

Direct Analysis of Solids by Ultrasonic Slurry Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry

D. Conrad Grégoire

Geological Survey of Canada, 601 Booth St., Ottawa, Ontario, Canada K1A 0E8

Nancy J. Miller-Ihli

United States Department of Agriculture, Nutrient Composition Laboratory, Beltsville, MD 20705, USA

Ralph E. Sturgeon

Institute for Environmental Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R9

The direct analysis of solids using ultrasonic slurry electrothermal vaporization inductively coupled plasma mass spectrometry is reported. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1632a Trace Elements in Coal (Bituminous), Total Diet SRM 1548 and National Research Council of Canada LUTS-1 Lobster Hepatopancreas RM were analysed for a number of elements including Ni, Cu, Cr, Pb, Mn and Co. As a consequence of matrix effects, most analytes were determined using the method of standard additions, although Ni, Cu, Pb and Mn in NIST coal and Pb in LUTS-1 were successfully determined by external calibration using aqueous standards. With the exception of Cr in the coal sample, excellent agreement was obtained between the concentration determined and the certified range. Monitoring of the argon dimer during the high temperature vaporization cycle was shown to be an effective means of assessing matrix effects and selecting calibration strategies for individual analytes. Calculated limits of detection range from 0.07 ng g⁻¹ for Co to 3.2 ng g⁻¹ for Cr in 2 mg samples.

Keywords: *Slurry sampling; electrothermal vaporization; inductively coupled plasma mass spectrometry; ultrasonic mixing*

Recent studies¹⁻³ have shown that electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is effective for the ultratrace and micro-analysis of a variety of materials ranging from arctic snow¹ to single zircons.³ The ETV-ICP-MS technique allows for multi-element analysis of microlitre-sized samples while at the same time taking advantage of the very high sensitivity of ICP-MS.

The direct analysis of solids and/or slurries by any analytical technique offers advantages over more conventional sample preparation. Among these advantages are the reduced sample preparation time, the reduced possibility of sample contamination, increased sensitivity (no dilution), decreased likelihood of analyte loss through volatilization prior to analysis and the selective analysis of micro-amounts of solids. Slurry sampling offers additional advantages for samples that occur naturally as slurries, such as milk and blood, and for the completion of surveys where the analysis of large numbers of samples, such as contaminated soils, is required. Furthermore, slurry sampling combines the benefits of solid and liquid sampling and permits the use of conventional liquid sample handling apparatus such as autosamplers.

Electrothermal atomic absorption spectrometry (ETAAS) has been successfully applied to the analysis of slurries.⁴⁻¹¹ Bendicho and de Loos-Vollebregt¹² and Miller-Ihli⁶ have reviewed the available literature and quantified the importance of certain factors such as particle size, sample density and analyte partitioning.^{6,11} Accurate results were obtained for the determination of As, Fe, Mn and Pb in sediment⁴ and for the determination of many elements in a wide variety of matrices ranging from glass¹³ to spinach.⁹

Ebdon *et al.*¹⁴ analysed coal using slurry nebulization ICP-MS. Agreement between determined analyte concentration and the certified values for the semi-quantitative determination of 67 elements in seven reference coal samples was

within a factor of two. When a more quantitative approach was used, excellent agreement was obtained between determined analyte concentration and the certified range for 16 elements. In other studies, Totland *et al.*¹⁵ determined the platinum group elements and gold in a number of reference materials using slurries nebulized directly into the plasma of an ICP mass spectrometer. Limits of quantitative analysis for the platinum group elements in samples ranged from 0.04 to 0.2 µg g⁻¹. Huang *et al.*¹⁶ used slurry sampling for the determination of Zr, V, Cr, W, Mo, B and Ti by ETV-ICP-AES. By using a suspension of poly(tetrafluoroethylene), these workers¹⁶ were able to improve limits of detection for these elements by factors ranging from 7 to 119 over those obtained by simple volatilization of sample into the ICP atomic emission spectrometer without the use of a fluorinating agent.

