3114

Arsenic and Selenium by Hydride Generation Atomic Absorption Spectrometry

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3114 A. Introduction

For general introductory material on atomic absorption spectrometric methods, see Section 3111 A.

The two methods presented in this section are a manual method and a continuous-flow method especially recommended for selenium. Continuous-flow automated systems are preferable to manual hydride generators because the effect of sudden hydrogen generation on light-path transparency is removed and any blank response from contamination of the HCl reagent by the elements being determined is incorporated into the background baseline.

3114 B. Manual Hydride Generation Atomic Absorption Spectrometric Method

1. General Discussion

a. Principle: This method is applicable to the determination of arsenic and selenium by conversion to their hydrides by sodium borohydride reagent and transport into an atomic absorption atomizer.

Arsenous acid and selenous acid, the As(III) and Se(IV) oxidation states of arsenic and selenium, respectively, are instantaneously converted by sodium borohydride reagent in acid solution to their volatile hydrides. The hydrides are purged continuously by argon or nitrogen into a quartz cell heated electrically or by the flame of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of the elemental hydrides in an appropriate reaction cell, minimizes dilution of the hydrides by the carrier gas and provides rapid, sensitive determinations of arsenic and selenium.

Caution: Arsenic and selenium and their hydrides are toxic. Handle with care.

At room temperature and solution pH values of 1 or less, arsenic acid, the As(V) oxidation state of arsenic, is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atomic absorption peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before reaction with sodium borohydride.

Selenic acid, the Se(VI) oxidation state of selenium, is not measurably reduced by sodium borohydride. To determine total selenium by atomic absorption and sodium borohydride, first reduce Se(VI) formed during the acid digestion procedure to Se(IV), being careful to prevent reoxidation by chlorine. Efficiency of reduction depends on temperature, reduction time, and HCl concentration. For 4 N HCl, heat 1 h at 100 °C. For 6 N HCl, boiling for 10 min is sufficient.[1-3] Alternatively, autoclave samples in sealed containers at 121 °C for 1 h. Note: Autoclaving in sealed containers may result in incomplete reduction, apparently due to the buildup of chlorine gas. To obtain equal instrument responses for reduced Se(VI) and Se (IV) solutions of equal concentrations, manipulate HCl concentration and heating time. For further details, see Section 3500-Se.

b. Equipment selection: Certain atomic absorption atomizers and hydride reaction cells are available commercially for use with the sodium borohydride reagent. A functional manual system that can be constructed in the laboratory is presented in Figure 3114:1. Irrespective of the hydride reaction cell-atomizer system selected, it must meet the following quality-control considerations:

- it must provide a precise and reproducible standard curve between 0 and 20 g As or Se per liter and an instrument detection limit between 0.1 and 0.5 g As or Se per liter;
- when carried through the entire procedure, oxidation state couples [As(III) – As(V) or Se(IV) – Se(VI)] must cause equal instrument response; and
- sample digestion must yield 80% or greater recovery of added cacodylic acid (dimethyl arsinic acid) and 90% or greater recovery of added As(III), As(V), Se(VI), or Se(IV).

Quartz atomization cells provide for the most sensitive arsenic and selenium hydride determinations. The quartz cell can be heated electrically or by an air-acetylene flame in an atomic absorption unit.

c. Digestion techniques: Waters and wastewaters may contain varying amounts of organic arsenic compounds and inorganic compounds of As(III), As(V), Se(IV), and Se(VI). To measure total arsenic and selenium in these samples requires sample digestion to solubilize particulate forms, oxidize reduced forms of arsenic and selenium, and convert any organic compounds to inorganic ones. Organic selenium compounds rarely have been demonstrated in water. It is left to the experienced analyst's judgment whether sample digestion is required.

