

Elemental and Isotopic Analysis by Inductively Coupled Plasma Mass Spectrometry

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Chemists generally think of mass spectrometry (MS) as a method for determining the molecular weight and structure of molecules and for identification and quantification of trace compounds. However, MS was originally used for the discovery of naturally occurring isotopes of the various elements. In fact, in the earliest MS experiments, a plasma ion source was used to convert the sample into atomic ions!^{1,2} MS remained a potentially valuable measurement method for elemental analysis for many years, but the lack of a convenient and effective source capable of generating atomic ions on a multielement basis limited practical applications.

Meanwhile, elemental analysis had been transformed by the growth of atomic spectroscopy, particularly with the widespread adoption of atomic absorption in the 1960s. In 1964, the inductively coupled plasma (ICP) poked its nose through the door and achieved remarkable success as an emission source for multielemental analysis.^{3,4} Most of the best emission lines from the ICP were from singly charged atomic ions, so use of the ICP as an ion source for MS was a natural development. The early work of Gray on MS with a dc capillary arc plasma⁵ showed substantial promise and influenced us to attempt similar experiments with the much more robust and reliable ICP. Ions were first extracted from the analytical ICP in 1975, and mass spectra were first observed in 1978.⁶ Important practical improvements to the ion extraction process came largely from Douglas and French^{7,8} and Gray and Date⁹ in 1982. These early studies led to rapid commercialization and procreation among analysts, which transformed ICP-MS from a research curiosity into a practical analytical method capable of tolerating tough real samples.

ICP-MS is now widely used to support scientific activity in a variety of disciplines, primarily environmental monitoring, geochemistry, material sciences, semiconductor fabrication, nuclear technology, and biomedicine. Perhaps this Account will help spur interest in and use of the technique among chemists.

Robert Samuel Houk was born in New Castle, PA. He graduated from Slippery Rock State College in 1974 with a B.S. in secondary education. He then attended graduate school at Iowa State University, where he received the Ph.D. in analytical chemistry in 1980. Under the direction of V. A. Fassel and H. J. Svec, he constructed the first analytical ICP-MS device for his graduate degree. After a postdoctoral appointment at Iowa State, he joined the faculty there in 1981 and is now professor of chemistry. He has won the Lester W. Strock Award from the Society for Applied Spectroscopy (1986), the Maurice F. Hasler Award from Fisons Instruments and Applied Research Laboratories (1993), and the Chemical Instrumentation Award of the American Chemical Society (1993), primarily for his work in ICP-MS. Iowa State also presented him with the Wilkinson Teaching Award in 1993. His research interests include analytical atomic spectrometry, fundamental studies of analytical plasmas (particularly the ICP), improvements in sample introduction methodology for atomic spectroscopy, and electrospray MS for measuring elemental species and long-lived radionuclides.

Instrumentation

ICP and Ion Extraction. A schematic diagram of the ICP and ion extraction device is given in Figure 1.¹⁰ The ICP is an atmospheric pressure electrical discharge. It is usually supported in argon by power added to the load coil at rf frequencies, typically 27 or 40 MHz. The current through the coil sets up time-varying electric and magnetic fields, which influence the motion of free electrons inside the plasma. These fast electrons soon collide with neutral gas. In this fashion, energy added to the coil is transferred to and heats up the plasma. The energy is added primarily to the outer torus, leaving a cooler central hole, often called the axial channel, into which the sample is injected.

Many types of samples can be put into the ICP.¹¹ Gases can be injected directly. Condensed phase samples are usually subdivided into fine droplets or particulates first. Liquids are converted to an aerosol by a nebulizer. Solids can be dissolved or ground and suspended as slurries, then nebulized. Alternatively, a bulk solid can be converted directly into particulates by a variety of ablation methods employing a laser or an auxiliary arc or spark. Improving the efficiency, speed, and precision of the sample introduction process is a major area of research interest in atomic spectroscopy.

The axial channel is hot enough to convert these analyte particles largely into atomic ions. This is a key dimension to the selectivity of the technique, because the analyst can then identify the elements present on the basis of their known isotope patterns. The term "temperature" is a vague one for the ICP, because conditions therein deviate significantly from

