INTRODUCTION

The field of inorganic mass spectrometry has seen substantial change in the author’s professional lifetime (over 30 years). Techniques in their infancy 30 years ago have matured; some have almost disappeared. New and previously unthought of techniques have come into being; some of these, such as ICP-MS, are reasonably mature now, while others have some distance to go before they can be so considered. Most of these new areas provide fertile fields for researchers, both in the development of new analytical techniques and by allowing fundamental studies to be undertaken that were previously difficult, impossible, or completely unforeseen. As full coverage of the field is manifestly impossible within the framework of this paper, only those areas with which the author has personal contact will be discussed. Most of the work originated in his own laboratory, but that of other laboratories is covered where it seemed appropriate.

Inorganic mass spectrometry has historically addressed three analytical challenges. These are the measurement of isotopic abundances, determination of elemental concentrations, and investigation of fundamental properties such as measuring ionization potentials and bond strengths. To these historical interests has recently been added the area of speciation of inorganic components of complex mixtures. It is probable that this area will become increasingly important in the future.

Much of the inspiration for development of techniques to measure isotopic abundances came from the nuclear and geological communities. In nuclear applications, isotopic ratio information allows verification of enrichment processes and evaluation of the operation of nuclear reactors. Isotope ratios play a crucial role in
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various geochronological schemes and have more recently been applied to the measurement of isotopic fractionation in natural processes to help answer questions concerning, for example, mineral origin. Determination of elemental concentrations had its origins in the materials science community and has found added importance in the environmental arena. Speciation is driven largely by health concerns. Underlying all these applications, of course, lies the fundamental chemistry and physics that control the events. Without full understanding of the fundamental issues, progress can be achieved only by luck and not by design.

Many instrumental techniques can address both isotopic composition and elemental concentrations; almost all can be used to address fundamental issues. Inorganic speciation is relatively new, but it seems clear that more often than not it will require a combination of techniques to attack the problem. In what follows, I have organized the text according to technique; contributions to each area will be noted as appropriate.

**THERMAL IONIZATION MASS SPECTROMETRY**

Thermal ionization can in many ways be considered a mature field. This does not mean, however, that new and exciting developments are not occurring. Delmore, et al. of Idaho National Engineering Laboratory have recently devised an ingenious method to study the ionization process itself(1). Images of ions forming on emitters can be obtained and provide insight not previously available of the details of the ionization process. This has allowed Delmore and his group to develop highly efficient emitters that produce strong ion currents (both positive and negative) for use in secondary ionization mass spectrometry.

One of the more frustrating aspects of thermal ionization has always been that for many elements only a small fraction (often less than 0.001) of the sample is ionized. Elements of high first ionization potential (U, Pb, etc.) do not leave the filament predominantly as ions but as neutral species. Olivares and co-workers at Los Alamos National Laboratory have recently reported a tube ionization source from which substantially improved ionization efficiency was realized (2). The crucible like tube
was made of high-purity tungsten and was formed by 0.5 mm hole 1.25 cm deep drilled in a piece of rod. Temperatures as high as 3000° C were achieved using electron heating from a tantalum wire. Reported ionization efficiency for uranium was 8%, at least a tenfold increase over conventional methods. The authors adapted a source common in accelerator mass spectrometry for use in a more conventional instrument. The new source has the potential of having profound impact on thermal ionization mass spectrometry.

