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# Elemental and isotopic analysis of solutions by mass spectrometry using a plasma ion source[1]

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## Abstract

Solution aerosols are introduced into an atmospheric pressure inert gas plasma where elemental constituents are ionized. An ion sampling interface extracts gas from the plasma into a vacuum system where the ions are mass analyzed and detected. The feasibility of this analytical concept for trace elemental and isotopic analysis was first demonstrated using a capillary arc plasma. Recent work is described which was performed with an inductively coupled plasma. The relative standard deviations obtained for determination of relative abundances of Cu and Rb isotopes are approximately ±1 percent. Samples are directly introduced into the plasma ionization source and can be changed in approximately two minutes by simple procedures performed completely outside the vacuum system. Dissolution and nebulization are the only sample preparation procedures required. Ions from most of the elements studied are obtained under the same operating parameters. Continued improvements in ion extraction techniques are expected to make plasma ion sources valuable for rapid mass spectrometric analysis of solutions.

## Introduction

Despite the widespread use of mass spectrometry as a measurement method for geological applications, there still exists room for innovations in techniques for sample introduction and ionization. In particular, there is no widely-used ion source suitable for rapid multielemental and isotopic analysis of solutions. Recent publications indicate that electrical discharges (plasmas) generated in inert gases at atmospheric pressure are potentially valuable ion sources for direct mass spectrometric analysis of solutions. The objectives of this paper are to review these developments and to indicate the feasibility of this technique for rapid determinations of relative isotopic abundances of elements in solutions.

The operations and instrumental components involved in mass spectrometry with a plasma ionization source are illustrated in Figure 1. Solution samples are introduced into a nebulizer where aerosol droplets are generated using either pneumatic or ultrasonic processes. This aerosol is then transported into an argon plasma, where analyte species from the aerosol particles are vaporized, atomized, and ionized. However, the operating temperature and pressure of the plasma are too high for the mass spectrometer. Therefore, a fraction of the plasma particles is extracted through an ion sampling interface into a vacuum system housing a mass spectrometer and ion detector. The crucial component of the ion sampling interface is an orifice in the wall of the vacuum system. Ions from the plasma are entrained in the flow of gas through the orifice. The ions are collected from the sampled gas by an ion optical system and are focussed and transmitted to the mass analyzer and ion detector. Because of the large gas load from the atmospheric pressure source, two or more stages of differential pumping are used to successively reduce the pressure so that the mass analyzer operates under high vacuum conditions. The instruments constructed to date employ a quadrupole mass analyzer and Channeltron electron multiplier operated in a pulse counting mode.

A. L. Gray was the first investigator to evaluate a plasma ion source for mass spectrometric analysis of solutions. He used a direct current capillary arc plasma (Jones *et al.*, 1971). Particles were extracted from this plasma through a 75–125 μm diameter orifice in a platinum disk. The disk was sealed into

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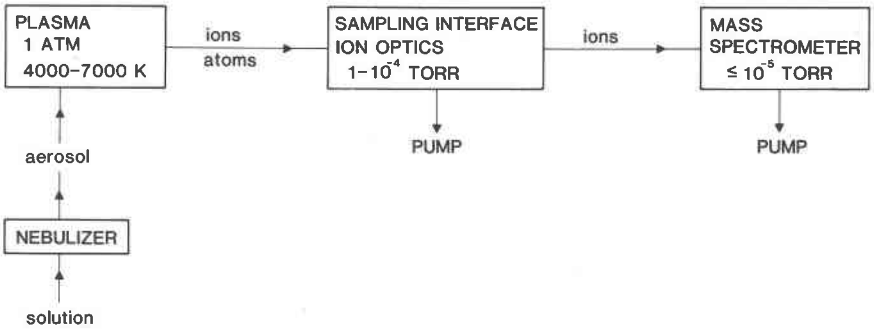

Fig. 1. Schematic diagram describing plasma mass spectrometry.

the tip of a copper cone mounted on a two-stage vacuum system housing an electrostatic ion lens and quadrupole mass spectrometer.

