ABSTRACT:
Trends in the application of inductively coupled plasma-source mass spectrometry to inorganic analysis are reviewed. Instrumentation, system performance, analytical difficulties and their solution are addressed. Current literature is used to illustrate the power and versatility of the technique. Comments on likely innovations in ICP-MS in the near future conclude the article.

1. HISTORICAL INTRODUCTION
In the mid-seventies, following studies using a D.C. plasma as an ion source for mass spectrometry, it was apparent that a plasma-mass spectrometer combination was a potentially powerful instrument for inorganic analysis. However, the D.C. plasma-spectrometer duo suffered from severe interelement effects and partly because of this an alternative was sought. The ICP was chosen and R.S. Houk, working at the Ames Laboratory, Iowa State University, published an account of the collection of the first spectra obtained from an ICP-MS system in 1980 [2]. Following this progress was rapid with work proceeding in the USA, Canada and the UK. The first commercial instruments were available in 1983 and 1984 (Sciex and VG isotopes, respectively). Recently, French and Japanese companies have also entered the field.

2. INSTRUMENTATION
Fig. 1. is a simplified illustration of a typical ICP-MS system. Briefly, it consists of: a quartz torch which is fed with argon; a pneumatic nebulizer for the introduction of sample solution to the torch in the form of microdroplets; a loadcoil supplied with R.F. power; an interface to extract ions from the plasma; a quadrupole to separate the ions on the basis of their charge to mass ratio; a detection and data handling system.
where \( n \) is the electron density, \( m_e \) is the electron mass, \( h \) Plank's constant, \( Q^+ \) and \( Q^0 \) the partition functions of the ions and neutral atoms respectively, \( k \) Boltzmann's constant and \( I \) the ionization potential of the element. According to (1), most of the elements of the periodic table are ionized under typical plasma conditions [3].

The principal novel feature of the system is the plasma-spectrometer interface which allows the extraction of ions from the plasma at 5000 - 10000 K and atmospheric pressure, directly into a spectrometer whose final stage is at about 2 x 10^-6 torr. This is possible because of the nickel sampling cone which contains a small aperture, and which is watercooled and therefore able to remain in the tailflame of the plasma. Gas flows so rapidly through the 0.5 - 1.0 mm diameter aperture that the composition of the ion beam is effectively frozen. The core of the rapidly expanding ion beam is intercepted by a sharp-edged aperture in the tip of a skimmer cone. This aperture is usually 1.0 mm in diameter and located 5 to 10 mm behind the cone aperture. The ion beam may be focused by ion optics and the ions separated on the basis of their m/z ratio. Detection is by a channel electron multiplier operating in the pulse counting mode. A multichannel analyzer (MCA) of 1024 or 2048 channels is traditionally used to record the spectra. The mass scan of the quadrupole is correlated with the scan of the MCA so that ions with a particular m/z ratio are always recorded in the same channel or group of channels.

The quadrupole is computer controlled. Commercial instruments now include sophisticated software to: (i) control all of the instrumentation; (ii) manipulate data. For example, the instrument may be started and shut-down by computer command.

In addition, particular masses or mass ranges can be scanned. Calculations of the concentrations of specified elements in analyzed samples, based on the integrals obtained from the analysis of standard solutions, may be made. Mathematical corrections of interferences may also be done automatically.

3. PERFORMANCE

Comprehensive elemental coverage, detection limits in the sub ng mL^-1 region and rapid sample throughput, make ICP-MS an impressive method of inorganic analysis. The quadrupoles used exhibit good abundance sensitivity (10^-5) and can comfortably resolve masses one dalton apart. Thus isotope ratios may also be determined. A linear dynamic range of six orders of magnitude and good matrix tolerance in solutions of up to about 1 % solids content are also important features, giving the analyst freedom in the choice of dilution factors.

Usually the spectra obtained are simple, even for complex matrices, and this makes them straight forward to interpret. Fig. 3 shows the full mass range spectrum obtained from a multielement standard containing the following elements at 1 µg mL^-1; Li, B, Zn, Sc, Fe, Ga, Rb, Y, Nb, Sb, Te, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Th, U. Palladium and samarium are present at 0.1 µg mL^-1; Cs and Tl at 1.02 µg mL^-1.

