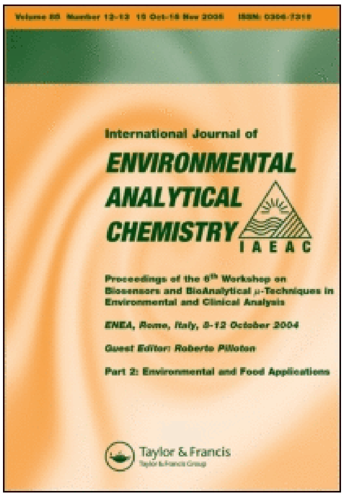

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Determination of Arsenic (III, V, Total) in Polluted Waters by Graphite Furnace Atomic Absorption Spectrometry and Anodic Stripping Voltammetry

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An ammonium pyrrolidinedithiocarbamate-methyl isobutyl ketone-electrothermal atomic absorption spectrophotometric (APDC-MIBK-ETA) procedure and a toluene extraction-anodic stripping voltammetric (ASV) procedure were applied for the determination of As (III, V, Total) in some polluted waters. The total arsenic content of these water samples was also determined using the direct ETA and the nickel-matrix modification-ETA methods. There was good agreement among the various methods on the total arsenic content of the water samples. Neither the container material (Pyrex glass or linear polyethylene), nor filtration, nor preservation with 1% HCl had any significant effect on the total arsenic concentration of the polluted river water and mine leachate samples studied. Also, no As(III) could be detected in the samples.

KEY WORDS: Arsenic, Polluted Waters, Graphite furnace atomic absorption spectrometry, Anodic stripping voltammetry.

INTRODUCTION

The determination of arsenic and its speciation in the aquatic environment has generated considerable interest in recent years especially since the presence of arsenic in drinking water supplies is considered to represent a significant health hazard.[1] For example, arsenic contamination of potable water has been linked with skin pigmentation changes, keratoses, cancer and neurological effects.[2,3] The potential toxicity of arsenic is now known to depend on its oxidation state.[4] Therefore there is a requirement to develop methods for quantifying the different oxidation forms of arsenic. The most predominant oxidation states of arsenic in natural waters including drinking water appear to be +3 and +5.[4]

Electrothermal atomic absorption spectrometry (ETA) is one of the popular techniques now in use for measuring ng/ml levels of arsenic in water samples. The ETA technique coupled with hydride evolution[5] or ammonium pyrrolidinedithiocarbamate-methyl isobutyl ketone (APDC-MIBK) extraction[6] has been used to differentiate between As(III) and As(V). Another potential analytical technique that can be used to distinguish between As(III) and As(V) is linear scan anodic stripping voltammetry (LSASV).

In this paper we present our results on the use of the APCD-MIBK-ETA system and LSASV to determine As(III), As(V) and total inorganic As in a polluted river water sample and in a polluted mine leachate. In addition, we have determined total arsenic using the direct ETA and nickel-matrix modification-ETA methods.

EXPERIMENTAL SECTION

Apparatus

A Perkin–Elmer Model 603 atomic absorption spectrophotometer equipped with a Perkin–Elmer Model HGA-2100 graphite furnace, a deuterium arc background corrector and a Perkin–Elmer Model M-1356 EDL was used for the atomic absorption measurement of arsenic. The nitrogen purge gas flow was interrupted during atomization.

The anodic stripping voltammetric measurements of arsenic were made using an ESA (Environmental Sciences Associates, Inc., Massachusettes, U.S.A.) Model 3040 Charge Transfer Analyzer equipped with an ESA Model 3600-01 electrochemical cell and a Heath-Schlumberger (Michigan, U.S.A.) Model SR-207 X-Y recorder. The electrochemical cell was a three-electrodes system consisting of a tubular pyrolytic graphite working electrode with a gold film plated on the active inner surface (2 cm^2), a platinum wire counter electrode in 0.05 M hydroxylamine hydrochloride and a Ag/AgCl reference electrode in saturated NaCl solution.