With this apparatus the major ions in the mass spectrum of a deionized water blank solution were attributed to $NO^+$, $O_2^+$, $H_3O^+$, $NH_4^+$, $Na^+$, $K^+$, $(H_3O^+) \cdot H_2O$, and $(H_3O^+) \cdot 2H_2O$. A relatively small peak due to $Ar^+$ was observed. These peaks were superimposed on a very low background of approximately 1 count/sec. The analyte elements Ag, Al, Cd, Co, Hg, Mn, and Pb were detected as singly charged, monatomic, positive ions ($M^+$). The detection limits were 0.00005–0.1 mg/l. The detection limits obtained for elements with first ionization energies below 8.5 eV rivalled the best detection limits obtained using any analytical technique (Gray, 1974, 1975a,b,c). The relative abundances of the naturally-occurring isotopes of Sr and Pb were determined with relative precision of ±0.5–1 percent standard deviation. The determinations were performed directly on trace levels (20 $\mu$g/ml) of these elements in solutions (Gray, 1976, 1978).

Gray's pioneering work clearly demonstrated the feasibility of an atmospheric pressure plasma ion source for mass spectrometric analysis of solutions. However, severe matrix or interelement interference problems were observed. These problems were probably caused by the capillary arc plasma used in these initial studies (Gray, 1981b). Inductively coupled argon plasmas (ICPs) are commonly used as excitation sources for emission spectrometry largely because they exhibit a much greater freedom from interelement effects (Fassel, 1978; Larson *et al.*, 1975). For example, ICPs have been used for the rapid determination of 50 or more elements by atomic emission spectrometry in dissolved geological matrices (Floyd *et al.*, 1980). Emission spectrometric data also indicates that most of the elements are efficiently ionized in ICPs (Winge *et al.*, 1979). For these reasons we have used an ICP ion source with ion sampling and mass analysis techniques similar to those of Gray's work.

## Apparatus and procedures

Our prototype ICP-mass spectrometer (Houk *et al.*, 1980a,b, 1981b) with recent modifications (Houk *et al.*, 1981c) has been described in detail. The aerosol generated by our ultrasonic nebulizer (Olson *et al.*, 1977) was desolvated prior to its introduction into the ICP. The results shown below were obtained at a forward power level of 1.0 kW, an aerosol carrier gas flow rate of 1.0 l/min, and with a 70 $\mu$m diameter sampling orifice.

Isotopically-certified standard reference materials (SRMs) of Cu (#976) and Rb (#984) were obtained from the National Bureau of Standards. These materials were dissolved in nitric acid and diluted to yield various solutions that were 5–20 $\mu$g/ml of the metal dissolved in 1 percent $HNO_3$ in deionized $H_2O$. While one of these solutions was being introduced into the ICP the mass analyzer was repetitively scanned 128 times. Repetitive scans were summed and stored by a multichannel signal averager (Gray, 1981a; Houk *et al.*, 1981c). There was no separate source of ionization inside the vacuum system.

## Results and discussion

Other publications describe initial analytical results obtained by mass spectrometry with an ICP ion source (Houk *et al.*, 1980a,b, 1981a,b,c; Gray and Date, 1981a,b). As shown in Figure 2, the major ions detected in the mass spectrum of the reference blank solution are $ArH^+$, $Ar^+$, $NO^+$, $H_3O^+$, $H^+$, $O_2^+$, $HO_2^+$, $H_2O^+$, and $OH^+$. Although not evident in Figure 2, $Ar_2^+$, $Ar_2H^+$, and $Ar^{+2}$ are also usually

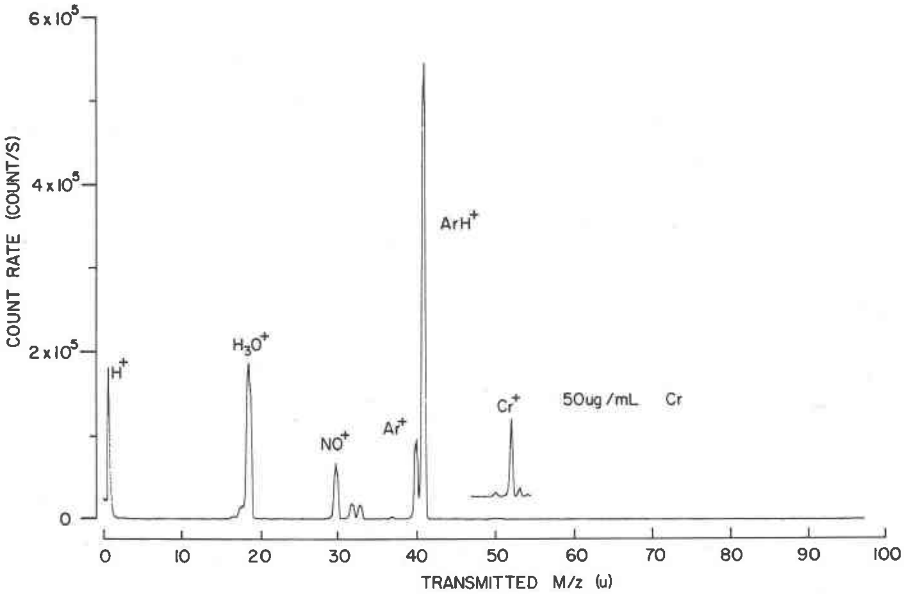

Fig. 2. Mass spectrum of 1 percent $HNO_3$ in deionized $H_2O$. The superimposed spectrum was obtained during nebulization of 50 µg/ml Cr in 1 percent $HNO_3$. The baseline count rate was approximately 50 counts/sec.