The analysis of slurries by ETV-ICP-MS has not been reported in the literature. The characteristics of ETAAS and ETV-ICP-MS techniques have been compared by Grégoire *et al.*¹⁷ These workers have shown that the requirements for successful ETV-ICP-MS analysis are perhaps less demanding than for ETAAS. Complete vaporization of sample and efficient transport of volatilized material to the argon plasma (provided complete atomization occurs within the plasma) are all that is required for ETV-ICP-MS. Electrothermal atomic absorption spectrometry, on the other hand, requires not only complete vaporization, but also complete *in situ* atomization of sample material. For ETV-ICP-MS, breakdown of analyte-containing vapour (molecules) or aerosols, followed by atomization and ionization, ideally takes place within the argon plasma. The ETV serves only as a means of thermally pre-treating and vaporizing (in whatever form) the sample into a stream of argon flowing into the argon plasma. Electrothermal vaporization ICP-MS promises an effective technique for the analysis of diverse, complex materials for a large number of analytes.

The objective of this study was to demonstrate the feasibility of direct analysis of solids by ultrasonic slurry ETV-ICP-MS and to highlight the strengths and weaknesses of this approach.

Experimental

Instrumentation

A Perkin-Elmer Sciex Elan 5000 ICP mass spectrometer equipped with an HGA-600MS electrothermal vaporizer was used. The electrothermal vaporizer system was fitted with a Model AS-60 autosampler equipped with a USS-100 ultrasonic mixing probe. The ultrasonic mixing probe was constructed of high-purity titanium. Pyrolytic graphite coated graphite tubes were used throughout. The experimental conditions for the Elan 5000 and the HGA 600MS are given in Table 1. Optimization of the USS-100 was accomplished by lowering the probe into an autosampler cup containing sample solution and activating the device. While in operation, the power level of the ultrasonic probe was adjusted to provide maximum, smooth (rolling) agitation of the sample without spillage. A power level of 30 (12 W) and a mixing time of 30 s were selected for optimum performance of the ultrasonic mixing probe. To facilitate accurate sampling of larger particle sizes, the Teflon tip provided on the AS-60 autosampler was replaced with a larger thin-walled Teflon capillary tube (i.d. 0.81 mm).

Optimization of plasma and mass spectrometer conditions was accomplished using solution nebulization sample introduction and aqueous standards (High Purity Standards, Charleston, NC, USA). The HGA-600MS was interfaced to the argon plasma *via* an 80 cm length of 6 mm i.d. Teflon tubing. The operation of the HGA-600MS was completely computer controlled. During the dry and char stages of the temperature programme, opposing flows of argon gas (300 ml min⁻¹) originating from both ends of the graphite tube, removed water and other vapours through the dosing hole of the graphite tube. Prior to and during the high temperature or vaporization step, a graphite probe was pneumatically activated to seal the dosing hole. Once the graphite tube was sealed, a valve located at one end of the HGA-600MS workhead directed the carrier argon flow originating from the far end of the graphite tube directly to the argon plasma at a flow rate of 900 ml min⁻¹.

Some of the analytes studied are considered refractory (Cr and Ni) and require relatively high temperatures for complete vaporization. Accordingly, the ETV heating cycle (Table 1) comprises the highest heating rates available and a high

vaporization temperature. A high temperature clean-up step (2700 °C) was included as part of the temperature programme to minimize the effects of carry-over, particularly from un-vaporized matrix material.

Preparation of Slurries

A weighed portion of reference material (sample) was placed in a 20 ml plastic centrifuge tube. A diluent consisting of 5% Ultrex (Baker) HNO₃ containing 0.005% Triton X-100 was added to the sample and mixed on a vortex mixer. An aliquot of sample slurry was then immediately withdrawn from the centrifuge tube using an Eppendorf pipette and placed into a clean Teflon auto-sampler cup. In preparing the slurries, care was taken to ensure that an appropriate ratio of sample: diluent was used by taking into account the particle size and the density of the reference material in order to minimize effects arising from poor sampling statistics.^{10,11}

The coal [National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 1632a Trace Elements in Coal (Bituminous)] slurry was prepared by mixing 4 mg of sample per 4 ml of diluent. The density of the coal was approximately 0.7 g cm⁻³ and the particle size was apparently less than 50 µm. A 20 µl aliquot of sample slurry would require a minimum of 0.08 mg ml⁻¹ of coal to give 50 particles, ensuring a representative sampling of the bulk slurry.^{10,11}

The NIST SRM 1548 Total Diet was prepared in a similar fashion, except that 400 mg of sample were suspended in 4 ml of diluent. With a density of about 1 g cm⁻³ and a particle size of less than 250 µm, only 20 mg ml⁻¹ was required to ensure that each 20 µl aliquot contained 50 particles. This criterion was met with a concentration of 100 mg ml⁻¹.

