November 3, 2005 (revised)

To: Water Resources Discipline

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

Subject: Approval of a Water Quality Analytical Method for the Determination of Elements in Natural Water, Biota, Sediment, and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry

The Office of Water Quality has approved new water-quality analytical methods by the National Water Quality Laboratory (NWQL) for the determination of trace and common elements in filtered water (I-2020-05), whole water (I-4020-05), biota (I-9030-05), and sediment and soils (I-5050-05) by collision/reaction cell inductively coupled plasma-mass spectrometry (cICP/MS). The previous ICP/MS versions of these methods were assigned USGS method numbers I-2477-92 in filtered water and I-4472-97 in whole-water digests. This water-quality analytical method approval follows the technical procedure specified in OWQ Tech Memo 98.05, except that the report will be published as a Techniques and Methods Report, Book 5, Chapter B1. The draft report is entitled:

> Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory-Determination of Elements in Natural-Water, Biota, Sediment, and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry, by John R. Garbarino, Leslie K. Kanagy, Mark E. Cree.

The new method uses inductively coupled plasma ionization source and a quadrupole mass spectrometric detector source, as in earlier ICP/MS methods. The difference in the new method lies primarily in a gas-filled collision/reaction cell between the source and the mass spectrometer, which effectively eliminates the polyatomic interferents that were troubling for several elemental determinations, including chromium, iron, and arsenic. The new cICP/MS method and earlier ICP/MS methods produce similar results when elemental concentrations are comparable and polyatomic interferences are not present

Because of general technological improvements, cICP/MS detection limits are somewhat improved over earlier methods, and results show lower variability at low trace-element concentrations. Method detection limits for the cICP/MS method are typically less than 0.1 ug/L, except for boron and iron, which are about 1.0 ug/L because of reagent blank concentrations. The upper calibration standards for the method are 100 ug/L, except for aluminum, barium, manganese, strontium, and zinc, which are calibrated to 2,500 ug/L. Alkali and alkaline earth elements are typically calibrated to 100 mg/L.

The new method improves arsenic speciation determinations due to elimination of polyatomic interferences. Therefore, this method is also applied to arsenic speciation methods previously established by an OWQ Methods Approval Announcement dated April 3, 2002. The new methods, updated using the same earlier preparation and separation techniques, but followed by the new cICP/MS detection method are as follows:

1. Method I-2195-05 uses an HPLC phosphate mobile phase to separate 4 arsenic species with determination by hydride generation inductively-coupled plasma mass spectrometry (cICP/MS). Advantages: highest sensitivity, lowest analytical interference effects, all 4 arsenic species determined. This method replaces I-2191-02**.**

2. Method I-2193-05 uses an HPLC nitric acid mobile phase to separate 4 arsenic species with determination by cICP/MS. Advantages: good sensitivity, all 4 arsenic species determined, acid mine drainage samples can be analyzed, other organoarsenic species also can be determined on a custom basis, lower cost. This method replaces I-2193-02.

3. Method I-2196-05 uses an HPLC malonate/acetate mobile phase to separate arsenate (H2AsO4-) from arsenite (H3AsO3) with determination by cICP/MS. Advantages: good sensitivity, determines 2 major inorganic arsenic species, lowest cost. This method replaces I-2192-02.

4. Method I-2197-05 uses field solid phase extraction to separate arsenate (H2AsO4-) from arsenite (H3AsO3) with determination by cICP/MS. Advantages: minimizes loss of speciation, determines 2 major inorganic arsenic species. This method replaces I-1190-02.

For current information and method codes, please consult the NWQL on-line catalog at: http://rstalcoarv.cr.usgs.gov/USGS/USGS_gen.html. If you have questions about the method approval process, or if you need more information about the process, please contact Pete Rogerson (rogerson@usgs.gov), (303) 236-1836.

For further information about the cICP/MS method please contact the senior author, John Garbarino (jrgarb@usgs.gov), (303) 236-3945.