

Analysis of Soils by Glow Discharge Mass Spectrometry*

Douglas C. Duckworth, Christopher M. Barshick and David H. Smith

Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375, USA

The analysis of soils by conventional solution-based techniques, such as inductively coupled plasma and thermal ionization mass spectrometry, is complicated by the need for sample dissolution or the combination of a solids atomizer with an auxiliary ionization source. Since time is an important consideration in waste remediation, there exists a need for a method of rapidly analysing many soil samples with little sample preparation; glow discharge mass spectrometry (GDMS) has the potential to meet this need. Because GDMS is a bulk solids technique, sample preparation is simplified in comparison to other methods. It appears that, even with the most difficult samples (geological materials, such as soils and volcanic rock), all that is required is grinding, drying and mixing with a conducting host material prior to electrode formation. As a first test of GDMS for soil analysis, a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) was analysed by direct current GDMS. Fifty-one elements were quantified from a single cathode using ion beam ratios and 'standard' relative elemental sensitivity factors (RSF). Average errors for the suite of elements were less than a factor of 4 and 1.4 for uncorrected and corrected values, respectively. User-generated RSF values were applied to the analysis of several elements in NIST SRM 2704 Buffalo River Sediment. In the absence of isobaric interferences, accuracies ranging from 0.6 to 73% were observed, demonstrating the potential of the technique for the determination of many elements. The presence of entrained water and inhomogeneity resulting from cathode preparation is thought to affect matrix-to-matrix reproducibility. While further success depends on developing means of circumventing mass spectral interferences and addressing factors affecting plasma chemistry, the immediate goal of developing a screening method for priority metals in soils was met.

Keywords: *Glow discharge mass spectrometry; elemental analysis; solid sampling; soil analysis; environmental waste remediation*

The analysis of soils has long been a serious analytical challenge. Traditional approaches usually involve dissolution of the sample,¹ and most soils contain refractory silicates and other compounds that resist being dissolved. For some soils, even the most drastic efforts (use of HF, microwave digestion, *etc.*) do not succeed completely. The problem is exacerbated by the fact that the elements of interest are often present in the low ppm range, which necessitates meticulous attention to cleanliness to prevent contamination of the sample. It also requires at least gram amounts of soil to provide enough of the analyte element for analysis. The fact that some analytes, such as arsenic and mercury, are volatile contributes additional challenges for the analyst. Dissolution is tedious. Modern requirements for waste remediation and other environmentally driven concerns demand analysis of numerous elements in a single sample, often at concentrations in the ppm range. Compounding this is the fact that the sample load for environmental restoration, while unknown, is anticipated to be quite large.

It is clearly desirable to develop a method that would significantly reduce sample preparation time, provide multi-element analysis, demonstrate similar elemental sensitivities and be reliable. Glow discharge mass spectrometry (GDMS) offers promise to meet all of these demands.

Like its better-known counterpart, the inductively coupled plasma (ICP),^{2,3} the GD has been shown to be capable of providing multi-element quantification.⁴⁻⁶ Unlike the ICP, however, this can be accomplished directly from the solid without the need for some auxiliary form of atomization, such as a laser.⁷ The GDMS technique has also been shown to be a good method for obtaining isotopic information,^{8,9} and a recent experiment showed that uranium isotopic abundances could be measured with fair accuracy directly from a soil sample.¹⁰ Other than this proof of principle experiment, the application of GDMS to soils has been

limited. However, GD atomic emission spectrometry (GD-AES) has been successfully employed for the analysis of various geological materials.^{11,12} These GD-AES studies demonstrated quantitative results for a variety of major and minor elements, and reproducibilities of approximately 5%. In comparison, GDMS affords a relatively simple spectrum and the ability to perform 'standardless' semiquantitative analyses, making GDMS an attractive alternative.

In this study, advantage is taken of the multi-element capabilities of GDMS for the identification and quantification of a number of elements in a soil electrode. Using standard sample preparation techniques (drying, mixing with silver powder and pressing into an electrode), a semiquantitative multi-element analysis was performed for 51 elements on National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 4355 Environ Radioactivity Peruvian Soil (hereafter referred to as Peruvian Soil). Analytical performance and full quantification capabilities were investigated. The problems that are associated with mass spectral interpretation of this complex matrix are addressed.