4. ANALYTICAL DIFFICULTIES

At the temperatures existing along the central axis of the ICP microdroplets of sample solution are rapidly desolvated, vaporized and ionized. Generally, singly-charged positive ions are produced, though in practice a few doubly-charged ions with second ionization energies less than the first ionization energy of argon (15.76 eV) are also produced. Some polyatomic species are also formed, probably in the plasma-spectrometer interface. In addition, a small proportion of the population of ions of highly refractory elements, tend to exist as oxides. Thus two types of spectral interference arise: polyatomic species such as H_2O^+, ArO^+, and ArAr^+; double-charged ions such as Ba^{2+}. Such species are undesirable since, as noted above, the quadrupole effectively resolves only to one mass unit. Hence 56ArO^+ coincides with the iron isotope 56Fe^2+. Barium doubly-charged ions of mass 138 are detected at mass 69 i.e. coincident with 69Ga. A third type of problem is the so-called isobaric interference. This arises because isotopes of different elements sometimes match.
have the same mass e.g. $^{98}\text{Ru}$ and $^{98}\text{Mo}$.

Most of the polyatomic species, being combinations of $\text{H}$, $\text{N}$, $\text{O}$ and $\text{Ar}$, occur below mass 80. Since many of these species derive from the water in which the sample is dissolved, they occur at essentially the same levels in a "blank" of water (or of 1% v/v nitric acid solution which is typically used for analysis). Subtraction of a blank spectrum thus removes the interference. Also, interference-free isotopes are often available, thereby allowing the calculation of elemental concentrations. For example, as noted above, $^{56}\text{Fe}$ suffers from a large interference, but there are iron isotopes at mass 54 and 57. The $^{54}\text{Fe}$ isotope also suffers from an interference viz $^{40}\text{Ar}^{14}\text{N}$, so integrals at mass 57 are often used for the determination of iron. Alternatively, the spray-chamber, into which the nebulized sample droplets pass, may be water-cooled. This reduces the amount of water vapour present and thus $\text{ArO}^+$ levels, thereby allowing blank subtraction to correct for the $^{40}\text{Ar}^{16}\text{O}^+$ interference [4].

Also, levels of oxides and doubly-charged ions depend on the system parameters and may be reduced by a suitable choice of the argon gas flows and forward R.F. plasma power.

High (thousands of $\mu$g mL$^{-1}$) levels of elements such as Na in the sample solution can cause suppression of the integrals of elements present at trace levels. Greater sample dilution obviates this problem at the expense of poorer sensitivity. Alternatively the suppressing specie may be removed from the sample solution by an ion-exchange procedure.

Memory effects are typically very small, a washout between samples of one or two minutes being sufficient to reduce residual counts to negligible levels. Exceptions include elements such as Hg and I which tend to stick tenaciously to the walls of the spray-chamber and injector tube. Flushing the system with dilute nitric acid solves this difficulty at the cost of reduced sample throughput.

Integrals of an element at a fixed concentration may drift over prolonged periods, but this tendency has been diminished since the early days of ICP-MS. Moreover, the use of standards run at intervals during the analysis, or the inclusion of an internal standard in the sample solution can be used to correct this effect.

5. APPLICATIONS

5.1. Biological Materials

The number of applications of ICP-MS to real analytical problems has recently
been growing rapidly. Biological analyses have been particularly prominent. Amongst others, liquid and powdered milk [5, 6], urine [7], bovine liver [8], seminal plasma [9], and oyster tissue [10] have been analyzed since 1988. Two minireviews of biological applications have recently been presented [11, 12].

Typically, samples are digested prior to analysis. The aim of digestion is to completely dissolve the sample matrix, giving a solution which is readily nebulized and causes no blockage of the injector tube or sampling cone aperture. Sulphuric, hydrochloric and nitric acids are commonly used for the digestions, but the final solution is usually made up in nitric acid since this produces few spectral interferences. Teflon-lined digestion vessels are frequently employed to hold the acid and the sample material. Often the vessels have to be heated to achieve sample digestion. Recently, microwave digestion procedures, using controlled heating cycles, have been developed.