detected. Some slight deviations from previously published spectra are expected due to variable ion extraction conditions. Nevertheless, the m/z regions 3–13, 20–30, and above 42 u are free of spectral overlap between analyte ions and major ions in the blank spectrum. Small peaks ($\leq$ 1000 counts/sec) due to minor ions are also detected in the m/z range 48–78 u. These ions are probably cluster species formed by collisions in the extraction process, *e.g.*, $NO^+ \cdot H_2O$ would be detected at 48 u. Elimination of these minor ions is one objective for continued development of ion sampling techniques.

Most of the elements studied so far are detected as $M^+$ ions. The isotopic peaks of Cr are shown in the superimposed spectrum in Figure 2. Elements known to form stable or refractory metal oxide or hydroxide species are detected as a distribution of $M^+$ with $MO^+$ or $MOH^+$. For example, As is detected as both $As^+$ and $AsO^+$ with roughly equal intensities. Ions observed for several elements of geological interest are listed in Table 1. Analytical calibration curves have a working range of 0.02–100 mg/l with detection limits of 0.002–0.06 mg/l. The classical interference effect caused by shifts of analyte ionization equilibria due to variable concentrations of Na is less severe for the ICP ion source than for the DC capillary arc plasma (Houk *et al.*, 1980a,b).

Figure 3 shows the mass spectrum of copper recorded from the memory of the signal averager. These peaks are more than adequately resolved for relative abundance determinations. No other ions from the blank solution were detected at these masses. The background count rate was approximately 50 counts/sec, which was presumably caused by photons and RF noise from the ICP detected by the electron multiplier. The powers of detection would further improve if this background could be reduced closer to the natural background of the electron multiplier (approximately 1 count/sec).

The relative abundances of the stable isotopes of Cu and Rb were determined in reference solutions

Table 1. Positive ions observed for several elements of geological interest

| Element | Ion(s) | Reference |
|---|---|---|
| Li | $Li^+$ | Houk, 1980a |
| K | $K^+$ | Houk, 1980a |
| Rb | $Rb^+$ | Houk _et_ _al_., 1980b |
| Sr | $Sr^+$, $Sr^{2+}$, $SrOH^+$ | Houk _et_ _al_., 1981a |
| Pr | $PrO^+$ | Houk, _et_ _al_., 1981b |
| Pb | $Pb^+$ | Houk, 1980a<br>Gray and Date, 1981a |
| U | $U^+$, $UO^+$, $UO_2{}^+$ | Gray and Date, 1981a |

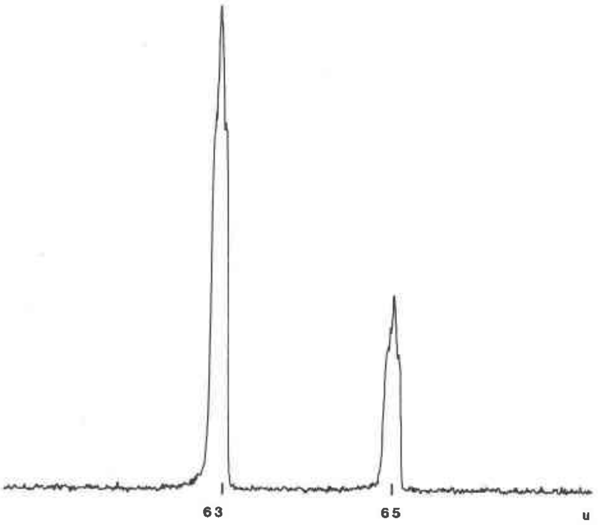

Fig. 3. Isotopic peaks for $Cu^+$ at 5 μg/ml, NBS Standard Reference Material 976. The spectrum shown is the sum of 128 sweeps and the peak count rate for $^{63}Cu^+$ is approximately 3000 counts/sec. The certified value for the ratio $^{63}Cu/^{65}Cu$ is 2.24.

by integrating each isotopic peak in the signal averaged spectra. Representative data are shown for Rb in Table 2. The standard deviation of replicate determinations was of the order of ±1 percent. The abundance of the major isotope was consistently low by approximately 1 percent. This disagreement could have been caused by pulse pileup or dead time losses at the higher count rates obtained as the mass analyzer scanned over the most abundant peak (Gray and Anderson, 1976).

