Microwave Dissolution of Lake Sediments and Mine Tailings and Determination of Arsenic and Selenium by Atomic Absorption Spectrometry

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MICROWAVE DISSOLUTION OF LAKE SEDIMENTS AND MINE TAILINGS AND DETERMINATION OF ARSENIC AND SELENIUM BY ATOMIC ABSORPTION SPECTROMETRY

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A close-vessel microwave dissolution method for the determination of arsenic and selenium in lake sediments and mine tailings is compared with a conventional hot plate digestion technique. The utilization of a mixture of $HCl-HNO_3-HF$ allowed the best recovery of As (105% and 100%) and Se (109%) present in certified reference materials analysed by Hydride Generation Atomic Absorption Spectrometry when the hot plate technique only led to poor recovery of both elements. Relationships between the total concentration of arsenic and total iron and between the total concentration of selenium and total sulfur have been observed in surficial lake sediments and mine tailings.

KEY WORDS: Microwave, arsenic, selenium, lake sediments, mine tailings, AAS.

INTRODUCTION

Dissolution techniques of geological samples such as rocks, soils and sediments usually involve different mixtures of acids. In open systems, the risk of contamination and/or loss of volatile elements is high and digestion procedures are generally time-consuming. This is the reason why microwave digestion procedures in closed Teflon containers have gained interest in the recent years owing to rapid sample dissolution and reduced contamination risks. Closed vessels provide the elevated pressures and temperatures necessary for rapid decomposition of samples[1]. Microwave digestion techniques have been used for a wide variety of environmental samples such as ore and smelter sample[2,3], soils[4-6], sediments and sludges[6-9] and biological samples[9,10].

Arsenic and selenium can enter the aquatic environment via natural processes such as rock and soil weathering and geothermal activity. They are also introduced as by-products of industrial activity such as mining and metal refining processes, the use of herbicides and pesticides and the burning of fossil fuels. The geochemical behaviour of both elements can be strongly influenced by changes in environmental conditions: pH, redox potential, the presence of reactive minerals (oxides and sulfides), and the action of microbial organisms[11]. An important aspect of arsenic and selenium chemistry is the

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existence of many oxidation states in aquatic systems. It has been shown that the toxicity of both elements is strongly related to the oxidation state and in the case of selenium, to the presence of other trace elements namely Hg, Cd, and Co. The environmental importance of both elements justifies the development of very accurate determination procedures.

In this paper, a conventional hot plate digestion technique is compared to close-vessel microwave methods for the determination of arsenic and selenium in lake sediments and mine tailings by Hydride Generation coupled to Atomic Absorption Spectrometry and by Graphite Furnace Atomic Absorption Spectrometry. Information on the geochemistry of both elements in lake sediments and mine tailings is also presented.

METHODOLOGY

Sampling

Surface sediment samples were collected from four lakes located in the Sudbury area using a sediment grab. Trace element loadings in these lakes are mainly due to the mining activities in the region. Tailing samples were collected with a plastic spatula from three different mines located in Northern Ontario, Inco and Flaconbridge located in the Sudbury region and Rio Algom located at Elliot Lake, Ontario.

Digestion equipment

A hot plate digestion technique developed by Inco Mine laboratory for multi-element analysis of biological and solid samples was used for comparison. Digestion was performed in 50 mL Teflon beakers covered with watch glasses and heated on hot plates. A CEM microwave digestion system (Model MDS-2000) was modified to allow both the pressure and time to be monitored during digestion. A 120 mL Teflon PFA digestion vessel (Savillex) equipped with a safety pressure-relief disk was used. This type of vessel can hold a maximum pressure of 8 kPa, our samples were microwaved at a pressure of 4.5 kPa to avoid the loss of any volatile compounds of As and Se. All sample preparation were carried out in a clean laboratory, equipped with laminar flow bench and fume hood.

Procedure

Hot plate (Procedure A):   A 0.5000 g portion of dried solid was mixed with 15 mL of HNO_3 in the Teflon beaker, boiled on hot plate until all nitric acid had boiled off. After cooling, 15 mL of HCl and 2 mL of HF were added and the sample was evaporated to dryness. Another 4 mL of HCl and 10 mL of double distilled water were added and the sample was heated until 2–3 mL of solution remained. The sample was removed from the heat, cooled and filtrated through a 0.45 μm cellulose nitrate membrane and stored in cleaned polypropylene bottles prior to analysis.

