METHODS OF ANALYSIS BY THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY— DETERMINATION OF ARSENIC AND SELENIUM IN WATER AND SEDIMENT BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY

U.S. GEOLOGICAL SURVEY

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By Sandra R. Jones and John R. Garbarino

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CONVERSION FACTORS, ABBREVIATED WATER-QUALITY UNITS AND ADDITIONAL ABBREVIATIONS

Multiply	*By*	*To obtain*
gram (g)	3.53×10^{-2}	ounce, avoirdupois
liter (L)	3.38×10^{1}	ounce, fluid
microgram (µg)	3.53×10^{-8}	ounce, avoirdupois
microliter (µL)	3.38×10^{-5}	ounce, fluid
milligram (mg)	3.53×10^{-5}	ounce, avoirdupois
milliliter (mL)	3.38×10^{-5}	ounce, fluid
nanometer (nm)	3.94×10^{-8}	inch
picogram (pg)	3.53×10^{-14}	ounce, avoirdupois

Degree Celsius (^{o}C) may be converted to degree Fahrenheit (^{o}F) by using the following equation:

$$^{o}F = 9/5\ (^{o}C)+32.$$

Abbreviated water-quality units used in this report:

mg/L	milligram per liter
mL/min	milliliters per minute
µg/g	microgram per gram
µg/L	microgram per liter
µS/cm	microsiemens per centimeter at 25 degrees Celsius

Other abbreviations used in this report:

As	arsenic
a-s	absorbance-seconds
ASTM	American Society for Testing and Materials
GFAAS	graphite furnace atomic absorption spectrometry
HGAAS	hydride generation atomic absorption spectrometry
HGA	heated graphite atomizer
ICP–MS	inductively coupled plasma–mass spectrometry
M	molarity (moles per liter)
MDL	method detection limit
M_o	characteristic mass
MRL	method reporting level
NWQL	National Water Quality Laboratory
Se	selenium
sp gr	specific gravity

Other abbreviations used in this report – continued

SRWS	Standard Reference Water Samples
STPF	stabilized temperature platform furnace
THGA	transverse heated graphite atomizer
USGS	U.S. Geological Survey
v/v	volume per volume
w/v	weight per volume
WWR	whole-water recoverable

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ABSTRACT

Graphite furnace atomic absorption spectrometry (GFAAS) is a sensitive, precise, and accurate technique that can be used to determine arsenic and selenium in water samples and sediment samples. Because the method detection limits are similar, bias and variability are comparable, and interferences are minimal, the GFAAS method has been developed to replace the hydride generation atomic absorption spectrometry (HGAAS) methods. Advantages of the GFAAS method include shorter sample preparation time, increased sample throughput from simultaneous multielement analysis, reduced amount of chemical waste, reduced sample volume requirements, increased linear concentration range, and the use of a more accurate digestion procedure. The linear concentration range for arsenic and selenium is 1 to 50 micrograms per liter (µg/L) in solution; the current method detection limit for arsenic in solution is 0.9 µg/L; the method detection limit for selenium in solution is 1 µg/L.

This report describes results that were obtained using stop-flow and low-flow conditions during atomization. The bias and variability of the simultaneous determination of arsenic and selenium by GFAAS under both conditions are supported with results from standard reference materials – water and sediment, spike recoveries, and natural-water samples. Arsenic and selenium results for all Standard Reference Water Samples analyzed were within one standard deviation of the most probable values. Long-term spike recoveries at 6.25, 25.0, and 37.5 µg/L in reagent-, ground-, and surface-water samples for arsenic averaged 103±2 percent using low-flow conditions and 104±4 percent using stop-flow conditions. Corresponding recoveries for selenium were 98±13 percent using low-flow conditions and 87±24 percent using stop-flow conditions. Spike recoveries at 25 µg/L in 120 water samples ranged between 97 and 99 percent for arsenic and between 82 and 93 percent for selenium, depending on the flow conditions used. Statistical analysis of dissolved and whole-water recoverable analytical results for the same set of water samples indicated there are no significant difference between the GFAAS and HGAAS methods.

Interferences related to various chemical constituents were also identified. Although sulfate and chloride in association with various cations might interfere with the determination of arsenic and selenium by GFAAS, the use of a magnesium nitrate/palladium matrix modifier and low-flow argon during atomization helped to

minimize such interferences. When using stabilized temperature platform furnace conditions where stop flow is used during atomization, the addition of hydrogen (5 percent volume/volume) to the argon minimized chemical interferences. Nevertheless, stop flow during atomization was found to be less effective than low flow in reducing interference effects.

INTRODUCTION

Arsenic is a metallic element whose compounds are used in insecticides, weed killers, lead shot, semiconductor devices, various alloys, pressure-treated wood products, and in glass, enamel, and ceramic manufacturing. Selenium, a nonmetallic element, is used in pigments, photographic exposure meters, electronics, and xerography. In addition, both elements can be found in naturally occurring minerals that can be solubilized through erosion processes. Their significance to water quality is important because arsenic and selenium can be toxic to organisms and humans causing problems from skin disorders to deformities and death.

The U.S. Geological Survey National Water Quality Laboratory (NWQL) has developed a new graphite furnace atomic spectrometry (GFAAS) method to replace the hydride generation atomic absorption spectrometry (HGAAS) methods for the analysis of arsenic and selenium found in “Methods for determination of inorganic substances in water and fluvial sediments” (Fishman and Friedman, 1989). The arsenic method (I-2062-85, I-4062-85, I-6062-85) has a method reporting limit (MRL) of 1 μg/L and a linear analytical range to 20 μg/L; the selenium method (I-2667-85, I-4667-85, I6667-85) has a MRL of 1 μg/L and a linear analytical range to 15 μg/L. The GFAAS method was developed for the simultaneous determination of arsenic and selenium in water and sediment and offers comparable sensitivity, bias and variability, reduces chemical waste, and extends the analytical concentration range to 50 μg/L.

The HGAAS methods each require about 15 mL of sample, a digestion procedure to oxidize organic species, and a procedure to reduce the analyte to the appropriate oxidation state. In contrast, GFAAS requires less than 1 mL of sample and no additional preparatory procedures. In the GFAAS method, about 30 microliters of aqueous sample is placed directly into a graphite tube, dried and atomized into ground-state atoms. The ground-state atoms absorb light from an electrodeless discharge lamp in an amount that is directly proportional to the concentration of arsenic or selenium in the sample.

Arsenic and selenium determination by GFAAS requires four basic steps: drying, pyrolysis, atomization, and clean out. After the sample is pipetted into the pyrolytically coated graphite tube, the tube is purged with a continuous flow of argon and gently heated to dryness. Following the drying step, the temperature is raised to the pyrolysis or charring temperature. After pyrolysis, the tube may be cooled to a uniform temperature followed by rapid heating (less than 1 second) to the atomization temperature. Gas flow through the tube then is lowered or stopped, and the sample is atomized into the optical path where the light absorption is measured. Following atomization, the gas flow is increased and a high-temperature clean-out step is used to prepare the graphite tube for the next sample.

This report describes a method developed by the U.S. Geological Survey (USGS) for use at the NWQL for the simultaneous determination of arsenic and selenium by GFAAS. The method supplements other methods of the USGS for determination of arsenic and selenium in water and sediment samples that are described by Fishman and Friedman (1989). This method was implemented at the NWQL on October 1, 1998.

ANALYTICAL METHOD

Inorganic Constituents and Watstore Codes

Arsenic, dissolved, I-2063-98 (µg/L as As): 01000
Arsenic, whole water recoverable, I-4063-98 (µg/L as As): 01002
Arsenic, total recoverable in bed sediment, dry weight, I-6063-98 (µg/g as As): 01003
Selenium, dissolved, I-2668-98 (µg/L as Se): 01145
Selenium, whole water recoverable, I-4668-98 (µg/L as Se): 01147
Selenium, total recoverable in bed sediment, dry weight, I-6668-98 (µg/g as Se): 01148

1. Application

1.1 This method is used to analyze filtered and nonfiltered (also referred as whole-water) water samples for the determination of dissolved and whole-water recoverable (WWR) arsenic and selenium and bed sediment (also referred to as bottom material) for total recoverable arsenic and selenium. Using a 30-µL sample-injection, the linear analytical range is 1 to 50 µg/L for arsenic and selenium. Samples that contain arsenic or selenium concentrations exceeding the upper limit of the analytical range need to be diluted and re-analyzed or analyzed by an alternate method.

1.2 Furnace temperature programs, volumes, matrix modifiers, and other instrumental settings may be modified provided that characteristic mass (±20 percent) is maintained, and the method detection limit (MDL) is equivalent or lower. Characteristic mass (M_O) best describes instrumental and operational performance; it is defined as the mass of an analyte in picograms required to produce a signal of 0.0044 absorbance-seconds (a-s). The characteristic mass is used to optimize and evaluate instrument performance (Beaty, 1988).

2. Summary of method

The simultaneous determination of arsenic and selenium by GFAAS requires that a small (microliter) volume of sample be pipetted into a graphite tube. The tube is held between two graphite rings with quartz windows at each end, which produces a somewhat closed environment to enhance the absorbance signal. The tube is pyrolytically coated with high-density carbon to reduce the formation of nonvolatile carbides to prevent surface adsorption of the sample onto the walls of the graphite tube, and increase tube life (Ghe and others, 1983). The sample is evaporated to dryness, charred, and atomized by using specified temperatures and high-temperature ramping. The absorbance signal is measured and compared to standards.

3. Interferences

Two types of interferences affect GFAAS analyses—spectral and nonspectral. The most common type of spectral interference is background absorption where undissociated molecular forms of matrix materials produce broadband absorption spectra. Zeeman background correction compensates for broadband absorption by using a strong magnetic field to shift the electronic energy levels of an analyte atom. The shifted atomic spectrum can then be differentiated from the background spectrum (Beaty, 1988). Atoms having absorption wavelengths unresolved from the analyte absorption wavelength cause either positive or negative errors when measuring the analyte concentration profile (Flajnik-Riveria and Delles, 1996).

Sufficient energy must be available during atomization to dissociate the analyte and create free atoms. The composition of the sample matrix may interfere with this process and result in either positive or negative errors. Matrix vapor condensation takes place not only in end-heated graphite atomizer-type furnaces, but also in spatially isothermal, transverse heated graphite atomizer-type furnaces (Frech and L'Vov, 1993). It has also been shown that atoms can be trapped on the surface of condensed matrix particles and deposited at the cooler tube ends, resulting in a depression of the analyte signal. Introducing a low flow of inert gas during the atomization step can eliminate this type of interference. However, using low flow causes some loss of sensitivity for more volatile elements (Frech and L'Vov, 1993). This report demonstrates that either stop-flow or low-flow conditions can be used to determine arsenic and selenium. Nevertheless, low-flow conditions are recommended for routine sample analysis at the NWQL.

3.1 Arsenic interferences

The determination of 25-µg/L arsenic in solutions containing increasing concentrations of various compounds of sulfate and chloride, including aluminum sulfate, calcium sulfate, iron sulfate, manganese sulfate, sodium sulfate, and sodium chloride is shown in figure 1. Up to 3,000 mg/L of each sulfate compound and 7,500 mg/L of sodium chloride were tested. Arsenic measurements are generally unaffected using stop-flow or low-flow conditions for all metal salts added except for aluminum sulfate. All recovery measurements are within the acceptance criteria of 25±7.5 μg/L (±30 percent). However, although recoveries in aluminum sulfate are acceptable, the measurements were not reliable because of spectral interference. Aluminum interferes with arsenic at 193.7 nm, causing false positive results (Flajnik-Riviera and Delles 1996). Results showed that the spectral interference is significant for aluminum concentrations as low as 19 mg/L (100 mg-sulfate/L). Fortunately, aluminum concentrations in natural-water samples analyzed at the NWQL rarely exceed 19 mg/L (the 75th percentile is about 0.6 mg/L). In addition, the aluminum interference produces a unique atomization profile (see figure 2) when using either low-flow or stop-flow conditions. A low, broad peak formation and a high background peak formation with numerous spikes characterize the profile.

3.2 Selenium interferences

Lindberg and others (1988) have reported spectral and volatilization interferences on selenium. Selenium may be lost either by volatilization or by the formation of decomposition products, such as hydrogen selenide and selenium monoxide, which are not dissociated during the ashing and atomizing steps. Different modifiers, such as palladium, have been used to reduce volatilization losses (Lindberg and others, 1988).

The determination of 25-μg/L selenium in the same series of interference solutions as used for arsenic (see section 3.1) is shown in figure 3. As with arsenic, selenium absorption 196.0 nm is affected by a spectral interference from aluminum. Unlike arsenic, selenium is not affected until aluminum concentrations reach greater than 90 mg Al/L (500-1000 mg-sulfate/L) depending on the flow conditions.

Selenium is more prone to nonspectral type interferences than arsenic. It is especially susceptible to compounds such as iron sulfate and manganese sulfate, which are often present in natural-water samples. Recoveries for selenium fell outside 25±7.5 μg/L at 500 mg/L iron sulfate and at 1,000 mg/L manganese sulfate using stop-flow conditions, while low-flow conditions provided a stable environment up to 3,000 mg/L. Figure 3 demonstrates that low-flow conditions during atomization are advantageous in reducing such interferences. Sodium sulfate interferes at 3,000 mg/L for both stop- and low-flow conditions. Calcium sulfate does not interfere at 1,000 mg/L. Selenium is stable in sodium chloride concentrations up to 7,500 mg/L.

