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Evolution and revolution in instrumentation for plasma-source mass spectrometry*

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Abstract: Plasma-source mass spectrometry, usually in the form of inductively coupled plasma mass spectrometry (ICP-MS), has matured into a widely accepted method for ultra-trace multielemental analysis. However, the method exhibits shortcomings. For example, it does not provide adequate precision for isotope ratio measurements if many isotopes are to be determined. Moreover, isobaric overlaps (spectral interferences) can be very troublesome in some situations. Similarly, matrix interferences can adversely affect many determinations. Yet, it is in the area of high-speed transient measurements that ICP-MS perhaps suffers its greatest weakness. When sampling devices such as flow injection, laser ablation, electrothermal vaporization, or chromatography are employed, the user must choose between broad elemental or isotopic coverage and signal-to-noise ratio (S/N). In turn, compromised S/N means lower precision or poorer detection limits. Here, new instrumentation aimed at overcoming these limitations will be described. One system, based on a time-of-flight mass spectrometer, provides excellent detection limits, resolving power better than commercial quadrupole mass filters, precision of at least 0.02% rsd in a ratioing mode, and extraordinarily high speed for use with transient sampling devices. The second instrument is based on a sector-field mass spectrometer but, unlike other such units, is equipped with a focal-plane array detector. So equipped, the system can detect a broad mass range at once.

INTRODUCTION

Most users desire a set of features from plasma-source mass spectrometry such as those listed in Table 1. Unfortunately, when we compare these features to what is ordinarily experienced in ICP-MS, a number of critical shortcomings are found. In particular, although detection limits are low in terms of concentration, they are often inadequate on an absolute (mass) basis for extremely tiny or precious samples, such as those found in nanotechnology, in the biosciences, and in fields such as art and archeology.

Similarly, precision is often inadequate for isotope-ratio determinations, especially when a number of elements or isotopes must be examined. Although spectral and matrix interferences are undeniably less severe than in ICP-emission spectrometry, they certainly exist and are frequently very trou-

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Table 1 What we want in plasma-source mass spectrometry.

Low detection limits (single atom?)
Excellent precision (<0.1% rsd)
Broad dynamic range (>10^7)
No spectral or matrix interferences
Complete, simultaneous elemental coverage
Isotope-analysis capability
Absolute (standardless) analysis
No sample preparation
Macro, micro, or transient samples
Amenable to speciation
Spatial resolution in solid samples
Rapid (10 s per sample)
Inexpensive (initial and continuing)
Simple, automated, and compact

blesome [1–4]. Further, quadrupole mass filters and sector-field mass spectrometers of the sort commonly employed for ICP-MS are inherently sequential instruments, which limits their speed, precision, and applicability to many kinds of samples or sample-introduction equipment. Lack of absolute (standardless) analysis, too, is a shortcoming, especially in the analysis of solid samples such as often performed with laser ablation. In turn, these limitations complicate sample preparation and make it difficult for ICP-MS to be employed with micro or transient samples like those produced by flow-injection, electrothermal vaporization, laser ablation, or chromatography. This latter difficulty makes multielemental speciation unnecessarily inconvenient.

From this brief analysis, it seems that the most critical bottlenecks in ICP-MS are the following: borderline precision for isotope-ratio measurements, especially in a multielement mode; the existence of troublesome matrix and spectral interferences; difficulty with micro and transient samples; consequently, compromised speciation; the need for matrix-matched standards when laser ablation is employed; and speed that is limited by a sequential-scanning process. Of course, every one of these "bottlenecks" represents an opportunity—for research, discovery, and improvement.

