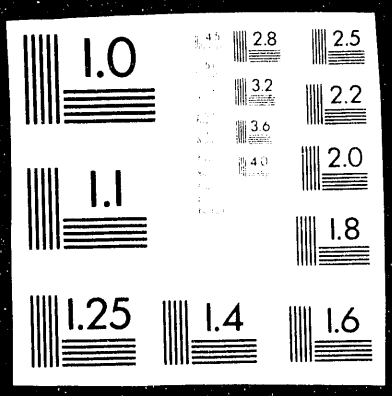

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Topical Report

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N.D. Niss
T.H. Brown

November 1991

Work Performed Under Cooperative Agreement No.: DE-FC21-86MC11076

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
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DISCLAIMER

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

SUMMARY

Methods of sample preparation for the determination of total selenium, and selenite, selenate, arsenite, and arsenate in coal fly ash materials were evaluated. The measurement methods use atomic spectroscopy for the determination of total concentrations and ion chromatography (IC) for the determination of individual ionic species. Sample preparation procedures which minimize the loss or alteration of the species of interest were explored and defined. The utility of the sample preparation methods can be sample dependent, so caution is advised in their use. IC conditions were established for the determination in extract solutions of selenite, selenate, arsenite, and arsenate with minimal interference from common anions.

SUMMARY

Methods of sample preparation for the determination of total selenium, and selenite, selenate, arsenite, and arsenate in coal fly ash materials were evaluated. The measurement methods use atomic spectroscopy for the determination of total concentrations and ion chromatography (IC) for the determination of individual ionic species. Sample preparation procedures which minimize the loss or alteration of the species of interest were explored and defined. The utility of the sample preparation methods can be sample dependent, so caution is advised in their use. IC conditions were established for the determination in extract solutions of selenite, selenate, arsenite, and arsenate with minimal interference from common anions.

INTRODUCTION

Background

The determination of arsenic (As) and selenium (Se) in coal fly ash material is of special concern because of the contemplated uses of coal combustion by-products for roadbed stabilization, construction materials, and other applications. The analysis of such materials for total arsenic is relatively straightforward, but the determination of total selenium is difficult. In addition, the species, or ionic forms of selenium and arsenic are of interest since the ionic forms can determine how these species could become mobile or stabilized under various conditions. Current ion chromatography methods do not work well because of interferences from common anions. An objective of this project was to develop a suppressed ion chromatography method to separate inorganic selenium and arsenic species in the presence of other anions common to aqueous systems. This report evaluates various aspects of the issues related to the determination of arsenic and selenium and their ionic species in coal fly ash, and presents some improved analytical methodology.

Digestion Using EPA 3050

EPA SW846 Method 3050 is a widely used standard method for digesting solid samples such as sediments, sludges, and soils for the determination of total concentrations of several trace metals, including arsenic and selenium (USEPA 1986). Subsequent measurement is by inductively coupled plasma (ICP) or graphite furnace atomic absorption (GFAA) spectroscopy, with the latter being more sensitive for arsenic and selenium. The 3050 method involves heating a sample in nitric acid and hydrogen peroxide followed by refluxing with either nitric acid or hydrochloric acid. This method was found to work acceptably for preparing samples for the determination of arsenic in materials such as coal fly ash. Thus, new approaches for preparing samples for total arsenic determination were not pursued in the current study.

Problems occur, however when the 3050 digestion is used for preparing samples for the determination of selenium. The precision for the determination of Se with the 3050 digestion is unreliable. The results of USEPA Method study 37 (Edgell 1989) list the overall percent relative standard deviation (RSD) for selenium at 29.6%, and the single analyst RSD at 23.0%. In addition, we have found that with certain matrices the recoveries from Method 3050 do not correlate with the results from paste extracts or fusion techniques for different samples. This is described in the Experimental section below.

Zeeman Background Correction

For the determination of total arsenic and selenium concentrations, a Zeeman GFAA system was used. Zeeman background correction for atomic absorption (AA) is accomplished by applying a magnetic field to the sample at the wavelength of the particular analyte being determined (Carnrick et al. 1986). Only the analyte source lamp is used. The signal is detected through polarizing light filters parallel and perpendicular to the magnetic field. Absorption of light at the analyte wavelength occurs only in the parallel component (Hideaki and Yasuda 1976). This provides the benefit of seeing only the actual background

and not interferences due to spectral lines associated with other elements. This is true particularly for selenium in an iron-containing matrix (Fernandez et al. 1981). Iron has several lines which border the selenium line at 196 nm. With a conventional continuum source such as deuterium lamp background correction, the bordering lines of iron absorb a large amount of light from the deuterium source and none from the analytical source. This causes an oversubtraction of background resulting in low selenium recoveries. A Zeeman system offers a significant advantage over deuterium background correction. With a Zeeman system, the analyte light source wavelength is used for both background correction and analytical detection so that interference from nearby lines from other elements is minimized. In some cases, however ICP provides a better measurement than Zeeman AA. For example, our observations are that for many complex sample matrices, ICP exhibits fewer interference problems with Se than Zeeman AA. The opposite is true for As. Zeeman AA provides a better methodology for determining total As than does ICP. The many spectral interferences which occur in ICP are sparsely apparent for As by Zeeman AA.

Arsenic and Selenium Species

The names and chemical formulas of the four anions which are the focus of this study are provided in Table 1. These are arsenite, arsenate, selenite, and selenate.

Table 1. Chemical Species Investigated in This Study

Chemical Name	Chemical Formula
Arsenite	AsO_2^-
Arsenate	AsO_4^{3-}
Selenite	SeO_3^{2-}
Selenate	SeO_4^{2-}

Note: The degree of dissociation of these mineral acids may vary in natural systems depending on the redox conditions.

Selenium can exist in solid matrices as selenide, elemental selenium, selenite, selenate, and as organically bound compounds. (Rosenfeld and Beath 1964). Inorganic selenide may be found in solid phases as metal selenides of low solubility, or as ferroselite, an analog of pyrite (Howard 1977). Selenite and selenate may exist in solid phases as carbonates, ferric oxides, and manganese oxides.

Elemental selenium may be found in the solid phase, depending on the redox conditions of the system (Cutter 1986). The redox potential (pe + pH) of the solid system controls the selenium speciation in solution. The electron activity at equilibrium, pe is defined as the negative logarithm of electron concentration, which is similar to the definition of pH as the negative logarithm of hydronium ion concentration (Stumm and Major 1981). According to Elrashidi et al. (1987), selenate is the major ion in solution under high redox (pe + pH > 15.0) conditions. In the moderate redox range (pe + pH 7.5 to 15.0), selenite, as SeO_3^{2-} or $HSeO_3^-$ may be present. At low redox conditions (pe + pH < 7.5), selenide (HSe^-) is the major ion present.

Arsenic can exist as arsenide As(-III), elemental arsenic As(0), arsenite As(III), and arsenate As(V) in aqueous systems. The main factors controlling the chemical form of arsenic present are the pH and pe of the system. Arsenite will be dominant only at low pH and low pe, and arsenate will be dominant at all other pH and pe values. The occurrence of As(0) metal is very rare, and arsenide occurs only at extremely low Eh values, and in very low concentrations (Crecelius et al. 1986). Arsenic can exist in solid matrices as arsenite, arsenate, and organically bound forms. Organically bound arsenic has been detected as monomethylarsonate (MMA), and dimethylarsinate (DMA) in soils and sediments from the methylation of arsenic by microbial action (Takamatsu et al. 1982).

Extraction of Arsenic and Selenium Species

As discussed above, the chemical forms of selenium and arsenic solubilized from solid matrices are governed by various parameters including pH, dissociation constants and oxidation-reduction potentials. To determine the chemical species of selenium and arsenic in solid matrices, a leaching method must remove the extractable selenium and arsenic species quantitatively, while preserving their chemical forms. Most techniques for the determination of total selenium and arsenic in solid matrices employ oxidative digestions such as the 3050 digestion which generate selenate and arsenate from reduced forms of the species present in the material (Campbell 1984). Phase-selective leaching methods as developed by Tessier et al. (1979) determine the concentrations of selenium and arsenic associated with sedimentary phases such as carbonates, iron and manganese oxides, organic matter, and primary mineral. The Tessier leaching methods do not preserve the chemical forms of selenium and arsenic due to the conditions used.