The National Research Council of Canada (NRCC) LUTS-1 Lobster Hepatopancreas reference material (RM) was provided as 10.3 g of homogeneous slurry. The material was diluted by adding (in a calibrated flask) diluent to a total volume of 100 ml. The suspension was sonicated for 30 min in an ultrasonic bath and, following mixing on a vortex mixer, a 1 ml aliquot of the diluted LUTS-1 slurry was removed using an Eppendorf pipette and placed in a Teflon autosampler cup. Although no data are available characterizing the actual particle size of the LUTS-1 material, we believe it to be less than 50 µm and certainly less than 100 µm. Looking at the guidelines for minimum mass,^{10,11} only 1.3 mg ml⁻¹ was needed for 100 µm particles of a density of 1 g cm⁻² to provide the minimum 50 particles per 20 µl analytical sample aliquot.

Table 1 Instrumental operating parameters and data acquisition parameters

ICP mass spectrometer	
R.f. power	1000 W
Coolant argon flow rate	15.0 l min ⁻¹
Intermediate argon flow rate	850 ml min ⁻¹
Carrier argon flow rate	900 ml min ⁻¹
Sampler/skimmer	Nickel
HGA-600MS Electrothermal vaporizer	
Sample volume	10 µl
Drying stage (2 second ramp)	110 °C for 50 s
Internal argon flow rate	300 ml min ⁻¹
Charring stage (10 second ramp)	400 °C for 50 s
Internal argon flow rate	300 ml min ⁻¹
Vaporization stage	2600 °C
Heating rate	2000 °C s ⁻¹
Time at maximum temperature	6 s
Clean-up stage	2700 °C for 8 s
Data acquisition	
Dwell time	10 ms
Scan mode	Peak-hopping
Points per spectral peak	1
Isotopes monitored per measurement cycle	5
Signal measurement mode	Integrated

Reagents

All acids were produced by sub-boiling distillation in Teflon distillation vessels. Distilled water (18 MΩ cm) was obtained from a Millipore RO system. For ultrasonic slurry ETV-ICP-MS determinations, the addition of 5 µl of NASS-3 Open Ocean Sea Water Reference Material (NRCC) (diluted 500-fold) chemical modifier was added to both standard and sample solutions. The addition of this solution provides 0.7 ng of salt containing Na, Cl, Mg and Sr which acts as a physical carrier^{1,18} ensuring efficient transport of vaporized analyte from the graphite tube to the argon plasma. Prior to use, NASS-3 was purified of trace metals using chelating resins¹⁹ and diluted to strength with ultra-pure water.

The use of a carrier such as NASS-3 results in both an enhancement in signal and a linearization of calibration curves.^{20,21} Linear calibration curves were obtained for all analytes from the limit of detection to masses giving a signal intensity of approximately 10⁶ counts s⁻¹ in ICP-MS. Absolute limits of detection in pg (parentheses) for the analytes studied¹ were Ni (0.47); Cr (3.2); Cu (0.42); Pb (0.086); Mn (0.12) and Co (0.14). The limit of detection is defined as the mass of element which produces a response equivalent to three times

the standard deviation of the blank. The blank is the integrated response obtained from the vaporization of 5 μ l of NASS-3 carrier. A 1 pg mass of analyte results in an integrated signal of from 1000 to 2000 counts depending on the analyte and the experimental conditions.

Signal Measurement and Data Acquisition

Fig. 1 illustrates typical ETV-ICP-MS signal pulses obtained for the volatilization of 100 pg of analyte in the presence of NASS-3 carrier. Because of the transient nature of ETV-ICP-MS signal pulses, the number of analyte isotopes monitored was limited to five to ensure recording of accurate analyte signal pulse shapes. The peak-hopping mode of data acquisition was used with a 10 ms dwell time for each analyte isotope monitored. Single (one m/z per mass) sequential measurements were made for each analyte isotope on a continuous basis from the start of the vaporization cycle until the signal returned to baseline values.

