since the ionization potential of Ar is lower than the energies of the two metastable states of He. However, there seems to be more involved than simply an increase in electron concentration since the presence of O_2 is necessary to prevent the deposition of carbonaceous material. Presumably, carbon is removed as CO and CO_2.

Analytical Implications. An inspection of Figure 3 reveals that, while the presence of oxygen is necessary to observe chromium atomic emission, there is an optimum P_{O_2} due to the quenching properties of oxygen. The advantages of adding oxygen are as follows: 1) The addition of oxygen increases the atomic Cr emission. This, of course, improves sensitivity for the chromium chelate. 2) The addition of oxygen reduces molecular emissions from species such as N_2 and N_2^+, introduced through leaks in the system. This means a reduction in background, and is especially important if the 3579-Å chromium line is used for analysis, since there is a very intense N_2 band in this region. 3) The addition of oxygen quenches molecular emissions from species such as CH and CN, which are the result of fragmentation. This is important in improving selectivity.

The following disadvantages are the result of adding oxygen: 1) The chromium emission reaches a maximum and then decreases rather quickly with the addition of oxygen. Curve 1 in Figure 3 shows the importance of maintaining the flow of oxygen constant to maximize precision. 2) Curve 6 in Figure 2 shows that the background in the 3100- to 3000-Å region is high due to the formation of OH. This precludes the use of this region for sensitive analysis unless water can be rigorously excluded.

LITERATURE CITED

(1) A. J. McCormack, S. C. Tong, and W. D. Cooke, *Anal. Chem.*, **37**, 1470 (1965).
(2) C. A. Bache and D. J. Lisk, *Anal. Chem.*, **37**, 1477 (1965).
(3) C. A. Bache and D. J. Lisk, *Anal. Chem.*, **37**, 783 (1965).
(4) C. A. Bache and D. J. Lisk, *Anal. Chem.*, **38**, 1757 (1966).
(5) C. A. Bache and D. J. Lisk, *Anal. Chem.*, **39**, 786 (1967).
(6) H. A. Moye, *Anal. Chem.*, **39**, 1441 (1967).
(7) C. A. Bache and D. J. Lisk, *J. Gas Chromatogr.*, **6**, 301 (1968).
(8) R. M. Dagnall, S. J. Pratt, T. S. West, and D. R. Deans, *Talanta*, **16**, 797 (1969).
(9) R. M. Dagnall, S. J. Pratt, T. S. West, and D. R. Deans, *Talanta*, **17**, 1009 (1970).
(10) W. Braun, N. C. Peterson, A. M. Bass, and M. J. Kurylo, *J. Chromatogr.*, **55**, 237 (1971).
(11) R. M. Dagnall, T. S. West, and P. Whitehead, *Anal. Chim. Acta*, **60**, 25 (1972).
(12) W. R. McLean, D. L. Stanton, and G. E. Penketh, *Analyst (London)*, **98**, 432 (1973).
(13) R. M. Dagnall, T. S. West, and P. Whitehead, *Anal. Chem.* **44**, 2074 (1972).
(14) D. A. Luippold and J. L. Beauchamp, *Anal. Chem.*, **42**, 1374 (1970).
(15) C. A. Bache and D. J. Lisk, *Anal. Chem.*, **43**, 950 (1971).
(16) R. M. Dagnall, T. S. West, and P. Whitehead, *Analyst (London)*, **98**, 647 (1973).
(17) Y. Talmi and A. W. Andren, *Anal. Chem.*, **46**, 2122 (1974).
(18) F. A. Serravallo and T. H. Risby, *J. Chromatogr. Sci.*, **12**, r585 (1974).
(19) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 500 (1963).
(20) F. W. Lampe, "Ionizing Collision Reactions of Electronically Excited Atoms and Molecules", in "Ion-Molecule Reactions", Volume 2, J. L. Franklin, Ed., Plenum Press, New York, N.Y., 1972.
(21) R. Schade, *Z. Phys.*, **105**, 595 (1937).
(22) R. Schade, *Z. Phys.*, **108**, 353 (1938).
(23) H. Buttner, *Z. Phys.*, **111**, 750 (1939).
(24) O. Tuxen, *Z. Phys.*, **103**, 463 (1936).
(25) F. L. Arnot and M. B. M'Ewen, *Proc. Roy. Soc. London, Ser. A*, **171**, 106 (1939).
(26) J. A. Hornbeck, *Phys. Rev.*, **84**, 615 (1951).
(27) J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951).
(28) W. Kaul and R. Taubert, *Z. Naturforsch. A*, **17**, 88 (1962).
(29) F. J. Comes, *Z. Naturforsch. A*, **17**, 1031 (1962).
(30) M. S. B. Munson, J. L. Franklin, and F. H. Field. *J. Phys. Chem.*, **67**, 1542 (1963).
(31) R. K. Curran, *J. Chem. Phys.*, **38**, 2974 (1963).
(32) D. Morris, *Proc. Phys. Soc., London, Sect. A*, **68**, 11 (1955).
(33) M. Pahl and V. Weimer, *Z. Naturforsch. A*, **13**, 753 (1958).
(34) M. Pahl, *Z. Naturforsch. A*, **14**, 239 (1959).
(35) J. P. Gaus and L. M. Chanin, *J. Appl. Phys.*, **40**, 256 (1969).
(36) J. L. Franklin, P. K. Ghosh, and S. Studniarz, *Adv. Chem. Ser.*, **80**, 59 (1969).
(37) J. Franck and P. Knipping, *Z. Phys.*, **1**, 320 (1920).
(38) F. M. Penning, *Naturwissenschaften*, **15**, 818 (1927).
(39) F. M. Penning, *Z. Phys.*, **46**, 335 (1928).
(40) F. M. Penning, *Z. Phys.*, **57**, 723 (1929).
(41) F. M. Penning, *Z. Phys.*, **72**, 338 (1931).
(42) W. L. Fite, *Adv. Chem. Ser.*, **80**, 1 (1969).
(43) F. K. McTaggart, "Plasma Chemistry in Electrical Discharges", Elsevier Publishing Co., New York, N.Y., 1967, p 19.
(44) R. H. Tourin, "Spectroscopic Gas Temperature Measurement", Elsevier Publishing Co., New York, N.Y., 1966, p 47.
(45) W. L. Wiese, M. W. Smith, and B. M. Glennon, "Atomic Transition Probabilities, Volume I, Hydrogen through Neon", National Bureau of Standards, Washington, D.C., 1966.
(46) C. H. Corliss and W. R. Bozmann, "Experimental Transition Probabilities for Spectral Lines of Seventy Elements", National Bureau of Standards, Monograph 53 (1962).

