

(4)

REPORT DOCUMENTATION PAGE

AD-A197 732

DTIC FILE COPY

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE
NA

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

INDU/DC/GMH/TR-88-41

6a. NAME OF PERFORMING ORGANIZATION
Indiana University6b. OFFICE SYMBOL
(If applicable)
NA1b. RESTRICTIVE MARKINGS
NA

3. DISTRIBUTION/AVAILABILITY OF REPORT

Distribution Unlimited; Approved for
Public Release

5. MONITORING ORGANIZATION REPORT NUMBER(S)

NA

6c. ADDRESS (City, State, and ZIP Code)

Department of Chemistry
Bloomington, IN 47405

7b. ADDRESS (City, State, and ZIP Code)

800 N. Quincy Street
Arlington, VA 222178a. NAME OF FUNDING/SPONSORING
ORGANIZATION8b. OFFICE SYMBOL
(If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

Contract N00014-86-K-0366

8c. ADDRESS (City, State, and ZIP Code)

10. SOURCE OF FUNDING NUMBERS

PROGRAM
ELEMENT NO.PROJECT
NO.TASK
NO. R&T
Code
4134006WORK UNIT
ACCESSION NO.

11. TITLE (Include Security Classification)

Developments in Plasma-Source Mass Spectrometry

12. PERSONAL AUTHOR(S)

Gary M. Hieftje and George H. Vickers

13a. TYPE OF REPORT
Technical13b. TIME COVERED
FROM TO14. DATE OF REPORT (Year, Month, Day)
11 July 198815. PAGE COUNT
54

16. SUPPLEMENTARY NOTATION

Accepted for publication in Analytica Chimica Acta

17. COSATI CODES

FIELD GROUP SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Plasma-Source Mass Spectrometry, Review, Multielement
Analysis.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The field of plasma-source mass spectrometry is critically reviewed and its current status assessed. An overview of PS-MS applications is provided and a discussion is offered of key problem areas that currently exist in the field. Areas that are now receiving strong research attention are outlined and a view is offered for future prospects of plasma-source mass spectrometry as a technique for elemental analysis.

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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

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21. ABSTRACT SECURITY CLASSIFICATION

Distribution Unlimited

22a. NAME OF RESPONSIBLE INDIVIDUAL

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22b. TELEPHONE (Include Area Code)

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22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N14-86-K-0366

R&T Code 4134006

TECHNICAL REPORT NO. 41

DEVELOPMENTS IN PLASMA-SOURCE MASS SPECTROMETRY

by

Gary M. Hieftje and George H. Vickers

Prepared for Publication

in

ANALYTICA CHIMICA ACTA

Indiana University
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Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
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11 July 1988

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It is a privilege to participate in a symposium and in a special issue of *Analytica Chimica Acta* in which the outstanding contributions of Dr. Alison M. G. Macdonald are recognized. Her stewardship of *ACA* in recent years and her service as editor since 1961 have been important not only in maintaining the distinction of the journal but in shaping the field of analytical chemistry as a whole.

Individuals who attended the symposium to honor Dr. Macdonald in Beatenberg, Switzerland will note that the title of this paper is different from the one selected for the original presentation, which was "Recent Developments in Atomic Spectrometry". Clearly, to review the entire scope of atomic spectrometry and to assess its current trends would consume far more space than would be appropriate in this volume. As a result, we have elected to concentrate on one of the most important and exciting new aspects of atomic spectrometry--the development of atmospheric-pressure plasma-source mass spectrometry (PS-MS) as a method for elemental analysis.

Despite its relative youth, PS-MS is already extremely important. It has experienced rapid, nearly explosive growth since commercial instrumentation appeared on the marketplace a few years ago. Perhaps this growth can best be documented by examining the publications in the field [1-132]. When viewed in the manner displayed in Fig. 1, these publications exhibit a nearly exponential growth over the period from 1980 to the present. Interestingly (but facetiously), if this trend is extrapolated to the year 2000, we learn that there should be over 37,000 publications on PS-MS in that year alone! Extending these data even further, there would be over 7 million papers in the year 2010, nearly as many as emanate each year from a typical governmental office.

Happily, Fig. 1 suggests that the growth in ICP manuscripts might be leveling off, so our libraries may still be saved.

The citations at the end of this manuscript are intentionally listed in chronological order so the reader can examine the growth and development of PS-MS. No comprehensive overview of these trends will be attempted here. Rather, the reader is referred to the many excellent reviews that have appeared in the past [9,11,19,24,26,30,38,54,55,66,67,98].

From a perusal of the earlier papers on PS-MS, it is apparent that the inductively coupled plasma (ICP) is a relatively recent ion source for use with mass spectrometry [4]. Publications before 1980 and a number that have appeared afterward have employed plasmas such as a capillary arc [1-3] or a microwave-induced plasma [5]. Indeed, despite the glowing comments by many of its early proponents, the combination of ICP-MS was not universally accepted.

In part, the reason for this early lack of acceptance is the high degree of success enjoyed by 1980 of optical emission spectrometry (OES) performed with an ICP. Added to this fact is the complication that a number of individuals and firms who originally designed mass spectrometers for use with an atmospheric-pressure ion source viewed the system differently from the likely "customers". These ultimate users of PS-MS instruments are those engaged in the field of elemental analysis.

The discrepancy between these two viewpoints can be appreciated by an examination of Figs. 2 and 3. Figure 2 represents the view of PS-MS held by many who are professional mass spectrometrists. To them, an atmospheric-pressure plasma such as an ICP is simply a new kind of ion source. Such individuals are accustomed to "high-technology" systems and to the attendant complexities of vacuum-based instrumentation. In

contrast, Fig. 3 shows the view of ICP-MS held by most atomic spectrometrists. To those in the business of elemental analysis, the most important feature in any block diagram is the sample itself. They view the ICP as something complex in its own right and worthy of considerable attention. Beyond the plasma lies a poorly understood interface between the ICP and mass spectrometer, something that places great demands of its own on the use of the instrument. The interface, they recognize, has associated with it a "Big Pump" and leads to a rather dramatic and impressive but forbidding array of plumbing termed a mass spectrometer.

Because the ultimate users and purchasers of ICP-MS instrumentation understandably view the new combination with some suspicion, it is appropriate to question why the method has become so attractive in recent years. To provide some perspective, let us examine briefly the alternatives that such a user has and why those alternatives fall short in capability.

Figure 4 portrays schematically the options that ordinarily are available for atomic spectrometric analysis. Of these alternatives, those most commonly employed are atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES). As indicated above, mass spectrometry (MS) is making inroads on these other methods. Coherent forward scattering (CFS) spectrometry and atomic fluorescence spectrometry (AFS) are attractive also for samples of some kinds.

Of course, the clear competitor to PS-MS in terms of capability is ICP-OES. Indeed, this powerful combination is now responsible for more elemental determinations than any other technique. The reasons for this choice are clear: ICP-OES features high sensitivity (parts per billion

for most elements), a broad linear dynamic range (10^6 in most cases), reasonable precision (0.5% when an internal standard is employed), limited and increasingly understood matrix interferences, modest initial cost (US \$40,000 - \$200,000) and low continuing expense, relative simplicity of operation, compactness, microsampling capability, and relatively rapid analyses (approximately 10 seconds per sample, with 30-60 elements per sample being determined).

With these attributes of ICP-OES being so strong, it might at first seem surprising that ICP-MS (or PS-MS in general) is appealing at all. Yet, in its ideal embodiment, a combined PS-MS instrument retains most of the attributes of the ICP that are found in ICP-OES but adds a number of the strengths unique to mass spectrometry. These strengths include a simpler spectral background and correspondingly reduced spectral interferences, even higher sensitivity (parts per trillion for most elements), almost complete elemental coverage across the periodic table, and the ability to provide information about the isotopic composition of samples.