Cutter and Bruland (1984) developed an alkaline leaching method using one molar sodium hydroxide to solubilize selenite and selenate from biogenic particles. The samples were first sonically disrupted and then leached with sodium hydroxide solution for four hours. Radiotracer studies using ^{75}Se-labeled selenite and selenate were performed to test the efficiency of the leaching technique. The results showed that 94% of the labels were recovered. Non-radiogenic selenite standards were also subjected to the leaching procedure to see if any oxidation to selenate occurred. After a four hour leach, no speciation change from selenite to selenate was detected.

The alkaline leaching procedure was tested further by Cutter (1986) on National Bureau of Standards River Sediment, Estuarine Sediment, and Coal Fly Ash standards. Since selenite and selenate are concentrated in the inorganic phases of a sediment, the concentrations of selenite and selenate obtained from the alkaline leach procedure were compared with the sum of the total selenium concentrations from the exchangeable, carbonate, and iron and manganese oxide phases obtained from the selective dissolution method of Tessier et al. (1979). In all cases, the selenite and selenate concentrations obtained from the alkaline leach procedure compared very closely to the total selenium concentrations obtained from the selective dissolution procedure.

Aqueous extraction techniques also were developed and tested by Karlsen and Frankenberger (1986a and b). Two soils were extracted with water at a 1:5 solid to solution ratio for one hour. The extracts were filtered and subsequently analyzed for selenite or selenate by single column ion chromatography (SCIC) and hydride generation-AA and ICP. The results from the SCIC and AA/ICP analyses agreed favorably, but no experiments were conducted to determine the extraction efficiency of the aqueous technique on the soil samples. All spiking experiments were performed on the extracts, and not on the soils prior to extraction.

Previous work by Maher (1981) showed that arsenite and arsenate are quantitatively extracted at different pH values. The maximum recovery of arsenite occurs at low pH values, while maximum recovery of arsenate occurs at a pH > 12. This work was tested further by Crecelius et al. (1986) using phosphate buffers. They confirmed that the maximum recovery of As(III) occurs at about pH 2.8 and the maximum recovery of As(V) occurs at a pH > 12.

Single Column Ion Chromatography Methods

Karlsen and Frankenberger (1986a and b) developed SCIC methods for the determination of selenite and selenate using separate runs with different eluents. For the determination of selenite, a phthalic acid eluent adjusted to pH 2.7 was used with a low capacity anion exchange column. Karlsen and Frankenberger (1986a) tested the method using standard solutions of selenite, chloride, phosphate, nitrite, and nitrate ions, as well as aqueous extracts of soil solutions. High levels of chloride in the soil extracts interfered with the analysis, but were removed with a silver-saturated cation exchange resin. Sulfate and selenate did not elute as detectable peaks with this separation. Karlsen and Frankenberger (1986b) determined selenate using a 4 mM phthalic acid eluent adjusted to pH 4.6, with a low-capacity anion exchange column. The method was tested using standard solutions of selenate, chloride, nitrate, sulfate ions, and aqueous soil extracts. Interferences from sulfate in the aqueous extracts were removed with a barium-saturated cation exchange resin.

Mehra and Frankenberger (1988) determined selenite and selenate in aqueous soil extracts with a single SCIC separation. A low capacity resin-based anion exchange column and conductivity detection was used with a 4 mM p-hydroxybenzoic acid (PHBA) eluent. Although no interferences were present, high levels of nitrate and sulfate, which

are common in many soil extracts, can pose serious problems. Wescan Instruments Inc. (1988) used similar conditions with standard solutions of selenite and selenate, and aqueous soil extracts.

Suppressed Ion Chromatography Methods

Suppressed ion chromatography offers some distinct advantages over SCIC. One of the most important is the pH stability of the columns. The silica-based columns used in SCIC are only stable between pH 3 and 9, whereas the resin-based columns used in suppressed IC are stable at all pH values. The pH stability of the resin-based columns is important when analyzing extracts with extreme pH values, such as highly alkaline coal fly-ash leachates (Johnson 1986).

Williams (1983) developed a method for the separation of selenite and selenate using suppressed ion chromatography with ultraviolet (UV) absorbance detection. The method is free of sulfate interferences because sulfate does not display UV absorbance above 190 nm, however nitrate still presents an interference problem with the detection of selenite. Another major disadvantage of this method is its lack of sensitivity. The limits of detection are about 15 mg/L.

The determination of As(III) species by ion chromatography after oxidation to AsO_4^{3-} with aqua regia was developed by Hansen et al. (1979). As(V) can be detected directly as arsenate (AsO_4^{3-}), but arsenite is not detectable using conductivity because of the low dissociation constant of arsenious acid. Dionex Corp. (1984) developed a separation for the simultaneous detection of arsenite and arsenate using combined electrochemical and conductivity detection. The separation is performed with a sodium carbonate/sodium bicarbonate eluent and a high capacity resin-based anion exchange column. Arsenate is detected via suppressed conductivity and arsenite is detected using an electrochemical detector equipped with a platinum working electrode at 0.50 V. The determination of As(III) and As(V) by ion chromatography with combined electrochemical and conductivity detection has also been studied by Tan and Dutrizac (1986).

EXPERIMENTAL

Samples Used in This Study

Four coal fly ash samples were used in this study. These were the NIST 1633a fly ash standard reference material (SRM) from the National Institute for Standards and Technology (NIST) in Gaithersburg, MD, and three fly ashes from commercial sources labeled A, B, and C. A certification sheet for NIST 1633a SRM is provided in Appendix A. Fly ash A is from a conventional pulverized coal (PC) process. Fly ash B is from a process using a calcium-based sorbent for sulfur dioxide removal. Fly ash C was generated in an experimental process study where sodium carbonate-bicarbonate was blown into the combustion gas ahead of the spray dryer.

Sample Preparation for the Determination of Selenium by Atomic Spectroscopy

Digestates containing high levels of sodium proved to be difficult to analyze for Se by AA or ICP due to spectral interferences. A cation exchange cleanup step was incorporated prior to the analysis of these samples. This included samples with high sodium content subjected to paste extraction, and solutions from sodium fusion procedures which are described in the next section. This approach eliminated the spectral interferences due to sodium. The method for the cation exchange cleanup is provided in Appendix B. Spiking of sample extracts with selenium atomic spectroscopy standards was performed to confirm quantitative recovery.

There are several considerations involved in selecting the optimal digestion method for the determination of total selenium in coal fly ash samples. The main consideration seems to be the sample type and its source. It is beyond the scope of the current study to define the causes of this relationship. Our results show that caution is required in selecting an appropriate method and in interpreting the results. Trial and error with extensive quality control checks are required.

In some preliminary experimental work, the sodium carbonate-bicarbonate blown fly ash C gave a total selenium value of 3.18 mg/kg following a 3050 digestion on a dry sample basis, and a value of 6.88 mg/kg from a direct determination from a highly alkaline solid:water (2:1) paste extract. When the remaining solid material from the paste extract was digested by the 3050 procedure, an additional 0.53 mg/kg Se was obtained. When the 3050 digestion was performed twice sequentially on a portion of fly ash C in a separate experiment, the results were 3.94 and 0.08 mg/kg Se, respectively. The phenomenon is possibly similar to the results of acid and base extraction experiments by Kolm (1975). They observed that base extracts from soil samples typically show higher total selenium values than acid extracts. When we applied the 3050 method to the NIST 1633a SRM fly ash, the result was triplicate values of 11.3, 12.9, and 11.5 mg/kg Se in one set of analyses, and a value of 10.8 mg/kg on a different day. The certified value is 10.3 mg/kg Se. This difference between the certified and measured values is reflective of the standard deviation problem with Se noted in the Introduction section. An alkaline paste extraction described in Appendix B of the NIST 1633a SRM gave a value of 3.18 mg/kg, whereas an ultrasonic alkaline extraction procedure discussed in a later section gave a value of 10.8 mg/kg, near the certified value of 10.3 mg/kg.

