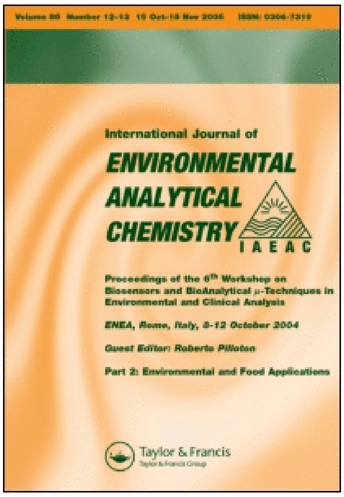

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# Analysis and Speciation of Arsenic in Herbicide-Treated Soils by DC Helium Emission Spectrometry

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The analysis and speciation of arsenic in two South Texas soil samples treated with arsenical herbicides was carried out utilizing hydride generation-dc helium emission spectrometry. Extractions with Bray P-1 solution ($0.03\,M\,NH_4FF + 0.025\,M\,HCl$) showed that the extractability of arsenic decreased in the order dmaa (dimethylarsinic acid or its salts) > maa (methanearsonic acid or its salts) > arsenate. It was found that maa underwent degradative changes such as oxidation of the C-As bond or methylation most easily. In general the herbicides were more strongly sorbed on clay than on loam.

KEY WORDS: Arsenical herbicides; soils; DC emission spectrometry; hydride generation: speciation.

## INTRODUCTION

During the past 25 years organic arsenicals have found extensive use as herbicides and pesticides. Since they are effective at lower rates of application and exhibit less residual phytotoxicity, they have largely replaced inorganic arsenicals such as lead and calcium arsenates and sodium arsenite. With their increased use, considerable interest has been expressed in the development of accurate and sensitive procedures for the quantitative determination of these substances. Speciation is of particular importance, since the toxicity and ecological fate of an element is determined by its chemical form. Speciation is especially relevant in the case of arsenicals which can undergo a variety of chemical transformations in the soil through microbial action. Two such changes which are mediated by microbial action are the oxidation[1] of the C—As bond to form $CO_2$ or the formation of methylated arsines under anaerobic conditions.[2] One of the other mechanisms by which the applied arsenicals may undergo change is the formation of iron and aluminium arsenates which are sparingly soluble.[3] Some of these are rather slow processes and may require up to six months to reach equilibrium.[4] The soil pH (5–7) also determines the chemical forms which the arsenicals assume and, hence, their uptake by plants.

Because there exist a number of mechanisms by which arsenic is redistributed, it is not surprising that the phytotoxicity of the arsenicals is more closely related to the extractable forms of arsenic than to the total arsenic content.[5] Speciation procedures have been applied to only a limited number of organic compounds. Methanearsonic (MAA) and dimethylarsinic (cacodylic) acid (DMAA) are the most widely determined since these acids and their salts find common use as herbicides. Interest in these compounds and their corresponding arsines as well as in trimethylarsine has also been generated by evidence that they may occur in nature as a result of bacterial reduction and methylation of inorganic arsenic.[2]

Among the analytical methods which have been developed reduction of the arsenic compounds to the corresponding arsines has been found to be the most promising procedure for releasing the element from its matrix.[6] Since there is evidence that only the undissociated forms of the arsenic acids are capable of being reduced to the corresponding arsines, some measure of selectivity can be achieved by controlling the pH of the medium. The differences in their boiling points permit the separation of the arsines by fractional volatilization,[7,8] although gas chromatography may prove to be useful in the separation of a wider range of compounds.[9] Various techniques including atomic absorption,[10] DC helium emission spectrometry[8,11] and microwave emission spectrometry[7,9] have been employed for the determinatiion of the arsines. DC emission spectrometry provides high sensitivity and element selectivity and is considerably less prone to interferences than is atomic absorption. This study evaluates the capability of hydride generation–DC helium emission spectrometry as an analytical tool in the speciation of arsenic in two South Texas soils treated with arsenical herbicides.

## EXPERIMENTAL

### Materials

The two soil samples, a fine sandy loam and the underlying clay, belonged to the well-characterized Lufkin series and were sampled from a location in

Brazos County near College Station, Texas.[12] The particle size analysis and mineralogy data of the two samples are given in Tables I and II.

