peaks. Because this file does have areas for *m*/*z* 28, 29, and 30, respectively as columns G, H, and I, one could sum the entries in columns G, H, and I, using *e.g.* “=SUM(G8:I8)” and use this sum for the “Area All N” column. A better solution, if it is possible, is to modify the data export so that one of the columns is the sum of the peak areas for *m*/*z* 28, 29, and 30.
8. Enter “Area All C” in cell X1. As in the step above, it would be better if this were an “Area All” peak column containing the sum of the areas of the *m*/*z* 44, 45, and 46. If the data export can be modified, this modification is recommended.
9. The entries in X8:X10 are “No Beam” and are not numeric. Delete them.
10. Enter ”Delta N-15” in cell V1.
11. Enter “Delta C-13” in cell AM1.
12. Delete rows 2 through 7, save the file, and close the file, which is now ready to import (Fig. 22.26).
13. To save time on future imports, make an Excel template of the column headings and the first column. To create this Excel template, one can delete all the information in the Excel range A2:AP54 in the file just created. This template is named “Nu Instruments C&N template.xlsx” and is found in the folder named “22.5 Nu Instruments.” It appears in Figure 22.27.If desired, additional columns can be added to the Excel file to be imported (Figs. 22.26), which might include “Mass Spec”, “Analysis”, “Port”, “Extraction ID”, “Comment”, or (and) “Ignore”.

To import the Nu Instruments file:

1. On the LIMS main page click “Import Data from Mass Specs” and the Analysis Import Format form (Fig. 19.12 or similar) will open.
2. Select “P --> Pegasus” the Nu Instruments IRMS and click “Import.”
3. Navigate to the file created, “Nu Instruments C&N v1.xlsx,” click “Select,” and LIMS will identify the delta values to be imported (Fig. 22.17).
4. Click “OK” and LIMS will display the Import Criteria for Mass Spectrometer form (Fig. 22.28).
5. There can be an increase (or decrease) in peak area over time for the same mass of the same reference with an EA or TC/EA. LIMS can adjust for an increase (or decrease) in peak area of all peak of the same gas type based on values of the ratios of the peak areas and masses of a selected reference over time. This normalization should improve elemental mass fraction (element concentration) determinations. To perform this evaluation for CO_2 areas, click the “Area Adjust” check

Nu Instruments C&N v1.xlsx

	A	B	C	D	E	F	G	H	I
1	Line		OurLabID	Amount	Date-Time Analyzed		Area All N		
2	1	Sam	G-4	0	20 May 2016 17:51	C:\N	1.32E-08	9.61E-11	-6.40E-12
3	2	Sam	G-4	0	20 May 2016 18:00	C:\N	1.36E-09	9.30E-12	3.33E-12
4	3	Sam	G-4	0	20 May 2016 18:08	C:\N	8.13E-10	5.35E-12	3.57E-12
5	4	Sam	G-1	560	20 May 2016 18:17	C:\N	9.86E-08	7.26E-10	3.39E-11
6	5	Sam	G-1	550	20 May 2016 18:25	C:\N	1.02E-07	7.52E-10	3.44E-11
7	6	Sam	G-40	500	20 May 2016 18:33	C:\N	6.08E-08	4.42E-10	2.10E-11
8	7	Sam	G-40	510	20 May 2016 18:42	C:\N	6.22E-08	4.53E-10	2.12E-11
9	8	Sam	G-40	500	20 May 2016 18:50	C:\N	6.09E-08	4.43E-10	2.08E-11
10	9	Sam	G-41	510	20 May 2016 18:59	C:\N	6.83E-08	5.23E-10	2.32E-11
11	10	Sam	G-41	520	20 May 2016 19:07	C:\N	6.40E-08	4.90E-10	1.60E-11
12	11	Sam	G-41	520	20 May 2016 19:16	C:\N	6.67E-08	5.11E-10	2.25E-11
13	12	Sam	G-42	500	20 May 2016 19:25	C:\N	9.06E-08	6.68E-10	2.97E-11
14	13	Sam	G-42	500	20 May 2016 19:33	C:\N	9.61E-08	7.08E-10	3.11E-11
15	14	Sam	G-42	490	20 May 2016 19:41	C:\N	9.52E-08	7.02E-10	3.02E-11
16	15	Sam	G-42	500	20 May 2016 19:50	C:\N	9.72E-08	7.17E-10	3.15E-11
17	16	Sam	G-42	510	20 May 2016 19:58	C:\N	9.92E-08	7.31E-10	3.22E-11
18	17	Sam	G-43	510	20 May 2016 20:06	C:\N	9.22E-08	6.80E-10	3.00E-11
19	18	Sam	G-43	500	20 May 2016 20:15	C:\N	9.46E-08	6.98E-10	3.05E-11
20	19	Sam	G-43	510	20 May 2016 20:23	C:\N	9.56E-08	7.05E-10	3.12E-11
21	20	Sam	G-43	510	20 May 2016 20:32	C:\N	9.53E-08	7.03E-10	2.69E-11
22	21	Sam	G-43	520	20 May 2016 20:41	C:\N	1.00E-07	7.40E-10	3.26E-11
23	22	Sam	G-1112	510	20 May 2016 20:49	C:\N	6.37E-08	4.64E-10	2.16E-11
24	23	Sam	G-1112	510	20 May 2016 20:58	C:\N	6.43E-08	4.68E-10	1.24E-11

Nu Instruments C&N v0

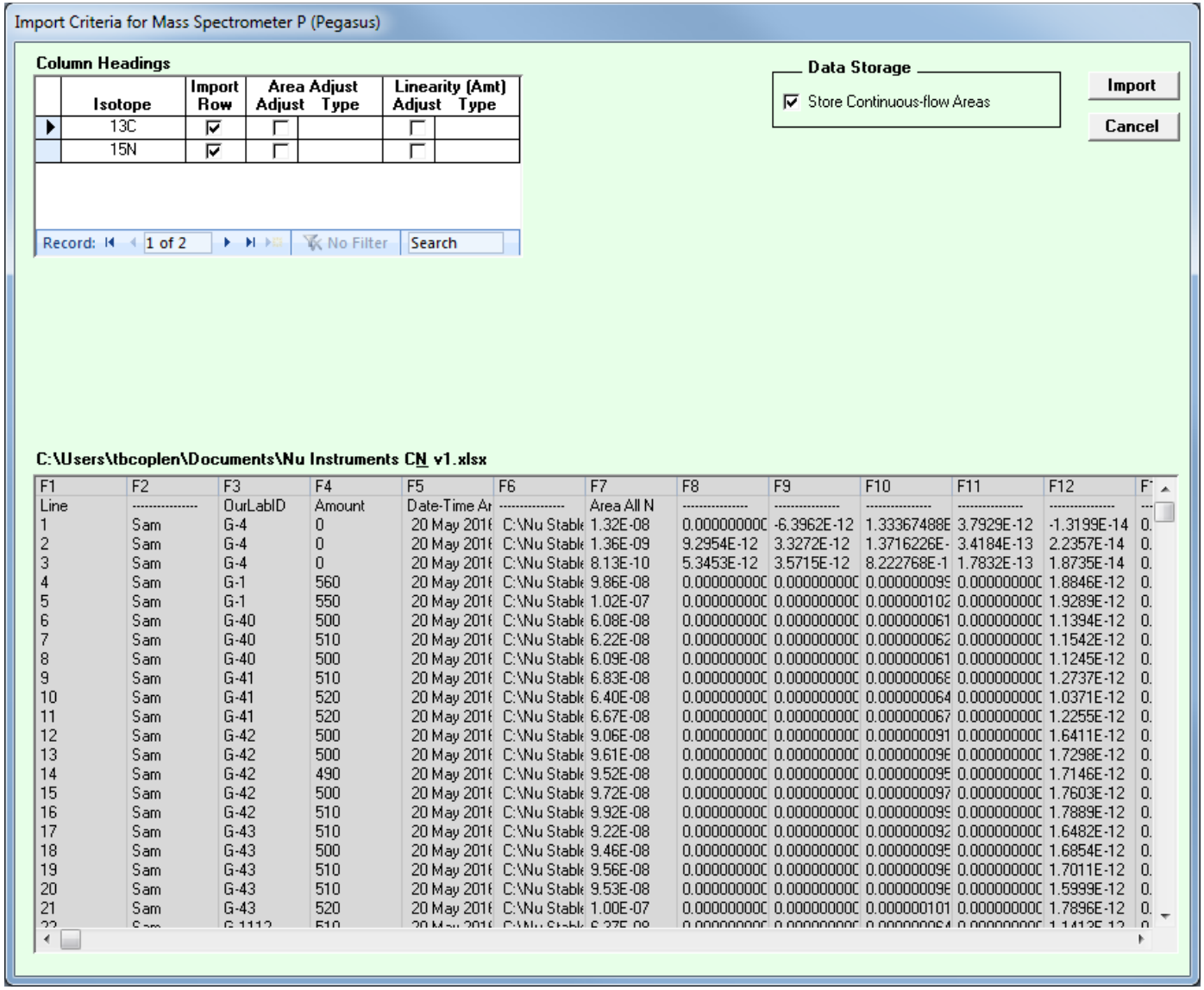
Fig. 22.26. Section of an example Nu Instruments csv file after modification for importing using the LIMS Abbreviated import format.

Nu Instruments C&N template.xlsx

	A	B	C	D	E	F	G	H	I	J
1	Line		OurLabID	Amount	Date-Time Analyzed		Area All N			
2										
3										
4										

Nu Instruments C&N Template

Fig. 22.27. Example Nu Instruments template for C&N data importing using the LIMS Abbreviated import format.



F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F
Line	----------	OurLabID	Amount	Date-Time Ar	----------	Area All N	----------	----------	----------	----------	----------	---
1	Sam	G-4	0	20 May 201(	C:\Nu Stable	1.32E-08	0.000000000	-6.3962E-12	1.33367488E	3.7929E-12	-1.3199E-14	0.
2	Sam	G-4	0	20 May 201(	C:\Nu Stable	1.36E-09	9.2954E-12	3.3272E-12	1.3716226E-	3.4184E-13	2.2357E-14	0.
3	Sam	G-4	0	20 May 201(	C:\Nu Stable	8.13E-10	5.3453E-12	3.5715E-12	8.222768E-1	1.7832E-13	1.8735E-14	0.
4	Sam	G-1	560	20 May 201(	C:\Nu Stable	9.86E-08	0.000000000	0.000000000	0.000000095	0.000000000	1.8846E-12	0.
5	Sam	G-1	550	20 May 201(	C:\Nu Stable	1.02E-07	0.000000000	0.000000000	0.000000102	0.000000000	1.9289E-12	0.
6	Sam	G-40	500	20 May 201(	C:\Nu Stable	6.08E-08	0.000000000	0.000000000	0.000000061	0.000000000	1.1394E-12	0.
7	Sam	G-40	510	20 May 201(	C:\Nu Stable	6.22E-08	0.000000000	0.000000000	0.000000062	0.000000000	1.1542E-12	0.
8	Sam	G-40	500	20 May 201(	C:\Nu Stable	6.09E-08	0.000000000	0.000000000	0.000000061	0.000000000	1.1245E-12	0.
9	Sam	G-41	510	20 May 201(	C:\Nu Stable	6.83E-08	0.000000000	0.000000000	0.000000068	0.000000000	1.2737E-12	0.
10	Sam	G-41	520	20 May 201(	C:\Nu Stable	6.40E-08	0.000000000	0.000000000	0.000000064	0.000000000	1.0371E-12	0.
11	Sam	G-41	520	20 May 201(	C:\Nu Stable	6.67E-08	0.000000000	0.000000000	0.000000067	0.000000000	1.2255E-12	0.
12	Sam	G-42	500	20 May 201(	C:\Nu Stable	9.06E-08	0.000000000	0.000000000	0.000000091	0.000000000	1.6411E-12	0.
13	Sam	G-42	500	20 May 201(	C:\Nu Stable	9.61E-08	0.000000000	0.000000000	0.000000096	0.000000000	1.7298E-12	0.
14	Sam	G-42	490	20 May 201(	C:\Nu Stable	9.52E-08	0.000000000	0.000000000	0.000000095	0.000000000	1.7146E-12	0.
15	Sam	G-42	500	20 May 201(	C:\Nu Stable	9.72E-08	0.000000000	0.000000000	0.000000097	0.000000000	1.7603E-12	0.
16	Sam	G-42	510	20 May 201(	C:\Nu Stable	9.92E-08	0.000000000	0.000000000	0.000000099	0.000000000	1.7889E-12	0.
17	Sam	G-43	510	20 May 201(	C:\Nu Stable	9.22E-08	0.000000000	0.000000000	0.000000092	0.000000000	1.6482E-12	0.
18	Sam	G-43	500	20 May 201(	C:\Nu Stable	9.46E-08	0.000000000	0.000000000	0.000000095	0.000000000	1.6854E-12	0.
19	Sam	G-43	510	20 May 201(	C:\Nu Stable	9.56E-08	0.000000000	0.000000000	0.000000096	0.000000000	1.7011E-12	0.
20	Sam	G-43	510	20 May 201(	C:\Nu Stable	9.53E-08	0.000000000	0.000000000	0.000000096	0.000000000	1.5999E-12	0.
21	Sam	G-43	520	20 May 201(	C:\Nu Stable	1.00E-07	0.000000000	0.000000000	0.000000101	0.000000000	1.7896E-12	0.

Fig. 22.28. The Import Criteria for Mass Spectrometer form for Nu Instruments samples.

box in the row having “13C” in the “Isotope” column and LIMS will display the Area Adjust form (Fig. 22.29).

6. The Area Adjust form (Fig. 22.29) shows a plot of analysis number versus CO_2 area of the reference G-40 divided by the sample mass of G-40. The user can select a choice of regressions (linear, quadratic, logarithmic, or power) to fit their data. The *R* squared value of the fit is shown. The user can select other references from the “Our Lab ID” dropdown control. By clicking “Import Adjusted Areas” all of the CO_2 areas in the imported file will be adjusted (normalized) using the algorithm in the “Trend line.” In figure 22.29, the first analysis (P-6) shows an anomalously high value for the ratio Area / Amount. The first sample in any run may be anomalous and is routinely ignored in many laboratories. Ignore analysis P-6 by clicking the check box in the row for analysis P-6 and the plot will be updated immediately (Fig. 22.30).

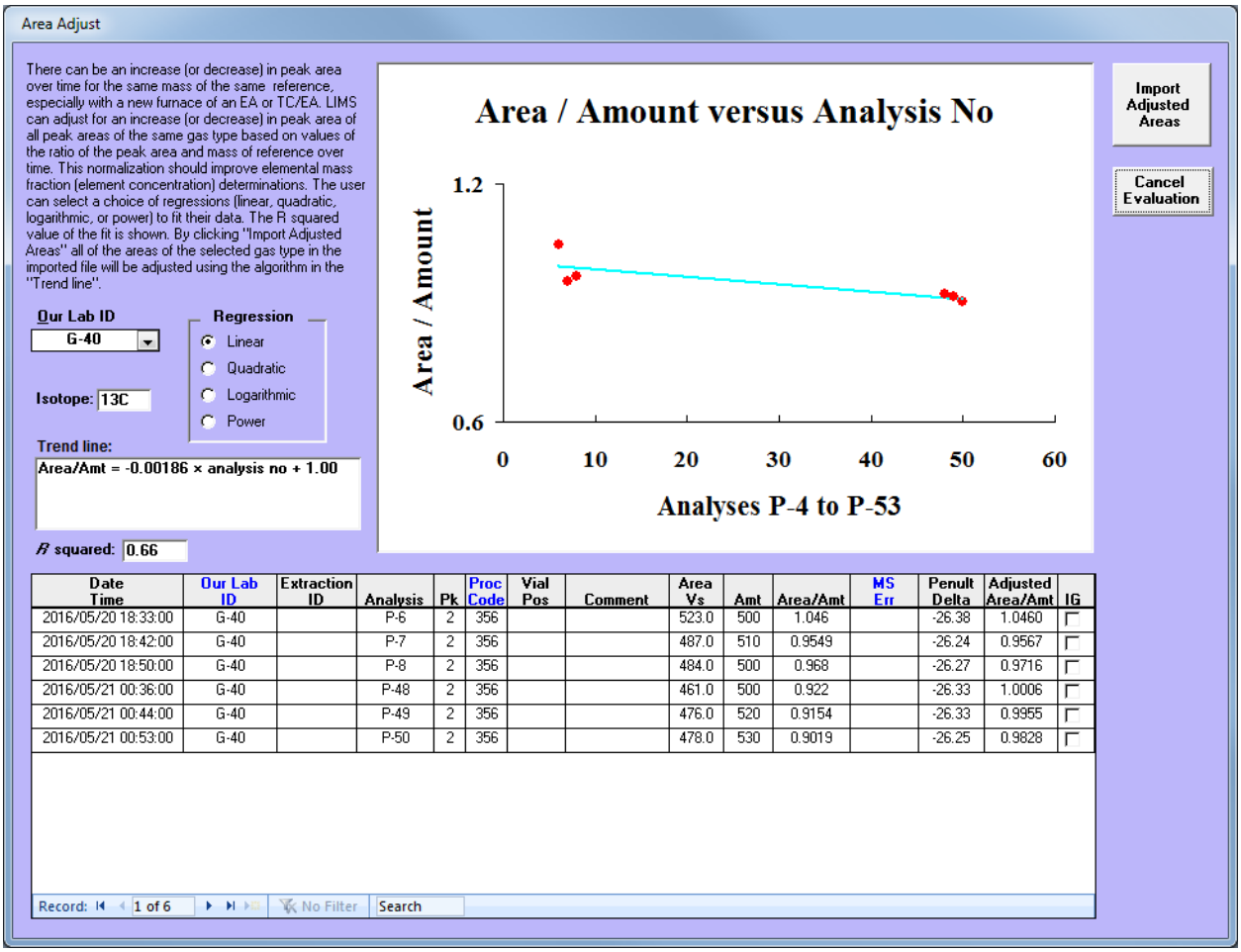


Fig. 22.29. The Area Adjust form showing analysis number versus CO_2 area / amount of standard for the Nu Instruments import.

7. The *R* squared value has improved from 0.66 to 0.91 and appears reasonable. Therefore, click "Import Adjusted Areas" and LIMS will notify the user that all peak areas will be updated with the linear regression (Fig. 22.31). If a user changes their mind, the file can be reimported.
8. Click "OK."
9. To evaluate the so-called "Linearity" from a plot of peak area versus $\delta^{13}C$ values of G-40, click the "Linearity (Amt)" check box for the row having the isotope "13C," and LIMS displays the Adjustment for Variation in Delta Value with Variation in Amount of Sample form (Fig. 22.32).
10. Select G-43 for the reference "Our Lab ID" and note that the *R* squared value improves from 0.35 to 0.80. Therefore, click "Import Adjusted Delta Values,"
11. Repeat the Area Adjust for "15N," and import the adjusted areas.
12. Click the "Linearity (Amt)" check box for "15N" and observe that the *R* squared values are relatively low. There is no justification to apply a linearity adjustment. Therefore, click "Cancel Evaluation," and the updated Column Headings in the upper left panel of the Import Criteria for Mass Spectrometer form are shown in Figure 22.33.
13. The "Store Continuous-flow Areas" check box is enabled, which is correct, so it can be retained as is.
14. These data are ready to import. Click "Import" and LIMS displays the informational message in Figure 21.8.
15. Click "OK" and LIMS imports the analyses and displays a summary message (Fig. 22.34). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking "Special Features" then "ImportLog."
16. Click "OK" and this completes the importing of the Nu Instruments C&N example file "Nu Instruments C&N v1.xlsx."

Normalization of the $\delta^{13}C$ and $\delta^{15}N$ results with determination of element mass fractions (element concentrations) is the next step and is discussed in Section 24.

⚠ Users need to remember that Nu Instruments files do not have an analysis number. Therefore, if they are imported more than once, analyses will be replicated in LIMS. One way to avoid this conundrum is to add an "Analysis" column to each Excel file and populate with regularly increasing integers.

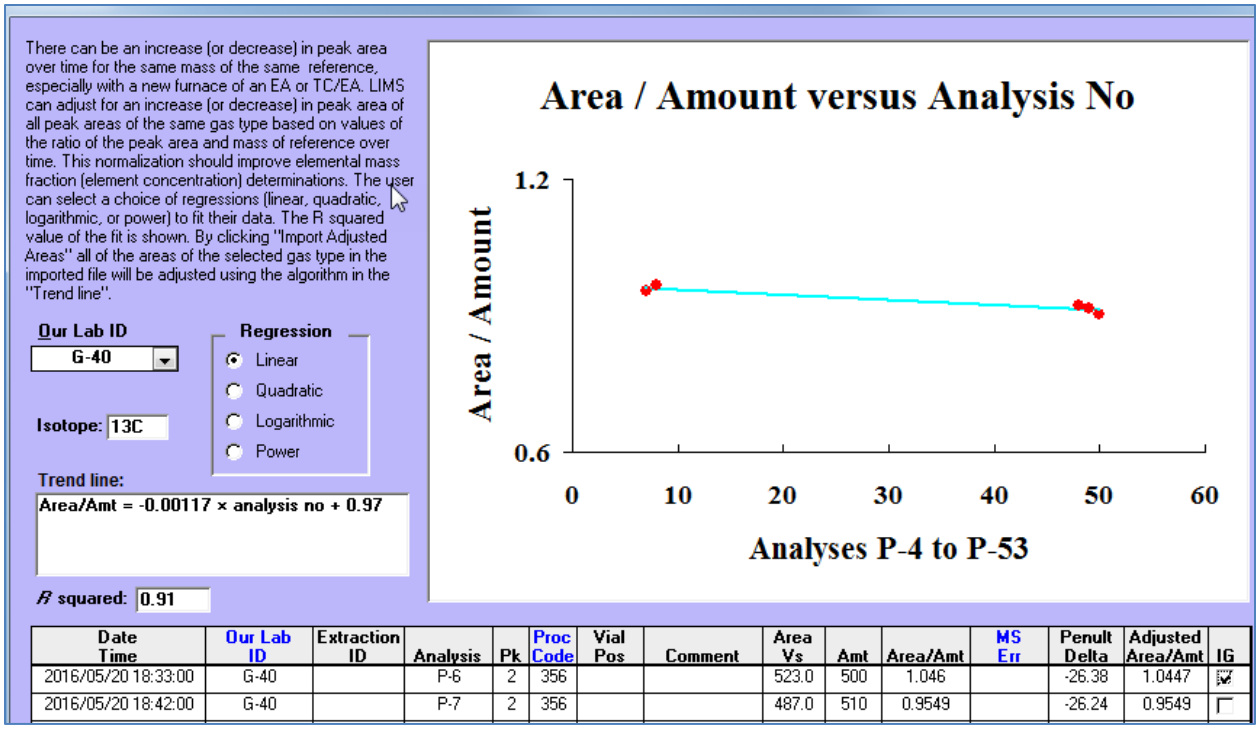


Fig. 22.30. Updated Area Adjust form after ignoring analysis P-6.

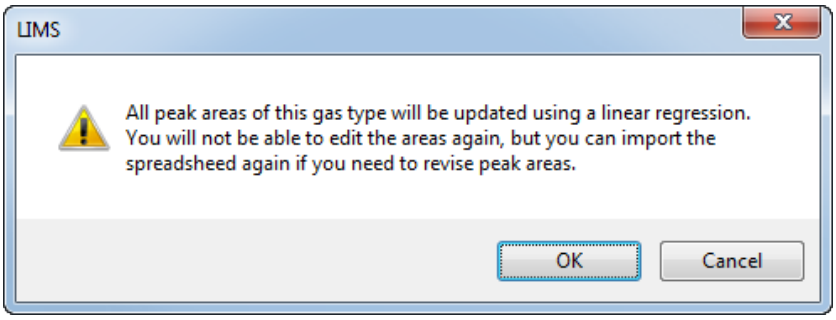
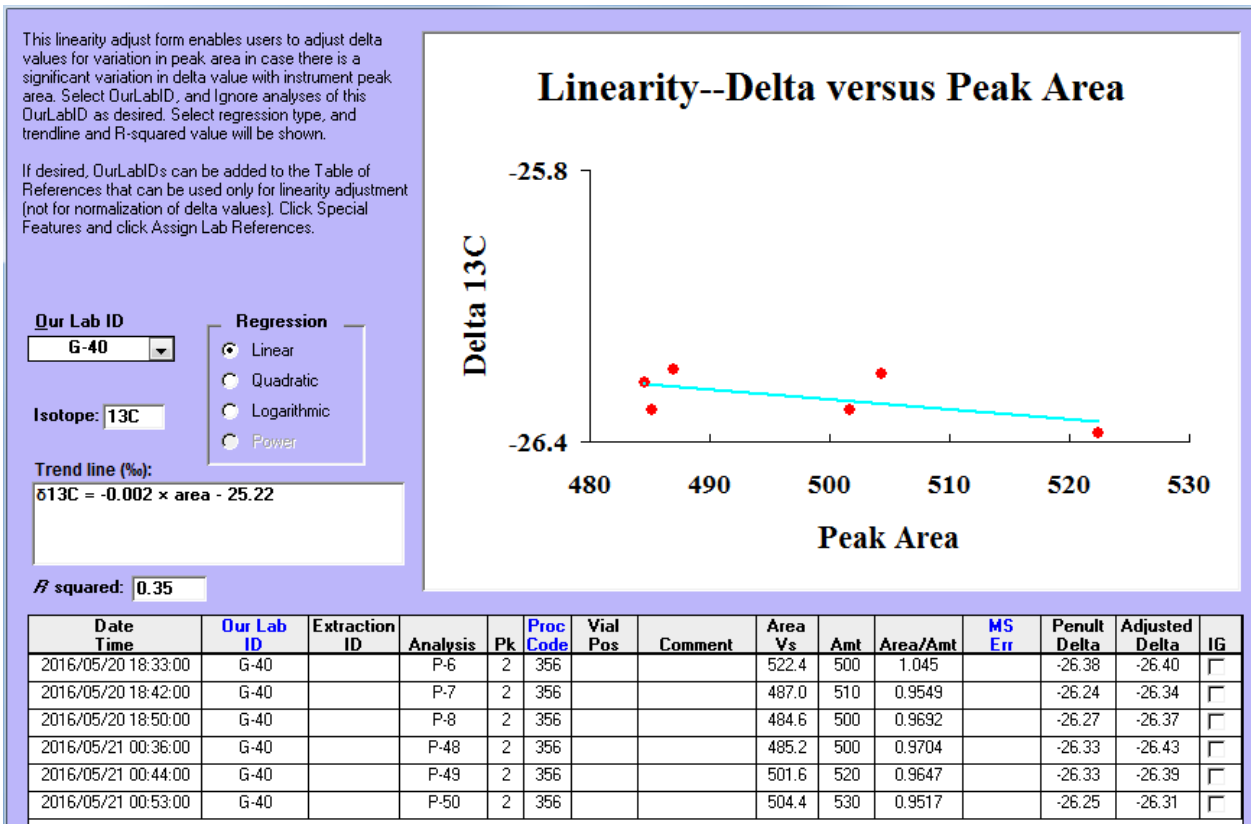


Fig. 22.31. LIMS notification that peak areas will be updated.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Area Vs	Amt	Area/Amt	MS Err	Penult Delta	Adjusted Delta	IG
2016/05/20 18:33:00	G-40		P-6	2	356			522.4	500	1.045		-26.38	-26.40	☐
2016/05/20 18:42:00	G-40		P-7	2	356			487.0	510	0.9549		-26.24	-26.34	☐
2016/05/20 18:50:00	G-40		P-8	2	356			484.6	500	0.9692		-26.27	-26.37	☐
2016/05/21 00:36:00	G-40		P-48	2	356			485.2	500	0.9704		-26.33	-26.43	☐
2016/05/21 00:44:00	G-40		P-49	2	356			501.6	520	0.9647		-26.33	-26.39	☐
2016/05/21 00:53:00	G-40		P-50	2	356			504.4	530	0.9517		-26.25	-26.31	☐

Fig. 22.32. The Adjustment for Variation in Delta Value with Variation in Amount of Sample (linearity adjustment) form for Nu Instruments samples.

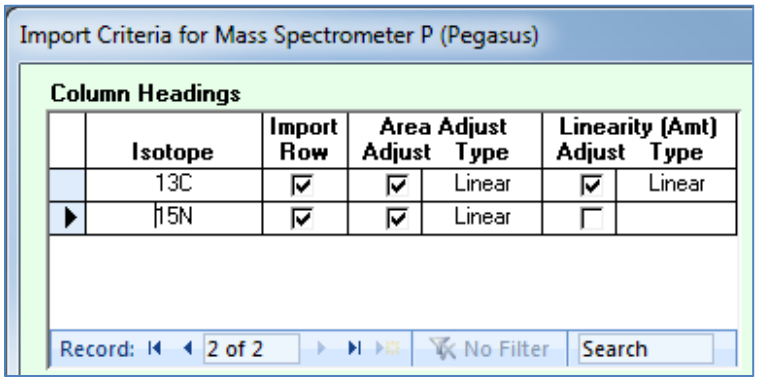


Fig. 22.33. Updated Column Headings in the Import Criteria of Mass Spectrometer form.

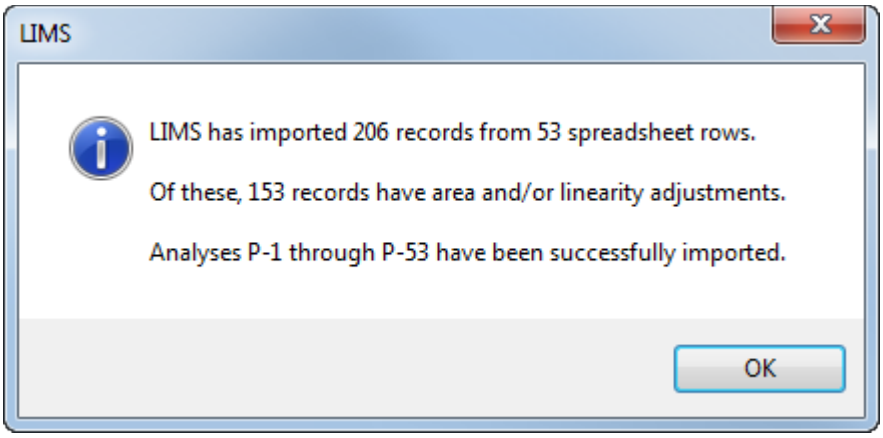


Fig. 22.34. LIMS Nu Instruments C&N sample import summary.

22.6 Importing Data Files from a Sercon Mass Spectrometer

This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had a Sercon mass spectrometer named "Artemis" added to it in Section 17.6. In the event the "Lakes_Backend_DB.accdb" backend database with "Artemis" is not available, a backend database for use in this section can be extracted from a file named "Sercon_Artemis_Backend_DB.zip" that is provided in a folder named "Section 22.6" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this section a Sercon data file having $\delta^{13}C$ and $\delta^{15}N$ results will be imported into LIMS. Before proceeding, the reader should be fully familiar with the information in Section 17.1. Sercon data files are tab formatted (space delimited) text files with the suffix prn. The suffix "prn" can be replaced by "txt" so that the file can be opened with recent versions of Excel, modified as needed, and saved as either an Excel xls or xlsx file. The example file "Sercon C&N v0.prn" is located in the folder named "22.6 Sercon" that accompanies this manual. The reader will create a file named "Sercon C&N v1.xlsx" and this file is provided in folder "22.6 Sercon" for reference. In case Excel is not set up as a default program to open prn files automatically, to create a file that LIMS can import:

1. Open Excel.
2. From the "File" tab select "Open."
3. For the filter in the lower right of the Windows Open dialog box, select text files.
4. If "*.prn" is not one of the file choices, change the suffix of "Sercon C&N v0" from "prn" to "txt."
5. Navigate to the file "Sercon C&N v0.prn" (or "Sercon C&N v0.txt" as needed).
6. Click "Open" and the Excel text Import Wizard should open (Fig. 22.35).

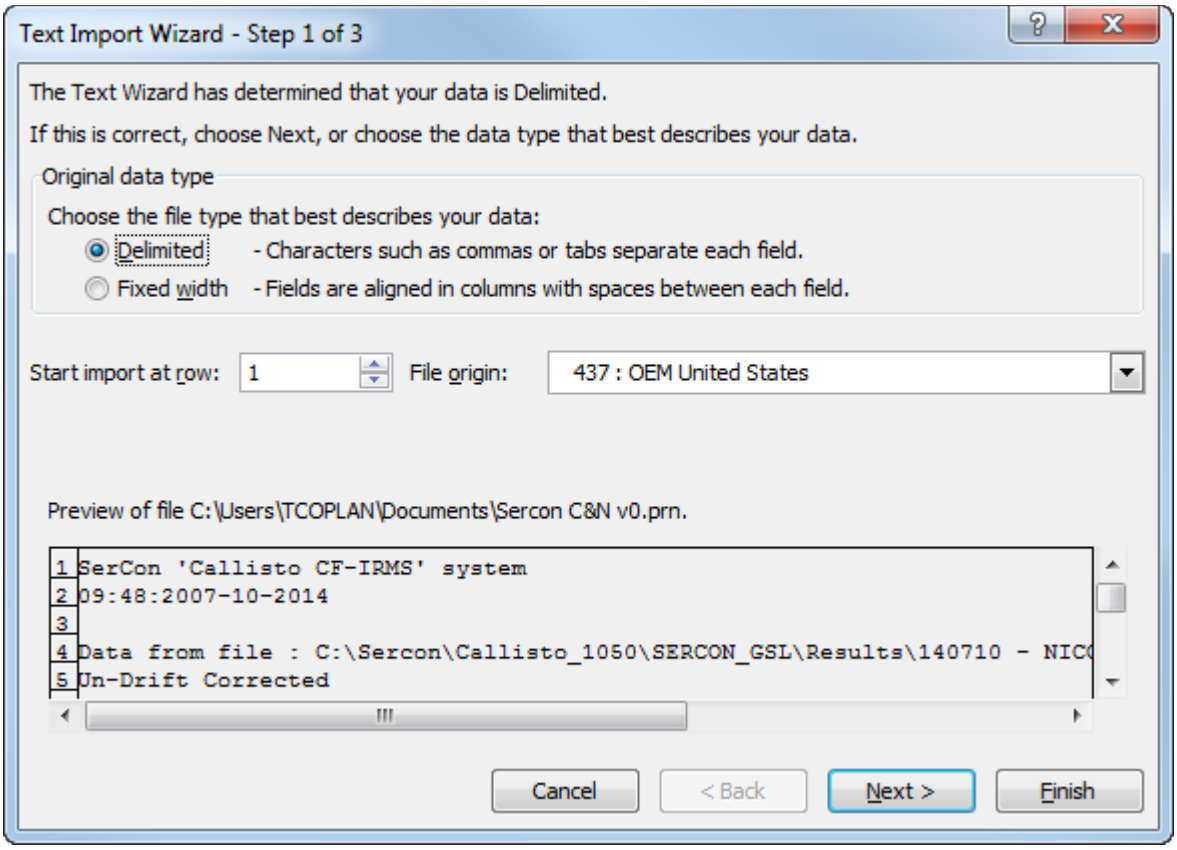


Fig. 22.35. Step 1 of the Excel Text Import Wizard.

7. Ensure that the "Delimited" option is selected, click "Next >," and Excel should show step 2 of the wizard.
8. Ensure that "Tab" is selected as the delimiter and that "{none}" is selected as the "Text qualifier" (Fig. 22.12).
9. Click "Next >" and step 3 of the Excel import wizard will enable one to set the date format. Because there are no dates, click "Finish," and Excel will display the text file (Fig. 22.37). To avoid having to use the Text Import Wizard, assign Excel as one of the programs that can open prn files. Right click on a prn file, select "Open With," select "Choose default program," and browse for and select Excel.
10. Save the file with a new name. The name "Sercon C&N v1.xlsx" is used in this example and this file is provided in the folder named "22.6 Sercon."
11. Replace "SerCon 'Callisto CF-IRMS' system" in cell A1 by "Line."
12. Enter "OurLabID" (with no spaces) in cell B1.
13. Enter "Amount" in cell C1.
14. Enter "Area All N" in cell D1.
15. Enter "Delta N-15" in cell G1.

16. Enter “Area All C” in cell K1
17. Enter ”Delta C-13” in cell N1.
18. Delete Excel rows 26 to 47 to eliminate duplicate analyses data.
19. Delete Excel row 2 through 7 and save the file, which is now ready to import (Fig. 22.38).
20. To save time on future imports, make an Excel template of the column headings. To create this Excel template, one can delete all the information in the Excel range A2:R19 in the file just created. This template is named “Sercon C&N template.xlsx” and is found in the folder named “22.6 Sercon.” It appears in Figure 22.39.

If desired, additional columns can be added to the Excel file to be imported (Figs. 22.38 and 22.39), which might include “Mass Spec”, “Analysis”, “Date-Time Analyzed”, “Port”, “Extraction ID”, “Comment”, or (and) “Ignore”.

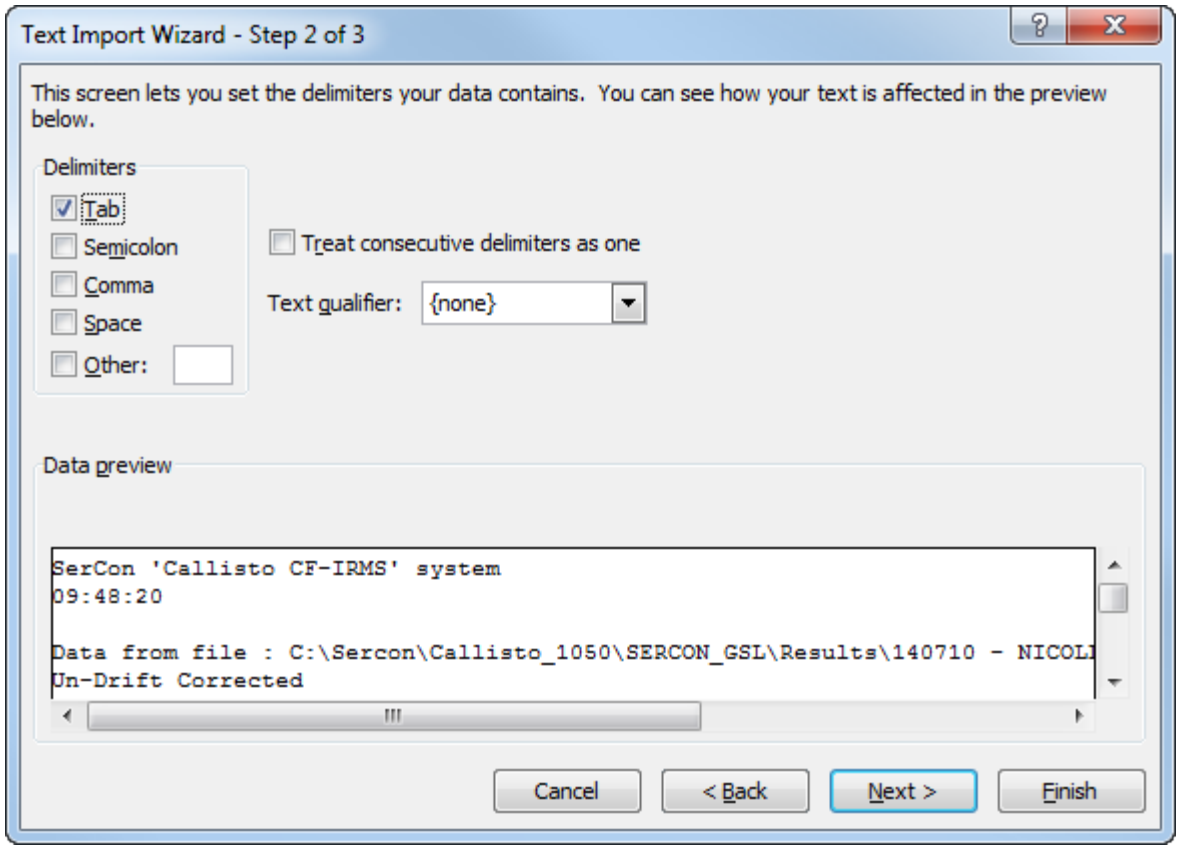
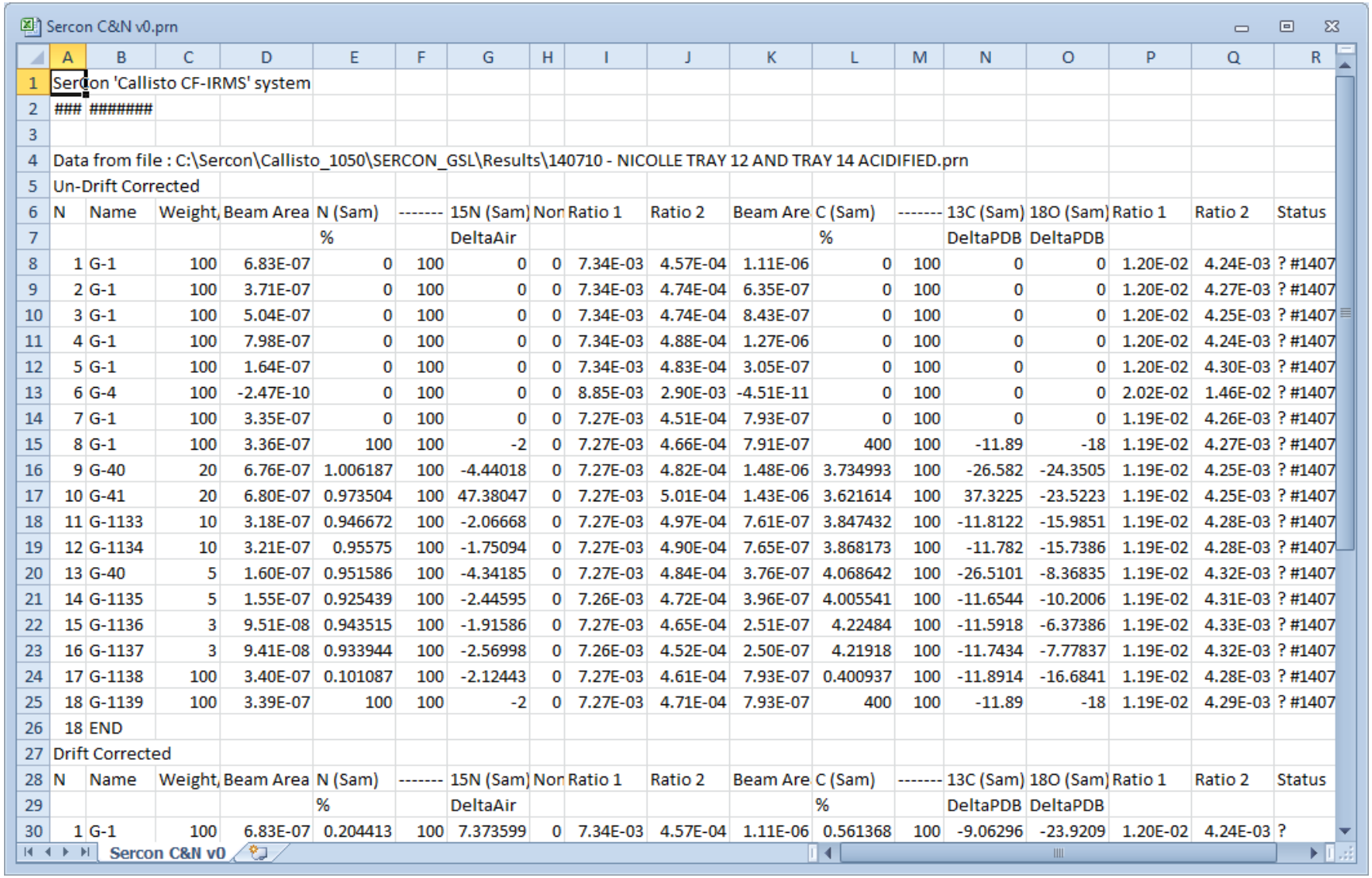


Fig. 22.36. Step 2 of the Excel Text Import Wizard. The “Text qualifier” needs to be set to “{none}.”

To import the Sercon file:

1. On the LIMS main page click “Import Data from Mass Specs” and the Analysis Import Format form (Fig. 19.12 or similar) will open.
2. Select “A --> Artemis” the Sercon IRMS and click “Import.”
3. Navigate to the file created, “Sercon C&N v1.xlsx,” click “Select,” and LIMS will prompt for a date (Fig. 22.16).
4. Click “OK” and LIMS will identify the delta values to be imported (Fig. 22.17).
5. Click “OK” and LIMS will open the Import Criteria for Mass Spectrometer form (Fig. 22.40).
6. There can be an increase (or decrease) in peak area over time for the same mass of the same reference with an EA or TC/EA. LIMS can adjust for an increase (or decrease) in peak area of all peak of the same gas type based on values of the ratios of the peak areas and masses of a selected reference over time. This normalization should improve elemental mass fraction (element concentration) determinations. To perform this evaluation for CO_2 areas, click the “Area Adjust” check box in the row having “13C” in the “Isotope” column and LIMS will display the Area Adjust form (Fig. 22.41).
7. The Area Adjust form (Fig. 22.41) shows a plot of analysis number versus CO_2 area of the reference G-40 divided by the sample mass of G-40. The user can select a choice of regressions (linear, quadratic, logarithmic, or power) to fit their data. The *R* squared value of the fit is shown. The user can select other references from the “Our Lab ID” dropdown control. By clicking “Import Adjusted Areas” all of the CO_2 areas in the imported file will be adjusted (normalized) using the algorithm in the “Trend line.” If there are more than two analyses in the lower panel, the user can ignore analyses by clicking “IG” check boxes (see the example in Section 22.5).
8. Click “Import Adjusted Areas” and LIMS will notify the user that all peak areas will be updated with the linear regression (Fig. 22.31). If a user changes their mind, the file can be reimported.
9. Click “OK.”
10. To evaluate the so-called “Linearity” from a plot of peak area versus $\delta^{13}C$ values of G-40, click the “Linearity (Amt)” check box for the row having the isotope “13C,” and LIMS displays the Adjustment for Variation in Delta Value with Variation in Amount of Sample form (Fig. 22.42).
11. There is a small variation in $\delta^{13}C$ with amount of sample; therefore, click “Import Adjusted Delta Values.”
12. Repeat the Area Adjust for “15N,” and import the adjusted areas.
13. Repeat the Linearity Adjust for “15N,” and the upper left panel of the Import Criteria for Mass Spectrometer form is shown in Figure 22.43.



Sercon C&N v0.prn

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1	Sercon 'Callisto CF-IRMS' system																	
2	###	########																
3																		
4	Data from file : C:\Sercon\Callisto_1050\SERCON_GSL\Results\140710 - NICOLLE TRAY 12 AND TRAY 14 ACIDIFIED.prn																	
5	Un-Drift Corrected																	
6	N	Name	Weight,	Beam Area	N (Sam)	-------	15N (Sam)	Nor	Ratio 1	Ratio 2	Beam Are	C (Sam)	-------	13C (Sam)	18O (Sam)	Ratio 1	Ratio 2	Status
7					%		DeltaAir					%		DeltaPDB	DeltaPDB			
8	1	G-1	100	6.83E-07	0	100	0	0	7.34E-03	4.57E-04	1.11E-06	0	100	0	0	1.20E-02	4.24E-03	? #1407
9	2	G-1	100	3.71E-07	0	100	0	0	7.34E-03	4.74E-04	6.35E-07	0	100	0	0	1.20E-02	4.27E-03	? #1407
10	3	G-1	100	5.04E-07	0	100	0	0	7.34E-03	4.74E-04	8.43E-07	0	100	0	0	1.20E-02	4.25E-03	? #1407
11	4	G-1	100	7.98E-07	0	100	0	0	7.34E-03	4.88E-04	1.27E-06	0	100	0	0	1.20E-02	4.24E-03	? #1407
12	5	G-1	100	1.64E-07	0	100	0	0	7.34E-03	4.83E-04	3.05E-07	0	100	0	0	1.20E-02	4.30E-03	? #1407
13	6	G-4	100	-2.47E-10	0	100	0	0	8.85E-03	2.90E-03	-4.51E-11	0	100	0	0	2.02E-02	1.46E-02	? #1407
14	7	G-1	100	3.35E-07	0	100	0	0	7.27E-03	4.51E-04	7.93E-07	0	100	0	0	1.19E-02	4.26E-03	? #1407
15	8	G-1	100	3.36E-07	100	100	-2	0	7.27E-03	4.66E-04	7.91E-07	400	100	-11.89	-18	1.19E-02	4.27E-03	? #1407
16	9	G-40	20	6.76E-07	1.006187	100	-4.44018	0	7.27E-03	4.82E-04	1.48E-06	3.734993	100	-26.582	-24.3505	1.19E-02	4.25E-03	? #1407
17	10	G-41	20	6.80E-07	0.973504	100	47.38047	0	7.27E-03	5.01E-04	1.43E-06	3.621614	100	37.3225	-23.5223	1.19E-02	4.25E-03	? #1407
18	11	G-1133	10	3.18E-07	0.946672	100	-2.06668	0	7.27E-03	4.97E-04	7.61E-07	3.847432	100	-11.8122	-15.9851	1.19E-02	4.28E-03	? #1407
19	12	G-1134	10	3.21E-07	0.95575	100	-1.75094	0	7.27E-03	4.90E-04	7.65E-07	3.868173	100	-11.782	-15.7386	1.19E-02	4.28E-03	? #1407
20	13	G-40	5	1.60E-07	0.951586	100	-4.34185	0	7.27E-03	4.84E-04	3.76E-07	4.068642	100	-26.5101	-8.36835	1.19E-02	4.32E-03	? #1407
21	14	G-1135	5	1.55E-07	0.925439	100	-2.44595	0	7.26E-03	4.72E-04	3.96E-07	4.005541	100	-11.6544	-10.2006	1.19E-02	4.31E-03	? #1407
22	15	G-1136	3	9.51E-08	0.943515	100	-1.91586	0	7.27E-03	4.65E-04	2.51E-07	4.22484	100	-11.5918	-6.37386	1.19E-02	4.33E-03	? #1407
23	16	G-1137	3	9.41E-08	0.933944	100	-2.56998	0	7.26E-03	4.52E-04	2.50E-07	4.21918	100	-11.7434	-7.77837	1.19E-02	4.32E-03	? #1407
24	17	G-1138	100	3.40E-07	0.101087	100	-2.12443	0	7.27E-03	4.61E-04	7.93E-07	0.400937	100	-11.8914	-16.6841	1.19E-02	4.28E-03	? #1407
25	18	G-1139	100	3.39E-07	100	100	-2	0	7.27E-03	4.71E-04	7.93E-07	400	100	-11.89	-18	1.19E-02	4.29E-03	? #1407
26	18	END																
27	Drift Corrected																	
28	N	Name	Weight,	Beam Area	N (Sam)	-------	15N (Sam)	Nor	Ratio 1	Ratio 2	Beam Are	C (Sam)	-------	13C (Sam)	18O (Sam)	Ratio 1	Ratio 2	Status
29					%		DeltaAir					%		DeltaPDB	DeltaPDB			
30	1	G-1	100	6.83E-07	0.204413	100	7.373599	0	7.34E-03	4.57E-04	1.11E-06	0.561368	100	-9.06296	-23.9209	1.20E-02	4.24E-03	?

Sercon C&N v0

Fig. 22.37. Sercon prn text file opened with Excel.

Sercon C&N v1.xlsx

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1	Line	OurLabID	Amount	Area All N			Delta N-15				Area All C			Delta C-13				
2	1	G-1	100	6.83E-07	0	100	0	0	7.34E-03	4.57E-04	1.11E-06	0	100	0	0	1.20E-02	4.24E-03	? #1407
3	2	G-1	100	3.71E-07	0	100	0	0	7.34E-03	4.74E-04	6.35E-07	0	100	0	0	1.20E-02	4.27E-03	? #1407
4	3	G-1	100	5.04E-07	0	100	0	0	7.34E-03	4.74E-04	8.43E-07	0	100	0	0	1.20E-02	4.25E-03	? #1407
5	4	G-1	100	7.98E-07	0	100	0	0	7.34E-03	4.88E-04	1.27E-06	0	100	0	0	1.20E-02	4.24E-03	? #1407
6	5	G-1	100	1.64E-07	0	100	0	0	7.34E-03	4.83E-04	3.05E-07	0	100	0	0	1.20E-02	4.30E-03	? #1407
7	6	G-4	100	-2.47E-10	0	100	0	0	8.85E-03	2.90E-03	-4.51E-11	0	100	0	0	2.02E-02	1.46E-02	? #1407
8	7	G-1	100	3.35E-07	0	100	0	0	7.27E-03	4.51E-04	7.93E-07	0	100	0	0	1.19E-02	4.26E-03	? #1407
9	8	G-1	100	3.36E-07	100	100	-2	0	7.27E-03	4.66E-04	7.91E-07	400	100	-11.89	-18	1.19E-02	4.27E-03	? #1407
10	9	G-40	20	6.76E-07	1.01	100	-4.440175	0	7.27E-03	4.82E-04	1.48E-06	3.73	100	-26.58201	-24.351	1.19E-02	4.25E-03	? #1407
11	10	G-41	20	6.80E-07	0.97	100	47.380474	0	7.27E-03	5.01E-04	1.43E-06	3.62	100	37.3225	-23.522	1.19E-02	4.25E-03	? #1407
12	11	G-1133	10	3.18E-07	0.95	100	-2.066684	0	7.27E-03	4.97E-04	7.61E-07	3.85	100	-11.81219	-15.985	1.19E-02	4.28E-03	? #1407
13	12	G-1134	10	3.21E-07	0.96	100	-1.750942	0	7.27E-03	4.90E-04	7.65E-07	3.87	100	-11.78204	-15.739	1.19E-02	4.28E-03	? #1407
14	13	G-40	5	1.60E-07	0.95	100	-4.341854	0	7.27E-03	4.84E-04	3.76E-07	4.07	100	-26.5101	-8.3683	1.19E-02	4.32E-03	? #1407
15	14	G-1135	5	1.55E-07	0.93	100	-2.445953	0	7.26E-03	4.72E-04	3.96E-07	4.01	100	-11.6544	-10.201	1.19E-02	4.31E-03	? #1407
16	15	G-1136	3	9.51E-08	0.94	100	-1.915855	0	7.27E-03	4.65E-04	2.51E-07	4.22	100	-11.59175	-6.3739	1.19E-02	4.33E-03	? #1407
17	16	G-1137	3	9.41E-08	0.93	100	-2.569977	0	7.26E-03	4.52E-04	2.50E-07	4.22	100	-11.7434	-7.7784	1.19E-02	4.32E-03	? #1407
18	17	G-1138	100	3.40E-07	0.1	100	-2.124425	0	7.27E-03	4.61E-04	7.93E-07	0.4	100	-11.89141	-16.684	1.19E-02	4.28E-03	? #1407
19	18	G-1139	100	3.39E-07	100	100	-2	0	7.27E-03	4.71E-04	7.93E-07	400	100	-11.89	-18	1.19E-02	4.29E-03	? #1407
20																		

Sercon C&N v0

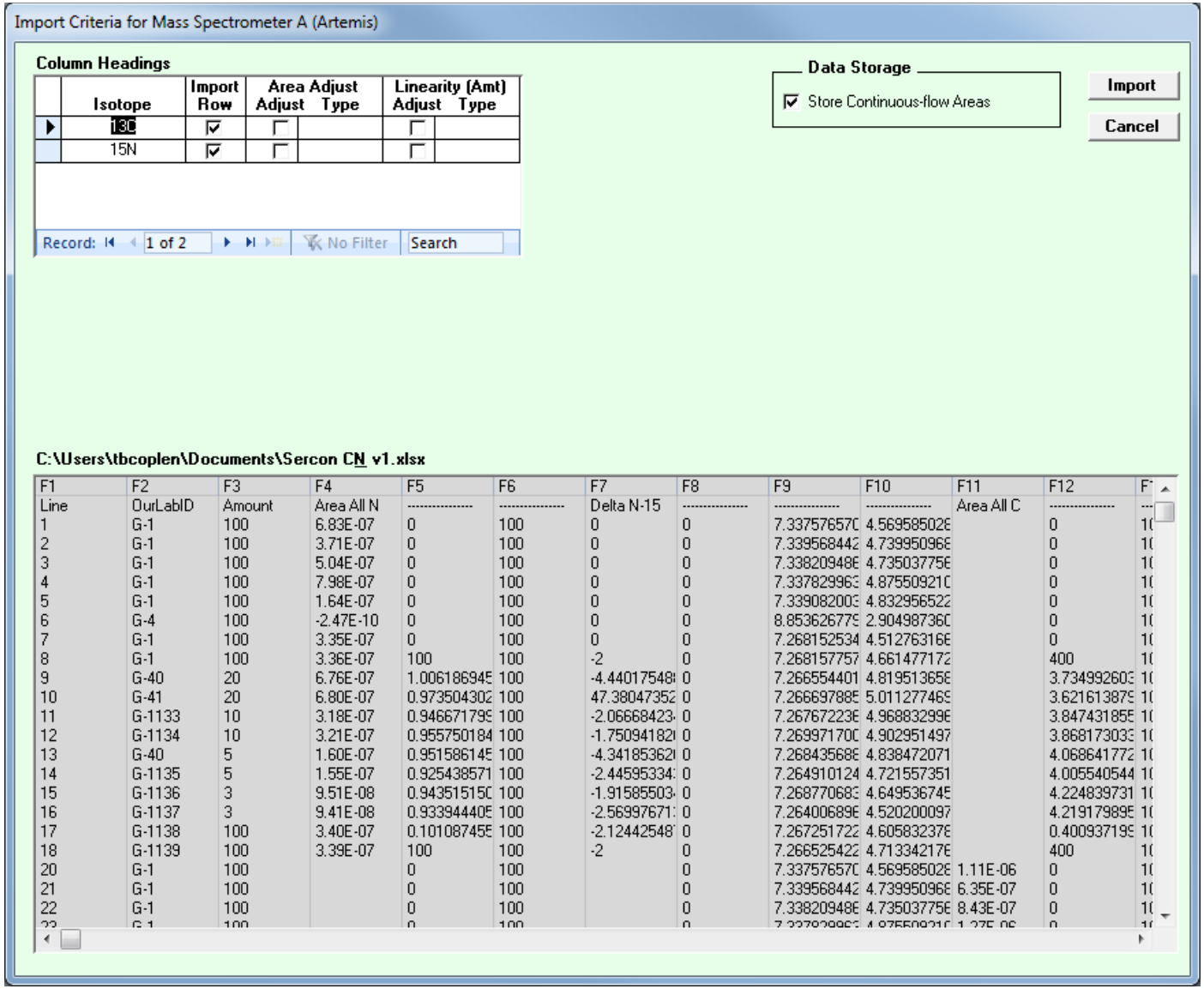
Fig. 22.38. Sercon Excel file after modification for importing using the LIMS Abbreviated import format.

Sercon C&N template.xlsx

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1	Line	OurLabID	Amount	Area All N			Delta N-15				Area All C			Delta C-13
2														
3														

Sercon C&N v0

Fig. 22.39. Sercon template for C&N data importing using the LIMS Abbreviated import format.



F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F12	F
Line	OurLabID	Amount	Area All N	----------	----------	Delta N-15	----------	----------	----------	Area All C	----------	---
1	G-1	100	6.83E-07	0	100	0	0	7.337576570	4.569585028		0	10
2	G-1	100	3.71E-07	0	100	0	0	7.339568442	4.739950968		0	10
3	G-1	100	5.04E-07	0	100	0	0	7.338209488	4.735037758		0	10
4	G-1	100	7.98E-07	0	100	0	0	7.337829963	4.875509210		0	10
5	G-1	100	1.64E-07	0	100	0	0	7.339082003	4.832956522		0	10
6	G-4	100	-2.47E-10	0	100	0	0	8.853626779	2.904987360		0	10
7	G-1	100	3.35E-07	0	100	0	0	7.268152534	4.512763168		0	10
8	G-1	100	3.36E-07	100	100	-2	0	7.268157757	4.661477172		400	10
9	G-40	20	6.76E-07	1.006186945	100	-4.440175481	0	7.266554401	4.819513658		3.734992603	10
10	G-41	20	6.80E-07	0.973504302	100	47.38047352	0	7.266697885	5.011277469		3.621613879	10
11	G-1133	10	3.18E-07	0.946671795	100	-2.066684234	0	7.267672238	4.968832998		3.847431855	10
12	G-1134	10	3.21E-07	0.955750184	100	-1.750941821	0	7.269971700	4.902951497		3.868173033	10
13	G-40	5	1.60E-07	0.951586145	100	-4.341853621	0	7.268435688	4.838472071		4.068641772	10
14	G-1135	5	1.55E-07	0.925438571	100	-2.445953341	0	7.264910124	4.721557351		4.005540544	10
15	G-1136	3	9.51E-08	0.943515150	100	-1.915855034	0	7.268770683	4.649536745		4.224839731	10
16	G-1137	3	9.41E-08	0.933944405	100	-2.569976711	0	7.264006898	4.520200097		4.219179895	10
17	G-1138	100	3.40E-07	0.101087455	100	-2.124425481	0	7.267251722	4.605823785		0.400937195	10
18	G-1139	100	3.39E-07	100	100	-2	0	7.266525422	4.713342176		400	10
20	G-1	100		0	100		0	7.337576570	4.569585028	1.11E-06	0	10
21	G-1	100		0	100		0	7.339568442	4.739950968	6.35E-07	0	10
22	G-1	100		0	100		0	7.338209488	4.735037758	8.43E-07	0	10

Fig. 22.40. The Import Criteria for Mass Spectrometer form for Sercon C&N samples.

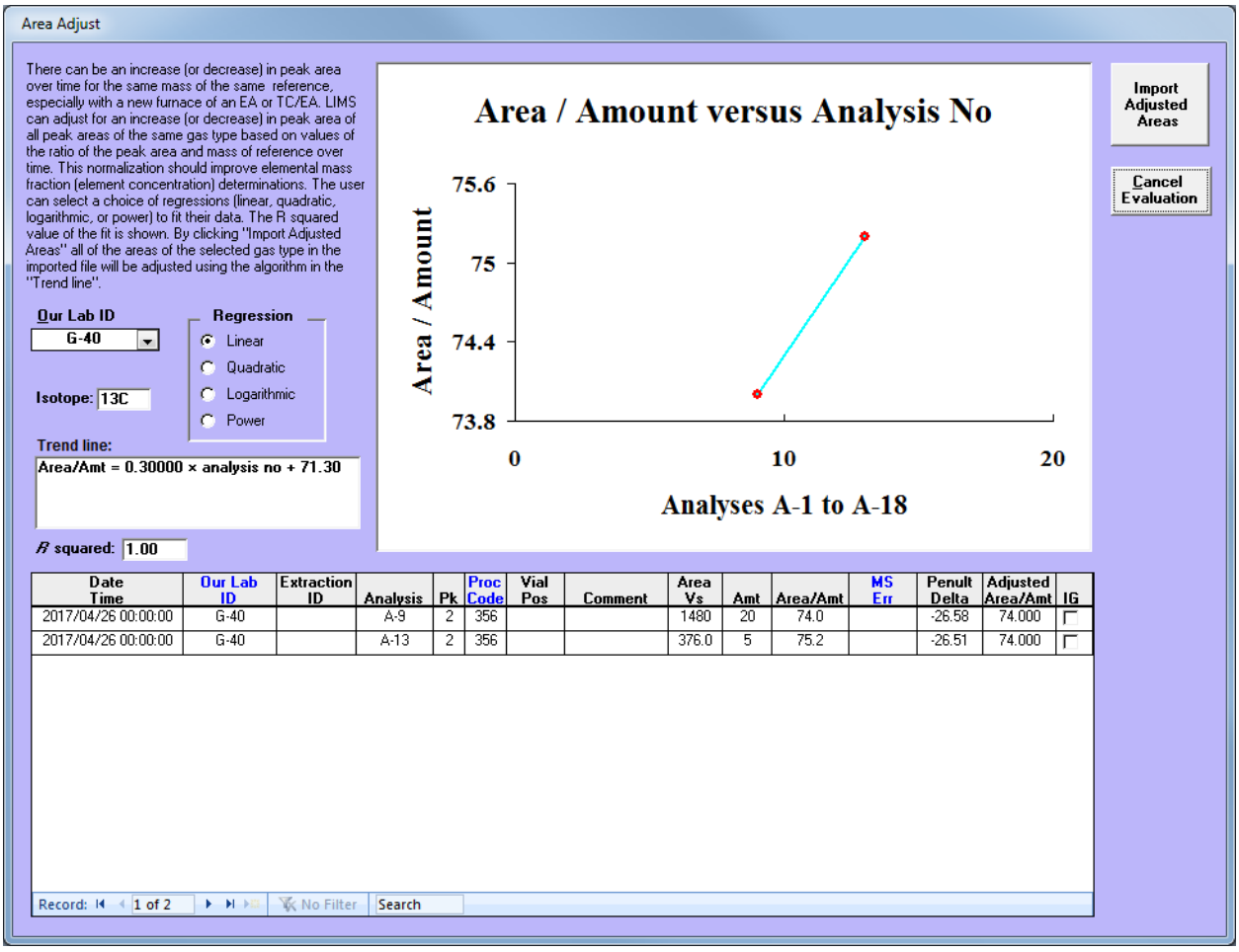


Fig. 22.41. The Area Adjust form showing analysis number versus CO_2 area / amount of standard for the Sercon C&N EA import.

⚠ Users need to remember that Sercon files do not have an analysis number. Therefore, if they are imported more than once, analyses will be replicated in LIMS. One way to avoid this conundrum is to add an "Analysis" column to each Excel file and populate with regularly increasing integers.

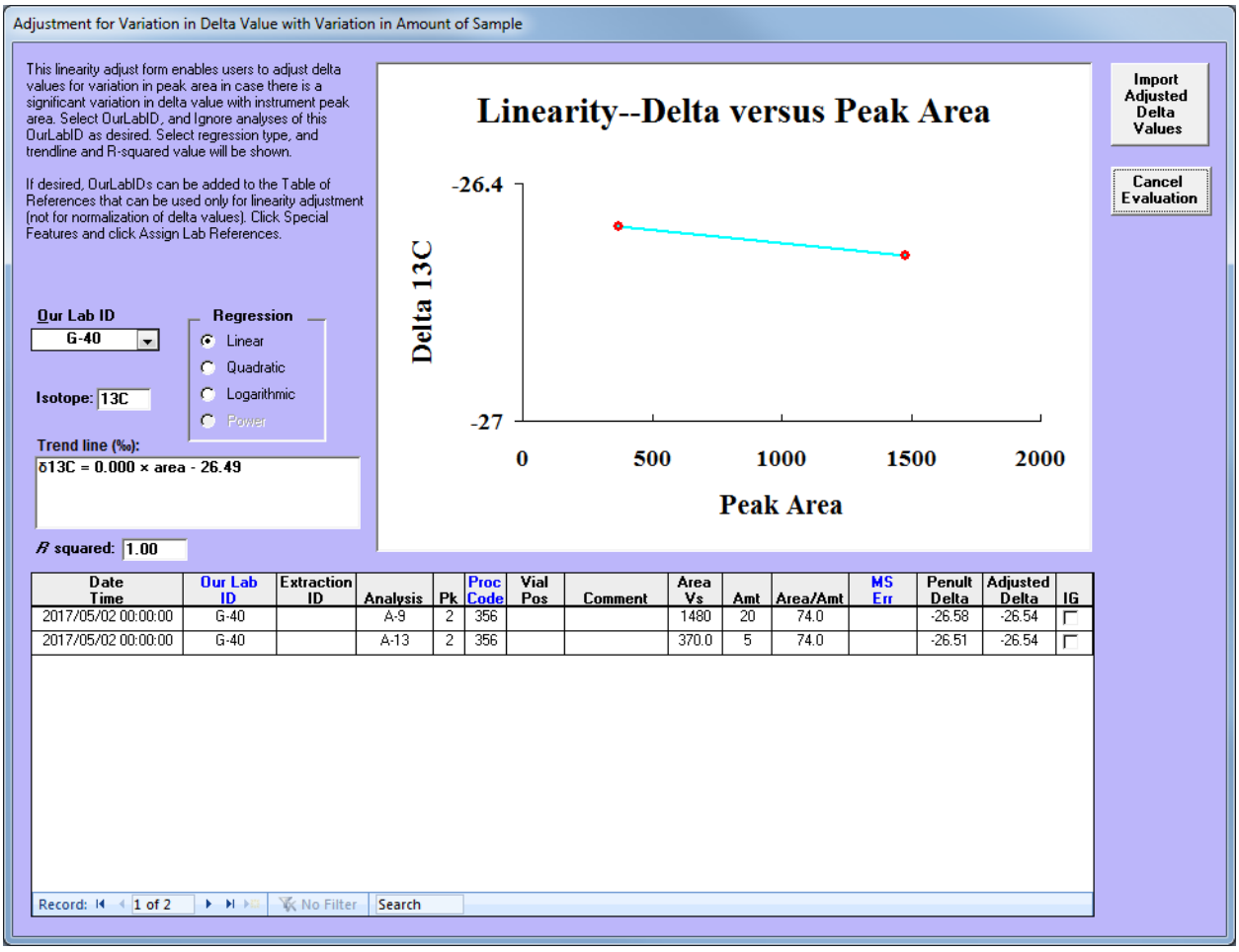


Fig. 22.42. The Adjustment for Variation in Delta Value with Variation in Amount of Sample (linearity adjustment) form for the Sercon import.

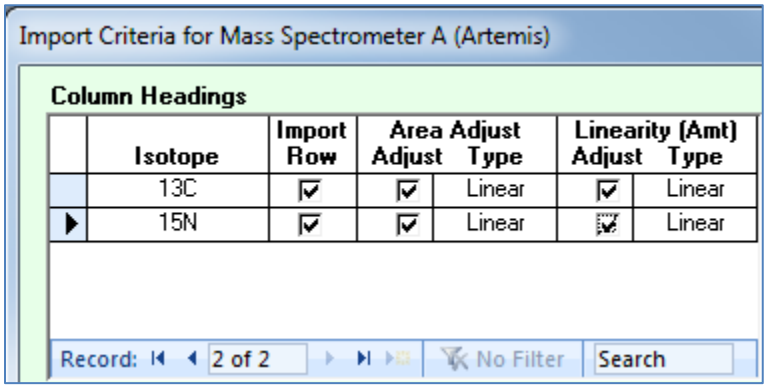


Fig. 22.43. Updated Column Headings in the Import Criteria of Mass Spectrometer form.

14. The “Store Continuous-flow Areas” check box is enabled, which is correct, so it can be retained as is.
15. These data are ready to import. Click “Import” and LIMS displays the informational message in Figure 22.19.
16. Click “OK” and LIMS imports the analyses and displays a summary message (Fig. 22.44). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking “Special Features” then “ImportLog.”
17. Click “OK” and this completes importing of the Sercon C&N EA example file “Sercon C&N v1.xlsx.”

Normalization of the $\delta^{13}C$ and $\delta^{15}N$ results with determination of element mass fractions (element concentrations) is the next step and is discussed in Section 24.

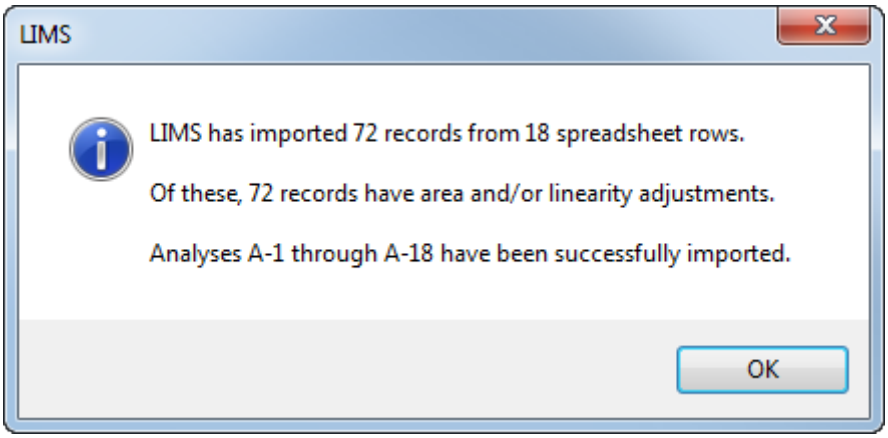


Fig. 22.44. LIMS Sercon C&N EA sample import summary.

22.7 Importing Data from a Carbon-14 Scintillation Counter

This example assumes that LIMS is connected to the “Lakes_Backend_DB.accdb” backend database that was set up in Section 4.8 and that had a carbon-14 counter named “Beta” added to it in Section 17.7. In the event the “Lakes_Backend_DB.accdb” backend database with “Beta” is not available, a backend database for use in this section can be extracted from a file named “Beta_14C_Backend_DB.zip” that is provided in a folder named “Section 22.7” in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this section the reader will create a carbon-14 data file named "Samples_for_carbon-14.xlsx" and this file is provided in the folder named "22.7 Carbon-14" for reference. Before proceeding, the reader should be fully familiar with the information in Section 17.1. In this example, three samples have arrived at the laboratory for carbon-14 analysis. They are:

TG1A1
TG1A2
TG1A3

Create a new project by manually logging in these samples (see Section 7.3) using the medium code 140 for ^{14}C-bearing material. Suppose the project created is G-1480 to G-1482. Create the Excel file having columns for line, Our Lab IDs, and ^{14}C value. From Table 17.1, the column heading for ^{14}C data is "C-14." The Excel file should appear as shown in Figure 22.45. To import this file:

1. On the main page click "Import Data from Mass Specs" and the Analysis Import Format form will open (Fig. 19.12 or similar).
2. Select "B --> Beta" the carbon-14 counter.
3. Click "Import."
4. Navigate to the Excel file just created, click "Select" and LIMS will prompt for the analysis date (Fig. 22.16). The suggested date will be today's date.
5. Enter the desired date and click ""OK" (Fig. 22.16), and LIMS provide an informational message (Fig. 22.46).
6. Click "OK" and LIMS provide an import summary message (Fig. 22.47). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking "Special Features" then "ImportLog."
7. Click "OK" and that completes importing the carbon-14 data from Beta--Carbon-14.

The next step is to apply data normalization, which is discussed in Section 24.

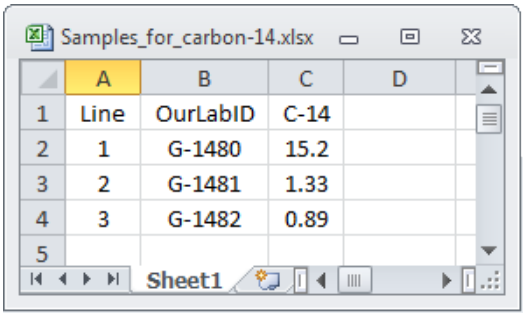


Fig. 22.45. LIMS Abbreviated import format Excel file with carbon-14 results.

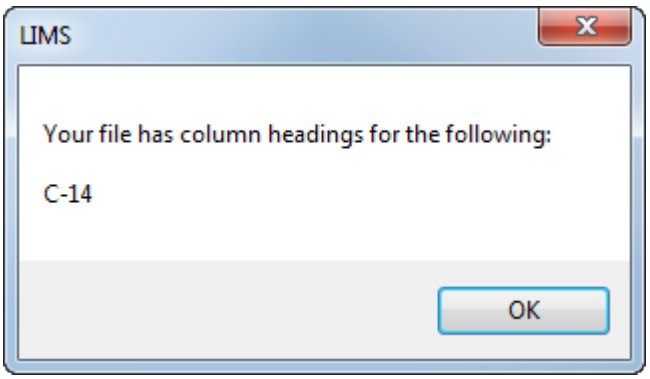


Fig. 22.46. LIMS isotope informational message.

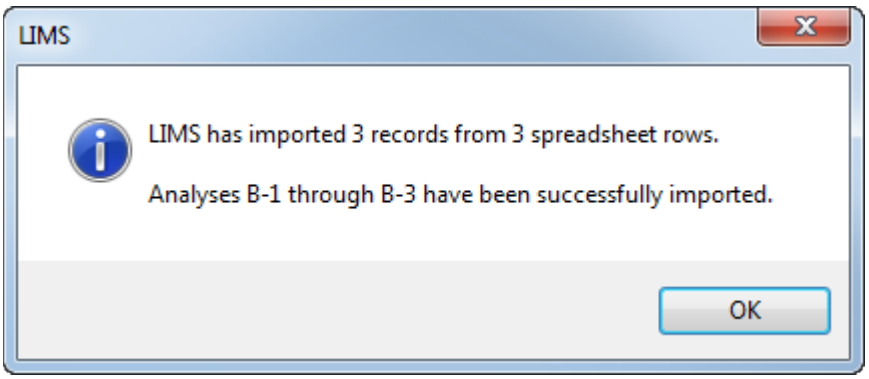


Fig. 22.47. LIMS summary import message.

23 Importing Data from a Mass Spectrometer having the "LIMS Default" Import Format

23.1 Importing Continuous-flow Results

This example assumes that LIMS is connected to the "Lakes_Backend_DB.accdb" backend database that was set up in Section 4.8 and that had an IRMS named "Zeus" with the LIMS Default import format added to it in Section 18. In the event the "Lakes_Backend_DB.accdb" backend database with "Zeus" is not available, a backend database for use in this section can be extracted from a file named "LIMS_Default_Zeus_Backend_DB.zip" that is provided in a folder named "Section 23" in the files that accompany this manual. Section 4.4 provides instructions for connecting to a different backend database.

In this example, a file named "Zeus_CF.accdb," which is found in the folder "Section 23" in the files that accompany this manual, has the LIMS Default format. To import this file:

1. On the main page click "Import Data from Mass Specs" and the Analysis Import Format form will open (Fig. 19.12 or similar).
2. Select "Z --> Zeus" the IRMS having a LIMS Default import format.
3. Click "Import."
4. Navigate to "Section 23" and select "Zeus_CF.accdb" and, depending upon the location of the file, a Microsoft Access Security Notice may appear (Fig. 21.1). If it does appear, click "Open." The Import Criteria for Mass Spectrometer form should open and is nearly identical to Figure 21.2. The upper left pane of this form contains the "Isotope" and rows for check boxes for importing, area adjust, and linearity adjust. The upper right panel has check boxes to enable importing of continuous-flow areas and importing of continuous-flow reference injection data. The lower panel displays data in the Microsoft Access file being imported.
5. There can be an increase (or decrease) in peak area over time for the same mass of the same reference with an EA or TC/EA. LIMS can adjust for an increase (or decrease) in peak area of all peak of the same gas type based on values of the ratios of the peak areas and masses of a selected reference over time. This normalization should improve elemental mass fraction (element concentration) determinations. To perform this evaluation, click the "Area Adjust" check box in the row having "13C" in the "Isotope" column and LIMS will display the Area Adjust form, which is nearly identical to Figure 21.3.
6. The Area Adjust form (nearly identical to Fig. 21.3) shows a plot of analysis number versus CO2 area of the reference G-40 divided by the mass of G-40. The user can select a choice of regressions (linear, quadratic, logarithmic, or power) to fit their data. The *R* squared value of the fit is shown. By clicking "Import Adjusted Areas" all of the CO_2 areas in the imported file will be adjusted (normalized) using the algorithm in the

"Trend line." The first analysis (Z-48050) shows an anomalously high value for the ratio Area / Amount. The first sample in any run may be anomalous and is routinely ignored in many laboratories. To ignore the data point for Z-48050, click the check box in the row for analysis Z-48050 and the plot will be updated immediately.

7. The linear plot has an *R* squared value of 0.79 and appears reasonable. Therefore, click "Import Adjusted Areas" and LIMS will notify the user that all peak areas will be updated with the linear regression. If a user changes their mind, the file can be reimported.
8. Click "OK."
9. To evaluate the so-called "Linearity" from a plot of peak area versus δ^{13}C values of G-40, click the "Linearity (Amt)" check box for the row having the isotope "13C," and LIMS will display the Adjustment for Variation in Delta Value with Variation in Amount of Sample form (nearly identical to Fig. 21.5).
10. Over the peak area interval of 11 to 102 Vs, the δ^{13}C value of G-40 (USGS40) remains relatively constant with an *R* squared value of 0.07. There is no justification to apply a linearity adjustment. Therefore, click "Cancel Evaluation."
11. Perform the same steps for "15N." Click the Area Adjust check box for "15N," and the Area Adjust form open.
12. Ignore analysis "Z-48050" as done above by clicking the "IG" check box for this analysis.
13. The *R* squared value is 0.16 so that there is no justification to apply an adjustment. Click "Cancel Evaluation."
14. Evaluate the need for a linearity adjustment by clicking the "Linearity (Amt)" check box for the isotope "15N," and LIMS prompts the user with the message shown in Figure 21.6 to perform the Area Adjust first. Because in the step above, there was no justification to perform an Area Adjust owing to the low *R* squared value, click "No," and LIMS will display the Adjustment for Variation in Delta Value with Variation in Amount of Sample form.
15. Note that the *R* squared value is very low, 0.08. Therefore, click "Cancel Evaluation" and the updated upper portion of the Import Criteria for Mass Spectrometer form is shown in Figure 21.7.
16. The "Store Continuous-flow Areas" check box is enabled, which is correct, so it can be retained as is. The "Import CF Reference Injection Peaks" check box is not checked, but can be checked if the user prefers to import continuous-flow reference injection peak data. In this example, retain it unchecked.
17. These data are ready to import. Click "Import" and LIMS displays a message similar to that of Figure 21.8.
18. Click "OK;" LIMS imports the results and provides a summary message (Fig. 23.1). If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and

notify the user with a dialog box. The import log is opened by clicking “Special Features” then “ImportLog.”

19. Click “OK” and this completes the importing of the Access file “Zeus_CF.accdb.”

Normalization of the $\delta^{13}C$ and $\delta^{15}N$ results and determinations of element mass fractions (element concentrations) is the next step, and they are discussed in Section 24.

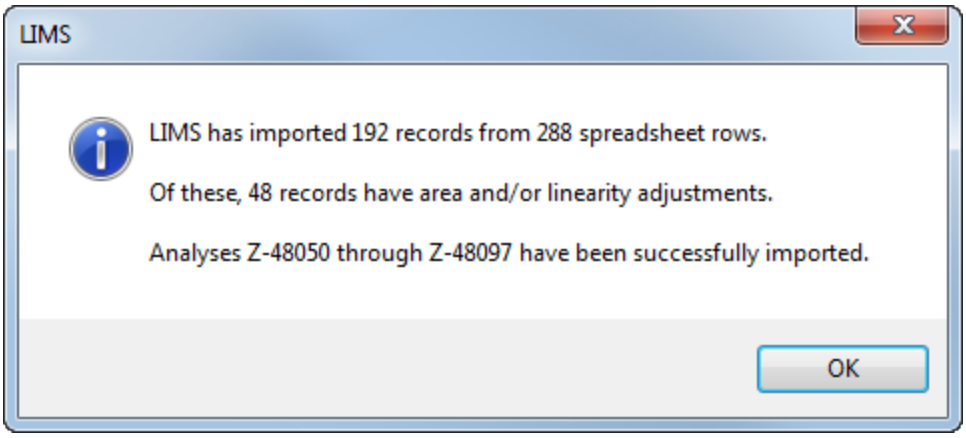


Fig. 23.1. LIMS continuous-flow import summary.

23.2 Importing Dual-inlet Results

Importing dual-inlet results is straight forward. In the following example, an Access file named “Zeus_DI.accdb,” which is found in the folder “Section 23” in the files that accompany this manual, has the LIMS Default format. To import this file:

1. On the main page click “Import Data from Mass Specs” and the Analysis Import Format form will open (Fig. 19.12 or similar).
2. Select “Z --> Zeus” the LIMS Default IRMS.
3. Click “Import.”
4. Navigate to “Section 23” and select “Zeus_DI.accdb`” and, depending upon the location of the file, a Microsoft Access Security Notice may appear (Fig. 21.1). If it does appear, click “Open.”
5. LIMS will import the file provide the summary message shown in Figure 23.2. If there are invalid Our Lab IDs or invalid procedure codes, LIMS will log the errors and notify the user with a dialog box. The import log is opened by clicking “Special Features” then “ImportLog.”
6. Click “OK” and this completes importing of the dual-inlet file.

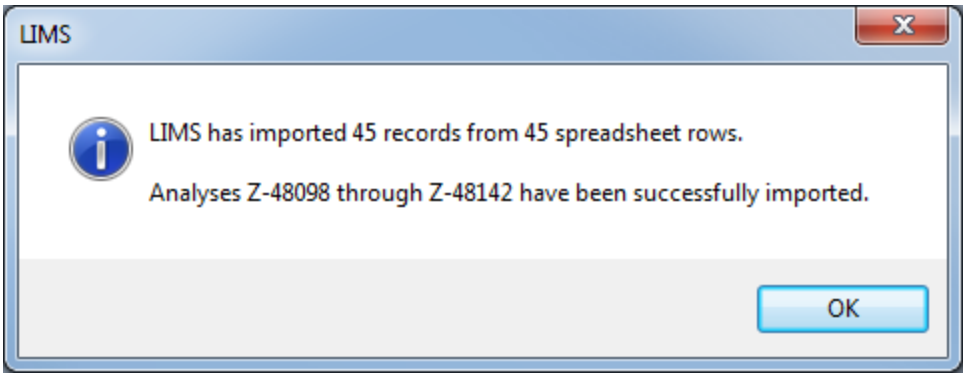


Fig. 23.2. LIMS dual-inlet import summary.

Normalization of these dual inlet results is the next step and is discussed in Section 24.

24 Normalization and Determination of Element Mass Fractions (Concentrations)

24.1 General Information

Normalization of isotope-delta results in LIMS is based on Coplen[4] and analytical methods used in LIMS are documented in Appendix E. It is recommended that samples be analyzed with secondary internationally distributed, isotopic reference materials, if available, of a similar matrix whose delta values bracket the samples of interest. This has been termed the Identical Treatment principle (IT principle) [5] and is discussed by Brand et al.[7] The delta value of a sample is determined by linear least squares regression by LIMS, that is by using the relation:

$$y = mx + b$$

In LIMS, y is termed the **final delta**, m the **expansion coefficient**, x the **penultimate delta**, and b the **additive correction factor**. Thus:

final delta = expansion coefficient × penultimate delta + additive correction factor

In addition to linear least squares regression, users can apply a linear drift correction over the period of analytical run and users can apply a blank correction, which may be important in some EA and TC/EA analyses; these are termed the **hourly drift correction** and the **blank correction**, respectively, in LIMS. When all parameters are applied by the user, a final delta is calculated using the relation:

final delta = (((penultimate delta + blank correction) + hourly drift correction) × expansion coefficient) + additive correction factor

24.2 The Data Normalization form

Once analytical results from a mass spectrometer have been imported, they are considered to be "in progress." They remain in progress until they are normalized to internationally accepted isotope-delta scales, such as the VSMOW-SLAP scale for δ^2H measurements, evaluated, and "stored" to projects. Samples having two isotopes will need to be normalized twice, one after the other. The user can click "Apply Data Normalization" on the main page and the Data Normalization form (Fig. 24.1) opens. This form enables a user to select a mass spectrometric range of analyses and isotope to perform normalization. In the case of δ^{18}O measurements, users can normalize δ^{18}O values of water samples separately from δ^{18}O measurements of all other oxygen-bearing materials. This feature retains the strategy used at the University of Chicago (and other universities) since the 1950s to normalize carbonates and waters using different algorithms. LIMS is able to maintain two normalization scales for water and for other oxygen-bearing substances by assigning them different procedure codes. Procedure codes between 800 and 809

are used for water (Fig. 6.3) and codes between 810 and 899 are used for all other oxygen-bearing materials (all samples having an Our Lab ID prefix of C, G, J, N, R, and S). This form will display the analysis number, peak number, date-time of the analysis, the Our Lab ID, vial position (also called the port), and name or value of the reference. Once normalization has been completed, the correction coefficients (expansion coefficient, additive correction factor, etc.) will be shown in the "Correction Coefs" column. The last column is the "Range" column and it displays any LIMS Range Markers indicating the range in analysis numbers to which a set of correction coefficients apply.

