

Determination of Tungsten and Molybdenum at Low Levels in Geological Materials by Inductively Coupled Plasma Mass Spectrometry*

Gwendy E. M. Hall, Chang J. Park and J. C. Pelchat

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

The determination of tungsten and molybdenum in geological materials by isotope dilution and internal standardisation inductively coupled plasma mass spectrometry (ICP-MS) is reported. The sample is first decomposed by an alkaline fusion, the elements are then leached from the melt as their soluble oxy-anions, and taken through a separation procedure based on selective formation of their oxinate complexes with subsequent adsorption on activated charcoal. Rhenium is used as the internal standard for tungsten and ruthenium as the internal standard for molybdenum. This technique is shown to compensate well for any possible interferences, such as that arising from the presence of sodium. Relative standard deviations of 7 and 5%, and determination limits of 0.07 and 0.08 $\mu\text{g g}^{-1}$ are obtained for tungsten and molybdenum, respectively, by isotope dilution ICP-MS. This precision is degraded only slightly when using internal standardisation ICP-MS. Results by both calibration methods are shown to be accurate and comparable to literature values of international reference materials.

Keywords: Tungsten and molybdenum determination; inductively coupled plasma mass spectrometry; geological materials; internal standardisation; isotope dilution

In designing a useful and practical method to analyse geological materials for trace elements, one of the objectives should be to achieve a determination limit significantly lower than the crustal abundance of each element. The average content of both tungsten and molybdenum in rocks lies in the 1–2 $\mu\text{g g}^{-1}$ range¹ and, therefore, a determination limit of ca. 0.1 $\mu\text{g g}^{-1}$ is desirable for each element.

To date, most methods used to determine tungsten and molybdenum at low levels in geological materials have been based on two analytical techniques: spectrophotometry and neutron activation. In the former technique, the reagent most frequently used is dithiol,^{2–4} wherein the metal - dithiol complex is selectively extracted into an organic solvent such as isoamyl acetate and its absorbance measured. The less sensitive and less selective colorimetric complexing reagent, thiocyanate, has also been used routinely.^{5,6} Terashima² reported a detection limit as low as 0.1 $\mu\text{g g}^{-1}$ for both elements after separate treatments of 0.5-g sample aliquots in order to avoid mutual interferences. A method employing the latter technique, neutron activation, described by Simon and Rollinson⁷ is capable of detecting tungsten to 0.005 $\mu\text{g g}^{-1}$ with a relative standard deviation of ca. 20%. The procedure is based on the extraction of tungsten into chloroform with α -benzoin oxime, back-extraction into potassium hydroxide solution and final precipitation with σ -benzoin oxime. The activities of the 0.13 and 0.48 MeV gamma rays are measured and the yield determined by measurement of the 0.155 MeV gamma ray of ¹⁸⁸Re in equilibrium with ¹⁸⁸W added prior to sample fusion with peroxide. Other neutron activation methods have been reported, capable of determining tungsten⁸ to 0.01 $\mu\text{g g}^{-1}$ and molybdenum⁹ to 0.04 $\mu\text{g g}^{-1}$, but both also involve long irradiation times and complex separation procedures using ion exchange.

Until recently, rocks, soils and sediments were analysed at the Geological Survey of Canada for tungsten by the colorimetric dithiol procedure and for molybdenum by atomic absorption spectrometry; each technique yields a determination limit of 2 $\mu\text{g g}^{-1}$. Examination of a newly developed method¹⁰ to determine boron by inductively coupled plasma

atomic emission spectrometry (ICP-AES) after decomposition by alkali fusion led to the extension of this procedure to include the determination of tungsten to 5 $\mu\text{g g}^{-1}$ and molybdenum to 2 $\mu\text{g g}^{-1}$ in geological materials. A study was then initiated to lower the determination limit to a more practical level of 0.1 $\mu\text{g g}^{-1}$ for both elements by separating them from the alkaline solution obtained after fusion and measuring their content in a more concentrated and "cleaner" solution by inductively coupled plasma mass spectrometry (ICP-MS). The detection limit (3σ) in solution by ICP-MS is reported to be 0.05 ng ml⁻¹ for tungsten and 0.04 ng ml⁻¹ for molybdenum.¹¹ Since the first paper describing the ICP as an ion source for mass spectrometric determination of trace elements was published in 1980,¹² about 60 reports on this technique have appeared in the literature. As spectroscopists are still in the early stages of identifying interferences,^{13,14} and as salt build-up on the sampling orifice remains a problem, it was considered expedient to present to the ICP mass spectrometer a solution as free as possible from potential interferences. Furthermore, a ten-fold dilution of the alkaline solution used to determine boron¹⁰ could not be analysed by ICP-MS due to rapid salt build-up on the sampling orifice.

Vanderborcht and co-workers^{15–17} have made extensive use of chelation with 8-hydroxyquinoline (oxine) and subsequent adsorption of the metal oxinate on to activated charcoal as a means of concentrating trace elements in waters and brines, in preparation for measurement by energy-dispersive X-ray fluorescence. This separation technique appeared favourable in that alkali and alkaline earth elements, particularly sodium originating from the sodium carbonate - sodium nitrate flux, would not be appreciably adsorbed on to the charcoal. This study reports the combination of such a separation procedure with measurement of tungsten and molybdenum in the final solution by ICP-MS with calibration by internal standardisation and isotope dilution.

Experimental

Reagents

De-ionised, distilled water was used throughout. Sodium carbonate, sodium nitrate, hydrochloric acid, oxine and ethanol were all "Baker analysed" reagent grade. The

* Presented at the Third Biennial National Atomic Spectroscopy Symposium (BNASS), Bristol, UK, 23rd–25th July, 1986.

GSC contribution 27386.

activated charcoal (Darco, G-60) was obtained from Matheson, Coleman and Bell, OH, USA. Individual standard stock solutions (W, Mo, Re and Ru) were obtained from Spex Industries Inc., Metuchen, NJ, USA. The enriched isotopes of ¹⁸²W (93.75% ¹⁸²W, 2.55% ¹⁸⁴W) and ⁹⁵Mo (95.88% ⁹⁵Mo, 0.76% ⁹⁸Mo) were obtained from US Services Inc., Summit, NJ, USA. All glassware was washed in 30% nitric acid and repeatedly rinsed with de-ionised, distilled water.

Instrumentation

The ICP-MS system used for this work was the Elan 250 made by Sciex, Thornhill, Ontario, Canada. A peristaltic pump (Minipuls II, Gilson Medical Electronics, Inc., WI, USA) was placed in line with the sample delivery tube. At this time, a mass flow controller was not used to minimise fluctuation in delivery of the sample aerosol. Details of the instrumentation and operating conditions used are given in Table 1.

Inductively coupled plasma atomic emission spectrometry was used for comparison purposes and for optimisation of the conditions specified in the separation procedure. A Jobin-Yvon (ISA, Metuchen, NJ, USA) Model 38 high-resolution sequential ICP emission spectrometer was used. Details of the instrumentation and operating conditions are given in Table 2.