Various alternative digestion procedures are provided in 3114 B.4*c* and B.4*d*. Consider sulfuric-nitric-perchloric acid

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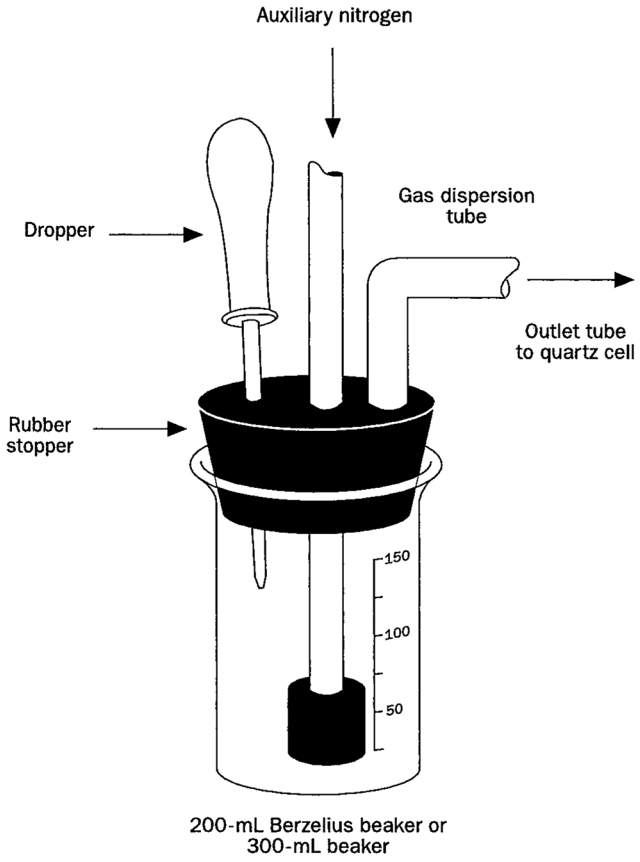

Figure 3114:1. Manual reaction cell for producing As and Se hydrides.

digestion (3114 B.4*c*) or sulfuric-nitric acid digestion (Section 3030 F) as providing a measure of total recoverable arsenic rather than total arsenic because they do not completely convert certain organic arsenic compounds to As(V). Sulfuric-nitric-perchloric acid digestion effectively destroys organics and most particulates in untreated wastewater or solid samples, but does not convert all organic arsenicals to As(V). Potassium persulfate digestion (3114 B.4*d*) is effective for converting organic arsenic and selenium compounds to As(V) and Se(VI) in potable and surface waters and in most wastewaters.[4]

The HCl-autoclave reduction of Se(VI) described above and in 3114 B.4*f* is an effective digestion procedure for total inorganic selenium; however, it has not been found effective for converting benzene-substituted selenium compounds to inorganic selenium. In all cases, verify the effectiveness of digestion methods by carrying samples with known additions of organic As or Se(IV) through the entire procedure.

d. Interferences: Interferences are minimized because the As and Se hydrides are removed from the solution containing most potentially interfering substances. Slight response variations occur when acid matrices are varied. Control these variations by treating standards and samples in the same manner. Low concentrations of noble metals (approximately 100 µg/L of Ag, Au, Pt, Pd, etc.); concentrations of copper, lead, and nickel at or greater than 1 mg/L; and concentrations between 0.1 and 1 mg/L of hydride-forming elements (Bi, Sb, Sn, and Te) may suppress the response of As and Se hydrides. Interference by transition metals depends strongly on HCl concentration. Interferences are less pronounced at 4 to 6 N HCl than at lower concentrations.[5] The presence of As or Se in each other's matrices can cause similar suppression. Reduced nitrogen oxides resulting from HNO_3 digestion and nitrite also can suppress instrumental response for both elements. Large concentrations of iodide interfere with the Se determination by reducing Se to its elemental form. When determining Se, do not use any glassware that has been used for iodide reduction of As(V).