3.3 The high concentrations of metal salts used in this study to determine arsenic and selenium interferences are not normally encountered in water samples analyzed at the NWQL. However, such concentration levels can be present in acid mine drainage, saline estuaries, and some ground water. The primary purpose of using high metal salt concentrations was to establish the limitations of arsenic and selenium determined by GFAAS.

4. Instrumentation

4.1 The GFAAS instrumentation used in this method must have a Zeeman-background correction system, a digital integrator to quantitate peak area, a programmable temperature controller for high-temperature ramping, an autosampler, and a controllable gas flowrate. The graphite furnace must be capable of reaching a temperature sufficient to atomize arsenic and selenium. At present (1998) two types of graphite furnaces are acceptable for use—the heated graphite atomizer (HGA) and the transverse heated graphite atomizer (THGA). Data presented in this report were obtained using a simultaneous multielement GFAAS with a THGA furnace. The multielement GFAAS uses a beam combiner and enhanced detector system to determine up to six elements simultaneously. However, arsenic and selenium may be determined on a single-element basis with somewhat improved method detection limits. Refer to Beaty (1988) and Beaty and Kerber (1993) for a complete description of furnace conditions and instrumental performance.

4.2 Furnace Conditions

Arsenic and selenium are determined simultaneously using conditions slightly different than what might be used on a conventional graphite furnace. Compromise pyrolysis and atomization temperatures are chosen for arsenic and selenium by adding 50 to 100 °C to the lowest elemental pyrolysis temperature and by subtracting 50 to 100 °C from the highest elemental atomization temperature.

The length of hold time maintained during pyrolysis is generally 25 to 30 seconds. However, because the sample matrix may broaden normal peak formations, it was found that a longer pyrolysis time of 50 to 60 seconds helped reduce matrix interferences. Consequently, in order to accommodate all matrices, a slightly higher atomization temperature with a longer hold time is used than might be used for more pristine sample matrices.

Both stop flow and low flow during atomization were investigated. Stabilized temperature platform (STPF) technology is a proven, accepted, and valuable technique for the analysis of samples by GFAAS. One of its key requirements is to stop the flow of gas during atomization thereby enhancing sensitivity. However, it may not always be advantageous to use stop flow because the use of low flow during atomization has been shown to reduce vapor-phase and matrix interferences. All samples were analyzed using stop flow and low flow during atomization to demonstrate the usefulness of low-flow during atomization.

Furnace conditions vary slightly between stop flow and low flow. Stop flow conditions include argon mixed with 5 percent hydrogen to help reduce chloride interferences during the drying and pyrolysis steps (Creed and others, 1992). During pyrolysis, the furnace is purged with pure argon because the selenium signal might be suppressed if the matrix components are not purged prior to atomization. Although the THGA design by definition is transversely heated and should not have temperature gradients along the tube, inconsistencies are present (Frech and L'Vov, 1993). Since selenium is especially prone to vapor-phase interferences, a pre-atomization cooldown is also implemented to help promote a constant temperature along the tube during atomization.

Low-flow conditions consist of using an argon flow rate of 50 mL/min through the furnace tube during atomization. Lower gas flows were not examined because the THGA design does not have that capability. Argon mixed with 5 percent hydrogen was used during drying and pyrolysis followed by a purge with pure argon, but the use of this gas mixture is considered optional. Its effectiveness under low-flow conditions was not determined. End-capped tubes are recommended for low-flow conditions because they provide enhanced sensitivity and stability over the open-end tubes.

The use of palladium and magnesium nitrate as a matrix modifier is widely accepted for the determination of arsenic and selenium. Perkin Elmer™ has recommended modifier concentrations for each of its furnace designs; however, little or no difference was found for most sample matrices between the HGA or THGA concentrations. Nevertheless, the modifier concentration suggested for the HGA was found to be advantageous for complex sample matrices, especially matrices with higher concentrations of iron.

5. Apparatus

5.1 *Graphite furnace atomic absorption spectrometer.* See section 4, Instrumentation.

5.2 *Graphite tubes with platform.* Pyrolytically coated graphite tubes for HGA or pyrolytically coated open-end or end-capped tubes for THGA usage.

5.3 *Labware.* Many metals adsorb easily to glassware surfaces. The use of fluorinated ethylene propylene (FEP) labware minimizes such loss.

5.4 *Argon*

5.5 *Argon with 5 percent hydrogen.*

5.6 *Arsenic electrodeless discharge lamp*. Designed for a wavelength setting of 193.7 nanometers (nm).

5.7 *Selenium electrodeless discharge lamp*. Designed for a wavelength setting of 196.0 nm.

6. Reagents

6.1 *Matrix modifier solution*, 0.3 percent weight/volume (w/v) palladium and 0.2 percent w/v Mg $(NO_3)_2$ in deionized water. Note that palladium is available in a solution of either hydrochloric acid (HCl) or nitric acid (HNO_3). Using palladium in HCl increases the likelihood of interferences because of the chloride present.

6.2 *Nitric acid*, concentrated, ultrapure (sp gr 1.41): J.T. Baker Ultrex brand HNO_3 has been found to be adequately pure; however, check each lot for contamination. Used for sample preservation.

6.3 *Deionized water*: All references to deionized water shall be understood to mean Type I reagent water (American Society for Testing and Materials, 1995, p. 122-124).

6.4 *Nitric acid*, 10 percent: In a 1-L volumetric flask containing about 500 mL of deionized water, add 100 mL of concentrated HNO_3 (sp gr 1.41), then fill to volume with deionized water.

6.5 *Deionized water, acidified:* Add 4.0 mL ultrapure concentrated HNO_3 (sp gr 1.41) to each liter of deionized water for a final concentration of 0.4 percent.

7. Standards

7.1 *Arsenic, selenium standard solution I*, 1.00 mL = 1,000 µg As and Se: Use commercially prepared and certified As and Se calibration standards, 1,000 mg/L, 0.100 percent w/v.

7.2 *Arsenic, selenium standard solution II*, 1.00 mL = 100.0 µg As and Se: Dilute 10.0 mL each As, Se standard solution I to 100 mL (NOTE 1).

NOTE 1. Use acidified deionized water to prepare all dilutions. Store all standards in sealed FEP containers. Standards stored for 12 months yielded concentrations equal to freshly prepared solutions.

7.3 *Arsenic, selenium standard solution III*, 1.00 mL = 1.00 µg As and Se: Dilute 10.0 mL of As, Se standard solution II to 1,000 mL.

7.4 *Arsenic, selenium working standard solution I*, 1.00 mL = 0.010 µg As and Se: Dilute 10.0 mL of As, Se standard solution III to 1,000 mL.

7.5 *Arsenic, selenium working standard solution II*, 1.00 mL = 0.025 µg As and Se: Dilute 25.0 mL of As, Se standard solution III to 1,000 mL.

7.6 *Arsenic, selenium working standard solution III*, 1.00 mL = 0.050 µg As and Se: Dilute 50.0 mL of As, Se standard solution III to 1,000 mL.

8. Sample preparation

8.1 Filtered, acidified water samples analyzed by GFAAS for dissolved arsenic and selenium do not require additional sample preparation.

8.2 Nonfiltered, acidified water samples analyzed by GFAAS for WWR arsenic and selenium require either the HCl in-bottle digestion procedure described by Hoffman and others (1996) or the modified procedure using only HNO_3 described in the following section 8.4. All of the GFAAS results for nonfiltered samples provided in this report are based from the standard in-bottle digestion.

8.3 Prepare bed sediment using method P-0520-85 prior to sampling. Obtain a representative sample of the bed sediment by either coring (method P-0810-85) or splitting (method P-0811-85) (Fishman and Friedman, 1989, p. 45-48). Weigh a 100-mg subsample into a clean 250-mL polyethylene bottle and add 100 mL of acidified water (see section 6.5). Digest this mixture using either the standard in-bottle digestion procedure (Hoffman and others, 1996) or the HNO_3 procedure described in section 8.4.

8.4 An in-bottle digestion using only HNO_3 is advantageous for reducing interference effects from chloride. The standard in-bottle digestion procedure described by Hoffman and others (1996) is modified to use 1.6 mL of concentrated HNO_3 instead of concentrated HCl for each 50 mL of sample— the proportion by volume. The remainder of the digestion procedure is unchanged. The accuracy of using the HNO_3 digestion procedure was validated with results obtained for a series of standard reference materials. Synthetic whole-water samples were prepared by weighing 200-600 mg of each standard reference material (National Institute of Standards and Technology's 2704 Buffalo River Sediment, 1645 Riverine Sediment, or 1646 Estuarine Sediment) into 400-mL of acidified deionized water. In addition, U.S. Geological Survey whole-water standard reference WW-1 was used. These synthetic whole-water samples were digested using the standard in-bottle procedure, the HNO_3 in-bottle procedure, and two other on-line digestion procedures specific to the HGAAS methods;

the arsenic and selenium hydride methods use a sulfuric acid/potassium persulfate digestion. Since bed sediment samples are prepared in a manner similar to whole-water samples, the same synthetic whole-water samples can be used to represent bed sediment samples.

Results from GFAAS, HGAAS, and inductively coupled plasma mass spectrometry (ICPMS) for each of the digestion procedures is shown in table 1. The results from GFAAS and ICPMS indicate that there is no significant difference in the arsenic concentration measured in the synthetic whole-water samples whether HCl or HNO_3 is used, although there is a slight difference between methods. The effects of high concentrations of HCL on the determination of arsenic by GFAAS were determined by removing the HCl from an aliquot of synthetic whole-water digest from the standard in-bottle procedure. The HCl was removed by evaporating the aliquot to dryness at 85 °C and reconstituting the residue in 3 percent HNO_3. Results for two of the synthetic whole-water samples indicated that removing the HCl had negligible effect. However, when HCl was removed from the reverine sediment based whole-water digest, the arsenic concentration was substantially higher (see table 1). The HGAAS digestion procedure gave arsenic concentrations 25 to 300 percent less than the in-bottle procedures. Such negative bias most likely results from an incomplete digestion, or particulate settling out in the sample tube prior to sample introduction, or both. This problem is exasperated because the synthetic whole-water samples have coarser sediment and higher sediment concentrations than are normally present in water samples submitted to NWQL. Data presented in the Discussion of Results section indicates there is no significant bias in WWR arsenic results from GFAAS presumably because of the low sediment concentrations in the natural-water samples.

Table 1 near here.

Selenium concentrations for WW-1 indicate there is no significant difference between the HGAAS on-line digestion procedure and the standard in-bottle procedure (see table 1). However, at concentrations near the MDLs for low-flow GFAAS possible interferences from chloride are indicated. Selenium was not detected in any NIST-based whole water digested using the HCl (standard) in-bottle digestion by GFAAS. However, when the HCl is removed, selenium concentrations correspond to the HNO_3 in-bottle results for 2 of the 3 samples. Even though the selenium concentrations are near the MDLs for GFAAS and HGAAS, the results compare reasonably well with ICPMS results. Results presented in the Discussion of Results section show that there is no significant difference between results from HGAAS and GFAAS even though different digestion procedures were used.

Table 1.—*Arsenic and selenium concentrations in synthetic whole-water standards digested using hydrochloric acid in-bottle, nitric acid in-bottle, and other digestion procedures*

[µg/g, microgram per gram; GFAAS, graphite furnace atomic absorption spectrometry; ICPMS, inductively coupled plasma mass spectrometry; HGAAS, hydride generation atomic absorption spectrometry using sulfuric acid/potassium persulfate digestion for arsenic and potassium persulfate/hydrochloric acid/oxalic acid digestion for selenium; HCl, standard in-bottle digestion using hydrochloric acid; -HCl, standard in-bottle digestion but hydrochloric acid removed by evaporation; HNO_3, in-bottle digestion using nitric acid; WW1, U.S. Geological Survey whole-water reference standard WW-1; BR, National Institute of Standards and Technology (NIST) Buffalo River sediment 2704; RS, NIST Riverine sediment 1645; ES, NIST Estuarine sediment 1646; na, not available; nd, none detected; ±, plus or minus; the number of replicate digestions was 4]

	GFAAS (low flow)			ICPMS		HGAAS
µg/g	HCl	-HCl	HNO_3	-HCl	HNO_3	On-line
ARSENIC						
WW1, in µg/L	19.8±0.3	21±1	na	18.13±0.09	na	5±1
BR	15.3±0.4	15.4±0.6	16.8±0.3	14.3±0.2	13.4±0.1	11.0±0.9
RS	44±1	51±3	46±2	42±1	36.6±0.9	27.6±0.4
ES	9.0±0.2	9.7±0.1	10.08±0.05	7.72±0.05	7.34±0.05	3.2±0.8
SELENIUM						
WW1, in µg/L	4.3±0.2	4.7±0.7	na	4.8±0.1	na	4.7±0.3
BR	nd	1.0±0.8	1.0±0.8	0.8±0.1	0.44±0.08	0.6±0.05
RS	nd	nd	nd	0.64±0.08	0.36±0.04	0.8±0.1
ES	nd	1.0±0.1	0.78±0.06	0.67±0.03	0.69±0.05	0.43±0.07

9. Instrumental performance

Instrumental performance (see section 1.2) is best demonstrated by characteristic mass and MDL measurements. See section 12 for calculating characteristic mass. Typical Perkin-Elmer characteristic mass settings for different instrumentation is provided in the following table:

Instrument	Tube type	Arsenic, pg	Selenium, pg
HGA	Grooved tube	15	28
THGA	Open-end	40	45
THGA	Closed-end	22	28

These characteristic mass measurements are obtained using stop flow during atomization and in a non-simultaneous mode. Perkin-Elmer has not established instrumental characteristic mass measurements for low flow during atomization. Using a 50 μg/L standard and a 30-μL injection, the characteristic mass measurements for arsenic and selenium by simultaneous analysis on a THGA using a closed-end tube and stop flow during atomization averaged 25 pg (+14 percent) for arsenic and 33 pg (+16 percent) for selenium. Using low-flow conditions, the characteristic mass was 46 pg for arsenic and 56 pg for selenium. These measurements, calculated using the instrumental settings specified for a THGA open-end tube under stop-flow conditions indicated the difference for arsenic is +15 percent and selenium is +24 percent, demonstrating that the sensitivity using low-flow conditions is comparable to that of using an open-end tube with stop flow atomization.