Recommended Procedure

- 1. Mix 200 mg of sample with 1 g of Na₂CO₃ - NaNO₃ (5 + 1) flux in a nickel crucible and fuse at 870 °C for 15 min.
- 2. Leach the melt with 10 ml of H₂O. If calibration is carried out by isotope dilution, add known amounts of ¹⁸²W and ⁹⁵Mo. Leave the mixture to stand overnight.
- 3. After warming, transfer the contents of the crucible into a test-tube, rinsing the crucible with 10 ml of H₂O.
- 4. Heat the test-tube in a hot-water bath at 90 °C for 1 h with frequent shaking. After cooling, centrifuge and decant the clear solution into a 50-ml beaker.
- 5. Add ca. 10 ml of H₂O and adjust the pH to 1.5–2.0 with HCl (initially with 12 M HCl, and then with 1.2 M HCl). With the volume at ca. 45 ml, add 1 ml of oxine dissolved in ethanol (25 mg ml⁻¹) and 200 mg of activated charcoal. Stir for 1 h with a magnetic stirrer.
- 6. Filter off the activated charcoal residue through a 0.45-µm membrane filter (Millipore, HAWP) under vacuum and transfer into a porcelain crucible and ash at 650 °C for 2 h.
- 7. Transfer the ash into a calibrated test-tube. Rinse the crucible first with 0.5 ml of 12 M HCl and then with ca. 1 ml of

H₂O and add the washings to the test-tube. Heat the test-tube and contents for several minutes with shaking. After cooling, adjust to ca. 4 ml with H₂O and centrifuge. Decant the solutions and make up to 5 ml with H₂O.

8. If calibration is carried out using isotope dilution, dilute this solution by a factor of five and analyse by ICP-MS. If calibration is carried out using internal standardisation, take 2 ml of the solution from step 7 and add 8 ml of a solution containing 20 ng ml⁻¹ of Re and 20 ng ml⁻¹ of Ru. If analysis by ICP-AES is to be carried out, take 3 ml of the solution from step 7 (i.e., the remaining solution after the aliquot for ICP-MS analysis by internal standardisation has been withdrawn). Thus, the dilution factor for analysis by ICP-MS is 125, in 0.24 M HCl, whereas the dilution factor for analysis by ICP-AES is 25, in 1.2 M HCl.

Calibration

Blanks and calibration standards, in duplicate, were taken through procedures identical with the sample decomposition and separation using Eppendorf microlitre pipettes to deliver accurate amounts of standard stock solutions directly on to the flux itself. Aliquots of standard solutions were chosen such that they would be equivalent to 0, 2.5, 5.0, 10.0 and 50.0 µg g⁻¹ of W or Mo in the original sample. Results were compared to calibration standards prepared directly in 1.2 M HCl and treated as in step 8. Analysis by isotope dilution ICP-MS was carried out after analysis by ICP-AES in order to estimate the optimum amount of enriched isotope to add in step 2 (see Results and Discussion). Five readings for each solution were taken and the relative standard deviation (RSD) recorded.

Analysis of International Reference Materials

Twenty-two reference materials from the US Geological Survey (USGS), the Canadian Certified Reference Materials Project (CCRMP) and the Institute of Geophysical and Geochemical Prospecting, China (IGGE) were analysed by ICP-MS, using the two methods of calibration, and by ICP-AES. Eight separate decompositions were carried out for each sample at random intervals over a three-month period; four were analysed by internal standardisation ICP-MS and by ICP-AES, while the other four were analysed by isotope dilution ICP-MS.

Table 1. ICP-MS hardware and operating conditions

<i>Inductively coupled plasma—</i>			
R.f. generator	2.5 kW, frequency 27.12 MHz	
Nebuliser	Meinhard C concentric glass	
Spray chamber	Scott-type	
Torch	Sciex, "long"	
Distance from load coil to sampler orifice	22 mm	
R.f. power	1.1 kW	
Plasma Ar flow-rate	12 l min ⁻¹	
Auxiliary Ar flow-rate	2.1 l min ⁻¹	
Nebuliser pressure	40 p.s.i.	
Solution uptake rate	1.0 ml min ⁻¹	
<i>Mass spectrometer—</i>			
Sampler	Nickel, 1.14-mm orifice	
Skimmer	Nickel, 0.89-mm orifice	
Ion lens settings	B = 10, E1 = 70, P = 20, S2 = 48	
Data acquisition parameters	Measurement time = 1 s; dwell time = 50 ms in multi-channel mode, 5 readings each solution	

Table 2. ICP-AES hardware and operating conditions

<i>Inductively coupled plasma—</i>			
R.f. generator	2.5 kW, frequency 27.12 MHz	
Nebuliser	Meinhard C concentric glass	
Spray chamber	Scott-type	
Torch	Jobin-Yvon demountable quartz	
Observation zone	12 mm above initial radiation zone	
R.f. power	1.05 kW	
Plasma Ar flow-rate	13 l min ⁻¹	
Auxiliary Ar flow-rate	0.15 l min ⁻¹	
Nebuliser pressure	38 p.s.i.	
Solution uptake rate	1.4 ml min ⁻¹	
<i>Atomic emission spectrometer—</i>			
Slit widths	Entrance and exit 50 µm	
Grating	Holographic, 3600 grooves mm ⁻¹	
Wavelengths	Mo II 202.030 nm with background correction at -0.016 and +0.019 nm	
		W II 207.911 nm with background correction at +0.024 nm	
Data acquisition parameters	Integration time 500 ms, 3 measurements for each solution	

Results and Discussion

Sample Preparation Procedure

Chelation by oxine with subsequent adsorption on to activated charcoal at a pH of 8 is an efficient means of concentrating many trace metal ions in waters. The collection substrate is then most frequently suitable for analysis by X-ray fluorescence or neutron activation. However, the objective of this separation procedure was to minimise the adsorption of other trace metal ions and major ions such as Na⁺ (from the flux) and to recover efficiently W and Mo subsequently from the charcoal into solution. Details of the optimisation of para-

meters are given in a separate publication.¹⁸ The point to note is that selectivity of formation of the metal oxinate is achieved by lowering the pH of separation to *ca.* 1.5 where W and Mo oxinates are quantitatively formed and adsorbed. This actually prohibits extension of this method to include the determination of elements such as Cr and V, which are not quantitatively adsorbed at this pH. Solutions of the international reference materials and in-house controls analysed by isotope dilution ICP-MS were also analysed by atomic absorption spectrometry for Na and Pb to test the efficiency of separation. The highest Na concentration found was only 3 µg ml⁻¹ and Pb was not detectable (<0.1 µg ml⁻¹).

