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# Decomposition of organoarsenic compounds by using a microwave oven and subsequent determination by flow injection–hydride generation–atomic absorption spectrometry

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**Environmentally important organoarsenicals such as arsenobetaine, arsenocholine and tetramethylarsonium ion do not form volatile hydrides under the commonly used analytical conditions on treatment with borohydride and it has been difficult to determine their concentrations without further derivatization. This paper describes a rapid method which completely decomposes and oxidizes these arsenicals to arsenate by using potassium persulphate and sodium hydroxide with the aid of microwave energy. The quantitative decomposition of these species permits their determination at low nanogram levels, by hydride generation atomic absorption spectrometry (HG AA). A new hydride generator which has high efficiency and minimum dead volume and therefore is suitable for flow injection analysis (FIA) is also described. A system combining flow injection analysis, online microwave oven digestion, and hydride generation followed by atomic absorption measurement, is developed. This system is capable of performing analysis at a sample throughput of 100–120 per hour. Calibration curves were linear from 10 to 200 ng cm$^{-3}$ of arsenic and the detection limit was 5 ng cm$^{-3}$ for a 100-µl injection or 0.5 ng of arsenic. All ten organoarsenic compounds studied gave arsenate as the decomposition product, which was confirmed by using molybdenum blue photometric measurement.**

**Keywords: Arsenic, microwave oven digestion, hydride generation, atomic absorption spectrometry, flow injection analysis, determination, decomposition, arsenobetaine**

## INTRODUCTION

Studies of arsenic in the environment have been of interest to chemists for many years.[1] Naturally occurring arsenic species include arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), all of which have been found in natural waters. Other organoarsenicals such as arsenobetaine (AB), arsenocholine (AC), tetramethylarsonium ion ($Me_4As^+$), and arsenosugars occur in biological tissue. It is important to distinguish between these species since toxicity varies greatly among arsenicals. Whilst inorganic arsenic species are well known to be very toxic, organoarsenicals are generally much less so. Arsenobetaine, for example, which is a major arsenic compound found in many seafoods,[2] is essentially non-toxic.[3,4] Studies of these organoarsenicals in environmental and biological systems are currently receiving much attention.[5–10]

Because trace amounts of arsenicals are usually encountered in environmental and biological samples, analytical methods with high sensitivity are required. Hydride generation has been recognized as a very useful technique in trace analysis due to its ability to enhance sensitivity. It has been widely used in conjunction with spectrometric detection, for the determination of trace amounts of As(III), As(V), MMA and DMA.[11–15] However, arsenobetaine, arsenocholine and a number of other organoarsenicals do not form volatile hydrides under the commonly used analytical conditions. It is therefore necessary to convert these organoarsenicals to some hydride-forming arsenic species in order to determine trace amounts of organoarsenicals and/or total arsenic by hydride generation.

Wet digestion methods with a nitric–sulphuric–perchloric acids mixture,[8,16] and a nitric–perchloric–chloric acids mixture,[17] have been

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reported to digest samples prior to the determination of total arsenic. Andreae[18] has reported that some organoarsenicals such as arsenobetaine are resistant to acid digestion. Thus heating with magnesium oxide in a muffle furnace was applied for complete decomposition. Similarly, dry ashing with a mixture of magnesium nitrate and magnesium oxide has been reported.[19] Wet digestion with strong base,[9,20–22] for example 40% aqueous sodium hydroxide, has also been investigated, although this in general does not result in complete breakdown to species detectable by the hydride generation method.[22,23] Stringer and Attrep[24] applied ultraviolet (UV) radiation to arsenicals in the presence of hydrogen peroxide and sulphuric acid. A 4 h irradiation time was required to photodecompose disodium methylarsonate, dimethylarsinic acid, and triphenylarsine oxide spiked into a waste water sample. Cullen and Dodd[25] further investigated the photo-oxidation of a range of organoarsenicals to arsenate in the presence of different mineral acids. One hour of UV irradiation (1200 W medium-pressure lamp) completely oxidized samples in fused silica tubes to As(V). Recently, Atallah and Kalman[26] have modified the batch-type photo-oxidation procedure to an on-line process. A Teflon tubing (5 m × 0.5 mm i.d.) coiled around a mercury lamp (UV source) was used as a photoreactor. Decomposed arsenicals, exiting from the photoreactor, were subsequently determined by using hydride generation AA.

Microwave oven sample dissolution[27–29] has been shown to possess advantages over the commonly used thermal heating methods. We were interested in applying the rapid and efficient heating possible with a microwave oven to decompose organoarsenicals to a form suitable for readily generating arsines. We describe here the successful on-line coupling of microwave oven decomposition with flow injection and hydride generation AA for the determination of organoarsenicals and total arsenic.

## EXPERIMENTAL

A Varian Model AA-1275 atomic absorption spectrophotometer equipped with a standard Varian air–acetylene flame atomizer, as described previously,[30] was used throughout this work. An arsenic hollow-cathode lamp (Hamamatsu Photonics, Japan) was used with an 8 mA current. Background correction was performed with a deuterium background correction system. Hydrides were introduced into an open-ended T-shaped quartz tube (11.5 cm long × 0.8 cm i.d.) which was mounted in the AA flame. Atomic absorption signals, measured at 193.7 nm wavelength, were recorded on a Hewlett–Packard 3390A integrator.