Experimental

The analysis of non-conducting materials, such as soils, when blended with a conductive host matrix has been shown to be an acceptable analytical method for GD applications.¹¹⁻¹⁴ Glow discharge sample cathodes were prepared by mixing approximately 50 mg of soil with 0.50 g of silver powder (99.99+%, -325 mesh, Aldrich, Milwaukee, WI, USA) in a Wig-L-Bug amalgamator (Model 3110-3A, Crescent Dental, Lyons, IL, USA) for 5 min. Before mixing, all samples and the silver powder were dried at 120 °C for 2 h. This temperature was chosen to drive off water and was low enough so that loss of volatile elements would not be excessive. The homogenized mixture was then pressed at 15000 psi (1 psi = 6895 Pa) into the shape of a pin electrode 1.5 mm in diameter × 18.0 mm in length; no further sample preparation was performed.

The samples were analysed using a VG9000 glow dis-

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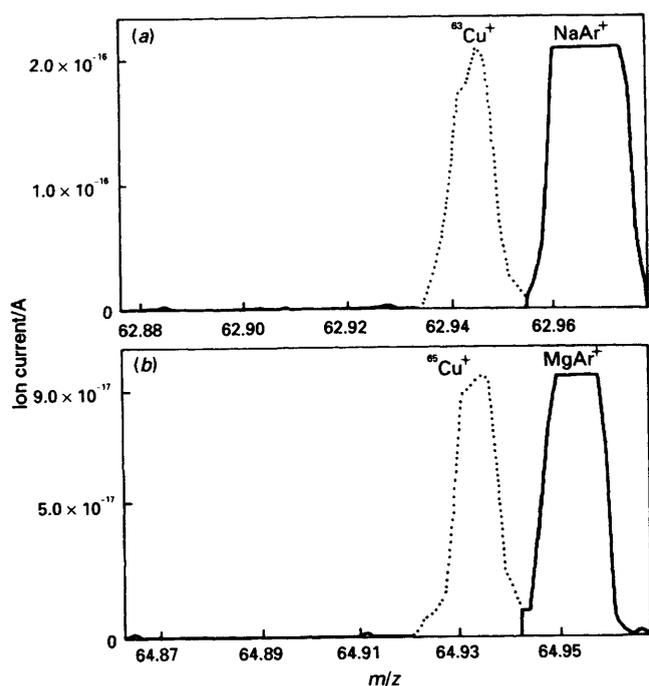


Fig. 1 Glow discharge mass spectra of copper isotopes (a) $^{63}\text{Cu}^+$ and (b) $^{65}\text{Cu}^+$ in NIST SRM 4355 Environ Radioactivity Peruvian Soil ($\approx 1.33 \times 10^2$ Pa, 1 kV, 2 mA, mass resolution ≈ 3500)

charge mass spectrometer (Fisons Instruments, Elemental, Winsford, Cheshire, UK) and its cryo-cooled 'Gallium' cell. This double-focusing, reverse Nier-Johnson geometry instrument has both a Faraday cup and a Daly detector that work in combination to provide a dynamic range in excess of 10^9 (*i.e.*, 1×10^{-18} – 1×10^{-9} A). For quantification, a resolving power of $m/\Delta m \approx 3000$ (at 5% peak height) was utilized and appeared adequate to resolve interferences from most isotopes.

The GD was supported by high-purity argon that was further purified by an in-line, heated, active-metal getter system (400 °C). In addition, the discharge cell was cooled to about -130 °C to reduce problems associated with oxide

and hydride species. The discharge voltage for these studies was -1000 V (d.c.) at a constant 2 mA current, and the pressure inside the ion source was estimated to be 1.33×10^1 – 1.33×10^2 Pa; source pressure cannot be measured directly and is estimated based on pin geometry and V - I considerations.

