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The Determination of Arsenic by Flame AAS Using the Zeeman Effect and its Application to the Analysis of Sediment Extracts

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A polarized Zeeman Effect Atomic Absorption Spectrometer has been used for the analysis of arsenic in chemical extracts of sediments using a procedure designed to provide information on the potential availability of trace elements. The limit of determination for arsenic was found to be $0.09 \mu\text{g}/\text{ml}^{-1}$ for standard solutions. The minimal baseline noise associated with the instrument afforded very good stability of the calibration conditions at the $0.50 \mu\text{g}/\text{ml}^{-1}$ concentration level. Accuracy tests performed with standard reference materials showed good agreement for the determinations in the extracts. The analysis of a lake bottom sediment is used to demonstrate the value of this instrumental technique in the determination of arsenic in difficult matrices.

KEY WORDS: Arsenic, Zeeman effect, flame AAS.

INTRODUCTION

In a recent review of instrumental methods for the determination of arsenic, atomic absorption spectrometry was shown to be the most common technique for the analysis of this element.¹ Using the air-acetylene flame, the $3 \mu\text{g}/\text{ml}^{-1}$ detection limit¹ is generally inadequate for most studies. Thus, many workers have elected to use hydride generation for separation of the arsenic to achieve lower detection limits.²⁻⁴ Others have opted for arsenic measurement by electrothermal atomization in a graphite furnace.⁵⁻⁸ The hydride generation method suffers from a number of disadvantages,⁹ the most significant of which, in the context of sediment extract analysis, is the reduction of generation efficiency caused by the often high concentration of concomitant metals in samples. Similarly, although the graphite furnace offers limits of the order of $1 \mu\text{g}/\text{l}^{-1}$, this technique is also prone to severe background and matrix interferences. These problems are not intractable ones and solutions have been found to overcome a variety of interferences. In most cases the increased time required in sample manipulation prior to analysis detracts from the advantages offered by these procedures.

Recently, the value of the Zeeman Effect in reducing background interferences and in enhancing signal-to-noise ratios has been established for atomization using the air-acetylene flame.¹⁰ Because of the simplicity of the flame determination, we have determined the analytical potential of this technique for the analysis of arsenic with special reference to sediment extracts.

EXPERIMENTAL

Spectrometer

The atomic absorption measurements were made on a Hitachi Model 180-80 system, equipped with a water cooled, premix type burner for air-acetylene. The configuration and operation of the Zeeman flame system has previously been described.¹¹ A conventional (Hamamatsu) hollow cathode lamp was used, and was operated at a current of 12 mA. Operating conditions for the AAS measurements were those recommended by the manufacturer.

Sequential extraction procedure

The sediment samples were subjected to the chemical extraction procedure outlined in Figure 1. This scheme is a modification of that developed by Tessier *et al.*¹² Apart from the residual fraction, all extracts were obtained by centrifugation at 20,000 g for 30 min. The supernatants were removed by decantation and made up to a final volume of 25 ml. Chemicals were of reagent grade or better quality.