When reducing Se(VI) to Se(IV), to prevent chlorine gas produced from reoxidizing Se(IV), generate the hydride within a few hours of the reduction steps or purge the chlorine from the samples by sparging.[6]

Interferences depend on system design and defy quantitative description because of their synergistic effects. Certain waters and wastewaters can contain interferences in sufficient concentration to suppress absorption responses of As and Se. For representative samples in a given laboratory and for initial analyses of unknown wastewaters, add appropriate inorganic forms of As or Se to digested sample portions and measure recovery. If average recoveries are less than 90%, consider using alternative analytical procedures.

e. Detection level and optimum concentration range: For both arsenic and selenium analyzed by aspiration into a nitrogen-hydrogen or argon-hydrogen flame after reduction, the method detection level is 2 µg/L or lower and the optimum concentration range is 2 to 20 µg/L.

For both arsenic and selenium analyzed by atomization into a nitrogen-hydrogen flame after reduction, the method detection limit should be 2 µg/L, with an optimum concentration range of 2 to 20 µg/L. Lower detection limits can be expected with a quartz tube atomizer.

f. Quality control (QC): The QC practices considered to be an integral part of each method can be found in Section 3020.

2. Apparatus

a. Atomic absorption spectrometer, equipped with air-acetylene flame and quartz cell with mounting bracket or an electrically heated quartz cell, As and Se electrodeless discharge lamps with power supply, background correction at measurement wavelengths, and appropriate strip-chart recorder. A good-quality 10-mV recorder with high sensitivity and a fast response time is needed.

b. Atomizer: Use one of the following:

1) *Cylindrical quartz cell,* 10 to 20 cm long, bracket-mountable above air-acetylene burner.

2) *Cylindrical quartz cell*, 10 to 20 cm long, electrically heated by external nichrome wire to 800 to 900 °C.[7]

3) *Cylindrical quartz cell* with internal fuel-rich hydrogen-oxygen (air) flame.[8]

The sensitivity of quartz cells deteriorates over several months of use. Sensitivity sometimes may be restored by treatment with 40% HF. **Caution: HF is extremely corrosive. Avoid all contact with exposed skin. Handle with care**.

c. Reaction cell for producing As or Se hydrides: See Figure 3114:1 for an example of a manual, laboratory-made system. A commercially available system is acceptable if it uses liquid sodium borohydride reagents, accepts samples digested in

accordance with 3114 B.4*c-e*, accepts 4 to 6 N HCl, and is efficiently purged with a high purity inert gas.

d. Eye dropper or syringe capable of delivering 0.5 to 3.0 mL sodium borohydride reagent. Exact and reproducible addition is required so production of hydrogen gas does not vary significantly between determinations.

e. Vent: See Section 3111 A.6*f*.

3. Reagents

a. Sodium borohydride reagent: Dissolve 8 g $NaBH_4$ in 200 mL 0.1 N NaOH. Prepare fresh daily.

b. Sodium iodide prereductant solution: Dissolve 50 g Nal in 500 mL water. Prepare fresh daily. Alternatively, use an equivalent KI solution.

c. Sulfuric acid (H_2SO_4), 18 N.

d. Sulfuric acid, 2.5*N*: Cautiously add 35 mL conc H_2SO_4 to about 400 mL water, let cool, and adjust volume to 500 mL.

e. Potassium persulfate, 5% solution: Dissolve 25 g $K_2S_2O_8$ in water and dilute to 500 mL. Store in glass and refrigerate. Prepare weekly.

f. Nitric acid (HNO_3), conc.

g. Perchloric acid ($HClO_4$), conc.

h. Hydrochloric acid (HCl), conc.

i. Argon (or nitrogen), commercial grade.

j. Arsenic(III) solutions:

1) *Stock As(III) solution*—Dissolve 1.320 g arsenic trioxide, As_2O_3, in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(III).

2) *Intermediate As(III) solution*—Dilute 10 mL stock As solution to 1000 mL with water containing 5 mL conc HCl; 1.00 mL = 10.0 µg As(III).

3) *Standard As(III) solution*—Dilute 10 mL intermediate As(III) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3); 1.00 mL = 0.100 µg As(III). Prepare diluted solutions daily.

k. Arsenic(V) solutions:

1) *Stock As(V) solution*—Dissolve 1.534 g arsenic pentoxide (As_2O_5) in distilled water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As(V).