Sodium peroxide fusion was tested also to determine total selenium, with and without the addition of sodium hydroxide to lower the fusion temperature. The results for fly ash C were 5.54 and 4.34 mg/kg Se for fusion with and without sodium hydroxide, respectively. The 1633a SRM fly ash gave values of 7.07 and 5.86 for fusion with and without the addition of sodium hydroxide, respectively. The resulting values are between the values obtained by the 3050 acid digestion procedure and the paste extraction in both cases. This indicates that sodium peroxide fusion is not the optimal sample preparation step for either of these samples.

Optimization of Ion Chromatography Parameters

Our observations show when standard anion separation methods (i.e., bicarbonate/carbonate eluant) are used, interference problems with selenite and selenate exist from nitrate, phosphate, and sulfate. Arsenate is strongly retained on the column, and will not elute in a reasonable amount of time. To alleviate these problems, several combinations of anion exchange columns and eluant compositions were tested. The optimal separation of all the anions of interest was achieved using a HPIC-AG5/AS4A column combination with two different eluants. A sodium carbonate/sodium hydroxide eluant was used to elute selenite and selenate in the presence of common anions. A sodium bicarbonate/sodium carbonate eluant was used to elute arsenite and arsenate with a run time of about 20 minutes. Detailed descriptions of the methods are contained in Appendix B.

The use of an AG5 anion exchange guard column instead of the customary AG4 anion exchange guard column with an AS4A analytical anion exchange column separates nitrate and sulfate from selenite and selenate, respectively. This is because the AG5 packing has a different selectivity than the AG4 packing due to differences in the hydrophobic nature of the functional groups in the packings. The use of a sodium carbonate/sodium hydroxide eluant eliminates the interference of phosphate with selenite because the valency of phosphate is highly dependent on the eluant pH. The dissociation of orthophosphoric acid involves three steps, and as the eluant pH rises, the proportion of phosphate in the PO_4^{3-} also increases, lengthening the retention time. This eliminates the interference from any phosphate ion present in an extract. The eluant used to separate the selenium species consisted of 2.0 mM sodium carbonate and 1.0 mM sodium hydroxide at a flow rate of 2 mL/minute. All anions were detected via conductivity at 1 micro Siemens full scale (μSFS). Figure 1 shows a chromatogram of selenite and selenate with other common anions in reagent water. In samples with very high levels of sulfate, problems may still occur with the detection of selenate or arsenate. In these cases, the samples may be pretreated with commercially available solid phase cation exchange extraction cartridges containing barium.

The AG5/AS4A column combination was also used to separate arsenite and arsenate from other common anions. The eluant consisted of 2.0 mM sodium carbonate and 1.5 mM sodium bicarbonate. Arsenite was detected using electrochemical detection with a platinum working electrode at a potential of 0.50 V. The electrochemical detector was installed between the column and the suppressor device. Arsenate was detected using conductivity detection set at 1 μSFS. A flow rate of 1 mL/minute was used because higher flow rates cause an unstable baseline with the electrochemical detector. Figure 2 shows a chromatogram of arsenite and arsenate with other anions in reagent water.

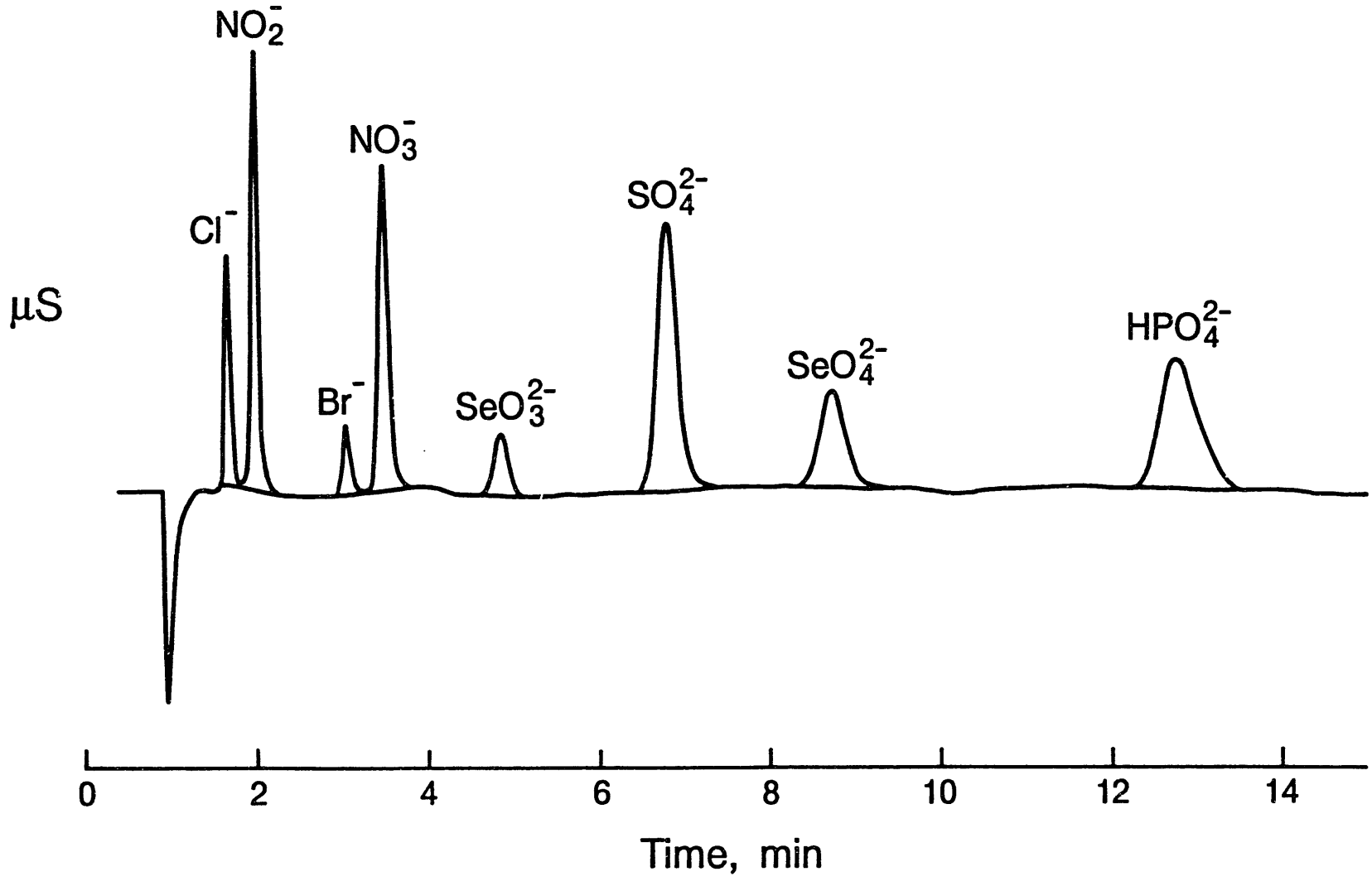

Figure 1. Ion Chromatogram of Selenite and Selenate in the Presence of Common Anions. Column, Dionex AG5 + AS4A; Eluant, 2.0 mM Na_2CO_3, 1.0 mM NaOH; Conductivity Detection.