Standard stock solutions of As(III) and As(V) were prepared by dissolving reagent grade sodium arsenite ($NaAsO_2$) and sodium arsenate ($NaH_2AsO_4$) in water so as to give final concentrations of 1000 ppm arsenic in each case. Standard solutions of the organo-arsenicals were prepared at the same concentration of arsenic by dissolving appropriate amounts of disodium methanearsonate (Pfaltz and Bauer) and dimethylarsinic (cacodylic) acid. The dimethylarsinic acid was recrystallized twice from a product (98% purity) purchased from the Sigma Chemical Co. Sodium borohydride (99% purity) was obtained from the Alpha-Ventron Corp. and was found to contain a measurable amount (10–40 ppb) of arsenic(V). All other chemicals used were of reagent grade. The herbicides used in the study were the following:

1) "Bueno-6" containing monosodium methanearsonate (MSMA), manufactured by the Diamond Shamrock Corp., Cleveland, Ohio.

2) "DSMA Liquid" (with surfactant) containing disodium methanearsonate (Diamond Shamrock).

3) "Phytar 560" (with surfactant) containing sodium cacodylate and cacodylic acid, manufactured by Ansul Company, Marinette, Wisconsin.

## Sample preparation

After removal of extraneous matter, 100 g aliquots of the soil samples were carefully weighed out into 250 ml Erlenmeyer flasks. Sufficient water was added to each portion so as to convert it into a moist paste and 10 ml of the spiking solution (100 ppm in arsenic) was added. The spiked samples were shaken on a wrist-shaker for four hours and each sample was quantitatively transferred to a 250 ml beaker and dried in air at 40°C. The dried samples were ground so as to pass through a No. 14 mesh sieve and stored in polyethylene bottles for a minimum period of six months before extraction and analysis.

A weighed quantity (25 g) of equilibrated sample was extracted with 250 ml of the Bray P-1 solution[4] (0.03 M $NH_4F + 0.025$ M HCl) for two hour periods. After filtration, the filtrate and the distilled water washing were combined and reserved for speciation.

## Instrumentation and procedure

The details of the arsine generator and the plasma emission detection system have been described elsewhere.[13] These were slightly modified for use in the present study (Figure 1). An empty U-tube otherwise identical with the sample trap immersed in a Dry-Ice-isopropanol bath[7] was interposed between the

TABLE I

Particle size analysis of the soil samples[a]

| | | | Per Cent Composition | | | |
|---|---|---|---|---|---|---|
| Sample | Horizon | Depth (inches) | Sand (2–0.05 mm) | Silt (0.05–0.002 mm) | | Clay (<0.002 mm) |
| Loam | A1/A2 | 0–7 | 50.2 | 43.0 | | 6.7 |
| Clay | B21tg | 07–21 | 22.0 | 29.7 | | 48.3 |
| | | | | | coarse clay (0.002–0.0002 mm) | fine clay (<0.0002 mm) |
| Loam | A1/A2 | 0–7 | | | 32 | 68 |
| Clay | B21tg | 07–21 | | | 16 | 84 |

[a] Based on Ref. 12.

TABLE II

Mineralogic composition of the soil samples[a]

| Soil sample | Horizon | Sand | Silt | Clay |
|---|---|---|---|---|
| Loam | A1/A2 | QZ > 40%<br>FD < 10% | QZ > 40%<br>FD 10–40%<br>CR < 10% | QZ < 10%<br>MT > 40%<br>KK 10–40% |
| Clay | B21tg | QZ > 40%<br>FD < 10% | QZ > 40%<br>FD < 10%<br>CR < 10% | QZ < 10%<br>MT > 40%<br>KK 10–40% |

QZ: Quartz; FD: Feldspar; CR; Cristobalite; MT: Montmorillonite; KK: Kaolinite.
[a]Based on Ref. 12.