A modified version of the reduction-distillation apparatus devised by Davis *et al.*[7] was used to separate As(III) from the original sample for the ASV analyses. To minimize contamination and facilitate rapid changing of the apparatus in between distillation, a quickfit B-10 ground glass joint instead of the original tight-fitting rubber septum connected the nitrogen line to the distillation apparatus. Variations in the flow rate of the nitrogen carrier gas were eliminated using regulator-equipped flow meters (Brooks Instruments Model Sho-Rate 150) to monitor the gas flow through each set up during the distillation process.

Reagents

High-purity water was obtained by distilling doubly deionized water in a Corning Model AG-11 distillation unit.

The APDC (2% and 5%) and the ammonium citrate buffer (20%) used in the solvent extraction study were prepared and purified as described in a previous publication.[6] A 10% solution Cu_2Cl_2 in conc. HCl used in the ASV reduction-distillation process was prepared according to the procedure of Davis *et al.*[7]

A stock arsenic standard solution certified to contain 1.0 mg As(V)/ml was purchased from Fisher Scientific for the atomic absorption work. Ultrapure As_2O_5 (Alfa Products, Ventron Corporation) was used for the preparation of standard As(V) solution in the ASV experiments.

A stock solution containing 1.0 mg As(III)/ml was prepared as follows: Exactly 0.1320 g of high-purity As_2O_3 (NBS Standard Reference Material 83c, dried at 100°C for 2 h) was dissolved in 2 ml of 1 M NaOH followed by the addition of 25 ml of water plus 4 ml of 1 M HCl and dilution to 100 ml with high-purity water. The solution was stored in a precleaned linear polyethylene bottle.

All other reagents and solutions used were of the highest purity available.

Sample Collection

Nalgene linear polyethylene, 1000-ml screw-cap bottles and Corning Pyrex glass, 2500-ml screw-cap bottles were used as containers for the samples. Prior to use the bottles were cleaned sequentially as follows: a detergent wash, tap water rinse, soaking in 1% HNO_3 for 24 h, and high-purity water rinse (10 times).

To check the effect of suspended solids on arsenic concentrations duplicate filtered and unfiltered samples were obtained from the same locations. Filtration was done using a 0.45-μm Millipore filtering system. The membrane filters had been washed with 1% HCl followed by rinsing in high-purity water prior to filtration. The filtered samples were acidified to contain 1 ml conc. HCl (Baker Ultrex) for every 100 ml of sample.

The samples were brought to the laboratory within 6 h of collection and refrigerated at 4°C until analyzed.

Analytical procedure

i) Direct ETA. A known aliquot of the sample was diluted suitably with high-purity water and HNO_3 (Baker Ultrex) so that the arsenic concentration in the diluted sample would be between 20–30 ng/ml and the HNO_3 concentration would be 2%. A 10 μl aliquot of the dilutes sample was then introduced into the pyrolytically coated graphite tube with an Eppendorf pipette fitted with disposable polypropylene tips. Prior to use the tips were cleaned by soaking them overnight in 1% HNO_3 followed by four rinses with high-purity water.

ii) Nickel matrix modification-ETA. A known aliquot of the sample was diluted with HNO_3 and a 10% solution of nickel (as nitrate) so that the final solution concentration of these reagents would be 1% and 0.05%, respectively. The dilution factor used was such that the arsenic concentration in the matrix-modified sample would be 20–30 ng/ml.

iii) APCD-MIBK-ETA. The procedure is basically the same as that described in a previous publication.[6] To determine As(III), a suitable aliquot (25 ml for samples containing up to 10 ng As/ml; for arsenic concentrations greater than 10 ng/ml, a smaller aliquot was diluted to 25 ml with water) was neutralized with 1 M NaOH, if necessary. The solution was then transferred to a 125-ml Pyrex glass separatory funnel fitted with Teflon stopcocks and polyethylene stoppers. Ammonium citrate buffer (5 ml) was added, the pH was adjusted between 3.0–5.5 with 1 M HC1, 5 ml of 2% APDC was added followed by 5 ml of water-saturated MIBK, and the solution was extracted for 1 min. The aqueous layer was drained off. The organic phase was washed twice with 10 ml of high-purity water. The amount of As(III) was determined by injecting 10 μl of the MIBK phase into the pyrocoated graphite tube.

