upon reaction with nitrous acid. Attempts to analyze such mixtures by titration with sodium nitrite would fail because of consumption of nitrous acid by compounds other than the primary aromatic amine. The highly colored N-nitroso and C-nitroso compounds formed with secondary and tertiary amines similarly might interfere with colorimetric methods. Simple gas chromatography would be unsuitable for nonvolatile amines. Yet, only the diazonium salt liberates nitrogen upon mild pyrolysis, thus providing a specific measure of primary aromatic amine content.

Analysis of nitrite in nitrate required special modification of the diazotization conditions. Anthranilic acid was chosen for diazotization because its diazonium salt has good water solubility. Hydrochloric acid was unsuitable for reaction in the presence of high concentrations of nitrate because of the potential formation of aqua regia. Since a strong acid was required to achieve rapid, quantitative diazotization, trifluoroacetic acid was substituted. Trifluoroacetic acid is completely dissociated in aqueous solution and is readily removed upon vacuum drying. It was necessary to run reactions in dilute solution rather than platinum boats to prevent small, but significant losses of nitrous acid by volatilization. The results of analysis of synthetic nitrite-nitrate mixtures are given in Table III.

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# Determination of Cacodylic Acid (Hydroxydimethylarsine Oxide) by Gas Chromatography

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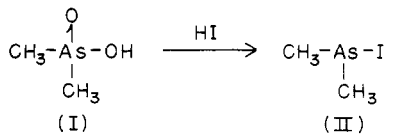
Despite the introduction of synthetic organic pesticides during the last 30 years, arsenic compounds still find extensive use in agriculture. In 1972, over 1.2 million pounds of arsenicals were applied by permit in California, about 70% as inorganics including sodium arsenite and lead arsenate and the remainder as the herbicides hydroxydimethylarsine oxide (cacodylic acid) and salts of methanearsonic acid (MSMA and DSMA) (*1*). Although most of the inorganic arsenicals were used for agricultural and structural pest control, about 30% of the organic arsenicals were used by irrigation, flood control, and water resource organizations. Significant residues of the arsenicals have been found in soil and water (*2, 3*).

Most methods for the determination of arsenic compounds are based on their conversion to arsenic trioxide ($As_2O_3$) which subsequently is reduced to arsine ($AsH_3$) and quantitated by colorimetry (*2, 4*), atomic absorption spectrophotometry (*5, 6*), or emission spectroscopy (*7*). Still others [atomic absorption (*8, 9*), single-sweep polarographic (*10*), neutron activation (*3*), and X-ray fluorescence (*11*)] measure the original arsenical directly. While the majority provide adequate recoveries and sensitivity, the determination represents only total arsenic; contributions from arsenite, arsenate, cacodylate, or methanearsonate cannot be differentiated. Paper chromatography followed by colorimetric determination of the separated arsenicals is the only selective analysis reported (*12*).

This nonselectivity may be prohibitive. For example, determination of applied cacodylic acid in a waterway may be hindered by a background of other arsenicals arising from natural water content and runoff from treated fields areas. Furthermore, some cacodylic acid formulations contain nearly equal amounts of MSMA.

We report here a procedure whereby cacodylic acid and its salts can be determined rapidly with a detectability limit below 0.05 ppm in water and 0.5 ppm in soil. The method, which excludes other arsenicals, is based on conversion of cacodylic acid (I) to iododimethylarsine (II) with hydriodic acid (Equation 1), followed by determination with electron-capture gas chromatography.




(I) (II)

## EXPERIMENTAL

**Apparatus.** Gas-liquid chromatography was performed with a Varian Model 1700 gas chromatograph equipped with a tritium electron-capture detector (ECD) and a 15-ft × ⅛-in. (o.d.) stainless steel column containing 10% DC-200 on 60/80 mesh Gas Chrom Q. Oven temperature was 105 °C; injection port, 125 °C; detector, 200 °C; carrier gas (nitrogen) flow was 20-30 ml/minute. Iododimethylarsine had a retention time of 5 minutes. Mass spectra were obtained with a Finnigan Model 3000 gas chromatograph-mass spectrometer operated at 70 eV and equipped with a 4-ft × ⅛-in. (i.d.) glass column containing 2% OV-1 on 60/80 mesh Chromosorb G.