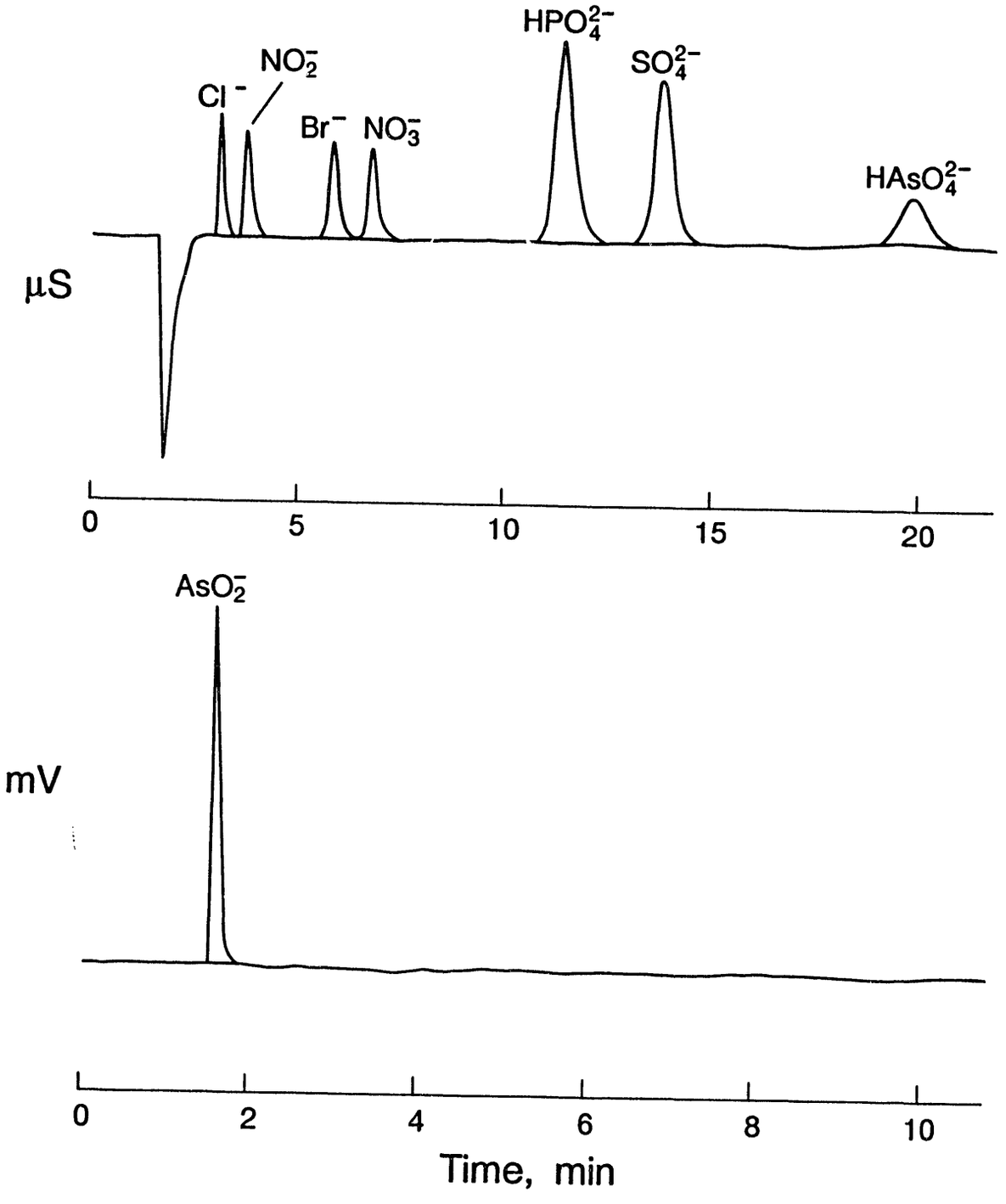

Figure 2. Ion Chromatogram of Arsenite and Arsenate in the Presence of Common Anions. Column, Dionex AG5 + AS4A; Eluant, 2.0 mM Na_2CO_3, 1.5 mM $NaHCO_3$; Conductivity Detection with Electrochemical Detection for Arsenite.

Extraction of Selenium and Arsenic Species from Coal Fly Ash

To determine the selenium and arsenic species present in coal fly ash samples, methods must first be developed to quantitatively extract the elements without changing their chemical forms. The NIST 1633a SRM fly ash material was used for the exploratory work. Experiments were performed using an ultrasonic bath with 0.5M, 2M, and 4M sodium hydroxide solutions and distilled and deionized (ASTM Type I) water to extract selenite, selenate, and arsenate. A 1M hydrochloric acid solution was used to extract arsenite. The fly ash was extracted with each solution for different lengths of time ranging from 4 to 24 hours. The complete extraction method is detailed in Appendix B. The optimum extraction conditions for selenite, selenate, and arsenate uses a 0.5M sodium hydroxide solution with an extraction time of four hours. Longer times did not result in any appreciable increase in the levels of selenium or arsenic detected in the leachates. Use of stronger sodium hydroxide solutions (i.e., 2M or 4M) led to baseline interruption problems with the test species, and secondary complex formations. Type I water did not extract detectable levels of the anions of interest, even after a 24 hour extraction period. Experiments also were conducted using 1M hydrochloric acid to release arsenite. Arsenite was not detected in any samples, but spike recoveries for a four hour extraction were between 90-110%.

To ensure that no speciation change was occurring during the extraction process, the four fly ash samples used in this study were spiked with selenite, selenate, arsenite, and arsenate prior to extraction. Solutions of the sodium salts of the anions in the appropriate extraction fluid were added to extraction fluid and the sample prior to the ultrasonic extraction. Tables 2 and 3 show the spiking levels and recoveries for the selenium and arsenic species of interest. The results show no detectable speciation changes over the chosen extraction time of four hours. The quantitative recoveries of all the species of interest also indicate that they are not altered or adsorbed by the sample with this procedure. Spiking experiments should be performed whenever different fly ash matrices are analyzed.

Table 2. Recovery of Selenium Species From Coal Fly Ash

Fly Ash	SeO_3^{2-} Conc. in Spike, mg/kg	SeO_3^{2-} Recovery, mg/kg	%	SeO_4^{2-} Conc. in Spike, mg/kg	SeO_4^{2-} Recovery, mg/kg	%
NIST 1633a	1.27	1.33	105	1.27	1.24	98
A	1.23	1.24	101	1.23	1.22	99
B	1.24	1.18	95	1.24	1.15	93
C	1.27	1.33	105	1.27	1.24	98
Mean			102			97
Standard Deviation			4.7			2.7

Table 3. Recovery of Arsenic Species From Coal Fly Ash

Fly Ash	AsO_2^- Conc. in Spike, mg/kg	AsO_2^- Recovery, mg/kg	%	AsO_4^{3-} Conc. in Spike, mg/kg	AsO_4^{3-} Recovery, mg/kg	%
NIST 1633a	1.55	1.53	98	1.27	1.30	102
A	1.57	1.45	92	1.53	1.45	95
B	1.52	1.42	93	1.55	1.53	99
C	1.60	1.53	95	1.27	1.40	110
Mean			94			102
Standard Deviation			2.6			6.4

The leachates were also analyzed for total selenium and arsenic by Zeeman AA spectroscopy to provide a comparison with the IC results for the ion species. These data are presented in Tables 4 and 5. Also shown are the results for total As and Se as determined by AA or ICP following the 3050 digestion. The results for Se show that the only specie detected in the NIST 1633a SRM, and fly ashes A and B is selenite (Table 4). Selenate was the only specie detected in the extract from fly ash C. The total Se concentrations closely match the selenite or selenate-Se values. The ultrasonic extraction provided a value of 10.8 mg/kg for the NIST 1633a SRM, close to its certified value of 10.3 mg/kg Se (Appendix A). This extraction procedure also gave the highest value of Se of any of the methods evaluated in this study for the highly alkaline fly ash C.

Table 4. Comparison of Selenium Results by IC and AA/ICP

	Ultrasonic Extraction			3050 Digestion
	IC		AA	AA/ICP
Fly Ash	SeO_3^{2-}-Se mg/kg	SeO_4^{2-}-Se mg/kg	Total Se mg/kg	Total Se mg/kg
NIST 1633a	11.2	<0.08	10.8	11.6*
A	7.70	<0.08	7.70	10.3**
B	8.10	<0.08	8.45	23.3**
C	<0.08	9.13	9.60	3.18

* Average of four determinations.
** ICP values.

