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Techniques of Water-Resources Investigations
of the United States Geological Survey

Chapter A6

QUALITY ASSURANCE PRACTICES FOR THE CHEMICAL AND BIOLOGICAL ANALYSES OF WATER AND FLUVIAL SEDIMENTS

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Book 5

Laboratory Analysis

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Standard Quantitative Analysis Techniques

The production of quantitative analyses requires the use of standard quantitative analysis techniques. Some of the more common techniques are included in this section. Familiarity with them is mandatory for anyone working in an analytical laboratory.

Cleaning Glassware

1. Application or scope

1.1 This practice details some basic procedures to be followed in cleaning laboratory glassware.

1.2 The type and amount of cleaning which is necessary depends on the analysis to be done and on the contaminant present in the vessel to be cleaned.

2. Practice

2.1 Washing

2.1.1 Remove wax or grease pencil markings by hand (usually with the aid of acetone).

2.1.2 Wash glassware either by hand or in a specially designed automatic washer which has a distilled rinse capability (laboratory washer). Glassware will be suitable for use in making analysis of most inorganic constituents which have concentrations reported in the milligram per liter range (such as calcium or sulfate).

2.1.3 Use phosphate-free detergent for glassware used for phosphorus determinations.

2.1.4 If washing by hand, chromic acid cleaning solution may be used (NOTE 1 and 2). Follow the wash by rinsing with tap water and at least four distilled water rinses.

NOTE 1. The cleaning solution may be prepared by adding 1 liter concentrated H_2SO_4 to 35 mL saturated sodium dichromate solution.

NOTE 2. Because of safety hazards associated with chromic acid cleaning solutions, its use is discouraged unless absolutely necessary. Substitutes are now available which can be used; for example, Lab Safety Supply Co. (1980) advertises "Nochromix" as a substitute solution.

2.1.5 Do not use strong caustic solution on volumetric glassware.

2.1.6 Do not soak spectrometer absorption cells in caustic or in strong cleaning solution and never use abrasive material on them.

2.1.7 For glassware to be used in the determination of organic constituents, rinse, after washing, with an organic solvent such as acetone, or follow the wash by baking at 350°C for at least 8 hours.

2.1.8 Wash glassware used for trace-metal analysis with 1:1 nitric acid-water solution. Follow the wash by at least four deionized-water rinses.

2.1.9 Acetone or a warm sodium hydroxide solution followed by an acid rinse may be used to eliminate grease.

2.1.10 Glassware to be used in bacteriological analysis should be rinsed at least three times with distilled water which has not come in contact with copper tubing or other toxic material (glass or stainless steel plumbing is acceptable).

2.1.11 Clean glassware until the surface drains uniformly, in a thin film. Droplets, instead of a thin film, indicate glassware is not completely clean and must be rewashed.

2.2 Drying

2.2.1 If air drying or oven drying, be sure glassware does not become contaminated from the air.

2.2.2 If drying on a rack, be careful the glassware does not become contaminated from the rack (as from metal or a paint chip).

2.2.3 Sterilize glassware to be used in

bacteriological analysis for 1 hour at 170°C. Heat glassware in metal containers for 2 hours at 170°C (American Public Health Association and others, 1976).

Selected References

American Public Health Association and others, 1976, Standard methods for the examination of water and wastewater (14th ed.): Washington, D.C., American Public Health Association, p. 885.

Bordner, Robert, Winter, John, and Scarpino, Pasquale, 1978, Microbiological methods for monitoring the environment, water and wastes: U.S. Environmental Protection Agency EPA–600/8–78–017, Cincinnati, p. 36.

Lab Safety Supply Co., 1980, Safe handling of toxic and hazardous chemicals: 1981 Catalog, Janesville, Wis., Lab Safety Supply Co., p. 93.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 4–5—4–9.

Correction for Color Interference

1. Application or scope

1.1 This practice describes corrective actions to be taken when color interferes with an analysis. The natural color in many water samples shows an appreciable absorbance at the wavelengths used in a number of colorimetric determinations; if the absorbance changes the apparent concentration of the constituent being determined, it must be compensated for or eliminated.

1.2 Also see practice "Standard-addition technique."

2. Practice

2.1 Highly sensitive analytical method

2.1.1 If the absorbance due to the constituent sought exceeds the absorbance due to natural color by a factor of at least 50, no compensation for natural color is required for most analyses (NOTE 1).

NOTE 1. If the factor is 50, the error introduced is 2 percent.

2.1.2 If the sensitivity of the method is sufficient (Skougstad and others, 1979) so that the color interference can be eliminated by diluting the sample and an accurate concentration value still can be obtained, dilute the sample and proceed with the analysis (NOTE 2).

NOTE 2. The sensitivity of the method for the constituent being determined must be known and must be high relative to the interference.

2.2 Preparation of a color "blank"

2.2.1 If the sensitivity of the method relative to the interference is not known or if there is any doubt as to the effect of color on the absorbance of the element sought, use two equal volumes of the sample.

2.2.2 To one volume of sample, add all reagents. To the other volume of sample, add all reagents except the indicator reagent; instead add a volume of indicator solvent which is equal to the volume of indicator reagent normally added.

2.2.3 Measure the absorbance of both samples.

2.2.4 Calculate the difference between the absorbances to obtain a corrected absorbance. Use this corrected absorbance in determining the concentration of the constituent (NOTE 3).

NOTE 3. This procedure will work for most waters. However, if the indicator reagent reacts with or affects the natural color or turbidity in the water sample, this method should not be used. Filtration of excessively turbid samples may be required prior to analysis.

2.3 Bleaching or adsorption

2.3.1 If the above procedure proves inadequate, try a bleaching procedure (such as hydrogen peroxide) or adsorption procedure (such as activated carbon) provided these procedures do not change the chemical equilibrium or contaminate the sample.

2.3.2 Be extremely careful, since it is relatively easy to contaminate the sample by either adding or removing constituents from the water sample (NOTE 4).

NOTE 4. Because of the problems associated with the removal of color, it is usually preferable to use an alternative, noncolorimetric procedure to make the analysis.

2.3.3 Consult an applicable reference before trying either bleaching or adsorption.

Reference

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Gravimetry

1. Application or scope

1.1 This describes some of the basic principles and techniques to be followed in making gravimetric analyses.

1.2 Operating procedures for analytical balances, discussed in the practice "Analytical balances," in the section "Instrumental Techniques," must be followed.

2. Practice

2.1 Requirements

2.1.1 Use desiccators of sufficient size and limit the number of samples placed in them so that samples will have achieved room temperature at the end of the specified drying period.

2.1.2 Use a desiccant which conforms to that specified in the applicable procedure. Replace or regenerate before its drying power has diminished (NOTE 1).

NOTE 1. Many desiccants contain a moisture absorption indicator to indicate need for regeneration or replacement.