SECONDARY IONIZATION MASS SPECTROMETRY

The strengths of secondary ionization mass spectrometry (SIMS) have always been its excellent spatial resolution both horizontally (1-10 μm) and vertically (a few atomic layers), and its superb sensitivity for most elements. Aside from sample mounting requirements, three serious obstacles impede application of the technique. The first is the sensitivity of ion yields, which vary over orders of magnitude and are dependent on the composition of the sample matrix. Matrix-matched standards are therefore required for quantitative analysis. Lack of suitable solid standards, which are difficult to develop due to cost and homogeneity concerns, have limited application of the technique. The second problem is that a wide variety of molecular species are present in the secondary ion spectrum, and often form isobaric interferences on the elemental peaks of interest. Interfering peaks can either be resolved using high mass resolution, or the relative intensity of the molecular ions can be greatly reduced by applying an energy offset and analyzing secondary ions with high initial kinetic energies. The third major problem is that of sample charging, particularly when the sample is an insulator and a negatively charged primary ion beam (e.g., O-) cannot be used. This has been particularly problematic for the high precision analysis (0.1% or less) of oxygen isotopes in natural samples, the vast majority of which are insulators. The conventional SIMS approach to measuring light isotope ratios, using high mass resolution to resolve interferences, has proven nearly impossible to implement, even when electron flood guns are utilized for charge compensation. These problems probably result from the fact that even minor sample charging can cause large shifts (1-
4%) in the measured isotope ratios. The dependence of mass bias on kinetic energy of the secondary ions makes it nearly impossible to obtain stable analytical conditions. Hervig, et al. (3) discovered, however, that there was very little variation in mass bias when secondary ions with high initial kinetic energies were analyzed (>300 eV), and that, under these conditions, molecular interferences were essentially absent. Work at ORNL (4) demonstrated that utilizing this method, termed extreme energy filtering, analyses with reproducibility of ± 0.07% (18O/16O) could be obtained on a variety of insulating specimens. This technique allows analysis of isotope variations on an unprecedented spatial scale, with precision that approaches that of conventional analyses.

Problems with matrix effects continue to affect the accuracy of this technique; measured 18O/16O ratios can vary by over 5% with the substitution of a single cation (e.g. Fe for Mg) in the measured phase. Recent efforts to characterize these effects, however, indicate that they are systematic and can be predicted to some degree. We found that solid solutions of two oxides (e.g., FeSiO₄ and MgSiO₄) exhibited biases that could be calculated from those of two end-members using a linear approximation. Further work has shown that this concept holds true for mixtures of multiple oxides and indicates that the bias of solid solutions can be empirically determined by knowledge of that of the various compositional end members and the composition of the sample. These developments suggest that it may be possible vastly to reduce the number of standards required for high precision and accuracy analyses. Although a purely theoretical model that allows prediction of mass bias with high precision has not yet been developed, these results indicate that the atomic mass and radius of the analyte element are important factors in determining the mass bias.

**INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**

Inductively coupled plasma mass spectrometry (ICP-MS) has mostly been associated with elemental assay of solutions. It has unparalleled sensitivity, being able to measure reliably concentrations for most elements at the parts-per-trillion level. There is, however, a constant push to extend detection limits even lower, driven
primarily by environmental concerns. In addition, matrix effects can contribute molecular interferences and cause signal suppression. One way of addressing both of these issues is to concentrate and separate the element of interest before introduction to the mass spectrometer. Such a concentration step leads to improved detection limits, and separation of a target element from the rest of the sample reduces or eliminates matrix effects.

One way of achieving this is with an on-line electrochemical cell. Both anodic stripping and adsorptive stripping voltammetry have been successfully interfaced to a conventional ICP-MS (5). A flow-through cell was used in this work; it has a dead volume of about 1 µl, which allows for efficient volumetric concentration of analytes from larger samples. The matrix and all other constituents remain in the original solution and are sent to waste. Anodic stripping is illustrated schematically in Figure 1. Deposition occurs at one voltage and, when enough analyte has been collected, stripping occurs at another. This results in a pulse of the analyte element reaching the mass spectrometer in a very short time and yields a sharp spike along the time axis, as shown in the bottom trace in Figure 1. The intensity of this response, when normalized for time of deposition, yields a straight line with concentration over five orders of magnitude.

Anodic stripping from a thin-film mercury electrode was demonstrated for thallium using a quadrupole-based system. The detection limit was calculated to be 50 pg/l or 50 ppq (part per quadrillion). This represents and improvement in the detection limit of about one hundred over conventional ICP-MS using pneumatic nebulization.