**Reagents.** Hydriodic acid (Fisher Scientific Co.) was a 57% w/v certified grade. Cacodylic acid (K & K Laboratories) was recrystallized twice from aqueous ethanol, mp 194-6 °C [reported (*13*) 200 °C]. All solvents were redistilled twice before use.

Standard iododimethylarsine was prepared (*14*) by combining 5.0 g cacodylic acid, 16.0 g potassium iodide, and 20 ml of water in a small separatory funnel; sulfur dioxide (Matheson Gas Products) was bubbled in for about 10 minutes until the solution was saturated, and 5-ml portions of 6*N* hydrochloric acid were added

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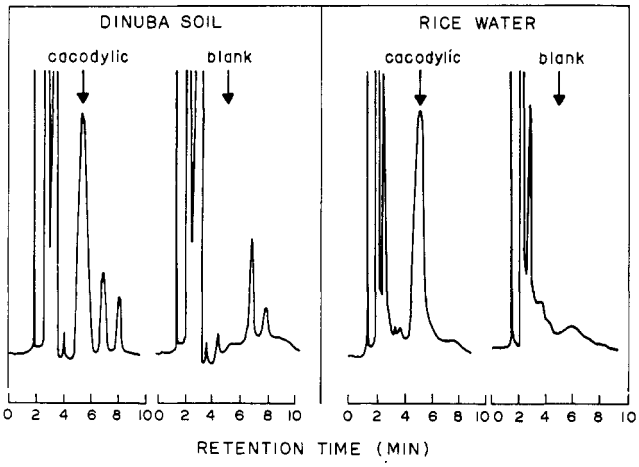


**Figure 1.** Sample chromatograms of iododimethylarsine in Dinuba soil at 1.5 ppm cacodylic acid and rice field water at 0.15 ppm cacodylic acid

until the yellow lower layer of product separated. The crude iododimethylarsine (7.8 g, 94% yield) was removed, purified by vacuum distillation, and stored cold in a sealed glass vial. *Poison.* Identity was confirmed by mass spectrometry: *m/e* 232 ($IAsMe_2$, parent), 217 (IAsMe), 202 (IAs), 105 ($AsMe_2$, base). The pure product was homogeneous in GLC.

**Procedure.** *Water.* Water samples (collected from a rice field in Sutter County, Calif.) were filtered through Whatman No. 1 filter paper to remove suspended debris, and analyzed in triplicate. A 15-ml test tube containing a 10.0-ml subsample was placed in a water bath (80–90 °C) and evaporated to dryness with a stream of filtered air. The sides of the tube were rinsed with about 1 ml of methanol and the contents were again evaporated to dryness. The residue was swirled with 100 μl of hydriodic acid for about 30 seconds, 5.0 ml of hexane were added, and the contents were mixed thoroughly with a vortex stirrer to extract all of the iododimethylarsine into the hexane. Quantitative injections of 1 to 3 μl of the hexane phase were introduced into the gas chromatograph within 15 minutes of derivatization.

*Soil.* Soil samples (Dinuba fine sandy loam from Modesto, Calif.) were air dried and pulverized; subsamples were analyzed in triplicate. Hydriodic acid (1.0 ml) was added to a 15-ml test tube containing a 1.0-g subsample. After swirling for about 30 seconds, 5.0 ml of hexane was added, the contents were mixed thoroughly with a vortex stirrer, and the soil was allowed to settle. Quantitative injections of 1 to 3 μl of the hexane phase were introduced into the gas chromatograph within 15 minutes of derivatization.

*Standard Curves.* Residues were quantitated by comparison of gas chromatogram peak heights with values from a standard curve prepared from known amounts of cacodylic acid near the expected residue level. For example, 10-, 20-, and 30-μl aliquots of a standard solution containing 0.10 μg/μl of cacodylic acid in distilled water were added to a series of test tubes; the contents were evaporated, treated with 100 μl of hydriodic acid each, and extracted with 5.0 ml of hexane. GLC peak heights resulting from equivolume injections of these standards plotted against original cacodylic acid concentration resulted in an acceptable straight line. To determine recoveries, water samples (10.0 ml) were fortified at 0.15 ppm with the cacodylic acid standard solution after being placed in a test tube for evaporation, and soil samples (1.0 g) were fortified at 1.5 ppm with an equal amount of cacodylic acid solution before addition of hydriodic acid; resultant values were compared to the standard curve.

