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Direct Determination of Arsenic in Sugar by GFAAS With Transversely Heated Graphite Atomizer and Longitudinal Zeeman-Effect Background Correction

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ABSTRACT

A method has been developed for the direct determination of As in sugar by graphite furnace atomic absorption spectrometry with a transversely heated graphite atomizer (end-capped THGA) and longitudinal Zeeman-effect background correction. The thermal behavior of As during the pyrolysis and atomization steps was investigated in sugar solutions containing 0.2% (v/v) HNO_3 using Pd, Ni, and a mixture of Pd + Mg as the chemical modifiers. For a 60-µL sugar solution, an aliquot of 8% (m/v) in 0.2% (v/v)HNO_3 was dispensed into a pre-heated graphite tube at 70ºC. Linear analytical curves were obtained in the 0.25 - 1.50-µg L^{-1} As range. Using 5 µg Pd and a first pyrolysis step at 600ºC assisted by air during 40 s, the formation of a large amount of carbonaceous residue inside the atomizer was avoided. The characteristic mass was calculated as 24 pg As and the lifetime of the graphite tube was around 280 firings. The limit of detection (L.O.D.) based on integrated absorbance was 0.08 µg L^{-1} (4.8 pg As) and the typical relative standard deviation (n = 12) was 7% for a sugar solution containing 0.5 µg L^{-1}. Recoveries of As added to sugar samples varied from 86 to 98%. The accuracy was checked in the direct analysis of eight sugar samples. A paired *t*-test showed that the results were in agreement at the 95% confidence level with those obtained for acid-digested sugar samples by GFAAS.

INTRODUCTION

The monitoring of arsenic in environmental, biological, and food samples is important because As-based compounds are still used in some agroindustrial areas as fungicide, herbicide, insecticide, algaecide, defoliant, and wood preservative (1). Indeed, arsenic compounds are also used in the metallurgical industry (to improve both hardening and corrosion resistance of metallic alloy), in semiconductor materials, pigments, anti-fouling paints, and in therapeutic and veterinary medicine (1,2). As inorganic arsenic and its related compounds are considered toxic to human health (3,4) and may accumulate in soils used for agriculture (5), an accurate determination of arsenic in foodstuffs and agroindustrial products is relevant.

Among analytical techniques used in the routine determination of arsenic, the most common methods are hydride generation atomic absorption spectrometry (6), atomic fluorescence spectrometry (7), inductively coupled plasma mass spectrometry (8), inductively coupled plasma atomic emission spectrometry (9), and electrothermal atomic absorption spectrometry (10).

Electrothermal atomic absorption spectrometry (ETAAS) is a suitable and widely used technique for the determination of elements at trace levels due to its selectivity, simplicity, high sensitivity, and capability for direct analysis with minimal sample preparation (11-15). This last characteristic is attractive for laboratories that routinely analyze samples in large-scale (16). The shortcomings associated with dry or wet ashing procedures are circumvented and then analytical costs can be drastically reduced.

Several works have been published on the application of ETAAS for As determination in foodstuffs (17,18), biological tissue (19,20), water (10, 21-25), and beverages (15,26). However, the literature dealing with the determination of As in sugar by ETAAS is very limited. Only few methods have been described that use different procedures for sugar sample preparation for ETAAS analysis (18) or hydride generation AAS (27-28). The most widely used methods used the dry ashing sample preparation procedure. Because arsenic is usually present in sugars at ultra-trace levels (29), the use of direct analysis is attractive and relevant from the quality control point of view.

The aim of this study was to develop a simple and fast method for the direct determination of trace As in table sugars using ETAAS with transversely heated graphite atomizer (THGA™) (end-capped configuration) and longitudinal Zeeman-effect background corrector. The proposed method was applied for sugar samples produced in Brazil for export.

EXPERIMENTAL

Instrumentation

A PerkinElmer SIMAA™ 6000 simultaneous multielement atomic absorption spectrometer with a longitudinal Zeeman-effect background correction system, furnished with end-capped graphite tubes inserted on a transversely-heated graphite atomizer

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(PerkinElmer Part No. B3 000653) and an AS-72 autosampler were used. A PerkinElmer electrodeless discharge lamp (EDL) was used for As measurements at the analytical wavelength recommended by manufacturer (193.7 nm and slit 0.7 nm). The EDL lamp was operated applying 380 mA. High-purity argon (99.999%, White Martins, Brazil) was used as the purge gas and synthetic air (White Martins, Brazil) was used in the oxygen-assisted pyrolysis. It should be pointed out that the experiments were carried out under Stabilized Temperature Platform Furnace (STPF) conditions (12) including Zeeman-effect background correction.

Reagents, Reference Solutions and Samples

High-purity de-ionized water using a Milli-Q™ water purification system (Millipore) was used throughout. Hydrochloric acid, nitric acid, hydrogen peroxide, and sodium hydroxide used were Suprapur® grade (Merck). All reference solutions and samples were acidified to 0.2% (v/v) HNO_3. All 0.1% (m/v) Pd, Mg, and Ni solutions used as chemical modifiers were prepared by appropriate dilution from individual 1% (m/v) stock solutions in water.

Arsenic stock solution (1000 mg L^{-1}) was prepared by dissolving 1.320 g As_2O_3 (Fluka Chemical) in about 20 ml 1.0 mol L^{-1} NaOH. A volume of 50 ml of 0.5 mol L^{-1} HCl was added to this solution and the volume was made up to 1000 ml with water. For calibration, five reference solutions (0.25, 0.50, 0.75, 1.00, and 1.50 µg L^{-1}) were prepared daily in 0.2% (v/v) HNO_3 by appropriate dilution of the stock solution. The autosampler washing solution was 0.1% (v/v) of Triton®X-100 in 0.2% (v/v) HNO_3. In each measurement, 60 µL of sample or reference solution plus 5 µL of 0.1% (m/v) Pd solution as chemical modifier were injected into the pre-heated tube at 70ºC. All measurements of integrated absorbance were made with at least three replicates.

The electrothermal behavior of As in diluted nitric acid and sample solutions was studied using pyrolysis and atomization curves without a chemical modifier and with $Pd(NO_3)_2$, $Ni(NO_3)_2$, and $Pd(NO_3)_2$ plus $Mg(NO_3)_2$. This study was made with the following solutions containing 0.5 ng As: (a) 0.2% (v/v) HNO_3; (b) 0.2% HNO_3 plus 5% (m/v) sugar; (c) acid-digested sugar.

Sugar samples were supplied by Copersucar (Sugar-cane, Alcohol and Sugar Fabricator Association of São Paulo State, Brazil) and were collected from different Brazilian producers.

A different procedure for sample preparation was used to compare the results and to check the accuracy of the developed procedure. The wet ashing digestion procedure in a closed vessel system employed the ETHOS 1600 microwave oven (Milestone, Sousole, Italy) and the procedure used was as follows: 250 mg of sugar sample was placed into acid-cleaned PFA flasks and 2.5 mL concentrated nitric acid was added. The flasks were placed on the microwave oven cavity and the heating program listed in Table I was run. All digests were clear solutions and the final volume was made up to 5 mL with Milli-Q water.

Before analysis, a simple sample dilution of the sugar samples was carried out by dissolving the samples in 0.2% (v/v) HNO_3 prior to direct analysis in order to obtain an 8% (m/v) sugar solution.

The heating program of the graphite atomizer used for As determination is shown in Table II.

RESULTS AND DISCUSSION

All measurements were initially carried out according to the conditions recommended by the manufacturer. Although GFAAS with

TABLE I
Microwave Digestion Temperature Program

Step	Hold Time (min)	Power (W)
1	1	250
2	1	0
3	5	250
4	5	400
5	5	600
6	5	vent

TABLE II
Heating Program of Atomizer for the Determination of As in Sugar

Step	Temperature (ºC)	Time (Ramp, Hold)(s)	Gas Flow (mL/min)
1	110	15, 35	250 (Ar)
2	180	15, 30	250 (Ar)
3	600	20, 40	250 (air)
4	20	1, 40	250 (Ar)
5	1400	10, 10	250 (Ar)
6	2200	0, 5	0 (reading)
7	2500	1, 5	250 (Ar)

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Zeeman-effect background corrector is a potentially efficient technique for the determination of As at trace levels in sugar with a simple dilution of the sample prior to analysis, the large amount of carbonaceous residue generated after a few firings impaired the performance of the spectrometer. This drawback can be circumvented by using an additional air-assisted pyrolysis step at 600ºC for 40 s for the determination of the analyte. The electrothermal behavior of As in diluted nitric acid, sugar digest, and diluted sugar was studied without and in the presence of the following modifiers: $Pd(NO_3)_2$, $Ni(NO_3)_2$, and $Pd(NO_3)_2$ plus $Mg(NO_3)_2$. The modifier volume of either 5 µL Pd, 20 µL Ni, or 5 µL Pd + 3 µL Mg was added to a 20-µL volume of sample. Pyrolysis and atomization curves were employed to determine the optimal pyrolysis and atomization temperatures for each medium with and without modifiers. All results were based on peak area measurements, which are summarized in Table III. For this study, the digest and the diluted sugar sample were spiked with 0.5 ng As. The effect of the chemical modifier on sensitivity and stabilization of the analyte in the presence of sugar was relevant. Although Ni stabilized As up to 1600ºC, the selected modifier in this work was Pd because it gave the best characteristic mass (Table III), the peak profiles in presence of Pd were narrower than those obtained with Pd/Mg, or Ni and background attenuation were more pronounced. For arsenic determination in sugars, the optimized heating program of the atomizer with two pyrolysis steps is summarized in Table II. It should be noted here that the measurement of atomic signals using end-capped transversely heated graphite atomizers led to integrated absorbances of 60% higher than those obtained with conventional tubes. The former atomizer was then selected for

TABLE III
Optimized Pyrolysis/Atomization Temperatures and Characteristic Mass (m_0) in pg for As in 0.2% (v/v) HNO_3
[Acid-digest (dig.) and Solution (direct) of Sugars]

Modifier	HNO_3	Dig.	Direct
None	1000/2300ºC m_0 = 34.3	400/2200ºC m_0 = 121	400/2000ºC m_0 = 440
Ni	1800/2200ºC m_0 = 34.0	1400/2200ºC m_0 = 76.1	1600/2200ºC m_0 = 78.6
Pd	1800/2200ºC m_0 = 32.3	1400/2200ºC m_0 = 33.8	1400/2200ºC m_0 = 27.6
Pd/Mg	1600/2200ºC m_0 = 31.3	1400/2200ºC m_0 = 34.4	1400/2200ºC m_0 = 38.1

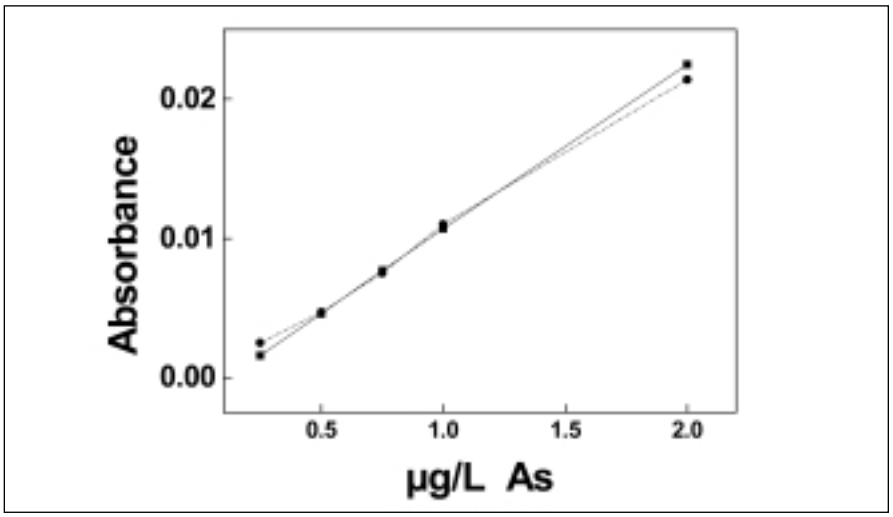

Fig. 1. Influence of matrix on calibration for As. Curves correspond to reference solutions prepared in 0.2% (v/v) HNO_3 (solid line) and 8% (m/v) sugar solution plus 0.2% (v/v) HNO_3 (dotted line).

further experiments in order to maximize sensitivity. The influence of the injected sample volume was studied by injecting 40, 60, and 80 µL aliquots into the graphite tube. Although higher absorbance was generated for higher injected volumes, the relative standard deviations (RSD) relative to an 80-µL volume were around 11%. For 60 µL of sample volume and 5 µL of modifier, the typical RSD was ~1.3%. The selected injection volume was 60 µL as a compromise between sensitivity and precision of the measurements. The samples were dispensed into a preheated graphite tube with the pipette speed fixed at 40%. When the temperature was increased from 70 to 90ºC, the atomic signals and precision did not change, so 70ºC was the temperature selected for further experiments. It should be stressed that under these conditions, no problems were observed with mixing of the modifier with the sample or with the platform holding 65 µL of sample.