To determine total arsenic, a suitable aliquot of the sample (25 ml of a smaller aliquot diluted to 25 ml with high-purity water) was acidified to 0.3–0.4 M with 6 M HCl and 3 ml of a 2% solution of sodium thiosulphate was added with swirling. After 5 min, 5 ml of a 5% solution of APDC and 5 ml of water-saturated MIBK were added. The solution was extracted for 5 min and the arsenic content in the sample was measured as described above.

The amount of As(V) in the sample was obtained by subtracting the As(III) value from the total arsenic content.

The concentration of arsenic in the water samples using the three procedures described above was obtained by direct comparison to linear working curves. The working curves were prepared using standard As(V) solutions in 2% HNO_3 for method (i); in 1% HNO_3 plus 0.05% Ni for method (ii); and extracting the standards containing As(III) and As(V) under the same conditions as the sample for method (iii). Also, in all the cases, the method of standard addition was used to check for quantitative recovery.

iv) Anodic stripping voltammetry. The solvent extraction method of Yasui *et al.*,[8] was used for differentiating between As(III) and As(V). To determine As(III), a 10 ml aliquot of the sample was acidified to 9 M with conc. HCl and extracted for 2 min with 10 ml of toluene. The extraction was repeated twice. The As(III) in the combined toluene extract (30 ml) was then back-extracted using two 5-ml portions of high-purity water. A 1 ml aliquot of the combined aqueous extract was then transfered into the reduction-distillation apparatus, 6 ml of conc. HCl was added and the $AsCl_3$ liberated was distilled off at 105°C into 4 ml of high-purity water contained in the ESA Model 3040 Analysis Cell using nitrogen (flow rate, 140 ml/min) as the carrier gas. The distillation was continued for 16 min. After adjusting the volume to 5 ml with 12 M HCl, the resulting solution was directly analyzed using the Charge Transfer Analyzer under the optimized instrumental conditions recommended by Lee and Méranger.[9]

To determine As(V), an aliquot of the acidic aqueous phase from the toluene extraction was digested with a 24:24:1 mixture of nitric, perchloric and sulphuric acids at 200°C to near dryness. The digestate was taken up in 7 ml of 1% Cu_2Cl_2 in conc. HCl, and the $AsCl_3$ was distilled off as described above.

The As(V) in the sample was also determined using an alternate approach. This involved digestion of the water sample (rather than the acidic aqueous phase from the toluene extract) with the nitric-perchloric-sulphuric acid mixture and determination of the total arsenic using the reduction-distillation-ASV procedure described earlier. The concentration of As(V) was obtained by difference between the values of total As and As(III).

RESULTS AND DISCUSSION

Optimum instrumental and solution variables

Table I shows the optimum instrumental parameters we obtained for the direct ETA, nickel-matrix modification-ETA and the APDC-MIBK-ETA methods.

TABLE I

Optimized graphite furnace atomic absorption spectrophotometric parameters for arsenic

	Methods		
Parameters[a]	Direct ETA	Nickel matrix modification-ETA	APDC-MIBK-ETA[b]
Line, nm	193.7	193.7	193.7
Slit, nm	0.7	0.7	0.7
Dry temp, °C	100	100	80
Dry time, s	40	40	50
Ash temp, °C	500	900	200
Ash time, s	30	30	60
Atom temp, °C	2500	2500	2600
Atom time, s	7	7	7
Integration time, s	5	5	5
EDL power, W	8	8	8

[a] Temperatures represent the meter settings on the control panel of the HGA-2100 temperature programmer.
[b] The parameters given are for the MIBK phase.

In the direct ETA method, we used an ashing temperature of 500°C for 30s. Above 500°C there was loss of arsenic as has also been reported by Edigar.[10] The acidity was maintained at 2% HNO_3 since some workers[11,12] had noted considerable variations in the slope (i.e., arsenic atomic absorption signal vs. arsenic concentration) with changes in acidity.