Results and Discussion

Spectral Characteristics

Soil is a complex matrix, and it was anticipated that many molecular ions would be produced in the GD. Molecular species such as dimers and oxides of silicon, aluminium, iron and other elements abundant in soil were expected in addition to argides and other species originating from the support gas. The presence of such undesired species almost invariably leads to isobaric interferences with elemental ions of interest. This problem has been addressed in various ways, including use of gettering agents^{15,16} and cryogenic cooling¹⁷ to reduce the amounts of residual gas species in the plasma. An alternative approach is to minimize the contribution of polyatomic species through gas-phase collisional dissociation. This has been accomplished with some success through energetic collisions with a variety of target gases in both double¹⁸ and triple¹⁹ quadrupole mass analysers. Early investigations on this matter using an ion trap mass spectrometer have been reported²⁰ where dissociation was effected through multiple collisions with a helium buffer gas; dissociation efficiencies for strongly bound hydroxides approached 100%. In the present experiment, the mass resolving capability of the instrument was exploited to resolve many molecular species from the elemental.

Figs. 1–3 are spectra illustrating some of the problems encountered during this study of soil analysis by GDMS. These spectra were obtained from a pressed silver electrode containing $\approx 9\%$ Peruvian Soil. At least 57 elements have been previously quantified in this soil at levels ranging from sub-ppm to per cent. Owing to the multiplicity of species in soils, several of which are present at the per cent level, many interferences were encountered. For soils and other complex matrices, it is clear that some means of dealing with molecular interferences are necessary.

Fig. 1 shows how an isobaric interference can dominate

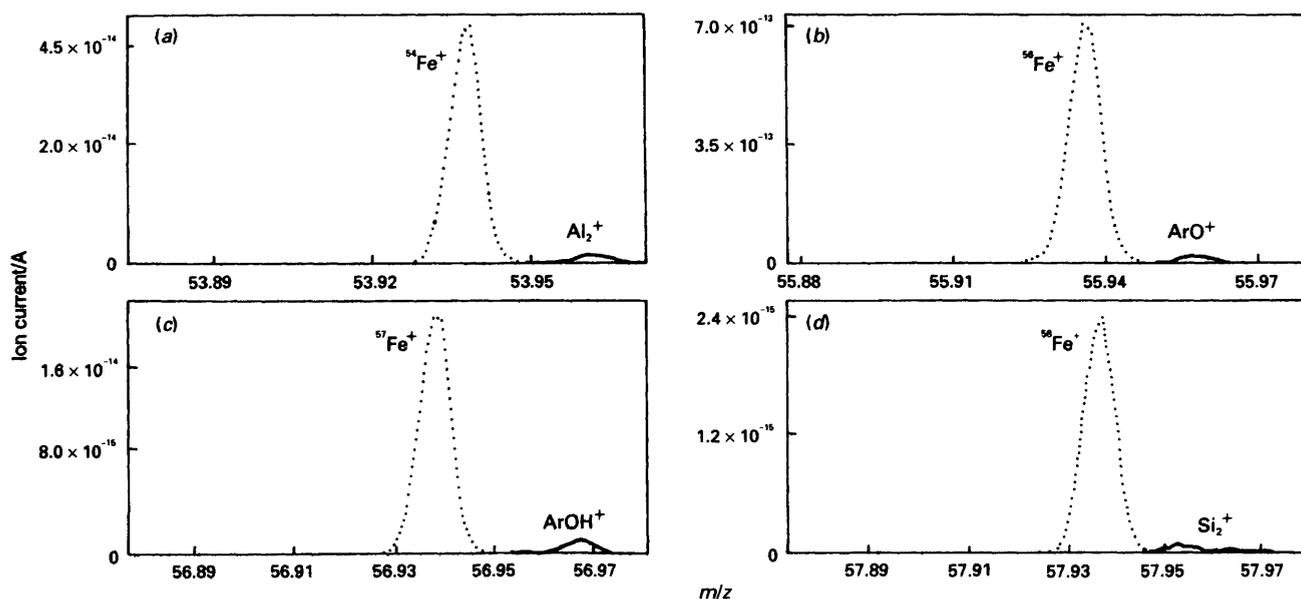


Fig. 2 Glow discharge mass spectra of iron isotopes (a) $^{54}\text{Fe}^+$; (b) $^{56}\text{Fe}^+$; (c) $^{57}\text{Fe}^+$; and (d) $^{58}\text{Fe}^+$ in NIST SRM 4355 Environ Radioactivity Peruvian Soil ($\approx 1.33 \times 10^2$ Pa, 1 kV, 2 mA)