The matrix effects were evaluated by comparing the slopes between curves built up from aqueous reference solutions and matrix-matched solutions in the 0.25 – 2.00 µg L^{-1} As range (Figure 1). The figure shows no appreciable matrix effects. The errors associated with absorbance measurements by per-

forming the calibration with aqueous reference solutions are less than 10%, which is acceptable for trace and direct analysis of sugars. Reference solutions in the 0.25 - 1.50 μg L^{-1} range were used for calibration and good linear correlation coefficients (r= 0.9999) were usually attained. Typical absorbance and background signals for sugar samples using the end-capped THGA configuration are shown in Figure 2.

The performance of the developed procedure was assessed by determining As in eight sugar samples. A comparison of the results of our method using a simple dilution of the sample with those obtained for acid-digested samples by GFAAS is showed in Table IV. Applying a paired *t*-test, it was observed that all results are in agreement at the 95% confidence level and recoveries were found to be within 86 - 98% for the spiked samples. The limit of detection (LOD) was 0.08 μg L^{-1} (4.8 pg As) and the relative standard deviation was 7% after 12 consecutive analyses of a sugar solution spiked with 0.5 μg L^{-1} As. The lifetime of the graphite tube using the established conditions is around 280 firings.

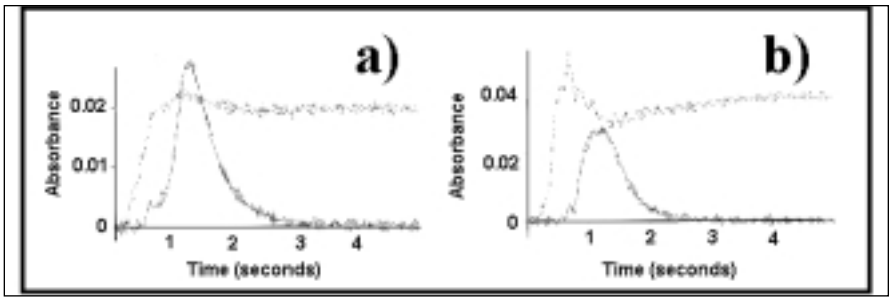

Fig. 2. Absorbance-time profiles for As determination (solid lines) and background (dotted lines) with 5 μg Pd as modifier. (a) 60 μL of 0.2% (v/v) HNO_3 solution containing 2.0 μg L^{-1} As; (b) 60 μL of 8% (m/v) sugar solution containing 0.2% (v/v) HNO_3 and 2.0 μg L^{-1} As.

TABLE IV
Results in μg/kg Obtained for As in Sugar Samples Using the Developed Procedure Without Digestion and With Digestion

Sample No.	Without Digestion	With Digestion
1	2.9 ± 0.6	3.9 ± 0.2
2	< 0.08	< 0.08
3	2.8 ± 0.7	3.1 ± 0.2
4	3.5 ± 0.2	5.6 ± 0.7
5	< 0.08	< 0.08
6	5.5 ± 0.1	6.5 ± 0.7
7	< 0.08	< 0.08
8	< 0.08	< 0.08

CONCLUSION

This work presents a new strategy for the direct determination of As in sugar samples by graphite furnace atomic absorption spectrometry. The comparative results and recovery values of the spiked samples indicated that a simple dilution of the sample in diluted nitric acid was sufficient to accurately determine arsenic in white sugar. The limit of quantification obtained is three orders of magnitude lower than those required by international regulations (1 mg Kg^{-1}) and with the proposed method up to 15 measurements per hour can be performed requiring only a simple dilution of the sample. These characteristics of the method are attractive for quality control purposes.

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Analysis of Wear Metals and Additive Package Elements in New and Used Oil Using the Optima 4300 DV ICP-OES

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ABSTRACT

New and Used Oil is analyzed for wear metals and additive elements by simultaneous ICP-OES using a solid-state SCD detector. Complete methodology is included along with sample and standard preparation. Data shows typical results for samples and QCs while analyzing a sample every 45 seconds.

INTRODUCTION

The analysis of new and used oil for concentration trends of wear metals and for formulation or depletion of additive package metals has been around for over 30 years. Wear metals such as copper and iron may indicate wear in an engine or any oil-wetted compartment. Boron, silicon, sodium, or potassium may indicate contamination from dirt or antifreeze leading to a failure. Additive elements such as calcium, phosphorus, and zinc are analyzed for depletion, which contributes to wear since these elements contribute to certain key lubrication characteristics. A sound maintenance program that routinely measures metals in the lubricating oils not only reduces the expense of routinely dismantling the components for visual inspection, but can indicate unexpected wear before component failure.

Atomic Absorption Spectrometers (AAs) were first used for these applications in the early to mid-1960s. As the number of elements and samples grew over the years, Inductively Coupled Plasma Emission Spectrometers (ICPs) were used for oil analysis starting in the early to mid-1980s. Most of these ICPs were sequential instruments that scanned from one element to the next. Simultaneous ICPs were usually too expensive for this application.

Today, many oil analysis labs will handle between 500 to 2000 samples per day and determine between 15 to 21 elements per sample. In these busy labs, the Optima 4300™ DV ICP-OES is rapidly becoming the instrument of choice. The Optima 4300 has a Segmented-array Charged-coupled Device (SCD) detector, which can measure all ICP elements simultaneously for over 6000 wavelengths. Along with the ability for very high sample throughput, the Optima 4300 permits the end-user to easily add new elements as their oil programs change. Add to these features:

- A 40-MHz free-running RF generator rugged enough to handle organic solvents as easily as aqueous solutions.
- A sample introduction system requiring no internal maintenance and exhibiting no carbon buildup during oil analysis.
- An ICP nebulizer that will not clog even with the high soot often seen in used oils.
- An autosampler with a SmartRinse™ feature that virtually eliminates analyte carryover.

It is easy to see why the Optima 4300 is such a robust instrument for busy oil analysis laboratories.

EXPERIMENTAL

All data were collected using the PerkinElmer Optima 4300 DV with a PerkinElmer AS-90plus autosampler. Modifications to the standard system are as follows:

1. Cross-flow nebulizer was replaced with the low-flow GemCone™ nebulizer (part number N077-0358).
2. Scott spray chamber was replaced with a baffled cyclonic spray chamber (part number N077-6053).
3. Standard 2.0 mm i.d. alumina injector was replaced with a 1.2 mm i.d. alumina injector (part number N077-5228).

All solutions were prepared with a Bohdan Automated Robotics Workstation (Mettler-Toledo-Bohdan, Vernon Hills, IL USA).

REAGENTS

Calibration standards were made using Conostan S-21+K blended standard, which contains 22 elements (Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, and Zn) at 500, 100, and 30 mg/g in a hydrocarbon oil. A custom-blended standard was used from Conostan which contains Ca at 5000 ppm, P at 1600 ppm, and Zn at 1600 ppm. A single-element standard was 5000 mg/g from Conostan for Co (Conostan Division, Conoco Inc. P.O. Box 1267, Ponca City, Oklahoma 74601 USA.

The diluent used in all cases was deodorized kerosene (Baker Analyzed, J.T. Baker Chemical Co., Phillipsburg, NJ USA).

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ICP WinLab32™ Method

Listed below are some important parameters from the WinLab32™ oil method

Method Name: Oil
Inst: Symbol, Wavelength, Name, and Function

Element	Wavelength (nm)	Name	Function
Al	308.215	Al	Analyte
Ca	315.885	Ca	Analyte
Cr	205.558	Cr	Analyte
Cu	324.751	Cu	Analyte
Fe	259.937	Fe	Analyte
K	766.492	K	Analyte
Mg	279.075	Mg	Analyte
Mo	203.843	Mo	Analyte
Na	588.983	Na	Analyte
Ni	231.603	Ni	Analyte
P	214.913	P	Analyte
Pb	220.351	Pb	Analyte
Si	288.155	Si	Analyte
Sn	189.925	Sn	Analyte
Zn	213.856	Zn	Analyte
Co	238.890	Co IS	Internal Standard

Inst: Spectrometer, Read Time, Replicates

Spectral Profiling: No Resolution: High
Read Delay Time (sec) : 18
Replicates : 2
Read Time : Auto Min. Time : 0.100 sec Max. Time: 2.000 sec

Sampler: Plasma Parameters

Source Equilibration Delay : 0 sec
Plasma Aerosol Type : Wet
Nebulizer Start-up Conditions: Instant

Element	Plasma (L/min)	Aux (L/min)	Neb (L/min)	Power (Watts)	View Dist	Plasma View
All	15	1.4	0.5	1500	15.0	Radial

Sampler: Peristatic Pump Parameters

Sample Flow Rate : 3.00 mL/min
Sample Flush Time(sec) : 6

Sampler: Wash Parameters

Wash Frequency : After every sample + extra time if sample concentrations exceed limits.
Wash Location : 0
Wash Rate(mL/min) : 4.00
Wash Time (sec) : 7

Analyte	Calibration Units	Concentration
Al	ppm	
Ca	ppm	
Cr	ppm	300
Cu	ppm	300
Fe	ppm	300
K	ppm	
Mg	ppm	
Mo	ppm	
Na	ppm	300
Ni	ppm	
P	ppm	
Pb	ppm	
Si	ppm	300
Sn	ppm	
Zn	ppm	

Additional Wash Time : 15 sec

SAMPLE AND STANDARD PREPARATION

All samples and standards were diluted 1:10 with kerosene on a Bohdan Automated Robotics Workstation. The Workstation picks up the oil from a standard 2-oz or 4-oz bottle, dispenses the oil into an autosampler tube, adds kerosene, vortex-mixes the sample and returns the tube to the AS-90*plus* autosampler rack. The sample preparation is done on a volume-to-volume or if needed, a weight-to-weight basis (as required by ASTM Standard D5185). Forty-five or 80 samples can be prepared at a time and requires a one-minute sample preparation time per sample. All sample information is transferred directly from the Bohdan software into the Winlab32 software, eliminating the need to enter the data twice. Only 4 mL of diluted solution is required for the analysis. Cobalt is used during the analysis as an internal standard for the additive elements to overcome the matrix suppression caused by different oil viscosities. Since the additive elements are organic-metallic and soluble in the oil, the use of an internal standard provides a more accurate result. The wear metal elements are suspended in the oil matrix and the results compare more favorably to other analysis techniques (such as AA) if an internal standard is not used for these elements.

RESULTS AND DISCUSSION

Below are the results obtained for the analysis of used oil utilizing the Optima 4300 DV. Analysis time per sample is 45 seconds, which includes washing between samples and two replicate readings per sample. Two check standards for low (wear metal - 30 ppm) and high concentrations (additive elements – 1600 ppm), are analyzed every 10 to 15 samples with limits set at ±10%. With the stability of the Optima 4300, the check standards

rarely fail in an 8-10 hour period. If a check standard should fail, the action selected in the software is to recalibrate, rerun the check standard to verify it is within limits, and then rerun all samples since the last acceptable check standard.

CONCLUSION

The Optima 4300 handles the diluted oil matrix very easily and increases sample throughput over previous Optima models to 45 seconds per samples with no carryover between samples. The Optima 4300 is the ideal ICP spectrophotometer for oil laboratories with moderate to very heavy workloads.

Note:
This paper was also published in Petro Industry News, pg. 10 (October 2000).