Table 3. Intensities obtained at ¹⁸⁴W, ¹⁸⁷Re, ⁹⁵Mo, ¹⁰²Ru of 100 ng ml⁻¹ standard solution in the presence of 100 µg ml⁻¹ of Pb, Cu and Na at r.f. power of 1.1 kW, *n* = 5

Matrix element	W		Re		W/Re		Mo		Ru		Mo/Ru	
	Counts s ⁻¹	RSD, %	Counts s ⁻¹	RSD, %	Ratio	RSD, %	Count s ⁻¹	RSD, %	Counts s ⁻¹	RSD, %	Ratio	RSD, %
At <i>P</i> _{neb} = 42 p.s.i., <i>S2</i> = 48												
—	20 796	2.00	51 532	2.77	0.404	2.03	18 640	1.82	24 934	1.97	0.748	1.39
Pb	18 165	0.94	41 195	2.45	0.441	1.25	16 435	1.10	21 410	2.72	0.768	0.85
Cu	21 232	2.68	51 380	3.73	0.413	1.97	20 968	1.89	27 754	3.41	0.755	1.79
Na	20 378	5.57	47 096	5.76	0.432	2.08	18 440	3.23	23 934	2.68	0.770	1.74
At <i>P</i> _{neb} = 40 p.s.i., <i>S2</i> = 40												
—	8 244	1.42	17 380	2.35	0.474	1.96	14 642	2.05	18 782	3.07	0.780	1.95
Pb	14 944	2.44	31 778	3.11	0.471	1.88	20 780	3.08	25 448	2.75	0.817	2.04
Cu	10 262	1.71	20 775	2.68	0.493	0.82	15 108	4.09	18 768	5.66	0.804	2.05
Na	10 454	3.38	21 836	4.09	0.478	1.82	14 758	2.14	18 848	2.50	0.783	1.28

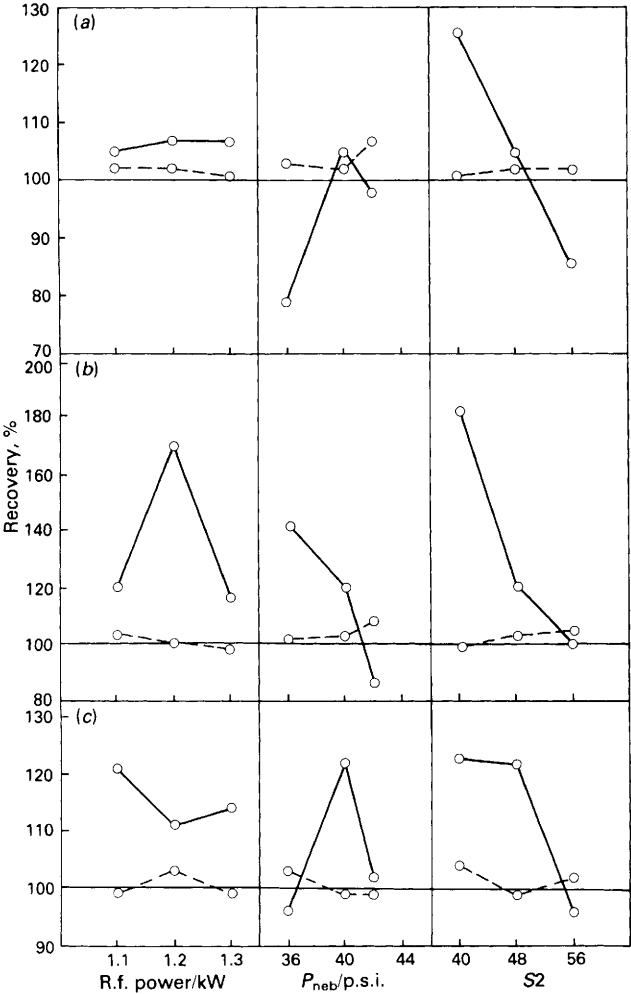


Fig. 1. Effect of 100 µg ml⁻¹ of Na (a), Pb (b) and Cu (c) on 100 ng ml⁻¹ W with and without internal standardisation with Re: solid line, without internal standardisation; and broken line with internal standardisation

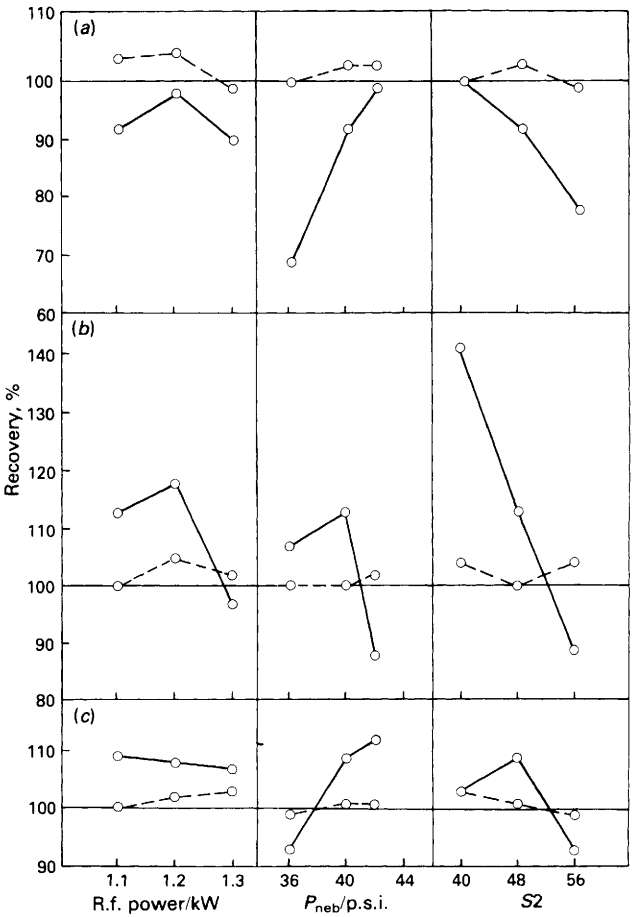


Fig. 2. Effect of 100 µg ml⁻¹ of Na (a), Pb (b) and Cu (c) on 100 ng ml⁻¹ Mo with and without internal standardisation with Ru: solid line, without internal standardisation; and broken line, with internal standardisation

Internal Standardisation

Initially, settings of r.f. power, nebuliser pressure (P_{neb}) and the photon stop lens (S2) were optimised with 100 ng ml⁻¹ standard solutions of W and Mo. Both elements produced maximum intensities at an r.f. power of 1.1 kW and an S2 of 48. However, a maximum count rate at P_{neb} of 40 p.s.i. was found for Mo, whereas the count rate for W peaked at 42 p.s.i. A compromise of 40 p.s.i. was chosen for the nebuliser pressure. Under these conditions, oxide formation was determined to be 1% for W and 0.2% for Mo.

