X-RAY SPECTROMETRIC DETERMINATIONS OF ARSENIC SORBED ONTO CELLULOSE AFTER SOLVENT EXTRACTION FROM FUSED SILICATE ROCKS

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UNITS AND ABBREVIATIONS

The metric system of units is used in this report. The abbreviations used are as follows:

µg (microgram)
mg (milligram)
g (gram)
ml (milliliter)
l (liter)
kV (kilovolts)
mA (milliamperes)
keV (kilo electron volts)
M (Molar, moles per liter)
mg/l (milligrams per liter)
ppm (parts per million)
cts/sec (counts per second)

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ABSTRACT

The determination of arsenic in silicate rocks is achieved by X-ray fluorescence spectrometry after the arsenic is sorbed onto cellulose and the cellulose briquetted into a sample specimen. The rocks are first decomposed by fusion with sodium hydroxide and then acidified with sulfuric acid. In order to remove any lead which will interfere with the As determination (Pb Lα peak on the As Kα peak), following reduction of any As(V) present to As(III) with ascorbic acid, NaI is added to form the arseno-iodide complex which is extracted with toluene. The extract is deposited on cellulose and the toluene is evaporated prior to final specimen preparation. The relative precision is from 0.7 to 5.7 percent for the range of 0.06 to 2.37 percent As in the rock. The detection limit is 15 ppm in 250 mg of rock. Results for As found in international rock standards and a series of jasperoid rocks are compared to previously reported values and to values obtained by inductively-coupled plasma emission spectrometry.

INTRODUCTION

Aside from classical and colormetric methods for determining arsenic in geologic samples (Hillebrand and others, 1953; Rader and Grimaldi, 1960; and Stauffer, 1980), instrumental methods developed recently were reviewed by Brooks and others (1981). These include atomic spectrometry (absorption, emission, and fluorescence), neutron activation-gamma-ray spectrometry, and X-ray spectrometry (X-ray fluorescence and proton-induced X-ray emission). More recent instrumental methodologies for arsenic were developed in U.S. Geological Survey laboratories (Hubert, 1983; Crock and Lichte, 1982; Crock and others, 1983; and Ehrlick and Horowitz, 1985).

Atomic spectrometric and neutron activation techniques have limited working ranges at low concentrations and require diluted sample specimens to determine higher concentrations. The advantage of X-ray fluorescence spectrometry (XRFS) being applicable to a wide range of analyte concentration prompted this investigation of XRFS for determining trace-to-minor concentrations of arsenic in geologic samples.

Lead is commonly present in rock bodies containing arsenic and will interfere with the analysis. The interference of Pb ($L\alpha$ line) with arsenic ($K\alpha$ line) is cited as an example of spectral line interference in XRFS (Bertin, 1975). By use of accurate deconvolution and matrix-correction computer programs (O'Reilly and King, in press), quantitation of both the As and Pb components of the X-ray spectral overlap is possible down to about the 10-ppm level or less in geological samples. Alternatively, without these physical-mathematical calculations, estimation of As concentration could be accomplished with XRFS after chemical separation of Pb from As.

Fabbi and Espos (1972) determined As in rocks using XRFS without mention of correcting for the potential Pb interference. Zsolnay and others (1984) and Lichtfuss and Bruemmer (1983) analyzed soils and sediments. In these latter two studies, the arsenic was simply corrected for lead by measuring lead at the $L\beta$ line, and the lead $L\alpha$ intensity was calculated and subtracted from the arsenic $K\alpha$ peak. Hubert (1984) separated As from Pb by digesting the sample with nitric-sulfuric acid and reducing the As(V) with ammonium thiosulfate and hydrochloric acid before extracting the As(III)-chloro complex into benzene. The extract was then transferred to a filter paper disk, and the solvent was evaporated prior to irradiation of the disk. Arsenic-spiked samples were carried through the digestion and extraction in order to compensate for losses of arsenic.

A solvent extraction procedure used for coal (Aruscavage, 1977) based on the partitioning of arsenic iodide into toluene (Byrne and Gorenc, 1972) provides separation of arsenic from lead after fusion of the sample with NaOH used as a powerful alkaline flux (W. D'Angelo, oral communication). Deposition of liquid solution on cellulose yields a material which can be briquetted and taken to analysis by XRFS (Rose and others, 1965). A combination of these two procedures isolates As into a "clean" matrix apart from lead and other unextracted elements. This permits use of synthetically-prepared calibration standards which can be used repeatedly.