When the method of standard additions was used for calibration purposes, three additions were used in addition to the unspiked sample. The concentration of added aqueous standard was adjusted to bracket the concentration of analyte present in the sample. Analytical results presented in the tables are the means of five separate determinations for each sample or standard addition. Integrated data (counts) for analyte signal pulses were used for all measurements.

Fig. 1 also shows the signal pulse for the argon dimer, $^{40}\text{Ar}^{40}\text{Ar}^+$. The argon dimer is produced in the argon plasma and behaves in a similar manner to²² any other (analyte) ion in the plasma, both in terms of non-spectroscopic interferences and plasma effects. Beauchemin *et al.*²³ used the argon dimer as an internal standard to correct for changes in signal intensity due to the presence of concomitant elements and/or signal drift. These workers found that the argon dimer could not be effectively applied to correct interferences and drift over the entire mass range, but only for an m/z range from 63–114. We decided to investigate the use of the argon dimer as a semi-quantitative indicator of possible matrix suppression (or enhancement) effects. The argon dimer signal pulse (Fig. 1) shows a large increase in signal about 1.8 s into the high-temperature vaporization step. This 'bulge' in signal is the result of the expansion of gases within the graphite tube during rapid heating. This 'pressure-pulse' reflects a change in the sampling depth at the ICP mass spectrometer interface. The utility of monitoring the intensity of this molecular ion is discussed below.

Selection of Analyte Isotopes

The selection of analyte isotopes was determined by considering a number of factors including the background spectral

features of ETV-ICP-MS, the concentration of analyte in the sample, the abundance of the analyte isotope and possible molecular ion species produced within the ETV or in the argon plasma which are isobaric with the analyte isotope.

Of the six elements studied, only ^{55}Mn and ^{59}Co are monoisotopic. Chromium has three isotopes at m/z 52 (83.76% abundance), 53 (9.55) and 54 (2.38). The major isotope of Cr is interfered with by a significant background molecular ion arising from the formation of $^{40}\text{Ar}^{12}\text{C}^+$, precluding its use as an analyte isotope. Chromium analyses were completed using ^{53}Cr .

Nickel has five isotopes at m/z 58 (67.77), 60 (26.16), 61 (1.25), 62 (3.66) and 64 (1.16). Of the two major (abundance) Ni isotopes, ^{60}Ni was selected as the analyte isotope because the more abundant ^{58}Ni is isobaric with ^{58}Fe and some of the materials studied may be high in iron.

Copper has two isotopes at m/z 63 (69.09) and 65 (30.91). The major isotope of Cu is free of isobaric interferences from other elements and molecular ions produced from matrix components. The ^{65}Cu , however, is interfered with by a molecular ion produced from the combination of $^{25}\text{Mg}^+$ with $^{40}\text{Ar}^+$ to form an argide in the plasma.¹⁸

The four isotopes of Pb are free of isobaric interferences and each can be used for detection. The abundance (%) of each of these isotopes is: ^{204}Pb (1.37); ^{206}Pb (25.15); ^{207}Pb (21.11) and ^{208}Pb (52.37). Because of the relatively large variation in concentration of Pb present in the reference materials studied, ^{207}Pb was used for the determination of Pb in the coal, ^{208}Pb was used for the determination of Pb in LUTS-1 and ^{204}Pb was used for the determination of Pb in the Total Diet RM.

Results and Discussion

NIST SRM Coal 1632a Reference Material

Coal has a fairly simple matrix comprised primarily of carbon with small quantities of inorganic impurities. The analysis of this material by ultrasonic slurry ETV-ICP-MS was not expected to be difficult since the signal pulse for the argon dimer (Fig. 2) was identical with that observed for a vaporization cycle carried out in the absence of any matrix (Fig. 1). The results presented in Table 2 show that external calibration could be used for the analysis of coal for Cu, Ni, Pb and Mn. The results obtained for these elements were in agreement with the certified values. The result for the determination of Cr, however, was low, indicating a matrix effect or interference causing inaccuracy. Application of the method of standard additions did not yield the correct concentration value for this element. These results, together with the knowledge that analyte signals were probably not perturbed (argon dimer) by the presence of matrix, indicate that possibly, on reaching the argon plasma, coal particles physically transported to the argon