Measurement using internal standardisation was pursued in an attempt to improve upon the precision obtained by direct calibration, often greater than $\pm 2\%$ RSD, and to minimise possible interferences. The elements, Re and Ru, were chosen as internal standards for W and Mo, respectively, because of their closeness in mass and their low crustal abundances (ca. 1 ng g⁻¹).¹ Moreover, their degrees of ionisation are similar, a critical parameter in an interference study.¹⁹ At $T = 7500$ K, the percentages of ionisation for W⁺, Re⁺, Mo⁺ and Ru⁺ are calculated to be 94, 93, 98 and 96, respectively. The only mutual isobaric interference is that of ⁹⁸Ru on ⁹⁸Mo where 1.9% of the element, Ru, exists as that isotope.

In order to investigate their effectiveness as internal standards to correct for matrix interference, a stock solution containing 100 ng ml⁻¹ of W, Re, Mo and Ru was made and sub-divided into four. Three portions were then spiked to contain 100 µg ml⁻¹ each of Pb, Cu and Na. Lead was chosen as it was thought that it might exhibit a mass effect in the spectrometer, Na because of its probable ionisation interference effect and Cu as a less problematic matrix element. The masses chosen for calibration purposes were ¹⁸⁴W, ¹⁸⁷Re, ⁹⁵Mo and ¹⁰²Ru as there are no apparent isobaric interferences from other isotopes, oxides or plasma species. Another reason to choose the ⁹⁵Mo⁺ line, in preference to ⁹⁸Mo⁺ in these interference studies, is that ⁶³Cu³⁵Cl⁺ is isobaric with ⁹⁸Mo⁺. Stock solutions of the three "matrix" elements were checked for their W, Re, Mo and Ru content and found to be negligible. The intensities of all four solutions were measured at the four masses and two different combinations of P_{neb} and S2 settings. The data presented in Table 3 indicate three points in particular. Firstly, the presence of a 1000-fold excess of these "matrix" elements affects the intensity of ⁹⁵Mo and ¹⁸⁴W signals. Lead, in particular, produces a dramatic enhancement

under one set of conditions for both W and Mo and a slight suppression under another set of conditions. The second point to note is that these enhancements and suppressions are effectively offset by ratioing to their internal standard. Thirdly, the RSDs obtained by internal standardisation are now in the 1–2% range, down from the 1–5% range. This implies that better precision could be expected by calibration with internal standardisation than by the method of standard addition (not studied in this work).

This study was expanded to include effects seen by varying the r.f. power from 1.1 to 1.3 kW, the nebuliser pressure from 36 to 42 p.s.i., and the photon stop lens setting from 40 to 56. As each parameter was varied in turn, the other two were set to their optimum values (r.f. power 1.1 kW, P_{neb} 40 p.s.i. and S2 48). This investigation was carried out in order to observe the changes in the magnitudes of the interferences with changes in parameter settings and hence to comprehend the nature of such interferences better; this is not to imply that these settings of power, pressure and photon stop lens would ever drift to any appreciable extent from the individual values chosen within these ranges. Results are displayed graphically in Figs. 1 and 2 for W and Mo, respectively.

Recovery without internal standardisation is defined as

$$\frac{(^{95}\text{Mo or }^{184}\text{W counts s}^{-1})_{\text{with matrix element}}}{(^{95}\text{Mo or }^{184}\text{W counts s}^{-1})_{\text{without matrix element}}} \times 100$$

whereas recovery with internal standardisation is defined as

$$\frac{\left(\frac{^{95}\text{Mo or }^{184}\text{W counts s}^{-1}}{^{102}\text{Ru or }^{187}\text{Re counts s}^{-1}} \right)_{\text{with matrix element}}}{\left(\frac{^{95}\text{Mo or }^{184}\text{W counts s}^{-1}}{^{102}\text{Ru or }^{187}\text{Re counts s}^{-1}} \right)_{\text{without matrix element}}} \times 100$$

The greatest interferences are seen to be: Na on W and Mo at P_{neb} of 36 p.s.i. (79 and 69%, respectively); Pb on W and Mo at an S2 of 40 (181 and 141%, respectively); Pb on W at an r.f. power of 1.2 kW (169%); and Na on W and Mo at an S2 of 56 (86 and 78%, respectively). The enhancement caused by Cu on W to about 120% at four sets of conditions was unexpected. Work is continuing with the objective of elucidating the types of interferences encountered and of formulating models to predict their likelihood. In summary, the method of internal standardisation is seen to compensate well for these interferences, to within a range of 99–103% of the true W or Mo value under the conditions chosen for analysis (r.f. power 1.1 kW; P_{neb} 40 p.s.i.; and S2 48). The magnitude of these interferences decreased (not proportionately) at the 10 µg ml⁻¹ level of Pb, Cu and Na, ranging from 91 to 112% of the true W or Mo concentration (100 ng ml⁻¹) and, again, internal standardisation minimised such effects to 99–102% of the correct value. Hence, analysis by internal standardisation should provide good accuracy, especially in light of the efficiency of separation of W and Mo from Na achieved in this procedure.

Isotope Dilution

Measurement by isotope dilution should compensate for the possible interferences of ionisation, transport and ion sampling effects and mass-dependent signal drift,²⁰ provided that there are no isobaric interferences on either isotopic mass

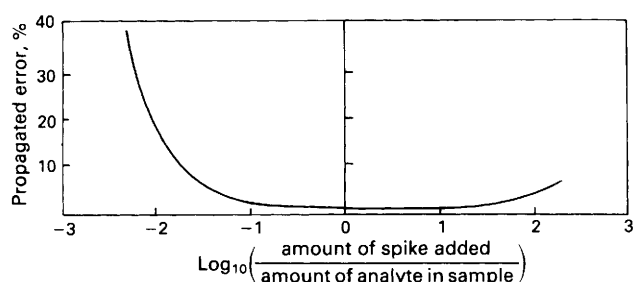


Fig. 3. Propagation of error in isotope dilution ICP-MS: determination of Mo as an example. Assumptions made: (i) RSD for isotope ratio measurement of spiked solution = 1%; (ii) abundance of ⁹⁵Mo in sample = 15.9% and abundance of ⁹⁸Mo in sample = 24.4%; and (iii) abundance of ⁹⁵Mo in spike solution = 95.88% and abundance of ⁹⁸Mo in spike solution = 0.76%

Table 4. Isotope ratio measurements of ¹⁸²W/¹⁸⁴W and ⁹⁵Mo/⁹⁸Mo in solutions of GSD-3, GSD-6 and SGR-1, $n = 5$

Sample	¹⁸² W/ ¹⁸⁴ W			⁹⁵ Mo/ ⁹⁸ Mo		
	Mean	SD	RSD, %	Mean	SD	RSD, %
GSD-3	0.8572	0.0196	2.29	0.6486	0.0048	0.74
GSD-6	0.8610	0.0063	0.73	0.6543	0.0146	2.23
SGR-1	0.8586	0.0200	2.33	0.6480	0.0046	0.71
Natural abundance ratio	0.8567			0.6516		

being counted. If the isotope is added in the early stages of sample treatment, it should also compensate for loss of analyte through the separation procedure but this has been found to be insignificant, as determined by standard solutions similarly treated. Care must be taken to ensure that the isotope spike added is in chemical equilibrium with the analyte. Although analysis by isotope dilution appears ideal, there is one major drawback. In order to minimise the propagation of error in the isotope ratio measurement of the spiked sample, the molar ratio (R) of the spike to the analyte in the sample should be within the range $0.1 < R < 10$.²¹ Thus, the approximate concentration of the analyte, to an order of magnitude, must be known. This propagation of error is illustrated graphically for Mo in Fig. 3, assuming an RSD of 1% for the isotope ratio measurement of the spiked solution. Thus, if the amount of spike added equals 100 times the amount of Mo in the sample, the propagated error would be 4%, whereas it would be as high as 18% if the ratio of spike to analyte was 1:100.