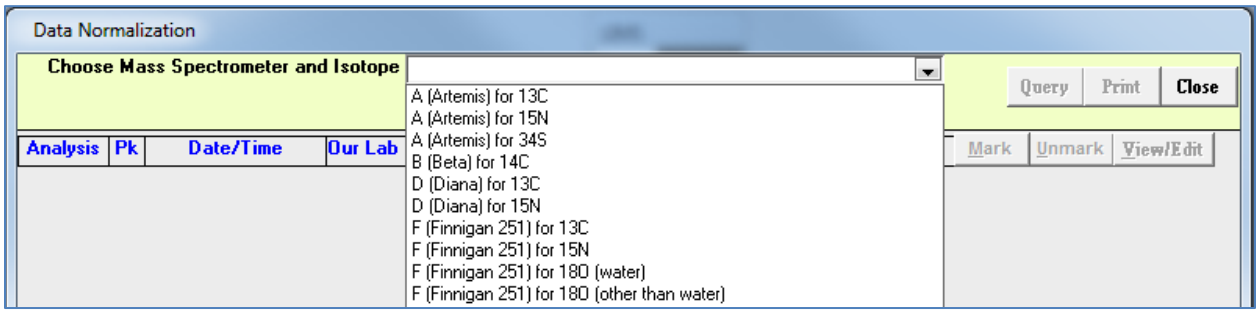


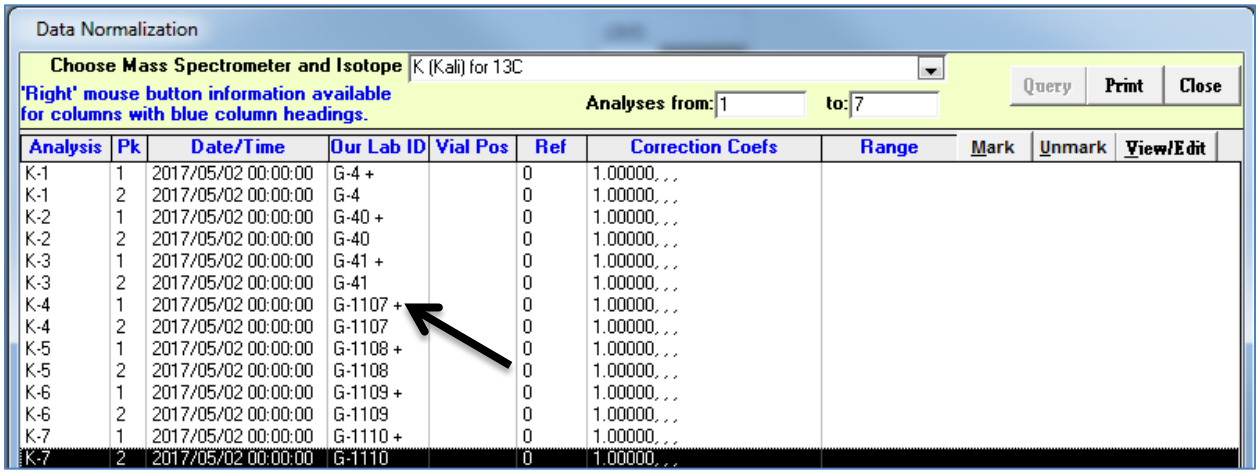
Fig. 24.1. The Data Normalization form.

Upon selecting a mass spectrometer and isotope for normalization, and clicking "Query," either of two possibilities can occur:

- The range of analyses will contain analyses that can be normalized, and these are indicated by a plus symbol "+" following the Our Lab ID as shown in Figure 24.2.
- The range of analyses will not contain analyses that can be normalized (Fig 24.3). In this case, the range of analysis numbers may need to be expanded or the isotope may be incorrect.

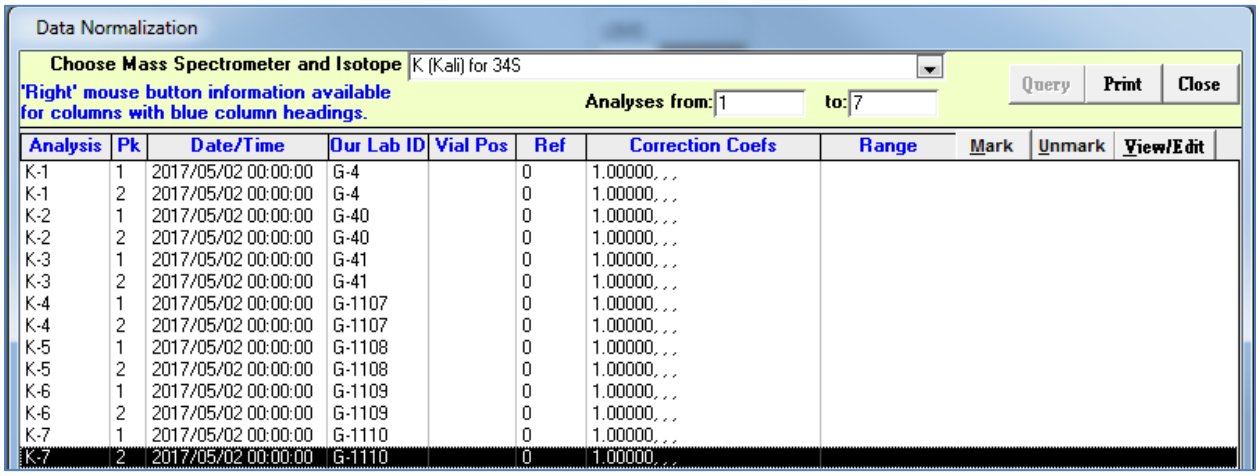
In the event that a range of analyses does not contain any references from the LIMS table of references, the expansion coefficient and additive correction factor are assigned using this form. For example, considering the following:

1. On the Data Normalization form select "B (Beta--Carbon-14) for 14C," click "Query" and LIMS displays Figure 24.4.
2. The last analysis (B-3) is highlighted and the Our Lab ID has a "+" following G-1212. Therefore, double-click on this analysis, and LIMS displays the message that no reference sample is found in the selected range (Fig. 25.5), which is correct because no carbon-14 references have been added to the Lakes Isotope Laboratory database.
3. The final carbon-14 value = 1 × penultimate carbon-14 value + 0. The expansion coefficient will be 1 and the additive correction factor will be 0. To enter these values



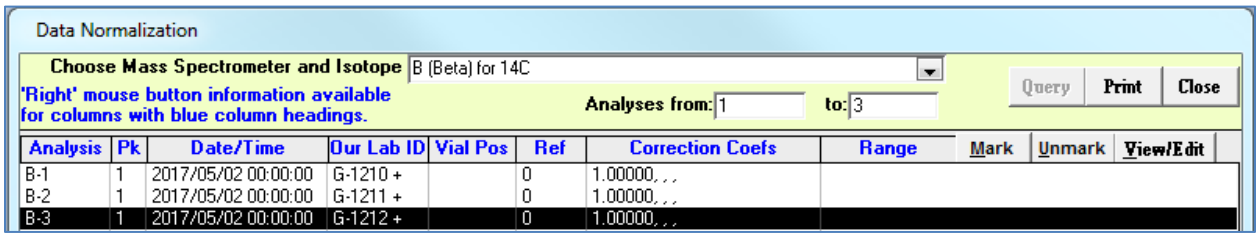
Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Ref	Correction Coefs	Range
K-1	1	2017/05/02 00:00:00	G-4 +		0	1.00000, , ,	
K-1	2	2017/05/02 00:00:00	G-4		0	1.00000, , ,	
K-2	1	2017/05/02 00:00:00	G-40 +		0	1.00000, , ,	
K-2	2	2017/05/02 00:00:00	G-40		0	1.00000, , ,	
K-3	1	2017/05/02 00:00:00	G-41 +		0	1.00000, , ,	
K-3	2	2017/05/02 00:00:00	G-41		0	1.00000, , ,	
K-4	1	2017/05/02 00:00:00	G-1107 +		0	1.00000, , ,	
K-4	2	2017/05/02 00:00:00	G-1107		0	1.00000, , ,	
K-5	1	2017/05/02 00:00:00	G-1108 +		0	1.00000, , ,	
K-5	2	2017/05/02 00:00:00	G-1108		0	1.00000, , ,	
K-6	1	2017/05/02 00:00:00	G-1109 +		0	1.00000, , ,	
K-6	2	2017/05/02 00:00:00	G-1109		0	1.00000, , ,	
K-7	1	2017/05/02 00:00:00	G-1110 +		0	1.00000, , ,	
K-7	2	2017/05/02 00:00:00	G-1110		0	1.00000, , ,	

Fig. 24.2. Example of a mass spectrometer, range, and isotope that does shows analyses that can be normalized. Each analysis having peak number of 1 (a $\delta^{13}C$ analysis) can be normalized as indicated by "+" following the Our Lab ID.



Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Ref	Correction Coefs	Range
K-1	1	2017/05/02 00:00:00	G-4		0	1.00000, , ,	
K-1	2	2017/05/02 00:00:00	G-4		0	1.00000, , ,	
K-2	1	2017/05/02 00:00:00	G-40		0	1.00000, , ,	
K-2	2	2017/05/02 00:00:00	G-40		0	1.00000, , ,	
K-3	1	2017/05/02 00:00:00	G-41		0	1.00000, , ,	
K-3	2	2017/05/02 00:00:00	G-41		0	1.00000, , ,	
K-4	1	2017/05/02 00:00:00	G-1107		0	1.00000, , ,	
K-4	2	2017/05/02 00:00:00	G-1107		0	1.00000, , ,	
K-5	1	2017/05/02 00:00:00	G-1108		0	1.00000, , ,	
K-5	2	2017/05/02 00:00:00	G-1108		0	1.00000, , ,	
K-6	1	2017/05/02 00:00:00	G-1109		0	1.00000, , ,	
K-6	2	2017/05/02 00:00:00	G-1109		0	1.00000, , ,	
K-7	1	2017/05/02 00:00:00	G-1110		0	1.00000, , ,	
K-7	2	2017/05/02 00:00:00	G-1110		0	1.00000, , ,	

Fig. 24.3. Example of a mass spectrometer, range, and isotope that does not show analyses to normalize.



Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Ref	Correction Coefs	Range
B-1	1	2017/05/02 00:00:00	G-1210 +		0	1.00000, , ,	
B-2	1	2017/05/02 00:00:00	G-1211 +		0	1.00000, , ,	
B-3	1	2017/05/02 00:00:00	G-1212 +		0	1.00000, , ,	

Fig. 24.4. The Data Normalization form with analyses of Beta, the carbon-14 counter .

click “Mark,” and the Expansion Coefficient Entry form open (Fig. 24.6).

4. Accept the entry of “1.00000” and click “OK,” and LIMS opens the Correction Factor Entry dialog box (Fig. 24.7).
5. Enter “0,” click “OK,” and LIMS adds “Corrections Coefficients” and updates the Range Marker to “1.000 – 3; 1.00000*pd+0.0” in the “Range” column (Fig. 24.8). The components of the “Correction Coefs” and “Range” are identified in Figure 24.9.

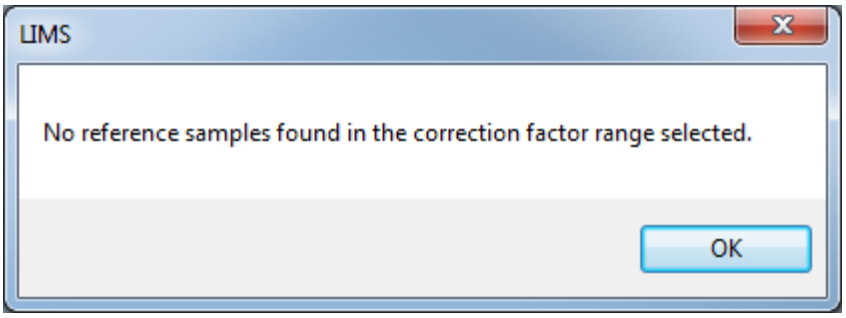


Fig. 24.5. LIMS indication that no reference exists in the selected range.

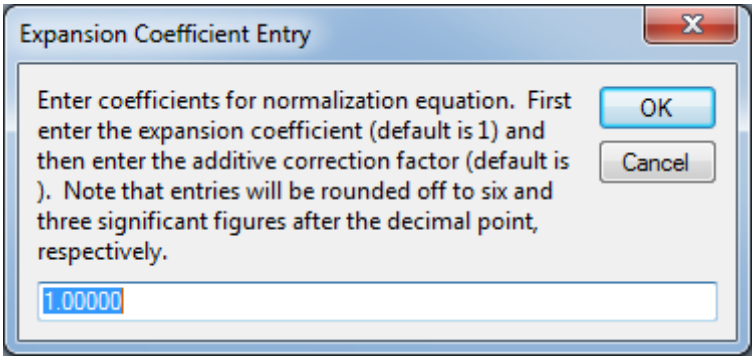


Fig. 24.6. Expansion Coefficient Entry dialog box.

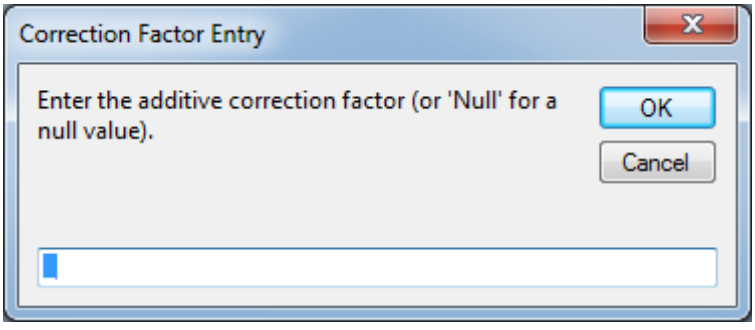


Fig. 24.7. Correction Factor Entry dialog box.

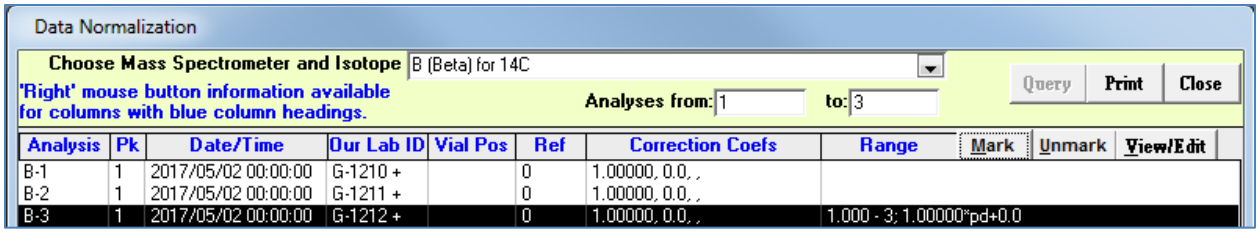


Fig. 24.8. Updated Range Marker.

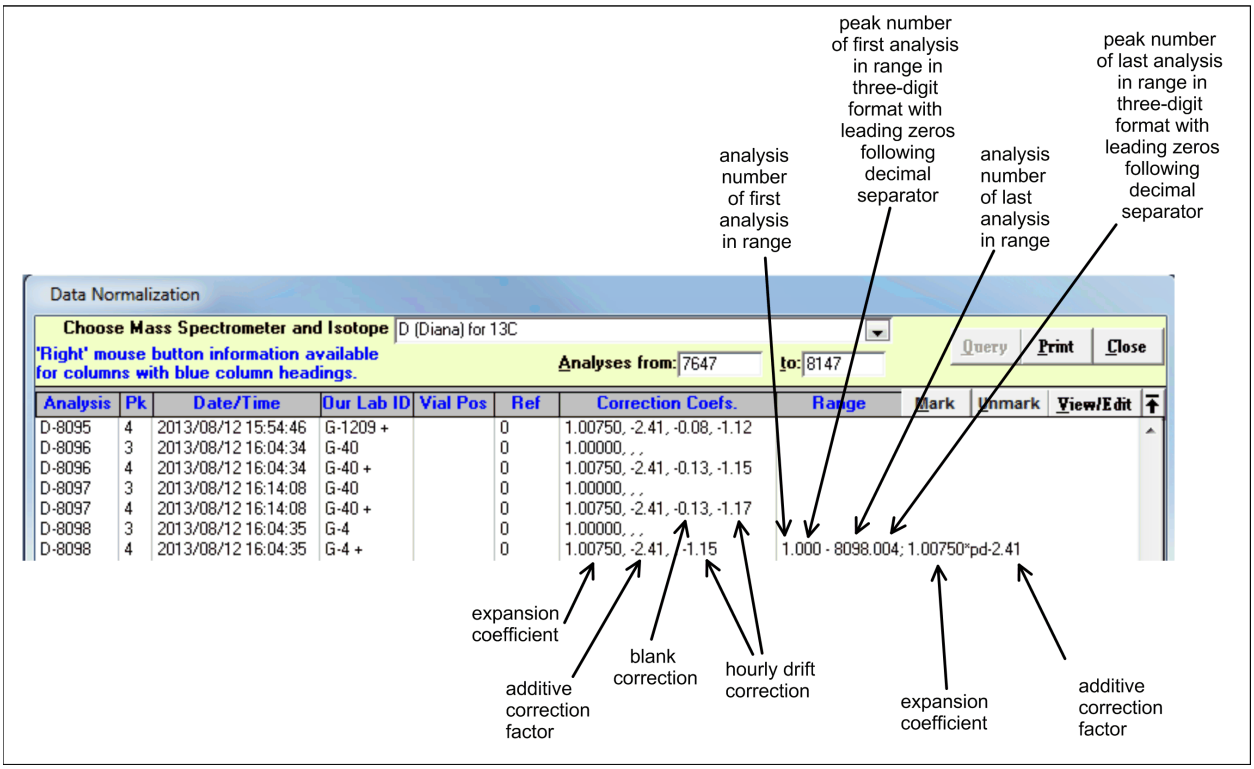


Fig. 24.9. Example of correction coefficients and the LIMS Range Marker. Note that G-4 does not have a blank correction value in this example because G-4 is a blank. The order of correction coefficients ("Correction Ceofs.") is expansion coefficient, additive correction factor, blank correction, and hourly drift correction, except for sample blanks, in which case the blank correction is null. In the range marker "pd" is penultimate delta.

The "Unmark" button is used to delete a range marker. Deleting a range marker does not delete any analyses from LIMS. If either the expansion coefficient or the additive correction factor needs to be updated for a range of analyses not having references, the range marker would be deleted and recreated by clicking "Mark;" the updated expansion coefficient and additive correction factor would then be entered.

The “View/Edit” button opens the Normalization Equation Coefficients form, which is discussed in the next section. This completes the normalization of these carbon-14 results and the next step is to evaluate carbon-14 results (Section xx).

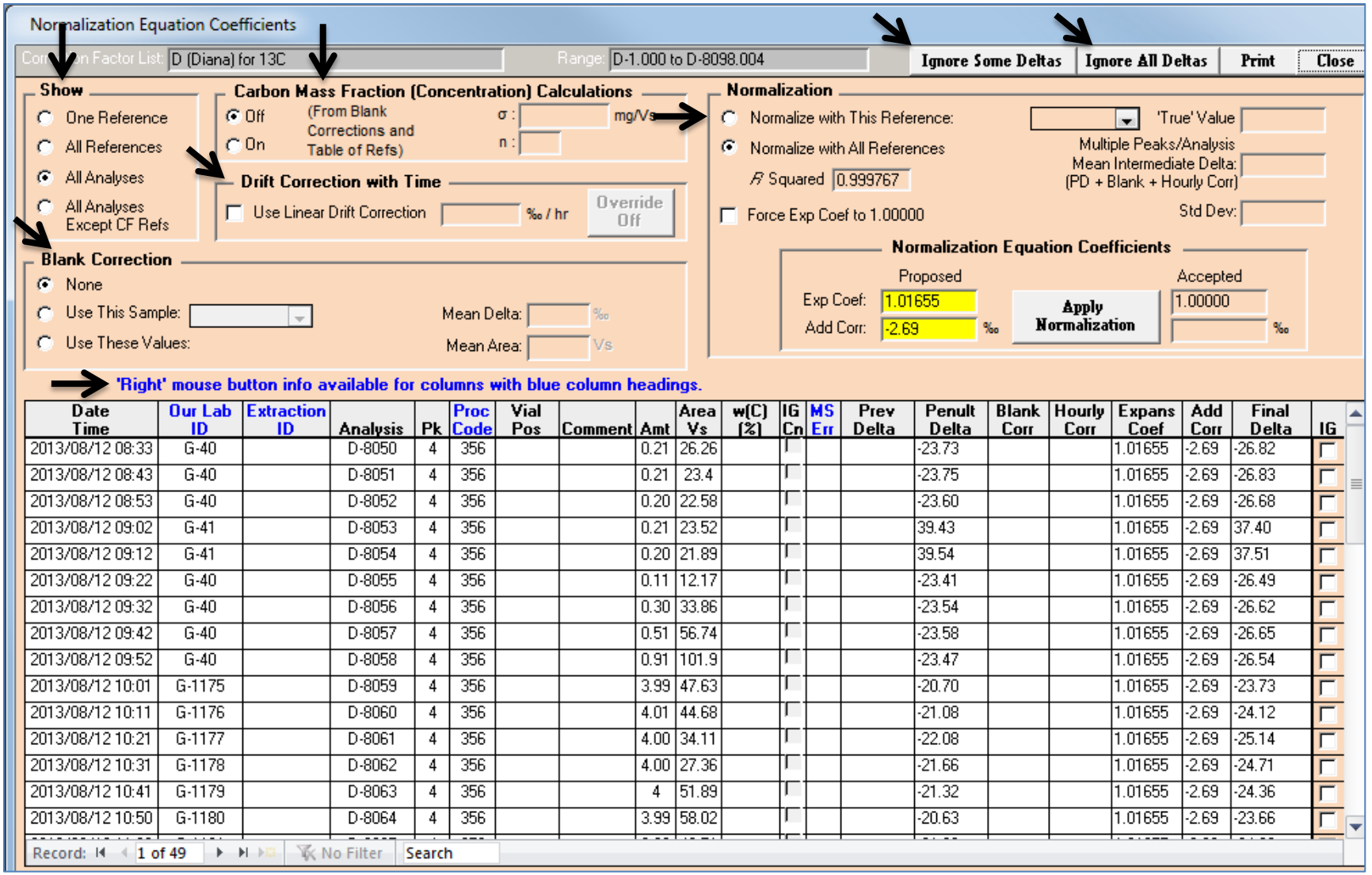
24.3 Normalizing Results using the Normalization Equation Coefficients form

The Normalization Equation Coefficients form is one of the most useful forms in LIMS. To demonstrate its use

1. On the main page click “Apply Data Normalization” and the Data Normalization form will open (Fig. 24.1).
2. Select “D (Diana) for 13C,” and LIMS will enter the last 500 analyses in the “Analyses from” and “to” fields.
3. Click “Query” and LIMS will display analyses D-8050 to D-8098.
4. Double-click on the last analysis that has a “+” symbol following the Our Lab ID value, which is peak 4 of analysis D-8098, and the Normalization Equation Coefficients form will open.
5. LIMS may prompt that it will determine best fitting normalization equation coefficients. Click “OK” and the Normalization Equation Coefficients form should appear as shown in Figure 24.10.

The “Show” panel in the upper left of the form enables the user to show one reference, all references, all analyses, or all analyses except continuous-flow reference injection analyses that might have been imported. The Mass Concentration Calculations panel labelled “Carbon Mass Fraction (Concentration) Calculations” is discussed in Section 24.6. The “Drift Correction with Time” panel is discussed in Section 24.4. Corrections for sample blank are made using the controls in the “Blank Correction” panel, which is discussed in Section 22.5. The lower panel in the Normalization Equation Coefficients form (Fig. 24.10) displays information about each analysis:

- The date-time of each analysis (“Date Time”)
- The “Our Lab ID”
- The “Extraction ID,” which is also known as the Aliquot ID
- The mass spectrometric analysis number consisting of the mass spectrometer prefix (code), a hyphen, and the integer analysis number (“Analysis”)
- The peak number (“Pk”)
- The procedure code (see Section 6.4) (“Proc Code”)
- The vial position, which is also known as the Port (“Vial Pos”)
- A “Comment”



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(C) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2013/08/12 08:33	G-40		D-8050	4	356			0.21	26.26					-23.73			1.01655	-2.69	-26.82	
2013/08/12 08:43	G-40		D-8051	4	356			0.21	23.4					-23.75			1.01655	-2.69	-26.83	
2013/08/12 08:53	G-40		D-8052	4	356			0.20	22.58					-23.60			1.01655	-2.69	-26.68	
2013/08/12 09:02	G-41		D-8053	4	356			0.21	23.52					39.43			1.01655	-2.69	37.40	
2013/08/12 09:12	G-41		D-8054	4	356			0.20	21.89					39.54			1.01655	-2.69	37.51	
2013/08/12 09:22	G-40		D-8055	4	356			0.11	12.17					-23.41			1.01655	-2.69	-26.49	
2013/08/12 09:32	G-40		D-8056	4	356			0.30	33.86					-23.54			1.01655	-2.69	-26.62	
2013/08/12 09:42	G-40		D-8057	4	356			0.51	56.74					-23.58			1.01655	-2.69	-26.65	
2013/08/12 09:52	G-40		D-8058	4	356			0.91	101.9					-23.47			1.01655	-2.69	-26.54	
2013/08/12 10:01	G-1175		D-8059	4	356			3.99	47.63					-20.70			1.01655	-2.69	-23.73	
2013/08/12 10:11	G-1176		D-8060	4	356			4.01	44.68					-21.08			1.01655	-2.69	-24.12	
2013/08/12 10:21	G-1177		D-8061	4	356			4.00	34.11					-22.08			1.01655	-2.69	-25.14	
2013/08/12 10:31	G-1178		D-8062	4	356			4.00	27.36					-21.66			1.01655	-2.69	-24.71	
2013/08/12 10:41	G-1179		D-8063	4	356			4	51.89					-21.32			1.01655	-2.69	-24.36	
2013/08/12 10:50	G-1180		D-8064	4	356			3.99	58.02					-20.63			1.01655	-2.69	-23.66	

Fig. 24.10. The Normalization Equation Coefficients form. Normalization coefficients are determined using two-point normalization with G-40 and G-41.

- The amount of sample (“Amt”)
- The continuous-flow area, which is the sum of the areas of the *m*/*z* values of the gas; also call the Area All (“Area Vs”).
- The mass fraction of the element [*e.g.* symbol *w*(C) for carbon] (“w(C) (%)”).
- Check boxes to enable to user to ignore an analysis for calculating mass fraction of an element (“IG Cn”)
- The mass spectrometric error code (“MS Err”)
- The imported delta value in the case that linearity adjustments were performed to determine updated penultimate delta values (“Prev Delta”)
- The penultimate delta value (“Penult Delta”)
- The blank correction value (“Blank Corr”)
- The hourly drift correction value (“Hourly Corr”)
- The expansion coefficient (“Expans Coef”)
- The additive correction factor (“Add Corr”)
- The final delta value calculated using the equations in Section 24.1 (“Final Delta”)
- A check box to enable the user to ignore the analysis in all isotope-delta calculations (“IG”). The analysis can still be used in mass fraction calculations (unless the “IG Cn” check box is enabled).
- In the situation that there are multiple peaks of a reference for the same analysis number, the mean and standard deviation are provided in the “Multiple Peaks Analysis Summary” pane near the bottom of the Normalization Equation Coefficients form—see example in Figure 32.11.

Many of the column-heading labels in LIMS are shown in blue font, and the blue font indicates that additional information is available by right-clicking. For example, scrolling to Analysis D-8089 and right clicking the entry in the “Extraction ID” column displays the dialog box shown in Figure 24.11.

Users are able to perform one-point or two-point normalization. Two-point normalization commonly is termed full normalization if there are three or more references. To perform a one-point normalization using G-40 (USGS40 L-glutamic acid):

1. Click “One Reference” in the “Show” panel.
2. Click “Normalize with This Reference” in the “Normalization” panel.
3. Select “G-40” for the reference if it is not already selected, and LIMS displays the information shown in Figure 24.12.

The proposed expansion coefficient is 1 by default because normalization with a single reference was selected. However, using additional information the user may want to update the expansion coefficient and the additive correction factor. Neither field is locked and for an example one can update the expansion coefficient and additive correction factor to 1.01234 and –2.88 ‰ as shown

in Figure 24.13. The values in the "Final Delta" column update immediately. In addition to performing one-point normalization with G-40, one can normalize with G-41 by selecting G-41 as the reference for single-point normalization ("Normalize with This Reference" selected) as shown in Figures 24.14 and 24.15. To improve normalization, one can click "IG" check boxes as shown in Figure 24.16 in which the "IG" check box of D-8078 (G-41) was checked, and the standard deviation of the $\delta^{13}C$ values of G-41 improves from 0.31 ‰ (Fig. 24.15) to 0.08 ‰. In some cases, the results from an entire run need to be ignored. This is accomplished in one step by clicking "Ignore All Deltas" at the top of the form. Clicking "Ignore All Deltas" causes the button label to change to "Clear All Deltas" and vice versa. To check "IG" check boxes of selected peak numbers of all analyses, one can click "Ignore Some Deltas." After clicking "Ignore Some Deltas" the button label changes to "Clear Some Deltas," which enables the user to unclick "IG" check boxes of selected peak numbers.

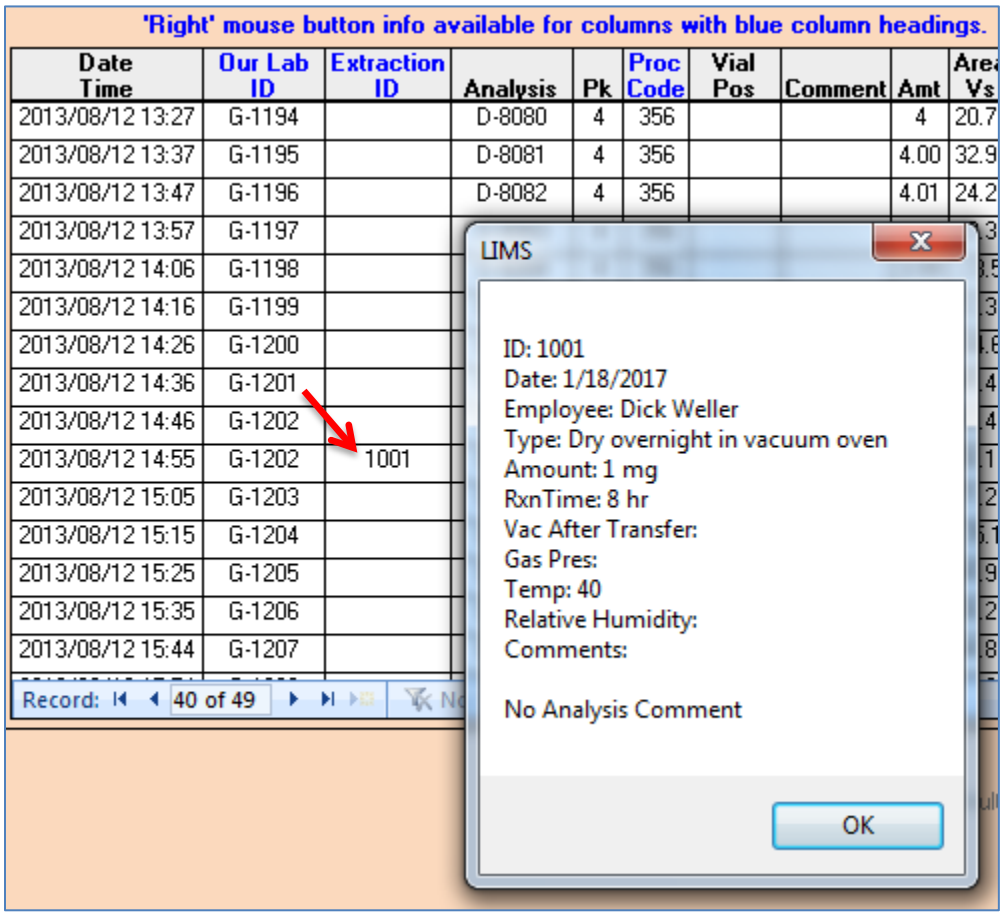
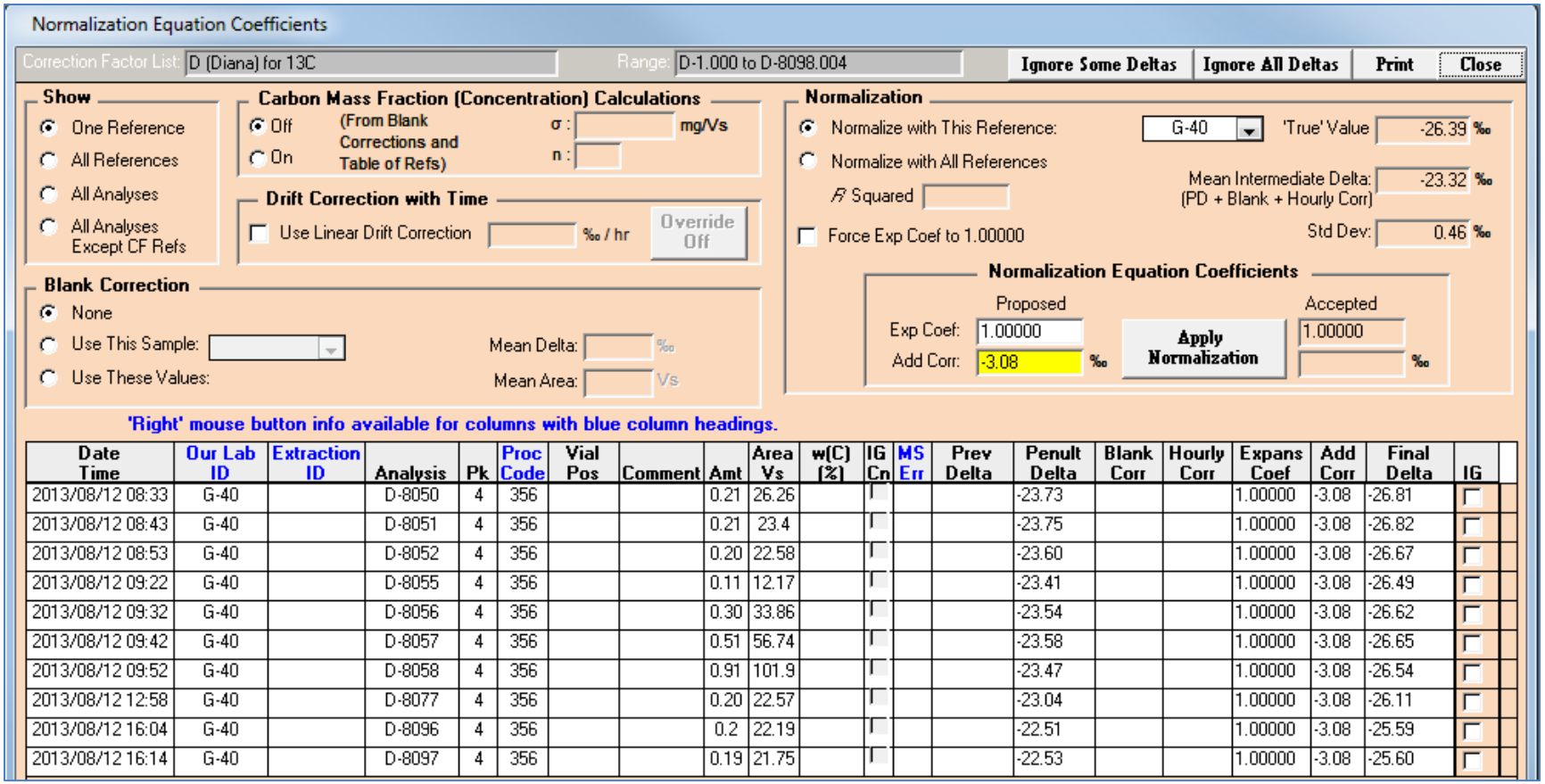


Fig. 24.11. Example information provided by right-clicking entries in column headings having a blue font. Here the user right-clicked the "Extraction ID" entry labelled "1001." This Extraction ID information was entered in the Extraction form in Section 11 (see Fig. 11.1).



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(C) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2013/08/12 08:33	G-40		D-8050	4	356			0.21	26.26					-23.73			1.00000	-3.08	-26.81	
2013/08/12 08:43	G-40		D-8051	4	356			0.21	23.4					-23.75			1.00000	-3.08	-26.82	
2013/08/12 08:53	G-40		D-8052	4	356			0.20	22.58					-23.60			1.00000	-3.08	-26.67	
2013/08/12 09:22	G-40		D-8055	4	356			0.11	12.17					-23.41			1.00000	-3.08	-26.49	
2013/08/12 09:32	G-40		D-8056	4	356			0.30	33.86					-23.54			1.00000	-3.08	-26.62	
2013/08/12 09:42	G-40		D-8057	4	356			0.51	56.74					-23.58			1.00000	-3.08	-26.65	
2013/08/12 09:52	G-40		D-8058	4	356			0.91	101.9					-23.47			1.00000	-3.08	-26.54	
2013/08/12 12:58	G-40		D-8077	4	356			0.20	22.57					-23.04			1.00000	-3.08	-26.11	
2013/08/12 16:04	G-40		D-8096	4	356			0.2	22.19					-22.51			1.00000	-3.08	-25.59	
2013/08/12 16:14	G-40		D-8097	4	356			0.19	21.75					-22.53			1.00000	-3.08	-25.60	

Fig. 24.12. Single-point normalization using 10 samples of G-40 USGS40.

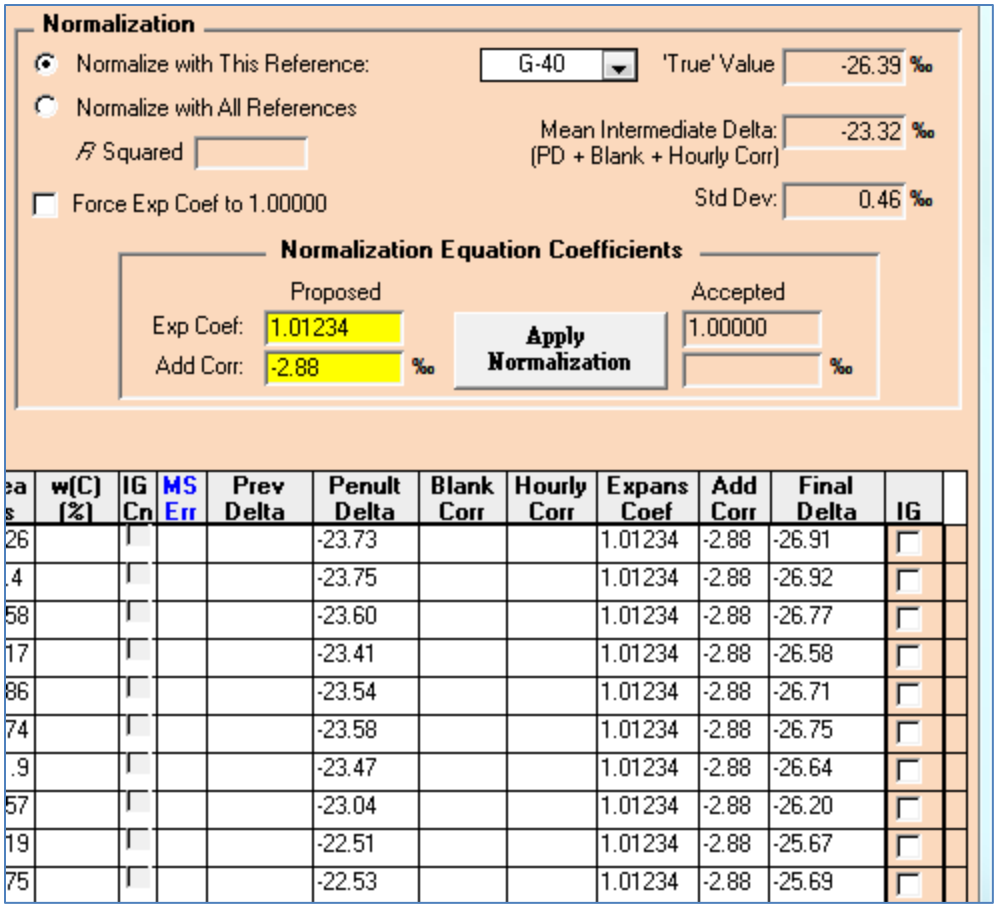


Fig. 24.13. Example of manually updating the "Exp Coef" and "Add Corr" fields to perform one-point normalization using an expansion coefficient that is not 1.00000.

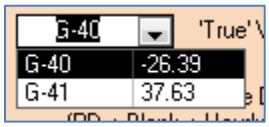


Fig. 24.14. The reference dropdown control showing the assigned delta values of references.

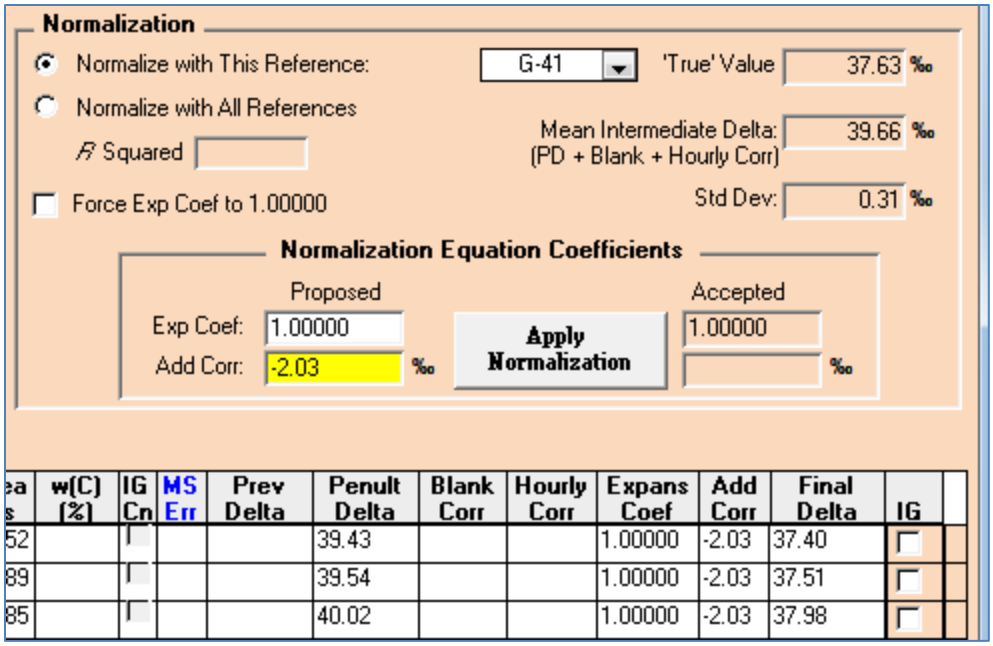


Fig. 24.15. Single-point normalization using all three samples of G-41 USGS41.

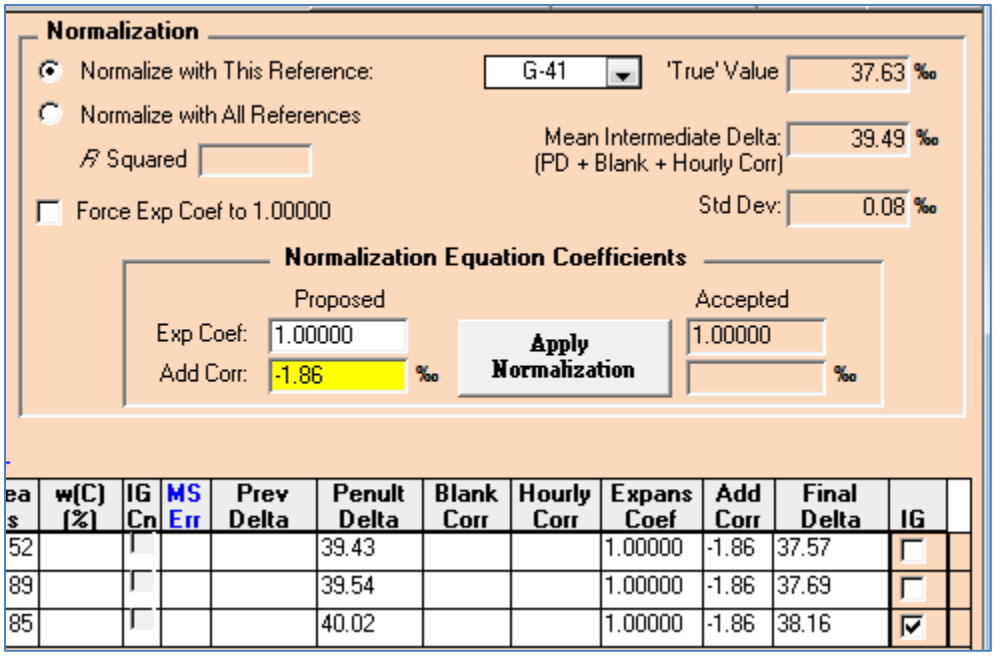


Fig. 24.16. Ignoring analyses to improve the standard deviation.

To perform two-point normalization:

1. Click “All Reference” in the “Show” panel.
2. Click “Normalize with All References” in the “Normalization” panel.
3. Ensure that the “IG” check boxes of analysis D-8078 is unchecked.
4. Based on the references interspersed among the unknowns, LIMS is proposing to normalize the 49 $\delta^{13}C$ analyses between D-1 and D-8098, shown in the bottom panel, with an expansion coefficient of 1.01655 and an additive correction factor of –2.69 ‰ (Fig. 24.10). The *R* squared value for these coefficients is 0.999767 as shown in the Normalization panel. Click “Apply Normalization,” and the “Accepted” fields for the expansion coefficient and additive correction factor are updated, the backgrounds of the “Proposed” values changes from yellow to white, and the values in the “Final Delta” column are updated (Fig. 24.17).
5. For QA/QC documentation users may decide to click “Print” at the top of the form, and LIMS will print the QA/QC documentation report shown in Figure 24.18.
6. Click “Close” to exit the Normalization Equation Coefficients form, and LIMS may prompt with the dialog box shown in Figure 24.19. Click “Yes” or “No” as desired and the Range Marker is shown on the Data Normalization form (Fig. 24.20).
7. To document Range Markers in the analysis interval specified on the Data Normalization form (7598 to 8098), click “Print” and LIMS prints the report shown in Figure. 24.21. Because a Range Marker exists, clicking “View/Edit” will open the Normalization Equation Coefficients form.

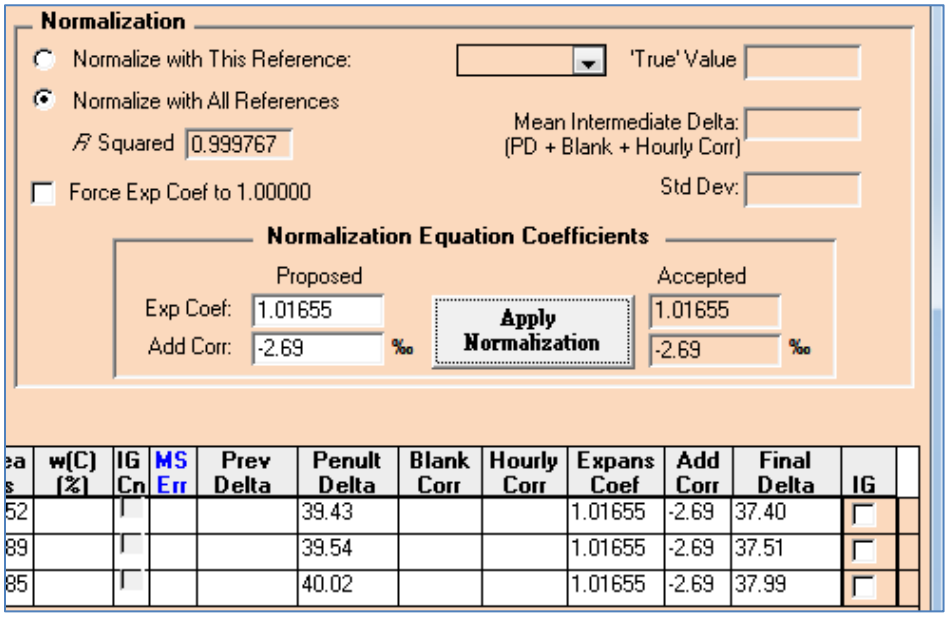


Fig. 24.17. Normalization equation coefficients and final delta values for two-point normalization.

References for D (Diana) for 13C
Between 1.000 And 8098.004

4/22/2017 8:10:10 AM

Expansion Coefficient: 1.01655
Additive Correction Factor: -2.69
***R* Squared:** 0.999767

Date	Analysis	Pk	Vial Pos	Proc. Code	Error Messages	Area	Penultimate Delta	Blank Corr	Hourly Corr	Intermediate Delta	IG
G-40	USGS40, L-Glutamic Acid										
8/12/2013 8:33:32 AM	8050	4		356		26.3	-23.73			-23.73	
8/12/2013 8:43:20 AM	8051	4		356		23.4	-23.75			-23.75	
8/12/2013 8:53:09 AM	8052	4		356		22.6	-23.60			-23.60	
8/12/2013 9:22:34 AM	8055	4		356		12.2	-23.41			-23.41	
8/12/2013 9:32:23 AM	8056	4		356		33.9	-23.54			-23.54	
8/12/2013 9:42:12 AM	8057	4		356		56.7	-23.58			-23.58	
8/12/2013 9:52:00 AM	8058	4		356		101.9	-23.47			-23.47	
8/12/2013 12:58:17 PM	8077	4		356		22.6	-23.04			-23.04	
8/12/2013 4:04:34 PM	8096	4		356		22.2	-22.51			-22.51	
8/12/2013 4:14:08 PM	8097	4		356		21.7	-22.53			-22.53	
										-23.32 ± 0.46	

Computed delta value of G-40 relative to VPDB: -26.39 per mil
Value should be (from reference table): -26.39 per mil.

G-41	USGS41, L-Glutamic Acid										
8/12/2013 9:02:57 AM	8053	4		356		23.5	39.43			39.43	
8/12/2013 9:12:45 AM	8054	4		356		21.9	39.54			39.54	
8/12/2013 1:08:06 PM	8078	4		356		23.8	40.02			40.02	
										39.66 ± 0.31	

Computed delta value of G-41 relative to VPDB: 37.63 per mil
Value should be (from reference table): 37.63 per mil.

Fig. 24.18. Example QA/QC documentation report of normalization equation coefficients.

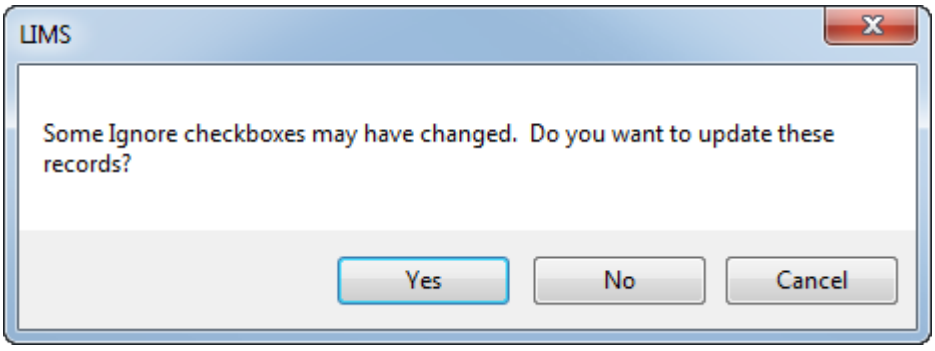
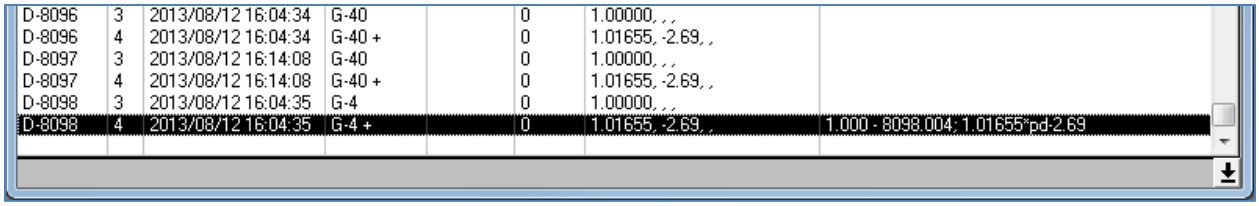


Fig. 24.19. LIMS dialog box upon closing Normalization Equation Coefficients form if "IG" check boxes were clicked after clicking "Apply Normalization."



D-8096	3	2013/08/12 16:04:34	G-40		0	1.00000, , ,	
D-8096	4	2013/08/12 16:04:34	G-40 +		0	1.01655, -2.69, ,	
D-8097	3	2013/08/12 16:14:08	G-40		0	1.00000, , ,	
D-8097	4	2013/08/12 16:14:08	G-40 +		0	1.01655, -2.69, ,	
D-8098	3	2013/08/12 16:04:35	G-4		0	1.00000, , ,	
D-8098	4	2013/08/12 16:04:35	G-4 +		0	1.01655, -2.69, ,	1.000 - 8098.004; 1.01655*pd-2.69

Fig. 24.20. New Range Marker on the Data Normalization form.

Summary of Correction Factor Ranges 4/22/2017 8:35:43 AM

Correction Factor List: D (Diana) for 13C

8/12/2013 1.000 to 8098.004 1.01655 x Penultimate Delta - 2.69

Fig. 24.21. Example report documenting Range Markers.

Occasionally, users may include several different references in a daily run and subsequently want to treat one of them (*e.g.* Ref A) as a blind sample to determine its delta values without its being included in the normalization process. The solution is to click the "IG" check box for each analysis of Ref A. This is facilitated by selecting “Normalize with This Reference” in the Normalize panel and selecting “One Reference” in the Show panel. After ignoring all analyses of Ref A, normalize as desired including applying drift correction with time (Section 24.4) if desired and correcting for sample blank (Section 24.5) if desired. Click “Apply Normalization,” close the form and return to the LIMS main page. Use the Add or Edit Analyses form (Section 27) to un-check each of the analyses of Ref A that was ignored. Now you can use the Print or Export Samples in Progress form (Section 26) to print or export to an Excel file the analyses in the normalization range.

Two-point normalization using the Normalization Equation Coefficients form was discussed in this section. Additional correction and normalization tools are discussed in the next sections.

Useful tip: Items in columns having column names with blue font can provide additional information by right-clicking. Right-clicking on an Our Lab ID displays information about the sample. Right-clicking on a procedure code provides a description of the analytical procedure. Right-clicking on "MS Err" provides a description of the mass spectrometer error code.

24.4 Applying Drift Correction with Time

LIMS can apply a linear drift correction with time to results the delta values of references interspersed among unknowns in the run. To demonstrate this feature:

1. On the main page click "Apply Data Normalization" and the Data Normalization form will open (Fig. 24.1).
2. Select "D (Diana) for 13C," and LIMS will enter the last 500 analyses in the "Analyses from" and "to" fields.
3. Click "Query" and LIMS will display analyses D-8050 to D-8098, and the last analysis will be highlighted as shown in Figure 24.20.
4. Click "View/Edit" (or double-click on the highlighted analysis) and LIMS will prompt that it will determine best fitting normalization equation coefficients.
5. Click "OK" and the Normalization Equation Coefficients form should appear with two-point normalization performed (Fig. 24.17).
6. Click "One Reference" in the "Show" panel.
7. Select "Normalize with This Reference" in the "Normalization" panel, select reference G-40 if not already selected, and note that the standard deviation is 0.46 ‰.
8. Click the "Use Linear Drift Correction" check box in the "Drift Correction with Time" panel, and LIMS displays the dialog box shown in Figure 24.22, which indicates that an hourly drift correction value of –0.154 ‰/hr was calculated by least squares regression from $\delta^{13}C$ results of G-40 by assigning a time of 0 hours to the first analysis (D-8050) and a time of 7.7 hr to the last analysis (D-8097) that resulted in an *R* squared value of 0.98. These results are based on 10 measurements of G-40.
9. Click "Cancel" to discontinue displaying this message and note that the hourly drift correction value of –0.154 ‰/hr is displayed in red font (Fig. 24.23). Note that the standard deviation has improved from 0.46 ‰ to 0.07 ‰.
10. Change the reference from G-40 to G-41 and the hourly drift correction value decreases to –0.133 ‰/hr based on three measurements of G-41.
11. To use the mean hourly drift correction value determined from all references, click "Override Off" shown in the "Drift Correction with Time" panel (Fig. 24.23), and LIMS changes the label of this control to "Override On" and displays the dialog box shown in Figure 24.24.
12. Click "OK" and the mean hourly drift correction value of –0.143 ‰/hr is displayed. With the override on, the hourly drift correction field is unlocked and a user can edit it as desired—this feature should be used with care.
13. Click "Override On" and change the reference to G-40 so that the hourly drift correction value is –0.154 ‰/hr.
14. Click "Normalize with All References" in the "Normalization" panel.
15. Click "All Analyses" in the "Show" panel.

16. Click “Apply Normalization” and LIMS will update the “Final Delta” values and the hourly drift correction values are shown in the “Hourly Corr” column (Fig. 24.25). Note that the *R* squared value has improved to 0.999995.
17. Click “Close” and “Close” to return to the main page.

This completes the discussion of linear drift correction. The one final correction that can be performed is correction for sample blank, which is discussed in the next section.

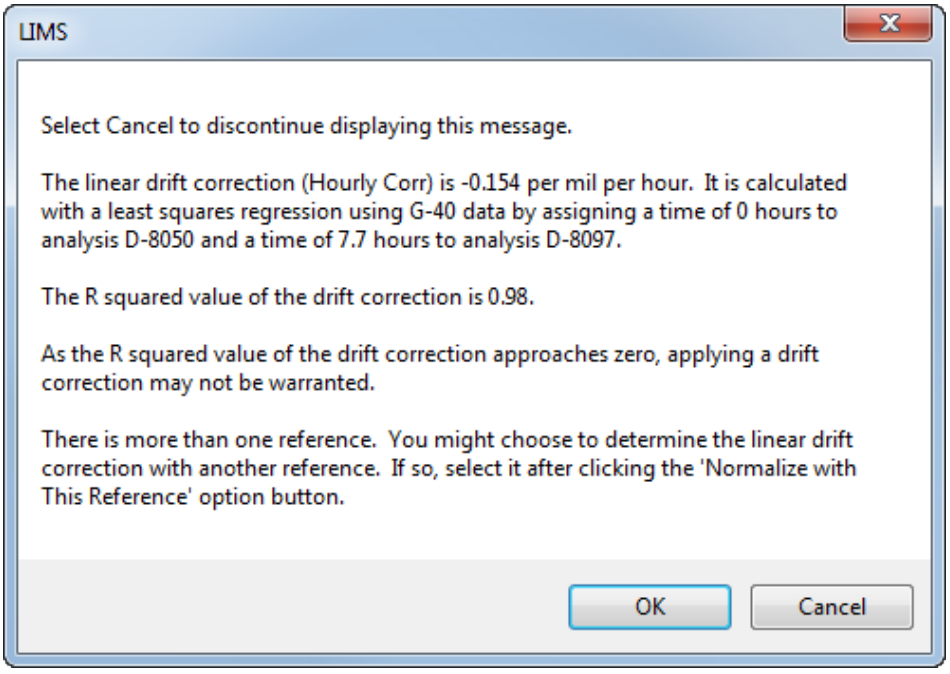


Fig. 24.22. Drift correction dialog box.

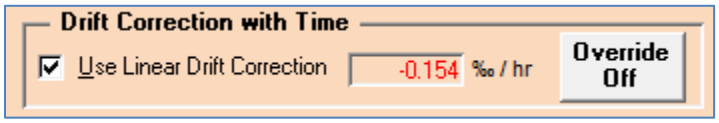


Fig. 24.23. Hourly drift correction.

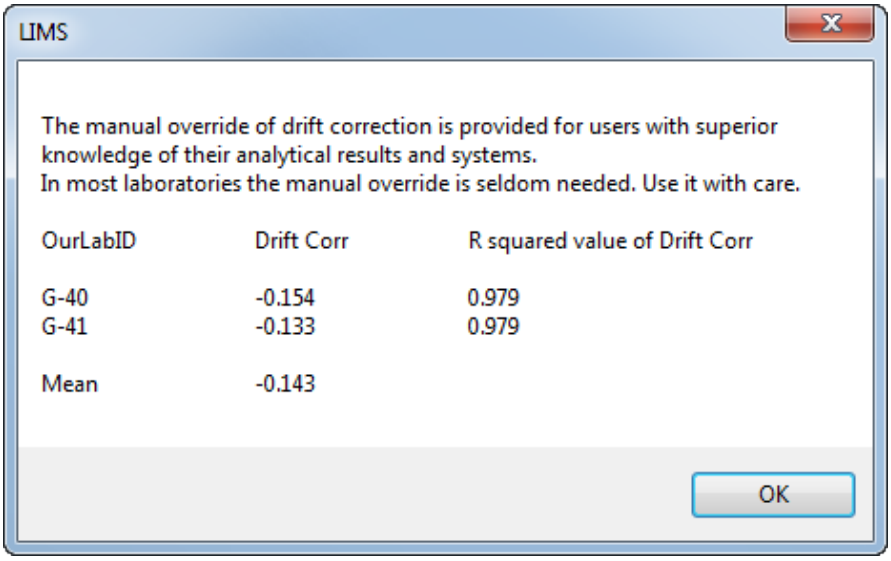
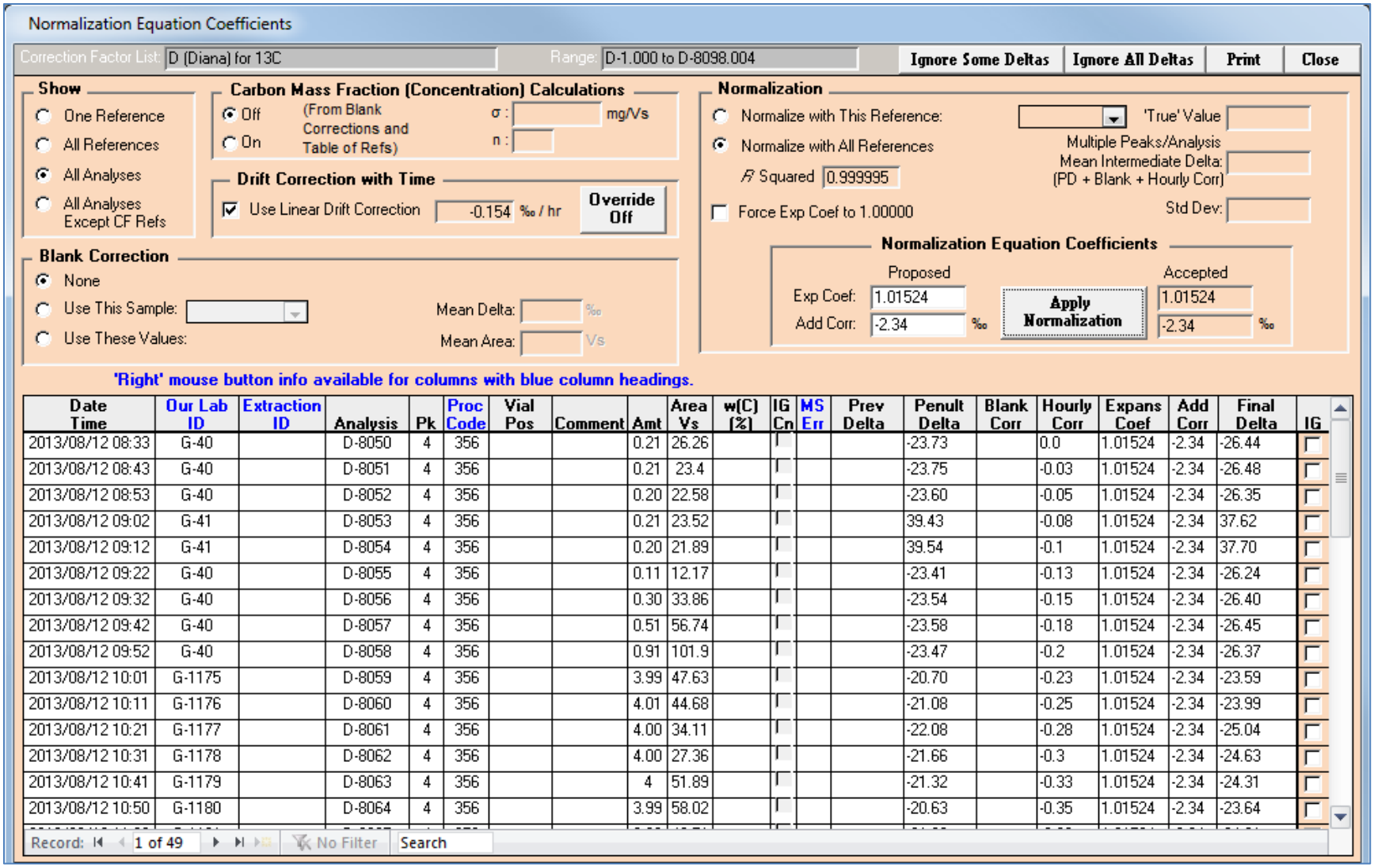


Fig. 24.24. Hourly drift correction calculated from mean values of G-40 and G-41.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(C) (%)	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2013/08/12 08:33	G-40		D-8050	4	356			0.21	26.26					-23.73		0.0	1.01524	-2.34	-26.44	
2013/08/12 08:43	G-40		D-8051	4	356			0.21	23.4					-23.75		-0.03	1.01524	-2.34	-26.48	
2013/08/12 08:53	G-40		D-8052	4	356			0.20	22.58					-23.60		-0.05	1.01524	-2.34	-26.35	
2013/08/12 09:02	G-41		D-8053	4	356			0.21	23.52					39.43		-0.08	1.01524	-2.34	37.62	
2013/08/12 09:12	G-41		D-8054	4	356			0.20	21.89					39.54		-0.1	1.01524	-2.34	37.70	
2013/08/12 09:22	G-40		D-8055	4	356			0.11	12.17					-23.41		-0.13	1.01524	-2.34	-26.24	
2013/08/12 09:32	G-40		D-8056	4	356			0.30	33.86					-23.54		-0.15	1.01524	-2.34	-26.40	
2013/08/12 09:42	G-40		D-8057	4	356			0.51	56.74					-23.58		-0.18	1.01524	-2.34	-26.45	
2013/08/12 09:52	G-40		D-8058	4	356			0.91	101.9					-23.47		-0.2	1.01524	-2.34	-26.37	
2013/08/12 10:01	G-1175		D-8059	4	356			3.99	47.63					-20.70		-0.23	1.01524	-2.34	-23.59	
2013/08/12 10:11	G-1176		D-8060	4	356			4.01	44.68					-21.08		-0.25	1.01524	-2.34	-23.99	
2013/08/12 10:21	G-1177		D-8061	4	356			4.00	34.11					-22.08		-0.28	1.01524	-2.34	-25.04	
2013/08/12 10:31	G-1178		D-8062	4	356			4.00	27.36					-21.66		-0.3	1.01524	-2.34	-24.63	
2013/08/12 10:41	G-1179		D-8063	4	356			4	51.89					-21.32		-0.33	1.01524	-2.34	-24.31	
2013/08/12 10:50	G-1180		D-8064	4	356			3.99	58.02					-20.63		-0.35	1.01524	-2.34	-23.64	

Fig. 24.25. The Normalization Equation Coefficients form with linear drift correction. Drift correction determined using G-40.

24.5 Applying Blank Correction

LIMS can make a correction for sample blank using either data from a blank or estimated delta values and areas using the controls and fields in the "Blank Correction" panel in the Normalization Equation Coefficients form (as in Fig. 24.10). In the database for a new laboratory, G-4 is identified as an empty cup for use as a blank in a continuous-flow method or empty cup in an EA or TC/EA method (Fig. 24.26). G-4 was analyzed in the example analyses discussed in Sections 24.3 and 24.4.

To demonstrate blank correction with G-4:

1. On the main page click "Apply Data Normalization" and the Data Normalization form will open (Fig. 24.1).
2. Select "D (Diana) for 13C," and LIMS will enter the last 500 analyses in the "Analyses from" and "to" fields.
3. Click "Query" and LIMS will display analyses D-8050 to D-8098, and the last analysis will be highlighted as shown in Figure 24.20.
4. Click "View/Edit" (or double-click on the highlighted analysis) and LIMS will prompt that it has determined linear drift correction (Fig. 24.22).

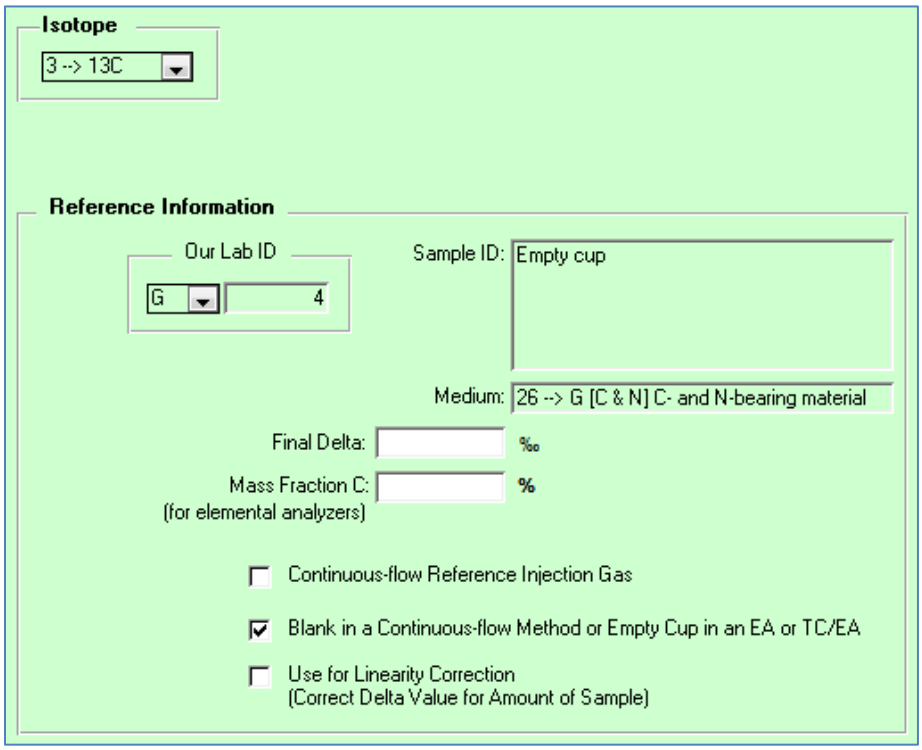


Fig. 24.26. G-4 identified in the Reference Samples form as an empty cup for use as a blank.

5. Click “OK” and LIMS will prompt that it will determine best fitting normalization equation coefficients.
6. Click “OK” and the Normalization Equation Coefficients form should appear with two-point normalization and linear drift correction performed (Fig. 24.25).
7. Select the “Use This Sample” option in the “Blank Correction” panel, and LIMS displays the Our Lab IDs of all of the references in the run identified as blanks, which in this example is only G-4 (Fig. 24.27).
8. Select G-4 and LIMS will recalculate the linear drift correction based on correction for the blank, G-4, and displays a dialog box similar to Figure 24.22. LIMS uses a mean $\delta^{13}C$ value of –7.2 ‰ and a mean area of 0.18 Vs for blank correction calculations (Fig. 24.28), which are documented in Appendix E. Note that the hourly drift correction has changed from a value of –0.154 ‰/hr to –0.152 ‰/hr, the proposed expansion coefficient value has changed from a value of 1.01524 to 1.00750, and the additive correction factor has changed from a value of –2.34 ‰ to –2.41 ‰, both shown with yellow background indicating revised values (Fig. 24.28).
9. Click “OK” and click “Apply Normalization” to update the “Accepted” values of the expansion coefficient and the additive correction factor (Fig. 24.29).

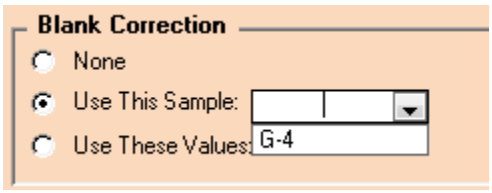


Fig. 24.27. LIMS displaying all references identified as blanks. In this case the only reference identified as a blank in the run was G-4.

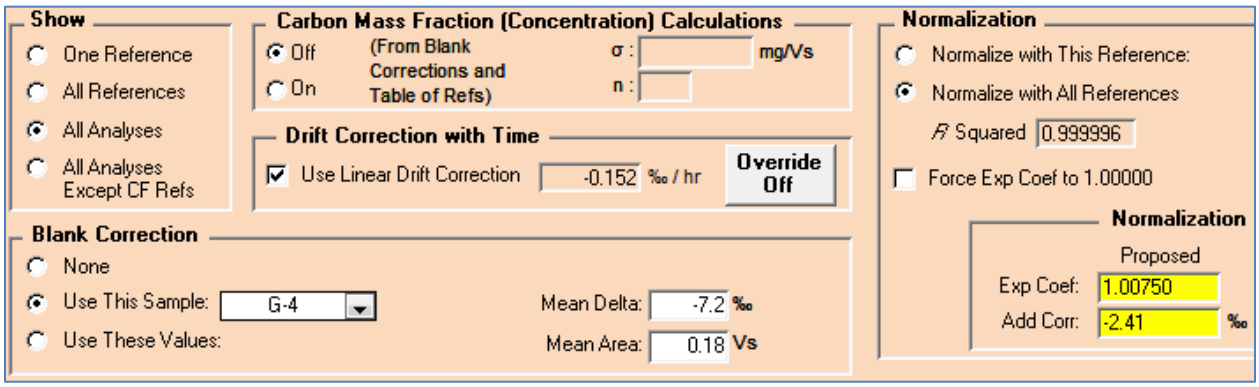
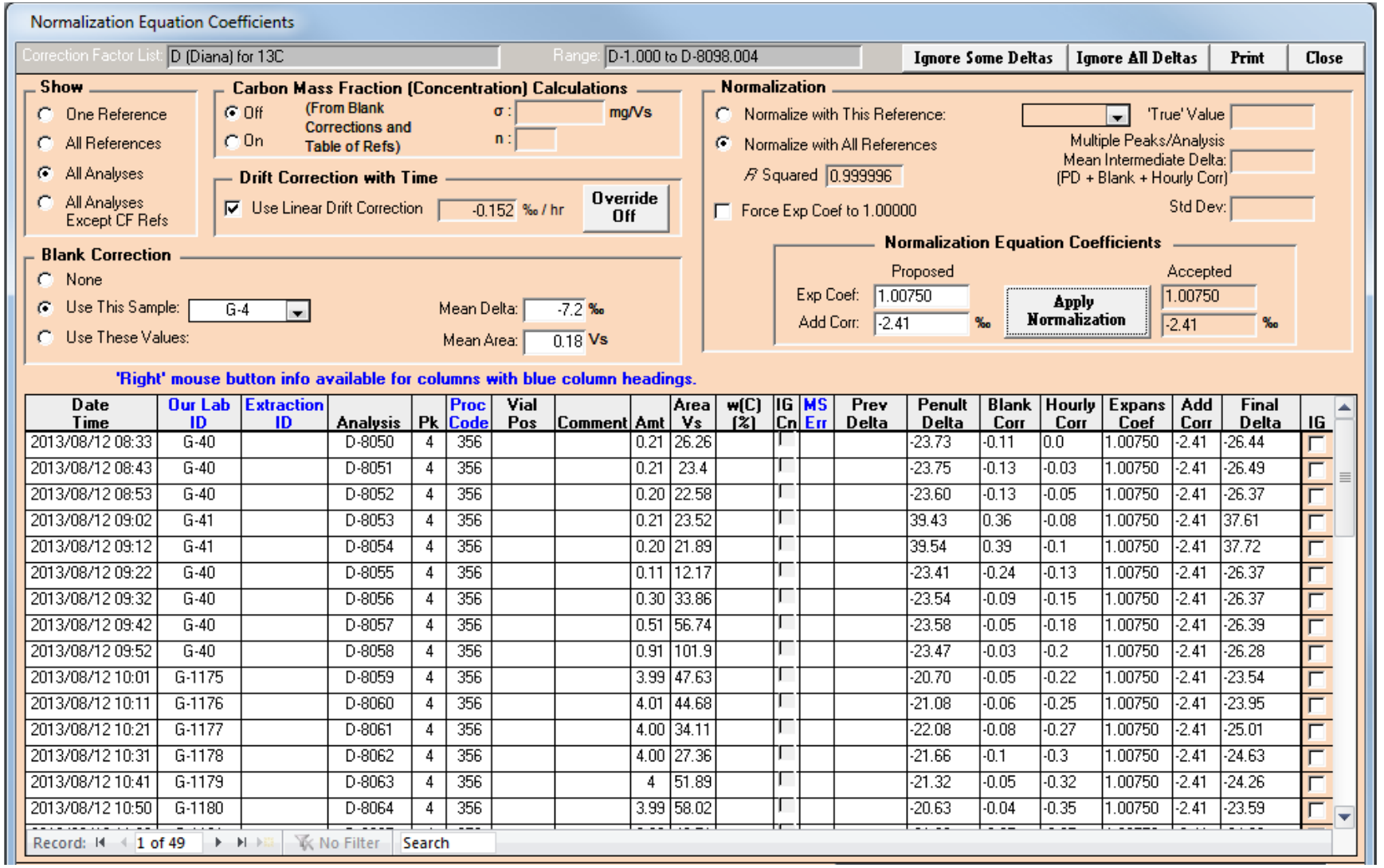


Fig. 24.28. Changes to the Normalization Equation Coefficients form using G-4 for correction of blank.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(C) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2013/08/12 08:33	G-40		D-8050	4	356			0.21	26.26					-23.73	-0.11	0.0	1.00750	-2.41	-26.44	
2013/08/12 08:43	G-40		D-8051	4	356			0.21	23.4					-23.75	-0.13	-0.03	1.00750	-2.41	-26.49	
2013/08/12 08:53	G-40		D-8052	4	356			0.20	22.58					-23.60	-0.13	-0.05	1.00750	-2.41	-26.37	
2013/08/12 09:02	G-41		D-8053	4	356			0.21	23.52					39.43	0.36	-0.08	1.00750	-2.41	37.61	
2013/08/12 09:12	G-41		D-8054	4	356			0.20	21.89					39.54	0.39	-0.1	1.00750	-2.41	37.72	
2013/08/12 09:22	G-40		D-8055	4	356			0.11	12.17					-23.41	-0.24	-0.13	1.00750	-2.41	-26.37	
2013/08/12 09:32	G-40		D-8056	4	356			0.30	33.86					-23.54	-0.09	-0.15	1.00750	-2.41	-26.37	
2013/08/12 09:42	G-40		D-8057	4	356			0.51	56.74					-23.58	-0.05	-0.18	1.00750	-2.41	-26.39	
2013/08/12 09:52	G-40		D-8058	4	356			0.91	101.9					-23.47	-0.03	-0.2	1.00750	-2.41	-26.28	
2013/08/12 10:01	G-1175		D-8059	4	356			3.99	47.63					-20.70	-0.05	-0.22	1.00750	-2.41	-23.54	
2013/08/12 10:11	G-1176		D-8060	4	356			4.01	44.68					-21.08	-0.06	-0.25	1.00750	-2.41	-23.95	
2013/08/12 10:21	G-1177		D-8061	4	356			4.00	34.11					-22.08	-0.08	-0.27	1.00750	-2.41	-25.01	
2013/08/12 10:31	G-1178		D-8062	4	356			4.00	27.36					-21.66	-0.1	-0.3	1.00750	-2.41	-24.63	
2013/08/12 10:41	G-1179		D-8063	4	356			4	51.89					-21.32	-0.05	-0.32	1.00750	-2.41	-24.26	
2013/08/12 10:50	G-1180		D-8064	4	356			3.99	58.02					-20.63	-0.04	-0.35	1.00750	-2.41	-23.59	

Fig. 24.29. The Normalization Equation Coefficients form with linear drift correction using G-40 and with blank correction using G-4.

The blank correction values are shown in the column labelled “Blank Corr” (Fig. 24.29). An alternative to using the “Use This Sample” option in the “Blank Correction” panel, one can select the “Use These Values” option. LIMS will unlock the “Mean Delta” and “Mean Area” fields, and the user can enter values as appropriate. This feature should be used with care.

To demonstrate that the Data Normalization form has been updated with all coefficients discussed in Section 24.1, click “Close” to return to the Data Normalization form, whose four correction coefficients for each $\delta^{13}C$ analysis and Range Marker have been updated (Fig. 24.30).

This completes the discussion of blank correction. Determination of element mass fractions (concentrations) continues in the next section using the Normalization Equation Coefficients form shown in Figure 24.29.

D-8093	4	2013/08/12 15:35:09	G-1207 +		0	1.00750, -2.41, -0.08, -1.07	
D-8094	3	2013/08/12 15:44:57	G-1208		0	1.00000, , ,	
D-8094	4	2013/08/12 15:44:57	G-1208 +		0	1.00750, -2.41, -0.06, -1.1	
D-8095	3	2013/08/12 15:54:46	G-1209		0	1.00000, , ,	
D-8095	4	2013/08/12 15:54:46	G-1209 +		0	1.00750, -2.41, -0.08, -1.12	
D-8096	3	2013/08/12 16:04:34	G-40		0	1.00000, , ,	
D-8096	4	2013/08/12 16:04:34	G-40 +		0	1.00750, -2.41, -0.13, -1.15	
D-8097	3	2013/08/12 16:14:08	G-40		0	1.00000, , ,	
D-8097	4	2013/08/12 16:14:08	G-40 +		0	1.00750, -2.41, -0.13, -1.17	
D-8098	3	2013/08/12 16:04:35	G-4		0	1.00000, , ,	
D-8098	4	2013/08/12 16:04:35	G-4 +		0	1.00750, -2.41, , -1.15	1.000 - 8098.004; 1.00750*pd-2.41

Fig. 24.30. The Data Normalization form showing updated Range Marker and correction coefficients. Four normalization coefficients (expansion coefficient, additive correction factor, blank correction, and hourly drift correction) delineated by commas are shown for each $\delta^{13}C$ analysis except for G-4 which does not have a blank correction value.

24.6 Determining Element Mass Fractions (Concentrations)

LIMS is able to calculate the mass fractions (concentrations) of hydrogen, carbon, nitrogen, oxygen, and sulfur in material analyzed by EA or TC/EA if reference materials with known mass fractions are analyzed along with the unknowns. If several reference materials having different element mass fractions are analyzed, the user can choose to base calculation on any one, or on all of, the reference materials by checking the desired check boxes in the column “IG Cn” on the Normalization Equation Coefficients form (Fig. 24.29). The symbol for mass fraction is *w*; thus the symbol for the mass fraction of carbon is *w*(C), which is a column heading in the Normalization Equation Coefficients form (Fig. 24.29).

To demonstrate determining carbon mass fractions:

1. On the main page click “Apply Data Normalization” and the Data Normalization form will open (Fig. 24.1).
2. Select “D (Diana) for 13C,” and LIMS will enter the last 500 analyses in the “Analyses from” and “to” fields.
3. Click “Query” and LIMS will display analyses D-8050 to D-8098, and the last analysis will be highlighted as shown in Figure 24.30.
4. Click “View/Edit” (or double-click on the highlighted analysis) and LIMS will prompt that the proposed and accepted normalization coefficients may have changed since the last time they were saved (Fig. 24.31).
5. Click “OK” and LIMS indicates that it has determined a linear drift correction (Fig. 24.22).
6. Click “OK” and LIMS will prompt that it will determine best fitting normalization equation coefficients.
7. Click “OK” and the Normalization Equation Coefficients form should appear with two-point normalization and linear drift correction performed (Fig. 24.25), but blank correction has not been performed because LIMS does not store the blank Our Lab ID.
8. Select the “Use This Sample” option in the “Blank Correction” panel, and LIMS displays the Our Lab IDs of all of the references in the run identified as blanks, which in this example is only G-4 (Fig. 24.27).
9. Select G-4 and LIMS will provide a dialog box similar to that of Figure 24.22, indicating that the updated hourly drift correction is –0.152 ‰/hr.
10. Click “OK” and the Normalization Equation Coefficients form will appear as shown in Figure 24.29.
11. Select “All References” in the “Show” panel.
12. Select “On” in the “Carbon Mass Fraction (Concentration) Calculations” panel, and LIMS will populate the column “w(C) (%).”
13. Because USGS41 and USGS41a L-glutamic acid, respectively, have an excess of 3 and 0.7 percent carbon by mass than USGS40 L-glutamic acid, users should not use either USGS41 or USGS41a for mass fraction calculations.[9] This is because both USGS41 and USGS41a contain pyroglutamic acid formed during their preparation.[9] Deselect all mass fraction calculations with G-41 by clicking the “IG Cn” check boxes of each G-41 analysis (Fig. 24.32).
14. Review the mass fractions of the remaining analyses and ignore any that appear to be problematic. Click the “IG Cn” check box of analyses D-8050 because it is substantially too high—probably because it was the first analysis of the run. Note that the standard deviation of the ratio mass / peak area in the “Carbon Mass Fraction (Concentration) Calculations” panel of all the unchecked references improves from 0.01435 to 0.00209 mg/Vs when the “IG Cn” check box of D-8050 is checked (Fig. 24.33).
15. Click “Apply Normalization” to save the “IG Cn” check box updates.

16. Select “All Analyses” in the “Show” panel and carbon mass fraction calculations are completed (Fig. 24.34).

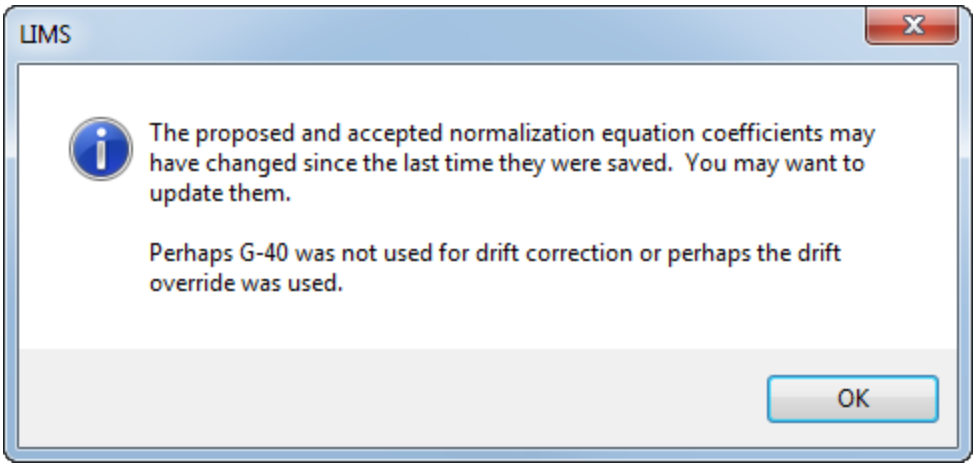


Fig. 24.31. LIMS dialog box that the proposed and accepted normalization coefficients may have changed.

Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(C) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expa Cor
G-40		D-8050	4	356			0.21	26.26	46.5	☑			-23.73		0.0	1.015
G-40		D-8051	4	356			0.21	23.4	41	☐			-23.75		-0.03	1.015
G-40		D-8052	4	356			0.20	22.58	40.4	☐			-23.60		-0.05	1.015
G-40		D-8055	4	356			0.11	12.17	41.1	☐			-23.41		-0.13	1.015
G-40		D-8056	4	356			0.30	33.86	40.9	☐			-23.54		-0.15	1.015
G-40		D-8057	4	356			0.51	56.74	40.6	☐			-23.58		-0.18	1.015
G-40		D-8058	4	356			0.91	101.9	40.9	☐			-23.47		-0.2	1.015
G-40		D-8077	4	356			0.20	22.57	40.9	☐			-23.04		-0.68	1.015
G-40		D-8096	4	356			0.2	22.19	40.7	☐			-22.51		-1.16	1.015
G-40		D-8097	4	356			0.19	21.75	40.9	☐			-22.53		-1.18	1.015
G-41		D-8053	4	356			0.21	23.52	41.2	☑			39.43		-0.08	1.015
G-41		D-8054	4	356			0.20	21.89	39.5	☑			39.54		-0.1	1.015
G-41		D-8078	4	356			0.21	23.85	41.8	☑			40.02		-0.7	1.015

Fig. 24.32. Mass fraction calculations with G-41 L-glutamic acid disabled.