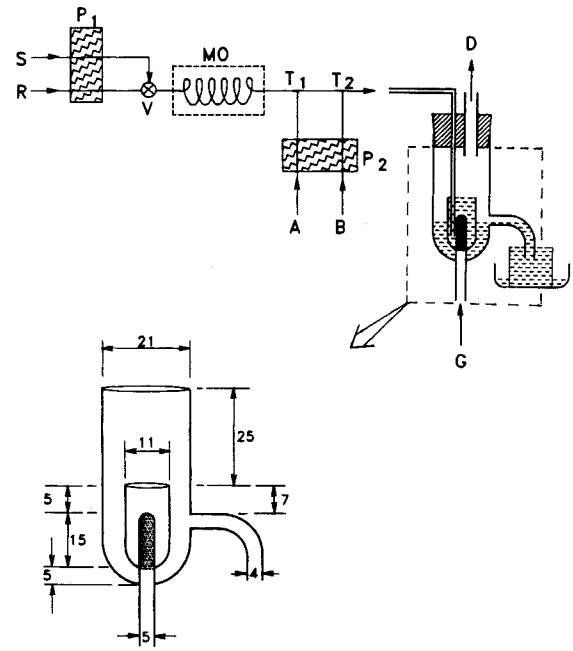


**Figure 1** A schematic diagram of an on-line coupled flow injection–microwave oven decomposition–hydride generation system. S, sample flow; R, reagent flow; V, sample injection valve; $P_1$, $P_2$, peristaltic pumps; MO, microwave oven; $T_1$, $T_2$, T-joints; A, acid flow; B, borohydride flow; G, carrier gas ($N_2$); D, to detector (AA). Dimensions are in mm.

A domestic microwave oven (Toshiba Co., Japan) with a maximum power output of 500 W (variable in nine steps from 100 W to 500 W) and an operating frequency of 2450 MHz was used for digestions. The power outputs at different settings were calibrated by using the literature method.[27] A digestion coil (3 m × 0.5 mm i.d.) and a cooling coil (1 m × 4 mm i.d.), both made of Teflon, were placed inside the miocrowave oven. Two upper inlet holes and two lower outlet holes were drilled on the same side of the oven and the holes were shielded with proper metal fittings to prevent microwave leakage. A continuous flow of tap water (approximately 10 $cm^3$ $min^{-1}$) through the cooling coil was used to prevent damage to the oven through continuous operation.

A schematic of the combined flow injection analysis–microwave oven digestion–hydride generation system is shown in Fig. 1. Sample injection was accomplished by means of a Rheodyne six-port sample injection valve (V) fitted with a 100-μl sample loop. Peristaltic pumps ($P_1$ and $P_2$) (Gilson Minipuls 2 and Isamatec ISP) were used to deliver sample and reagent solutions. A continuous flow of digestion reagent (R) carries the sample into the digestion coil located inside the microwave oven (MO) for decomposition. After the decomposition, the solution mixes with the acid flow (A) at the first T-joint ($T_1$), and then borohydride (B) at the second T-joint ($T_2$). The evolution of hydrides begins in the second T-joint ($T_2$) and continues in the reactor-gas/liquid separator apparatus. Inside this apparatus a flow of carrier gas (G) assists mixing and reaction and subsequently carries hydrides to the atomic absorption spectrometric detector (D). Waste solution from the hydride generation constantly drains out via a side-arm arranged to be at constant pressure.

The glass reactor-gas/liquid separator unit is also shown in Fig. 1. A medium-porosity gas-dispersion tube is located in the centre. As the carrier gas flows through the porous glass gas dispersion tube, fine bubbles are generated. These fine bubbles assist mixing and reaction as well as creating an efficient gas/liquid separation.

As has been shown previously[30] by radioactive tracer studies, fast reaction and efficient gas/liquid separation are achieved by using this type of hydride generator and no reaction coil is needed. The distance from the first T-joint ($T_1$) and the gas/liquid separator is kept short (20 cm) to reduce dispersion. Compared with the previously described hydride generator, the present version is smaller, has minimum dead volume, and it is therefore particularly suitable for the FIA system.