10. Calibration

A calibration curve is constructed using a blank and a minimum of three working standards using a calculated intercept linear regression analysis. The correlation coefficient must be at least 0.999 or better.

11. Procedure and data evaluation

11.1 Analyze samples in a clean contaminant-free environment.

11.2 Rinse the sample cups at least twice with sample before filling. Place the cups in sample tray and cover. Adjust the autosampler so that only the injection tip contacts the sample.

11.3 Analyze blanks prior to sample analysis to condition a new graphite tube and to verify that acidified water and modifier are not contaminated. If contamination is present, which is indicated by a distinct peak formation generally 0.005 a-s or greater, then use another aliquot of blank or modifier, or both. If the acidified water, the modifier, or both are contaminated, prepare fresh solutions by using a new bottle or lot of acid or matrix modifier chemicals as necessary. If contamination persists, troubleshoot by replacing the graphite tube or cleaning the contact rings, or both.

11.4 Inject matrix modifier (see note 2) with each aliquot of blank and a minimum of three standards to construct the calibration curve from the absorbance-second measurements.

11.5 Similarly, analyze samples by injecting matrix modifier (see note 2) with each sample.

11.6 Analyze a quality-control sample (i.e. a USGS Standard Reference Water Sample, SRWS) immediately following calibration and after every tenth sample (minimum). Analyze a reagent blank with each set of samples. See the *Quality Assurance* section for more information regarding quality control.

NOTE 2: Currently (1998), 7 µL of matrix modifier is used for each 30-µL sample.

12. Calculations

12.1 Calculation of characteristic mass (M_O) in picograms

$$M_O = \frac{\text{sample volume } (\mu\text{L}) \times \text{analyte concentration } (\mu\text{g/L}) \times 0.0044 \text{ A-s}}{\text{observed peak area (A-s)}}$$

Acceptable ranges include an interval difference of ± 20%

$$\text{Percent difference} = [(\text{calculated } M_O - \text{instrument } M_O) / (\text{instrument } M_O)] \times (100)$$

12.2 Calculation of percent spike recovery

$$\text{Percent spike recovery} = [(S_{sp} - S) / Spk] \times 100$$

Where S_{sp} equals the spiked sample concentration, S equals the unspiked sample concentration, and *Spk* equals the theoretical spike concentration.

12.3 Calculation of concentration in bed sediment

$$\text{As or Se } (\mu\text{g/g}) = \frac{\mu\text{g/L As or Se} \times 0.1 \text{ L}}{\text{Wt of sample (g)}}$$

13. Reporting of results

Currently (1998), report dissolved (01000), and WWR (01002) arsenic, and dissolved (01145), and WWR (01147) selenium concentrations as follows: Less than 1.0 µg/L, as less than 1 µg/L; 1 to 100 µg/L, to the nearest microgram per liter; 100 µg/L and greater, two significant figures. Report recoverable bed sediment (01003) arsenic and (01148) selenium as follows: Less than 1.0 µg/g as less than 1 µg/g; 1 to 100 µg/g, to the nearest microgram per gram; 100 µg/g and greater, two significant figures.

14. Bias and variability

The bias and variability of the method are determined by comparing results from the new method and a former official method with standard reference materials and natural-water samples. See the following discussion for results.

DISCUSSION OF RESULTS

Method Detection Limit

The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the analyte concentration is greater than zero (U.S. Environmental Protection Agency, 1994). The MDLs for low-flow and stop-flow conditions are listed in table 2. These MDLs were determined using the procedure described by the U.S. Environmental Protection Agency (1994).

The current (1998) MDLs listed in table 2 were determined by analyzing the MDL standard solution as part of a set of real water samples. This practice provides a MDL that more likely represents a level of detection that would be expected during routine analyses.

Table 2 near here

Bias and Variability Data

Standard reference materials

The bias and variability of arsenic and selenium determinations by GFAAS were verified by analyzing SRWS. Results for all standard reference materials were well within an acceptable one standard deviation of the mean (see tables 3 through 6). Every SRWS was treated and analyzed as a dissolved and WWR sample.

Tables 3 through 6 near here.

Validation of the new method requires bias and variability measurements be obtained on three different types of water matrices (Fishman and others, 1998). Matrices consist of laboratory-reagent water, ground-water, and surface-water samples. Each sample was fortified with 6.25, 25.0, and 37.5 μg/L arsenic and selenium and analyzed under low-flow and stop-flow conditions on nine nonconsecutive days to determine percent recovery. Percent recovery results are listed in table 7. The mean percent recoveries for all matrix types are 103±2 and 104±4 percent for arsenic using low-flow and stop-flow conditions, respectively; corresponding recoveries for selenium using low-flow and stop-flow conditions were 98±13 and 87±24 percent, respectively. Arsenic recoveries in all matrix types indicated negligible bias when using either low-flow or stop-flow conditions. However, selenium recoveries in the ground-water matrix were negatively biased by at least 30 percent when using either low-flow or stop-flow conditions. This bias results from the interference associated with high iron sulfate concentration (as shown in fig. 3); the ground-water matrix has 340 mg-iron/L and 2,300 mg-sulfate/L. In general, the variability in the selenium spike recoveries is about a factor of 5 greater than arsenic.

Table 7 near here.

Table 2.—*Method detection limits and analytical precision for low-flow and stop-flow graphite furnace atomic absorption spectrometry*

[µg/L, micrograms per liter; % RSD, percent relative standard deviation; MDL, method detection limit]

Theoretical concentration was 2.5 µg/L	Experimental mean concentration (µg/L)	Standard deviation (µg/L)	% RSD	*t*-value	Degrees of freedom (n - 1)	MDL (µg/L)
Low flow						
Arsenic	2.5	0.3	12	2.602	15	0.9
Selenium	2.6	0.4	15	2.602	15	1.1
Stop flow						
Arsenic	2.2	0.3	14	2.583	16	0.7
Selenium	2.3	0.4	17	2.583	16	1.1

Table 3.—*Bias and variability for the determination of* ***arsenic*** *in standard reference materials using* ***low-flow*** *graphite furnace atomic absorption spectrometry*

[µg/L, micrograms per liter; n, number of determinations; % RSD, percent relative standard deviation; SRWS, U.S. Geological Survey Standard Reference Water Sample; WWR, whole-water recoverable digestion using in-bottle procedure Hoffman and others (1996), Theoretical measurements are derived from interlaboratory results using various analytical methods]

	Experimental				Theoretical	
Reference material	Mean (µg/L)	Standard deviation (µg/L)	% RSD	n	Mean (µg/L)	Standard deviation (µg/L)
SRWS 119	4.4	0.6	13.6	19	4.2	1.2
WWR SRWS 119	3.7	0.5	13.5	8		
SRWS 123	20.9	1.5	7.2	20	20.2	3.4
WWR SRWS 123	20.0	1.1	5.5	8		
SRWS 125	9.9	0.8	8.1	17	10.2	2.0
WWR SRWS 125	10.1	0.4	4.0	5		
SRWS 133	27.5	1.2	4.4	28	27.1	4.3
WWR SRWS 133	26.3	0.6	2.3	12		
SRWS 135	10.7	0.8	7.5	15	10.0	2.0
WWR SRWS 135	10.2	0.6	5.9	6		
SRWS 139	5.8	0.5	8.6	20	5.6	1.4
WWR SRWS 139	5.0	0.6	12.0	6		
SRWS 143	16.2	1.0	6.2	15	15.2	2.7
WWR SRWS 143	15.5	0.8	5.2	3		
SRWS 145	10.2	0.7	6.9	13	9.9	2.0
WWR SRWS 145	9.0	0.7	7.8	10		

Table 4.—*Bias and variability for the determination of* ***arsenic*** *in standard reference materials using* ***stop-flow*** *graphite furnace atomic absorption spectrometry*

[µg/L, micrograms per liter; n, number of determinations; % RSD, percent relative standard deviation; SRWS, U.S. Geological Survey Standard Reference Water Sample; WWR, whole-water recoverable digestion using in-bottle procedure Hoffman and others (1996), Theoretical measurements are derived from interlaboratory results using various analytical methods by the Branch of Quality Systems]

	Experimental				Theoretical	
Reference material	Mean (µg/L)	Standard deviation (µg/L)	% RSD	n	Mean (µg/L)	Standard deviation (µg/L)
SRWS 119	4.3	0.4	9.3	12	4.2	1.2
WWR SRWS 119	3.7	0.7	18.9	7		
SRWS 123	21.2	1.0	4.7	11	20.2	3.4
WWR SRWS 123	20.7	0.5	2.4	5		
SRWS 125	10.1	0.5	5.0	5	10.2	2.0
WWR SRWS 125	9.8	0.9	9.2	4		
SRWS 133	27.0	1.3	4.8	19	27.1	4.3
WWR SRWS 133	26.3	1.0	3.8	6		
SRWS 135	10.3	0.6	5.8	8	10.0	2.0
WWR SRWS 135	10.4	1.6	15.4	7		
SRWS 139	5.5	0.6	10.9	13	5.6	1.4
WWR SRWS 139	6.2	1.1	17.7	4		
SRWS 143	15.9	1.3	8.2	9	15.2	2.7
WWR SRWS 143	14.1	1.0	7.1	3		
SRWS 145	9.6	0.8	8.3	12	9.9	2.0
WWR SRWS 145	9.6	0.4	4.2	7		

Table 5.—*Bias and variability for the determination of* ***selenium*** *in standard reference materials using* ***low-flow*** *graphite furnace atomic absorption spectrometry*
[µg/L, micrograms per liter; n, number of determinations; % RSD, percent relative standard deviation; SRWS, U.S. Geological Survey Standard Reference Water Sample; WWR, whole-water recoverable digestion using in-bottle procedure Hoffman and others (1996), Theoretical measurements are derived from interlaboratory results using various analytical methods by the Branch of Quality Systems]

	Experimental				Theoretical	
Reference material	Mean (µg/L)	Standard deviation (µg/L)	% RSD	n	Mean (µg/L)	Standard deviation (µg/L)
SRWS 119	9.8	0.7	7.1	19	9.8	2.6
WWR SRWS 119	8.9	0.7	7.9	9		
SRWS 123	5.2	0.6	11.5	20	5.2	1.5
WWR SRWS 123	4.8	0.5	10.4	8		
SRWS 125	10.0	0.7	7.0	18	9.8	2.6
WWR SRWS 125	10.2	0.3	2.9	3		
SRWS 133	21.9	1.2	5.5	28	21.4	5.4
WWR SRWS 133	22.3	0.6	2.7	12		
SRWS 135	10.8	0.6	5.6	13	10.0	2.7
WWR SRWS 135	10.1	1.4	13.9	9		
SRWS 139	4.7	0.6	12.8	20	4.8	1.4
WWR SRWS 139	4.3	0.8	18.6	6		
SRWS 143	10.1	1.0	9.9	15	9.6	2.6
WWR SRWS 143	10.3	0.2	1.9	3		
SRWS 145	10.3	0.7	6.8	13	10.1	2.7
WWR SRWS 145	10.0	1.1	11.0	10		

Table 6.—*Bias and variability for the determination of* ***selenium*** *in standard reference materials using* ***stop-flow*** *graphite furnace atomic absorption spectrometry*

[µg/L, micrograms per liter; n, number of determinations; % RSD, percent relative standard deviation; SRWS, U.S. Geological Survey Standard Reference Water Sample; WWR, whole-water recoverable digestion using in-bottle procedure Hoffman and others (1996), theoretical measurements are derived from interlaboratory results using various analytical methods by the Branch of Quality Systems]