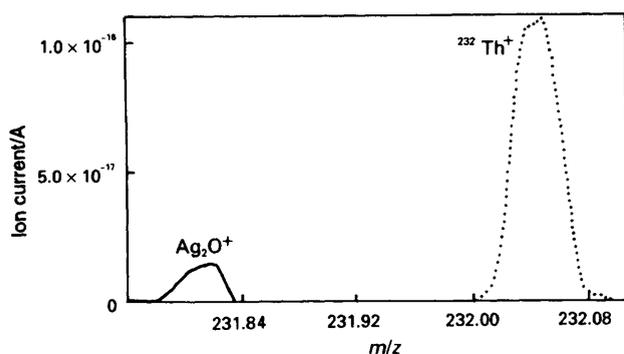


Fig. 3 Glow discharge mass spectrum of thorium in NIST SRM 4355 Environ Radioactivity Peruvian Soil ($\approx 1.33 \times 10^2$ Pa, 1 kV, 2 mA)

the spectrum of a given element; in this example, argides of sodium and magnesium interfere with both isotopes of copper at m/z 63 and 65. In these spectra NaAr^+ interferes with $^{63}\text{Cu}^+$ and MgAr^+ interferes with $^{65}\text{Cu}^+$. This illustrates an extreme case, where relatively small elemental peaks are adjacent to peaks of a much larger molecular species.

The spectral region of the first row transition elements is very complicated owing to dimers, argides and residual gas adducts of low mass species. This region is also complicated by multiply-charged species of higher mass. The mass spectra of the four stable isotopes of iron are presented in Fig. 2 to illustrate the complexity of this spectral region. Like copper in Fig. 1, each isotope has a resolved interference. The interfering peaks assigned to the iron isotopes in Fig. 2(a)–(d) are $^{27}\text{Al}^+$, $^{40}\text{Ar}^{16}\text{O}$, $^{40}\text{Ar}^{16}\text{O}^+\text{H}$ and Si_2^+ ($^{28}\text{Si}^{29}\text{Si}^+$ and $^{29}\text{Si}_2^+$), respectively. While the analyte is of greater abundance, the interfering species are present at appreciable relative abundance. In the absence of sufficient mass resolving power, there are often no interference free isotopes available for quantification, unlike GDMS analysis of high purity metals and alloys.

While the first row transition metal spectral region is the most complicated, interferences were also noted for many analytes of high and low mass. For example, Fig. 3 shows ^{232}Th (11.3 ppm in soil) which has been resolved from $^{107}\text{Ag}^{109}\text{Ag}^{16}\text{O}^+$. Thorium, being mononuclidic, has no alternative isotopes available. In this case, a different electrically conductive binder could have been utilized, but this example is representative of several mononuclidic elements which are subject to isobaric interferences (e.g., As, Al, Mn, V and Co).

Isobaric interferences, such as those presented in Figs. 1–3, were observed for most elements. Fortunately, little contribution from organic species and carbides was noted. The positive mass defect associated with hydrogen would, however, make organic species easy to resolve in most cases. In the present experiments, other species were more prominent and less easily resolved. For the determination of most elements in soils by GDMS, and in the absence of alternative means of polyatomic ion reduction, sufficient mass resolving power is mandatory.

Multi-element Analysis of Soil

To establish the capability of the GDMS technique for the multi-element analysis of soil, the Peruvian Soil electrode was analysed for 51 elements relative to the silver matrix ($\approx 91\%$). Elements determined included metals and non-metals. Owing to the seemingly infinite combinations of polyatomic and multiply-charged interferences, all isotopes of each element were measured and their ratios to ^{107}Ag

calculated. This analysis comprised 177 isotope measurements and required approximately 45 min, excluding a pre-sputter period of approximately 20 min duration. This pre-sputter period has been observed to be sufficient for signal stabilization. After blank correction, the isotopes resulting in the lowest elemental concentration represented the isotopes with least interference. These isotopes, presented in Table 1, were selected for this, and all subsequent, analysis.