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Determination of Alkylarsenic Acids in Pesticide and Environmental Samples by Gas Chromatography with a Microwave Emission Spectrometric Detection System

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The applicability of a gas chromatograph with a microwave emission spectrometric detector (GC-MES) to the determination of alkylarsenic acids in commercial pesticides and in environmental samples is described. The analytical procedure involves $NaBH_4$ reduction of the arsenic acids to the corresponding arsines, followed by either extraction of these arsines or their flushing from the sample solution and collection in cold toluene at −5 °C. In either case, the arsines are separated on a GC column and determined by a MES detector by measuring the emission intensity of the As 228.8-nm spectral line. Various parameters affecting the production and collection of the arsines, such as the reduction conditions, sample volume, losses due to volatilization, and arsine rearrangement side reactions are discussed along with instrumentation parameters such as column operation and microwave power. The various alkylarsines separated on the GC column were positively identified by a mass spectrometer. Since the MES detector is highly selective to arsenic ($>10^4$), the absolute sensitivity (20 pg of arsenic) is very little dependent on the molecular structure of the arsines. The relative sensitivity for water samples is at least 0.25 μg/l.

Table I. Operating Conditions

Parameter	6
GC column length, ft[a]	5% Carbowax 20M on 80/100 mesh,
GC column packing	Chromosorb 101
Quartz capillary, i.d., o.d., mm[b]	0.5, 6.5
Carrier gas[c]	Argon
Carrier gas flow rate	100 ml/min
Column temperature, °C	175
Inlet temperature, °C	180
Capillary heater temperature, °C	210
Microwave generator output, watts	20
Monochromator setting	
Slit height, mm	10
Slit width, μm	30
Wavelength, nm	228.8
Photomultiplier tube	RCA 1P28
Photomultiplier voltage, V	630
Optics[d]	
Lens focal length, mm	100
Lens diameter, mm	50

[a] Pyrex column dimensions: i.d., 3.5 mm; o.d., 6.5 mm. [b] Quartz capillary length, 25 cm. [c] The plasma was operated at 5–10 Torr. [d] Plasma image was focused on the entrace slit.

In recent years, extensive use has been made of sodium and ammonium salts of monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMMA) as nonselective, postemergent, foliar contact herbicides. There is evidence concerning the bioaccumulation of these arsenicals (*1*), as well as their reduction by soil microorganisms to the corresponding toxic and highly volatile arsines (*2–4*). To study the environmental impact of these herbicides, accurate and sensitive analytical methods are required which are capable of providing information concerning the molecular form of these arsenicals in addition to their arsenic content. Within the past few years, several GC methods have been described for the separation and identification of inorganic arsenic species (*5–7*) as well as MMAA and DMAA (*8–10*). However, to date none of these methods have been applied to environmental samples.