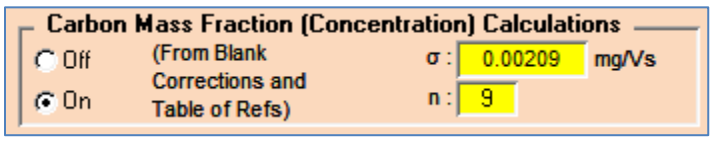
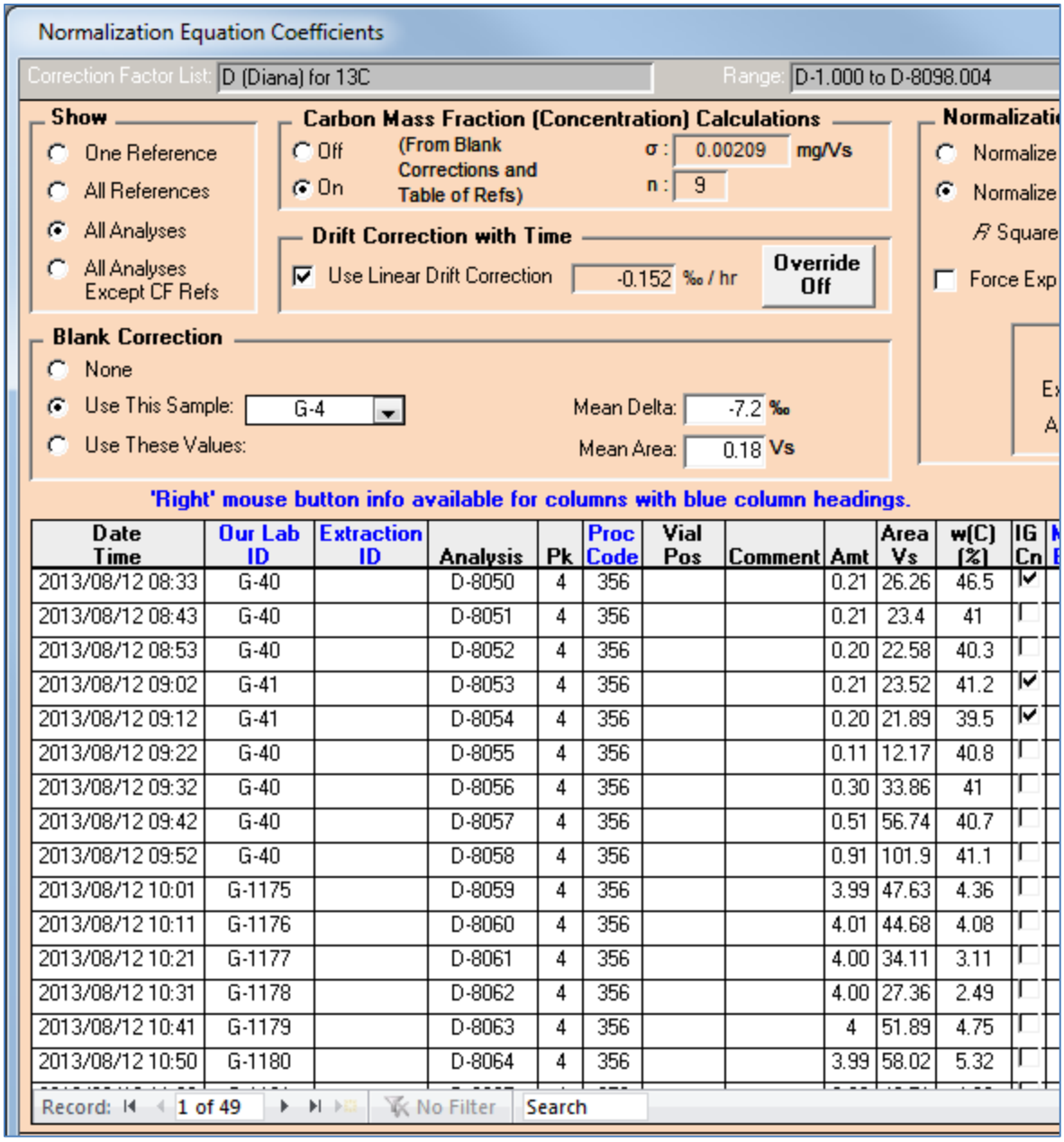


Fig. 24.33. Standard deviation of the ratio mass / peak area.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(C) (%)	IG Cn
2013/08/12 08:33	G-40		D-8050	4	356			0.21	26.26	46.5	☑
2013/08/12 08:43	G-40		D-8051	4	356			0.21	23.4	41	☐
2013/08/12 08:53	G-40		D-8052	4	356			0.20	22.58	40.3	☐
2013/08/12 09:02	G-41		D-8053	4	356			0.21	23.52	41.2	☑
2013/08/12 09:12	G-41		D-8054	4	356			0.20	21.89	39.5	☑
2013/08/12 09:22	G-40		D-8055	4	356			0.11	12.17	40.8	☐
2013/08/12 09:32	G-40		D-8056	4	356			0.30	33.86	41	☐
2013/08/12 09:42	G-40		D-8057	4	356			0.51	56.74	40.7	☐
2013/08/12 09:52	G-40		D-8058	4	356			0.91	101.9	41.1	☐
2013/08/12 10:01	G-1175		D-8059	4	356			3.99	47.63	4.36	☐
2013/08/12 10:11	G-1176		D-8060	4	356			4.01	44.68	4.08	☐
2013/08/12 10:21	G-1177		D-8061	4	356			4.00	34.11	3.11	☐
2013/08/12 10:31	G-1178		D-8062	4	356			4.00	27.36	2.49	☐
2013/08/12 10:41	G-1179		D-8063	4	356			4	51.89	4.75	☐
2013/08/12 10:50	G-1180		D-8064	4	356			3.99	58.02	5.32	☐

Fig. 24.34. Carbon mass fractions (concentrations) determined by LIMS. Values in the *w*(C) field include correction for blank G-4, ignoring all G-41 measurements, and ignoring one G-40 measurement (the first analysis of the run).

Users have the capability to have LIMS save hydrogen, carbon, nitrogen, oxygen, and (or) sulfur mass fractions (concentrations) of EA measurements in comment fields of sample tables and project reports by enabling this option on the LIMS Option form (Figs. 24.35, 24.36, and 24.37).

Useful tip: The accuracy of mass fractions of hydrogen, carbon, nitrogen, oxygen, and sulfur determined with LIMS may be equal to or better than those determined with a standard EA because the user can (1) account for variation in the ratio area / amount of references over time (see *e.g.* Fig. 22.29), (2) utilize several USGS40 references interspersed throughout the run, and (3) automatically account for blank with one or more sample blanks in the run.

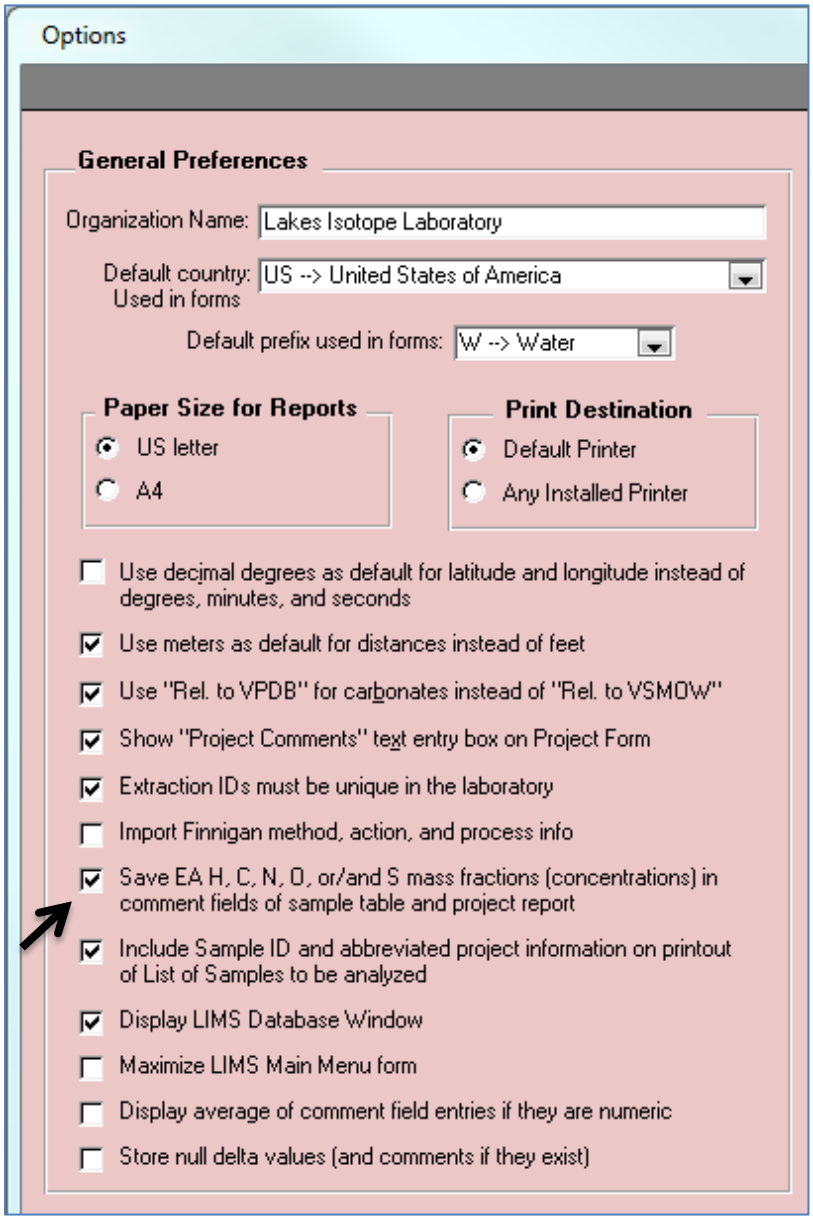


Fig. 24.35. Check box on Options form to enable saving EA mass fractions (concentrations) in comment fields of sample table and project report.

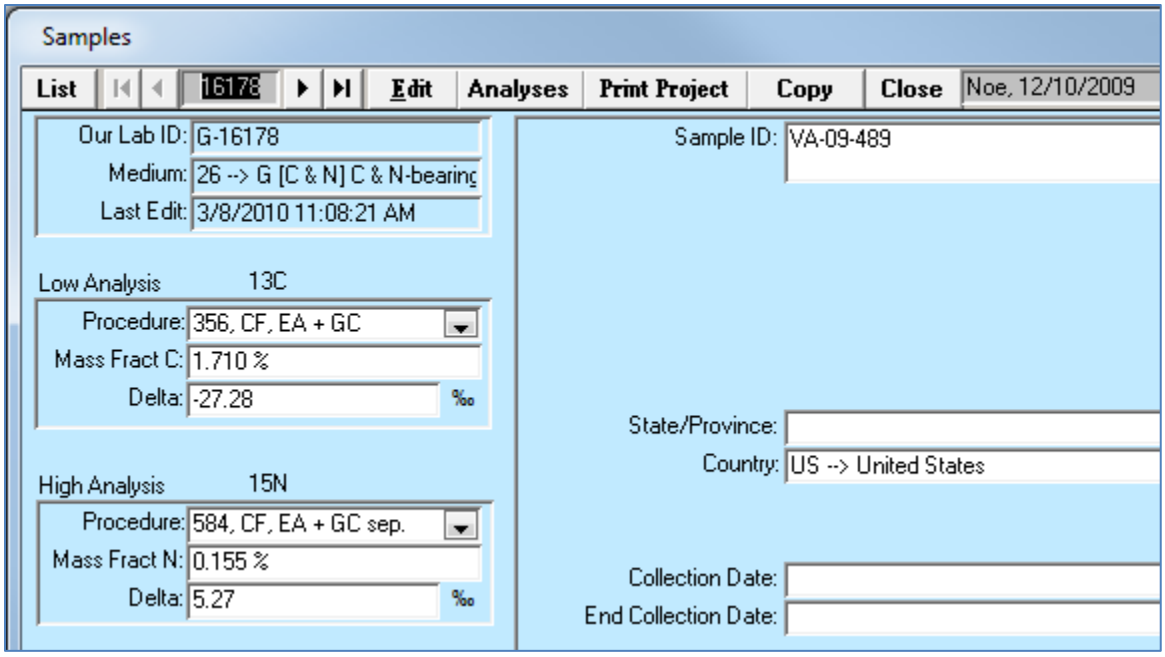


Fig. 24.36. Example of Samples form with carbon and nitrogen mass fractions saved in the comment fields.

Submission: 12/10/2009 Noe, Greg **G-16178 to G-16183** 4/23/2017

Medium: 26 --> G [C & N] C & N-bearing material
Purpose: NOE CN

Location:

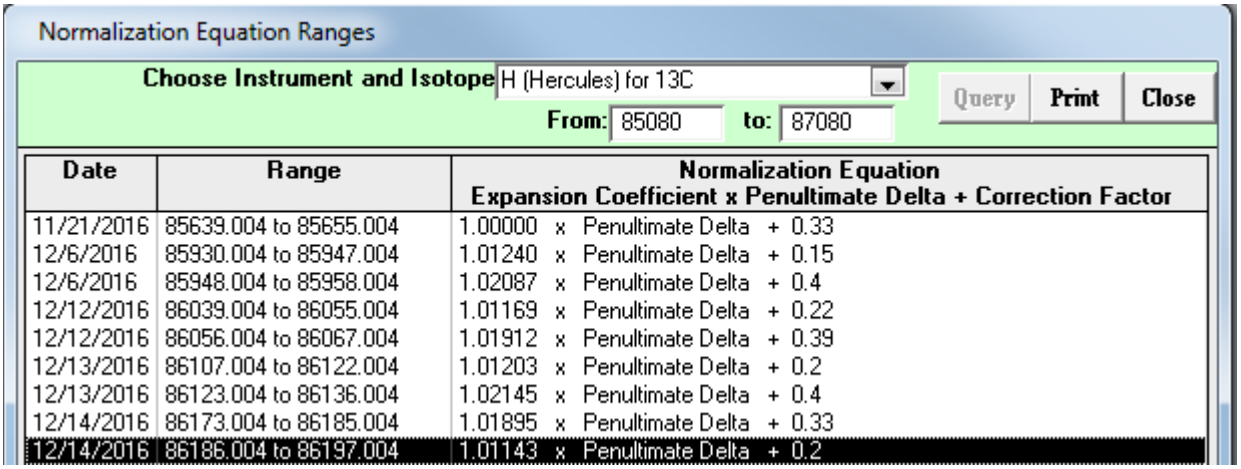
Sample ID:	Collection Date	Our Lab ID	$1000\,\delta^{13}C_{VPDB}$ Value	Mass Fraction C	$1000\,\delta^{15}N_{AIR}$ Value	Mass Fraction N
VA-09-489		G-16178	-27.28	1.710 %	5.27	0.155 %
VA-09-490		G-16179	-27.51	1.530 %	4.96	0.146 %
VA-09-491		G-16180	-27.81	2.100 %	4.61	0.199 %
VA-09-492		G-16181	-27.81	1.830 %	5.97	0.171 %
VA-09-493		G-16182	-27.39	1.960 %	5.85	0.179 %
VA-09-494		G-16183	-28.49	2.060 %	5.36	0.183 %

Fig. 24.37. Example of Project report with carbon and nitrogen mass fractions saved in the comment fields.

⚠ **Caution:** Do not use either USGS41 or USGS41a L-glutamic acid to determine carbon mass fractions (carbon concentrations) because they have 3 and 0.7 percent, respectively, more carbon by mass than USGS40 L-glutamic acid.

24.7 Viewing Data Normalization Ranges

It is sometimes useful to have a summary of the Range Markers in LIMS. By clicking on "View Data Normalization Ranges" on the main page, one can open the Normalization Equation Ranges form and view Range Markers for a selected mass spectrometer and isotope as shown in the example in Figure 24.38. Click "Print" to print a report of selected Range Markers.



Date	Range	Normalization Equation Expansion Coefficient x Penultimate Delta + Correction Factor
11/21/2016	85639.004 to 85655.004	1.00000 x Penultimate Delta + 0.33
12/6/2016	85930.004 to 85947.004	1.01240 x Penultimate Delta + 0.15
12/6/2016	85948.004 to 85958.004	1.02087 x Penultimate Delta + 0.4
12/12/2016	86039.004 to 86055.004	1.01169 x Penultimate Delta + 0.22
12/12/2016	86056.004 to 86067.004	1.01912 x Penultimate Delta + 0.39
12/13/2016	86107.004 to 86122.004	1.01203 x Penultimate Delta + 0.2
12/13/2016	86123.004 to 86136.004	1.02145 x Penultimate Delta + 0.4
12/14/2016	86173.004 to 86185.004	1.01895 x Penultimate Delta + 0.33
12/14/2016	86186.004 to 86197.004	1.01143 x Penultimate Delta + 0.2

Fig. 24.38. Example list of Range Markers for $\delta^{13}C$ analyses of the H mass spectrometer.

25 Evaluating Samples in Progress

25.1 General Information

Once customer samples have been measured, preferably twice is there is sufficient sample, and all of the delta values are normalized, they remain "in progress" until they are evaluated by the analyst and stored to projects. The analyst should evaluate all results before storing them and releasing them to customers. The LIMS data evaluation consists of two parts: (1) checking the repeatability of all normalized samples that were measured at least twice, and (2) checking the performance of control standards included in each run, and over time (see Section 30).

Evaluation of analyses of samples in progress is performed with the Evaluate Samples in Progress form. This section requires the user to connect to the backend database named "Evaluate_SIP_BACKEND_DB.accdb" that can be extracted from a file named "Evaluate_SIP_BACKEND_DB.zip" that is found in the folder named "Section 25" in the files that accompany this manual. To demonstrate use of the Evaluate Samples in Progress form:

1. On the LIMS main page click "Special Features" and click "Backend db" to open the BackEnd and FrontEnd Databases form.
2. Extract **"**Evaluate_SIP_BACKEND_DB.accdb" from the file named "Evaluate_SIP_BACKEND_DB.zip" in the folder named "Section 25".
3. Follow the instructions in Section 4.4 and connect to the backend database "Evaluate_SIP_BACKEND_DB.accdb."
4. Click "Evaluate Samples in Progress" on the main page.
5. Select "G" for the "Prefix" if not already selected.
6. For the "Isotope" select "13C" and LIMS will populate the "From" and "To" fields of the "Our Lab ID Range" panel with 1 and 1208, respectively, the lowest and highest Our Lab IDs in the "in progress" $\delta^{13}C$ queue having a G prefix.
7. Click "Query" and LIMS displays the dialog box in Figure 25.1.
8. Click "OK" and LIMS displays the $\delta^{13}C$ analyses of G-1 (Fig. 25.2).

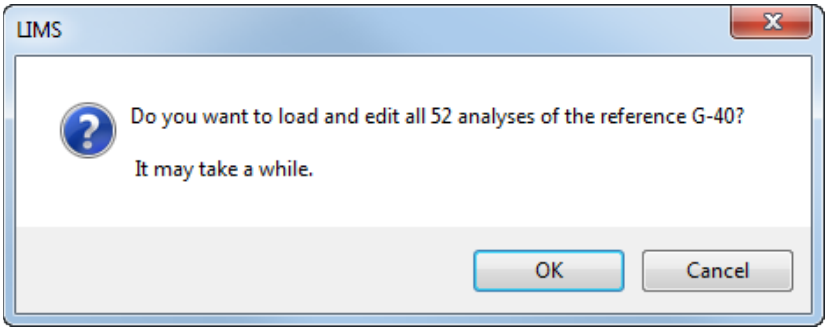
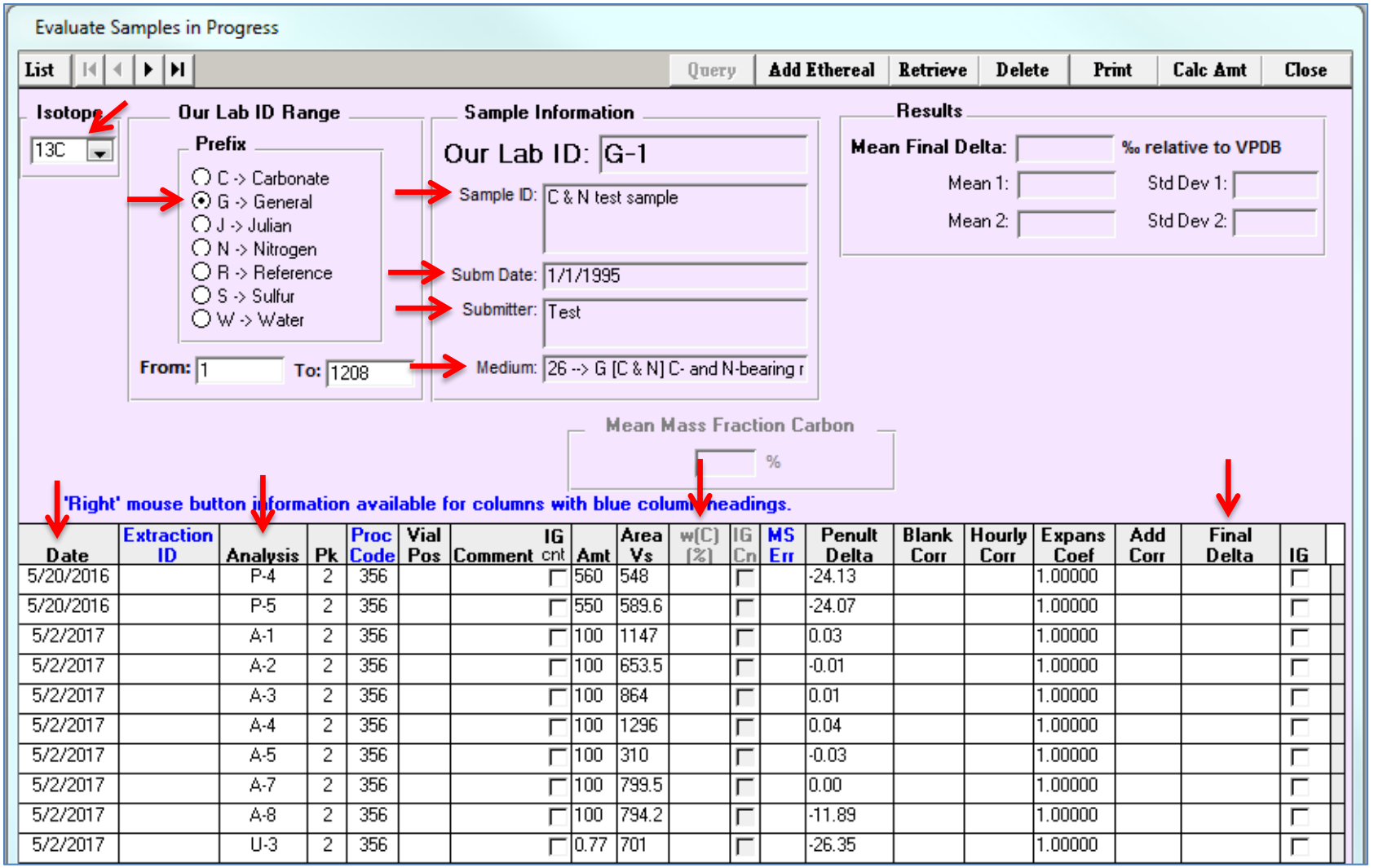


Fig. 25.1. LIMS query to display reference materials.



Date	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	IG Comment	IG cnt	Amt	Area Vs	w(C) [%]	IG Cn	MS Err	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
5/20/2016		P-4	2	356				560	548				-24.13			1.00000			
5/20/2016		P-5	2	356				550	589.6				-24.07			1.00000			
5/2/2017		A-1	2	356				100	1147				0.03			1.00000			
5/2/2017		A-2	2	356				100	653.5				-0.01			1.00000			
5/2/2017		A-3	2	356				100	864				0.01			1.00000			
5/2/2017		A-4	2	356				100	1296				0.04			1.00000			
5/2/2017		A-5	2	356				100	310				-0.03			1.00000			
5/2/2017		A-7	2	356				100	799.5				0.00			1.00000			
5/2/2017		A-8	2	356				100	794.2				-11.89			1.00000			
5/2/2017		U-3	2	356				0.77	701				-26.35			1.00000			

Fig. 25.2. The Evaluate Samples in Progress form. This test sample has been analyzed by three mass spectrometers (A, P, and U). None of these analyses have been normalized so that the mean $\delta^{13}C$ cannot be stored to the project form and G-1 removed from the $\delta^{13}C$ "in progress" queue.

Viewing the example Evaluate Samples in Progress form in Figure 25.2, one can ascertain that

- The Sample ID is "C & N test sample."
- The submission date of the project containing this sample is 1/1/1995.
- The submitter is "Test."
- The sample has been analyzed 10 times by three mass spectrometers (A, P, and U) between May 20, 2016 and May 2, 2017.
- None of these analyses has been normalized; thus, there are no values in the "Final Delta" column. Likewise, there are no carbon mass fraction values in the "w(C) (%)" column.

To view a sample whose analyses have been normalized, navigate to G-1202 using the "List" button in the upper left corner of the form, and LIMS shows Figure 25.3. The mean mass fraction of carbon is 5.44 %. LIMS calculates the mean final $\delta^{13}C$ value and standard deviation (–27.49 ± 0.10 ‰). The standard deviation is low; therefore, the mean $\delta^{13}C$ value is ready to be "stored" to the project, which is demonstrated in Section 28.

The "Add Ethereal" button is discussed in Section 25.4. If a sample was previously stored and is no longer in the Samples in Progress table, one can click "Retrieve" to add the sample to the Samples in Progress table with the "Isotope" currently selected. Clicking "Print" generates a "Print Samples in Progress" report (Section 26) of all samples in the Our Lab ID Range having the specified "Isotope." Caution is advised in clicking "Print" because the number of pages printed can be large, depending upon the size of the Our Lab ID Range. Users may prefer to use the Print or Export Samples in Progress form (Section 26) because it is more flexible; for example, it allows users to print or export analyses from a single mass spectrometer to an Excel file. Clicking "Calc Amt" opens a dialog box showing the amount of sample needed to create sample peaks having a variety of areas. An example of this dialog box is generated using atom fraction data is available in Appendix B (Fig. B.19).

⚠ **Helpful Hint:** Many of the fields (text boxes) in LIMS forms allow users to copy and paste their values. For example, in Figure 25.3 one can copy and paste values of the "Mean 1", "Mean Final Delta", "Mean Mass Fraction Carbon", "From", "To", and other fields.

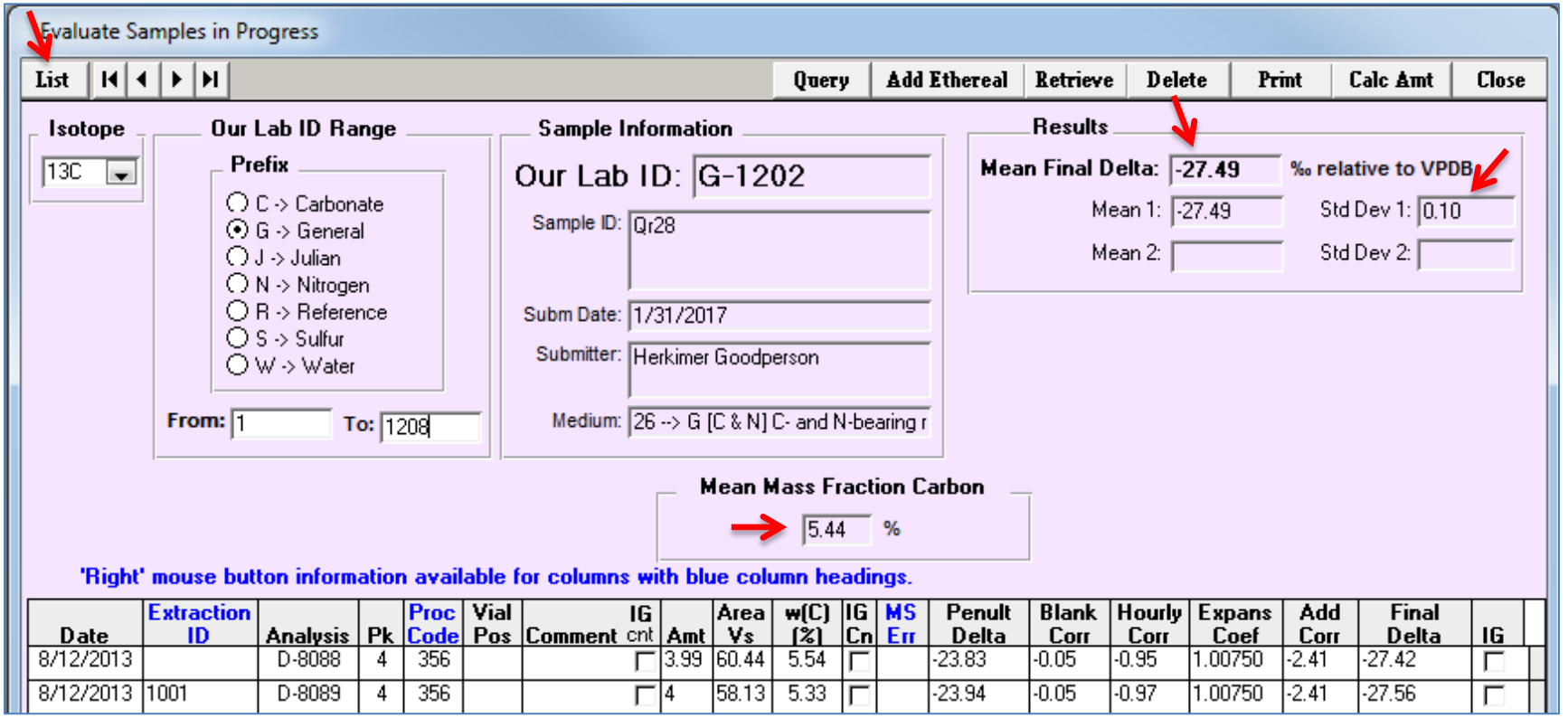


Fig. 25.3. The Evaluate Samples in Progress form for $\delta^{13}C$ of G-1202. Because there are two analyses that have been normalized, LIMS can calculate a mean final $\delta^{13}C$ value and standard deviation (–27.49 ± 0.10 ‰).

25.2 Multiple Peaks for the Same Analysis Number

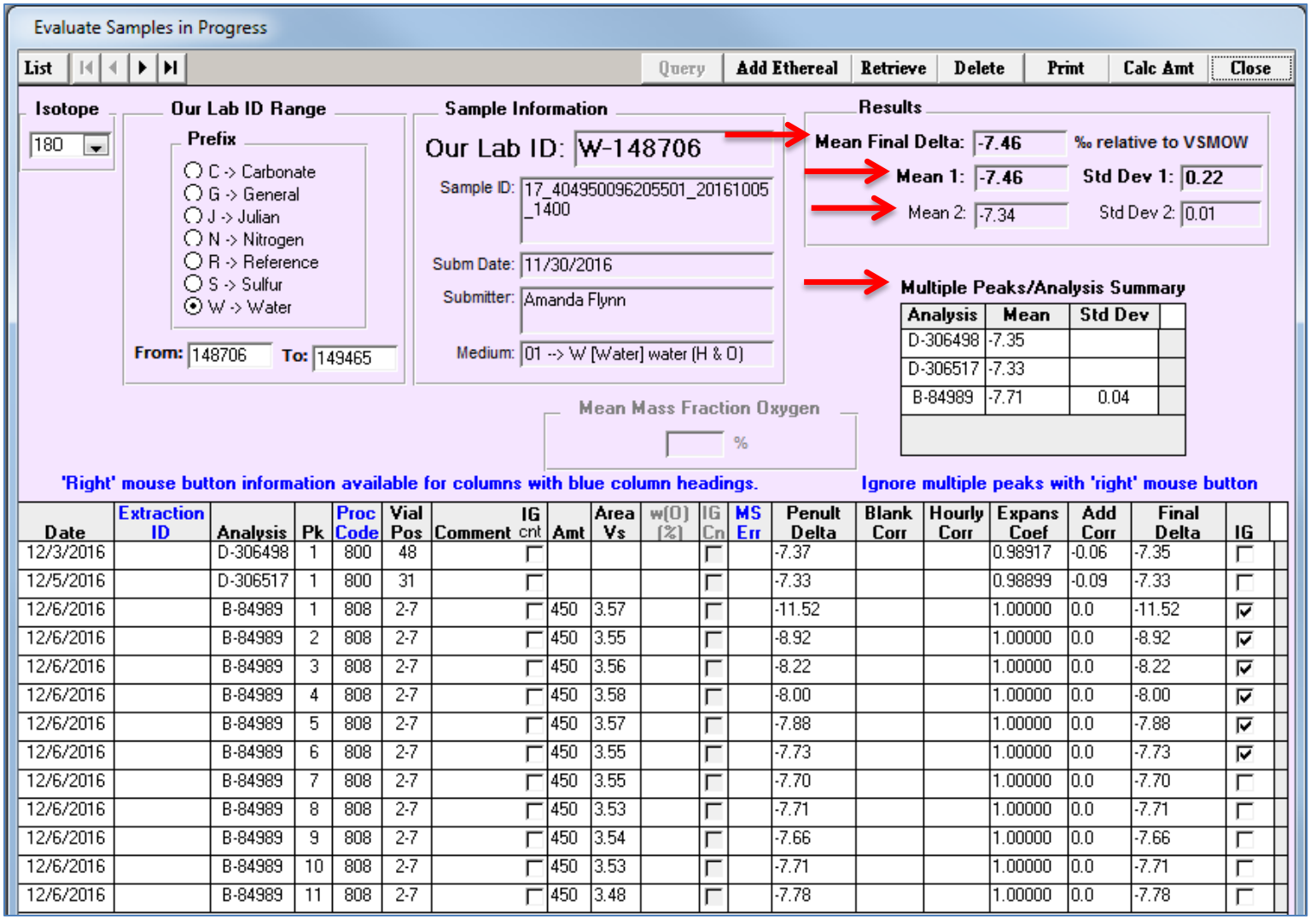
Some analytical methods, such as those using a Thermo GasBench or a laser absorption spectrometer, can generate multiple peaks for each analysis number. Figure 25.4 shows water sample W-148706, which was analyzed twice with a dual-inlet IRMS (analyses D-306498 and D-306517) and with multiple injections of a liquid water laser absorption spectrometer (analysis number B-84989). This is an example of LIMS for Light Stable Isotopes and LIMS for Lasers 2015 being connected to the same backend database. A number of features are displayed by this example:

- Because at least one of the analyses is an analysis with multiple peaks, LIMS displays the "Multiple Peaks/Analysis Summary" panel.
- For analysis B-84989 LIMS calculates a standard deviation of 0.04 ‰ using the $\delta^{18}O$ values of the five peaks whose "IG" check boxes are not checked and displays the mean and standard deviation in the "Multiple Peaks/Analysis Summary" panel.
- The $\delta^{18}O$ values of the dual-inlet IRMS analyses performed on different days are –7.35 and –7.33 ‰ and they are in excellent agreement.
- Using all three analyses LIMS calculates a mean $\delta^{18}O$ value of –2.46 ‰, identified as "Mean 1;" a standard deviation of 0.22 ‰ is calculated and identified as "Std Dev1."
- LIMS identifies the $\delta^{18}O$ outlier (–7.71 ‰) and calculates a mean and standard deviation from the remaining $\delta^{18}O$ values, which is identifies as "Mean 2" and "Std Dev 2," respectively. Their values are –7.34 ‰ and 0.01 ‰, respectively.
- LIMS presents a "Mean Final Delta" value, which is that of "Mean 1" (in bold font) having a value of –7.46 ‰.

The two dual-inlet IRMS analyses analyzed on different days are in good agreement. Because analysis B-84989 is not in satisfactory agreement with the dual-inlet IRMS measurement, it is justifiable to ignore analysis B-84989. To ignore this analysis one would:

1. Right-click any of the check boxes in the "IG" column having peak numbers between 7 and 11, and LIMS will display the dialog box shown in Figure 25.5.
2. Click "OK" and LIMS will check the ignore check boxes for peaks 7 through 11 of B-84989, indicating that these measurements are ignored. Because there are now no analyses with multiple peaks to display, LIMS hides the "Multiple Peaks/Analysis Summary" panel and LIMS updates the "Mean Final Delta" (–7.34 ‰), "Mean 1", "Std Dev 1", "Mean 2", and "Std Dev 2" fields as shown in Figure 25.6.

The $\delta^{18}O$ value of W-148706 is ready to be stored (Section 28).



Date	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	IG Comment	IG cnt	Amt	Area Vs	w(O) (%)	IG Cn	MS Err	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
12/3/2016		D-306498	1	800	48								-7.37			0.98917	-0.06	-7.35	
12/5/2016		D-306517	1	800	31								-7.33			0.98899	-0.09	-7.33	
12/6/2016		B-84989	1	808	2-7			450	3.57				-11.52			1.00000	0.0	-11.52	☑
12/6/2016		B-84989	2	808	2-7			450	3.55				-8.92			1.00000	0.0	-8.92	☑
12/6/2016		B-84989	3	808	2-7			450	3.56				-8.22			1.00000	0.0	-8.22	☑
12/6/2016		B-84989	4	808	2-7			450	3.58				-8.00			1.00000	0.0	-8.00	☑
12/6/2016		B-84989	5	808	2-7			450	3.57				-7.88			1.00000	0.0	-7.88	☑
12/6/2016		B-84989	6	808	2-7			450	3.55				-7.73			1.00000	0.0	-7.73	☑
12/6/2016		B-84989	7	808	2-7			450	3.55				-7.70			1.00000	0.0	-7.70	
12/6/2016		B-84989	8	808	2-7			450	3.53				-7.71			1.00000	0.0	-7.71	
12/6/2016		B-84989	9	808	2-7			450	3.54				-7.66			1.00000	0.0	-7.66	
12/6/2016		B-84989	10	808	2-7			450	3.53				-7.71			1.00000	0.0	-7.71	
12/6/2016		B-84989	11	808	2-7			450	3.48				-7.78			1.00000	0.0	-7.78	

Fig. 25.4. Example of a sample analyzed with an instrument generating multiple $\delta^{18}O$ peaks per analysis. Analyses D-306498 and D-306517 are dual-inlet IRMS. Analysis B-84989 is a liquid water laser absorption spectrometer having 11 peaks (injections), the first six of which are ignored.

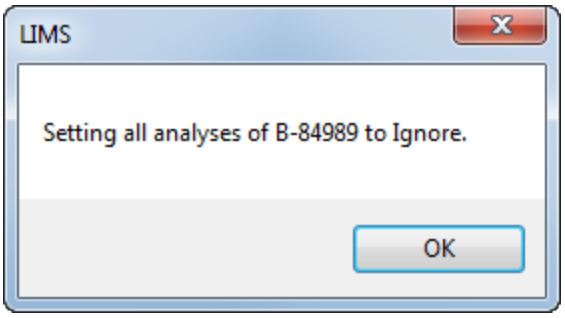
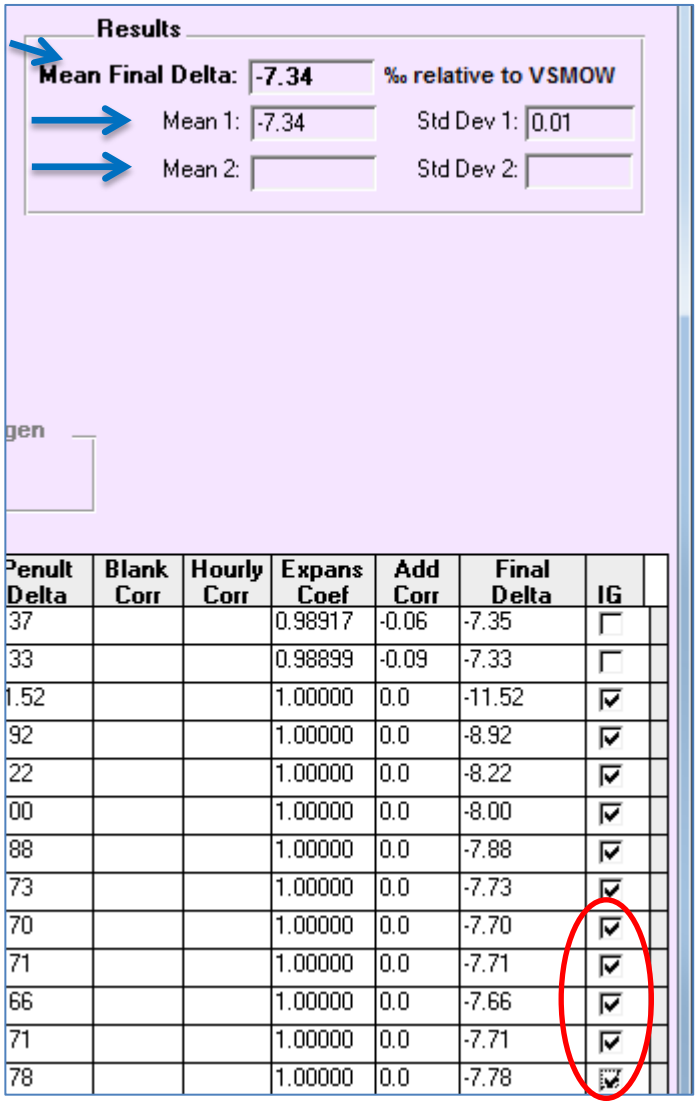


Fig. 25.5. Dialog box setting all analyses of B-84989 to ignore.



Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
37			0.98917	-0.06	-7.35	☐
33			0.98899	-0.09	-7.33	☐
1.52			1.00000	0.0	-11.52	☑
92			1.00000	0.0	-8.92	☑
22			1.00000	0.0	-8.22	☑
00			1.00000	0.0	-8.00	☑
88			1.00000	0.0	-7.88	☑
73			1.00000	0.0	-7.73	☑
70			1.00000	0.0	-7.70	☑
71			1.00000	0.0	-7.71	☑
66			1.00000	0.0	-7.66	☑
71			1.00000	0.0	-7.71	☑
78			1.00000	0.0	-7.78	☑

Fig. 25.6. Delta values and standard deviations are updated accordingly when all analyses of B-84989 are ignored.

25.3 Numerical Comments

Section 4.3 showed how users can enable LIMS to display averages of comment field entries if they are numeric by enabling the "Display average of comment field entries if they are numeric" check box on the Option form (Fig. 4.12 and Table 4.1). These values might be mass fractions (concentrations) or any other quantity. A user might populate the Comment field of a mass spectrometer data file imported into LIMS or they might use the Add or Edit Analyses form (Section 27).

For example, Figure 25.7 shows an analysis of CO_2 evolved by off-line phosphoric acid reaction with calcite. The yield of CO_2 (in percent) measured by a manometer was entered into the Comment field of the analysis. Figure 25.7 demonstrates several features:

- Two analyses of this sample have yields of 98.3 and 97.9 %.
- A field labelled "Mean of Analyses Comments (If Numeric)" displays a value of "98.100 ± 0.283 (n = 2)." This value will be included in "in Progress" Excel files created by users in Section 26.
- An ignore concentration column ("IG cnt") is visible. Clicking an "IG cnt" check box of an analysis updates the mean and standard deviation of the Comment entries (Fig. 25.8).

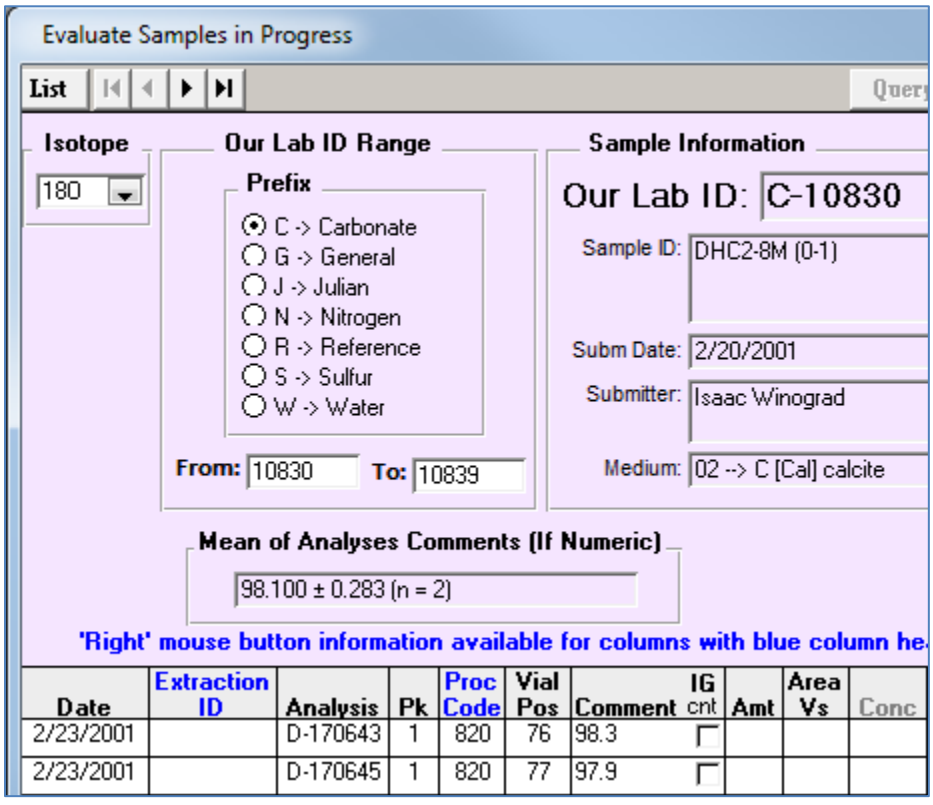


Fig. 25.7. Mean and standard deviation of Comment field entries.

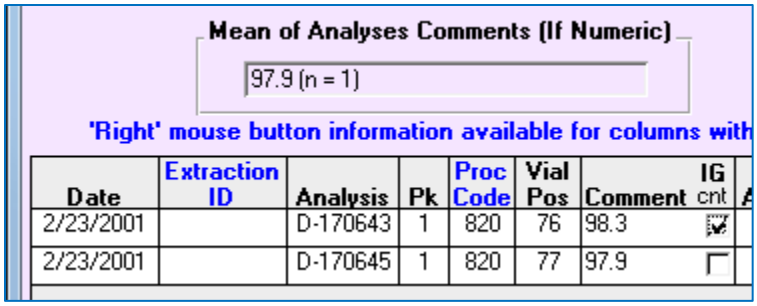
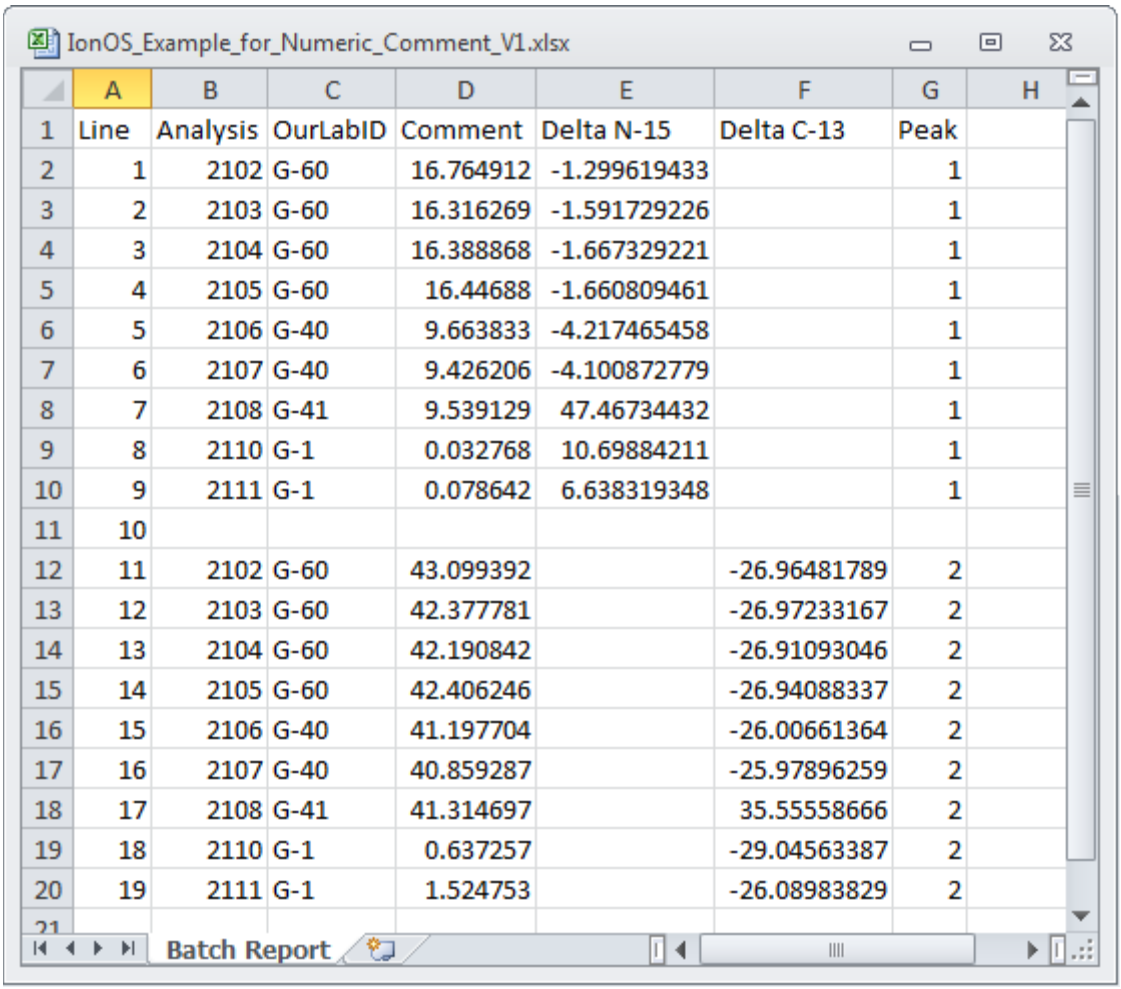


Fig. 25.8. Updated mean and standard deviation of Comment field entries. Clicking the "IG cnt" check box of analysis D-170643 updates the mean and standard deviation of the Comment field entries to "97.9 (n = 1)."

Some data files generated by mass spectrometers have element mass fractions (concentrations) and they are missing either an amount column or a peak area column. Thus, LIMS is not able to determine mass fractions. The numerical comment feature of LIMS can be used to import mass fractions in the comment field. Subsequently, mean and standard deviations of comment entries can be exported to an Excel file (Section 26) or the mean can be saved to the "Comment" field of each sample on a Project form (Section 28). For example, the file "IonOS_Example_for_Numeric_Comment.xlsx," which is found in the folder named "Section 25" that accompanies this manual, is an IonOS file having mass fractions for carbon, nitrogen, and sulfur. This file has no amounts and no area data. By rearranging these data and adding columns the columns "Line", "Analysis", "OurLabID", "Comment", "Delta N-15", "Delta C-13", and "Peak", one is able to create an Excel data file that can be imported into LIMS (Fig. 25.9). This file is named "IonOS_Example_for_Numeric_Comment_V1.xlsx" and is found in the folder named "Section 25." After importing and normalizing these data, Figure 25.10 shows nitrogen mass fractions in the "Comment" field. The mean value of "16.479 ± 0.198 (n = 4)" can be saved in an Excel file (Section 26) or the mean value (16.48 %) can be saved to the "Comment" field of sample G-60 on the Project form containing G-60 (Section 28).

This completes the discussion of the Evaluate Samples in Progress form. The next action of the user could be

- Store the results just evaluated if they are satisfactory, which is discussed in Section 28.
- Print or save to an Excel file "in progress" analyses, which is discussed in Section 26.
- Add samples that need another analysis to the appropriate "Samples To Be Analyzed" queue (Section 29).



IonOS_Example_for_Numeric_Comment_V1.xlsx

	A	B	C	D	E	F	G	H
1	Line	Analysis	OurLabID	Comment	Delta N-15	Delta C-13	Peak	
2	1	2102	G-60	16.764912	-1.299619433		1	
3	2	2103	G-60	16.316269	-1.591729226		1	
4	3	2104	G-60	16.388868	-1.667329221		1	
5	4	2105	G-60	16.44688	-1.660809461		1	
6	5	2106	G-40	9.663833	-4.217465458		1	
7	6	2107	G-40	9.426206	-4.100872779		1	
8	7	2108	G-41	9.539129	47.46734432		1	
9	8	2110	G-1	0.032768	10.69884211		1	
10	9	2111	G-1	0.078642	6.638319348		1	
11	10							
12	11	2102	G-60	43.099392		-26.96481789	2	
13	12	2103	G-60	42.377781		-26.97233167	2	
14	13	2104	G-60	42.190842		-26.91093046	2	
15	14	2105	G-60	42.406246		-26.94088337	2	
16	15	2106	G-40	41.197704		-26.00661364	2	
17	16	2107	G-40	40.859287		-25.97896259	2	
18	17	2108	G-41	41.314697		35.55558666	2	
19	18	2110	G-1	0.637257		-29.04563387	2	
20	19	2111	G-1	1.524753		-26.08983829	2	
21								

Batch Report

Fig. 25.9. Example file ("IonOS_Example_for_Numeric_Comment_V1.xlsx") used for importing carbon and nitrogen mass fractions (concentrations) in the "Comment" column.

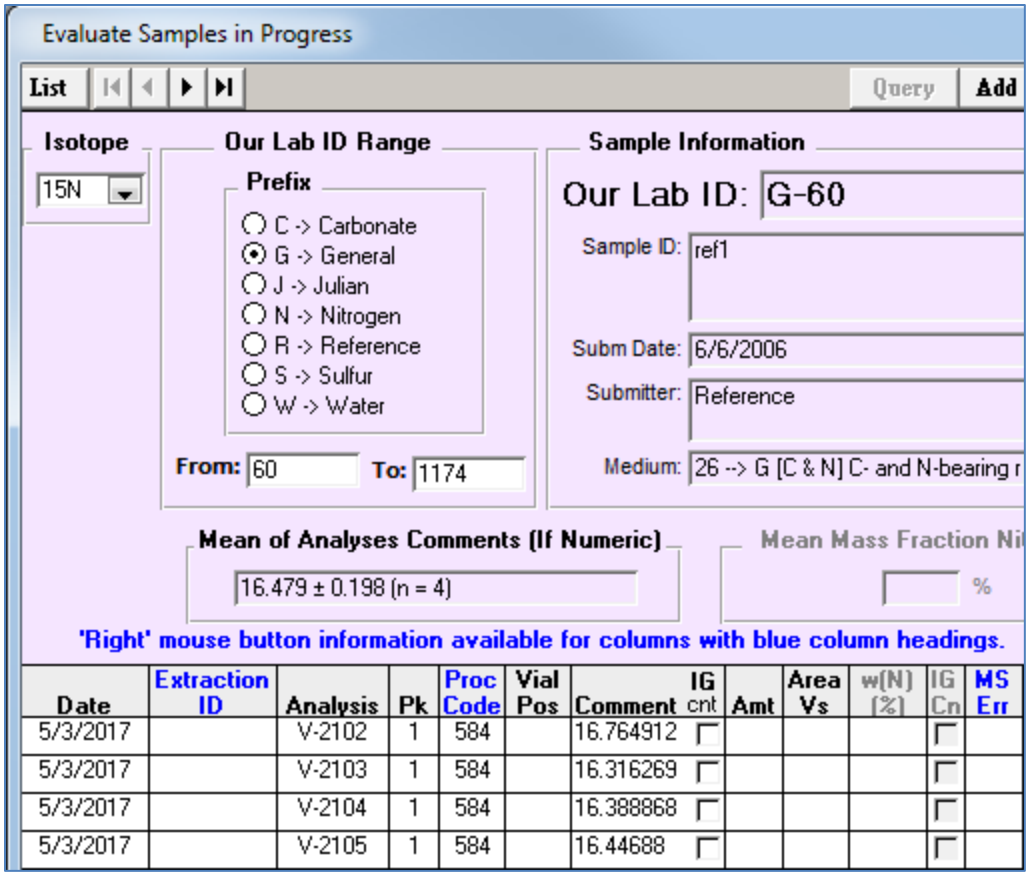


Fig. 25.10. Numerical comment field used for nitrogen mass fractions (concentration).

25.4 The Ethereal Mass Spectrometer

Occasionally one may realize that the mean delta value calculated from two or more mass spectrometer analyses is in error and needs to be adjusted. For example, if an analytical run were suspicious because of a specific factor, such as contaminated helium or a higher than normal drift with time, preference might be given to analyses from an analytical run not having any of these issues. The user may be able to estimate the best delta value, and it can be added by clicking "Add Ethereal." Clicking this button brings up the "Ethereal mass spectrometer" shown in Figure 13.2. The user can then enter the final delta value for the sample (not a penultimate delta value). All of the analyses except the analysis from the Ethereal mass spectrometer can be ignored by checking the "IG" check boxes, and then the value from the Ethereal mass spectrometer is stored when the "Store Single Analysis" check box of the Store Sample Results to Projects form is checked (Section 28).

26 Printing or Exporting Samples in Progress

Some analysts (and clients) prefer to see and evaluate individual analyses offline using Excel or view print-outs of detailed summaries and the statistics for individual samples before they are stored. This is facilitated by clicking "Print/Export Samples in Progress" on the main page, which opens the Print or Export Samples in Progress form.

This section continues from Section 25 and assumes that the reader has connected to the backend database name "Evaluate_SIP_BACKEND_DB.accdb" as discussed in Section 25.1. To demonstrate use of the Print or Export Samples in Progress form:

1. On the LIMS main page click "Print/Export Samples in Progress" and the Print or Export Samples in Progress form opens.
2. Select "13C" for the "Isotope."
3. Select "G" for the "Prefix."
4. Enter "1202" for both the "From" and "to" fields.
5. Check the "Print Extraction IDs, Comments, Concentrations, Amounts, and Area" check box.
6. Check the "Print Extraction ID Details" check box and the Print or Export Samples in Progress form should appear as shown in Figure 26.1.
7. Click "Print" to generate the report shown in Figure 26.2.

Perhaps the most common use of the Print or Export Samples in Progress form is to export results to Excel files. Clicking the "Save as Excel File" check box changes the "Print" button to a "Save" button. Clicking "Save" causes LIMS to create two Excel files:

- The first is an Excel file containing one row of data for each analysis number of each sample in the selection. An example file named"G-25000--G-25148_15N_BriefSummary.xlsx" is provided in the folder named "Section 26" that accompanies this manual. Summary information for each Our Lab ID is contained in approximately 40 columns, including columns for mean delta values and standard deviation, element mass fractions if available, project submission date, etc. This summary file is provided to clients by some LIMS users.

  If the "Display average of comment field entries if they are numeric" check box on the Options form is checked (Fig. 4.12 and Sections 4.3 and 25.3), LIMS will include a "Mean_Numeric_Comment" column in the Excel file. This column can be used for element mass fractions (concentration) as shown in Figure 25.9 (Section 25.3).

- The second is a file containing one row of data for each peak number of each analysis. In a folder named "Section 26" an example file name is "G-25000--G-25148_15N.xlsx" is provided. Details of each analysis are contained in approximately 50 columns of data

including penultimate delta value, blank correction, hourly drift correction, expansion coefficient, and additive correction factor. In case of questions at a later data by a client about analysis of one or more samples, this file can be easily generated by LIMS users and provided to clients.

Clicking the "Export with references" check box (Fig. 26.1) enables users to include the results of all reference materials analyzed with the "Our Lab ID" and "Isotope" selection. This additional information in an Excel file is of use for clients that request that delta values of all references be provided with results of their samples.

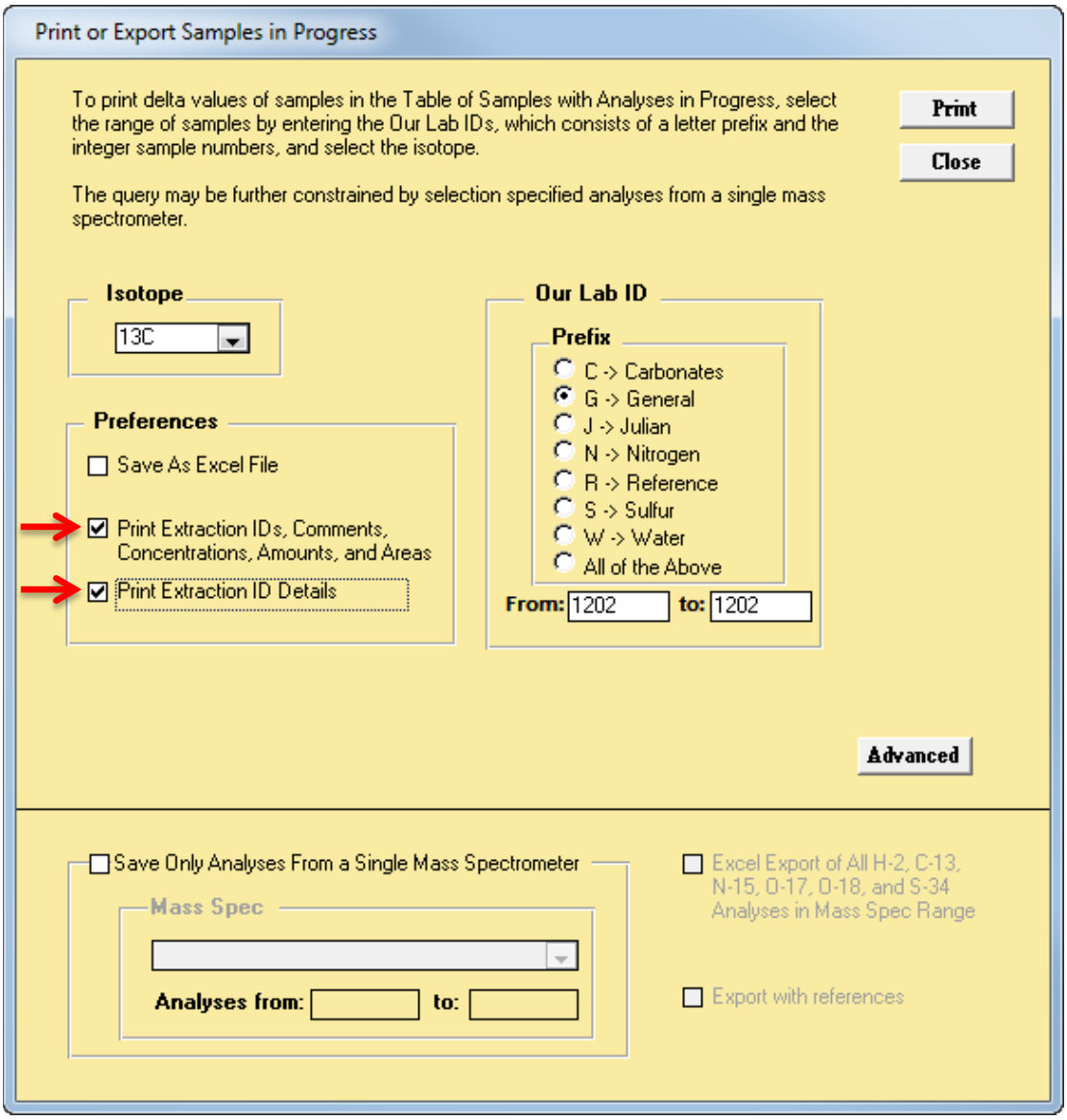
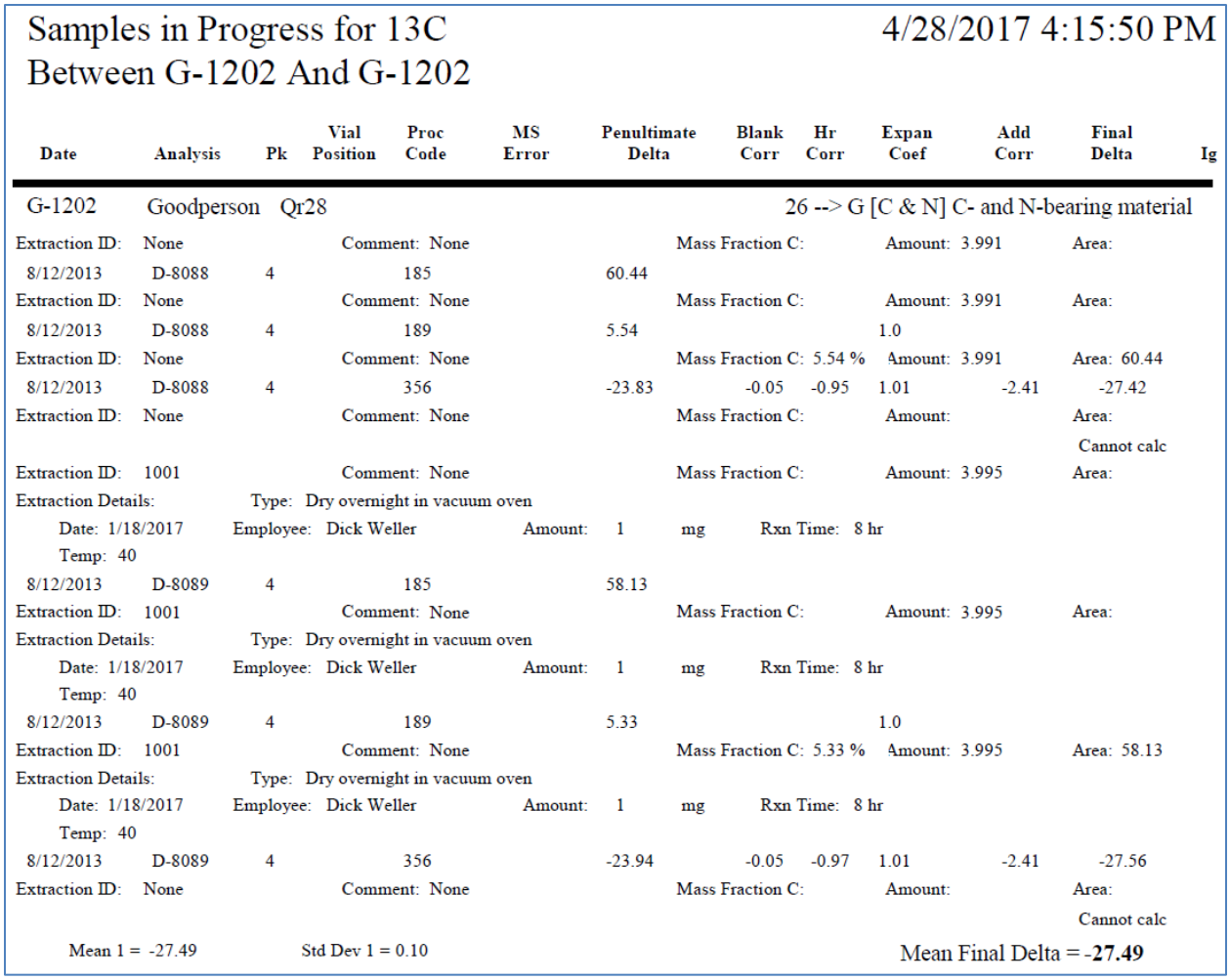


Fig. 26.1. Example of the Print or Export Samples in Progress form.



Samples in Progress for 13C
Between G-1202 And G-1202

4/28/2017 4:15:50 PM

Date	Analysis	Pk	Vial Position	Proc Code	MS Error	Penultimate Delta	Blank Corr	Hr Corr	Expan Coef	Add Corr	Final Delta	Ig
G-1202	Goodperson	Qr28									26 --> G [C & N] C- and N-bearing material	
Extraction ID: None				Comment: None				Mass Fraction C:		Amount: 3.991	Area:	
8/12/2013	D-8088	4		185		60.44						
Extraction ID: None				Comment: None				Mass Fraction C:		Amount: 3.991	Area:	
8/12/2013	D-8088	4		189		5.54			1.0			
Extraction ID: None				Comment: None				Mass Fraction C: 5.54 %		Amount: 3.991	Area: 60.44	
8/12/2013	D-8088	4		356		-23.83	-0.05	-0.95	1.01	-2.41	-27.42	
Extraction ID: None				Comment: None				Mass Fraction C:		Amount:	Area: Cannot calc	
Extraction ID: 1001				Comment: None				Mass Fraction C:		Amount: 3.995	Area:	
Extraction Details:			Type: Dry overnight in vacuum oven									
Date: 1/18/2017		Employee: Dick Weller			Amount: 1	mg		Rxn Time: 8 hr				
Temp: 40												
8/12/2013	D-8089	4		185		58.13						
Extraction ID: 1001				Comment: None				Mass Fraction C:		Amount: 3.995	Area:	
Extraction Details:			Type: Dry overnight in vacuum oven									
Date: 1/18/2017		Employee: Dick Weller			Amount: 1	mg		Rxn Time: 8 hr				
Temp: 40												
8/12/2013	D-8089	4		189		5.33			1.0			
Extraction ID: 1001				Comment: None				Mass Fraction C: 5.33 %		Amount: 3.995	Area: 58.13	
Extraction Details:			Type: Dry overnight in vacuum oven									
Date: 1/18/2017		Employee: Dick Weller			Amount: 1	mg		Rxn Time: 8 hr				
Temp: 40												
8/12/2013	D-8089	4		356		-23.94	-0.05	-0.97	1.01	-2.41	-27.56	
Extraction ID: None				Comment: None				Mass Fraction C:		Amount:	Area: Cannot calc	

Mean 1 = -27.49 Std Dev 1 = 0.10 Mean Final Delta = **-27.49**

Fig. 26.2. Example of the Print Samples in Progress Report. This report displaysExtractions ID details from Table of Extractions, as well as Extraction IDs, Comments, Amounts, and Areas. Deselect the "Print Extraction ID Details" to print a shorter report.

Commonly, it is important to evaluate performance of a mass spectrometer over a day or several days, and LIMS provides the ability to constrain the file export to a specified range of analyses and mass spectrometer as exemplified by Figure 26.3.
Clicking "Advanced" hides the lower portion of the Print or Export Samples in Progress form. Any selections of check boxes or text boxes will be discarded by LIMS.

One of the exports that is performed daily for some IRMSs in the Reston Stable Isotope Laboratory (RSIL) of the U.S. Geological Survey is a special export of all samples and all isotopes in a selected range of analyses of an IRMS. This export is enabled by clicking the "Excel Export of All H-2, C-13, N-15, O-17, O-18, and S-34 Analyses in Mass Spec Range"

check box as exemplified in Figure 26.4. File "H-86760__H-86973.xls," which is provided in the folder named "Section 26" that accompanies this manual, is an example of this special Excel export. This file contains nitrogen-, oxygen-, and sulfur-isotope data for each analysis number of the H mass spectrometer. Columns for sulfur mass fraction, blank correction for each isotope, and additive correction factor for each isotope are included.

This completes discussion of the Print or Export Samples in Progress form.

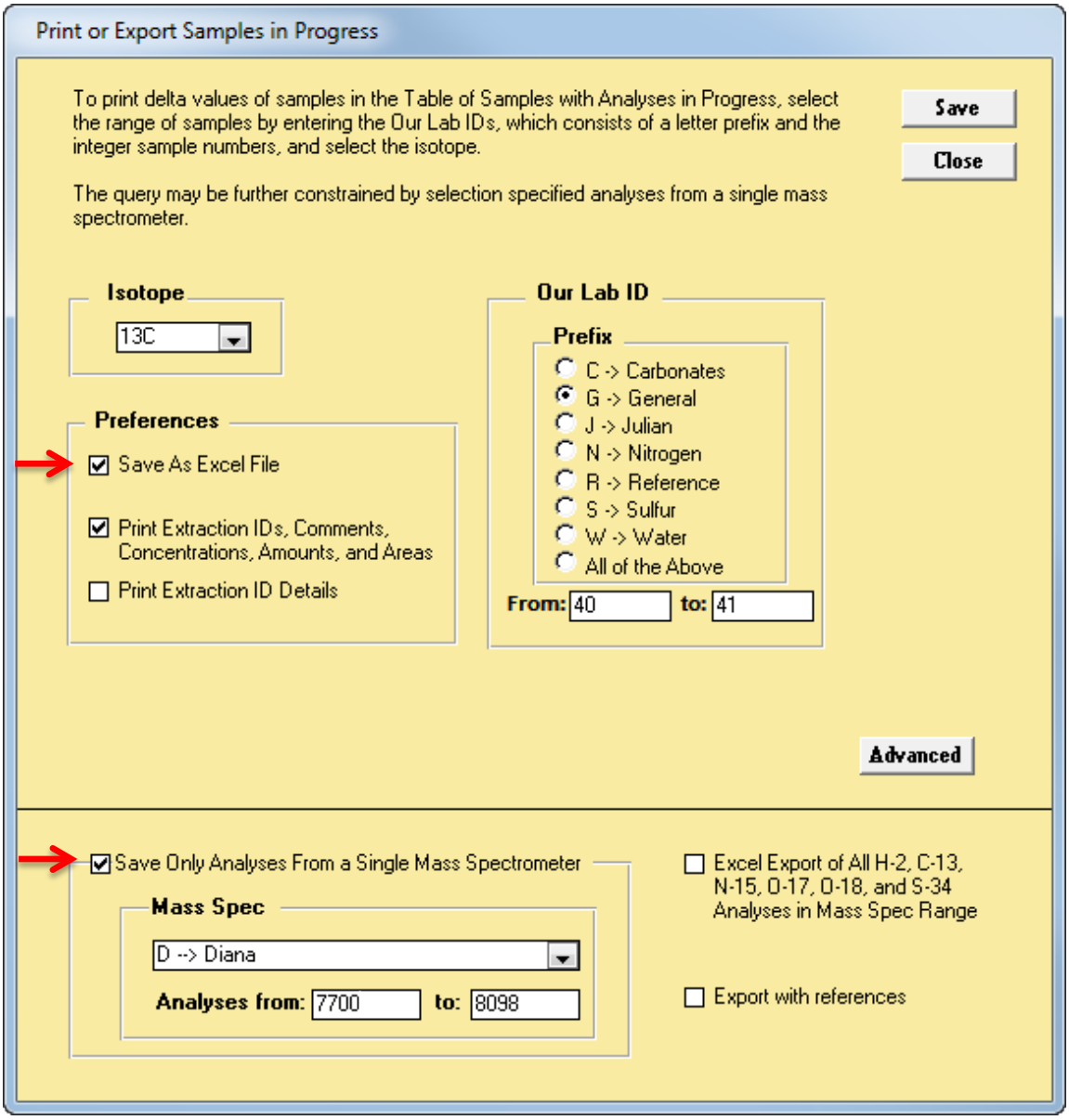


Fig. 26.3. Exporting Samples in Progress data from a specified range of analyses from one mass spectrometer.

⚠ **Helpful Hint:** Even though there are fields for both "From" and "to," if one wants to print just one sample, one only needs to enter in the numeric part of the Our Lab ID into the "From" box and click the Enter key three times to print (or save) the sample. LIMS will automatically fill in the blank "to" field.

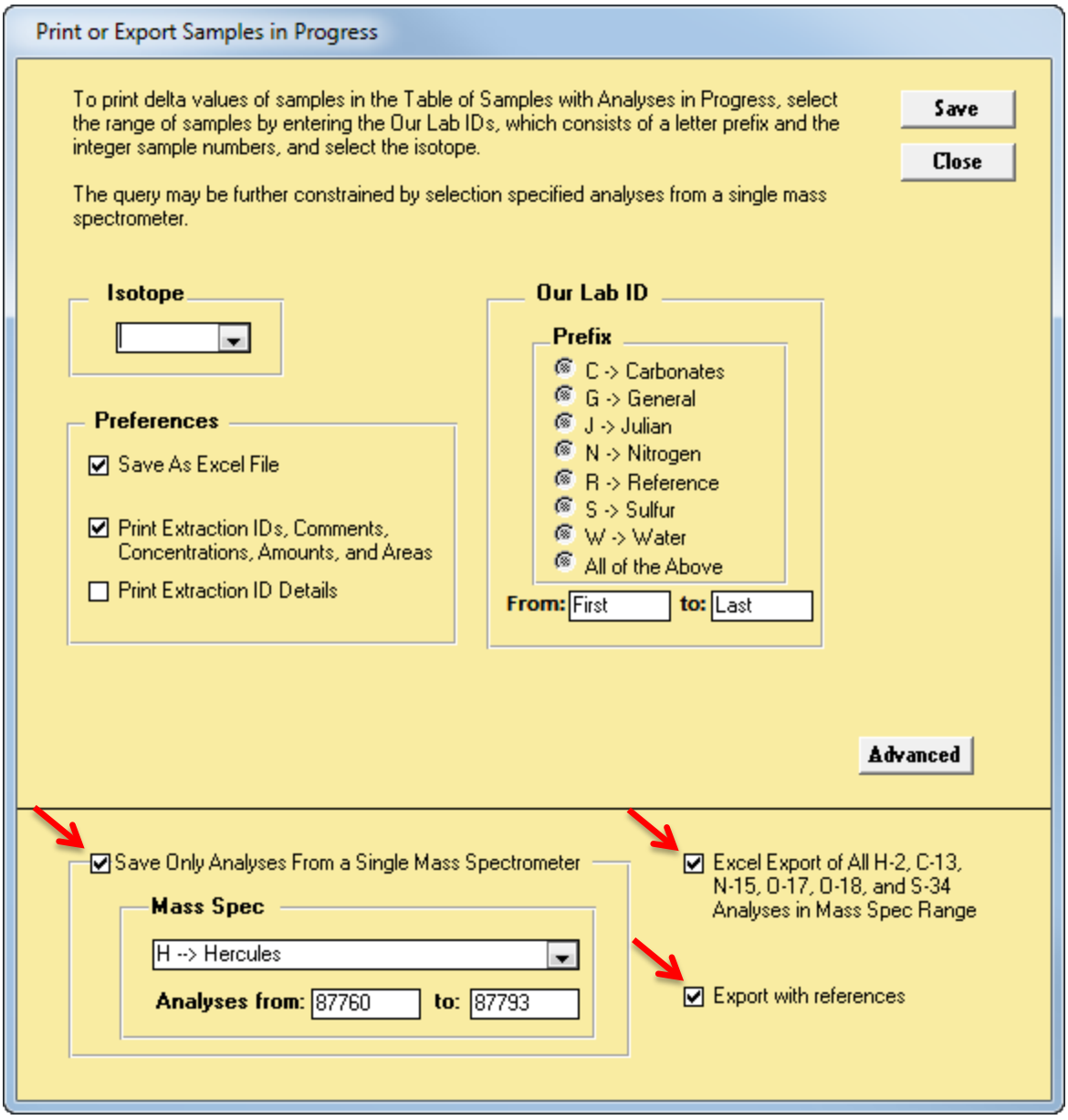
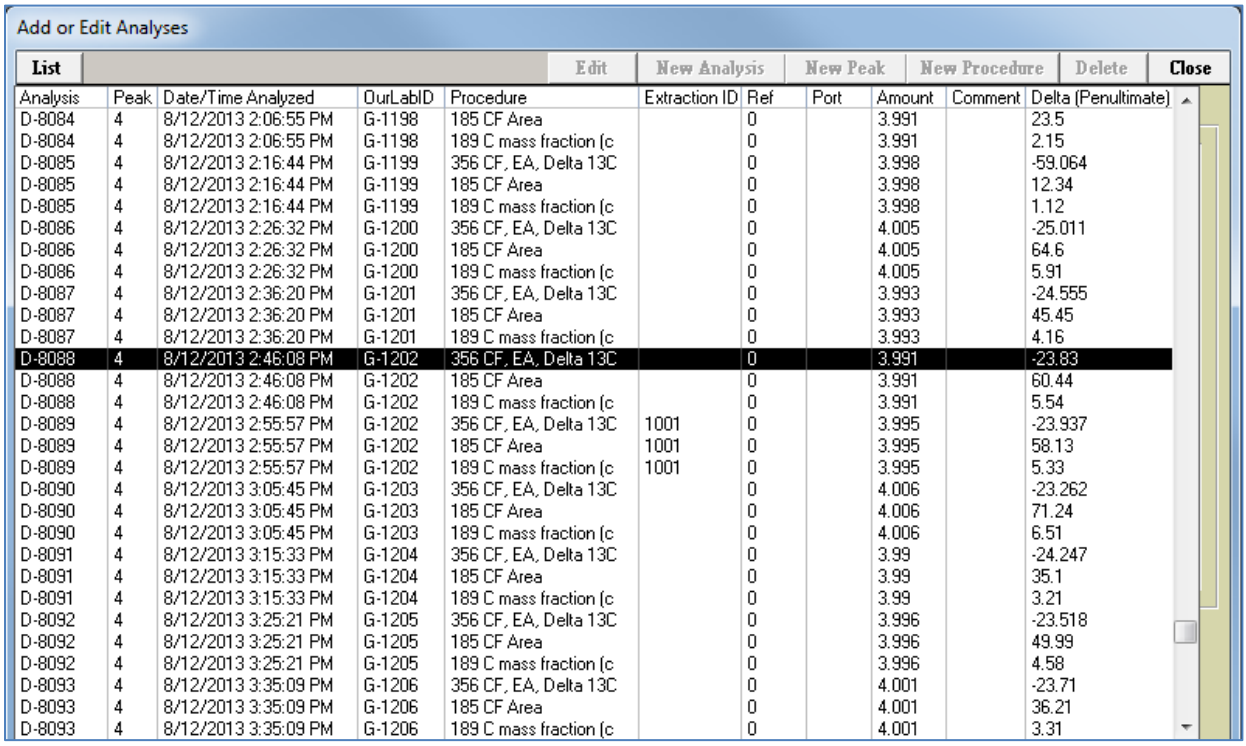


Fig. 26.4. Special export of all results of all samples and all isotopes analyzed in a selected analysis range of a mass spectrometer.

27 Viewing and Editing Sample Analysis Results

There are occasions when information associated with a sample analysis needs to be changed. A common problem is to correct sample identifiers when the wrong sample was analyzed. Users are able to view, edit, or add analyses using the Add or Edit Analysis form. This section continues from Section 26 and assumes that the reader has connected to the backend database name "Evaluate_SIP_BACKEND_DB.accdb" as discussed in Section 25.1. To demonstrate use of this form consider an example in which the analyst has learned after the daily analysis that they misread a sample container and sample G-1205 of Herkimer Goodperson was inadvertently misread as G-1202 and analyzed as mass spectrometer analysis D-8088. To correct this issue in LIMS:

1. On the LIMS main page click "View / Edit Information about Samples Analyses" and the Add or Edit Analyses form will open.
2. For the "Mass Spec," select "D --> Diana."
3. Click "List"
4. Select procedure 356 of peak number 4 of analysis D-8088 (Fig. 27.1), and LIMS will populate fields in the form with this analysis (Fig. 27.2).
5. Click "Edit" and the backgrounds of the fields that can be edited will be white (Fig 27.3).



Analysis	Peak	Date/Time Analyzed	OurLabID	Procedure	Extraction ID	Ref	Port	Amount	Comment	Delta (Penultimate)
D-8084	4	8/12/2013 2:06:55 PM	G-1198	185 CF Area		0		3.991		23.5
D-8084	4	8/12/2013 2:06:55 PM	G-1198	189 C mass fraction (c		0		3.991		2.15
D-8085	4	8/12/2013 2:16:44 PM	G-1199	356 CF, EA, Delta 13C		0		3.998		-59.064
D-8085	4	8/12/2013 2:16:44 PM	G-1199	185 CF Area		0		3.998		12.34
D-8085	4	8/12/2013 2:16:44 PM	G-1199	189 C mass fraction (c		0		3.998		1.12
D-8086	4	8/12/2013 2:26:32 PM	G-1200	356 CF, EA, Delta 13C		0		4.005		-25.011
D-8086	4	8/12/2013 2:26:32 PM	G-1200	185 CF Area		0		4.005		64.6
D-8086	4	8/12/2013 2:26:32 PM	G-1200	189 C mass fraction (c		0		4.005		5.91
D-8087	4	8/12/2013 2:36:20 PM	G-1201	356 CF, EA, Delta 13C		0		3.993		-24.555
D-8087	4	8/12/2013 2:36:20 PM	G-1201	185 CF Area		0		3.993		45.45
D-8087	4	8/12/2013 2:36:20 PM	G-1201	189 C mass fraction (c		0		3.993		4.16
D-8088	4	8/12/2013 2:46:08 PM	G-1202	356 CF, EA, Delta 13C		0		3.991		-23.83
D-8088	4	8/12/2013 2:46:08 PM	G-1202	185 CF Area		0		3.991		60.44
D-8088	4	8/12/2013 2:46:08 PM	G-1202	189 C mass fraction (c		0		3.991		5.54
D-8089	4	8/12/2013 2:55:57 PM	G-1202	356 CF, EA, Delta 13C	1001	0		3.995		-23.937
D-8089	4	8/12/2013 2:55:57 PM	G-1202	185 CF Area	1001	0		3.995		58.13
D-8089	4	8/12/2013 2:55:57 PM	G-1202	189 C mass fraction (c	1001	0		3.995		5.33
D-8090	4	8/12/2013 3:05:45 PM	G-1203	356 CF, EA, Delta 13C		0		4.006		-23.262
D-8090	4	8/12/2013 3:05:45 PM	G-1203	185 CF Area		0		4.006		71.24
D-8090	4	8/12/2013 3:05:45 PM	G-1203	189 C mass fraction (c		0		4.006		6.51
D-8091	4	8/12/2013 3:15:33 PM	G-1204	356 CF, EA, Delta 13C		0		3.99		-24.247
D-8091	4	8/12/2013 3:15:33 PM	G-1204	185 CF Area		0		3.99		35.1
D-8091	4	8/12/2013 3:15:33 PM	G-1204	189 C mass fraction (c		0		3.99		3.21
D-8092	4	8/12/2013 3:25:21 PM	G-1205	356 CF, EA, Delta 13C		0		3.996		-23.518
D-8092	4	8/12/2013 3:25:21 PM	G-1205	185 CF Area		0		3.996		49.99
D-8092	4	8/12/2013 3:25:21 PM	G-1205	189 C mass fraction (c		0		3.996		4.58
D-8093	4	8/12/2013 3:35:09 PM	G-1206	356 CF, EA, Delta 13C		0		4.001		-23.71
D-8093	4	8/12/2013 3:35:09 PM	G-1206	185 CF Area		0		4.001		36.21
D-8093	4	8/12/2013 3:35:09 PM	G-1206	189 C mass fraction (c		0		4.001		3.31

Fig. 27.1. Upper section of Add or Edit form with List dropdown open .

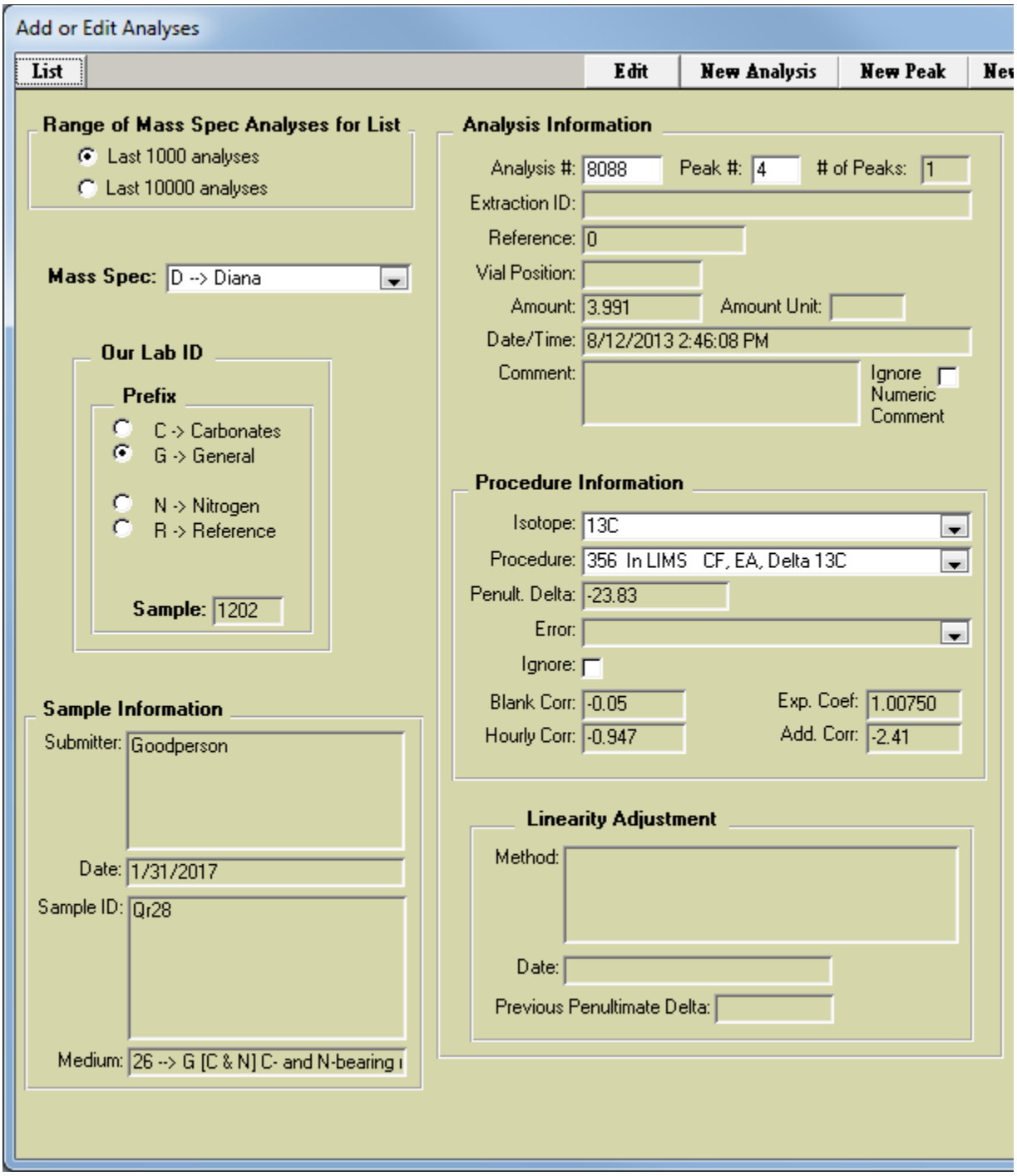


Fig. 27.2. Add or Edit form displaying the $\delta^{13}C$ analysis of D-8088 .

6. Replace the value of "1202" by "1205" in the "Sample" field of the Our Lab ID panel.
7. Click "Save," enter 0 for error code if prompted, and the analysis will be updated.