Several other aspects of the isotopic abundance determinations shown in Table 2 render these levels of precision and accuracy worthy of improvement. These determinations were performed directly on a trace level of Rb in solution. Sample was continuously nebulized with dissolution as the only chemical preparation step. For the eight separate determinations the same sample was nebulized eight times in approximately three minute periods. The nebulizer was rinsed with blank solution for approximately two minutes in between each sample run. In this forty minute time period the relative Rb isotopic abundances could have been determined for eight different samples. Furthermore, ions from most of the elements would have been obtained under these operating conditions. At the end of one scanning cycle the mass analyzer could have been adjusted to transmit a different m/z range for isotopic abundance determinations of other elements. Thus mass spectrometry with a plasma ion source is potentially valuable for rapid, sequential determinations of isotopic abundances on a multielement basis provided isotopic peaks of different elements do not overlap. If necessary, the element-specific chemical separation procedures developed for radiochemistry or thermal ionization mass spectrometry should be equally useful (a) to alleviate overlap of isotopic peaks for elements such as Rb and Sr, or (b) to optimize the solution concentration of one element or a small group of elements prior to analysis. The analytical evaluation of ICP mass spectrometry is continuing in our laboratory for more difficult elements than Cu and Rb. For example, Cr, Sr, and Pb have several isotopes at adjacent masses and also have one isotope with a low relative natural abundance.

## Conclusion

The results obtained to date merely indicate the feasibility of plasma ion sources for both elemental and isotopic analysis of solutions. Of the various plasmas used an ICP will probably become the most useful because of its relative freedom from interelement effects. However, potential interference phenomena in analysis of real samples by ICP-mass spectrometry have not yet been comprehensively evaluated. The pinhole-size sampling orifices used tend to plug with solid deposits during nebulization of concentrated solutions (≥250 mg/l) (Houk *et al.*, 1980b).

Workers at Sciex, Inc. (Toronto, Canada) have recently described a solution to the orifice plugging problem. The initial sampling of gas from their microwave-induced plasma occurs through a relatively large orifice (350 μm diameter) in a stainless steel cone. The pressure in the first stage of their vacuum system is maintained at approximately 1 torr using a mechanical vacuum pump. A conical skimmer is used to collimate particles and conduct them into the mass analyzer chamber (Douglas and

Table 2. Relative abundance determination of stable Rb isotopes in NBS Standard Reference Material 984

| Isotope | Relative Abundances (%)<br>determined | certified |
|---|---|---|
| 85 | 71.14 | 72.17 |
| 87 | 28.86 ± 0.88* | 27.83 |

*This uncertainty represents one standard deviation for 8 separate determinations. The total Rb concentration was 15 mg/L.

French, 1981a,b). The Sciex group is currently beginning studies using an ICP ion source with this sampling interface. Gray and Date (personal communication) have recently described some potentially desirable features of this type of sampling interface used with an ICP. Essentially, the larger the sampling orifice the more ions extracted through it and the less likely it is to plug. Also, the larger sampling orifice extracts ions directly from the plasma so that the effects of collisions during the extraction process are less significant (Houk *et al.*, 1981a,b). Therefore, this sort of sampling interface should be an improvement over the pinhole orifice types used initially.

It is expected that continued development of ion sampling techniques will lead to improved powers of detection for elemental analysis and simpler spectra for the blank solution and analyte elements. The present values of precision (relative standard deviations approximately 1 percent) are perhaps useful for studies involving highly variable or anomalous isotopic abundances, *e.g.*, distinguishing radiogenic Pb from anthropogenic Pb (Stukas and Wang, 1981). It remains to be seen whether the precision can be improved to values useful for other geochemical applications (relative standard deviation $\leq$0.1 percent). Ions from carbon have not yet been observed. Isotopic abundance determinations for H, O, and N are likely to be difficult because these elements are generally present as impurity gases in the argon used to support the plasma. For the reasons outlined above plasma ion sources should serve to complement electron impact and thermal ionization techniques rather than replace them, particularly for applications requiring isotopic analysis of metallic elements in large numbers of solutions.

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