Braman and Foreback (*11*) have since succeeded in separating and quantitatively determining As(III), As(V), MMAA, and DMAA by a procedure formally analogous to thermal volatilization. Their analytical procedure is based on $NaBH_4$ reduction of the arsenicals to the corresponding gaseous arsines and their collection in a liquid nitrogen trap. Separation of the arsines is subsequently achieved by heating the trap and thus selectively volatilizing them according to their boiling points. Detection of the arsines is accomplished by their introduction into a helium dc-discharge detector and the measurement of the resultant emission intensity of the As 228.8-nm spectral line. Using this technique, arsenic species at the sub-ppm concentration level have been determined in various environmental samples including water, egg shells, sea shells, etc.

This article describes a new analytical method for the determination of arsenicals in industrial and environmental samples. As in the previous method, the $NaBH_4$ reduction scheme is used, but the arsine separation is achieved by GC and is therefore more efficient and reproducible. The highly selective and sensitive microwave emission spectrometric (MES) GC detector has been utilized throughout the study. The necessary conditions for the quantitative reduction and collection of several alkylarsenic compounds as well as their GC separation and MES detection are described.

EXPERIMENTAL

Apparatus. The GC-MES system used in this study has been described previously (*12, 13*). The detection procedure for the alkylarsines involves their GC separation and elution into a low-power microwave argon plasma and measurement of the resultant emission intensity of As 228.8 nm. The GC-MES operating conditions are summarized in Table I.

Reagents. Highly purified MMAA and DMAA obtained from Ansul Corp. were used to prepare the corresponding 1000 μg/ml aqueous standard stock solutions. Three commercial pesticide samples received for comparative analysis (Ansul) were similarly diluted with water to prepare 1000 μg/ml stock solutions. Other arsenic acids including ethyl, *n*-propyl- and *n*-butylarsonic acids were obtained from Eastman Kodak. $NaBH_4$ pellets (250 mg) from Ventron Corp. were used as the reducing agent. The trimethylarsine (TMA) was also obtained from Ventron.

Procedure. Two alternative procedures were employed to quantitatively collect the volatile arsines evolved during the reduction reaction.

Extraction Method. Aqueous samples were acidified to pH 1 with either oxalic acid (2%) or HCl. Ten ml of benzene or toluene were then added and reduction was initiated by dropping a $NaBH_4$ pellet into the aqueous sample. The extraction vessel (a long test tube) was left open to permit the H_2 formed to escape. To ensure an efficient extraction, the vessel was shaken throughout the reaction (3 min). The two layers were then allowed to separate before an aliquot of the organic layer was removed for subsequent analysis by the GC-MES.

Cold Trap Method. This method requires the use of an air-tight reaction vessel (Figure 1) in which the volatile arsines are collected in a −5 °C toluene cold trap. The low temperature is maintained by submerging the trap in an ethylene glycol–ice bath. The reduction procedure is identical with that of the above method but the arsines are flushed through a glass-frit bubbler into the toluene trap instead of being extracted.

DISCUSSION

Reduction. The overall accuracy and precision of the analytical procedure strongly depend on the rate and degree of completion of the reduction of the arsenic acids, as well as on the rapid removal and the efficient collection of the generated arsines. Various parameters, including pH, temperature, and initial concentration of $NaBH_4$ which affect these processes, also determine the degree to which the undesirable side reactions of arsine molecular rearrangement take place. Because of these side reactions, the reduction of MMAA resulted in the partial production of AsH_3, DMA, and TMA in addition to the expected MMA. The reduction of DMAA produced small amounts of MMA. Molecular rearrangements of a similar nature have been previously observed for other arsines (*14, 15*). Although the nature of these rearrangements is not entirely understood, they can be easily controlled and practically eliminated as shown by the following observations and Table II:

1) The arsine's rearrangement did not occur in the GC system.

2) The degree of rearrangement could be reduced if $NaBH_4$ pellet rather than an aqueous $NaBH_4$ solution was used as the reducing agent (Table II). Further addition of $NaBH_4$ did not seem to reduce or reverse the rearrangement.

3) A drastic reduction in arsine rearrangement was achieved when the dissolved oxygen present in the aqueous samples was removed prior to reduction (Table II).

4) A decrease in the degree of rearrangement was also observed upon lowering the pH, Figure 2.

These observations indicate that the degree of rearrangement is reduced when the rate of reduction is increased; e.g., low pH and the instantaneous increase in $NaBH_4$ concentration in the aqueous solution upon introduction of a pellet. Fortunately, the completeness of reduction is also optimized under the same set of conditions. Thus, while DMA production (from DMAA) remained essentially con-

