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3114 METALS BY HYDRIDE GENERATION/ATOMIC ABSORPTION SPECTROMETRY*

3114 A. Introduction

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

Two methods are presented in this section: A manual method and a continuous-flow method especially recommended for se-

lenium. 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 base line.

* Approved by Standard Methods Committee, 1989.

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 aspiration 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 an appropriate atomizer 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 4N HCl, heat 1 h at 100°C. For 6N 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 system is presented in Figure 3114:1. Irrespective of the hydride reaction cell-atomizer system selected, it must meet the following quality-control considerations: (a) it must provide a precise and reproducible standard curve between 1 and 20 μg As or Se/L and an instrumental detection limit between 0.1 and 0.5 μg As or Se/L; (b) when carried through the entire procedure, oxidation state couples [As(III) - As(V) or Se(IV) - Se(VI)] must cause equal instrument response; and (c) 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).

Three types of atomic absorption atomizers commonly are used in the measurement of arsenic and selenium. Most instrument manufacturers can provide a Boling-type burner for argon (or nitrogen)-air entrained-hydrogen flames. Alternatively use an externally heated quartz cell or a quartz cell with an internal fuel rich oxygen-hydrogen or air-hydrogen flame. Quartz atomization cells provide for the most sensitive arsenic and selenium hydride determinations and minimize background noise associated with the argon-air entrained-hydrogen flame.

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 and oxidize reduced forms of arsenic and selenium and to 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.

Two digestion procedures are provided in § 4c below. Consider sulfuric-nitric-perchloric acid digestion or sulfuric-nitric acid digestion 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). The sulfuric-nitric-perchloric acid digestion effectively destroys organics and most particulates in untreated wastewaters or solid samples. The potassium persulfate digestion (§ 4d) 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 is an effective digestion procedure for total inorganic Se; however, it has not been found effective for converting benzene substituted selenium compounds to inorganic selenium.

d. Interferences: Interferences are minimized because the As and Se hydrides are removed from the solution containing most potential 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 $\mu\text{g/L}$ 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 6N HCl than at lower concentrations.⁵ The

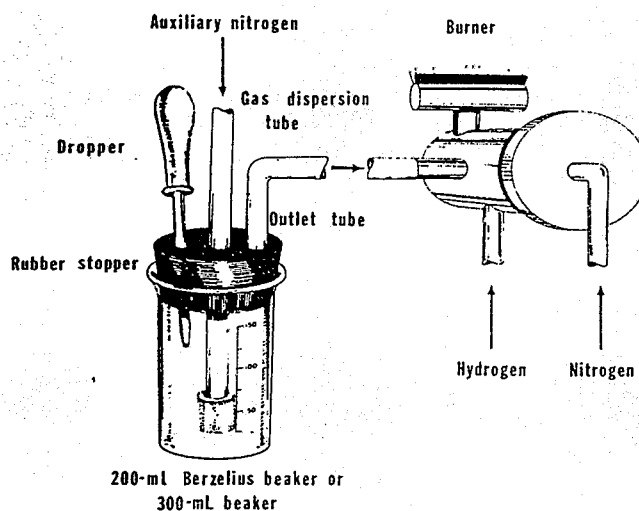


Figure 3114:1. Manual reaction cell for producing As and Se hydrides.

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. Do not use any glassware for determining Se that has been used for iodide reduction of As(V).

To prevent chlorine gas produced in the reduction of Se(VI) to Se(IV) from reoxidizing the 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 limit and optimum concentration range: For both arsenic and selenium, analyzed by aspiration into a nitrogen-hydrogen flame after reduction, the method detection limit is 0.002 mg/L and the optimum concentration range 0.002 to 0.02 mg/L.

2. Apparatus

a. Atomic absorption spectrometer equipped with gas flow meters for argon (or nitrogen) and hydrogen, 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) *Boling-type burner head* for argon (or nitrogen)-air entrained-hydrogen flame.
- 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. A commercially available system is acceptable if it utilizes liquid sodium borohydride reagents; accepts samples digested in accordance with 1s 4c, d, and e; accepts 4 to 6N HCl; and is efficiently and precisely stirred by the purging gas and/or a magnetic stirrer.

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

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

3. Reagents

a. *Sodium borohydride reagent*: Dissolve 8 g NaBH₄ in 200 mL 0.1N NaOH. Prepare fresh daily.