The derivation of the simplified isotope dilution formula used in the calculation of analyte concentration is as follows. If x is the unknown molar amount of analyte (W or Mo) in the sample, y is the molar amount of spike added and R is the ratio of isotope (1) (e.g., ⁹⁵Mo, ¹⁸²W) to isotope (2) (e.g., ⁹⁸Mo, ¹⁸⁴W) in the spiked sample, then

$$R = \frac{x \times \text{natural abundance}(1) + y \times \text{abundance}(1) \text{ in spike}}{x \times \text{natural abundance}(2) + y \times \text{abundance}(2) \text{ in spike}}$$

Thus,

$$x = y \times \frac{\text{abundance}(1) \text{ in spike} - R \times \text{abundance}(2) \text{ in spike}}{R \times \text{natural abundance}(2) - \text{natural abundance}(1)}$$

$$\text{Analyte concentration} = \frac{x \times \text{atomic mass of analyte}}{\text{sample mass}}$$

The abundances of ⁹⁵Mo and ⁹⁸Mo in the spike were 95.88 and 0.76%, respectively, while the abundances of ¹⁸²W and ¹⁸⁴W were 93.75 and 2.55%, respectively.

The validity of assuming the ratio of ¹⁸²W to ¹⁸⁴W and ⁹⁵Mo to ⁹⁸Mo in the unspiked samples to be equal to their natural abundances was investigated by determining these values in solutions of GSD-3, GSD-6 and SGR-1 obtained by carrying out the recommended decomposition and separation procedures. Results shown in Table 4 confirm that this assumption is justified as each mean is within a standard deviation of the natural abundance ratio. Mass discrimination is not evident for these elements.

The interference study using 1000-fold excesses of Na, Pb and Cu discussed in the previous section were repeated by isotope dilution ICP-MS. For all settings of r.f. power, nebuliser pressure and photon stop lens indicated in Figs 1 and 2, this measurement technique produced results within 99–102% of the true W and Mo concentration of 100 ng ml⁻¹.

Analytical Results for the International Reference Materials

Results of four separate analyses of 22 international reference materials by both ICP-MS and ICP-AES are shown in Tables 5 and 6 for tungsten and molybdenum, respectively. There are few recommended values in the literature for these samples, and, as noted in the tables, only the GSD series is attributed with such certainty. Overall, the agreement amongst the three measurement techniques is very good and these values match well with those reported in the literature with a few exceptions.

Tungsten results by this ICP-MS method (Table 5) appear high for GXR-6 and low for SCo-1, STM-1 and MRG-1. However, these values cited for comparison are obtained from individual colorimetric or neutron activation methods and do not represent recommended values based upon a variety of analytical techniques. Such controversy is readily apparent upon examining the literature and is evident in results quoted for MRG-1 and GXR-6, for example. The value of 1.78 µg g⁻¹ W for GXR-6 obtained by isotope dilution ICP-MS does not agree with the 1.1 µg g⁻¹ quoted by Gladney *et al.*,²³ 0.88

Table 5. Tungsten content of standard reference materials analysed by ICP-MS and ICP-AES. Each result is quoted as the mean ± standard deviation based on four separate decompositions

Sample	ICP-MS, isotope dilution		ICP-MS, internal standardisation		ICP-AES, direct calibration		Literature value/ µg g ⁻¹	Reference
	W content/ µg g ⁻¹	RSD, %	W content/ µg g ⁻¹	RSD, %	W content/ µg g ⁻¹	RSD, %		
AGV-1 (andesite)	0.56 ± 0.04	7.1	0.59 ± 0.04	6.7	0.6 ± 0.1	16.6	0.53	22
BHVO-1 (basalt)	0.23 ± 0.03	13.0	0.26 ± 0.03	11.5	<0.4	—	0.21	2
MAG-1 (marine sediment)	1.56 ± 0.16	10.2	1.41 ± 0.20	14.2	1.5 ± 0.2	13.3	1.67	2
QLO-1 (quartz latite)	0.62 ± 0.09	14.5	0.51 ± 0.12	23.5	0.6 ± 0.2	33.3	0.58	2
RGM-1 (rhyolite)	1.46 ± 0.07	4.8	1.41 ± 0.10	7.1	1.3 ± 0.2	15.4	1.6	22
SCo-1 (Cody shale)	1.34 ± 0.08	6.0	1.31 ± 0.12	9.1	1.1 ± 0.2	18.2	1.61	2
SDC-1 (mica schist)	0.77 ± 0.09	11.6	0.71 ± 0.11	15.5	0.8 ± 0.3	37.5	0.8	22
SGR-1 (petroleum shale)	2.52 ± 0.12	4.8	2.61 ± 0.13	5.0	2.5 ± 0.1	4.0	2.64	2
STM-1 (syenite)	3.36 ± 0.11	3.3	3.30 ± 0.18	5.5	3.1 ± 0.2	6.5	3.8	22
GXR-2 (soil)	1.60 ± 0.18	11.2	1.55 ± 0.20	12.9	1.5 ± 0.3	20.0	1.8 ± 0.5	23
GXR-5 (soil)	0.99 ± 0.09	9.1	1.05 ± 0.15	14.3	1.1 ± 0.2	18.2	1.1 ± 0.5	23
GXR-6 (soil)	1.78 ± 0.14	7.8	1.68 ± 0.19	11.3	1.8 ± 0.3	16.6	1.1	23
GSD-1 (stream sediment)	0.99 ± 0.11	11.1	1.03 ± 0.15	14.6	0.9 ± 0.2	22.2	1.04 ± 0.3*	24
GSD-3 (stream sediment)	5.03 ± 0.10	2.0	4.91 ± 0.15	3.0	4.7 ± 0.3	6.4	4.9 ± 0.7*	24
GSD-4 (stream sediment)	2.51 ± 0.07	2.8	2.41 ± 0.20	8.3	2.3 ± 0.3	13.0	2.5 ± 0.8*	24
GSD-5 (stream sediment)	3.26 ± 0.08	2.4	3.37 ± 0.28	8.3	3.2 ± 0.4	12.5	3.2 ± 0.6*	24
GSD-6 (stream sediment)	24.6 ± 0.8	3.2	25.8 ± 1.1	4.3	24 ± 2	8.7	25 ± 3*	24
GSD-7 (stream sediment)	5.54 ± 0.19	3.4	5.48 ± 0.19	3.5	5.3 ± 0.4	7.5	5.5 ± 1.0*	24
GSD-8 (stream sediment)	2.02 ± 0.13	6.4	1.88 ± 0.22	11.7	2.1 ± 0.3	14.3	1.95 ± 0.44*	24
SY-3 (syenite)	1.14 ± 0.07	6.1	1.03 ± 0.10	9.7	1.0 ± 0.1	10.0	1.27	2
MRG-1 (gabbro)	0.27 ± 0.03	11.1	0.24 ± 0.05	20.8	0.4 ± 0.2	50.0	0.54	2
FeR-1 (iron formation)	1.04 ± 0.09	8.6	1.12 ± 0.12	10.7	1.1 ± 0.3	27.3	—	—

* Recommended values.