ICP-MS INSTRUMENTATION

Now that the reader's taste is presumably whetted and he is preparing to rush out and purchase one of the several available commercial ICP-MS instruments, let us briefly review the nature of such instruments. Figure 5 shows in block form the components important in a PS-MS instrument. Although all components are important, let us dwell here on the interface, ion optics, and mass spectrometer. The familiarity of the ICP to most analytical chemists argues that it not be treated in detail.

Interface. The interface assembly is similar in almost all PS-MS instruments and is portrayed schematically in Fig. 6. Figure 6 shows the ICP-MS interface as being oriented vertically, such as in the instrument employed in our laboratory. However, most systems employ a horizontal configuration. There is in our experience no clear advantage to either orientation.

The customary ICP-MS interface is derived from those employed many years ago to sample gases from atmospheric-pressure combustion flames. In the conventional arrangement, a tapered plate, termed a "sampling cone", is inserted into the plasma tail flame; an orifice (ordinarily about 1 millimeter in diameter) in the tip of the cone then permits plasma gases to expand into a moderate-pressure (approximately 1 torr) region. If allowed to flow uninterrupted into this lower pressure zone, the gases would form a supersonic jet and assume the shape of a typical "barrel shock" [30] which would ordinarily terminate in a mach disk. During this expansion process the plasma gases are cooled tremendously and their thermal energy is converted to a directed supersonic velocity. Interestingly, because the predominant gas sampled from the ICP is argon, the directed velocity that is assumed by virtually all species is the same as that of the argon "bath gas". Because the ions so sampled possess nearly the same velocity, their energies vary directly with their masses. Determination of ion energies as a function of mass then allows a straight line to be plotted (ion kinetic energy vs. mass) from which the gas-kinetic temperature of the sampled gases can be determined [50].

Placed in the expanding sample stream ahead of the mach disk is a second cone (the "skimmer") at the tip of which another orifice is

located. Of course, because of the expansion of plasma gases in the barrel-shock region, this second orifice passes only a small fraction of species originally admitted from the atmospheric-pressure discharge. However, the ion beam that emerges from the skimmer orifice is relatively collimated and passes into an even lower-pressure zone where ion optics and possibly the mass spectrometer are located. The various commercial configurations differ in this region and will be described in more detail below.

It is important that the sampling and skimmer orifices be sufficiently large to permit plasma gases to flow freely into and through the interface. If the first (sampler) orifice is too small, a boundary layer of stagnant gases can form over it in which collisions will take place [16,28]. These occurrences can distort an elemental mass spectrum, produce interelement interferences, and increase mass spectral complexity. Although the optimal size of each orifice will depend upon the plasma temperature and the ratio of pressures inside and outside the sampling orifice, experience shows that an ICP can be sampled adequately with an orifice on the order of 1 mm in diameter. In turn, to extract ions from the resulting supersonic expansion in the most effective manner, the skimmer orifice is ordinarily held at approximately the same size.

It might at first seem surprising that an ICP can simply be moved into close proximity with a grounded metallic (sampling) plate. Of course, the orifice assembly is water-cooled to prevent its damage or degradation. Nonetheless, the relatively high fields and the presence of charged species in the ICP would suggest that an added discharge might occur between the sampling plate and the plasma. Indeed, such is

the case unless care is taken. Early studies in ICP-MS were compromised by the presence of a noticeable discharge near the sampling orifice. Erroneously termed a "pinch" discharge, this secondary, orifice-linked event is attributable to both radio-frequency voltage swings in the plasma and to a resulting dc potential difference between the ICP and the orifice plate itself [21,36,80]. These features can be explained with the aid of Figs. 7 and 8.

As shown in Fig. 7, a conventional ICP is operated with one end of its load coil grounded and the other end free to undergo voltage swings at the applied radio frequency. Unfortunately, these voltage swings not only induce a magnetic field in the plasma but also couple capacitively into the discharge. As a result, when the "live" end of the ICP load coil swings positively, a capacitively coupled negative voltage appears in the plasma itself. Similarly, when the load coils swings negatively, the plasma becomes positively charged. These potential swings in the plasma can be rather large, in excess of 100 V, and can generate a discharge that appears strongest at the sampling orifice. This orifice-linked discharge (OLD) not only alters the mass spectrum and increases the fraction of doubly charged ions which appear, but also produces gradual orifice plate erosion. From a fundamental point of view, the OLD also produces a distorted view of species that intrinsically exist in the plasma.

Plasma rectification can intensify the OLD (see Fig. 8). When the capacitively-induced voltage in the plasma swings positive, highly mobile electrons are attracted to and collected by the grounded orifice plate, leaving an excess of positive charges in the plasma. In contrast, when the induced plasma voltage becomes positive, argon ions

(the predominant positive-charge carriers) are too massive to move very far and fewer are captured by the orifice plate than was the case for electrons. Because the orifice plate is not a particularly effective electron emitter, the positive voltage swing in the discharge is far greater in magnitude than is the negative half-cycle. This effective rectification yields a positive dc voltage in the discharge which far exceeds the intrinsic plasma potential and which can alter, among other things, the kinetic energy of ions extracted from the discharge.

Clearly, it is desirable to overcome the foregoing effects. Perhaps the most effective approach is that taken by Douglas, *et al.* [21,36] in which the center of the load coil is grounded. The ends of the load coil are then allowed to go through equal but opposite voltage swings and thereby capacitively couple opposing voltages into the discharge. Because the plasma is relatively conductive, these capacitively generated voltages tend to cancel each other, so the magnitude of voltage change is minimized. Of course, the resulting dc voltage is also diminished. An alternative approach is to intentionally couple onto the sampling orifice plate a voltage equal to that in the plasma itself. In this way, species in the plasma "see" no voltage difference with the orifice plate, and an orifice-linked discharge is minimized. Importantly, once ions pass the first (sampling) orifice plate, they experience few collisions with other species, so that potential differences with respect to later ion-optic elements have less effect.

Commercial ICP Instruments. At present, there are only five manufacturers of ICP-MS instruments throughout the world. The two largest are Sciex of Canada and VG Elemental of Great Britain. In

Japan, instruments are manufactured by Seiko and Yokogawa. In France, an instrument is offered by Nermag. With the exception of the Sciex system, all instruments offer a three-stage vacuum arrangement. As stated earlier, the first stage (between the sampler and skimmer orifice plates) is held near 1 torr and is evacuated by a large rotary-vane pump. A second vacuum stage, just behind the skimmer orifice, is then held at approximately 10^{-3} torr by a combination of a mechanical forepump and a diffusion pump. A similar evacuation system is used to maintain a third stage between 10^{-5} and 10^{-6} torr. Ordinarily, ion optics are located in both the second and third vacuum stages while the mass spectrometer and ion detector are located in the lowest-pressure regime.

The Sciex unit differs from the others in its use of a cryopump. Like the others, it utilizes a 1-torr first-stage vacuum region but follows that zone with one held at 10^{-5} torr by a high-capacity cryopump. As a result, its ion optics are somewhat different from those found in the other instruments.