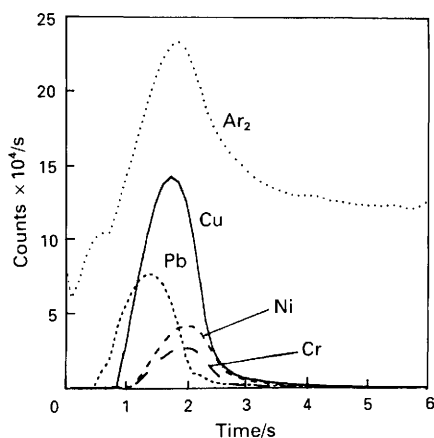


Fig. 1 ETV-ICP-MS signal pulses for 100 pg of Pb, Cu, Ni and Cr

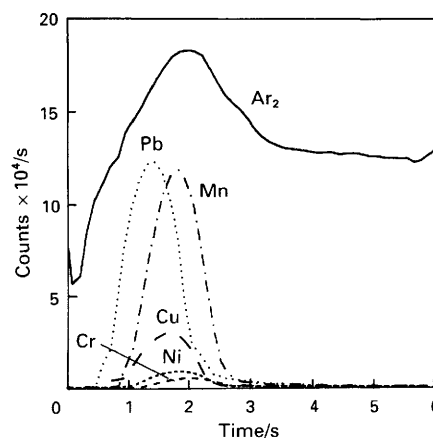


Fig. 2 ETV-ICP-MS signal pulses for 20 μ g of NIST SRM Coal 1632a

Table 2 Analysis of NIST SRM Coal 1632a Trace Elements in Coal (Bituminous) by slurry sampling ETV-ICP-MS

	Concentration/ $\mu\text{g g}^{-1}$				
	Cu	Cr	Ni	Pb	Mn
External calibration	16.8 ± 0.1	22.7 ± 2.8	20.0 ± 3.5	11.0 ± 0.5	30.8 ± 2.2
Certified	16.5 ± 1.0	34.4 ± 1.5	19.4 ± 1.0	12.4 ± 0.6	28 ± 2

plasma are not completely vaporized during the short residence time (1–3 ms) of analyte in the argon plasma. A second explanation, which is complementary to the above, involves the degree of mobilization of analyte into the diluent solution. Of all the elements determined in the coal sample, Cr is the least likely to be extracted into the mobile phase. In Fig. 2, the Cr analyte signal pulse clearly has the latest appearance time and is also the last element to ‘peak’ during the high-temperature vaporization cycle. The appearance time is defined as the time elapsed from the on-set of the high-temperature vaporization cycle to the point when the analyte signal is first measurable above background noise. Whereas the other elements were partially or perhaps completely extracted from the solid phase (coal) to the liquid phase (diluent), Cr remained partially trapped in the coal matrix. Analysis using either external calibration or the method of standard additions would give incorrect results.

NRCC LUTS-1 Lobster Hepatopancreas Reference Material

Fig. 3 shows the slurry sampling ETV-ICP-MS analyte signal pulses for Cr, Pb, Co and Ni for a 2 mg sample size of LUTS-1 RM. As was shown for coal, Pb is the most volatile analyte with the earliest appearance time and Cr is the least volatile with the latest appearance time. The ultrasonic slurry ETV-ICP-MS signal pulse for the argon dimer for LUTS-1 is qualitatively different from that in both the coal slurry and the aqueous standard. At about 0.8 s from the start of the high temperature vaporization cycle, there is a small peak corresponding to the initial expansion of the argon gas flowing through the graphite tube. At about 2.5 s, a second, much larger peak maximum occurs indicating some signal enhance-

ment due to volatilized matrix components. The LUTS-1 RM comprises a highly organic matrix composed of complex proteins, carbohydrates and lipids. All of these materials are prone to decomposition during the char step of the heating cycle, resulting in the formation of a carbon char composed of carbon chains covering a wide range of molecular weights. This material is relatively refractory and vaporizes only at high temperatures. The use of oxygen ashing to reduce the quantity of carbonaceous material present was tried, but the alternate gas valve configuration on the ETV unit did not allow for the use of air during the char step without extinguishing the argon plasma during the vaporization step.