In the paragraphs below, it will be argued that many of these remaining complications can be overcome by use of simultaneous detection in atomic mass spectrometry. Simultaneous detection inherently provides a number of important benefits. Because all the channels are being monitored all the time, precision and detection limits improve as the square root of the number of channels that are being monitored. In atomic mass spectrometry, there are 207 isotopes that are ordinarily examined. If one wishes to monitor every one of those isotopes, simultaneous coverage will therefore improve precision and detection limits by roughly a factor of 14 for a fixed observation time. In addition, simultaneous detection can result in improved precision when ratioing techniques are utilized [5]. This advantage arises from the fact that much of the noise that is encountered in ICP-MS is correlated; that is, it affects all elemental signals in much the same way. Thus, the signal fluctuations from one element tend to follow those of others closely in time; ratioing the signals in perfect time registry can then compensate for the fluctuations, whereas any temporal offset (such as that produced by sequential scanning) cannot fully compensate. Similarly, simultaneous detection avoids a problem commonly termed "spectral skew". Spectral skew arises when a transient sample is being examined. In such a transient, the sample concentration changes continuously, so mass-spectral peaks measured at one point in the transient correspond to a different instantaneous sample concentration than those examined at any other point in time. The changing concentration therefore leads to quantitation errors that are difficult to correct. Lastly, higher sample throughput and improved background detection and correction naturally flow from simultaneous detection.

There are several sorts of mass spectrometers that lend themselves to simultaneous measurement. Included in the list are an ion trap, a Fourier-transform mass spectrometer (FTMS), a time-of-flight mass spectrometer (TOFMS), and a sector-field mass spectrometer equipped with a focal-plane array detector. Here, we will term the last of these devices ADAMS, for array-detector atomic mass spectrometer. Of these instruments, the ion trap and FTMS suffer from relatively slow scan times, compared to TOFMS and ADAMS. Often, an FTMS operated in high-resolution mode will require a 10-second scan, whereas the scan frequency of an ion trap is limited to approximately 10 full scans per second. For the fastest of transients, it therefore seems most attractive to pursue further the possibility of employing a TOFMS or ADAMS device. These systems will constitute the balance of our discussion below.

PLASMA-SOURCE TOFMS

Conveniently, ICP-TOFMS instruments are already commercially available from two manufacturers (Leco in the United States and GBC in Australia), with a third planning to introduce one shortly. Such instruments possess a number of important features, including resolving power of roughly 1200 (better than a quadrupole mass filter but less than obtainable with a high-resolution sector-field instrument), precision that is often limited by counting statistics or by analog electronics to levels of approximately 0.02% rsd, and the capability of generating between 20 000 and 30 000 complete elemental mass spectra per second [6,7]. The main shortcoming of the current commercial systems is that the detection limits they offer are roughly a factor of 5 to 10 higher (poorer) than is claimed for commercial quadrupole mass filters. In part, this disparity might be the result of the relatively recent commercial introduction of these instruments, within the last three years. Presumably, things will continue to get better as the recently introduced instruments are improved and as additional manufacturers enter the market.

To illustrate the utility of a TOFMS, we offer here two brief examples, the use of flow-injection techniques to investigate and reduce matrix interferences in ICP-MS, and the use of a TOFMS to approach standardless (absolute) analysis of alloy samples by means of laser ablation.

Flow-injection ICP-TOFMS

It has long been realized that flow injection is a natural complement to ICP-MS for elemental analysis [8–10]. However, the high speed and lack of spectral skew available from a TOFMS enhances this capability. Not only does ICP-TOFMS enable the entire elemental and isotopic pattern of a sample to be followed during the course of an FIA transient, it also permits high-precision isotope ratios to be measured at the same time and allows the true shape of an FI peak to be traced. This latter capability is essential if gradient dilution techniques are to be employed.

In this context, gradient dilution refers to the well-defined peak shape that arises in flow injection because of dispersion in the flow-injection tubing [11]. In turn, this dispersion arises from a combination of events including diffusion and the parabolic velocity profile in the tubing. The result is an FI peak shape that can be mathematically characterized and that ideally is the same for all species injected at the same moment. Controlled dispersion has made it possible to generate complete calibration curves from a single FIA injection, since the concentration at each point on the FIA peak can be established beforehand. Here, the same capability makes it possible to study interferences, to characterize them, and in some cases to reduce or eliminate them.