All commercial instruments and most employed elsewhere for exploratory studies employ a radio-frequency quadrupole mass filter. Such devices are relatively inexpensive, simple to use, compact, and provide adequate resolution over the desired mass range. A figure of merit having some importance in ICP-MS is the so-called "abundance sensitivity". Stated simply, abundance sensitivity is a measure of "leakage" from one mass unit to adjacent ones and has its analog in optical spectrometry in the form of stray light. A typical abundance sensitivity for commercial mass spectrometers of 10^6 indicates that an ion peak having an amplitude of 10^6 counts per second at, say, 138

daltons (Ba) will produce only one count per second at either masses 137 or 139.

All commercial mass spectrometers incorporate some means of reducing background signals that are generated by photons emitted by the plasma gases. It is not surprising that in a hot, highly ionized medium such as an ICP that a substantial number of excited argon species are formed. Because the lowest excited state of argon has an energy over 11.5 eV above the ground state, a photon emitted by such an excited species is capable of eliciting a response from most ion detectors. Therefore, all commercial instruments employ ion optics which force sampled ions to follow a curved path around a central photon stop. Because photons and neutral species are not affected by the ion-optical potential fields, they are intercepted by the stop. An alternative is found on the Yokogawa instrument, in which a bent rf-only, quadrupole pre-filter is employed. Furthermore, all systems utilize an off-axis detector into which ions must be electrostatically deflected. The curved paths through which the ions must pass further reduce photon-caused events and ordinarily reduce background counts to no more than a few per second.

The detector which is universally incorporated into commercial ICP-MS instruments is of the continuous-dynode type. This form of detector is relatively compact and inexpensive and yields an extremely low dark-count rate. In our own instrument [59,88], we use a discrete-dynode electron multiplier which, we have found, is capable of higher counting rates than the continuous-dynode systems and is not subject to paralysis caused by a high ion flux. These attributes arise from the ability of a

dynode bias network to supply more current to individual dynodes than is possible in a channel-multiplier unit.

It is common in commercial ICP-MS units to offer ion-counting electronics. Because of the low background signals ordinarily encountered in ICP-MS, ion counting offers high sensitivity, for which ICP-MS has become appropriately known. Our own experience [59,88,90,92] is that a high-quality current-measuring (analog) detection system can provide the same level of ion detectability but does not suffer from count losses at large signal peaks. With an ion-counting system, the ability to detect individual ion-arrival events is limited by the interval between ions. If two charged species arrive within the response time of the counting electronics, they are registered as a single event. However, because two arriving ions produce a current which is statistically twice that of a single ion, analog detection systems suffer from no such limitation.

CAPABILITIES OF ICP-MS

Let us now examine the level of performance which can be produced by instruments of the kind described in the preceding section. Key among the capabilities offered by ICP-MS are extremely low detection limits, broad linear working range, and isotope-analysis capability. Table 1 compiles detection limits for most elements in the periodic table. It will be noted that most concentration values are in the low part-per-trillion range and are therefore competitive with or superior to those offered by graphite-furnace atomic absorption spectrometry. Importantly, however, such detection limits can be obtained simultaneously for a large number of elements in each sample.

The linear dynamic range available in ICP-MS rivals that of the corresponding emission technique and far exceeds that offered by atomic absorption spectrometry. With ion-counting detection, a linear range of 10^5 or 10^6 is not uncommon; with analog detection that range is extended by at least one order of magnitude.

Isotope-ratio determination is, of course, an area in which mass spectrometry offers one of its greatest strengths. Isotope ratios have been measured in samples of various kinds by many workers [18,44,53,58,60,61,77,89,103,106,107,109,119-121,126]. It is important in these isotope-ratio measurements that the selected isotopic peaks be monitored as closely in time as possible. However, because a quadrupole mass filter is necessarily a scanned device, it is necessary to hop back and forth between the masses of interest. In this way, the effects of instrumental drift are minimized. Regrettably, this requirement precludes the determination of isotope ratios for a large number of elements at one time. For this capability to be established, systems of improved stability must be developed. This matter will be addressed in greater detail later.

The attainable precision in ICP-MS measurements is on the order of 0.1-0.5%, essentially the same as that found in ICP-OES. For this level of reproducibility to be achieved, however, an internal standard [91] or isotope dilution techniques [71,86] must be utilized. Again, for best precision, it is important that the analyte and the internal standard be monitored as closely in time as possible.

KEY PROBLEM AREAS IN PS-MS

The development of plasma-source mass spectrometry has now reached the stage where workers no longer view the technique as a panacea for their elemental-measurement problems. A large number of difficulties with ICP-MS have appeared and have been described openly over the last several years. A number of those difficulties have now been addressed and solutions to them are being offered.

Isobaric Overlap (Spectral Interferences)

Many reviewers of ICP-MS developments have remarked how kind nature has been in offering essentially no element without interference-free isotopes. Only a few elements are mono-isotopic (possess only one isotope), and they suffer no interference from isotopes of other elements. In other mass regions, where overlap is common, each element seems to have at least one isotope that lies alone.

Unfortunately, plasma-source mass spectra do not consist only of peaks attributable to atomic ions. Doubly charged ions are found in appreciable abundance and appear at a position on the mass spectral axis at a location half the nominal atomic weight. For example, the most abundant isotope of Ba (atomic weight 138) produces a doubly charged ion which appears at $m/z = 69$, where the most abundant isotope of gallium is found.

Far more troublesome than doubly charged ions are those of polyatomic species. Polyatomics are generated by interaction with the plasma gas, through atmospheric entrainment, from the solvent employed in the sample solution, and from the sample itself. A growing list of

these spectral overlaps is being assembled in the literature [40,41, 57,74,88,100].

The solvent has a particularly marked effect on background spectra observed in ICP-MS [41,88]. Importantly, water and nitric acid both yield relatively simple background spectra in the region from 3-80 daltons. In contrast, hydrochloric acid produces a number of additional peaks attributable to chlorine-containing species. These additional features introduce a number of spectral interferences, several of which are devastating. For example, the major ArCl peak at 75 daltons overlaps with As, which is monoisotopic. Arsenic can therefore not be determined in a chloride-containing matrix unless its concentration is extremely high. Sulfuric acid produces an even more complex background spectrum and a correspondingly greater number of spectral interferences. A large number of such overlaps have been documented [41] but an especially significant example is the interference of the SO peak at 48 daltons with the major isotope of titanium.

It is interesting that so many polyatomic ions survive the harsh environment of the ICP and the sampling interface that leads to a mass spectrometer. One cannot but wonder whether a more energetic source might serve to dissociate these species. It is possible also that a collision cell interposed between the plasma source and mass spectrometer might be able to fragment many polyatomic species. Finally, charge exchange might serve to diminish the contribution of polyatomics to selected mass regions. A suitable reagent gas, placed within a collision chamber, might be selected to undergo charge exchange with a particularly troublesome polyatomic. Because it is unlikely that the analyte atom of interest would match the ionization characteristics

of the reagent gas well enough to undergo charge exchange, it might then be able to be detected in the presence of high concentrations of the polyatomic interferent.

It is interesting also that background mass spectra obtained from an ICP are relatively complex in the mass range below 80 daltons but amazingly clean above that. This situation can be contrasted with that experienced in optical emission spectrometry, where the heaviest elements produce the most complex background spectra. Perhaps future instrumental configurations might incorporate a mass spectrometer for detection of elements of atomic element number above 80 while an auxiliary emission spectrometer is utilized to determine the lighter elements.

Sample Matrix Interferences

A substantial number of matrix interferences have been documented in ICP-MS [31,32,35,76,88,93,94,110]. A number of these effects are identical to those observed in the corresponding emission procedures. Still others are unique to the ICP-MS combination.