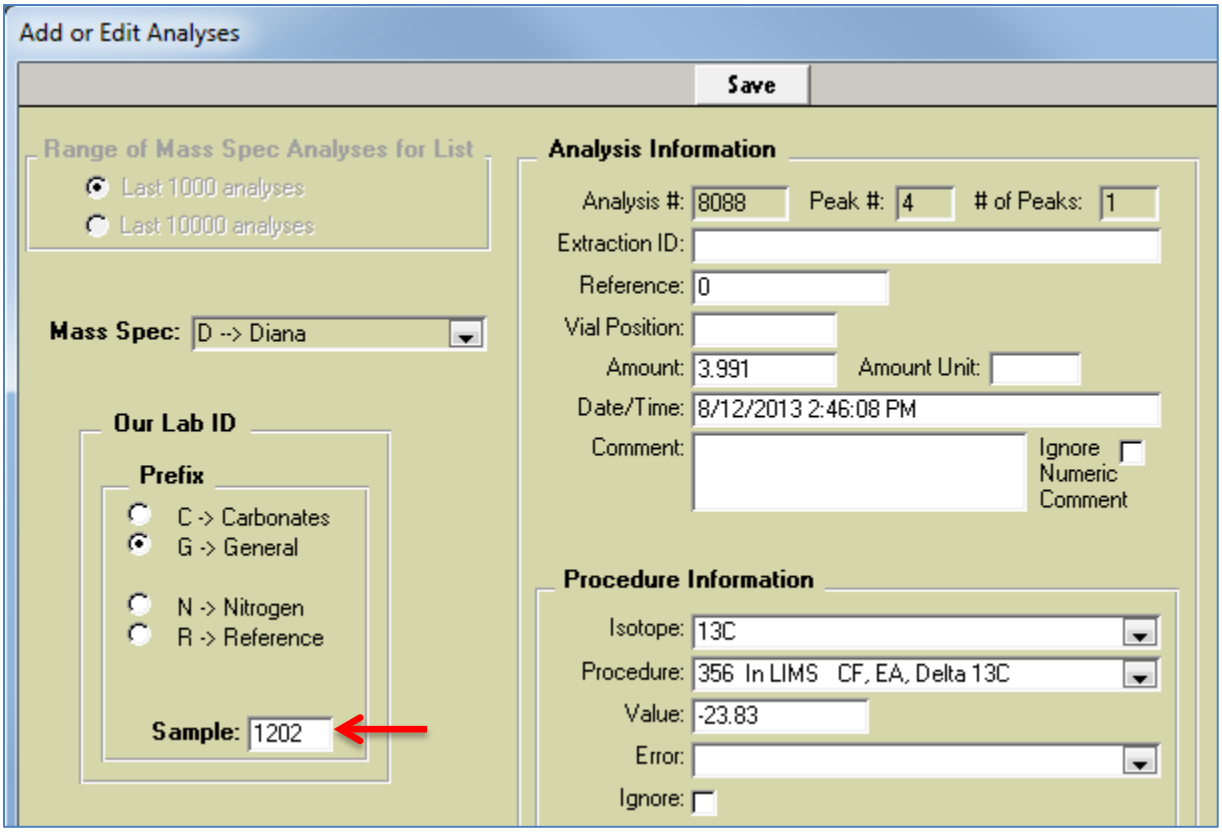


Fig. 27.3. Add or Edit form displaying editable fields with white backgrounds.

In addition to updating procedure 356 of analysis D-8088, the user can confirm that procedures 185 (continuous-flow area) and 189 (carbon mass fraction) have been updated by clicking "List." In addition to editing information for a procedure, a new procedure can be added by clicking "New Procedure." A new peak number and a new analysis can be added by clicking "New Peak" and "New Analysis," respectively. But adding data in this manner is laborious. It is usually better to import a new file that includes the missing information.

⚠ These advanced editing features are intended to facilitate repair of faulty analyses, where the analyst has corrected the data offline. However, a daily analytical run of bad results is better repeated entirely than manually edited. **In short, manual editing of sample results is rarely used under normal operations.**

28 Storing Sample Analysis Results to Projects

28.1 General Information

Final delta values that have been normalized, reviewed, and accepted (and mass fractions if they exist) can be "stored" to a project using the Store Sample Results to Projects form so that they can be reported to a client. This section continues from Section 27 and assumes that the reader has connected to the backend database name "Evaluate_SIP_BACKEND_DB.accdb" as discussed in Section 25.1. To demonstrate use of this form:

1. On the LIMS main page click "Store Sample Results to Projects" and the Store Sample Results to Projects form will open.
2. For the "Prefix," select "G" if not already selected.
3. For the "Isotope" select "13C."
4. For the "From" and "To" fields, enter "1175" and "1208," respectively, which are Herkimer Goodperson's carbon- and nitrogen-bearing samples submitted January 31, 2017.
5. Enable the "Store Single Analysis" check box because many of these samples were analyzed only once and the form appears as shown in Figure 28.1.
6. Click "Store" and LIMS will store δ^{13}C sample results of all selected samples in the "In Progress" queue. This may take a minute. Upon completion, LIMS displays the dialog box shown in Figure 28.2.

Once the results have been stored, the project form is updated as shown in Figure 28.3. Specifically, the "Number of samples completed for 13C" field has been updated to 34. Clicking "Samples" opens the Samples form (Fig. 28.4) and displays G-1175, which has a δ^{13}C value of –23.54 ‰ and a carbon mass fraction (concentration) of 4.36 %. Clicking "Analyses" displays the Analysis form (Fig. 28.5). By clicking "List," LIMS displays the List dropdown of isotope-delta values, continuous-flow areas, and mass fractions of G-1175 (Fig. 28.6). A user can choose to view the δ^{13}C information, the continuous-flow area results, or the carbon mass fraction results. Had a linearity adjustment been performed, the regression type, equation, and previous penultimate delta (see for example Section 19.6.1) would be shown at the bottom of the form in the "Linearity Adjustment" panel. Clicking "Edit" on the Analysis form opens the Edit Analysis form (Fig. 28.7), which is discussed in Section 27. Clicking "Edit" on the Edit Analysis form changes the background of the fields that can be edited to white (Fig. 28.8).

In addition to opening the Store Samples Results to Projects form from the LIMS main page, one can click "Store Samples in Progress" on the Projects form (Fig. 28.3), which opens the Store Sample Results to Projects with the "From" and "to" fields populated as discussed in Section 7.6.3.

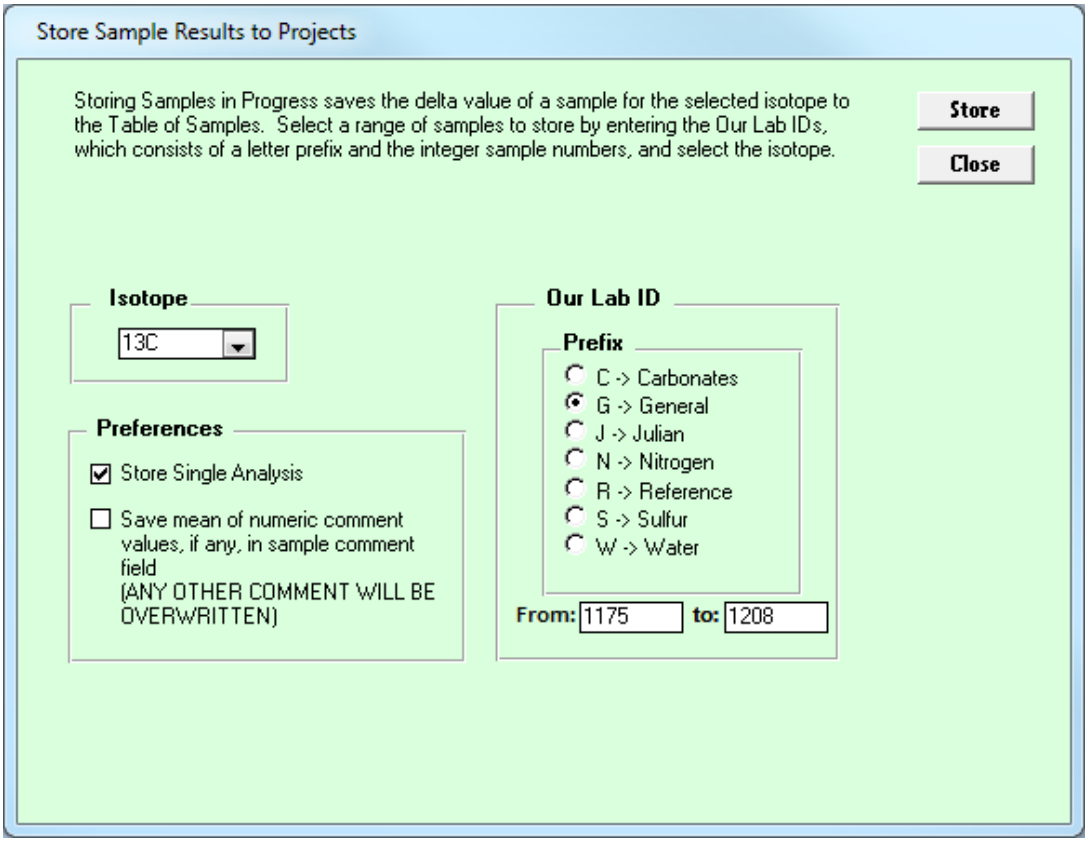


Fig. 28.1. Store Sample Results to Projects form.

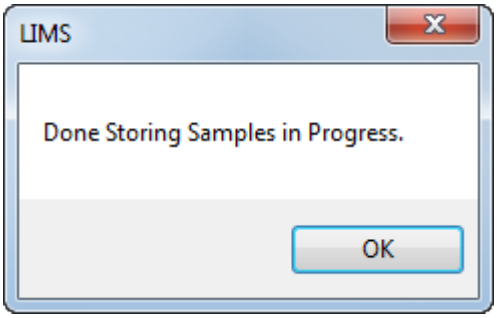


Fig. 28.2. Dialog box upon completion of storing sample results.

⚠ Users need to remember that LIMS does not store final data unless samples have been analyzed twice, or more. To override this feature, enable the "Store Single Analysis" check box—only then will samples analyzed once be stored.
Duplicate analyses are recommended.

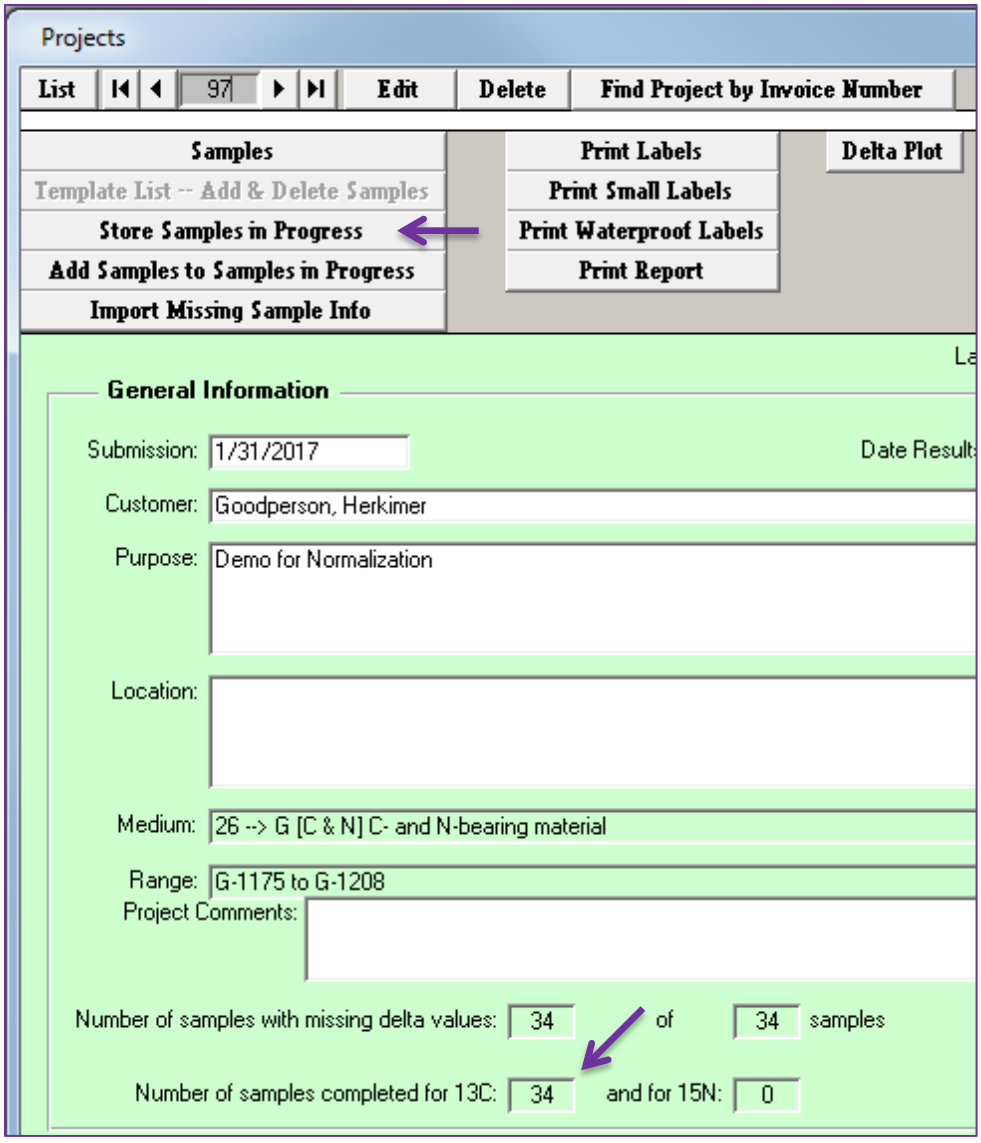


Fig. 28.3. Updated project form of the project having samples G-1175 to G-1208.

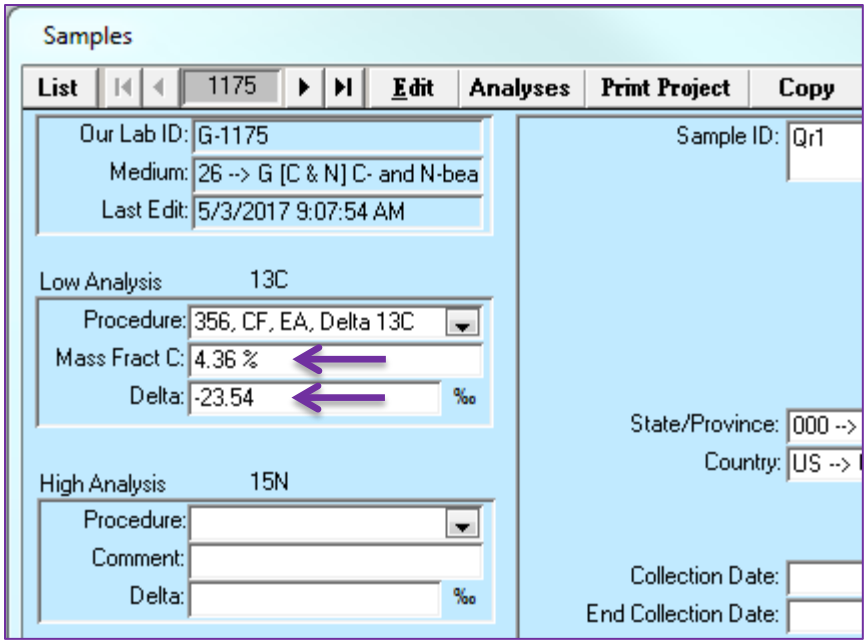


Fig. 28.4. Updated project form of the project having samples G-1175 to G-1208.

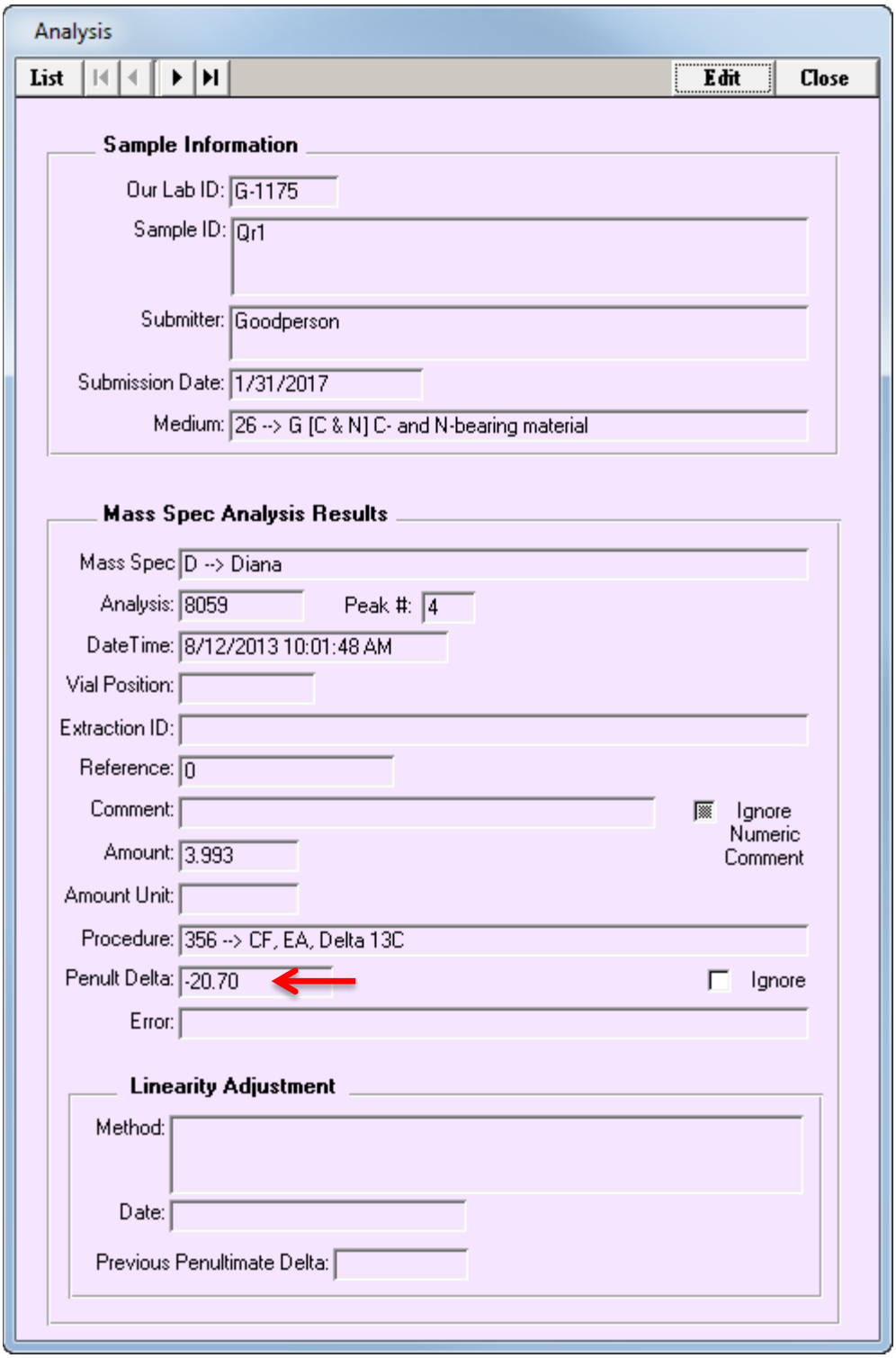


Fig. 28.5. Analysis form showing the penultimate $\delta^{13}C$ value of G-1175. The mass spectrometer analysis number is D-8059 and the peak number is 4.

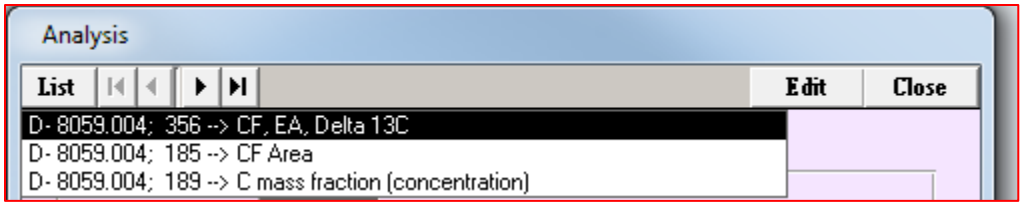


Fig. 28.6. List dropdown of G-1175 on the Analysis form. User can view the $\delta^{13}C$ information, the continuous-flow area results, or the carbon mass fraction results.

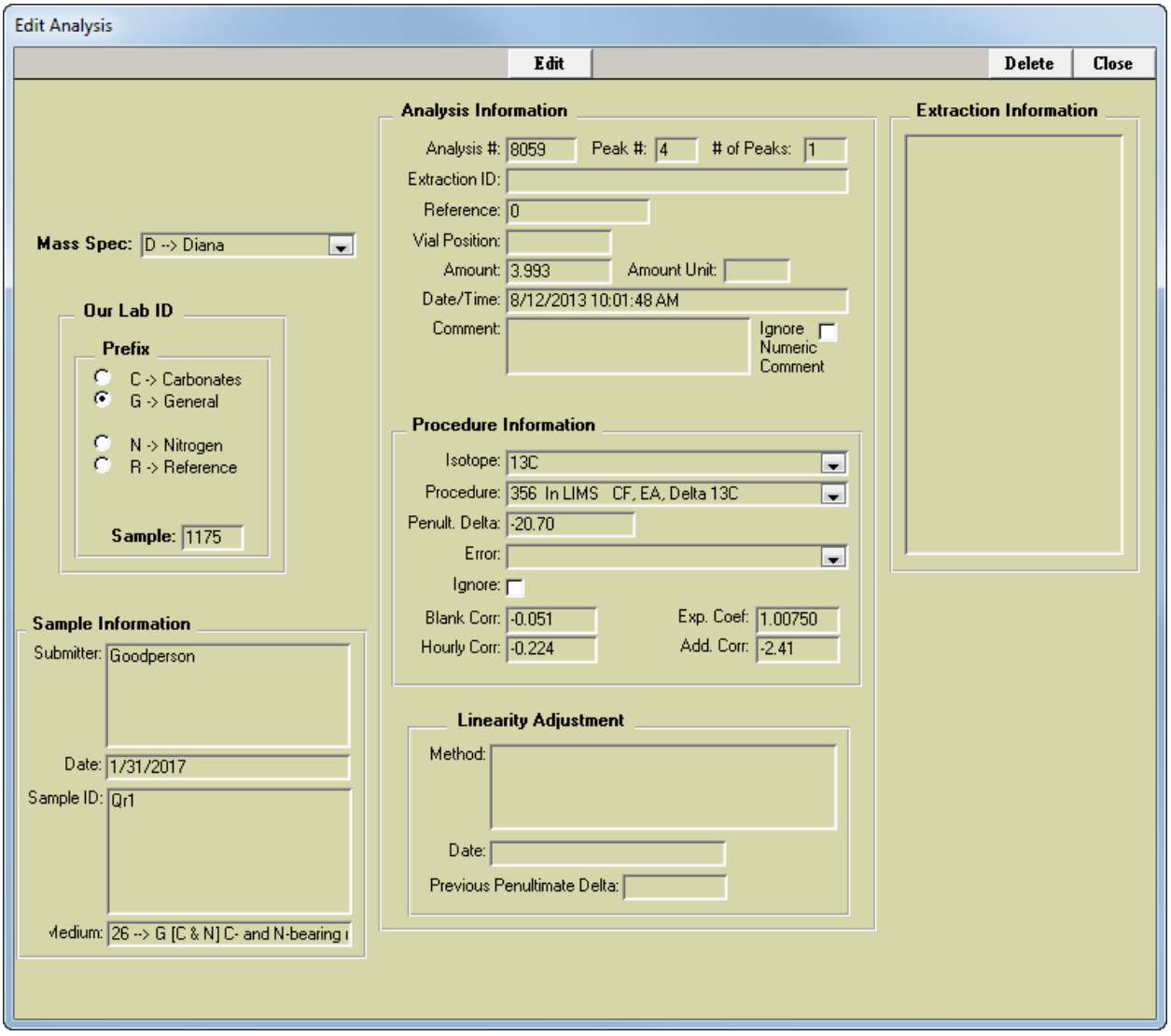


Fig. 28.7. Edit Analysis form displaying the $\delta^{13}C$ results of G-1175.

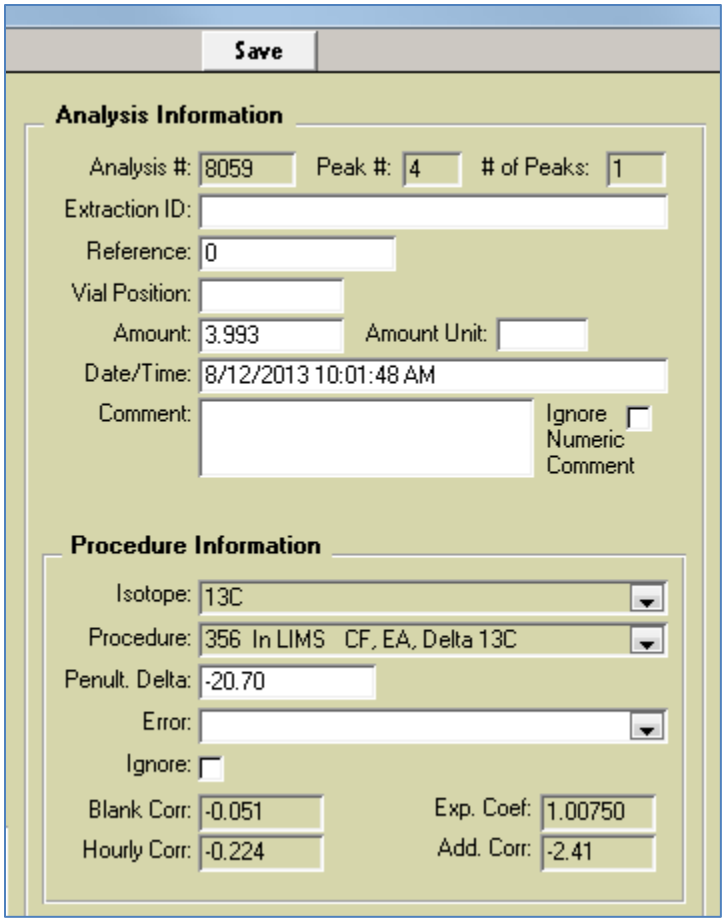


Fig. 28.8. Editable fields of the Edit Analysis form $\delta^{13}C$ results of G-1175.

28.2 Storing Sample Analysis Results from Multiple Mass Spectrometers

If a sample has been analyzed by more than one mass spectrometer, LIMS gives the user the option to store the average value or to store the analyses from a single mass spectrometer and set the ignore field of all analyses from other mass spectrometers to "True" to ignore these results.

Consider water sample W-148706, which is shown in Fig. 25.4. This sample was analyzed twice with one mass spectrometer and once with a laser absorption spectrometer. Suppose one enters the range W-148700 and W-148755 and clicks "Store," LIMS will display the dialog box shown in Figure 28.9. To determine the final delta value from only the D mass spectrometer, ignoring all analyses of the B instrument, one would enter "3" and click "OK."

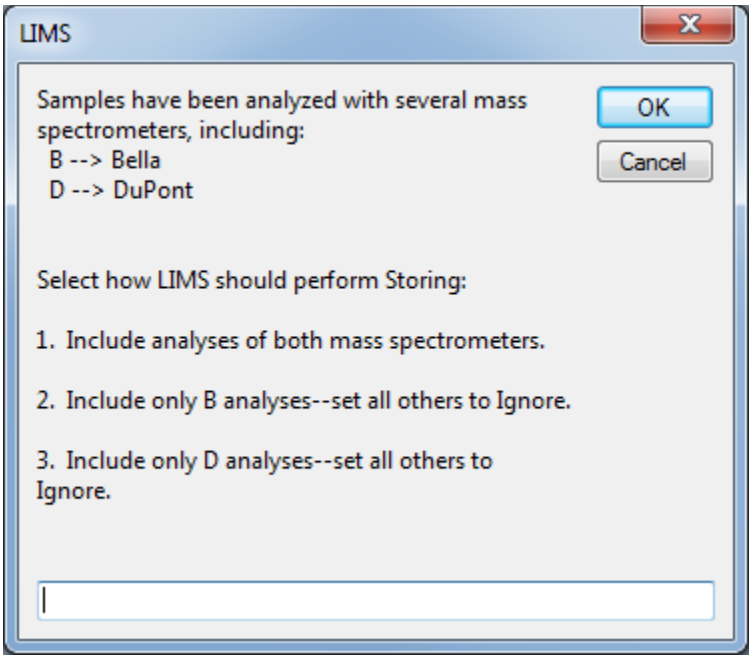


Fig. 28.9. How-to-store dialog box. Entering "1" uses analyses of all mass spectrometers to calculate a final delta value that is stored.

28.3 Storing Analysis Results of Samples Having Numerical Comments

LIMS can determine the average of numerical comments (Section 25.3) if this option is enabled on the Options form (Fig. 4.12 and Table 4.1). Consider sample C-10830 shown in Figure 25.7. If one enables the check box labelled "Save mean numeric comment values, if any, in sample comment field (ANY OTHER COMMENT WILL BE OVERWRITTEN)" on the Store Sample Results to Projects form (Fig. 28.10), clicking store will cause LIMS to store the mean numerical value in the comment of the Sample form for the appropriate isotope. After storing C-10830, the "Comment" for the $\delta^{18}O$ result is updated on the Sample form to "98.100±0.283" (Fig. 28.11). A project report (Fig. 28.12) includes the mean numerical value in the comment field.

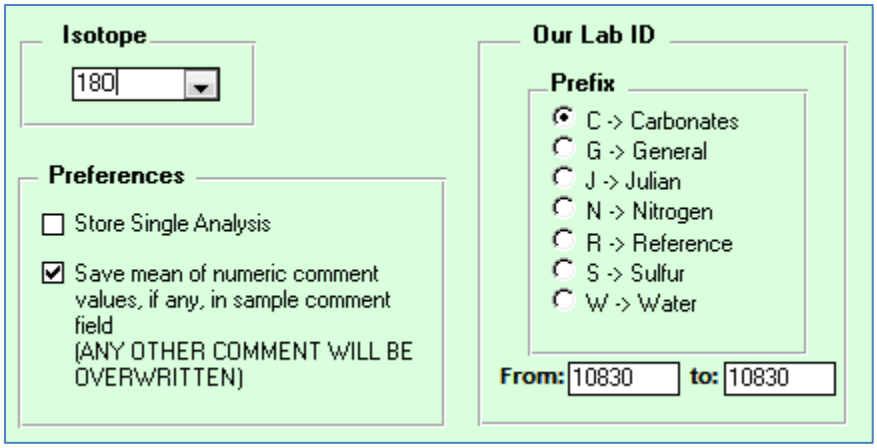


Fig. 28.10. Storing sample analysis results of samples with numerical comments.

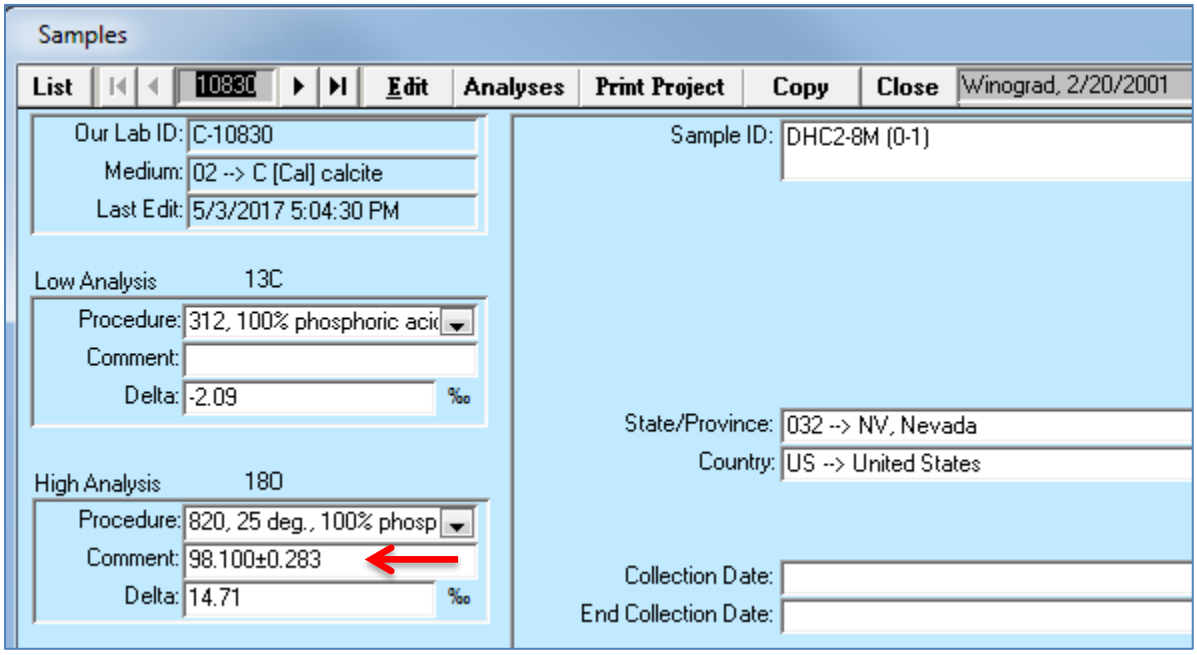


Fig. 28.11. Sample form after storing analyses having numerical comments.

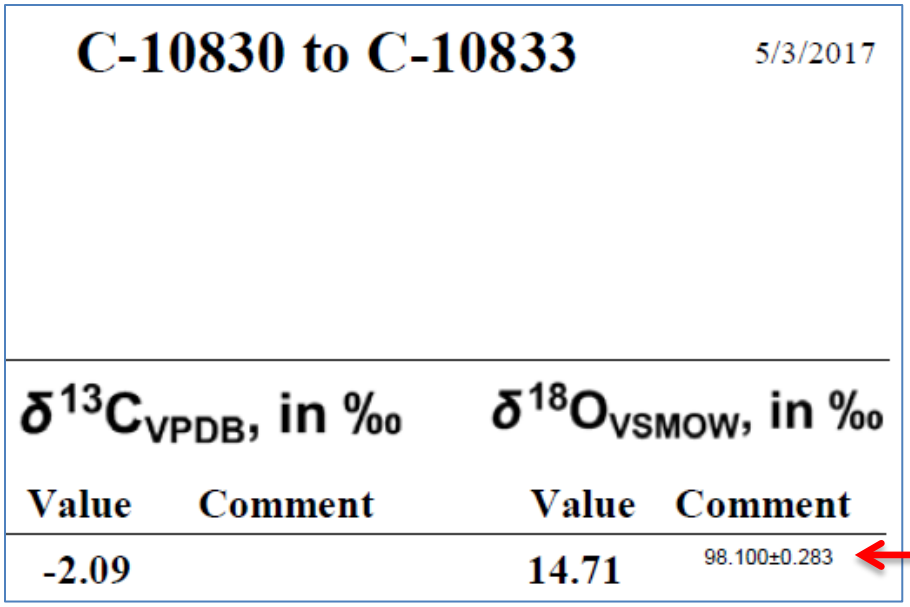


Fig. 28.12. Section of a project report displaying a mean numerical comment for a δ^{18}O value.

29 Adding Samples Back to the "In Progress" Queue for Reevaluation

Occasionally samples will need to be reevaluated, and this occurs because of a variety of reasons, including:

- There was a mix-up in samples analyzed and the Our Lab ID of an analysis is incorrect.
- Correction factors were changed.
- A client requests results of each analysis of a sample.

Adding samples back to "In Progress" enables the user to re-process data, correct or ignore errors, and remove faulty data from a client's project. Note that if a sample was previously stored and is re-analyzed, LIMS automatically loads that sample back to the "In Progress" queue.

This section continues from Section 28 and assumes that the reader has connected to the backend database name "Evaluate_SIP_BACKEND_DB.accdb" as discussed in Section 25.1. To demonstrate use of the Add Stored Samples Back to In Progress form:

1. On the LIMS main page click "Add Stored Samples Back to In Progress" and the Add Stored Samples Back to In Progress form will open.
2. Select "13C" for the "Isotope" if not already selected.
3. Select "G" for the "Prefix" is not already selected.
4. Enter "1202" and "1205" in the "From" and "to" fields, respectively.
5. Click the "Set any previously stored delta values in Table of Samples to null" check box to avoid incorrect results being reported to a client and the form should appear as in Figure 29.1.
6. Click "Add" and LIMS displays the dialog box shown in Figure 29.2.
7. The samples remain in the "In Progress" queue until restored.

⚠ Be sure to "Store" updated data once corrections are made, or the Project will retain the incorrect data that was previously stored.

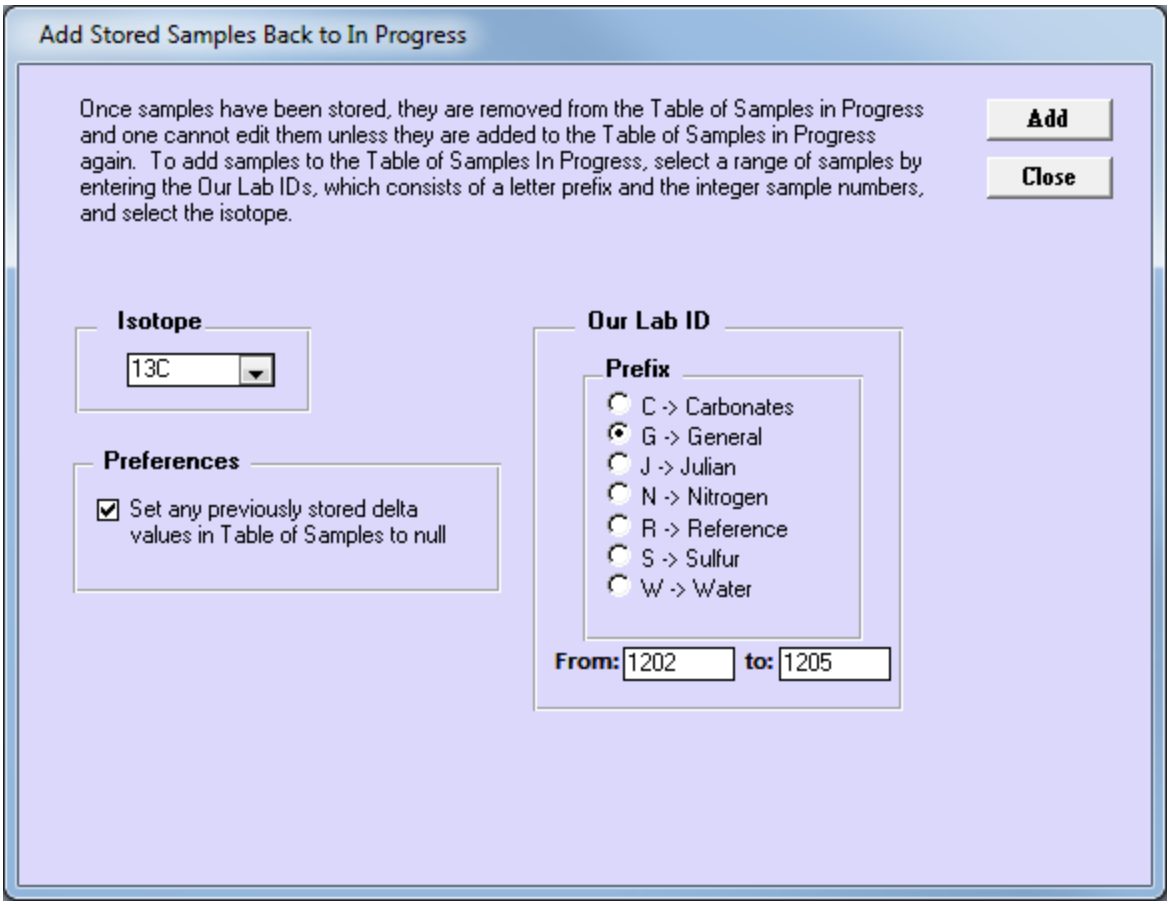


Fig. 29.1. Add Stored Sample Back to In Progress form and success dialog box.

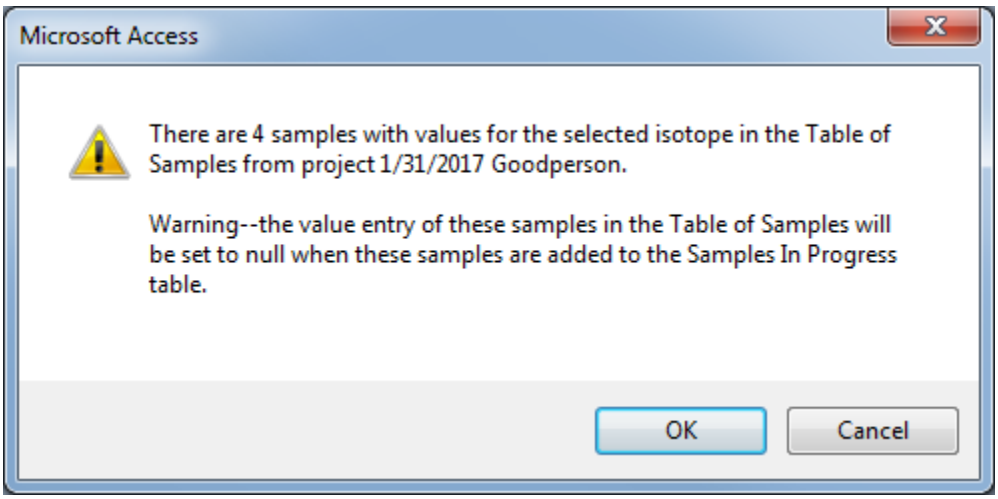


Fig. 29.2. Confirmation message that delta values in the selected range will be set to null.

30 Track My Lab QA/QC

An important part of laboratory quality assurance/quality control (QA/QC) activities is to monitor the accuracy of a control standard over time. An abrupt change in the delta value of a control standard could indicate a mix-up of samples in a daily analytical run. An evaluation of control standards before reporting results to clients is helpful in many isotope laboratories. LIMS provides this capability with the Track My Laboratory QA/QC form, which is opened by clicking "Track My Lab QA/QC" on the LIMS main menu. The sample being evaluated can be any sample in LIMS—this form is not restricted to a control or reference sample.

Measurements from the Reston Stable Isotope Laboratory are presented on this form in Figure 30.1. In addition to constraining the graph by beginning and ending date, the user may also constrain the plot by selecting a range of analyses from a specified IRMS. Optionally, data may be exported as an Excel file for offline analysis or may be used for annual reporting of laboratory performance and audits.

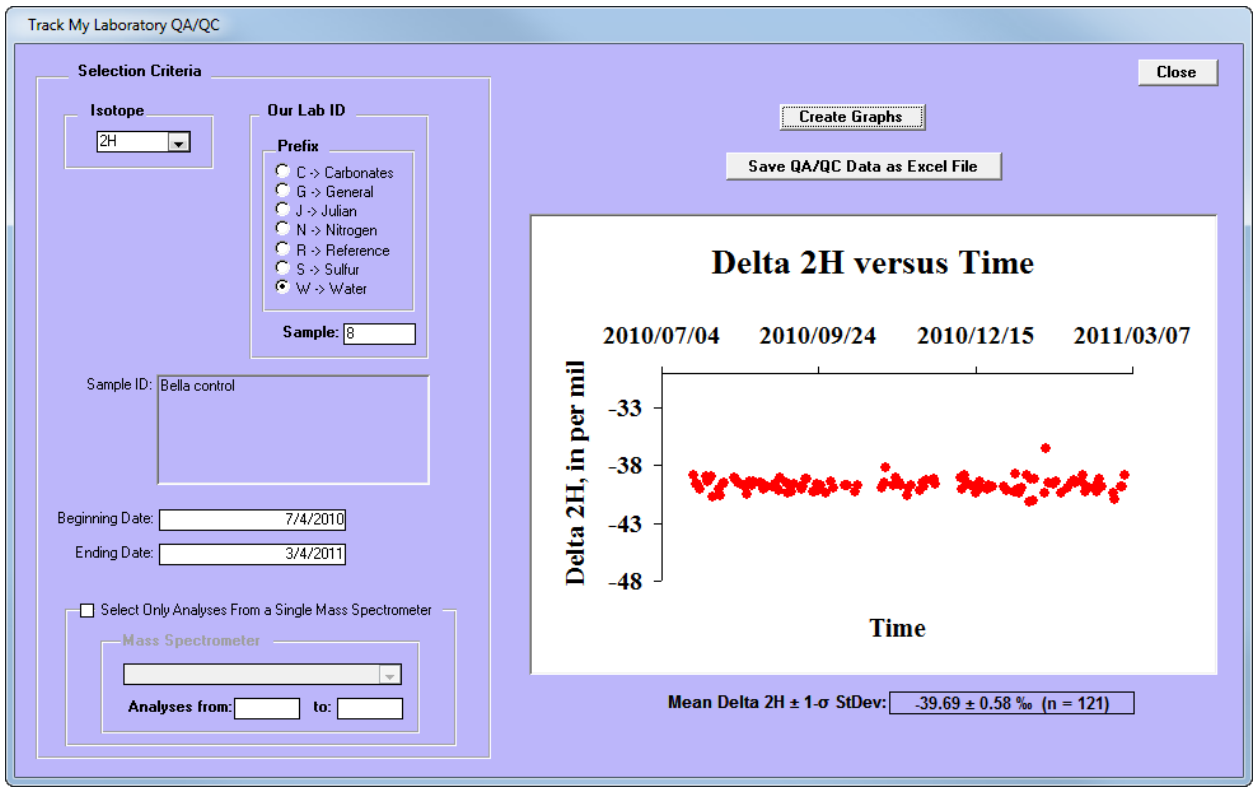


Fig. 30.1. Example of Track My Lab QA/QC form.

31 Reporting Customer Results

31.1 General Information

Once all results have been normalized, reviewed, accepted, and stored, results are reported to the customer using the Projects form (*e.g.* Fig. 31.1). Usually the "Project Ready to Report" field with the yellow background (Fig. 31.1) will be displayed when a project is ready to report. LIMS identifies "Ready to Report" projects by checking if the project is missing delta values and by checking for an entry in the "Date Results Reported" field. If the project has medium 1 (water for hydrogen and oxygen isotopes), it is recommended that the user click "Delta Plot" to make a $\delta^{2}H$ versus $\delta^{18}O$ crossplot shown in Figure 7.30. If there are samples lying off the meteoric water line, they should be investigated to confirm that their isotopic compositions are correct and not the result of a sample mix-up, nor some other issue.

There are a number of options for reporting. Clients may receive a printed report, an Excel file, an ASCII text file prepared for an email, a pdf file (if a pdf creator is installed), or a combination of these. In the example report shown in Figure 31.1,

- Clicking "Print Report" automatically prints the project report shown in Figure 31.2. If a pdf creator is installed, a pdf can be created.
- Clicking "Export Results" gives the user the possibility to export an Excel file of the results, a text file (Section 31.2), or both. When one clicks "Export Results," LIMS populates the "Date Results Reported" field with the current date and LIMS hides the "Project Ready to Report" field with the yellow background.

As discussed in Section 7.2, selected files or all files from a client or a query of projects in the backend database can be printed, exported as individual Excel files, or combined into a single Excel file using the Find Project form. For example, in the Find Projects form, entering "Goodperson, Herkimer" for the "Name," entering "26 --> G [C & N] C- and N-bearing material" for the "Medium," and clicking "Search" displays the 10 projects that can be printed, exported as individual Excel files, or combined into a single Excel file using the command buttons on the right side of the form (Fig. 31.3).

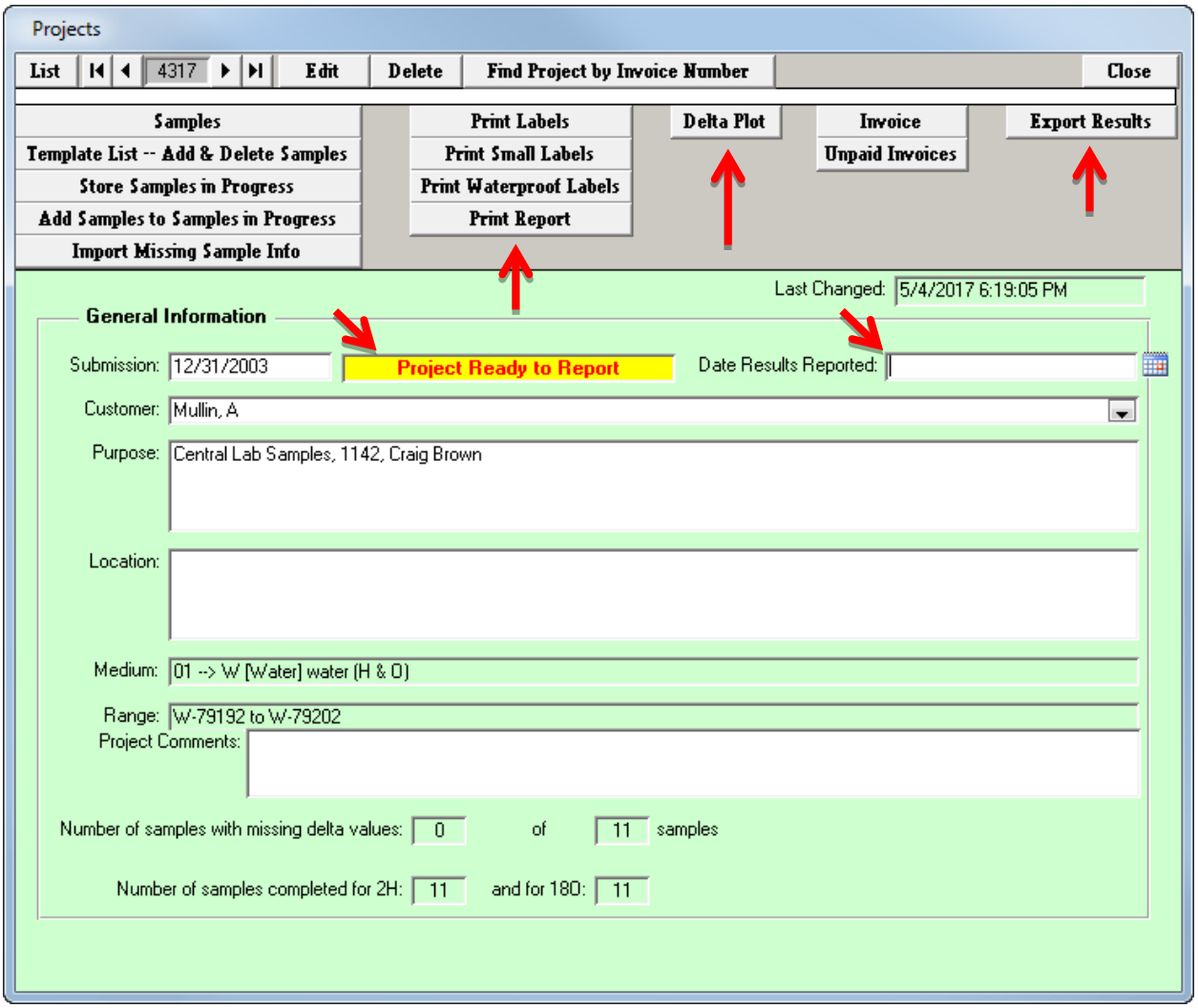


Fig. 31.1. Example of a project report ready to be reported.

Submission: 12/31/2003 Mullin, A **W-79192 to W-79202** 5/4/2017

Medium: 01 --> W [Water] water (H & O)
Purpose: Central Lab Samples, 1142, Craig Brown

Location:

Sample ID:	Collection Date	Our Lab ID	δ^2H_{VSMOW}, in ‰ Value	Comment	$\delta^{18}O_{VSMOW}$, in ‰ Value	Comment
QC-000202		W-79192	-115.20		-14.69	
033659500	11/5/2003	W-79193	-44.94		-7.23	n=1
033659501	11/20/2003	W-79194	-44.60		-7.30	n=1
033659502	12/9/2003	W-79195	-50.07		-7.93	
033659503	12/1/2003	W-79196	-46.23		-7.56	n=1
033659504	11/24/2003	W-79197	-46.82		-7.55	n=1
033659505	11/6/2003	W-79198	-49.83		-8.00	
033659506	12/17/2003	W-79199	-48.24		-7.83	n=1
033659507	12/16/2003	W-79200	-49.23		-7.90	n=1
033659508	12/30/2003	W-79201	-44.99		-7.52	
033659509	12/30/2003	W-79202	-47.49		-7.87	n=1

Fig. 31.2. Example of a project report.

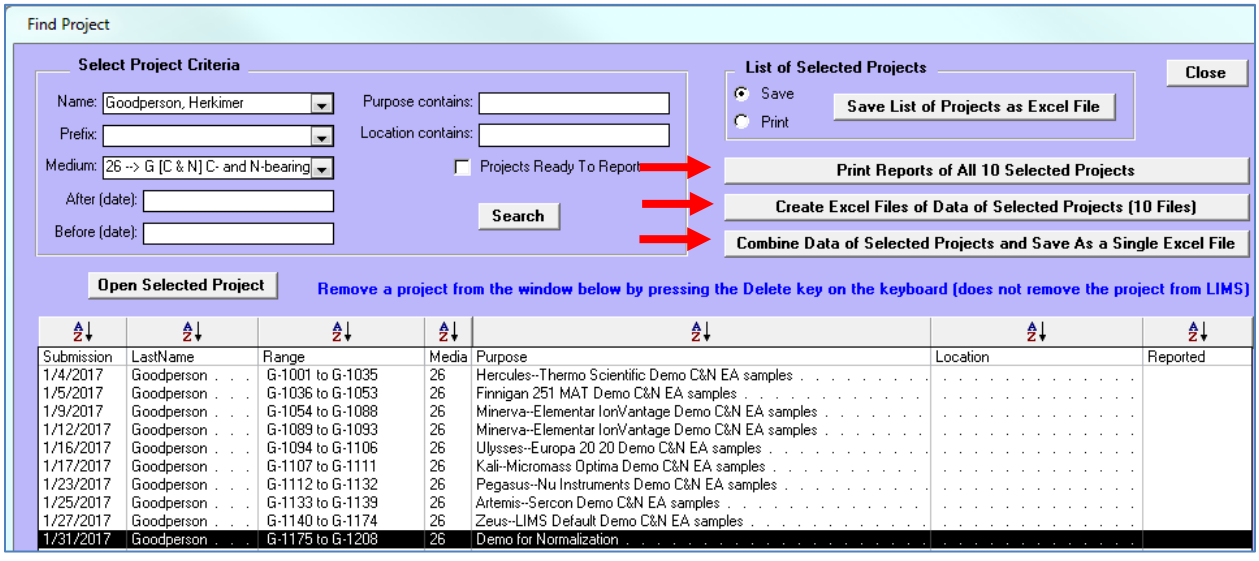


Fig. 31.3. Printing and Exporting selected projects using the Find Project form.

31.2 Reporting Text

The ASCII text file that can be created when the user clicks "Export Results" lists analytical results as well as any or all of the following:

- Contact information
- Methods used for analysis
- Isotopic reference materials used
- Uncertainty values
- References to the analytical method

To add or edit reporting text, click "Reporting Text" in the Special Features window and the Reporting Text form will open (Fig. 31.4).

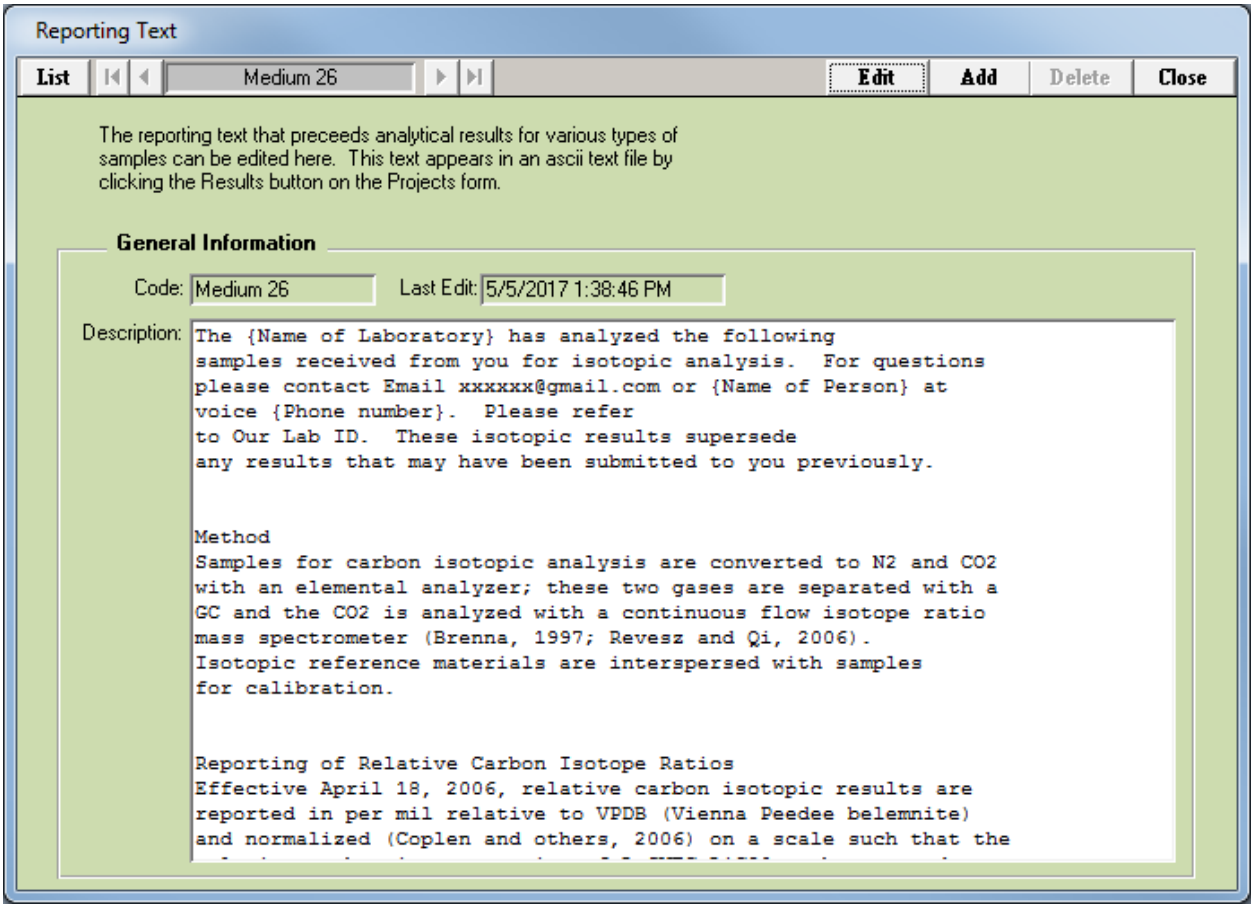


Fig. 31.4. Reporting text for displaying preliminary text for a new laboratory.

Example reporting text is provided in the backend database for a new laboratory for "Medium 26" (δ^{13}C and δ^{15}N measurements by EA and IRMS of carbon- and nitrogen-bearing substances). The example reporting text is:

The {Name of Laboratory} has analyzed the following samples received from you for isotopic analysis. For questions please contact Email xxxxxx@gmail.com or {Name of Person} at voice {Phone number}. Please refer to Our Lab ID. These isotopic results supersede any results that may have been submitted to you previously.

Method

Samples for carbon isotopic analysis are converted to N2 and CO2 with an elemental analyzer; these two gases are separated with a GC and the CO2 is analyzed with a continuous flow isotope ratio mass spectrometer (Brenna, 1997; Revesz and Qi, 2006). Isotopic reference materials are interspersed with samples for calibration.

Reporting of Relative Carbon Isotope Ratios

Effective April 18, 2006, relative carbon isotopic results are reported in per mil relative to VPDB (Vienna Peedee belemnite) and normalized (Coplen and others, 2006) on a scale such that the relative carbon isotope ratios of USGS44 calcium carbonate and NBS 19 CaCO3 are -42.1 and +1.95 per mil, respectively.

The carbon isotopic compositions of carbon-bearing internationally distributed isotopic reference materials, had they been analyzed in this laboratory with your samples, are in accord with Coplen and other (2006) and are:

NBS 19	CaCO3	+1.95 (exactly)
NBS 18	CaCO3	-5.01
IAEA-CO-1	CaCO3	+2.49
IAEA-CO-8	CaCO3	-5.76
USGS44	CaCO3	-42.1
IAEA-CO-9	BaCO3	-47.32
USGS24	graphite	-16.05
NBS 22	oil	-30.03
IAEA-CH-3	cellulose	-24.72
IAEA-CH-6	sucrose	-10.45
IAEA-CH-7	polyethylene	-32.15
IAEA-600	caffeine	-27.77
IAEA-601	benzoic acid	-28.81
USGS40	glutamic acid	-26.39
USGS41	glutamic acid	+37.63
RM 8562	CO2	-3.72
RM 8563	CO2	-41.59
RM 8564	CO2	-10.45

The 2-sigma uncertainty of carbon isotopic results is 0.5 per mil unless otherwise indicated. This means that if the same sample were resubmitted for isotopic analysis, the newly measured value would lie within the uncertainty bounds 95 percent of the time.

References

Brenna, J. T., Corso, T. N., Tobias, H. J., and Caimi, R. J.,

1997, High-precision continuous-flow isotope ratio mass spectrometry: Mass Spectrometry Reviews, v. 16, p. 227-258.

Coplen, T.B., Brand, W.A., Gehre, M., Gröning, M., Meijer, H. A. J., Toman, B, and Verkouteren, R. M., 2006, New guidelines for delta 13C measurements: Analytical Chemistry, v. 78, p. 2439-2441.

Révész, Kinga, and Qi, Haiping, 2006, Determination of the delta(15N/14N) and delta(13C/12C) of total N and C in solids: RSIL lab code 1832. C5 of Révész, Kinga, and Coplen, Tyler B., eds., Methods of the Reston Stable Isotope Laboratory: Reston, Virginia, U.S. Geological Survey, Techniques and Methods, book 10, sec. C, chap. 5, 30 p. http://pubs.water.usgs.gov/tm10C5/

32 Compound Specific Isotope Analyses

32.1 General Information

Compound specific isotope analysis involves separating a mixture into its constituent compounds, converting the separated compound into gases that can be analyzed by an IRMS (typically H_2, N_2, and CO_2), and determining isotope-delta values of each of these gas peaks in a time series. The compounds are identified by their retention time during chromatographic separation. For example, $\delta^{13}C$ analysis of a natural gas sample might produce $\delta^{13}C$ values sequentially for methane, ethane, *n*-propane, iso-butane, and *n*-butane. Each of these delta values typically will have the same analysis number, but different peak numbers. Following analysis of the sample, a user might analyze a standard, such as NGS 2, which contains methane, ethane, *n*-propane, iso-butane, and *n*-butane with known $\delta^{13}C$ values. The challenge is to use the $\delta^{13}C$ values of methane, ethane, *n*-propane, iso-butane, and *n*-butane in NGS 2 to normalize, respectively, the $\delta^{13}C$ values of methane, ethane, *n*-propane, iso-butane, and *n*-butane in the sample. The solution is to adjust the analysis and peak numbers before importing into LIMS so that all the $\delta^{13}C$ peaks of methane are grouped together, all the $\delta^{13}C$ peaks of ethane are grouped together, and so on. Example files are provided in a folder named "Section 32" in the files that accompany this manual. To set up this demonstration:

1. Create a new folder. It can be within a LIMS folder or elsewhere.
2. Identify the folder as an Access Trusted Location (Section 3.2.2).
3. Copy the zip file "CSIA_Demo.zip," which is located in a folder named "Section 32" that accompanies this manual, into this new folder and extract the files from it, keeping them in this new folder. The six extracted files should be: "LIMS_CSIA_Demo_Backend_DB.accdb", "LM9PREFS.ACCDB", "CSIA_Demo_v0.xlsx", "CSIA_Demo_v1.xlsx", "G-240--G-1006_13C.xlsx", and "G-240--G-1006_13C_BriefSummary.xlsx".
4. Transfer into this new folder a fresh copy of the LIMS frontend, which is named "Lims9.202.zip" (or similar) and is located in a folder named "Section 4" that accompanies this manual. Extract the frontend database file from this zip file, keeping it in the same folder—it will be named "Lims9.202.accdb" or similar.
5. Double-click the new frontend (Lims9.202.accdb or similar) to open it. It should open with the message that LIMS cannot find the backend database (Fig. 4.1).
6. Click "OK" and navigate to "LIMS_CSIA_Demo_Backend_DB.accdb."
7. LIMS will display a message that it needs to close.
8. Click "OK."
9. Reopen this frontend database and LIMS should display the welcome message in Figure 4.18.
10. Click "Yes" and LIMS will prompt that it needs to update settings and close.
11. Click "OK" and LIMS will perform cleanup activities upon closing.

12. Reopen this frontend database and LIMS should open with the main page (similar to Fig. 4.8).
13. Click “Special Features” and click “Options.”
14. Set the paper size to A4 if needed, and set the print destination to “Any Installed Printer” if there is more than one printer available. A pdf creator might be one of the printers.
15. Click “Close” to close the Options form.

This completes the installation of the CSIA Demo database for use in this section. Click “View Projects -->” and open the project having the Our Lab ID Range G-240 to G-245 (Fig. 32.1).

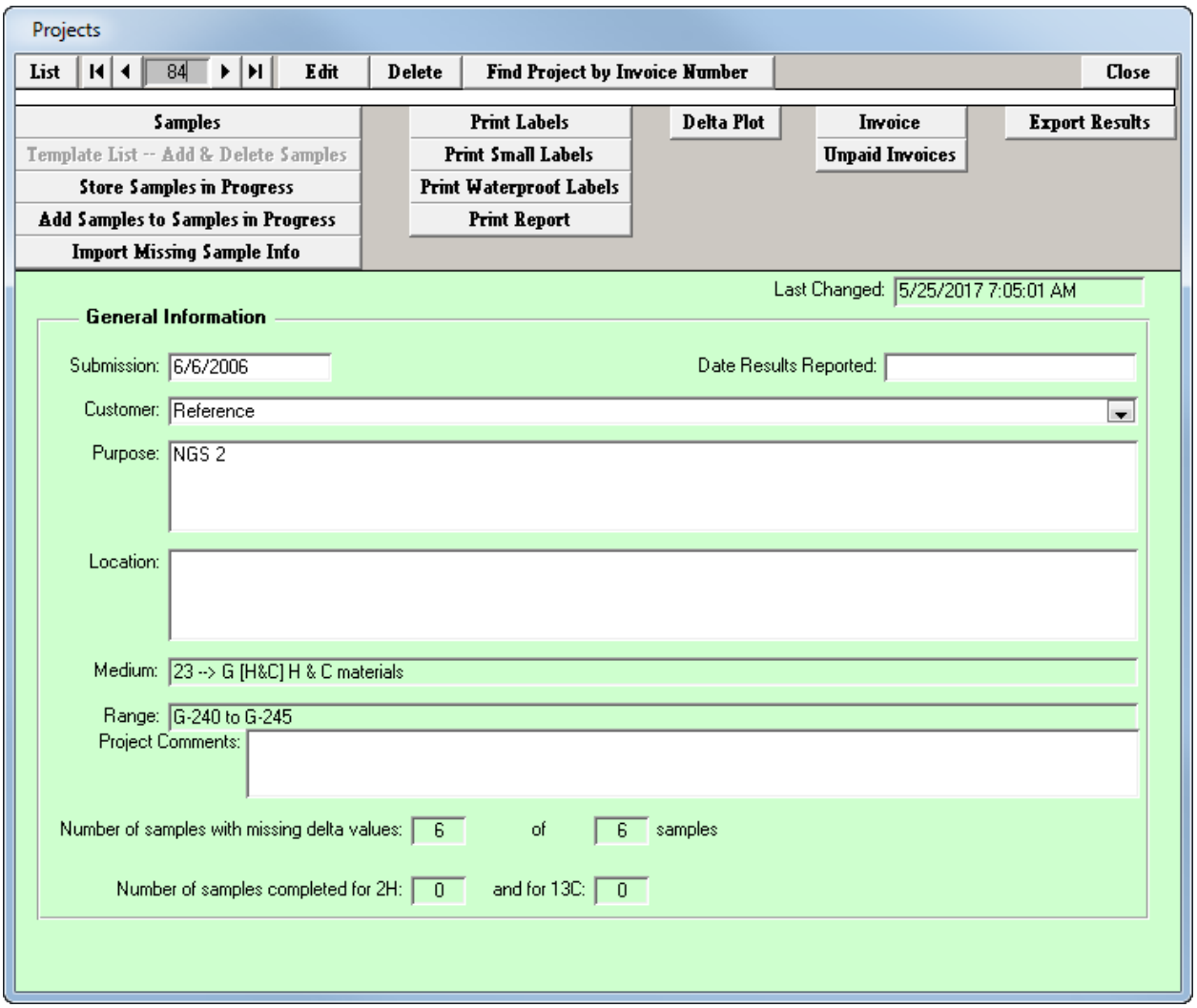


Fig. 32.1. CSIA project for NGS 2 compounds.

Click “Samples” then “List” to display the samples in this project (Fig. 32.2). Note that G-240 is a placeholder. No delta values need to be entered on the Samples form for any of these samples. Instead, the $\delta^{13}C$ values of methane, ethane, *n*-propane, iso-butane, and *n*-butane are entered into the LIMS Table of References using the Reference Samples form, which is accessed by clicking “Assign Lab References” in the Special Features window (Section 12). Clicking “List” on the Reference Samples form and navigating to G-241 displays the information shown in Figure 32.3.

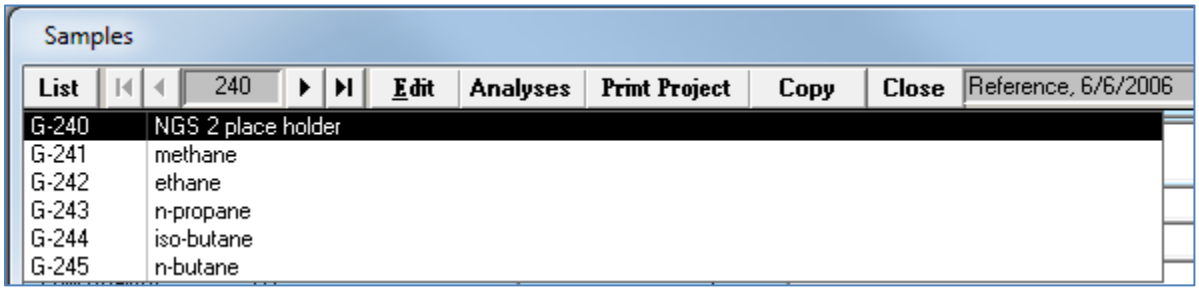


Fig. 32.2. Reference samples in CSIA project G-240 to G-245.

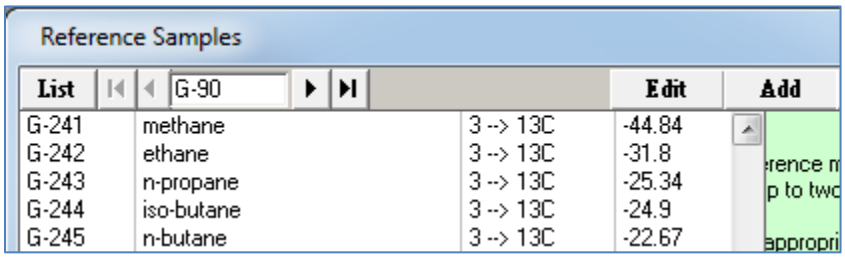


Fig. 32.3. Reference samples in CSIA project G-240 to G-245.

In LIMS each CSIA project must be logged in as its own separate project because each CSIA sample will contain multiple compounds for analysis. The example database contains a CSIA project. Viewing projects, one can observe that G-1001 to 1006 is a “CSIA Demo” project. G-1001 is a placeholder for the bulk sample and the other five samples are methane, ethane, *n*-propane, iso-butane, and *n*-butane in this example (Fig. 32.4). Commonly it is not known prior to analysis which compounds might be in the CSIA sample. There are at least two approaches to deal with this situation:

- One might create one or more test projects consisting of a single sample and use them for analyses. Once the analyses are completed and compounds identified for each CSIA sample, a project can be created for each CSIA sample, which contains the specific compounds found in each CSIA sample.

- Alternatively, based on previous information about the compounds that may appear in a CSIA sample, prior to analysis of each CSIA sample a user can login a default project with possible compounds that may appear in a client's CSIA sample. A project is required for each CSIA sample. For example, a default project might contain Our Lab IDs for:
    - the bulk CSIA sample used as a placeholder
    - methane
    - ethane
    - *n*-propane
    - iso-butane
    - *n*-butane
    - iso-pentane
    - *n*-pentane
    - iso-hexane
    - *n*-hexane

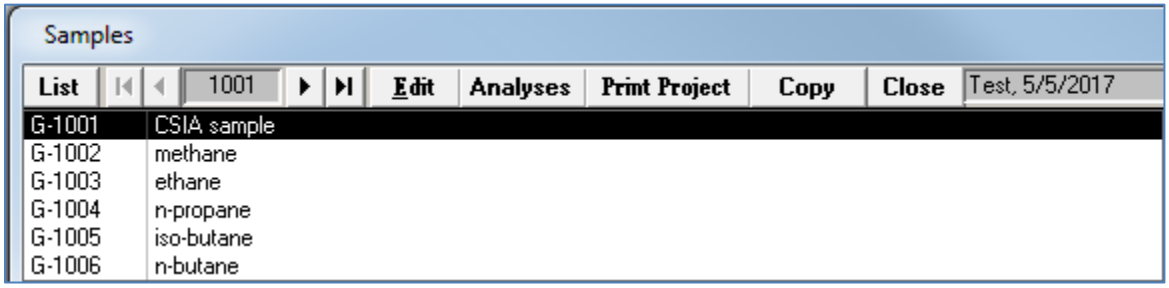


Fig. 32.4. CSIA samples in the project G-1001 to G-1006.

32.2 Importing CSIA Results

Prior to importing, CSIA results need to be edited so that normalization can be performed satisfactorily. Figure 32.5 shows selected analysis numbers and peak numbers in an unedited Excel file named "CSIA_Demo_v0.xlsx" that can be extracted from the file named "CSIA_Demo.zip," which is located in the folder named "Section 32." This file results from the analysis of a CSIA sample (G-1001) and reference (G-240) with a Delta V Plus IRMS. Although this example uses data from ISODAT, the process is the same for Excel files for the LIMS Abbreviated import format (Section 17). Note that only the placeholders G-240 and G-1001 appear in the file. The steps to modify this file for importing are:

1. Insert a new column after the "Peak Nr" column (column C).
2. Enter "Peak Nr" in cell D1.
3. Insert a new column after the "Analysis" column (column B).

4. Enter “Analysis” in cell C1.
5. Rename cell B1 “Old Analysis” and rename cell D1 “Old Peak Nr.”
6. Sort the file by the “Component” column and then by the “Old Analysis” column.
7. Find the lowest “Old Analysis” entry, which is “T-1974” (which appears twice), and enter it in cell C2.
8. Copy cell C2 to C3:C23 so that all rows have the same analysis number of “T-1974.”
9. Enter “101” for the “Peak Nr” in cell E2.
10. Increment the values in the “Peak Nr” column so they range from “101” in cell E2 to “122” in cell E23.
11. Delete column D (“Old Peak Nr”).
12. Delete column B (“Old Analysis”).
13. Save the file as “CSIA_Demo_v2.xlsx,” which is ready for importing and should appear as shown in Figure 32.6. It should be identical to the file named “CSIA_Demo_v1.xlsx” that can be extracted from the file named “CSIA_Demo.zip,” which is located in the folder named “Section 32.”

CSIA_Demo_v0.xlsx

	A	B	C	D	E	F	G	H	I	J
1	Identifier 1	Analysis	Peak Nr	Gasconfi	Rt	Component	Is Ref _	Area All	d 13C/12C	Time Code
2	G-1001	T-1974	5	CO2	713.1	ethane	0	124.476	-29.009	2015/04/15 13:42:50
3	G-1001	T-1974	6	CO2	1143.4	n-propane	0	90.532	-33.424	2015/04/15 13:42:50
4	G-1001	T-1974	7	CO2	1503.3	iso-butane	0	49.17	-28.664	2015/04/15 13:42:50
5	G-1001	T-1974	8	CO2	1582.5	n-butane	0	48.541	-27.469	2015/04/15 13:42:50
6	G-1001	T-1975	5	CO2	713.5	ethane	0	126.751	-28.808	2015/04/15 14:35:55
7	G-1001	T-1975	6	CO2	1144.1	n-propane	0	90.732	-31.39	2015/04/15 14:35:55
8	G-1001	T-1975	7	CO2	1187.1	n-propane	0	26.327	-32.972	2015/04/15 14:35:55
9	G-1001	T-1975	8	CO2	1504	iso-butane	0	24.664	-30.009	2015/04/15 14:35:55
10	G-1001	T-1975	9	CO2	1583	n-butane	0	50.642	-27.092	2015/04/15 14:35:55
11	G-1001	T-1976	5	CO2	446	methane	0	39.536	-36.896	2015/04/15 15:03:28
12	G-1001	T-1977	5	CO2	446.6	methane	0	39.518	-36.963	2015/04/15 15:23:26
13	G-240	T-1982	5	CO2	446.4	methane	0	34.416	-44.937	2015/04/15 16:55:43
14	G-240	T-1983	5	CO2	446.4	methane	0	36.874	-44.565	2015/04/15 17:11:24
15	G-240	T-1984	5	CO2	446.2	methane	0	38.354	-44.44	2015/04/15 17:29:09
16	G-240	T-1986	5	CO2	713.7	ethane	0	126.889	-31	2015/04/15 18:04:36
17	G-240	T-1986	8	CO2	1144.3	n-propane	0	89.327	-24.226	2015/04/15 18:04:36
18	G-240	T-1986	15	CO2	1504.8	iso-butane	0	20.914	-24.457	2015/04/15 18:04:36
19	G-240	T-1986	18	CO2	1583.8	n-butane	0	50.342	-22.172	2015/04/15 18:04:36
20	G-240	T-1987	5	CO2	714.4	ethane	0	131.347	-32.634	2015/04/15 18:49:28
21	G-240	T-1987	6	CO2	1144.7	n-propane	0	91.065	-24.46	2015/04/15 18:49:28
22	G-240	T-1987	9	CO2	1583.8	iso-butane	0	51.049	-21.722	2015/04/15 18:49:28
23	G-240	T-1987	11	CO2	1917.8	n-butane	0	22.671	-21.651	2015/04/15 18:49:28
24										

Sheet1

Fig. 32.5. Selected analyses and peak numbers of a CSIA run (“CSIA_Demo_v0.xlsx.”

CSIA_Demo_v2.xlsx

	A	B	C	D	E	F	G	H	I	J
1	Identifier 1	Analysis	Peak Nr	Gasconfi	Rt	Component	Is Ref _	Area All	d 13C/12C	Time Code
2	G-1001	T-1974	101	CO2	713.1	ethane	0	124.476	-29.009	2015/04/15 13:42:50
3	G-1001	T-1974	102	CO2	713.5	ethane	0	126.751	-28.808	2015/04/15 14:35:55
4	G-240	T-1974	103	CO2	713.7	ethane	0	126.889	-31	2015/04/15 18:04:36
5	G-240	T-1974	104	CO2	714.4	ethane	0	131.347	-32.634	2015/04/15 18:49:28
6	G-1001	T-1974	105	CO2	1503.3	iso-butane	0	49.17	-28.664	2015/04/15 13:42:50
7	G-1001	T-1974	106	CO2	1504	iso-butane	0	24.664	-30.009	2015/04/15 14:35:55
8	G-240	T-1974	107	CO2	1504.8	iso-butane	0	20.914	-24.457	2015/04/15 18:04:36
9	G-240	T-1974	108	CO2	1583.8	iso-butane	0	51.049	-21.722	2015/04/15 18:49:28
10	G-1001	T-1974	109	CO2	446	methane	0	39.536	-36.896	2015/04/15 15:03:28
11	G-1001	T-1974	110	CO2	446.6	methane	0	39.518	-36.963	2015/04/15 15:23:26
12	G-240	T-1974	111	CO2	446.4	methane	0	34.416	-44.937	2015/04/15 16:55:43
13	G-240	T-1974	112	CO2	446.4	methane	0	36.874	-44.565	2015/04/15 17:11:24
14	G-240	T-1974	113	CO2	446.2	methane	0	38.354	-44.44	2015/04/15 17:29:09
15	G-1001	T-1974	114	CO2	1582.5	n-butane	0	48.541	-27.469	2015/04/15 13:42:50
16	G-1001	T-1974	115	CO2	1583	n-butane	0	50.642	-27.092	2015/04/15 14:35:55
17	G-240	T-1974	116	CO2	1583.8	n-butane	0	50.342	-22.172	2015/04/15 18:04:36
18	G-240	T-1974	117	CO2	1917.8	n-butane	0	22.671	-21.651	2015/04/15 18:49:28
19	G-1001	T-1974	118	CO2	1143.4	n-propane	0	90.532	-33.424	2015/04/15 13:42:50
20	G-1001	T-1974	119	CO2	1144.1	n-propane	0	90.732	-31.39	2015/04/15 14:35:55
21	G-1001	T-1974	120	CO2	1187.1	n-propane	0	26.327	-32.972	2015/04/15 14:35:55
22	G-240	T-1974	121	CO2	1144.3	n-propane	0	89.327	-24.226	2015/04/15 18:04:36
23	G-240	T-1974	122	CO2	1144.7	n-propane	0	91.065	-24.46	2015/04/15 18:49:28
24										

Sheet1

Fig. 32.6. Modified CSIA Excel file ready for importing. This file should be identical to the file named "CSIA_Demo_v1.xlsx," which can be extracted from the file named "CSIA_Demo.zip" that is located in a folder named "Section 32" in files that accompany this manual.

The modified file (Fig. 32.6) has the ethane, iso-butane, methane, *n*-butane, and *n*-propane grouped together. In this manner, setting range markers at peak numbers 104, 108, 113, 117, and 122 will enable the user to normalize δ^{13}C values of ethane, iso-butane, methane, *n*-butane, and *n*-propane, respectively. To import the modified file:

1. Click "Import Data from Mass Specs" on the main page and the Analysis Import Format form will open.
2. Click "Import" and navigate to "CSIA_Demo_v2.xlsx."
3. Click "Select" and the Import Criteria for Mass Spectrometer form will open (Fig. 32.7).
4. Enter "F9" for the column heading for the row having isotope "13C."

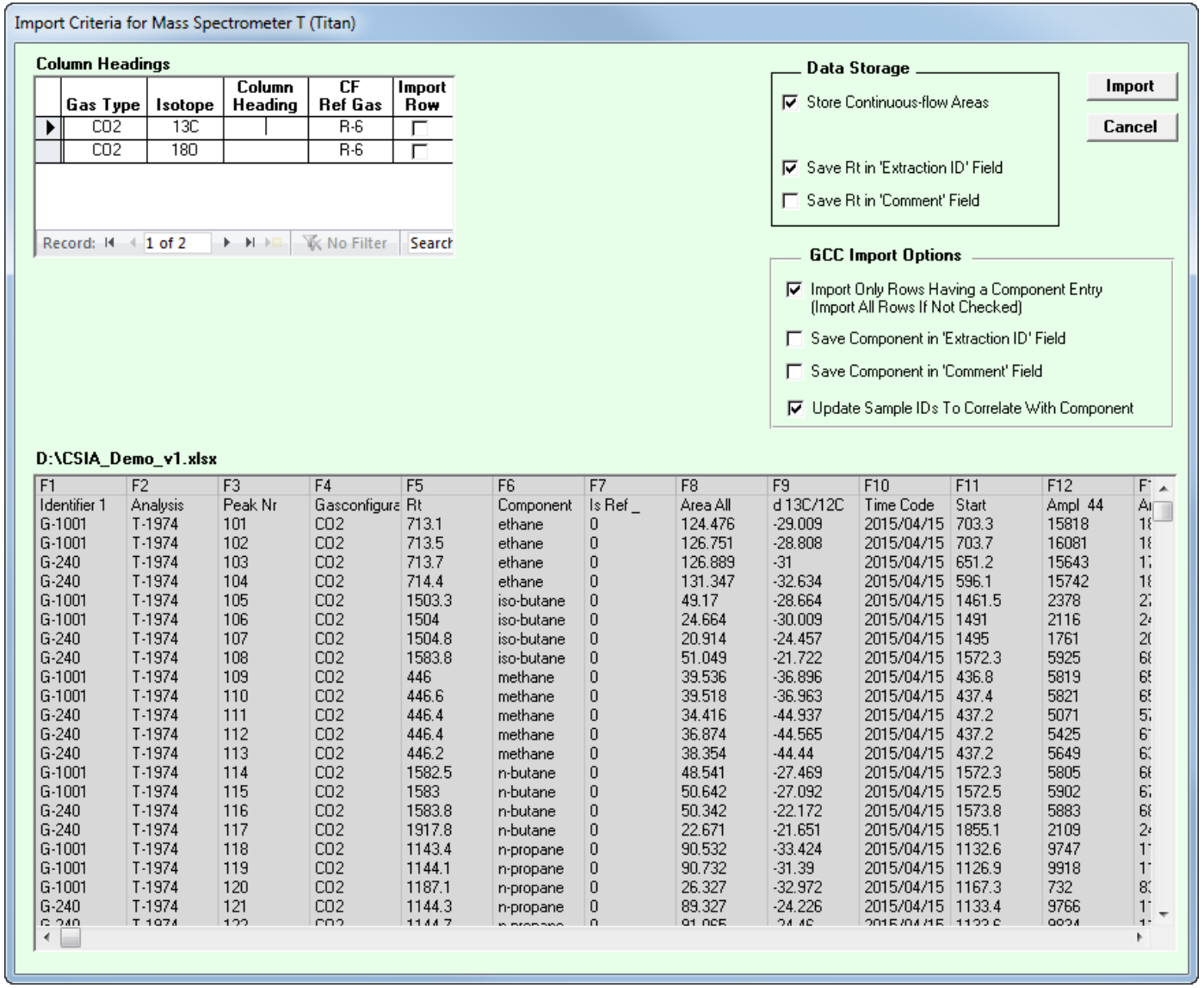


Fig. 32.7. Import Criteria for Mass Spectrometer form for CSIA analyses.

5. Click the "Import Row" check box for the row having isotope "13C." Because the "Update Sample IDs to Correlate with Component" check box is already enabled, nothing further is needed. The form should appear as shown in Figure 32.8.
6. Click "Import" and a dialog box will indicate that $\delta^{13}C$ values of CO_2 will be imported.
7. Click "OK" and LIMS will display the import success dialog box in Figure 32.9.
8. Click "OK" to complete the data import.

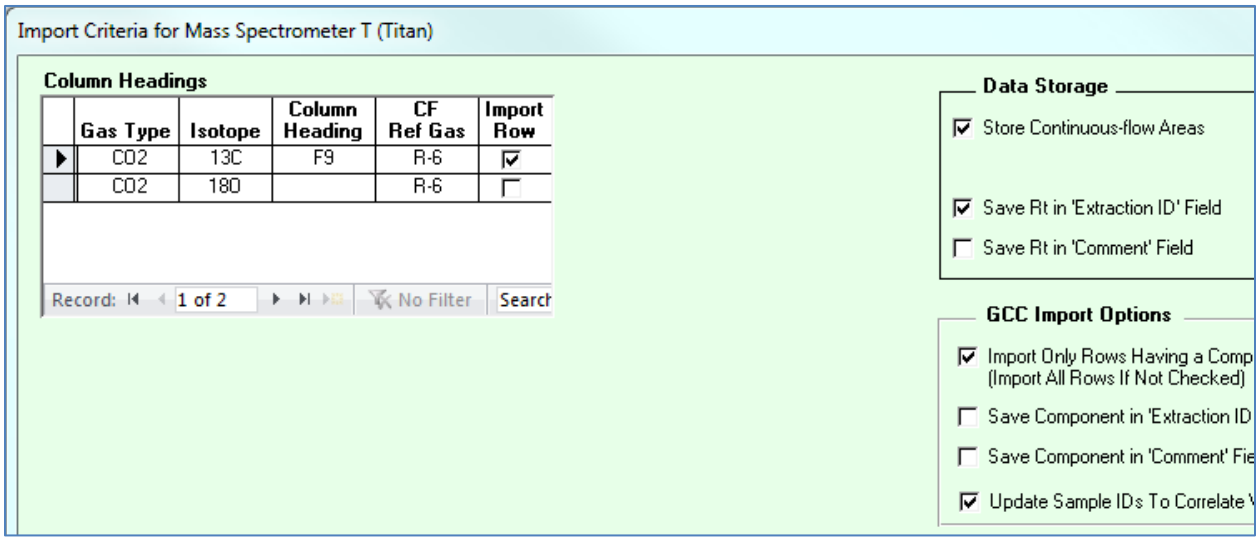


Fig. 32.8. Import Criteria for Mass Spectrometer form set up for CSIA importing.

