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Matrix Interferences in Arsenic Determinations by Graphite Furnace Atomic Absorption Spectrometry: Recommendations for the Determination of Arsenic in Water Samples

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The interferences of phosphate, sodium sulfate and chloride, aluminum nitrate, potassium chloride and selenous acid (singly and in combination) with the determination of arsenic by graphite furnace atomic absorption spectrometry were investigated. The arsenic signals were not only dependent on the phosphate concentration but also on the phosphate/arsenic ratio. Ashing curves (As signals as a function of ashing temperature) showed that arsenite and arsenate in salt-free solutions with 400 mg/L Ni (as nitrate, sulfate or chloride) can be determined at ashing temperatures $< 1100^{\circ}$. In the absence of Ni the signals are less intense and the ashing temperature should not be higher than 900° . Ni addition to solutions of methylarsonic acid, dimethylarsinic acid, arsenocholine and arsenobetaine enhanced the signal intensity but did not change the range of usable ashing temperatures. When

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salts are present at levels commonly found in freshwater, even addition of Ni does not produce acceptable results at ashing temperatures $>900^{\circ}$. The determination of an ashing curve is recommended before a water sample is analyzed for arsenic. A procedure for the determination of arsenic was developed and successfully applied to a synthetic and natural freshwater samples.

KEY WORDS: Arsenic determinations, interferences, graphite furnace AA, freshwater analyses.

INTRODUCTION

Graphite furnace atomic absorption spectrometry (GFAA) has become one of the most widely used analytical methods for the determination of arsenic^{1,2} in a variety of samples such as drinking water, sea water and brines, biological fluids, soils and industrial products and wastes. Water may contain arsenite, arsenate and methylated arsenic compounds. Biological samples may have arsenite, arsenate, methylated arsenic compounds, arsenobetaine, arsenocholine and other organic arsenic compounds. The advantages of GFAA (high sensitivity, only μL volumes of samples required, rapid analysis) are counteracted to some degree by matrix interferences,^{3,4} many of which are still unknown. Such interferences may be caused by the interaction of arsenic with hot carbon of the graphite cup or tube⁵⁻⁷ and the presence of cations and anions.⁸⁻¹²

Arsenic signals generated by GFAA are, for instance, dependent on the nitric acid concentration,¹³ on the concentration of sodium sulfate,^{9,14} various metal ions,^{14,15} phosphate^{10,11,13} and other anions.^{10,15} A detailed study¹⁴ of the interferences of several cations led to the conclusion that the determination of arsenic at low concentrations becomes difficult when sodium or potassium and sulfate are present at levels of a few mg/L. Concentrations of alkali metals and sulfate exceed these levels in nearly all biological and environmental samples including drinking water.

Although interfering cations and anions have been studied separately, no prediction can be made from such data about the influence of several salts simultaneously present in the solution, in which arsenic has to be determined. The degree of interference will not only depend on the concentration of the interfering species, but very likely also on the ratio of the concentrations of arsenic compound/interfering species.

Volatilization of arsenic during ashing may also be responsible for erroneous results.^{14,16,17} Modifications of the matrix through addition of nickel salts¹⁸ to reduce volatility and repress interferences is helpful in many but not in all cases.¹⁴ To counteract interferences tantalum-lined,^{6,19} tantalum-coated or niobium-coated graphite tubes¹⁷ and molybdenum microtubes²⁰ were recommended. Separation of arsenic compounds from the matrix by coprecipitation²¹ and solvent extraction^{22,23} were also used to avoid interferences. These procedures are time-consuming.

Under ideal conditions, the various arsenic compounds in a sample should be converted during the ashing cycle to one single species and should produce a signal dependent on the total amount of arsenic present. Should different compounds with different volatilities be present or formed, some of the arsenic might be lost during ashing, and atomization might occur in stages. Both events would produce erroneous results. Different sensitivities were in fact observed for various organic and inorganic arsenic compounds.^{24,25} If several arsenic compounds are present, matrix effects can probably not be eliminated in a simple manner by the standard addition technique. To successfully apply the standard addition technique under these circumstances, the chemical nature of the arsenic compounds and their concentrations must be known. Such knowledge is not available and its availability would obviate the analysis.