The results of the analysis for 51 elements, both with and without the application of relative sensitivity factors (RSF), and the accepted concentrations (not all elements were certified) are presented in Table 1. Relative sensitivity factors used were 'standard' values supplied with the commercial software as opposed to matrix-specific ones. These 'standard' RSFs are correction factors between measured analyte/matrix ion beam ratios and certified concentrations. 'Standard' RSFs were determined, for the most part, from a variety of metals and alloys. Because of the large matrix differences (soils *versus* metals), 'standard' RSF values are expected to differ from those of soil. The absolute error associated with the uncorrected (*i.e.*, no RSFs applied) elemental concentrations ranges from 0.044 to 1360% with an average of 283%. Since no attempts were made to correct for relative sensitivities, the results are encouraging. Many analyses, such as rapid screening for elements of interest, can be performed successfully with accuracy within a factor of ≈ 4 relative to the true value.

After RSF adjustment of the elemental concentrations using the 'standard' RSF values, the spread in absolute error ranged from 1.48 to 98.6%, with an average error of 39.6%. This is a significant improvement and suggests that better accuracies can be attained with matrix-specific RSF values. The correlation between certified and RSF adjusted concentrations also indicates that relative ion yields from a soil matrix are similar to those of solid metals, from which the 'standard' RSF values were generated. This observation supports the long-standing claim of GDMS to be only minimally dependent on the matrix.

Of particular importance in Table 1 are several elements listed as hazardous in the Resource Conservation and Recovery Act (RCRA). These include Cr, As, Se, Ba, Cd and Pb, and were measured with a promising degree of success. The ability to analyse such materials, even semi-quantitatively, with little sample preparation will clearly benefit environmental waste remediation efforts.

Analytical Performance

Analytical characteristics of GDMS as applied to the analysis of soil are presented in Table 2. Certified concentrations and sensitivity factors (relative to Ag) for Al, Fe, As, Pb and U in Peruvian Soil are shown in columns two and three, respectively. The RSF values fall within a factor of 10 for these elements, indicating a similar elemental response across the Periodic Table. Internal precisions of the ion beam ratios were measured, following a 20 min pre-sputter period, and represent ten replicate analyses obtained at roughly 2 min intervals. The stability of the discharge is indicated by the good precision, which ranges from 1.2% for Al (8.19%) to 3.6% for the less abundant U (3.63 ppm).

External precision was determined by analysing the same sample five times. The cryo-cooled sample was removed to atmosphere and allowed to warm to room temperature between measurements. Each element, with the exception of As, exhibited only a slight decrease in precision with respect to internal precision, with each being better than 6.0%. Since As is the only element demonstrating a marked decrease in sensitivity, a residual gas polyatomic interference is suspected. Upon close observation, an incompletely

Table 1 Results of multi-element analyses of NIST SRM 4355 Environ Radioactivity, Peruvian Soil