	Experimental				Theoretical	
Reference material	Mean (µg/L)	Standard deviation (µg/L)	% RSD	n	Mean (µg/L)	Standard Deviation (µg/L)
SRWS 119	9.4	0.5	5.3	12	9.8	2.6
WWR SRWS 119	8.8	0.9	10.2	7		
SRWS 123	4.7	0.3	6.4	11	5.2	1.5
WWR SRWS 123	5.5	1.1	20.0	5		
SRWS 125	9.4	0.6	6.4	9	9.8	2.6
WWR SRWS 125	9.7	1.3	13.4	4		
SRWS 133	21.6	0.8	3.7	19	21.4	5.4
WWR SRWS 133	22.9	0.9	3.9	6		
SRWS 135	9.8	0.8	8.2	9	10.0	2.7
WWR SRWS 135	10.3	1.1	11.4	7		
SRWS 139	4.4	0.5	11.4	14	4.8	1.4
WWR SRWS 139	5.4	0.7	13.0	4		
SRWS 143	10.3	2.0	19.4	9	9.6	2.6
WWR SRWS 143	9.0	1.3	14.4	3		
SRWS 145	9.3	0.6	6.5	12	10.1	2.7
WWR SRWS 145	10.4	0.7	6.7	7		

Table 7.—*Percent recoveries in spiked laboratory reagent-water, ground-water, and surface-water samples by graphite furnace atomic absorption spectrometry*

[µg/L, micrograms per liter; ±, plus or minus]

Spike (µg/L)	Arsenic (percent recovery)		Selenium (percent recovery)	
	Low Flow	Stop Flow	Low flow	Stop Flow
Reagent-water matrix				
6.25	102±5	104±6	111±7	99±10
25.0	104±5	102±7	105±5	105±6
37.5	102±6	99±5	103±6	101±4
Ground-water matrix				
6.25	100±11	97±15	72±12	98±7
25.0	101±7	103±9	71±7	105±4
37.5	105±5	106±6	72±8	105±5
Surface-water matrix				
6.25	102±13	106±8	97±16	98±7
25.0	106±7	108±6	99±4	105±4
37.5	105±6	107±6	101±4	105±5

Spike recoveries in natural-water samples

A representative set of about 120 natural-water samples were chosen from the various types of water submitted to NWQL—surface water, ground water, acid mine drainage, and storm water runoff. Every water sample chosen was spiked with 25 µg/L arsenic and selenium to identify possible interferences. Sample specific conductance, sulfate concentration, and chloride concentration were used as indicators of potential interferences. The range of concentrations of arsenic, selenium, chloride, and sulfate and the specific conductance for the set of samples is provided in table 8.

Table 8 near here

The relation of spike recoveries for arsenic to specific conductance, sulfate concentration, and chloride concentration is shown in figures 4 through 6. The total number of samples plotted for each depends on the analyses requested for each sample; for example, chloride was not determined for all samples. Spike recovery between 70 and 130 percent was established as the acceptance criteria.

Table 8.—*Chemical characteristics of all natural-water samples used to evaluate graphite furnace atomic absorption spectrometry*

µg/L, microgram per liter; mg/L, milligram per liter; <MDL, less than the method detection limit; SC, specific conductance; µS/cm, microsiemens per centimeter at 25 degrees Celsius]

Element or constituent	25th percentile	Median	75th percentile	Maximum
Arsenic, in µg/L	1.7	2.9	7.4	104
Selenium, in µg/L	2.9	4.5	8.2	34
Chloride, in mg/L	9.8	68	501	9,176
SC, in µS/cm [1]	455	944	2,490	52,600
Sulfate, in mg/L	108	309	1,306	16,832

[1] Specific conductance for whole-water samples prior to digestion.

Both dissolved and WWR sample spike recoveries for arsenic (figures 4-6) showed no significant trends with respect to specific conductance, sulfate, or chloride concentrations. Only one spike recovery did not satisfy the acceptance criteria when using low-flow conditions (the recovery was biased low). This sample had a specific conductance of 23,000 µS/cm, 16,000 mg-sulfate/L, and 280 mg-chloride/L; all concentrations were considerably above the 90th percentile of the samples submitted to NWQL. When using stop-flow conditions four samples did not give acceptable recoveries (positive and negative bias). Specific conductance for these samples ranged from 600 to over 27,000 µS/cm. In general, results for the sample set indicated that the determination of arsenic using low-flow conditions is only marginally better than stop-flow conditions. Either flow condition was demonstrated to be accurate for samples with specific conductance as high as 29,000 µS/cm, with sulfate concentrations in excess of 3,500 mg/L, and with chloride concentrations in excess of 8,000 mg/L. Specific conductance generally is a good indicator of possible interferences; high specific conductance often translates to high concentrations of chloride or sulfate. However, to preclude the possibility of additional non-spectral interferences seen in more complex matrices using stop-flow conditions, low-flow conditions are indicated for routine sample analysis at the NWQL.

With acceptance criteria of 70 to 130 percent, dissolved and WWR spike recoveries for selenium (figures 7-9) showed a distinct negative bias with increasing specific conductance, and corresponding sulfate and chloride concentrations. Significant negative bias in dissolved selenium recoveries was measured for the majority of samples analyzed using stop-flow conditions when the specific conductance was greater than 1,300 µS/cm; chloride ranged from about 150 to 8,000 mg/L and sulfate ranged from about 250 to 17,000 mg/L. This trend was less significant when low-flow conditions were used.

In contrast, spike recoveries in the WWR matrix also demonstrated downward trends, however the trend is scattered and unpredictable in relation to specific conductance. When using low-flow conditions, 126 of 136 (93 percent) dissolved and WWR samples had acceptable recoveries. However, when stop-flow conditions were used 112 of 136 (82 percent) had acceptable recoveries. Since selenium determinations using stop-flow conditions have a greater degree of interference, low-flow conditions are recommended for the routine analyses. However, stop-flow conditions should be considered for pristine samples. As with arsenic, specific conductance might be a good indicator of potential interferences.

Analysis of natural-water samples by GFAAS in relation to HGAAS

The same set of samples used to determine spike recoveries also was analyzed by the current HGAAS methods and the new GFAAS methods (for a description of the sample set, see the preceding section entitled "*Spike recoveries in water samples*". Arsenic and selenium results were evaluated using linear regression analysis and the One Sample Sign Test - the One Sample Sign Test is used to determine whether there is a significant difference between the median values for GFAAS and HGAAS at the 95-percent confidence level. Both low-flow and stop-flow results from GFAAS were used in the comparison.

Slopes, y-intercepts, and correlation coefficients from the linear regression analyses, and the p-values from the One Sample Sign Test are listed in table 9; the data points used in the linear regression analysis are plotted in figures 10 through 13. The regression analysis results show that there is no significant difference between the arsenic and selenium results from either the low-flow or stop-flow GFAAS and HGAAS methods. All the slopes are nearly 1.0, and with the exception of dissolved selenium using stop-flow conditions, the y-intercepts are less than the MDL. The One Sample Sign Test results indicate that the difference between the methods is not significant for WWR arsenic by using stop flow, dissolved selenium by using low flow, and WWR selenium by using stop flow; all other results show significant difference at the 95-percent confidence level. However, most median differences for those results showing significant difference were less than or equal to the MDLs, therefore, for the wide range of sample concentrations in the data set, the difference is negligible. Only WWR selenium results using low-flow (-0.96 µg/L) and stop-flow conditions (1.4 µg/L) have median differences near the MDL.

Table 9 near here.

Table 9. – *Summary of statistical analysis results for graphite furnace atomic absorption spectrometry and hydride generation atomic absorption spectrometry*

[GFAAS, graphite furnace atomic absorption spectrometry; HGAAS, hydride generation atomic absorption spectrometry; n, number of samples; µg/L, microgram per liter; R^2, correlation coefficient; WWR, whole-water recoverable; <, less than]

	Linear regression of HGAAS in relation to GFAAS				One Sample Sign Test
Matrix and technique	n	Slope	y-intercept (µg/L)	R^2	p-value[1]
Arsenic, dissolved					
Low flow	68	0.97	0.60	0.9689	0.0035
Stop flow	68	1.1	0.85	0.8940	<0.0001
Arsenic, WWR					
Low flow	51	1.0	0.62	0.9577	0.0500
Stop flow	50	1.0	0.15	0.9473	1.000
Selenium, dissolved					
Low flow	68	0.96	0.67	0.9435	0.0684
Stop flow	67	0.93	-1.6	0.8028	<0.0001
Selenium, WWR					
Low flow	70	0.99	1.0	0.9125	0.0017
Stop flow	70	1.0	1.6	0.8059	0.1306

[1] The null hypothesis is that the difference between GFAAS and HGAAS results is zero.

QUALITY ASSURANCE

Minimum quality-control requirements per set must include analysis of a laboratory reagent blank and quality-control samples, such as SRWS, and may include check standards, sample duplicates, and sample spikes. A WWR or bed sediment sample set must include a synthetic whole-water sample based on a standard reference material and reagent blank carried through the digestion process to verify the accuracy of the procedure. Field spikes are encouraged as an additional check. Detailed descriptions of quality control requirements and corrective measures are included in the method SOP IM####.# (S.R. Jones, U.S. Geological Survey, written commun, 1998). Refer to Pritt and Raese (1995) for a further description of inorganic quality-control requirements.

CONCLUSIONS

The GFAAS technique has been shown to be capable of accurately determining arsenic and selenium in water and sediment. Performance of the method for the determination of arsenic and selenium was supported by the accuracy obtained for standard reference materials, spike recovery samples, and water samples. The method provides the following advantages:

- The method detection limits are similar to the HGAAS methods (about 1 μg/L).
- Arsenic and selenium are determined simultaneously on a single sample aliquot.
- The bias and variability is comparable to the former methods.
- The potential of chemical interferences is minimal for routine sample matrices.
- The in-bottle digestion procedure is more accurate than the former on-line digestion procedure for the determination of recoverable arsenic in unfiltered water and bed sediment. Either the HCl in-bottle or the HNO3 in-bottle digestion procedure can be used, however the HNO3 in-bottle procedure reduces the potential for interferences.
- The in-bottle digestion procedure used in the subject method is used by other methods at NWQL thereby reducing the number of required digestion procedures.
- Sample throughput is increased.
- Smaller sample volumes are required.
- The number of chemical reagents required is substantially reduced.
- The amount of chemical waste produced is substantially reduced.

This new method most likely will not impact long-term water-quality trend analysis studies that use dissolved arsenic and selenium results. However, possible bias may be identified in whole-water recoverable water analysis and total-recoverable bed sediment analysis for arsenic and selenium results depending on the sample matrix.

REFERENCES CITED

American Society for Testing and Materials, 1995, Annual book of ASTM standards, Section II, Water: Philadelphia, v. 11.01, p. 122-124.

Beaty, R.D., 1988, Concepts, instrumentation and techniques in atomic absorption spectrometry: Perkin-Elmer Corp., chaps. 5 and 6, variable pagination.

Beaty, R.D., and Kerber, J.D., 1993, Concepts, instrumentation and techniques in atomic absorption spectrometry: Perkin-Elmer Corp., chaps. 5 and 6.

Creed, J., Martin, T., Lobring, L., and O'Dell, J., 1992, Minimizing chloride interferences produced by combination acid digestion using palladium and hydrogen as a matrix modifier in graphite furnace atomic absorption spectrometry, Environmental Science Technology: V. 26, p. 102, 106.

Fishman, M.J., and Friedman, L.C., 1989, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p.

Fishman, M.J., Pritt, J.W., and Raese, J.W., 1998, Guideline for method validation and publication: U.S. Geological Survey National Water Quality Laboratory, Standard Operating Procedure MX0015.1, accessed August 13, 1998, at URL http://wwwnwql.cr.usgs.gov/nwql/sop/mrdp.w-list.html

Frech, W., and L'Vov, B.V., 1993, Matrix vapours and physical interference effects in graphite furnace atomic absorption spectrometery –II. Side-heated tubes: Spectrochimica Acta, v. 48B, no. 11, p. 1371-1379.

Flajnik-Riviera, C. and Delles, F., 1996, Evaluation of deuterium and Zeeman background correction with the presence of spectral interferences, Determinations of arsenic and selenium in an iron matrix by GFAA: American Environmental Laboratory, p. 24-27.

Ghe, A.M., Carati, Daniela, and Stefanelli, Claudio, 1983, Determination of trace amounts of arsenic and selenium by flame and flameless atomic absorption spectrometry: Annali di Chimica, p. 711.

Hoffman, G.L., Fishman, M.N., and Garbarino, J.R., 1996, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory--In-bottle acid digestion of whole-water samples: U.S. Geological Survey Open-File Report 96-225, 28 p.

Lindberg, I., Lundberg, E., Arkhammar, P., and Berggren, P., 1988, Direct determination of selenium in solid biological materials by graphite furnace atomic absorption spectrometry: Journal of Analytical Spectrometry, v. 3, p. 497.

Pritt, J.W., and Raese, J.W., 1995, Quality assurance/quality control manual--National Water Quality Laboratory: U.S. Geological Survey Open-File Report 95-443, 35 p.

U.S. Environmental Protection Agency, 1994, Guidelines establishing test procedures for the analysis of pollutants (Part 136, Appendix B. Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11): U.S. Code of Federal Regulations, Title 40, Revised as of July 1, 1994, p. 635–637.