A Shimadzu UV-2100 UV–visible spectrophotometer was used for the photometric determination of arsenaste by the molybdenum blue method.[31]

## Reagents

Standard solutions of arsenite, arsenate, monomethylarsonic acid and dimethylarsinic acid were prepared as previously described. Arsenobetaine,[32] arsenocholine,[33] and tetramethylarsonium iodide[6] were synthesized and characterized by literature methods. Stock solutions (1000.0 μg $cm^{-3}$ of arsenic) were prepared by dissolving appropriate amounts of these compounds in 0.01 mol $dm^{-3}$ hydrochloric acid. Appropriate amounts of butylarsonic acid [$C_4H_9AsO(OH)_2$], *p*-arsanilic acid [$NH_2C_6H_4AsO(OH)_2$, Eastman Kodak], 4-nitrobenzenearsonic acid [4-$NO_2C_6H_4$-$AsO(OH)_2$, Aldrich], *p*-hydroxyphenylarsonic acid [p-$HOC_6H_4AsO(OH)_2$, Eastman Kodak), and α-toluenearsonic acid [$C_6H_5CH_2AsO(OH)_2$, Eastman Kodak] were dissolved in 0.01 mol $dm^{-3}$ hydrochloric acid to make individual stock solutions (1000.0 μg $cm^{-3}$ of arsenic). These solutions were standardized against arsenite by using both flame AA and inductively coupled plasma atomic emission spectrometry (ICP AES). Standard solutions were prepared by serial dilutions with 0.01 mol $dm^{-3}$ hydrochloric acid.

Potassium persulphate (BDH) solutions were made fresh daily. Sodium borohydride (Aldrich) solutions in 0.1 mol $dm^{-3}$ sodium hydroxide (BDH) were prepared fresh and filtered prior to use. All other reagents used were of analytical reagent grade or better.

## Procedures

### FIA mode

A 100-μl sample was injected into a digestion reagent stream. The reagent carried the sample to the microwave oven operating at a chosen power setting. Hydride generation and gas/liquid separation took place and the evolved hydrides were introduced into a flame-heated quartz tube for atomic absorption measurement. A peak signal was recorded by using an integrator capable of both peak height and peak area measurements. It was found that peak height measurement gave better reproducibility and lower standard deviation. Thus the peak height of the signal was measured for quantitation. Experimental conditions are summarized in Table 1.

### Continuous mode

In the continuous operation mode, the sample injection valve (V) in Fig. 1 was replaced by a T-joint. Sample and reagent solutions were continuously taken up by the peristaltic pump and met at the T-joint before flowing into the digestion coil. As a result of continuous introduction of the sample, a continuous steady state signal was observed and recorded on the integrator.

### Batch-type digestion

A sample solution (1.0 $cm^3$) and the digestion reagent solution (5.0 $cm^3$) were combined in a

polyethylene bottle. The bottle was *loosely* capped and placed in the microwave oven. The microwave oven was then operated at the full power setting (500 W) for 2 min followed by a 5-min cooling period and finally another 2 min of microwave heating. After the sample was cooled, it was diluted to 10.0 $cm^3$. Determination of the decomposition product, arsenate, in the sample was carried out by using FIA–hydride generation–AA, as shown in Fig. 1, except that the microwave oven was not used.

### Analysis of the decomposed product

A photometric method[31] based on the formation of arseno-molybdenum blue was used to measure the concentration of arsenate in the digested solution. Arsenate is the only arsenic species to form the blue complex, whose absorption can be measured for quantitative purposes.

A 10-$cm^3$ digested solution was collected from the outlet of the digestion coil after four repetitive injections of 100 µl of a sample (containing 10 µg $cm^{-3}$ of arsenic). A 5-$cm^3$ aliquot of this solution was pipetted into a dry and clean 50-$cm^3$ Erlenmeyer flask. To the flask 1 $cm^3$ of 1 mol $dm^{-3}$ hydrochloric acid and 1 $cm^3$ of a mixed reagent containing 0.6% (w/v) ammonium molybdate, 1.1% (w/v) ascorbic acid, 0.014% (w/v) potassium antimonyl tartrate, and 1.2 mol $dm^{-3}$ sulphuric acid were added. A blue complex slowly formed and the absorbance at 860 nm was measured after 3 h. Distilled water containing potassium persulphate and the same amount of colour-formation reagents was used as a blank. An arsenate solution containing the same amount of potassium persulphate as in the digested solution was used as standard. It is found to be important to have the same amount of persulphate in the sample and the standard solutions, as the presence of persulphate enhanced absorption signals by approximately 20%.

## RESULTS AND DISCUSSION

### Batch-type digestion: preliminary studies

In a preliminary study, the microwave oven was used for open vessel batch-type digestion to investigate the possibility of decomposing organoarsenicals and to search for appropriate reagents. A 4-min microwave heating time was applied to each sample and reagents studied include 1–6 mol $dm^{-3}$ sulphuric acid, 1–4 mol $dm^{-3}$ sodium hydroxide, 5–20% hydrogen peroxide, 2–6 mol $dm^{-3}$ nitric acid, and 2.5% (w/v) potassium persulphate in 0.1 mol $dm^{-3}$ sodium hydroxide. It was found that when sulphuric acid, sodium hydroxide, hydrogen peroxide and nitric acid were used, the decomposition efficiencies for arsenobetaine, arsenocholine and tetramethylarsonium were all less than 30%. Increasing the concentration of reagents was not further attempted because sparks were observed from the digesting solution when a high concentration of sodium hydroxide (4 mol $dm^{-3}$) was used. When 2.5% (w/v) potassium persulphate in 0.1 mol $dm^{-3}$ sodium hydroxide aqueous solution was used, complete conversion of arsenobetaine, arsenocholine and tetramethylarsonium to arsenate was achieved. Therefore, potassium persulphate and sodium hydroxide were chosen as the digestion reagents for further studies.