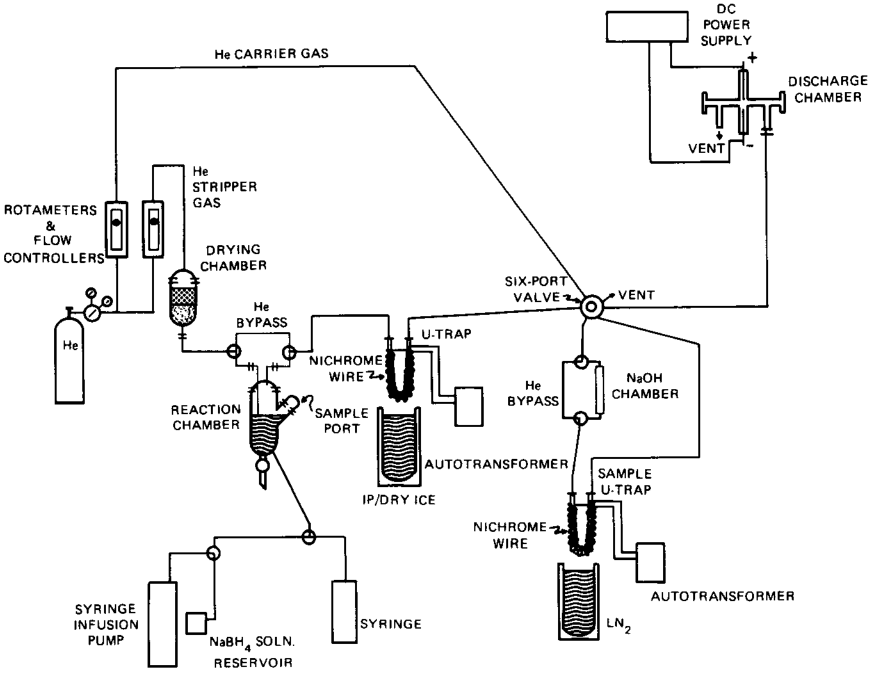

FIGURE 1 Schematic diagram of the arsine generation system.

arsine generator and the sample trap to serve as a water trap. This device was found to be very efficient, allowing only a fraction of a microliter of water to enter the chamber during analysis without any significant loss of the arsines. A glass-tube (18 cm long, 6 mm i.d.) packed with powdered sodium hydroxide (Fisher Scientific, Cat. No. 78608) was connected to the sample exit to absorb residual carbon dioxide. A Whitey three-way ball valve at each end of the absorber tube provided the option of directing the gas flow through a stainless steel bypass tubing (0.125 inch i.d.).

Impurities in the commercial grade of helium used are readily observable because of the high sensitivity of the detector. Air components, carbon dioxide, moisture and light hydrocarbons constitute the major impurities. Band emissions from carbon-containing compounds are very pronounced at the arsenic wavelength. The helium gas is purified adequately by passing it first through molecular sieve 5A and then through a chamber containing Ascarite and anhydrous magnesium perchlorate.

The experimental conditions for the determination of the organoarsines were identical with those for total inorganic arsenic[13] (pH ~ 1.3 provided by a 5% oxalic acid medium) although the two were determined in separate runs due to the different sensitivity settings required on the photometer. The sample volume was variable ranging from 1.0 to 10.0 ml. About 30 seconds after the heating (200 watts) of the sample trap was started, the effluent was routed around the $CO_2$ absorber. This maneuver ensured effective removal of $CO_2$ and at the same time prevented absorption of the organoarsines. The emission signal peaks were well separated and the following "retention times" (time between application of heat to the sample trap and appearance of the peak) were observed: $AsH_3$ (22.5 ± 1.5 s), $(CH_3)AsH_2$ (42 ± 2 s), $(CH_3)_2AsH$ (55 ± 2 s).

The arsine from As(III) was determined by carrying out the reduction in 0.5 M phosphate buffer at a pH of 6.5. The procedure was identical with the total arsenic procedure except that half the volume of borohydride was used and delivered to the reaction chamber in a single injection. Under these conditions no conversion of arsenate or organic arsenic acids to the arsines was observed.