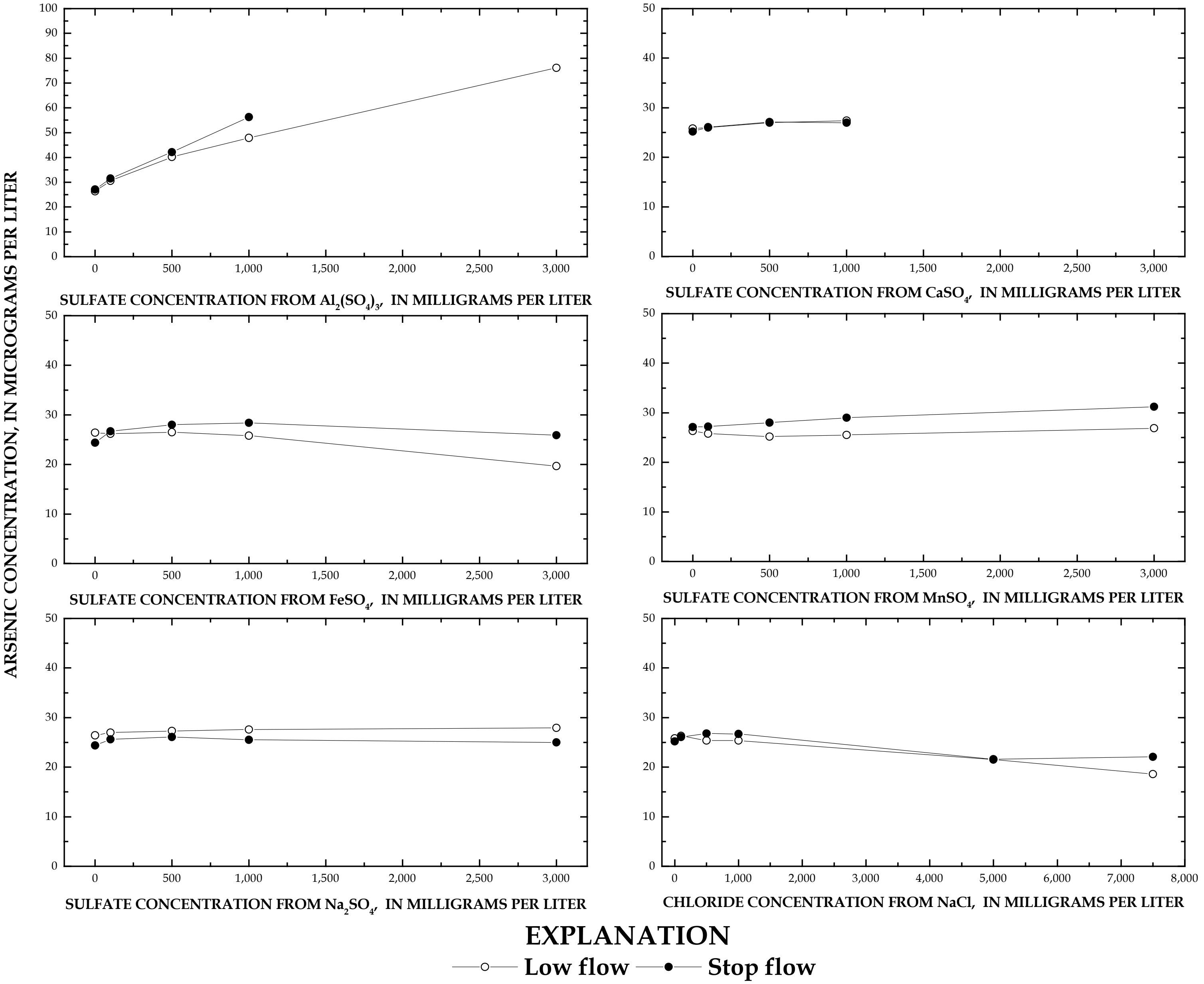

Figure 1.—*Arsenic* *measurements using low-flow and stop-flow conditions during atomization of solutions containing increasing concentrations of sulfate and chloride from aluminum sulfate, calcium sulfate, iron sulfate, manganese sulfate, sodium sulfate, and sodium chloride.*

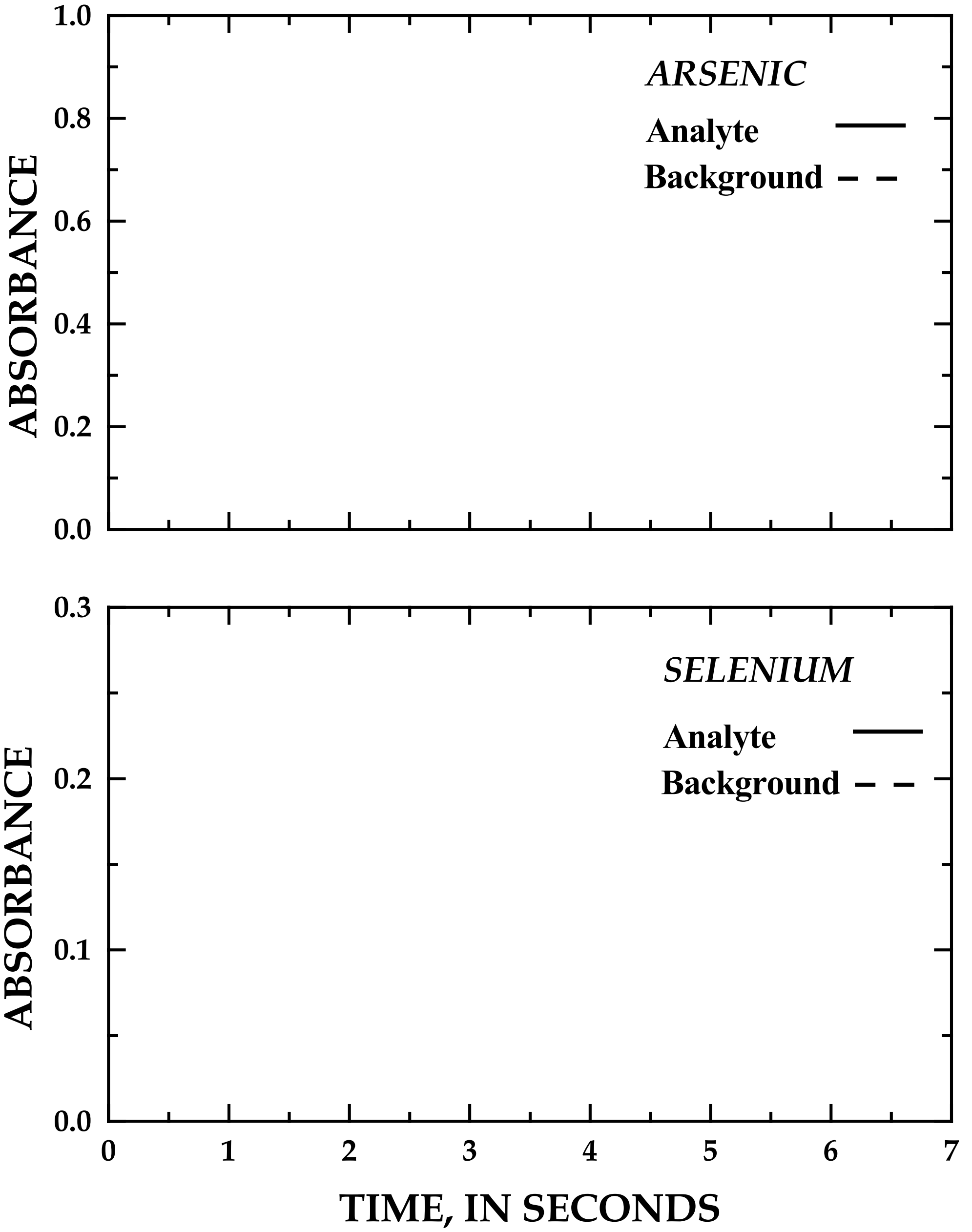

Figure 2.–*Typical arsenic and selenium atomization profiles for a sample having 1,000 milligrams per liter aluminum.*

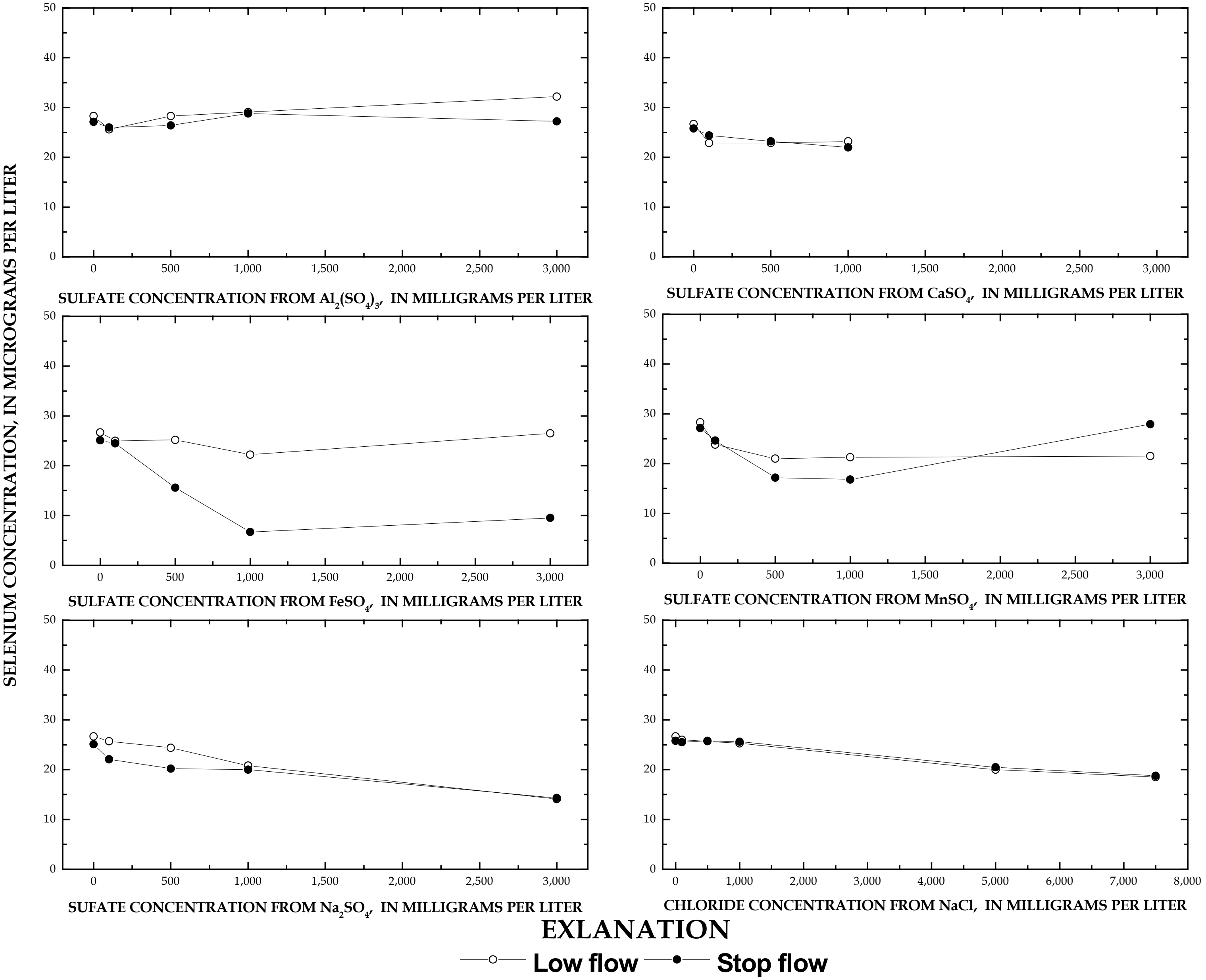

Figure 3.—***Selenium*** *measurements using low-flow and stop-flow conditions during atomization of solutions containing increasing concentrations of sulfate and chloride from aluminum sulfate, calcium sulfate, iron sulfate, manganese sulfate, sodium sulfate, and sodium chloride.*