EXPERIMENTAL PROCEDURE

Arsenic standard, 1000 mg/l. Dissolve 0.2461 g As_2O_3 (99.99 percent pure) in 10 ml of 20 percent (w/v) KOH solution. Neutralize with 20 percent (v/v) H_2SO_4 to the phenolphthalein endpoint. Dilute to 200.0 ml with 1 percent H_2SO_4 (Perkin-Elmer Corporation, 1982).

Lead standard, 1000 mg/l. Dissolve 0.2154 g PbO in 2 ml concentrated HNO_3 and dilute with H_2O to 200.0 ml.

Working standards. Prepare As working standard solutions by appropriately diluting the arsenic standard with 1 percent H_2SO_4 to give end concentrations of 25, 50, 100, 150, and 200 mg/l. Pipet 2.00 ml of a standard solution into a 10-ml teflon beaker containing 1.000 g of chromatographic cellulose (Whatman CF11). Add one drop of a 0.05 percent methylorange indicator solution and mix the moistened mass with a small glass stir rod until there is a uniform pink color. Leave the stir rod in the beaker and place beaker on a steam bath or a hot plate at 80°C overnight in order to dry the cellulose.

Mix the dried cellulose with the stir rod until the mixture appears to be homogeneous. Quantitatively transfer the cellulose to a boron carbide mortar and continue to grind and mix for five minutes. Transfer the solid to the pelletizing die lined with a glass disk (Fabbi, 1972) and press the cellulose with a 72 percent cellulose acetate-28 percent paraffin wax backing at 25,000 psi for one minute.

Working Pb standards of 5, 10, 25, 50, and 100 mg/l were prepared so that pure Pb specimens could be prepared for testing instrumental sensitivity to Pb using measurement conditions for As.

Sample preparation. Accurately weigh a 250-mg portion of sample (<200 mesh) and transfer to a zirconium crucible (30-50 ml capacity). Add 20 pellets of NaOH, cover, and fuse sample over a Meker burner with an oxidizing flame. Cool crucible on a hotplate heated to 80°C.

Add 25 ml water to the cooled melt. Stir slurry with a small stir rod and transfer slurry to a 250-ml separatory funnel. Rinse crucible and cover with two 25-ml portions of 1:1 sulfuric acid and transfer rinsings to the separatory funnel.

Add 7.5 ml 20 percent ascorbic acid to the funnel and mix. Then add 7.5 ml 6 M NaI to the funnel and mix. Allow contents in the separatory funnel to stand for 10 to 15 minutes.

Extract the arseno-iodide complex by adding 25 ml toluene to the funnel and shaking the contents for two minutes. Allow up to one hour for the phases to separate and draw off and discard the aqueous (bottom) phase. Collect the organic phase and immediately pipet 20.00 ml of the extract into a 25-ml teflon beaker containing 1.000 g chromatographic cellulose. Stir slurry with a small glass stir rod and place beaker with stir rod on a steam bath or a hotplate at 80°C.

Allow the toluene to completely evaporate. Remove the teflon beaker from the hotplate and break up and thoroughly stir the dry cellulose, containing the arsenic, with the small stir rod.

Quantitatively transfer the cellulose to a boron carbide mortar and grind and mix for five minutes.

Transfer the cellulose to the pelletizing die and prepare a sample briquet in a like manner described for the working standards.

Recovery specimens. Artificial recovery samples were prepared by diluting randomly varying amounts of the As and Pb standards together in 3 M NaOH to give solutions of various final concentrations. In a like manner as the sample preparation, the basic solutions were then acidified with 1:1 sulfuric acid, the arsenic extracted and sorbed onto chromatographic cellulose, and the cellulose briquetted.

X-ray fluorescence spectrometric analysis. A Kevex 0700/7000 energy-dispersive X-ray fluorescence (EDXRF) spectrometer was used to measure the intensity of the As $K\alpha$ X-ray line. All samples were counted for 200 seconds. A molybdenum secondary target was used with typical excitation conditions of 33 kV and 0.7 mA. The energy regions of interest are 10.36 to 10.74 keV for the As $K\alpha$ line and 16.20 to 17.08 keV for the molybdenum Compton scatter region. The ratio of the As intensity to the intensity of the Compton scatter in the given energy regions is used to quantify As concentrations in the pressed pellets.