Process: Spectral Overlap and Background Correction (BGC)

F'n	Analyte	Overlap Correction	Background Correction	BGC1	BGC2
A	Al	None	2-Point	-0.039	0.023
A	Ca	None	2-Point	-0.038	0.041
A	Cr	None	2-Point	-0.027	0.019
A	Cu	None	2-Point	-0.043	0.039
A	Fe	None	2-Point	-0.027	0.027
A	K	MSF	None		
A	Mg	None	2-Point	-0.025	0.022
A	Mo	None	2-Point	-0.017	0.018
A	Na	MSF	None		
A	Ni	None	2-Point	-0.026	0.036
A	P	None	1-Point	0.017	
A	Pb	None	2-Point	-0.033	0.020
A	Si	None	2-Point	-0.030	0.020
A	Sn	None	2-Point	-0.010	0.021
A	Zn	None	2-Point	-0.030	0.036
IS	Co IS	None	1-Point	0.044	

IEC Table : None MSF Table : oil.msf

QC Samples: Concentrations and Limits

QC 1: 30 S-21+K Concentration Units: Calibration

Analyte	Units	Conc	Lower Limit	Upper Limit
Al	ppm	30	27.0	33.0
Cr	ppm	30	27.0	33.0
Cu	ppm	30	27.0	33.0
Fe	ppm	30	27.0	33.0
K	ppm	30	27.0	33.0
Mo	ppm	30	27.0	33.0
Na	ppm	30	27.0	33.0
Ni	ppm	30	27.0	33.0
Pb	ppm	30	27.0	33.0
Si	ppm	30	27.0	33.0
Sn	ppm	30	27.0	33.0

QC 2: Ca, P, Zn Concentration Units: Calibration

Analyte	Units	Conc	Lower Limit	Upper Limit
Ca	ppm	5000	4500.0	5500.0
P	ppm	1600	1440.0	1760.0
Zn	ppm	1600	1440.0	1760.0

Schedule for QC Analyses

ID	QC Sample	After Init.Cal	After Recal	Periodic	Freq	At End
QC1	30 S-21+K	Yes	Yes	Yes	1	Yes
QC2	Ca, P, Zn	Yes	Yes	Yes	1	Yes

Periodic timing of Analyses

Frequency
Same for all QCs : 11

Failure Actions for QCs

QC	Sample ID	Times to Retry QC	When All Tries Fail	Additional Message
QC1	30 S-21+K	1	Recal & Rerun	
QC2	Ca, P, Zn	1	Recal & Rerun	