Table 5. Comparison of Arsenic Results by IC and AA

Fly Ash	Ultrasonic Extraction IC AsO_2^--As mg/kg	Ultrasonic Extraction IC $HAsO_4^{2-}$-As mg/kg	Ultrasonic Extraction AA Total As mg/kg	3050 Digestion AA Total As mg/kg
NIST 1633a	<0.02	130	135	122
A	<0.02	<0.20	0.34	21
B	<0.02	<0.20	0.35	31
C	<0.02	<20.*	7.62	<12

* This fly ash contained very high sulfate levels, so the sample was diluted 100x before injection.

Arsenite was measured in the 1M hydrochloric acid ultrasonic extract solutions and arsenate was determined in the 0.5M alkaline ultrasonic extract solutions (Table 5). Arsenic was not detected by IC in any of the sample extracts except for the NIST 1633a SRM, where it occurs as arsenate. Zeeman AA determinations for total arsenic were performed on the alkaline ultrasonic extract solutions. The IC and AA values from the 1633a extract fall within 20% of the certified value of 145 mg/kg As (Appendix A), which is within EPA acceptance criteria. Some As was detected by AA in the extracts from the other three samples. For fly ashes A and B, the level detected was near the IC detection limit of 0.20 mg/kg. A large sulfate interference was present in the fly ash C extract which required sample dilution with a resulting increase in the IC quantitation limit.

For the NIST 1633a SRM, the Se results by AA for the ultrasonic extracts compare well with the 3050 digestion values (Table 4). As previously noted, the acid digestion yields lower results for fly ash C than an alkaline extraction. The reason for this is unknown. The other two fly ashes yield higher values for the 3050 digestion than for the ultrasonic alkaline extraction. Possibly some species are present that are not solubilized in the latter procedure.

The As results by AA are within 20% of the certified value for the NIST 1633a SRM for both the ultrasonic extraction and 3050 digestion (Table 5). About two orders of magnitude more As was detected in the fly ash A and B digestates than in their corresponding alkaline ultrasonic extracts. This is probably due to a form of As which is neither arsenite nor arsenate. The 3050 result for fly ash C did not show any detectable arsenic on analysis of a diluted digestate solution. These results indicate that for determining total As, both the 3050 digestion and the ultrasonic digestion should be performed. Although the 3050 digestion appears to put all the As in solution, a lower

detection limit was achieved for fly ash C by Zeeman AA for the ultrasonic extract than for the 3050 digestate due to dilutions required for the latter solution because of sulfate interference.

The total Se values obtained for the two fly ash materials extracted using the four sample extraction methods provided in Appendix B, are presented in Table 6. These include the paste extraction, the sodium peroxide fusion with sodium hydroxide addition, the 3050 acid digestion, and the ultrasonic extraction. The 3050 digestion and the ultrasonic extraction give essentially the same values for the NIST 1633a SRM. These values are significantly higher than those obtained by the other two methods. The ultrasonic extraction gives the highest value of all four sample preparation methods for fly ash C. The reasons for the above results are not fully understood. These observations should not necessarily be extrapolated to other fly ash materials. Caution should be applied in selecting the optimal analytical scheme.

Table 6. Results for Total Se by AA for Four Sample Extraction Methods

	Total Se on Dry Sample Basis, mg/kg			
Fly Ash	Paste Extraction	Fusion with NaOH Added	3050 Digestion	Ultrasonic Extraction
NIST 1633a	3.18	7.07	11.6	10.8*
C	6.88	5.54	3.18	9.60

* Average of four determinations.

CONCLUSIONS

Analytical methods for the preparation of coal fly ash samples and extracts for the determination of total Se by Zeeman GFAA or ICP were evaluated. Methods for the extraction of As and Se species from fly ash, and their determination by ion chromatography were developed. The methods were documented in a format for use in research efforts in the measurement and speciation of arsenic and selenium in a variety of aqueous and solid matrices.

Four methods for extraction of total selenium were evaluated with two coal fly ash materials. The methods included paste extraction, sodium peroxide fusion, ultrasonic extraction, and acid digestion. The acid digestion and sodium peroxide fusion gave the highest recoveries for one sample, the NIST 1633a SRM, while the ultrasonic extraction gave the highest recovery for the other sample.

New separation conditions were established for the determination of selenite, selenate, arsenite, and arsenate in the presence of common anions by ion chromatography. Four fly ash samples were extracted with a new ultrasonic extraction procedure. Spiking experiments showed that the selenium and arsenic species were not altered under the conditions of the extraction, and that the recoveries were quantitative.

The results for total arsenic and selenium measured by atomic spectroscopy from the ultrasonic extracts and acid digestates of four fly ash samples were compared with the ion chromatography analysis results of the ultrasonic extracts. The results for selenium were essentially the same for the 1633a SRM. For two fly ashes, the acid digestion yielded higher total Se values than the ultrasonic extraction. The selenium in the NIST 1633a SRM and these two fly ashes from the ultrasonic extract was all in the form of selenite. The fourth fly ash gave a higher total selenium value for the ultrasonic extract than for the acid digestate. The selenium in this extract was in the form of selenate.

Analysis of the ultrasonic extracts showed that only one fly ash, the NIST 1633a SRM had detectable arsenic by IC, all in the form of arsenate. The value was essentially the same as detected by AA in both the ultrasonic extract and the 3050 acid digestate. Some total arsenic was detected by AA in the ultrasonic extracts for the other three fly ashes. For two of these, the total arsenic was higher in the 3050 acid digestate than in the ultrasonic digestate. Another fly ash had detectable arsenic only in the ultrasonic extract by AA, but dilutions due to a complex matrix raised the detection limits so that a comparison with the IC measurement in the ultrasonic extract and AA measurement in the acid digestate was not possible.

The results of the current study show that, at minimum, both the alkaline ultrasonic extraction and the acid 3050 digestion should be used for total Se determination in unknown samples. Only the 3050 digestion should be required for the determination of total arsenic. The alkaline ultrasonic extraction is the preferred sample preparation method for the determination of selenite, selenate and arsenate by ion chromatography. The ultrasonic hydrochloric acid extraction is required for the determination of arsenite. The ion chromatography results should be compared with the results of total As or Se determination by atomic spectroscopy since other As or Se containing compounds might be present. Additional work is needed to establish optimized and practical analytical approaches for the determination of other species, such as selenide or organically-bound As and Se species.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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APPENDIX A

Certification Sheet for NIST 1633a SRM

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1633a

Trace Elements in Coal Fly Ash

This Standard Reference Material (SRM) is intended for use in the evaluation of analytical methods for the determination of constituent elements in coal fly ash or materials with a similar matrix.

SRM 1633a is a fly ash that was sieved through a No. 170 sieve with a nominal sieve opening of 90 μm.

Certified Values of Constituent Elements: The certified values for the constituent elements are shown in Table 1. The analytical techniques used and the analysts are given in Table 3. The certified values are based on results obtained by reference methods of known accuracy or from two or more independent, reliable analytical methods. Noncertified values are given for information only in Table 2.

Notice and Warnings to Users: This certification is invalid 5 years from date of purchase of the SRM. The constituents certified or analyzed are reviewed periodically and may be updated to reflect improved measurement. Updated certificates will be made available upon request.

Use: This material should be dried to a constant weight before using. Recommended procedures for drying are: (1) Vacuum drying for 24 hours at ambient temperature using a cold trap at or below −50 ° C and a pressure not greater than 30 Pa (0.2 mm Hg); (2) drying for 2 hours in an oven at 105 ° C; (3) drying in a dessicator over P_2O_5 or Mg_2ClO_4. Samples of the dried material weighing at least 250-mg should be used for analysis. When not in use the material should be kept in a tightly sealed bottle.

Source and Preparation of Material: The fly ash material was supplied by a coal fired power plant and is a product of Pennsylvania and West Virginia coals. It was selected as a typical fly ash and is not intended as a fly ash from a specific coal or combustion process. The material was sieved and blended for 2 hours in a Vee blender. The material was then removed and placed in a series of bulk containers from which specific samples were taken for homogeneity testing and certification analysis. Twelve bottles were selected for the homogeneity test. Samples from each bottle were analyzed for cobalt, chromium, europium, iron, scandium, and thorium using nondestructive neutron activation analysis. The observed standard deviations for both 50 and 250 mg sample sizes were consistent with counting statistics, indicating that the fly ash is homogeneous within ± 5% (relative) based on these elements. The homogeneity testing and certification analyses were performed in the NBS Center for Analytical Chemistry.