## RESULTS AND DISCUSSION

### Precision and detection limits

Typical calibration lines for the three arsines are given in Figure 2. The sensitivity of the instrument for the analytes decreased in the order $AsH_3 > CH_3AsH_2 > (CH_3)_2AsH$ and the detection limits were 0.3, 1.0 and 2.9 ng, respectively. The precision of multiple analyses of all of the aqueous samples analyzed for total inorganic arsenic varied within the range ± 1.0% to

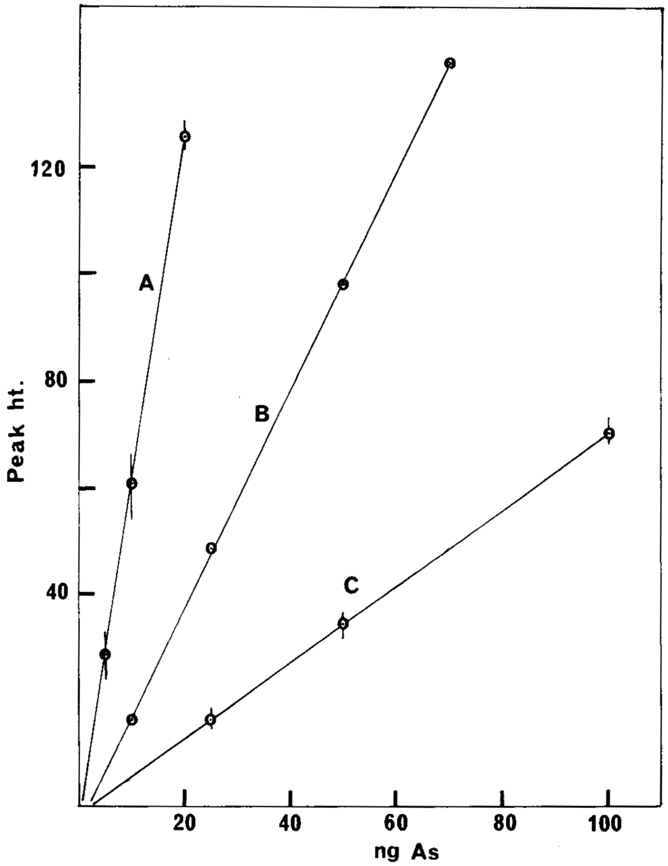

FIGURE 2 Calibration curves for the arsines.
A: $AsH_3$, B: $CH_3AsH_2$, C: $(CH_3)_2AsH$.

±8.9% (relative) with an average of ±4.0%. The precision in the analysis $CH_3AsH_2$ varied from ±1.3% to ±8.2% (relative) the average being 5.2%. The precision was significantly lower in the case of $(CH_3)_2AsH$ the range being from ±4.2% to ±8.8% (relative) with an average of ±7.0%. A significant reagent blank correction was necessary in the determination of total inorganic arsenic (pH ~ 1.3). (Further purification of the oxalic acid had no effect on the blank values. This led us to the conclusion that the borohydride contained a small amount of arsenate). Reagent blanks in determination of As(III) were negligibly small. The As(V) content was determined as the difference between total inorganic arsenic and the As(III) content. The precision in the determination of As(III) ranged between ±4.1% and ±1.7% (relative) with an average of ±2.7%.

The extractions were carried out in duplicate and the determinations in triplicate.

## Analysis of the herbicides

The herbicides used in the study were analyzed by the DC-helium plasma emission method so as to test its analytical capability. From the results given in Table III it can be seen that there is good agreement between the manufacturers' values and ours. In addition to the major components reported to be present (manufacturers' label) small amounts of inorganic arsenic were found in all of the herbicides, the amount in Bueno 6 being significantly higher. Substantial amounts of methanearsonic acid and/or its salts were also found to be present in Phytar 560.

TABLE III

Analysis of the Herbicides by DC helium emission spectrometry[a]

| | maa[b] | | dmaa[c] | | |
|---|---|---|---|---|---|
| Sample | Present work | Mfgr.'s value | Present work | Mfgr.'s value | Total Inorganic arsenic |
| DSMA | | | | | |
| Liquid | 9.4±0.4 | 8.9 | — | — | 0.37±0.06 |
| Bueno 6 | 21.9±0.7 | 22.37 | — | — | 1.21±0.04 |
| Phytar 560 | 1.0±0.1 | N.R.[d] | 11.1±0.5 | 12.64 | 0.21±0.01 |

[a] All values expressed as % As by weight.