## RESULTS AND DISCUSSION

The present research sought a rapid, simple, quantitative method by which common arsenic herbicides could be determined with specificity in environmental samples. The widely-available technique of electron-capture gas chromatography would provide such a method if the herbicides were converted to a volatile form detectable by the instrument. The haloarsines offered the necessary properties.

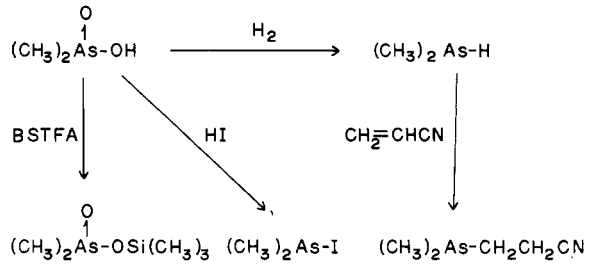


**Figure 2.** Volatile derivatives of cacodylic acid

**Table I. Recovery of Cacodylic Acid from Water and Soil**

| Sample | Added, ppm | Found ppm[a] | Recovery, %[a] |
|---|---|---|---|
| Distilled water | 0.15 | 0.137 ± 0.012 | 92.3 ± 7.4 |
| Rice water | 0.15 | 0.150 ± 0.004 | 100 ± 2.6 |
| Rice water (blank) | 0 | <0.050 | 0 |
| Dinuba soil | 1.5 | 1.22 ± 0.11 | 81.3 ± 5.1 |
| Dinuba soil (blank) | 0 | <0.50 | 0 |

[a] Mean and standard deviation from three samples.

Chlorodimethylarsine, dichloromethylarsine, and arsenic trichloride formed readily from cacodylic acid, methanearsonic acid, and arsenious acid, respectively (*15*), but they eluted poorly in submicrogram amounts and tended to corrode columns and detectors. Iododimethylarsine also formed readily, the necessary hydriodic acid serving as both reducing and iodinating agent. Iododimethylarsine was hexane-soluble, volatile, powerfully electron-capturing, and could be chromatographed in nanogram amounts under conditions where interfering arsenic halides did not appear. The GLC conditions precluded interference by other electron-capturing environmental contaminants such as chlorinated hydrocarbon insecticides.

**Recovery of Cacodylic Acid.** Various parameters which might affect the analytical recovery of cacodylic acid were examined. Distilled water samples (10 ml) fortified with 1.0 ppm cacodylic acid were adjusted to pH 11, 9, 7, 5, and 3, and processed in the usual manner; recoveries were independent of sample pH. Reaction with hydriodic acid was complete and quantitative within 15 seconds provided that less than 20 μl of sample water remained per 100 μl of added hydriodic acid. To demonstrate the selectivity of the method, cacodylic acid (10 μg) was derivatized alone and in the presence of 100 μg each of sodium arsenite, sodium arsenate, and methanearsonic acid with equal recovery of cacodylic acid in all cases.

While neat iododimethylarsine was fairly stable (especially when stored in a chilled, sealed vial), solutions in organic solvent at ng/μl levels indicated decomposition within 30 minutes. A stock solution (1.0 μg/μl) in hexane, prepared in an amber glass volumetric flask and stored in a refrigerator, was stable for about one week. This solution was diluted to 1.0 ng/μl in hexane for gas chromatography to define the retention time of iododimethylarsine and establish the linearity of the ECD detector. However, both convenience and the instability of standards dictated that standard curves be prepared by the described method and that sample solutions be analyzed within a few minutes of derivatization. If analysis indicated residues greater than the 0.05 to 0.5 ppm range in water or 0.5 to 5.0 ppm range in soil, smaller samples were used. This precluded the possibility of a nonlinear derivatization response. In addition, it was observed that sodium sul-

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fate caused rapid disappearance of iododimethylarsine and therefore was not suitable to dry extracts. Although the preparation of standard iododimethylarsine was not difficult, the compound must be recognized as VOLATILE AND POISONOUS, and both standards and derivatized samples should be handled with adequate ventilation and precautions against skin contact.