Remarks

Torch position -4.0, 1.2 alumina injector

Results for a used oil and a QC showing analysis time and QC recovery values are shown below.

```
============================================================
Sequence No.: 1                              Autosampler Location: 24
Sample ID: 003016                            Date Collected: 8/16/00 10:07:16 AM

------------------------------------------------------------
Mean Data: 003016
                  Mean Corrected          Calib                        Sample
Analyte              Intensity      Conc. Units      Std.Dev.      Conc. Units      Std.Dev.   RSD
Co IS                 26445.7         75 %              0.5                                    0.63%
Al                      172.5          1 ppm            0.1          1 ppm              0.1   5.29%
Ca†                  1393084.4       2271 ppm           11.1       2271 ppm             11.1   0.49%
Cr                      16.7          0 ppm            0.1          0 ppm              0.1  33.27%
Cu                    1235.8          1 ppm            0.0          1 ppm              0.0   0.14%
Fe                    3516.5          5 ppm            0.0          5 ppm              0.0   0.91%
K                      108.0          1 ppm            0.1          1 ppm              0.1  10.91%
Mg†                  37480.0        442 ppm            4.9        442 ppm              4.9   1.11%
Mo                      12.9          0 ppm            0.1          0 ppm              0.1  29.56%
Na                    1260.2          2 ppm            0.2          2 ppm              0.2  14.89%
Ni                     -19.8          0 ppm            0.0          0 ppm              0.0  23.98%
P†                   16770.2        928 ppm            8.1        928 ppm              8.1   0.88%
Pb                      15.3          1 ppm            0.1          1 ppm              0.1  20.53%
Si                     149.0          1 ppm            0.0          1 ppm              0.0   2.17%
Sn                     -11.1         -1 ppm            0.0         -1 ppm              0.0   4.19%
Zn†                  484250.5       1080 ppm            0.8       1080 ppm              0.8   0.07%


============================================================
Sequence No.: 36                              Autosampler Location: 2
Sample ID: 30 S-21+K                         Date Collected: 8/16/00 10:08:00 AM

------------------------------------------------------------
Mean Data: 30 S-21+K
                  Mean Corrected          Calib                        Sample
Analyte              Intensity      Conc. Units      Std.Dev.      Conc. Units      Std.Dev.   RSD
Co IS                 31348.6         89 %              0.6                                    0.63%
Al                     4732.3         29 ppm            0.6          29 ppm             0.6   2.05%
   QC value within limits for Al  Recovery = 97.59%
Ca†                   18675.3         30 ppm            0.0          30 ppm             0.0   0.15%
Cr                     2407.3         30 ppm            0.3          30 ppm             0.3   0.98%
   QC value within limits for Cr  Recovery = 99.21%
Cu                    63358.6         30 ppm            0.8          30 ppm             0.8   2.85%
   QC value within limits for Cu  Recovery = 98.86%
Fe                    23325.1         31 ppm            0.2          31 ppm             0.2   0.65%
   QC value within limits for Fe  Recovery = 102.38%
K                      2916.9         30 ppm            0.4          30 ppm             0.4   1.46%
   QC value within limits for K  Recovery = 98.40%
Mg†                    3621.8         43 ppm            3.2          43 ppm             3.2   7.39%
Mo                      992.9         30 ppm            0.3          30 ppm             0.3   0.97%
   QC value within limits for Mo  Recovery = 99.24%
Na                    23789.4         28 ppm            2.3          28 ppm             2.3   8.01%
   QC value within limits for Na  Recovery = 94.54%
Ni                     5303.5         29 ppm            0.0          29 ppm             0.0   0.09%
   QC value within limits for Ni  Recovery = 97.90%
P†                      535.9         30 ppm            0.2          30 ppm             0.2   0.60%
Pb                      703.8         30 ppm            0.2          30 ppm             0.2   0.65%
   QC value within limits for Pb  Recovery = 99.22%
Si                     4670.4         28 ppm            0.2          28 ppm             0.2   0.75%
   QC value within limits for Si  Recovery = 94.80%
Sn                      332.7         29 ppm            0.2          29 ppm             0.2   0.62%
   QC value within limits for Sn  Recovery = 96.58%
Zn†                   15946.5         36 ppm            1.3          36 ppm             1.3   3.71%
All analytes passed QC.
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A Random Testing of Table Wines for Arsenic Using Electrothermal Atomic Absorption Spectrometry

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ABSTRACT

An atomic absorption spectrometric method is described for the determination of total arsenic in table wines. A Zeeman background correction atomic absorption spectrometer was used for this study. The complex matrices in the wine were considerably reduced by evaporating the aqueous phase and then digesting the residue with concentrated nitric acid. Using palladium nitrate as the matrix modifier, the determination was successfully carried out in wines containing different levels of dissolved solids. An arsenic electrodeless discharge lamp was used to get better detection limits. Calibration curves from aqueous standards were used to calculate the detection limits of the analyte. The average detection limit (15 repetitive measurements of the blank), calculated as 3σ/slope of the calibration curve, was 0.5 µg/L. A random survey of a limited number of domestic and imported table wines was conducted to monitor the concentration levels of arsenic. The arsenic concentrations in these samples were found to be significantly lower than the maximum tolerance level of 50 µg/L in bottled water and in drinking water, set by the United States Food and Drug Administration and the Environmental Protection Agency.

INTRODUCTION

One of the strategic goals of the Bureau of Alcohol, Tobacco and Firearms (ATF) is to ensure public safety through random analyses of regulated products for toxic metals. Wines, distilled spirits, and malt beverages are the three major classes of alcoholic beverages that are monitored by the bureau through its laboratories. The ATF National Laboratory Center located at Rockville, Maryland, USA, conducted a random survey of the concentrations of some of the commonly occurring toxic metals in alcoholic beverages. This paper summarizes the methodology and the results of a study on arsenic concentrations in table wines. In some wine-producing countries, arsenic-bearing pesticides are permitted for use in viticulture. Thus, this study was undertaken to screen some wines for arsenic and to ensure that table wines will not have any health implication for the consumer.

The arsenic in table wines may originate from the soil, irrigation water, or pesticides used in viticulture. There are several papers on the determination of total arsenic in different matrices with atomic absorption spectrometry. But, most of the recent papers describe the speciation of arsenic compounds, because the toxicity depends on the chemical form of the element, with As(III) being the most potent, followed by As(V), then monomethylarsenate, and finally dimethylarsenate (1). When ingested, inorganic arsenic may cause acute or chronic toxicity. Arsenic is also of concern as a carcinogen, causing skin cancer (2). Epidemiological evidence supports the conclusion that arsenic is a human carcinogen associated mainly with skin cancer by ingestion, with lung cancer by inhalation, and with bladder cancer by drinking water (3). These facts demonstrate the need for determining arsenic concentrations in wines. Arsenic is found in all waters, with an average concentration approaching 1 to 2 µg/L (4). The dissociation of arsenic-bearing minerals is the most important source of inorganic arsenic in groundwater (5). In addition, anthropogenic, plant, and animal sources can add to the arsenic content in surface water. Recent papers on arsenic describe speciation with High Pressure Liquid Chromatography (HPLC) and hydride generation atomic absorption spectrometry (6). The speciation has also been achieved by coupling HPLC with inductively coupled plasma atomic emission spectrometry (ICP-AES) (7-9). Although HPLC/IC-AES has been very useful, it does not have the high sensitivity needed for arsenic trace determination. The coupling of HPLC with inductively coupled plasma mass spectrometery (ICP-MS) has been found to be extremely effective in determining ultra-trace elements because of its high sensitivity, large dynamic range, and isotope ratio measurement capability. This technique has been used for arsenic speciation of biological samples in recent years (10-14). Atomic absorption spectrometry (AAS) with both flame and graphite furnace atomizers has been used as a method of HPLC detection (HPLC/AAS) for the speciation of arsenic (15-16). In this paper, a simple method of wine analysis for total arsenic using graphite furnace atomic absorption spectrometry has been described. The data generated by this study revealed that arsenic in wines is significantly lower than the levels in drinking water established by the U.S. Food and Drug Administration and the U.S. Environmental Protection Agency.

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EXPERIMENTAL

Instrumentation

A PerkinElmer Model 5100 PC atomic absorption spectrometer with Zeeman background correction (PerkinElmer, Norwalk, CT, USA) was used for this study. The spectrometer was equipped with an AS-60 autosampler, an HGA®-600 furnace, and a Hewlett-Packard DeskJet® 695C printer. Graphite tubes (PerkinElmer Part No.B0 137111) and L'vov platforms (Perkin-Elmer Part No.B0 137112) were used for this study. An arsenic electrodeless discharge lamp (PerkinElmer Part No.N305-0605) was kept at 300 mA. The slit width was 0.7 nm and measurements were made at the 193.7-nm wavelength. The time of integration was 5 seconds for all measurements. Pure argon (99.99%) was used for purging. The instrumental parameters for the furnace analysis are listed in Table I. Peak area measurements were used for data calculation.

Reagents and Standard Solutions

All chemicals and reagents used were of analytical grade. Arsenic standard and nitric acid were obtained from Fisher Scientific (Chicago, IL, USA). Palladium nitrate [Pd $(NO_3)_2$] was purchased from Sigma Chemical Company (St. Louis, MO, USA). Arsenic standards for calibration (5, 10, 20 ppb) were prepared from a 100-ppb stock solution. Water for this study was deionized with a deionizer (Solution Consultants Inc., Jasper, GA, USA). A standard reference material containing trace metals in Drinking Water (Lot #904020) was obtained from High Purity Standards (Charleston, SC, USA). This standard was used to check the accuracy of the calibration method.

TABLE I
Furnace Time/Temperature Program

Step	1	2	3	4	5
Temp (ºC)	120	1300	20	2100	2600
Ramp (s)	10	1	1	0	1
Hold (s)	50	30	15	5	5

TABLE II
Recovery Data for Arsenic in Wines

Sample No.	Present (µg/L)	Added (µg/L)	Found (µg/L)	%Recovery[a]
1 Red wine	0	10	10	100
2 Red wine	1	10	12	109
3 White wine	0	15	15	100
4 White wine	1	15	15	94

[a]Each value is an average of three measurements with RSD <10%.

Sample Preparation

Exactly 10 mL of the wine sample was transferred into a 50-mL Teflon® beaker and evaporated at 100ºC in a Labconco Rapid Digestor (Labconco Corp. Kansas City, MO, USA) to dryness. The residue was then digested with 5 mL of concentrated nitric acid at 110ºC until the volume was reduced to approximately 1 mL. At this stage, the solution was cooled to room temperature and then diluted to 10 mL with deionized water. All of the wine samples gave clear solutions upon acid digestion. These solutions were directly analyzed with the graphite furnace atomic absorption spectrometer. The matrix modifier, palladium nitrate, was prepared by digesting the powder in 10 mL aqua regia and evaporating the acid at 110ºC. The residue was then redissolved in a 4M nitric acid to make the 200 ppm Pd solution.

Calibration

Standard solutions of arsenic (2, 5, 10, 20 ppb) were used to obtain calibration curves. Throughout this study, the sensitivity, the correlation coefficient, and the detection limit were regularly monitored. The correlation coefficient ranged from 0.9995 to 0.9999. The detection limit was calculated as 3σ/slope of the calibration curve. The average detection limit was 0.5 µg/L. The average measurement limit (10σ/slope of calibration curve) was 2 µg/L.

Autosampler Program

The autosampler was programmed to inject microliter amounts of 2, 5, 10, and 20 µg/L arsenic standards. A typical 30-µL injection consists of 20 µL of standard, blank, or sample; 5 mL of the matrix modifier, and 5 mL of the diluent [0.3% (v/v) nitric acid]. The sample analysis was followed by recovery determination. The autosampler was programmed to inject 20 mL of sample, 5 µL of matrix modifier, and 5 µL of 20 µg/L arsenic standard for spike recovery. Thus, a set of data consisting of calibration, sample analysis, and spike recovery was obtained for each sample.

RESULTS AND DISCUSSION

Matrix Modifier