The results obtained for the analysis of LUTS-1 by ultrasonic slurry ETV-ICP-MS using both external calibration and the method of standard additions are summarized in Table 3. The results obtained by external calibration do not agree with certified values for any element except Pb. Of the four elements studied, only Pb is virtually completely volatilized before the second pulse maximum occurs in the argon dimer signal. Because Pb is vaporized before the major matrix components are volatilized from the graphite tube, Pb ions in the argon plasma and the mass spectrometer are not subject to signal alteration due to space-charge or other effects. When the method of standard additions was applied, excellent agreement with certified values was obtained for all of the elements studied.

NIST Total Diet 1548 Reference Material

Fig. 4 shows typical analyte signal pulses for the slurry sampling ETV-ICP-MS volatilization of 2 mg of Total Diet SRM. Perhaps the most notable feature of this figure is the signal

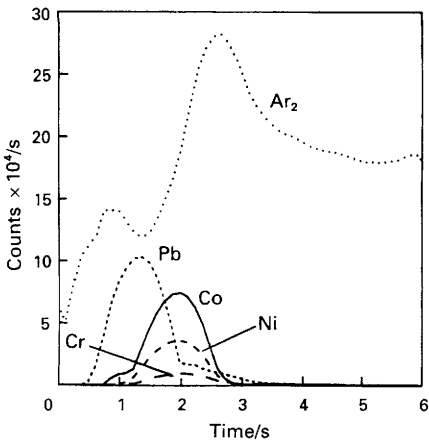


Fig. 3 ETV-ICP-MS signal pulses for 2 mg of NRCC LUTS-1 Lobster Hepatopancreas reference material

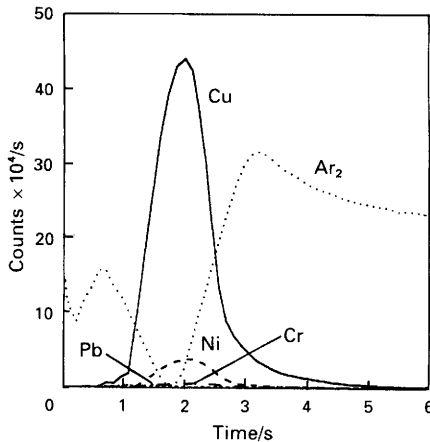


Fig. 4 ETV-ICP-MS signal pulses for 2 mg of NIST SRM 1548 Total Diet

Table 3 Analysis of NRCC LUTS-1 Lobster Hepatopancreas by slurry sampling ETV-ICP-MS

	Concentration/ $\mu\text{g g}^{-1}$			
	Co	Cr	Ni	Pb
External calibration	0.17 ± 0.02	0.45 ± 0.07	0.59 ± 0.03	0.013 ± 0.001
Standard additions	0.048 ± 0.006	0.081 ± 0.013	0.159 ± 0.009	0.007 ± 0.001
Certified	0.051 ± 0.006	0.079 ± 0.012	0.200 ± 0.034	0.010 ± 0.002

pulse for the argon dimer. The Total Diet 1548 SRM is a composite material comprising foodstuffs representative of the total dietary intake for the average person. This sample contains large amounts of organic material (as does LUTS-1) in addition to substantial quantities of salts. During the high-temperature vaporization step (following the dry and char step), the first component to volatilize is the salt matrix, which corresponds to the virtual total suppression of the argon dimer signal at 1.8 s into the vaporization step. At higher temperatures and at later times, carbonaceous material is volatilized, resulting in some enhancement of the argon dimer signal (3.2 s). All of the analyte signal pulses occur during the volatilization of the salt matrix and therefore all should be subject to interference effects in the plasma and/or mass spectrometer. The analytical results obtained for the diet sample using both external calibration and the method of standard additions are summarized in Table 4. Only one elemental concentration for the analytes studied is certified (Cr) for this material, but information values are given in the certificate for both Ni and Pb. Additional values were obtained separately for comparison purposes for Cr and Ni using independent analytical methods.

The results in Table 4 show that values obtained for Cr, Ni and Pb using external calibration do not agree with certified or analysed values. Only Cu was in agreement with the certified range. Although the Cu was volatilized at the same time as the salt matrix in the sample, the concentration of Cu in the sample was very high. It has been shown that the severity of interference effects is related to the molar ratio of analyte to matrix component.²² The higher the ratio, the smaller the matrix effect. The much higher ratio of Cu to matrix compared with other analytes studied probably resulted in a Cu^+ ion signal which was relatively insensitive to interference effects compared with Cr, Ni and Pb. When the method of standard additions was used, excellent agreement was obtained between determined concentrations and the certified or reference values for all of the elements studied.