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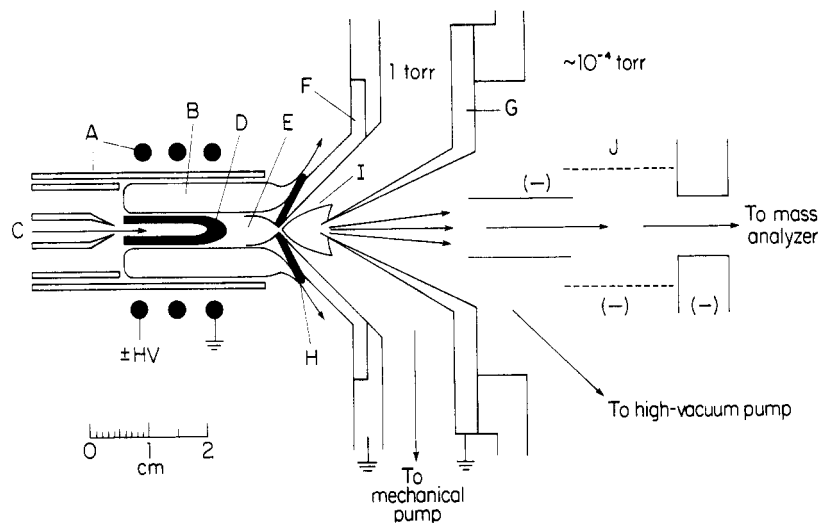


Figure 1. Schematic diagram of ICP and ion extraction device: A, torch and load coil; B, hot outer torus of ICP; C, sample flowing into central channel of ICP; D, emission from oxides and neutral atoms; E, emission from ions; F, sampling nozzle with 1-mm hole in tip; G, skimmer; H, boundary layer of cold gas around outside of sampler; I, supersonic jet between sampler and skimmer; J, ion lens. Reproduced with permission.^{10a}

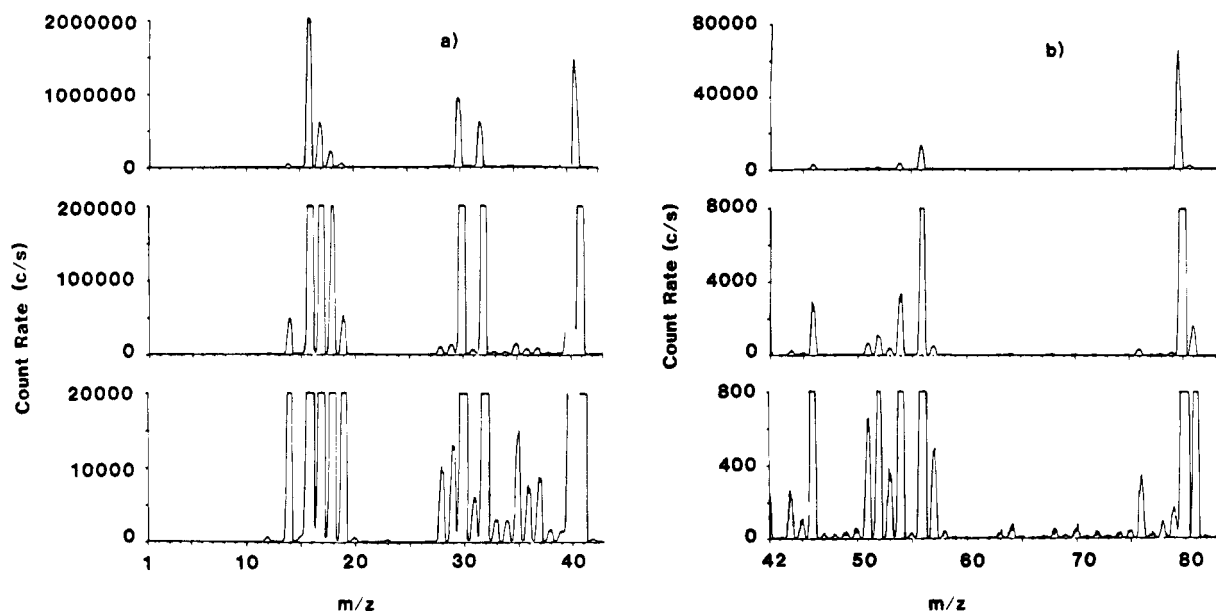


Figure 2. Background mass spectra obtained during nebulization of 1% HNO_3 in deionized water. The same spectra are plotted with different vertical scales for clarity. The detector was shut off as the MS scanned over the intense peak from $^{40}\text{Ar}^+$.

equilibrium.¹² Nevertheless, one position can generally be found in the plasma where atomic ions are produced in high yield from most of the elements for a wide range of samples.

Next, the ions are extracted into the vacuum system. Essentially, the nozzle of a supersonic jet sampling device is thrust into the plasma along the central axis. This sampling device is usually a water-cooled metal cone with a circular orifice (~ 1 mm diameter) in the center. Ions are entrained in the flow of neutrals through the orifice. The central section of the resulting supersonic jet passes through a skimmer into another high-vacuum stage. Surprisingly, the ions apparently pass through both the sampler and the skimmer with relatively little chemical reaction.^{7,8} The resulting beam is reasonably representative of the

ionic composition of the ICP region sampled, with the notable exceptions of argon adduct ions like ArO^+ , Ar_2^+ , and ArM^+ (M^+ = atomic metal ion).