Table 6. Molybdenum content of standard reference materials analysed by ICP-MS and ICP-AES. Each result is quoted as the mean \pm standard deviation based on four separate decompositions

Sample	ICP-MS, isotope dilution		ICP-MS, internal standardisation		ICP-AES, direct calibration		Literature value/ $\mu\text{g g}^{-1}$	Reference
	Mo content/ $\mu\text{g g}^{-1}$	RSD, %	Mo content/ $\mu\text{g g}^{-1}$	RSD, %	Mo content/ $\mu\text{g g}^{-1}$	RSD, %		
AGV-1 (andesite)	2.13 ± 0.06	2.8	2.18 ± 0.09	4.1	2.1 ± 0.1	4.8	2.02	25
BHVO-1 (basalt)	1.11 ± 0.04	3.6	1.20 ± 0.06	5.0	1.1 ± 0.1	9.0	1.01	25
MAG-1 (marine sediment)	1.41 ± 0.08	5.7	1.37 ± 0.08	5.8	1.3 ± 0.1	7.7	1.46	25
QLO-1 (quartz latite)	2.53 ± 0.06	2.4	2.63 ± 0.07	2.7	2.5 ± 0.1	4.0	2.55	25
RGM-1 (rhyolite)	2.48 ± 0.08	3.2	2.53 ± 0.08	3.2	2.5 ± 0.1	4.0	2.44	25
SCo-1 (Cody shale)	1.39 ± 0.10	7.2	1.42 ± 0.08	5.6	1.3 ± 0.1	7.7	1.69	25
SDC-1 (mica schist)	0.39 ± 0.10	25.6	0.32 ± 0.12	37.5	0.4 ± 0.3	75.0	0.10	25
SGR-1 (petroleum shale)	34.1 ± 0.2	0.6	35.1 ± 0.3	0.9	34 ± 1	2.3	36.64	25
STM-1 (syenite)	5.02 ± 0.06	1.2	4.95 ± 0.08	1.6	4.9 ± 0.2	4.1	4.86	25
GXR-2 (soil)	1.57 ± 0.04	2.5	1.44 ± 0.06	4.2	1.5 ± 0.1	6.7	1.5 ± 0.2	23
GXR-5 (soil)	31.8 ± 0.6	1.9	31.9 ± 1.0	3.1	30 ± 1	3.3	28 ± 6	23
GXR-6 (soil)	2.28 ± 0.06	2.6	2.17 ± 0.08	3.7	2.2 ± 0.2	9.1	2.1 ± 0.3	23
GSD-1 (stream sediment)	0.84 ± 0.03	3.6	0.76 ± 0.03	3.9	0.8 ± 0.1	12.5	$0.74 \pm 0.20^*$	24
GSD-3 (stream sediment)	91.5 ± 1.7	1.9	90.2 ± 2.0	2.2	89 ± 4	4.5	$92 \pm 7^*$	24
GSD-4 (stream sediment)	0.84 ± 0.02	2.4	0.81 ± 0.04	4.9	0.9 ± 0.1	11.1	$0.86 \pm 0.27^*$	24
GSD-5 (stream sediment)	1.34 ± 0.03	2.2	1.28 ± 0.06	4.7	1.3 ± 0.1	7.7	$1.2 \pm 0.3^*$	24
GSD-6 (stream sediment)	7.88 ± 0.30	3.8	7.92 ± 0.32	4.1	8.0 ± 0.3	3.8	$7.7 \pm 1.2^*$	24
GSD-7 (stream sediment)	1.74 ± 0.12	6.9	1.61 ± 0.18	11.2	1.7 ± 0.2	11.8	$1.4 \pm 0.2^*$	24
GSD-8 (stream sediment)	0.67 ± 0.03	4.4	0.59 ± 0.03	5.1	0.6 ± 0.1	16.7	$0.54 \pm 0.19^*$	24
SY-3 (syenite)	0.78 ± 0.13	16.7	0.87 ± 0.14	16.1	0.8 ± 0.2	25.0	0.58	2
MRG-1 (gabbro)	1.01 ± 0.07	6.9	1.03 ± 0.08	7.7	0.9 ± 0.1	11.1	0.84	2
FeR-1 (iron-formation)	3.42 ± 0.08	2.3	3.36 ± 0.10	3.0	3.3 ± 0.3	9.0	—	—

* Recommended values.

Table 7. Comparison of the precision of the measurement step *versus* the precision of the over-all procedure in the determination of tungsten by ICP-MS and ICP-AES, $n = 5$

Sample	ICP-MS, isotope dilution		ICP-MS, internal standardisation		ICP-AES, direct calibration	
	W content/ $\mu\text{g g}^{-1}$	RSD, %	W content/ $\mu\text{g g}^{-1}$	RSD, %	W content/ $\mu\text{g g}^{-1}$	RSD, %
GSD-4 (stream sediment)	2.57	0.65	2.46	0.89	2.39	11.4
	2.50	1.35	2.26	1.46	2.71	11.9
	2.44	1.52	2.52	1.11	2.07	0.4
	2.44	1.45	2.40	1.60	2.17	7.6
	2.49	1.10	2.36	0.99	2.29	23.3
Mean and RSD of 5 replicates	2.49	1.91	2.40	4.12	2.33	10.6
XY-03 (composite from carbonaceous cherty mudstone)	1.39	1.00	1.33	2.87	1.15	27.6
	1.31	0.80	1.45	4.34	1.28	7.9
	1.36	1.25	1.34	1.81	1.14	19.2
	1.20	1.38	1.37	2.35	1.07	10.5
	1.53	1.95	1.67	1.17	1.44	18.9
Mean and RSD of 5 replicates	1.36	7.17	1.43	10.08	1.22	12.00

$\mu\text{g g}^{-1}$ quoted by Abbey,²⁶ or the $1.39 \mu\text{g g}^{-1}$ figure quoted by Terashima.² Perhaps a problem of inhomogeneity exists with this sample in addition to the occurrence of variability between methods. Although the result of $0.27 \mu\text{g g}^{-1}$ W for MRG-1 obtained by isotope dilution ICP-MS is significantly different from the value of $0.54 \mu\text{g g}^{-1}$ quoted by Terashima,² it does agree well with the $0.28 \mu\text{g g}^{-1}$ result published by Steel *et al.*²⁷