RESULTS AND DISCUSSION

With the spectrometer at the As Kα energy region, As intensity increases linearly with As concentration for the pure element calibration disks ranging from from 0 to 400 ppm As with a sensitivity factor of 0.16 (cts/sec per µg). At the As Kα region, the intensity of Pb increases linearly with Pb concentration (0 to 200 ppm Pb) with a sensitivity factor of 0.085. At the As Kβ energy region (11.54-11.88 keV), where there is no Pb interference, the sensitivity factor for As is only 0.025. The sensitivity factor for Pb in the Pb Lβ region (12.44-12.82 keV) is 0.083.

With the laboratory-prepared recovery samples, international rock standards, and jasperoid specimens, lead was not detected in the Pb Lβ region.

The ratio of the intensity of the As Kα region to the intensity of the Compton scatter region of the molybdenum secondary target increases linearly with As concentration. This method is more suitable than raw intensities for calibration because it is not readily influenced by absorption-enhancement effects, effects due to particle size and surface texture, packing density variations, and instrument errors (Bertin, 1975).

Initially, the amount of sample used in the analyses of jasperoid rocks in this study was 50 mg, and the amount of toluene extract deposited on the cellulose was only 2 ml with the limit of detection being equivalent to 150 ppm in the original samples. Since the amounts of arsenic measured in the final specimens were in range of the lowest arsenic standard, the sample amount was increased to 250 mg and all reagent amounts increased five-fold. In addition, the amount of toluene extract deposited on the cellulose was increased to a maximum of 20 ml. These two changes would yield a fifty-fold increase in measurable arsenic in the pellet and a limit of detection of 15 ppm in the original sample.

The arsenic recovered in cellulose pellets prepared from 3 M NaOH solutions are shown in Table 1. These results had been corrected for an As blank which was found to be 3.4 µg. Lower recoveries for 80 and 120 µg As sorbed on cellulose could be attributed to inhomogeneous distributions of As in the pellets despite grinding and mixing of the cellulose prior to briquetting. The results for the mixed As and Pb solutions suggest that the Pb is not carried over in the extraction. Pb was not detected in the pellets prepared from the As + Pb solutions when analyzed at the Pb Lβ line.

Table 2 lists the results obtained by taking 250 mg of geologic reference material to analysis. The reported values are from Gladney and Burns (1984) and the U.S. National Bureau of Standards certified values. In addition to possible specimen inhomogeneity errors discussed earlier with the recoveries in Table 1, during the extraction step for rock specimens, the time required for satisfactory phase separation approaches one hour. The presence of small amounts of aqueous solution in the toluene extracts deposited on cellulose would give low recoveries of As.

Table 1. Recoveries of arsenic extracted from 3 M NaOH solutions

Solution As	 Pb	As in Pellet Sorbed	 Found	Recovery Percent
--------μg--------		----------μg--------		
10	0	4	3.2	80
40	0	16	16.7	104
100	0	40	40.5	101
200	0	80	60.3	75
300	0	120	89.3	74
400	0	160	146	91
10	50	4	4.2	105
50	50	20	19.8	99
100	250	40	35.4	89
300	400	120	105	87

Table 2. Arsenic (ppm) in geologic reference standards.

Sample	Found	Mean	Percent RSD*	Reported
GXR-1 jasperoid	410		---	400±50
GXR-3 Fe-Mn deposit	4030 4070	4050	0.7	4200±400
NBS-91 opal glass	2260 2150	2210	3.5	1350

* Relative standard deviation

Presently, there is no reasonable explanation for the conflicting data of the NBS-91. Although Pb is present at a certified value of 900 ppm in the original sample, after the extraction step, no Pb could be detected in the pellet (<40 ppm) at the Pb Lβ region.

Table 3 gives the arsenic concentrations found in a series of jasperoid rocks. The mean concentrations determined by the extraction-XRF method agreed with those determined by the acid digestion-ICP method (Crock and others, 1983) except for Sample 84GJ166C. Sample inhomogeneity at the time of analysis by each of the two methods could result in the 20 percent difference in As levels found for this sample.

Table 3. Arsenic (ppm) in six jasperoids determined by different methods.

Sample No.	Solvent Extraction/XRF			Acid Digestion/ICP
	Replicate	Mean	Percent RSD*	
84GJ159B	2120			
	2190	2160	2.3	2100
84GJ159C	24,300			
	23,100			
	23,900			
	23,300	23,700	2.3	23,000
84GJ163B	930			
	860	895	5.5	920
84GJ166A	1090			
	1060	1080	2.0	1100
84GJ166C	590			
	640	615	5.7	740
84GJ166D	980			
	1000	990	1.4	1000

*Relative standard deviation

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