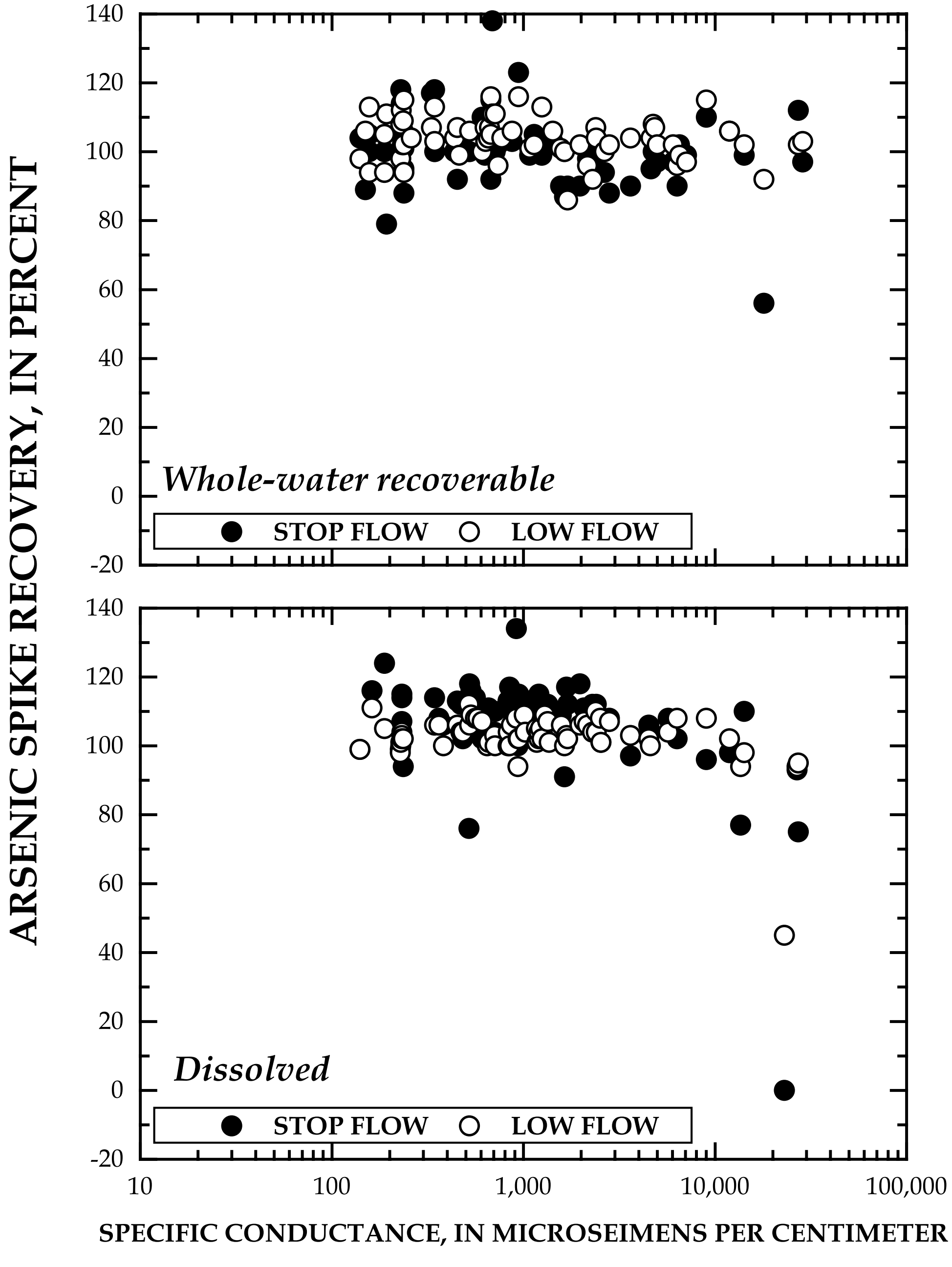

Figure 4.-- Spike recovery measurements for dissolved and whole-water recoverable **arsenic** by graphite furnace atomic absorption spectrometry using stop flow and low flow during atomization in association with specific conductance.

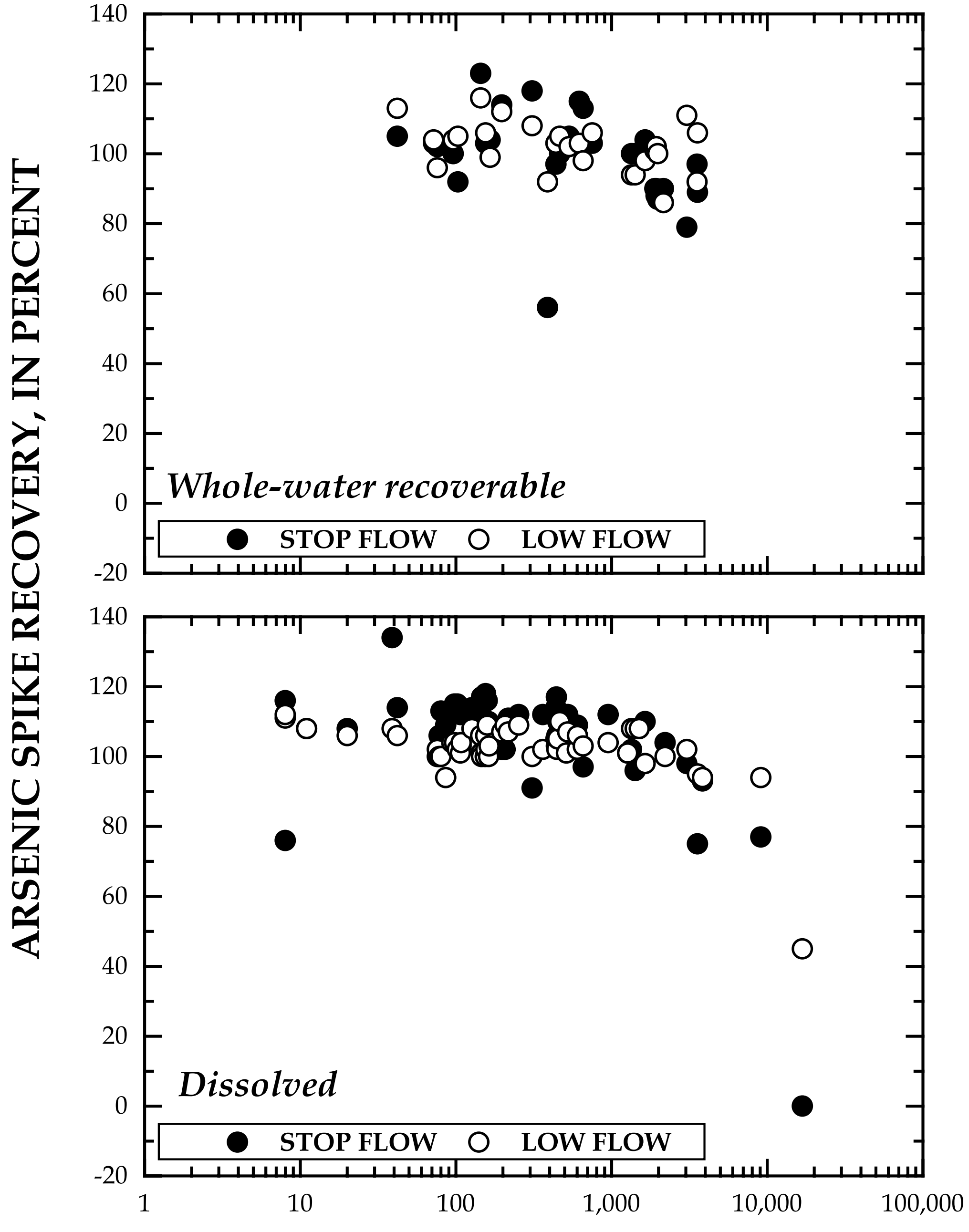

Figure 5.-- Spike recovery measurements for dissolved and whole-water recoverable **arsenic** by graphite furnace atomic absorption spectrometry using stop flow and low flow during atomization in association with sulfate concentration.

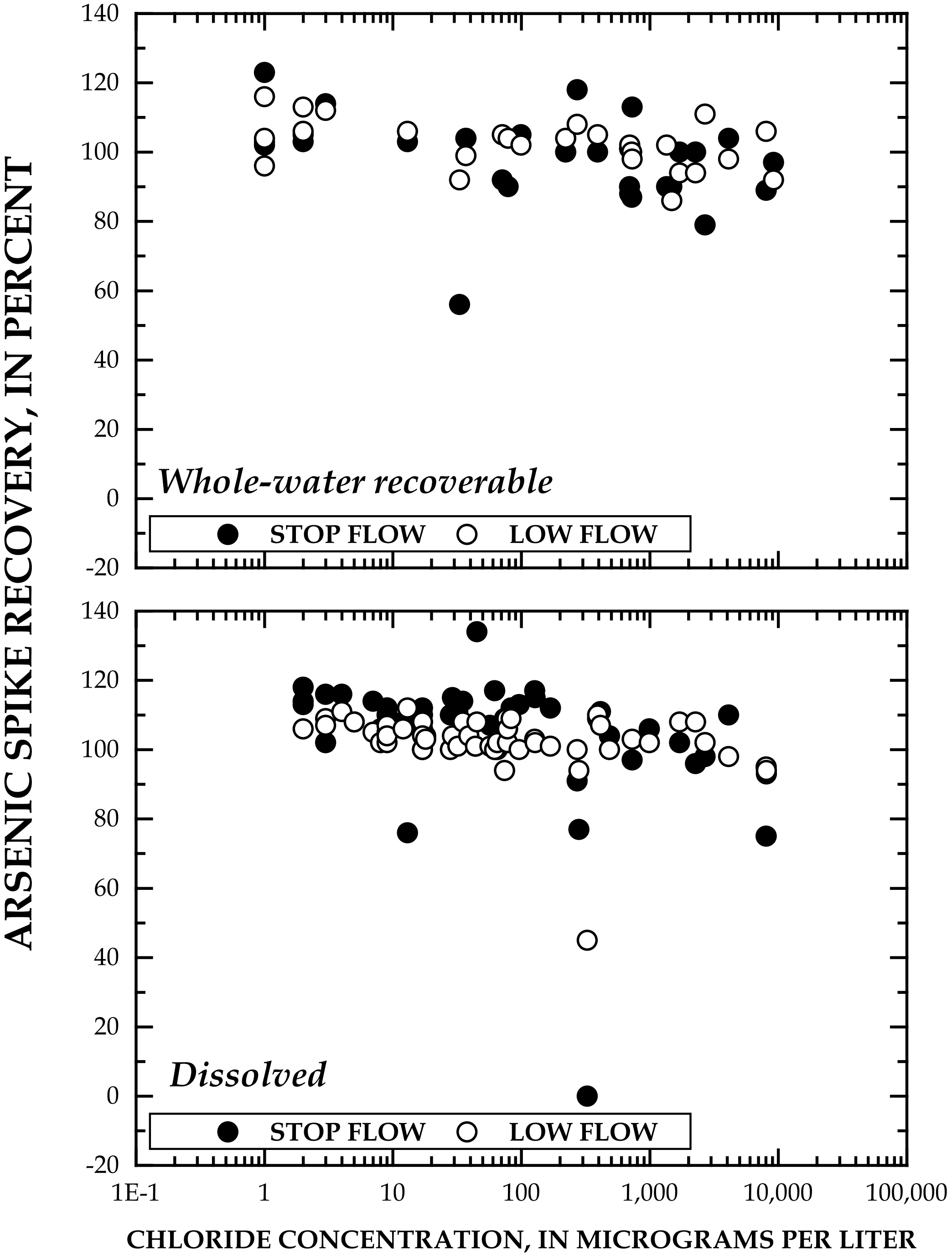

Figure 6.-- Spike recovery measurements for dissolved and whole-water recoverable **arsenic** by graphite furnace atomic absorption spectrometry using stop flow and low flow during atomization in association with chloride concentration.

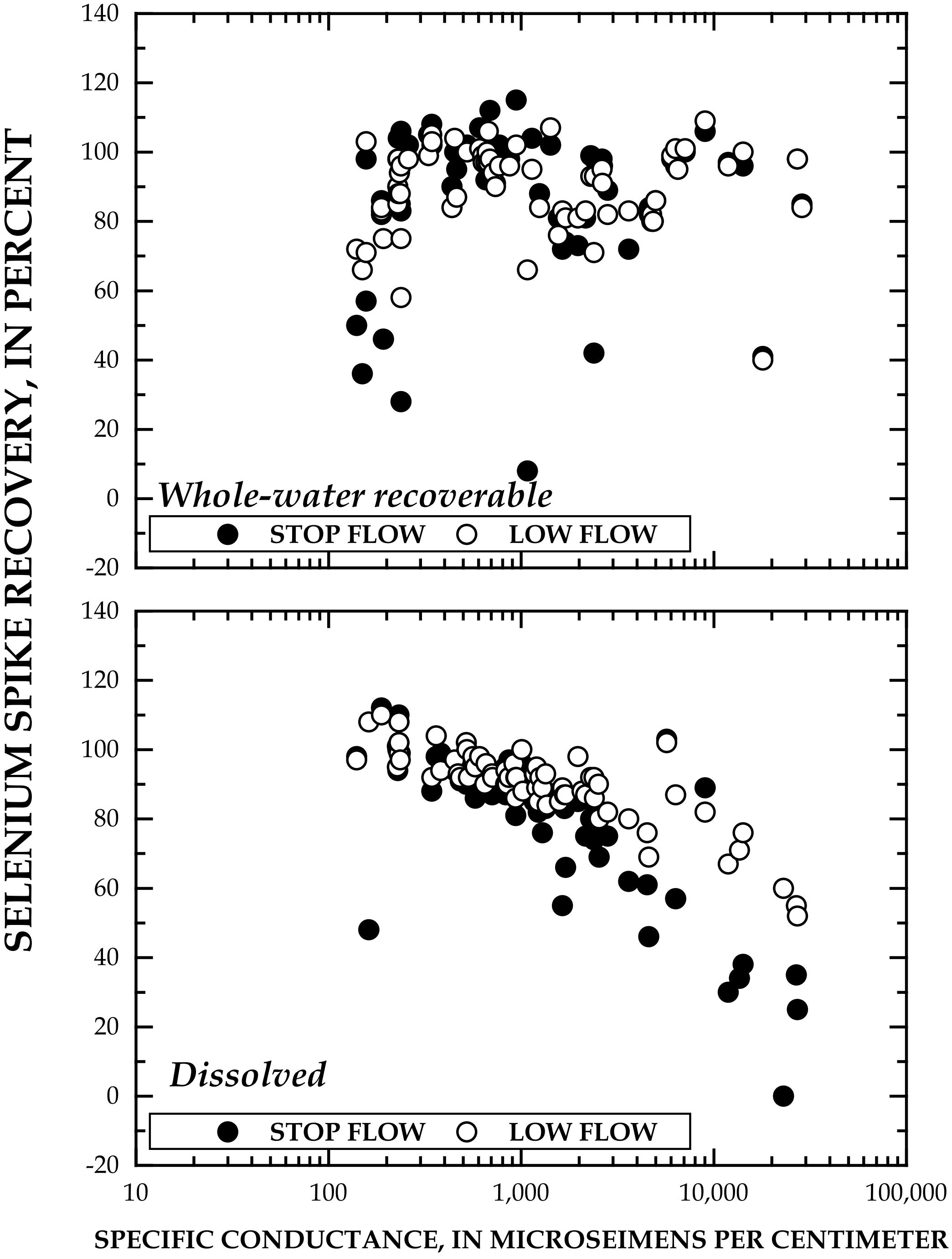

Figure 7.-- Spike recovery measurements for dissolved and whole-water recoverable **selenium** by graphite furnace atomic absorption spectrometry using stop flow and low flow during atomization in association with specific conductance.