Our interference studies have employed the injection of a plug of a chosen interferent into a flowing stream that contains a number of analyte elements [12]. This approach is shown schematically in Fig. 1. This single injection permits us to ascertain the effect of a range of interferent concentrations on a host of analyte elements simultaneously. Of course, this capability exists only because a TOFMS is being employed. At present, we are using this capability to study interferences fundamentally. However,

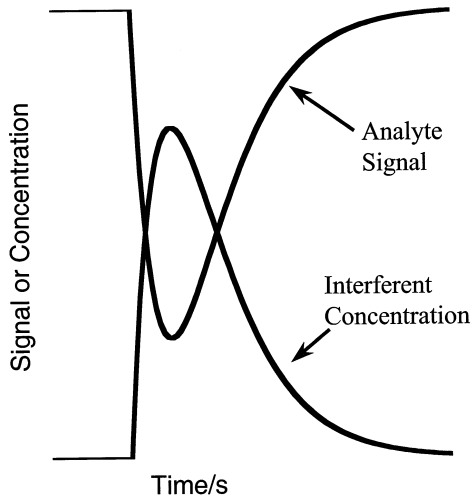

Fig. 1 Schematic diagram showing method of characterizing matrix interferences by means of flow injection. In this method, an aliquot of a solution containing a matrix interferent is injected into a flowing stream containing a number of analyte elements. Because the change in interferent concentration with time is known and reproducible, it is possible quickly and simultaneously to determine the effect of the interferent concentration on many analytes.

a modification allows the same concept to be used to characterize interferences in a real sample more fully and possibly to eliminate them.

This new approach relies upon two facts: 1) ideally, the time-dependent change in concentration for all elements should be the same in flow injection; and 2) matrix interferences in ICP-MS depend upon the absolute concentration of the interfering species and not on the interferent/analyte concentration ratio. Because the concentration of all analyte species changes proportionately during FI, and because TOFMS enables all the concentrations to be sampled at exactly the same time, the ratio of any two analyte signals should be constant at all times during the FI pulse, in the absence of an interference (see Fig. 2a). In contrast, when an interfering species is present, its concentration, too, will change in direct proportion to the concentrations of the analyte species. Because the level of interference depends upon the absolute concentration of the interfering species, its presence will be apparent and therefore troublesome only at the FI peak. Earlier or later during the FI pulse, the interference should vanish for all practical purposes. Because analyte elements differ in their susceptibility to each interference, the analyte ratios should therefore exhibit a deviation from a constant value during the peak of the FI transient, which later returns to the same constant value they display during the initial, low-concentration portion of the transient (see Fig. 2b)

This behavior can be exploited in two important ways. First, learning where the analyte signal ratios return to a constant value reveals the time during the FI pulse where the interference has vanished, for all practical purposes. Because the time-dependent concentration of all species during the pulse is known, this return to a constant level indicates the dilution of the original sample that is necessary to overcome the interference. Second, and potentially even more useful, the signal of each analyte species can be measured directly (i.e., not as a ratio) at the time the signal ratios return to a constant level. Again, because the concentration vs. time profile of the FI process is known, the original analyte concentration can be determined as easily from this point as from the peak of the FI pulse. In this way, interference-free measurements should be possible from even a single sample injection.

There are two complications with this approach. First, as Fig. 3 shows, analyte-signal ratios become noisy at low concentrations such as those found at the beginning and end of a FI peak. To be