Over the past several years, a number of workers have noted that a sufficiently high concentration of almost any element seems to have an effect on the detection of virtually any other element. Understandably, high concentrations of dissolved solute are not particularly compatible with the orifice-sampling arrangement necessary in ICP-MS. Most practitioners attempt to keep the concentration of total dissolved solids in their sample solutions below 0.1% if possible and below 1% at all costs. At higher concentrations, interelement effects become even

more pronounced and, at the highest concentrations, sample deposits can accumulate on the sampling and skimmer-orifice plates.

At more modest concentration levels, additional effects persist [110]. Apparently, what occurs is attributable to a space-charge effect [133]. Because the ion optics in the reduced-pressure zones of an ICP-MS instrument are configured for the manipulation of positive ions, electrons are lost from the sampled plasma gases. The resulting stream is then highly charged and coulombic repulsion (space-charge) effects occur within it. Not surprisingly, lighter ions are influenced more strongly by this charge repulsion than are heavier ones and are preferentially lost from the ion beam.

As long as a sampled ion beam consists mostly of the plasma support gas (argon), ions of any particular mass (light or heavy) are lost from the beam in a reproducible fashion. However, when sample concentration is increased, a greater fraction of the positively charged beam consists of ions attributable to the sample. As a result, heavier ions from the sample solution can be enhanced at the expense of lighter ones, while lighter ions lose intensity when heavier elements are present.

Attempts to overcome interelement interferences caused by this space-charge effect depend mostly on decreasing the concentration of ions in the sampled beam. This goal can be achieved by detuning the ICP-MS ion optics, by operating the ICP in a mode where fewer ions are effectively sampled (under lower sensitivity conditions) or simply by diluting the original sample solution. All approaches require an approximately ten fold loss in overall sensitivity for individual ions. An interesting challenge here, and one probably best left to the

manufacturers, is to produce an ion-optical arrangement which is designed to handle space-charge limited beams.

Other Problem Areas

Long-term drift is an insidious difficulty in most ICP-MS instruments and is documented excellently in the study by Ting and Janghorbani [58]. They noted a downward drift in individual iron isotopic signals of more than 50% over a 1 1/2 hour period. Yet, the iron isotope ratio varied by only a few percent over the same interval. It is because of this poorly understood drift that users are well advised to employ internal standardization [91] or isotope dilution [71,86] whenever ICP-MS is utilized.

Instrumental cost is another factor which is partly responsible for limiting the growth of ICP-MS. Whereas highly effective ICP emission instruments are available commercially for approximately US \$40,000, an ICP-MS unit will command a price approximately five times higher. To be sure, there is a certain level of glamor associated with the possession of the "newest instrument on the block" and with the concept of owning a mass spectrometer. Nonetheless, users are finding it increasingly difficult to justify the purchase of such a costly instrument unless their needs (unusually high sensitivity or isotope analysis) require it.

Practitioners of conventional atomic spectrometry are unaccustomed also to the level of maintenance required by an ICP-MS instrument. Although quadrupole mass filters are relatively trouble-free, the need to concern oneself with vacuum systems, pump oil, and the like introduces new concerns. Photons are, after all, clean; introducing

them into a spectrometer seldom contaminates it; they leave no residue; and they are incapable of shorting out high-voltage power supplies.

Despite reports in which ICP-MS has been used in conjunction with flow-injection analysis [51,122] and with electrothermal (carbon-furnace) atomization [82,97], the method does not lend itself naturally to the introduction of transient samples. A quadrupole mass filter, as stated above, is necessarily a scanned device, although the scanning speed can be very high. A dwell time of 1 ms per unit mass interval is not uncommon for a quadrupole unit; it is therefore possible to scan an entire mass spectrum in something approaching 0.1 s. Nonetheless, for a rapidly changing sample pulse, a substantial change in incoming analyte concentration might occur between the times when the lowest and highest mass values are being observed. Successful approaches to transient sample introduction in ICP-MS have utilized expansion chambers which serve to stretch the sample-introduction pulse to time scales compatible with quadrupole scanning speeds. Although this approach is successful, it also degrades detection limits because of the need to dilute the sample pulse.

Finally, ICP-MS now suffers in part from its early stage of development. Every new analytical method has its own natural gestation period during which its capabilities and limitations are delimited, while operating conditions are optimized, and when reliable "cookbook" procedures are developed for the analysis of various sample types. The increasing number of papers describing applications of ICP-MS to samples of various types will surely help to overcome this limitation.

APPLICATIONS OF PLASMA SOURCE MASS SPECTROMETRY

An ever-increasing number of applications of ICP-MS is appearing in the scientific literature. The greatest number of applications have occurred in the area of geological analysis [20,23,34,75,78,83,96,102,116,123] while others have arisen in environmental analysis [79,108,128,129], open water samples [29,72,115], alloy and metals analysis [33,37,65], in clinical [114,121], or food [45] analysis, and in the examination of materials in organics [48,62]. At least two of these applications deserve elaboration.

In a study involving the determination of lead concentrations and lead isotope ratios in whole blood, Delves and Campbell [121] showed that adequate precision in the metal determination could be achieved in approximately one minute of running time, while more than three minutes was required to produce the desired precision for isotope-ratio measurements. Perhaps the world's record in ICP-MS sensitivity is held by a group at the National Research Council laboratory in Ottawa, Canada [115]. Using a 50-fold preconcentration technique, they were able to determine a number of elements in open sea water with precision levels, probably limited by sampling uncertainties, of one part per trillion. The same workers, in an earlier study [29] employed the same procedure to obtain detection limits as low as 0.2 parts per trillion of cobalt.

SOME AREAS OF CURRENT INTENSE ACTIVITY

It is not surprising that a great deal of effort is being expended to overcome the limitations which still plague plasma-source mass spectrometry. Such activities are oriented toward a better understanding of the ion-sampling process which occurs in the PS-MS interface

(much of which, we are now learning, was already familiar in other fields), improved ion-optic systems, and an improved characterization of both spectral and interelement interference effects.

Other work is oriented toward the development of improved sample-introduction systems for ICP-MS [98]. For example, the effect of solvent loading on both the plasma and on the mass-spectrometer characteristics has been examined [99]. Also, a variety of alternative sampling approaches are being explored, including the introduction of microsamples [15], the use of a wire-loop atomizer [39], arc nebulization [47,64], laser ablation [22,85], flow-injection analysis [51,122], hydride generation [52], the introduction of slurries [95], and the addition of an electrothermal atomizer for microsample analysis [82,97]. ICP-MS systems have also been coupled with gas chromatography [56] and high-performance liquid chromatography [101,104,112].

Studies continue in hopes of understanding better the operation of ICP instrumentation and in an effort to select optimal sets of parameters under which the systems can be operated [27,43,49,63,73,100,111]. In addition, ICP-MS is being employed as an aid to fundamental characterization of the ICP itself [6,17,69,92]. A number of workers, including ourselves [132] and others [117,124] have examined the possibility of using negative-ion mass spectrometry to detect elements with high electron affinities. Results to date suggest that only the halogens, sulfur, oxygen and possibly nitrogen can be satisfactorily detected in the negative-ion mode. Our own experience [132] suggests that only fluorine, chlorine, and bromine are best detected as negative ions. All other elements produce stronger and more stable signals when they are detected as positive ions.

An area of substantial continuing interest is the improvement of instrumentation for plasma-source mass spectrometry. Not surprisingly, the plasma source itself figures prominently in these studies. It is now recognized by most workers that the conventional inductively coupled plasma is not ideally suited for producing ions to be extracted into a mass spectrometer. Its excessively high gas flows produce an enormous sample dilution; the consequent passage of ions into the mass spectrometer compounds this inefficiency.