Depending on the analytical requirements, elemental concentrations may be determined by external calibration, isotope dilution analysis or the method of standard additions.

ICP-MS generally compares favourably with other analytical techniques for the inorganic analysis of biological materials. As an illustration, analyses of National Institute of Standards Technology (NIST) Standard Reference Material 1577 Bovine Liver by ICP-MS and neutron activation analysis (NAA) for the elements B, Mg, Al, Ca, V, Cr, Fe, Mn, Ni, Co, Cu, Zn, As, Se, Sr, Mo, and Cd, yielded similar accuracies and precisions, but the NAA analyses required various irradiations for different groups of elements, some of up to five days [13].

Another important feature of ICP-MS is its ability to obtain isotopic information. Numerous successful determinations of isotope ratios have been completed. A typical example is the determination of $^{63}$Cu:$^{65}$Cu ratios in blood plasma or serum following desalting using size-exclusion chromatography [14]. This was necessary since ArNa$^+$ and PO$_4^-$ interferences lie at mass sixty-three.

The group of Janghorbani, at the University of Chicago, has been especially active in isotope ratio analysis, and their work provides a good starting point for interested readers [15] (and references therein).

5.2. Geological Materials

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is a particularly powerful technique for the analysis of geological materials. However, the spectra of geological materials obtained by ICP-MS are much simpler than the equivalent spectra obtained by the optical technique. In particular, the rare earth elements are amenable to ICP-MS analysis [16]. For the reader interested in this area of applications, work published last year should provide a useful introduction [17, 18].

6. ALTERNATIVE METHODS OF SAMPLE INTRODUCTION

Since sample digestion is time-consuming and involves the use of hazardous materials, alternative methods to the use of a pneumatic nebulizer for sample introduction have been sought. Such alternatives include electrothermal vaporization (ETV), direct sample insertion, flow injection, and laser ablation (LA). Two of these, ETV and LA, are outlined here.

Electrothermal vaporization involves the use of a rod or filament which can be heated by a flow of current. Small solid or liquid samples (a few µg or µL) may be rapidly vaporized if they are placed on the rod. The vapour generated may be swept into the central channel of the ICP by an argon flow. Whittaker et al [19] used ETV in their determination of isotope ratios in blood samples, and from the data obtained deduced iron absorption in healthy women.

Laser ablation is an attractive option for sample introduction in many applications. Pulses from a ruby [20] or Nd:YAG laser [21] have been used to mobilise solid sample material into the central channel flow. Some matrices require no preparation; depth profiling is possible; interferences reduced, and sample throughput rapid. However, accuracy and precision are inferior to those routinely achieved with solution nebulization. Currently there is considerable scope for improvement in the design and optimization of alternative sample introduction methods. Each offers specific analytical advantages depending on the matrix and elements of interest.

7. FUTURE TRENDS

The literature reveals a continuing concern with fundamental aspects of ICP-MS. Renewed interest has been shown for example in the processes which occur at the plasma-spectrometer interface. Molecular gases are being investigated as additives to argon plasmas to improve
analytical performance and there is also interest in using helium rather than argon to support the plasma.

In addition, the numbers of applications papers is likely to continue to rise in the near future. This is due to the proven ability of ICP-MS to determine many elements in a diverse range of matrices. Moreover, its isotope ratio capabilities have received some detailed treatment and this opens up literally endless possibilities for stable isotope tracer studies. ICP-MS has also been used as a detector in speciation studies – another field capable of tremendous expansion.

Studies showing what ICP-MS can do in real analyses are still needed because the number of permutations of matrices and elements is virtually endless. Nevertheless, more and more "pure applications", that is those which aim to answer particular biological, medical, geological, or metallurgical problems, are being produced and well illustrate the maturity of the technique.

Other analytical techniques are sometimes used to obtain data for comparison with those obtained by ICP-MS. Additional comprehensive interanalytical comparisons are needed so that users can decide which method will best meet their needs.

Finally, it should be of interest to spectroscopists that spectra from a high resolution ICP mass spectrometer have recently been obtained [22]. This instrumentation allows the resolution of analyte isotopes from interferences very close in mass. As yet it is too early to assess the significance of this development.

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9. REFERENCES


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