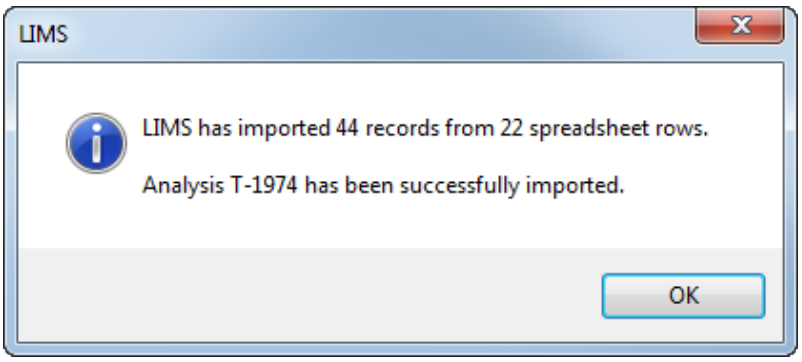


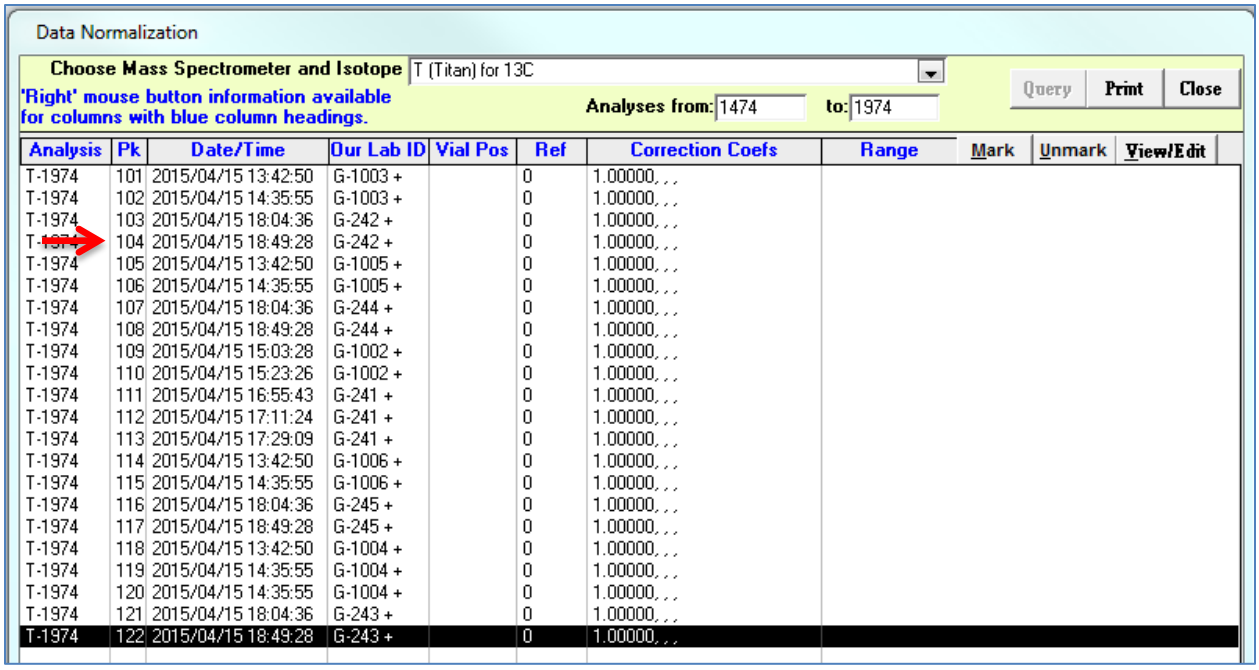
Fig. 32.9. Import success dialog box.

32.3 Normalizing CSIA Results

To normalize the results:

1. Click "Apply Data Normalization" on the main page and the Data Normalization form will open (Section 24.2).
2. Select "T (Titan) for 13C."
3. Click "Query" and the Data Normalization form (Section 24.3) will appear as shown in Figure 32.10. Note that the Our Lab IDs G-240 and G-1001 have been replaced. LIMS has replaced each Our Lab ID with the correct one in the two projects based on the entries in the "Component" columns.
4. As noted above, the last ethane sample is peak number ("Pk") 104. Right-click on any of the column in the Data Normalization form in the peak number-104 row and LIMS displays a dialog box with the description of the Our Lab ID (G-242) as shown in Figure 32.11.
5. Click "Close" to close the dialog box.
6. Double-click on the row having peak number 104 and the Normalization Equation Coefficients form will open showing only the ethane peaks (Fig. 32.12). Note that the "Force Exp Coef to 1.00000" check box is checked. If there were two or more references, this check box would be unchecked and LIMS would have normalized the ethane δ^{13}C values using all the references. If a user has knowledge of what the Proposed "Exp Coef" and "Add Corr" values should be, they can uncheck the "Force Exp Coef to 1.00000" check box and enter the "Exp Coef" and "Add Corr" values manually in these two "Proposed" fields.
7. Right-click on any of the entries in the "Our Lab ID" column and LIMS opens a dialog box similar to that shown in Figure 32.11.
8. Click "OK."
9. Click "Apply Normalization" and the Accepted "Exp Coef" and "Add Corr" fields are updated to 1.00000 and 0.02, respectively. This completes normalization of the ethane δ^{13}C values.
10. Click "Close" to return to the Data Normalization form.
11. Repeat steps 6–10 for the rows having peak number 108, 113, 117, and 122, respectively, to normalize the iso-butane, methane, *n*-butane, and *n*-propane δ^{13}C values, and the Data Normalization form should appear as shown in Figure 32.13.
12. Click "Close" to return to the main page.

This completes normalization the CSIA data and the Data Normalization form. Note that the order of normalizing results is important. Begin with the lowest peak number (104 in this example) and end with the highest peak number (122 in this example).



Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Ref	Correction Coefs	Range
T-1974	101	2015/04/15 13:42:50	G-1003 +		0	1.00000, , ,	
T-1974	102	2015/04/15 14:35:55	G-1003 +		0	1.00000, , ,	
T-1974	103	2015/04/15 18:04:36	G-242 +		0	1.00000, , ,	
T-1974	104	2015/04/15 18:49:28	G-242 +		0	1.00000, , ,	
T-1974	105	2015/04/15 13:42:50	G-1005 +		0	1.00000, , ,	
T-1974	106	2015/04/15 14:35:55	G-1005 +		0	1.00000, , ,	
T-1974	107	2015/04/15 18:04:36	G-244 +		0	1.00000, , ,	
T-1974	108	2015/04/15 18:49:28	G-244 +		0	1.00000, , ,	
T-1974	109	2015/04/15 15:03:28	G-1002 +		0	1.00000, , ,	
T-1974	110	2015/04/15 15:23:26	G-1002 +		0	1.00000, , ,	
T-1974	111	2015/04/15 16:55:43	G-241 +		0	1.00000, , ,	
T-1974	112	2015/04/15 17:11:24	G-241 +		0	1.00000, , ,	
T-1974	113	2015/04/15 17:29:09	G-241 +		0	1.00000, , ,	
T-1974	114	2015/04/15 13:42:50	G-1006 +		0	1.00000, , ,	
T-1974	115	2015/04/15 14:35:55	G-1006 +		0	1.00000, , ,	
T-1974	116	2015/04/15 18:04:36	G-245 +		0	1.00000, , ,	
T-1974	117	2015/04/15 18:49:28	G-245 +		0	1.00000, , ,	
T-1974	118	2015/04/15 13:42:50	G-1004 +		0	1.00000, , ,	
T-1974	119	2015/04/15 14:35:55	G-1004 +		0	1.00000, , ,	
T-1974	120	2015/04/15 14:35:55	G-1004 +		0	1.00000, , ,	
T-1974	121	2015/04/15 18:04:36	G-243 +		0	1.00000, , ,	
T-1974	122	2015/04/15 18:49:28	G-243 +		0	1.00000, , ,	

Fig. 32.10. Data Normalization form for CSIA analyses.

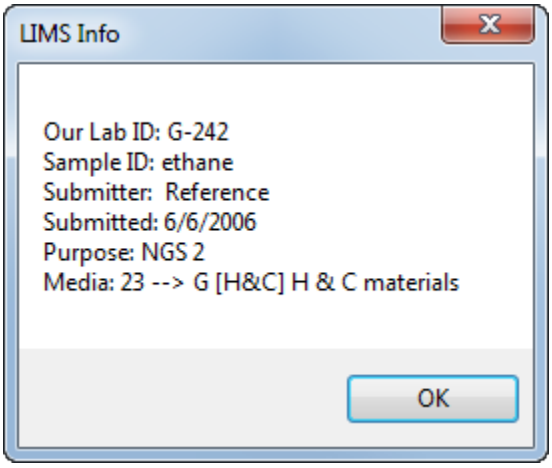


Fig. 32.11. Our Lab ID description obtained by right-clicking any entry in the peak number-104 row of the Data Normalization form.

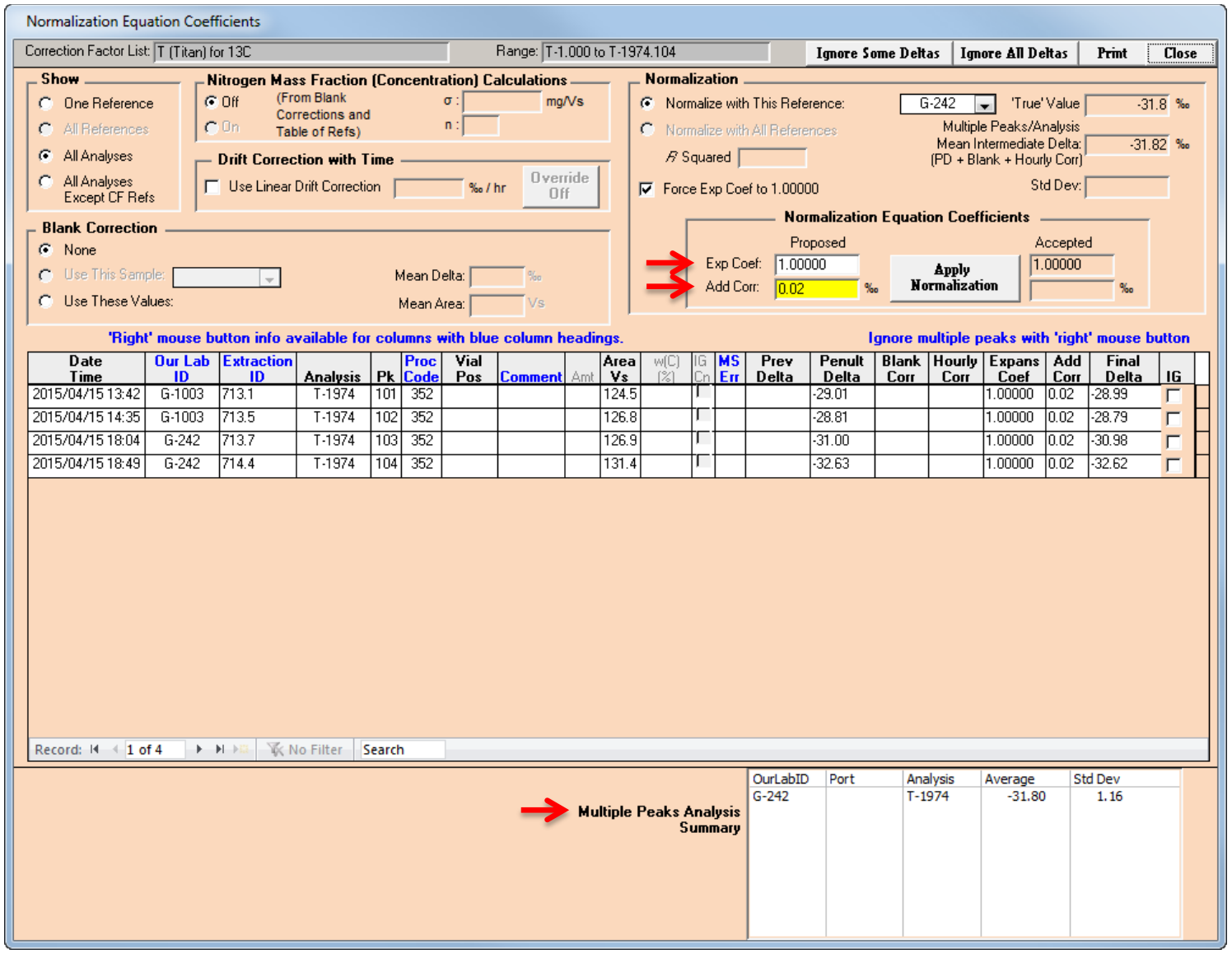
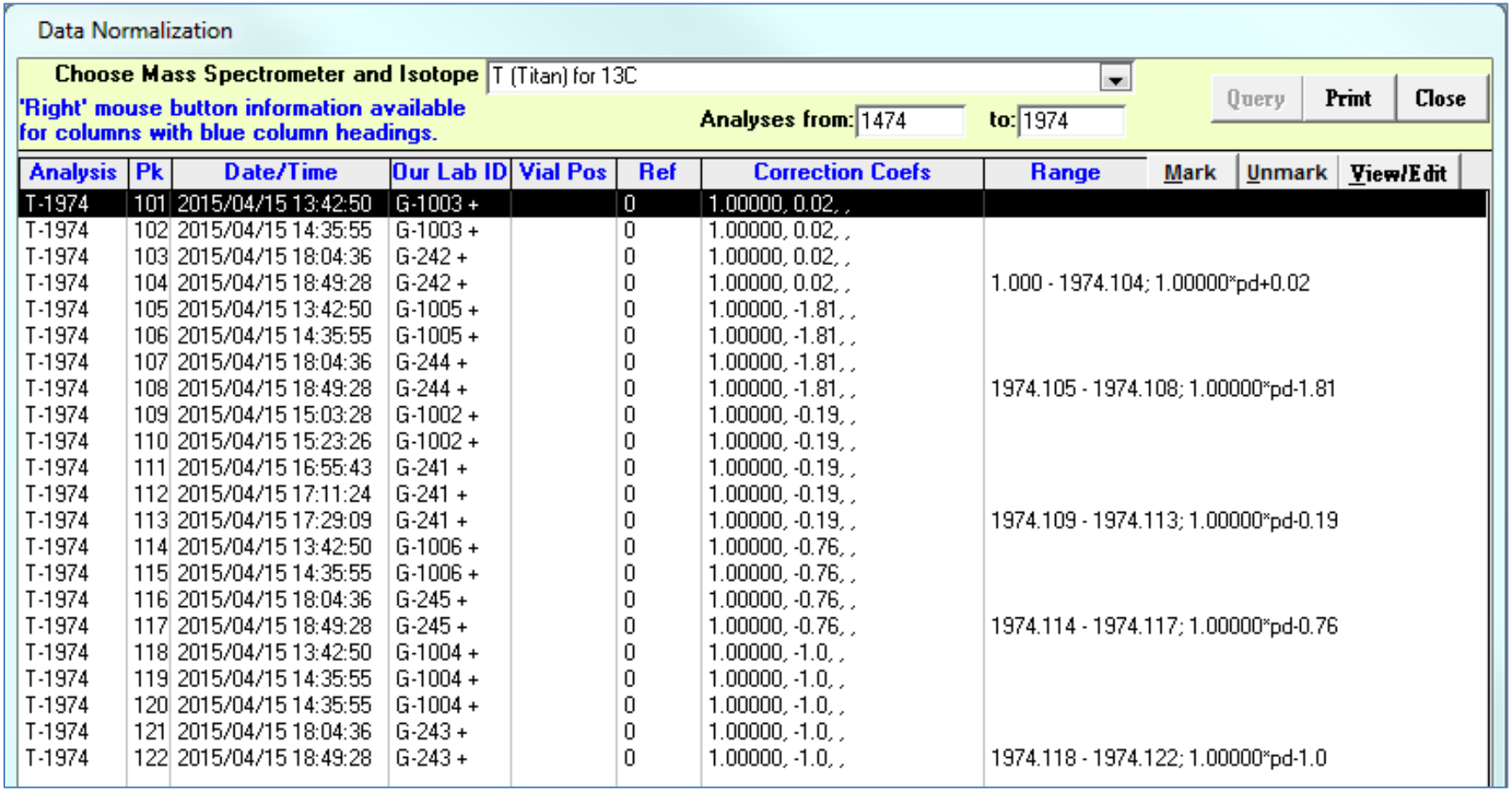


Fig. 32.12. Normalization Equation Coefficients form for peak numbers 101–104.



Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Ref	Correction Coefs	Range
T-1974	101	2015/04/15 13:42:50	G-1003 +		0	1.00000, 0.02, ,	
T-1974	102	2015/04/15 14:35:55	G-1003 +		0	1.00000, 0.02, ,	
T-1974	103	2015/04/15 18:04:36	G-242 +		0	1.00000, 0.02, ,	
T-1974	104	2015/04/15 18:49:28	G-242 +		0	1.00000, 0.02, ,	1.000 - 1974.104; 1.00000*pd+0.02
T-1974	105	2015/04/15 13:42:50	G-1005 +		0	1.00000, -1.81, ,	
T-1974	106	2015/04/15 14:35:55	G-1005 +		0	1.00000, -1.81, ,	
T-1974	107	2015/04/15 18:04:36	G-244 +		0	1.00000, -1.81, ,	
T-1974	108	2015/04/15 18:49:28	G-244 +		0	1.00000, -1.81, ,	1974.105 - 1974.108; 1.00000*pd-1.81
T-1974	109	2015/04/15 15:03:28	G-1002 +		0	1.00000, -0.19, ,	
T-1974	110	2015/04/15 15:23:26	G-1002 +		0	1.00000, -0.19, ,	
T-1974	111	2015/04/15 16:55:43	G-241 +		0	1.00000, -0.19, ,	
T-1974	112	2015/04/15 17:11:24	G-241 +		0	1.00000, -0.19, ,	
T-1974	113	2015/04/15 17:29:09	G-241 +		0	1.00000, -0.19, ,	1974.109 - 1974.113; 1.00000*pd-0.19
T-1974	114	2015/04/15 13:42:50	G-1006 +		0	1.00000, -0.76, ,	
T-1974	115	2015/04/15 14:35:55	G-1006 +		0	1.00000, -0.76, ,	
T-1974	116	2015/04/15 18:04:36	G-245 +		0	1.00000, -0.76, ,	
T-1974	117	2015/04/15 18:49:28	G-245 +		0	1.00000, -0.76, ,	1974.114 - 1974.117; 1.00000*pd-0.76
T-1974	118	2015/04/15 13:42:50	G-1004 +		0	1.00000, -1.0, ,	
T-1974	119	2015/04/15 14:35:55	G-1004 +		0	1.00000, -1.0, ,	
T-1974	120	2015/04/15 14:35:55	G-1004 +		0	1.00000, -1.0, ,	
T-1974	121	2015/04/15 18:04:36	G-243 +		0	1.00000, -1.0, ,	
T-1974	122	2015/04/15 18:49:28	G-243 +		0	1.00000, -1.0, ,	1974.118 - 1974.122; 1.00000*pd-1.0

Fig. 32.13. Data Normalization form with five range markers for ethane, iso-butane, methane, *n*-butane, and *n*-propane δ^{13}C data.

32.4 Evaluating CSIA Data of Samples in Progress

To evaluate these CSIA data:

1. Click “Evaluate Samples in Progress” on the main page and the Evaluate Samples in Progress form will open (Section 25).
2. Select “G” for the “Prefix” if not already selected.
3. Select “13C” for the “Isotope.”
4. Click “Query” and the Evaluate Samples in Progress form will appear as shown in Figure 32.14.
5. Click “Close” to return to the main page.

Note that the “Multiple Peaks/Analysis Summary” panel (Fig. 32.14) provides the mean and standard deviation of each analysis. Because there is only one analysis number (T-1974), LIMS does not calculate a “Mean Final Delta” value, but only calculates a “Mean 1” value.

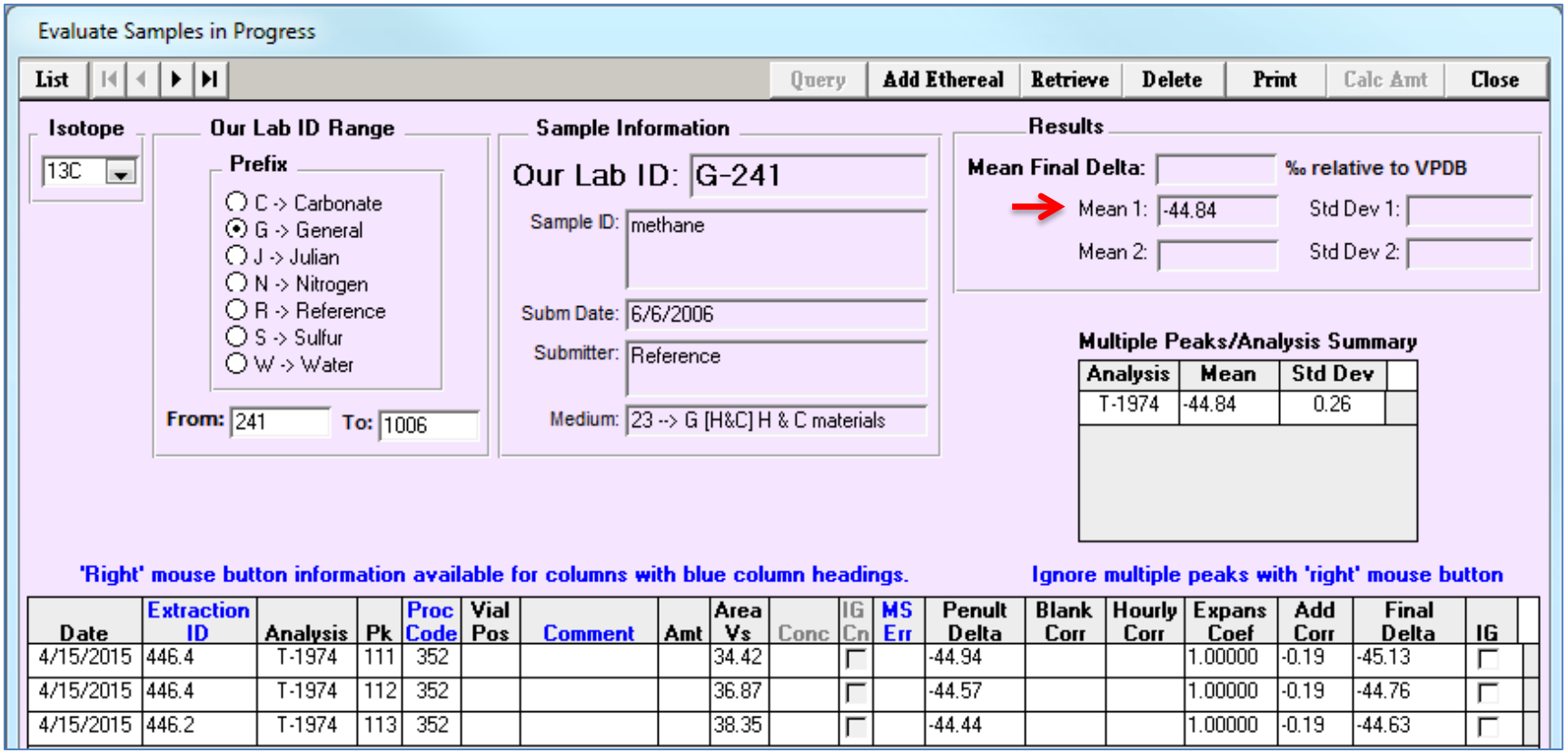


Fig. 32.14. Example of Evauate Samples in Progress for CSIA results.

32.5 Printing and Exporting CSIA Results of Samples in Progress

Samples in Progress results are printed and exported using the Print or Export Samples in Progress form (Section 26). To demonstrate printing and exporting:

1. Click “Print / Export Samples in Progress” on the main page and the Print or Export Samples in Progress form will open.
2. Select “G” for the “Prefix” if not already selected.
3. Select “13C” for the “Isotope.”
4. Enter 240 and 1006 in the “From” and “to” fields, respectively.
5. Click “Print” and LIMS will prompt with a dialog box asking if you want to print all of the analyses of the reference sample G-241.
6. Click “Yes” and LIMS prints a Samples in Progress report (Fig. 32.15). Compare with Figure 26.2.
7. Click the “Save As Excel File” check box.
8. Click “Save” and LIMS will prompt with a dialog box asking if you want to save all of the analyses of the reference sample G-241.
9. Click “Yes” and LIMS exports two Excel files, “G-240--G-1006_13C_BriefSummary.xlsx” and “G-240--G-1006_13C.xlsx”. Commonly one or both of these Excel files is provided to the client. These two files are provided as examples in the file “CSIA_Demo.zip” in a folder named “Section 32” in files that accompany this manual.

This completes the discussion of Printing and Exporting CSIA Results of Samples in Progress.

Samples in Progress for 13C
Between G-240 And G-1006

6/2/2017 9:01:19 AM

Date	Analysis	Pk	Vial Position	Proc Code	MS Error	Penultimate Delta	Blank Corr	Hr Corr	Exp Coef	Add Corr	Final Delta	Ig
G-241	Reference	methane					23 --> G [H&C] H & C materials					
4/15/2015	T-1974	111		352		-44.94			1.0	-0.19	-45.13	
4/15/2015	T-1974	112		352		-44.57			1.0	-0.19	-44.76	
4/15/2015	T-1974	113		352		-44.44			1.0	-0.19	-44.63	
Mean 1 = -44.84												
G-242	Reference	ethane					23 --> G [H&C] H & C materials					
4/15/2015	T-1974	103		352		-31.0			1.0	0.02	-30.98	
4/15/2015	T-1974	104		352		-32.63			1.0	0.02	-32.62	
Mean 1 = -31.80												
G-243	Reference	n-propane					23 --> G [H&C] H & C materials					
4/15/2015	T-1974	121		352		-24.23			1.0	-1.0	-25.22	
4/15/2015	T-1974	122		352		-24.46			1.0	-1.0	-25.46	
Mean 1 = -25.34												
G-244	Reference	iso-butane					23 --> G [H&C] H & C materials					
4/15/2015	T-1974	107		352		-24.46			1.0	-1.81	-26.27	
4/15/2015	T-1974	108		352		-21.72			1.0	-1.81	-23.53	
Mean 1 = -24.90												
G-245	Reference	n-butane					23 --> G [H&C] H & C materials					
4/15/2015	T-1974	116		352		-22.17			1.0	-0.76	-22.93	
4/15/2015	T-1974	117		352		-21.65			1.0	-0.76	-22.41	
Mean 1 = -22.67												
G-1002	Test	methane					23 --> G [H&C] H & C materials					
4/15/2015	T-1974	109		352		-36.9			1.0	-0.19	-37.09	
4/15/2015	T-1974	110		352		-36.96			1.0	-0.19	-37.16	
Mean 1 = -37.12												

Fig. 32.15. Page 1 of a Samples in Progress report to CSIA sample results.

32.6 Storing CSIA Results to Projects

To store these CSIA results to projects:

1. Click “Store Sample Results to Projects” on the main page and the Store Sample Results to Projects form will open.
2. Select “G” for the “Prefix” if not already selected.
3. Select “13C” for the “Isotope.”
4. Enter 1002 and 1006 in the “From” and “to” fields, respectively.
5. Click the “Store Single Analysis” check box because only one analysis number of each sample (Our Lab ID) exists. The Store Sample Results to Projects form should appear as shown in Figure 32.16.
6. Click “Store” and LIMS saves the results in the Table of Samples and displays the dialog box and status form shown in Figure 32.17.
7. Click “OK” and “Close”, and this completes storing of the CSIA results.
8. Navigating to the project and printing a project report results in the report shown in Figure 32.18.

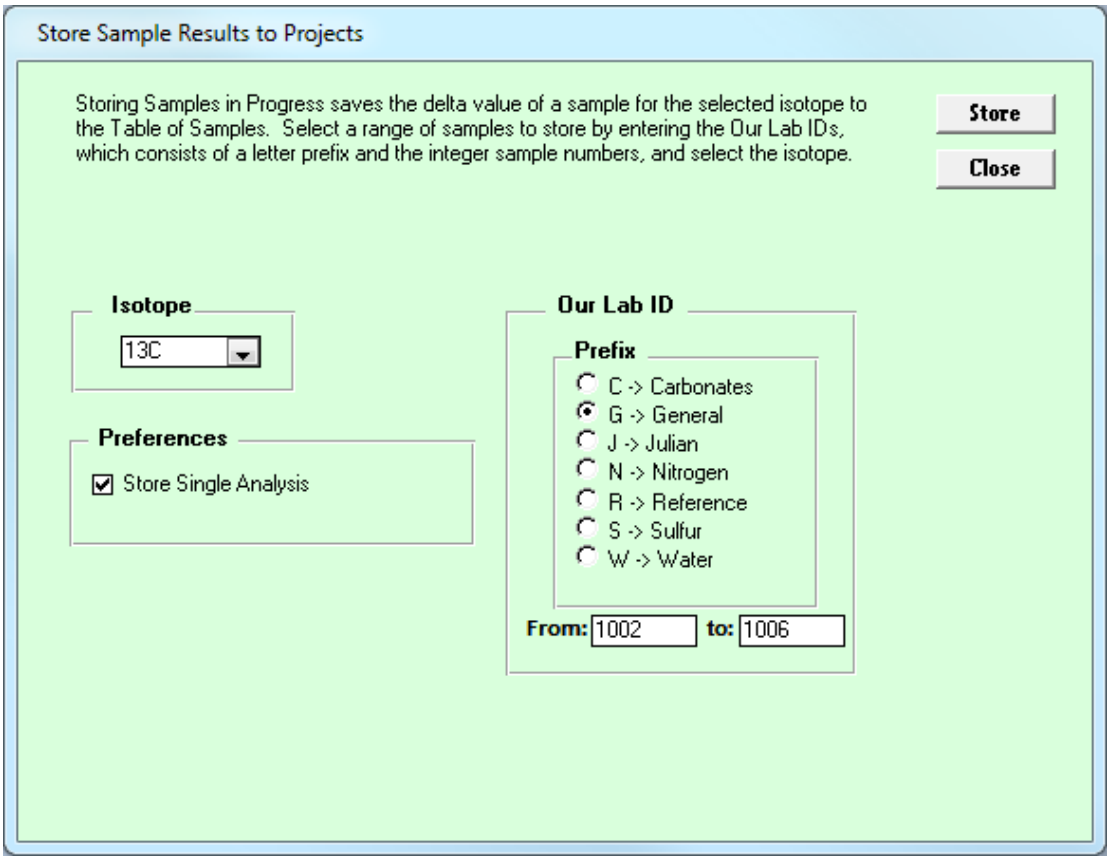


Fig. 32.16. Store Sample Results to Projects form for selected CSIA samples.

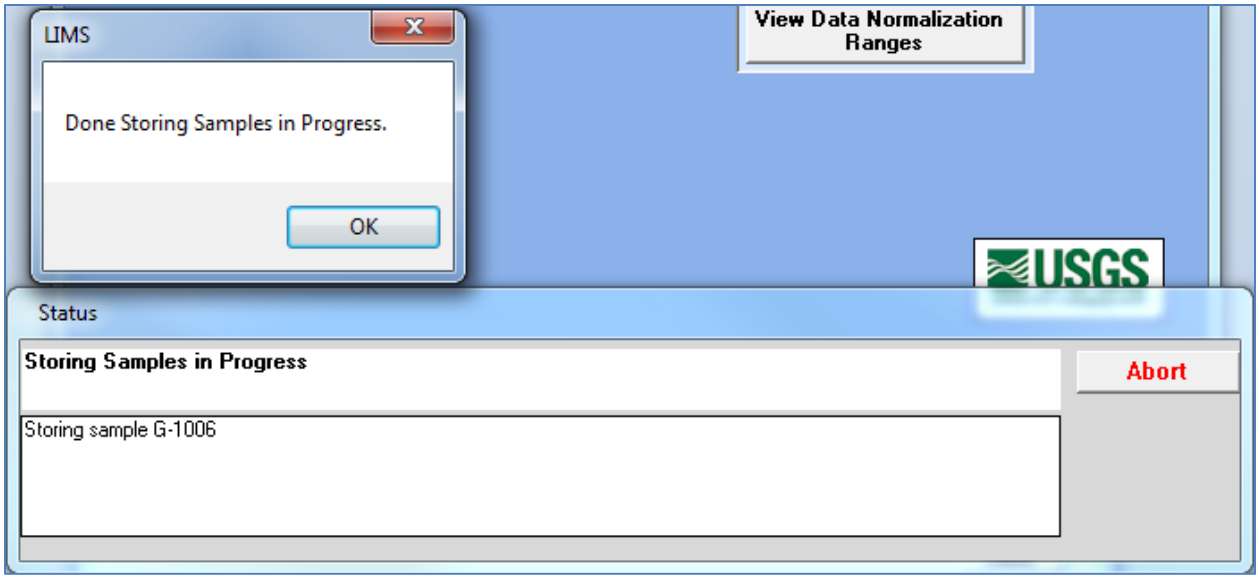


Fig. 32.17. Dialog box indicating successful storing of samples.

Submission: 5/5/2017 Test **G-1001 to G-1006** 5/26/2017

Medium: 23 --> G [H&C] H & C materials
Purpose: CSIA Demo

Location:

Sample ID:	Collection Date	Our Lab ID	δ^2H_{VSMOW}, in ‰ Value	Comment	$\delta^{13}C_{VPDB}$, in ‰ Value	Comment
CSIA sample		G-1001				
methane		G-1002			-37.12	
ethane		G-1003			-28.89	
n-propane		G-1004			-33.59	
iso-butane		G-1005			-31.15	
n-butane		G-1006			-28.04	

Fig. 32.18. Project report of the CSIA samples G-1001 to G-1006. Note that G-1001 is a placeholder and does not have a $\delta^{13}C$ value.

33 Creating Sample Lists

33.1 General Information

Many laboratories find it helpful to use tools in LIMS to create sample lists for routine analysis of samples submitted to the laboratory. It is useful if these lists of samples have two references having substantially different isotopic compositions interspersed among the unknowns to be measured. In this manner, a daily analytical run can be normalized to isotope-delta scales (Section 24). There are three strategies for automating or semi automating the creation of sample lists:

- Employ a USGS weighing template for mass spectrometers having EAs and TC/EAs (Section 33.2).
- Optimize the laboratory sample submission file (Section 7.5.1) so that it can be used easily to create a file that can be imported by an IRMS or can be copy and pasted to the sequence table of an IRMS (Section 33.3).
- Create a template in LIMS for an analytical method that has an associated Samples to be Analyzed queue with which one can generate a sample list (with interspersed references) in a file format that can be transferred to the IRMS. For a Thermo Scientific IRMS this file format would be an Excel file. For IonVantage and MassLynx this file format would be a Microsoft Access file with a suffix of spl. When samples are logged into LIMS, they are added to the appropriate Samples to be Analyzed queue by clicking "Template List – Add & Delete Samples" (Section 7.6.3) on a Project form (Fig. 7.26) as discussed in Section 33.5.2.

33.2 Excel Weighing Templates for EA and TC/EA Analyses

The RSIL uses an 84-position Excel weighing template for EA and TC/EA sample analyses (Fig. 33.1), which it named "USGS_weighing_template_84_pos.xls" and is found in a folder named "Section 33.2" in files that accompany this manual. Each sample has cells for:

- Our Lab ID
- Desired weight taking into account the mass fraction(s) of element(s) to be analyzed for isotopic composition
- Weight measured with a microbalance
- Comment

A microbalance is connected to a laptop so that the measured weight can be automatically transferred to the cell containing the specimen weight. This minimizes typographic errors. The cells in a second worksheet of this file ("Sequence Table Headings"), shown in Figure 33.2, are linked to the cells in the "Template" worksheet. It is an easy process to cut and paste the information in the Sequence Table Headings worksheet to the sequence table of the IRMS. It is

recommended that reference materials be interspersed among every dozen or so samples. For example, for an RSIL EA weighing temple, USGS40 L-glutamic acid would be loaded into lines (positions) 1, 2, 3, 4, 5, 18, 19, 32, 33, 46, and 47. USGS41 L-glutamic acid would be loaded into lines (positions) 6, 7, 20, 21, 34, 35, 48, and 49.

In addition to the file for 84 samples, the folder named "Section 33.2" also contains the following files for as many as 192 samples that may be of use to laboratories.

- USGS_weighing_template_96_pos_letter.xls
- USGS_weighing_template_96_pos_A4.xls
- USGS_weighing_template_97-192_pos_letter.xls
- USGS_weighing_template_97-192_pos_A4.xls

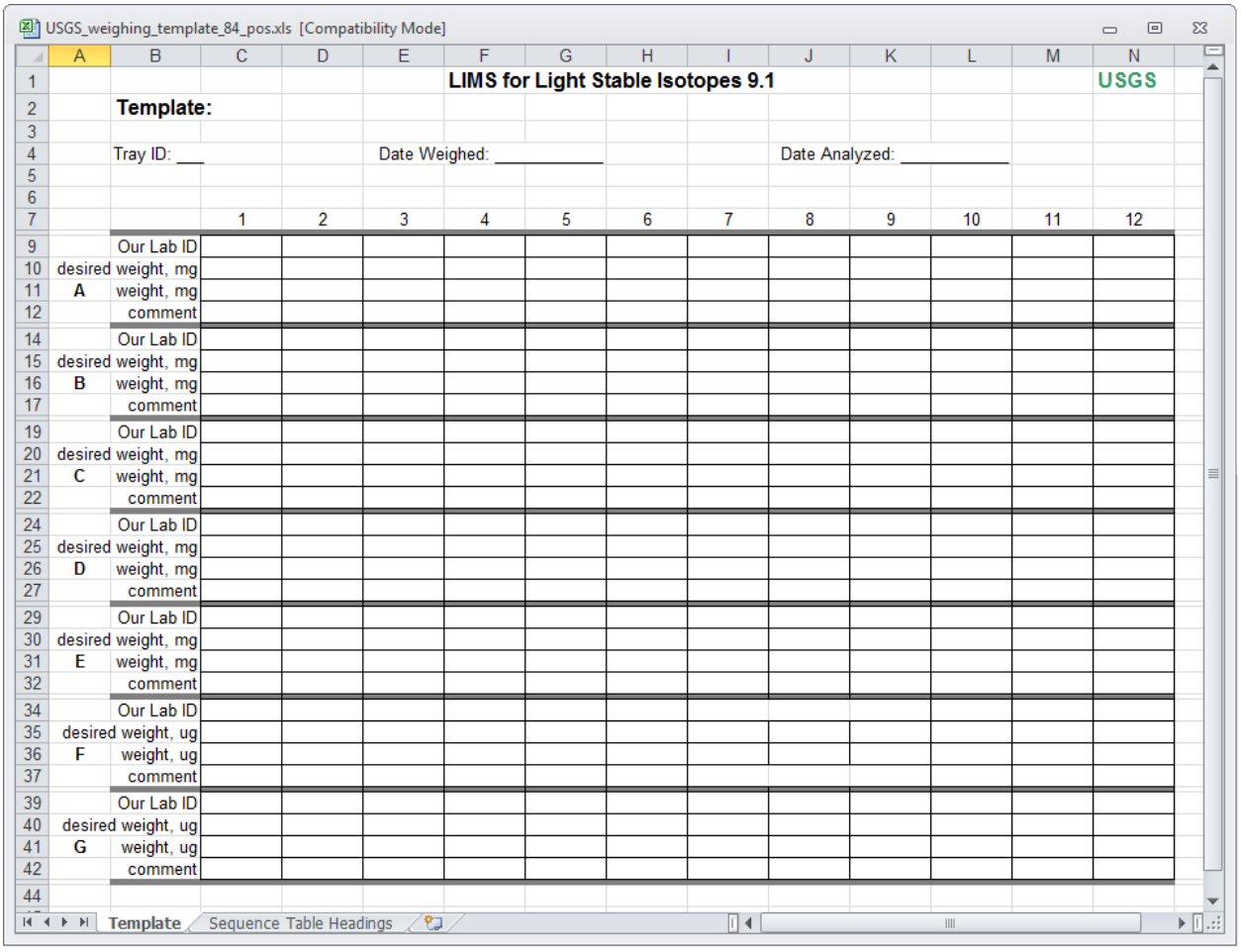
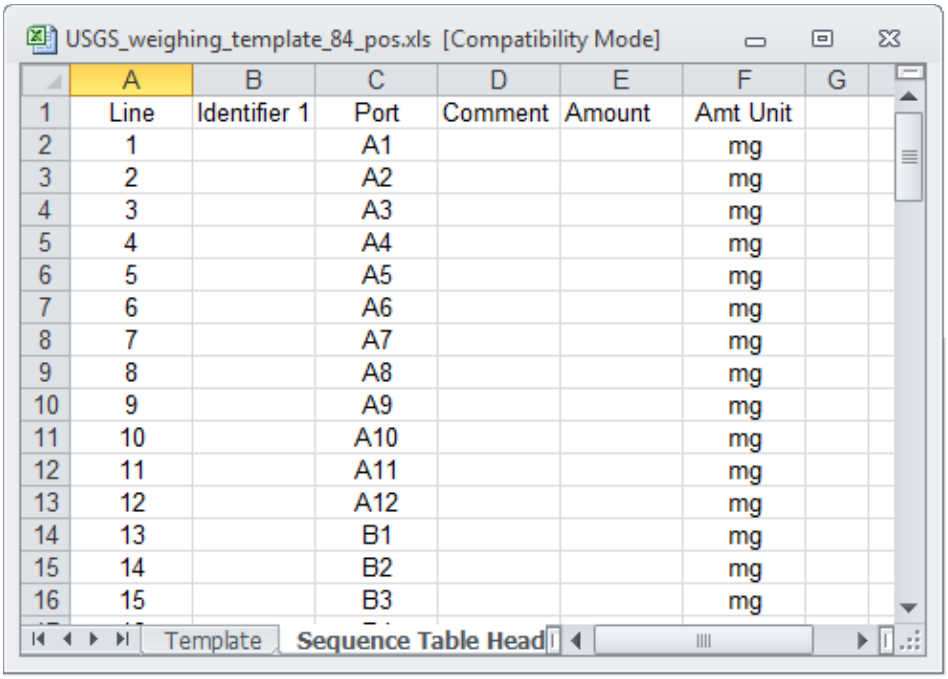


Fig. 33.1. USGS weighing template for an IRMS having an EA or TC/EA . This Excel file is suitable for weighing as many as 84 samples.



	A	B	C	D	E	F	G
1	Line	Identifier 1	Port	Comment	Amount	Amt Unit	
2	1		A1			mg	
3	2		A2			mg	
4	3		A3			mg	
5	4		A4			mg	
6	5		A5			mg	
7	6		A6			mg	
8	7		A7			mg	
9	8		A8			mg	
10	9		A9			mg	
11	10		A10			mg	
12	11		A11			mg	
13	12		A12			mg	
14	13		B1			mg	
15	14		B2			mg	
16	15		B3			mg	

Fig. 33.2. Sequence Table Headings worksheet of weighing template. At the RSIL, USGS40 L-glutamic acid is loaded into lines (positions) 1, 2, 3, 4, 5, 18, 19, 32, 33, 46, and 47. USGS41 L-glutamic acid is loaded into lines (positions) 6, 7, 20, 21, 34, 35, 48, and 49.

33.3 Using Sample Submission Files to Create EA, TC/EA, and Other Sample Lists

Laboratories can optimize their sample submission files for the types of analyses they perform most. Solutions to analyzing EA samples, where the client weighs their own samples and provides sample IDs, tray locations, and weights, are shown in Figures 7.15 (Washington State University), 7.16 (Memorial University of Newfoundland), and 7.17 (University of Ottawa). Any of these worksheets could be modified to blank out rows for reference materials in the tray. Either the laboratory or the client could weigh out reference materials that would be interspersed among the unknowns. For rows (tray positions) having references, such as USGS40 and USGS41, there should be no entry in the Sample ID column to ensure that USGS40 and USGS41 are not assigned new Our Lab IDs.

33.4 LIMS Sample Export Formats

33.4.1 Introduction

When a user creates a sample list from the Samples to be Analyzed queue, LIMS creates an export file that contains the sample names, the position of the samples in the preparation system, and information about the isotopic analyses requested. This information can be transferred to the data acquisition and control software of the mass spectrometer that uses this information to perform the requested isotopic analyses. This technique eliminates typing in sample headings, which may result in typographic errors. The sample export format is specific to each mass spectrometer (Table 13.2) and is designated when editing or adding a mass spectrometer using the Mass Spec form (Section 13). These sample export formats are discussed below.

33.4.2 LIMS Default Sample Export Format

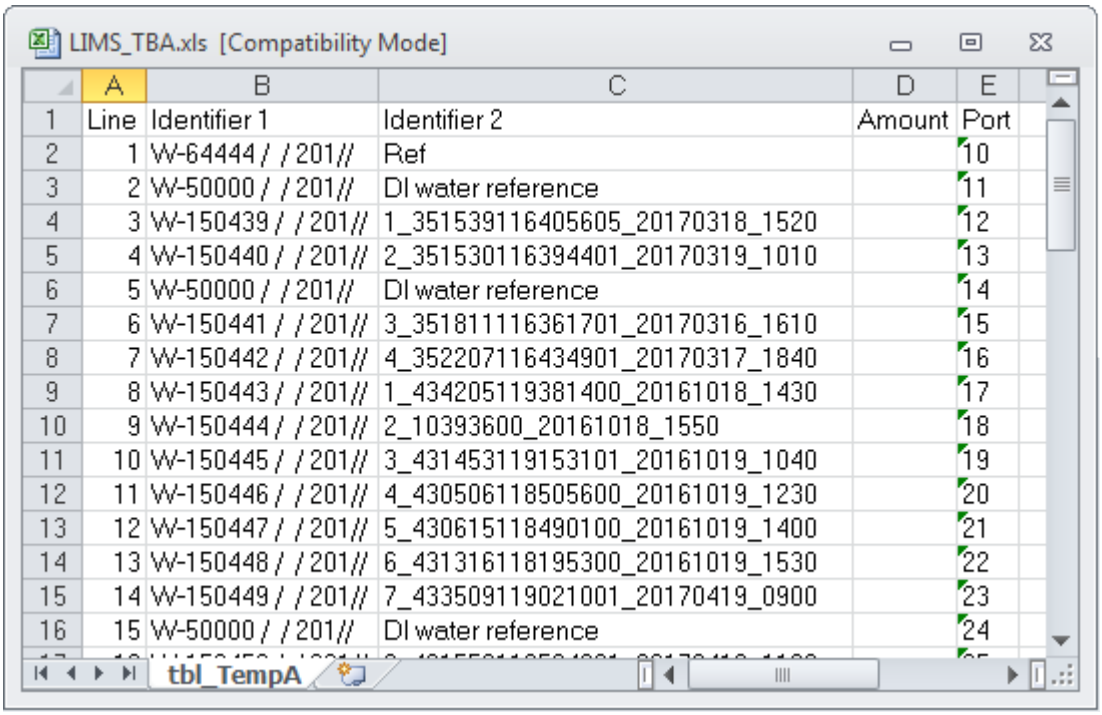
The LIMS Default sample export format is the default export format for many mass spectrometers. LIMS saves the export information as a Microsoft Excel file named "LIMS_TBA.xls." The file has five columns of information (Table 33.1 and Fig. 33.2). LIMS is able to concatenate as many as five data items in either the "Identifier 1" or "Identifier 2" fields. In this manner, LIMS can create a sample list having low and high procedure codes and pass this information to the mass spectrometer data system. Subsequently, the mass spectrometer data system will pass this information back to LIMS along with isotope-delta results. In this manner, LIMS isotope-delta values and specified procedure codes (as opposed to default procedure codes) are automatically imported into LIMS with no additional data entry. Five data items can be concatenated in either of the fields "Identifier 1" or "Identifier 2," but not both. When all five data items are provided, they are delimited with forward slashes as:

Our Lab ID / Extraction ID / Low Procedure Code / High Procedure Code / Comment

The minimum information needed by LIMS to import an analysis is the Our Lab ID. Section 19.2 provides additional discussion of the "Identifier 1" and "Identifier 2" use.

Table 33.1. LIMS Default field headings and information that can be imported into the mass spectrometer data system

Field Name	Description
Line	Row number in Excel (required)
Identifier 1	Identifies one to five items, including Our Lab ID, Extraction ID, low procedure code, high procedure code, and comment (required)
Identifier 2	Additional sample information, such as Sample ID or reference name (not required)
Amount	Amount of sample (not required)
Port	Vial position or port number the sample will be loaded into (not required)

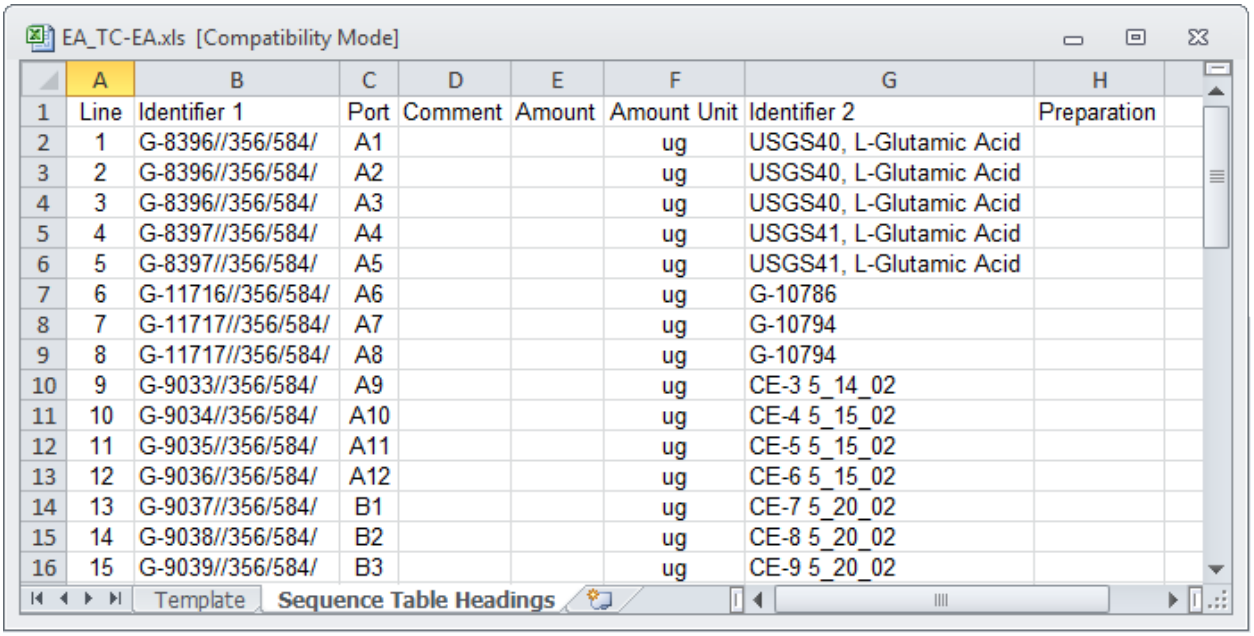


	A	B	C	D	E
1	Line	Identifier 1	Identifier 2	Amount	Port
2	1	W-64444 / / 201//	Ref		10
3	2	W-50000 / / 201//	DI water reference		11
4	3	W-150439 / / 201//	1_351539116405605_20170318_1520		12
5	4	W-150440 / / 201//	2_351530116394401_20170319_1010		13
6	5	W-50000 / / 201//	DI water reference		14
7	6	W-150441 / / 201//	3_351811116361701_20170316_1610		15
8	7	W-150442 / / 201//	4_352207116434901_20170317_1840		16
9	8	W-150443 / / 201//	1_434205119381400_20161018_1430		17
10	9	W-150444 / / 201//	2_10393600_20161018_1550		18
11	10	W-150445 / / 201//	3_431453119153101_20161019_1040		19
12	11	W-150446 / / 201//	4_430506118505600_20161019_1230		20
13	12	W-150447 / / 201//	5_430615118490100_20161019_1400		21
14	13	W-150448 / / 201//	6_431316118195300_20161019_1530		22
15	14	W-150449 / / 201//	7_433509119021001_20170419_0900		23
16	15	W-50000 / / 201//	DI water reference		24

Fig. 33.3. Example LIMS Default Sample Export Excel file. The "Identifier 1" column contains Our Lab IDs and low procedure codes ("201" for this δ^2H analysis). The "Identifier 2" column contains the LIMS Sample ID.

33.4.3 LIMS EA + TC/EA Sample Export Format

With the LIMS EA + TC/EA sample export format users are able to create an Excel file named "EA_TC-EA.xls," having two worksheets ("Template" and "Sequence Table Headings"). The "Template" worksheet is similar to that shown in Figure 33.1. An example of the "Sequence Table Headings" worksheet is shown in Figure 33.4. The user can weigh desired amounts of samples and references, and the weights can be copied from the "Sequence Table Headings" worksheet to the sample sequence table of the mass spectrometer data system.


EA_TC-EA.xls [Compatibility Mode]

	A	B	C	D	E	F	G	H
1	Line	Identifier 1	Port	Comment	Amount	Amount Unit	Identifier 2	Preparation
2	1	G-8396//356/584/	A1			ug	USGS40, L-Glutamic Acid	
3	2	G-8396//356/584/	A2			ug	USGS40, L-Glutamic Acid	
4	3	G-8396//356/584/	A3			ug	USGS40, L-Glutamic Acid	
5	4	G-8397//356/584/	A4			ug	USGS41, L-Glutamic Acid	
6	5	G-8397//356/584/	A5			ug	USGS41, L-Glutamic Acid	
7	6	G-11716//356/584/	A6			ug	G-10786	
8	7	G-11717//356/584/	A7			ug	G-10794	
9	8	G-11717//356/584/	A8			ug	G-10794	
10	9	G-9033//356/584/	A9			ug	CE-3 5_14_02	
11	10	G-9034//356/584/	A10			ug	CE-4 5_15_02	
12	11	G-9035//356/584/	A11			ug	CE-5 5_15_02	
13	12	G-9036//356/584/	A12			ug	CE-6 5_15_02	
14	13	G-9037//356/584/	B1			ug	CE-7 5_20_02	
15	14	G-9038//356/584/	B2			ug	CE-8 5_20_02	
16	15	G-9039//356/584/	B3			ug	CE-9 5_20_02	

Template | Sequence Table Headings

Fig. 33.4. "Sequence Table Headings" worksheet of an example LIMS EA + TC/EA Sample Export Excel file. The "Identifier 1" column contains Our Lab IDs and low and high procedure codes ("356" for this δ13C analysis and "584" for δ15N analysis). The "Identifier 2" column contains the LIMS Sample ID.

33.4.4 IonVantage and MassLynx Sample Export Format

A table describing the contents of fields of the IonVantage and MassLynx Access export file, which has the suffix spl, is provided in section 5.2.3 ("Editing sample lists before use") in the file named "MassLynx-LIMS interface manual-SCN1022ib5.pdf." This pdf can be found in a folder named "Section 16" that accompanies this manual.

33.4.5 LIMS Default for "Old" ISODAT

The export file for LIMS Default for Finnigan "Old" ISODAT is identical to the LIMS Default export format, except the Excel filename is "Old_Isod.xls." See Section 33.4.2, Section 33.4.3, Table 33.1, Figure 33.1, and Figure 33.4 for details.

33.5 Creating Sample Lists Using Templates

33.5.1 Creating a Sample Analysis Template

Sample analysis templates are instrument specific queues used to manage samples that need to be analyzed. After a template has been created, a user will be able to (1) add samples to its queue, (2) export samples and references to a file for use by the IRMS software, and (3) print a sample list. These templates are designed by the user and specify mass spectrometer, media, low and high procedures, default samples, order of analysis according to a list number and vial (port) number, and location of references.

The first step in creating an analysis template is to identify references of the media to be analyzed and ensure that they have assigned isotope-delta values in the Table of References (Section 12.2). The next step is to determine the order in which sample and references in vials (or ports) will be analyzed. For some peripherals, such as a carousel, this is trivial because the list order and carousel number are one-to-one. However, for other peripherals it may be beneficial to sketch the peripheral and devise the optimum list order of vials (ports). Consider the heated block used for carbonates (Fig. 33.5) that was discussed by P. Higgins in her "LIMS for Light Stable Isotopes – A guide to implementation." This peripheral requires a template for 48 samples and references with the vials analyzed in the order shown in Figure 33.6. The auto sampler analyses vial 1 first, vial 13 second, 25 third, etc. Superimposed upon the 48 vial positions are four yellow rectangles each containing 12 positions. In LIMS, each yellow rectangle emulates a sheet of paper onto which a technician has placed 12 samples and references (three across and four down). To set up this demonstration:

1. Create a new folder. It can be within a LIMS folder or elsewhere.
2. Identify the folder as an Access Trusted Location (Section 3.2.2).
3. Copy the zip file "LIMS_Analysis_Template_Demo_Backend_DB.zip," which is located in a folder named "Section 33.5" that accompanies this manual, into this new folder and extract the files from it, keeping them in this new folder. The extracted files are: "LIMS_Analysis_Template_Demo_Backend_DB.accdb", "Lm9prefs.accdb", and "Vial_Tray_Details_PAL carbonate.xlsx".

Fig. 33.5. Heated block used for carbonate-acid reactions at the University of Rochester. Right shows vial numbers used by the IRMS. Courtesy P. Higgins, University of Rochester, Rochester, NY.

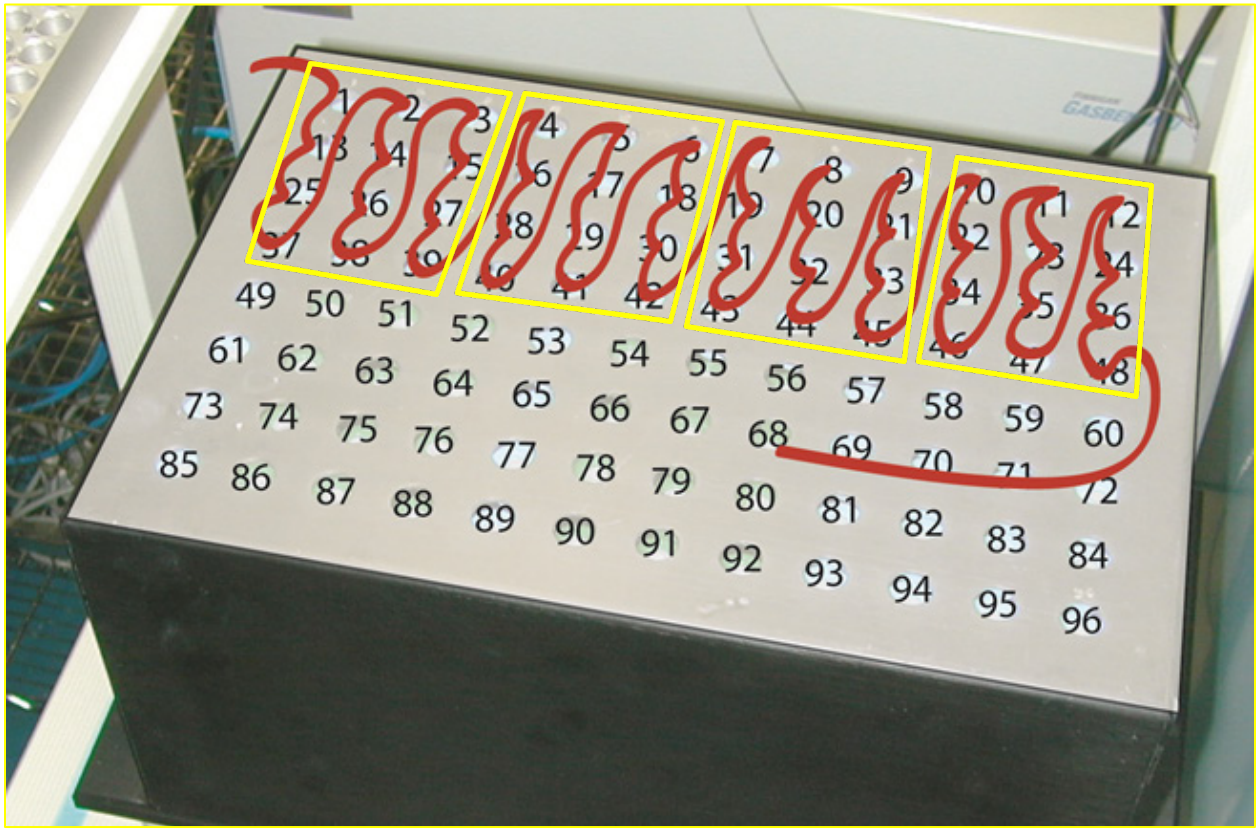


Fig. 33.6. Order of analysis of 48 samples and references in heated block. Superimposed upon the 48 vial positions are four yellow rectangles each containing 12 positions. In LIMS, each yellow rectangle represents a sheet of paper onto which a technician has placed 12 samples and references (three across and four down). Courtesy P. Higgins, University of Rochester, Rochester, New York.

4. Transfer into this new folder a fresh copy of the LIMS frontend, which is named "Lims9.202.zip" (or similar) and is located in a folder named "Section 4" that accompanies this manual. Extract the frontend database file from this zip file, keeping it in the same folder—it will be named "Lims9.202.accdb" or similar.
5. Double-click the new frontend (Lims9.202.accdb or similar) to open it. It should open with the message that LIMS cannot find the backend database (Fig. 4.1).
6. Click "OK" and navigate to "LIMS_Analysis_Template_Demo_Backend_DB.accdb."
7. LIMS will display a message that it needs to close.
8. Click "OK."
9. Reopen this frontend database and LIMS should display the welcome message in Figure 4.18.
10. Click "Yes" and LIMS will prompt that it needs to update settings and close.
11. Click "OK" and LIMS will perform cleanup activities upon closing.
12. Reopen this frontend database and LIMS should open with the main page (similar to Fig. 4.8).
13. Click "Special Features" and click "Options."
14. Set the paper size to A4 if needed, and set the print destination to "Any Installed Printer" if there is more than one printer available. A pdf creator might be one of the printers.
15. Click "Close" to close the Options form. The backend database is now ready.
16. The first step is to ensure that references exist and create them if they do not. For this demonstration, the two calcite references (C-51 and C-52) have been added to the Table of References. Click "Assign Lab References" in the Special Features Window, click "List," and navigate to "C-51" to confirm that these references are in the Table of References (Fig. 33.7), both for $\delta^{13}C$ and $\delta^{18}O$ values. Viewing the Reference Samples form for C-51 (Fig. 33.8), the reader will note that in addition to a "Final Delta" being provided, the "Use for Linearity Correction" check box has been check. This will enable this reference to be used for a linearity correction (adjust a delta value for amount of sample) as shown in Figures 19.18, 21.5, and 22.32.
17. Click "List" and navigate to control standard C-53 (Fig. 33.9). Note that "–999 ‰" is assigned as its "Final Delta" so that it appears as a reference, but cannot be used for normalization.

Fig. 33.7. References C-51 and C-52.

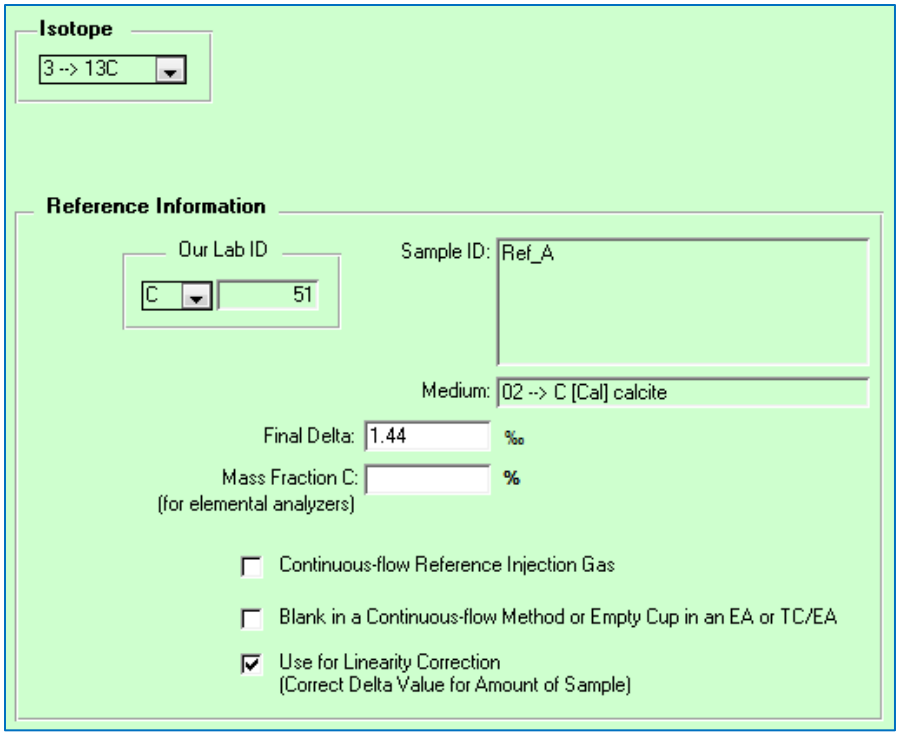


Fig. 33.8. Reference Samples form displaying C-51.

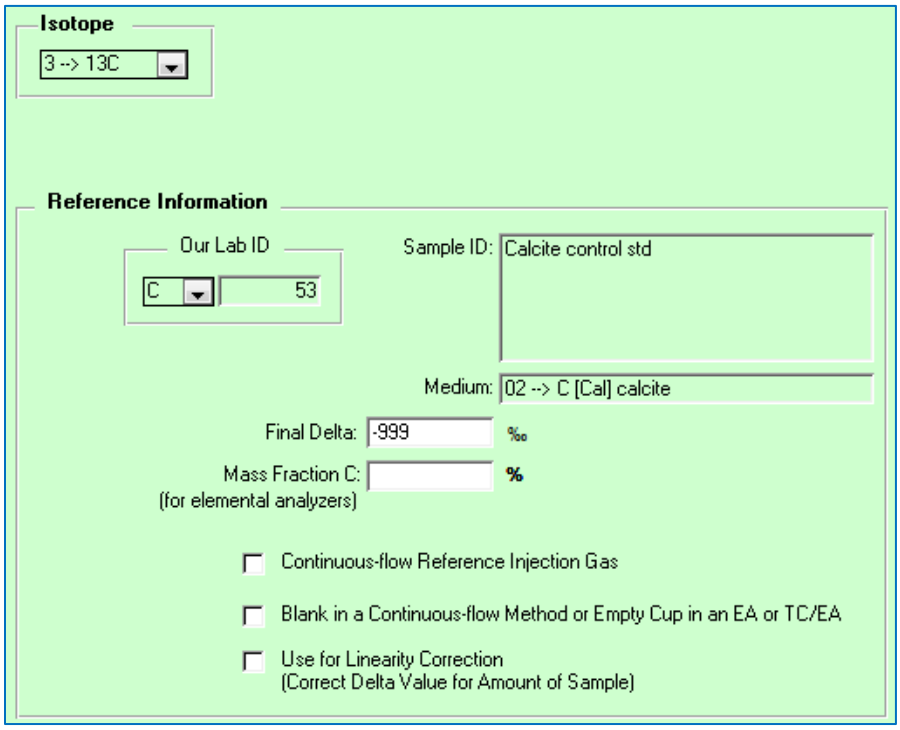


Fig. 33.9. Reference Samples form displaying calcite control standard C-53.

18. Click “Close.”
19. Click “Analysis Templates” in the Special Features Window and the Design Templates form will open (Fig. 33.10).
20. Click “Create a New Template.”
21. Enter “PAL carbonate” for the “Name” field.
22. Enter “For measurement of carbonates” for the “Description” field.
23. Select “T --> Titan” for the “Mass Spec” field.
24. Select “LIMS Default” for the “Export Format” field.
25. For the “Available Media” select “02 --> C (Cal) calcite” and click “Add.” Additional media, such as dolomite and aragonite, can be added as desired.
26. Select “312 --> DI, 100 % phosphoric acid, Delta 13C” for the Default Procedure for the Low Isotope.
27. Select “821 --> DI, 50 deg., 100% phosphoric acid, Delta 18O” for the Default Procedure for the High Isotope.

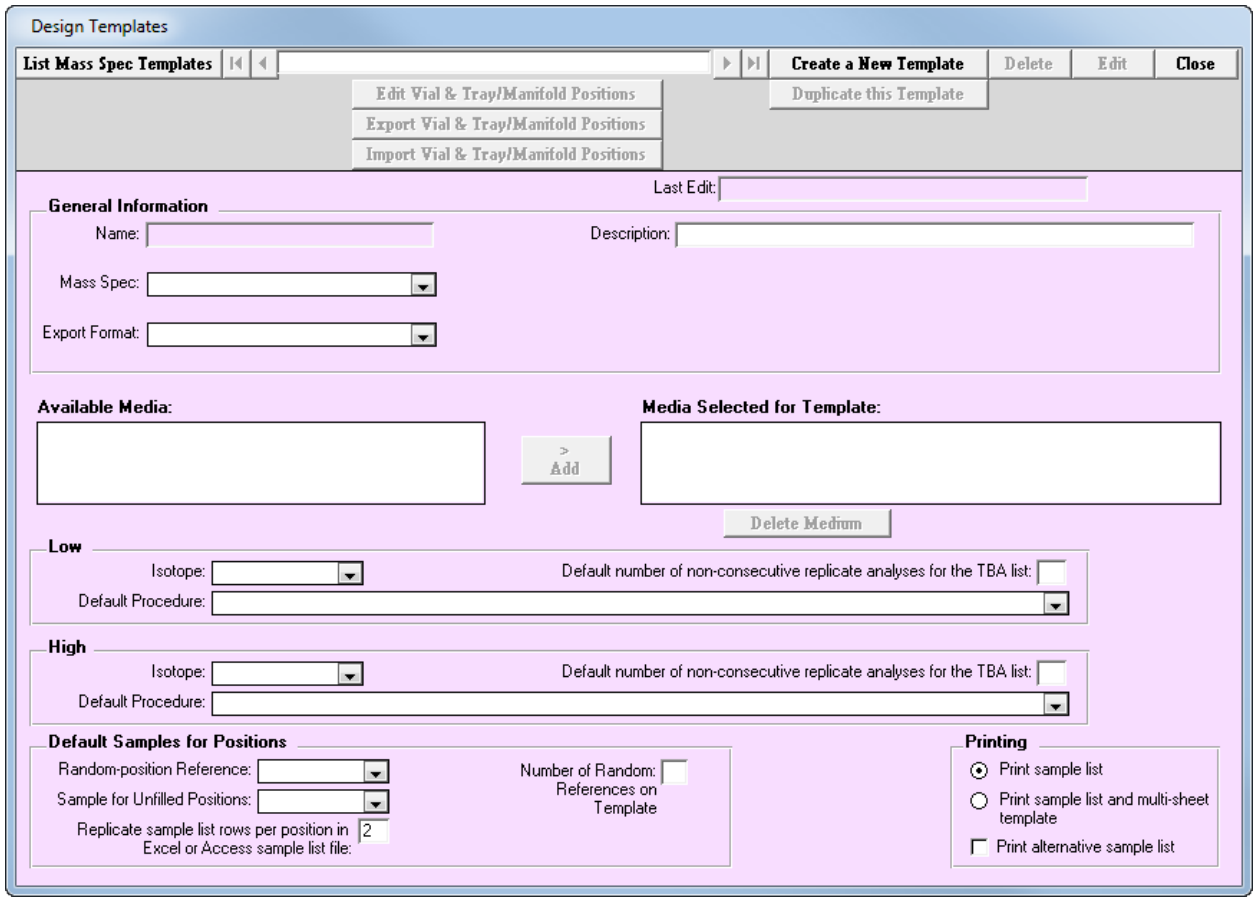


Fig. 33.10. Design Templates form.

28. For the Low Isotope, enter “2” for the “Default number of non-consecutive replicate analyses for the TBA list.” This indicates that by default each sample (and reference) will analysed twice for $\delta^{13}C$ value, once on each of two sample lists.
29. For the High Isotope, enter “2” for the “Default number of non-consecutive replicate analyses for the TBA list.” This indicates that by default each sample (and reference) will analysed twice for $\delta^{18}O$ value, once on each of two sample lists.
30. LIMS has the option to randomly insert references a specified number of times among the ports. For example, to enter four randomly positioned references in a template, one would enter “4” in the “Number of Random References on Template” field and select the desired Our Lab ID of the reference from the “Random-position Reference” field. For this example, no randomly positioned references will be used. Therefore, enter “0” for the “Number of Random References on Template” and leave the “Random-position Reference” field as is.
31. Select “C-1” for the “Sample for Unfilled Positions.” This dummy sample is used, for example, when only 20 samples are available for analysis on a 48-position template. This field cannot be left blank.
32. Enter “1” for the “Replicate sample list rows per port in Excel or Access sample list file.” This is the number of rows that are generated for each vial (or port) in the LIMS export file. For example, if seven aliquots (or injections) are desired for each vial, then for some IRMS manufacturers, the entry is this field would be “7” in order to create 7 rows for each sample.
33. For the “Printing” panel option, select “Print sample list and multi-sheet template” so that LIMS will print a sample list plus a four-page printout that will emulate the four rectangles in Figure 33.6 and can be used for setting up samples and references to be analysed prior to loading the samples and references.
34. Click “Save” and the basic template is created (Fig. 33.11). Once created, all fields are modifiable, except the “Name” filed, which cannot be edited. In the case that the “Name” field has a mistake, the template may be deleted and re-created.

The Design Templates form will display two additional fields for “IonVantage 1.1”, “MassLynx 4.0”, and “Micromass MassLynx 3.6” sample export formats. These fields are named “MS Method (MassLynx)” and “Inlet Method (MassLynx)” and their use is discussed in the handbook that is provided as a file named “MassLynx-LIMS interface manual-SCN1022ib5.pdf” in a folder named “Section 16” that accompanies this manual. An example of the Design Templates form for an IonVantage sample export is shown in Figure 33.12.

The analysis sequence of local measurement standards, control standards, and client samples are set up next and the two options to set them up are (1) click “Edit Vial & Tray/Manifold Positions” and populate fields in the mass spectrometer run sequence form that opens (Fig. 33.13), or (2) click “Import Vial & Tray/Manifold Positions.” In this demonstration, both

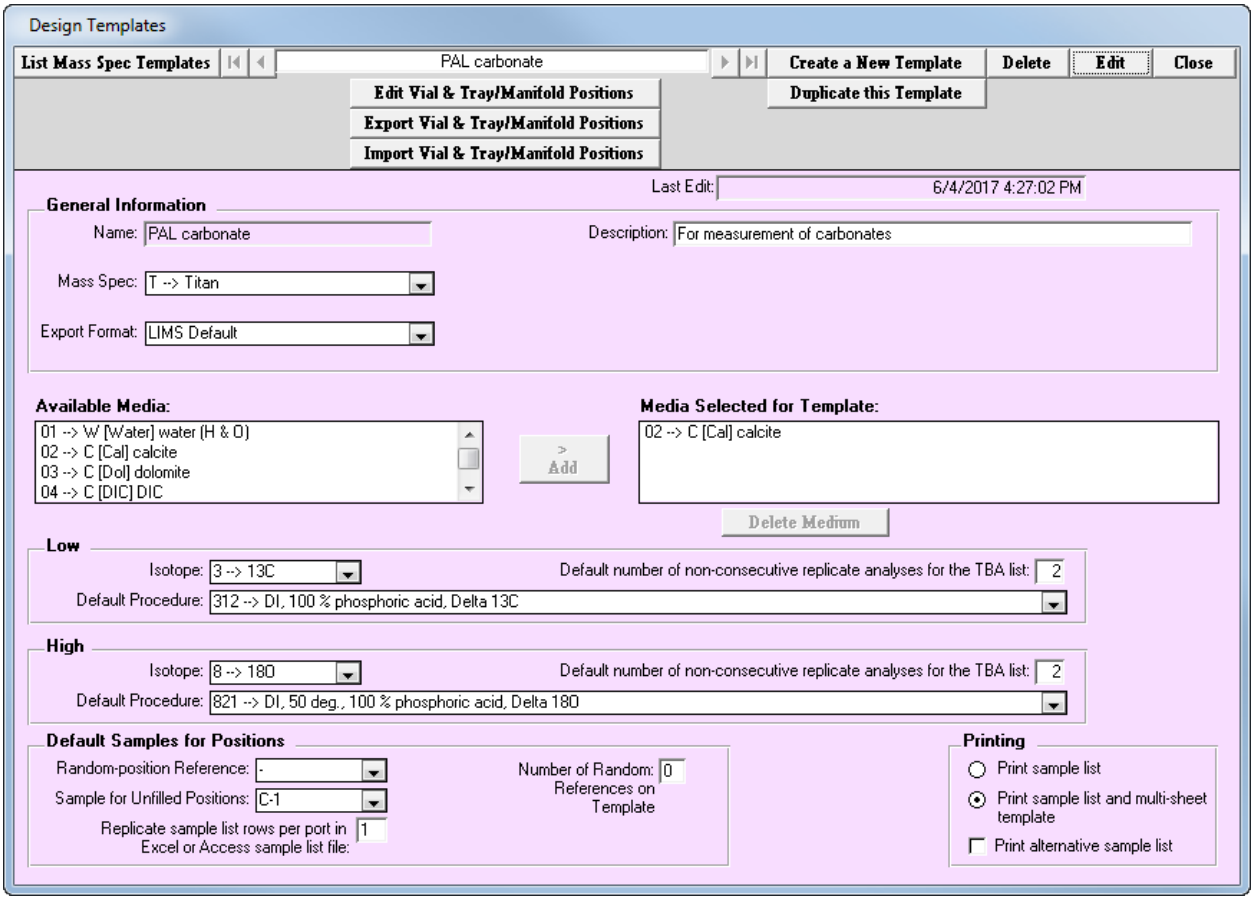


Fig. 33.11. The 48-sample PAL carbonate template.

options are discussed. The form in Figure 33.13 represents one of the rectangles (or pages) shown in Figure 33.6 and the vial positions within that rectangle. When all vial positions and run-order indicators have been accounted for in the template, there will be four pages. To add these positions to the template:

1. Click “Edit Vial & Tray/Manifold Positions” and the mass spectrometer run sequence form opens (Fig. 33.13).
2. Click “Edit.”
3. Populate the form with the data shown in Figure 33.14.
4. Click “Save.”
5. Click “Add Page” and populate “Page 2” with the data shown in Figure 33.15.
6. Click “Save.”
7. Click “Add Page” and populate “Page 3” with the data shown in Figure 33.16.
8. Click “Save.”
9. Click “Add Page” and populate “Page 4” with the data shown in Figure 33.17.

10. Click “Save” to complete the entry of the vial/port data.
11. Click “Close” to return to the Design Templates form. This completes the “PAL carbonate” template.

To make modifications to vial and tray/manifold positions, it may be easier for many users to export the position data to an Excel file, edit the Excel file, and then import it. The Excel file generated by clicking “Export Vial & Tray/Manifold Positions” (Fig. 33.18) is named “Vial_Tray_Details_PAL Carbonate.xlsx” and it was extracted from “LIMS_Analysis_Template_Demo_Backend_DB.zip” when setting up the examples for this section. This zip file is provided in a folder named “Section 33.5” in the files that accompany this manual. This Excel file is sorted by Page and Page_Position in Figure 33.18. The last column of the Excel file has page positions between 1 and 12. The 12 positions on each page (Figs. 33.13–33.17) begin with position 1 in the upper left, position 3 in the upper right, and position 12 in the bottom right of the page, just as one reads a book.

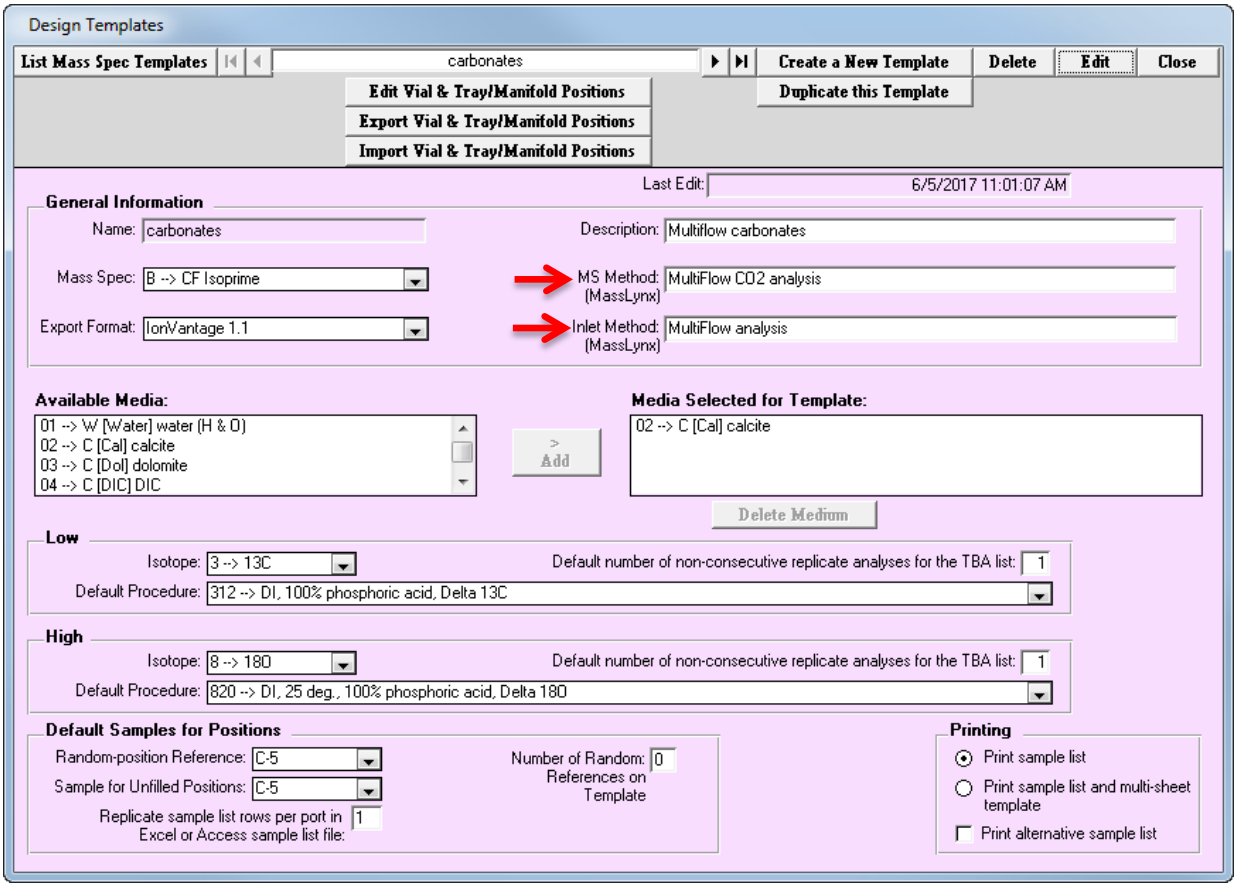


Fig. 33.12. Design Templates form for an IonVantage 1.1 sample export format. For IonVantage and MassLynx export formats two additional forms, fields (“MS Method (MassLynx)” and “Inlet Method (MassLynx)”) are required.

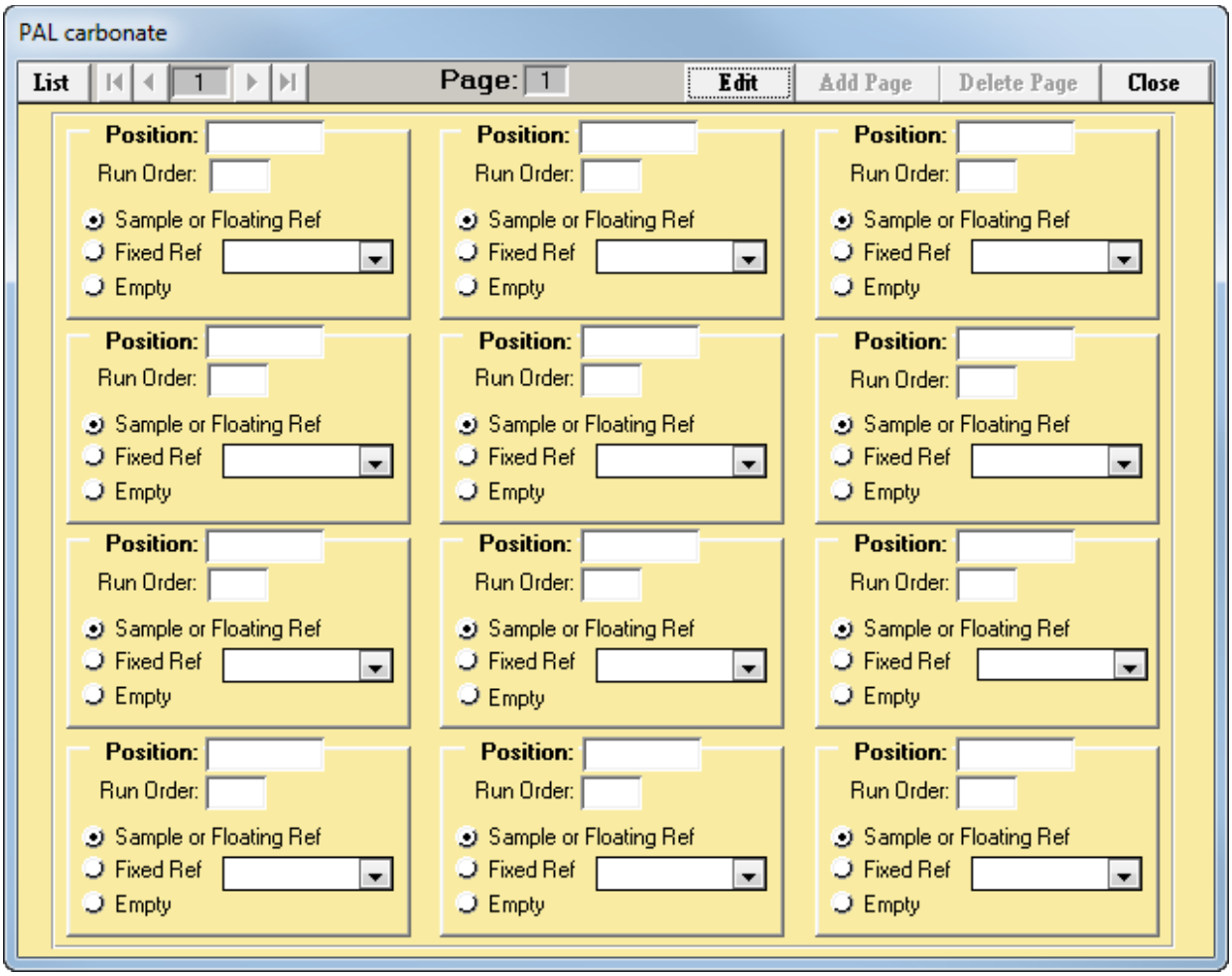


Fig. 33.13. Run sequence form for setting up the tray/manifold positions.

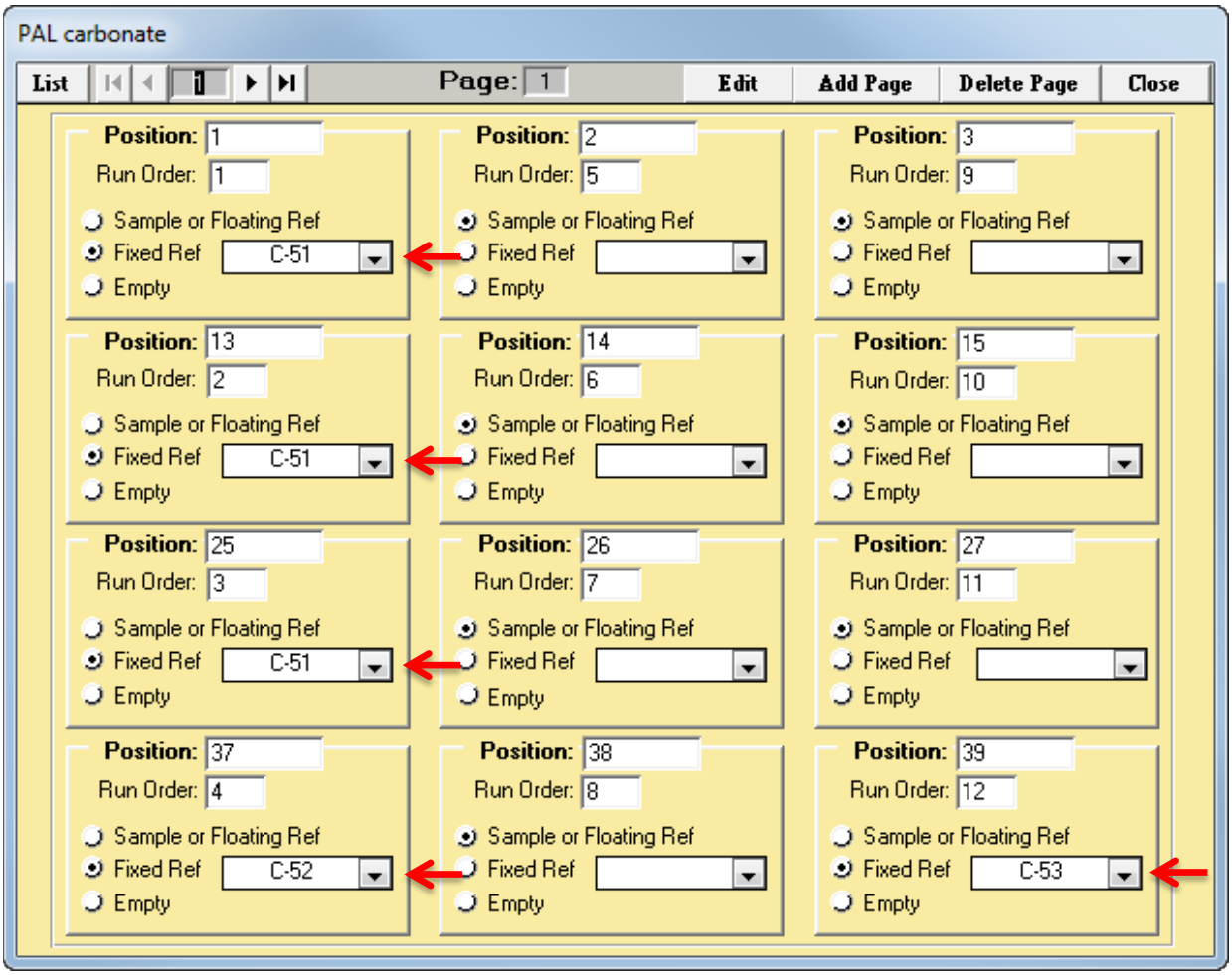


Fig. 33.14. First page of sequence for PAL caronate tray/manifold positions. Note the three occurrences of reference C-51, the single occurrence of reference C-52, and the control standard C-53.

