Chapter L

Arsenic and selenium by flow injection or continuous flow-hydride generation-atomic absorption spectrophotometry

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Principle

Geologic samples are digested using a multi-acid procedure in an open Teflon vessel. At the end of the digestion period, arsenic and selenium are reduced to oxidation states, +3 and +4, respectively. Sodium borohydride is added to the solution resulting in rapid formation of the hydrides as illustrated by:

$$3\ NaBH_4 + 4H_3AsO_3 \rightarrow 4\ AsH_3(g) + 3\ H_3BO_3 + 3\ NaOH$$

$$3\ NaBH_4 + 4H_2SeO_3 \rightarrow 4\ H_2Se(g) + 3\ H_3BO_3 + 3\ NaOH$$

The gaseous hydrides are stripped from the analytical stream and transported with inert gas to the atomizer (a heated quartz furnace) of the atomic absorption spectrophotometer. For selenium, the quartz furnace is heated by an air acetylene flame to 2000°C; and the arsenic furnace is electrically heated to 900°C. Concentrations of the elements are determined using calibration standards in solutions of similar matrix.

Interferences

Interferences usually associated with atomic absorption analysis are negligible, but incomplete recoveries of the elements from the digest solution may yield low analytical results. Incomplete recoveries are principally due to:

1. Concentration of certain transition and heavy metals (e.g. Cu, Fe, Ni, and Sn) of more than 500 ppm in the sample compete with As and Se for available $NaBH_4$. This competition may result in insufficient $NaBH_4$ for completion of the hydride-forming reaction.

2. Concentrations of one or more of the hydride forming elements in excess of 1,000 ppm. Competing hydride elements deplete the oxygen supply in the furnace which is needed to convert hydrides to ground state elements.

3. Interference of hydride formation from the incomplete digestion of organic material.

4. Possible volatility losses of the analyte in an organic rich matrix due to organometallic compounds.

5. Coprecipitation of the hydride elements if a metal is reduced to the metallic form, as is seen with Ag or Au.

Interferences one and two are generally of minimal concern in non-ore samples because the probability of high concentrations of these elements is quite low. More often, interference problems occur in mineral studies, but can be resolved by dilution of the sample solution (after KI-$C_6H_8O_6$ is added to samples for As determination only). This dilution will raise the appropriate detection limits. Special care should be taken to ensure that all the organic material in organic-rich sample is thoroughly and rapidly digested (i.e., oxidized) to enable the reaction to reach completion and to avoid loss through volatilization.

Scope

This hydride generation-atomic absorption spectrophotometric method (HG-AAS) is useful for the determination of As and Se, in a variety of geochemical samples. The optimum concentration ranges without sample dilution for these elements in various sample media are as follows:

Matrix	*Concentration range*	
	Selenium	*Arsenic*
Rock	0.1 to 4 ppm	0.2 to 20 ppm
Coal	0.1 to 10 ppm	0.2 to 50 ppm
Plant	0.03 to 1 ppm	0.05 to 12.5 ppm
Water	1 to 40 ppb	2 to 50 ppb

Above these ranges, the options of sample dilutions versus alternative techniques, e.g. energy dispersive X-ray fluorescence for selenium, should be considered. One day is required to complete digestion of 40 samples. The analyses of 40 samples requires about 1.5 hours of instrument time for each element.

Apparatus

- Standard laboratory hot plate with a 30x60-cm heating surface
- 2.5-cm-thick x 25-cm-wide x 50-cm-long aluminum heating block with 34-mm holes drilled through in a 5x10 matrix
- Thick-walled, 30-mL Teflon bottles, #0201 T from Savillex Corp., Minnetonka, Minnesota
- 125-mL Erlenmeyer flasks, with condensor tubes #ASG-CT03 from Allen Scientific Glass
- 60 mL plastic bottles with screw tops
- Gilson 212b autosampler
- Perkin Elmer 2100 AA with FIAS 400, AS 90 autosampler, PC controller and printer, for arsenic determination.
- Perkin Elmer 603 AA with Varian hydride generator Model VGA77 and strip chart recorder, for selenium determination.

Reagents

- Deionized water (DI)
- Nitric acid, HNO_3 'INSTRA-ANALYZED' grade
- Hydrochloric acid, HCl 'INSTRA-ANALYZED' grade
- Perchloric acid, $HClO_4$ 'INSTRA-ANALYZED' grade
- Sulfuric acid, H_2SO_4 'INSTRA-ANALYZED' grade
- Hydrofluoric acid, HF reagent grade
- Ascorbic acid, $C_6H_8O_6$ reagent grade
- Potassium iodide, KI reagent grade
- Sodium borohydride, $NaBH_4$ reagent grade
- Sodium hydroxide, NaOH reagent grade
- Potasium Persulfate, $K_2S_2O_8$ reagent grade

6 N HCl solution: Dilute 'INSTRA-ANALYZED' grade HCL suitable for trace metals analysis, with an equal volume of DI water. The use of the 'INSTRA-ANALYZED' grade or HCl of similar purity is advised throughout the procedure.