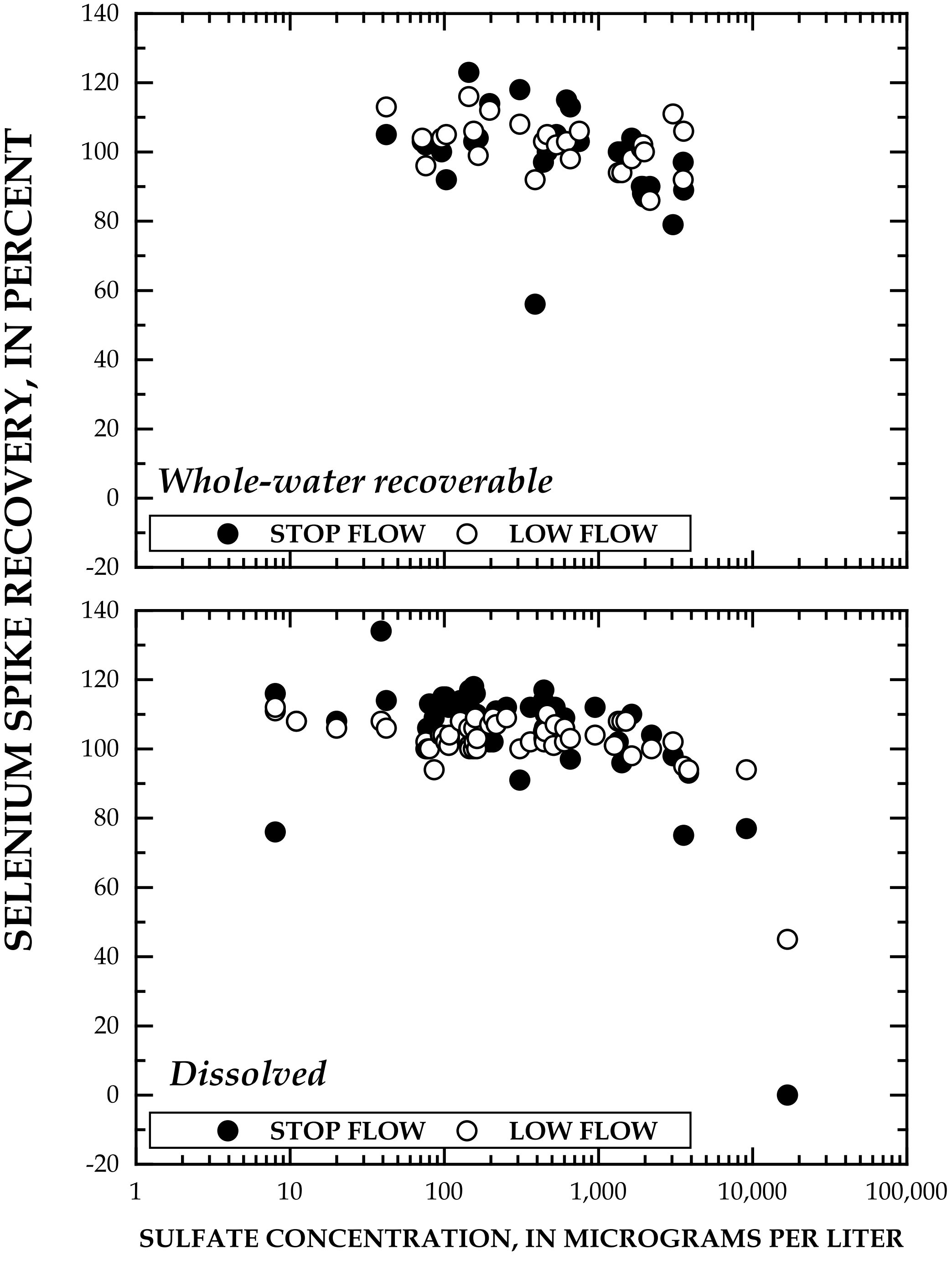

Figure 8.--Spike recovery measurements for dissolved and whole-water recoverable **selenium** by graphite furnace atomic absorption spectrometry using stop flow and low flow during atomization in association with sulfate concentration.

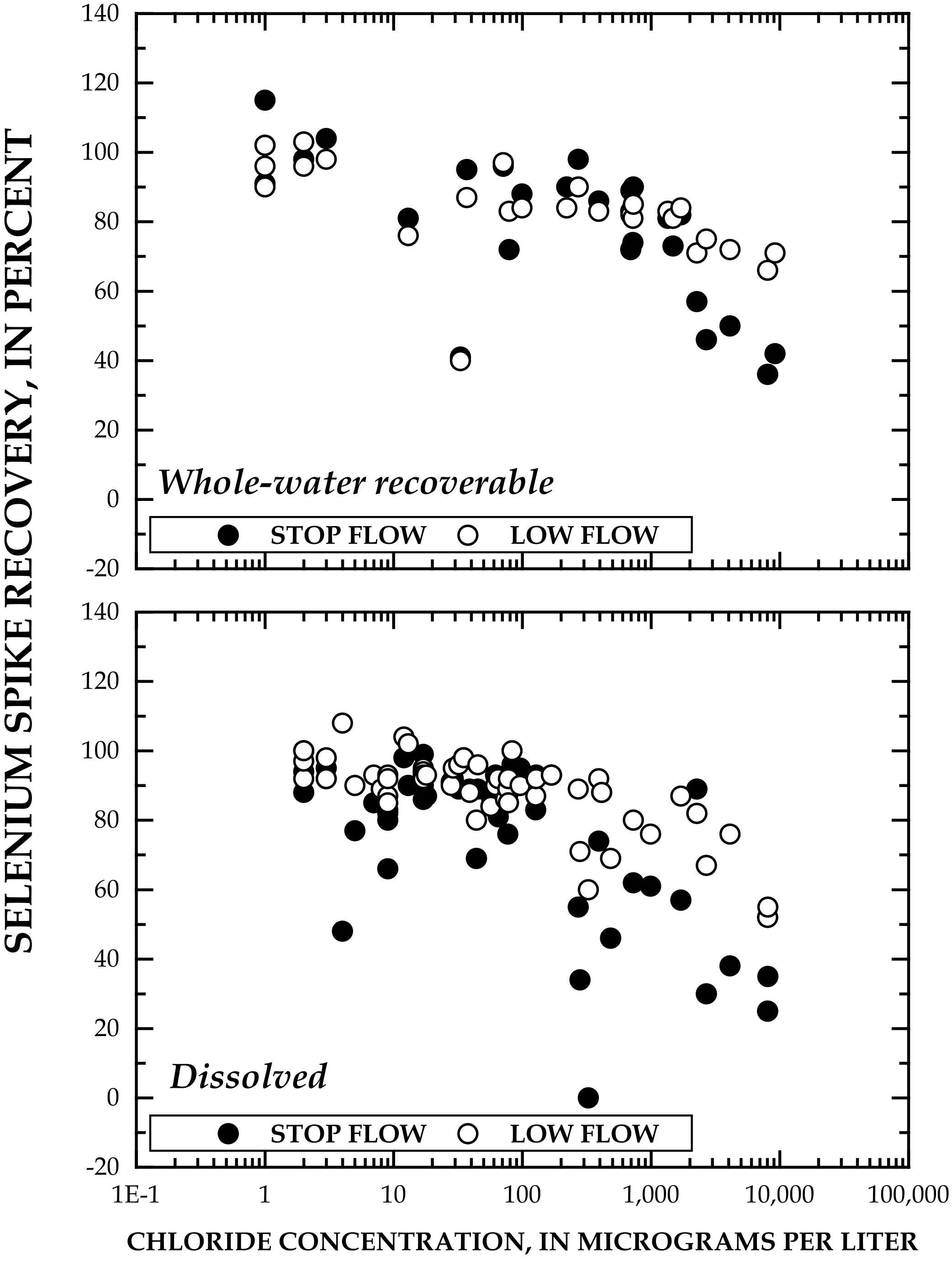

Figure 9.--Spike recovery measurements for dissolved and whole-water recoverable **selenium** by graphite furnace atomic absorption spectrometry using stop flow and low flow during atomization in association with chloride concentration.

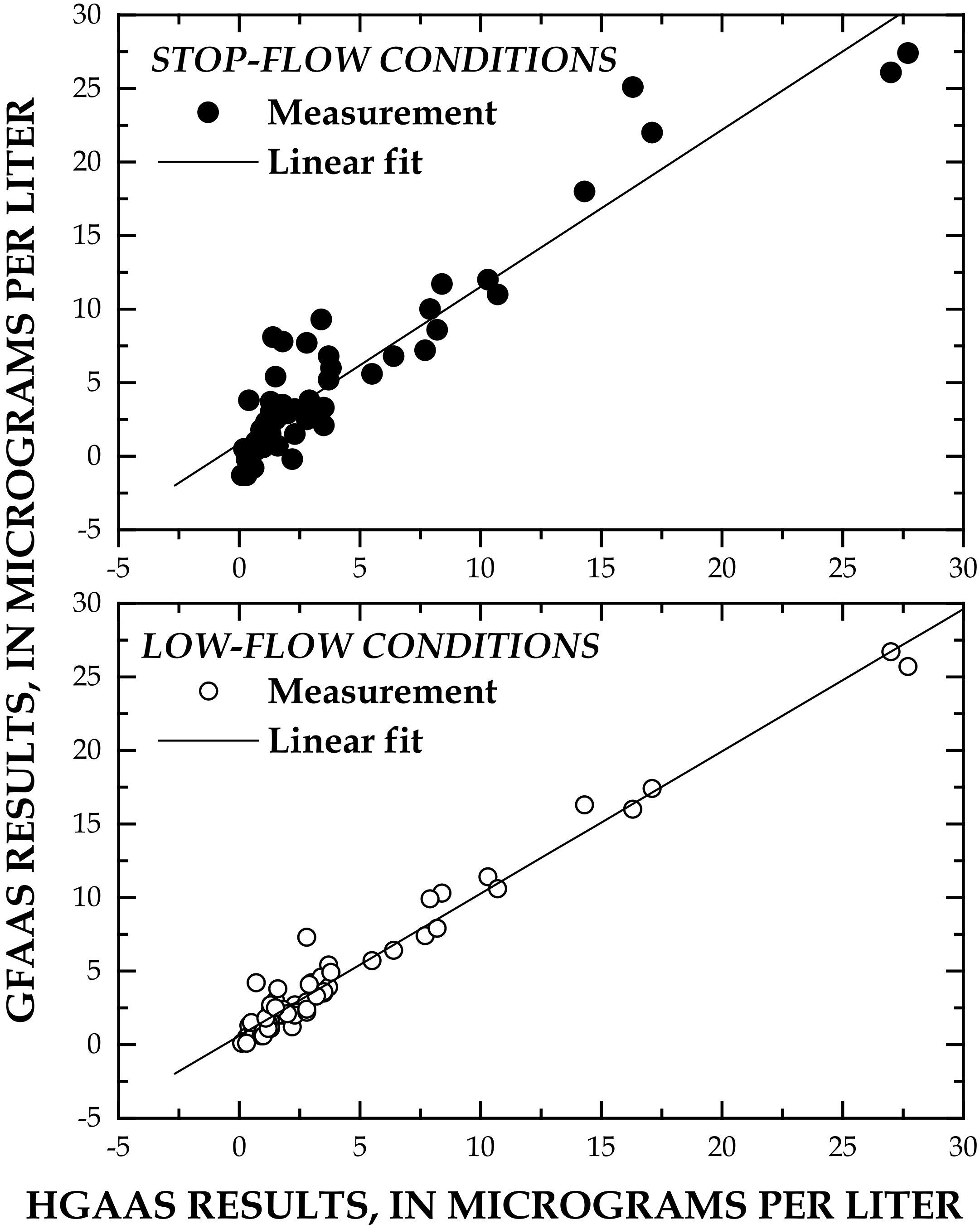

Figure 10.--Results for the determination of **dissolved arsenic** in filtered water samples analyzed by graphite furnace atomic absorption spectrometry (GFAAS) using **stop-flow** and **low-flow** conditions relative to hydride generation atomic absorption spectrometry (HGAAS).