Adapting adsorptive stripping to this purpose greatly expands the number of elements that can be addressed. Adsorptive stripping works through use of a complexing agent rather than by purely electrolytical processes. For example, early work with uranium showed that cupferron was a suitable agent for this application (6). Chemical stripping of the adsorbed U film with nitric acid was found to be superior to electrochemical stripping. Using this approach yielded U⁺ ion beam intensities that varied linearly with adsorption time.

The combination of anodic and adsorptive stripping gives access to about 50 elements. While this approach may not be suitable for cases where many elements need
to be quantified for large numbers of samples, it holds promise for situations where concentrations of specific target elements are required at trace and ultra-trace levels, or when a hostile matrix (such as brine solutions) is involved.

**GLOW DISCHARGE MASS SPECTROMETRY**

Glow discharge mass spectrometry (GDMS) in many ways complements ICP-MS. Its forte is elemental bulk analysis of solid materials, whereas the strength of ICP-MS is analysis of solutions. While most samples can be dissolved for ICP-MS analysis, this involves an extra and time-consuming processing step with all the attendant risk of introducing contamination. In any case, there are samples for which not all elements can be held simultaneously in solution. Glow discharge mass spectrometry has proven to be a reliable technique and the preferred one in many applications where ICP-MS is not suitable. Such situations can be as disparate as direct analysis of soil and analysis of the iridium-tungsten alloy used in deep space probes.

Among the more difficult problems to overcome in elemental mass spectrometry is the presence of isobaric interferences in the mass spectrum. These interferences are due to polyatomic species, doubly charged ions, or isotopes of the same nominal mass as that of the ion of interest. A combination of several techniques that discriminate between or suppress these species has been used to overcome this problem with varying degrees of success (7-10). Much of the work described below is directed toward solving this problem.

Quadrupole mass spectrometers have been considered in many quarters to be unsuitable for glow discharge applications because of their inability to resolve molecular interferences from analyte peaks. In consequence, elements such as iron, where its major isotope (56) has an interference from ArO⁺ and chromium (ArC⁺) were believed to have limits of detection too high for many applications. A recent investigation at ORNL showed that this is not necessarily the case (11). Studies using a quadruple-based system revealed the crucial importance of gas purity in reducing interference peaks in the mass spectrum. Sector-based instruments can often deal with this problem by using high enough mass resolution to separate elemental peaks from
molecular, something not possible with a quadrupole mass filter. A newly designed support gas delivery system produced argon that was measured to be pure to the ppb level. This high-purity support gas allowed analysis of metal samples for C, N, and O at the ppm level; detection limits for all elements of interest range from 0.1 to 1 ppm. This instrument is adequate to address many analytical problems and is much less expensive than a sector-based instrument. In this configuration it can be considered a legitimate successor of spark source mass spectrometry.

The ion trap is an intriguing device. Small enough to be held in one's hand, it is nonetheless a powerful tool for research and holds promise for practical applications as well. It has recently been investigated for its suitability for inorganic applications. Koppenaal and co-workers at Pacific Northwest National Laboratory have interfaced a trap to an ICP ion source (12, 13). At ORNL, Duckworth, et al. have interfaced a trap to a glow discharge ion source to investigate the trap's potential in that area (14, 15). The trap has several characteristics that can be exploited for fundamental and practical purposes. These include its relatively high operating pressure (~1 mtorr) and long ion storage times (milliseconds to seconds). There is thus a high density of gas-phase atoms, which leads to high collision frequency. Trapped ions therefore undergo a large number of collisions during an experiment. As a result, chemical and collisional processes can be effected for fundamental studies and for their analytical utility. Examples are shown in Figures 2 and 3. Figure 2a shows a typical linear quadrupole glow discharge mass spectrum of Mo in a Ti matrix. Peaks due to polyatomic TiAr+ ion are clearly seen. Figure 2b, the quadrupole ion trap glow discharge mass spectrum of the same sample, shows the effect of low energy collisional decomposition of the metal argides; note the vast reduction of TiAr+. Figure 3a shows a mass spectrum of Os and Re. The spectrum resulting from the chemical reaction of Os with methane in the ion trap is shown in Figure 3b. A post-ionization chemical separation of the atomic isobars of Os and Re (m/z 187) results, illustrating one way in which gas-phase chemistry in the trap can be exploited for analytical purposes, as previously demonstrated by Beauchamp, et al. (16). Though not shown, charge exchange processes are also important in the reduction of discharge gas related ions (e.g., Ar2+, Ar+, Ar2+).
Another important fundamental capability of the trap is its resonance-selective excitation of trapped ions according to their mass-to-charge ratio. Such resonance excitation causes supra-thermal collisions, effecting dissociation of even the most strongly bound polyatomic ions; both fundamental information and analytical benefit can be obtained through judicious use. An example is shown in Figure 4, in which TaO⁺ is dissociated and the Ta⁺ product ion trapped with an efficiency of over 30%. This ms/ms efficiency is quite high given the 8.2 eV bond energy involved.