2) *Intermediate As(V) solution*—Prepare as for As(III) above; 1.00 mL = 10.0 µg As(V).

3) *Standard As(V) solution*—Prepare as for As(III) above; 1.00 mL = 0.100 µg As(V).

l. Organic arsenic solutions:

1) *Stock organic arsenic solution*—Dissolve 1.842 g dimethylarsinic acid (cacodylic acid) [$(CH_3)_2AsOOH$] in water containing 4 g NaOH. Dilute to 1 L; 1.00 mL = 1.00 mg As. [Note: Check purity of cacodylic acid reagent against an intermediate arsenic standard (50 to 100 mg/L As) using flame atomic absorption.]

2) *Intermediate organic arsenic solution*—Prepare as for As(III) above; 1.00 mL = 10.0 µg As.

3) *Standard organic arsenic solution*—Prepare as for As(III) above; 1.00 mL = 0.100 µg As.

m. Selenium(IV) solutions:

1) *Stock Se(IV) solution*—Dissolve 2.190 g sodium selenite (Na_2SeO_3) in water containing 10 mL HCl and dilute to 1 L; 1.00 mL = 1.00 mg Se(IV).

2) *Intermediate Se(IV) solution*—Dilute 10 mL stock Se(IV) to 1000 mL with water containing 10 mL conc HCl; 1.00 mL = 10.0 µg Se(IV).

3) *Standard Se(IV) solution*—Dilute 10 mL intermediate Se(IV) solution to 1000 mL with water containing the same concentration of acid used for sample preservation (2 to 5 mL conc HNO_3). Prepare solution daily when checking the equivalency of instrument response for Se(IV) and Se(VI); 1.00 mL = 0.100 µg Se(IV).

n. Selenium(VI) solutions:

1) *Stock Se(VI) solution*—Dissolve 2.393 g sodium selenate (Na_2SeO_4), in water containing 10 mL conc HNO_3. Dilute to 1 L; 1.00 mL = 1.00 mg Se(VI).

2) *Intermediate Se(VI) solution*—Prepare as for Se(IV) above; 1.00 mL = 10.0 µg Se (VI).

3) *Standard Se(VI) solution*—Prepare as for Se(IV) above; 1.00 mL = 0.100 µg Se(VI).

4. Procedure

a. Apparatus setup: Either see Figure 3114:1 or follow manufacturer's instructions. Connect the inlet of the reaction cell with auxiliary purging gas controlled by a flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous $CaCl_2$ but not $CaSO_4$ because it may retain SeH_2. Before using the hydride generation analysis system, optimize the operating parameters. Align the quartz atomizers for maximum absorbance. Aspirate a blank until memory effects are removed. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent, solution volume, and stirring rate for optimum instrument response for the chemical species to be analyzed. Optimize the quartz cell temperature. Rapid injection of sodium borohydride reagent will increase sensitivities, so injection rates should be both consistent and as rapid as the system will tolerate. Recommended wavelengths are 193.7 and 196.0 nm for As and Se, respectively.

b. Instrument calibration standards: Prepare at least 3 standards and a blank by transferring appropriate volumes of AS(III) or Se(IV) standard solutions to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (typically 2 to 5 mL/L conc HNO_3). Standards should be prepared to cover the linear range of the instrument used (generally from 1 to 20 µg/L). Prepare fresh daily. In all cases, standards must be carried through the same digestion protocol as the samples to monitor digestion effectiveness.