The overall direction and coordination of the analytical measurements leading to the initial certification were performed in the Center for Analytical Chemistry under the chairmanship of L.A. Machlan.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W.P. Reed and T.E. Gills.

Gaithersburg, MD 20899
January 5, 1985
(Revision of certificate
dated April 18, 1979)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Table 1. Certified Values of Constituent Elements

Major Constituents	Content Wt. Percent	Minor Constituents	Content Wt. Percent
Aluminum	14.3 ± 1.0[a]	Magnesium	0.455 ± 0.010
Iron	9.4 ± 0.1	Sodium	0.17 ± 0.01
Potassium	1.88 ± 0.06		
Silicon	22.8 ± 0.8		
Calcium	1.11 ± 0.01		

Trace Constituents

Element	Content µg/g	Element	Content µg/g
Antimony	6.8 ± 0.4	Rubidium	131 ± 2
Arsenic	145 ± 15	Selenium	10.3 ± 0.6
Cadmium	1.00 ± 0.15	Strontium	830 ± 30
Chromium	196 ± 6	Thorium	24.7 ± 0.3
Copper	118 ± 3	Thallium	5.7 ± 0.2
Manganese	179 ± 8	Uranium	10.2 ± 0.1
Mercury	0.16 ± 0.01	Vanadium	297 ± 6
Nickel	127 ± 4	Zinc	220 ± 10
Lead	72.4 ± 0.4		

[a]The uncertainties of the certified values are based on judgment and represent an evaluation of the combined effects of method imprecision, possible systematic errors among methods, and material variability for samples of 250-mg or more. (No attempt was made to derive exact statistical measures of imprecision because several methods were involved in the determination of most constituents).

Supplemental Information

Note: The following values are not certified because they are not based on the results of either a reference method or of two or more independent methods. These values are included for information only.

Table 2. Noncertified Values for Constituent Elements

Element	Content Wt. Percent	Element	Content µg/g
Barium	0.15	Beryllium	12
Titanium	0.8	Cerium	180
Sulfur	0.18	Cobalt	46
		Cesium	11
		Europium	4
		Gallium	58
		Hafnium	8
		Molybdenum	29
		Scandium	40

APPENDIX B

Analytical Methods

CONTENTS OF APPENDIX B

WESTERN RESEARCH INSTITUTE
ANALYTICAL METHOD

Method Title: Paste Extraction for the Determination of Total Selenium by Atomic Spectroscopy

1. Summary of Method

In some solids, selenium exists in a form which is more mobile in a basic media than in an acidic media. In one case, twice as much Se was extracted using a NaOH paste than was extracted using the acid digestion described in SW846 Method 3050. For samples to be analyzed by graphite furnace atomic absorption (GFAA) spectroscopy, this extraction must be followed by the cation removal procedure described in the following standard operating procedure prior to the determination of selenium.

2. Apparatus and Materials

2.1 A wrist action shaker or sample rotator. It is necessary to use a shaker which changes the horizontal axis of the sample container. Use of a shaker with only one dimension of motion will allow the sample to settle and cause an inefficient extraction.

2.2 50-mL polypropylene centrifuge tubes with lids

2.3 Centrifuge

3. Reagents

3.1 ASTM Type I water [American Society for Testing and Materials (ASTM) D1193].

3.2 0.5 N NaOH solution.

4. Extraction

4.1 Mix the sample thoroughly.

4.2 Add 20 g of as-received sample, weighed to the nearest milligram, and 20 mL 0.5 N NaOH to each centrifuge tube.

(Note: If the paste extract is at a pH of 12 or greater with just the addition of Type I water, then Type I water may be used in place of 0.5 N NaOH.)

4.3 Place the centrifuge tubes on the shaker and allow to shake for 24 hours.

4.4 Centrifuge the samples and decant off the liquid into a 100-mL volumetric flask.

4.5 Add 20 mL Type I water to the tube and shake for 30 minutes.

4.6 Centrifuge the sample and decant the liquid into the volumetric flask with the rest of the sample extract.

4.7 Repeat the above washing two more times. Bring the sample extract volume to 100 mL.

4.8 Particulates in the extract that may clog the ICP nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

5. Calculation

The concentration of selenium may be calculated by the equation:

$$C = A \times V / M$$

Where C = Concentration of Se in the original sample, mg/kg
A = Concentration of Se in the extract, mg/L
V = Total volume of extract, mL
M = Mass of the sample extracted, g

6. Quality Control

6.1 A lab control sample such as NIST 1633a SRM must be extracted at a 10% frequency.

6.2 Duplicate samples must be extracted at a 10% frequency.

6.3 Spikes must be extracted at a 10% frequency.

6.4 Neither this method nor SW846 Method 3050 may extract all the Se in all cases. In many cases a combination of this method followed by SW846 Method 3050 may be required to obtain a true idea of the amount of leachable Se.

WESTERN RESEARCH INSTITUTE
ANALYTICAL METHOD

Method Title: Sodium Peroxide Fusion for the Determination of Metals by Atomic Spectroscopy

1. Summary of Method

For materials which contain silicates, mineral acid digestions such as SW846 Method 3050 will leave much of the sample undigested. Hydrofluoric acid-based digestions will decompose the entire sample, but will also cause a loss of Si. A method which completely decomposes the sample and still allows for the determination of Si and other metals is the sodium peroxide fusion. A sodium peroxide fusion has the advantage over other fusions of being able to decompose a wide range of samples at relatively low temperatures, < 500°C, with an analytically pure compound. A variation of the method which uses sodium peroxide:sodium hydroxide (1:1) instead of sodium peroxide alone can result in a lower fusion temperature and might prove advantageous for determining certain elements in specific samples.

2. Apparatus and Materials

2.1 A temperature control furnace capable of reaching 600 °C

2.2 50-mL zirconium crucibles

3. Reagents

3.1 ASTM Type I water

3.2 Sodium peroxide pellets, 93%+ pure

3.3 Hydrochloric acid, concentrated - trace metals grade

3.4 Nitric acid, concentrated - trace metals grade

4. Fusion

4.1 Add 0.5 grams of well mixed sample, weighed to the nearest milligram, and 2.0 grams sodium peroxide to each zirconium crucible. An alternative fusion mix uses 1.0 g of sodium peroxide and 1.0 g sodium hydroxide.

4.2 Place the zirconium crucibles in the furnace and allow the temperature to come to 400°C.

4.3 Hold the temperature at 400°C for 15 minutes.

4.4 Raise the temperature to 600°C and hold for 30 minutes.

4.5 Remove crucibles and allow them to cool to room temperature. Caution: crucibles are hot.

4.6 Carefully rinse peroxide pellet into a 100-mL volumetric flask using a funnel and small aliquots of water. Caution: crucibles will heat up as reaction occurs and some sample loss may occur due to excessive effervescence. Use multiple washings.

4.7 Add about 5 mL nitric acid:Type I water (1:1) mix to the crucible to rinse out any remaining residue.

4.8 Add nitric acid to the rinsate until it is clear. Then add 5 mL HCl.

4.9 Particulates in the rinsate that may clog the ICP nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

5. Calculation

The concentration of selenium may be calculated by the equation:

$$C = A \times V / M$$

Where C = concentration of analyte, mg/kg
A = Concentration of analyte in the rinsate, mg/L
V = Total volume of rinsate in mL
M = Mass of the sample, g

6. Quality Control

6.1 A lab control sample such as NIST 1633a SRM must be run at a 10% frequency.

6.2 Duplicate samples must be run at a 10% frequency.

6.3 A NIST SRM should be run with each batch for the elements of interest.

7. References

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WESTERN RESEARCH INSTITUTE
ANALYTICAL METHOD

Method Title: Cation Removal for the Determination of Total Selenium by Atomic Spectroscopy

1. Summary of Method

High concentrations of cations such as sodium, potassium, magnesium, iron, etc., make the determination of selenium by graphite furnace atomic absorption (GFAA) spectroscopy very difficult if not impossible. By using a cation exchange resin the interfering cations can be removed while leaving selenium, which exists in anionic form. This allows for the simple and rapid determination of selenium by GFAA.