A largely unexplored aspect of glow discharge mass spectrometry is its ability to measure isotope ratios. There is no inherent reason why high quality measurements cannot be made. Investigatory work done at ORNL reported ratios with precisions of ± 0.03% for copper and silver using the pure metals as samples (17). A VG-9000 double-focussing mass spectrometer equipped with a single collector was used. The level of precision did not approach that predicted by counting statistics, and was interpreted as reflecting a system limitation, probably due to instability in the discharge. There is no doubt that much better performance could be obtained using an instrument using a multi-collector array, as has recently been reported for an ICP-based system (18). Multi-collectors tend to normalize instabilities in the source and provide precision significantly better than that attainable with single collector configurations.

An alternative approach to combating interferences in glow discharge mass spectrometry is to put them to work for you. Metal argide ions, metal dimeric ions, and doubly charged metal ions can be used instead of singly charged ions for quantification (19). Although the use of species other than the singly charged ions for elemental quantification is rare in GDMS, it is not new in other types of mass spectrometry such as spark source and secondary ion mass spectrometry where the doubly charged ions are often found in high abundance (20). In glow discharge ion sources, these species showed behavior similar to that of the metal ion when glow discharge power was varied, and similar to that of the metal atom when glow discharge pressure was varied. Quantification was feasible using species with concentrations as low as a few parts-per-million in the gas phase. These species provided quantification of better than 15% relative error in most cases for elements with concentration of 0.1% and above in the sample. In contrast, relative errors of approximately 50% were observed when M⁺ ions
were used for quantification; these large errors were due to a plethora of polyatomic interferences.

The most common approach to addressing isobaric interferences has been to use a double focussing mass spectrometer to resolve them from analyte ions. With working resolutions of ~ 6000 - 20,000, it is possible to resolve most interferences. It should be noted, however, that, for some typical diatomic ion interferences such as dimers, oxides, and argides, the mass resolution required to effect separation from the analyte of the same nominal mass varies from a few thousand to in excess of 60,000; such resolution is not available on conventional commercial instruments designed for inorganic applications.

By coupling an elemental ion source with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, resolution far in excess of any other instrumentation can be achieved (21, 22). Figure 5 illustrates a high resolution mass spectrum generated from a cathode prepared by pressing mercury oxide powder (10% mercury by weight) and platinum powder (10% platinum by weight) with silver powder. Resolution was more than 650,000 (full width half height). The $^{199}\text{Hg}^+$ and $^{199}\text{Pt}^+$ isotopes differ in mass by 1 part in 176,000, and complete baseline separation is achieved, as shown in Figure 5.

Currently the cost and complexity of such instrumentation preclude its widespread use. Such instrumentation may be justified in certain situations, however, particularly where costly and time-consuming chemical separation is necessary prior to isotopic analysis. One such example may be in the analysis of low levels of plutonium in the presence of uranium. Here radiological hazards place a premium on minimizing sample handling, a strength of the GD-FTICR technique, and the ability to resolve $^{238}\text{U}$ from $^{238}\text{Pu}$ is of great potential value.