| Element (isotope used) | Certified concentration (ppm) | Measured concentration (ppm)* | Error (%) | RSF adjusted concentrations (ppm)† | Error (%) |
|------------------------|-------------------------------|-------------------------------|-----------|------------------------------------|-----------|
| ⁷ Li | 52.1 | 159 | 205 | 61.5 | 18.0 |
| ⁹ Be | 1.77 | 4.44 | 151 | 1.57 | -11.3 |
| ¹¹ B | 63.0 | 311 | 393 | 83.4 | 32.4 |
| ¹⁹ F | 682 | 41.7 | -93.9 | 9.68 | -98.6 |
| ²³ Na | 19 200 | 37 100 | 93.1 | 17 200 | -10.4 |
| ²⁴ Mg | 15 000 | 26 200 | 74.8 | 9 360 | -37.6 |
| ²⁷ Al | 81 900 | 26 3000 | 222 | 83 800 | 2.35 |
| ³⁰ Si | 330 000 | 584 000 | 76.9 | 250 000 | -24.2 |
| ³¹ P | 1 100 | 1 100 | -0.0437 | 805 | -26.8 |
| ³⁹ K | 18 600 | 2 080 | -88.8 | 564 | -97.0 |
| ⁴² Ca | 22 000 | 115 000 | 424 | 14 700 | -33.3 |
| ⁴⁵ Sc | 14.8 | 70.2 | 374 | 6.39 | -56.8 |
| ⁴⁷ Ti | 4 700 | 33 500 | 613 | 3 700 | -21.3 |
| ⁵² Cr | 28.9 | 31.5 | 9.07 | 10.4 | -64.1 |
| ⁵⁵ Mn | 852 | 2 070 | 143 | 699 | -18.0 |
| ⁵⁶ Fe | 44 500 | 138 000 | 210 | 31 600 | -29.0 |
| ⁵⁹ Co | 14.8 | 35.7 | 141 | 8.99 | -39.3 |
| ⁶¹ Ni | 13.0 | 46.6 | 259 | 14.8 | 14.1 |
| ⁶³ Cu | 77.1 | 51.1 | -33.7 | 64.8 | -16.0 |
| ⁶⁶ Zn | 368 | 331 | -10.2 | 444 | 20.6 |
| ⁷¹ Ga | 18.4 | 26.8 | 45.5 | 28.3 | 53.9 |
| ⁷⁵ As | 93.9 | 78.1 | -16.8 | 92.5 | -1.48 |
| ⁸² Se | 1.40 | 28.7 | 1 950 | 1.56 | 11.3 |
| ⁸⁵ Rb | 138 | 200 | 44.6 | 45.8 | -66.8 |
| ⁸⁸ Sr | 330 | 1 800 | 445 | 273 | -17.3 |
| ⁸⁹ Y | 21.0 | 101 | 380 | 12.6 | -39.9 |
| ⁹⁰ Zr | 221 | 901 | 308 | 178 | -19.6 |
| ⁹³ Nb | 9.00 | 41.1 | 357 | 6.81 | -24.4 |
| ⁹⁸ Mo | 1.70 | 15.3 | 799 | 2.84 | 67.3 |
| ¹¹³ Cd | 1.50 | 3.69 | 146 | 4.94 | 2.30 |
| ¹³³ Cs | 56.7 | 102 | 79.0 | 19.1 | -66.4 |
| ¹³⁸ Ba | 561 | 1510 | 169 | 400 | -28.7 |
| ¹³⁹ La | 28.1 | 108 | 285 | 16.6 | -40.8 |
| ¹⁴⁰ Ce | 59.7 | 195 | 227 | 33.6 | -43.8 |
| ¹⁴¹ Pr | 5.00 | 21.7 | 333 | 3.99 | -20.3 |
| ¹⁴² Nd | 29.9 | 192 | 541 | 31.8 | 6.27 |
| ¹⁴⁸ Sm | 5.42 | 79.1 | 1 360 | 10.6 | 95.6 |
| ¹⁵³ Eu | 1.18 | 8.37 | 609 | 1.57 | 33.1 |
| ¹⁵⁷ Gd | 35.0 | 28.6 | -18.3 | 2.83 | -91.9 |
| ¹⁵⁹ Tb | 0.665 | 3.22 | 384 | 0.157 | -76.5 |
| ¹⁶⁴ Dy | 4.00 | 18.9 | 371 | 3.30 | -17.4 |
| ¹⁶⁵ Ho | 0.820 | 3.18 | 288 | 0.533 | -35.0 |
| ¹⁶⁹ Tm | 0.420 | 1.16 | 176 | 0.184 | -56.3 |
| ¹⁷² Yb | 2.24 | 6.84 | 205 | 1.33 | -40.4 |
| ¹⁷⁵ Lu | 0.336 | 1.13 | 236 | 0.117 | -65.3 |
| ¹⁷⁷ Hf | 6.30 | 19.0 | 202 | 2.85 | -54.7 |
| ¹⁸⁴ W | 5.10 | 25.4 | 397 | 7.47 | 46.5 |
| ²⁰⁸ Pb | 129 | 240 | 85.7 | 142 | 9.88 |
| ²⁰⁹ Bi | 12.0 | 0.460 | -96.2 | 0.428 | -96.4 |
| ²³² Th | 11.3 | 23.7 | 110 | 3.39 | -70.0 |
| ²³⁸ U | 3.04 | 8.48 | 179 | 1.57 | -48.5 |

* Concentrations determined from ion beam ratios.