Calculations based on our own instrumental configuration reveal how inefficient this sampling process is. Our sampling orifice, 1.2 mm in diameter, passes a total of 1.2×10^{21} species (atoms, molecules, and ions) per second, a number which corresponds to 2.9 L min^{-1} at STP. The orifice therefore draws in only approximately 25% of the gases that are used in the plasma. In turn, our skimmer orifice, 1 mm in diameter, passes only 8.7×10^{18} molecules per second, about 0.73% of the flow through the sampling orifice.

This substantial inefficiency is exacerbated by losses in the ion optics and mass spectrometer which can be estimated by comparing the analyte flow through the skimmer to the ion count rate produced at our detector. Considering nebulizer losses, the dilution by gases, and expansion in the ICP, a one ppm solution concentration of a chosen analyte will generate approximately $10^{10} \text{ atoms cm}^{-3}$ in the observation zone of an ICP. At the plasma temperature, there are approximately 10^{18} argon atoms cm^{-3} , producing an atom fraction of the analyte equal to 10^{-8} . Because approximately 8.7×10^{18} total species per second flow through the skimmer orifice, approximately 9×10^{10} analyte atoms per second enter the lowest-pressure regime. Yet, experience reveals that a

1 ppm solution of a highly ionized analyte will produce only about 10^6 counts per second from our detector. The efficiency of ion detection is therefore approximately 10^{-5} . That is, only one atom out of every 10^5 which enter the low-pressure zone of our system is ever detected.

This astounding inefficiency suggests the sensitivity of which plasma-source mass spectrometry might ultimately be capable. Of course, to realize that sensitivity will require that problems caused by spectral and interelement interferences first be overcome and that means of handling extremely low sample concentrations or sample quantities be developed.

Attempts have already been made to modify an ICP so it is more compatible with mass-spectrometric operation. A water-cooled plasma torch has been utilized [125] which requires far lower gas flows than the conventional unit. Our own, somewhat similar work has focused on the use of optimized and reduced-size torches. Helium as a support gas has also been examined [84].

Because of its lower operating-power and support-gas requirements, a microwave-induced plasma is a reasonable alternative to the ICP as an ion source for mass spectrometry. Microwave plasmas supported in argon [5,13,118], helium [81], and nitrogen [90] have all been examined. It is not surprising, however, given the past performance of such plasmas, that their attractiveness in PS-MS is still limited. At even moderate microwave input power levels, the MIP seems incapable of efficiently atomizing a sample and of generating atomic ions from it.

Perhaps a better approach is to employ a reduced-pressure MIP. Such a discharge is known to possess unusually high electron and ionization temperatures and would serve admirably as an ionization

medium for mass spectrometric sampling. Unfortunately, the reduced-pressure MIP also possesses a lower thermal temperature than its atmospheric-pressure counterpart. As a consequence, it is not well suited for atomizing a sample. This behavior was noted in a recent study in which a clever coupling between an MIP and mass spectrometer was achieved [131].

Arguably the optimal source for mass spectrometry would have the configuration shown in Fig. 9. Here, two sources are employed in tandem, with the first being used for sample vaporization and atomization and the second for excitation or ionization of the resulting atoms. With this combination, the first source can be optimized for its intended purpose. It might have a high thermal temperature or might employ an alternative mechanism for sample atomization (e.g. inert-gas ion sputtering). In contrast, the second source can be one whose input energy is targeted for excitation or ionization. As such, it would be far from thermal equilibrium and would not be thermally hot but would possess a high electron temperature. Such features are common in reduced-pressure discharges such as the MIP mentioned above. The low thermal temperature and reduced pressure of the second source provides an additional benefit in that it can be more easily coupled to a mass spectrometer. Work on this tandem-source concept is currently under way in our laboratory.

CONCLUDING REMARKS

It should be clear from the foregoing narrative that the field of plasma-source mass spectrometry is in a state of substantial flux. New developments appear in the literature monthly and rumors persist that

additional instrument companies will enter the marketplace. However, it is equally clear that most "easy" instrument sales have already been made. Most scientists who wish principally to study the method and improve its characteristics have already purchased or assembled their own instrumentation. Similarly, most users with unusual needs (e.g. extremely low sample concentration or the requirement of isotope measurement) have acquired their units. The next round of sales must be made on the basis of a head-to-head comparison with competitive methods, principally ICP-emission spectrometry. The emotional and psychological appeal of possessing a mass spectrometer is not sufficient to overcome rumors of persistent difficulty with instrumentation or the complications that surround the learning of a new technology.

Despite these concerns and the apparent hiatus in growth of PS-MS apparent in Fig. 1, we remain confident that the technique will grow. The inherent sensitivity of mass spectrometry, coupled with its information content and the simplicity of mass spectra, argue strongly for the acceptance of the method. Our current problems are largely technological and should be solved in time. If our return from euphoria to reality is not too devastating and we take the time to learn the fundamental characteristics of mass spectrometry, ion optics, and atmospheric-pressure ion sampling, we are confident that mass spectrometry will emerge by the end of the next decade as a dominant method for elemental analysis.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation through Grant CHE 87-22639, by the Office of Naval Research, and by the Perkin-Elmer Corporation.

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TABLE 1

Summary of ICP-MS detection limits (ng mL^{-1} , 3σ).

<u>Element</u>	<u>Detection Limit</u>	<u>Reference</u>
Li	0.1	32
B	0.4	32
F	110	124
Mg	0.13	38
Al	0.16	38
P	20	124
S	100	124
Cl	1	124
Ti	0.32	68 ^a
V	0.08	79
Cr	0.01	38
Mn	0.03	38
Co	0.01	29
Ni	0.04	29
Cu	0.02	29
Zn	0.01	38
Ge	0.02	32
As	0.04	32
Se	0.8	38
Br	1	124
Y	0.05	63
Zr	0.03	68
Mo	0.04	32
Ru	0.06	68
Ag	0.03	32
Cd	0.03	38
In	0.06	38
Sn	0.06	32
Sb	0.06	68
Te	0.08	32
I	0.01	124
Cs	0.02	63
Ba	0.15	63
La	0.01	83
Ce	0.01	38
Pr	0.01	83
Nd	0.045	83
Sm	0.03	83
Eu	0.015	83
Gd	0.05	68
Tb	0.01	83
Dy	0.035	83
Ho	0.01	83
Er	0.035	83
Tm	0.01	83
Yb	0.03	83
Lu	0.01	83
Hf	0.01	68
Ta	0.05	68
W	0.05	38
Au	0.06	32
Hg	0.02	32
Pb	0.01	38
Th	0.02	32
U	0.01	38

^aValues from ref. 68 have been converted from a 2σ definition.

FIGURE LEGENDS

- Figure 1. Growth in the number of publications in PS-MS has been nearly exponential since 1980, the year when the ICP was first introduced as an ion source.
- Figure 2. To most mass spectrometrists, the atmospheric-pressure plasma is merely one more ion source useful for mass spectrometric determination.
- Figure 3. To an individual experienced in atomic spectrometric analysis, mass spectrometry represents just one more detection method for determining the elemental composition of samples.
- Figure 4. A number of options exist for measuring atoms or atomic ions produced from a sample: MS, mass spectrometry; CFS, coherent forward scattering; AAS, atomic absorption spectrometry; AFS, atomic fluorescence spectrometry; AES, atomic emission spectrometry. The component L represents a laser or primary light source needed for AAS, CFS, or AFS. It can also represent the laser source used for multiphoton-ionization mass spectrometry.
- Figure 5. Instrumental components required for performing plasma-source mass spectrometry. See text for discussion.