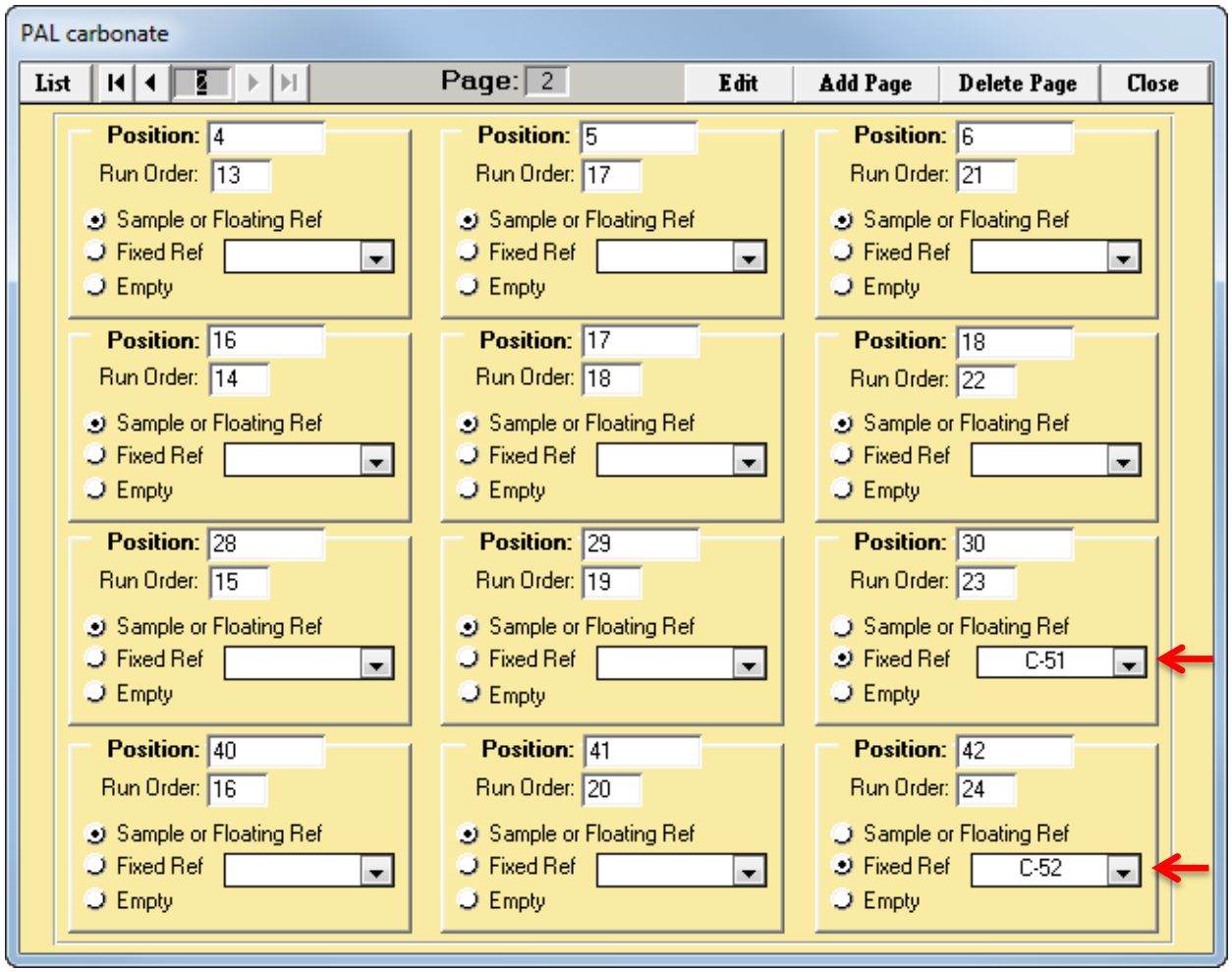


Fig. 33.15. Second page of sequence for PAL caronate tray/manifold positions. Note the single occurrence of reference C-51 and of reference C-52.

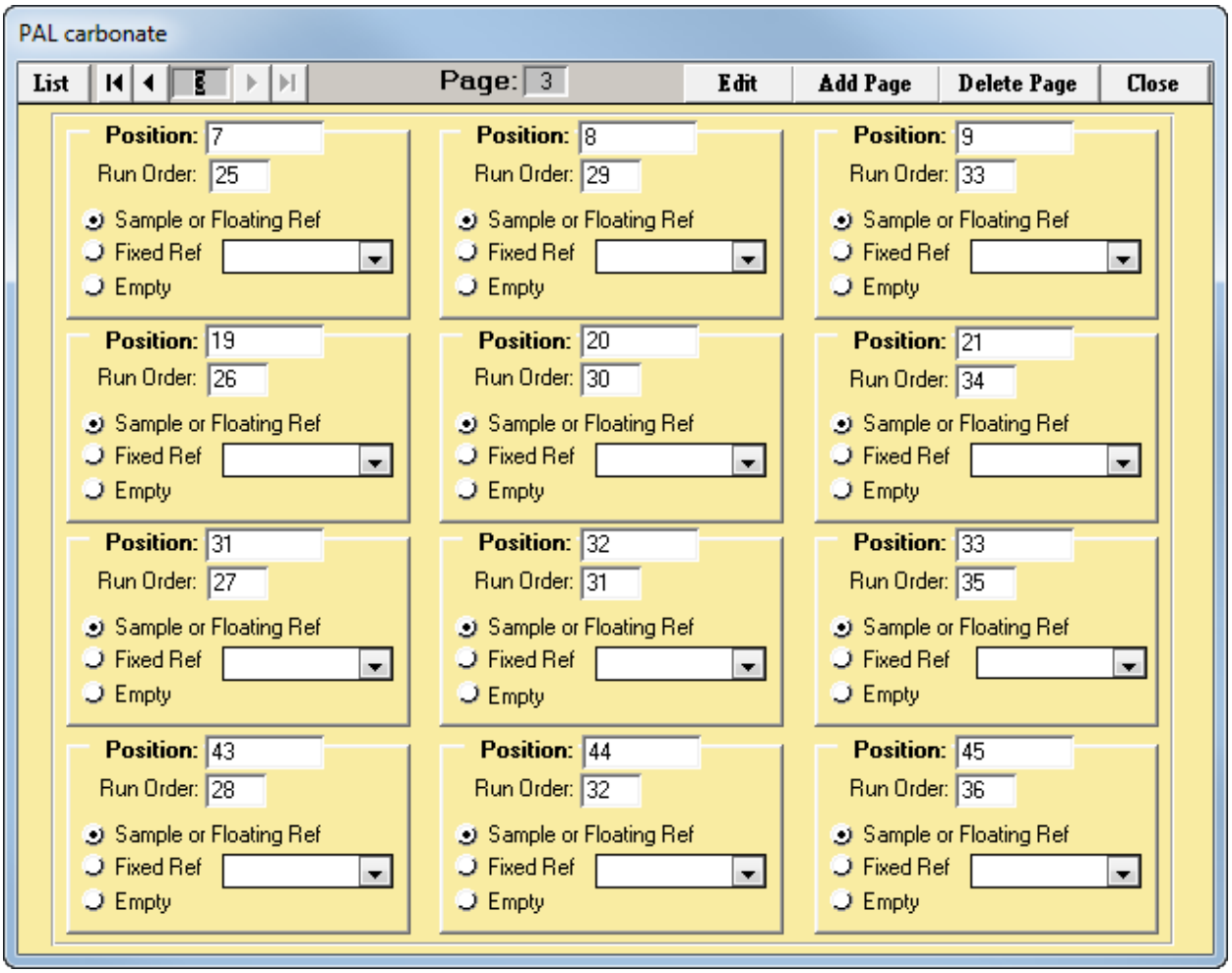


Fig. 33.16. Third page of sequence for PAL caronate tray/manifold positions.

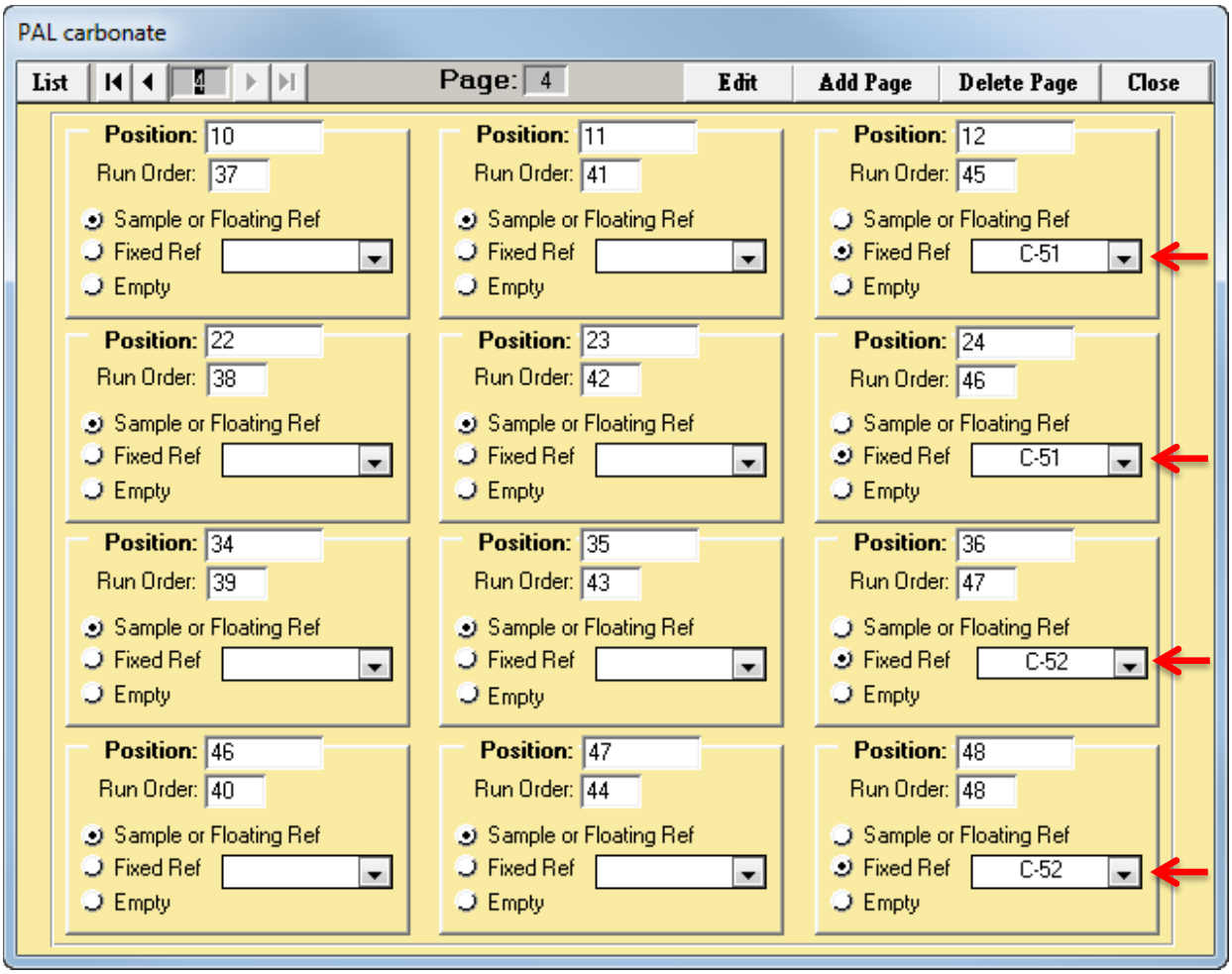
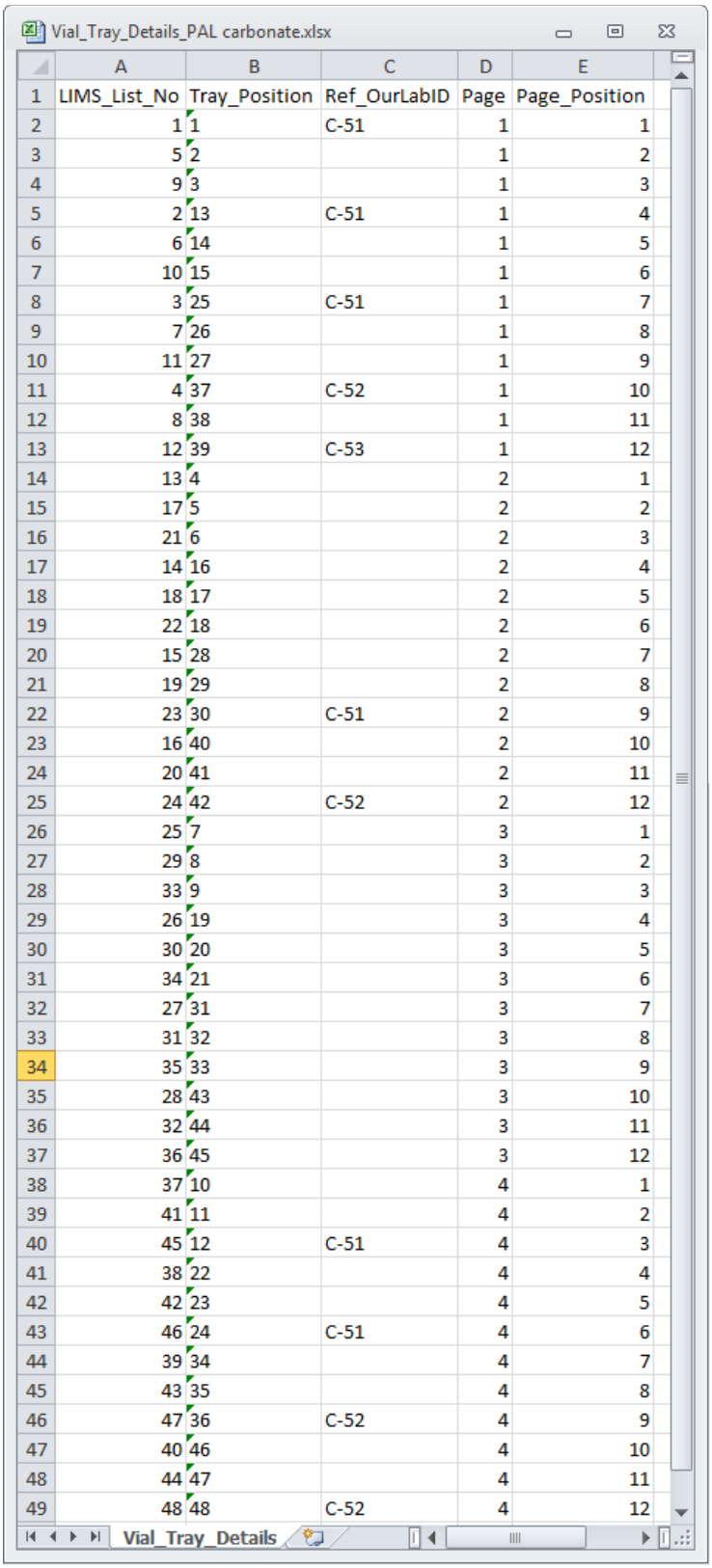


Fig. 33.17. Fourth page of sequence for PAL caronate tray/manifold positions. Note the two occurrences of reference C-51 and the two occurrences of reference C-52.



Vial_Tray_Details_PAL carbonate.xlsx

	A	B	C	D	E
1	LIMS_List_No	Tray_Position	Ref_OurLabID	Page	Page_Position
2	1	1	C-51	1	1
3	5	2		1	2
4	9	3		1	3
5	2	13	C-51	1	4
6	6	14		1	5
7	10	15		1	6
8	3	25	C-51	1	7
9	7	26		1	8
10	11	27		1	9
11	4	37	C-52	1	10
12	8	38		1	11
13	12	39	C-53	1	12
14	13	4		2	1
15	17	5		2	2
16	21	6		2	3
17	14	16		2	4
18	18	17		2	5
19	22	18		2	6
20	15	28		2	7
21	19	29		2	8
22	23	30	C-51	2	9
23	16	40		2	10
24	20	41		2	11
25	24	42	C-52	2	12
26	25	7		3	1
27	29	8		3	2
28	33	9		3	3
29	26	19		3	4
30	30	20		3	5
31	34	21		3	6
32	27	31		3	7
33	31	32		3	8
34	35	33		3	9
35	28	43		3	10
36	32	44		3	11
37	36	45		3	12
38	37	10		4	1
39	41	11		4	2
40	45	12	C-51	4	3
41	38	22		4	4
42	42	23		4	5
43	46	24	C-51	4	6
44	39	34		4	7
45	43	35		4	8
46	47	36	C-52	4	9
47	40	46		4	10
48	44	47		4	11
49	48	48	C-52	4	12

Vial_Tray_Details

Fig. 33.18. The “Vial_Tray_Details_PAL carbonate.xlsx” file.

33.5.2 Adding Client Samples to a Sample Analysis List

When an analysis template is created, a companion sample analysis list for samples needing analysis is created. To access this list, click “Create a Sample List -->” on the LIMS main page and the Create a Sample List form (Fig. 33.19) opens. This is the only sample list so it opens automatically. If there are two or more sample lists, the desired list is easily accessed using the navigation controls.

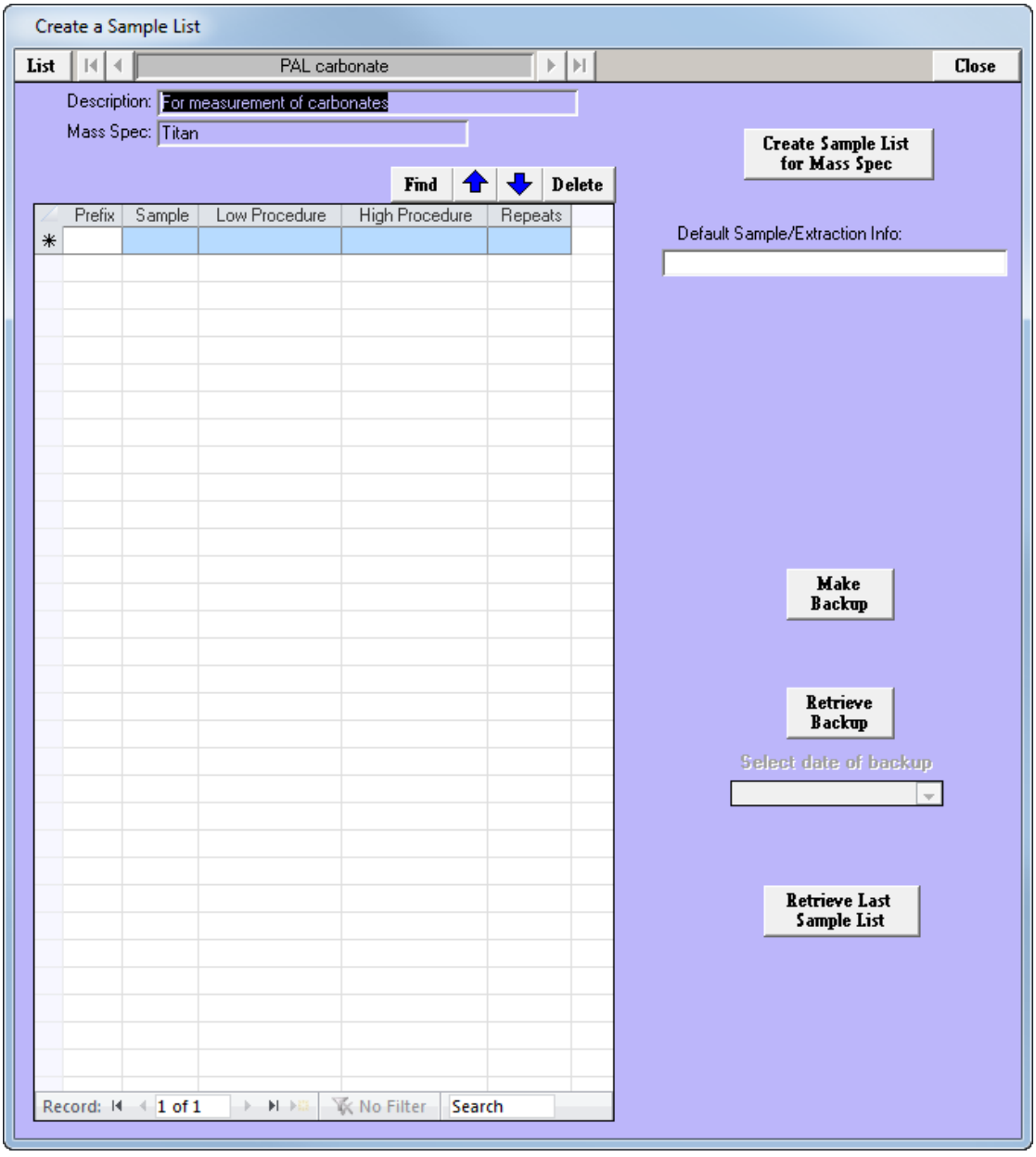


Fig. 33.19. Create a Sample List form.

Although one can add samples to the Create a Sample List form one at a time, it is usually faster to add samples to the desired sample list using shortcut buttons on the Projects form (Section 7.6.3). To demonstrate this feature:

1. Click "View Projects -->" on the LIMS main page and the Find Project form opens.
2. Double-click on the last project (C-1001 to C-1070) and the Projects form opens.
3. Click "Template List – Add & Delete Samples" and the Add Samples To Be Analyzed form for the project C-1001 to C-1070 opens.
4. Click "Add" and the dialog box "The repeats have been added." opens.
5. Click "OK" and the samples have been added to the sample list for PAL carbonates.
6. Click "Close", "Close", and "Close" to return to the main page.

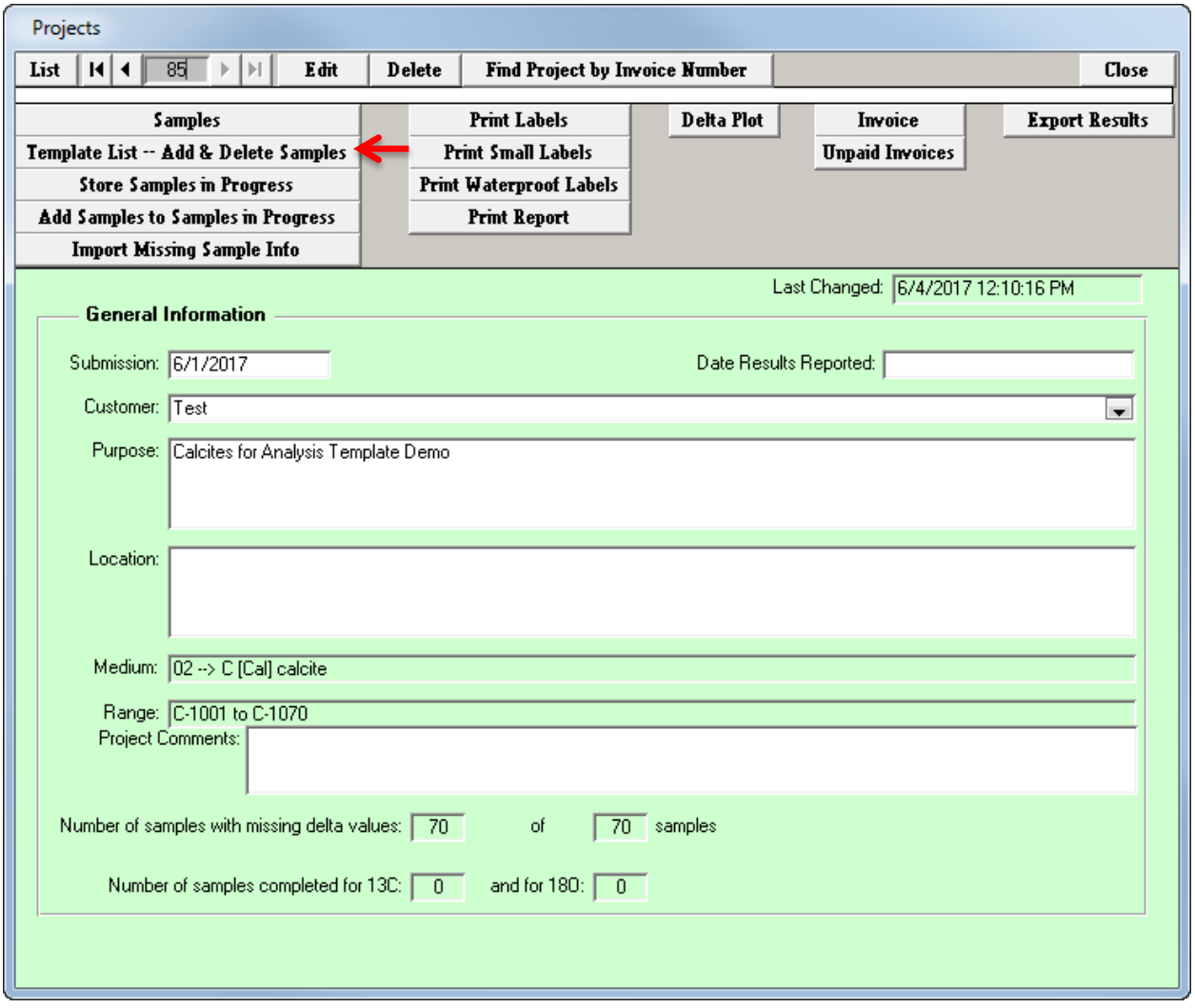


Fig. 33.20. Project for C-1001 to C-1070.

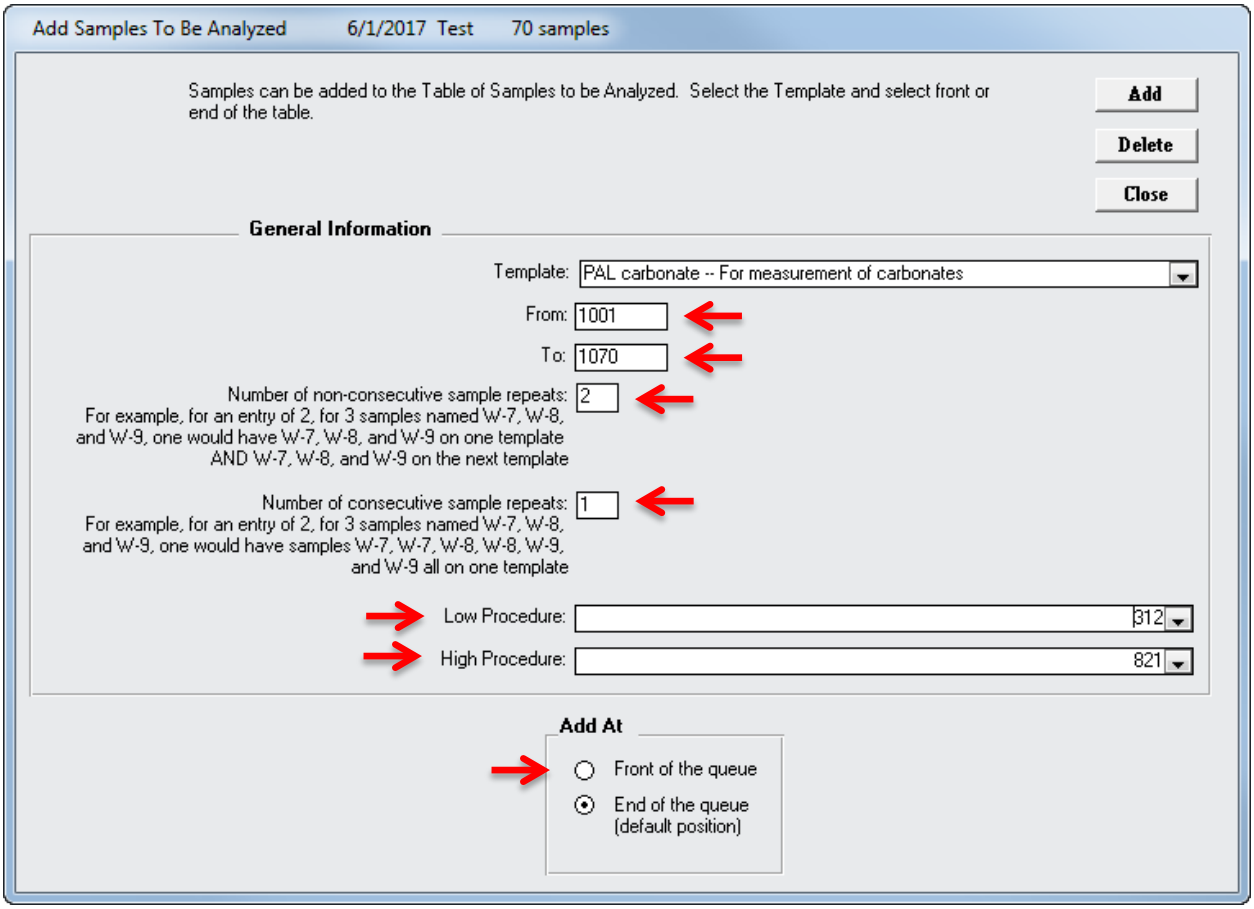


Fig. 33.21. Add Samples To Be Analyzed form for the project C-1001 to C-1070.

The Add Sample To Be Analyzed form (Fig. 33.21) is very flexible. There are a number of useful options for adding samples:

- "From" and "To" fields by default are populated with the first and last Our Lab IDs of the project. These values can be adjusted as needed.
- The "Add At" option by default is set to add samples to the end of the sample queue. For emergency or high priority analyses, samples may be added to the front of the queue.
- The "Number of non-consecutive sample repeats" field is populated with the value entered in the "Default number of non-consecutive replicate analyses for the TBA list" field for the low isotope on the Design Templates form, which is "2" as shown in Figure 33.11. Setting this value to "2" indicates that the laboratory will analyze these samples two times on different days.
- The "Number of consecutive sample repeats" is "1" by default. Setting this value to "3" would cause LIMS to add each Our Lab ID consecutively three times to the sample list. Clicking "Add" with the "Number of consecutive sample repeats" set to "3" and the

"Number of non-consecutive sample repeats" retained as "2" creates the sample list shown in Figure 33.22.

- The low and high procedure codes can be adjusted if alternative codes exist for the medium by changing the "Low Procedure" and (or) "High Procedure" fields.

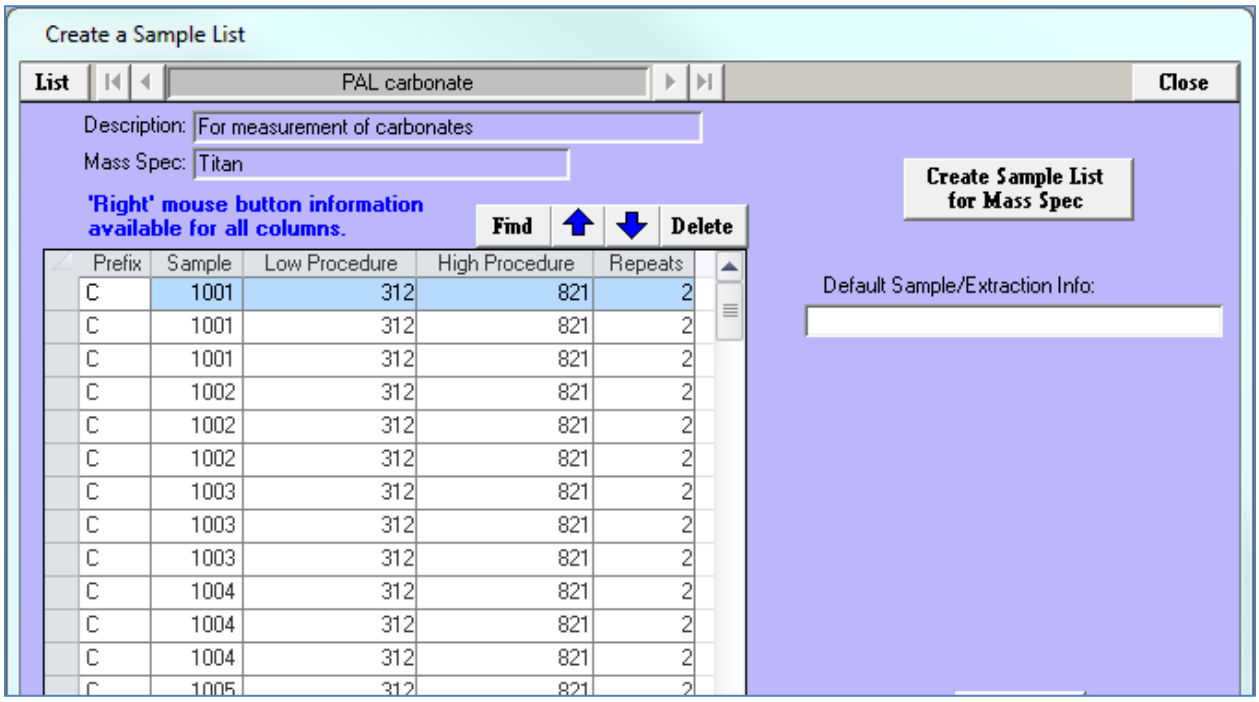


Fig. 33.22. Example sample list with three occurrences of each Our Lab ID and "Repeats" retained at the default of "2."

33.5.3 Generating Sample Lists

Assuming that the reader clicked "Add" on the Add Samples To Be Analyzed form for the project C-1001 to C-1070 using the default settings shown in Figure 33.21, a list of 70 Our Lab IDs is added to the "PAL carbonate sample" queue. To generate a sample list:

1. Click "Create a Sample List -->" on the LIMS main page and the Create a Sample List form opens with the "PAL carbonate" queue displayed (similar to that in Figure 33.22). If there is a question about a sample, right-clicking the row with the sample opens a dialog box such as shown in Figure 33.23.
2. Click "Create Sample List for Mass Spec" and LIMS displays the dialog box shown in Figure 33.24.
3. Click OK" and LIMS displays the proposed samples and references to be analyzed (Fig. 33.25).

4. Click “Save and Print” and LIMS provides a file dialog to save the sample list as an Excel file with the name “For_T_ISODAT NT Seq Tbl Info.xls.” Usually the file is saved to a flash drive, which is attached to the sample list report.
5. Navigate to the preferred folder and click “Select” and LIMS will (1) save the Excel file, which has five columns (Fig. 33.3) and is discussed in Section 33.4.2 and Table 33.1, (2) print a sample list report (Fig. 33.26), (3) print a multi-sheet report for setting up the samples (Fig. 33.27), and (4) display a dialog box indicating that the backup of the sample queue has been made (Fig. 33.28).
6. Click “OK” and the “Repeats” in the “PAL carbonate” sample queue are decremented by one (Fig. 33.29).
7. Click “Close” to return to the main page.

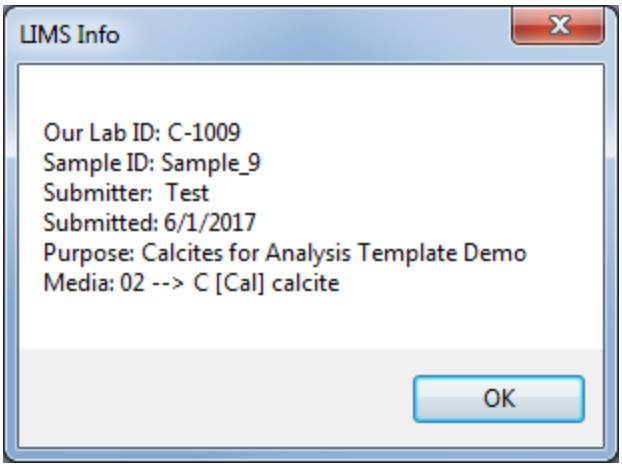


Fig. 33.23. Dialog box providing sample information.

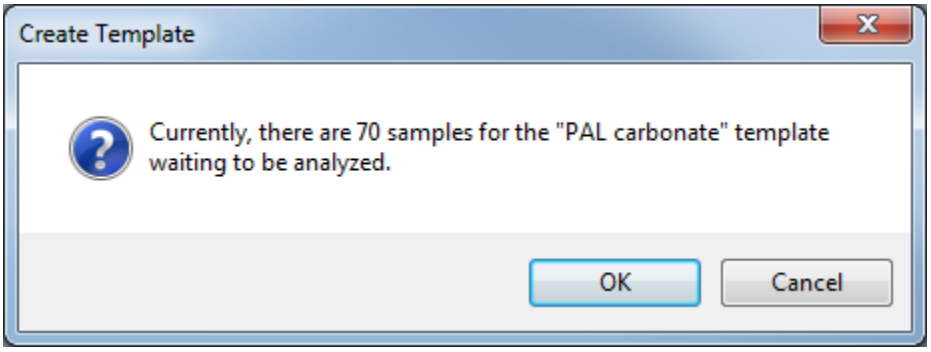


Fig. 33.24. Dialog box indicating number of samples in the sample list needing to be analyzed. Samples having a “Repeat” value of zero are not counted.

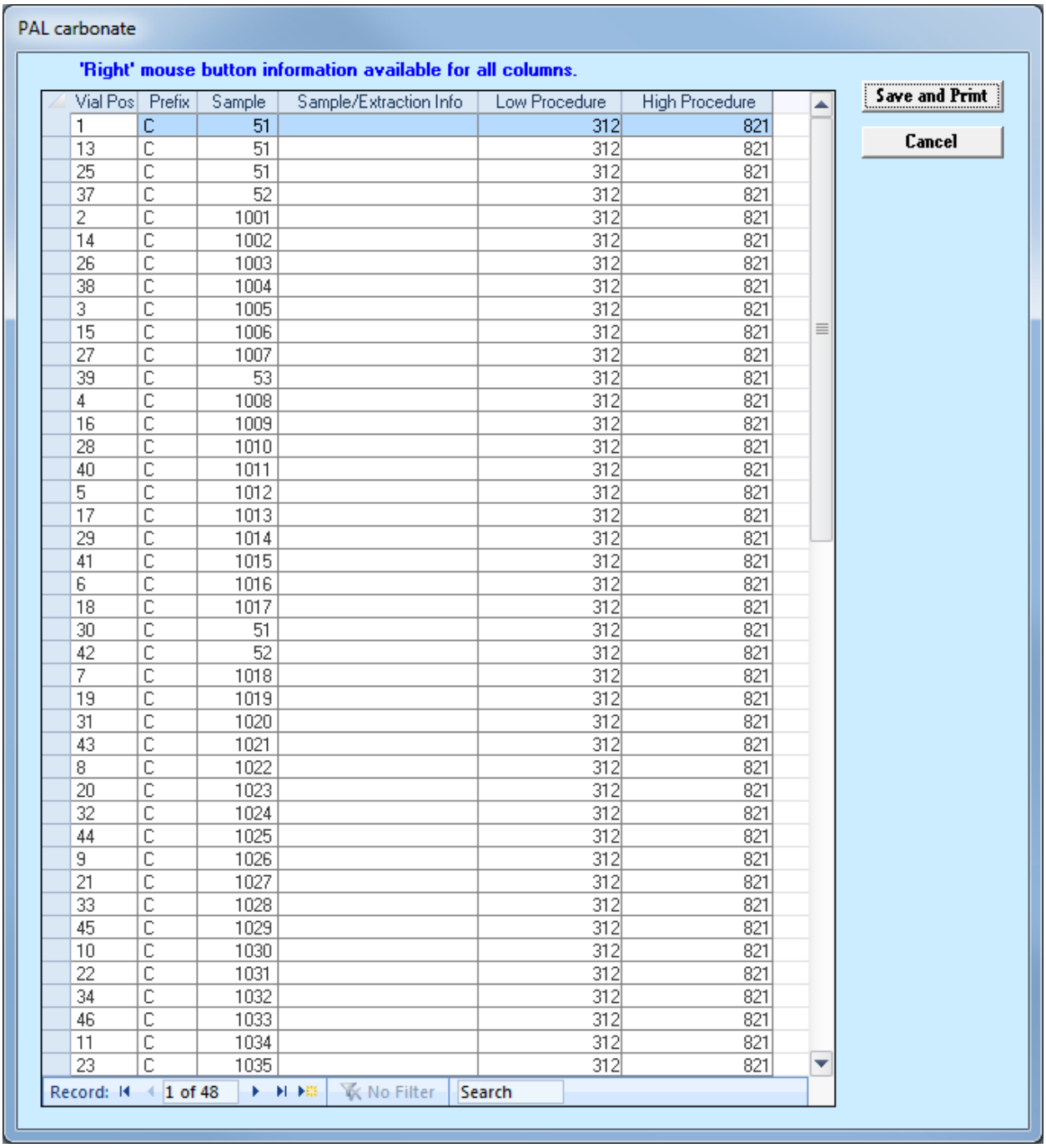


Fig. 33.25. Proposed samples and references to be analyzed.

6/5/2017 2:54:52 PM

PAL carbonate Samples To Be Analyzed

Vial Pos	Our Lab ID	Sample #	Project	Notes
1	C-51	Ref_A	Laboratory Calc	
13	C-51	Ref_A	Laboratory Calc	
25	C-51	Ref_A	Laboratory Calc	
37	C-52	Ref_B	Laboratory Calc	
2	C-1001	Sample_1	Calcites for An	
14	C-1002	Sample_2	Calcites for An	
26	C-1003	Sample_3	Calcites for An	
38	C-1004	Sample_4	Calcites for An	
3	C-1005	Sample_5	Calcites for An	
15	C-1006	Sample_6	Calcites for An	
27	C-1007	Sample_7	Calcites for An	
39	C-53	Calcite control	Laboratory Calc	
4	C-1008	Sample_8	Calcites for An	
16	C-1009	Sample_9	Calcites for An	
28	C-1010	Sample_10	Calcites for An	
40	C-1011	Sample_11	Calcites for An	
5	C-1012	Sample_12	Calcites for An	
17	C-1013	Sample_13	Calcites for An	
29	C-1014	Sample_14	Calcites for An	
41	C-1015	Sample_15	Calcites for An	
6	C-1016	Sample_16	Calcites for An	
18	C-1017	Sample_17	Calcites for An	
30	C-51	Ref_A	Laboratory Calc	
42	C-52	Ref_B	Laboratory Calc	
7	C-1018	Sample_18	Calcites for An	
19	C-1019	Sample_19	Calcites for An	
31	C-1020	Sample_20	Calcites for An	
43	C-1021	Sample_21	Calcites for An	
8	C-1022	Sample_22	Calcites for An	
20	C-1023	Sample_23	Calcites for An	
32	C-1024	Sample_24	Calcites for An	
44	C-1025	Sample_25	Calcites for An	
9	C-1026	Sample_26	Calcites for An	
21	C-1027	Sample_27	Calcites for An	
33	C-1028	Sample_28	Calcites for An	
45	C-1029	Sample_29	Calcites for An	
10	C-1030	Sample_30	Calcites for An	
22	C-1031	Sample_31	Calcites for An	
34	C-1032	Sample_32	Calcites for An	
46	C-1033	Sample_33	Calcites for An	
11	C-1034	Sample_34	Calcites for An	
23	C-1035	Sample_35	Calcites for An	
35	C-1036	Sample_36	Calcites for An	
47	C-1037	Sample_37	Calcites for An	
12	C-51	Ref_A	Laboratory Calc	
24	C-51	Ref_A	Laboratory Calc	
36	C-52	Ref_B	Laboratory Calc	
48	C-52	Ref_B	Laboratory Calc	

Fig. 33.26. Example sample list report for samples to be analyzed.

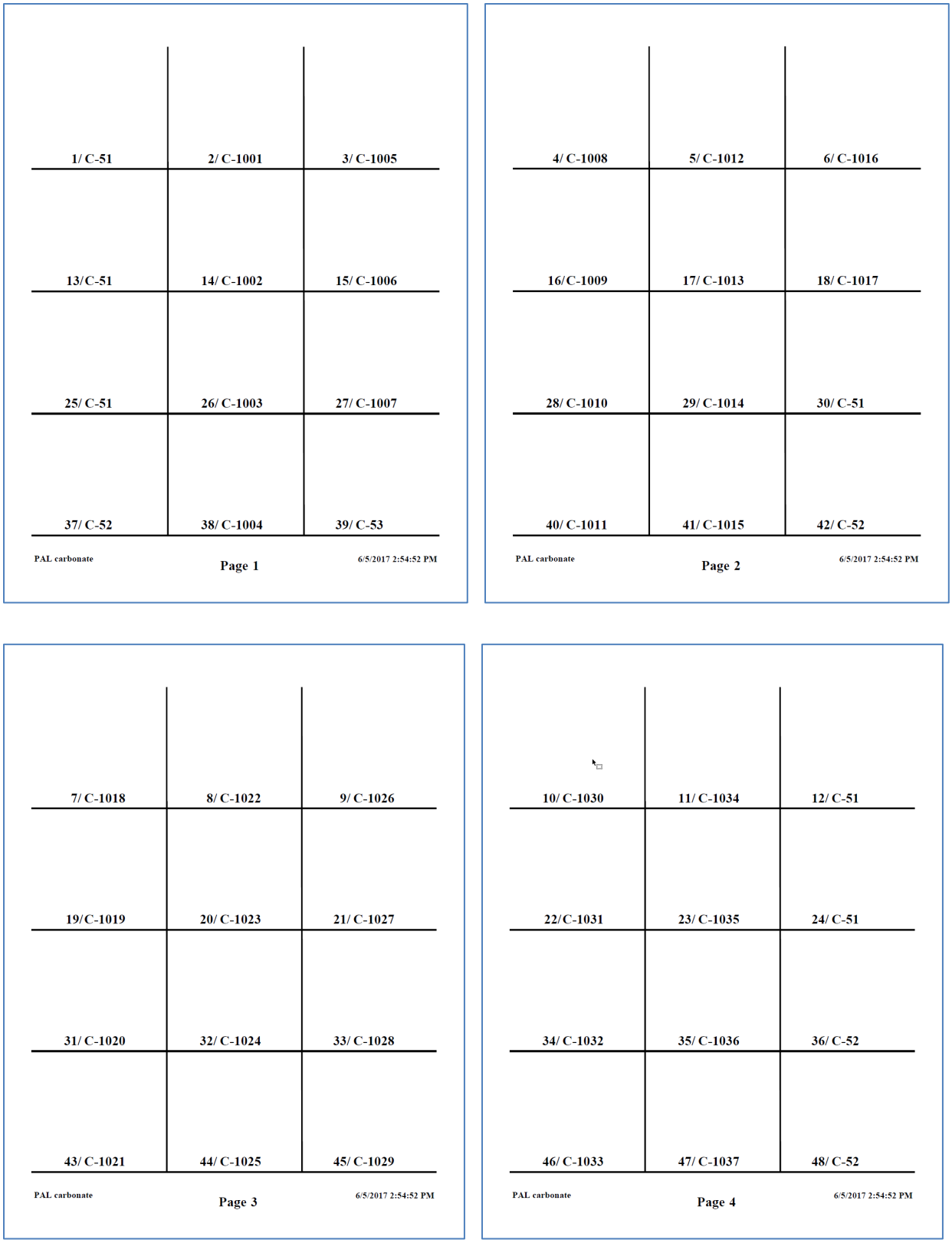


Fig. 33.27. Example multi-sheet report for setting up samples to be analyzed.

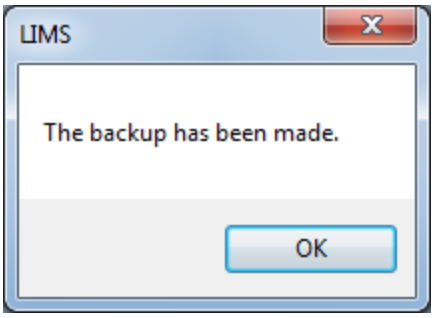
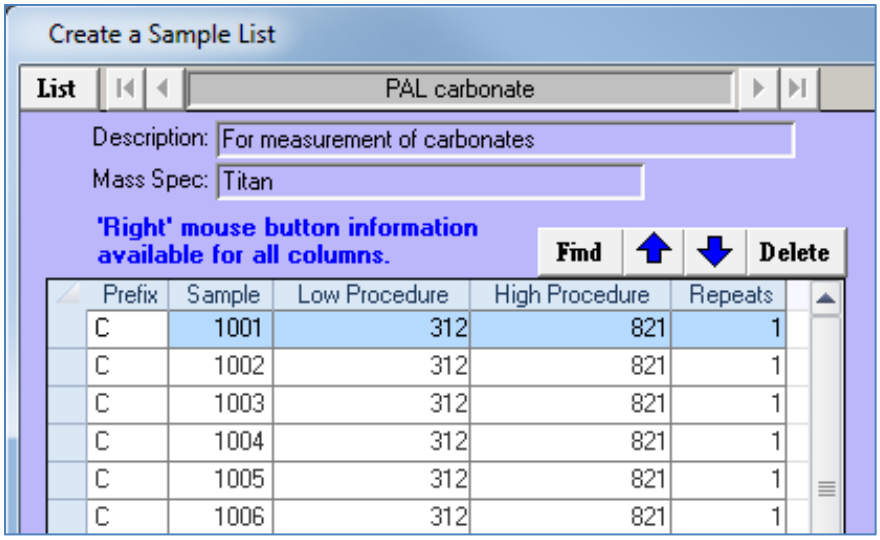


Fig. 33.28. Dialog indicating that a backup of the sample queue has been completed.



Prefix	Sample	Low Procedure	High Procedure	Repeats
C	1001	312	821	1
C	1002	312	821	1
C	1003	312	821	1
C	1004	312	821	1
C	1005	312	821	1
C	1006	312	821	1

Fig. 33.29. "Repeats" column of the "PAL carbonate" sample list decremented by one.

The Create a Sample List form (Fig. 33.19) has a number of useful features:

- The "Make Backup" button enables the user to make a backup of all sample queues when clicked.
- The "Retrieve Backup" button enables the user to select the date-time of a previous backup and update all sample queues based on the selected backup.
- The "Retrieve Last Sample List" is useful when one needs to reprint the sample list report and resave the file to a flash drive or other storage location.

Had the LIMS EA + TC/EA sample export format been selected for the "PAL carbonate" sample template, the format of the Excel file would be that shown in Figure 33.4 (Section 33.4.3).

33.5.4 Removing and Managing Client Samples Added to a Sample Analysis List

There are two ways to delete samples from a sample analysis queue. This action may be required, for example, if one mistakenly added samples to the wrong IRMS sample queue, or one wishes to remove some samples that do not need to be analyzed. The first method is to highlight the samples to be removed on the Create a Sample List form (*e.g*. Fig. 33.29) and click the "Delete" button near the top of the form or click the "Delete" key on the keyboard. To remove all the samples from a given project, open the project in the Projects form (e.g. Fig. 33.20) and click "Template List – Add & Delete Samples" to open the Add Samples To Be Analyzed form (Fig. 33.21). Clicking "Delete" will remove all sample in the project from all sample lists. If samples should only be removed from one sample list, select the "Template" and then click "Delete." Samples will only be deleted from the selected sample list. To delete a specific interval of Our Lab IDs enter the minimum and maximum sample numbers in the "From" and "To" fields, be sure the "Template" is selected, and click "Delete."

To move one or more samples to the bottom or top of the sample queue, highlight them and then click the down or up arrow, respectively.

33.5.5 Repeated Samples

It is recommended that samples be measured at least twice. The benefit of having two or more analyses per sample helps catch vial/sample placement errors, allows the operator to check the consistency between two or more analyses of the same sample, helps identify problematic samples (*e.g*. poor repeats), and allows the operator to compare the performance of sample repetitions with control standards in the same run. This approach gives realistic metrics of overall mass spectrometer performance.

34 Sources of Internationally Distributed, Isotopic Reference Materials

The three major sources of light element isotopic reference materials are:

- International Atomic Energy Agency, Vienna, Austria (https://nucleus.iaea.org/rpst/)
- National Institute of Standards and Technology, Gaithersburg, Maryland (https://www.nist.gov/srm)
- Reston Stable Isotope Laboratory (RSIL) of the U.S. Geological Survey, Reston, Virginia, USA (http://isotopes.usgs.gov/lab/referencematerials.html)

In addition to providing single-use materials, the RSIL also provide daily-use secondary isotopic reference materials such as cases of 144 glass ampoules each containing 5 mL of water, USGS42 and USGS43 human hair, and USGS40 and USGS41a l-glutamic acid for EA-IRMS use.

References

[1] Coplen, T. B., 2000, A Guide for the Laboratory Information Management System (LIMS) for Light Stable Isotopes—Versions 7 and 8: U. S. Geological Survey Open-File Report 00-345, 110 p. https://water.usgs.gov/software/code/geochemical/lims/doc/ofr00345.pdf

[2] Coplen, T. B., 2011, Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results: Rapid Communications in Mass Spectrometry: v. 25, p. 2538–2560. http://dx.doi.org/10.1002/rcm.5129

[3] Rozanski, K., Araguas-Araguas, L., Gonfiantini, R., 1993, Isotopic patterns in modern global precipitation, in Climate Change in Continental Isotopic Records: Geophysical Monograph 78, (Eds: P. K. Swart, K. C. Lohmann, J. McKenzie, S. Savin), American Geophysical Union, Washington DC, p. 1–36. http://onlinelibrary.wiley.com/doi/10.1029/GM078p0001/pdf

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[5] Werner, R. A., Brand, W. A., 2001, Referencing strategies and techniques in stable isotope ratio analysis: Rapid Communications in Mass Spectrometry, v. 15, p 501–519. http://dx.doi.org/10.1002/rcm.258

[6] Schimmelmann, A., Qi, H., Coplen, T. B., Brand, W. A., Fong, J., Meier-Augenstein, W., Kemp, H. F., Toman, B., Ackermann, A., Assonov, S., Aerts-Bijma, A. T., Brejcha, R., Chikaraishi, Y., Darwish, T., Elsner, M., Gehre, M., Geilmann, H., Gröning, M., Hélie, J-F., Herrero-Martín, S., Meijer, H. A. J., Sauer, P. E., Sessions, A. L., and Werner, R. A., 2016, New organic reference materials for hydrogen, carbon, and nitrogen stable isotope-ratio measurements: caffeines, n-alkanes, fatty acid methyl esters, glycines, L-valines, polyethylenes, and oils: Analytical Chemistry, v. 88, p. 4294–4302. http://dx.doi.org/10.1021/acs.analchem.5b04392

[7] Brand, W. A., Coplen, T.B., Vogl, J., Rosner, M., and Prohaska, T., 2014, Assessment of international reference materials for isotope-ratio analysis: Pure and Applied Chemistry, v. 86, p. 425–467. DOI: 10.1515/pac-2013-1023. https://doi.org/10.1515/pac-2013-1023

[8] MassLynx 3.6i LIMS interface handbook, Version 1.1, Micromass UK Ltd., 28 p., 2002. Provided in the Section 16 electronic files to this user manual.

[9] Qi, H., Coplen, T. B., Mroczkowski, S. J., Brand, W. A., Brandes, L., Geilmann, H., Schimmelmann, A., 2016, A new organic reference material, L-glutamic acid, USGS41a, for $\delta^{13}C$ and $\delta^{15}N$ measurements—a replacement for USGS41: Rapid Communications in Mass Spectrometry: v. 30, p.859–866. http://dx.doi.org/10.1002/rcm.7510

Appendix A Editing and Adding Media

A.1 Editing Media Codes

Media codes and isotope codes are discussed in Section 6.1. Each medium has one of seven Prefixes (see Table 6.3) and can have one or two isotopes as exemplified in Table 6.1. The Prefix can be changed if and only if no samples using this medium have been logged into the database. The isotopes, isotope ratios, and CFCs to be measured cannot usually be changed because typically they are used in other tables in LIMS. If a medium has two check boxes enabled, the check box with the higher isotope code (see Table 6.2) can be deselected if the medium is not used in other tables in LIMS. This example should function properly using LIMS connected to any of the backend databases in files that accompany this manual. To edit a media code:

1. Click "Special Features" and then "Media," and the Media form will open (Fig. A.1).

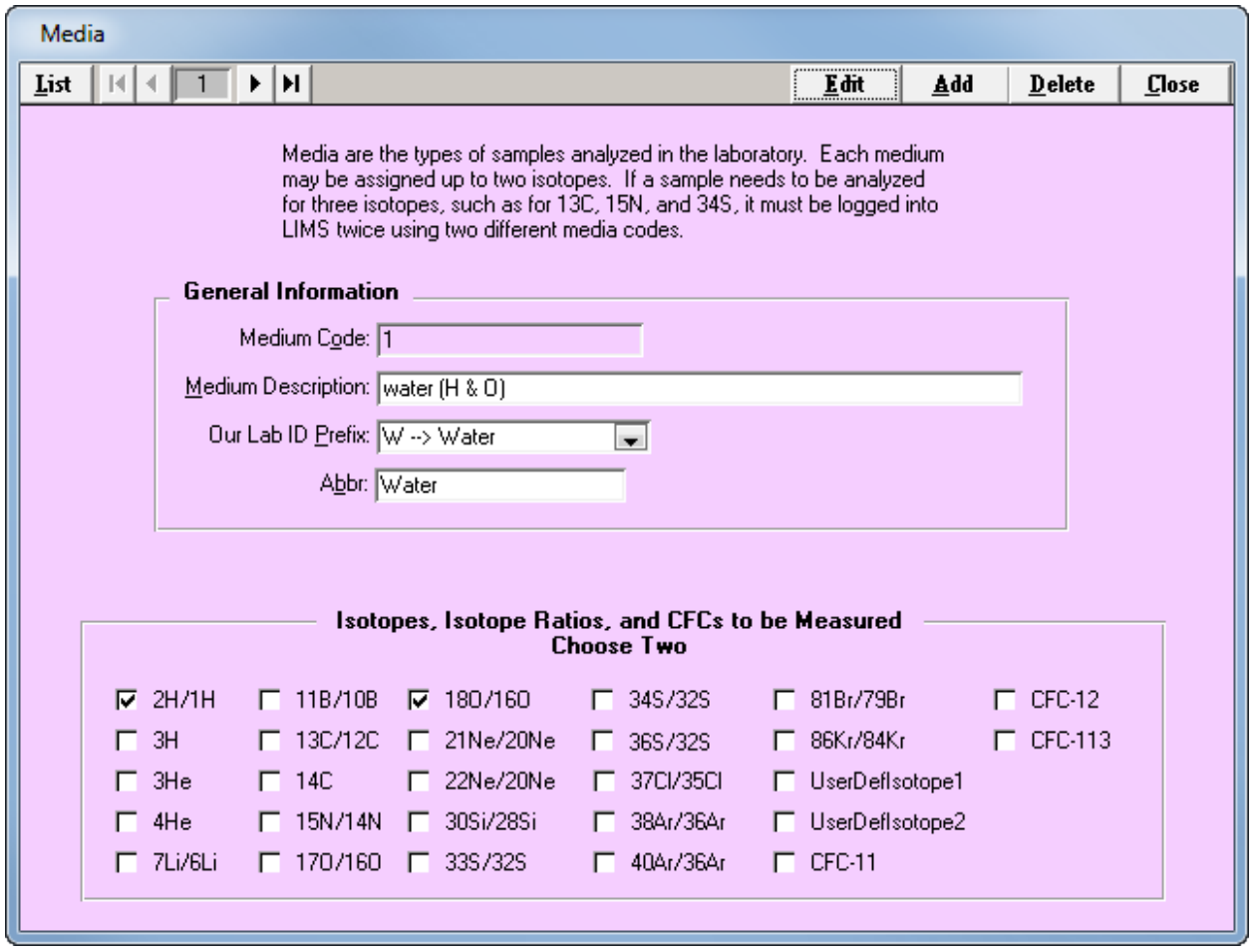


Fig. A.1. Media form.

2. Click on “List” and navigate to the media code to be edited.
3. Click “Edit.”
4. The medium description and the abbreviation can be edited as desired. Depending upon use of the medium in other tables in LIMS, the Prefix and check boxes for the isotopes, isotope ratios, and CFCs to be measured might not be available for editing. LIMS will provide a message if they cannot be changed.
5. Click “Save” and “Close” to close the Media form.

A.2 Adding a Medium

To add a new medium:

1. Click “Special Features” and then “Media,” and the Media form will open (Fig. A.1).
2. Click on “List” to view existing media codes in LIMS, and select an integer code that does not exist.
3. Click “Add.”
4. Assign one or two isotopes (or isotope ratios or CFCs) by enabling one or two check boxes.
5. Enter a code, medium description, abbreviation, and prefix for the Our Lab ID. Click “Save.”
6. Click “Close” to return to the main page.

Example

The laboratory has agreed to accept samples from a tracer test using heavy water (^2H_2O or D_2O). The hydrogen-isotope results will be reported as atom fraction (see Section 6.1) and the oxygen isotope results will be reported as $\delta^{18}O$ values. Create medium with code 99 and Prefix “W” for these samples. To set up this demonstration:

1. Create a new folder. It can be within a LIMS folder or elsewhere.
2. Identify the folder as an Access Trusted Location (Section 3.2.2).
3. Copy the zip file “Appendix_A_Demo.zip,” which is located in a folder named “Appendix A” that accompanies this manual, into this new folder and extract the file from it, keeping it in this new folder. The extracted file is named “Appendix_A_Demo.accdb.”
4. Transfer into this new folder a fresh copy of the LIMS frontend, which is named “Lims9.202.zip” (or similar) and is located in a folder named “Section 4” that accompanies this manual. Extract the frontend database from this zip file, keeping it in the same folder—it will be named “Lims9.202.accdb” or similar.

5. Double-click the new frontend (Lims9.202.accdb or similar) to open it. It should open with the message that LIMS cannot find the backend database (Fig. 4.1).
6. Click “OK” and navigate to “Appendix_A_Demo.accdb.”
7. LIMS will display a message that it needs to close.
8. Click “OK.”
9. Reopen this frontend database and LIMS should display the welcome message in Figure 4.18.
10. Click “Yes” and LIMS will prompt that it needs to update settings and close.
11. Click “OK” and LIMS will perform cleanup activities upon closing.
12. Reopen this frontend database and LIMS will open with a dialog box that LIMS can now make a backup for each day of the week (Fig. A.2).
13. Click “OK” and LIMS will display the main page (similar to Fig. 4.8).
14. Click “Special Features.”
15. Click “Backend db” and the BackEnd and FrontEnd Databases form will open.
16. Uncheck the “Enable creation of as many as 7 backups (Monday, Tuesday, Wednesday, Thursday, Friday, Saturday, and Sunday)” check box, because this is only a LIMS example.
17. Click “Close” to close the BackEnd and FrontEnd Databases form.
18. Click Media” to open the Media form (Fig. A.1).
19. Click on “List” to view existing media codes in LIMS and to confirm that 99 is unused.
20. Click “Add.”
21. Click the “2H/1H” check box and the “18O/16O” check box.
22. Enter “99” for the medium code.
23. Enter “water, x(2H) enriched & O” for the medium description. The character string “x(2H)” will cause hydrogen isotopic compositions to be expressed on reports as an atom fraction. Normally atom fractions values are measured and reported in percent. The oxygen isotopic composition will be reported as an isotope-delta value.
24. Enter “x(2H) H2O” in the “Abbr” field.
25. Enter “W” for the Prefix and the Media form should appear as in Fig. A.3.
26. Click “Save” and a dialog box reminds the user to add this medium to the worksheet titled “Media” if using LIMS Excel sample submission files for clients.
27. Click “OK” and the new medium has been created.
28. Click “Close” to return to the main page.

This backend database will be used in Appendix C to demonstrate addition of procedure codes to LIMS. It may be most convenient for user to skip Appendix B and continue immediately with Appendix C.

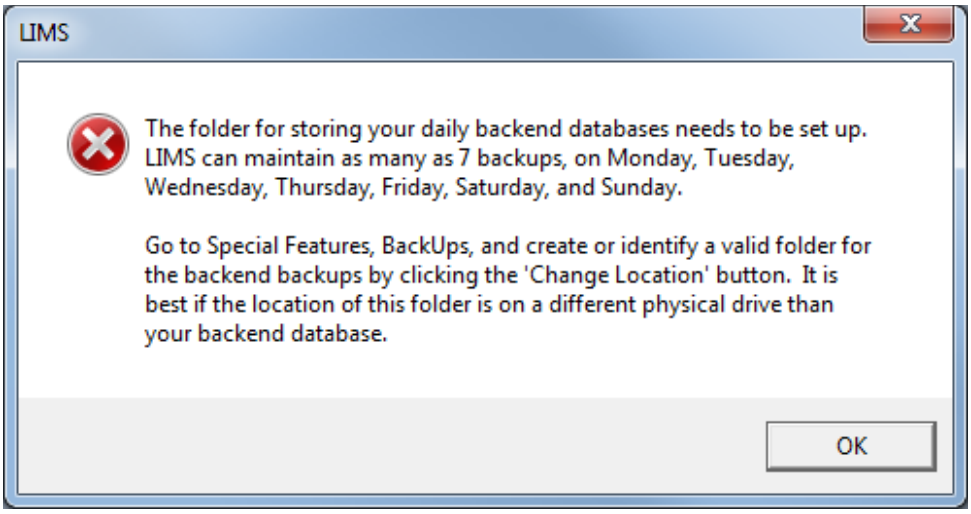


Fig. A.2. Dialog box indicating the folder for daily backups of the backend database need to be set up.

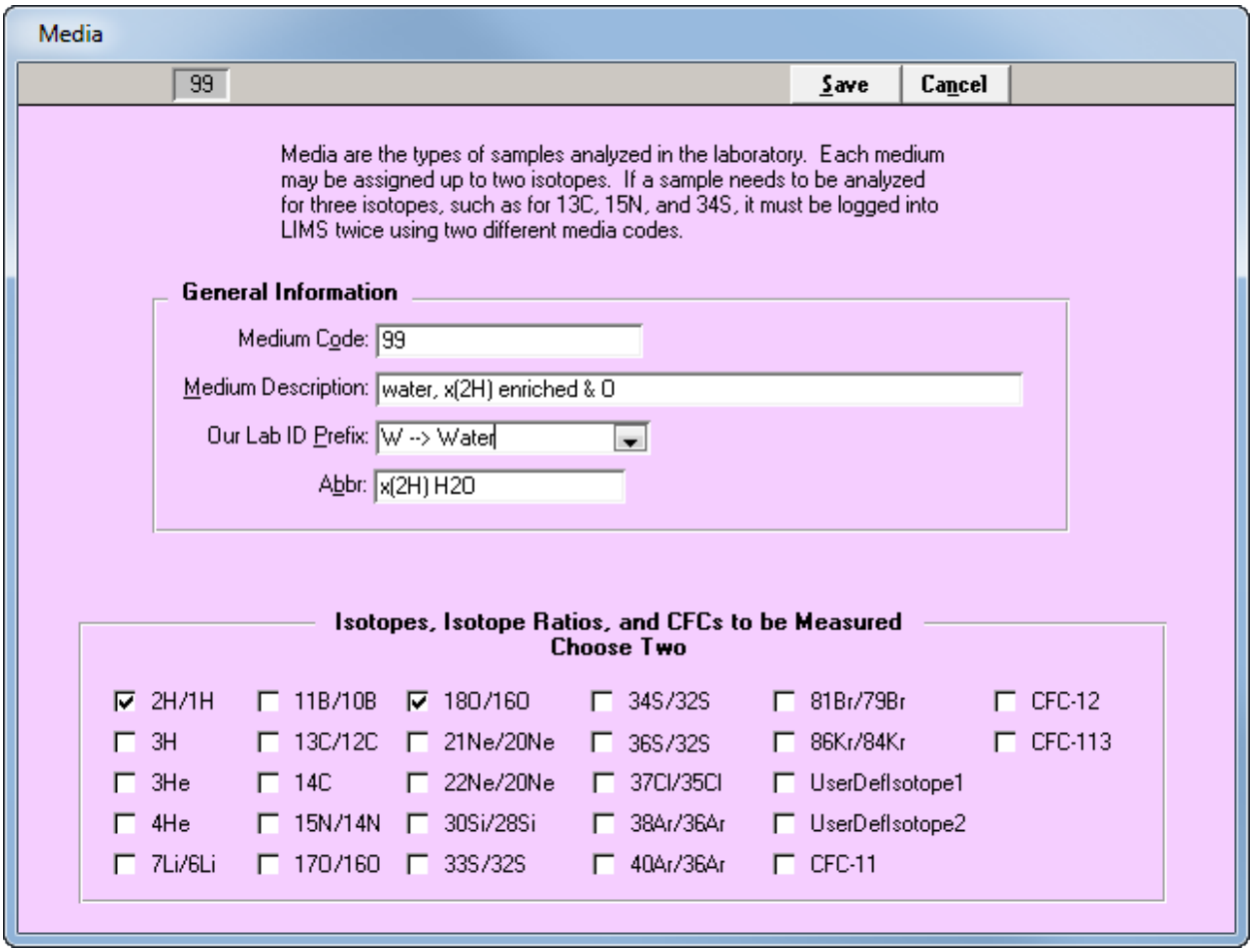


Fig. A.3. A new medium 99 for a tracer-test water enriched in ^{2}H.

If a new medium is added to LIMS, make sure to update the Media worksheet of your Excel sample submission file that is provided to clients (see Sections 7.5.1 and 7.5.5 for more information).

A.3 Deleting a Medium

Deleting a medium is accomplished by clicking the "Delete" button. If samples have been logged in using the medium or if the medium is used in other tables in LIMS, LIMS will prevent the user from deleting the medium.

Appendix B Importing, Normalizing, Evaluating, Storing, and Reporting Atom Fractions for Tracer Studies

B.1 General Information

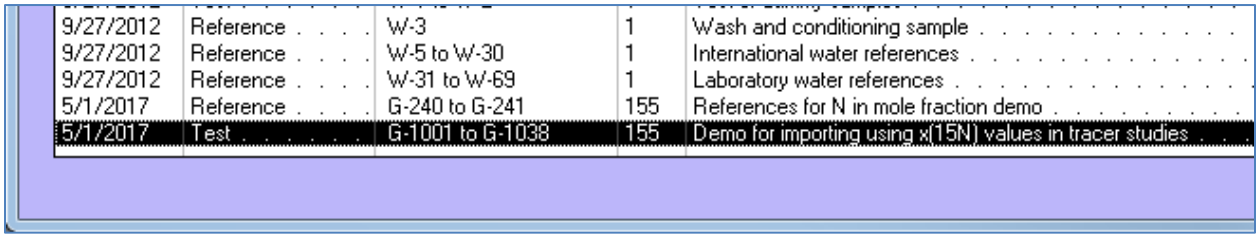
Some IRMSs have the capability of reporting isotopic abundances as atom fractions,[2] sometimes incorrectly termed atom percent.[2] LIMS can import, normalize, store, report, and export ten isotopes (^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{36}S, ^{30}Si, and ^{37}Cl) as atom fractions. The low isotope or the high isotope in media can either be an isotope-delta value (column 4 of Table 6.1) or an atom fraction value (Table 6.2). To designate that an isotope of a medium should be treated and expressed as an atom fraction, the description of that medium must contain the "x(2H)", "x(13C)", "x(15N)", "x(17O)", "x(18O)", "x(33S)", "x(34S)", "x(36S)", "*x*(^{30}Si)", and "x(37Cl)", respectively, to designate atom fraction of the isotope ^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{36}S, ^{30}Si, or ^{37}Cl. For example, 155 is a default medium included in the backend database for tracer studies for a new isotope laboratory (Fig. 6.2). The "Medium Description" is "13C & x(15N) 15N enriched." The character string "x(15N)" enables nitrogen-15 to be imported, normalized, stored, reported, and exported as the atom fraction *x*(^{15}N) for isotope-tracer studies. Atom fractions may be used with any LIMS import format.

B.2 Importing Results

A backend example database named "Backend_DB_N-15_Fraction_Example.accdb" can be extracted from a file named "Backend_DB_N-15_Fraction_Example.zip" that is provided in a folder named "Appendix B" in files that accompany this manual. To demonstrate the use of atom fractions in LIMS:

1. Create a new folder and make it an Access Trusted folder if it is not already (Section 3.2.2).
2. Copy "Backend_DB_N-15_Fraction_Example.accdb" into this folder.
3. From the folder named "Section 4" that accompanies this manual, copy an unopened frontend, which will be named "LIMS9.202.zip" (or similar), into this new folder.
4. Extract the frontend database, keeping it in the same folder.
5. Open the frontend database, which will be named "Lims9.202.accdb" (or similar) and attach it to "Backend_DB_N-15_Fraction_Example.accdb" created in step 2 following the instructions in Section 4.1 for setting up LIMS in a new laboratory.
6. Once set up, from the LIMS main menu click "View Projects -->" and LIMS should display two projects having medium 155 (Fig. B.1).
7. Click "Close" to return to the main menu.

8. Click “Import Data from Mass Specs” and LIMS will open the Analysis Import Format form. The mass spectrometer “D --> Diana” will be displayed because it is the only mass spectrometer in this backend database.
9. Click “Import” and navigate to the file named “N-15_fraction_example.xls,” which is located in the folder named “Section B.”
10. Click “Select” and LIMS should display the Import Criteria for Mass Spectrometer form (Fig. B.3).
11. For the column heading for “13C” and “15N,” enter “F11” and “F12,” respectively.
12. Click the “Import Row” check boxes for “13C” and “15N” and the form should appear as shown in Figure B.4.
13. To determine if these carbon-isotope results can be improved by an area adjust, click the “Area Adjust” check box for “13C” and LIMS opens the Area Adjust form shown in Figure B.5.
14. Because the *R* squared value is relative low (0.21), click “Cancel Evaluation” and LIMS returns to the Import Criteria for Mass Spectrometer form.



9/27/2012	Reference	W-3	1	Wash and conditioning sample
9/27/2012	Reference	W-5 to W-30	1	International water references
9/27/2012	Reference	W-31 to W-69	1	Laboratory water references
5/1/2017	Reference	G-240 to G-241	155	References for N in mole fraction demo
5/1/2017	Test	G-1001 to G-1038	155	Demo for importing using x(15N) values in tracer studies

Fig. B.1. Portion of the Find Project form showing projects having medium 155.

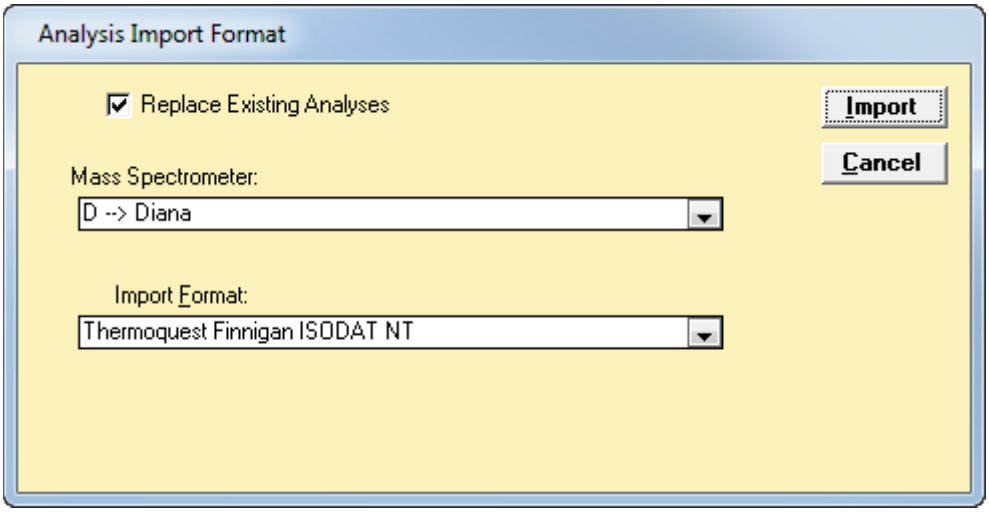


Fig. B.2. Analysis Import Format form.

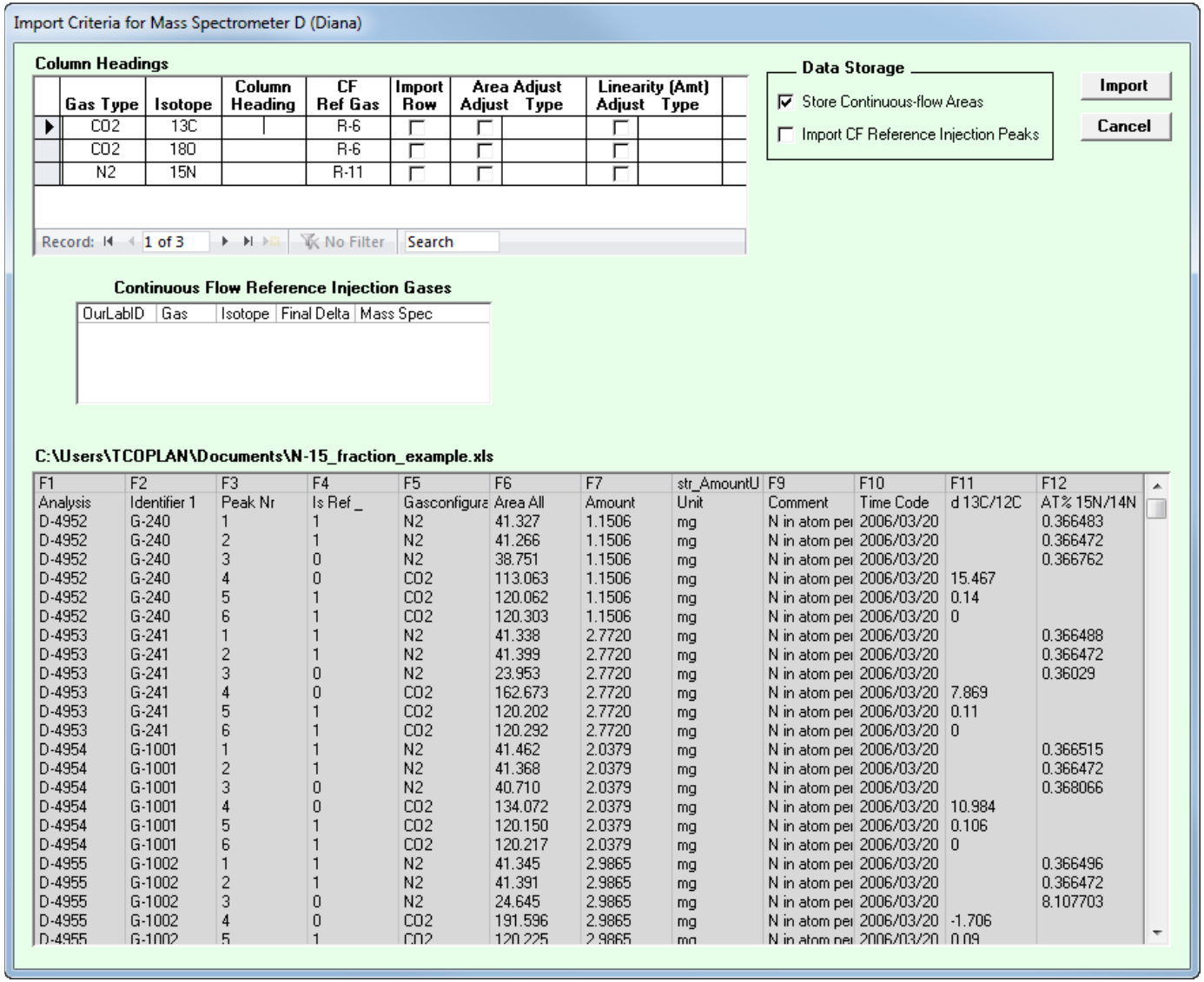


Fig. B.3. Import Criteria for Mass Spectrometer form.

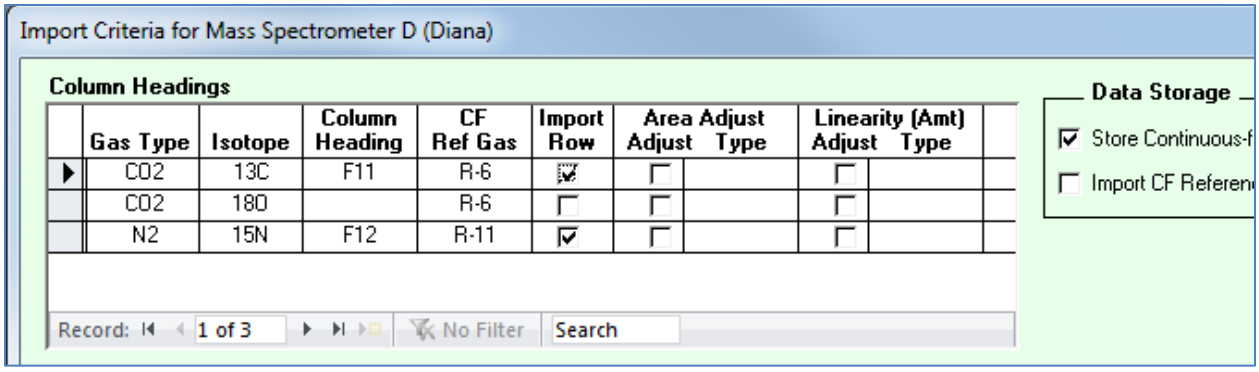


Fig. B.4. Analysis Import Format form set up for import.

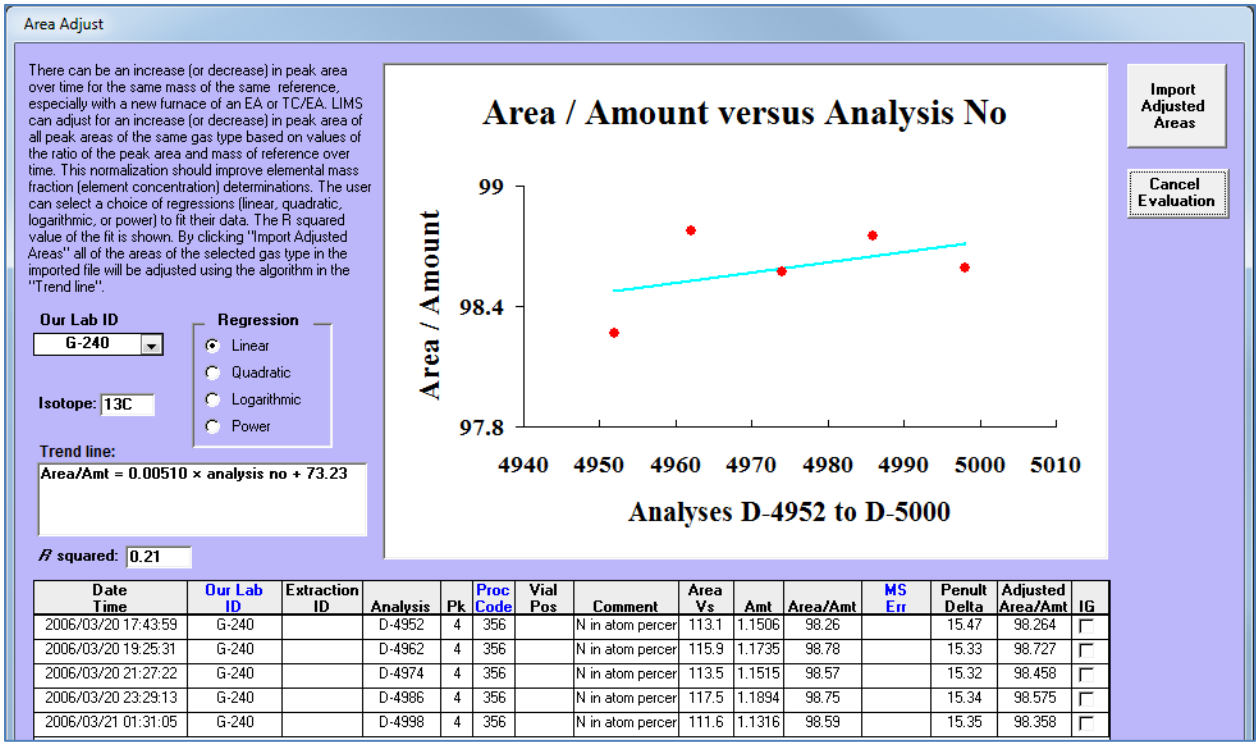


Fig. B.5. Area Adjust form for carbon-isotope measurements.

15. To determine if a linearity amount adjustment is merited for the $\delta^{13}C$ measurements, click the "Linearity (Amt)" check box for "13C" and LIMS opens a dialog box (Fig. B.6).
16. Click "No" to carry out the adjustment and LIMS displays the Adjustment for Variation in Delta Value with Variation in Amount of Sample form for $\delta^{13}C$ (Fig. B.7).
17. Because the *R* squared value is relatively low (0.12), click "Cancel Evaluation" and LIMS returns to the Import Criteria for Mass Spectrometer form.

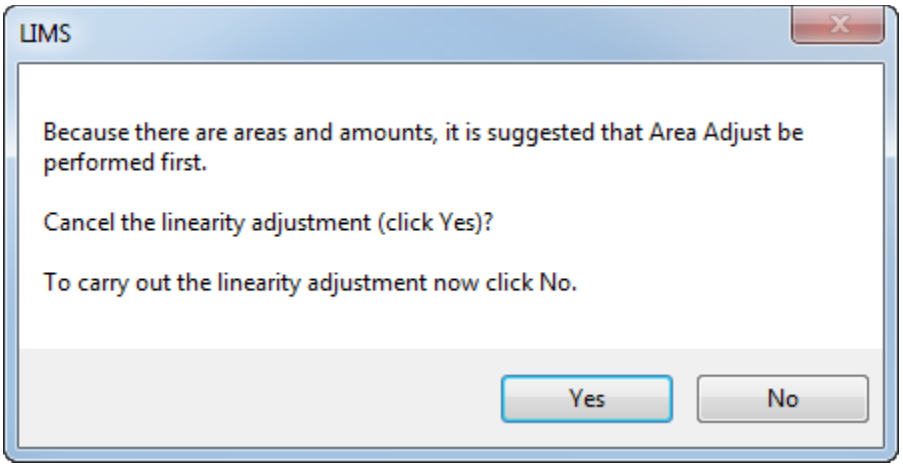


Fig. B.6. Dialog box for linearity adjustment.

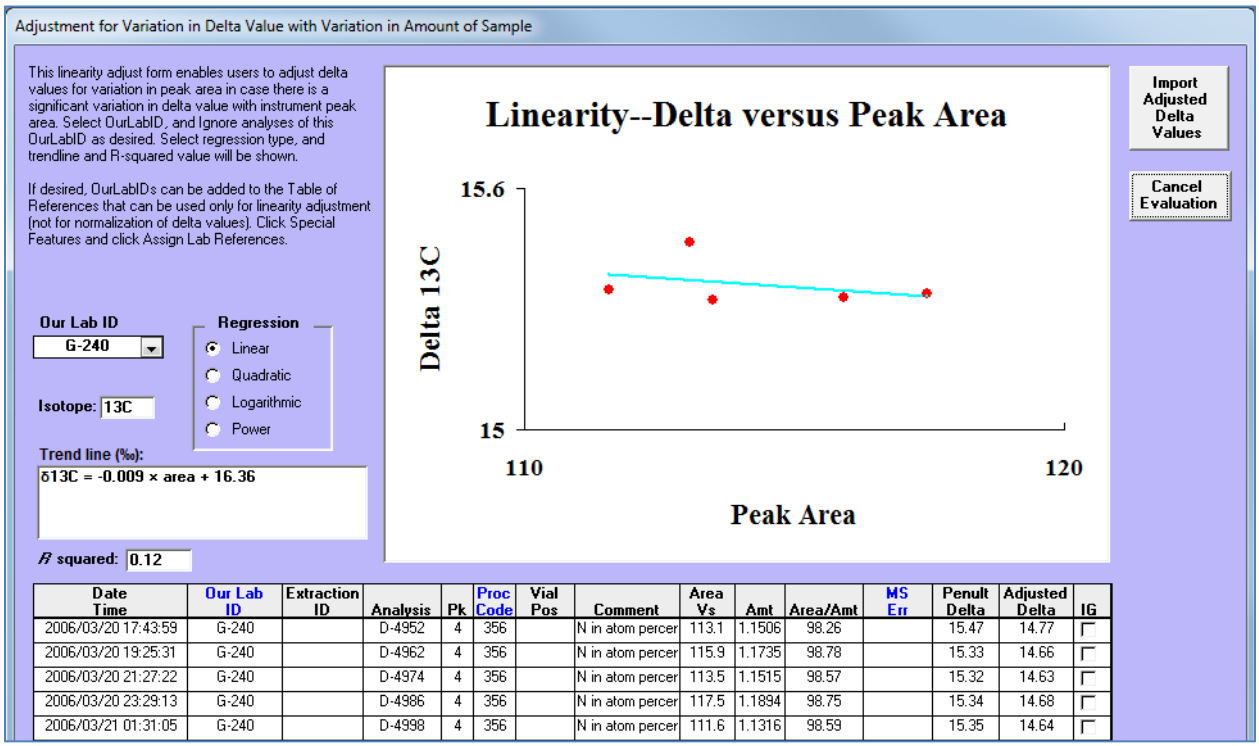
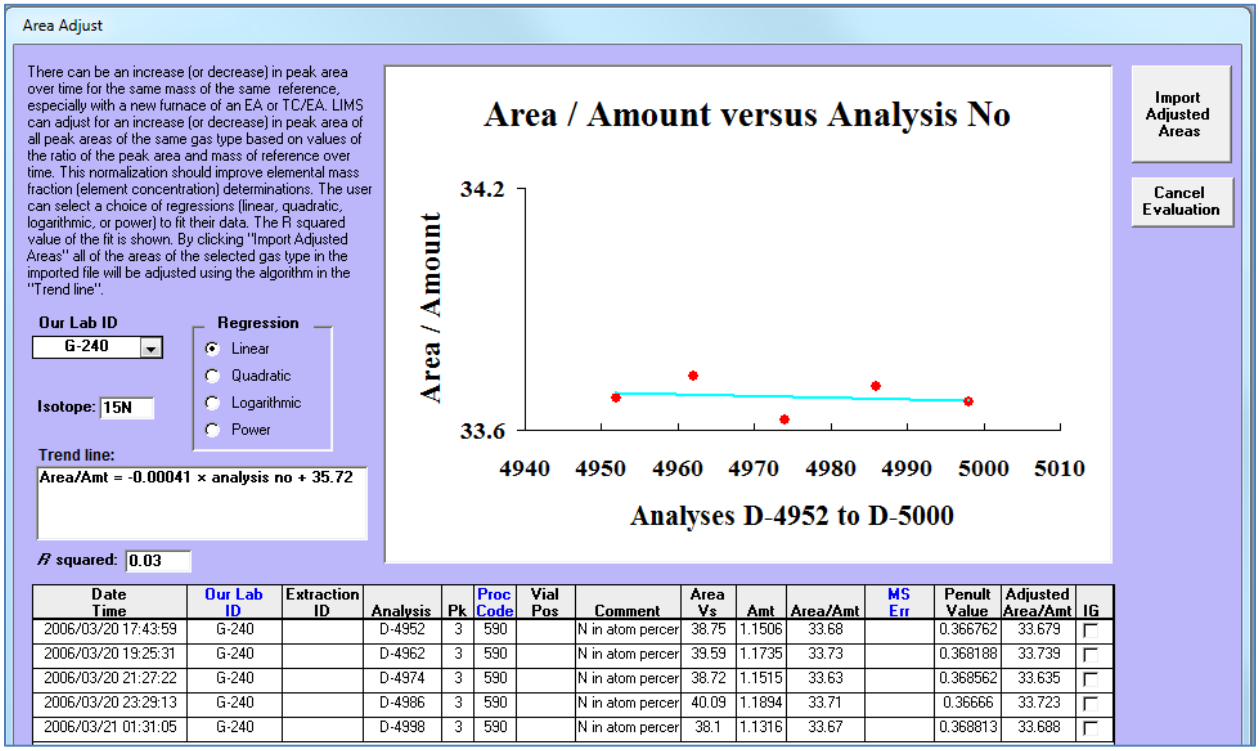


Fig. B.7. Adjustment for Variation in Delta Value with Variation in Amount of Sample form for $\delta^{13}C$.