Some typical background spectra are shown in Figure 2. The major background ions are generally Ar^+ , ArH^+ , O^+ , H_2O^+ , O_2^+ , and Ar_2^+ . Additional minor ions include ArO^+ , ArN^+ , and N_2^+ . The major constituents of the sample or solvent contribute other troublesome ions such as ClO^+ , ArCl^+ , SO^+ , and SO_2^+ . Some of these polyatomic ions persist in the ICP, which is apparently not quite hot enough to atomize everything, whereas others are probably made by collisions in the extraction process.

In either case, polyatomic ions interfere with some important analytes such as Ca^+ , K^+ , Si^+ , Fe^+ , V^+ , and As^+ . Investigation of means for minimizing these interferences is an area of substantial activity. These include (a) high spectral resolution (10 000 is sufficient in most cases), (b) removal of solvent by desolvation or by introducing the sample in as dry a form as

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possible, and (c) corrections based on known isotope patterns. Use of argon ICPs with small doses of other gases, such as $N_2^{13a,b}$ or Xe^{13c} or ICPs or microwave plasmas sustained in He^{13d-f} also can attenuate the severity of many of these interfaces.

The plasma is quasineutral; i.e., the ion and electron densities are essentially equal. Thus, the absolute ion current passing through the sampler and skimmer can be very high, because the current carried by the ions is neutralized by an equal current from electrons.^{7,8} This happy situation breaks down somewhere aft of the skimmer tip, where charge separation occurs. The total ion current of ~ 1 mA now is far too high to be focused and transmitted by most ion lenses, and repulsive interactions between positive ions disperse the ion beam substantially. As a result, only a small fraction ($\sim 10^{-3}$) of the ions leaving the skimmer are eventually detected. Furthermore, the trajectories of ions are also sensitive to the mass and abundance of ions from matrix elements (i.e., Na, K, Ca, and Mg from sea water) in the sample.^{14,15} Generally, the sensitivity for analyte ions decreases when a concentrated matrix is present. The extent of the decrease is greatest for light analytes and heavy matrices. Thus, from the standpoint of matrix effects, determination of U impurity in a Li matrix is much easier than measurement of Li impurity in a U matrix.¹⁴⁻¹⁷

These space charge problems adversely affect both accuracy and detection limits. Internal standardization or isotope dilution is generally employed to compensate for the interferences, and the loss of ions is tolerated ruefully. Solids from the sample can also coat onto the sampler and skimmer, primarily the former. These phenomena generally limit the maximum total solute level to $\sim 0.1\%$ by weight in the solution.

Mass Analysis and Detection. As shown in Figure 1, ions are conducted to the mass analyzer through an ion lens. A quadrupole mass analyzer is by far the most common, because of its moderate cost and size and its ability to tolerate relatively high operating pressures. The spectral resolution is only ~ 1 Da, so the ability of the plasma to efficiently atomize the sample is critical. The m/z resolved ions are detected by an electron multiplier, which is usually operated in the pulse counting mode. Fortunately, the background can be made low enough to see detectable signals from only a few ions at the detector, which helps compensate for the inefficiency of collecting ions behind the skimmer. Typically, some 10^6 atoms of the analyte element are required in the ICP to generate a significant signal at the detector.

Recent research has demonstrated some remarkable improvements with other kinds of mass analyzers. Double focusing devices are capable of high enough

spectral resolution to separate most atomic analyte ions from the remaining diatomic and polyatomic interfering ions.^{18,19} Sensitivity is better than that obtained with quadrupoles, and the background is essentially the dark current of the detector. So far, the best absolute detection limit reported corresponds to 500 atoms of the analyte element in the plasma. With these devices, ICP-MS thus approaches single atom detection limits. A different type of double focusing analyzer with multiple Faraday cup collectors is capable of isotope ratio measurements with a precision of 0.01% relative standard deviation.^{20,21} This value is comparable to that achieved by thermal ionization, with the added advantages that ICP-MS is much faster and does not suffer from isotope fractionation. Ion traps^{22a} and time-of-flight mass analyzers^{22b} can also be used with the ICP, with potential advantages for simultaneous multielement measurements.

Analytical Performance

Analyte Mass Spectra. A typical analyte spectrum is shown in Figure 3. Operating conditions are generally selected to maximize the yield of atomic M^+ ions from the analytes of interest. Metal oxide ions (MO^+) are usually the next most abundant ion after M^+ . These MO^+ ions also interfere with analyte ions. For example, the various Mo isotope peaks of MoO^+ overlap all the major isotopes of Cd, which prevents measurement of trace levels of Cd if a large excess of Mo is present.