c. Preparation of samples and standards for total recoverable arsenic and selenium: Use digestion procedure described in Section 3030 F for samples and standards. Alternatively, add 50 mL sample, As(III) standard, or Se(IV) standard to 200-mL Berzelius beaker or 100-mL micro-Kjeldahl flask. Add 7 mL 18 N H_2SO_4 and 5 mL conc HNO_3. Add a small boiling chip or glass beads if necessary. Evaporate to SO_3 fumes. Maintain oxidizing conditions at all times by adding small amounts of HNO_3 to prevent solution from darkening. Maintain an excess of HNO_3 until all organic matter is destroyed. Complete digestion usually is indicated by a light-colored solution. Cool slightly, add 25 mL water and 1 mL conc $HClO_4$ and again evaporate to SO_3 fumes to expel oxides of nitrogen. **Caution: See Section 3030 H for cautions on use of $HClO_4$.** Monitor effectiveness of either digestion procedure used by adding 5 mL of standard organic arsenic solution or 5 mL of a standard selenium

solution to a 50-mL sample and measuring recovery, carrying standards and the sample with known addition through entire procedure. To report total recoverable arsenic as total arsenic, average recoveries of cacodylic acid must exceed 80%. After final evaporation of SO_3 fumes, dilute to 50 mL for arsenic measurements or to 30 mL for selenium measurements. For analysis of both elements in a single sample, increase the sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating results.

d. Preparation of samples and standards for total arsenic and selenium: Add 50 mL undigested sample or standard to a 200-mL Berzelius beaker or 100-mL micro-Kjeldahl flask. Add 1 mL 2.5 N H_2SO_4 and 5 mL 5% $K_2S_2O_8$. Boil gently on a preheated hot plate for approximately 30 to 40 min or until a final volume of 10 mL is reached. Do not let sample go to dryness. Alternatively, heat in an autoclave at 121 °C for 1 h in capped containers. After manual digestion, dilute to 50 mL for subsequent arsenic measurements and to 30 mL for selenium measurements. Monitor digestion effectiveness by measuring recovery of As or Se as above. If poor recovery of arsenic added as cacodylic acid is obtained, re-analyze using double the amount of $K_2S_2O_8$. For analysis of both elements in a single sample, increase sample volume to 100 mL and double the volumes of acids used in the digestion. Adjust final digestate volume to 100 mL. Use 50 mL for As and 30 mL for Se determinations, making appropriate volume corrections in calculating the results.

e. Determination of arsenic with sodium borohydride: To 50 mL digested standard or sample in a 200-mL Berzelius beaker (see Figure 3114:1), add 5 mL conc HCl and mix. Add 5 mL NaI prereductant solution, mix, and wait at least 30 min. [Note: The NaI reagent has not been found necessary for certain hydride reaction cell designs if a 20% to 30% loss in instrument sensitivity is not important and variables of solution acid conditions, temperatures, and volumes for production of As(V) and arsine can be controlled strictly. Such control requires an automated delivery system (see 3114 C.)]

Attach one Berzelius beaker at a time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the quartz cell. Turn on the strip-chart recorder and wait until the baseline is established by the purging gas and all air is expelled from the reaction cell. Add 0.5 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the baseline, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Periodically compare standard As(III) and As(V) curves for response consistency. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 µg/L As(III) or As(V), as appropriate. Average recoveries should be not less than 90%.

f. Determination of selenium with sodium borohydride: To 30 mL digested standard or sample in a 200-mL Berzelius beaker or 100-mL micro-Kjeldahl flask, add 15 mL conc HCl and mix. Heat for a predetermined period at 90 to 100 °C. Alternatively, autoclave at 121 °C in capped containers for 60 min, or heat for a predetermined time in open test tubes using a 90 to 100 °C hot water bath or an aluminum block digester. Check effectiveness of the selected heating time by demonstrating equal instrument responses for calibration curves prepared either from standard Se(IV) or from Se(VI) solutions. Effective heat exposure for converting Se(VI) to Se(IV), with no loss of Se(IV), ranges between 5 and 60 min when open beakers or test tubes are used. Establish a heating time for effective conversion and apply this time to all samples and standards. Do not digest standard Se(IV) and Se(VI) solutions used for this check of equivalency. After prereduction of Se(VI) to Se(IV), attach Berzelius beakers, one at a time, to the purge apparatus. For each, turn on the strip-chart recorder and wait until the baseline is established. Add 0.50 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the baseline, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Check for the presence of chemical interferences that suppress selenium hydride instrument response by treating a digested sample with 10 µg Se (IV)/L. Average recoveries should be not less than 90%.