Sodium borohydride solution: For As, dissolve 0.5 g NaOH and 2.0 g $NaBH_4$ in DI water and dilute to 1 L in a volumetric flask. For Se dissolve 3.5 g $NaBH_4$ and 5 g NaOH in DI water and dilute to 1 L. All solutions should be made weekly and kept refrigerated between analyses.

Potassium iodide-ascorbic acid solution: (For As analysis only.) Dissolve 100 g KI in DI water. Add 50 g $C_6H_8O_6$. Dilute to 1 L with DI water. Stable for at least 2 weeks.

Saturated persulfate: (For water analysis only.) Dissolve sufficient $K_2S_2O_8$ into one liter of DI so that crystals remain and no more will go into solution.

Arsenic standard solutions: Commercially prepared As standards are used to make a 10 ppm stock solution in 10 percent HCl. The 10 ppm stock is used to prepare 20, 40, and 80 ppb working standards by transferring 0.2 mL, 0.4 mL, and 0.8 mL aliquots to three 100-mL volumetric flasks. To these add 50 mL of 6 *N* HCl, 20 mL of KI/C_6HO_6 solution, and enough DI water to bring the volume to 100 mL. The working standards are stable for at least 1 week and should be refrigerated between analyses.

Selenium standard solutions: A commercially prepared selenium stock is used to make a 10 ppm standard in 10 percent HCl. From this 0.05, 0.10, and 0.20 mL aliquots are transferred to three 100 mL volumetric flasks and brought to volume with 50 mL 6 *N* HCl, 4 mL H_2SO_4, and DI water. These standards should be stable for at least 1 week and kept refrigerated between analyses. NOTE: for water analysis, do not add H_2SO_4 to the standard solutions.

Safety precautions

The principal hazards associated with the technique deal primarily with the decomposition of the samples and the use of concentrated acids. Most dangerous is HF which inflicts painful and lasting bone and neural damage. Gloves, goggles or safety glasses, and a laboratory coat should be used whenever handling chemical reagents. Extra care should be taken in the dispensing of this acid and all equipment used in this operation should be rinsed thoroughly afterward. A salve such as calcium gluconate or magnesium sulfate should be prominently located in the laboratory and applied if an HF burn is detected. A chemical exhaust hood should be used for the digestion procedure and over the atomic absorption instrument due to the evolution of toxic hydrides and HCl vapors. There is a danger of H_2 ignition and flashback if the inert carrier gas is not turned on in advance. Review the *CHP* and *MSDS* for further information.

Procedure (rock, soil, and sediment)

1. Weigh 0.25 g sample (<80-mesh) into a 30-mL Teflon vessel, add 9 mL HNO_3 and 0.25 mL of 10 percent HCl. Allow to stand for 3 hours.
2. Add 2 mL $HClO_4$, 2 mL H_2SO_4, 10 mL HF and heat overnight at 125°C. Evaporate to ≈ 2 mLs
3. Cool, add 25 mL 6 *N* HCl and let stand for half an hour.
4. Transfer the sample solution to a 60-mL polyethylene bottle. Place bottle on digital balance, tare balance, and bring up to 55 g with DI water.
5. For selenium, approximately 8 mL of the solution is decanted into 13x100-mm test tubes and Se is determined using a Varian hydride generation system in conjunction with a Perkin Elmer-603AA.
6. For arsenic, 8 mL is mixed with 2 mL of $KI\text{-}C_6H_8O_6$ solution in 17x100-mm test tubes and is allowed to stand for 1 hour before analysis. Arsenic is determined using a Perkin Elmer-2100AA and FIAS-400 hydride system.
7. Sample peaks are compared to standard peaks recorded on a strip chart recorder for selenium while the 4100 software does the data reduction mathematically for arsenic.

Procedure (coal and plant)

1. Weigh a 0.1 g sample of coal or a 1.0 g sample of plant material into a 125 mL Erlenmeyer flask.
2. Add 20 mL HNO_3, 2 mL H_2SO_4, and let stand overnight.
3. Then add 3 mL of $HClO_4$, insert refluxers, and heat at about 175°C for 30 min.
4. Remove refluxers and continue to heat to dense white fumes.
5. Continue with step 3 of the rock procedure above.