This paper describes the effects of the addition of nickel salts to solutions of inorganic and organic arsenic compounds on the behavior of these arsenic compounds during the ashing cycle, discusses interferences caused by phosphate and by various salts, present singly or in combination, and presents a procedure for the determination of arsenic by GFAA in freshwater samples.

EXPERIMENTAL

A Hitachi Model 170-70 Zeeman graphite furnace atomic absorption spectrometer equipped with a graphite cup capable of holding 50 μ L and an Instrument Laboratory arsenic hollow cathode lamp operated at 12 mA were used throughout the study. One pen of the Hitachi Model 056 dual-pen recorder traced the absorbance signal caused by arsenic while the other pen recorded the signal

generated by non-atomic absorption. The peak heights of the signals were measured in millimeters. The operating conditions for the graphite furnace were (cycle, mode, ramp rate or time, current): drying, ramp-6, 22 A; ashing, various temperatures; atomization, 7.5 s, 300 A. The temperatures for the ashing cycles were set by adjusting the current to values taken from the temperature-ampere graph in the operating manual. The spectrometer monitored the 193.7 nm line at slit width No. 2, scale expansion $\times 3$, pen response 3 and a sheath gas flow rate of 4 L/min of nitrogen. The carrier gas flow of 0.2 L/min was stopped during the atomization cycle. The samples (20 μ L) were transferred into the graphite cup using a 20 μ L Eppendorf pipette fitted with a polypropylene tip. The GFAA signals obtained with the same graphite cup and averaged over the useful lifetime of the cup had relative standard deviations of not more than 5 percent. However, these deviations were generally less than 2 percent when a small number of samples to be compared were analyzed during a short period of time with a cup not close to the end of its useful life. The experiments related to the influence of salts and salt mixtures (Tables I, II) were carried out in this manner. The same solution measured with different cups gave signals with deviations of 10–15 percent.

A Spectronic-20 spectrometer was used in the determination of arsenic with the silver diethyldithiocarbamate method.²⁶ A Bausch & Lomb ARL Model 34 000 simultaneous inductively coupled argon plasma emission spectrometer was employed to quantitate arsenic by atomic emission spectroscopy. The reduction of arsenic compounds to arsines and their determination by DC helium arc emission spectrometry was carried out as described in the literature.²⁷

Standard solutions of arsenate and arsenite were prepared from Baker Analyzed $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and NaAsO_2 . Methylarsonic acid (99.9%) and dimethylarsinic acid (99.9%) were obtained from the Ansul Corporation, Weslaco, Texas. Arsenobetaine bromide, $[(\text{CH}_3)_3\text{AsCH}_2\text{COOH}]^+\text{Br}^-$, (97%) and arsenocholine iodide, $[(\text{CH}_3)_3\text{AsCH}_2\text{CH}_2\text{OH}]^+\text{I}^-$, (96%) were synthesized in our laboratory.²⁸ All standard materials were dissolved in distilled, deionized water.

The solutions used for the study of the phosphate interference were prepared from 1000 mg/L As(arsenite) or 1000 mg/L As(arsenate) stock solutions by dilution in 50-mL volumetric flasks.

Appropriate volumes of H_3PO_4 solutions (10 mg PO_4/mL or more dilute solutions) were added to the flasks followed by 5 mL of 1 M nitric acid. The flasks were filled to the mark with distilled, deionized water.

RESULTS AND DISCUSSION

Our laboratory is engaged not only in the determination of total arsenic in a variety of samples including drinking water, but also in the identification of arsenic compounds. To gain confidence in the results of "total arsenic" determinations and determinations of arsenic compounds by GFAA in freshwater samples the influence of salts commonly found in freshwaters and of the temperature during the ashing cycle on the determination of inorganic and organic arsenic compounds was investigated.