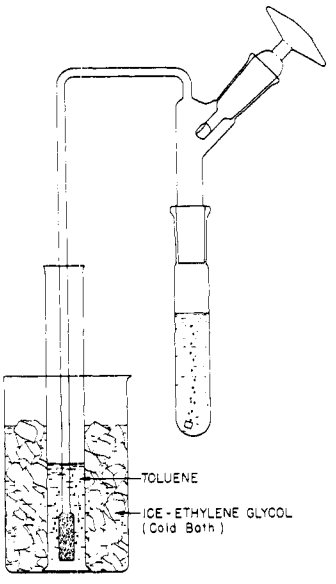

Figure 1. Reaction vessel used in the cold toluene trap method

Table II. Effect of Reducing Agents and Oxygen Removal on Arsine Rearrangement

	Reducing agent		Oxygen removal from sample[a]
	1% $NaBH_4$ Solution	$NaBH_4$ Pellet	
% DMA produced by MMA rearrangement	5–7, traces of AsH_3 and TMA	2	< 0.4
% MMA produced by DMA rearrangement	2–4	2	0.1

[a] Reduction of sample with a $NaBH_4$ pellet at pH 1.

stant between pH 0.2 and 1.0, it was less than 50% complete at pH 1.2 and practically zero above pH 1.5. Temperature (25–50 °C), on the other hand, seemed to have no effect on DMA generation.

The drastic increase in arsine rearrangement in the presence of oxygen can probably be linked to the fact that alkylarsines are characteristically very reactive and readily attacked by oxygen (*16*). This also suggests that the rearrangement occurs after or simultaneously with the generation of the arsines rather than with the acids themselves.

Efficiency of Alkyl Arsine Collection Extraction Method. The quantitative collection of each arsine generated depends on its volatility and its solubility in the organic solvent. Extracts of DMA obtained by reduction of DMAA aqueous samples at the 0.03–10 μg/ml concentration range produced linear calibration curves with correlation coefficients better than 0.999. These curves were highly reproducible, despite the fact that the extraction efficiency of DMA was only 91 ± 2%. Increase in the solvent volume by a factor of 3 (30 ml) improved the extraction efficiency to more than 99% but also proportionally reduced the relative sensitivity. Unlike DMA (bp 36 °C), MMA (bp −2 °C) was not extracted efficiently and reproducibly by the solvents used. Other solvents, including diethyl ether and ethanol, which were more efficient extractants were incompatible with the GC column.

Cold Trap Method. In the cold trap method, the overall arsine collection efficiency depends on the efficiency of both the flushing of arsine from the aqueous sample and

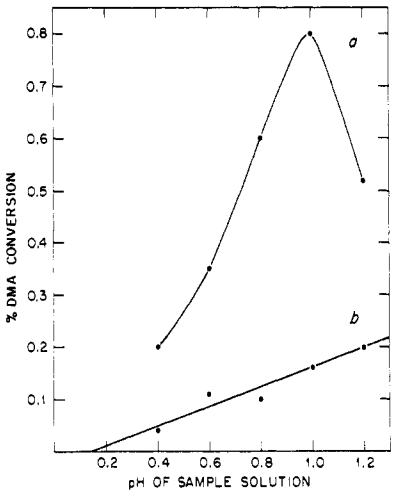

Figure 2. Effect of pH on the rearrangement of DMA to MMA

(*a*) DMAA reduction in the presence of oxygen. (*b*) DMAA reduction in the absence of oxygen

the collection of these arsines by the cold toluene (−5 °C) trap. The efficiency of the cold trap for capturing MMA and DMA was 94 ± 2% and 96 ± 2%, respectively, regardless of the toluene volume (5–25 ml) or of the concentrations of the MMAA (up to 10 μg) and DMAA (up to 100 μg). Lowering the trap temperature below −5 °C should further improve the trapping efficiency, although attempts to accomplish this by using a Dry Ice bath resulted in blockage of the glass frit with frozen toluene. A more promising cooling approach should involve the use of a well regulated cryogenic device.

The flushing efficiencies of MMA and DMA from the aqueous solution into the cold trap were 99 ± 2% and 85 ± 2% correspondingly. It should be noted, however, that these values were determined by directly comparing the peak heights of MMA and DMA GC peaks to those of TMA standards. This approach was employed in the absence of certified MMA and DMA standards. Attempts to improve the flushing efficiency by introducing a second $NaBH_4$ pellet only caused losses due to escape of MMA and DMA already trapped in the cold toluene.

The overall collection recoveries of MMA and DMA in the cold trap were 93 ± 2% and 81 ± 2% correspondingly. Despite their incompleteness, these recoveries were highly reproducible. Satisfactory accuracies have been obtained by comparing MMAA and DMAA samples to their respective standards, rather than utilizing the TMA standard (see analytical results section). The reproducibilities of MMA determinations obtained for five different samples (each 0.1 μg/ml MMA and 10 μg/ml DMAA) and five consecutive injections of the same MMA sample are shown in Figure 3. The relative standard deviation values were 4.5% for the former case and 2.1% for the latter.