Surprisingly, doubly charged ions are of rather low intensity and seldom cause serious interference problems. For example, the La^{2+} peak ($m/z = 69.5$) in Figure 3 is barely observable, even though the second ionization energy of La is rather low (11.06 eV).

In general, the ion yields for various elements can be maximized at a single set of operating conditions (i.e., plasma power, aerosol gas flow rate, and sampling position), which simplifies multielement analysis. Elements with ionization energies less than about 8 eV are believed to be present primarily (i.e., 90–100%) as M^+ . This includes some 60 elements, most of which are metals. Approximate values for the degree of ionization of the elements can be estimated from the Saha equation.^{10,12,23}

Because of the relative uniformity of ionization in the ICP, the response for a variety of elements can be calibrated using standards prepared from only a few elements. Usually, a suite of about five calibration elements are chosen to span the m/z range. For example, Li, Y, In, Ho, Ta, and Tl would be typical. Some 60 or 70 elements can be quantified in this fashion using standards containing only about five elements, which greatly reduces time, errors, and contamination in the preparation of standards. The

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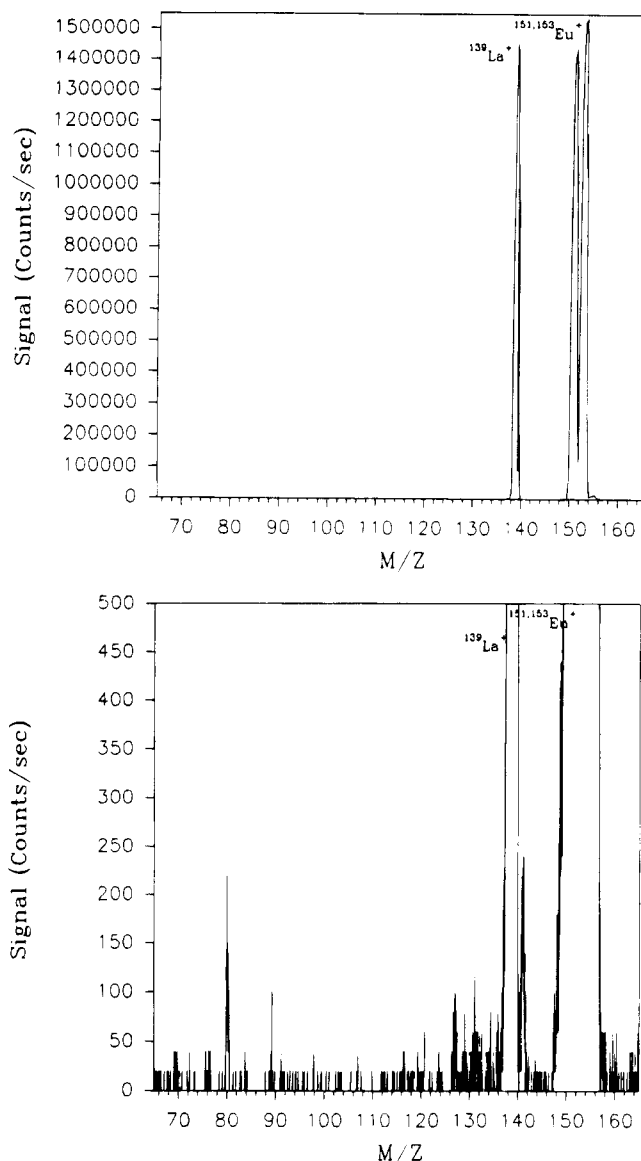


Figure 3. Spectrum of La and Eu, each at 0.5 ppm. Note the small peaks for LaO^+ , La^{2+} , and $^{140}\text{Ce}^+$.

calibrations are not perfect due to element-to-element differences in the degree of ionization in the ICP, matrix interferences induced by space charge, other effects that cause the sensitivity to be dependent on the atomic mass of the element, and low levels of unsuspected polyatomic ions. Nevertheless, this semi-quantitative calibration method generally provides results that are accurate within 50%, often within 20%, which is adequate for many analytical purposes. This method is also convenient when standards of variable analyte concentration are not available, which is common in solid sampling methods like laser ablation.

Figures of Merit. General values characteristic of routine analytical performance are discussed in this section. Detection limits are 1–10 ppt (part per trillion by weight) with quadrupole instruments. These values improve to 10–50 ppq (part per quadrillion) with magnetic sector devices because of the very low background. The reader should distinguish between the detection limit in the solution presented to the instrument and the detection limit in the original sample, usually a solid. The solute level in the final solution is typically 0.1%, so a detection limit of 1 ppt

in the solution corresponds to 1 ppb in the original solid. At high signal levels, the precision is roughly 1–3% relative standard deviation (RSD) in the ion signal. At low signal levels, the precision is poorer and is limited by statistical variations in the number of ion counts observed. Most quantification is done by ratio measurements, either with an internal standard of a different element or with a different stable isotope of the analyte element. Isotope ratios can be measured with a precision of 0.1–0.5% RSD with quadrupole devices, or 0.01% RSD with a multicollector magnetic sector device.