Phosphate interference

The influence of phosphate added to the solutions as H_3PO_4 on the determination of arsenate (Na_2HAsO_4) and arsenite (NaAsO_2) is shown in Figure 1. With increasing phosphate concentration, the arsenic signals are enhanced until a phosphate/As ($\mu\text{g L}^{-1}/\mu\text{g L}^{-1}$) ratio of 100 is reached. At higher ratios the arsenic signals are depressed. The signal intensities obtained at a ratio of 1000 are one fourth or less of those observed at a ratio of 100. The curves showing the dependence of the arsenic signals on the PO_4/As ratio (Figure 1) have the same shape with maxima at a ratio of 100 for arsenite at 200 $\mu\text{g/L}$ As and arsenate at 50, 100 and 200 $\mu\text{g/L}$ As.

The GFAA signals generated by arsenate solutions with 50, 100 and 200 $\mu\text{g/L}$ As in the presence of 0, 2.5, 5.0 and 7.5 mg/L PO_4 produce straight-line calibration curves with zero intercept. At higher phosphate concentrations sets of three points corresponding to a particular phosphate concentration do not lie on a straight line. Similarly, the arsenic signals for 50, 100 and 200 $\mu\text{g/L}$ As (arsenate) and PO_4/As ratios of 0, 50, 100 and 150 produce straight lines through the origin, whereas lines for higher ratios have a sizeable intercept on the concentration axis and are non-linear. This dependence of the response on the phosphate concentration and the

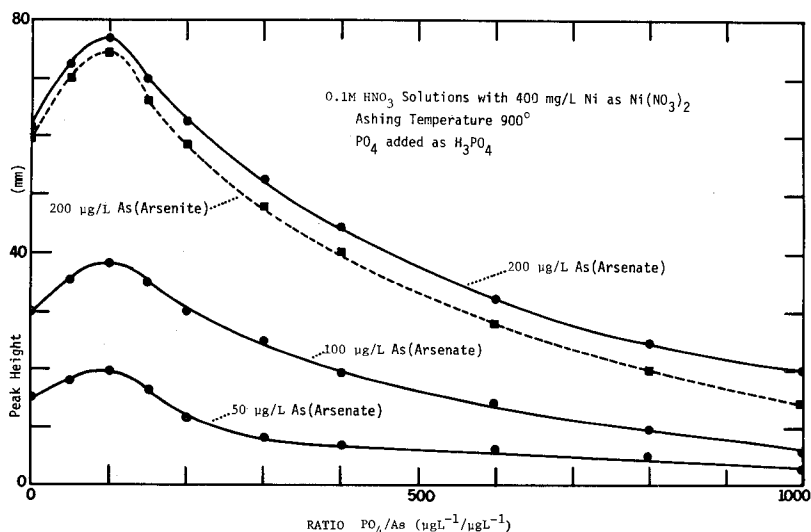


FIGURE 1 The dependence of the GFAA arsenic signals on the PO₄/As ratios at an ashing temperature of 900°.

phosphate/arsenic ratio indicates that even results obtained by the standard addition technique, which changes the phosphate arsenic ratio, could be erroneous. The recommended use of phosphoric acid or phosphates to adjust the pH of aqueous mobile phases in liquid chromatography will cause interferences when arsenic is determined in the effluent either manually or by automated systems.²⁹ Additional experiments with a wider range of arsenic concentrations and arsenic compounds on spectrometers with and without background correction are needed to better define phosphate interferences. It is certainly not advantageous to rely on calibration curves obtained with distilled water solutions of arsenic compounds when phosphate is present in the samples to be analyzed.

Ashing curves

To check the influence of the ashing temperature on the arsenic analyses, 0.1 M HNO₃ solutions of arsenic compounds were analyzed by GFAA with and without the addition of various nickel salts. The conditions under which drying and atomization took place were kept

constant. The ashing temperature was varied. The following arsenic compounds were investigated: NaAsO_2 , $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, $(\text{CH}_3)_2\text{AsO}_2\text{H}$, $\text{CH}_3\text{AsO}_3\text{H}_2$, $[(\text{CH}_3)_3\text{AsCH}_2\text{CH}_2\text{OH}]^+\text{Br}^-$, $[(\text{CH}_3)_3\text{AsCH}_2\text{COOH}]^+\text{I}^-$. Nickel chloride, nitrate and sulfate were used as matrix modification reagents at concentrations of 400 mg/L Ni. The results of these investigations are shown in Figures 2–5.