The effect of sample volume was also studied. Equivalent amounts of MMAA and DMAA were added to degassed and acidified water, 15–200 ml in volume. Arsine recoveries from these samples were compared relative to that of the 15-ml sample, Table III. Complete arsine recovery from the 200-ml samples was accomplished only when two $NaBH_4$ pellets were introduced simultaneously. This experiment reinforces the previous conclusion that large quantities of $NaBH_4$ have to be introduced rapidly into the system to ensure the instantaneous reduction of the acids and their removal from the sample solution. Since the arsine generated from aqueous samples larger than 200 ml can be collected in less than 5 ml of toluene, a preconcentration factor of at least 40 can be achieved.

Table III. Effect of Reduction Conditions on Recovery of MMA

Reduction conditions	% MMA Recovered[a] 100-ml sample	200-ml sample
1) Reduction with 1 $NaBH_4$ pellet	55.3	15.3
2) Same as No. 1 but with argon flushing of the aqueous sample (3 min.) following initial reduction	80.0	48.8
3) Same as No. 1 but with addition of a second $NaBH_4$ pellet following the initial reduction	56.0	60.0
4) Reduction with 2 $NaBH_4$ pellets added simultaneously	100	100

[a] Recoveries were determined relative to a 15-ml sample containing the same amount of MMAA and reduced with a single $NaBH_4$ pellet.

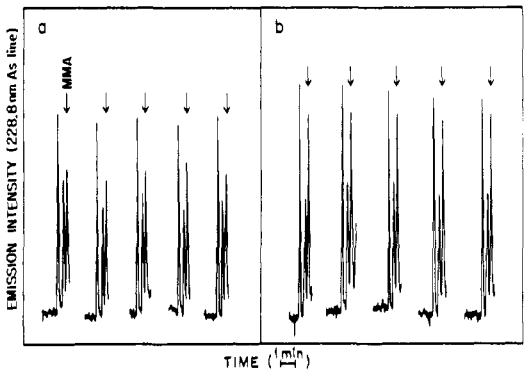

Figure 3. Reproducibility in determining MMAA using the cold toluene trap method

(*a*) 4-μl injection of 0.1 μg/ml MMA benzene solutions. (*b*) 6-μl injections of a 0.1 μg/ml MMA benzene solution

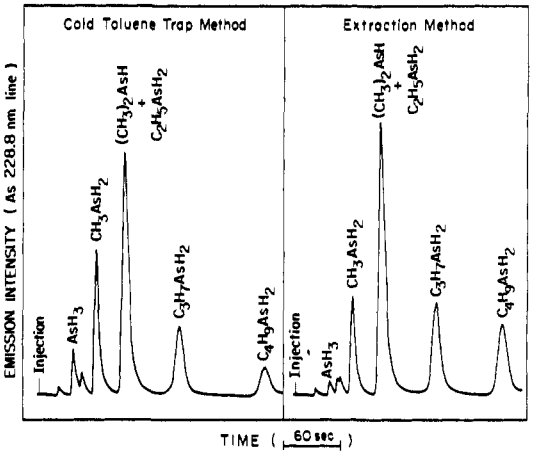

Figure 4. Relative collection efficiencies of the cold toluene trap and extraction methods for various alkylarsines

5-μl injection of alkylarsine toluene solutions

Liquid Nitrogen Cold Trap Method. A significant improvement in relative sensitivity and more complete arsine collection can be achieved by utilizing a liquid nitrogen cold trap (*11*). After sample collection, the trap (interfaced to the GC column inlet) should be instantaneously heated in order to provide adequate chromatographic resolution. The cold toluene method, however, has two distinct advantages over the liquid nitrogen one: every sample can be analyzed several times (several injections) to improve accuracy and, since the arsine–toluene solutions are stable for at least 24 hours, a large number of samples can be first collected and then analyzed, a very desirable feature in routine-type analysis.

