

I.C.P. magnetic sector multicollector mass spectrometry and its applications to geochemistry

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The I.C.P. magnetic sector multi-collector mass spectrometer (Plasma 54) is a high precision double focusing instrument with extended geometry in which the instability of the plasma is circumvented by using simultaneous static multi-collection (Walder and Freedman, 1992). The plasma source utilizes Ar as the support gas, in a similar manner to that commonly deployed in conventional quadrupole I.C.P.M.S. The ions are extracted at high voltage and a quadrupole d.c. lens is used to focus the ion beam onto the analyzer entrance slit. An electrostatic analyzer is used to match the energy dispersion of the plasma source with that of the magnetic sector analyzer. The instrument has a mass resolution of > 400 . The magnet provides double dispersion with effective 54 cm extended geometry and z focusing. The exit pole face is adjustable to rotate the exiting ion beams and produce an ion image perpendicular to the optic axis. The collector assembly can provide flat topped peaks for the simultaneous detection of up to nine masses using eight independently adjustable Faraday collectors and a fixed axial Faraday collector that can be lowered to allow the ion beam access to a Daly detector with pulse counting. The Plasma 54 has a higher transmission efficiency than most quadrupole instruments (currently $> 100 \times 10^6$ ions sec^{-1} ppm^{-1} indium using conventional aspiration methods). In order to test the instrument at high precision for peak flatness a relatively simple gas source can be temporarily substituted for the plasma source. Alternatively the peak flat can be determined by sequentially moving a collector across a mass and measuring the isotopic ratio in the static mode at high precision for different collector positions. Recently a new wide flight tube and magnet with an additional Faraday detector located on the high mass side have been developed and commissioned.

This can be used to detect U at the same time as Pb is measured using the main collector array (or ^7Li at the same time as ^6Li) (Halliday *et al.*, 1993). This facilitates simultaneous U-Pb measurements for spatial resolution work.

The standard method of sample admission utilizes a peristaltic pump to deliver dissolved samples to a pneumatic nebulizer. The nebulizer converts the solution into an aerosol which is then passed into the plasma source where it is desolvated, dissociated and ionized. The minimum solution volume required is about 1 ml. A Mistral desolvating higher efficiency nebulizer can be incorporated in the plasma source resulting in significant (factor of 10) increases in signal size (Walder *et al.*, 1993b). Whereas by thermal ionization it is difficult to obtain high precision concentration and/or isotopic data for certain elements such as Sn, Hf, W, Pt and Ir, simply because they are difficult to ionize, high precision ($< 0.002\%$ RSD) is achievable with 300ng of Hf (Walder *et al.*, 1993b) using the Plasma 54. The design is currently being modified to increase the transmission further by a factor of > 10 .

The mass discrimination in the source of the Plasma 54 is a relatively simple function of mass (close to a power law) and, unlike the case for a thermal source, is independent of time, the chemical properties of the element, or the admixing of other elements (Russ and Bazan, 1987; Walder and Freedman, 1992, Walder *et al.*, 1993c). This significant feature of this kind of mass spectrometer contrasts with thermal ionization mass spectrometry in which mass discrimination is a function of work function and in some instances, poorly understood reactions that occur on the filament during heating. Thus, using a solution containing a mixture of elements with overlapping mass ranges, the mass discrimination

observed in an element of known isotopic composition can be used to determine accurately the unknown isotopic composition of the other element. The implications of this are far reaching. Normal isotopic compositions, natural fractionations, natural isotopic anomalies and artificial isotopic enrichments can be measured to higher precision. Elements such as Pb, the isotopic compositions of which cannot be normalized with internal normalization, can be corrected for mass discrimination to high levels of accuracy by admixing a standard such as Tl of known isotopic composition and monitoring masses ^{205}Tl and ^{203}Tl . Isobaric interferences such as ^{87}Rb on ^{87}Sr , ^{144}Sm on ^{144}Nd or ^{176}Lu on ^{176}Hf can be corrected for to higher degrees of accuracy than has hitherto been possible. The isotopic composition of Hf can be determined to high precision, even with a Lu/Hf ratio of 0.5. Similarly Nd isotopic compositions can be determined to high precision even with 50:50 mixture of Sm and Nd. The Pb, Hf, Sr and Nd data generated so far demonstrate a remarkable performance and open the way for isotopic studies in which the elements of interest cannot be separated. For example, there is no reason why laser ablation Sr and Hf isotopic analyses should not be feasible, even in the presence of Rb and Lu (respectively).

A Nd-YAG laser has been coupled with a Plasma 54 and the number of Pb ions detected per number of Pb atoms ablated in NIST SRM 610 glass has been shown to be 1 in 450 (Walder *et al.*, 1993a). Direct micro sampling isotopic analysis for Pb, Sr and Hf in complex matrices is relatively straightforward, even in the presence of isobaric interferences such as ^{87}Rb on ^{87}Sr . Molecular isobaric interferences are usually negligible. Using conventional aspiration methods the analysis of isotopes between masses 14 and 80 may well be complicated by the presence of interfering simple molecular species (usually with a maximum of two atoms) from major components of the solution and plasma support gas. However, the use of laser ablation and hence a dry plasma (rather than aqueous aspiration techniques) reduces oxide and hydride formation. The simplicity of molecular species in the plasma (nearly always a maximum of

two atoms combined) contrasts with secondary ionization mass spectrometry (S.I.M.S.) which requires very high mass resolution in order to separate complex molecular interfering species (Compston *et al.*, 1982; Shimizu and Hart, 1982).

Although development of the Plasma 54 is ongoing it is already very apparent that this instrument offers considerable potential for new and improved isotopic and trace element measurements. These include, for example, greater accuracy for Pb isotopic data, Rb/Sr ratios, U-Th disequilibrium data and Hf isotopic compositions. Certain isotopic anomalies in meteorites can be measured very precisely. New long half-life chronometers such as In-Sn dating of sulfides should be feasible. High precision isotope dilution trace element data for the platinum group elements and transition metals will be straightforward. Laser ablation *in situ* measurements of Sr, Hf and Pb isotopic compositions, together with U-Pb ages of accessory minerals can be made. Finally, measurements of natural isotopic fractionation of low mass elements such as Li, B, Cl should be possible but have yet to be evaluated.

References

- Compston, W., Williams, I.S. and Clemens, S.W. (1982) *Abstr. 30th Ann. Conf. Am. Assoc. Mass Spectrometry*, 593-5
- Halliday, A.N., Christensen, J.N., Jones, C.E., Walder, A.J. and Freedman, P.A. (1993) *Trans. Amer. Geophys. Un.*, **74**, 626-7.
- Russ, G.P. and Bazan, J.M. (1987) *Spectrochim. Acta*, **42B**, 49. Shimizu, N. and Hart, S.R. (1982) *Ann. Rev. Earth Planet. Sci.*, **10**, 483-526.
- Walder, A.J., Abell, I.D., Freedman, P.A. and Platzner, I. (1993a) *Spectrochim Acta*, **48B**, 397-402.
- Walder, A.J. and Freedman, P.A., (1992) *J. Anal. Atomic Spectr.*, **7**, 571-5.
- Walder, A.J., Koller, D., Reed, N.M., Hutton, R.C. and Freedman, P.A., (1993b) *J. Anal. At. Spectrom.*, **8**, 1037-41.
- Walder, A.J., Platzner, I. and Freedman, P.A., (1993c) *J. Anal. At. Spectrom.*, **8**, 19-23.