Typical recoveries (Table I) were based on the standard curve derived directly from cacodylic acid. Attempts to determine the exact yield of the derivatization step with a standard curve based on iododimethylarsine gave recoveries greater than 100%, due to instability of the standard solution. Interferences in the water analyses were not serious (Figure 1), and the detectability limit of 0.05 ppm or less could be lowered further by derivatization of a larger water sample. Attempts to lower the detectability limit in soil (about 0.5 ppm) by prior extraction of the cacodylic acid with methanol or aqueous methanol failed, probably because of its binding to soil particles (*13*). Previous methods for determination of arsenic in soil have avoided this problem by converting the bound cacodylic acid to arsenic trioxide, which is then removed as arsine.

Major advantages include simplicity and rapid analysis; dried soil samples can be weighed, derivatized, and analyzed in less than 10 minutes, and water samples, once evaporated, require a similar amount of time. The instability of iododimethylarsine was circumvented by using a standard curve based on fortification, and by analyzing each sample in triplicate.

**Other Arsenic Derivatives.** Trimethylsilyl (TMS) derivatives (Figure 2) of arsenite, arsenate, cacodylate, and methanearsonate were prepared (*16*) from 5 mg of the arsenical, 200 μl of bis(trimethylsilyl)trifluoroacetamide (BSTFA), and 200 μl of dimethylformamide in a septum capped vial. While the four derivatives were separated by GLC (5 ft, 5% SE-30), the reaction was never reproducible, perhaps because of the hydrolytic instability of the products.

Cyanoethylated derivatives (Figure 2) were prepared by trapping the effluent of a nitrogen-swept arsine generator (*7, 17, 18*) in chilled acrylonitrile containing sodium methoxide catalyst. Although the previously described methanearsonate derivative (*17*) and the cacodylate derivative were separated by GLC (5 ft, 5% OV-17), the reaction proved too slow for practical use. Heating and/or additional catalysis produced chromatograms obscured by polymerization products of acrylonitrile.

The major impediment to the development of a general procedure for arsenicals was the gas chromatography of the highly reactive arsenic derivatives. Work is in progress on solving this difficulty so that the hydriodic acid procedure may be extended to methanearsonic acid and the inorganic arsenicals.


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# Detailed High Resolution Gas Chromatography–Mass Spectrometry Analysis of a Pyrolysis Naphtha


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Modern gasolines are complex blends of many hydrocarbon streams which are, in turn, complex mixtures. Most of these blending components are explicitly manufactured for gasoline production. Occasionally a by-product stream from an unrelated process is of such boiling range and octane number that with little or no processing it can be utilized as a gasoline blending stock.

The liquid recovered from the pyrolysis of naphtha to make ethylene is such a product. It consists of unconverted hydrocarbons of the feed naphtha and large quantities of olefins and aromatic compounds formed during the pyrolysis step.

This paper describes use of mass chromatography (MC) to make compound-type identifications so that a routine high resolution capillary gas chromatography (HRCGC) method could be used to make analyses of pyrolysis naphthas. The MC method (*1–5*), when combined with known HRCGC retention data, provided a uniquely rapid way to correctly analyze pyrolysis naphthas whose compositions were unlike those of the typical gasoline blending components.

## EXPERIMENTAL

Data presented here were obtained using a 1000-ft squalane-coated 0.02-in. i.d. capillary column in a Hewlett-Packard F and M 810 gas chromatograph. The column is interfaced to a Nuclide 12-90-G mass spectrometer through a single-stage 3-mm o.d., 1-mil thick dimethyl silicone membrane enricher. The enricher is maintained at about 150 °C. A comparison of total ion monitor (TIM) and flame ionization detector (FID) traces shows negligible resolution loss due to interfacing. The column was programmed from 30 to 100 °C at 1 °C/minute. Helium was used as carrier gas.


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