2.1.3 Maintain temperature of drying ovens within the specified limits of the required drying temperature.

2.1.4 An analytical balance is an essential part of every gravimetric procedure. The type commonly used for this purpose is a single-pan, direct-reading balance which is capable of determining the mass of an object to 0.1 mg. Be certain that it receives regular maintenance and is properly calibrated with Class S weights.

2.2 Measurement procedures

2.2.1 Prepare sample solutions as directed in the method used. If a determination involves precipitation, it is of importance that conditions be carefully controlled as directed in the analytical procedure in order to optimize the purity and percent recovery of the precipitate.

2.2.2 The validity of a gravimetric procedure does not depend on standard solutions; however, carefully prepare reagents, if any, as specified in the analytical procedure.

2.2.3 In any direct gravimetric analysis, separate the constituent being determined from the other constituents of the sample, either in the form of the constituent itself or as a compound of known, definite composition. In the latter case, calculate the weight of the constituent from its theoretical percent of the compound.

2.2.4 In any indirect gravimetric analysis, determine the weight of the residue remaining after the volatilization of the constituent. Determine the amount of the constituent sought from the loss in weight.

2.2.5 Follow the appropriate concentration range specified in the analytical method. If the concentration of a constituent falls outside of this range, use a smaller sample volume, dilute the sample, or use an alternate approved method. If the working range of the method is exceeded, the procedure must be repeated because the amount of residue will be so great that it is very likely that water will be entrapped and not completely driven off during the drying period.

2.2.6 Regulate the temperature of the drying oven, the drying time, and the cooling time in the desiccator.

2.2.7 Never weigh chemicals directly on the balance pan. Use a weighing paper or other container.

2.3 Calculations

2.3.1 The calculations for gravimetric analyses are relatively simple. For determinations of dissolved and suspended solids, convert the weight of the residue per volume of sample evaporated to weight of residue per liter.

2.3.2 For procedures involving compound formation and precipitation, a factor must be applied to convert the weight of the precipitate to the weight of the constituent sought.

2.3.3 Consult the appropriate method for specific directions.

Selected References

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, Stanley, 1969, Quantitative chemical analysis (4th ed.): Toronto, Macmillian, p. 565.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 551–578.

Reagents and Gases

1. Application or scope

1.1 This practice lists the grades of chemicals and gases used in analytical work, gives general guidelines for their use, and describes quantitative practices which must be followed in preparation of all standard solutions.

2. Practice

2.1 Purity

2.1.1 As noted in Skougstad and others (1979), "Unless indicated to the contrary, all chemicals specified for use in the analytical procedures shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. Those chemicals not listed by this organization may be tested as indicated by Rosin (1955). Chemicals used for primary standards may be obtained from the U.S. National Bureau of Standards or from manufacturers marketing chemicals of comparable purity."

2.1.2 The grade of purity of chemicals and solvents and of gases are listed in table 4 and table 5, respectively. Table 6 is a general guideline which may be followed in determining the purity needed (NOTE 1).

NOTE 1. The specific purity needed will depend on the instrument, analytical method, and so forth. Use only chemicals that are within the allowable date of use.

2.2 Dilution water

2.2.1 Demineralized water is the most commonly used reagent in the laboratory. For inorganic analysis, prepare demineralized water either by distillation, by use of mixed cation-anion exchange resins, or by reverse osmosis. A combination of the above procedures may be necessary, especially if the distillation is carried out in a metal still, to produce water of adequate purity. The specific conductance of the demineralized water should not exceed 1.5 μmho/cm at 25°C.

2.2.2 Prepare carbon dioxide-free water by boiling and cooling demineralized water immediately before use. Its pH should be between 6.2 and 7.2.

2.2.3 Prepare ammonia-free water by passing distilled water through a mixed-bed ion-exchange resin or through a cation-bed in the hydrogen ion form.

2.2.4 Use water from an all-glass or glass-lined still for organic determinations. It may be necessary to redistill from alkaline permanganate solution in order to obtain a water with low organic residual.

2.2.5 Use water which is free from traces of dissolved metals, nutrients, residual chlorine and other bactericidal compounds for bacteriological analyses.

2.3 Measurement accuracy

2.3.1. Weigh materials to the precision required by the method. As noted in Book 5, Chapter A1 of Techniques for Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979), "a mass designated as 4.532 g must be weighed accurately to +0.0005 g, whereas a mass designated as 4.5 g must be weighed accurately to +0.05 g."

2.3.2 Use borosilicate glass for volumetric glassware.

2.3.3 Select volumetric glassware which will give the accuracy required by the method. Again as noted in Skougstad and others (1979), " 'add 2.00 mL of reagent' shows that a volumetric pipet must be used for the addition, but 'add 2 mL' or 'add 1.5 mL' shows that a serological pipet may be used; 'dilute to 1,000 mL' shows that a volumetric flask is essential, but 'dilute to 1 liter' permits the use of a graduated cylinder."

2.3.4 Volumetric glassware is calibrated either to deliver (marked TD) or to contain (marked TC). Know which is being used. Almost all volumetric pipets are calibrated to deliver. Allow a pipet marked TD to drain freely for the time stated on its side (for example, 25 s). Then hold the tip against the inner wall of the vessel into which it is draining, being careful not to touch the liquid already in the container. Some liquid always should remain in the tip of the pipet.

Table 4.—Grades of chemicals and solvents

Grade	Abbreviation	Description
Ultra pure	Ultrex, Nanograde, and so forth.[1/]	Ultrahigh-purity materials. Certificate showing actual concentration of impurities furnished.
Primary standard	PS	Exceptional purity for standardization and preparing standards.
Spectroquality	--	Specially purified to provide insignificant background in absorption and emission spectroscopy.
Analytical reagent	AR	High purity for laboratory use. Lot analysis usually on label of container.
American Chemical Society	ACS	Meets specifications published by the American Chemical Society.
Chemically pure	CP	Suitable for most routine use. Lot analysis not specified on label.
National Formulary	NF	Meets specifications of the National Formulary.
United States Pharamacopeia	USP	Meets specifications of the United States Pharmacopeia.
Food Chemicals Codex	FCC	Meets specification of Food Chemicals Codex.
Purified	PURI	Higher quality than technical but no official standards. Used principally for bulk applications.
Practical	PRACT	Sufficiently high quality for most organic synthesis.
Technical	TECH	Suitable for most general industrial uses.

[1/] These and other trademarks are used by chemical companies to designate their highest purity solvents.

2.3.5 Note also that, as indicated in Skougstad and others (1979), "although the glassware is calibrated to deliver a specific volume at 20°C, the error in measurement incurred by pipetting samples at room temperature is insignificant for water analysis. One gram of pure water is contained in 1.002 mL at 20°C and in 1.007 mL at 38°C; the maximum error in volume that will result from those temperature differences is only 0.5 percent. Brine samples should be brought to as near 20°C as possible before making dilutions for analysis."