Nitric/hydrochloric acids (Procedure B): A 0.2250 g portion of dried solid was mixed in the Teflon digestion vessel with 10 mL (4:1) of the HNO_3/HCl mixture. The content of the vessel was rapidly heated at maximum power until the internal pressure reached

4.5 kPa. This pressure was maintained for 14 minutes. The vessel was cooled down in either an ice bath or liquid nitrogen and the content was filtered on a 0.45 μm cellulose nitrate filtration membrane and stored in cleaned polypropylene bottles prior to analysis.

Nitric/hydrochloric/hydrofluoric acids (Procedure C): This procedure is similar to procedure B with the acid mixture of $HNO_3/HCl/HF$ (4:1:0.5).

Analysis

The determination of total arsenic and selenium from the acid digestions were carried out on two different devices:

1. A Zeeman Graphite Furnace (HGA 500) Atomic Absorption Spectrometer (GFAAS) Perkin-Elmer (Model 5000); a 20 μL aliquot of the sample and the same volume of a 10% $Ni(NO_3)_2$ solution used as matrix modifier[12] were introduced into the pyrolytic graphite-coated tube (without platform) of the furnace, the sample was dried at 140°C for 40 sec., ashed at 1500°C (As)–1000°C (Se) for 30 sec. and atomized at 2500°C (As)–2300°C (Se) for 7 sec. A cleaning step of 5 sec. at 2700°C was added at the end and measurements were performed using the peak height mode.

2. A Hydride Generation System (HGS) Perkin-Elmer (Model MHS-10) coupled to an Atomic Absorption Spectrometer (AAS) Perkin-Elmer (Model 5000); variable volumes of the samples were diluted in 1M HCl, a 10% (w/v) KI solution was used as pre-reductant reagent and a 1.5% $NaBH_4$ in 0.1 M NaOH solution to generate the hydride. Electrodeless discharge lamps were used as sources and the concentration was determined from peak height measurements on a strip chart. Total concentration of iron and sulfur were obtained by x-ray fluorescence spectrometry (Philips 1404) using the powder pellet and glass disc preparation methods[13].

RESULTS

The precision and the accuracy of the three digestion methods were determined by analysing two certified reference materials (CRM) from the National Research Council of Canada (NRCC): BCSS-1 and PACS-1. The standards were prepared and digested using the same acid combination and digestion technique as the samples and they were analysed using both analytical methods GFAAS and HGAAS.

There is a significant difference between values obtained by GFAAS and those obtained by HGAAS, GFAAS values being systematically lower than the others (Table 1). Some interferences commonly related to the graphite furnace technique can lead to lower signals and the loss of volatile compounds of As and Se during the ashing step is not excluded. Nevertheless, the concentrations of As and Se measured by GFAAS fall within the 95% confidence lower limit of the certified materials (Note 1 in Table 1).

It appears clearly that the hot plate method (Proc. A) is not appropriate for the determination of As and Se since the recoveries by HGAAS are poor for As (57 & 74% for BCSS-1 and PACS-1 respectively) and most of the Se is lost during the digestion. Procedure B does not permit to extract all As and Se present in the certified material but

Table 1 Total concentration of arsenic and selenium (μg/g) in certified reference materials (CRM) BCSS-1 and PACS-1.

CRM		Cert.Value[1]	GFAAS			HGAAS		
			A	B	C	A	B	C[2]
BCSS-1	As	11.1	4.8	7.2	9.9	6.3	9.0	11.7
			(4.0)	(0.5)	(1.8)	(3.0)	(1.3)	(2.0)[3]
	Se	0.43	ND[4]	0.23	0.41	ND	0.30	0.47
			–	(0.1)	(2.0)	–	(2.3)	(1.1)
PACS-1	As	211.0	148.7	182.9	201.4	156.7	193.8	211.9
			(2.0)	(3.0)	(1.2)	(2.0)	(1.2)	(0.8)
	Se	1.09	ND	0.59	0.99	ND	0.80	1.19
			–	(1.0)	(0.5)	–	(0.9)	(2.0)

[1] Certified values for BCSS-1 As: 11.1 ± 1.4; Se: 0.43 ± 0.06, for PACS-1 As: 211 ± 11; Se: 1.09 ± 0.11
[2] Procedure A: Hot Plate; Procedure B: Microwave with HNO_3/HCl; Procedure C: Microwave with $HNO_3/HCl/HF$
[3] Numbers in parentheses represent the coefficient of variation (%) N=6
[4] ND: not detectable

the addition of a small volume of hydrofluoric acid in Procedure C destroys the remaining crystalline matrix and leads to the total recovery of both As (105% and 100%) and Se (109%) present in the certified reference materials analysed by HGAAS. This particular technique eliminates most of the interferences coming from the acid matrix since only the generated hydride are transported into the flame.