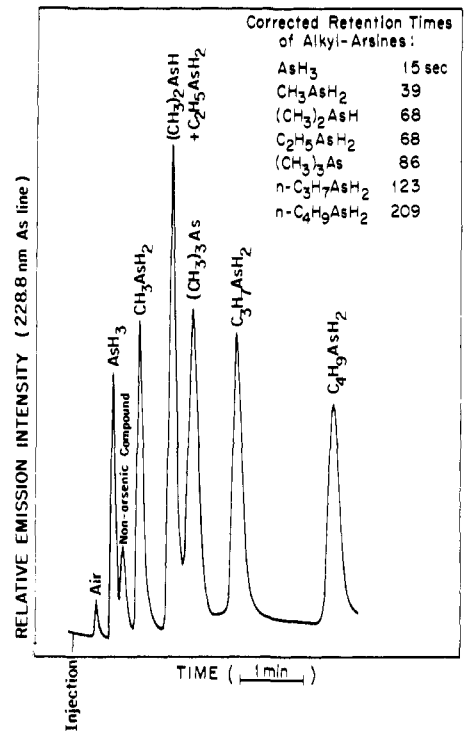

Figure 5. GC chromatogram of alkylarsines

Solid Adsorbent Trap Method. Braman and Foreback (*11*) utilized a column consisting of glass microbeads coated with a thin film of metallic silver to preconcentrate volatile alkylarsines from air. After collection, the adsorbed arsines were removed from the column by flushing it with concentrated KOH (oxidizing the arsines to the corresponding acids). For determination, these acids had to be reduced again to the corresponding arsines. We tried to modify the above procedure by eliminating the KOH desorption step. Unfortunately, neither flushing the column with benzene (or toluene) nor heating it, brought about the elution of the adsorbed arsines. Consequently, a different approach was adopted. A similar column (4 inches long) consisting of the same packing material utilized in the GC column was used to adsorb the arsines. The collection efficiency was 100%. After collection, the column was heated and the desorbed arsines were flushed (argon or helium) into a cold toluene trap. This method should provide a rather simple preconcentration step for arsines from either water or air samples.

GC Separation of Alkylarsines. In addition to MMAA and DMAA, the $NaBH_4$ reduction method can be applied to the determination of other alkylarsenic acids as well. The method, however, is limited to those arsines whose re-

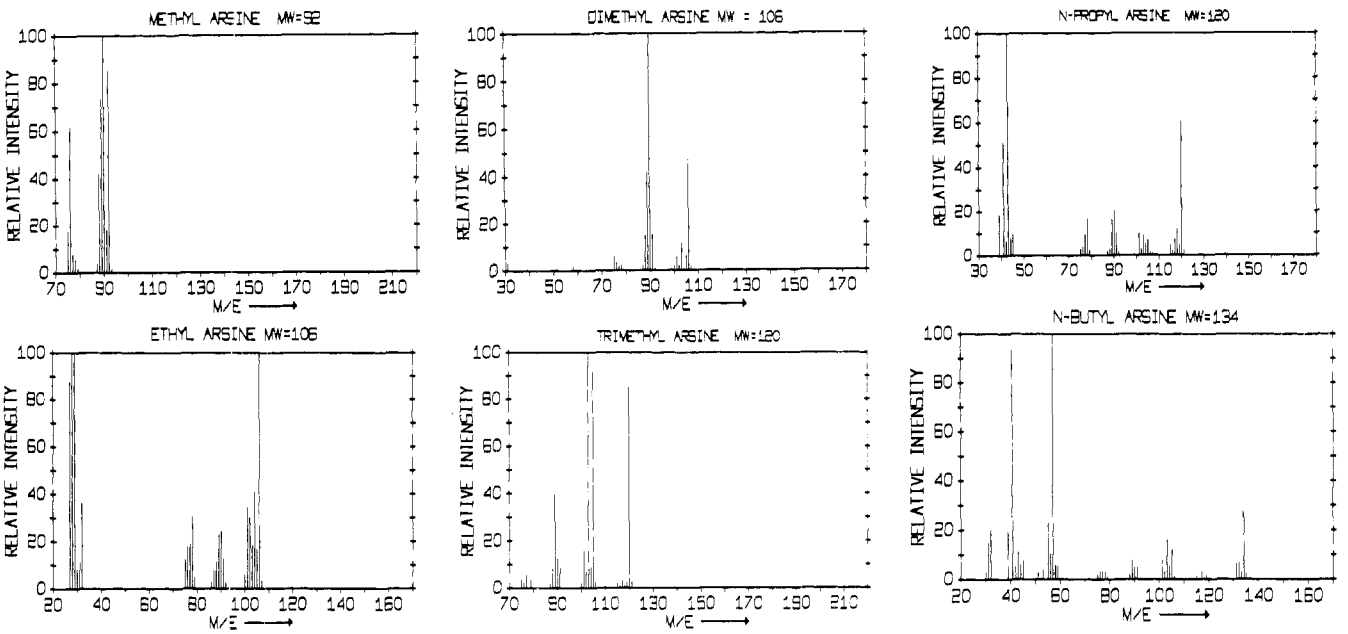

Figure 6. Mass spectrograms of the alkylarsines

Conditions: 70 eV, helium carrier gas

tention time does not exceed that of the toluene solvent (t_R = 250 sec.). This, therefore, excludes the determination of acids with alkyl moieties greater than C_5. A sample containing 50 μg each of $Na_2AsO_4 \cdot 7H_2O$, MMAA, DMAA, ethyl-, *n*-propyl-, and *n*-butylarsonic acids was reduced and its arsine products were collected in 10 ml of toluene by both the extraction and the toluene cold trap procedures. As previously discussed, the collection efficiency depends on the volatility of each arsine. AsH_3 (bp −55 °C) was too volatile to be quantitatively collected by either procedure. MMA was efficiently collected only by the cold toluene trap. DMA and ethylarsine, because of their moderate volatility were reproducibly collected by either method. The low-volatility *n*-propyl- and *n*-butylarsines were only partially volatilized (50% retained in water) and, therefore, were quantitatively collected only by the extraction method. The relative efficiency of the two collection methods for each of the arsines is demonstrated by Figure 4. A more complete chromatogram, including the TMA, is shown in Figure 5. The positive identification of the arsines was accomplished by GC-MS. The mass spectrograms obtained for each arsine appear in Figure 6.