Several matrix modifiers that are commonly used in atomic absorption spectrometry were tried during

the method development phase. These included magnesium, palladium, sulfuric acid, ammonium chloride, phosphoric acid, and ammonium dihydrogen phosphate [$NH_4H_2PO_4$]. The effects of these compounds were evaluated individually and in combination. All of the modifiers except palladium showed only moderate effect in reducing the background absorption. The spike recoveries were in the 50-80% range. Only a solution of palladium nitrate containing 200 ppm Pd was found to be effective in reducing the background and facilitating spike recoveries that ranged 94 to 109%.

Method Validation

The evaporation and acid digestion of wine samples at 100ºC and 110ºC, respectively, were investigated to check for any loss of arsenic. To accomplish this, wines with known arsenic concentrations were spiked with known quantities of arsenic before evaporation and acid digestion. The acid-digested samples were then analyzed with the GFAAS technique using palladium nitrate as the matrix modifier. The recoveries ranged from 94 to 109%, showing that the acid digestion and evaporation do not result in loss of arsenic. Because a standard reference sample for arsenic in wines was unavailable, the validation was based on comparison of the results from the calibration method with those obtained by standard addition and on the results of the spike recoveries.

Applications

The analytical method described above was applied to determine total arsenic concentration (i.e., both free and bound arsenic) in domestic and imported wines. Tables III and IV provide data on total arsenic content in domestic wines. The concentrations of arsenic in most of the domestic samples were lower than the detection limit (0.5 ppb) and those samples that were found to contain arsenic had only about 1 to 3 ppb. These results indicate that the arsenic concentrations in domestic wines are significantly lower than the maximum tolerance level of 50 µg/L in bottled water and in drinking water set by the United States Food and Drug Administration (17) and the Environmental Protection Agency (18), respectively. The concentrations of arsenic in some of the imported wines are given in Tables V and VI. None of the samples showed an arsenic level higher than the FDA/EPA tolerance limit in water. The arsenic concentrations in imported wines ranged from

TABLE III
Arsenic in U.S. Wines
White Wines

No.	State	As (µg/L)[a]
1	California	2
2	Florida	1
3	Louisiana	0
4	Maryland	1
5	Michigan	0
6	New Jersey	2
7	New York	0
8	North Carolina	0
9	Oregon	0
10	Texas	0
11	Virginia	0
12	Washington	0

[a]Each value is an average of three measurements with RSD <10%.

TABLE IV
Arsenic in U.S. Wines
Red Wines

No.	State	As (µg/L)[a]
1	Arkansas	2
2	Colorado	1
3	Georgia	1
4	Idaho	1
5	Indiana	3
6	Maryland	0
7	Michigan	1
8	Missouri	1
9	New York	1
10	North Carolina	0
11	Oregon	1
12	Texas	2
13	Utah	0
14	Virginia	0
15	Washington	0
16	Wisconsin	2

[a]Each value is an average of three measurements with RSD <10%.

TABLE V
Arsenic in Imported Wines
White Wines

No.	Country of Origin	As (µg/L)[a]
1	Argentina	2
2	Australia	6
3	Austria	7
4	Brazil	9
5	Chile	14
6	France	7
7	Germany	12
8	Greece	0
9	Hungary	6
10	Israel	0
11	Italy	3
12	New Zealand	5
13	Portugal	4
14	Slovenia	20
15	Spain	0

[a]Each value is an average of three measurements with RSD <10%.

TABLE VI
Arsenic in Imported Wines
Red Wines

No.	Country of Origin	As (µg/L)[a]
1	Argentina	16
2	Australia	7
3	Austria	4
4	Bulgaria	9
5	Chile	8
6	France	4
7	Georgia	3
8	Germany	12
9	Greece	2
10	Hungary	2
11	Israel	0
12	Italy	3
13	Portugal	4
14	Romania	5
15	Slovenia	3
16	South Africa	6
17	Spain	7

[a]Each value is an average of three measurements with RSD <10%

0 to 20 ppb and in domestic wines, the range was 0 to 3 ppb. This study suggests that arsenic levels in table wines should not be a matter of health concern for consumers.

CONCLUSION

The method described above can be used to determine total arsenic content in table wines on a routine basis. The data generated by this study show that the arsenic concentrations in the wines tested are significantly lower than the maximum tolerance limit of 50 ppb established by the U.S. Food and Drug Administration and the Environmental Protection Agency for drinking water.

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Determination of Mercury in Blood by Cold Vapor Atomic Spectrometry

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ABSTRACT

The determination of mercury in biological matrices, such as blood, urine, and hair, is an important indicator in the assessment of mercury contamination in the environment and at the work place.

Non-reactive alkyl compounds with stannous salts have been used by some authors for the differential determination of inorganic and organic mercury in cold vapor atomic spectrometry (CVAAS). However, this procedure does not allow for complete digestion of blood, which is an essential condition for flow injection systems in order to avoid the generation of foam that would block the flow of the carrier gas. Thus, a suitable and easy-to-use routine method for the determination of mercury based on appropriate sample digestion, followed by automated flow injection cold vapor reduction with $NaBH_4$, has been developed.

The method was optimized by varying the carrier gas flow rate and the concentration of the diluent solution. A carrier flow rate of 75 mL/min provides a high enough absorbance peak with adequate resolution in peak shape. Best results were obtained by diluting the digested samples and aqueous standards with 10% nitric acid and 20% sulfuric acid.

The limit of detection for whole blood was 0.95 nmol/L, with a linear range up to 600 nmol/L.

To determine the precision and accuracy of the method, three levels of Seronorm trace elements whole blood were analyzed. The precision had a mean value of 3.7%. The accuracy was confirmed with the analysis of 24 samples of unknown concentration from the Quebec Interlaboratory Quality Control Program.

INTRODUCTION

Humans can be exposed to inorganic and organic mercury compounds from different sources. The general population is exposed to mercury primarily through diet and dental amalgam. Although the average daily intake from dental amalgam fillings is low, there is a considerable variation as some people have a higher mercury uptake from the amalgam fillings (1). Depending on the concentrations found in air and water, significant contributions to the daily intake of total mercury can occur (2).

The determination of mercury in various biological matrices, particularly blood, urine, and hair, is important for the assessment of mercury contamination in the environment and at the work place. Biological monitoring has become an important tool in environmental and occupational medicine for the assessment of the level of internal exposure to harmful substances taken up from the general environment (3). Biological monitoring is used to assess exposure, absorbed dose, body burden, or concentration in critical organs, or risk of adverse effects. The maximum value of mercury concentration in blood (B-Hg) is seen on the day of exposure, after which it decreases, with a half-time of about 3 days after a single low-level exposure (4). Its rapid rise after exposure makes B-Hg an excellent indicator of recent peaks in mercury exposure (5).

Techniques such as electrothermal atomic absorption spectrometry (ETAAS) (6,7), inductively coupled plasma mass spectrometry (ICP-MS) (8-11), nuclear magnetic resonance (NMR) (12), gas chromatography with mass spectrometry (GC-MS) (13), and potentiometric stripping analysis (PSA) (14) have been used for the determination of mercury. However, cold vapor atomic absorption spectrometry (CVAAS) (15-24) is preferably employed, because of its extremely high sensitivity, the absence of background attenuation-type spectral interferences, and the relatively low operating costs (15, 25,26). To improve the sensitivity of this technique, a preconcentration step with gold amalgamation (27,28) or a fluorescence detector in cold vapor atomic fluorescence spectrometry has been utilized (CVAFS) (29-31), as well as both of them in cold vapor atomic fluorescence spectrometry with gold amalgamation (32).

A review of the literature describing the determination of mercury suggests that a simple strong acid-permanganate digestion is not adequate to totally oxidize alkylmercury compounds. When this digestion scheme was applied to samples containing methyl or ethyl mercury, complete recovery was never attained regardless of the concentration of potassium permanganate (21). It is significant to note that the acid digestion-reduction procedures of the methods described in the seventies are still in general use today (21).
A bewildering variety of combinations of strong acids (HCl, $H2_SO_4$, HNO_3), oxidants (H_2O_2, $KMnO_4$, $K_2Cr_2O_7$, $K_2S_2O_8$), UV irradiation, and elevated temperatures and pressure have been used and recommended for off-line digestion (33). Although stannous chloride

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or stannous sulfate is a more specific Hg reductant than tetrahydroborate, most authors utilized either stannous chloride or stannous sulfate to reduce Hg(II) (15-21). Some authors have reported methods using sodium tetrahydroborate as the reductant (22-24), which can more readily attack organic mercury compounds (22).

The non-reactive alkyl compounds, especially with stannous salts, have been used by some authors for the differential determination of inorganic and organic mercury (21,28,34). However, complete digestion of blood is an essential step for analysis of the samples with currently available flow injection systems in order to avoid the generation of foam, which would block the flow of the carrier gas. Besides, this non-reactivity is not completely specific, approximately 2% of the methylmercury is degraded (28).

The purpose of this study was to develop an easy to use and reliable routine method for the determination of mercury, based on a sample digestion, followed by automated flow injection cold vapor reduction with $NaBH_4$.

EXPERIMENTAL

Instrumentation

A PerkinElmer flow injection mercury system FIMS™-400, equipped with an AS-90 autosampler, was used. A flow cell with a pathlength of 260 mm was used. The source was a low-pressure mercury lamp. A PTFE gas-liquid separator, with a PTFE-membrane to prevent humidity going to the cell, was used. The pump tubes used are summarized in Table I. The instrumental parameters are listed in Table II.

The FIMS program used is shown in Table III. The prefill time was 7 seconds, and the sampling time, performed in step 1, was 10 seconds. Subsequently, the sample (500 µL) was injected into the carrier stream and mixed with $NaBH_4$ solution in the chemifold. After mixing with the carrier gas, argon, the reaction products (mercury vapor, hydrogen, etc.) and the remaining liquid entered the gas-liquid separator. The absorption of the mercury vapor was measured into a cell where the gas was swept. This process was completed in step 2 within 25 seconds. The argon flow-rate was 75 mL/min.

TABLE I
Pump Tubes Used

	Pump tubing	Inner diameter (mm)	Color Code
Pump 1	Sample	1.52	Blue-yellow
Pump 2	Reagent carrier	1.52	Blue-yellow
	Reducing solution	1.14	Red-red
	Waste	3.18	Black-white

TABLE II
Instrumental Parameters

Wavelength	253.7 nm
Slit width	0.7 nm
Peak height mode	
Baseline offset correction time	2 s
Read delay	0 s
Smoothing points	9

TABLE III
Flow Injection Program (Sample volume 500 µL)

Step number	Time (s)	Pump 1 (rpm)	Pump 2 (rpm)	Valve	Read
Prefill	7	100	120	Fill	No
1	10	100	120	Fill	No
2	25	0	120	Inject	Yes

Reagents and Solutions

Water of 18 MΩ·cm of resistivity from a Milli-Q™ system (Millipore, Milford, USA) was always used for the solutions.

Silicon antifoaming agent: Dow Corning antifoaming 110 A, PerkinElmer Part No. B0507226.

Triton® X-100 reagent: p.a. grade, Merck, Darmstadt, Germany.

Nitric acid: Suprapur grade, Merck, Darmstadt, Germany.

Sulfuric acid: p.a. grade, maximum 0.0000005% Hg, Merck, Darmstadt, Germany.

Hydrochloric acid: p.a. grade, maximum 0.0000005% Hg, Merck, Darmstadt, Germany.

Reducing solution: 0.2% (w/v) $NaBH_4$; 0.05% (w/v) NaOH and with 0.1% of Dow Corning antifoaming 110 A. The solution must be freshly prepared.

Stabilizing solution: 0.5% $K_2Cr_2O_7$; 50% (v/v) HNO_3.

Carrier solution: 10% (v/v) HCl.

Stock reference solution: 10 mg/L of Hg (II) (PerkinElmer Part No. N930-0253).

Calibration solutions: Solutions having mercury concentrations of 0.0, 100, 250, and 500 nmol/L were prepared by further dilution of the

stock solution in water with 1% (v/v) of stabilizing solution.

Diluent solution: 10% (v/v) HNO_3 and 20% (v/v) H_2SO_4 in water.

Analytical Procedure

Place 1 mL of 0.2% Triton X-100 solution and add 0.5 mL of blood sample or calibration solution in a 50-mL polypropylene tube. Then add 0.1 mL of stabilizing solution. Add 1 mL of concentrated HNO_3 acid and 2 mL of concentrated H_2SO_4. Close the tube with a plastic stopper and let the mixture stand overnight at 60ºC. On the following day, and after cooling to room temperature, dilute to 10 mL with diluent solution. The determination is carried out according to the instrumentation parameters.

RESULTS AND DISCUSSION

Variation of Instrumental Parameters: Gas Flow Rate

With the same standard aqueous solution of 30 nmol/L, the argon flow rate was varied from 40 to 150 mL/min (see Figure 1). Although a gas flow rate of 50 mL/min provided the best absorbance, the 75 mL/min carrier flow rate was selected because of better resolution in peak shape.