2.3.6 For highly precise work or when volumetric glassware has been frequently used

Table 5.—Typical grades of gases

Grade	Description	Application
Research	99.995-99.999 percent pure; highest level of purity obtainable; certificate of impurities available.	Research and development.
Ultrahigh purity	99.99-99.999 percent pure; certificate of impurities available.	Gas chromatographic and spectrophotometric.
High purity	99.99-99.999 percent pure; certificate of impurities available.	Gas chromatographic and spectrophotometric.
Zero	Low total hydrocarbon content; certificate of impurities available.	Reference gases for hydrocarbon analyses.
Commercial, industrial, or technical	93-99 percent pure; no certification.	Welding, atomic absorption, normal commercial and laboratory uses.

Table 6.—General useage guide for chemicals, solvents, and gases

Chemical process	Grade of purity
Inorganic standards	PS, AR, ACS
Organic standards	Ultra Pure, PS
Gas chromatography, carrier gas	Carrier, Zero
Atomic absorption, fuel gases	Zero, Commercial
Extractions and separations	AR,ACS
Definitive reactions	AR, ACS
Additive chemicals	AR, ACS, CP
Biological nutrients and media	USP, NF
Cleaning solutions	PURI, TECH
Organic synthesis	PURI, PRACT

to measure strong alkaline solutions, the glassware should be calibrated. Directions for calibration are found in standard quantitative texts and in the U.S. National Bureau of Standards Circular 602 (1959).

2.4 Storage

2.4.1 Store reagents and stock standard solutions according to the manufacturer's directions. If sensitive to light, keep in a dark bottle. If sensitive to heat, store in a refrigerator. Include the expected shelf-life of the reagent on the label.

2.4.2 Store most neutral and acid solutions in borosilicate glass containers (NOTE 1). Plastic containers may be substituted only if they will not absorb or contaminate the constituent of interest.

NOTE 1. Volumetric glassware should not be used to store solutions.

2.4.3 Use polyethylene or Teflon containers to store alkaline solutions and solutions containing boron or silica.

2.4.4 Store all reagent solutions used for organic analyses in glass containers.

2.4.5 Discard chemicals and solutions if there is any possibility of contamination or deterioration or if the date for safe use has expired. Unless the analytical procedure states specifically that a change in color of a reagent does not affect its usefulness, discard immediately if any change in color or concentration is noticed. If a time limit is specified in an analytical method for a reagent or standard, do not exceed it.

References

Rosin, Joseph, 1955, Reagent chemicals and standards: New York, D. Van Nostrand, 561 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 13–14.

U.S. National Bureau of Standards, 1959, Testing of glass volumetric apparatus: Circular 602, 21 p.

Standard-Addition Technique

1. Application or scope

1.1 This practice can be used to compensate for known or suspected matrix effects or analytical interferences. However, this method can be used only if the measured absorbance is linear with respect to concentration and if the observable interference is independent of the concentration of constituent being analyzed (NOTE 1).

NOTE 1. In general, the slope of the plotted line should be similar to the slope of the corresponding aqueous standard curve.

1.2 Since both samples and standards are affected equally, it is not necessary to prepare matrix water comparable to the unknown sample in order to correct the analyses.

2. Practice

2.1 Preliminary analysis and preparation

2.1.1 Make a preliminary analysis for the constituent in question.

2.1.2 Prepare a blank and three standards containing different amounts of the constituent to be analyzed (NOTE 2).

NOTE 2. Volume of blank and standards must be the same.

2.1.3 Select volumes of sample and highest standard such that, when mixed together, the resulting concentration will not exceed the analytical range specified in the method.

2.1.4 Add equal volumes of sample to the blank and three standards.

2.2 Determination of concentration

2.2.1 Measure the absorbance of the constituent being analyzed in the spiked (with sample) blank and standards.

2.2.2 Plot the absorbances on the vertical axis and the known concentrations of the constituent prior to the addition of the sample on the horizontal axis. Continue the horizontal axis to the left of the vertical axis, scaling it backwards from the zero (blank) concentration (see fig. 3).

2.2.3 Draw a line through the plotted points and extrapolate back to zero absorbance.

2.2.4 Record the concentration at the intercept as the concentration of the constituent in the sample. Retain all records.

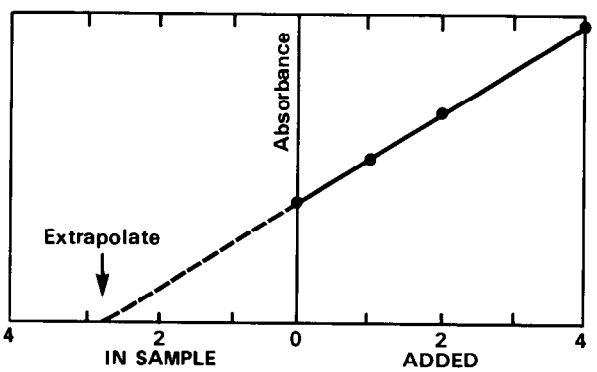

Figure 3.—Example of standard-addition method (from Skougstad and others, 1979).

Selected References

Klein, Robert, Jr., and Hach, Clifford, 1977, Standard additions, uses and limitations in spectrophotometric analysis: American Laboratory, v. 9, no. 7, p. 21–27.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the analysis of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 32.

U.S. Environmental Protection Agency, 1979, Methods for chemical analyses of water and wastes: U.S. Environmental Protection Agency EPA–600/4–79–020, Cincinnati, p. Metals 12—Metals 13.

Youden, W. J., 1960, The sample, the procedure, and the laboratory: Analytical Chemistry, v. 32, no. 13, p. 23A-37A.

Titrimetry

1. Application or scope

1.1 This practice describes some of the basic principles and standard techniques necessary for reliable titrimetric analyses.

1.2 The basic equipment employed in titrimetric procedures consists of pipets, burets, and other glassware. The appropriate glassware specifications and cleaning procedures must be rigorously observed.

1.3 If pH meters or spectrophotometers, are used to detect the titrimetric end point, operating procedures discussed in the section on instrumental quality control should be followed. If automated instruments are used, the manufacturer's manual should be consulted for operating instructions. An instrument of this type may be used only if its accuracy is equal to or superior to that obtained by manual procedures.

2. Practice

2.1 Requirements

2.1.1 To be suitable as a basis for a titrimetric determination, the chemical reaction involved must proceed rapidly to completion with no side reactions. In addition, other substances present in the sample should not react or interfere with the desired reaction, and the end point should be readily detectable by visual or instrumental means.

2.1.2 The end point does not as a rule coincide exactly with the equivalence point. The difference between the amount of titrant corresponding to the end point and that corresponding to the equivalence point represents the titration error. This difference should be as small as possible for a given procedure, and care should be taken to titrate every sample to the same end point.

2.1.3 Ideally, the standard solution used in titrimetry should be simple to prepare and be stable for a comparatively long time to avoid the need for frequent restandardization. Quite commonly, the standard is prepared at a concentration very close to that desired and then standardized by titrating an accurately measured amount of a primary standard. The primary standard must be of high purity, stable, and easily dried and weighed. Primary standards are available on specification from most chemical supply houses and often from the National Bureau of Standards.