The effect of the digestion time in the microwave oven on the decomposition efficiency of three organoarsenicals is shown in Fig. 2, where the relative peak height is obtained by comparing signals obtained from the organoarsenicals with those obtained from arsenate upon hydride generation AA measurements. Only a 30, 20 and 45-s microwave oven heating time is needed to decompose completely 100 µl of 200 ng $cm^{-3}$ AB, AC and $Me_4As^+$, respectively in a 5-$cm^3$ solution containing 2.5% $K_2S_2O_8$ in 0.1 mol $dm^{-3}$ NaOH.

**Table 1** Experimental conditions

| | |
|---|---|
| HCl concentration | 3.0 mol $dm^{-3}$ |
| HCl flow rate | 3.4 $cm^3$ $min^{-1}$ |
| $NaBH_4$ concentration | 0.65 mol $dm^{-3}$ in 0.1 mol $dm^{-3}$ NaOH |
| $NaBH_4$ flow rate | 3.4 $cm^3$ $min^{-1}$ |
| Carrier gas ($N_2$) flow rate | 160 $cm^3$ $min^{-1}$ |
| Microwave oven power | 500 W (full power) |
| Digestion coil | 3 m × 0.5 mm i.d. Teflon |
| Digestion reagents | 0.1 mol $dm^{-3}$ $K_2S_2O_8$ and 0.3 mol $dm^{-3}$ NaOH |
| Digestion reagent flow rate | 5.0 $cm_3$ $min^{-1}$ |

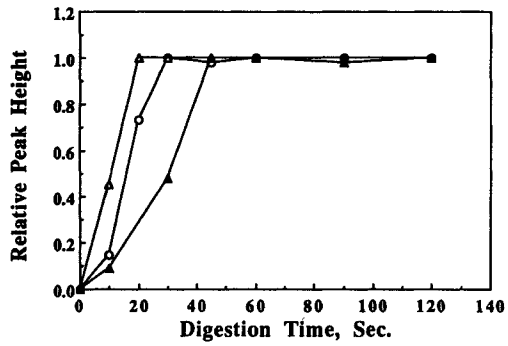


**Figure 2** Effect of digestion time on the decomposition efficiency with a batch-type digestion procedure: ○, AB; △, AC; ▲, $Me_4As^+$.

This high efficiency of decomposition within such a short period of time seemed suitable for development into an on-line decomposition system.

## FIA–microwave oven digestion–HG AA

The coupling of microwave oven digestion to flow injection analysis (FIA) and hydride generation atomic absorption spectrometry (HG AA) is shown schematically in Fig. 1. With this system, organoarsenicals were completely decomposed and gave quantitative absorption signals upon hydride generation AA measurements. Figure 3 compares signals obtained for arsenobetaine (AB), arsenocholine (AC), tetramethylarsonium ion ($Me_4As^+$), arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) when no digestion was applied (Fig. 3a); when a 50 °C water bath was used (Fig. 3b); and when a microwave oven was operated at 500 W for digestion (Fig. 3c). It is clear from Fig. 3(a) that AB, AC and $Me_4As^+$ do not form hydrides without a proper digestion procedure, whereas As(III), As(V), MMA and