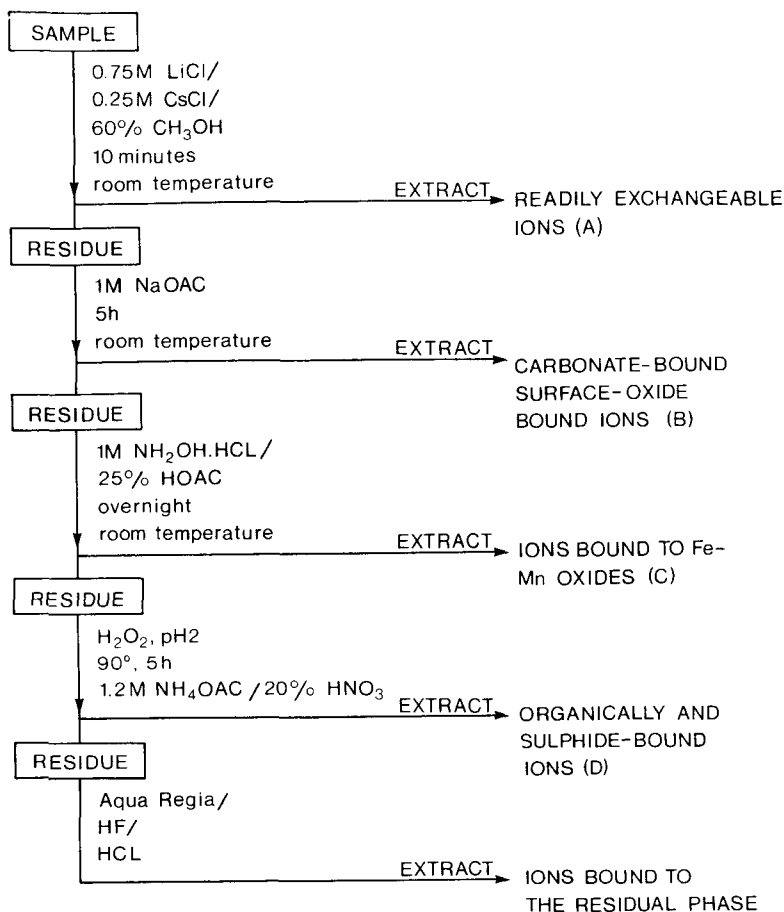


FIGURE 1 Outline of the sequential chemical extraction procedure.

RESULTS AND DISCUSSION

Calibration curves and detection limit

Calibration curves were prepared for the following arsenic concentrations: 0.00, 0.250, 0.500 and 1.00 $\mu\text{g}/\text{ml}^{-1}$ (in 0.2% v/v H_2SO_4). On separate occasions, and with fresh standards, the correlation coefficient for the four points was in the range 0.95–0.96. Typical recorder tracings for a $10\times$ scale expansion (0.02 \AA full scale) using three 10-second integrations are shown in Figure 2. The signals have been stored by the instrument computer during the integration time and the integrated signal subsequently displayed as a pulse. For a standard curve of 0.000, 0.250, 1.00 and 5.00 $\mu\text{g}/\text{ml}^{-1}$, a correlation coefficient of 1.00 was obtained.

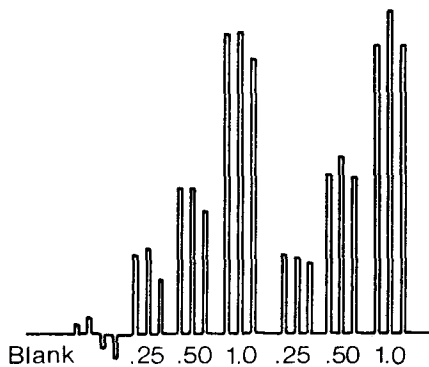


FIGURE 2 Recorder tracings for As calibration curve.

The reagent blank and standards were then run as samples to check on the stability of the calibration conditions which were stored in the instrument's data system. Calibration stability was found to be good (Table I). During this period, the calibration curve was not updated and the 0.250 $\mu\text{g}/\text{ml}^{-1}$ standard was run 21 times in triplicate. The average of the standard deviations of these measurements was 0.090 $\mu\text{g}/\text{ml}^{-1}$ and is here referred to as the limit of determination. The conventional definition of the reciprocal sensitivity of an element, which is used in the calculation of the detection limit, is the concentration which will absorb 1% of the

TABLE I
Calibration stability of the arsenic determination by
Zeeman flame AAS

Standard	Analysis	Standard deviation
Blank	0.042	± 0.006
0.250	0.250	± 0.02
	0.261	± 0.01
	0.245	± 0.003
	0.270	± 0.06
	0.500	± 0.01
0.500	0.547	± 0.01
	0.486	± 0.09
	0.507	± 0.06
0.750	0.770	± 0.014
	0.818	± 0.03
1.00	1.029	± 0.09
	1.040	± 0.02
	0.958	± 0.06
5.00	4.81	± 0.05

incident resonance radiation of that element, which is equivalent to an absorbance of 0.0044.¹³ This definition is not applicable in this analysis because the absorbance of the 1.00 $\mu\text{g}/\text{ml}^{-1}$ standard is 0.0047.

A range of detection limits has been reported for the determination of arsenic using an air-acetylene flame, e.g. 3.00 $\mu\text{g}/\text{ml}^{-1}$,¹ 0.20 $\mu\text{g}/\text{ml}^{-1}$,¹³ 1.80 $\mu\text{g}/\text{ml}^{-1}$,¹⁴ and 0.67 $\mu\text{g}/\text{ml}^{-1}$.¹¹ In spite of this wide variation, it is clear that the present system offers considerable improvement in achieving lower detection limits. The elimination of flame noise (the major source of signal-to-noise degradation) by the Zeeman Effect has been recently demonstrated.¹¹

Accuracy of the arsenic determination

Duplicate 1 g sub-samples of the National Research Council of Canada Marine Sediment Reference Material MESS-1 were subjected to a modified room temperature dissolution procedure.¹⁵ The samples, in polyethylene bottles, were first wetted with 2 ml of distilled water, then 3 ml of aqua regia and 20 ml of HF were added.