2.2 Standardization

2.2.1 Standardize titrant solutions according to the procedures listed in the analytical methods in order to determine their exact normalities. Store and preserve properly. Restandardize as specified in the procedure or whenever there is reason to believe that the concentration has changed.

2.2.2 Include a primary standard solution with each set of samples or at weekly intervals, whichever is less frequent, to ensure that the titrant has not changed or become contaminated. Keep a written record of the original standardization value and also of the values obtained for subsequent restandardizations.

2.3 Measurement procedure

2.3.1 Observe the appropriate concentration range specified in the method. If the concentration of a constituent falls outside this range, adjust the concentration by dilution or use an alternative method.

2.3.2 For visual and spectrophotometric titrations, titrate a solution consisting of demineralized water plus all necessary reagents to the end point to determine the blank correction.

2.4 Calculations

2.4.1 Subtract the volume of standard solution required for the titration of the blank from all sample titration volumes to determine the actual volume of standard solution involved in the reaction.

2.4.2 After the normality of a standard solution has been determined, each unit volume can be equated to a known amount of sample constituent. Determine the concentration of the constituent by considering this factor in addition to the volume of sample, the volume of titrant required, and the blank titration volume.

Consult each method for more specific calculation directions.

Selected References

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, Stanley, 1969, Quantitative Chemical Analysis (4th ed.): Toronto, Macmillian, p. 681.

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the analysis of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 579–580.

Instrumental Techniques

The proper use of analytical instruments is important in the production of reliable analytical values. The following practices confront this problem with special emphasis on the operation and calibration of instruments normally encountered in a water-analysis laboratory. Laboratories that analyze samples for the U.S. Geological Survey are expected to follow the detailed recommended procedures for the operation and calibration of instruments.

Instrument Maintenance

1. Application or scope

1.1 This practice is applicable to field equipment as well as to laboratory instruments.

1.2 In order to obtain valid responses, instruments must be checked on a regular basis. Where instrument maintenance schemes have not been established, 25 percent or more of the measuring equipment is often found to give erroneous answers (Juran and Gryna, 1976).

2. Practice

2.1 Identification number

2.1.1 Assign a number to each instrument. Although numbers used for inventory control (U.S. Geological Survey "W" numbers) may be used, a separate series for each type of instrument may be easier to use (for example, pH meter 001, 002, and so forth).

2.1.2 Number each instrument with a permanent marking.

2.2 Record card

2.2.1 Prepare a record card for each instrument. Record the type of instument, the model number, and its assigned number at the top of the card.

2.2.2 Indicate on the card the calibration limits of the instrument, the frequency with which the instrument should be checked, and the tests which should be made.

2.2.3 Indicate to whom the instrument is assigned and the date. Change this information whenever necessary (but keep a record).

2.2.4 Keep a record of the dates on which the instrument was checked. Include the name of the person who checked it, whether any changes were necessary, and so forth.

2.3 Frequency of maintenance check

2.3.1 Consider the amount of usage usual for a type of instrument (for example, atomic absorption spectrometers) and estimate the rate of instrument deteriortion.

2.3.2 Establish the necessary checking frequency for each type of instrument. This frequency may be based on units of time (for example, check every week) or may be based on use (for example, check every 200 samples).

2.3.3 Establish a maintenance schedule for each instrument and provide a way to keep track of it. For example, mark on a calendar (a couple of months in advance) the identification number of each instrument to be checked. Alternatively, mark the date of the next check on the instrument record card and maintain cards in a file, in order, by date. This frequency record file can be kept by a section leader for instruments in his section, or by an assigned person in a laboratory, district, or field office.

2.4 Record of findings

2.4.1 Record on the card the types of errors found and repairs needed.

2.4.2 Establish when the instrument last needed to be repaired. Determine the rates of repair or instrument change.

2.5 Analysis of record

2.5.1 Review records periodically. Be sure the schedule for maintenance checking is being adhered to.

2.5.2 If a particular model of instrument shows repeated problems, consider recommending a different model. If a particular type of

instrument shows repeated problems, increase the frequency of maintenance.

2.5.3 If no changes or problems are recorded, decrease the frequency of maintenance checks.

Selected References

Juran, J. M., 1974, Measurement, *in* Juran, J. M. and others, eds., Quality control handbook (3d ed): New York, McGraw-Hill, p. 13–15—13–18.

Juran, J. M., and Gryna, F. M., Jr., 1976, Quality planning and analysis: New York, McGraw-Hill, p. 393–398.

Analytical Balances

1. Application or scope

1.1 This practice details general procedures to be followed in using an analytical balance to prepare standards and reagents and to make gravimetric analyses.

1.2 The practice "Gravimetry," in the section "Standard Quantitative Analysis Techniques" should also be consulted.

2. Practice

2.1 Basic operational procedures

2.1.1 Mount and level the analytical balance on a heavy shock-proof table, located away from laboratory traffic, and protected from sudden drafts and humidity and temperature changes.

2.1.2 Clean up any material spilled in the balance case immediately.

2.1.3 Use ivory-tipped forceps or platinum-tipped tongs to handle objects to be weighed. Never use bare hands.

2.1.4 When not in use, raise the beam from the knife edges, return the weights to the beam, remove objects from the pan, and shut the side doors.

2.2 Calibration procedure

2.2.1 Check the calibration of a balance at least every 3 months using Class S weights.

2.2.2 If recalibration is necessary, consult and follow the manufacturer's instructions.

2.3 Measurement procedure

2.3.1 Set the meter to read zero when the balance is empty.

2.3.2 Set the object to be weighed on the balance pan using a pair of forceps or tongs, that have tips softer than brass (for example, ivory-tipped forceps, plastic-covered tongs, platinum-tipped tongs).

2.3.3 Add weights, generally starting with the largest, until balance is achieved. Consult the manufacturer's instructions for specific instructions.

Selected References

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the analysis of inorganic substances in water and fluvial sediment: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, p. 551.

U.S. Environmental Protection Agency, 1979, Handbook for analytical quality control in water and wastewater laboratories: U.S. Environmental Protection Agency EPA–600/4–79–019, Cincinnati, p. 3–1—3–15.

Atomic Absorption Spectrometers

1. Application or scope

1.1 This practice details procedures to be followed in using atomic absorption spectrometers.

1.2 Although all atomic absorption spectrometers must undergo similar operational optimization, calibration, and standardization procedures, some variation in instrumental quality control may be necessary since commercially available instruments vary somewhat with regard to features such as read-out devices, burners, background correction, and curvature correction devices. The analytical requirements of a laboratory dictate the instrument and optional features to be utilized.

2. Practice

2.1 Basic operational procedures

2.1.1 Set controls such as gain, slit width, flame type, and wavelength in accordance with either the manufacturer's manual or journal literature.