- Figure 6. Schematic diagram of the ICP-MS interface. Reproduced, with permission, from reference 113.
- Figure 7. A conventional ICP load coil, grounded on either end, can produce radio-frequency voltage swings in the plasma by capacitive coupling. In turn, these voltage swings can exacerbate the effects of a secondary discharge between the plasma and sampling-orifice plate.
- Figure 8. The radio-frequency voltage swings in the plasma, characterized by Fig. 7, can result in a dc voltage gradient between the ICP and the sampling orifice. See text for discussion.
- Figure 9. A tandem source for ion production. Source 1 has the task of sample vaporization and atomization and can be tailored for that purpose. In contrast, Source 2 directs its energy toward ionization events and is optimized accordingly. An example of Source 1 might be an electrothermal atomizer; an electron-impact beam would serve nicely as Source 2.

Publications in Plasma Source-Mass Spectrometry

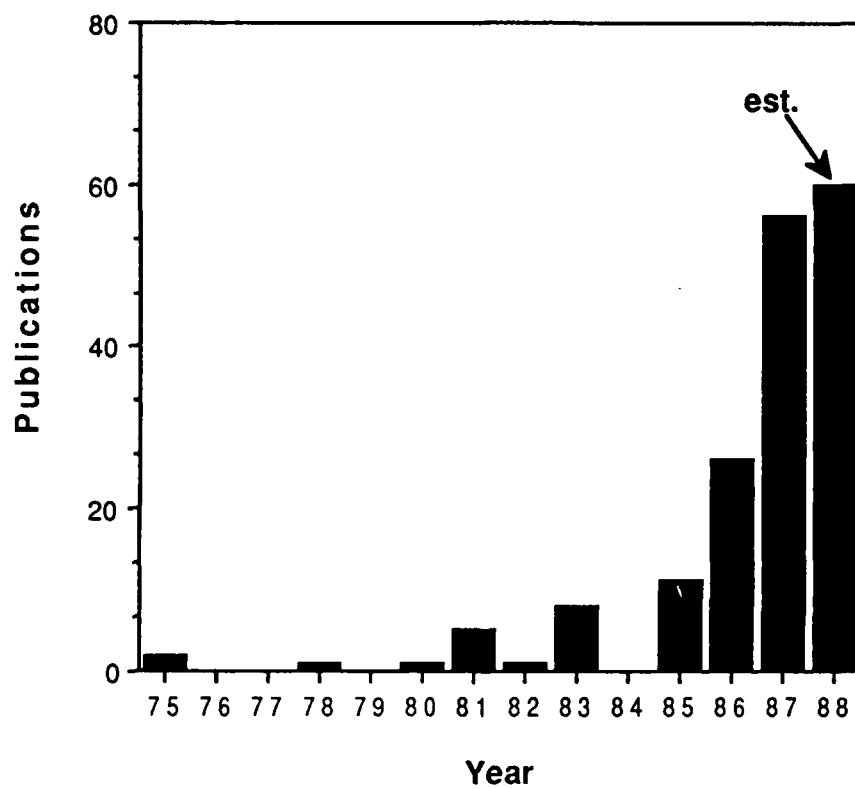