Procedure (water and extracts)

1. Weigh 10 g liquid sample into a 30-mL Teflon vessel.
2. Add 1 mL of saturated $K_2S_2O_8$ and let stand for 1 hour.
3. Add 1 mL conc HCl and heat at 110°C with watch glass in place.
4. Remove watch glass after 1 hour and continue heating for roughly 2½ to 3 hrs or until the volume is reduced to somewhere between 2 and 5 mL.
5. Add another 2 mL conc HCl, replace the watch glass, and heat for another hour.
6. Cool, add 25 mL 6 *N* HCl and let stand for half an hour.
7. Transfer to 60-mL polyethylene bottles with distilled water, and bring to a weight of 20 g.

Operating Conditions

The analyte content of the digest solution is determined using the instrumental operating conditions shown in table 1.

Table 1.—Operating conditions for determination of As and Se by HG-AAS

	Arsenic	*Selenium*
Grating	ultraviolet	ultraviolet
Wavelength	193.7 to 197.2 nm	196.0 nm
Slit	0.7 nm	0.7 nm
Lamp setting	8 W	6 W
Source	EDL	EDL
Cell (furnace) temp	900°C	2,000°C
Mode	absorbance	absorbance
Strip chart recorder	n/a	10 mV, 5 mm
Concentration mode, 10 µg	0.45 *A*	30 *A*

Calculations

Instrument software calculates element concentration by comparing sample concentration to pre-established matrix matched calibration curve. The instrument calculates final concentration by use of a regression equation.

Assignment of uncertainty

The analytical results for As and Se in selected reference materials, duplicate samples, and method blanks are summarized in table 2.

Table 2.—Analytical performance summary for As and Se by HG-AAS (solid phase samples in ppm, water samples in ppb)

[A=National Institute of Standards and Technology (NIST), 1992; B=Water Resources Division; C=NIST, 1976; D=Harms, 1988; E=NIST, 1979; F=Wilson, 1994; remaining *pv* from Potts and others, 1992]. See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Reference	*Description*	*n*	*Mean*	*s*	*pv*		*% RSD*	*% R*
Arsenic, As								
T81	water (trace elements)	10	11ppb	1	10.3	B	9	108
SRM 1575	pine needles	10	0.20	0.01	**0.21**	C cv	5	95
SDC-1	mica schist	10	0.29	0.04	0.22		14	132
GSD-6	stream sediment	10	14	0.5	*13.6*		4	106
T89	water (trace elements)	10	17	2	17.7	B	12	98
SRM 2709	soil	10	18	0.8	**17.7**	A cv	4	102
Selenium, Se								
T81	water (trace elements)	10	14ppb	1	12.7	B	7	109
T89	water (trace elements)	20	23ppb	3	17.8	B	13	127
ALF	alfalfa leaves	20	0.18	0.02	0.19	D	11	95
SRM 1635	coal fly ash	10	1.0	0.1	0.9	E	10	106
SRM 2709	soil	20	1.5	0.1	**1.57**	A cv	7	95
CLB-1	coal	20	2.5	0.2	**2.1**	F	8	119

Table 2.—Duplicate samples results

Duplicate samples	*k*	*n*	*Mean*	*s*	*% RSD*	*Concentration range*	*No. of < (total)*	*No. of < (pairs)*
Arsenic								
Water	10	2	37.4ppb	1.1	2.9	5.1 to 108	6	3
Plant	7	2	1.03	0.07	7	0.04 to 6.8	0	0
Rock	31	2	8.0	0.2	3	0.2 to 22	6	3
Coal	5	2	14.62	0.02	0.1	0.1 to 70	4	2
Selenium								
Water	5	2	29ppb	2	8	1.4 to 79	10	5
Plant	8	2	0.98	0.02	2	0.04 to 5.8	2	1
Rock	44	2	1.33	0.04	3	0.05 to 9.0	5	2
Coal	10	2	2.59	0.08	3	0.4 to 8.4	0	0

Table 2.—Continued—Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

Method blank	*n*	*Mean*	*s*	*3s*	*5s*
Arsenic					
Water	14	0.1ppb	0.5	2	3
Coal	9	0.01	0.01	0.04	0.06
Plant	8	0.03	0.01	0.02	0.04
Rock	43	0.07	0.1	0.3	0.6
Selenium					
Water	21	0.002ppb	0.006	0.02	0.03
Rock	39	0.03	0.04	0.1	0.2
Plant	9	0.01	0.01	0.02	0.04
Coal	10	0.05	0.02	0.06	0.10

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