In the nickel-matrix modification-ETA method, we chose an ashing temperature of 900°C. Edigar[10] found no loss of arsenic up to an ashing temperature of 1400°C in the presence of 0.1% Ni. We confirmed this observation even at 0.05% Ni. Some workers[11,12] reported erratic readings and accelerated tube deterioration at acidities greater than 2% HNO_3 using the Ni-ETA procedure. Therefore, we used a 0.05% solution of nickel in 1% HNO_3. Under these conditions the signals were repeatable and the background was minimal.

In the APDC-MIBK-ETA procedure, the use of a charring temperature of 200°C and a charring time of 60s provided the best compromise between maximum sensitivity and minimum background absorbance. The optimum solution conditions required for the quantitative extraction of the As(III)-APDC complex into MIBK and for the quantitative reduction of As(V) to As(III) have been described in detail in a previous publication.[6] These studies showed that complete transfer of the As(III) chelate from aqeuous to organic phase occurred in a single extraction over the pH range 1.0–6.8 and acidity range 0.1–0.5 M HCl in an extraction time 20s and at an APDC to As(III) concentration ratio 250. Once extracted the chelate remained stable in the MIBK phase at least for 5 months in the pH range 1.0–5.0. The stability data was obtained by draining off the original acidic aqueous phase, rinsing the MIBK phase with water twice and transferring the MIBK layer into clean, dry Pyrex glass centrifuge tubes.

There was no extraction of As(V) in the pH range 1.0–10.0 and only incomplete extraction in 0.3 M–1.0 M HCl. Therefore the determination of both As(V) and total As required the reduction of As(V) to As(III) prior to APDC-MIBK extraction. Initially we tried KI as a reductant. Nearly 70 min was required for the quantitative conversion of As(V) to As(III) using a 0.5% solution of KI in $\geqq 0.3$ M HCl at 25°C. Increasing the KI concentration to 5% lowered the reduction time by 30 min but this was still slow. However, when the solution contained 0.1% $Na_2S_2O_3$ in addition to 0.5% KI, the reduction was complete in 1 min. Subsequent studies showed that the reduction could be effected using sodium thiosulphate alone. For a 50 ng As(V)/ml, the optimum thiosulphate and HCl concentrations required were 0.1%–0.4% and 0.1 M–0.4 M, respectively. When the thiosulphate concentration exceeded $>0.4\%$ it decomposed even at 0.1 M HCl whereas when the HCl concentration was 0.4 M, the thiosulphate decomposed even at 1%.

The instrumental variables and solution conditions affecting the ASV measurement of arsenic have been discussed by earlier workers.[7,9]

Analytical parameters

Table 2 shows the detection limit (2 × standard deviation of the blank), sensitivity (concentration corresponding to 0.0044 A unit), linear range and precision of the various atomic absorption methods used in the present study. Note that the detection limit and sensitivity of all the methods were sufficiently low to enable determination of arsenic in polluted waters. In fact the samples had to be diluted (10 × and 100 × for river water and leachate samples, respectively) to bring the As level within the linear working range. The precision was also acceptable although greater care was required with the direct method.

TABLE II

Analytical parameters for arsenic using some electrothermal atomic absorption spectrophotometric methods

Parameters[a]	Direct ETA	Ni-matrix modification ETA	APDC-MIBK-ETA
Sensitivity, $ng\,ml^{-1}$	2.8	2.3	1.3
Detection limit, $ng\,ml^{-1}$	4.0	1.5	0.7
Linear range, $ng\,ml^{-1}$	0–100	0–60	0–90
Precision (%) at 5 × d.l.	21	14	17
10 × d.l.	12	11	9

[a] Sensitivity is concentration in $ng\,m^{-1}$ for 0.0044 Absorbance units. Detection limit is twice the standard deviation of the blank. Precision refers to coefficient of variation at the 95% confidence level for 10 determinations.

In the ASV method, the detection limit (3SD of blank) and linear working range were 1.0 ng As/ml and 10–500 ng As/ml, respectively. The precision, expressed as the percent coefficient variation at the 95% confidence interval for four replicate measurements was 5.2 and 2.9 at 10 ng As/ml and 50 ng As/ml, respectively. Thus the detection limit and precision of the ASV method were also adequate for determining the levels of arsenic in the polluted water samples examined in this study.