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

c. *Sulfuric acid, 18N*.

d. *Sulfuric acid, 2.5N*: Cautiously add 35 mL conc H₂SO₄ to about 400 mL water, let cool, and adjust volume to 500 mL.

e. *Potassium persulfate, 5% solution*: Dissolve 25 g K₂S₂O₈ in water and dilute to 500 mL. Store in glass and refrigerate. Prepare weekly.

f. *Nitric acid, HNO₃, conc.*

g. *Perchloric acid, HClO₄, conc.*

h. *Hydrochloric acid, HCl, conc.*

i. *Argon (or nitrogen), commercial grade.*

j. *Hydrogen, commercial grade.*

k. *Arsenic(III) solutions*:

1) *Stock As(III) solution*: Dissolve 1.320 g arsenic trioxide, As₂O₃, 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 HNO₃); 1.00 mL = 0.100 µg As(III). Prepare diluted solutions daily.

l. *Arsenic(V) solutions*:

1) *Stock As(V) solution*: Dissolve 1.534 g arsenic pentoxide, As₂O₅, 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).

m. *Organic arsenic solutions*:

1) *Stock organic arsenic solution*: Dissolve 1.842 g dimethylarsinic acid (cacodylic acid), (CH₃)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 As/L) 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.

n. *Selenium(IV) solutions*:

1) *Stock Se(IV) solution*: Dissolve 2.190 g sodium selenite, Na₂SeO₃, 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 HNO₃). Prepare solution daily when checking the equivalency of instrument response for Se(IV) and Se(VI); 1.00 mL = 0.100 µg Se(IV).

o. *Selenium(VI) solutions*:

1) *Stock Se(VI) solution*: Dissolve 2.393 g sodium selenate, Na₂SeO₄, in water containing 10 mL conc HNO₃. 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 inlet of reaction cell with auxiliary purging gas controlled by flow meter. If a drying cell between the reaction cell and atomizer is necessary, use only anhydrous CaCl₂ but not CaSO₄ because it may retain SeH₂. Before using the hydride generation/analysis system, optimize operating parameters. Aspirate dilute aqueous solutions of As and Se directly into the flame to facilitate atomizer alignment. Align 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. If a quartz atomizer is used, optimize cell temperature. If sodium borohydride reagent is added too quickly, rapid evolution of hydrogen will unbalance the system. If the volume of solution being purged is too large, the absorption signal will be decreased. Recommended wavelengths are 193.7 and 196.0 nm for As and Se, respectively.

b. *Instrument calibration standards*: Transfer 0.00, 1.00, 2.00, 5.00, 10.00, 15.00, and 20.00 mL standard solutions of As(III) or Se(IV) to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (commonly 2 to 5 mL conc HNO₃/L). This yields blank and standard solutions of 0, 1, 2, 5, 10, 15, and 20 µg As or Se/L. Prepare fresh daily.

c. *Preparation of samples and standards for total recoverable arsenic and selenium*: Follow general procedures of Section 3030F; alternatively, add 50 mL sample, As(III), or Se(IV) standard to 200-mL Berzelius beaker. (Alternatively, prepare standards by

adding 100 µg/L standard As or Se solutions directly to the beaker and dilute to 50 mL in this beaker). Add 7 mL 18N H₂SO₄ and 5 mL conc HNO₃. Add a small boiling chip or glass beads if necessary. Evaporate to SO₃ fumes. Maintain oxidizing conditions at all times by adding small amounts of HNO₃ to prevent solution from darkening. Maintain an excess of HNO₃ 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 HClO₄ and again evaporate to SO₃ fumes to expel oxides of nitrogen. CAUTION: See Section 3030H for cautions on use of HClO₄. Monitor effectiveness of 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 through entire procedure. To report total recoverable arsenic as total arsenic, average recoveries of cacodylic acid must exceed 80%. Alternatively, use 100-mL micro-kjeldahl flasks for the digestion of total recoverable arsenic or selenium, thereby improving digestion effectiveness. After final evaporation of SO₃ fumes, dilute to 50 mL for arsenic measurements or to 30 mL for selenium measurements.

d. Preparation of samples and standards for total arsenic and selenium: Add 50 mL sample or standard to a 200-mL Berzelius beaker. Add 1 mL 2.5N H₂SO₄ and 5 mL 5% K₂S₂O₈. Boil gently on a pre-heated 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 effectiveness of digestion by measuring recovery of As or Se as above. If poor recovery of arsenic added as cacodylic acid is obtained, reanalyze using double the amount of K₂S₂O₈.

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 Section 3114C.)

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 atomizer. Turn on strip-chart recorder and wait until the base line 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 base line, 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, or to 30 mL undigested standard or sample in a 200-mL Berzelius beaker, add 15 mL conc HCl and mix. Heat for a predetermined period at 90 to 100°C. Al-

ternatively 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 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. 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 base line is established. Add 0.50 mL sodium borohydride reagent. After the instrument absorbance has reached a maximum and returned to the base line, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Check for 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 versus concentration of standards. Measure peak heights or areas of samples and read concentrations from curve. If 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 seven replicates are given below:

	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	—	—

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3114 C. Continuous Hydride Generation/Atomic Absorption Spectrometric Method (PROPOSED)

1. General Discussion

The continuous hydride generator, introduced recently, 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 3500-Se.B or 3114B.4c and d.

a. *Principle:* See Section 3114B.

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 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 over 50%. Moreover, during the reduction of Se(VI) to Se(IV) by digestion with HCl (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).

2. Apparatus

a. *Continuous hydride generator:* The basic unit is composed of two 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 (3114B.1b and 2b), 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; borohydride reagent, 1 mL/min. Argon flow usually is pre-fixed, typically at 90 mL/min.

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