These figures of merit drive the main scientific uses of ICP-MS. The detection limits achievable by ICP-MS are superior to those of any other multielement technique and are rivaled only by highly selective single elemental methods like laser atomic fluorescence or resonance ionization. Analysts often find that the detection limits are restricted more by the purity of blank solutions than by the performance of the instrument. The samples are generally prepared in a clean room to alleviate these problems, and sometimes the instrument is housed in a clean environment as well. These excellent detection limits are important in all applications but particularly in environmental analysis and in monitoring purity of materials used to make semiconductors. In the latter case, even minute levels of elements like Fe, U, and Th cause problems such as failure of memory circuits. The simplicity of the mass spectra produced by the ICP greatly facilitates analysis of geochemical and nuclear samples. Traditionally, these materials have proven difficult for emission spectrometry because of the rich spectra emitted when elements like iron, rare earths, and actinides are excited.

Applications

The cases selected are intended to illustrate some of the main scientific studies that can be facilitated by ICP-MS. Space prohibits a full list of applications of ICP-MS, which is provided anyway in the review issues of *Analytical Chemistry*.²⁴ Although these examples are primarily from the author's own work, the intent is to represent a broad spectrum of research and analysis by many researchers.

Analysis of Sea Water and Urine. As mentioned above, determination of many of the light elements is complicated by polyatomic ions from the major constituents of the sample, including the oxygen in the solvent. Recent work in our laboratory has demonstrated methods for removing the water and chloride by cryogenic desolvation. The aerosol is heated, and the bulk of the water is removed by a condenser at $\sim 0^\circ\text{C}$. The residual solvent is then frozen onto a series of cold loops ($\sim -80^\circ\text{C}$). The resulting solid aerosol particles are conducted into the plasma. Chloride is removed as HCl by the same method.^{25,26}

A "dry" plasma like this yields much lower levels of ArO^+ , MO^+ , ClO^+ , and ArCl^+ than usual. These ions cause interferences for $^{51}\text{V}^+$ (from $^{35}\text{Cl}^{16}\text{O}^+$), various Ni isotopes (from CaO^+), and $^{75}\text{As}^+$ (from $^{40}\text{Ar}^{35}\text{Cl}^+$).

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Table 1. Analytical Results for the Determination of Vanadium, Nickel, and Arsenic Using Cryogenic Desolvation. Reproduced with Permission²⁶

sample	V concn ($\mu\text{g L}^{-1}$)		Ni concn ($\mu\text{g L}^{-1}$)		As concn ($\mu\text{g L}^{-1}$)	
	measd	certified (info)	measd	certified (info)	measd	certified (info)
urine (normal), NIST 2670	20 ± 4^b		70 ± 1	(70)	60 ± 2	(60)
urine (elevated), ^a NIST 2670	100 ± 10	(120)	300 ± 1	(300)	510 ± 10	480 ± 100
estaurine water, NRCC SLEW-1	0.79 ± 0.001		nd ^c		0.74 ± 0.01	0.765 ± 0.07
near shore sea water, NRCC CASS-2	2.60 ± 0.009		nd ^c		1.05 ± 0.01	1.01 ± 0.07

^a This urine sample had been spiked with various trace elements. ^b Uncertainties represent standard deviations of triplicate analyses. ^c Not determined.

Table 1 shows results for the determination of these elements in sea water and urine standard reference materials. The sample was acidified by 10-fold dilution with 1% HNO_3 . The standard additions method was used to correct for matrix interference. ICP-MS aficionados quickly become adept at evaluating accuracy by comparing the measured concentration to the certified or information values for standard reference materials like these. Nickel was not determined in the sea water samples, for no particular reason.

As shown in Table 1, the determined values for Ni and As agree closely with the certified or suggested values. Only one target value is available for V, largely because this element could not be determined accurately in these materials before this method of removing interferences was available. Other, easier elements can be determined as well; the cryogenic desolvation process does not compromise their measurement.²⁶

Elemental Speciation and Preconcentration. By itself, ICP-MS does little to identify the chemical forms of the various elements present in a sample. Yet the chemical state of the element determines its biological role or toxicity. For example, of the various forms of arsenic, inorganic As(III) and As(V) are considered the most toxic, and methylated derivatives are somewhat less toxic, while the metabolite arsenobetaine (i.e., $(\text{CH}_3)_3\text{As}^+\text{CH}_2\text{CH}_2\text{COO}^-$) is innocuous.²⁷⁻²⁹ Under the usual operating conditions, a mixture of these forms of arsenic would all decompose into As^+ in the ICP. The resulting value for total arsenic concentration could be very misleading without concurrent information about the species present.