Solutions of Na_2HAsO_4 (200 $\mu\text{g/L}$ As) in 0.1 M HNO_3 produced in the absence of any other solutes signals which were independent of the ashing temperature in the range of 400° to 1100° when NiCl_2 , NiSO_4 or $\text{Ni}(\text{NO}_3)_2$ were present (Figure 2). At temperatures above 1200° the signal intensities decreased rapidly. The signals corresponding to the plateau region in the ashing curves measured 65 mm (NiSO_4), 60 mm (NiCl_2) and 55 mm [$\text{Ni}(\text{NO}_3)_2$] for an average of 60 ± 3 mm. This deviation, partly caused by the use of different graphite cups, is slightly larger than the deviation of ± 2 within a set of values obtained, for instance, with NiCl_2 . Without nickel salts the signal intensity is considerably lower and begins to decrease already at ashing temperatures above 900°. Sodium arsenite solutions behave similarly (Figure 3). Nickel salts increase the signal intensity of methylarsonic acid and dimethylarsinic acid slightly but do not influence the ashing temperature at which the signals begin to decrease (Figure 4). Increasing the Ni concentration from 400 mg/L to 1000 mg/L did not have any effect. Arsenocholine bromide and arsenocholine iodide (Figure 5) produced the same ashing curves as the methylarsenic compounds.

The responses obtained with solutions of various arsenic compounds at 200 $\mu\text{g/L}$ As at temperatures in the plateau region of the ashing curves varied sufficiently to question the use of one calibration curve for all the compounds investigated. Because these experiments required several graphite cups, which do not always give the same results, 200 $\mu\text{g/L}$ As solutions of arsenate, arsenite, methylarsonic acid, dimethylarsinic acid, arsenocholine bromide and arsenocholine iodide in 0.1 M HNO_3 with a Ni concentration of 400 mg/L [$\text{Ni}(\text{NO}_3)_2$] were analyzed using the same graphite cup at an ashing temperature of 900°. The signals based on arsenate (100%) were 96% for arsenocholine, 97% for arsenobetaine, 102% for methylarsonic acid, 100% for dimethylarsinic acid and 100% for arsenite. Under these conditions one calibration curve, which is

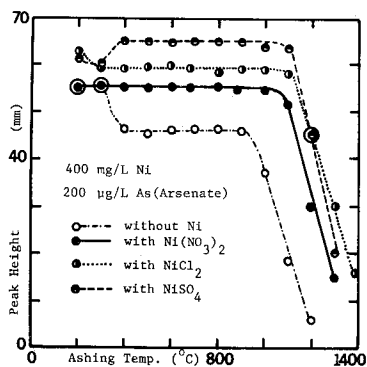


FIGURE 2 The dependence of the GFAA arsenic(arsenate) signals (0.1 M HNO_3 solutions without Ni or with various Ni salts) on the ashing temperature.

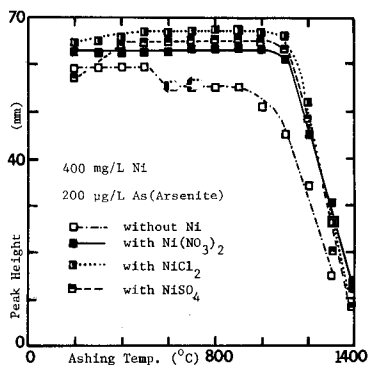


FIGURE 3 The dependence of the GFAA arsenic(arsenite) signals (0.1 M HNO_3 solutions without Ni or with various Ni salts) on the ashing temperature.

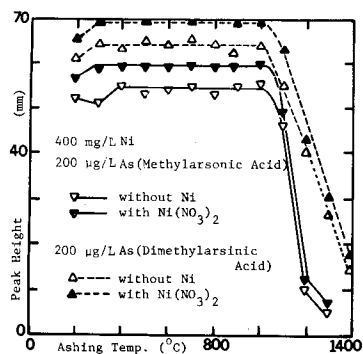


FIGURE 4 The dependence of the GFAA arsenic(methylarsonic acid, dimethylarsinic acid) signals (0.1 M HNO_3 solutions without Ni or with nickel nitrate) on the ashing temperature.