Included in each chromatogram are three peaks occurring at t_R = 20, 42, and 132 seconds. None of these components contain arsenic; they must be present in relatively high concentration to be detected at the arsenic wavelength (selectivity >10,000). The first peak has been identified as air and the last peak as a toluene impurity. The identity of the second peak is unknown, although it was present in a large number of doubly-distilled solvents studied. This peak was present even when more inert septums (Teflon and aluminum lined) were utilized. The high reproducibility and sharpness of this peak make it unlikely that it is a result of a column bleeding. The t_R for this ghost peak was very close to that of the MMA peak, thus setting a limit on the detection limit for this arsine.

Instrumental Parameters. *Column Operation.* Newly packed GC columns must be conditioned for at least 48 hours, preferably under reduced pressure (5–15 Torr), at 200 °C. Once conditioned, a column will operate satisfactorily for at least two months (over 2000 injections). Although the GC column can be operated at atmospheric pressure, its stability and longevity are poorer than under the conditions recommended. For routine work, the sample size should not exceed 100 ng of As. In operation, the microwave plasma is ignited prior to sample injection. Once the arsine components are eluted, the plasma is extinguished before the solvent enters the capillary. This is necessary to avoid carbon and polymer deposition on the quartz capillary walls. Up to 10 samples per hour can be injected, although this number should be smaller (about six) when operating at the detection limit level.

Microwave Power. Microwave power was found to have a small (although consistent) effect on the arsenic emission intensity. The intensity was constant between 15–35 watts, decreased by approximately 10% above 35 watts and remained at this level up to 90 watts. Below 15 watts, the plasma was unstable and was easily extinguished. Throughout these experiments, the microwave power was maintained at 20 watts.

Selectivity and Sensitivity. The arsines entering the plasma are fragmented and their arsenic atoms are electronically excited. The emission intensity of arsenic measured at 228.8 nm is directly proportional to the arsine concentration in the plasma. From a previous study (*17*), the selectivity of the detector to arsenic was found to be in excess of 20,000. Hence, very few spectral interferences are observed from trace impurities which are simultaneously eluted with the arsines. Also, because the selectivity of the MES detector is based on the detection of atomic arsenic, the sensitivity should be practically independent of the molecular structure of the arsines. In fact, the sensitivity ratio MMA/TMA for equivalent amounts of the two was 1.01. DMA was harder to compare because of its incomplete recovery. The arsenic detection limit, defined as the amount of the element which produces a signal twice the size of that obtained from the blank, is 20 pg. Because a preconcentration factor of at least 40 can be obtained, using the toluene cold trap procedure, the relative sensitivity is 0.25 μg/l. or better. For lower arsine levels (1–3 ng/l.), the liquid nitrogen trap should be utilized.

Analytical Results. The arsenic emission intensity (peak height) was linearly proportional to its concentration, at the 0.01–20 μg/ml range studied, Figure 7. Even

Table IV. Determination of MMAA and DMAA Content in Commercial Pesticide Samples

Sample	Manufacturer's analysis	Direct determination: Cold trap, % MMAA	Direct determination: Cold trap, % DMAA	Direct determination: Extraction, % DMAA	Standard addition (cold trap), % MMAA	Standard addition (cold trap), % DMAA	Estimate of % inorganic As (measured as AsH_3)
I	22.7% $(CH_3)_2AsO(ONa)$, 3.9% $(CH_3)_2AsO(OH)$, 6% NaCl, 17% surfactant	0.85 ± 0.05	24.8 ± 1.5	23.0[a]	0.81 ± 0.04	25.5[a]	Trace
II	60% $(CH_3)_2AsO(ONa)$, NaCl, Na_2SO_4	0.91 ± 0.04	46.0 ± 1.6	45.0[a]	0.96 ± 0.07	44.3[a]	>0.5
III	81% $(CH_3)_2AsO(OH)$, H_2O, NaCl, Na_2SO_4	8.0[a]	68.5 ± 1.5	69.0[a]	7.4[a]	69.7[a]	>4

[a] These values are based on the determination of a single sample.