5. Calculation

Construct a standard curve by plotting peak heights or areas of standards and blanks versus concentration of standards. Measure peak heights or areas of samples and read concentrations from curve. If a sample was diluted (or concentrated) before sample digestion, apply an appropriate factor. On instruments so equipped, read concentrations directly after standard calibration.

6. Precision and Bias

Single-laboratory, single-operator data were collected for As(III) and organic arsenic by both manual and automated methods, and for the manual determination of selenium. Recovery values (%) from 7 replicates are given below:

Method	As(III)	Org As	Se(IV)	Se(VI)
Manual with digestion	91.8	87.3	–	–
Manual without digestion	109.4	19.4	100.6	110.8
Automated with digestion	99.8	98.4	–	–
Automated without digestion	92.5	10.4	–	–

References

1. Vijan PN, Leung D. Reduction of chemical interference and speciation studies in the hydride generation-atomic absorption method for selenium. Anal Chim Acta. 1980;120:141–146.
2. Voth-Beach LM, Shrader DE. Reduction of interferences in the determination of arsenic and selenium by hydride generation. Spectroscopy. 1985;1:60–65.
3. Julshamn K, Ringdal O, Slinning KE, Braekkan OR. Optimization of the determination of selenium in marine samples by atomic absorption spectrometry: Comparison of a flameless graphite furnace atomic absorption system with a hydride generation atomic absorption system. Spectrochim Acta Part B. 1982;37(6):473–482.
4. Nygaard DD, Lowry JH. Sample digestion procedures for simultaneous determination of arsenic, antimony, and selenium by inductively coupled argon plasma emission spectrometry with hydride generation. Anal Chem. 1982;54(4):803–807.
5. Welz B, Melcher M. Mechanisms of transition metal interferences in hydride generation atomic-absorption spectrometry. Part 1. Influence of cobalt, copper, iron and nickel on selenium determination. Analyst. 1984;109:569–572.

6. Krivan V, Petrick K, Welz B, Melcher M. Radiotracer error-diagnostic investigation of selenium determination by hydride-generation atomic absorption spectrometry involving treatment with hydrogen peroxide and hydrochloric acid. Anal Chem. 1985;57(8):1703–1706.
7. Chu RC, Barron GP, Baumgarner PAW. Arsenic determination at submicrogram levels by arsine evolution and flameless atomic absorption spectrophotometric technique. Anal Chem. 1972;44(8):1476–1479.
8. Siemer DD, Koteel P, Jariwala V. Optimization of arsine generation in atomic absorption arsenic determinations. Anal Chem. 1976;48(6):836–840.

Bibliography

Fernandez FJ, Manning DC. The determination of arsenic at submicrogram levels by atomic absorption spectrophotometry. Atomic Absorption Newsletter. 1971;10:86.

Manning DC. A high sensitivity arsenic-selenium sampling system for atomic absorption spectroscopy. Atomic Absorption Newsletter. 1971;10:123.

Braman RS, Foreback CC. Methylated forms of arsenic in the environment. Science. 1973;182(4118):1247–1249.

Caldwell JS, Lishka RJ, McFarren EF. Evaluation of a low-cost arsenic and selenium determination of microgram-per-liter levels. J Amer Water Works Assoc. 1973;65:731.

Aggett J, Aspell AC. The determination of arsenic (III) and total arsenic by atomic-absorption spectroscopy. Analyst 1976;101(1202):341–347.

Fiorino JA, Jones JW, Capar SG. Sequential determination of arsenic, selenium, antimony, and tellurium in foods via rapid hydride evolution and atomic absorption spectrometry. Anal Chem. 1976;48(1):120–125.

Cutter GA. Species determination of selenium in natural waters. Anal Chim Acta. 1978;98(1):59–66.

Godden RG, Thomerson DR. Generation of covalent hydrides in atomic absorption spectroscopy. A Review. Analyst. 1980;105(1257):1137–1156.