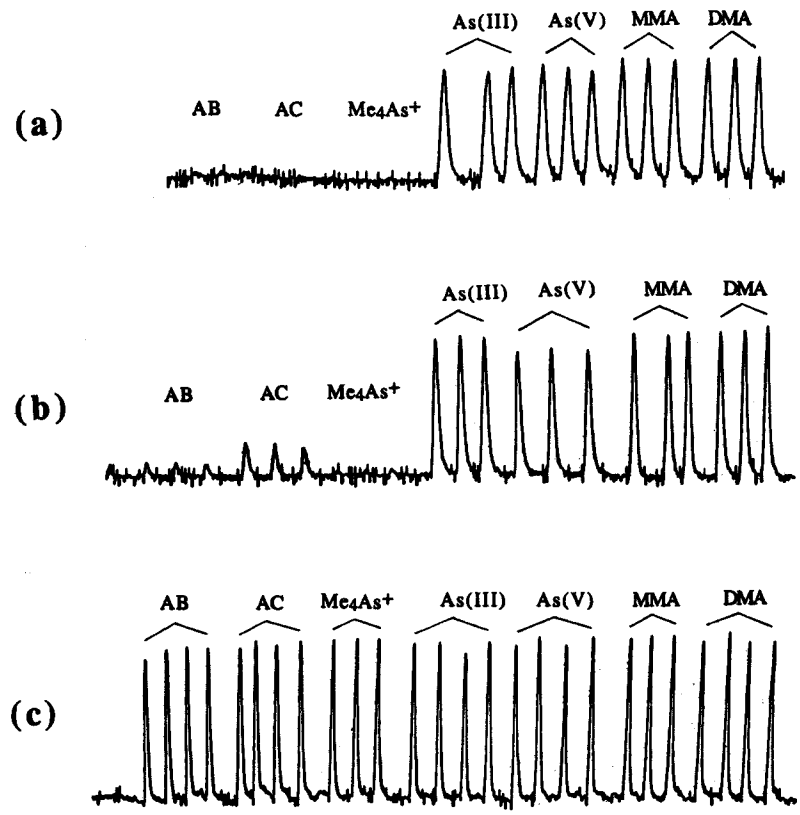


**Figure 3** Comparison of signals from 100 µl of seven arsenic compounds, each at 200 ng $cm^{-3}$ (as As), obtained by using different on-line digestion methods and HG AA. (a) No digestion, with distilled water as carrier; (b) 50 °C water bath, with 0.1 mol $dm^{-3}$ $K_2S_2O_8$ and 0.1 mol $dm^{-3}$ NaOH as carrier; (c) microwve oven digestion, with 0.1 mol $dm^{-3}$ $K_2S_2O_8$ and 0.1 mol $dm^{-3}$ NaOH as carrier.

DMA give quantitative signals. This is consistent with literature reports.[16,22,23,25,26] When a warm water bath is used along with 0.1 mol $dm^{-3}$ potassium persulphate and 0.1 mol $dm^{-3}$ sodium hydroxide as digestion reagents, only a small portion (5–25%) of these organoarsenicals is decomposed to form hydrides (Fig. 3b). Increasing the temperature of the water bath did not result in a complete decomposition of these organoarsenicals, although at 90 °C the decomposition efficiency was increased to approximately 50%. However, the utilization of microwave energy in combination with 0.1 mol $dm^{-3}$ potassium persulphate and 0.1 mol $dm^{-3}$ sodium hydroxide resulted in the decomposition of all arsenicals studied, and quantitative signals were obtained with hydride generation AA measurements (Fig. 3c).

**Digestion coil**

Teflon coils (3 m long) with various inner diameters (0.5, 0.8, 1.2 and 2.5 mm) were evaluated. When a 2.5-mm or a 1.2-mm i.d. coil was used, the signals observed were broad and sometimes split. This is probably due to dispersion of the analyte. Use of a Teflon coil with an i.d. of 0.5 mm results in sharp, narrow, and reproducible signals.

Investigation of the effect of the residence time of the sample being digested in the microwave oven was carried out by varying the length of the Teflon coil in the oven that was operating at its full power. AB, AC, $Me_4As^+$ and As(V) were chosen as examples to study the general decomposition efficiency. Thus the signals obtained from AB, AC and $Me_4As^+$ were compared with those obtained from As(V) under identical conditions. The peak heights of signals from these organoarsenicals relative to those from As(V) as a function of coil length are shown in Fig. 4. As the coil length was increased from 0.2 m to 0.5 m, the relative peak heights of all three organoarsenicals increased dramatically. Within the coil length range of 2.2–5 m, the three organoarsenicals gave signals of the same peak height as that from As(V), indicating complete conversion to hydride-forming arsenicals. On this basis a 3-m Teflon coil (0.5 mm i.d.) was chosen as optimum; under the given flow rate, the residence time of each sample in the microwave oven was only 15 s.

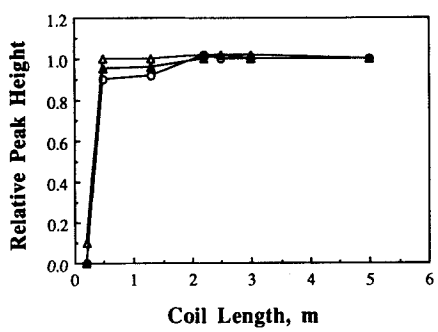


**Figure 4** Effect of digestion coil length on the decomposition efficiency with injection of 100 µl of (○) AB, (△) AC, and (▲) $Me_4As^+$, each at 200 ng $cm^{-3}$ (as As).

**Microwave oven power level and digestion reagents**

The power level of the microwave oven and the concentration of the digestion reagents are two other obvious important factors affecting a quantitative decomposition of organoarsenicals. A series of experiments was designed to study the effect of these two factors and to optimize them both at the same time. At each of the nine microwave oven power settings from 100 to 500 W, the concentration of potassium persulphate (made in 0.1 mol $dm^{-3}$ caustic soda) was varied between 3.7, 18, 37, 74, 110 and 150 mmol $dm^{-3}$. Determinations of arsenobetaine and arsenate were carried out under each of these conditions. Figure 5 shows relative peak heights of signals from 100 µl of 200 ng $cm^{-3}$ AB with respect to those from 100 µl of 200 ng $cm^{-3}$ of As(V) at various levels of microwave oven power and concentrations of persulphate. It demonstrates that increasing both microwave oven power and persulphate concentration within the ranges of study results in achieving maximum and constant signals from AB. A maximum signal region is seen when the concentration of persulphate ranges between 60 mmol $dm^{-3}$ and 150 mmol $dm^{-3}$ and microwave oven power is in the range of 300–500 W. A relative peak height of 1.0 with respect to As(V) obtained within this region indicates a complete decomposition of arsenobetaine.