Examination of Table 6 indicates that agreement between the results obtained by isotope dilution and internal standardisation ICP-MS for molybdenum is excellent and matches well with ICP-AES. As with tungsten, there are some results that are at variance with the few values so far reported elsewhere. The result of $0.39 \mu\text{g g}^{-1}$ Mo for SDC-1 is significantly higher than that of $0.10 \mu\text{g g}^{-1}$ quoted by Aruscavage and Campbell.²³ The value of $31.85 \mu\text{g g}^{-1}$ Mo for GXR-5 agrees better with that of $32.3 \mu\text{g g}^{-1}$ obtained by Terashima² than the mean of $28 \mu\text{g g}^{-1}$ calculated by Gladney *et al.*²² The concentration of $1.39 \mu\text{g g}^{-1}$ Mo for SCo-1 lies in between the $1.69 \mu\text{g g}^{-1}$

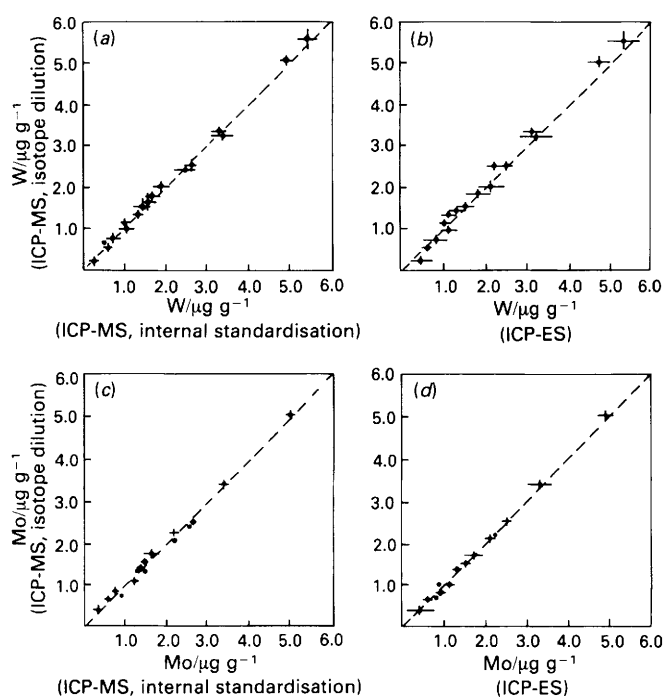
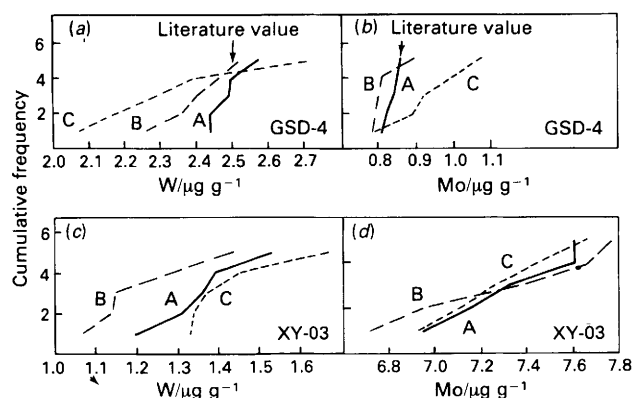
value obtained by Aruscavage and Campbell²⁵ and $1.15 \mu\text{g g}^{-1}$ quoted by Terashima.²

Fig. 4, showing $X - Y$ plots of these results obtained by ICP-MS and ICP-AES for tungsten and molybdenum, serves to emphasise the absence of bias between the methods of measurement and to illustrate the precision associated with each.

The only other publication to date that reports the analysis of geological materials for W and Mo by ICP-MS is that of Date and Hutchison.²⁸ These elements were determined in a leach solution derived from an $\text{HF} - \text{HClO}_4 - \text{HNO}_3$ attack carried out in a bomb, the dilution factor being 1000. Although this decomposition could well be incomplete for W, as mentioned by the authors, the results for GXR-2, GXR-5 and GXR-6 appear high for both elements in comparison with the data presented here and elsewhere. For example, duplicate results for GXR-2 are 4.5 and $4.2 \mu\text{g g}^{-1}$ W (*c.f.* $1.57 \mu\text{g g}^{-1}$). These values are probably close to the detection limit (not reported for W; $3.0 \mu\text{g g}^{-1}$ for Mo), and, therefore, the

Table 8. Comparison of the precision of the measurement step *versus* the precision of the over-all procedure in the determination of molybdenum by ICP-MS and ICP-AES, $n = 5$

Sample	ICP-MS, isotope dilution		ICP-MS, internal standardisation		ICP-AES, direct calibration	
	Mo content/ $\mu\text{g g}^{-1}$	RSD, %	Mo content/ $\mu\text{g g}^{-1}$	RSD, %	Mo content/ $\mu\text{g g}^{-1}$	RSD, %
GSD-4 (stream sediment)	0.86	1.02	0.89	1.32	0.79	5.6
	0.82	0.91	0.79	1.91	0.92	31.0
	0.84	0.94	0.80	0.94	1.07	23.0
	0.81	1.22	0.78	1.52	1.00	1.7
	0.85	1.43	0.81	1.43	0.89	6.9
Mean and RSD of 5 replicates	0.83	2.38	0.81	5.42	0.93	11.49
XY-03 (composite from carbonaceous cherty mudstone)	7.61	0.44	7.11	0.85	7.77	2.7
	6.95	0.33	7.25	0.67	7.36	0.4
	7.61	0.70	6.93	1.80	6.95	1.0
	7.15	0.48	7.45	0.95	6.72	4.2
	7.32	1.80	7.65	1.42	7.67	1.4
Mean and RSD of 5 replicates	7.33	4.14	7.28	3.91	7.29	6.21

**Fig. 4.** Graphical comparison of analytical results for the international reference materials using isotope dilution ICP-MS, internal standardisation ICP-MS and ICP-AES**Fig. 5** Cumulative frequency plots for W and Mo in five separate decompositions of GSD-4 and XY-03 by isotope dilution ICP-MS, internal standardisation ICP-MS and ICP-AES: A, isotope dilution ICP-MS; B, internal standardisation ICP-MS; and C, ICP-AES

associated lack of precision could be a factor. More likely, though, the high results are caused by positive interferences from concomitant elements as the method of calibration used was simply to bracket the samples with synthetic standards. The objective of the work was probably to analyse one solution for as many elements as thought reasonable from such a decomposition procedure rather than to design a method suitable for only a few elements.