Influence of Sulfuric and Nitric Acids

Because the final solution contains the acids used for the digestion and the concentration may vary, we need to know the influence of these acids on the analyte signal. We varied the concentration of these acids using a 30-nmol/L Hg(II) standard solution. First we varied the concentration of sulfuric acid with a fixed concentration (10%) of nitric acid. Figures 2 and 3 show that a sulfuric acid concentration of 20% (v/v) reults in the highest absorbance. In addition, small variations in the concentration of sulfuric acid do not result in a large change in peak height absorbance.

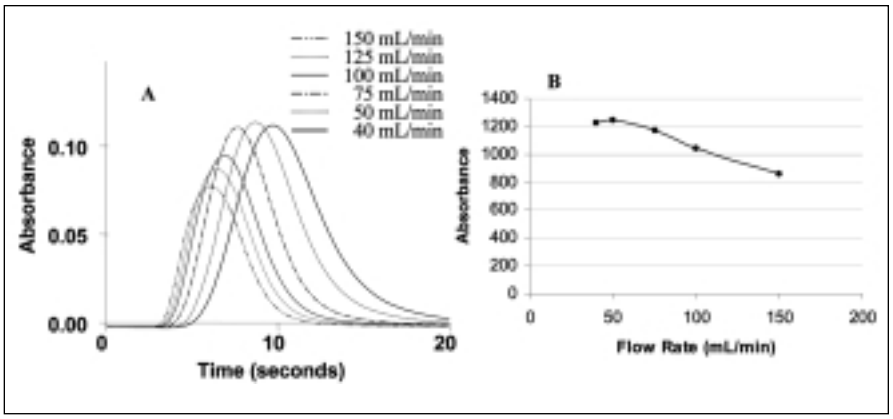

Fig. 1 (A and B). Variation of absorbance with the flow rate of the carrier gas. A: Different shapes of the absorbance peaks in relation to flow rate. B: Absorbance graph at different flow rates.

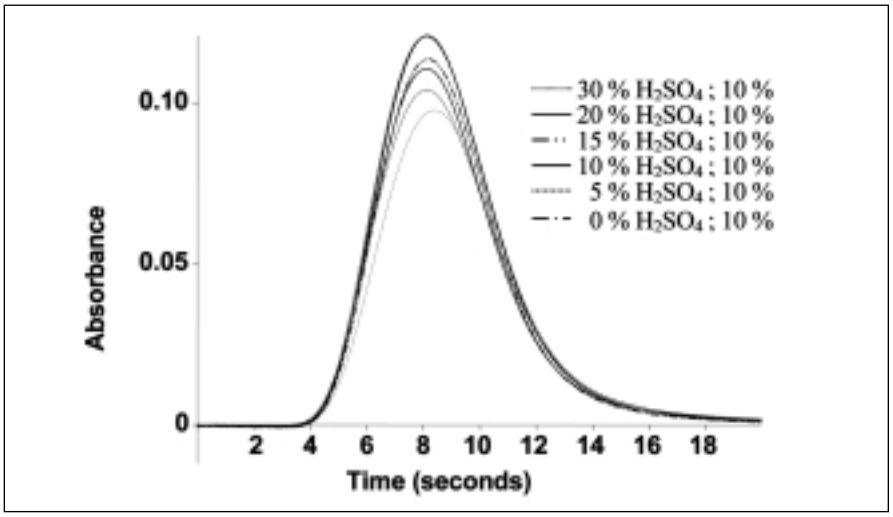

Fig. 2. Different absorbance peaks depending on the concentration of sulfuric acid.

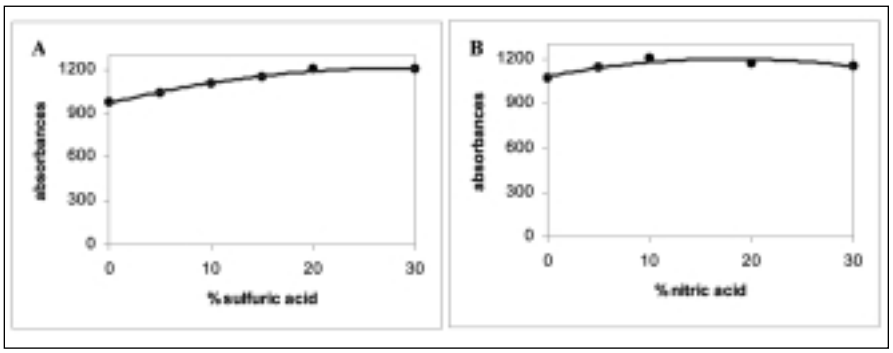

Fig. 3 (A and B). Variation of the absorbance with the concentration of sulfuric and nitric acids. A: Fixed concentration of nitric acid (10%) and variable concentration of sulfuric acid. B: Fixed concentration of sulfuric acid (20%) and variable concentration of nitric acid.

At a concentration of 20% sulfuric acid, we varied the concentration of nitric acid from 0% to 30%, which resulted in a maximum absorbance of 10% (v/v) nitric acid (see Figure 3B). The effect of nitric acid on absorbance is less important than the effect of sulfuric acid. It was found that small increments in the concentration of nitric acid did not cause a big variation in the absorbance. As a result of these experiments, a dilution solution containing 10% nitric acid and 20% sulfuric acid was used. It was found that the acid concentrations in the sample solutions (resulting from small variations in the acid concentrations due to the higher or lower presence of organic material in the digestion) resulted in only a small variation in the absorbance.

Interferences

The study of non-spectral interferences was carried out by comparing the slopes of the external calibration curves with those obtained by the method of standard additions. Each blood sample was analyzed three times using Seronorm level III, spiked with 100, 200 and 300 nmol of Hg(II) per liter.

The slope of the aqueous standard calibration curve ($2.301 \cdot 10^{-4}$ abs·L/nmol) was included within the confidence limits (p=0.05) of the standard additions curve ($2.333 \cdot 10^{-4} \pm 0.04 \cdot 10^{-4}$ abs·L/nmol). This implied the absence of non-spectral interferences in the CVAAS determination of mercury in whole blood under the proposed analytical conditions, and permitted the use of either external calibration curves or the standard additions method for quantification.

Linearity

A calibration curve with three aqueous standards of each of the concentrations 1, 2.5, 5, 10, 20, 30, 40 and 50 nmol/L was made. As can be seen in Figure 4, the calibration curve was linear up to 30 nmol/L. The slope of the calibration curve was $40.018 \cdot 10^{-4} \pm 0.388 \cdot 10^{-4}$ abs·L/nmol and the intercept $-4.898 \cdot 10^{-4} \pm 5.837 \cdot 10^{-4}$ abs·L/nmol, within the range up to 30 nmol/L, a determination coefficient of 0.9996, with a relative standard deviation (RSD) of the slope of 0.5%. The F parameter of the above-mentioned curve was 47320 with $p<0.001$.

Detection and Quantification Limits

Because the real blanks had no peak absorbance, the limit of detection was determined by extrapolating the standard deviation of the blank by a regression line of the standard deviations of the aqueous standards at low concentrations, within the range of 1 to 10 nmol/L of Hg(II). The intercept of this curve, 0.6334, was considered the standard deviation of the blank. Three times this parameter, divided by the slope of the calibration curve mentioned before, gives a limit of detection of 0.0475 nmol/L or 0.0095 µg/L. This result was confirmed with the repeated analysis of a mercury standard at the concentration of the determined limit of detection. For the blood sample using the method described, the limit of detection at 20 times dilution was found to be 0.95 nmol/L. Thus, the limit of quantification for the blood sample, based on 10 times the standard deviation of the blank, was 3.2 nmol/L.

Precision and Accuracy

To determine the precision and accuracy of the method, three levels of Seronorm trace elements whole blood, batches 404107, 404108, and 404109, were analyzed 10 times on three different days. This material is certified for total mercury. The results are shown in Table IV. The mean relative

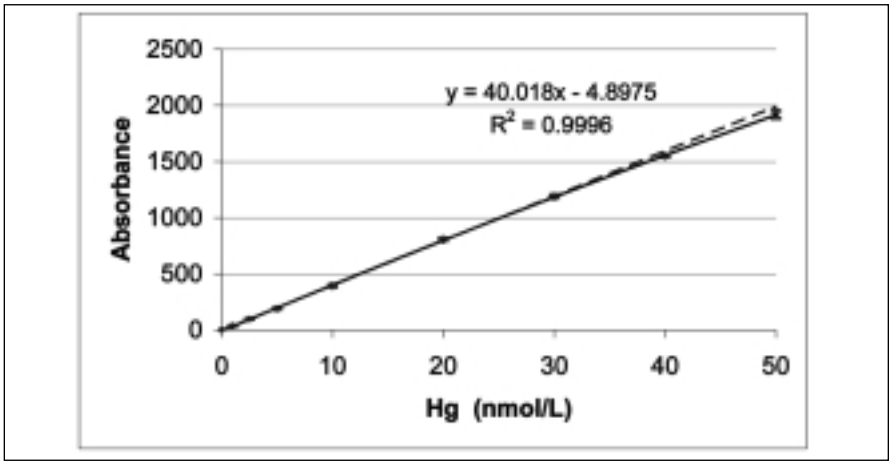

Fig. 4. Regression line for the mercury calibration up to 30 nmol/L and prolonged to 50 nmol/L in comparison with the curve obtained for all the concentrations up to 50 nmol/L.

TABLE IV
Determination of Hg in Three Levels of Seronorm Trace Elements Whole Blood Reference Control

Seromorm level	Observed Value		Recommended Value	
	(nmol/L)	RSD (%)	(nmol/L)	Range
1	13.1	5.0	15	11.0-16.5
2	41.8	2.6	40	33.5-42.0
3	69.8	2.5	70	67.5-82.0

standard deviation within-runs was 5.0%, 2.6%, and 2.5% for 15 nmol/L, 40 nmol/L, and 70 nmol/L, respectively. The mean relative standard deviation between-runs was 12.2%, 1.0%, and 3.4% for the same concentrations.

The precision had a mean value of 3.7% for the results obtained over three days.

The mean value of the three days for each concentration level was included within the given analytical range.

The accuracy was checked with the analysis of 24 samples of unknown concentration from the Quebec Interlaboratory Quality Control Program. Whole blood samples known to be supplemented with either inorganic or organic mercury from the Quebec Interlaboratory Quality Control Program were analyzed. The results are shown in Table V. Only one of the results of the 24 samples was out of acceptable range value (see Figure5).

CONCLUSION

This study shows that the dilution of the digested sample with 10% nitric acid and 20% of sulfuric acid gives a higher stability in a peak absorbance.

The linearity is lost starting with 30 nmol/L when aqueous standards are used. Taking into account the dilution factor used (1:20), a working range of up to 600 nmol/L in blood samples can be used. This working range is big enough to include almost all types of blood samples for this type of analysis.

The detection limit for the aqueous standards is excellent, 0.0475 nmol/L ($9.5 \cdot 10^{-3}$ µg/L). This implies that using the proposed method, a detection limit of 0.95 nmol/L can be obtained for whole blood, which enables to detect even the lowest concentrations that may occur.

TABLE V
Interlaboratory Comparison Program
(Samples received from the Centre de Toxicologie du Quebec)

ID	Specie	Observed value (nmol/L)	Target value (nmol/L)	Acceptable range (nmol/L)
M99-04	Organic	122	120	91-149
M99-05	Inorganic	59	55	39-71
M99-06	Organic	33	27	17-37
M99-07	Organic	19	8	1-15
M99-08	Organic	87	75	55-95
M99-09	Inorganic	54	45	31-59
M99-10	Inorganic	132	135	103-167
M99-11	Organic	29	27	17-37
M99-12	Inorganic	22	22	13-31
M99-13	Inorganic	22	14	6-22
M99-14	Inorganic	95	90	67-113
M99-15	Organic	40	35	23-47
M99-16	Organic	61	65	47-83
M99-17	Inorganic	15	15	7-23
M99-18	Inorganic	59	60	43-77
M00-01	Organic	242	235	184-286
M00-02	Organic	15	17	8-26
M00-03	Inorganic	54	57	41-73
M00-04	Inorganic	136	135	103-167
M00-05	Organic	74	75	55-95
M00-06	Inorganic	41	45	31-95
M00-07	Organic	43	40	27-53
M00-08	Inorganic	8	10	3-17
M00-09	Organic	166	165	127-203

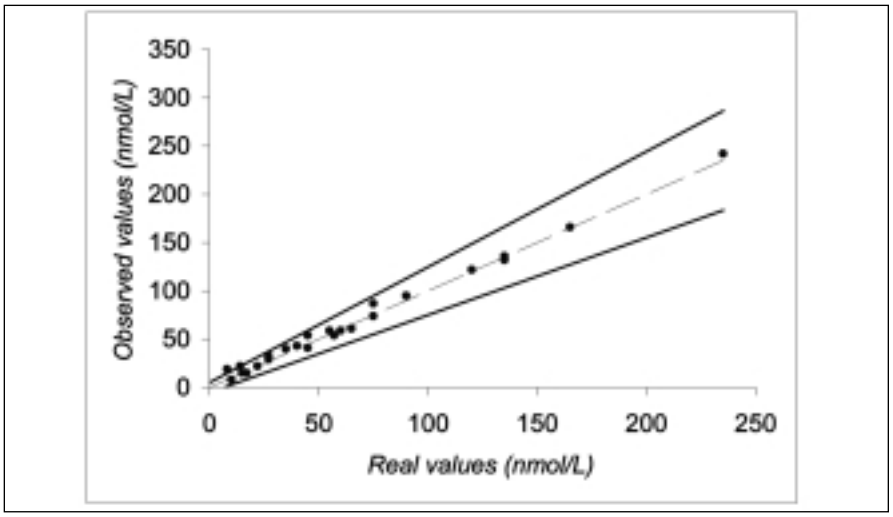

Fig. 5. Results obtained from samples provided by the Quebec Interlaboratory Comparison Program between lines representing the acceptable range and the target value.

The precision (RSD 3.7 %) is adequate to the objectives and to the low concentrations of analysis.

The results obtained for the Interlaboratory comparison program indicates that the method proposed provides accurate results.

Thus, a simple and routine method for the determination of total mercury in whole blood samples using the flow-injection mercury system has been described.

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Emulsion Liquid Membrane Separation of As(III) and As(V) With Subsequent Determination by Electrothermal AAS

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ABSTRACT

Liquid membranes consisting of L113A (surfactant), liquid paraffin (stabilizer), and kerosene (solvent) were used to separate arsenic(III) and arsenic(V) with HCl solution as the external phase and NaOH solution as the internal phase, followed by their determination with electrothermal atomic absorption spectrometry (ETAAS) using Ni salt as the matrix modifier. The effects on the recovery of arsenic were studied and the optimum conditions of separation and determination established. Total arsenic was determined after As(V) was reduced to As(III) by addition of sufficient KI and As(V) was determined by subtracting the value of As(III) from total arsenic. The RSD of As(III) and As(V) was less than 4% and the limit of detection up to several μg L^{-1}. The interference of most foreign ions was avoided. The method was applied to aqueous samples with satisfactory recoveries of more than 93.8%.

INTRODUCTION

The widespread occurrence of arsenic in the environment, resulting from natural processes and human activities (1,2), is hazardous due to the carcinogenic and mutagenic properties of arsenic. The predominant arsenic species are arsenite [As(III)] and arsenate [As(V)] (3). Because the toxicity of arsenic is dependent on its oxidation state (4), it is necessary to apply a method selective enough to determine As(III) and As(V) separately. The established method of extraction and separation of As(III) and As(V) with HCl has been proved to be an effective method for quantitative determination (5); however, poisonous solvents such as toluene are used in these extractions.

Emulsion liquid membrane (ELM) separation has the advantage of being efficient, rapid, selective, and simple (6). The system of using a liquid membrane solution with concentrated HCl (6•10 mol L^{-1}) has been used to recover As(III) in aqueous solutions (7). The determination of total arsenic was achieved by the emulsion liquid membrane separation with KI and HCl (8). The valence analysis of As(III) and As(V) was reported, but poisonous CCl_4 was used in this procedure, resulting in a detection limit up to 200 μg L^{-1} (9).

The purpose of this study was to establish a method for the valence analysis of trace arsenic, based on ELM separation without using hazardous solvents, and subsequent determination by electrothermal atomic absorption spectrometry (ETAAS). In concentrated HCl solutions, As(III) forms $AsCl_3$ which permeates through the liquid membrane (organic membrane) into the inner phase where $AsCl_3$ is hydrolyzed to AsO_3^{3-} and cannot go back to the external phase (7). However, As(V) probably forms $[AsCl_4]^+[AsCl_6]^-$ which cannot permeate the liquid membrane (10) and thus, As(III) and As(V) are effectively separated. The emulsion after separation is emulsified with isoamyl alcohol as the chemical emulsifier, followed by the determination of arsenic in the encapsulated phase (aqueous phase) by ETAAS using Ni salt as the matrix modifier. After reduction of As(V) to As(III) with sufficient KI, total arsenic can be determined and the concentration of As(V) can be obtained by subtracting the value of As(III) from total arsenic.

ETAAS is a sensitive method for the determination of trace substances after ELM separation. The recoveries of Pb (11,12), Au (13), Sc (14), and Cu (15) are excellent when using this combined technology. This investigation applied ELM and ETAAS to determine trace arsenic in aqueous samples with a limit of detection up to several μg L^{-1} and achieving a recovery of about 95%. The results were found to be satisfactory.

EXPERIMENTAL

Instrumentation

A Model JJ-1 motor-driven stirrer (o•2500 r min^{-1}) and an ONO SOKKI Model HT-431 tachometer (Japan) were used. For ETAAS analysis, a Model WFX-110 electrothermal atomic absorption spectrophotometer (Ruili Analytical Instrument Company, Beijing, China) was used. The instrumental parameters are given in Table I.

TABLE I
Instrumental Parameters

Lamp current	2.5 mA
Wavelength	193.7 nm
Carrier gas	Ar, 600–800 mL min^{-1} (stop flow during atomization)
Slit width	0.4 nm
Measuring mode	Peak absoption
Sample volume	10 μL

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Reagents and Standard Solutions

All reagents were of analytical reagent grade. Stock standard solutions of As(III) (500 mg L^{-1}) were prepared by dissolving 0.6600 g As(III) oxide in 10 mL of 20% NaOH solution, and adding 20 mL of 1 mol L^{-1} H_2SO_4 solution to make it acidic, then diluting to 1000 mL with distilled water. Other standard As(III) solutions were obtained daily from the 500 mg L^{-1} As (III) stock solution.

As(V) stock solution (50 mg L^{-1}) was prepared by adding 5 mL of 30% hydrogen peroxide solution to 10 mL of 500 mg L^{-1} As(III) standard solution, then drying by heating. Ten mL H_2O was added and the solution dried once more to remove the H_2O_2 completely. The sediment was dissolved by adding H_2O and then made up to 100-mL volume.

Kerosene bought from a local market was treated with concentrated H_2SO_4 and neutralized with $NaHCO_3$ solution.