A number of other decomposition reagents, such as $KClO_4$, $K_2Cr_2O_7$, $KIO_3$, and $H_2O_2$, all at concentrations of both 0.07 and 0.15 mol $dm^{-3}$, and 0.1–2 mol $dm^{-3}$ caustic soda were investigated. No signal was observed from AB, AC, or $Me_4As^+$ with any of these reagents in the same continuous-flow microwave oven digestion system. However, the addition of caustic soda to potassium persulphate promoted the complete

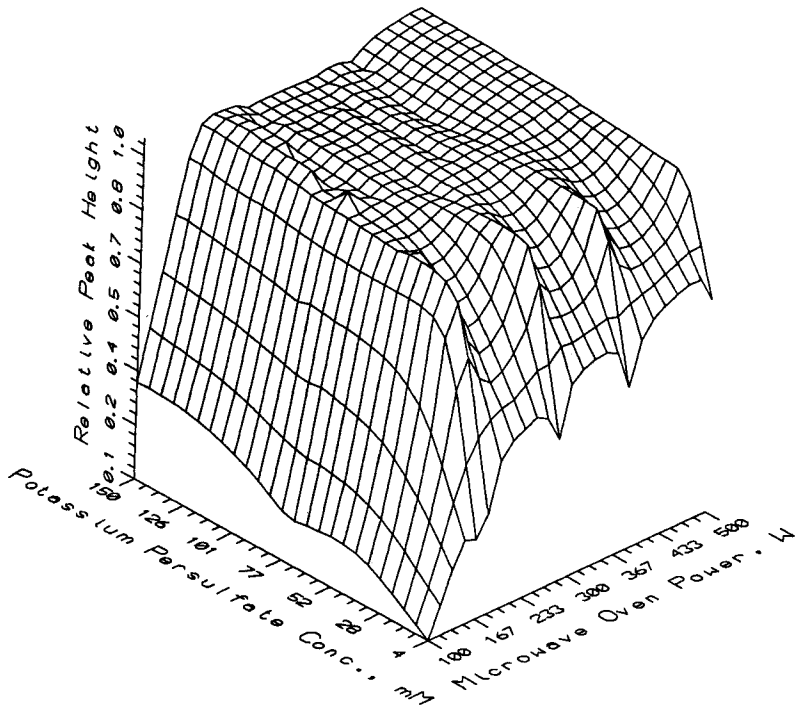


**Figure 5** A response surface showing the effect of potassium persulphate concentration and microwave oven power on the decomposition efficiency of 100 µl of 200 ng $cm^{-3}$ (as As) arsenobetaine.

digestion of AB and $Me_4As^+$. Figure 6 shows that the digestion of AB and $Me_4As^+$ is not complete when 0.1 mol $dm^{-3}$ potassium persulphate aqueous solution alone is used and microwave oven power is applied, whereas with 0.1 mol $dm^{-3}$ potassium persulphate in 0.1 mol $dm^{-3}$ NaOH solution, a complete digestion of AB and $Me_4AS^+$ is achieved, as has been seen from Fig. 3(c).

The effect of NaOH concentration and microwave oven power level on the decomposition

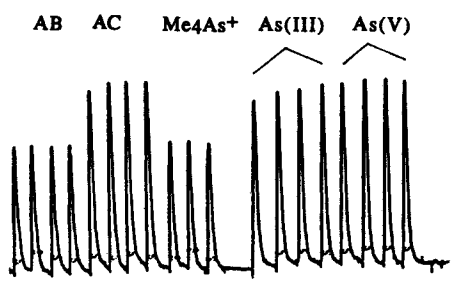


**Figure 6** Signals obtained by using FIA–microwave digestion–HG AA when the digestion reagent is 0.1 mol $dm^{-3}$ $K_2S_2O_8$ alone in distilled water. Note the incomplete decomposition of AB and $Me_4As^+$.

efficiency is shown in Fig. 7. Sodium hydroxide at various concentrations was made up in 0.1 mol $dm^{-3}$ potassium persulphate aqueous solution. As can be seen from Fig. 7, AB is not completely decomposed to arsenate in the absence of NaOH, at any microwave oven power setting. As the concentration of NaOH is increased, less microwave energy is needed to completely decompose AB, and the relative peak heights of signals from AB approaches to unity. A contour diagram also showed that, at full power (500 W), the optimum concentration of NaOH for achieving complete digestion of AB was in the range of 0.1–1.0 mol $dm^{-3}$. If the concentration of NaOH were increased further, the hydride generation reaction might be affected. Thus a solution containing 0.3 mol $dm^{-3}$ NaOH and 0.1 mol $dm^{-3}$ $K_2S_2O_8$ was chosen as the digestion reagent.