2.1.2 Commercial grade gases are adequate. If compressed air is to be used for an air-acetylene flame, provide a filter to remove water and oil.

2.1.3 Select the lamp to be used, adjust the lamp current, and allow the lamp to electronically stabilize as recommended in the manufacturer's manual. Aline the lamp by adjusting the vertical and horizontal lamp controls until maximum absorbance is achieved (NOTE 1).

NOTE 1. Hollow-cathode or electrodeless discharge lamps are usually used as the line source in atomic absorption spectrometry. Multielement hollowcathode lamps are available which contain from two to six elements. These lamps are less expensive than buying several single-element lamps; however, the useful life is usually shorter and sensitivity less. Furthermore, the utility of the lamp decreases considerably after one of the elements has completely vaporized from the cathode. The use of a multielement lamp, therefore, is often a bad trade off unless the several elements contained in the lamp are determined only infrequently.

2.1.4 When the burner head is correctly alined, the slot in the burner head is parallel to and slightly below the source beam. To adjust the burner head, raise it until it intercepts the light beam from the source, as indicated by an increase of absorbance on the display; then lower it slowly until the display again reads zero. Ignite the appropriate gases as described in the operator's manual, zero the instrument, and select a standard solution for the element of interest which gives an absorbance of from 0.2 to 0.6 absorbance units. While aspirating the standard, sequentially adjust the vertical, horizontal, and rotational positions to achieve maximum absorbance. Adjust the vertical height prior to determining different elements. Usually the rotational and horizontal positions need to be realined only when changing burner heads.

2.1.5 If it is necessary to adjust the nebulizer, aspirate a standard solution containing an element that has a wavelength above 250 nm and requires an oxidizing air-acetylene flame. Recommended elements are copper, magnesium, nickel (341.5 nm), and lead (283.3 nm). Change the aspiration rate slowly until maximum absorbance is reached.

2.1.6 Background correction devices, available for most atomic absorption instruments, must be used whenever there may be interfering substances such as gaseous molecular particles, smoke, or salt particles present in the source-light path. Always use background correction when elements are determined by heated-vaporization techniques utilizing equipment such as a graphite furnace.

2.1.7 Adjust the wavelength by setting the monochromator reading to the recommended wavelength for a particular element and then slowly changing the monochromator fine adjustment until maximum light passage is obtained. It is usually easier to optimize the monochromator setting if a slightly narrower than recommended slit width is used during this adjustment. The slit width must be returned

to the recommended setting after the wavelength setting has been optimized.

2.2 Calibration procedure

2.2.1 After the alinement procedures have been completed and the operating parameters adjusted according to instructions in an instrument manufacturer's manual or to literature procedures, turn on fuel and support gases and adjust to recommended flow rates. Ignite the burner and aspirate water until thermal equilibrium is reached.

2.2.2 Adjust the electronics of the instrument to read zero absorbance while aspirating a blank solution that contains all reagents, except for the elements of interest, in the same proportion as the calibration standards. Continue the aspiration until a stable signal is obtained.

2.2.3 Aspirate a standard solution containing the analyte at a concentration that will give an absorbance of between 0.2 and 0.6 and that will be within the linear absorbance range for the test element. Determine if adequate sensitivity has been obtained by reference to the manufacturer's manual. Keep a record of the sensitivity of each element for a particular intrument in order to detect deficiencies in the instrument or operating conditions.

2.2.4 The appropriate concentration ranges for each parameter are specified in Book 5, Chapter A1 of the series, Techniques of Water-Resources Investigations of the U.S. Geological Survey (Skougstad and others, 1979). Use a minimum of five standards, equally spaced over the concentration range. The blank, standards, and sample solutions all must contain the same concentration of added reagents.

2.2.5 When calibrating these instruments in the concentration mode, follow manufacturer's instructions. If less than five standards are employed in this procedure, use the remaining standards to confirm the validity of the calibration.

2.2.6 Reaspirate the five standards in random order to determine if the readings have remained constant. If there is a question about the stability of the operating parameters, the following procedure can be applied. Zero the instrument while aspirating a blank solution. Aspirate a standard solution having an absorbance of between 0.2 and 0.6 and record the reading. Repeat the process of alternately aspirating the blank and standard solution until a total of six readings have been obtained for the standard solution. The standard deviation obtained from these six measurements should not exceed 1 percent of the average reading of the standard solution. if the repeatability is less consistent, determine the source of variability before analyzing samples. If the solids content of the standard solution is too high, make an appropriate dilution to prevent either clogging of the burner or an erratic flame.

2.2.7 Each time an instrument is calibrated, keep a written record of the absorbance readings or, in cases where the direct concentration mode is used, the scale expansion of the instrument for each set of standards. A significant change ($\geq$10 percent) from previous results immediately indicates that a problem exists with the operational settings, the performance of the atomic absorption spectrometer, or the accuracy of the standard solutions. Corrective action must be taken before analyzing samples. Furthermore, an analyst must also be aware of subtle, but consistent changes in absorbance or expansion readings that may be indicative of such things as the gradual deterioration of the standard solutions, a dirty nebulizer system, a clogged burner, an instrument-part malfunction, or the initial stage of a lamp failure.

2.3 Measurement procedure

2.3.1 Prepare the sample solutions as directed in the appropriate analytical procedure. After calibration of the instrument, aspirate the sample solutions until a stable reading is obtained and recorded. If the concentration of a constituent in a sample falls outside of the analytical range, adjust the concentration dilution or use an alternative method.

2.3.2 Aspirate demineralized water or other sample solvent between each sample.

2.3.3 After every seventh sample, check the operating conditions of the instrument by aspirating a blank and, in random order, one of the calibration standards. If the reading of the calibration standard differs from the original calibration results by more than 2 percent or if baseline drift is indicated, take corrective measures immediately.

2.3.4 It is usually unnecessary to match the dissolved solids content of the standards

and samples unless the dissolved solids concentration of the samples exceeds 1 percent. If matrix effects are severe, dilute the sample, use a chelation-extraction technique, or use the standard-addition technique.

2.3.5 When a sample is to be analyzed by the method of standard additions, take four equal aliquots of sample. Add to three of these aliquots known amounts of analyte equal to one, two, and three times the approximate concentration of the sample. Dilute all four solutions to the same volume. Aspirate with solvent and adjust the absorbance read-out to zero. Aspirate, in random order, the above standard-addition solutions. If necessary, subtract any nonatomic absorbance from the absorbance readings. Prepare a calibration graph by plotting the absorbance against the added concentration. Extrapolate the resulting straight line through zero absorbance. The intercept on the absorbance axis gives the concentration of the constituent in the original sample. The standard-addition technique must show linear relationship between absorbance and concentration in order to be valid.

2.3.6 Atomic absorption procedures involving the use of flameless and electrothermal-vaporization techniques have become increasingly popular. The operation and calibration steps closely parallel those for flame determination although a recorder, if employed as a read-out device, must have a full-scale response time of 0.5 seconds or less. The matrix effects for electrothermal-vaporization techniques are much more severe, and the method of standard additions must be used routinely. Background correction must also be employed for electrothermal-vaporization procedures.