For these reasons, various groups have coupled chromatographic separations with on-line ICP-MS detection. The chromatographic retention time identifies the analytes, while the ICP-MS provides selectivity for the metal atom(s) of interest. Furthermore, ICP-MS provides the sensitivity necessary to monitor elemental species present at realistic levels.

An example is shown in Figure 4. A urine reference material is injected onto a reversed-phase LC column. Cationic species are separated as ion pairs and then injected into the plasma. A special nebulizer that introduces all the column effluent into the plasma is used.³¹ Only one peak due to Pb^{2+} in solution is seen from injection 1. Thus, nearly all the Pb in this sample is inorganic Pb^{2+} at a concentration of 10 ppb.

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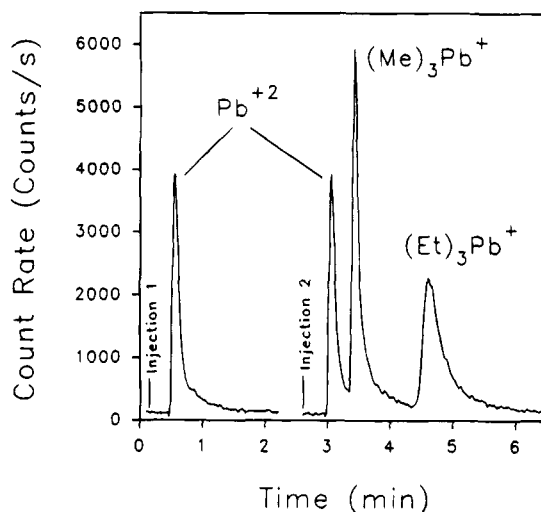


Figure 4. Separation of Pb species by LC-ICP-MS. The sample is a urine reference material (SRM 2670, National Institute of Standards and Technology). The mass analyzer monitors $^{208}\text{Pb}^+$. Injection 1: urine alone. Injection 2: urine spiked with each of the two trialkyllead species, 40 μg of Pb in each spike. Reproduced with permission.³⁰

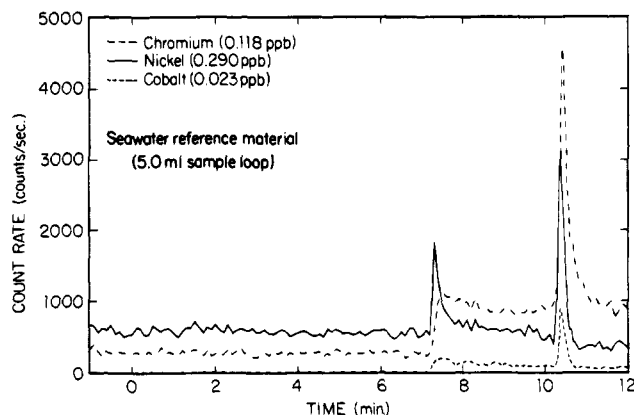


Figure 5. Preconcentration and elution of trace metals in near short sea water reference material CASS-1. The legend lists concentrations in the original sample. Reproduced with permission.³⁷

There are undoubtedly many other species in this sample, but only one gives a mass spectrometric signal for Pb^+ at $m/z = 208$. A second aliquot is spiked with $(\text{Me})_3\text{Pb}^+$ and $(\text{Et})_3\text{Pb}^+$, which yield the separate chromatographic peaks shown for injection 2. The urine sample is injected with no sample preparation or preliminary extraction procedures.

A variety of applications and separation methodologies have been addressed in this fashion, including Au drug metabolites in blood,³² As in seafood²⁷ and urine²⁹ by ion exchange, and various metals in proteins by