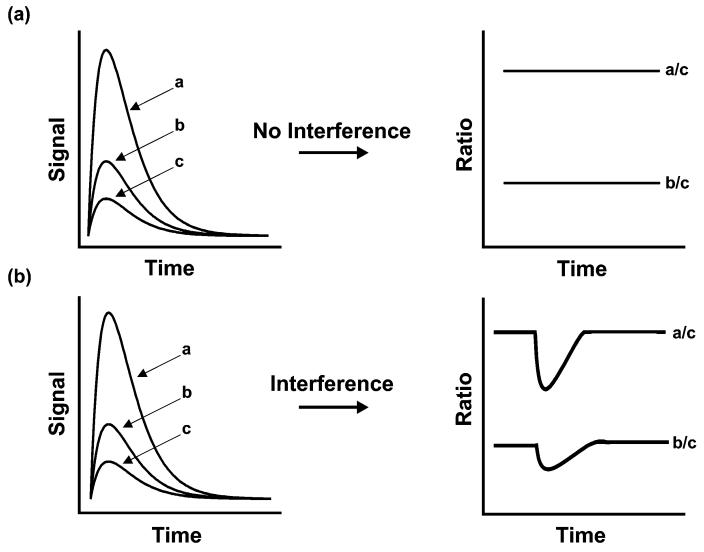

Fig. 2 Schematic diagram of a method for flagging and overcoming matrix interferences in ICP-TOFMS. Here, an aliquot of sample solution is injected into a flowing stream of solvent. a) Because all analyte elements change in concentration in exactly the same way, their ratios are constant with time in the absence of an interference. b) When an interferent is present, its concentration changes in proportion to the analytes. However, its effect is apparent only at the highest concentrations, causing the analyte signal ratios to deviate from a constant value only at the flow-injection peak. The deviation flags the existence of an interference. Also, observing when the analyte ratios return to a constant value enables one to calculate the dilution factor required to alleviate the interference.

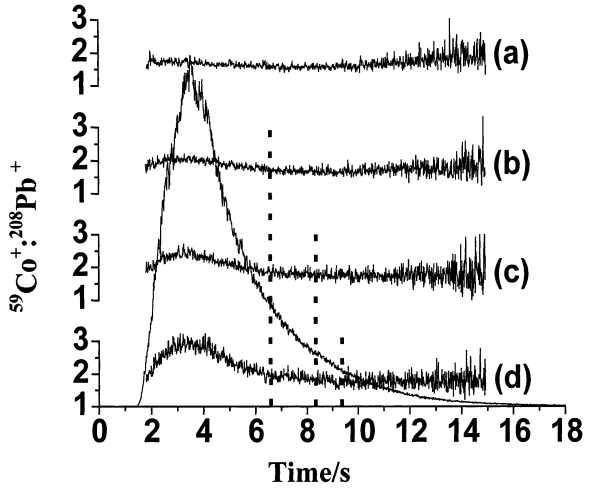

Fig. 3 Calculated $^{59}Co^{+}$:$^{208}Pb^{+}$ signal ratios across FIA profiles upon the injection of a multielemental solution containing (a) no added sodium, (b) 1000 ppm sodium, (c) 3000 ppm sodium, and (d) 5000 ppm sodium by means of FIA-ICP-TOFMS. A $^{59}Co^{+}$ FIA profile (no added interferent) is shown as a reference and the dotted lines indicate the point where the ratios have stabilized.

sure, the example shown in Fig. 3 is an extreme one; moreover, the amplitude of the noise can be reduced greatly through use of digital smoothing, something which was intentionally avoided in this example. Yet, determining the point where the signal ratios return to a constant value is not simple when the severity of the interference is substantial. Further, as Fig. 3 shows, later and later portions of the FIA pulse must be used to determine the original analyte concentration as the concentration of the interfering element rises. Second, the FI process is not as straightforward and ideal as many assume. Rather, some elements appear to be retained differently on FI tubing than others, leading to element-dependent dispersion curves. To date, we have found that at least three families of such dispersion behavior can be identified. It is therefore necessary to ratio only elements within a single family. Despite this potential complication, it seems clear that FI is a powerful tool for the investigation and perhaps elimination of matrix interferences in ICP-MS.