Brown RM Jr, Fry RC, Moyers JL, Northway SJ, Denton MB, Wilson GS. Interference by volatile nitrogen oxides and transition-metal catalysis in the preconcentration of arsenic and selenium as hydrides. Anal Chem. 1981;53:1560–1566.

Sinemus HW, Melcher M, Welz B. Influence of valence state on the determination of antimony, bismuth, selenium, and tellurium in lake water using the hydride AA technique. Atomic Spectrosc. 1981;2(3):81–86.

Dedina J. Interference of volatile hydride-forming elements in selenium determination by atomic absorption spectrometry with hydride generation. Anal Chem. 1982;54(12):2097–2102.

Van Wagenen S, Carter DE, Ragheb AG, Fernando Q. Kinetic control of peak shapes in atomic absorption arsenic determination arsine generations. Anal Chem. 1987;59(6):891–896.

3114 C. Continuous Hydride Generation Atomic Absorption Spectrometric Method

1. General Discussion

The continuous hydride generator offers the advantages of simplicity in operation, excellent reproducibility, low detection limits, and high sample volume throughput for selenium analysis following preparations as described in Sections 3500-Se B or 3114 B.4*c* and *d*.

a. Principle: See 3114 B.1*a.*

b. Interferences: Free chlorine in hydrochloric acid is a common but difficult-to-diagnose interference. (The amount of chlorine varies with manufacturer and with each lot from the same manufacturer.) Chlorine oxidizes the hydride and can contaminate the hydride generator to prevent recoveries under any conditions. When interference is encountered, or preferably before using each new bottle of HCl, eliminate chlorine from a 2.3-L bottle of conc HCl by bubbling with helium (commercial grade, 100 mL/min) for 3 h.

Excess oxidant (peroxide, persulfate, or permanganate) from the total selenium digestion can oxidize the hydride. Follow procedures in Section 3500-Se B.2, 3, or 4 to ensure removal of all oxidizing agents before hydride generation.

Nitrite is a common trace constituent in natural and waste waters, and at levels as low as 10 µg/L, nitrite can reduce the recovery of hydrogen selenide from Se(IV) by more than 50%. Moreover, during the reduction of Se(VI) to Se(IV) by digestion with HCl (Section 3500-Se B.5), some nitrate is converted to nitrite, which subsequently interferes. When this interference is suspected, add sulfanilamide after sample acidification (or HCl digestion). The diazotization reaction between nitrite and sulfanilamide completely removes the interferent effect (i.e., the standard addition slope is normal).

c. Quality control (QC): The QC practices considered to be an integral part of each method can be found in Section 3020.

2. Apparatus

a. Continuous hydride generator: The basic unit is composed of 2 parts: a precision peristaltic pump, which is used to meter and mix reagents and sample solutions, and the gas-liquid separator. At the gas-liquid separator, a constant flow of argon strips out the hydrogen and metal hydride gases formed in the reaction and carries them to the heated quartz absorption cell (3114 B.1*b* and 2*b*), which is supported by a metal bracket mounted on top of the regular air acetylene burner head. The spent liquid flows out of the separator via a constant level side drain to a waste bucket. Schematics and operating parameters are shown in Figure 3114:2.

Check flow rates frequently to ensure a steady flow; an uneven flow in any tubing will cause an erratic signal. Remove tubings from pump rollers when not in use. Typical flow rates are: sample, 7 mL/min; acid, 1 mL/min; and borohydride reagent, 1 mL/min. Argon flow usually is pre-fixed, typically at 90 mL/min.

b. Atomic absorption spectrometric equipment: See Section 3111 A.6.

3. Reagents

a. Hydrochloric acid (HCl), 5 + 1: Handle conc HCl under a fume hood. If necessary, remove free Cl_2 by stripping conc HCl with helium as described in 3114 C.1*b*.

b. Borohydride reagent: Dissolve 0.6 g $NaBH_4$ and 0.5 g NaOH in 100 mL water. **Caution: Sodium borohydride is toxic, flammable, and corrosive**.