Comparison of Sample and Calibration Standard Analyte ETV-ICP-MS Signal Pulses

Fig. 5 shows a comparison of analyte signal pulses for Ni obtained from the volatilization of sample and aqueous standard. This figure shows that for the Coal and Total Diet RMs, the Ni in the sample is volatilized at a later time than is Ni in the aqueous standard, whereas for the Lobster Hepatopancreas RM, Ni is volatilized at the same time for both sample and aqueous standards. These results may indicate that for the Coal and Total Diet RMs, analyte vaporization is delayed (compared with aqueous standard) because of adsorption of analyte onto coal particles or the delayed vaporization of analyte trapped in a salt melt. All of the elements determined in the diet sample experienced delayed vaporization and all elements determined in the Lobster Hepatopancreas sample were volatilized at the same time as were aqueous standards. Only Ni, Cr and Cu experienced delayed vaporization for the coal sample whereas Pb and Mn were not delayed relative to

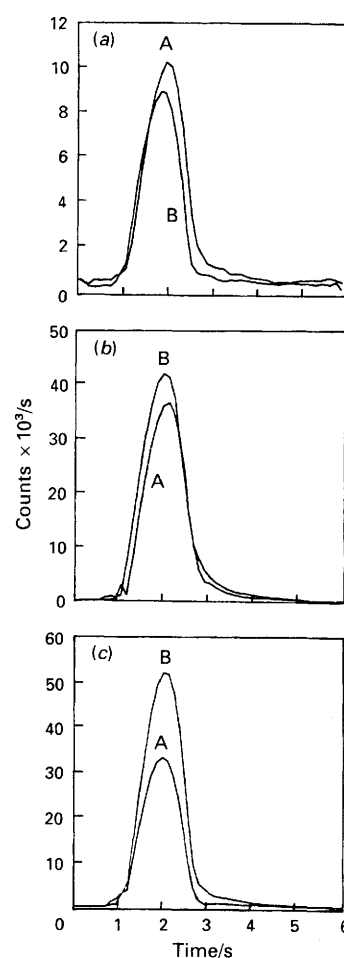


Fig. 5 Comparison of nickel ETV-ICP-MS signal pulses derived from A, reference materials and B, aqueous standards: (a) NIST SRM 1632a; (b) NIST SRM 1548; and (c) NRCC LUTS-1 Lobster Hepatopancreas

aqueous standard. Lead and magnesium were perhaps both quantitatively extracted from the coal matrix by the diluent, thus preventing delayed volatilization.

These data along with Tables 2–4 show that accurate and precise analytical results can be obtained even if the volatilization properties of the analyte are altered by the presence of matrix components.

Conclusion

This study has shown that ETV-ICP-MS can be used successfully for the direct analysis of slurries and that the technology developed for the analysis of slurries by ETAAS is directly transferrable to ETV-ICP-MS. The use of the argon dimer is demonstrated to be useful in monitoring non-spectroscopic or matrix effects and in selecting the appropriate calibration

Table 4 Analysis of NIST SRM 1548 Total Diet by slurry sampling ETV-ICP-MS

	Concentration/ $\mu\text{g g}^{-1}$			
	Cu	Cr	Ni	Pb
External calibration	2.1 ± 0.2	0.28 ± 0.02	0.75 ± 0.02	0.025 ± 0.005
Standard additions	2.9 ± 0.2	0.11 ± 0.02	0.29 ± 0.02	0.045 ± 0.006
Certified	2.6 ± 0.3	$0.094 \pm 0.014^*$	(0.41) [†] $0.30 \pm 0.01^\ddagger$	(0.05) [†]

* Acid digestion, determination by ETAAS.

[†] Certificate information values.

[‡] Acid digestion, solution nebulization ICP-MS determination.

strategy for individual analytes for the analysis of samples containing substantial matrix components.

Inductively coupled plasma mass spectrometry offers several advantages for the ETV determination of slurries (over ETAAS), including a multi-element capability and the ability to select different analyte isotopes having different natural abundances to extend the range of concentrations determinable on a single slurry sample preparation.

Although the presence of large amounts of salts in the samples lead to serious matrix effects, use of the method of standard additions gives results in excellent agreement with certified values, except for Cr in coal. For refractory materials such as coal, the partitioning of analyte between solid and liquid phases is important.