The bottles were then placed on a Burrell wrist-arm shaker and agitated for at least 16 hr. After shaking, 75 ml of saturated boric acid solution was added and the bottles replaced on the shaker for 4 hr. The supernatants were analyzed after allowing the small amounts of residue to settle. For the MESS-1 samples the As recovery was found to be 90.2 and 103.3% (Table II).

TABLE II
Recovery of arsenic in some standard reference materials

	Measured analytical concentration	Calculated recommended concentration	Recovery (%)
MESS-1	0.379	0.420	90.2
	0.484	0.469	103.2
Coal Fly Ash	1.83	1.90	96.3
SRM 633	1.16	1.12	104.0
	1.66	1.50	110.0
Urban Particulate Matter	0.319	0.413	77.2
	0.264	0.350	75.4
SRM 1648	0.269	0.368	73.2
River Sediment	0.925	1.20	77.5
SRM 1645			

A similar evaluation was done using triplicate sub-samples of the NBS Coal Fly Ash (SRM 1633) and Urban Particulate Matter (SRM 1648). In agreement with Silberman and Fisher, satisfactory recovery was obtained for the Coal Fly Ash (Table II). However, lower recoveries were found for the Urban Particulate Matter. This is probably caused by the higher carbon content of this material. Silberman and Fisher¹⁵ noted that the mass of the undissolved residue was correlated with the carbon content of various fly ashes. No carbon content is given for the Coal Fly Ash (SRM 1633) or the Urban Particulate Matter (SRM 1648). An extraction of the NBS River Sediment (SRM 1645) gave a 77.5% recovery of arsenic. Although the carbon content is not listed, the percent loss on ignition (10.72%) can be taken as an approximate measure of the high organic content of this material. In contrast, the Marine Sediment (MESS-1), is a fairly clean estuarine sediment collected

from the Miramichi River estuary (Gulf of St. Lawrence) and continued 2.99% carbon.

Chemical forms of arsenic in a sediment core from Moira Lake (Ontario)

Moira Lake lies about 100 miles east of Toronto in Ontario and drains an area in which the mining and smelting of gold, silver and arsenic occurred between 1900 and 1961. The lake sediments are sulphide rich and reducing and although massive algal blooms occur in summer, the bottom waters are always oxygenated.¹⁶ The analysis of the chemical forms of arsenic as operationally defined by the sequential extraction procedure, in 1 cm sections at intervals down the core, are shown in Table III. On the basis of Ambrosia (ragweed) pollen geochronology, a sediment depth of 22 cm corresponds to about 1900 when the smelting operations began; the calculated sedimentation rate was 2.36 mm year⁻¹.¹⁷

TABLE III
Chemical forms of arsenic in a sediment core from Moira Lake, Ontario. Concentrations in $\mu\text{g/g}$ dry wt.

Sediment depth	A	B	C	D	E	Total
0-1 cm	n.d.	17.9	155	389	43	605
9-10 cm	n.d.	157	320	305	25	807
14-15 cm	n.d.	79	210	225	17	531
18-19 cm	n.d.	115	172	148	11	446
21-22 cm	n.d.	53	125	192	12	282
32-33 cm	n.d.	80	89	156	14	339

n.d. = none detected.

A = readily exchangeable forms.

B = carbonate and surface-oxide bound forms.

C = Fe, Mn oxide bound forms.

D = forms bound to organic matter and sulphides.

E = residual forms.

The most important solid phases binding arsenic are (a) carbonates and surface oxides; (b) Fe—Mn oxides; (c) sulphides. The sulphide content in the sediments ranges from 1.6–2.1% and total iron 4.1–4.6%.¹⁶ Interestingly, significant amounts of arsenic can be extracted with NaOAc at pH 5.0. This fraction of the total arsenic

can be regarded as potentially available. Mobilization of other forms would be most unlikely under the well-oxygenated conditions of the lake's bottom waters.

These results are presented here to demonstrate the value of the Zeeman flame atomic absorption measurement of an element whose direct determination in difficult matrices poses problems for analysts.

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