

REDUCING INTERFERENCES, IN PLASMA SOURCE MASS SPECTROMETERS

This invention relates to mass spectrometers. It is particularly useful in mass spectrometers employing a plasma ion source such as an inductively-coupled plasma (ICP) or a microwave-induced plasma (MIP) source. Such instruments typically use a quadrupole mass filter but magnetic-sector mass filters are also used. The invention is applicable to both types.

ICP and MIP mass spectrometers are characterized by low background noise and high sensitivity and may have detection limits in the parts-per-trillion region across the mass range. However, with present instruments, a limiting factor on the detection limit at certain masses (or strictly mass-to-charge ratios) is the presence of an unwanted background signal at the mass to be monitored. Such spectral interferences (usually known as isobaric interferences) may be due to isotopes of two or more different elements having approximately the same mass, to charged molecular species for example ArO^+ , Ar_2^+ or oxide ions, or to doubly-charged species appearing at the same mass-to-charge ratio as a singly-charged ion.

Researchers in ICP mass spectroscopy have devoted considerable effort to establishing the mechanism of formation of these interfering molecular species in the hope that their formation can be reduced. For example, Vanhaecke, Vandecasteele, et al, in *Mikrochim. Acta*. 1992, vol. 108 pp 41-51 investigated the effect of various instrumental parameters (such as lens voltages, nebulizer and torch flow rates, etc) but were unable to form any general conclusions as to how isobaric interferences could be reduced. Similar work has been reported by Wang, Shen and Sheppard et al (*J. Anal. Atomic Spectrom.* 1990 vol 5 pp 445-449). Rowan and Houk (*Appl. Spectrosc.* 1989 vol 43 (6) pp 976-) teach the use of an instrument comprising two quadrupole mass analyzers in series. In this instrument the first quadrupole is not used as a mass analyzer but rather as an "RF only" quadrupole in which the pressure is deliberately kept quite high, at least in the region where the ions enter it. Molecular ions entering the first quadrupole are confined by the RF field and undergo collisions with the gas molecules therein and are lost by scattering. Atomic ions, having much smaller collisional cross-sections will however undergo fewer collisions and be transmitted to the mass analyzer. This arrangement was found to reduce some of the molecular ion interferences.

In order to further understand the processes by which different types of ions are formed in the plasma, several workers have attempted to measure the energy distribution of ions entering the mass analyzer. Peter and Höffer (*J. Vac. Sci. Technol.* 1987, vol A5 (4) pp 2285) report experiments carried out to determine the energy of various ions formed in an ICP using an energy filter combined with a quadrupole mass analyzer. However, the authors did not measure the energy distributions of molecular ions formed in the plasma, and merely report the results obtained without further comment as to how the information reported may be usefully employed.

A more detailed investigation of energy distributions was reported by Chambers and Hieftje (*Spectrochim. Acta*, 1991 vol 46B (6/7) pp 761-784). The authors used a quadrupole mass analyzer combined with a three-grid retarding potential energy filter and report the energy distributions of a variety of ions generated in an ICP. Theories are proposed concerning ion transport processes but no measurements are described on molecular ions and no conclusions are drawn

concerning distinguishing between interfering ion species in an ICPMS instrument.

It is the object of the invention to provide a method for the elemental analysis of a sample by ICP or MIP mass spectrometry in which isobaric interferences from molecular and multiply charged ions are reduced. It is a further objective to provide apparatus for carrying out such a method.

In accordance with these objectives the invention provides a method of determining the elemental composition of a sample by plasma mass spectroscopy comprising the steps of:

- a) introducing a said sample into an inductively-coupled or microwave-induced plasma formed in an inert gas to generate atomic ions from the elements present in it;
- b) passing at least some of said atomic ions through a nozzle-skimmer interface into an evacuated chamber, said interface comprising electrode means for determining the electrical potential at which said atomic ions enter said evacuated chamber so that atomic ions of a given mass-to-charge ratio enter said chamber with a particular kinetic energy; characterized by
- c) energy filtering the ions entering said chamber to reduce isobaric interferences from molecular and multiple charged ions by setting the lower cut-off energy to said particular kinetic energy of said atomic ions of a given mass-to-charge ratio so as to prevent at least the molecular ions of approximately said given mass-to-charge ratio having kinetic energies less than said particular kinetic energy from passing to step d); and
- d) mass filtering the ions passed by step c) and detecting those of said ions having said given mass-to-charge ratio.

Conveniently, step d) may be carried out using a quadrupole mass analyzer but a magnetic sector analyzer may also be used. The energy filtration step c) may be carried out with an energy filter having sufficient resolution to distinguish the wanted atomic ions from the unwanted ions. The requirements are further discussed below. Retarding grid or plate analyzers, parallel-plate or electrostatic cylindrical or spherical analyzers or cylindrical mirror analyzers may all be employed. Preferably there should be no line-of-sight path between the point of entry of the atomic ions into the evacuated chamber and the mass analyzer used in step d).

The inventor observed that in ICP mass spectrometers certain species produced in the ICP have markedly different ion energies from other species. In particular it was noted that whereas singly charged (i.e. atomic) "analyte" species such as Be, In and U were characterised by an ion energy distribution which steadily increased with mass (eg, from about 8 eV to 12 eV, depending on the conditions of the experiment), molecular species such as Ar_2 and ArO , and other oxide ions, showed substantially different ion energies, in most cases lower than those of the atomic ions of similar mass-to-charge ratio.

Multiply-charged species also were found to exhibit different ion energy characteristics from typical atomic ions. It was found by experiment that by placing an energy filter between the nozzle-skimmer interface and the mass analyzer of a prior ICP mass spectrometer it was possible to prevent ions having kinetic energies lower than the kinetic energy of the atomic ions (at any particular mass-to-charge ratio) from reaching the mass analyzer, so that the interferences due to the molecular ions in particular could be substantially reduced.

The reason for the variation of ion-energy with mass-to-charge ratio, and the difference in ion-energy for molecular