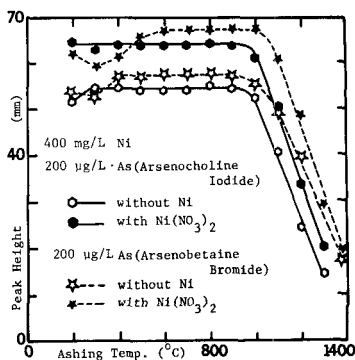


FIGURE 5 The dependence of the GFAA arsenic(arsenocholine iodide, arsenobetaine bromide) signals (0.1 M HNO_3 solutions without Ni or with nickel nitrate) on the ashing temperature.

linear from 25 to 250 µg/L As, can be used for these arsenic compounds. The signal intensities were independent of the nitric acid concentration in the range 0.08 M to 0.7 M.

Interference by salts and salt mixtures

Solutions of arsenic compounds (100 µg/L As, 400 mg/L $\text{Ni}[\text{Ni}(\text{NO}_3)_2]$, 0.1 M HNO_3) containing various salts were analyzed at an ashing temperature of 900° to find the concentrations at which the arsenic signals were 5 percent less than those obtained in the absence of the solutes. The results summarized in Table I indicate that sodium sulfate and phosphoric acid can certainly interfere with arsenic analyses. The interferences of these salts with the determination of arsenite and arsenate were also investigated at an ashing temperature of 1100°. Only sodium sulfate interfered more severely at 1100° than at 900° with a 5 percent signal reduction caused by 617 mg/L Na_2SO_4 . Such sodium and sulfate concentrations are not uncommon.^{30, 31}

Whereas these solutes with the exception of sodium sulfate and phosphoric acid do not influence the arsenic signals when present singly (Table I), severe signal reductions were caused by mixtures (Table II) of these salts. Mixture 1 which corresponds in composition to the concentrations identified in Table I reduced the arsenate

TABLE I
The influence of various salts and acids on the arsenic signals from 100 $\mu\text{g/L}$ As(arsenite) or As(arsenate) at an ashing temperature of 900°.

Salt	mg/L of salt causing signal reduction by 5 percent					
	Arsenite	Arsenate	$(\text{CH}_3)_2\text{AsOOH}$	$\text{CH}_3\text{AsO}_3\text{H}_2$	As-Betaine	As-Choline
Na_2SO_4	772	772	463	463	463	463
$\text{Al}(\text{NO}_3)_3$	> 3156 ^a	> 3156	> 3156	> 3156	> 3156	> 3156
KCl	> 763	> 763	> 763	> 763	> 763	> 763
H_3PO_4	41 ^b	41 ^b	41 ^b	41	41	41
NaCl	> 1017	> 1017	> 1017	> 1017	> 1017	> 1017
H_2SeO_3	> 327	> 327	> 327	> 327	327	> 327

^a > No interference observed at this concentration.

^b See discussion in section on phosphate interference.

TABLE II

The influence of various cations and anions simultaneously present in solution on the arsenic signals from 100 µg/L and 200 µg/L As(arsenate) [400 mg/L Ni(nickel nitrate), 0.1 M HNO₃].

Solution no.	Components of solution, mg/L ^a					As signal intensity in salt solution As signal intensity in distilled water × 100 ^b		
	NaCl	Na ₂ SO ₄	H ₃ PO ₄	Al(NO ₃) ₃	KCl	900°	Ashing temp.	1100°
1	400 (617) 1017 ^a	200 (417) 617 ^a	1 (40) 41 ^a	400 (2755) 3155 ^a	400 (363) 763 ^a	45 [40] ^b		15 [12] ^b
2	200 (308) 508	200 (417) 617	0.5 (20) 20.5	200 (1377) 1577	200 (181) 381	65 [60]		40 [35]
3	100 (154) 254	100 (208) 308	0.5 (20) 20.5	100 (688) 788	100 (90) 190	80 [76]		50 [45]
4	50 (77) 127	50 (104) 154	0.5 (20) 20.5	50 (344) 394	50 (45) 95	92 [90]		65 [60]
5	20 (31) 51	20 (42) 62	0.2 (10) 10.2	20 (138) 158	20 (18) 38	99 [97]		87 [84]
6	10 (15) 25	10 (21) 31	0.2 (10) 10.2	0 (0) 0	10 (9) 19	98 [98]		95 [94]

^aConcentrations refer to "mg/L cation (mg/L anion) mg/L salt".