Using reported ETV-ICP-MS limits of detection¹ for the analytes studied, the following limits of detection, in ng g^{-1} , can be estimated for a slurry sample size of 2 mg: Co, 0.070; Cu, 0.21; Cr, 3.2; Mn, 0.060; Ni, 0.24; and Pb, 0.012.

Clearly, the future of ETV-ICP-MS applied to the analysis of slurries is promising. Further work is required on the study of chemical modifiers which could either be used to remove matrix components and/or stabilize analytes, such that vaporization of analyte occurs after matrix components have left the graphite tube. The analysis of organic materials could be improved with the use of air or oxygen ashing to assist in the removal of carbon derived from sample material prior to the high temperature volatilization step.

The authors are grateful to the Perkin-Elmer Corporation for the loan of the HGA-600MS and the USS-100.

References

- 1 Sturgeon, R. E., Grégoire, D. C., Willie, S. N., Zheng, J. and Kudo, A., *J. Anal. At. Spectrom.*, 1993, **8**, 1053.
- 2 Grégoire, D. C. and Lee, J., *J. Anal. At. Spectrom.*, 1993, **9**, 393.
- 3 Grégoire, D. C., Ansdell, K., Goltz, D. M. and Chakrabarti, C. L., *Chem. Geol.*, in the press.
- 4 Epstein, M. S., Carnrick, G. R., Slavin, W., and Miller-Ihli, N., *Anal. Chem.*, 1989, **61**, 1415.
- 5 Bin, H., Zucheng, J., and Yun'e, Z., *J. Anal. At. Spectrom.*, 1991, **6**, 623.
- 6 Miller-Ihli, N. J., *Anal. Chem.*, 1992, **64**, 964A.
- 7 Miller-Ihli, N. J., *J. Anal. At. Spectrom.*, 1988, **3**, 73.
- 8 Miller-Ihli, N. J., *J. Anal. At. Spectrom.*, 1989, **4**, 295.
- 9 Miller-Ihli, N. J., *Fresenius' J. Anal. Chem.*, 1990, **337**, 271.
- 10 Miller-Ihli, N. J., *At. Spectrosc.*, 1992, **13**, 1.
- 11 Miller-Ihli, N. J., *Fresenius' J. Anal. Chem.*, 1993, **345**, 482.
- 12 Bendicho, C., and de Loos-Vollebregt, M. T. C., *J. Anal. At. Spectrom.*, 1991, **6**, 353.
- 13 Bendicho, C., and de Loos-Vollebregt, M. T. C., *Spectrochim. Acta, Part B*, 1990, **45**, 695.
- 14 Ebdon, L., Foulkes, M. E., Parry, H. G. M., and Tye, C. T., *J. Anal. At. Spectrom.*, 1988, **3**, 753.
- 15 Totland, M., Jarvis, I., and Jarvis, K. E., *Chem. Geol.*, 1993, **104**, 175.
- 16 Huang, M., Jiang, Z., and Zeng, Y., *J. Anal. At. Spectrom.*, 1991, **6**, 221.
- 17 Grégoire, D. C., Lamoureux, M., Chakrabarti, C. L., Al-Maawali, S., and Byrne, J. P., *J. Anal. At. Spectrom.*, 1992, **7**, 579.
- 18 Grégoire, D. C., and Sturgeon, R. E., *Spectrochim. Acta, Part B*, 1993, **48**, 1347.
- 19 Sturgeon, R. E., Berman, S. S., Willie, S. N., and Desaulniers, J. A. H., *Anal. Chem.*, 1981, **53**, 2337.
- 20 Grégoire, D. C., Al-Maawali, S., and Chakrabarti, C. L., *Spectrochim. Acta, Part B*, 1992, **47**, 1123.
- 21 Ediger, R. D., and Beres, S. A., *Spectrochim. Acta, Part B*, 1992, **47**, 907.
- 22 Grégoire, D. C., *Spectrochim. Acta, Part B*, 1987, **42**, 895.
- 23 Beauchemin, D., McLaren, J. W., and Berman, S. S., *Spectrochim. Acta, Part B*, 1987, **42**, 467.

Paper 3/06822F

Received November 15, 1993

Accepted January 10, 1994