Laser-ablation ICP-TOFMS

The second application of ICP-TOFMS to be highlighted here also takes advantage of its time-resolution capability. However, equally important is the fact that a TOFMS provides for each input ion packet a complete elemental mass spectrum. Together, these features are employed to obviate the necessity for using matrix-matched solid standards in laser-ablation (LA) ICP-TOFMS.

Ordinarily, quantitation in LA-ICP-TOFMS is compromised by changes in laser power, sample-surface albedo, and other factors that alter the interaction between the laser beam and the sample. Although the best method to overcome these difficulties has been through use of matrix-matched standards [13,14], the lack of availability of such standards has caused users to turn to alternative techniques. These techniques include normalization based on measurements of the ablated aerosol [15–17] or of the acoustic pulse [18] generated by the action of the laser on the sample surface. Here, we compensate for potential errors by recognizing that the sum of the peaks in a complete elemental mass spectrum should be proportional to the mass of sample that has been ablated. Normalization of each mass-spectral peak by this summed spectrum then not only provides an excellent means of compensating for pulse-to-pulse variations in the laser, but also permits virtually standardless analysis to be performed. In essence, the ratio of a particular isotopic peak to the sum of all such peaks in the mass spectrum is directly the concentration of that isotope within the original sample. Of course, for this procedure to be effective, it is necessary to take account of slight variations in ionization efficiency from element to element and also the natural mass bias that occurs in any mass spectrometer.

Our approach has been to employ a number of different alloys for standardization and to measure a range of elements in each [19]. A mass-bias factor and an empirical sensitivity value are then extracted from these data and applied to subsequent samples. We have found that a single set of such sensitivity and mass-bias factors allows the same calibration curve to be used with high fidelity for a broad range of sample types, including those having as their principal matrix component aluminum, cobalt, copper, iron, nickel, and brass. An example of this agreement can be found in Fig. 4. Despite a factor-of-six difference in the amount of material ablated from these different types of matrix, samples can be analyzed with a single laser pulse that consumes as little as 13 ng and with a depth resolution on the order of 200 nm. Applied to standards not in the original calibration set, the method offers semi-quantitative accuracy to within 3% for elements present at high concentration (above 10%) and less than 10% error for elements that range between 0.1 and 10% in composition (with the exception of Zn, which undergoes substantial fractionation).

Current limitations of the method include a restriction to metal-alloy samples, because of the greater difficulty of measuring non-metals by ICP-MS. We are currently in the process of assessing the severity of this restriction; because the new method must account for only the major elements in order to generate fractional concentrations, elements such as oxygen need be accounted for only if they constitute a substantial portion of the sample mass. In turn, such high concentrations generate strong mass-spectral signals that often can be measured over the background generated by atmospheric entrainment.

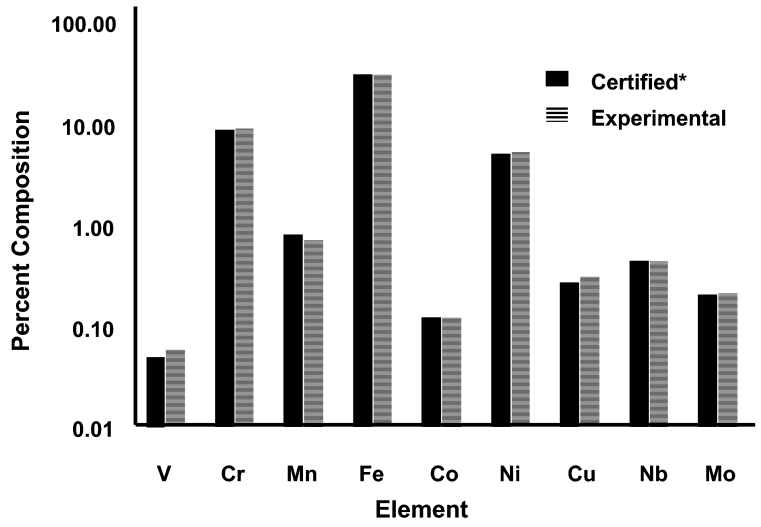

Fig. 4 Agreement between certified concentrations and those determined by a new virtually standardless method for analysis by laser-ablation ICP-TOFMS. The values are for steel standard BRNM 87E, from Brammer Standard Company, Inc., Houston, TX. Each analysis is obtained from a single laser pulse that ablated approximately 13 ng from the sample.