2.4 Read-out and graphical techniques

2.4.1 If Beer's law is followed or if a nonlinear curve can be electronically corrected by the atomic absorption spectrometer, obtain concentration readings directly from the instrument.

2.4.2 Alternatively determine the constituent concentration from a plot of the average absorbances obtained for the standard solutions versus their respective concentrations.

2.4.3 If the analytical curve is nonlinear and uncorrected, use the calibration values to obtain, by regression analysis, a parabolic equation, $y = a_0 + a_1x + a_2x^2$, where y = absorbance and x = concentration. Obtain the constituent concentrations for the sample solutions by the direct substitutiion of absorbance values into the equation, or use the derived parabolic equation to construct a graph of absorbances of standards versus their respective concentrations and use the graph to obtain the concentration values of the sample solutions.

2.4.4 If the analytical curve is linear at low concentrations and becomes curved as the concentration increases, plot the linear portion of the curve immediately and use the calibration values from the nonlinear portion of the curve to calculate the parabolic equation. This equation, of course, applies only to the nonlinear portion of the curve.

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Automated Analyzers

1. Application or scope

1.1 This practice details procedures to be followed in using automated wet-chemical analyzers.

1.2 The most commonly used automated analyzer system is the Technicon AutoAnalyzer which generally includes a sampler, proportioning pump, cartridge manifold, heating bath (if necessary), colorimeter or ion-selective electrode module, voltage stabilizer, recorder, and possibly a printer.

1.3 Other automated systems (for instance, discrete or batch analyzers) or modular components compatible with AutoAnalyzer modules may be substituted, but their precision and accuracy must be at least equivalent.

1.4 AutoAnalyzer modules, on occasion, have been used to automate instruments such as atomic absorption spectrometers. It is imperative that the applicable precautions, such as changing pump tubes routinely, which are recommended for the complete system, also be practiced when modules are used in this manner. Some automated atomic absorption procedures are designed to handle water-suspended sediment mixtures. A sampler with a stirring attachment is required in these situations.

2. Practice

2.1 Basic operational procedure

2.1.1 The platen pressure for the proportioning pump is adjusted at the factory and remains quite consistent if the platen is not used on different pumps. However, adjust the platen according to the manufacturer's instructions if the pump tubes wear rapidly because the platen pressure is too low (NOTE 1).

NOTE 1. There are many causes for erratic flow; improperly adjusted platen pressure is one of the less frequent causes.

2.1.2 The material of the pump tubes must be compatible with the solution being pumped. Inspect them frequently, and determine a routine replacement schedule based on the amount and frequency of use.

2.1.3 The Technicon "colorimeter" is a two-photocell filter photoelectric colorimeter. The procedures described in the practice, "Colorimetric spectrometers" are generally applicable to its operation.

2.1.4 The two most common flow-cell lengths are 15 mm and 50 mm; the length to be used is determined primarily by the sensitivity of the procedure. The flow cell is removed from the instrument infrequently; therefore, the opportunity for handling-contamination is reduced. When it is necessary to handle the cell, handle carefully and do not scratch it.

2.1.5 Handle the light source with care. Keep the light filters used in the instrument scrupulously clean.

2.1.6 Check and optimize the optical alinement periodically and follow the manufacturer's instructions, whenever a light source is replaced.

2.1.7 Replace the filter photometer with an ion-selective electrode module for electrometric determinations. Determinations are usually performed at temperatures exceeding 25°C and thermal stability as well as electronic stability is very important. Handle the ion-selective electrodes according to the manufacturer's instructions.

2.1.8 Set the indicator control on the filter photometer first to zero and then to full scale. The recorder should read zero and 100, respectively. If it does not, adjust the appropriate set screws on the photometer until the desired recorder readings are obtained.

2.1.9 Similar controls are also present in the ion-selective electrode module. In addition, another control switch contains four positions, two of which are labeled "Cal 1" and "Cal 2." Adjust these positions to give recorder readings of zero and 50, respectively. Adjustments are also available on the ion-selective electrode module to correct these readings, if necessary.

2.1.10 If results appear inconsistent or noisy, check to see if the following problems exist:

- Dirty transmission line
- Inadequate warm-up time
- Erratic bubble patterns
- Improper sample-to-wash ratio
- Worn pump tubing
- Improper sampling rate
- Improperly functioning air-bar
- Improper cooling of the flow cell.

Correct any of the above factors which are present. A properly operating system will contain evenly spaced sample segments which flow with little or no surging through the system.

2.2 Calibration procedure

2.2.1 Allow the instrument to electronically stabilize, and set the operating parameters as specified for the analytical method. Specified parameters should include sampling rate, sample-to-wash ratio, flow-cell length, heating bath temperature, filters, and wavelength. The size and type of pump tubing and the manifold arrangement are to be considered an integral part of the methodology for a particular determination.

2.2.2 Pumping all reagents through the system, but using wash solution (usually demineralized water) in the sample line, adjust the baseline on the recorder to read zero. Adjust the printer to read zero also.

2.2.3 After the baseline has stabilized with wash solution in the sample line, proceed with calibration and with analysis of samples. Beginning with the highest standard, place a minimum of five standards, equally spaced over the analytical range, in the first positions of the first sample tray.

2.2.4 Place individual standards of differing concentrations or a blank solution in every eighth position of this and subsequent sample trays, filling the remainder of each tray with unknown samples.

2.2.5 When the peak from the highest standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale. Adjust the printer to read the correct concentration value.

2.2.6 If the STD CAL setting and instrument noise are consistent with previous, acceptable determinations, proceed with the analysis. If a problem exists, locate and correct it; then recalibrate and continue.

2.2.7 Whenever an instrument is calibrated, keep a written record of the STD CAL setting for each set of standards. A significant change ($\geq$ 10 percent) from previously documented results immediately indicates that a problem exists with the operational settings, the performance of the system, or the accuracy of the standard solutions. Take corrective action before analysis of samples begins. Be aware that subtle but consistent changes in STD CAL settings may be indicative of such things as the gradual deterioration of standard solutions, an instrument part malfunction, or the initial stage of a lamp failure.

2.3 Measurement procedure

2.3.1 Appropriate analytical ranges for each parameter are specified in Skougstad and others (1979) and must be closely followed. If the concentration of a constituent falls outside of the recommended range, adjust the concentration by dilution, or use an alternative analytical method.

2.3.2 If the calibration standards which are in every "eighth" position differ from the original calibration results by more than 2 percent, or if baseline drift is indicated, take corrective measures immediately.

2.3.3 The information concerning colored waters in the practices "Correction for color interference" and "Colorimetric spectrometers," is generally applicable to automated, colorimetric procedures. Attempt to compensate for color by passing an additional stream containing the sample and all reagents, except for the indicator reagent, through the reference channel of the photometer. The points at which reagent solutions are added and the mixing schemes have to be identical for the two streams, and the sample solution must be phased to arrive at both cells at the same time. In applicable cases, the absorbance due to sample color will be subtracted.