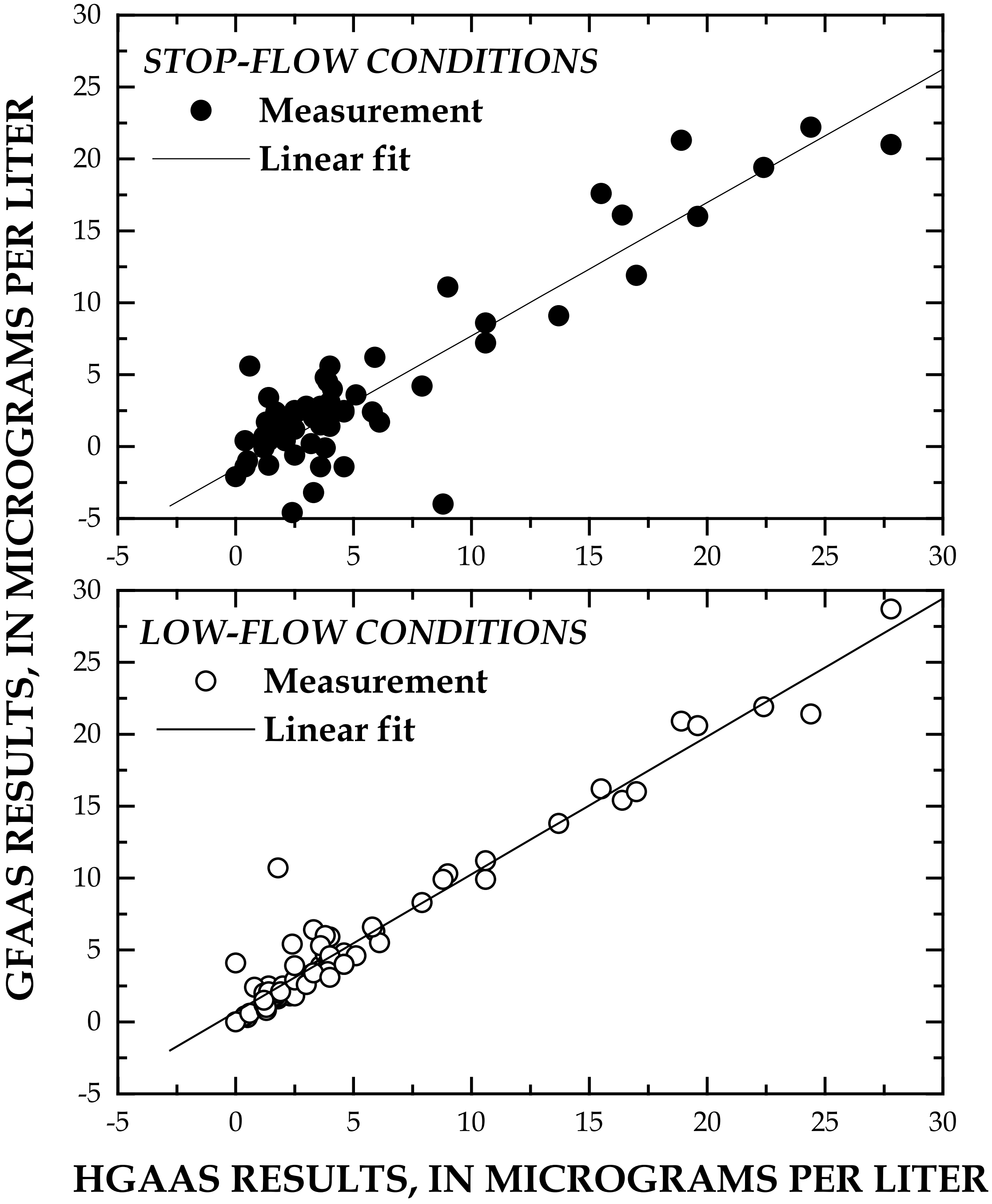

Figure 11.--Results for the determination of **dissolved selenium** in filtered water samples analyzed by graphite furnace atomic absorption spectrometry (GFAAS) using **stop-flow** and **low-flow** conditions relative to hydride generation atomic absorption spectrometry (HGAAS).

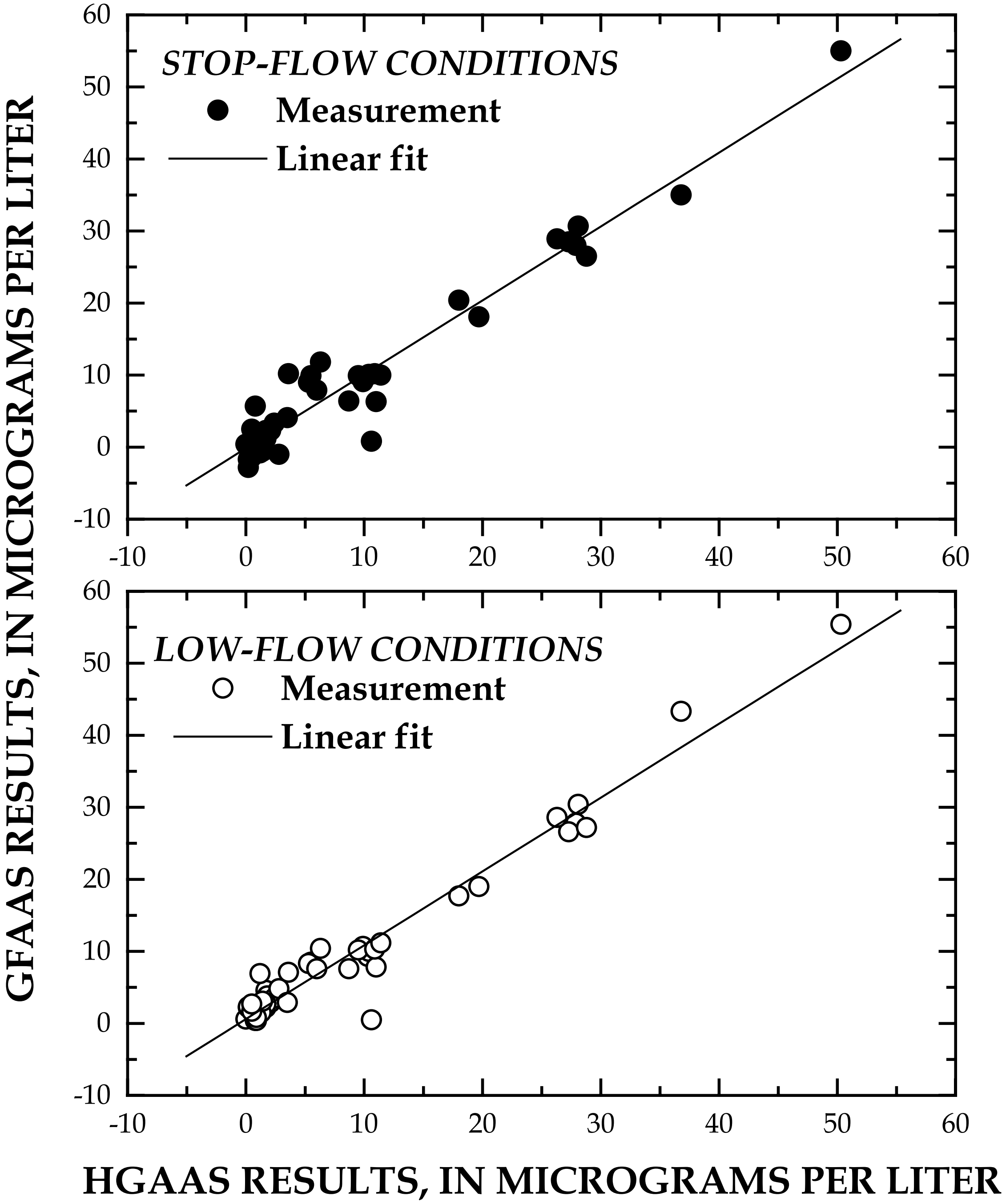

Figure 12.--Results for the determination of **whole water recoverable arsenic** in nonfiltered water samples analyzed by graphite furnace atomic absorption spectrometry (GFAAS) using **stop-flow** and **low-flow** conditions relative to hydride generation atomic absorption spectrometry (HGAAS). GFAAS uses the in-bottle digestion and HGAAS uses an on-line digestion procedure.

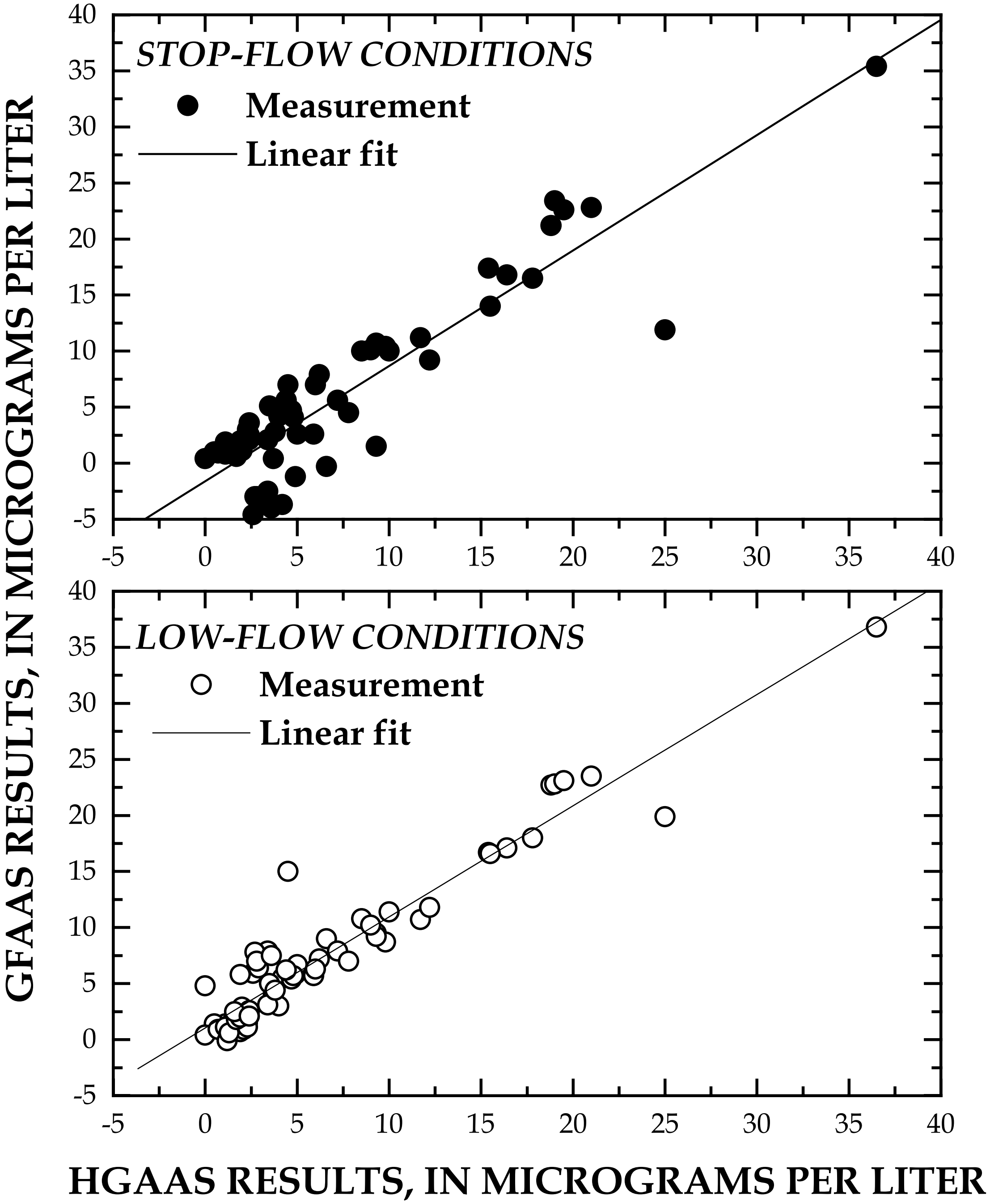

Figure 13.--Results for the determination of **whole water recoverable selenium** in nonfiltered water samples analyzed by graphite furnace atomic absorption spectrometry (GFAAS) using **stop-flow** and **low-flow** conditions relative to hydride generation atomic absorption spectrometry (HGAAS). GFAAS uses the in-bottle digestion and HGAAS uses an on-line digestion procedure.