The more serious complication at present is limited dynamic range, generally only about three orders of magnitude. Although we have found it possible to extend this range by a factor of 10 through use of minor isotopes, the high speed and limited dynamic range of typical TOFMS detectors make it seem unlikely that additional gains will be straightforward. We are currently pursuing alternative instrumental modifications to obtain at least another factor of 100 broader range.

ARRAY DETECTOR ATOMIC MASS SPECTROMETER (ADAMS)

Most atomic emission spectrometers that are now being sold employ focal-plane array detectors. This important development is the result of many years of research involving two-dimensional array detectors, cross-dispersion echelle spectrometers, and novel optical configurations that make it possible to employ linear detector arrays [20–23]. These rather complicated instrumental innovations are necessitated by the richness and complexity of an atomic emission spectrum. In order to avoid serious spectral interferences, atomic spectra must be measured at resolution levels on the order of 1 pm and over a spectral range of roughly 600 nm (from roughly 200 to 800 nm). At least 600 000 resolution elements are therefore needed to cover the full atomic emission range at the desired resolution.

Although clever ways have been found around this dilemma, a brief glance indicates how much more attractive it is to consider using a linear detector array to acquire a full atomic mass spectrum. Users of quadrupole mass filters have long argued that unit-mass resolution is adequate for most applications. In addition, there are only 207 isotopes that would commonly be measured in atomic mass spectrometry, even if coverage across the entire periodic table is needed. If as many as five points across each mass-spectral peak were then desired, a simple 1-inch (2.5 cm) 1024-element linear array detector should suffice. At present, such systems are available at extremely low cost.

Unfortunately, physics makes things somewhat more inconvenient. All spatially dispersive mass spectrometers that are now available produce a mass spectrum that varies quadratically rather than linearly with mass-to-charge ratio. As a result, mass-spectral peaks are crowded together at one end of the

mass scale but separated by a great distance at the other. As a result, if adequate mass resolution is to be achieved at the cluttered end of the spectrum, a great deal of wasted detector space would exist at the other.

Our solution to this quandary has been to divide the atomic mass range into two segments, each of which has a ratio of upper to lower mass that is roughly the same. This constant ratio is a necessary consequence of the quadratic mass display in typical spectrometers.

In our case, we have designed an instrument that can operate alternately over the mass range from ^{7}Li to ^{39}K (ratio of 39/7 = 5.6) and from ^{41}K to ^{238}U (ratio of 238/41 = 5.8). Conveniently, the two ranges avoid the troublesome peak at 40 u, ordinarily saturated because of the strong Ar^{+} signal in ICP-MS. Switching between the two ranges is accomplished in a straightforward fashion by adjusting the accelerating voltage in the spectrometer.

The resulting instrument, diagrammed in Fig. 5, is extremely compact (approximately 80 cm in length), and offers outstanding performance. Its resolving power is at least as good as would be expected from a quadrupole mass filter but, because it employs a higher accelerating voltage, it generates higher ion currents and low detector noise. Typical sensitivities with an ICP source are greater than 10^{8} cps/ppm-isotope, and when an electron multiplier detector is used, detection limits are generally in the tens of parts per quadrillion range, as shown in Table 2 [24].