2.3.4 Alternatively, use a bleaching or adsorption procedure to remove the color before the sample is placed on the sampler turntable. Be sure that the chemistry of the constituent being determined is not affected and be careful to avoid contamination and the problems associated with adsorption.

2.3.5 If excess turbidity is present, remove it by passing the sample through a 0.45-

μm filter or use an alternative procedure (NOTE 2).

NOTE 2. The sample also may be centrifuged, often after using a flocculating agent such as acidified sodium chloride, to remove turbidity. However, as noted in Skougstad and others (1979, p. 294), "Centrifuging is often useful, but it is less efficient than membrane filters for fine particles."

2.4 Read-out and graphical techniques

2.4.1 If the AutoAnalyzer procedure follows Beer's law, use the printer concentration directly.

2.4.2 If a printer is unavailable, plot standard concentration versus recorder readings and determine the concentrations of the samples from the graph.

2.4.3 If the analytical curve is nonlinear, use the calibration values to obtain, by regression analysis, a parabolic equation $y = a_0 + a_1x + a_2x^2$ where y = recorder reading and x = concentration. Sufficient standards must be used in the nonlinear portion of the curve to properly define it. Obtain the constituent concentrations by direct substitution of recorder readings into the equation, or use the derived parabolic equation to construct a graph of recorder values of standards versus their respective concentrations and use the graph to obtain the concentration values of the sample solutions.

2.4.4 If the analytical curve is linear at low concentrations and becomes curved as the concentration increases, plot the linear portion of the curve immediately and use the calibration values from the nonlinear part of the curve to calculate the parabolic equation. This equation, of course, applies only to to the nonlinear portion of the curve.

Reference

Skougstad, M. W., Fishman, M. J., Friedman, L. C., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.

Colorimetric Spectrometers

1. Application or scope

1.1 This practice details procedures to be followed in the calibration and operation of spectrometers.

1.2 A spectrophotometer consists essentially of a radiant-energy source; a device, such as a prism or grating with a selection slit, for isolation of relatively monochromatic radiant energy; one or more absorption cells to hold the sample, standards, and blank; and a photodetector to measure the radiant energy passed through the solution. Commercially available spectrophotometers vary with regard to such features as spectral bandpass, type and quality of monochromators, read-out devices, and availability of optional equipment.

1.3 A filter photometer uses a filter in place of a prism or grating. The resulting light is not as monochromatic; in addition, this instrument lacks the versatility of a spectrophotometer. However, in spite of these drawbacks, the recent trend towards automated procedures has increased the popularity of the filter photometer because it is well suited to individual determinations.

1.4 The addition of a semiautomated device to aspirate the samples directly into the cell, and then to a waste line after a reading has been obtained, is a very desirable feature if a large number of samples is being analyzed, because it is faster and eliminates most of the problems involved with cell handling and placement.

2. Practice

2.1 Basic operational procedures

2.1.1 The light source usually used in the visible region is a tungsten filament incandescent bulb. Align the bulb according to the manufacturer's manual whenever it is replaced or disturbed. Be careful not to touch the glass part of the lamp because serious deterioration of an instrument's performance may result.

2.1.2 Check the alinement of the cell holder periodically. If it is removed or disturbed, realine the cell holder according to the manufacturer's instructions.

2.1.3 When handling a cell, protect it from scratches and never permit it to rub against another cell or against other hard surfaces.

2.1.4 Avoid using abrasive, corrosive, or stain-producing cleaning agents in or on a cell.

2.1.5 Do not handle the part of the cell through which the light beam will pass.

2.1.6 Always rinse the cell with several portions of the solution before taking a measurement.

2.1.7 Wipe the outside of the cell with clean lens paper to eliminate any liquid drops or smudges. Inspect to ensure that no lint remains on the outside or that no small air bubbles cling to the inner surface of the cell.

2.1.8 If two cells are used simultaneously, always use one for the blank solution and the other for the various samples.

2.1.9 Carefully place the cells in the sample holder to avoid scratches. Position cells with identifying lines or marks as specified in the manufacturer's manual.

2.1.10 For maximum precision and accuracy, standardize and measure with matched cells. The placement of cells in a correct (exactly at right angles to the beam), reproducible manner cannot be overemphasized.

2.1.11 Check the wavelength calibration at least every 6 months. Many high quality standards having very sharp absorption or emission peaks that are isolated from nearby peaks can be used. Some of the more practical methods for calibration in the visible region involve the use of one of the following materials: holmium oxide glass, holmium oxide solution, mercury lamp, or deuterium lamp. Consult the manufacturer's manual for specific directions.

2.2 Calibration procedures

2.2.1 After the alinement procedures have been completed, allow the instrument to electronically stabilize and then set the

wavelength, slit width, if variable, and other operating parameters as specified in either the Techniques of Water-Resources Investigations (TWRI), Book 5, Chapters A1 and A3, or in the operator's manual.

2.2.2 If information on the optimum slit width for a particular determination is unavailable, it must be determined. This depends on the spectral characteristics of the sample and the dispersion of light in the spectrophotometer. Use the narrowest slit width that will give an acceptable signal-to-noise ratio. Block the source light from the photodetector and set the percent transmittance reading to 0.00. Insert a blank, consisting of demineralized water and reagents added in the same volume and manner as for standards and samples into the light path and set the percent transmittance to 100.0 (equivalent to an absorbance of 0.000). Refer to the manufacturer's manual for a complete description of the calibration procedures for the absorbance and concentration modes. Do not use the concentration mode if the calibration curve is not linear over the operating range. When reading concentration directly, do not measure absorbances of solutions that exceed the working range of the procedure.

2.2.3 The appropriate concentration ranges for each parameter are specified in the TWRI, Book 5, Chapters A1 and A3 or in other analytical methods manuals and technical journals. Use a minimum of four standards, equally spaced over the concentration range, to calibrate a visible-range spectrophotometer in the absorbance mode. The blank, standards, and sample solutions all must contain the same concentration of added reagents.

2.2.4 Follow the manufacturer's instructions when calibrating an instrument in the concentration mode. If less than four standards are employed in this procedure, use the remaining standards to confirm the validity of the calibration.

2.2.5 Recheck the 0.00 and 100.0 percent transmittance points, and if they and the readings for the standards are satisfactory, the instrument is correctly calibrated. If not, repeat the above procedure. If a problem still exists, locate and correct it before proceeding further.

2.2.6 Whenever an instrument is calibrated for a determination, keep a written record of the slit width, if applicable, and absorbance readings (percent transmittance readings should be used only if this is the only measurement scale available) for each set of standards. A significant change (≥ 10 percent) from previously documented results, immediately indicates that a problem exists with the operational settings, the performance of the spectrophotometer, or the accuracy of the standard solutions. Take immediate, corrective action. Be aware that subtle, but consistent changes in absorbance readings may be indicative of such things as the gradual deterioration of standard solutions, an instrument-part malfunction, or the initial stage of lamp failure.