It was not possible to obtain unequivocal proof of accuracy of the ETA and ASV methods used in our work, because no reference standards certified for As(III), As(V) and total As in natural water or polluted water are currently available. Nonetheless, an indirect measure of accuracy was obtained by doing recovery studies. The mean analytical recovery for total inorganic arsenic was 100 ± 15% at 10X and 20X detection limit of each of the direct-ETA and the nickel-matrix modification-ETA methods. Also, the recoveries for both As(III) and As(V) were close to 100% at 5 ×, 10 ×, 20 × and 40 × detection limit of the APDC-MIBK-ETA method.[6]

As shown in Table III, recoveries on spiked samples by the ASV method ranged from 96 to 101% for As(III) and 96–111% for As(V). A further proof of accuracy of the ASV method was obtained by analyzing the NBS multielement aqueous standard (SRM 1643). As against the NBS certified value of 77.1 ng total inorganic As ml^{-1}, the proposed method gave 76.4 ± 2.3 ng As ml^{-1} (average of 7 determinations).

Thus the satisfactory recoveries obtained by the various ETA and ASV methods attest to the accuracy of our procedures for As(III), As(V) and total arsenic.

TABLE III

Arsenic recoveries following toluene extraction and ASV analysis

As added (ng/ml)	Species	As recovered (ng/ml)	% Recovery
200	As(III)	201.7 ± 7.1[a]	101
100	As(III)	100.3 ± 4.8	100
100	As(V)	99.1 ± 4.3	99
50	As(III)	47.8 ± 1.4	96
50	As(V)	51.3 ± 0.7	103
10	As(III)	9.7 ± 0.5	97
10	As(V)	11.1 ± 0.8	111

[a] Based on 4 replicate measurements. The measure of precision is the average deviation.

Analyses of samples

The results obtained for arsenic in the river water and mine leachate samples using the three ETA methods and anodic stripping voltammetry are summarized in Table IV. There is reasonable agreement among the various methods for the arsenic content in the samples.

The values given in Table IV apply to the total inorganic arsenic content in the samples. Although the APDC-MIBK-ETA and the toluene extraction-ASV methods are capable of differentiating between As(III) and As(V), no As(III) could be detected in the samples. The reason for this is not clear to us. However, some workers[13-15] cite the oxidation of As(III) to As(V) in aqueous solutions at the 0.01 to 5.0 mg As(III) L^{-1} levels as one cause for the disappearance of As(III).

Also it is clear from Table IV that neither the container material (Pyrex glass or linear polyethylene), nor filtration, nor preservation with 1% HCl has any significant effect on the total inorganic arsenic content of the samples. Thus

TABLE IV

Total arsenic content of river water and mine leachate samples using some electrothermal atomic absorption spectrophotometric and anodic stripping voltammetric methods

	Total inorganic arsenic, mg/L							
Method	RWG	RWFAG	RWP	RWFAP	LWG	LWFAG	LWP	LWFAP
Direct ETA	0.21±0.02	0.23±0.02	0.25±0.02	0.23±0.01	8.03±0.3	8.5±0.1	8.0±0.3	8.4±0.1
Nickel-matrix modification-ETA	0.21±0.02	0.20±0.02	0.20±0.02	0.22±0.03	7.5±0.2	8.4±0.1	8.3±0.4	8.0±0.6
APDC-MIBK-ETA	0.22±0.01	0.22±0.01	0.22±0.01	0.23±0.01	7.0±0.3	7.2±0.2	7.6±0.4	7.8±0.2
Anodic Stripping Voltammetry	0.23±0.01	0.24±0.01	0.24±0.01	0.24±0.01	8.1±0.3	8.6±0.7	8.7±0.6	8.6±0.7

RWG, RWFAG, RWP, RWFAP: River water stored in glass; filtered and acidified river water stored in glass; river water stored in polyethylene; filtered and acidified river water stored in polyetheylene, respectively.

LWG, LWFAG, LWP, LWFAP: Some connotation as above but leach water.

The measure of precision in the standard deviation at the 95% confidence interval.

adsorption of arsenic on the container material or on particulates from the river water sample (0.23 mg As/L), and the mine leachate (7.9 mg As/L) appears to be negligible.

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