Even though the glow discharge is an old ionization source as such devices go, there is much still to be learned about the fundamental processes taking place in them. One study we have undertaken centers on the formation of metal argides and the observation that $\text{ZnAr}^+$ currents can measure as high as 10% of those of $\text{Zn}^+$. This value is twenty times greater than for most metals. This observation prompted a systematic study of metal-noble gas diatomic species.
Twenty-four elements were studied, using neon, argon, and krypton as support gases in each case. (23). Periodicity of behavior was observed from one row to the next with all three noble gases. Figure 6 shows this trend for transition metal neides, argides, and kryptides. Note that the y-axis is logarithmic. Minor differences were observed among various neides, argide, and kryptides, yet the increase in relative abundance of the rare gas-metal adduct from cobalt to nickel to copper to zinc was consistent from gas to gas. The periodicity observed as the identity of the noble gas was changed was consistent with the variation in the theoretical binding energy of the metal-gas adduct. Variations within any one gas, however, did not correlate with this parameter; the theoretical binding energy of ZnAr⁺ is smaller than that of the other metal argides, yet it showed the greatest population in the gas phase. Of all of the parameters evaluated, only sputter rate, which correlates with the metal atom number density, correlated with the observed MX⁺ abundances. This study is continuing.

GAS CHROMATOGRAPHY-MASS SPECTROMETRY

For most analyses one of the techniques discussed earlier in this paper is sufficient. There are occasions, however, when information other than the isotopic or elemental composition is desired. For example, many elements are substantially more toxic to humans when they are present as organometallic species rather than in the form of inorganic compounds. For many environmental samples, therefore, both inorganic and organometallic forms of the element need to be quantified. This concern has driven trace elemental analysis in the direction of chemical speciation.

Most elemental speciation involves the coupling of some form of chromatography (e.g., high-performance liquid or gas) to an ICP or a glow discharge. Although these techniques have met with some success, the atomization and ionization processes are so efficient in these plasmas that intact organometallic molecules are not observed in the spectrum, which makes quantification problematic. As an alternative to one of these combinations of techniques, we are investigating conventional gas chromatography mass spectrometry (GC/MS). GC/MS has always been a very powerful method for analyzing organic compounds, including organometallic species
(24, 25), but little has been done for inorganic analytes. A typical organic analysis involves solvent extraction to separate organometallic species from the matrix, followed by separation of the individual organometallic compounds on a chromatographic column and detection using a mass spectrometer.

Our approach is different. Instead of using conventional solvent extraction, we have been evaluating solid phase microextraction as a medium for concentrating organometallic compounds from both water and slurries of soil with water. Once the organometallic species are quantified, the inorganic compounds are chemically transformed to an organometallic compound, one not originally found in the sample. Preliminary results have been encouraging. Quantification of inorganic mercury salts was accomplished by using an alkylating reagent (methylpentacyanocobaltate (III)) to produce dimethylmercury, a volatile organomercury compound; this compound is then subjected to GC/MS analysis. Detection limits are on the order of 10 parts per billion for organometallic compounds and 1 part per million for inorganic mercury salts (26).

While considerable work remains, the concept of converting the inorganic species of a target element into an organometallic compound for subsequent analysis has proven to be feasible. The results suggest that a single sample can be analyzed for both inorganic and organic species of a given element, minimizing disturbance of the sample and eliminating possible contamination. Considerable savings in sample preparation time would also be realized.

ACKNOWLEDGEMENT

This research sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC05-96OR22464 with Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corporation.

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Figure 1. Principles of anodic stripping ICP-MS.
Figure 2. Glow discharge-ion trap spectra of Mo⁺ with and without TiAr⁺ interference.
Figure 3.  Glow discharge-ion trap spectra illustrating chemical separation of Re and Os.
Figure 4. Glow-discharge-ion trap spectra illustrating breaking of the TaO bond.
Figure 5. High resolution glow discharge-Fourier transform ion cyclotron mass spectrum illustrating complete resolution of $^{198}$Hg$^+$ and $^{198}$Pt$^+$. 

RESOLUTION = 650 K (FWHH)
Figure 6. Percent metal-noble gas adduct ions (MX⁺) for row 4 elements. Ne (■): 2 mA, 1100 V dc discharge; Ar (▼): 2 mA, 1500 V dc; Kr (●): 2 mA, 1800 V dc.