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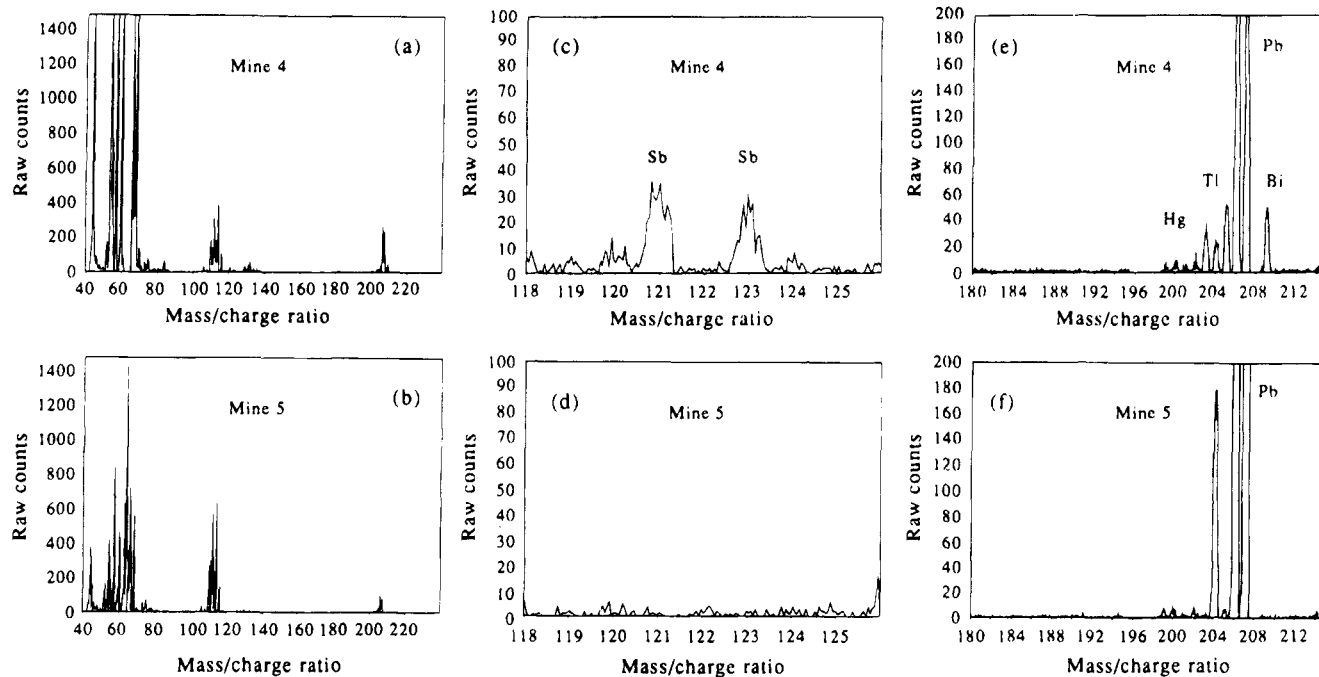


Figure 6. ICP mass spectra of trace impurities in gold from two mines in western Australia. Each sample contains substantial Cd ($m/z = 110-116$) and Pb ($m/z = 204, 206-208$). Note that the sample from mine 4 has much more Sb ($m/z = 121$ and 123), Tl ($m/z = 203$ and 205), and Bi ($m/z = 209$) than the sample from mine 5. Reproduced with permission.⁴¹

size exclusion.³³⁻³⁶ Future environmental regulations will probably require analyses that provide speciation information in addition to simple determination of the total element present. This goal is doubly challenging because other analytical issues such as sampling, sample preparation, and provision of standard reference materials for method validation are much more difficult for fragile elemental species than for simple elemental analysis.

Chromatographic separations can also be used to remove troublesome matrix elements and to preconcentrate analyte elements for more convenient measurement. An example is shown in Figure 5. Trace elements in sea water are complexed with a dithiocarbamate complexing agent and injected onto a resin column. The sample is loaded under acidic conditions, so the carboxylic acid groups on the dithiocarbamate complexes are protonated. The troublesome matrix elements Na, K, Ca, and Mg are not complexed, and most of them wash through the column to waste. A basic eluent is substituted at 7.0 min, as indicated by the arrow. The complexes either decompose or become deprotonated; in either case, they leave the resin and flow to the ICP-MS device. The original 5-mL sample now elutes in 0.5 mL, for a $10\times$ preconcentration factor. Thus, cobalt at only 23 ppt is easily seen as a well-defined peak, while the bulk of the difficult sea water matrix has been removed.³⁷ Chemical separation and preconcentration procedures such as this have recently seen a great deal of growth and interest for a variety of applications, including monitoring of trace radionuclides such as Np, Pu, ⁹⁹Tc, and ¹²⁹I.³⁸⁻⁴⁰

Gold Fingerprinting by Laser Ablation ICP-MS. Watling and co-workers have described a fascinating use of ICP-MS for analysis of solid gold samples.⁴¹ Australia currently produces gold with an annual worth of \$2 billion. Up to 2% of this gold is lost due to theft, a problem by no means unique to Australia. The idea is to trace the source of a particular gold sample by characterizing the trace impurity elements. Direct analysis of the solid by laser ablation saves time and precludes the effort and waste involved in dissolving gold. There is little point in proving the origin of a suspect gold specimen if the analysis consumes it all! Detection limits of ~ 1 ppb allow identification of a wide variety of elements, which improves the specificity of the fingerprint.