Precision and Determination Limit

The mean precision, expressed as the RSD, in the determination of W and Mo over the range of $0.2\text{--}5\ \mu\text{g g}^{-1}$ is 7 and 5%, respectively, by isotope dilution ICP-MS, and 10 and 7%, respectively, by internal standardisation ICP-MS, calculated from the analyses of the international reference materials. The RSD of the ICP-MS measurement itself is typically 0.5–2% and, thus, these increased values reflect the variability introduced in the sample decomposition and separation steps. Over the same concentration range, the average RSD obtained by ICP-AES is 18% for W and 13% for Mo. Here, the uncertainty in the measurement step is the dominating factor. Comparison of the precision of the measurement step and the precision of the over-all procedure for both elements is made in Tables 7 and 8 and shown graphically with cumulative frequency plots in Fig. 5. Five separate decompositions of GSD-4 and an in-house control sample, XY-03, were analysed by each of the three techniques. The RSDs of each solution measurement are also recorded; this value for GSD-4 lies in the 0.6–1.6% range for both elements by ICP-MS, whereas the range exhibited by ICP-AES broadens to 0.4–31%. The trend exhibited by most samples in the precision of the over-all procedure by the three techniques studied is exemplified by the increase in RSD for W in GSD-4, from 1.9% by isotope dilution ICP-MS to 4.1% by internal standardisation ICP-MS and, finally, to 10.6% by ICP-AES. The cumulative frequency plots in Fig. 5 make this readily apparent. The much greater scatter exhibited by XY-03 is probably due to inhomogeneity of this composite sample evidenced in other analyses; data for the majority of the international reference materials reflect behaviour very similar to GSD-4 shown here.

The determination limits for both ICP-MS calibration methods were derived from the analyses of five separate blanks (flux alone), treated as samples in the usual manner. Thus, the determination limit, defined as three times the standard deviation of the blank, is $0.07\ \mu\text{g g}^{-1}$ for W and $0.08\ \mu\text{g g}^{-1}$ for Mo by isotope dilution ICP-MS. The corresponding figures by internal standardisation ICP-MS are $0.1\ \mu\text{g g}^{-1}$ for

both elements. The actual blank values for W and Mo are equivalent to 0.33 and 0.72 $\mu\text{g g}^{-1}$, respectively, contributed by the activated charcoal and flux. Thus, by obtaining purer reagents, these determination limits could be lowered significantly; this is now under investigation. Care must be taken when changing to a new batch of reagent as the contamination level can alter drastically.

Conclusions

The determination of W and Mo at concentrations in the range of 0.2–5 $\mu\text{g g}^{-1}$ in geological materials by isotope dilution ICP-MS, using the described procedure, yields precisions of ca. 7 and 5% RSD, respectively, with determination limits of 0.07 and 0.08 $\mu\text{g g}^{-1}$, respectively. These figures of merit are degraded only slightly when using internal standardisation ICP-MS, wherein the ^{184}W intensity is normalised to that of ^{187}Re and the ^{95}Mo intensity is normalised to that of ^{102}Ru . Moreover, the interferences caused by the presence of 1000-fold excesses of Pb and Na are minimised to insignificant levels by internal standardisation, as they are by isotope dilution. A prior knowledge of the approximate concentration range is required for analysis by isotope dilution ICP-MS in order to add the optimum quantity of enriched isotope and hence maximise reproducibility. The accuracy of either technique appears most acceptable, as evidenced by results obtained on the international reference materials.

Sample introduction by electrothermal vapourisation is currently under investigation and, if successful, this may eliminate the need for separation of the analytes by the activated charcoal procedure.

References

1. Turekian, K. K., and Wedepohl, K. M., *Bull. Geol. Soc. Am.*, 1961, **72**, 175.
2. Terashima, S., *Geostand. Newsl.*, 1980, **IV**, 9.
3. Aruscavage, P., and Campbell, E. Y., *US Geol. Surv. J. Res.*, 1978, **6**, 697.
4. Quin, B. F., and Brooks, R. R., *Anal. Chim. Acta*, 1972, **58**, 301.
5. Lillie, E. G., and Greenland, L. P., *US Geol. Surv. J. Res.*, 1973, **1**, 555.
6. Lillie, E. G., and Greenland, L. P., *Anal. Chim. Acta*, 1974, **69**, 313.
7. Simon, F. O., and Rollinson, C. L., *US Geol. Surv. J. Res.*, 1975, **3**, 475.
8. Gladney, E. S., *Anal. Lett.*, 1978, **A11**, 429.
9. Nadkarni, R. A., and Morrison, G. H., *Anal. Chem.*, 1978, **50**, 294.
10. Hall, G. E. M., and Pelchat, J. C., *Analyst*, 1986, **111**, 1255.
11. Gray, A. L., *Spectrochim. Acta, Part B*, 1985, **40**, 1525.
12. Houk, R. S., Fassel, V. A., Flesch, G. D., Svec, H. J., Gray, A. L., and Taylor, C. E., *Anal. Chem.*, 1980, **52**, 2283.
13. Horlick, G., Tan, S. H., Vaughn, M. A., and Rose, C. A., *Spectrochim. Acta, Part B*, 1985, **40**, 1555.
14. Olivares, J. A., and Houk, R. S., *Anal. Chem.*, 1986, **58**, 20.
15. Vanderborght, B. M., and Van Grieken, R. E., *Anal. Chem.*, 1977, **49**, 311.
16. Vanderborght, B. M., and Van Grieken, R. E., *Int. J. Environ. Anal. Chem.*, 1978, **5**, 221.
17. Verbeeck, J., Vanderborght, B., Van Grieken, R., and Ex, G., *Anal. Chim. Acta*, 1981, **128**, 207.
18. Hall, G. E. M., Pelchat, J. C., and de Silva, N., *Analyst*, 1987, in the press (A6/359).
19. Gregoire, D. C., personal communication.
20. McLaren, J., Beauchemin, D., and Vander Voet, A., *Can. J. Spectrosc.*, 1985, **30**, 29A.
21. Heumann, K. G., *Int. J. Mass Spectrom. Ion Phys.*, 1982, **45**, 87.
22. Govindaraju, K., *Geostand. Newsl.*, 1984, Special Issue, 3.
23. Gladney, E. S., Burns, C. E., and Roelandts, I., *Geostand. Newsl.*, 1984, **2**, 119.
24. Xie, X., Yan, M., Li, L., and Shen, H., *Geostand. Newsl.*, 1985, **2**, 83.
25. Aruscavage, P. J., and Campbell, E. Y., *Geostand. Newsl.*, 1981, **2**, 171.
26. Abbey, S., "Studies in Standard Samples of Silicate Rocks and Minerals 1969–1982," Geological Survey of Canada, Ottawa, Paper 83–15, 1983, 114 pp.
27. Steel, T. W., Wilson, A., Goudvis, R., Ellis, P. J., and Radford, A. J., *Geostand. Newsl.*, 1978, **2**, 71.
28. Date, A. R., and Hutchison, D., *Spectrochim. Acta, Part B*, 1986, **41**, 175.

Paper J6/58

Received July 23rd, 1986

Accepted September 22nd, 1986