2. Handling of Samples

2.1 Containers and Preservatives

Samples may be collected in glass or polyethylene acid-washed bottles.

At least 100 mL of sample should be collected.

Cool to 4°C and extract as soon as possible.

2.2 Sample Preparation

The sample must be at a pH > 7 prior to contacting the resin.

If the sample contains carbonates it will react upon contact with the resin, forming carbon dioxide. This will result in gas being trapped in the resin and a greatly reduced efficiency in the column. A procedure is provided for the removal of carbonates prior to the addition of sample to the resin column.

3. Apparatus and Materials

3.1 An acid washed glass column with an approximately 0.5 inch I.D. and capacity of at least 30 mL. The column should have a glass wool filter and stopcock at one end. The use of a burette with a removable Teflon™ stopcock is ideal for this purpose.

3.2 Cation exchange resin, BIO-RAD AG 50W-X8, 100-200 mesh, hydrogen form.

3.3 Commercially available cation exchange solid-phase extraction cartridges for use on the end of a syringe, or an extraction manifold may also be used. The capacity of the resin must be consistent with the expected amount of sodium and other cations to be removed.

4. Reagents

4.1 ASTM Type I water [American Society for Testing and Materials (ASTM) D1193].

4.2 Hydrochloric acid, concentrated - trace metals grade.

4.3 Nitric acid, concentrated - trace metals grade.

4.4 10 N NaOH solution.

5. Sample Pretreatment

5.1 It is assumed that the sample is in a liquid state and that all the extractable selenium is in the aqueous solution. All preparatory methods i.e., SW846 Methods 7060 and 3050, paste extract, etc., should have been carried out prior to this extraction.

5.2 For samples with pH > 7, check for carbonates by adding 1 drop of concentrated nitric acid to the sample. If the sample effervesces, then continue to add nitric acid dropwise till there is no more effervescence.

5.3 Adjust the pH of the sample to > 7 using 10 N NaOH. Keep the pH as close to 7 as possible to avoid excess Na in the sample.

6. Cation Exchange

6.1 Place a glass wool plug at the outlet end of the glass column and put a stopcock on the outlet end.

6.2 Mix resin with Type I water. Add this mix to the column until the volume of resin is approximately 15 mL after settling.

6.3 Open the stopcock and rinse the column twice with approximately 15 mL of Type I water.

6.4 Allow the column to drain completely.

6.5 Place a 25-mL volumetric flask under the column.

6.6 Add 10 mL of sample to the column and allow to drain completely.

6.7 Rinse the column with 5 mL portions of Type I water, allowing the column to drain completely between additions. Continue till 25 mL of extract has been collected in the volumetric flask. The extract is now ready for analyses for Se by GFAA.

7. Resin Regeneration

7.1 Rinse the column with 50 mL HCl:Type 1 water (1:1).

7.2 Rinse the column with 50 mL Type I water. The column is now ready for the next extraction.

7.3 Mild positive pressure may be applied to the column to increase flow rate through the column.

8. Calculation

This cleanup procedure involves a 2.5 dilution of the original sample, so all subsequent results need to be multiplied by 2.5.

9. Quality Control

9.1 A lab control sample such as NIST 1633a SRM must be extracted at a 10% frequency.

9.2 Duplicate samples must be analyzed at a 10% frequency.

8. Reference

Hill, R.A., 1983, A Cleanup Technique for Samples Containing High-Level Interferences Prior to Ion Chromatographic Analysis. J. High Resolution Chromatogr. Comm. 6, May: 275-277.

WESTERN RESEARCH INSTITUTE
ANALYTICAL METHOD

Method Title: Ultrasonic Extraction for the Determination of Selenium and Arsenic Anion Species by Ion Chromatography.

1. Summary of Method

Few procedures are available for the extraction of selenium and arsenic species from solid materials while preserving their original chemical oxidation states. This method describes procedures for extracting inorganic selenium and arsenic species from solid materials in preparation for analysis by ion chromatography. Two different extraction solvents are used depending on the species to be determined. For the determination of selenite, selenate, and arsenate, the extraction is performed with 0.5 M sodium hydroxide. Arsenite is not extracted at this pH, so 1 M HCl is used for the extraction of arsenite.

2. Sample Handling and Preparation

2.1 Containers and Preservation

Samples may be collected in pre-cleaned glass or polyethylene bottles. A minimum sample size of 100 g is required.

Samples should be stored at 4°C prior to extraction.

2.2 Sample Preparation

The sample should be mixed thoroughly, and ground with a mortar and pestle to a fine powder.

3. Recommended Equipment

3.1 50-mL polypropylene centrifuge tubes with caps

3.2 Ultrasonic water bath

3.3 Centrifuge

3.4 Polypropylene sample containers for leachates

4. Reagents

4.1 Type I water [American Society for Testing and Materials (ASTM) D1193].

4.2 Extraction fluid for selenite, selenate, and arsenate: Sodium hydroxide, 0.5 M. Dissolve 20 g sodium hydroxide in Type I water and dilute to 1 L.

4.3 Extraction fluid for arsenite: Hydrochloric acid, 1 M. Add 85 mL concentrated trace metals grade HCl to Type I water and dilute to 1 L.

5. Extraction Procedure

5.1 Place approximately 10 g of air-dried and homogenized sample in a centrifuge tube, record the weight of sample added to the nearest mg, and add 4 mL Type I water.

5.2 Add 4 mL of the extraction fluid being used, cap tube, and place in ultrasonic bath for six hours. Be sure to record exact volume of extraction fluid and water added to centrifuge tube.

5.3 Remove centrifuge tube from ultrasonic bath and centrifuge at 10,000 rpm for 10 minutes.

5.4 Decant supernatant into polypropylene bottle. Add 2 mL of extraction fluid to centrifuge tube and centrifuge again at 10,000 rpm for 10 minutes. Decant supernatant into bottle. Repeat rinse procedure two more times.

5.5 Analyze leachate for the anions of interest by ion chromatography.

6. Calculation

6.1 The concentration of the anion of interest in the original solid is calculated as follows:

$$C = 1000\ L \times V / M$$

Where C = concentration of anion in the solid, mg/kg
L = concentration of anion in the leachate, mg/L
V = volume of leach solution added to the solid, L
M = mass of solid extracted, g

7. Quality Control

7.1 A lab control sample such as NIST 1633a SRM must be extracted at a 10% frequency.

7.2 Duplicate samples must be analyzed at a 10% frequency.

WESTERN RESEARCH INSTITUTE
ANALYTICAL METHOD

Method Title: Determination of Selenium and Arsenic Anion Species by Ion Chromatography

1. Scope and Application

1.1 Two methods are described for the determination of the following anions in water and extracts of solid materials.

Method A.

Bromide
Chloride
Nitrate-N
Nitrite-N
Ortho-Phosphate-P
Selenate-Se
Selenite-Se
Sulfate

Method B.

Arsenate-As
Arsenite-As
Sulfate

1.2 The Method Detection Limit (MDL) for the anions determined by Method A and Method B are listed in Tables 1 and 2, respectively. The MDL for certain samples may differ depending on the sample matrix.

2. Method Description

A 1-2 mL volume of sample is injected into an ion chromatograph with a loop injector. The anions of interest are separated by ion exchange mechanisms. The column effluent is directed to a suppressor, which chemically lowers the conductivity of the eluant, allowing for sensitive detection of the anions of interest. Method A uses a conductivity detector. Method B uses an electrochemical detector between the analytical column and the suppressor for the detection of arsenite, prior to conductivity detection of the other anions of interest. The composition of the eluant is different for the two methods.

3. Interferences

3.1 Interferences may be caused by anions having retention times that are similar to the anions of interest. Many interference problems can be addressed through sample dilution or spiking.

3.2 The negative peak that appears at the column void volume early in the analysis can be minimized by adding 1 mL of 100x concentrated eluant to 100 mL of each standard and sample.