10% (v/v) L113A solution (product code of monoalkenyl succinimide, produced by Lanzhou Oil Refinery, China) was prepared by adding 20 mL L113A to 180 mL kerosene.

For ETAAS analysis, a 10% $Ni(NO_3)_2 \cdot 6H_2O$ solution was used as the matrix modifier.

Analytical Procedures

Determination of As(III)

A water-in-oil emulsion was prepared just before use. L113A solution, liquid paraffin, kerosene, and NaOH solution were added in appropriate amounts to a 50-mL polyethylene vial. The mixture was stirred at about 2000 r min^{-1} with an inserted glass propeller for half an hour after which a pale yellow emulsion was obtained. Ten mL emulsifier was added to 50 mL feed solution containing trace As(III) and concentrated HCl. This solution was stirred at 450 r min^{-1} for 15 minutes. After letting the solution stand for 5 minutes, the aqueous layer below the emulsion was drained off. Ten mL H_2O was used to clean the propeller and 6 mL isoamyl alcohol was added as the chemical emulsifier. After slight stirring in a boiling water bath for about 5 minutes, the emulsion emulsified into two clear layers. The aqueous phase (the lower layer containing NaOH) was transferred into a 25-mL volumetric flask.

For ETAAS analysis, 6 mL of 2 mol L^{-1} HNO_3 solution was added to make the aqueous phase acidic and 0.5 mL of 10% $Ni(NO_3)_2$ solution was added as the matrix modifier. The solution was then brought to volume with water. Ten µL of the solution was transferred to the spectrophotometer by the autosampler and the peak absorption of arsenic was determined as specified. The optimum heating program for ETAAS analysis is listed in Table II.

TABLE II
Heating Program of AAS

Stage	Temperature (°C)	Time (s)
Drying	100	15
Ashing	800	15
Atomization	2500	3

Determination of As(V)

Total arsenic was determined using the same method as for the determination of As(III) by reducing As(V) to As(III) in a 50-mL solution containing arsenic and HCl after adding sufficient KI (see below). The concentration of As(V) was obtained by subtracting the value of As(III) from the total arsenic.

RESULTS AND DISCUSSION

Optimization of the Separation Conditions

Effect of agitation speed

The emulsion cannot disperse completely at very low stirrer speed; on the other hand, at very high stirrer speed, the breakage rate and agitation-induced swelling (water transport) were also high. In this experiment, the absorbance of arsenic increased with an agitation speed of 250 to 450 r min^{-1} and there was no obvious change in the absorbance over 450 r min^{-1}. The agitation speed of 450 r min^{-1} was selected for this study.

Effect of extraction time

Because of the rapid transport speed due to the thin membrane and the large surface areas, the needed extraction time is short. It was found that the absorbance of arsenic increased when the time was under 15 minutes. No obvious difference in absorbance appeared over 15 minutes. Thus, 15 minutes was sufficient for the extraction.

Effect of HCl concentration on the external phase

The absorbance of As(III) increased sharply with an increase in HCl concentration (see Figure 1). The feed solution containing 100 µg L^{-1} As(III) was stirred with the emulsifier (made up with 6% L113A, 4% liquid paraffin, 90% kerosene, and 2 mol L^{-1} NaOH solution) at 450 r min^{-1} for 15 minutes. R_{ew}=0.2 and R_{oi}=2/3. For ETAAS analysis, the ashing temperature used was 1100°C, while all other temperatures were the same as listed in Table I. There was no obvious change in the absorbance for HCl concentrations between 8 and 9 mol L^{-1}. It was clear that the HCl concentration was a decisive factor in this system. A feed solution containing 8 mol L^{-1} HCl seemed optimal.

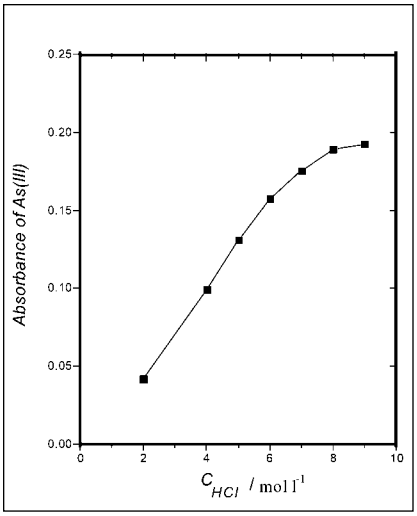

Fig. 1. Effect of HCl concentration on the absorbance of As(III).

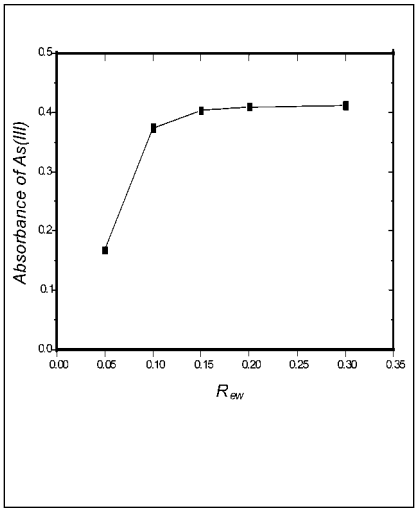

Fig. 2. Effect of R_{ew} on the absorbance of As(III).

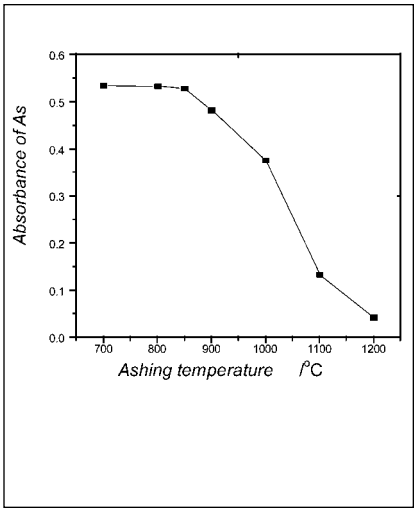

Fig. 3. Effect of ashing temperature on the absorbance of As.

Effect of NaOH concentration on the internal phase

NaOH solution was used to strip As(III) extracted into the organic membrane. The absorbance of As(III) increased slowly with an increase in concentration of NaOH from 0 to 2 mol L^{-1}, but there was no obvious difference in the absorbance for NaOH concentration over 2 mol L^{-1}. Thus, 2 mol L^{-1} NaOH solution was adopted.

Effect of surfactant

Surfactants are the most critical factors that influence the stability of the liquid membrane. Since L113A, a succinimide derivative, has the advantage of providing excellent stability with minimal swelling, it was chosen as the surfactant. A L113A concentration over 8% resulted in difficulties of emulsification, whereas a concentration under 4% resulted in unstable emulsions. There was no obvious change in the absorbance of As(III) for concentrations between 4% and 8%. It was found that L113A at 6% concentration was most suitable.

Effect of liquid paraffin

Liquid paraffin can increase the viscosity of the emulsion (thereby increasing the stability of the emulsion) and reduce the emulsion swelling. However, the mass transfer rate is decreased in the presence of a higher quantity of liquid paraffin. No obvious difference in the absorbance of As(III) was observed for the concentration of liquid paraffin from 2% to 8%. A liquid paraffin concentration of 4% was chosen to be optimal.

Effect of ratio of oil to internal phase (R_{oi})

The R_{oi} affects the stability of the emulsion and the mass transfer rate. The absorbance of As(III) decreased slightly with the R_{oi} due to lowering the viscosity of the emulsion. A low R_{oi} of 2 : 3 was adopted for this study.

Effect of ratio of emulsion to water (R_{ew})

The absorbance of As(III) increases with R_{ew}. But as Figure 2 shows (the ashing temperature used was 900°C, all other temperatures used were the same as in Figure 1), the absorbance of As(III) shows no obvious difference when the R_{ew} is over 0.15. For reasons of economic assessment and enrichment, a R_{ew} of 0.2 was found to be sufficient to achieve high % recoveries for As(III).

Optimization of the Determination Conditions

Effect of matrix modifier

In the absence of a modifier, the ashing temperature of As is only up to 400°C. Using $Ni(NO_3)_2$ as the matrix modifier, an ashing temperature of 800°C can be obtained. But the absorbance of As(III) decreases with a $Ni(NO_3)_2$ concentration of over 0.3%. A 2% $Ni(NO_3)_2$ concentration was chosen for this study.

Effect of ashing temperature

A stable and repeatable absorbance of As can be obtained for an ashing temperature of less than 800°C. However, when the ashing temperature was over 800°C, the absorbance of As decreased rapidly due to ashing loss. The results are shown in Figure 3 (the conditions being the same as in Figure 2). An ashing temperature of 800°C was found to be optimal.

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Recovery

Calibration procedure

Standard arsenic solutions in concentrations ranging from 0 to 280 μg L^{-1} were analyzed by ETAAS after emulsion liquid membrane separation using the conditions as stated above. As shown in Figure 4 (conditions being the same as in Figure 3), the absorbance of As was linear with an As concentration under 240 μg L^{-1}. The linear regression for Figure 4 was $A=0.038+0.0024C_{As}$, R=0.998 A = Absorbance of As).

Recovery of As(III)

Using optimum conditions, feed solutions containing various amounts of As(III) of less than 240 μg L^{-1} were studied and satisfactory recoveries of 93% to 99% were obtained. The results indicate that the method proposed is effective in the determination and recovery of trace arsenic.

Recovery of As(V)

Using optimum conditions, the recovery of As(V) was only 1.7% in the absence of the reductant when the feed solution contained 100 μg L-1 As(V). Thus, As(V) had a small interference effect on As(III). However, As(V) was quantitatively reduced to As(III) with 0.3% KI in the feed solution. Therefore, total arsenic can be conveniently determined in the presence of sufficient KI without requiring an extra reduction period prior to extraction. The recovery for As(V) was 96.2%.

Recovery of mixtures with different concentration ratios [As(III)/As(V)]

As can be seen in Table III, mixtures with different concentration ratios [As(III)/As(V)] were tested. The results show that the % recoveries for both As(III) and As(V) were excellent.

TABLE III
Recovery of Mixtures with Different Concentration Ratios [As(III)/As(V)]

Mixture	Present in mixture(μg L^{-1})		Found(μg L^{-1})		Recovery (%)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
1	10	200	10.9	196.0	109.0	98.0
2	10	100	11.0	96.7	110.0	96.7
3	20	80	18.5	78.5	92.5	98.1
4	50	50	47.6	47.0	95.2	94.0
5	80	20	78.2	19.7	97.8	98.5
6	100	10	99.6	11.7	99.6	117.0

TABLE IV
Recovery of As(III) and As(V) in Aqueous Samples

Samples	Found(μg L^{-1})		Added(μg L^{-1})		Found after added(μg L^{-1})		Recovery(%)	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
A	53.0	33.8	40.0	40.0	91.3	73.8	95.8	100
B	27.2	18.8	40.0	40.0	64.8	56.3	94.0	93.8
C	48.2	32.6	40.0	40.0	86.4	70.3	95.5	94.2

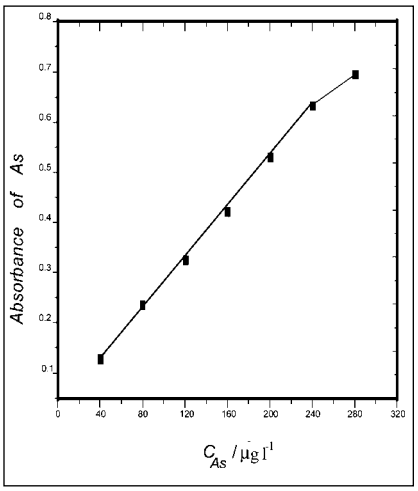

Fig. 4. Concentration range of As.

Precision

The precision of the method was determined by performing the analyses of arsenic mixtures containing 50 μg L^{-1} As(III) and 50 μg L^{-1} As(V). The procedure was repeated using the same standards on the same day (n=5). Recoveries of 95.6% (RSD=2.3%) and 95.4% (RSD=3.3%) for As(III) and As(V), respectively, were obtained.

Effect of foreign ions

The experiments show that most foreign ions were removed in the extraction. In the determination of As(III) (60 μg L^{-1}), an interference of less than 5% was observed in the presence of Cl^-, F^-, Zn^{2-}, Ba^{2+}, Co^{2+}, Mg^{2+}, NH_4^+, Sn^{2+}, PO_4^{3-}, Ca^{2+}, and Pb^{2+} at a concentration of 10 mg L^{-1}. However, strong oxidizing ions such as $Cr_2O_7^{2-}$ had serious effects on the recovery of As(III).

Application

The combined method of ELM and ETAAS was used to test the different aqueous samples (wastewater from our laboratory and water from our university's lake) for trace arsenic determination. The reliability of the method is illustrated using the method of standard additions. The results listed in Table IV show that satisfactory recoveries were obtained for both As(III) and As(V).

CONCLUSION

In this paper, we propose an effective separation method for arsenic followed by AAS detection. The optimum emulsion liquid membrane system consisted of 6% L113A, 4% liquid paraffin, 90% kerosene, and 2 mol/L NaOH. When the R_{oi} was 2/3 and R_{ew} was 0.2, with 8 mol/L HCl in the external phase, the recovery of As(III) was 93% to 99% after stirring at 450 r min^{-1} for 15minutes in contrast to a 1.7% recovery of As(V). But in the presence of 0.3% KI in the feed solution, As(V) was rapidly reduced to As(III) in order to enable the determination of total arsenic. A 96.2% recovery of As(V) was obtained by subtracting the As(III) amount from total arsenic.Thus, this method can be used for the valence analysis of arsenic.

The method was applied to the analysis of aqueous samples and the standard additions method was used to test the reliability of the method. The results show excellent recoveries of As(III) and As(V). The foreign ions such as Cl^-, Zn^{2+}, F^-, PO_4^{3-}, Ba^{2+}, Co^{2+}, Mg^{2+}, NH_4^+, Sn^{2+}, Ca^{2+} and Pb^{2+} with concentrations 160 times higher than the arsenic concentration effected a recovery of arsenic of less than 5%. The described method is very simple, convenient, rapid, and accurate with high sensitivity. It allows the determination of trace As(III) and As(V), respectively, in aqueous samples with satisfactory and reliable results.

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Determination of Cd in River Sediment Reference Material by GF-ETAAS Using Lithium Tetraborate as Chemical Modifier

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ABSTRACT

Lithium tetraborate was evaluated as a chemical modifier for the determination of cadmium by graphite furnace electrothermal atomization atomic absorption spectrometry. It was found that addition of 20 µg of $Li_2B_4O_7$ suffices to increase maximum pyrolysis temperature from 500ºC, in the absence of the modifier, to 800ºC. Pyrolysis temperature, characteristic mass (0.35 pg), and blank values (0.013 s) were comparable to those reported for other conventional modifiers. The performance of lithium tetraborate as a chemical modifier was evaluated for the determination of cadmium in a standard reference material, NIST Buffalo River Sediment (SRM 2704). The results (3.43 ± 0.03) agreed well with the certified values (3.45 ± 0.22). The detection limit of the methodology was 0.14 ng mL^{-1} (n= 10).

INTRODUCTION

The determination of volatile elements demands careful monitoring on part of the analyst during all stages of the analytical protocol, i.e., collection, preparation and analysis, in order to prevent losses, and therefore attain accurate and precise results. This is undoubtedly one of the reasons why microwave-assisted acid digestion has established itself as one of the most reliable sample preparation methods. However, though greatly overshadowed by the former, alkaline fusion with lithium tetraborate may provide a good alternative in terms of reliability, sample throughput, and cost. Even though the high temperatures required to obtain a fusion product amenable to dissolution limited this methodology to the determination of non-volatile analytes (1), several workers demonstrated that this is not the case (2-5). Alkaline fusion with lithium tetraborate has successfully been employed for the dissolution of some resilient samples, such as coal, fly ash, and silicon-containing materials (soils, sediments, and rocks).