^bValues in brackets refer to 100 µg/L As(arsenate) solutions. Values not in brackets pertain to 200 µg/L As(arsenate) solutions.

signal to 45 percent at an ashing temperature of 900° and to 15 percent at 1100° relative to the intensity obtained in the absence of the salt mixture. Only at considerably reduced salt concentrations (mixtures 5 and 6) are the expected signals observed (Table II). The results presented in Table II indicate that the determination of arsenic by GFAA in water samples, the compositions of which are unknown, may easily provide incorrect values especially when ashing temperatures above 900° are used.

A synthetic river water (composition given as footnote in Table III) was spiked with arsenite or arsenate and the ashing curves determined in the presence of 400 mg/L Ni as nickel chloride, nitrate or sulfate (Figure 6). The ashing curves clearly show that ashing temperatures above 900° are inappropriate, although temperatures between 1000 and 1200° were recommended for such analyses.^{10, 14, 23} Only half of the arsenic added to synthetic river water was recovered at an ashing temperature of 1100° , whereas determinations at 900° produced the expected amounts (Table III).

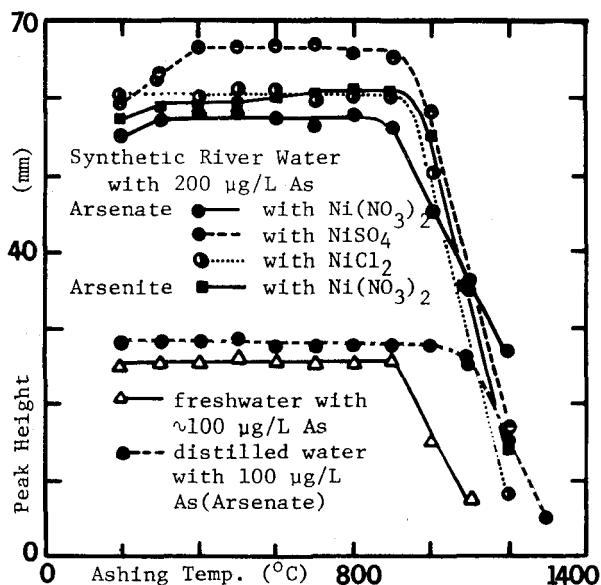


FIGURE 6 The dependence of the GFAA arsenic(arsenate, arsenite) signals (0.1 M HNO_3 solutions of synthetic river water or natural well water with 400 mg/L Ni from various nickel salts) on the ashing temperature.

TABLE III

Recovery of arsenic added to synthetic river water^a as arsenite or arsenate at ashing temperatures of 900° and 1100° [0.1 M HNO₃, 400 mg/L Ni(Nickel nitrate)].

As μg/L	As(arsenate) found, μg/L ^b		As(Arsenite) found, μg/L ^b	
	900°	1100°	900°	1100°
50	53 ± 4	27 ± 6	52 ± 4	29 ± 14
100	102 ± 3	65 ± 10	102 ± 3	68 ± 15
200	207 ± 4	125 ± 11	204 ± 5	110 ± 9

^aComposition in mg/L: Na 85, K 5.0, NH₄ 2.0, Mg 17, Ca 80, Cl 277, SO₄ 69, phosphate 5.4.

^bAverage/average deviation from 3 determinations.

Analysis of freshwater samples

The concentrations of cations and anions, which might interfere with GFAA analyses, are generally not known when samples are submitted for the determination of arsenic. It is, therefore, advisable to check the dependence of the arsenic signal on the ashing temperature. The ashing curve will identify the ashing temperature suitable for a particular sample.