### Concentration of sodium borohydride and hydrochloric acid

Both $NaBH_4$ and acid are necessary for the hydride generation reaction. Thus their concentrations need to be optimized for use. In order to examine the possible interdependence between

$NaBH_4$ and $K_2S_2O_8$ concentrations, both concentrations were varied and As(V) and AB were chosen as analytes. From the response surfaces obtained it was found that there was no interdependence between these two reagents within the concentration ranges of study, namely 1.8–150 mmol $dm^{-3}$ $K_2S_2O_8$ and 0.13–1.6 mol $dm^{-3}$ $NaBH_4$. This is understandable, considering the small molar concentration of $K_2S_2O_8$ relative to that of $NaBH_4$.

The effect of the concentration of HCl and $NaBH_4$ on the determination of arsenic was also studied, using AB and As(V) as examples. Response surfaces and contour diagrams of peak heights from AB and As(V) vs concentrations of $NaBH_4$ and HCl were obtained. The optimum ranges of concentrations are 2.5–5 mol $dm^{-3}$ HCl and 0.5–1.3 mol $dm^{-3}$ (2–5%, w/v) $NaBH_4$ in 0.1 mol $dm^{-3}$ NaOH and within these optimum ranges, 3 mol $dm^{-3}$ HCl and 0.65 mol $dm^{-3}$ $NaBH_4$ in 0.1 mol $dm^{-3}$ NaOH were chosen for the hydride generation.

Response surfaces clearly show the effect of two variables. However, a large number of experiments are usually required. With the present system, a sample throughput of 100–120 per hour is possible. Since the analysis is so fast, optimization of two factors could be achieved within 30 min.

### Other organoarsenicals

By using microwave oven digestion in the presence of 0.1 mol $dm^{-3}$ $K_2S_2O_8$ and 0.3 mol $dm^{-3}$ NaOH, *p*-hydroxyphenylarsonic acid, *p*-arsanilic acid, 4-nitrobenzenearsonic acid, α-toluenearsonic acid, and butylarsonic acid were all decomposed and 100% peak height signals relative to As(V) and As(III) were observed from the HG AA measurement.

### Decomposition product

In order to identify the decomposition product from the microwave digestion, the solution was collected from the outlet of the digestion coil. The molybdenum blue method,[31] in which only arsenate among arsenic species forms a blue compound, was used to measure the As(V) content in

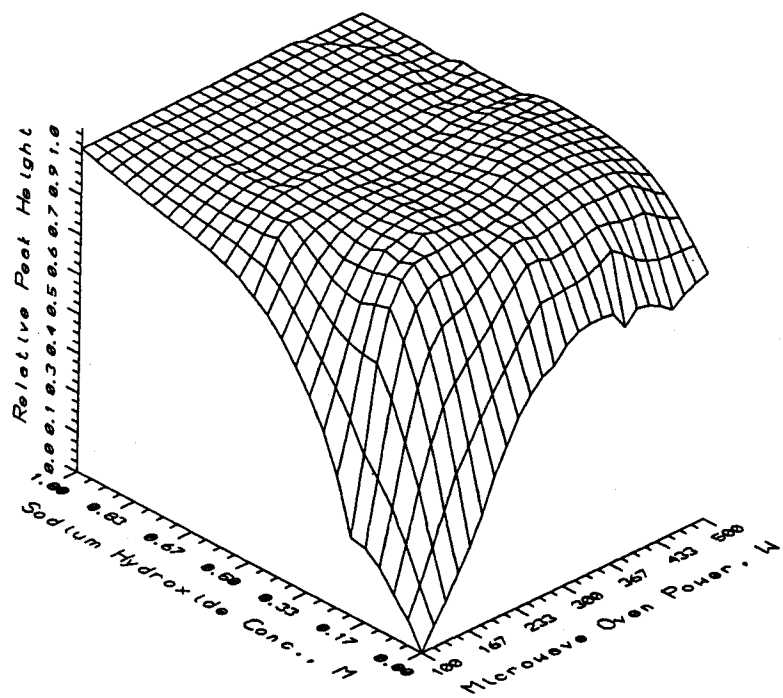


**Figure 7** A response surface showing the effect of sodium hydroxide concentration and microwave oven power on the decomposition efficiency of 100 µl of 200 ng $cm^{-3}$ (as As) of arsenobetaine.

the digested solution. It was found that all the arsenicals studied above were oxidized to As(V), with recoveries of 90–110%.

### Calibration

Figure 8 compares three-point calibration signals from AB with microwave oven digestion (Fig. 8a), As(V) with microwave oven digestion (Fig. 8b), and As(V) without microwave oven digestion (Fig. 8c). It is clear that the same degree of response is obtained from the same amount of arsenic, either as As(V) or in AB. Similar responses were also obtained from the other arsenic species, as is expected, since all these different arsenicals were oxidized to As(V), as discussed above. Therefore, it is possible to use a calibration curve from a single arsenical for all the arsenic species. A detailed calibration using AB as standard demonstrated that the concentration range 10–200 ng $cm^{-3}$ showed good linearity.

The detection limit, defined as three times the signal-to-noise ratio, was 5 ng $cm^{-3}$ for 100 µl sample injection or 0.5 ng of arsenic.