Unfortunately, the multichannel performance of the instrument has been disappointing, so most of our promising data have been obtained in a scanning mode with an electron multiplier detector. Now, however, a new generation of multichannel array detectors for mass spectrometry is about to appear. The detectors will rely upon Faraday cups for ion collection but, because of new techniques for reading the cups, extremely low background noise can be achieved. More importantly, each Faraday-cup detector can be examined in either a destructive or nondestructive fashion. This capability allows the detector to interrogate each channel as ions are being collected and to accumulate ions until a desired

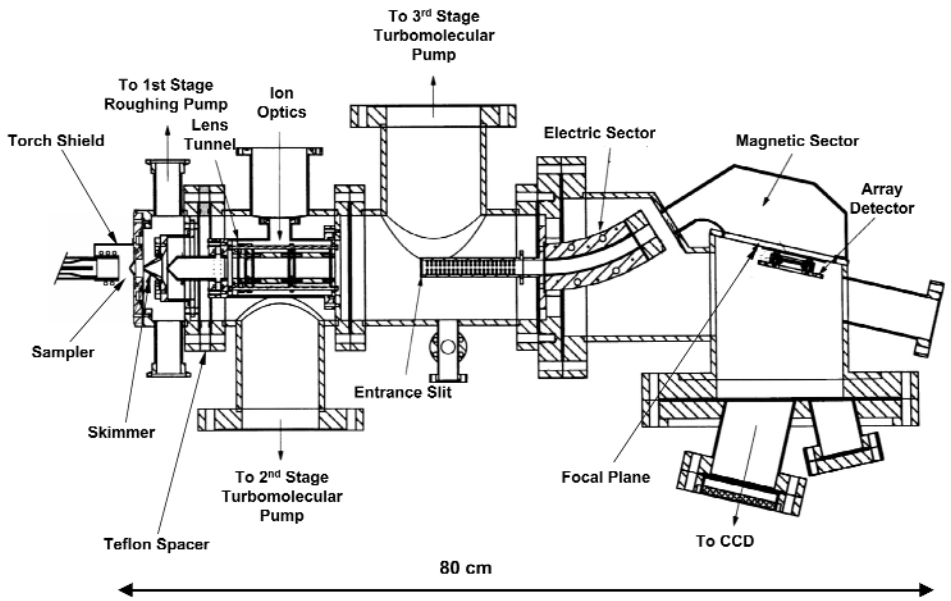

Fig. 5 Mechanical drawing of a Mattauch–Herzog double-focusing mass spectrometer designed for coupling with a linear detector array. So equipped, the spectrometer can measure the entire atomic mass range in two segments that straddle but avoid the troublesome Ar^{+} peak at 40 u.

Table 2 Detection limits obtained with ICP-ADAMS.

Element	Isotope	Detection limit (ppq)
Li	7	10
Ti	49	30
V	51	45
Co	59	20
Ni	60	50
Cu	65	5
Zn	66	5
As	75	50
Sr	88	55
Mo	100	50
Cd	114	50
Sb	123	103
Ho	165	35
W	186	30
Ir	193	90
Au	197	160
Tl	203	85
Pb	208	10
U	238	20

signal-to-noise ratio is achieved. Because some ions will naturally be arriving at a far greater rate than others, owing to their higher concentration in a sample, their channels can be read destructively more frequently and saturation thereby prevented. At the same time, weaker channels can be allowed to accumulate signal steadily. Thus, it becomes possible to extend the dynamic range of the instrument almost without limit.

It is anticipated that the detectors that will eventually be commercially available will be of a relatively small size, so they can fit not only along the flat focal plane of a Mattauch–Herzog spectrometer of the sort being used in our laboratory (cf. Fig. 5), but also they will able to be fit around the curved focal region of other mass-spectrometer designs. Further, because each detector chip will then be individual, it can be read extremely rapidly, at rates at least as high as 1000 spectra per second. In many ways, then, this new technology will offer the same benefits as the high-speed ICP-TOFMS systems outlined earlier in this paper.

CONCLUSIONS

From the foregoing comments, it should be clear that simultaneous mass spectrometers hold great promise for elemental analysis. They should provide higher signal-to-noise ratios, potentially lower detection limits, better precision, and higher speed than existing units. In turn, they hold the potential to open new doors for the analysis of transient samples, microsamples, and others of the sort being found with increasing frequency in the modern analytical laboratory.

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