Based on the results reported in this paper the following procedure is recommended for the determination of arsenic in freshwater samples: To an aliquot of the sample nitric acid and nickel nitrate are added to achieve concentrations of approximately 0.1 M HNO₃ and 400 mg/L Ni. The approximate arsenic concentration is determined by GFAA with an ashing temperature of 900°. Should the arsenic concentration be outside the linear calibration range, the sample is appropriately diluted with distilled water. The diluted sample, 0.1 M in HNO₃ with 400 mg/L Ni, is then used to obtain an ashing curve, from which the appropriate ashing temperature is selected for the analysis. The calibration curve is established under the same conditions.

Table IV summarizes the results of the analysis of two arsenic-containing freshwater samples by this procedure. Ashing curves are shown in Figure 6. Arsenic was also determined in these samples by several other methods as a check on the GFAA results. The values obtained by direct injection of the samples into the GFAA operating at an ashing temperature of 900° agree well with those produced by

TABLE IV

Arsenic concentrations in freshwater samples determined by various methods.

Sample no.	Total arsenic concentration ($\mu\text{g/L}$) by ^a					
	GFAA, 900°	GFAA, 1100°	Extr./GFAA	Ag DDC	ICP	HG/DC-He
1 ^b	277 \pm 4 ^c	70	290 \pm 5	288 \pm 4	258 \pm 5	280 \pm 5
2 ^b	460 \pm 5	98	470 \pm 3	487 \pm 6	473 \pm 8	490 \pm 4

^aMethods:

GFAA, 900°—procedure recommended in this paper with 900° ashing temperature.

GFAA, 1100°—direct injection into GFAA with 1100° ashing temperature.

Extr./GFAA—procedure given in ref. 20; extraction of arsenic into hexane sec-butyl dithiophosphate, reextraction into water, analysis of aqueous phase by GFAA with 1100° ashing temperature.

Ag DDC—reduction of arsenic compounds to arsine, formation of arsine/silver diethyldithiocarbamate complex and spectrophotometry (ref. 26).

ICP—inductively coupled argon plasma emission spectrometry.

HG/DC-He—reduction of arsenic compounds to arsine and detection by emission from a DC-helium arc (ref. 27).

^bThe samples were collected from private wells in New Hampshire. Composition of sample 1 (sample 2), mg/L: Al 1.2 (<0.4), Ca 0.3 (38.3), Fe 0.07 (0.07), K 3.4 (17.6), Mg 1.9 (11.3), Na 0.6 (46.3), S 0.1 (21.2), Si 0.2 (35.0).^cAverage/average deviation from 3 determinations.

other methods. At an ashing temperature of 1100° low, unacceptable concentrations were obtained. Removal of arsenic from the matrix by extraction with a hexane solution of ammonium sec-butyl dithiophosphate, reextraction of the arsenic into an aqueous phase free of other cations and anions, and injection of aliquots of these aqueous phases into the GFAA, gave correct results even at an ashing temperature of 1100°. The lengthy extraction procedure separated arsenic from the interfering salts.

When trace elements are to be analyzed by GFAA, high ashing temperatures are desirable to assure complete decomposition of organic materials present in the sample. However, when arsenic is to be determined in water samples, arsenic may be lost during ashing in the presence of dissolved salts. The determination of an ashing curve is recommended for the selection of an appropriate ashing temperature to avoid losses of arsenic during the ashing cycle. The water samples used in this investigation containing arsenite and arsenate could be successfully analyzed at an ashing temperature of 900° in the presence of nickel. Nickel addition will allow the determination of arsenic in salt-free media and media with low salt concentrations at ashing temperatures as high as 1300°.

CONCLUSIONS

Graphite furnace atomic absorption spectrometry, a sensitive method for the determination of arsenic, must be used with caution even when samples representing matrices as benign as freshwater are analyzed. Losses of arsenic may occur during the ashing cycle even in the presence of a nickel salt at ashing temperatures above 900°. The maximal, usable ashing temperature is determined by the concentrations of anions and cations in solution. In the case of phosphate it has been shown that arsenic signals are not only dependent on the phosphate concentration but also on the ratio arsenic/phosphate. To obtain reliable arsenic concentrations, an ashing curve should first be determined. The calibration of the instrument and the analyses of the samples should then be carried out at an ashing temperature corresponding to the high temperature part of the plateau in the ashing curve. The results obtained with freshwater samples using this procedure agreed with the values determined by our independent methods.

Acknowledgements

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