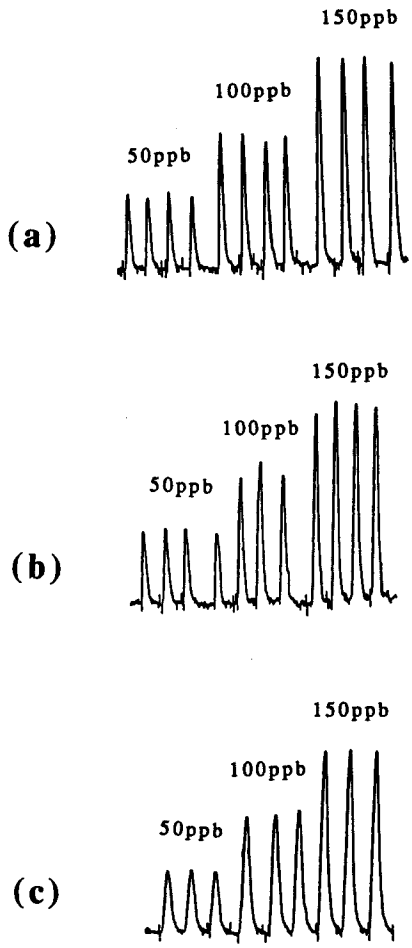


**Figure 8** Comparison of signals obtained from 100 µl of 50, 100 and 150 ng $cm^{-3}$ (as As) of arsenic compounds. (a) AB, with microwave digestion; (b) As(V), with microwave digestion; (c) As(V), without microwave digestion.

### Interference

A known amount of AB was spiked into a seawater and a urine sample matrix and recoveries were evaluated in order to study possible interference in analysing environmental and biological samples. No interference was encountered from the seawater matrix in the determination of AB and a quantitative recovery, 90–100%, was obtained. However, when AB was spiked into a urine sample, approximately 40% of the spiked AB was recovered based on the HG AA measurement. As(V) spiked into both seawater and urine samples was quantitatively recovered. Thus the interfernce from the urine matrix in the determination of AB is probably the result of incomplete digestion of AB in the presence of organic matrix in urine. Elimination of this interference remains to be studied in detail; presumably longer digestion times will be necessary.

## Continuous system

The microwave oven digestion was also adapted for continuous use. Solutions of sample and digestion reagent were continuously taken up and mixed at a T-joint before being introduced into the microwave oven operating at its full power. Steady-state signals are obtained as shown in Fig. 9. Without the microwave oven digestion (Fig. 9a), no signal is observed from AB, AC or $Me_4As^+$. With microwave oven digestion, quantitative decomposition of AB, AC, and $Me_4As^+$ is achieved and successful determination can be carried out by using hydride generation atomic absorption spectrometry (Figure 9b).

## CONCLUSION

Rapid and complete decomposition of organoarsenicals is achieved by using microwave oven digestion with $K_2S_2O_8$ and NaOH as digesting reagents. An on-line system is developed in which

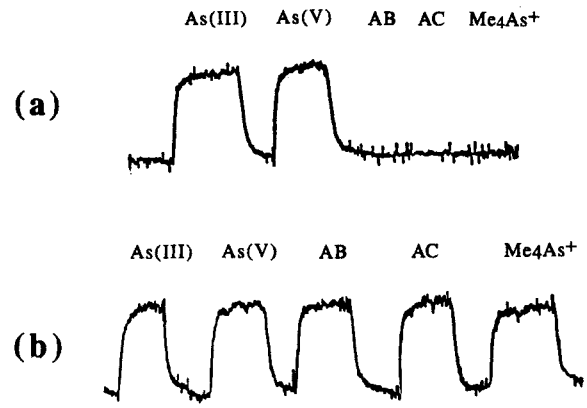


**Figure 9** Comparison of signals from 20 ng $cm^{-3}$ or arsenic compounds obtained by using the continuous HG AA system: (a) without microwave digestion; (b) with microwave digestion, using 0.1 mol $dm^{-3}$ $K_2S_2O_8$ and 0.3 mol $dm^{-3}$ NaOH as digestion reagents.

the decomposition product, arsenate, is quantitated by using a new hydride generator system. The use of microwave power to decompose organoarsenicals has shown the advantages of high efficiency, fast decomposition, and ease of operation. The on-line microwave oven digestion operates well with both continuous sample introduction and flow injection. A fast sample analysis (throughput 100–120 per hour) is achieved with the flow injection analysis operation.

Although the hydride generation technique coupled with spectrometric determination is very sensitive, it has not been well adopted for the determination of arsenic speciation because many species do not form hydrides. With the present system, arsenic species are converted to arsenate, which readily forms arsine. Therefore, it is possible to couple the microwave oven digestion–hydride generation–AA to a HPLC system to detect arsenic during speciation studies.

Since all arsenic compounds are converted to arsenate by the microwave digestion, it is also possible to determine total arsenic by a photometric method such as the molybdenum blue method, which only measures arsenate. Also because the digested product is the same for all the arsenic species studied, it is possible to use a single arsenic compound as a standard for all arsenicals.

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