2.2.7 The rate of development and the stability of the color formed in spectrophotometric procedures for water analysis vary considerably. Most procedures specify the time required for color development. The recommended time interval must be closely followed for both standards and samples.

2.3 Measurement procedure

2.3.1 Prepare sample solutions as directed in the analytical procedure. If the working range of the method is exceeded, dilute the sample or use an alternative procedure.

2.3.2 After every 10th sample, check the stability of the spectrophotometer by measuring a blank, and in random order, one of the calibration standards. If the reading of the calibration standard differs from the original calibration value by more than 2 percent, or if drift is indicated, take corrective measures before proceeding with the analysis. If the color complex is unstable, sufficient standards must be prepared in the order in which they will be read, so that a standard can be inserted after every tenth sample.

2.3.3 The natural color in many water samples shows an appreciable absorbance at the wavelengths used in a number of determinations; this effect requires either compensation or elimination. In some cases, a procedure has such high sensitivity that the absorbance of the constituent sought will exceed the absorbance of the natural color by a very large factor. If this factor is as high as 50 for a particular determination, the error introduced by the natural color will be only 2 percent and, in routine work, no compensation will be required. Simi-

larly, if the sensitivity of a procedure is sufficiently high, it is often possible to minimize the color absorbance by diluting the sample while still obtaining an accurate concentration value for the constituent. This technique requires a knowledge of the relative sensitivity for the constituent sought.

2.3.4 If the relative sensitivity is not known or if there is any doubt as to the effect of color on the absorbance of the element sought, attempt should be made to remove or compensate for the color present by using the following procedure. Take the same volume of sample water as was used for the test sample with one exception: do not add the indicator reagent. Instead, add an equal volume of indicator solvent, usually dilution water. Measure the absorbances of these two samples. The corrected absorbance, which is used to obtain concentration values, is the difference between the absorbance of the test sample with indicator reagent and the natural-color corrections. This method fails when the indicator reagent reacts with or affects the natural color or turbidity in the water sample. The latter qualification relates more to turbidity than color, and filtration of an excessively turbid sample through a 0.45 μm filter may be required.

2.3.5 If (such as with very highly colored waters), the above procedure is not applicable, procedures involving bleaching or adsorption can sometimes be used to advantage. These techniques must be applied with great care, however, because it is relatively easy to contaminate or change the sample by either adding or removing constituents from the water sample.

2.4 Read-out and graphical techniques

2.4.1 If Beer's law is followed, the concentration readings can be obtained directly from the instrument, if it has concentration mode capabilities.

2.4.2 Alternatively, the constituent concentration can be determined from a plot of absorbances obtained for the standard solutions versus their respective concentrations.

2.4.3 If the analytical curve is nonlinear, the calibration values of the standards must be used to obtain, by regression analysis, the parabolic equation $y = a_0 + a_1x + a_2x^2$ where y = absorbance and x = concentration. Sufficient standards must be used to properly define the equation. Obtain constituent concentrations by direct substitution of absorbance values into the above equation, or use the derived parabolic equation to construct a graph of the absorbances of standards versus their respective concentrations, and use the graph to obtain the concentration values of the samples.

2.4.4 If the analytical curve is linear at lower concentrations and becomes curved as the concentration increases, plot the linear portion of the curve immediately and use the calibration values from the nonlinear part of the curve to calculate the parabolic equation. This equation, of course, applies only to the curved portion.

2.4.5 If the scale of the spectrophotometer does not read directly in absorbance, it is most convenient to plot concentration against percent transmittance on semilogarithmic paper, using the logarithmic scale for the percent transmittance values.

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Conductivity Meters

1. Application or scope

1.1 This practice details procedures to follow in using conductivity meters. Conductivity meters are of relatively uncomplicated design and produce excellent results with simple quality control measures.

1.2 Conductivity meters consist essentially of a source of alternating current, a wheatstone bridge, a null indicator, and a conductivity cell. Conductivity cells usually consist of two thin plates of platinized metal, rigidly supported with a very precise parallel spacing. Pure platinum electrodes and circular carbon rings imbedded in an epoxy-type plastic cell are also used.

2. Practice

2.1 Basic operational procedure

2.1.1 At regular intervals, visually check the cell to insure that the platinized electrode surfaces are in good condition, that the electrodes are not bent, distorted, or fouled, and that the lead wires are properly separated and shielded to prevent electrolytic and capacitive current.

2.1.2 Clean and replatinize electrodes whenever the readings become erratic or inspection shows that any platinum black has flaked off. New electrodes must also undergo these cleaning and platinizing steps.

2.2 Calibration procedure

2.2.1 Allow the conductance instrument to electronically stabilize.

2.2.2 Prepare the KCl standard with care (NOTE 1). Compare the conductivity of a newly prepared standard with a previously prepared standard in order to ensure that the standard is correct.

NOTE 1. To prepare a 0.00702*N* potassium chloride solution, dissolve 0.5234 g KCl, dried at 180°C for 1 hour, in demineralized water and dilute to 1,000 mL (Skougstad and others, 1979); this solution has a specific conductance of 1,000 μmho/cm at 25°C. For potassium chloride solutions which will have other specific conductances, see Standard Methods (American Public Health Association and others, 1976).

2.2.3 Carefully measure the temperature of the standard solution (NOTE 2).

NOTE 2. Temperature significantly affects conductance measurements since conductance increases about 2 percent per degree Celsius. In the U.S. Geological Survey, specific conductance measurements are routinely reported at 25°C.

2.2.4 For direct-reading instruments with temperature compensation, measure the temperature of a 1,000 μmho/cm KCl standard, set the temperature control, and adjust the instrument to read 1,000. If another scale is used, check the calibration with another standard which is known to be in the range of the new scale.

2.2.5 For direct-reading instruments that are not temperature compensated, calibrate the instrument to read the conductance value of the KCl standard solution at the measured temperature by preparing a table of the conductivity of 0.00702*N* KCl versus temperature. If another scale is used, check the calibration with another standard which is known to be in the range of the selected scale.

2.2.6 For resistance measurements made using a wheatstone bridge, determine the cell constant of a particular cell according to directions in the methods manual. Inasmuch as the cell constant can change, it is necessary to recalculate this constant periodically. The resistance of sample solutions, and consequently their specific conductance, may be determined at 25.0°C by using a 25°C bath or by allowing samples to stabilize in a constant-temperature room (Skougstad and others, 1979). However, usually it is easier to determine experimentally the resistance of a standard KCl solution at 0.1°C intervals and make a correction to obtain the corresponding conductance at 25.0°C.

2.3 Measurement procedure

2.3.1 Carefully and thoroughly rinse the cell between each sample.

2.3.2 Record the temperature of each sample solution to the nearest 0.1°C.