Recently, Hernández Caraballo et al. (5) developed an alkaline fusion dissolution procedure based on a previous work by Bettinelli (3) for the determination of cadmium, lead, and zinc by atomic absorption spectrometric techniques. It was realized that lithium tetraborate not only stabilizes these volatile elements during the fusion procedure, as evidenced by quantitative recoveries in all the standard reference materials analyzed, but thermal stabilization was also provided during the determination of cadmium and lead by graphite furnace electrothermal atomization atomic absorption spectrometry (GF-ETAAS). Surprisingly enough, pyrolysis temperatures of 800 and 1000ºC could be applied for cadmium and lead, respectively, in the presence of lithium tetraborate matrix (5). In fact, the standard solutions had to be matrix-matched with the same amount of fluxing agent as was present in the final sample solution in order to level off the electrothermal atomization behavior of the analytes. Since this work (5) was mainly devoted to assess the applicability of alkaline fusion as a dissolution procedure for the analysis of soils and sediments, no attempts were made to further evaluate that flux as a chemical modifier.

The aim of the present work is to study the applicability of $Li_2B_4O_7$ as a chemical modifier for the determination of cadmium by GF-ETAAS. To test the accuracy and precision of the methodology proposed, the NIST (National Institute of Technology) standard reference material (SRM) Buffalo River Sediment (NIST SRM 2704), brought into solution by alkaline fusion using lithium tetraborate, was analyzed to determine its cadmium content.

EXPERIMENTAL

Instrumentation

A PerkinElmer Model 2100 atomic absorption spectrometer Model, equipped with an electrothermal atomization system Model HGA®-700, a Model AS-70 autosampler, and a deuterium lamp background correction system, was used for the determination of cadmium and lead. Pyrolytically coated graphite furnaces (PerkinElmer) with totally pyrolytic graphite platforms (PerkinElmer) were used after proper conditioning (6).

A PerkinElmer hollow cathode lamp, operated at 6 mA, was employed for the determination of Cd at the 228.8-nm line, with a 0.7-nm slit.

A Herbert-Arnold digital muffle oven Model N3, with programmable temperature settings from ambient temperature to 1100ºC, was used for alkaline fusion.

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Reagents

Stock and Working Solution.

A 1000-µg mL^{-1} cadmium standard solution (Merck) was used for standard preparation and calibration. Lithium tetraborate (Aldrich), 99.9+% purity, was used as both the chemical modifier for GF-ETAAS, and a fluxing agent for alkaline fusion dissolution. Nitric acid Suprapure® (Merck) was used for sample and modifier dissolution and stabilization of working standards. Distilled, de-ionized water, 18 MΩ cm^{-1} specific resistivity, from a Milli-Q™ water purifier system (Millipore), was used for the preparation of the sample and standards.

Standard Reference Materials

The NIST SRM 2704 Buffalo River Sediment standard reference material was used to verify the accuracy and precision of the proposed methodology.

Procedure

Standard and Chemical Modifier Solution Preparation

Cadmium standard solutions for calibration purposes were prepared by proper dilution with a 0.2 % (v/v) HNO_3 solution. A 10 000-µg mL^{-1} $Li_2B_4O_7$ solution was prepared by accurately weighing the corresponding amount of the salt, and adding the smallest volume of nitric acid (1% v/v) to yield a clear solution.

Alkaline Fusion Dissolution Procedure

The dissolution method was followed exactly as described Hernandez et al. (5). An accurately weighed amount (100 mg) of the NIST SRM 2704 material was thoroughly mixed with ~600 mg of lithium tetraborate. The mixture was carefully transferred to a graphite crucible and placed in a muffle oven. The oven temperature was automatically raised to 1000ºC in a gradual fashion (~45 minutes), and kept at this temperature for 15 minutes. After this time, the crucible was taken from the oven and allowed to cool to room temperature. The fusion product was transferred to a 250-mL beaker and 25 mL of a 10% (v/v) HNO_3 solution was added. The solution was magnetically stirred, and gently heated on a hot plate for about 20 minutes until complete dissolution of the melt was observed. The resulting solution was finally transferred to a 100-mL volumetric flask and brought to volume with distilled, de-ionized water.

Determination of Cd in NBS 2704 Buffalo River Sediment

Ten mL of the standards or samples and 10 µL of the $Li_2B_4O_7$ modifier were injected sequentially into the graphite furnace electrothermal atomizer, and cadmium was determined using the atomization program shown in Table I (5). The temperatures reported refers to nominal values given by the software controlling the spectrometer. No attempts were made to measure effective atomizer temperatures.

TABLE I
Atomization Program for the Determination of Cd by GF-ETAAS[a,b]

Step	Temp. (ºC)	Ramp (s)	Hold (s)
Dry	200	1	20
Pyrolysis	800	10	20
Cool-down	200	1	5
Cool-down	200	1	5
Atomization	1500	0	4 (Read)
Clean	2650	1	3
Cool-down	20	1	8

[a]Injection temperature: 120ºC.
[b]Gas flow 300 mL min^{-1} in all stages except during the second cool-down and the atomization stages (gas stop mode).

RESULTS AND DISCUSSION

Effect of Addition of Lithium Tetraborate

Alkaline fusion with lithium tetraborate has proven to be an effective way for preventing analyte losses during the high temperature fusion procedure (1000ºC) (2-5). It was therefore assumed that this fluxing agent could also be used as a chemical modifier in GF-ETAAS analysis for the determination of cadmium. Figure 1 shows that, effectively, addition of increasing amounts of $Li_2B_4O_7$ enhances cadmium thermal stability at a pyrolysis temperature (T_{pyr}= 900ºC), where no atomic absorption signal would be recorded in the absence of a chemical modifier. Twenty µg of the modifier are sufficient to achieve maximum sensitivity of the measurements. Higher amounts of

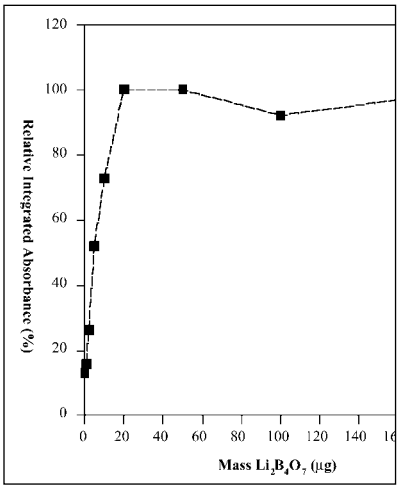

Fig. 1. Effect of the addition of lithium tetraborate on the sensitivity of the measurements of 0.2 ng Cd (T_{pyr}= 900 ºC).

the modifier do not seem to render additional benefit, at least in terms of increasing the sensitivity of the measurements.

To further study the capability of $Li_2B_4O_7$ for thermally stabilizing cadmium, pyrolysis curves were drawn. Different amounts of the modifier were evaluated in order to determine if an increase in the modifier meant increasing cadmium´s thermal stability. Figure 2 shows that a maximum pyrolysis temperature of 800ºC can be achieved in the presence of the modifier, irrespective of the amount of lithium tetraborate introduced into the atomizer. Table II shows characteristic mass values, maximum pyrolysis temperatures, and blank values for the $Li_2B_4O_7$ modifier. The same values, when available, are presented for the palladium + magnesium nitrate (7) and phosphate + magnesium nitrate (8) chemical modifiers. It is clear that lithium tetraborate compares favorably to other compounds more commonly used for chemical modification purposes.

Determination of Cd in NBS 2704 Buffalo River Sediment

Calibration against aqueous standard solutions is currently the simplest and easiest method for quantification by GF-ETAAS. However, for this method to be accurately applied, the analyte present in the sample and that present in the standard solutions must have the same electrothermal atomization behavior in the graphite furnace. Previously, it was found that the lithium tetraborate matrix present after alkaline fusion dissolution was sufficient to thermally stabilize cadmium in the samples (5). Effectively, Figure 3 shows that the maximum applicable pyrolysis temperature for cadmium in a sample of the NIST SRM 2704, brought into solution by alkaline fusion using lithium tetraborate, is the same as that achieved for an aqueous solution of cadmium to which at least 20 µg $Li_2B_4O_7$ has been added (see Figure 2). This implies that it is not necessary to match the matrix composition of the standard solution to that of the samples (5), but only to add the optimum amount of chemical modifier ($Li_2B_4O_7$) for proper quantification against aqueous solutions.

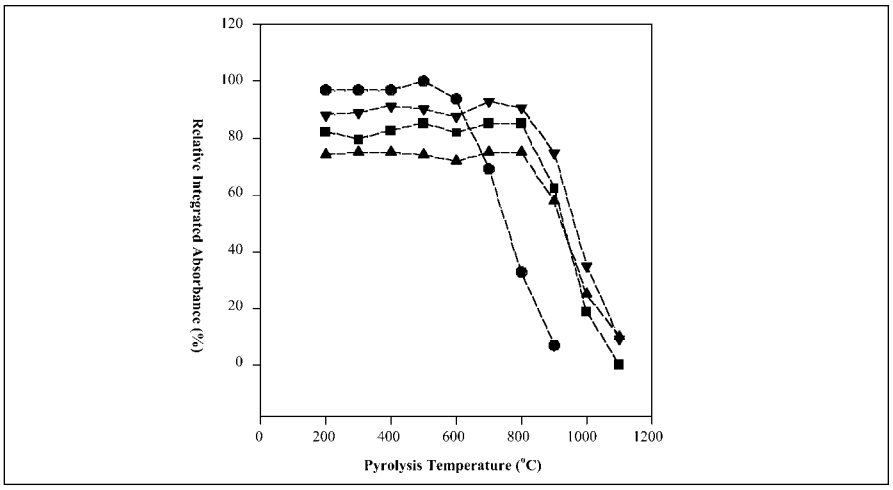

Fig. 2. Pyrolysis curves for 0.2 ng Cd: (●) no modifier; (■) 50 µg; (▲) 100 µg; and (▼) 200 µg $Li_2B_4O_7$ (T_{at}= 1500 ºC).

TABLE II
Comparison of Performance of Lithium Tetraborate With Other Chemical Modifiers Used in GF-ETAAS

Modifier	m_o (0.0044 s/pg)	T_{pyr} (ºC)	Blank values (s)
$Li_2B_4O_7$	0.35	800	0.013
Pd + Mg (7)	0.45	800	0.010
$NH_4H_2PO_4$ + $Mg(NO_3)_2$ (8)	0.40	1000	---

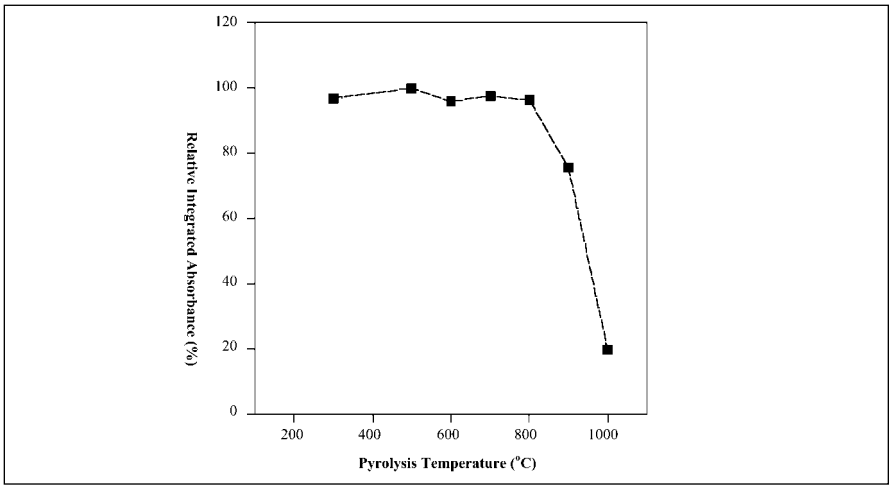

Fig. 3. Pyrolysis curve for 0.2 ng Cd in SRM 2704, after alkaline fusion dissolution with lithium tetraborate (T_{at}= 1500 ºC).

The above methodology was applied to the determination of cadmium in SRM 2704 with the results presented in Table III. It is clear that there is good agreement between the certified value (9) and that obtained with the proposed procedure. This implies two important findings. As shown previously (2-5), alkaline fusion with lithium tetraborate is an adequate procedure for dissolution of sediment samples, without risk of losing volatile elements. Secondly, addition of lithium tetraborate represents a good alternative for chemical modification of cadmium in GF-ETAAS analysis.

TABLE III
Determination of Cd by GF-ETAAS in NIST SRM 2704 Buffalo River Sediment

Certified ($\mu g\ g^{-1}$)[a]	Found ($\mu g\ g^{-1}$)[a]	% RSD	D.L. ($ng\ mL^{-1}$)[b]
3.45 (0.22)	3.43 (0.03)	0.88	0.14

[a]Values in parenthesis correspond to the standard deviation of the measurements.
[b]Detection limit corresponds to 3σ (n= 10).

CONCLUSION

The presence of lithium tetraborate increases cadmium thermal stability during its determination by GF-ETAAS similar to that achieved with other conventional modifiers. Besides, its low blank values, minimum contribution to background absorbance, the fact that conventional atomization programs can be used to reach its maximum performance, and the relative low cost make this compound attractive for chemical modification purposes.

The good performance of $Li_2B_4O_7$ in the determination of cadmium suggests that it could be used for the determination of other volatile elements as well, such as Pb, Zn, Sn, etc. Further studies are currently being carried out in our laboratory to evaluate this possibility.

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Presentation of the Bunsen-Kirchhoff Award for Analytical Spectroscopy

The Bunsen-Kirchhoff Award for Analytical Spectroscopy was awarded at the Colloquium on Analytical Atomic Spectroscopy (CANAS '01), held March 11-15, 2001, in Freiberg/Saxony, Germany, by the German Working Group for Applied Spectroscopy (DASp). The DASp regularly grants this award to younger scientists from universities, research institutes, or industry for their outstanding spectroscopic achievements.

The 2001 award winner was John A. McLean, Ph.D., George Washington University, Washington, DC, USA. The award was presented by Gerhard Schlemmer, PerkinElmer Instruments, Überlingen, Germany. The award consists of a certificate, an honorarium of DM 5000 granted by PerkinElmer Instruments, Norwalk, CT USA, and reimbursement of travel expenses to the conference.

Dr. McLean received this prize for his work in the field of plasma spectrometry, the development of a novel micronebulizer (DIHEN - direct injection high efficiency nebulizer), and work on plasma diagnostics. After studying chemistry at the University of Michigan, he began his research work in 1995 as a member of Professor A. Montaser's working group, successfully completing his PhD in April 2001.

For the development of the DIHEN, Dr. McLean was granted an American and European patent and received a number of awards including the R&D 100 Award, the 2000 American Chemical Society Division of Industrial & Engineering Chemistry Graduate Student Award in Applied Chemistry, the 1998 Federation of Analytical Chemistry, and the Spectroscopy Society (FACSS) Student Award, as well as other student awards. He is author of two chapters in the book, titled "Inductively Coupled Plasma Mass Spectrometry" (ed. A. Montaser, Wiley-VCH, New York, USA). He also published about 20 original papers in internationally respected and peer-reviewed journals and has given roughly 60 lectures and poster presentations.

In his lecture, "New Avenues in Plasma Source Atomic Spectrometry: Looking Towards the Future," Dr. McLean reported on the results of his successful research on ICP-MS using the DIHEN with respect to the application of micronebulization of μL sample volumes, e.g., for the trace and ultratrace analysis of Cr in DNA or to determine long-lived radionuclides in radioactive waste solutions. He also gave a comprehensive and interesting overview of direct solution input into the ICP-MS with micro- and nanonebulizers and presented his experimental observations concerning the formation of droplets during the μ-nebulization of aqueous solutions.

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