

April 3, 2002

To: Water Resources Division

From: Peter F. Rogerson, Senior Chemist
Office of Water Quality

For: LeRoy Schroder, Chief
Branch of Quality Systems

Subject: Approval of Water Quality Analytical Methods for the Determination of Field and Laboratory Arsenic Speciation in Filtered Water

The Office of Water Quality (OWQ) has approved 4 new Water Quality Analytical Methods for the determination of field and laboratory arsenic speciation in filtered water, developed by the National Water Quality Laboratory (NWQL). All methods, both field and laboratory, report all speciation results as micrograms of arsenic per liter.

The new field method, I-1190-02, uses a strong anion exchange cartridge to separate the anion arsenate (H_2AsO_4^-) from uncharged arsenite (H_3AsO_3) in the field, with laboratory determination by graphite furnace atomic absorption (GFAA) of the field-separated arsenic species. Advantage: no arsenic species stability questions.

There are 3 alternative laboratory arsenic speciation methods which all use high performance liquid chromatography (HPLC) to separate arsenic species in samples preserved with ethylenediamine tetraacetic acid (EDTA). Different HPLC conditions are used for each method. One method uses the more-sensitive hydride generation sample introduction system to enhance sensitivity and specificity, while one method only determines the 2 major inorganic arsenic species (see table below). The three laboratory methods are:

1. Method I-2191-02 uses an HPLC phosphate mobile phase to separate 4 arsenic species with determination by hydride generation inductively-coupled plasma mass spectrometry (ICP/MS). Advantages: highest sensitivity, lowest analytical interference effects, all 4 arsenic species determined.
2. Method I-2193-02 uses an HPLC nitrate mobile phase to separate 4 arsenic species with determination by ICP/MS. Advantages: good sensitivity, all 4 arsenic species determined, other organoarsenic species also can be determined on a custom basis, lower cost.
3. Method I-2192-02 uses an HPLC malonate/acetate mobile phase to separate arsenate (H_2AsO_4^-) from arsenite (H_3AsO_3) with determination by ICP/MS.

Advantages: good sensitivity, determines 2 major inorganic arsenic species, lowest cost.

I-1190-02 Field separation, Lab HGAA

| Constituent: | Parameter Code | Lab Code | Method Code | Detection Limit, est., ug/L as As |
|--|----------------|----------|-------------|-----------------------------------|
| arsenite (H ₃ AsO ₃ , As(III)) | 62452 | 2738 | A | 0.3 |
| arsenate (H ₂ AsO ₄ -, As(V)) | 62453 | 2739 | A | 0.3 |

I-2191-02 Lab separation by HPLC phosphate, Lab Hydride ICP/MS

| Constituent: | Parameter Code | Lab Code | Method Code | Detection Limit, est., ug/L as As |
|---|----------------|----------|-------------|-----------------------------------|
| arsenite (H ₃ AsO ₃ , As(III)) | 62452 | 2734 | B | 0.1 |
| arsenate (H ₂ AsO ₄ -, As(V)) | 62453 | 2735 | B | 0.2 |
| monomethylarsonate (MMA) ((CH ₃)HAsO ₃ -) | 62454 | 2736 | B | 0.1 |
| dimethylarsinate (DMA) ((CH ₃) ₂ HAsO ₂) | 62455 | 2737 | B | 0.1 |

I-2193-02 Lab separation by HPLC nitrate, Lab ICP/MS

| Constituent: | Parameter Code | Lab Code | Method Code | Detection Limit, est., ug/L as As |
|---|----------------|----------|-------------|-----------------------------------|
| arsenite (H ₃ AsO ₃ , As(III)) | 62452 | 2740 | D | 0.3 |
| arsenate (H ₂ AsO ₄ -, As(V)) | 62453 | 2741 | D | 0.3 |
| monomethylarsonate (MMA) ((CH ₃)HAsO ₃ -) | 62454 | 2742 | D | 0.2 |
| dimethylarsinate (DMA) ((CH ₃) ₂ HAsO ₂) | 62455 | 2743 | D | 0.2 |

I-2192-02 Lab separation by HPLC malonate/acetate, Lab ICP/MS

| Constituent: | Parameter Code | Lab Code | Method Code | Detection Limit, est., ug/L as As |
|--|----------------|----------|-------------|-----------------------------------|
| arsenite (H ₃ AsO ₃ , As(III)) | 62452 | 2744 | C | 0.6 |
| arsenate (H ₂ AsO ₄ -, As(V)) | 62453 | 2745 | C | 0.6 |

This method approval process follows the technical procedure specified in OWQ Tech Memo 98.05, except that this method is described in a Water Resources Investigations Report instead of an Open File Report. The method performance is described in:

Methods of Analysis by the U.S. Geological Survey National Water Quality laboratory – Arsenic Speciation in Natural-Water Samples using Laboratory and Field Methods, by John R. Garbarino, Anthony J. Bednar, and Mark R. Burkhardt.

U.S. Geological Survey Water Resources Investigations Report YY-XXXX (number to be assigned upon Director's approval).

When approved by the Director, the report will be made available through the NWQL web site at: <http://wwwnwql.cr.usgs.gov/USGS/Pubs/pubs.html> .

Information about the new method will be available later through the NWQL web site <http://wwwnwql.cr.usgs.gov/USGS>. Please click on SPiN and request information on the above Parameter or Lab codes. Note: This announcement predates information release in SPiN, so it may be a few days before information is available.

If you have questions about the new analytical method or would like a copy of the report, when it is available, please contact John Garbarino (jrgarb@usgs.gov) (303) 236-3945) or Mark Burkhardt (mrburk@usgs.gov (303) 236-3250) at the NWQL.

If you have questions about the method approval process, please contact Pete Rogerson (rogerson@usgs.gov, (303) 236-1836).