3.3 Samples containing particulate matter should be filtered prior to analysis to prevent damage to instrument columns and hydraulic systems.

4. Recommended Equipment

4.1 Ion chromatograph - A Dionex Ion Chromatograph system equipped with the following components:

Eluant reservoirs pressurized under a helium atmosphere to prevent eluant outgassing and subsequent bubbles in the detector cell.

Eluant pump with non-metallic parts, capable of pumping eluant at 1-5 mL/minute at pressures up to 2000 psig.

Conductivity detector equipped with a low-volume, flow-through, temperature-compensated cell, and an operating range of 0.001 to 1000 uS full scale.

Electrochemical detector equipped with a platinum working electrode and silver/silver chloride reference electrode. The detector should have an applied potential range of -9.99 V to +9.99 V, and an output range of 1 nA/V to 300 μA/V. The cell should be operable at pressures up to 300 psig.

Sample injection valve with low dead volume that will accommodate sample loops with volumes of 10 μL or greater.

Recorder or data system compatible with the detector output and capable of digital data acquisition at frequencies of 5 s^{-1} or higher. Dionex AI-400 Data Chromatography Software (Version 1.22) was used in this study.

4.2 Anion columns - Methods A and B both use a Dionex AG5 guard column (P/N 35396) and a Dionex AS4A analytical column (P/N 37041).

4.3 Suppressor system - Methods A and B both utilize a Dionex Anion Micromembrane Suppressor (P/N 37106).

5. Reagents and Materials

5.1 Type I water [American Society for Testing and Materials (ASTM) D1193]: water should have a specific resistance of at least 17.8 megohm-cm.

5.2 Eluant solution (Method A): Sodium carbonate, 2.0 mM, sodium hydroxide, 1.0 mM. Dissolve 0.2120 g sodium carbonate and 0.040 g sodium hydroxide in Type I water, and dilute to 1 liter.

5.3 Eluant solution (Method B): Sodium carbonate, 2.0 mM, sodium bicarbonate, 1.5 mM. Dissolve 0.2120 g sodium carbonate and 0.1260 g sodium bicarbonate in Type I water, and dilute to 1 liter.

5.4 Suppressor regenerant solution: 0.025 N sulfuric acid: dilute 1.4 mL concentrated sulfuric acid to 1 liter with Type I water.

5.5 Stock solutions, 1000 mg/L: Stock solutions used for calibration standards are prepared as specified below.

Arsenate ($HAsO_4^{2-}$-As) 1000 mg/L: Dissolve 0.4160 g sodium arsenate dibasic heptahydrate in Type I water and dilute to 100 mL.

Arsenite (AsO_2^--As) 1000 mg/L: Dissolve 0.1734 g sodium arsenite and dilute to 100 mL with 0.1M HCl.

Bromide (Br^-) 1000 mg/L: Dissolve 0.1288 g sodium bromide in Type I water and dilute to 100 mL.

Chloride (Cl^-) 1000 mg/L: Dissolve 0.1648 g sodium chloride in Type I water and dilute to 100 mL.

Nitrate-N (NO_3^--N) 1000 mg/L: Dissolve 0.6068 g sodium nitrate in Type I water and dilute to 100 mL.

Nitrite-N (NO_2^--N) 1000 mg/L: Dissolve 0.4926 g sodium nitrite in Type I water and dilute to 100 mL.

Phosphate (HPO_4^{2-}-P) 1000 mg/L: Dissolve 0.4394 g potassium phosphate, monobasic in Type I water and dilute to 100 mL.

Selenate (SeO_4^{2-}-Se) 1000 mg/L: Dissolve 0.2393 g sodium selenate in Type I water and dilute to 100 mL.

Selenite (SeO_3^{2-}-Se) 1000 mg/L: Dissolve 0.2190 g sodium selenite in Type I water and dilute to 100 mL.

Sulfate (SO_4^{2-}) 1000 mg/L: Dissolve 0.1814 g potassium sulfate in Type I water and dilute to 100 mL.

Stock standards are stable for at least one month when stored at 4° C. Working calibration standards should be prepared weekly. Standards containing arsenite, nitrite, selenite, and phosphate should be prepared daily.

6. Calibration

6.1 The ion chromatograph should be set up according to the manufacturer's instructions. The operating parameters for Methods A and B are listed in Tables 1 and 2 respectively. Method B uses both conductivity and electrochemical detection. The electrochemical detector should be plumbed into the system between the analytical column and the suppressor.

6.2 Prepare calibration standards at a minimum of three concentration levels and a blank for each anion of interest. Determine the retention times for each anion by injecting a calibration standard and recording the time when the peak elutes from the column. Retention times may vary slightly from day to day, so calibration check standards should be run at the beginning of each day.

6.3 Establish a calibration line by injecting a series of calibration standards. Tabulate peak area against the concentration of the calibration standard. Linear regression analysis is used to establish the slope, intercept, and correlation coefficient for each anion.

6.4 The calibration line must be verified at the beginning of every day, and whenever new eluant is prepared, and after every 20 samples. If the peak response or retention time for any anion varies by more than 10%, a new calibration standard should be run. If the response is still off, the system must be recalibrated for that anion.

7. Quality Control

7.1 A minimum of 10% of all samples should be spiked to monitor method performance. Field and laboratory duplicates should also be analyzed.

7.2 Before analyzing any samples, an aliquot of Type I water used in the preparation of calibration standards and sample dilutions should be injected to make sure no reagent interferences are present.

7.3 A laboratory control standard should be analyzed daily to confirm that calibration standards have been prepared correctly.

7.4 Samples must be diluted if the response is greater than the highest point on the calibration line.

8. Procedure

8.1 The recommended operating conditions for methods A and B are summarized in Tables 1 and 2 respectively.

8.2 Load a sample into the injection loop of the chromatograph using a syringe or autosampler. The same size injection loop should be used for standards and samples. Inject the sample onto the column and record the peak area of each analyte of interest. If the peak area exceeds the linear calibration range, dilute the sample with Type I water and repeat the analysis.

8.3 The width of the retention time window is generally three times the standard deviation of the retention time measured over a length of time. Experience is required for chromatographic peak identification. For example, peak retention time migration may occur when concentrations of analytes increase. Nitrate and sulfate are most affected, but all anions are affected to some degree. If the identification of anions is not clear, the samples should be spiked with a standard solution and reanalyzed.

8.4 Report results for aqueous samples in mg/L. For extracts from solid samples, the results should be reported in mg/kg of dried or as-received sample.

9. Reference

EPA Method 300.0, 1989, The Determination of Inorganic Anions in Water by Ion Chromatography, Methods for Chemical Analysis of Water and Wastes. U.S. EPA Environmental Monitoring and Support Laboratory, Cincinnati, OH.

Table 1. Chromatographic Conditions and Detection Limits - Method A

Chromatographic Conditions:

Eluant	2.0 mM sodium carbonate/1.0 mM sodium hydroxide
Flow Rate	2.0 mL/minute
Columns	Dionex HPIC AG5 and HPIC AS4A
Injection Volume	50 µL
Detector	Conductivity, 1 µSFS

Detection Limits in Type I Water:

Analyte	Retention Time (min)	MDL (mg/L)
Chloride	1.6	0.01
Nitrite-N	2.0	0.004
Bromide	3.1	0.01
Nitrate-N	3.3	0.002
Selenite-Se	4.7	0.01
Sulfate	6.8	0.01
Selenate-Se	8.7	0.01
O-Phosphate-P	13.1	0.003

Table 2. Chromatographic Conditions and Detection Limits - Method B

Chromatographic Conditions:

Eluant	2.0 mM sodium carbonate/1.5 mM sodium bicarbonate
Flow Rate	1.0 mL/minute
Columns	Dionex HPIC AG5 and HPIC AS4A
Injection Volume	50 µL
Detectors	Conductivity, 1 µSFS Electrochemical detection with platinum working electrode, 0.50V applied potential, 10 µAFS

Detection Limits in Type I Water:

Analyte	Retention Time (min)	MDL (mg/L)
Arsenite-As	1.6	0.002
Arsenate-As	20.1	0.10

END

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