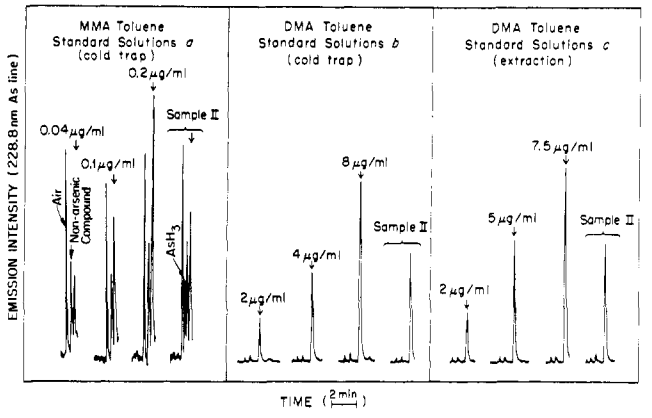

Figure 7. Chromatograms of MMA and DMA toluene solutions

(*a*) Standard solutions were prepared by reducing 0.004, 0.01, and 0.02 μg/ml aqueous solutions (15 ml) of MMAA and flushing the arsines generated into 5 ml toluene (−5 °C). Sample II is a 10 μg/ml solution of a commercial (pesticide quality) sodium cacodylate (Ansul Company). (*b*) DMA standards were prepared as described in *a*. Monochromator slit width was set at 20 μm for DNA and 30 μm for MMA determination. (*c*) DMA standards were prepared by reducing 2.0, 5.0, and 7.5 μg/ml aqueous solutions (15 ml) of DMAA and extracting the arsine generated with 5 ml toluene. A 10 μg/ml solution of Sample II was similarly prepared

though the MES detector appears to be equally sensitive to all arsines, regardless of their molecular structure, a single universal calibration curve cannot be used. Because of the different collection efficiencies of the various generated arsines, each arsenic acid in the sample should be compared to its corresponding standard, and both should be reduced and collected under identical conditions. On the other hand, the same standard can be utilized for the determination of its equivalent arsenic acid in various samples, with very little dependence on the matrix of the sample.

Table IV summaries the analytical results obtained for three commercial pesticides (Ansul). The manufacturer has determined the concentration of DMAA by acid titration, but lacking the necessary methodology was unable to determine the MMAA concentration of these samples. Both the extraction and the cold trap methods have been successfully employed (Figure 7), although the former was more efficient for DMA collection. The DMAA concentration values were only partially in agreement with those reported by the manufacturer. On the other hand, there was excellent agreement between the results obtained by the two collection methods and the standard addition method. The average RSD for all determinations was 4.9% and the average relative error was 2.4%. Precision should be improved if a better cold trap is utilized, and eventually be limited to 2.1%, the GC-MES measurement precision (see cold trap collection). To estimate the accuracy of the method for the determination of pesticides in water samples, both synthetic fresh and salt water samples were prepared. The samples were made 0.5 μg/l. MMAA and 1.0 μg/l. DMMA. The arsines generated by reduction of 200-ml aliquots of these samples were collected in a 5-ml cold toluene trap. Although operating close to the detection limit, the relative error accuracy (5%) was very similar to that obtained with the distilled water standards. Thus, the present analytical method can be used to determine arsenic acids as either major, minor, or trace components.

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LITERATURE CITED

(1) E. A. Woolson, "Arsenical Pesticides", E. A. Woolson, Ed., American Chemical Society, Washington, D.C., 1975, p 97.
(2) F. Challenger, *Chem. Rev.*, **36**, 315 (1945).
(3) D. P. Cox and M. Alexander, *Bull. Environ. Contam. Toxicol.*, **9**, 84 (1973).
(4) B. C. McBride and R. S. Wolfe, *Biochem.*, **10**, 4312 (1971).
(5) J. Tadmor, *J. Gas Chromatogr.*, **6**, 385 (1964).
(6) D. Vranti-Piscou, J. Kontoyannakos, and G. Parissakis, *J. Chromatogr. Sci.*, **9**, 499 (1971).
(7) W. C. Butts and W. T. Rainey, *Anal. Chem.*, **43**, 538 (1971).
(8) F. Roy, *J. Gas Chromatogr.*, **6**, 245 (1964).
(9) B. J. Gudzinowicz and J. L. Driscol, *J. Gas Chromatogr.*, **1**, 25 (1963).
(10) L. Johnson, K. Gerhardt, and W. Aue, *Sci. Total Environ.*, **1**, 108 (1972).
(11) R. S. Braman and C. C. Foreback, *Science*, **182**, 1247 (1973).
(12) Y. Talmi and A. W. Andren, *Anal. Chem.*, **46**, 2122 (1974).
(13) Y. Talmi and R. Crosmun, "Ecology and Analysis of Trace Contaminants", Progress Report, June 1973, ORNL-NSF-1, March 1973.
(14) L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Roch, *J. Am. Chem. Soc.*, **79**, 5884 (1957).
(15) B. J. Gudzinowicz and H. F. Martin, *Anal. Chem.*, **34**, 648 (1962).
(16) A. F. Trotman-Dickenson, Ed., "Comprehensive Inorganic Chemistry", Pergamon Press, New York, N.Y., 1973, pp 623–626.
(17) Y. Talmi and V. Norvell, *Anal. Chem.*, **47**, 1510 (1975).

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