[b] Salts of monomethylarsonic acid.

[c] Dimethylarsinic acid and its salts.

[d] Not reported.

## Analysis of the soil extracts

The arsenical levels in the doped soil samples are given in Table IV. The results of the speciation of the Bray P-1 extracts of these soil samples are detailed in Table V. Examination of the results in Table V reveals several intersting features:

1) In the C1 samples doped with sodium arsenite, the As(III) species are almost totally (>92%) oxidized after equilibration. This is not surprising since As(V) is expected to be the dominant form except under reducing conditions such as exist in flooded soils.[12]

2) In the sam'les C1, C2, and C7, the percentage of extractable arsenic

TABLE IV

Arsenical levels in the doped soil samples

| Sample | Form of arsenical added | Conc. of added arsenical (as ppm As) | | | |
|---|---|---|---|---|---|
| | | As(III) | As(V) | maa | dmaa |
| Loam C1 | As(III) standard | 10.00 | — | — | — |
| Clay C1 | As(III) standard | 10.00 | — | — | — |
| Loam C2 | As(V) standard | — | 10.00 | — | — |
| Clay C2 | As(V) standard | — | 10.00 | — | — |
| Loam C3 | DSMA standard | — | — | 10.00 | — |
| Clay C3 | DSMA standard | — | — | 10.00 | — |
| Loam C4 | "DSMA liq." | — | — | 14.20 | — |
| Clay C4 | "DSMA liq." | — | — | 14.20 | — |
| Loam C5 | "Bueno 6" | — | — | 14.30 | — |
| Clay C5 | "Bueno 6" | — | — | 14.30 | — |
| Loam C6 | "Phytar 560" | — | — | — | 14.20 |
| Clay C6 | "Phytar 560" | — | — | — | 14.20 |
| Loam C7 | As(III), As(V) stds | 10.00 | 10.00 | 0.57 | 0.79 |
| Clay C7 | +"Bueno 6"+"Phytar 560" | 10.00 | 10.00 | 0.57 | 0.79 |
| Loam C8 | — | — | — | — | — |
| Clay C8 | — | — | — | — | — |
| Loam C9 | SDMA standard | — | — | — | 10.00 |
| Clay C9 | SDMA standard | — | — | — | 10.00 |

is much lower from clay than from loam. This can be rationalized on the basis of increased sorption due to the finer particle size of the clays. The relatively greater difficulty of extraction of the inorganic aresenicals from clay is also largely due to the formation of sparingly soluble aluminium and iron arsenates.[14]

3) In the samples doped with salts of methanearsonic acid (C3, C4 and C5) the differences in extractability between loam and clay samples is much smaller than for the inorganic arsenicals. This behavior could be due to the solubilities of the iron and aluminium methane arsonates being greater than those of the corresponding arsenates although the actual solubility data are not available. It is noteworthy that in the case of the samples doped with aqueous maa (C3), substantially greater amounts of dmaa are formed than in the case of the herbicide treated samples (C4 and C5). A possible explanation for this difference is that the "inert" ingredients which constitute more than 50% of the commercial herbicides have an inhibitory effect on some methylation mechanisms in the soil.

4) Among the arsenicals examined, dimethylarsinic acid and its salts (C6 and C9) were the most easily extracted. Since DMAA is the least

TABLE V

Speciation of arsenic in the Bray P-1 extracts of doped soils[a, b, c]