Figure 1

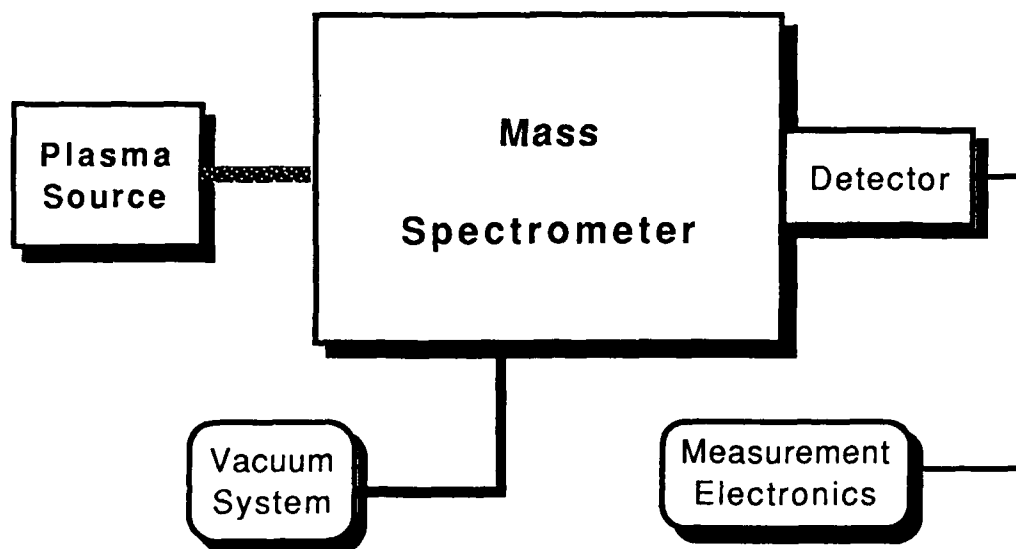


Fig. 2

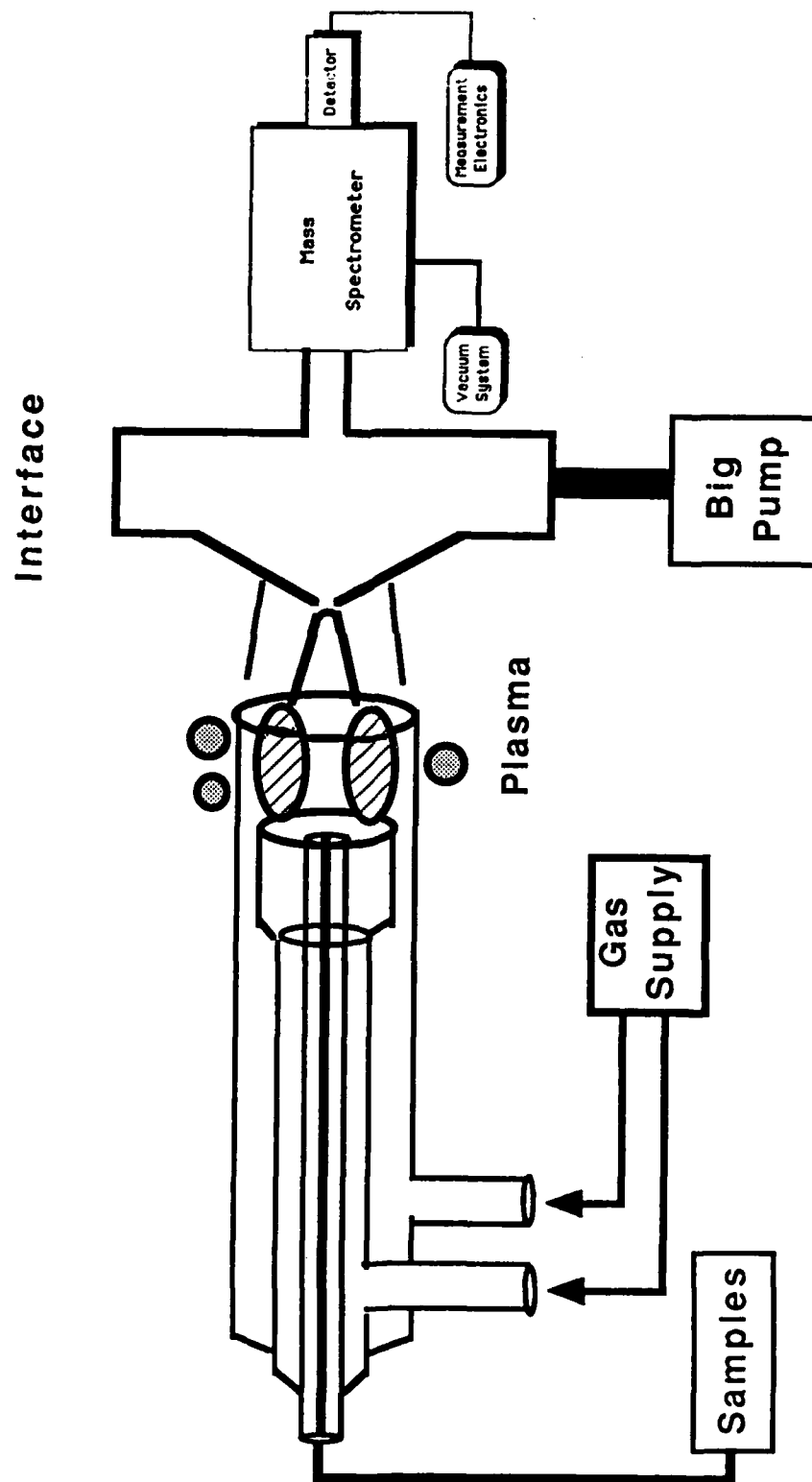


Fig. 3

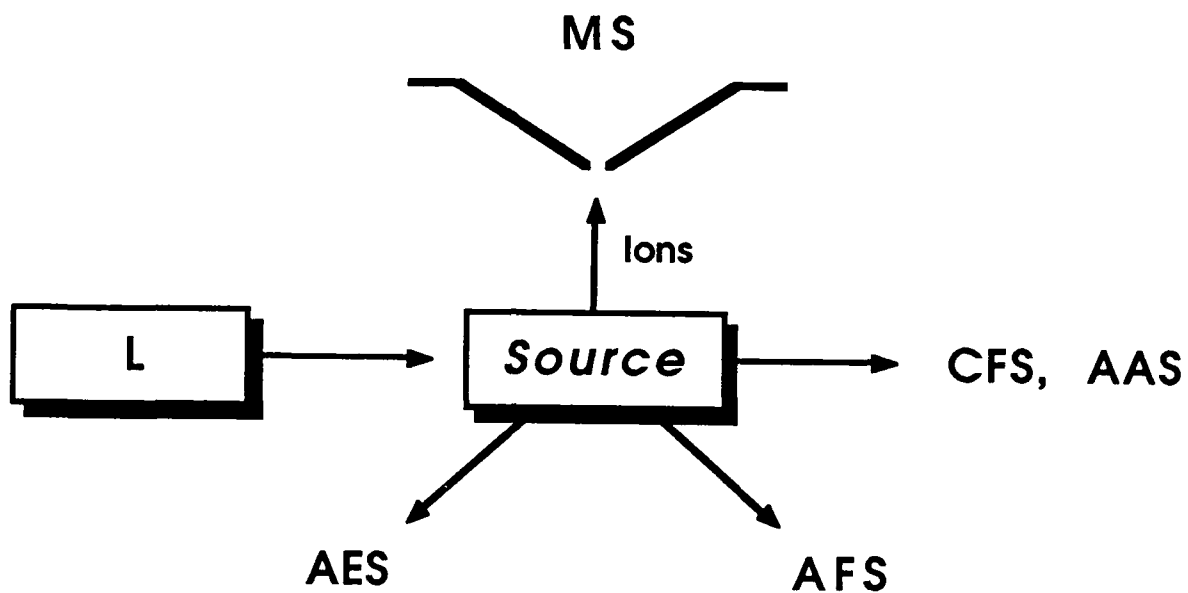


Fig. 4

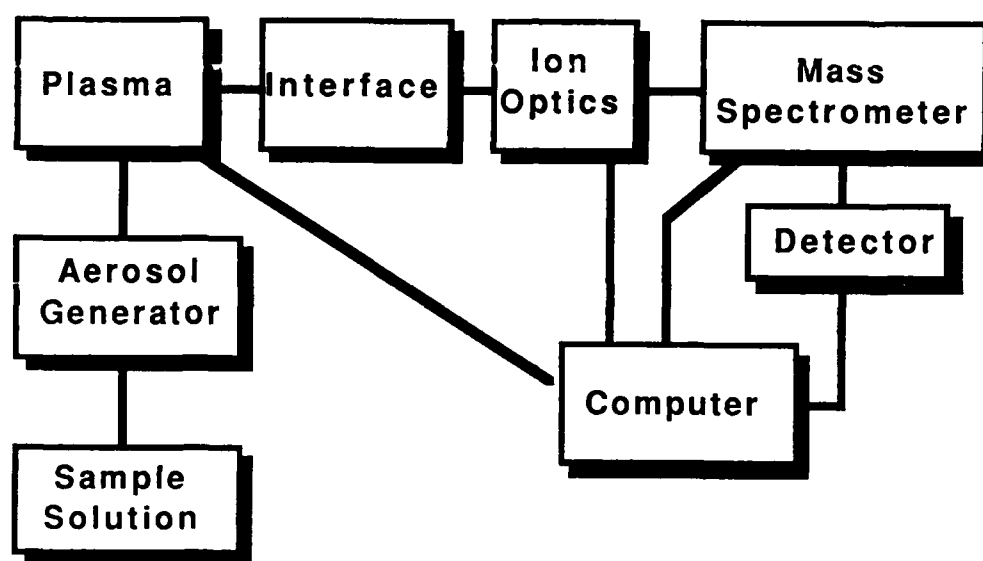


Fig. 5

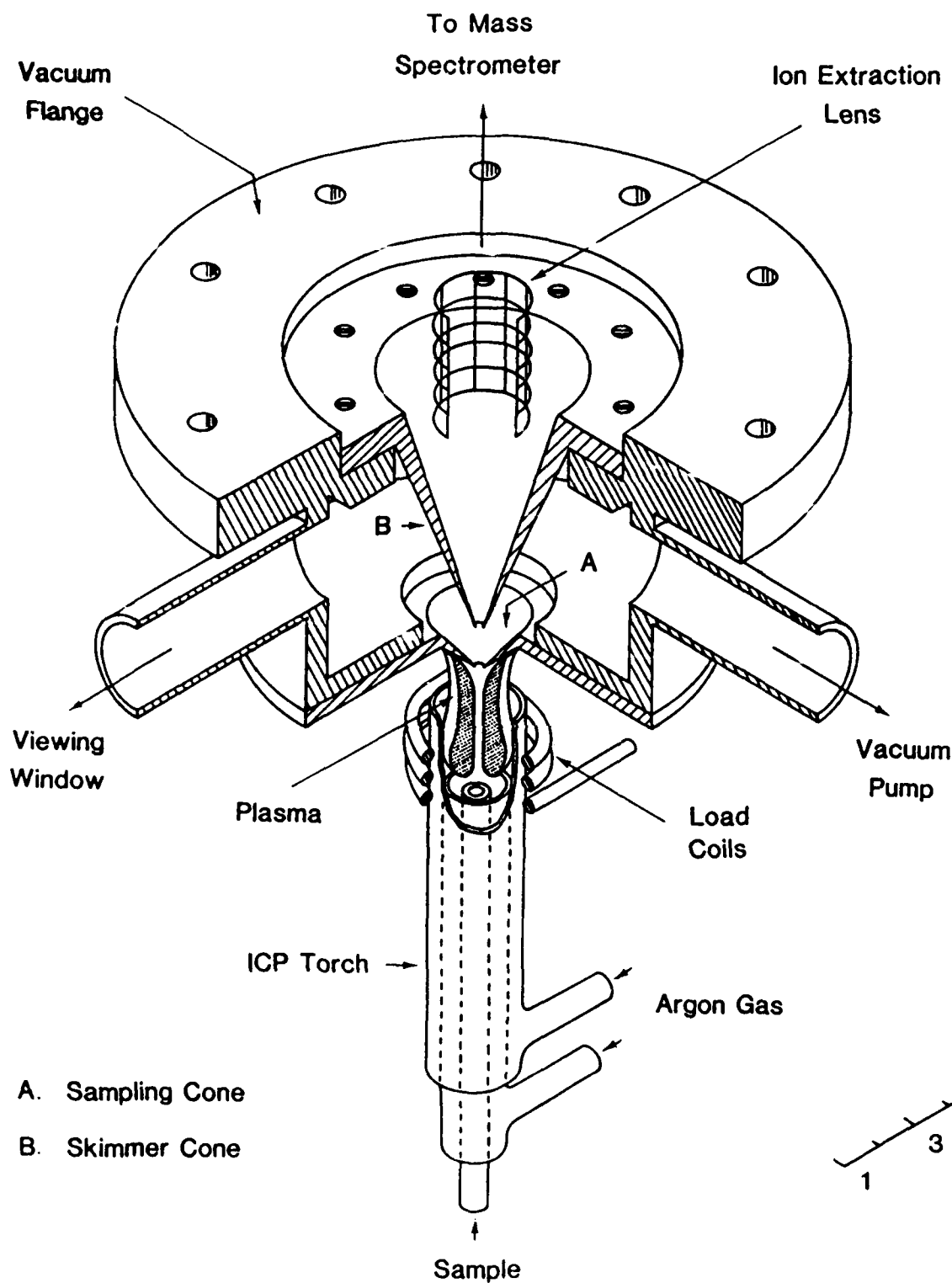


Fig. 6

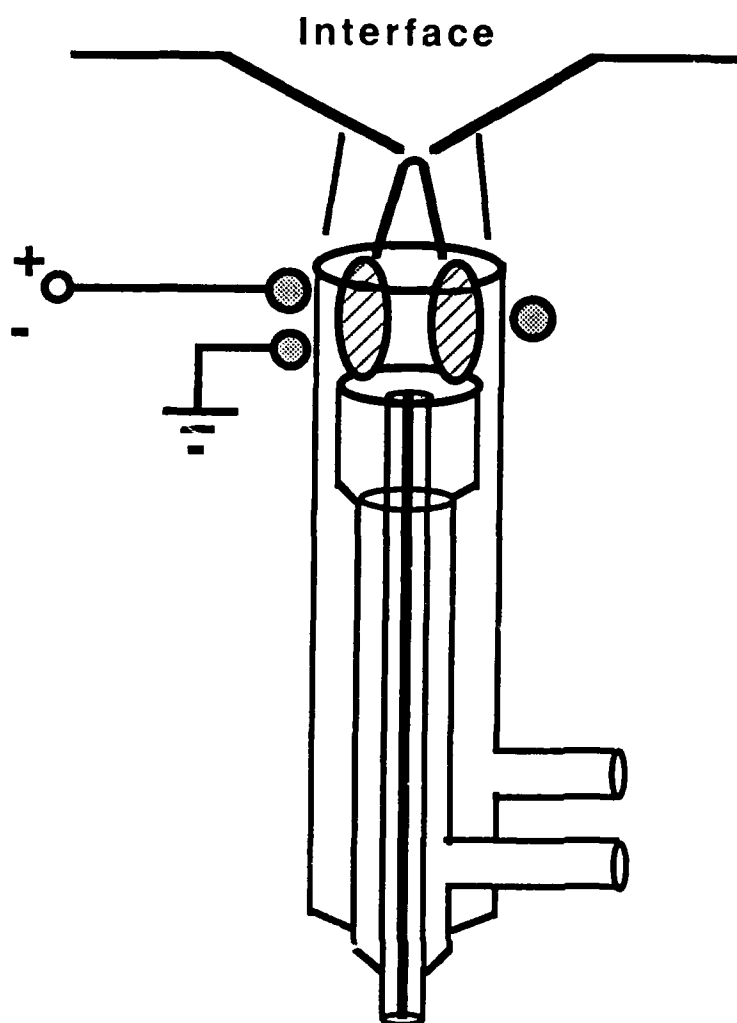
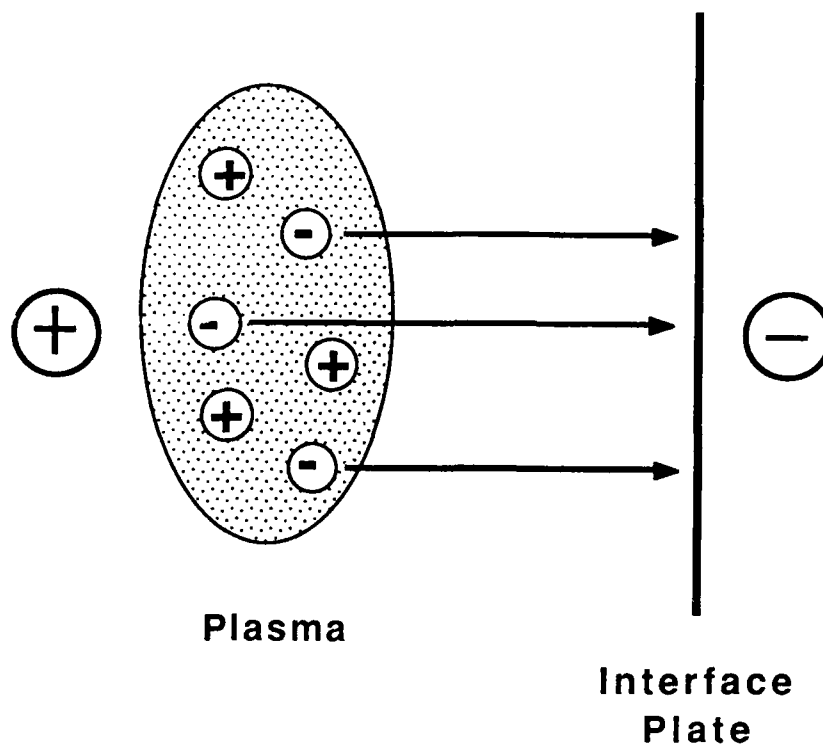


Fig. 7



Rectification Effect

Fig. 8

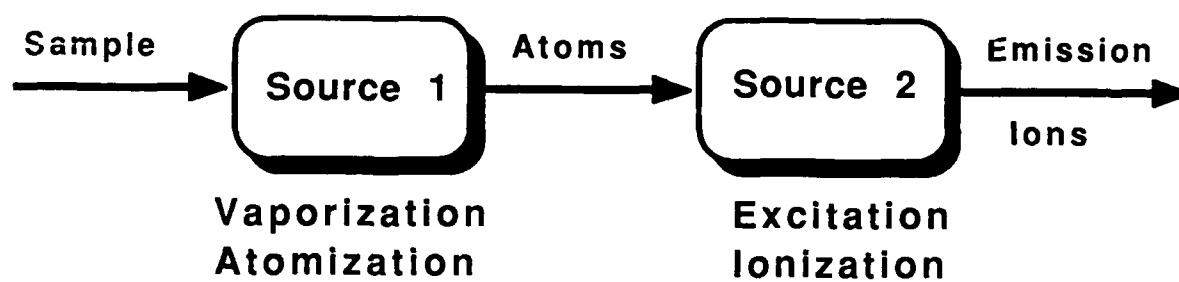


Fig. 9

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