† Concentrations determined from ion beam ratios, adjusted with 'standard' RSF values.

Table 2 Relative sensitivity factors and analytical figures of merit for the analysis of NIST SRM 4355 Environ Radioactivity, Peruvian Soil by GDMS

| Element | Certified concentration | RSF (X/Ag) | Internal precision (%) | External precision (%) | Pin-to-pin precision (%) |
|---------|-------------------------|------------|------------------------|------------------------|--------------------------|
| Al | 8.19* | 0.168 | 1.2 | 1.6 | 31 |
| Fe | 4.45* | 0.32 | 2.5 | 2.7 | 8.9 |
| As | 93.9† | 1.0 | 2.9 | 17 | 30 |
| Pb | 129† | 0.83 | 2.4 | 3.2 | 18 |
| U | 3.64† | 0.41 | 3.6 | 6.0 | 40 |

* Values given in %.

† Values given in ppm.

resolved peak was observed at $m/z=75$ and is as yet unidentified. Because arsenic is mononuclidic, no alterna-

tive isotopes are available. As will be demonstrated, this presents a problem in the determination of As.

Table 3 Analysis of NIST SRM 2704 Buffalo River Sediment

| Element | Certified concentration | Measured concentration |
|---------|-------------------------|------------------------|
| Al* | 6.11 ± 0.16 | 5.91 ± 0.16 |
| Fe* | 4.11 ± 0.10 | 5.39 ± 0.056 |
| As† | 23.4 ± 0.8 | 67.0 ± 2.8 |
| Pb† | 161 ± 17 | 162 ± 4.3 |
| U† | 3.13 ± 0.13 | 5.42 ± 0.73 |

* Values given in % ($n=5$).† Values given in ppm ($n=5$).

Pin-to-pin reproducibility is also indicated in Table 2. These results were obtained through the analysis of four pins prepared from the same mixture. Reproducibility ranges from 8.9 to 40% and is thought to be due largely to inhomogeneous distribution of soil in the silver powder. A comparison of the external and pin-to-pin precision for Al and U, relative to As, suggests that inhomogeneity, rather than residual gas contaminants, is the primary cause for the poorer reproducibility (*i.e.*, pin-to-pin reproducibility for As is better than for Al and U). If residual gas contamination were the cause of irreproducibility, As should be influenced to a greater extent than Al or U. As shown in Table 2, only As showed external precision that was significantly affected by exposure to residual gases. The degree of inhomogeneity and factors affecting homogeneity warrant further investigation.

The RSF values in Table 2 were applied to the analysis for the same elements of NIST SRM 2704 Buffalo River Sediment. The results are shown in Table 3 and are in good agreement with certified values. For As, the value is high, which supports the belief that an interferent is present. However, As is the worse case and differs by less than a factor of 3 from the expected value.

Inhomogeneity and the presence of residual gases are believed to be limiting factors in soil analyses. Reduction of inhomogeneity and elemental discrimination in sample preparation remains a formidable task. Much development will be required to improve the accuracy and precision of the technique. Residual gases, specifically water, are of primary concern owing to their affect on solid and gas-phase processes. Water can affect sputter and ionization efficiencies dramatically;^{21,22} the presence of hydrogen, which is generated from the dissociation of water, has recently been shown to affect relative ion yields.²³ Given the regionally varying water contents of soils, a method of reducing or reproducing water content might become necessary.

Conclusions

The feasibility of analysing soils by GDMS has been demonstrated, with drying, mixing and pressing an electrode being the only sample preparation. No chemical processing was required. Concentrations were obtained for 51 elements, with the added benefit of obtaining isotopic information as well. For rapid screening and multi-element semiquantitative analyses of soils, GDMS has shown great promise.

The results presented here are an encouraging start for an attack on a difficult analytical problem. The ability to obtain a multi-element analysis from a soil sample with so little preparation definitely warrants further attention. Issues to be addressed include reproducibility, variation of elemental sensitivity factors with soil matrix, the grain size of the soil and use of an r.f. instead of a d.c. discharge. There are, of course, many other difficult problems (water and oxide content, *etc.*), but the potential reward is large enough to justify significant effort.

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