The three digestion procedures were also used on sediment and tailing samples and the results for the HGAAS technique presented in Table 2 indicate that Procedure C is the most effective to extract As and Se from those samples. The results obtained with the GFAAS (not shown) gave slightly lower values than the HGAAS technique as it has already been mentioned for the CRM analysis. The hot plate procedure has led to significant losses of both elements leaving Se not detectable in low concentration tailing samples.

Arsenic and selenium inputs to the Sudbury area lakes originate mainly from atmospheric transport of these two elements emitted during smelting operations. The very high concentrations of both As and Se in Kelly Lake can also be related to the discharge of slags and tailing in this lake for many years. No correlation is observed between the total concentration of arsenic and selenium present in lake sediment and the pH of the lake but both element concentrations appear to be directly related to the proximity of the INCO smelter (Table 3). A correlation is observed between the total concentration of arsenic and that of iron (Table 3); the important role of iron oxyhydroxides on the distribution of arsenic in surficial lake sediments[14] can explain this correlation.

A similar relationship seems to exist between the total concentration of selenium and that of iron but a more clear trend can be observed between Se concentration and total sulfur (Table 3). This trend is expected since Se and S belong to the same group in the periodic table, have similar characteristics in the environment and since both elements are often associated in metal deposits[15] and can be released during the ore treatment. Similar trends were observed in mine tailing samples from the different locations.

Table 2 Total concentration of arsenic and selenium (μg/g) in lake sediments and mine tailings determined by HGAAS.

Sample location	As			Se		
	A	B	C	A	B	C[1]
Silver lake	98.2	118.3	131.6	5.0	7.7	10.5
	(1.7)	(3.3)	(2.0)	(3.2)	(0.6)	(2.0)[2]
St. Charles lake	108.5	122.1	141.8	5.4	8.0	9.6
	(3.2)	(1.3)	(2.0)	(1.9)	(2.4)	(0.5)
Tilton lake	19.6	23.7	30.4	1.8	3.0	4.4
	(2.4)	(3.0)	(1.4)	(1.4)	(3.1)	(0.8)
Kelly lake	195.7	248.4	263.5	86.3	143.6	161.1
	(1.5)	(0.8)	(0.6)	(3.0)	(2.0)	(4.5)
INCO tailing	3.8	6.2	8.5	7.0	10.1	12.5
	(3.4)	(2.2)	(1.2)	(1.7)	(2.4)	(0.8)
Falconbridge tailing	3.4	6.1	7.5	0.2	2.4	3.1
	(1.1)	(1.9)	(2.0)	(4.3)	(0.6)	(2.3)
Elliot lake tailing	6.4	8.3	14.1	ND[3]	0.9	1.7
	(2.4)	(2.0)	(1.9)	–	(2.3)	(0.5)

[1] Procedure A: Hot Plate; Procedure B: Microwave with HNO_3/HCl; Procedure C: Microwave with $HNO_3/HCl/HF$
[2] Numbers in parentheses represent the coefficient of variation (%) N=6
[3] ND: not detectable

Table 3 A comparison of lake pH and the total concentrations of As, Se, Fe, and S in the four studied lakes.

Sample location	Lake pH	As (μg/g)	Fe (%)	Se (μg/g)	S (%)
Silver lake (6.5)[1]	4.0	131.6	4.3	10.5	3.7
Tilton lake (13.7)	5.9	30.4	2.5	4.4	0.6
St. Charles lake (4.8)	6.9	141.8	5.0	9.6	2.1
Kelly lake (2.5)	7.5	263.5	8.6	161.1	9.3

[1] Numbers in parentheses represent the distance (km) from the INCO smelter.

CONCLUSION

The close-vessel microwave digestion procedure and the use of a HNO_3-HCl-HF combination have proven to bring arsenic and selenium quantitatively in solution and are, therefore suitable for the determination of these elements in lake sediments and mine tailings. The accuracy of the digestion procedure has been verified by the use of NRCC certified reference materials BCSS-1 and PACS-1. The hydride generation method showed better levels of accuracy than the graphite furnace method. The determination of total arsenic and selenium in lake sediments and mine tailings of the Sudbury area have permitted to identify correlations between the total concentrations of arsenic and iron and between the total concentrations of selenium and sulfur emphasizing then the close chemistries of these elements.

Acknowledgements

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