| Sample | Total inorg. As | "Corr." Total Inorg. As[d] | As(III) | maa | dmaa |
|---|---|---|---|---|---|
| Loam C1 | 7.45 ± 0.22(74) | | 0.69 ± 0.02 | — | — |
| Clay C1 | 2.03 ± 0.12(20) | | 0.07 ± 0.00 | — | — |
| Loam C2 | 7.47 ± 0.25(75) | | | — | — |
| Clay C2 | 1.95 ± 0.14(20) | | | — | — |
| Loam C3 | 2.48 ± 0.18 | | | 5,23 ± 0.43(52) | 2.35 ± 0.01 |
| Clay C3 | 0.13 ± 0.02 | | | 4.55 ± 0.29(45) | ~0.3 |
| Loam C4 | 2.97 ± 0.03 | 2.56 ± 0.04 | | 8.92 ± 0.36(63) | + |
| Clay C4 | 0.25 ± 0.02 | 0.12 ± 0.02 | | 7.12 ± 0.40(50) | + |
| Loam C5 | 4.32 ± 0.16 | 3.78 ± 0.16 | | 7.02 ± 0.41(49) | + |
| Clay C5 | 0.29 ± 0.00 | 0.12 ± 0.01 | | 6.64 ± 0.09(46) | — |
| Loam C6 | 1.64 ± 0.06 | 1.48 ± 0.06 | | + | 10.87 ± 0.76(76) |
| Clay C6 | 0.18 ± 0.00 | 0.13 ± 0.00 | | + | 11.33 ± 0.73(80) |
| Loam C7 | 13.92 ± 0.15(70) | | | + | + |
| Clay C7 | 4.32 ± 0.27(22) | | | — | — |
| Loam C8 | 1.58 ± 0.05 | | | — | — |
| Clay C8 | 0.08 ± 0.00 | | | — | — |
| Loam C9 | 1.63 ± 0.02 | | | — | 8.36 ± 0.07(84) |
| Clay C9 | 0.08 ± 0.00 | | | — | 9.63 ± 0.84(96) |

[a] Values expressed in μgs of arsenic extracted per g of soil.

[b] Percentage of arsenic extracted from the sample given within parentheses.

[c] + indicates species detected but present in too low a conc. to be quantified.

[d] Corrected for the inorganic arsenic in the added herbicide.

acidic of all the arsenicals ($pK_{a1} = 6.19$) it is likely that the extractability is influenced by the greater proportion of unionized DMAA at the soil pH.

5) The order of extractability of the arsenicals from the clay samples obtained in the present study, i.e., dmaa > maa > arsenate agrees very well with the sorption indices for a number of clays obtained by Wauchope,[15] i.e., aresenate > maa > dmaa.

6) In the samples doped with dmaa (C6 and C9) extractability from clay appears to be slightly greater than that from loam which is contrary to the behavior observed in the other samples. However, in view of the greater uncertainty involved in the analysis of dmaa, these differences are less significant.

7) In the samples C1 and C2 no evidence of either maa or dmaa could be found, indicating that, in these samples, biomethylation of the inorganic arsenicals was not significant. However, the possible loss of arsenic through the formation of volatile alkylarsines was not tested.

8) Regarding the interconversions among the arsenic species, methanearsonates on loam appeared to be the most mobile. In samples C4 and C5 the corrected total inorganic arsenic values were considerably higher than the corresponding values for the control blank (C8). This indicates oxidation of the C—As bond through biological mediation and/or exposure to atmospheric oxygen.[16] Amounts of dmaa too low to be quantified were also detected in these extracts, showing evidences of methylation. The corrected total inorganic arsenic values for samples C6 and C9 agreed closely with those for the control blank. This indicates that dimethylarsinic acid and its salts are more resistant to oxidation.

## Direct analysis of unextracted doped soils

The doped soil samples were directly analyzed without the extraction step. The procedures followed were identical with those used in the speciation of the extracts except that the soils were weighed and the solids were introduced directly into the arsine generator. The sample sizes ranged between 2.5 – 20.0 mg. The results (Table VI) followed the same pattern as in the speciation of the extracts although the precision was considerably lower. When corresponding samples were compared, the ratio,

$$\frac{\text{Total inorg. As in solid loam}}{\text{Total inorg. As in extract}}$$

had a value of 1.3 ± 0.2. The corresponding ratio in clay samples had a value of 4.0 ± 2.3. The values obtained in the case of the loams are comparable to the extractable arsenic values. In the case of the clay