18. To determine if these results can be improved by an area adjust, click the "Area Adjust" check box for "15N" and LIMS opens the Area Adjust form shown in Figure B.8.
19. Because the *R* squared value is low (0.03), click "Cancel Evaluation" and LIMS returns to the Import Criteria for Mass Spectrometer form.

20. To determine if a linearity amount adjustment is merited for the nitrogen-isotope measurements, click the "Linearity (Amt)" check box for "15N" and LIMS opens a dialog box (Fig. B6).
21. Click "No" to carry out the adjustment and LIMS displays the Adjustment for Variation in Atom Fraction with Variation in Amount of Sample form for the fraction of ^{15}N (Fig. B.9).
22. Because the *R* squared value is low (0.346), click "Cancel Evaluation" and LIMS returns to the Import Criteria for Mass Spectrometer form, which appears as shown in Figure B.4.
23. Click "Import" and LIMS displays the dialog box shown in Figure B.10.
24. Click "OK" and LIMS displays the import summary dialog box shown in Figure B.11 that 196 records have been successfully imported.
25. Click "OK" to complete the importing of $\delta^{13}C$ and $x(^{15}N)$ values.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Area Vs	Amt	Area/Amt	MS Err	Penult Value	Adjusted Area/Amt	IG
2006/03/20 17:43:59	G-240		D-4952	3	590		N in atom percer	38.75	1.1506	33.68		0.366762	33.679	☐
2006/03/20 19:25:31	G-240		D-4962	3	590		N in atom percer	39.59	1.1735	33.73		0.368188	33.739	☐
2006/03/20 21:27:22	G-240		D-4974	3	590		N in atom percer	38.72	1.1515	33.63		0.368562	33.635	☐
2006/03/20 23:29:13	G-240		D-4986	3	590		N in atom percer	40.09	1.1894	33.71		0.36666	33.723	☐
2006/03/21 01:31:05	G-240		D-4998	3	590		N in atom percer	38.1	1.1316	33.67		0.368813	33.688	☐

Fig. B.8. Area Adjust form for nitrogen-isotope measurements.

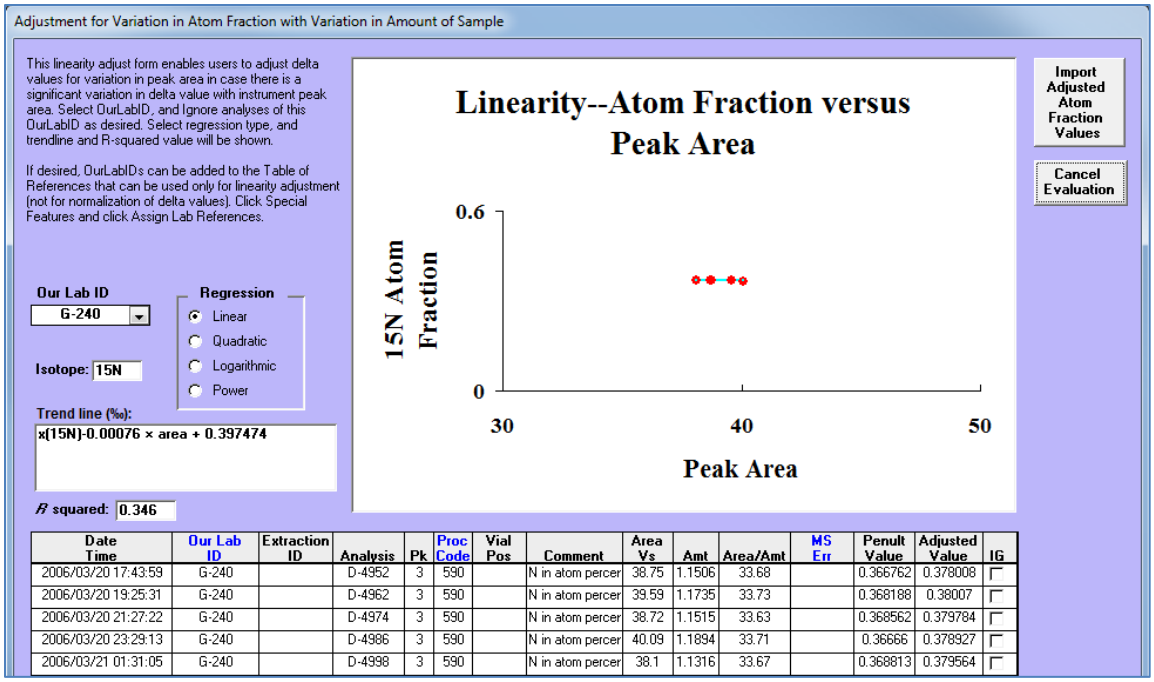


Fig. B.9. Adjustment for Variation in Atom Fraction with Variation in Amount of Sample form for nitrogen-isotope measurements.

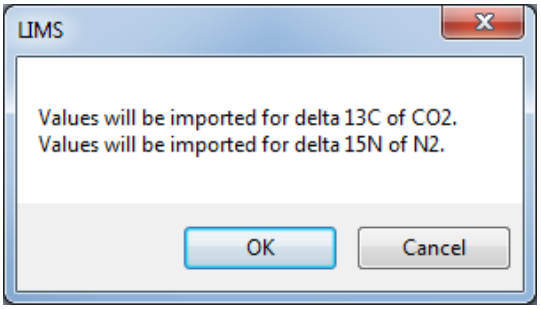


Fig. B.10. Import results dialog box.

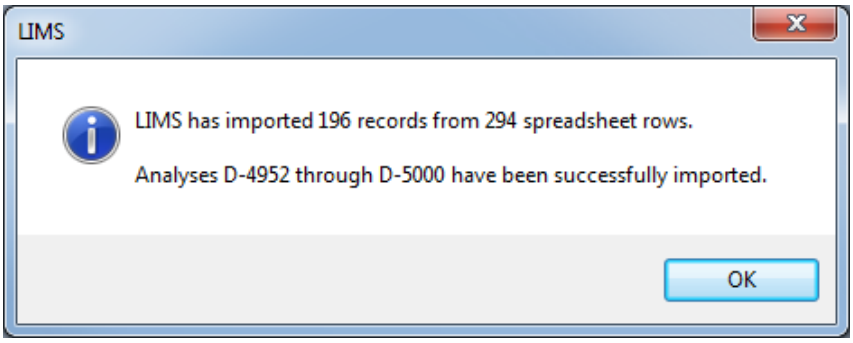
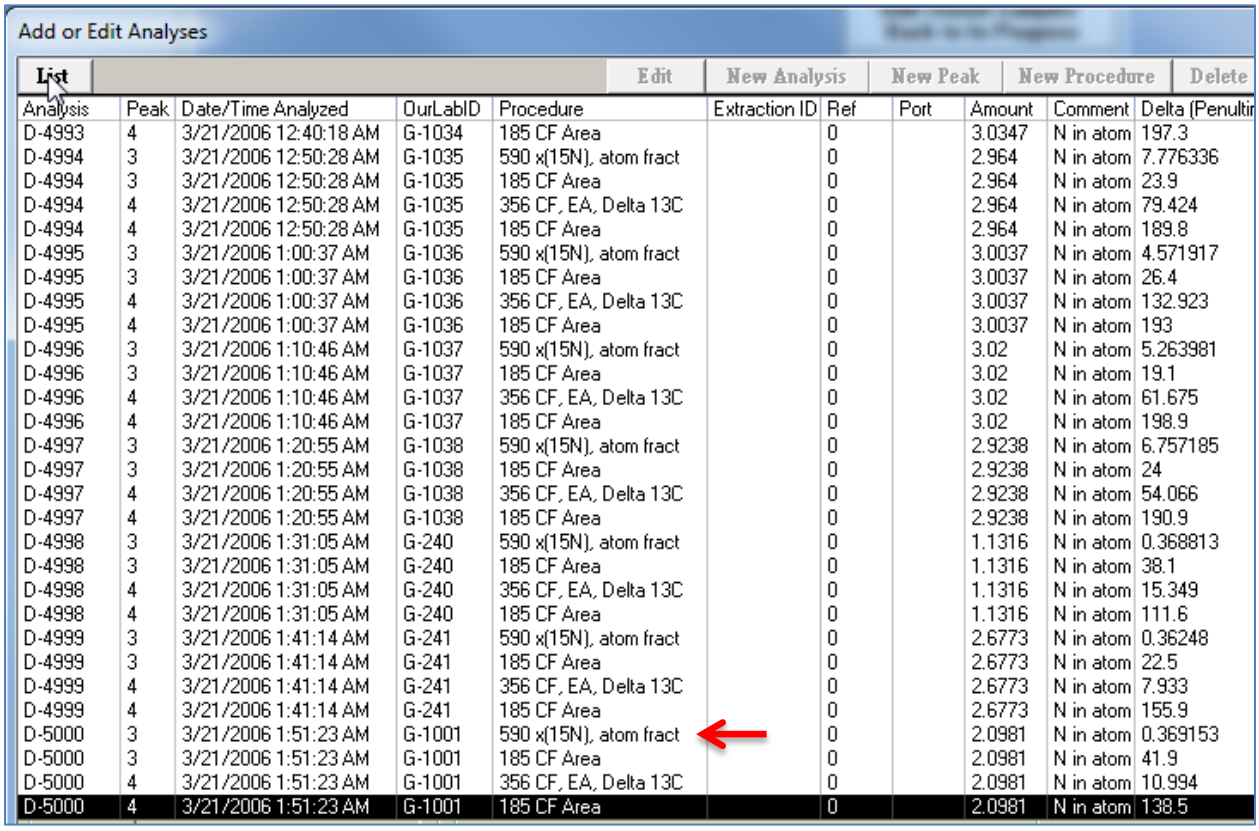


Fig. B.11. Import summary dialog box.

B.3 Viewing and Editing Atom Fraction Analyses

To demonstrate how LIMS stores delta values versus atom fractions:

1. Click "View / Edit Information about Samples Analyses" on the LIMS main page to open the Add or Edit Analyses form (Section 27).
2. Click "List" to display the most recent analyses (Fig. B.12).
3. Select the most recent atom fraction (peak number 3 of analysis D-5000 having a procedure code of 590) (Fig. B.13). Note that a penultimate value of 0.369153 is shown for the nitrogen-isotope measurement having a procedure code of 590.
4. Click "Close" to return to the main menu.



Analysis	Peak	Date/Time Analyzed	OurLabID	Procedure	Extraction ID	Ref	Port	Amount	Comment	Delta (Penultir
D-4993	4	3/21/2006 12:40:18 AM	G-1034	185 CF Area		0		3.0347	N in atom	197.3
D-4994	3	3/21/2006 12:50:28 AM	G-1035	590 x(15N), atom fract		0		2.964	N in atom	7.776336
D-4994	3	3/21/2006 12:50:28 AM	G-1035	185 CF Area		0		2.964	N in atom	23.9
D-4994	4	3/21/2006 12:50:28 AM	G-1035	356 CF, EA, Delta 13C		0		2.964	N in atom	79.424
D-4994	4	3/21/2006 12:50:28 AM	G-1035	185 CF Area		0		2.964	N in atom	189.8
D-4995	3	3/21/2006 1:00:37 AM	G-1036	590 x(15N), atom fract		0		3.0037	N in atom	4.571917
D-4995	3	3/21/2006 1:00:37 AM	G-1036	185 CF Area		0		3.0037	N in atom	26.4
D-4995	4	3/21/2006 1:00:37 AM	G-1036	356 CF, EA, Delta 13C		0		3.0037	N in atom	132.923
D-4995	4	3/21/2006 1:00:37 AM	G-1036	185 CF Area		0		3.0037	N in atom	193
D-4996	3	3/21/2006 1:10:46 AM	G-1037	590 x(15N), atom fract		0		3.02	N in atom	5.263981
D-4996	3	3/21/2006 1:10:46 AM	G-1037	185 CF Area		0		3.02	N in atom	19.1
D-4996	4	3/21/2006 1:10:46 AM	G-1037	356 CF, EA, Delta 13C		0		3.02	N in atom	61.675
D-4996	4	3/21/2006 1:10:46 AM	G-1037	185 CF Area		0		3.02	N in atom	198.9
D-4997	3	3/21/2006 1:20:55 AM	G-1038	590 x(15N), atom fract		0		2.9238	N in atom	6.757185
D-4997	3	3/21/2006 1:20:55 AM	G-1038	185 CF Area		0		2.9238	N in atom	24
D-4997	4	3/21/2006 1:20:55 AM	G-1038	356 CF, EA, Delta 13C		0		2.9238	N in atom	54.066
D-4997	4	3/21/2006 1:20:55 AM	G-1038	185 CF Area		0		2.9238	N in atom	190.9
D-4998	3	3/21/2006 1:31:05 AM	G-240	590 x(15N), atom fract		0		1.1316	N in atom	0.368813
D-4998	3	3/21/2006 1:31:05 AM	G-240	185 CF Area		0		1.1316	N in atom	38.1
D-4998	4	3/21/2006 1:31:05 AM	G-240	356 CF, EA, Delta 13C		0		1.1316	N in atom	15.349
D-4998	4	3/21/2006 1:31:05 AM	G-240	185 CF Area		0		1.1316	N in atom	111.6
D-4999	3	3/21/2006 1:41:14 AM	G-241	590 x(15N), atom fract		0		2.6773	N in atom	0.36248
D-4999	3	3/21/2006 1:41:14 AM	G-241	185 CF Area		0		2.6773	N in atom	22.5
D-4999	4	3/21/2006 1:41:14 AM	G-241	356 CF, EA, Delta 13C		0		2.6773	N in atom	7.933
D-4999	4	3/21/2006 1:41:14 AM	G-241	185 CF Area		0		2.6773	N in atom	155.9
D-5000	3	3/21/2006 1:51:23 AM	G-1001	590 x(15N), atom fract		0		2.0981	N in atom	0.369153
D-5000	3	3/21/2006 1:51:23 AM	G-1001	185 CF Area		0		2.0981	N in atom	41.9
D-5000	4	3/21/2006 1:51:23 AM	G-1001	356 CF, EA, Delta 13C		0		2.0981	N in atom	10.994
D-5000	4	3/21/2006 1:51:23 AM	G-1001	185 CF Area		0		2.0981	N in atom	138.5

Fig. B.12. Most recent analyses shown with the Add or Edit Analyses form.

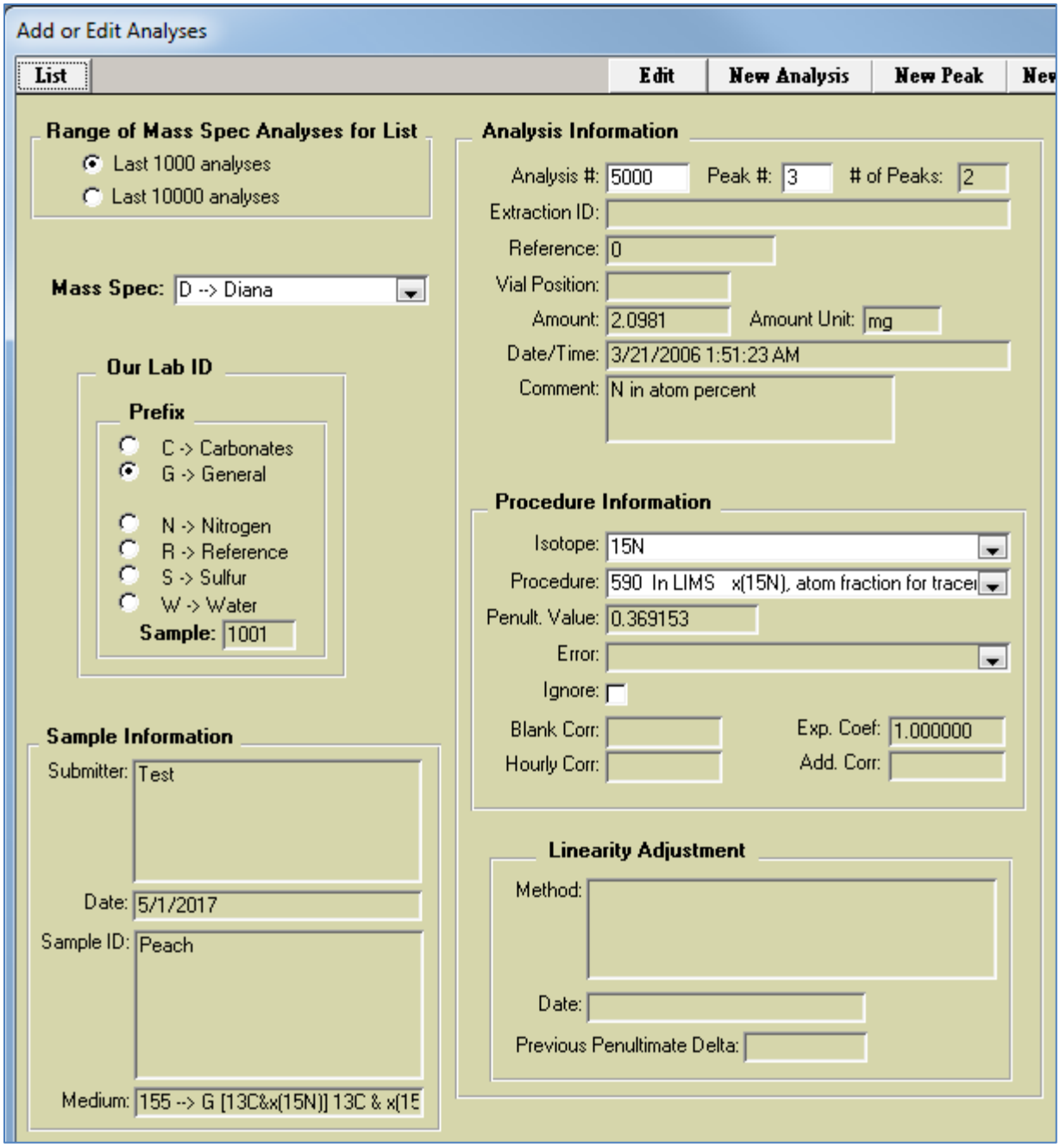


Fig. B.13. Add or Edit Analyses form showing ^{15}N fraction from a tracer study.

B.4 Normalizing Atom Fraction Values

The next step is to normalize the results:

1. Click "Apply Data Normalization" on the LIMS main page.
2. Select "D (Diana) for 15N" for the mass spectrometer and isotope.

3. Click “Query” and the Data Normalization form appears as shown in Figure B.14.
4. Double-click the last analysis having a “+” symbol after the Our Lab ID in column 4 (Analysis D-5000 having peak number 3) and LIMS prompts that it will determine best fitting normalization equation coefficients (Fig. B-15).

Data Normalization

Choose Mass Spectrometer and Isotope D (Diana) for 15N

'Right' mouse button information available for columns with blue column headings.

Analyses from: 4500 **to:** 5000

Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Ref	Correction Coefs	Range
D-4978	3	2006/03/20 22:07:59	G-1021 +		0	1.00000, , ,	
D-4978	4	2006/03/20 22:07:59	G-1021		0	1.00000, , ,	
D-4979	3	2006/03/20 22:18:08	G-1022 +		0	1.00000, , ,	
D-4979	4	2006/03/20 22:18:08	G-1022		0	1.00000, , ,	
D-4980	3	2006/03/20 22:28:18	G-1023 +		0	1.00000, , ,	
D-4980	4	2006/03/20 22:28:18	G-1023		0	1.00000, , ,	
D-4981	3	2006/03/20 22:38:27	G-1024 +		0	1.00000, , ,	
D-4981	4	2006/03/20 22:38:27	G-1024		0	1.00000, , ,	
D-4982	3	2006/03/20 22:48:36	G-1025 +		0	1.00000, , ,	
D-4982	4	2006/03/20 22:48:36	G-1025		0	1.00000, , ,	
D-4983	3	2006/03/20 22:58:45	G-1026 +		0	1.00000, , ,	
D-4983	4	2006/03/20 22:58:45	G-1026		0	1.00000, , ,	
D-4984	3	2006/03/20 23:08:55	G-1027 +		0	1.00000, , ,	
D-4984	4	2006/03/20 23:08:55	G-1027		0	1.00000, , ,	
D-4985	3	2006/03/20 23:19:04	G-1028 +		0	1.00000, , ,	
D-4985	4	2006/03/20 23:19:04	G-1028		0	1.00000, , ,	
D-4986	3	2006/03/20 23:29:13	G-240 +		0	1.00000, , ,	
D-4986	4	2006/03/20 23:29:13	G-240		0	1.00000, , ,	
D-4987	3	2006/03/20 23:39:23	G-241 +		0	1.00000, , ,	
D-4987	4	2006/03/20 23:39:23	G-241		0	1.00000, , ,	
D-4988	3	2006/03/20 23:49:32	G-1029 +		0	1.00000, , ,	
D-4988	4	2006/03/20 23:49:32	G-1029		0	1.00000, , ,	
D-4989	3	2006/03/20 23:59:41	G-1030 +		0	1.00000, , ,	
D-4989	4	2006/03/20 23:59:41	G-1030		0	1.00000, , ,	
D-4990	3	2006/03/21 00:09:50	G-1031 +		0	1.00000, , ,	
D-4990	4	2006/03/21 00:09:50	G-1031		0	1.00000, , ,	
D-4991	3	2006/03/21 00:20:00	G-1032 +		0	1.00000, , ,	
D-4991	4	2006/03/21 00:20:00	G-1032		0	1.00000, , ,	
D-4992	3	2006/03/21 00:30:09	G-1033 +		0	1.00000, , ,	
D-4992	4	2006/03/21 00:30:09	G-1033		0	1.00000, , ,	
D-4993	3	2006/03/21 00:40:18	G-1034 +		0	1.00000, , ,	
D-4993	4	2006/03/21 00:40:18	G-1034		0	1.00000, , ,	
D-4994	3	2006/03/21 00:50:28	G-1035 +		0	1.00000, , ,	
D-4994	4	2006/03/21 00:50:28	G-1035		0	1.00000, , ,	
D-4995	3	2006/03/21 01:00:37	G-1036 +		0	1.00000, , ,	
D-4995	4	2006/03/21 01:00:37	G-1036		0	1.00000, , ,	
D-4996	3	2006/03/21 01:10:46	G-1037 +		0	1.00000, , ,	
D-4996	4	2006/03/21 01:10:46	G-1037		0	1.00000, , ,	
D-4997	3	2006/03/21 01:20:55	G-1038 +		0	1.00000, , ,	
D-4997	4	2006/03/21 01:20:55	G-1038		0	1.00000, , ,	
D-4998	3	2006/03/21 01:31:05	G-240 +		0	1.00000, , ,	
D-4998	4	2006/03/21 01:31:05	G-240		0	1.00000, , ,	
D-4999	3	2006/03/21 01:41:14	G-241 +		0	1.00000, , ,	
D-4999	4	2006/03/21 01:41:14	G-241		0	1.00000, , ,	
D-5000	3	2006/03/21 01:51:23	G-1001 +		0	1.00000, , ,	
D-5000	4	2006/03/21 01:51:23	G-1001		0	1.00000, , ,	

Fig. B.14. Data Normalization form for ^{15}N.

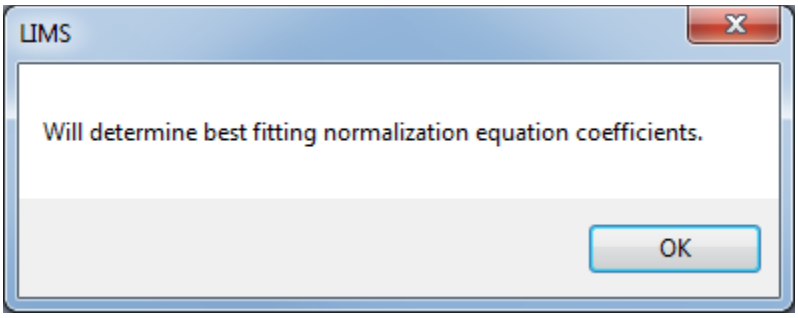
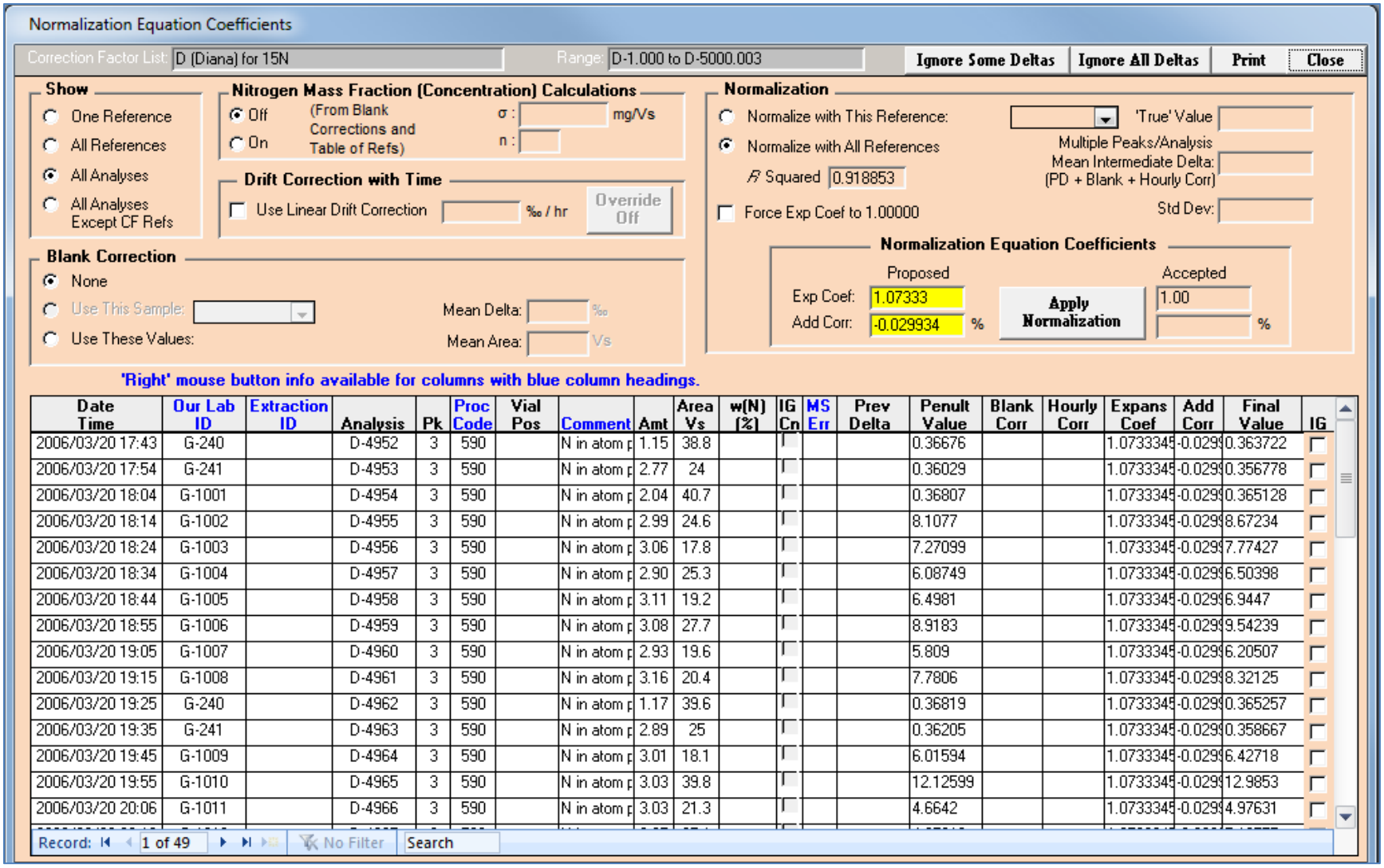


Fig. B.15. Normalization Equation Coefficients form dialog box.

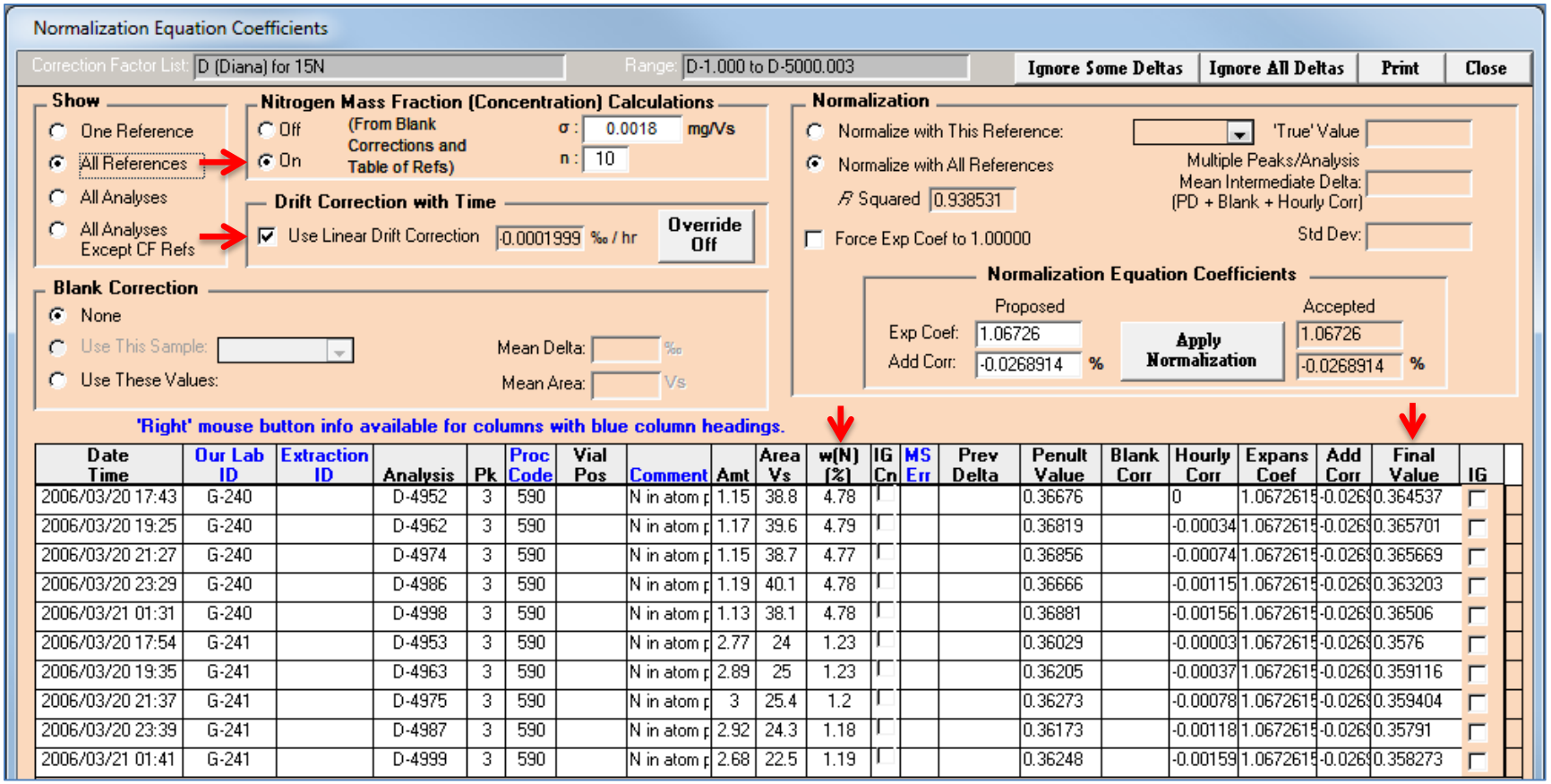
5. Click “OK” and the Normalization Equation Coefficients form appears as shown in Figure B.16.
6. All of the controls, including those for blank correction, drift correction with time, and nitrogen mass fraction (concentration) function the same as for delta values (Section 24), except that six-digit values generally are displayed and used for calculations. Click the “Use Linear Drift Correction” check box to perform drift correction with time and the entries in the “Final Delta” column are updated.
7. Select “All References” in the “Show” panel if not already selected.
8. Select “On” for “Nitrogen Mass Fraction (Concentration) Calculations” and the entries in the “w(N) (%)” column are populated.
9. Click “Apply Normalization” and the results are normalized (Fig. B.17).
10. Click “Close” and “Close” to return to the main menu.

This completes the normalization of nitrogen-isotope results expressed as atom fractions.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(N) [%]	IG Cn	MS Err	Prev Delta	Penult Value	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Value	IG
2006/03/20 17:43	G-240		D-4952	3	590		N in atom p	1.15	38.8					0.36676			1.0733345	-0.0299	0.363722	
2006/03/20 17:54	G-241		D-4953	3	590		N in atom p	2.77	24					0.36029			1.0733345	-0.0299	0.356778	
2006/03/20 18:04	G-1001		D-4954	3	590		N in atom p	2.04	40.7					0.36807			1.0733345	-0.0299	0.365128	
2006/03/20 18:14	G-1002		D-4955	3	590		N in atom p	2.99	24.6					8.1077			1.0733345	-0.0299	8.67234	
2006/03/20 18:24	G-1003		D-4956	3	590		N in atom p	3.06	17.8					7.27099			1.0733345	-0.0299	7.77427	
2006/03/20 18:34	G-1004		D-4957	3	590		N in atom p	2.90	25.3					6.08749			1.0733345	-0.0299	6.50398	
2006/03/20 18:44	G-1005		D-4958	3	590		N in atom p	3.11	19.2					6.4981			1.0733345	-0.0299	6.9447	
2006/03/20 18:55	G-1006		D-4959	3	590		N in atom p	3.08	27.7					8.9183			1.0733345	-0.0299	9.54239	
2006/03/20 19:05	G-1007		D-4960	3	590		N in atom p	2.93	19.6					5.809			1.0733345	-0.0299	6.20507	
2006/03/20 19:15	G-1008		D-4961	3	590		N in atom p	3.16	20.4					7.7806			1.0733345	-0.0299	8.32125	
2006/03/20 19:25	G-240		D-4962	3	590		N in atom p	1.17	39.6					0.36819			1.0733345	-0.0299	0.365257	
2006/03/20 19:35	G-241		D-4963	3	590		N in atom p	2.89	25					0.36205			1.0733345	-0.0299	0.358667	
2006/03/20 19:45	G-1009		D-4964	3	590		N in atom p	3.01	18.1					6.01594			1.0733345	-0.0299	6.42718	
2006/03/20 19:55	G-1010		D-4965	3	590		N in atom p	3.03	39.8					12.12599			1.0733345	-0.0299	12.9853	
2006/03/20 20:06	G-1011		D-4966	3	590		N in atom p	3.03	21.3					4.6642			1.0733345	-0.0299	4.97631	

Fig. B.16. Normalization Equation Coefficients form displaying nitrogen-isotope values as atom fractions. Six-digit final values are shown. Note that the nitrogen-15 fraction, $x(^{15}\mathrm{N})$, of G-1009 is nearly 13 percent.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(N) [%]	IG Cn	MS Err	Prev Delta	Penult Value	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Value	IG
2006/03/20 17:43	G-240		D-4952	3	590		N in atom p	1.15	38.8	4.78				0.36676		0	1.0672615	-0.0269	0.364537	
2006/03/20 19:25	G-240		D-4962	3	590		N in atom p	1.17	39.6	4.79				0.36819		-0.00034	1.0672615	-0.0269	0.365701	
2006/03/20 21:27	G-240		D-4974	3	590		N in atom p	1.15	38.7	4.77				0.36856		-0.00074	1.0672615	-0.0269	0.365669	
2006/03/20 23:29	G-240		D-4986	3	590		N in atom p	1.19	40.1	4.78				0.36666		-0.00115	1.0672615	-0.0269	0.363203	
2006/03/21 01:31	G-240		D-4998	3	590		N in atom p	1.13	38.1	4.78				0.36881		-0.00156	1.0672615	-0.0269	0.36506	
2006/03/20 17:54	G-241		D-4953	3	590		N in atom p	2.77	24	1.23				0.36029		-0.00003	1.0672615	-0.0269	0.3576	
2006/03/20 19:35	G-241		D-4963	3	590		N in atom p	2.89	25	1.23				0.36205		-0.00037	1.0672615	-0.0269	0.359116	
2006/03/20 21:37	G-241		D-4975	3	590		N in atom p	3	25.4	1.2				0.36273		-0.00078	1.0672615	-0.0269	0.359404	
2006/03/20 23:39	G-241		D-4987	3	590		N in atom p	2.92	24.3	1.18				0.36173		-0.00118	1.0672615	-0.0269	0.35791	
2006/03/21 01:41	G-241		D-4999	3	590		N in atom p	2.68	22.5	1.19				0.36248		-0.00159	1.0672615	-0.0269	0.358273	

Fig. B.17. Normalized, drift corrected nitrogen-15 fractions. All 10 references are shown. Mass fractions of nitrogen, *w*(N), have been calculated by enabling mass fraction calculations in the "Nitrogen Mass Fraction (Concentration) Calculations" panel.

B.5 Evaluating Atom Fraction Data of Samples in Progress

To evaluate the atom fraction data, which were normalized in the last section:

1. Click "Evaluate Samples in Progress" on the LIMS main page and the Evaluate Samples in Progress form will open. This form is discussed in detail in Section 25.
2. Select "G" for the "Prefix" if not already selected.
3. Select "15N" for the "Isotope" and the "From" and "To" fields will be filled with "240" and "1038," respectively.
4. Click "Query" and the Evaluate Samples in Progress form displays the results of the first Our Lab ID in the range, G-240 (Fig. B.18).

The Evaluate Samples in Progress form (Fig. B.18) functions the same for mass fraction values as for isotope-delta values. The mean of all x(15N) values is labelled "Mean 1" (0.364835). The "Mean 2" value is determined by removing the furthest outlier and recalculating the mean and standard deviation. Clicking one of the "IG" check boxes will cause LIMS to update the "Atom Fraction", "Mean 1", "Std Dev 1", "Mean 2", and "Std Dev 2" fields. Clicking one of the "IG Cn" check boxes will cause LIMS to update the mean mass fraction (concentration) value. Clicking "Add Ethereal" enables a user to add a value using the Ethereal mass spectrometer (Section 25.4). If a sample was previously stored and is no longer in the Samples in Progress table, one can click "Retrieve" to add the sample to the Samples in Progress table with the "Isotope" currently selected. Clicking "Print" generates a "Print Samples in Progress" report (Section 26) of all samples in the Our Lab ID Range having the specified "Isotope." Caution is advised in clicking "Print" because the number of pages printed can be large, depending upon the size of the Our Lab ID Range. Users may prefer to use the Print or Export Samples in Progress form (Section 26) because it is more flexible; for example, it allows users to print or export analyses from a single mass spectrometer to an Excel file. Clicking "Calc Amt" opens a dialog box (Fig. B.19) showing the amount of sample needed to create sample peaks having selected peak areas.

⚠ **Helpful Hint:** Many of the fields (text boxes) in LIMS forms allow users to copy and paste their values. For example, in Figure 25.3 one can copy and paste values of the "Mean 1", "Mean Final Delta", "Mean Mass Fraction Carbon", "From", "To", and other fields.

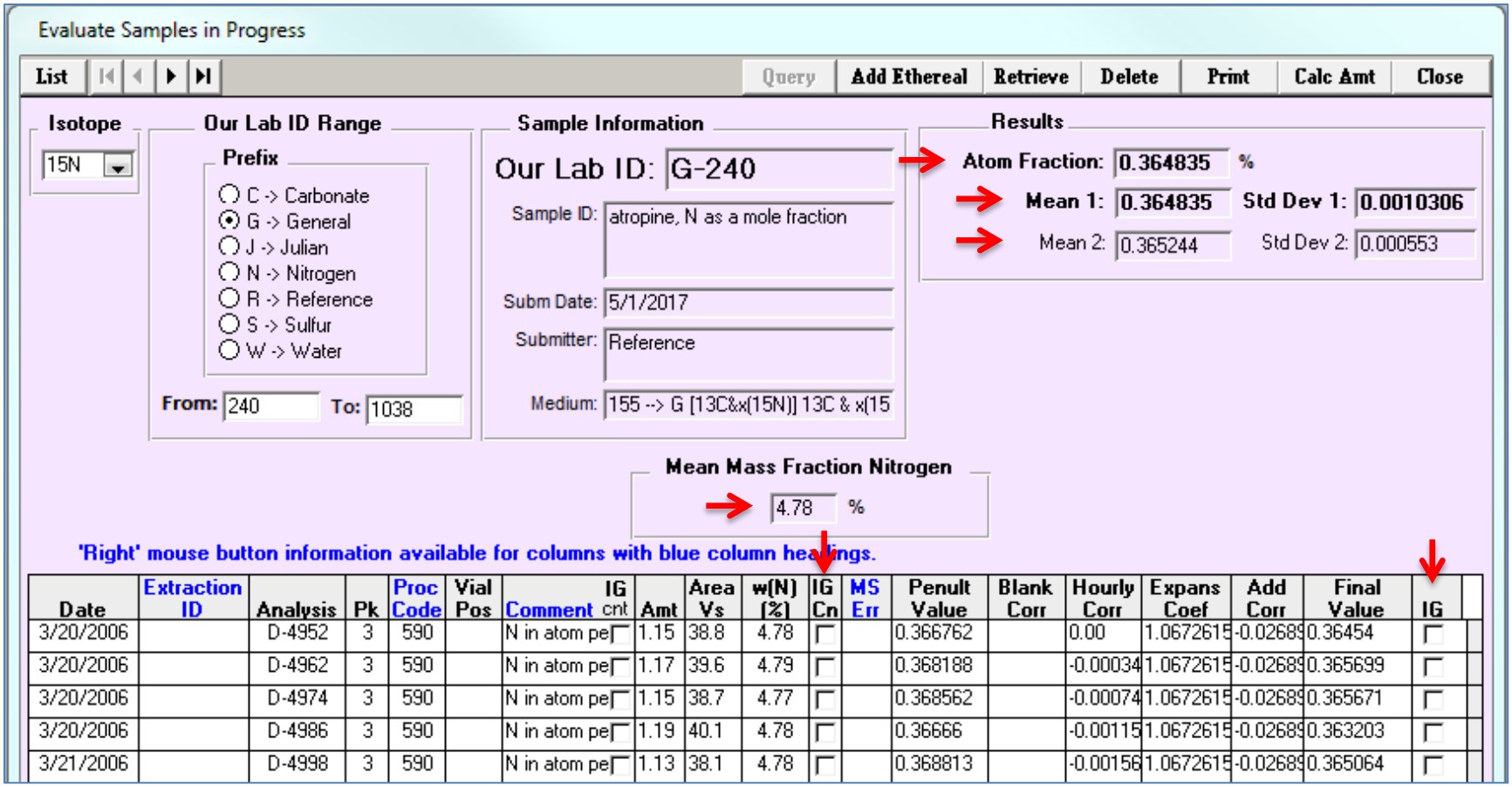


Fig. B.18. Evaluate Samples in Progress form with nitrogen-isotope values shown as ^{15}N atom fractions.

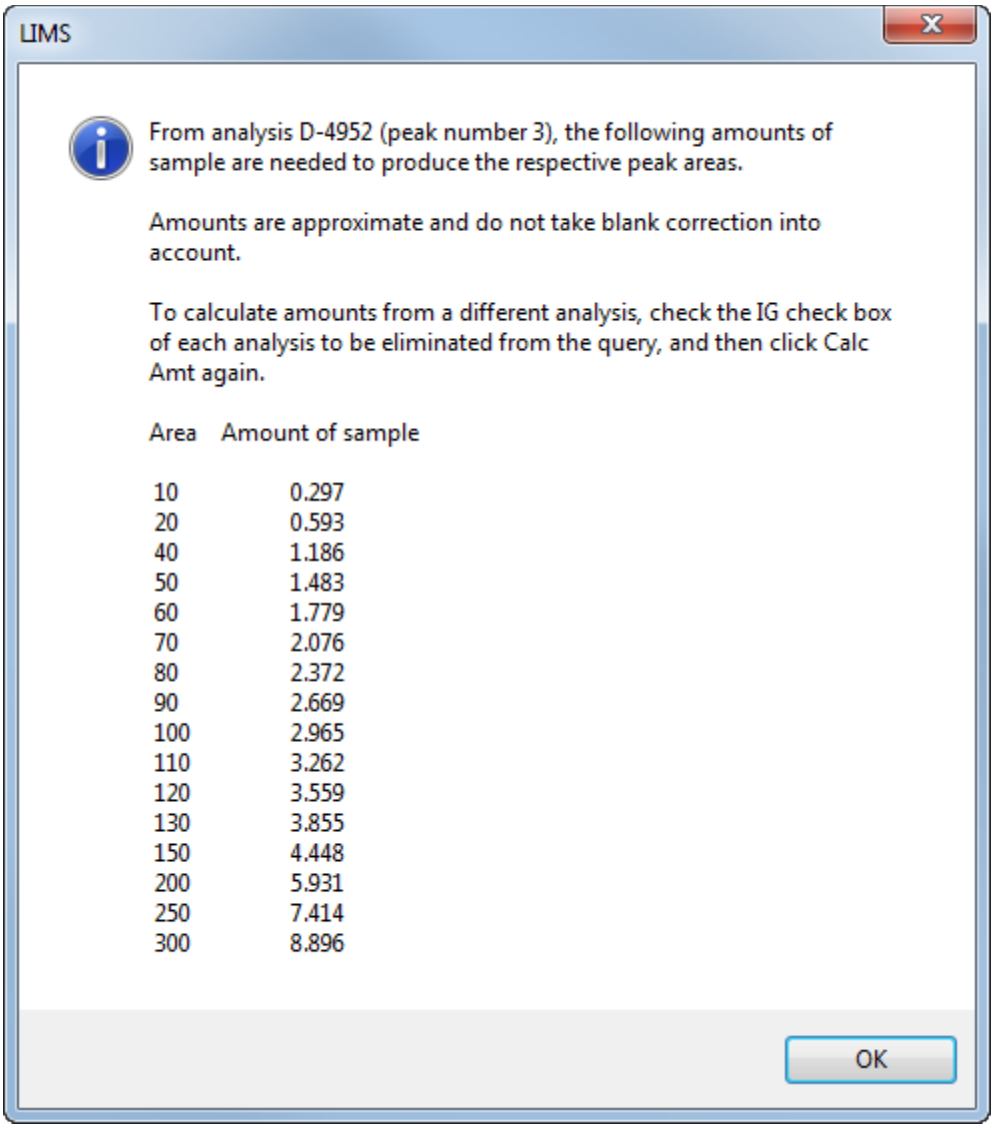


Fig. B.19. Dialog box showing the amount of sample needed for selected values of peak area. This dialog box is displayed by clicking "Cal Amt" on Evauate Samples in Progress form.

B.6 Printing and Exporting Atom Fraction Values of Samples in Progress

The Print or Export Samples in Progress form discussed in Section 26 can be used to print a report of atom fraction data, such as shown in Figure B.20 or to export Excel files. Two examples Excel files ("G-240--G-1038_15N_BriefSummary.xlsx" and "G-240--G-1038_15N.xlsx") are found in the folder named "Appendix B" in the files that accompany this manual.

Samples in Progress for 15N Between G-240 And G-240 — 5/13/2017 12:28:32 PM

Date	Analysis	Pk	Vial Position	Proc Code	MS Error	Penultimate Delta	Blank Corr	Hr Corr	Exp Coef	Add Corr	Final Delta	Ig
G-240	Reference	atropine, N as a mole fraction						155 --> G [13C&x(15N)] 13C & x(15N) 15N e				
3/20/2006	D-4952	3		590		0.366762		0.00	1.06726154	-0.0268914	0.36454	
3/20/2006	D-4962	3		590		0.368188		-0.000341	1.06726154	-0.0268914	0.365699	
3/20/2006	D-4974	3		590		0.368562		-0.000741	1.06726154	-0.0268914	0.365671	
3/20/2006	D-4986	3		590		0.36666		-0.001151	1.06726154	-0.0268914	0.363203	
3/21/2006	D-4998	3		590		0.368813		-0.001561	1.06726154	-0.0268914	0.365064	

Mean 1 = 0.364835 **Std Dev 1 = 0.0010306** Mean Final Delta = **0.364835**

Mean 2 = 0.365244 Std Dev 2 = 0.000553

Fig. B.20. Example of the Print Samples in Progress Report for atom fraction data.

B.7 Storing Atom Fraction Results to Projects

Users store sample results to projects with the Store Sample Results to Projects form (Section 28). To demonstrate this process for atom fraction data:

1. Click "Store Sample Results to Projects" on the LIMS main page.
2. Select G for the "Prefix."
3. Select "15N" for the "Isotope."
4. Click the "Store Single Analysis" check box.
5. Enter "1001" in the "From" field.
6. Enter "1038" in the "To" field and the form appears as shown in Figure B.21.
7. Click "Store" and LIMS stores the data to projects and displays a completion dialog box (Fig. B.22). This may take a minute.
8. Click "OK" and "Close" to return to the main page.

This completes storing of these atom fraction results. An example of the Samples form (Section 8.3) for sample G-1010 is shown in Figure B.23. Clicking "Print Project" prints a project report (Fig. B.24).

The Add Stored Samples Back to In Progress form (Section29) functions the same for samples have isotope-delta values and atom fraction values.

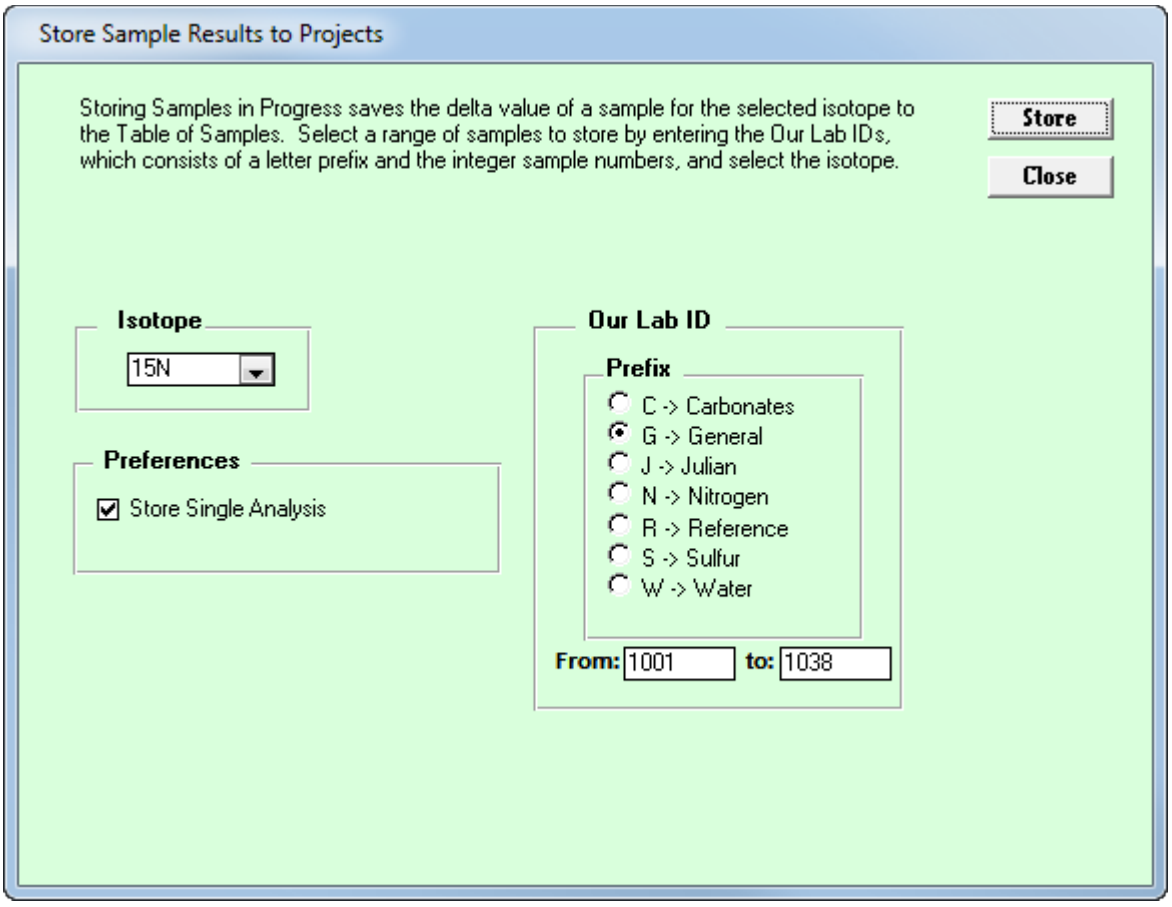


Fig. B.21. Example of the Store Sample Results to Projects form for storing atom fraction data.

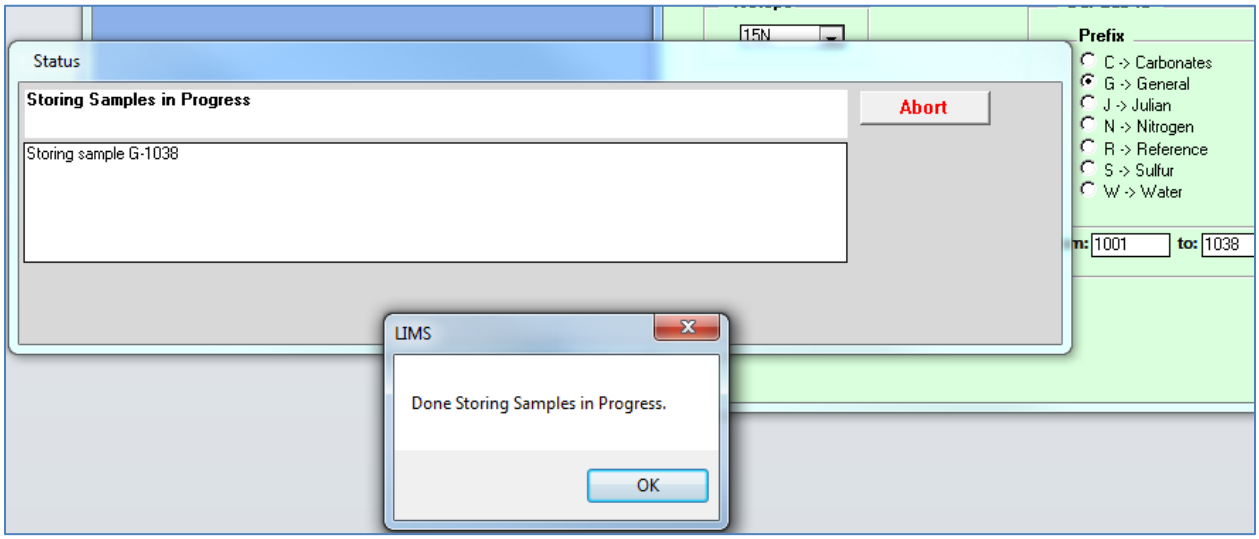


Fig. B.22. Store Sample Results to Projects completion dialog box.

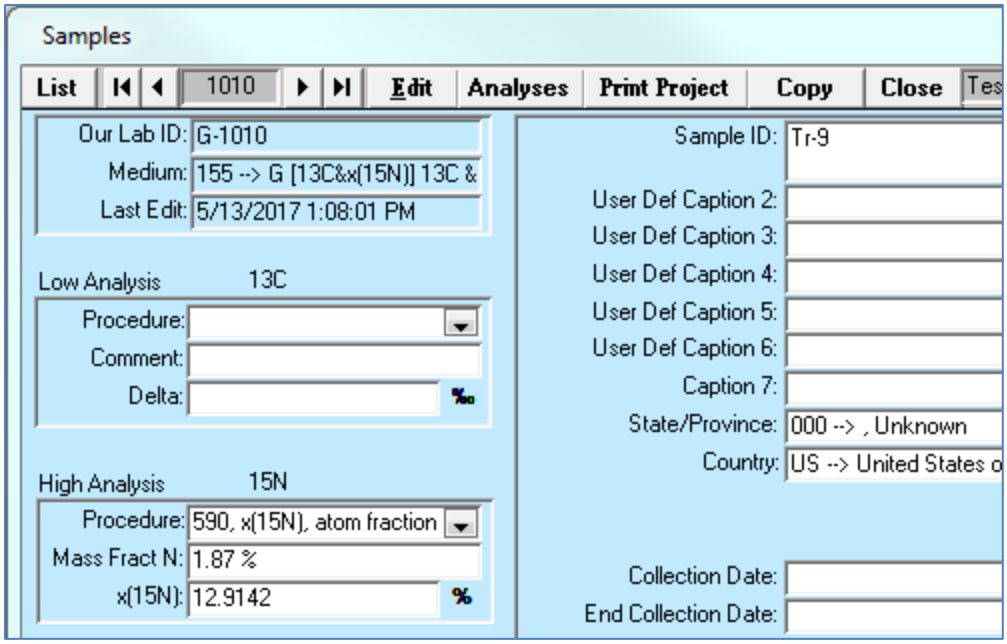


Fig. B.23. Example atom fraction data on the Sample form.

Submission: 5/1/2017 Test G-1001 to G-1038 5/13/2017

Medium: 155 --> G [13C&x(15N)] 13C & x(15N) 15N enriched

Purpose: Demo for importing using x(15N) values in tracer studies

Location:

Sample ID:	Collection Date	Our Lab ID	$\delta^{13}C_{VPDB}$, in ‰ Value	Comment	$x(^{15}N)$, in % Value	Mass Fraction N
Peach		**G-1001**			**0.36561**	2.83 %
Tr-1		**G-1002**			**8.62604**	1.17 %
Tr-2		**G-1003**			**7.73301**	0.82 %
Tr-3		**G-1004**			**6.46987**	1.24 %
Tr-4		**G-1005**			**6.90807**	0.88 %
Tr-5		**G-1006**			**9.49101**	1.27 %
Tr-6		**G-1007**			**6.17255**	0.95 %
Tr-7		**G-1008**			**8.27672**	0.92 %
Tr-8		**G-1009**			**6.39325**	0.85 %
Tr-9		**G-1010**			**12.9142**	1.87 %
Tr-10		**G-1011**			**4.95053**	1.00 %

Fig. B.24. Portion of a project report having atom fraction data.

B.8 Track My Lab QA/QC

Users can use the Track My Laboratory QA/QC form to evaluate laboratory performance of atom fraction measurements. Figure B.25 displays an example evaluation.

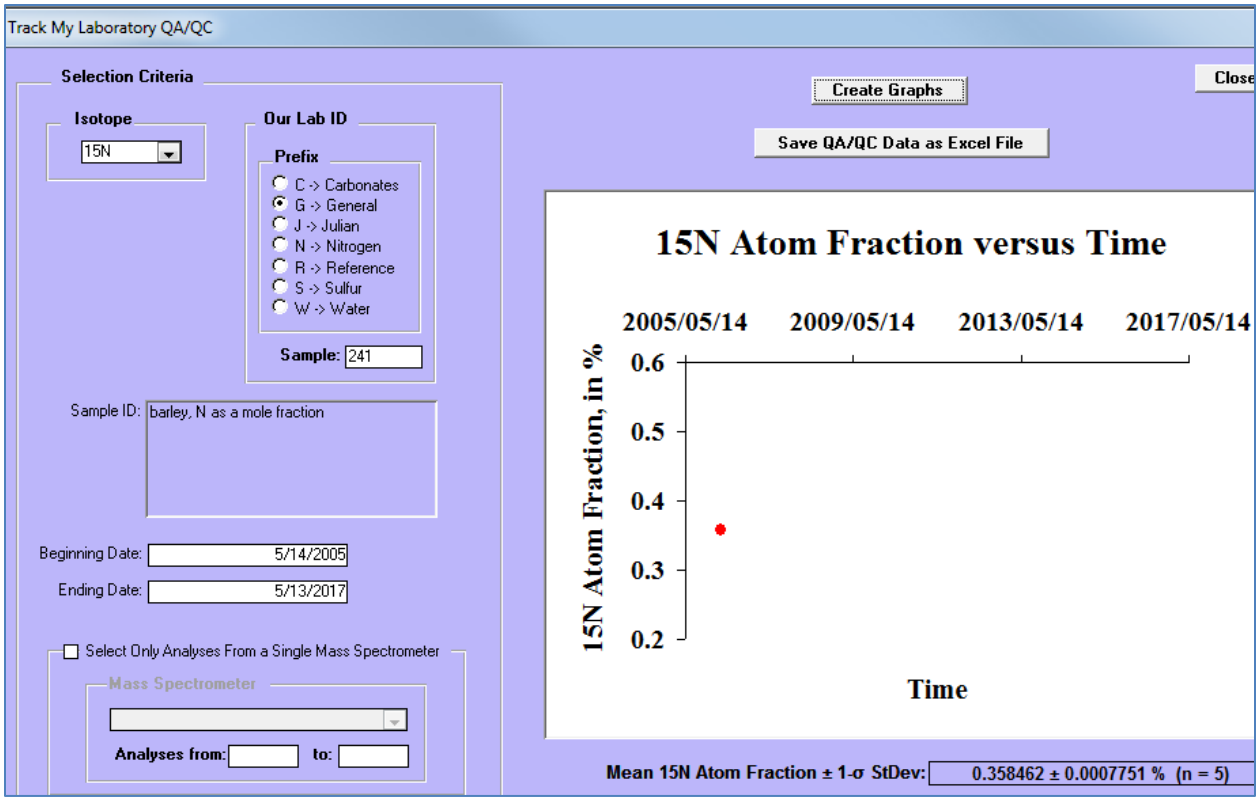


Fig. B.25. Example atom fraction data evaluated with the Track My Laboratory QA/QC form.

Appendix C Editing and Adding Procedures

C.1 The Procedure Codes form

Procedure codes are numerical values assigned to analytical methods by which samples are converted into gases (or equilibrated with gases) and (or) introduced into the mass spectrometer for analysis (see Section 6 and especially Section 6.4). This example assumes that the reader is using the same backend database as used in Sections A.1 and A.2. If needed, instructions for connecting to a different backend database are provided in Section 4.4. To open the Procedure Codes form:

1. Click "Special Features" and then "Procedures" and LIMS will display the message in Figure C.1.
2. Click "OK" to open the Procedure Codes form (Fig. C.2).
3. Click "List" to display procedure codes shown in Figure C.3.

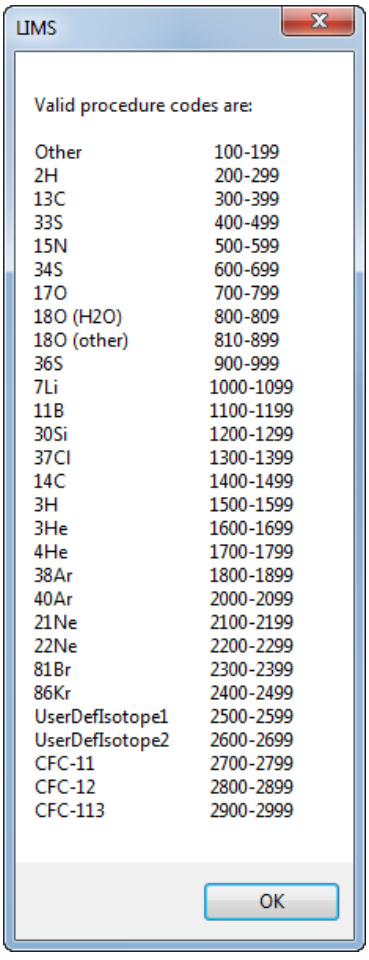


Fig. C.1. LIMS dialog box upon clicking the "Procedures" button.

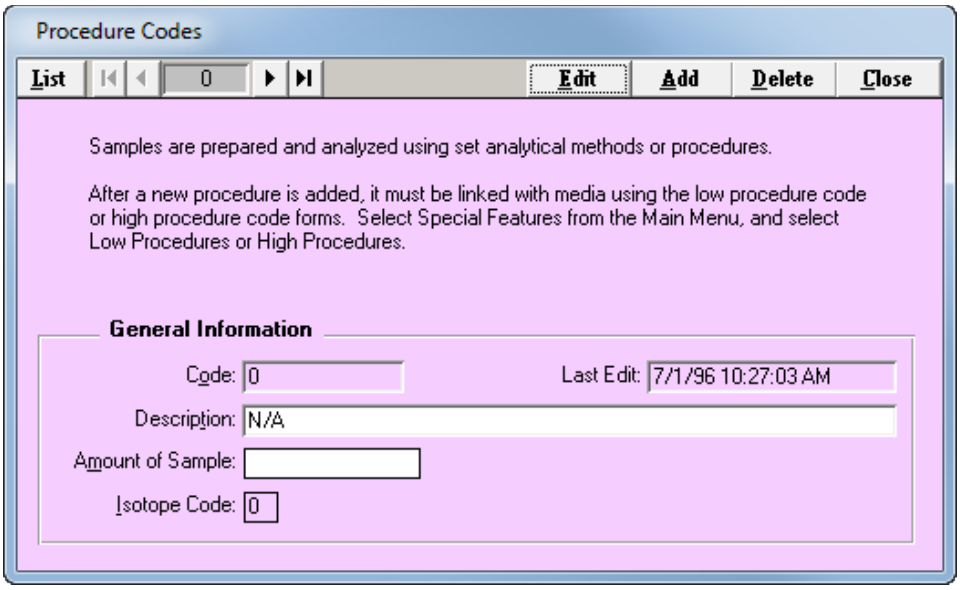


Fig. C.2. Procedure Codes form.

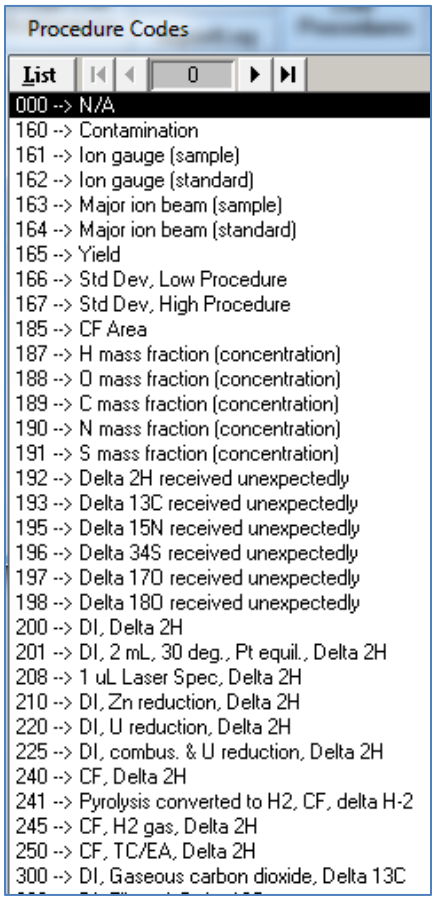


Fig. C.3. Procedure codes shown by clicking the “List” button.

Procedure codes 200–299 are designated for performing δ^2H analyses, all of which have isotope code 2 (Table 6.1). Procedure codes 300–399 are designated for performing δ^{13}C analyses, all of which have isotope code 3. Dividing the procedure code by 100 and taking the integer yields the isotope code. Although most procedure codes identify a specific analytical method, those with values between 100 and 199 indicate a quantity being measured, not an analytical method. For example, procedure codes 187–191 are hydrogen, carbon, nitrogen, sulfur, and oxygen mass fractions (concentrations), respectively (Fig. C.3). Code 185 is used in LIMS to store continuous-flow areas. Sometimes upon importing analytical results, an unexpected isotope-delta value is provided. For example, a spreadsheet might contain both a δ^{13}C and δ^{18}O value of a graphite sample analyzed with an EA. LIMS knows that a graphite sample has no oxygen, and the δ^{18}O value is a result of the reaction of the graphite with oxygen to produce carbon dioxide. LIMS can assign the unexpected δ^{18}O value a procedure code of 198 if desired (see Section 13.1).

In addition to the procedure code, the Procedure Codes form (Fig. C.3) also has fields for the procedure description, amount of sample, and the isotope code. The procedure description is editable. The amount of sample is for the user's information and this field is not used in LIMS.

C.2 Editing Procedures

To edit a procedure:

1. Navigate to the procedure code that needs to be edited. For example, navigate to procedure code 890 (DI, N-bearing material, Delta 18O) shown in Figure C.4.
2. Click "Edit."
3. Replace the existing description "DI, N-bearing material, Delta 18O" by "DI, N- and O-bearing material, Delta 18O" to indicate that the material has both nitrogen and oxygen in it.
4. Click "Save" to complete editing of this procedure.

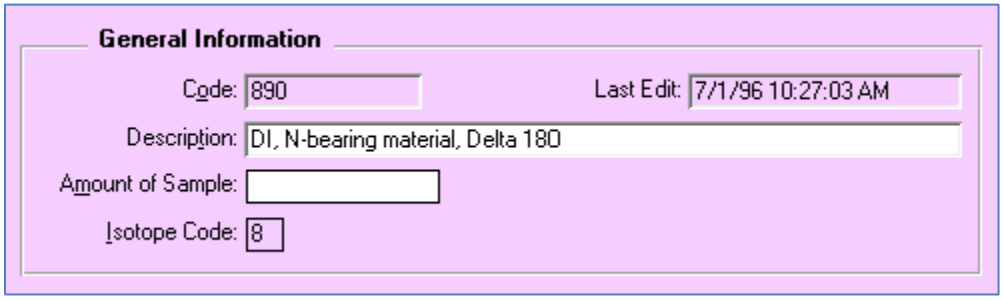


Fig. C.4. Procedure Codes form for code 890.

C.3 Adding Procedures

This demonstration assumes that the reader is using the same backend database as used in Sections A.1 and A.2. If needed, instructions for connecting to a different backend database are provided in Section 4.4. In Appendix A.2, an example was given in which a medium for a tracer test using heavy water was added (medium 99 with description "water, x(2H) enriched & O"). A procedure code for the hydrogen-isotope measurement needs to be added:

1. On the main page of LIMS click "Special Features," if the Special Features window is not already open.
2. Click "Procedures" and LIMS will display the message in Figure C.1.
3. Click "OK" to open the Procedure Codes form (Fig. C.2).
4. Click "List" to review the procedure codes for hydrogen, which range from 200 to 299 (Fig. C.3), and search for a code that is not used. Procedure code 260 is available, so it can be used for the new hydrogen-isotope procedure.
5. Click "Add."
6. For the "Code" field enter 260 and LIMS will prompt "You are entering a procedure code for 2H" when you click the "Tab" key or the "Enter" key on the keyboard.
7. Click "OK."
8. For the description field, enter "2H fraction of water (atom fraction in percent), x(2H)."
9. Click "Save" to create new procedure 260, $x(^2H)$ of water (Fig. C.5).
10. Click "Close" to return to the main page.

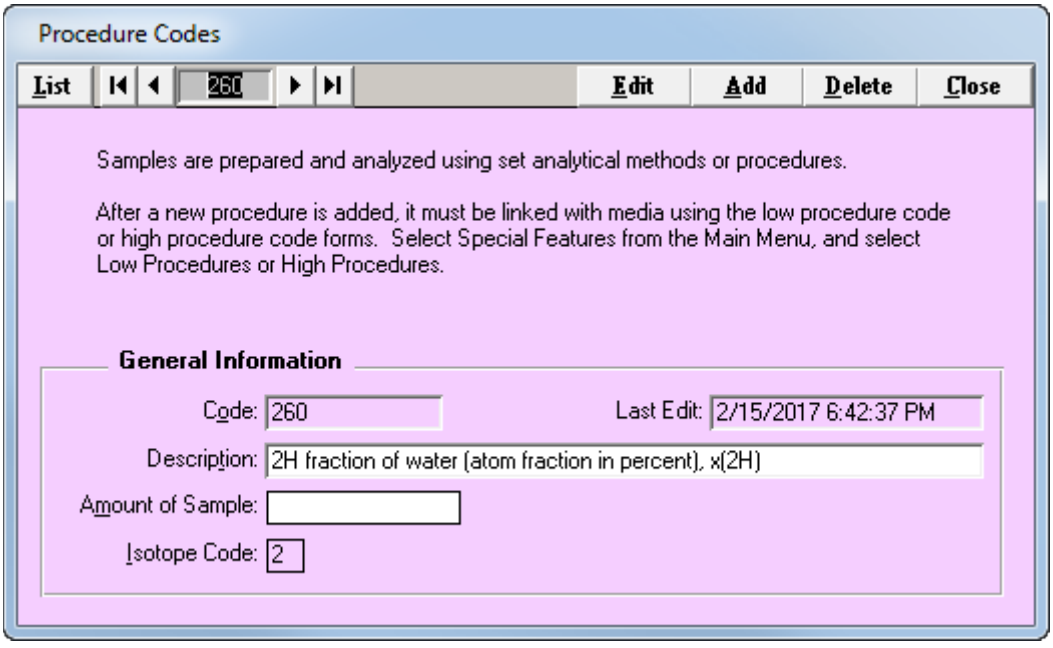


Fig. C.5. New procedure code 260, ^2H fraction of water for tracer samples.

C.4 Deleting Procedures

Procedure codes can be deleted only if they have not been used in tables in LIMS other than the table of procedure codes. LIMS will alert the user if a procedure code cannot be deleted.

C.5 Linking Procedures to the Low or High Isotope of a Medium—The Low Procedure Codes form and the High Procedure Codes form

As discussed in Section 6, media can have either one or two isotopes. The isotope with the lower isotope code (see Table 6.1 for isotope codes) is termed the low isotope. If a medium has a second isotope, it is the high isotope. As shown in Table 6.5, a nitrogen-isotope procedure code might be either a low procedure or a high procedure, depending upon the medium. For dissolved nitrate (medium 55), a δ^{15}N measurement (procedure code 587) would be a low procedure. However, for a carbon- and nitrogen-bearing material (medium 26), a δ^{15}N measurement (procedure code 584) would be a high procedure.

In order for LIMS to know whether an isotope measurement result should be stored in the low isotope field or the high isotope field of a sample (see panels labelled "Low Analysis" and "High Analysis" in Fig. 7.36), each procedure code needs to be linked to a medium as a low procedure or a high procedure. This linking is accomplished with the Low Procedure Codes form and the High Procedure Codes form. For example, click "Special Features" and "Low Procedures" to open the Low Procedures form, click "List," and navigate to the record "L(587), 55 --> N[NO3] dissolved nitrate" to see the linkage between the low isotope of medium 55 and the δ^{15}N procedure code 587, "CF, Denitrifier Method, P. aureofaciens, N-15" (Figs. C.6 and C.7). To view the linkage between the high isotope of medium 55 (isotope code 8, δ^{18}O) and a procedure code for δ^{18}O, close the Low Procedure Codes form and open the High Procedure Codes form by clicking "High Procedures." Click "List" and navigate to "H(889), 55 --> N[NO3] dissolved nitrate" to show the linkage between the high isotope of medium 55 and the δ^{18}O procedure code 889, "CF, Denitrifier Method, P. aureofaciens, O-18" (Fig. C.8).

C.6 Editing Low and High Procedure Codes forms

Commonly there is more than one procedure code for a medium. For example, for gaseous hydrogen (medium 10), the Low Procedure Codes form indicates that two procedure codes are available. The first is 200, which is a dual-inlet analysis, and the other is 245, which is a continuous-flow analysis. LIMS has the capability to designate either of these procedure codes as the default low procedure code for medium 10 in case a procedure code is not assigned during importing, which regularly occurs. Assigning a procedure code as the default is done by setting

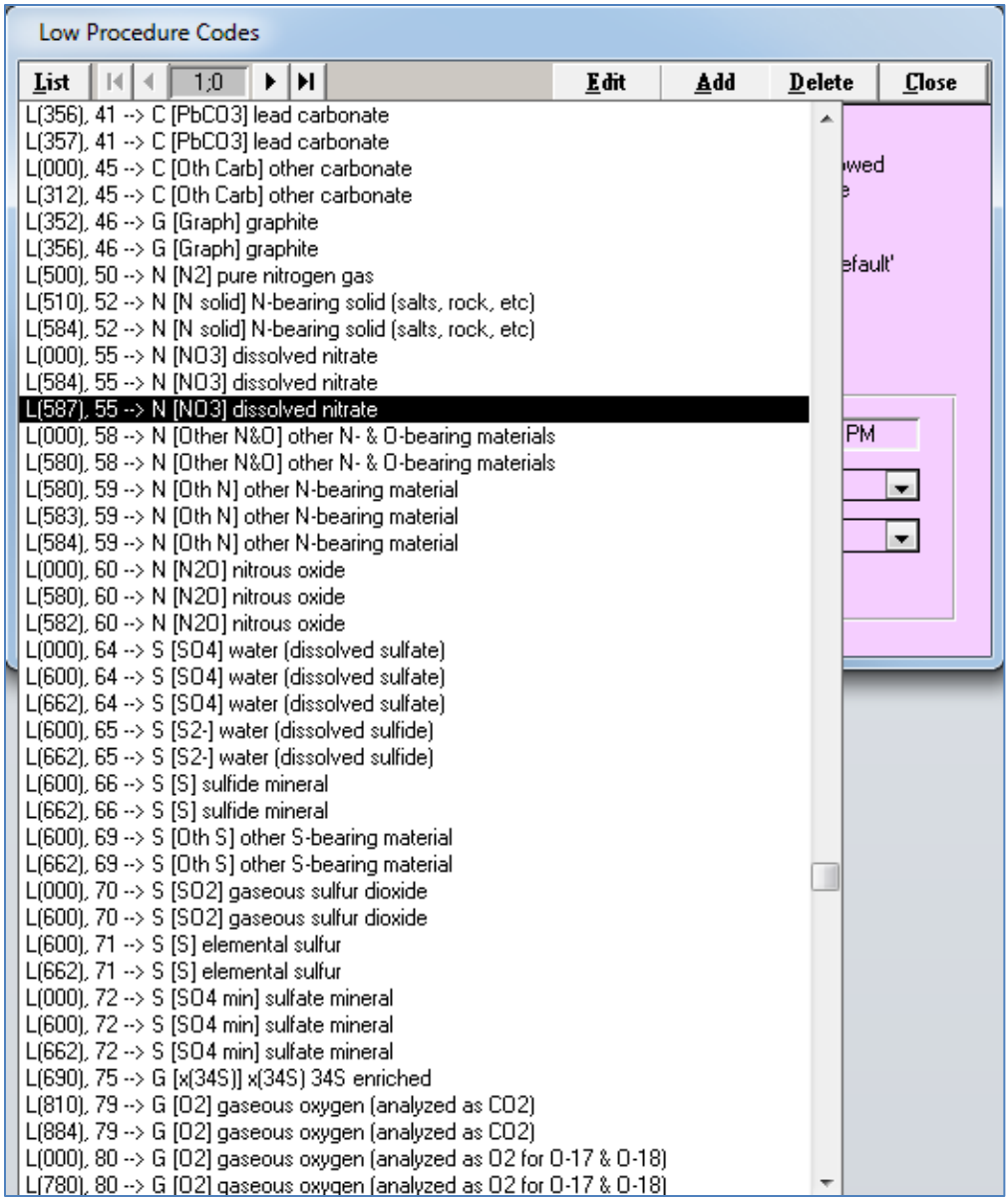


Fig. C.6. Navigation to the record "L(587), 55 --> N[NO3] dissolved nitrate" on the Low Procedure Codes form.

the "Default" field in the Low Procedure Codes (or High Procedure Codes) form to an asterisk (*). Currently, procedure code 200 is set as the default for medium 10 (Fig. C.9). To edit the default procedure code, click "Edit" and LIMS prompts that "You can only edit the field 'Default'. You may want to delete and add a low procedure." Click "OK" and change the "Default" field to a blank value. Click "Save." Navigate to the next procedure code, 245 for medium 10. Click "Edit," click "OK" to the LIMS prompt, set the "Default" field to "*," and click "Save" (Fig. C.10).

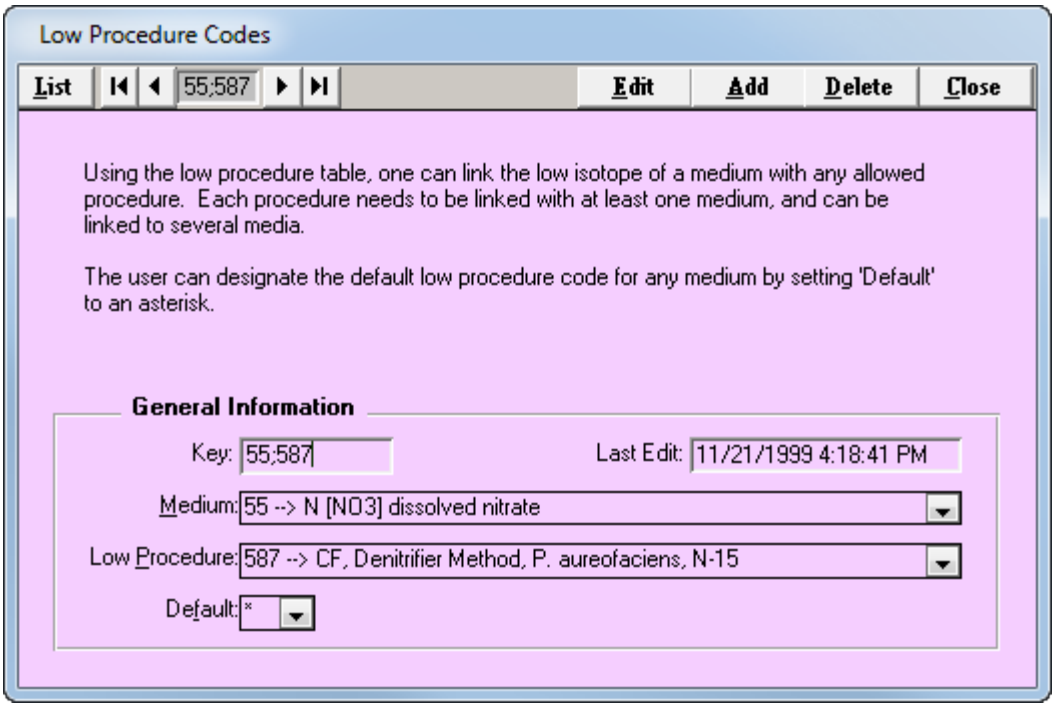


Fig. C.7. Low Procedure Codes form showing linkage between procedure code 587 and medium 55 (dissolved nitrate) for the low isotope.

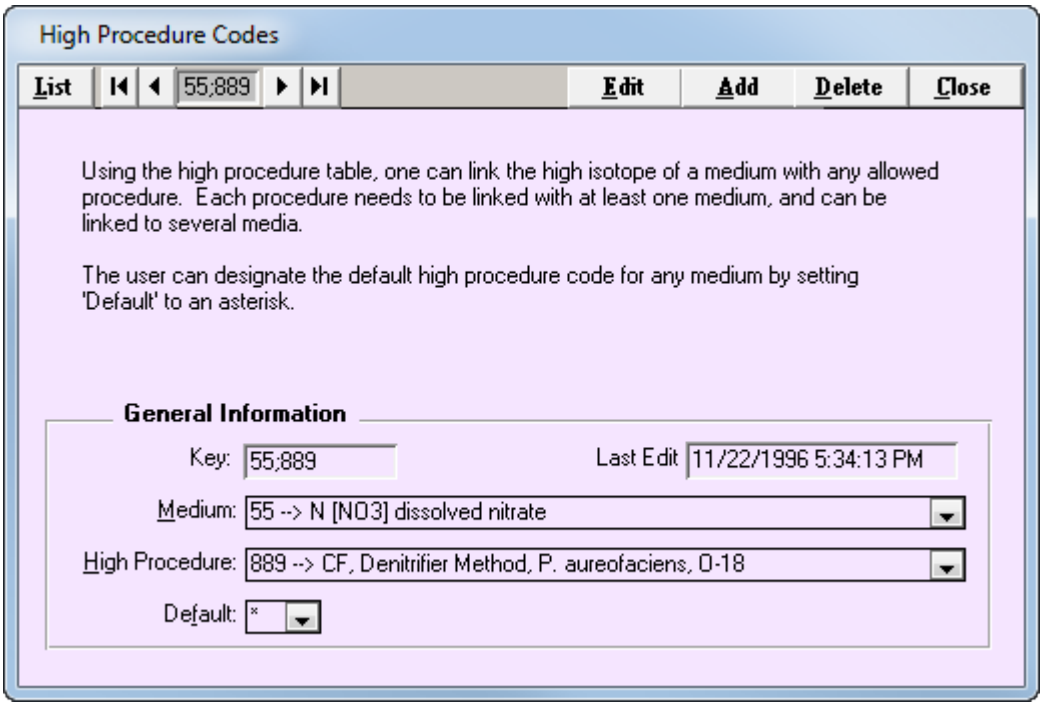


Fig. C.8. High Procedure Codes form showing linkage between procedure code 889 and medium 55 (dissolved nitrate) for the high isotope.

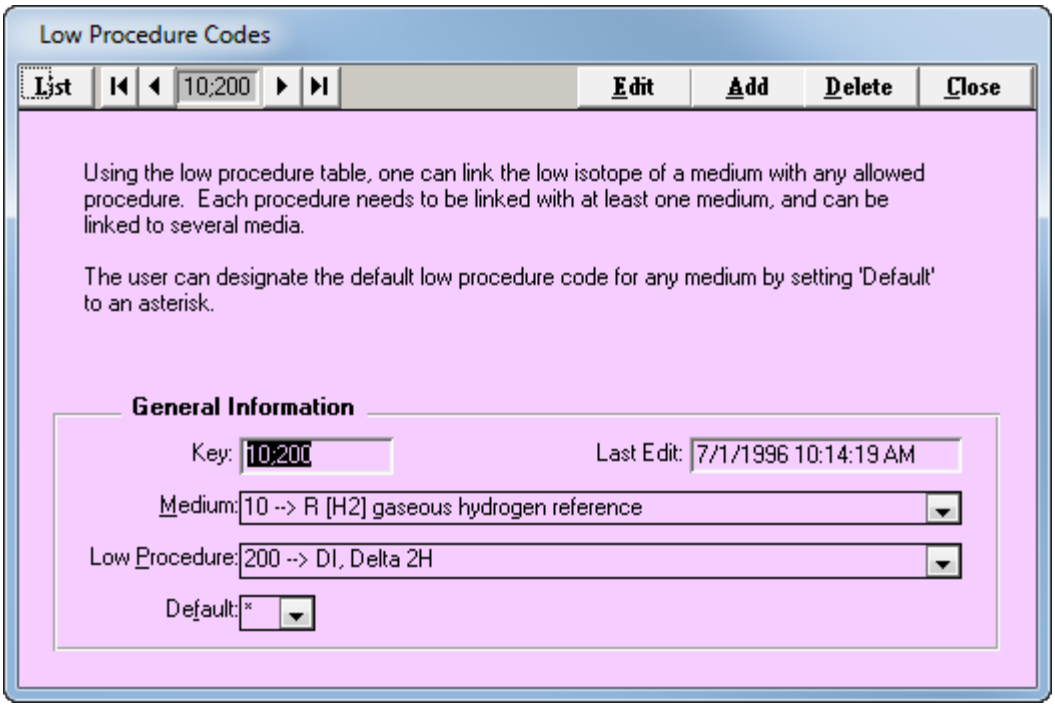


Fig. C.9. Low Procedure Codes form showing the default assignment of medium 10 to procedure code 200.