Portions of the mass spectra produced by two different mines in western Australia are shown in Figure 6. The gold from mine 4 clearly has more antimony than that from mine 5, as shown by the Sb^+ peaks of nearly equal abundance at m/z 121 and 123. The gold from mine 4 also has higher levels of Tl ($m/z = 203$ and 205) and Bi ($m/z = 209$). Similarly, gold from South Africa has much more Pd, Ru, Pt, Ir, and Os than Australian gold. Although there is substantial interest in improving methods of calibration for analysis of solids, there is little need for accurate quantification in this case. Simple identification and approximate quantification of the trace elements are sufficient.

These spectra provide definitive legal evidence as to the origin of a gold sample. Lay people on juries know that atoms of different elements have different

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atomic weights. With a little coaching, they can readily grasp, interpret, and act upon such evidence for themselves in these types of mass spectra.⁴¹

Stable Metal Isotope Tracer Studies. The applications discussed above deal primarily with elemental analysis, which is the main general use of ICP-MS. There is growing interest in the technique for isotope ratio measurements, particularly because samples may be analyzed and changed more rapidly by ICP-MS than by thermal ionization. A variety of studies of geological and environmental interest have been described, such as tracing the sources of Pb pollution⁴²⁻⁴⁴ and determining the age of the universe from the ¹⁸⁷Re/¹⁸⁷Os geological clock.^{42,45,46} The author, in collaboration with R. E. Serfass, has pursued some work in stable isotope tracing of the role of zinc in human nutrition. The advantage here is that a stable tracer can be used without radiation hazards. In fact, zinc has two viable minor tracer isotopes, ⁷⁰Zn and ⁶⁷Zn. Diets can be prepared with one or both isotopes without greatly perturbing the overall Zn level.

An example of the information provided is shown in Figure 7. The objective is to study the effect of the form of Zn dose on absorption and retention of Zn by human infants. Two different babies are fed formula labeled intrinsically with ⁶⁷Zn and extrinsically with ⁷⁰Zn (i.e., as a simple ZnCl₂ solution). Feces samples are collected, the Zn is isolated chemically, and the pertinent isotope ratios are measured by ICP-MS. The enrichment of each Zn isotope in the feces is then calculated.

In essence, the overlapping enrichment curves in Figure 7 show that extrinsic ⁷⁰Zn and intrinsic ⁶⁷Zn are absorbed and excreted identically. Thus, if supplementation of Zn in formula is necessary, the much easier and less expensive extrinsic procedure is adequate. Although the time characteristics of absorption and excretion differ for different infants, the two tracer isotopes are absorbed identically by each infant studied.⁴⁷ These types of isotope ratio studies represent a greatly underutilized capability of ICP-MS that must surely have some important chemical applications.

Concluding Remarks

There is still substantial room for improvement in the performance of ICP-MS, particularly in the reduction of interferences and improvement of precision and

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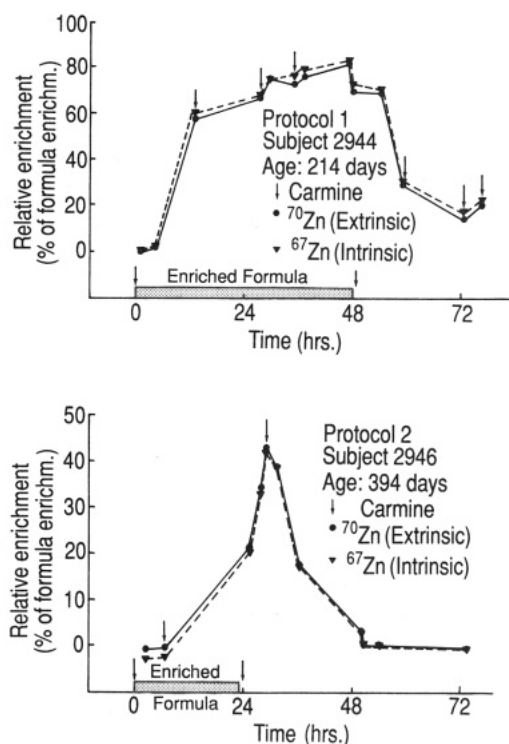


Figure 7. Enrichment curves for Zn isotope tracer study in one human infant. An enriched formula was administered for the first 48 h. The plotted points represent the measured enrichment of each isotope tracer in feces samples collected at the times shown. Reproduced with permission.⁴⁷

absolute sensitivity. These potential improvements stimulate research among a number of academic and government labs and instrument companies. ICP-MS is starting to displace atomic emission and atomic absorption spectrometry, although these established methods are still viable for many applications. In roughly 10 years since the technique became widely available due to the introduction of commercial devices, it has progressed from a research curiosity to a reliable analytical tool used by scientists in a wide range of disciplines. The early remarks of J. J. Thomson about the attractiveness of mass spectrometry compared to optical spectroscopy (emission, in those days) have been largely fulfilled,¹ although Thomson might not have predicted that mass spectrometrists would borrow a source from emission methodology to do so!

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