TABLE VI

DIRECT analysis and specification of doped soil samples

| Sample | Total inorg. As | As(III) | maa | dmaa |
|---|---|---|---|---|
| Loam C1 | 8.70±1.54 | 0.49±0.08 | | |
| Clay Cl | 5.53±0.53 | 0.31±0.03 | | |
| Loam C2 | 10.54±0.94 | | | |
| Clay C2 | 5.68±0.25 | | | |
| Loam C3 | 2.52±0.53 | | 3.75±0.49 | + |
| Clay C3 | 0.56±0.09 | | 5.41±0.55 | |
| Loam C4 | 3.96±0.39 | | 8.42±0.06 | + |
| Clay C4 | 0.91±0.04 | | 8.31±0.46 | |
| Loam C5 | 4.72±0.64 | | 6.23±0.23 | |
| Clay C5 | 1.00±0.01 | | 7.61±0.15 | |
| Loam C6 | 2.43±0.14 | | 0.42±0.03 | 11.00±0.28 |
| Clay C6 | 0.51±0.03 | | + | 11.56 |
| Loam C7 | 15.26±2.59 | 0.30±0.02 | | |
| Clay C7 | 10.35±0.38 | 0.51±0.02 | 0.28±0.08 | |
| Loam C8 | 2.38±0.39 | | 0.06±0.00 | |
| Clay C8 | 0.73±0.07 | | | |
| Loam C9 | 2.45±0.06 | | | 9.75±0.56 |
| Clay C9 | 0.49±0.03 | | | 9.81±0.42 |

samples it is evident that in addition to the extractable arsenic a substantial percentage of the more tightly bound arsenic is converted to arsine in the generator. Particle size is perhaps a factor in the greater reactivity of the clay samples towards the borohydride. With suitable adjustments of experimental conditions in the analysis, it may be possible to obtain acceptably precise values of either total or extractable inorganic arsenic. In the case of the organoarsenicals, particularly, dmaa, the agreement between values for the corresponding soils and extracts is much more acceptable. While several experimental parameters such as sample size and rate of borohydride injection need to be studied in greater detail, the direct analysis of solid samples appears to present a useful, rapid means of semiquantitative speciation.

## Acknowledgement

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## References

1. E. A. Woolson and P. C. Kearney, *Environ. Sci. Technol.* **7**, 47 (1973).
2. D. P. Cox and M. Alexander, *Bull. Env. Cont. Tox.* **9**, 84 (1973).
3. L. R. Johnson and A. E. Hiltbold, *Soil Sci. Soc. Amer. Proc.* **33**, 279–292 (1969).

4. L. W. Jacobs, J. K. Syers and D. R. Keeney, *Soil Sci. Soc. Amer. Proc.* **34,** 750 (1970).
5. E. A. Woolson, J. H. Axley and P. C. Kearney, *Soil Sci. Soc. Amer. Proc.* **35,** 101 (1971).
6. Y. Talmi and C. Feldman, "Arsenical Pesticides," E. A. Woolson, Ed., ACS Symposium Series No. 7, American Chemical Society, Washington, D.C., pp. 13–34 (1975).
7. M. O. Andreae, *Anal. Chem.* **49,** 820 (1977).
8. C. Feldman, *Anal. Chem.* **51,** 664 (1979).
9. Y. Talmi and D. T. Bostick, *Anal. Chem.* **47,** 2145 (1975).
10. R. Chu, G. P. Barron and P. Baumgarner, *Anal. Chem.* **44,** 1476 (1972).
11. R. S. Braman, D. L. Johnson, C. C. Foreback, T. M. Ammons and J. L. Bricker, *Anal. Chem.* **49,** 621 (1977).
12. Soil Survey Investigations Rept. No. 30, Soil Conservation Service, U.S.D.A. and Texas Agricultural Extension Service (1976).
13. P. J. Clark, R. A. Zingaro, K. J. Irgolic and A. N. McGinley, *Intern. J. Environ. Anal. Chem.* **7,** 295 (1980).
14. R. Dickens and A. E. Hiltbold, *Weeds,* **15,** 299 (1967).
15. R. G. Wauchope, *J. Environ. Qual.* **4,** 355 (1975).
16. R. A. Zingaro and A. Merijanian, *Inorg. Chem.* **5,** 187 (1966).