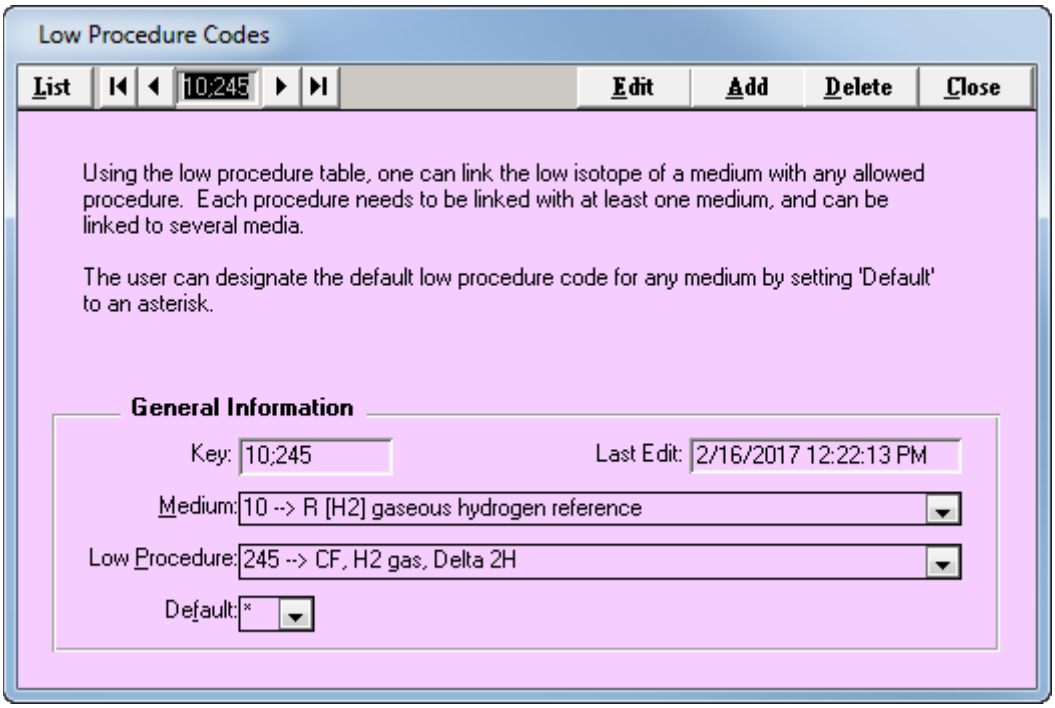


Fig. C.10. Low Procedure Codes form showing the default assignment of medium 10 changed to procedure code 245.

C.7 Adding a Record to the Low or High Procedure Codes form

In Appendix C.3, procedure code 260 ("2H fraction of water (atom fraction in percent), x(2H)") was added for analysis of water from a tracer test using heavy water. Procedure code 260 needs to be linked to the low isotope of medium 99 ("water, x(2H) enriched & O"), which was added in Appendix A.2. This is accomplished by the following steps:

1. Click "Special Features" if the Special Features window is not already open.
2. Click "Low Procedures" to open the Low Procedure Codes form (Figs. C.7–C.9).
3. Click "Add" and the "Medium" dropdown control will open.
4. Navigate to medium 99 (Fig. C.11).
5. Select "99 --> W [x(2H) H2O] water, x(2H) enriched & O" and the "Low Procedure" dropdown will open.
6. Navigate to procedure code 260 (Fig. C.12) and select this procedure code.
7. Set the "Default" field to "*" to indicate that this is the default low procedure code for medium 99 in case the procedure code is not specified during importing of isotopic data, which commonly is the case.
8. Click "Save" and the low isotope of medium 99 will be linked to procedure 260.
9. Click "Add" again, select medium 99, select procedure code "000," and click "Save" to create a second low procedure code linked to the low isotope of medium 99. Having this second procedure code of 0 minimizes minor irritations in creating LIMS templates for sample lists (Section 33.5.1).
10. Click "Close" to return to the main page.

Now that procedure code 260 has been linked to the low isotope of medium 99, the next step is to link an appropriate procedure code to the high isotope of medium 99. One can click "High Procedures" to open the High Procedure Codes form. Following the steps above, link procedure code 800 ("800 --> DI, 2 mL equilibration, Delta 18O") to medium 99 and set it as the default medium. Then, link procedure code 0 to medium 99. That completes linking the low and high isotopes of medium 99 to procedure codes.

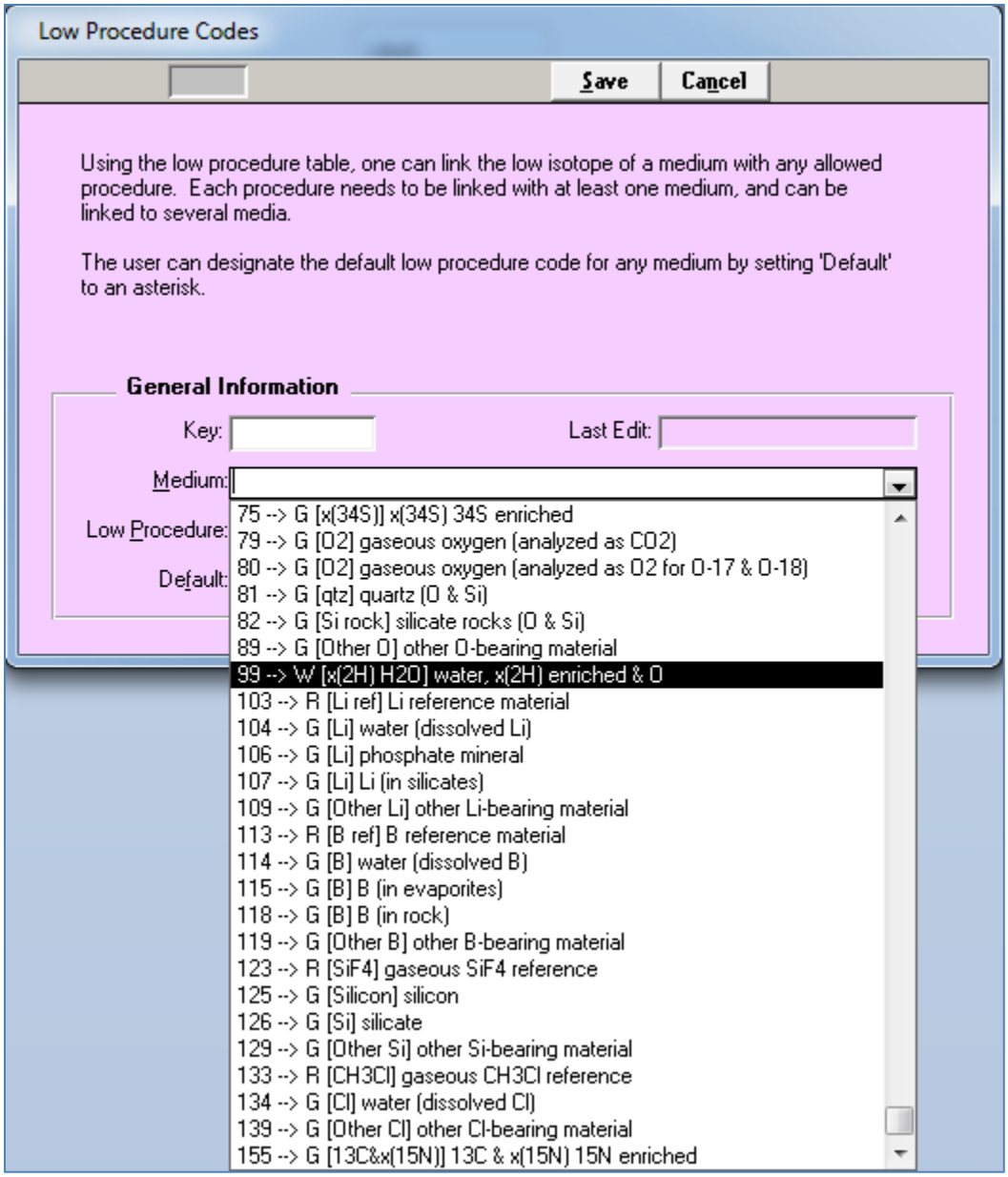


Fig. C.11. Low Procedure Codes form showing 99 for the "Medium" field.

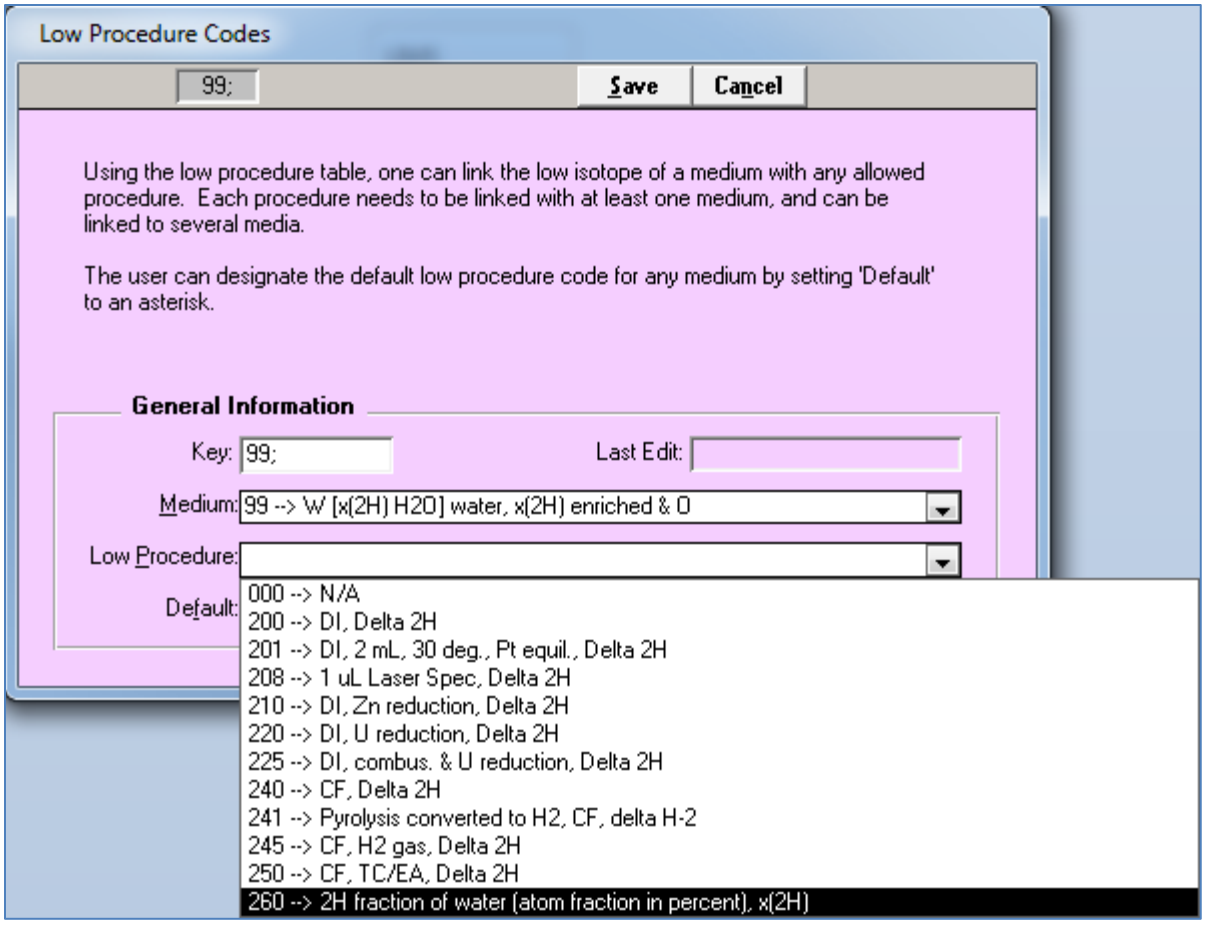


Fig. C.12. Low Procedure Codes form showing selection of 260 for the "Low Procedure" field.

Appendix D Mass Spectrometer Error Codes

One serious problem with isotope-ratio mass spectrometry is acquisition of incorrect isotopic compositions. One way this can occur is through the analysis of a sample that is so large that it saturates one of the electrometers (usually at about 12 V or 50 V, depending upon the instrument). It is important that isotopic data generated in such a manner is identified to the user. One method is to assign an error code indicating that an electrometer has exceeded a specified voltage. For example, one might assign a mass spectrometer error code of 110 to indicate that an electrometer exceeded 11 V during the measurement. Mass spectrometer vendors can detect such over-limit situations with their data acquisition and control software and can identify such analyses by using the appropriate error code in their data files.

The mass spectrometer error codes are accessed using the Mass Spectrometer Error Codes form (Fig. D.1), which is opened by clicking "Mass Spec Error Codes" in Special Features. The partial list of error codes in Figure D.2 was obtained by clicking "List." As with other forms in LIMS, click "Edit" to edit an error code and click "Add" to add an error code. When adding a new error code, we suggest copying and pasting the description from a similar, existent code into the "Description" field for the new code and modifying it as necessary. For example, to add a new code 270 having the description "<0.7 V Amplitude" note that the description of code 260 is similar ("<0.6 V Amplitude"); copy it and paste it into the "Description" field when creating new code 270.

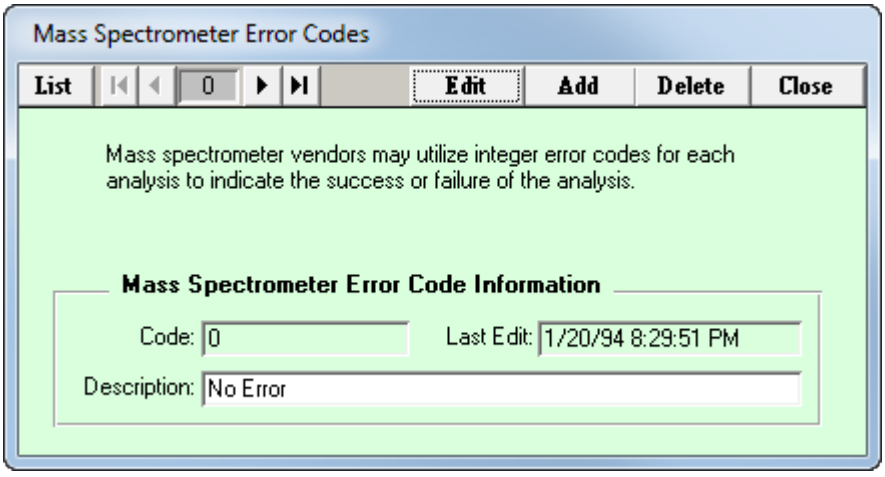


Fig. D.1. Mass Sectrometer Error Codes form.

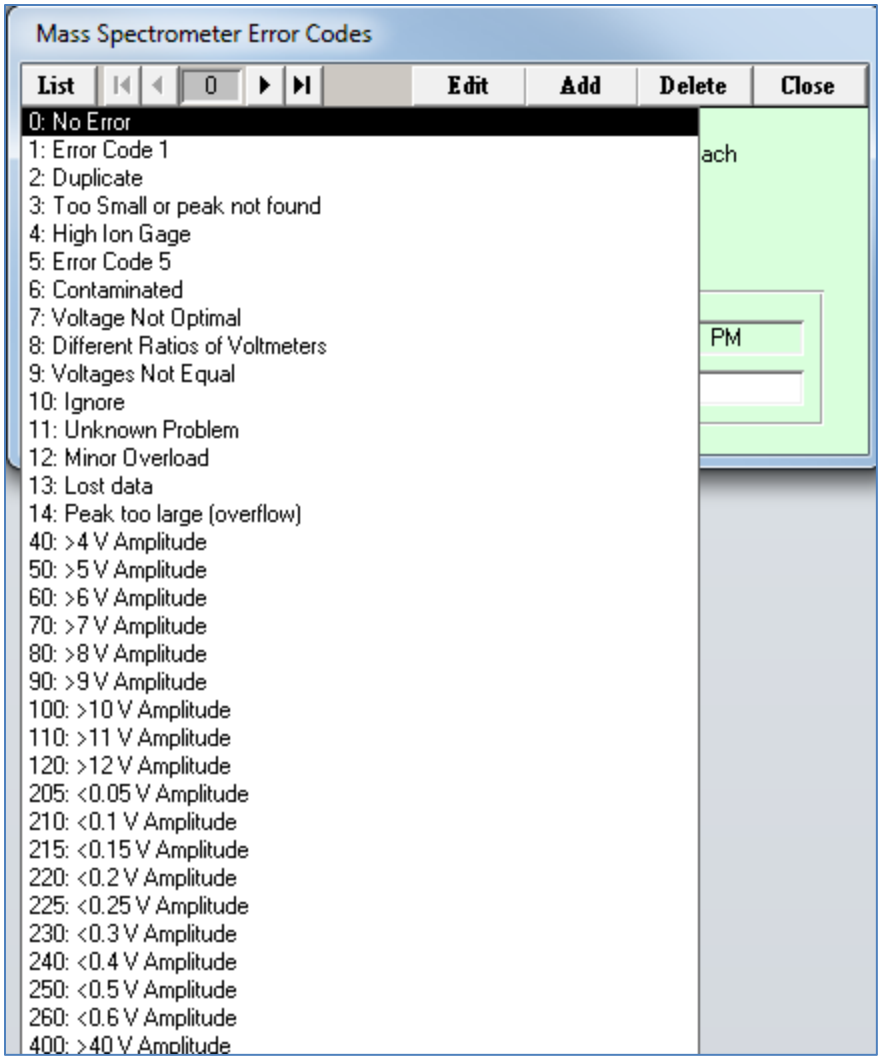


Fig. D.2. Selected mass spectrometer error codes .

Appendix E Documentation of Isotope-scale Normalization and Element Mass Fraction (Concentration) Calculations in LIMS for Light Stable Isotopes

E.1 General Information

Normalization of results in LIMS is based on Coplen.[4] Terms important for discussion of isotope-scale normalization calculations include the following:

penultimate delta	The delta value reported by ISODAT, IonOS, IonVantage, or equivalent data system. It is termed the penultimate delta because it is the one immediately calculated before the last (final) delta value that is reported to the sample submitter.
blank correction	Correction to delta value for the amount of blank in the analytical method.
hourly drift correction	The linear drift per hour over the period of the analysis of the unknowns and reference materials.
expansion coefficient	A value commonly near 1 that accounts for compression of the delta scale due to memory in the mass spectrometer and other factors.
additive correction factor	A parameter that accounts for offset in the delta value of isotopic reference materials from their assigned values.

For each dual-inlet analysis or each peak of a continuous-flow analysis, a final delta is calculated using the relation:

$$\text{final delta} = (((\text{penultimate delta} + \text{blank correction}) + \text{hourly drift correction}) \times \text{expansion coefficient}) + \text{additive correction factor} \quad (1)$$

In the case that the user applies no blank correction or hourly drift correction, Equation 1 reduces to y = mx + b format. Thus:

$$\text{final delta} = \text{penultimate delta} \times \text{expansion coefficient} + \text{additive correction factor} \quad (2)$$

The order in which calculations are performed to determine correction factors is as follows:

1. The mean blank delta value and the mean blank peak area value are determined from all analyses of the blank.
2. Using the value of mean blank delta and of mean blank peak area, LIMS updates the blank correction for each peak in LIMS (in Access table “tbl_TempAnalyses”). The sum of the penultimate delta and the blank correction is the blank corrected delta value.
3. Using the mean blank peak area and the mass fraction of the element in reference materials analyzed with the unknowns, LIMS uses mass balance to calculate the mass

fraction of element (elemental concentration) for each peak and updates Access table "tbl_TempAnalyses" accordingly.

4. Using the blank corrected delta values determined in step 2 above, LIMS calculates the hourly drift correction using linear least squares regression and updates "tbl_TempAnalyses." The sum of the blank corrected delta values and the hourly drift correction is termed the "blank and drift corrected delta value."
5. Using the blank and drift corrected delta values of each of the isotopic reference materials analyzed with the unknowns, LIMS uses linear least squares regression and calculates the expansion coefficient and additive correction factor (see Equation 1) and updates Access table "tbl_TempAnalyses."
6. With the expansion coefficient and additive correction factor, LIMS determines the final delta of each peak in the range of analyses and displays these values in the lower pane of the Normalization Equation Coefficients form (Section 24.3 and Figs. 24.10 and 24.28).

E.2 Sulfur Example

E.2.1 Isotope-scale Normalization

To demonstrate isotope-scale normalization and element mass fraction (concentration) calculations, the file "Documentation_Demo.zip" is provided in a folder named "Appendix E" that accompanies this manual. The following seven files can be extracted from this zip file:

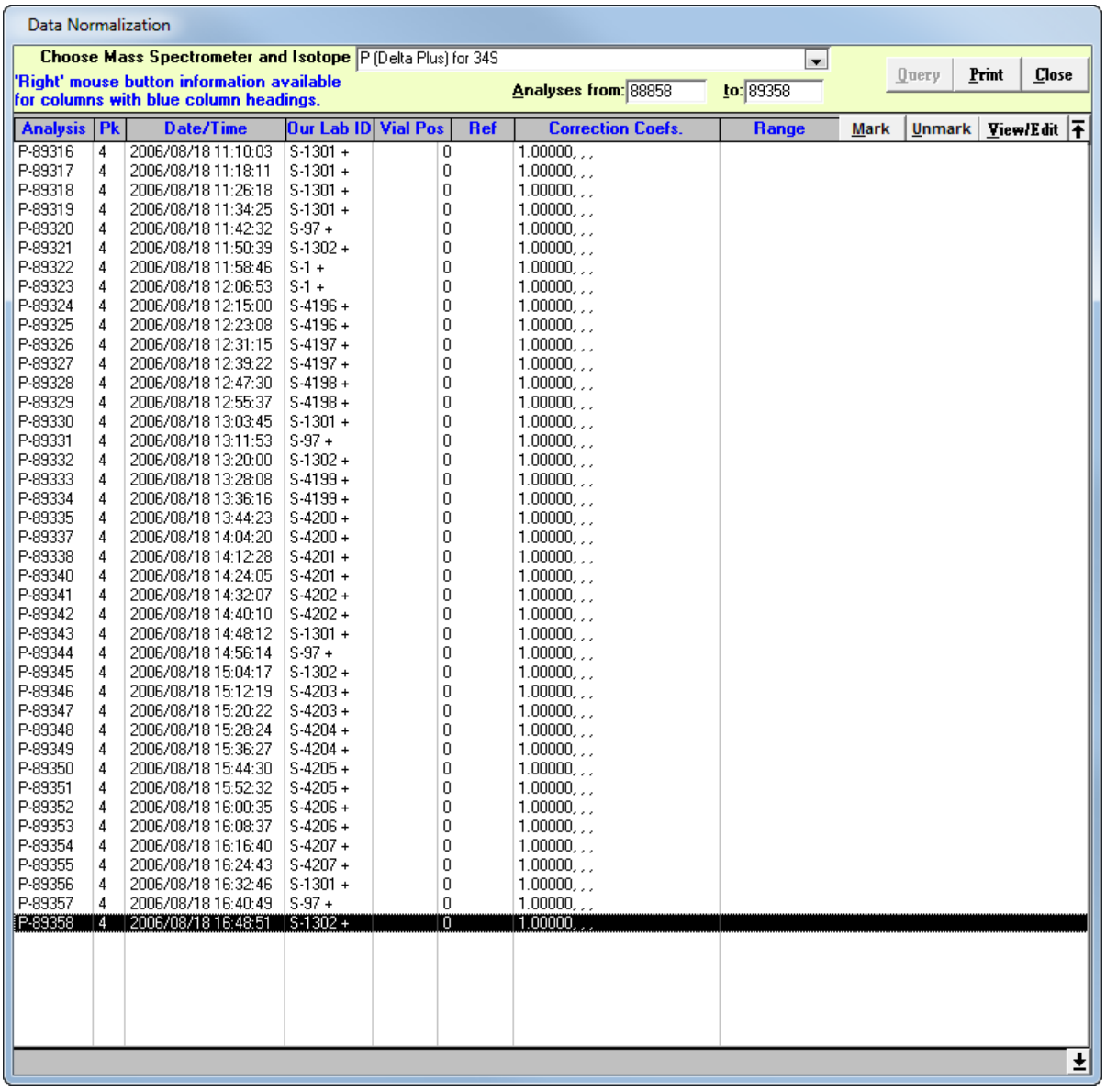
- Documentation Backend.accdb
- TempAnalyses.xlsx
- Drift Correction.xls
- ExpansionAndAdditiveCorr.xls
- TempAnalyses_with_3_ref_normalization.xlsx
- TempAnalyses_with_blank_correction&Norm.xlsx
- TempAnalyses_with_blank_&_drift_corr_&_norm.xlsx

To begin this demonstration:

1. Create a new folder. It can be within a LIMS folder or elsewhere.
2. Identify the folder as an Access Trusted Location (Section 3.2.2).
3. Copy the zip file "Documentation_Demo.zip," which is located in a folder named "Appendix E" that accompanies this manual, into this new folder and extract the files from it, keeping them in this new folder.
4. Transfer into this new folder a fresh copy of the LIMS frontend, which is named "Lims9.202.zip" (or similar) and is located in a folder named "Section 4" that accompanies this manual. Extract the file from this zip file into the same folder—it will be named "Lims9.202.accdb" or similar.

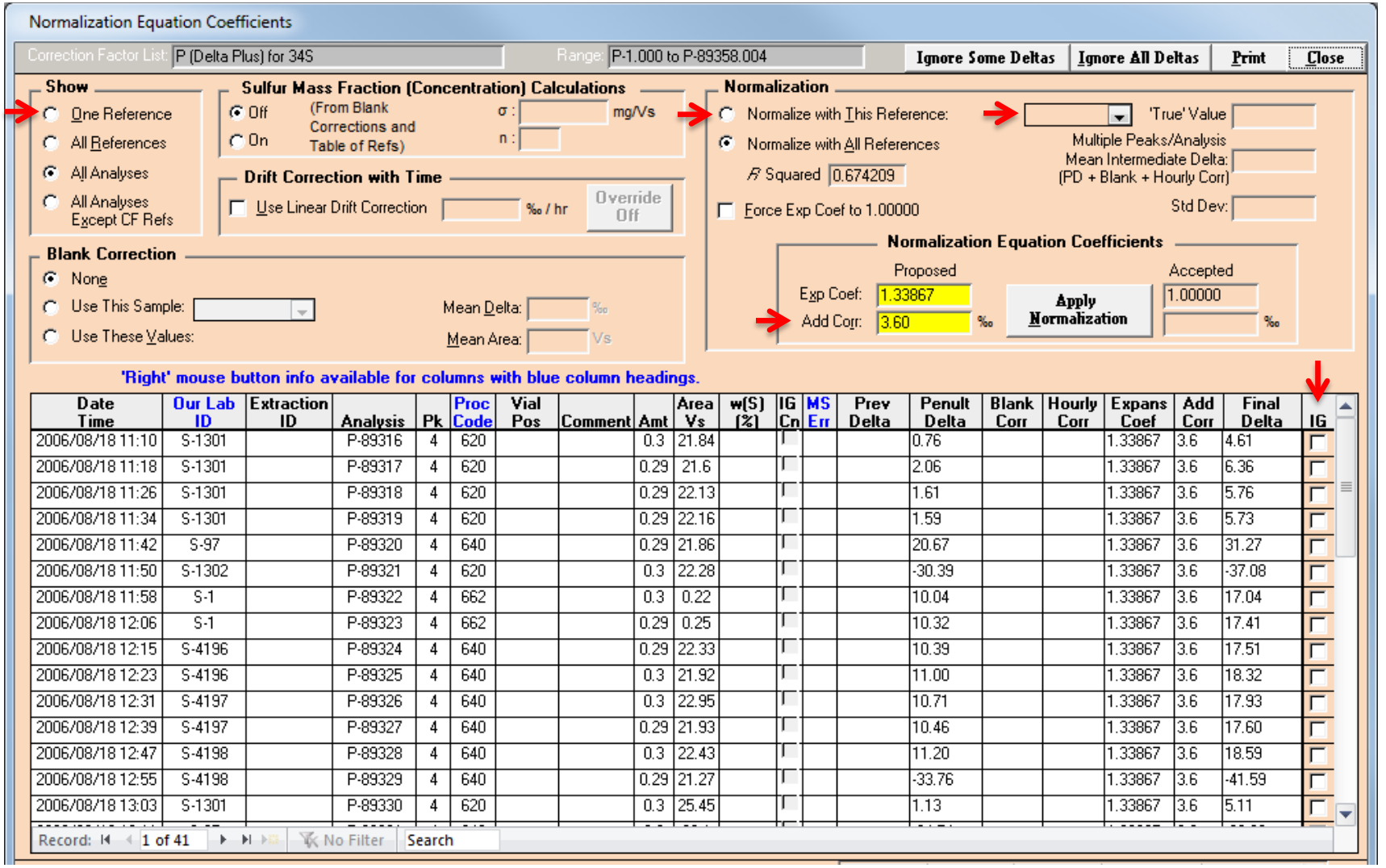
5. Double-click the new frontend (Lims9.202.accdb or similar) to open it. It should open with the message that LIMS cannot find the backend database (Fig. 4.1).
6. Click "OK" and navigate to "Documentation Backend.accdb."
7. LIMS will display a message that it needs to close.
8. Click "OK."
9. Reopen this frontend database and LIMS should display the welcome message in Figure 4.18.
10. Click "Yes" and LIMS will prompt that it needs to update settings and close.
11. Click "OK" and LIMS will perform cleanup activities upon closing.
12. Reopen this frontend database and LIMS will open with a dialog box that LIMS can now make a backup for each day of the week (Fig. A.2).
13. Click "OK" and LIMS will display the main page (similar to Fig. 4.8).
14. Click "Special Features."
15. Click "Backend db" and the BackEnd and FrontEnd Databases form will open.
16. Uncheck the "Enable creation of as many as 7 backups (Monday, Tuesday, Wednesday, Thursday, Friday, Saturday, and Sunday)" check box, because this is only a LIMS example.
17. Click "Close" to close the BackEnd and FrontEnd Databases form.
18. Click "Mass Specs" and the Mass Spec form will open.
19. Navigate to the P mass spectrometer ("Delta Plus") and note that this mass spectrometer is a continuous-flow IRMS with δ^{34}S capability.
20. Click "Close" to return to the main page.
21. One set of δ^{34}S data was previously imported. To view these data, click "Apply Data Normalization" and the Data Normalization form opens.
22. Select "P (Delta Plus) for 34S" (the only choice) for the mass spectrometer and isotope.
23. Click "Query" and the Data Normalization form shows the Delta Plus data (Fig. E.1).
24. Double click on the last analysis (P-86358), and LIMS opens the Normalization Equation Coefficients form and displays a message that it will determine best fitting normalization equation coefficients.
25. Click "OK" and the Normalization Equation Coefficients form appears (Fig. E.2.)
26. Review the δ^{34}S values of the references and ignore any that are obvious problems. Select "One Reference" in the Show panel in the upper left of the form.
27. Select "Normalize with This Reference" in the Normalization pane and LIMS shows the data for S-1301 (IAEA-SO-5) (Fig. E.3).
28. The standard deviation ("Std Dev" field in the "Normalization" panel in the upper right of the form) is 0.50 ‰, which is somewhat higher than expected. A common strategy is to ignore the lowest and highest delta values. Therefore, click the "IG" check boxes of the second and sixth analyses, and the standard deviation reduces to 0.36 ‰ (Fig. E.4). The proposed additive correction factor for normalization with one isotopic reference material (S-1301) is –0.79 ‰ and is shown in the text box with yellow background.

29. In the “Normalization” panel select reference S-97 (NBS 127) and notice that the standard deviation increases to 22.45 ‰.
30. Ignore analysis P-89331 by clicking the “IG” check box for analysis P-89311, and the standard deviation improves to 0.38 ‰.
31. In the “Normalization” panel select reference S-1302 (IAEA-SO-6) and note that the standard deviation is satisfactory (0.12 ‰).



Analysis	Pk	Date/Time	Our Lab ID	Vial Pos	Ref	Correction Coefs.	Range
P-89316	4	2006/08/18 11:10:03	S-1301 +		0	1.00000, , ,	
P-89317	4	2006/08/18 11:18:11	S-1301 +		0	1.00000, , ,	
P-89318	4	2006/08/18 11:26:18	S-1301 +		0	1.00000, , ,	
P-89319	4	2006/08/18 11:34:25	S-1301 +		0	1.00000, , ,	
P-89320	4	2006/08/18 11:42:32	S-97 +		0	1.00000, , ,	
P-89321	4	2006/08/18 11:50:39	S-1302 +		0	1.00000, , ,	
P-89322	4	2006/08/18 11:58:46	S-1 +		0	1.00000, , ,	
P-89323	4	2006/08/18 12:06:53	S-1 +		0	1.00000, , ,	
P-89324	4	2006/08/18 12:15:00	S-4196 +		0	1.00000, , ,	
P-89325	4	2006/08/18 12:23:08	S-4196 +		0	1.00000, , ,	
P-89326	4	2006/08/18 12:31:15	S-4197 +		0	1.00000, , ,	
P-89327	4	2006/08/18 12:39:22	S-4197 +		0	1.00000, , ,	
P-89328	4	2006/08/18 12:47:30	S-4198 +		0	1.00000, , ,	
P-89329	4	2006/08/18 12:55:37	S-4198 +		0	1.00000, , ,	
P-89330	4	2006/08/18 13:03:45	S-1301 +		0	1.00000, , ,	
P-89331	4	2006/08/18 13:11:53	S-97 +		0	1.00000, , ,	
P-89332	4	2006/08/18 13:20:00	S-1302 +		0	1.00000, , ,	
P-89333	4	2006/08/18 13:28:08	S-4199 +		0	1.00000, , ,	
P-89334	4	2006/08/18 13:36:16	S-4199 +		0	1.00000, , ,	
P-89335	4	2006/08/18 13:44:23	S-4200 +		0	1.00000, , ,	
P-89337	4	2006/08/18 14:04:20	S-4200 +		0	1.00000, , ,	
P-89338	4	2006/08/18 14:12:28	S-4201 +		0	1.00000, , ,	
P-89340	4	2006/08/18 14:24:05	S-4201 +		0	1.00000, , ,	
P-89341	4	2006/08/18 14:32:07	S-4202 +		0	1.00000, , ,	
P-89342	4	2006/08/18 14:40:10	S-4202 +		0	1.00000, , ,	
P-89343	4	2006/08/18 14:48:12	S-1301 +		0	1.00000, , ,	
P-89344	4	2006/08/18 14:56:14	S-97 +		0	1.00000, , ,	
P-89345	4	2006/08/18 15:04:17	S-1302 +		0	1.00000, , ,	
P-89346	4	2006/08/18 15:12:19	S-4203 +		0	1.00000, , ,	
P-89347	4	2006/08/18 15:20:22	S-4203 +		0	1.00000, , ,	
P-89348	4	2006/08/18 15:28:24	S-4204 +		0	1.00000, , ,	
P-89349	4	2006/08/18 15:36:27	S-4204 +		0	1.00000, , ,	
P-89350	4	2006/08/18 15:44:30	S-4205 +		0	1.00000, , ,	
P-89351	4	2006/08/18 15:52:32	S-4205 +		0	1.00000, , ,	
P-89352	4	2006/08/18 16:00:35	S-4206 +		0	1.00000, , ,	
P-89353	4	2006/08/18 16:08:37	S-4206 +		0	1.00000, , ,	
P-89354	4	2006/08/18 16:16:40	S-4207 +		0	1.00000, , ,	
P-89355	4	2006/08/18 16:24:43	S-4207 +		0	1.00000, , ,	
P-89356	4	2006/08/18 16:32:46	S-1301 +		0	1.00000, , ,	
P-89357	4	2006/08/18 16:40:49	S-97 +		0	1.00000, , ,	
P-89358	4	2006/08/18 16:48:51	S-1302 +		0	1.00000, , ,	

Fig. E.1. Data normalization form showing Delta Plus δ^{34}S data.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(S) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2006/08/18 11:10	S-1301		P-89316	4	620			0.3	21.84					0.76			1.33867	3.6	4.61	
2006/08/18 11:18	S-1301		P-89317	4	620			0.29	21.6					2.06			1.33867	3.6	6.36	
2006/08/18 11:26	S-1301		P-89318	4	620			0.29	22.13					1.61			1.33867	3.6	5.76	
2006/08/18 11:34	S-1301		P-89319	4	620			0.29	22.16					1.59			1.33867	3.6	5.73	
2006/08/18 11:42	S-97		P-89320	4	640			0.29	21.86					20.67			1.33867	3.6	31.27	
2006/08/18 11:50	S-1302		P-89321	4	620			0.3	22.28					-30.39			1.33867	3.6	-37.08	
2006/08/18 11:58	S-1		P-89322	4	662			0.3	0.22					10.04			1.33867	3.6	17.04	
2006/08/18 12:06	S-1		P-89323	4	662			0.29	0.25					10.32			1.33867	3.6	17.41	
2006/08/18 12:15	S-4196		P-89324	4	640			0.29	22.33					10.39			1.33867	3.6	17.51	
2006/08/18 12:23	S-4196		P-89325	4	640			0.3	21.92					11.00			1.33867	3.6	18.32	
2006/08/18 12:31	S-4197		P-89326	4	640			0.3	22.95					10.71			1.33867	3.6	17.93	
2006/08/18 12:39	S-4197		P-89327	4	640			0.29	21.93					10.46			1.33867	3.6	17.60	
2006/08/18 12:47	S-4198		P-89328	4	640			0.3	22.43					11.20			1.33867	3.6	18.59	
2006/08/18 12:55	S-4198		P-89329	4	640			0.29	21.27					-33.76			1.33867	3.6	-41.59	
2006/08/18 13:03	S-1301		P-89330	4	620			0.3	25.45					1.13			1.33867	3.6	5.11	

Fig. E.2. Data normalization form showing Delta Plus δ^{34}S data.

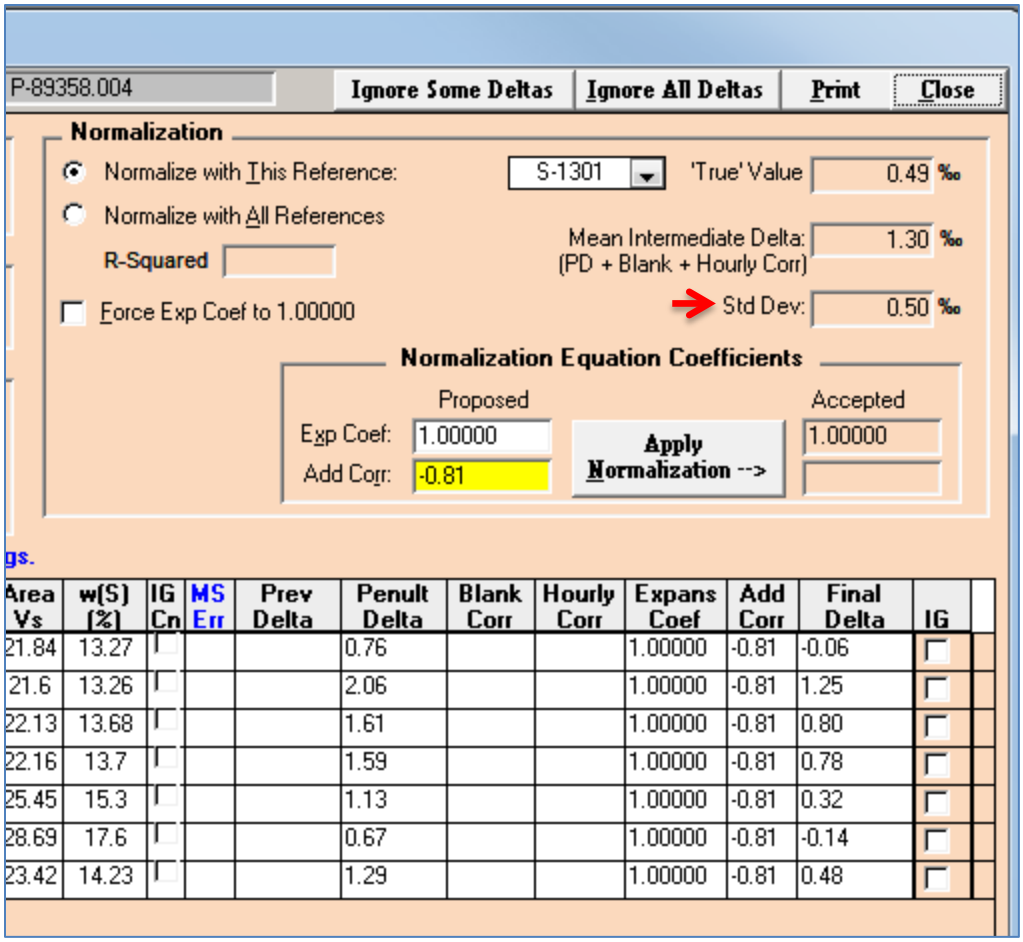


Fig. E.3. S-1301 δ^{34}S data.

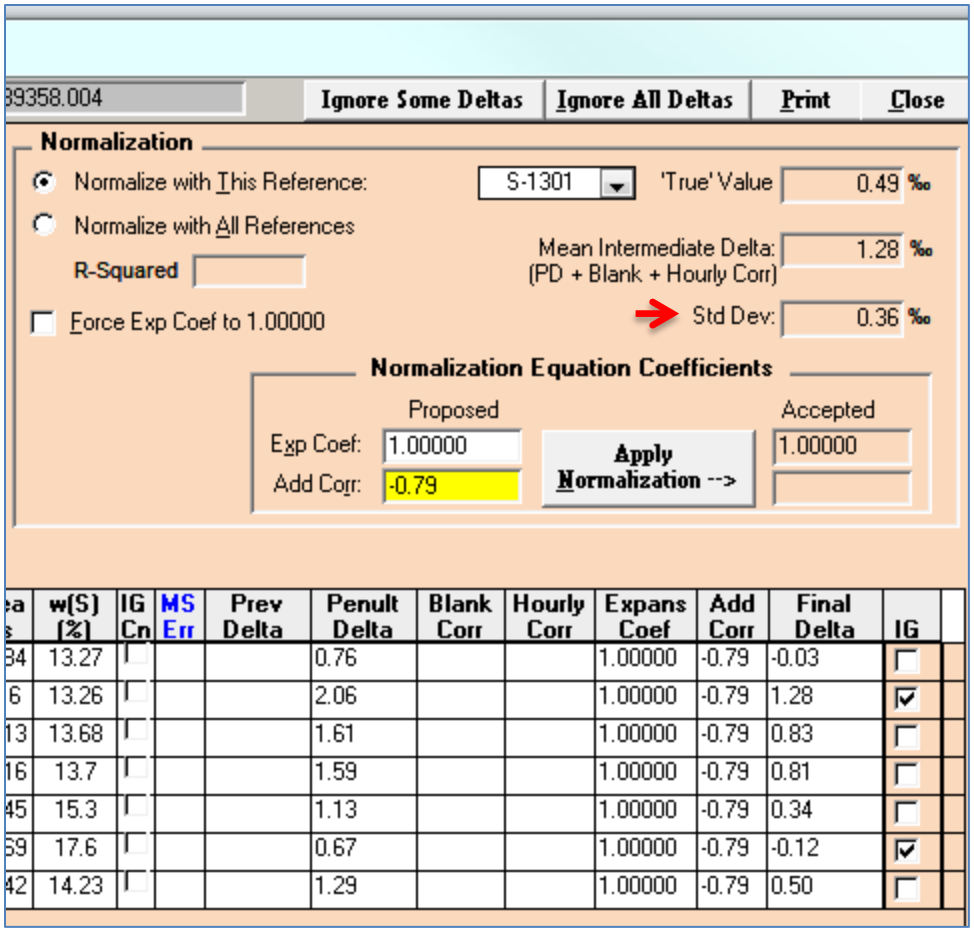
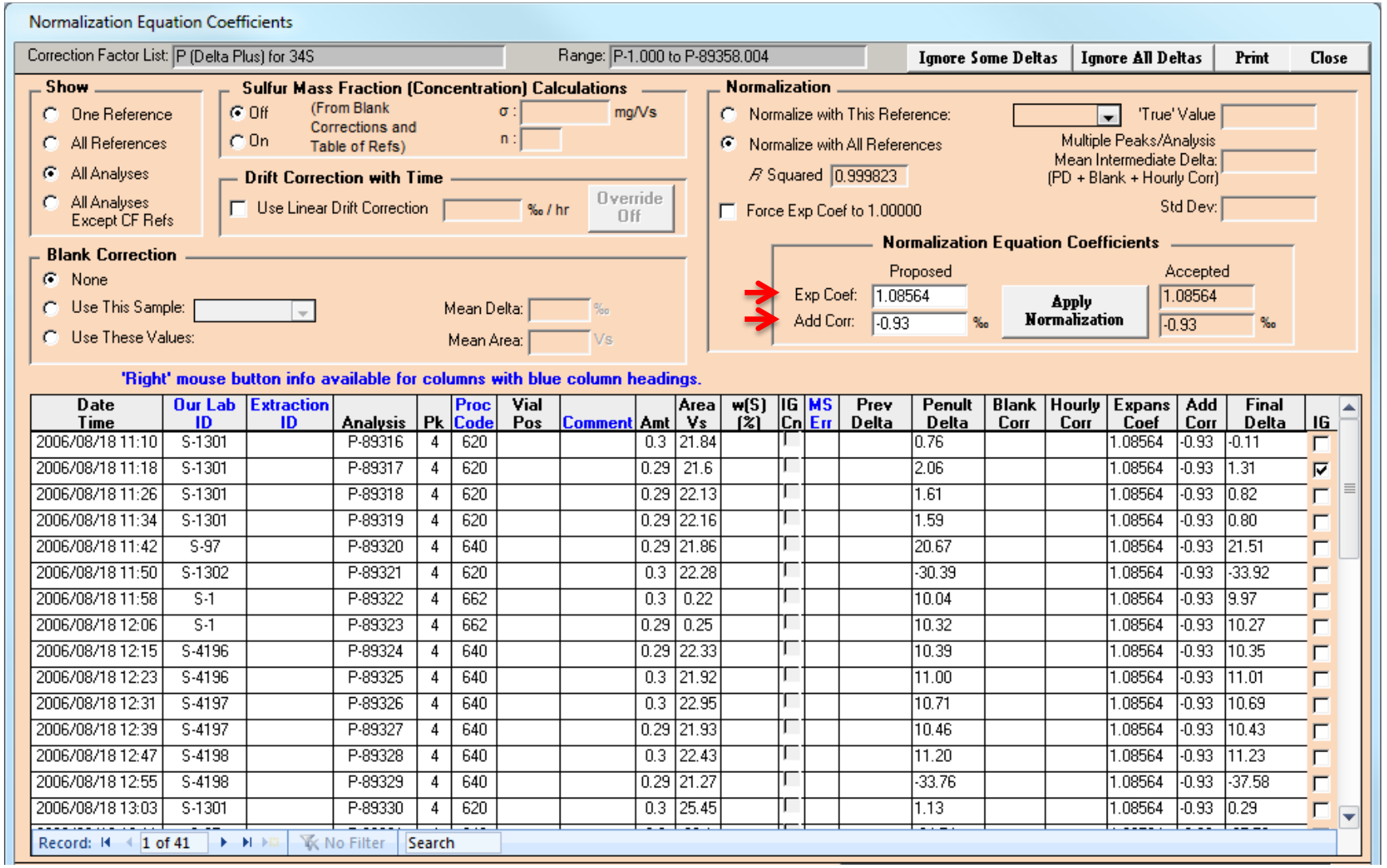


Fig. E.4. S-1301 δ^{34}S data with two analyses ignored. Standard deviation improves somewhat to 0.36 ‰.

32. Click the "Normalize with All References option" and note that expansion coefficient and additive correction factors change to 1.08564 and –0.93 ‰, respectively.
33. Click "Apply Normalization" to update the values in the "Final Delta" column.
34. Click the "All References" option in the Show panel and the Normalization Equation Coefficients form shows "Final Delta" values calculated using Equation 2 with an expansion coefficient of 1.08564 and an additive correction factor of –0.93 ‰ (Fig. E.5) because the blank correction and hourly drift correction values are null (treated as zero). These results can be documented by clicking "Print."
35. To view all analyses, click "All Analyses."

The "Final Delta" values are updated internally in the Access table "tbl_TempAnalyses," whose fields are described in Table E.1. The values for all analyses (step 35) have been exported to an



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(S) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2006/08/18 11:10	S-1301		P-89316	4	620			0.3	21.84					0.76			1.08564	-0.93	-0.11	
2006/08/18 11:18	S-1301		P-89317	4	620			0.29	21.6					2.06			1.08564	-0.93	1.31	☑
2006/08/18 11:26	S-1301		P-89318	4	620			0.29	22.13					1.61			1.08564	-0.93	0.82	
2006/08/18 11:34	S-1301		P-89319	4	620			0.29	22.16					1.59			1.08564	-0.93	0.80	
2006/08/18 11:42	S-97		P-89320	4	640			0.29	21.86					20.67			1.08564	-0.93	21.51	
2006/08/18 11:50	S-1302		P-89321	4	620			0.3	22.28					-30.39			1.08564	-0.93	-33.92	
2006/08/18 11:58	S-1		P-89322	4	662			0.3	0.22					10.04			1.08564	-0.93	9.97	
2006/08/18 12:06	S-1		P-89323	4	662			0.29	0.25					10.32			1.08564	-0.93	10.27	
2006/08/18 12:15	S-4196		P-89324	4	640			0.29	22.33					10.39			1.08564	-0.93	10.35	
2006/08/18 12:23	S-4196		P-89325	4	640			0.3	21.92					11.00			1.08564	-0.93	11.01	
2006/08/18 12:31	S-4197		P-89326	4	640			0.3	22.95					10.71			1.08564	-0.93	10.69	
2006/08/18 12:39	S-4197		P-89327	4	640			0.29	21.93					10.46			1.08564	-0.93	10.43	
2006/08/18 12:47	S-4198		P-89328	4	640			0.3	22.43					11.20			1.08564	-0.93	11.23	
2006/08/18 12:55	S-4198		P-89329	4	640			0.29	21.27					-33.76			1.08564	-0.93	-37.58	
2006/08/18 13:03	S-1301		P-89330	4	620			0.3	25.45					1.13			1.08564	-0.93	0.29	

Fig. E.5. Normalization Equation Coefficients form with normalization using all three isotopic reference materials.

Table E.1 Description of data in LIMS Access table tbl_TempAnalyses and the Excel file TempAnalyses.xls

Column	Name	Description
A	rstr_MassSpec	Single character mass spectrometer ID.
B	lng_Analysis	Analysis number, which is an integer greater than 1.
C	lng_PeakNumber	Peak number, which is an integer between 1 and 999.
D	rint_Procedure	LIMS procedure code (analytical method)
E	rstr_Prefix	Single character prefix of the LIMS OurLabID. Either C, G, J, N, R, S, or W.
F	rlng_Sample	Numeric part of the LIMS OurLabID. An integer.
G	str_AliquotID	Aliquot ID (also called Extraction ID) in an analysis.
H	str_Port	Port identifier of a peripheral device on which a sample is loaded or prepared for analysis.
I	str_Std	Name of standard or a value of -1, Yes, or True indicates the peak is a reference injection measurement.
J	dat_Analyzed	Date and time of start of analysis. All peaks in the same analysis number may have identical date-time values.
K	str_Comment	A comment entered in the ISODAT sequence table comment field or equivalent fields in IonOS or IonVantage, etc.
L	ysn_IgnoreNumericComment	The Options form has a check box to enable LIMS to display the average of comment field entries if they are numeric. True indicates that LIMS will not calculate and display the mean value even if the comments are numeric values.
M	dbl_Amount	Numerical amount of sample.
N	str_AmountUnit	Unit of amount, such as ug, mg, or mL.
O	dbl_Area	Peak area in Vs.
P	dbl_Conc	Elemental mass fraction (concentration) calculated by LIMS.
Q	ysn_IgnoreConc	True indicates that this analysis should not be used in

		mass fraction (element concentration) calculations.
R	dbl_PenultimateDelta	The delta value reported by ISODAT, IonOS, IonVantage, etc. to LIMS.
S	rint_Error	Mass spectrometer error code.
T	ysn_Ignore	True indicates that this analysis should not be used in delta calculations.
U	dbl_BlankCorrection	Value of the blank correction, which is determined by LIMS.
V	dbl_HourlyCorrection	Value of the hourly drift correction, which is calculated by LIMS.
W	dbl_ExpandCoef	Expansion coefficient calculated by LIMS.
X	dbl_Correction	Additive correction factor calculated by LIMS.
Y	cur_CorrRangeMin	Not visible in Normalization Equation Coefficients form. Contains information for the LIMS Range Marker.
Z	OurLabID	Not visible in Normalization Equation Coefficients form.
AA	Expr1	Not visible in Normalization Equation Coefficients form.
AB	Analysis	Not visible in Normalization Equation Coefficients form.
AC	FinalDelta	Final delta for each peak and analysis, calculated by LIMS.

Excel file named “TempAnalyses_with_3_ref_normalization.xlsx,” which is found in a folder named “Appendix E” that accompanies this manual

Equation (1) can be formulated for the Excel files “TempAnalyses.xls” and “TempAnalyses_with_3_ref_normalization.xlsx” as:

$$\text{column AC} = (((\text{column R} + \text{column U}) + \text{column V}) \times \text{column W}) + \text{column X} \quad (3)$$

where column R contains the penultimate delta, column U contains the blank correction values (if made), column V contains the hourly drift correction values (if made), column W contains the expansion factor, and column X contains the additive correction factor.

E.2.2 Blank Correction

The blank correction is performed by LIMS prior to determination of the hourly drift correction. The first step is to determine the mean blank delta value and the mean blank peak area value, and these are determined using the routine "s_UpdateBlankCorrDependencies" in LIMS. Three options are available to the user.

1. If the user has selected the "None" option button of the "Blank Correction" panel, LIMS uses a value of null for the average blank peak area in calculations, and the blank correction will be null.
2. If the user has specified an OurLabID to be used for blank calculations by selecting the "Use This Sample" option of the "Blank Correction" panel, LIMS first calculates for each analysis number the mean delta value and mean area of all of the peaks that are not marked "Ignore." There might be more than one peak for each analysis number. If there is only one peak per analysis number, as commonly is the case, the code in this routine uses these values as mean values. From the mean delta values and mean values of areas of each analysis number, LIMS calculates the average blank delta and average blank peak area and displays these values in the "Mean Delta" and "Mean Area" text boxes. In this manner, data from each analysis number is weighted equally even though some analyses may be comprised of more peaks than others. Note that if all the peaks in any analysis are marked ignore, no data from that analysis is included in calculations; however, the user may choose to use these data in determination of mass fraction of an element (elemental concentration).
3. If the user has specified the values of the mean delta of the blank and mean peak area of the blank by selecting the "Use These Values" option of the "Blank Correction" panel, LIMS uses the values the user has entered in the "Mean Delta" and "Mean Area" text boxes as the average blank delta and average blank peak area in calculations.

Step 2 of the blank correction calculations is to calculate the blank correction for each peak. In LIMS,

$$\text{blank correction} = \text{blank corrected delta value} - \text{penultimate delta} \tag{4}$$

Using the mean blank delta value and the mean blank peak area value determined above, correction for value of the blank is calculated in LIMS using the isotope mass balance relations

$$\begin{aligned}&\text{peak area from "Area All" ISODAT column} \times \text{penultimate delta}\\ &\quad = \text{blank corrected peak area of sample} \times \text{blank corrected delta value of sample}\\ &\qquad + \text{blank area} \times \text{blank delta}\end{aligned} \tag{5}$$

and

$$\begin{aligned}&\text{peak area from "Area All" ISODAT column}\\ &\quad = \text{blank area} + \text{blank corrected peak area of sample}\end{aligned} \tag{6}$$

where a sample is either an unknown or an isotopic reference material. The routine "s_BlankCorrUsingInputs" in LIMS updates the blank correction values in Access table tbl_TempAnalyses using Equations (4), (5), and (6). Combining the relations, one has the algorithm that is used in LIMS, which is:

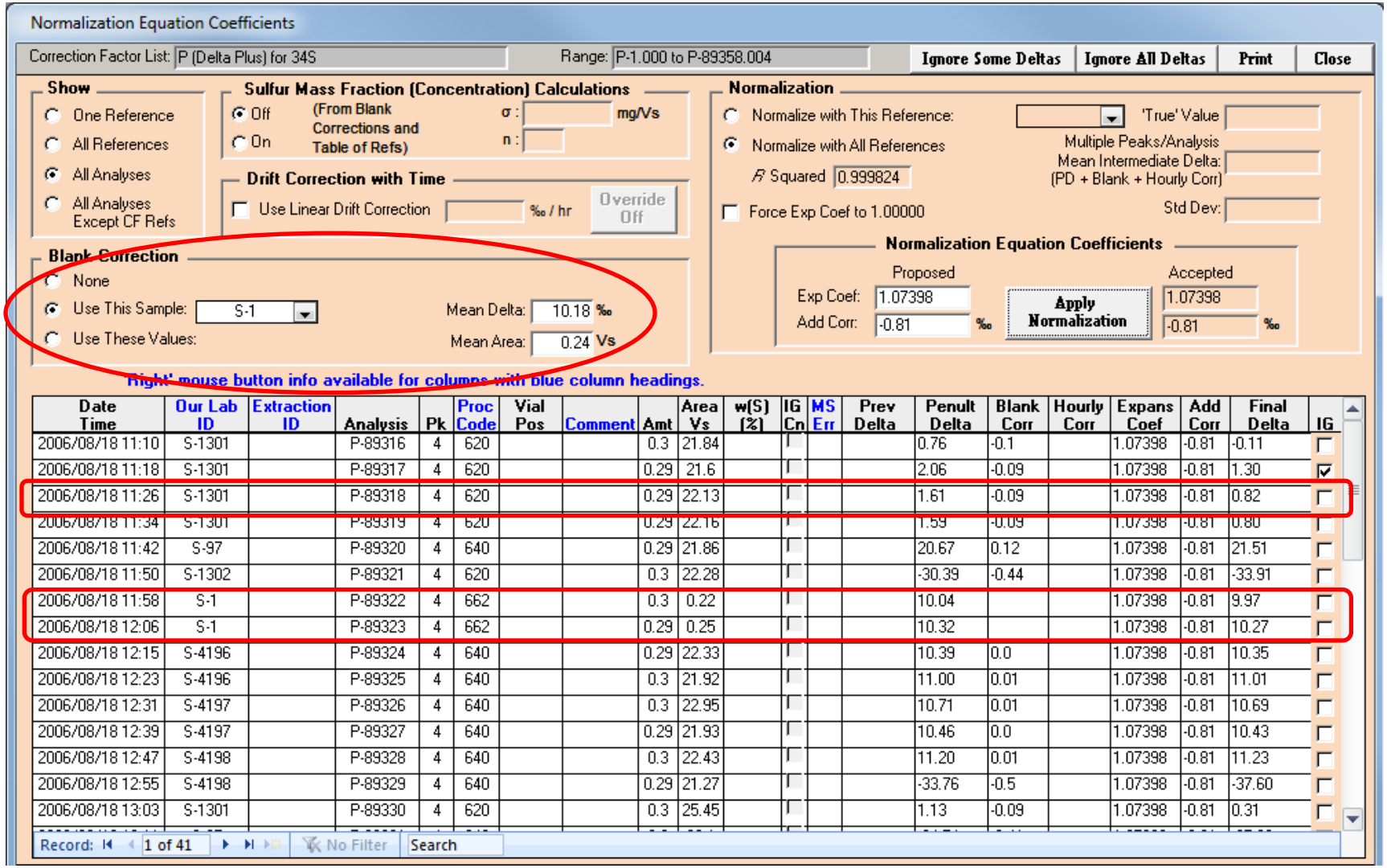
$$\begin{aligned}\text{blank correction} &= (((\text{penultimate delta}) \times (\text{peak area}) - (\text{blank delta}) \times (\text{blank area})) / \\ &\quad ((\text{peak area}) - (\text{area of blank}))) - \text{penultimate delta}\end{aligned} \tag{7}$$

Blank correction values are rounded to three significant figures after the decimal point for internal calculations of delta values of the isotopes ^{2}H, ^{13}C, ^{33}S, ^{15}N, ^{34}S, ^{17}O, ^{18}O, ^{36}S, ^{30}Si, and ^{37}Cl.

As an example of the application of these equations:

1. On the Normalization Equation Coefficients form shown in Figure E.5, select "Use This Sample" in the Blank Correction panel.
2. Select "S-1" for the blank.
3. Click "Apply Normalization -->" and LIMS updates the form to that shown in Figure E.6. The two analyses of S-1 are identified with an oval.

The underlying data source of the lower portion of Figure E.6 is the Access table "tbl_TempAnalyses." This table has been exported as an Excel file named "TempAnalyses_with_blank_correction&Norm.xlsx" and is provided in the folder named "Appendix E" that accompanies this manual. Blank S-1 was analyzed twice (analyses P-89322 and P-89323) and appears in rows 25 and 26 of the Excel file. Assuming the user selects the "Use This Sample" blank correction method, LIMS calculates a mean blank delta value of 10.18 ‰ by averaging the values in cells R25 and R26, and a mean blank peak area value of 0.2374785 Vs by averaging the values in cells O8 and O9, which is truncated in Figure E.6 to 0.24 Vs. The values in column O have been imported from the ISODAT "Area All" column. Consider determination of the blank correction for analysis P-89318 of S-1301 in row 21 of the Excel worksheet. For this analysis, the peak area (column O) is 22.129798 Vs, which is rounded to 22.13 Vs on the Normalization Equation Coefficients form. The penultimate delta (column R) is 1.613 ‰, which is rounded to 1.61 ‰ on the Normalization Equation Coefficients form. Using a blank area value of 0.2374785 Vs and a mean blank delta value of 10.18 ‰ in Equation (7), a blank correction value of –0.093 ‰ is calculated, and LIMS updates column U with this value. This value is rounded to –0.09 ‰ when displayed in the lower pane of the Normalization Equation Coefficients form (Fig. E.6).



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(S) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2006/08/18 11:10	S-1301		P-89316	4	620			0.3	21.84					0.76	-0.1		1.07398	-0.81	-0.11	
2006/08/18 11:18	S-1301		P-89317	4	620			0.29	21.6					2.06	-0.09		1.07398	-0.81	1.30	☑
2006/08/18 11:26	S-1301		P-89318	4	620			0.29	22.13					1.61	-0.09		1.07398	-0.81	0.82	
2006/08/18 11:34	S-1301		P-89319	4	620			0.29	22.16					1.59	-0.09		1.07398	-0.81	0.80	
2006/08/18 11:42	S-97		P-89320	4	640			0.29	21.86					20.67	0.12		1.07398	-0.81	21.51	
2006/08/18 11:50	S-1302		P-89321	4	620			0.3	22.28					-30.39	-0.44		1.07398	-0.81	-33.91	
2006/08/18 11:58	S-1		P-89322	4	662			0.3	0.22					10.04			1.07398	-0.81	9.97	
2006/08/18 12:06	S-1		P-89323	4	662			0.29	0.25					10.32			1.07398	-0.81	10.27	
2006/08/18 12:15	S-4196		P-89324	4	640			0.29	22.33					10.39	0.0		1.07398	-0.81	10.35	
2006/08/18 12:23	S-4196		P-89325	4	640			0.3	21.92					11.00	0.01		1.07398	-0.81	11.01	
2006/08/18 12:31	S-4197		P-89326	4	640			0.3	22.95					10.71	0.01		1.07398	-0.81	10.69	
2006/08/18 12:39	S-4197		P-89327	4	640			0.29	21.93					10.46	0.0		1.07398	-0.81	10.43	
2006/08/18 12:47	S-4198		P-89328	4	640			0.3	22.43					11.20	0.01		1.07398	-0.81	11.23	
2006/08/18 12:55	S-4198		P-89329	4	640			0.29	21.27					-33.76	-0.5		1.07398	-0.81	-37.60	
2006/08/18 13:03	S-1301		P-89330	4	620			0.3	25.45					1.13	-0.09		1.07398	-0.81	0.31	

Fig. E.6. Normalization Equation Coefficients form with blank correction using S-1 and normalization.

E.2.3 Hourly Drift Correction

Users can correct for linear drift in delta values over the period of the analysis run (typically hours or a few tens of hours) by checking the "Use Linear Drift Correction" check box on the Normalization Equation Coefficients form. When this check box is checked, LIMS will calculate hourly drift correction values based on a single references. When "Normalize with This Reference" option is selected, LIMS will use the most recently selected reference for hourly drift correction calculations. Because the hourly drift correction values rely on the blank correction values, LIMS will calculate blank correction values prior to calculating hourly drift correction values. As an example of the calculation of hourly drift correction:

1. On the Normalization Equation Coefficients form shown in Figure E.6, click the "Use Linear Drift Correction" check box in the Drift Correction with Time panel and LIMS provides the message shown in Figure E.7 on how LIMS calculates the hourly drift correction of –0.002 ‰/hr, which is shown in the Drift Correction with Time panel.
2. Click "OK."
3. Click "Apply Normalization -->" and LIMS updates the form (Fig. E.8). The hourly drift correction values are all 0.0 and are indicated with an oval, which indicates that the hourly drift correction values are less than 0.05 ‰ for the analyses shown. Scrolling down to analysis P-89334, one finds a value of –0.01 ‰. These values are determined from the five analyses of S-1301 that are not ignored (Table E.2).

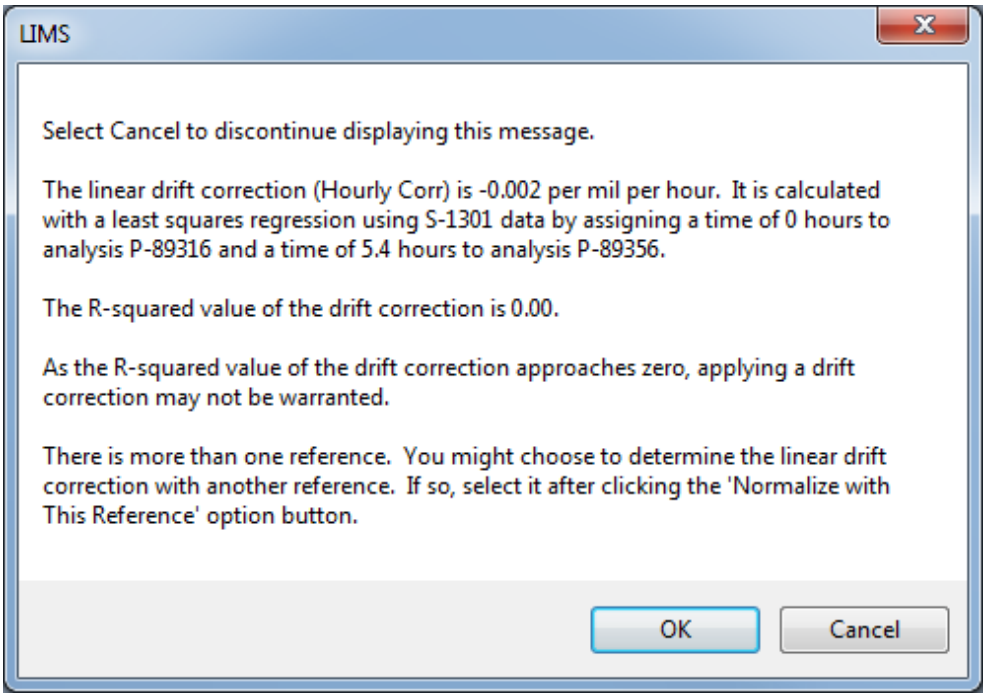
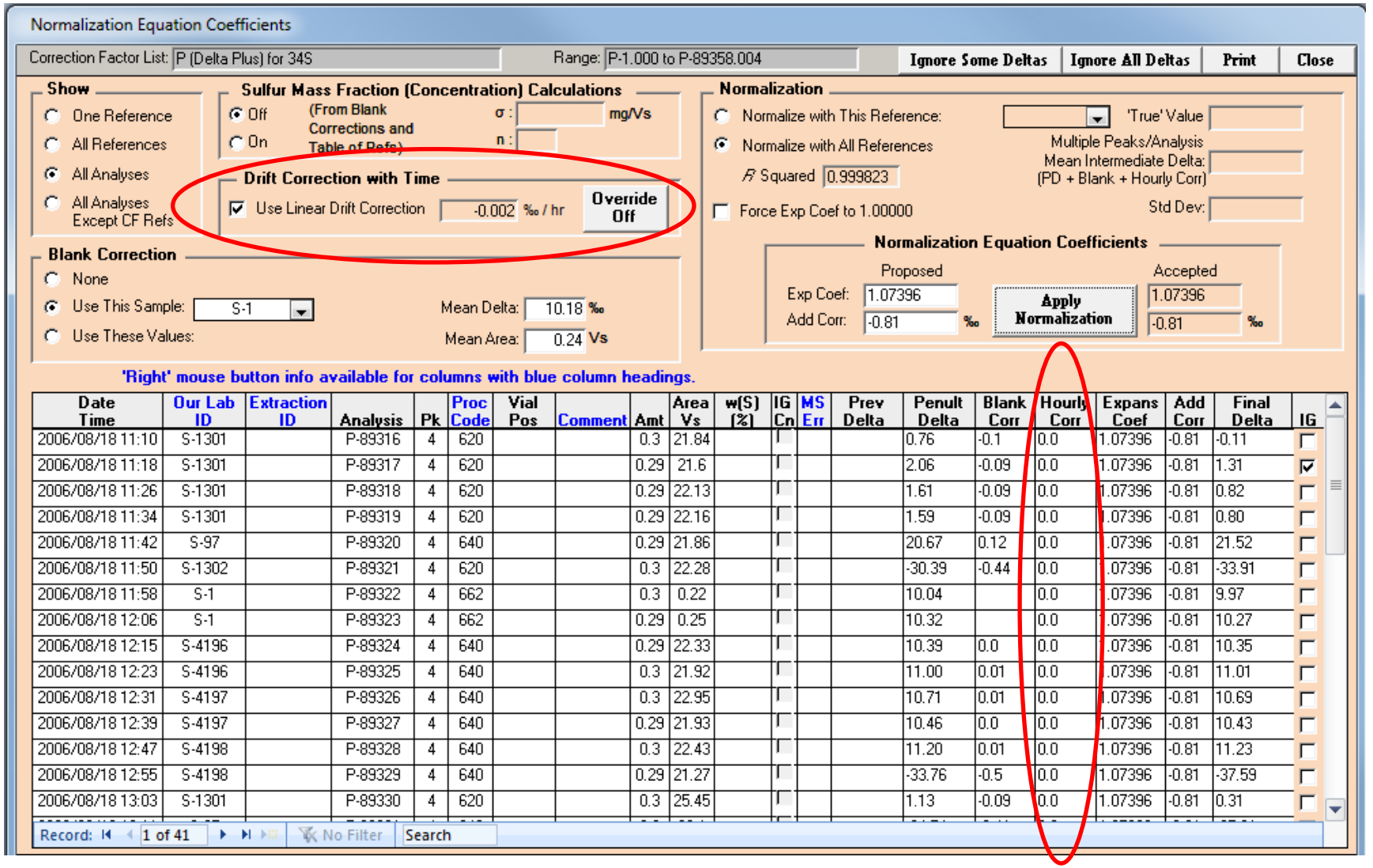


Fig. E.7. Drift correction message provided by LIMS.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(S) [%]	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2006/08/18 11:10	S-1301		P-89316	4	620			0.3	21.84					0.76	-0.1	0.0	1.07396	-0.81	-0.11	
2006/08/18 11:18	S-1301		P-89317	4	620			0.29	21.6					2.06	-0.09	0.0	1.07396	-0.81	1.31	☑
2006/08/18 11:26	S-1301		P-89318	4	620			0.29	22.13					1.61	-0.09	0.0	1.07396	-0.81	0.82	
2006/08/18 11:34	S-1301		P-89319	4	620			0.29	22.16					1.59	-0.09	0.0	1.07396	-0.81	0.80	
2006/08/18 11:42	S-97		P-89320	4	640			0.29	21.86					20.67	0.12	0.0	.07396	-0.81	21.52	
2006/08/18 11:50	S-1302		P-89321	4	620			0.3	22.28					-30.39	-0.44	0.0	.07396	-0.81	-33.91	
2006/08/18 11:58	S-1		P-89322	4	662			0.3	0.22					10.04		0.0	.07396	-0.81	9.97	
2006/08/18 12:06	S-1		P-89323	4	662			0.29	0.25					10.32		0.0	.07396	-0.81	10.27	
2006/08/18 12:15	S-4196		P-89324	4	640			0.29	22.33					10.39	0.0	0.0	.07396	-0.81	10.35	
2006/08/18 12:23	S-4196		P-89325	4	640			0.3	21.92					11.00	0.01	0.0	.07396	-0.81	11.01	
2006/08/18 12:31	S-4197		P-89326	4	640			0.3	22.95					10.71	0.01	0.0	.07396	-0.81	10.69	
2006/08/18 12:39	S-4197		P-89327	4	640			0.29	21.93					10.46	0.0	0.0	1.07396	-0.81	10.43	
2006/08/18 12:47	S-4198		P-89328	4	640			0.3	22.43					11.20	0.01	0.0	1.07396	-0.81	11.23	
2006/08/18 12:55	S-4198		P-89329	4	640			0.29	21.27					-33.76	-0.5	0.0	1.07396	-0.81	-37.59	
2006/08/18 13:03	S-1301		P-89330	4	620			0.3	25.45					1.13	-0.09	0.0	1.07396	-0.81	0.31	

Fig. E.8. Normalization Equation Coefficients form after blank correction, drift correction, and normalization.

Table E.2. Drift correction using S-1301

Analysis number	Analysis date-time	Time (hr)	Penultimate delta (‰)	Blank correction (‰)	Blank corrected delta (‰)
89316	8/18/06 11:10	0.000	0.755	–0.103	0.652
89318	8/18/06 11:26	0.271	1.613	–0.093	1.520
89319	8/18/06 11:34	0.406	1.59	–0.093	1.497
89330	8/18/06 13:03	1.895	1.127	–0.085	1.042
89356	8/18/06 16:32	5.377	1.288	–0.091	1.197

Table E.2 displays the analysis numbers, analysis date-time values, and penultimate delta values of the five analyses of S-1301 that are not ignored. The first analysis is assigned a time of zero in the third column. The values in the blank correction column were calculated with the routine "s_UpdateBlankCorrDependencies" as discussed in Appendix E.2.2. The last column of Table E.2 contains blank corrected delta values, the sum of values in columns four and five. LIMS uses the routine "s_CalcDriftCorrection" to calculate drift corrected delta values. This code next calculates the mean blank and drift corrected delta value and the mean date-time of each analysis of the selected reference (S-1301 in this example) and loads these data into the Access table "tbl_Temp_X_and_Y," which is used exclusively for determining linear least squares regressions. The date-time values are loaded into the independent variable (x) field and the delta values into the dependent variable (y) field. LIMS runs the routine "s_LeastSquaresRegression" to calculate the linear "least squares" slope, intercept, and R squared values, which are provided to the user in a pop-up message. In this example, the slope is –0.002 ‰/hr and R squared = 0.00 (Fig. E.7). These calculated values are identical to those that would be calculated with Excel's LINEST worksheet function. R squared is known as the coefficient of determination. Excel's Help File indicates that it

> "Compares estimated and actual y-values, and ranges in value from 0 to 1. If it is 1, there is a perfect correlation in the sample — there is no difference between the estimated y-value and the actual y-value. At the other extreme, if the coefficient of determination is 0, the regression equation is not helpful in predicting a y-value."

Using the slope and intercept, the routine "s_CalcDriftCorrection" updates hourly drift correction values of all analyses in the Access table "tbl_TempAnalyses." Hourly drift correction values are rounded to three significant figures after the decimal point for internal calculations for calculations of delta values involving isotopes ^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{36}S, ^{30}Si, and ^{37}Cl. For this example, these hourly drift correction values appear in column V of the Excel file named "TempAnalyses_with_blank_&_drift_corr_&_norm.xlsx," which is found in the folder named "Appendix E" that accompany this manual. These values are rounded to 2 significant figures

after the decimal point when displayed in the lower pane of the Normalization Equation Coefficients form.

E.2.4 Expansion Coefficient and Additive Correction Factor

The sum of the blank corrected delta value and the hourly drift correction is called the blank and drift corrected delta value. Using the blank and drift corrected delta value of each of the isotopic reference materials analyzed with the unknowns, LIMS uses linear least squares regression and calculates the expansion coefficient and additive correction factor (see Equation 1). LIMS will round the values of the expansion coefficient and additive correction factor for internal use, respectively, to six and three significant figures after the decimal point for calculations of delta values involving isotopes ^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{36}S, ^{30}Si, and ^{37}Cl. LIMS will subsequently round the values of the expansion coefficient and additive correction factor for display with the Normalization Equation Coefficients form and printing, respectively, to five and two significant figures after the decimal point for calculations of delta values involving isotopes ^{2}H, ^{13}C, ^{15}N, ^{17}O, ^{18}O, ^{33}S, ^{34}S, ^{36}S, ^{30}Si, and ^{37}Cl.

As an example, three isotopic reference materials are use in an Excel file named "TempAnalyses_with_blank_&_drift_corr_&_norm.xlsx" to calculate the expansion coefficient and additive correction factor, which are shown in Table E.3. Analyses having ignored delta values ("IG" check box) are not included in Table E.3. The second column contains the assigned delta values from the Table of References in LIMS. The last column shows the blank and drift corrected delta values calculated by Equation (1); this is the sum of the fourth, fifth, and sixth columns. The user can select to normalize with any one of these three reference materials by selecting the "Normalize with This Reference" option. The expansion coefficient can be forced to 1.00000 by checking the "Force Exp Coef to 1.00000" check box. When the user chooses to normalize with a single reference, the mean and 1-σ standard deviation of the blank and drift corrected delta values is displayed on Normalization Equation Coefficients form in the fields labelled "Mean Intermediate Delta" in the "Normalization" panel. In such a case, the additive correction factor will be the difference between the mean of the blank and drift corrected delta values and the assigned delta value of the reference. The user can choose "Normalize with All References"; the difference between the mean of the blank and drift corrected delta values and corresponding assigned delta values will be the additive correction factor. In either situation, the user can keep the expansion coefficient at 1.00000 or may change it as desired by entering the new value in the "Proposed Exp Coef" field. Likewise, a user is free to input any value of additive correction factor into the "Proposed Add Corr" field.

Table E.3. Data for determination of the expansion coefficient and additive correction factor

Our Lab ID	Assigned Value	Analysis number	Penultimate delta (‰)	Blank correction (‰)	Hourly correction (‰)
S-97	21.12	89344	19.935	0.104	–0.007
S-97	21.12	89320	20.671	0.115	–0.001
S-97	21.12	89357	20.428	0.11	–0.01
S-1301	0.49	89316	0.755	–0.103	0
S-1301	0.49	89318	1.613	–0.093	–0.001
S-1301	0.49	89319	1.59	–0.093	–0.001
S-1301	0.49	89330	1.127	–0.085	–0.004
S-1301	0.49	89356	1.288	–0.091	–0.01
S-1302	–34.05	89345	–30.531	–0.451	–0.007
S-1302	–34.05	89321	–30.385	–0.436	–0.001
S-1302	–34.05	89332	–30.636	–0.434	–0.004
S-1302	–34.05	89358	–30.417	–0.444	–0.011

When the "Normalize with All References" option is selected and the "Force Exp Coef to 1.00000" check box is deselected, LIMS will determine an expansion coefficient and additive correction factor using linear least squares regression. The routine "s_fmain_UpdateControls" loads data into Access table "tbl_Temp_X_and_Y" and executes the routine "s_LeastSquaresRegression" to determine slope, intercept, and *R* squared values. The "true" or accepted delta values of references are loaded into the independent variable (x) field and the Blank and Drift Corrected Delta values are loaded into the dependent variable (y) field. Therefore, the code must invert the slope and intercept to obtain the expansion coefficient and additive correction factor. That is,

$$\text{additive correction factor} = -\text{intercept} / \text{slope} \quad (8)$$

$$\text{expansion factor} = 1 / \text{slope} \quad (9)$$

For example, for the data in Table E.3 (see Excel file "TempAnalyses_with_blank_&_drift_corr_&_norm.xlsx"), the slope and intercept before inversion are 0.9311304976491 and 0.7518563108 ‰, respectively. After inversion, the expansion coefficient is 1.07396332 and the additive correction factor is – 0.807466 ‰; these are rounded to 1.07396 and –0.81 for display on the Normalization Equation Coefficients form. The *R* squared value of 0.999823 is determined by the routine "s_LeastSquaresRegression." It is displayed on Normalization Equation Coefficients form, and it is appears on the Correction Factor report. Using the expansion coefficient and additive correction factor, LIMS determines

the final delta of every peak in the range of analyses and displays these values in the lower pane of the Normalization Equation Coefficients form.

E.2.5 Mass Fraction (Concentration) Calculations

LIMS is able to calculate the mass fractions (concentrations) of hydrogen, carbon, nitrogen, oxygen, and sulfur in material analyzed by an IRMS having an EA or TC/EA if reference materials with known mass fractions are analyzed along with the unknown samples. If several reference materials having different element mass fractions are analyzed with unknowns, the user can choose to base calculation on any one of the reference materials or on all of them by checking the desired check boxes in the column in Figure E.8 labelled "IG Cn."

The total peak area is equal to the sum of the peak area of an unknown (or reference) and the peak area of the blank. Therefore,

peak area of unknown and blank (*e.g.* "Area All" column in ISODAT)
= blank corrected peak area of unknown + blank area (10)

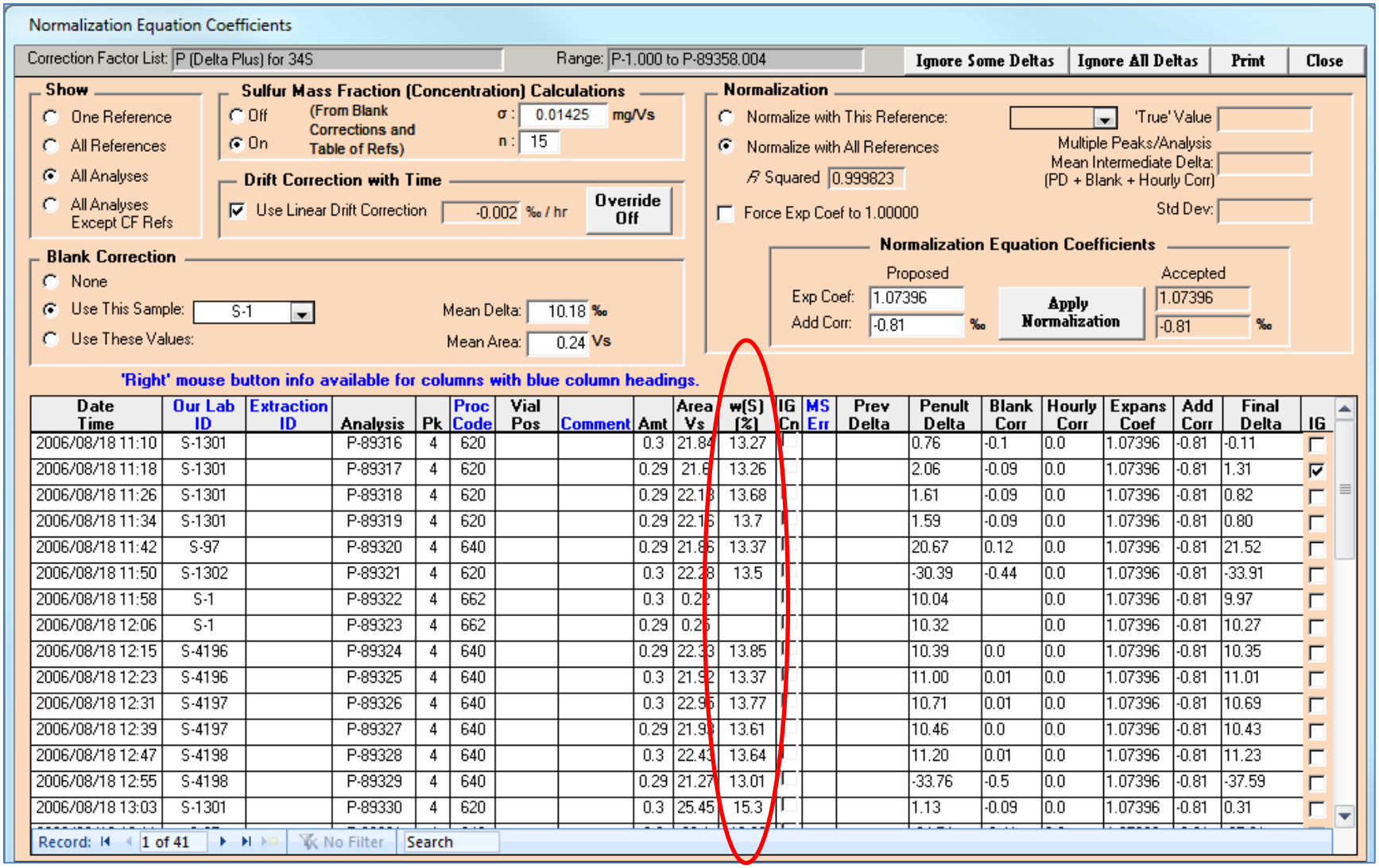
Because the blank corrected peak area of unknown is directly proportional to the element mass fraction (element concentration) and to the amount of substance:

peak area of unknown and blank (*e.g.* "Area All" column in ISODAT)
$= k \times w_A(E) \times m_A$ + blank area (11)

where k is a constant, $w_A(E)$ is the mass fraction of element E in substance A, and m_A is the mass of substance A. And likewise for a reference material B,

peak area of reference and blank (*e.g.* "Area All" column in ISODAT)
$= k \times w_B(E) \times m_B$ + blank area (12)

In Equation (12), the only unknown is k, and the LIMS routine "s_CalculateConcentrations" calculates a mean k value from analyses of a single reference material or more than one reference material as selected by the user using the check boxes in the "IG Cn" column. LIMS then uses the value of k from Equation (11) to calculate the element mass fractions, $w_A(E)$, of all of the peaks in the range of analyses. As an example of the application of Equations (10), (11), and (12), if the blank correction is set to use sample S-1 and "Base on All References Not Ignored" is used for sulfur mass fraction, column P of the Excel workbook "TempAnalyses_with_blank_&_drift_corr_&_norm.xlsx" displays the values of $w(S)$, and the values agree with those shown in Figure E.9.



Date Time	Our Lab ID	Extraction ID	Analysis	Pk	Proc Code	Vial Pos	Comment	Amt	Area Vs	w(S) (%)	IG Cn	MS Err	Prev Delta	Penult Delta	Blank Corr	Hourly Corr	Expans Coef	Add Corr	Final Delta	IG
2006/08/18 11:10	S-1301		P-89316	4	620			0.3	21.84	13.27				0.76	-0.1	0.0	1.07396	-0.81	-0.11	☐
2006/08/18 11:18	S-1301		P-89317	4	620			0.29	21.6	13.26				2.06	-0.09	0.0	1.07396	-0.81	1.31	☑
2006/08/18 11:26	S-1301		P-89318	4	620			0.29	22.1	13.68				1.61	-0.09	0.0	1.07396	-0.81	0.82	☐
2006/08/18 11:34	S-1301		P-89319	4	620			0.29	22.1	13.7				1.59	-0.09	0.0	1.07396	-0.81	0.80	☐
2006/08/18 11:42	S-97		P-89320	4	640			0.29	21.8	13.37				20.67	0.12	0.0	1.07396	-0.81	21.52	☐
2006/08/18 11:50	S-1302		P-89321	4	620			0.3	22.2	13.5				-30.39	-0.44	0.0	1.07396	-0.81	-33.91	☐
2006/08/18 11:58	S-1		P-89322	4	662			0.3	0.2					10.04		0.0	1.07396	-0.81	9.97	☐
2006/08/18 12:06	S-1		P-89323	4	662			0.29	0.2					10.32		0.0	1.07396	-0.81	10.27	☐
2006/08/18 12:15	S-4196		P-89324	4	640			0.29	22.3	13.85				10.39	0.0	0.0	1.07396	-0.81	10.35	☐
2006/08/18 12:23	S-4196		P-89325	4	640			0.3	21.9	13.37				11.00	0.01	0.0	1.07396	-0.81	11.01	☐
2006/08/18 12:31	S-4197		P-89326	4	640			0.3	22.9	13.77				10.71	0.01	0.0	1.07396	-0.81	10.69	☐
2006/08/18 12:39	S-4197		P-89327	4	640			0.29	21.9	13.61				10.46	0.0	0.0	1.07396	-0.81	10.43	☐
2006/08/18 12:47	S-4198		P-89328	4	640			0.3	22.4	13.64				11.20	0.01	0.0	1.07396	-0.81	11.23	☐
2006/08/18 12:55	S-4198		P-89329	4	640			0.29	21.2	13.01				-33.76	-0.5	0.0	1.07396	-0.81	-37.59	☐
2006/08/18 13:03	S-1301		P-89330	4	620			0.3	25.45	15.3				1.13	-0.09	0.0	1.07396	-0.81	0.31	☐

Fig. E.9. Normalization Equation Coefficients form after blank correction, drift correction, normalization, and calculation of sulfur mass fractions (concentrations).