

Inductively Coupled Plasma Mass Spectrometry A Review

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Inductively coupled plasma-mass spectrometry is a rapidly growing technique for multi-elemental analysis. In this review, instrumental developments, analytical performance and applications of this method achieved recently are described. Ion sampling interface, ion lens systems and various sample introduction systems are discussed. Suppression of analyte signals is usually observed in the presence of matrix salts at high concentration; this effect is generally more serious than those observed in inductively coupled plasma atomic emission spectrometry. The dependency of the suppression effect on the atomic weight of matrix elements is discussed. Applications to real samples for the determination of trace elements and isotope ratios are described.

Keywords Inductively coupled plasma, mass spectrometry, quadrupole mass spectrometer, ion sampling interface, matrix effect

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1 Introduction

The inductively coupled plasma (ICP), which has been developed for a light source of atomic emission spectrometry (AES) of solutions, was first used as an ion source of mass spectrometry (MS) in 1980 by Houk *et al.*¹, after the pioneering work by Gray², who used a capillary arc plasma as an ion source. Emission spectroscopists, who were considering only light emissions from the plasma, were greatly shocked at the attempt to count ions directly, although they knew well that analytes were highly ionized in the high-temperature plasmas such as ICP. Since then, many papers describing instrumental developments have been published. Commercial instruments of ICP-MS were introduced in 1983 by Sciex Inc. in Canada and by VG Isotopes Ltd. in England. In 1987, Seiko Instruments Inc. and Yokogawa Electric Corp. in Japan also commercialized their instruments.

Since the principles of ICP-MS and the early stages of the instrumental developments have already been described in the excellent reviews of Date³ and Houk⁴, this article will review the papers published after 1986 and will discuss recent trends of the instrumental developments. The instrument which has been

constructed in the author's laboratory will also be described.

2 Instrumental developments

2.1 Ion sampling interface

Ions generated in the plasma are introduced into a vacuum chamber containing a quadrupole mass spectrometer through two orifices called "sampler" and "skimmer". Usually a two- or three-stage differential vacuum system is used to maintain the pressure in the mass spectrometer chamber at 10^{-5} to 10^{-6} Torr. This basic principle of the sampling interface is generally used in all the recently reported ICP mass spectrometers including commercial ones. These orifices are usually made of copper or nickel, although platinum, ceramic-coated copper, *etc.* are sometimes used. The orifice diameter of the sampler in the recent instruments is 1 to 1.5 mm; slightly larger than the ones used earlier, and that of the skimmer is around 1 mm.

A problem arose in the early stage of the sampler development was the "pinch discharge" occurring at the orifice. The discharge causes erosion of the orifice, formation of ions from the orifice material and broadened peaks due to the increase of ion kinetic

energies. The pinch discharge was previously considered to be formed by compression of the free electron population of the plasma gas in the aperture mouth of the sampler. Douglas and French⁵ found that the discharge was an rf arc generated by a potential difference between the plasma and the grounded sampler. They were able to avoid the discharge by center-grounding the load coil. This principle was applied to the Sciex instruments. In other instruments, however, the discharge is weakened to the point where the effects of the discharge are negligible by grounding the upper end of the load coil and its elaborate shielding.

The distance between the sampler and skimmer orifices is usually about 10 mm. The behavior of the ion flow in this region and the importance of the distance between the orifices were discussed by Olivares and Houk⁶, referring to the literature of supersonic molecular beam experiments. In the latter experiments, it is well known that a shock wave called the Mach disk is formed behind the sampling orifice. Recently, Kawaguchi *et al.*⁷ observed the Mach disk by constructing a vacuum chamber consisting of a quartz cylinder and a water-cooled copper flange with an orifice. They showed that the position of the Mach disk in the extracted afterglow from an ICP can be expressed by the equation obtained in the supersonic molecular beam experiments. In other words, it has become apparent that the Mach disks generated in the charged particle beams behave similarly to those produced in the neutral gas beams.

2.2 Ion lens system

A cylindrical electrostatic lens system is used to focus the ions passed through the skimmer into the chamber containing a quadrupole mass spectrometer. A small optical baffle plate is commonly placed in the center axis of the lens system to prevent optical radiation of the ICP from reaching the electron multiplier. The channel electron multiplier, which has been generally used in the ICP mass spectrometer, is blind to visible and UV light but quite sensitive to photons below 120 nm. Argon has strong resonance lines in this wavelength region, *i.e.*, Ar I 104.82 and Ar I 106.67 nm.⁸ Olivares and Houk⁶, however, constructed an instrument with no baffle plate using an off-axis detector. Although they obtained a high ion transmission efficiency, the background was relatively high ($1000 - 10000 \text{ s}^{-1}$) compared to commercial instruments ($1 - 20^9$ or $30 - 100 \text{ s}^{-110}$).

Various types of ion lens system can be designed, but it is difficult to determine the most efficient design because the region containing the lens system is in transition from collision-dominated flow to molecular flow along the beam axis. Moreover, it is necessary to reduce the mass discrimination effect as low as possible.

Ion orbits in various lens systems were calculated in our laboratory during the construction of our instru-

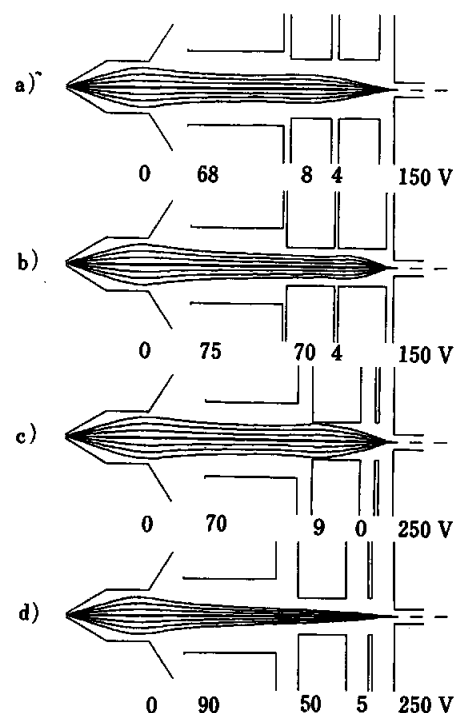


Fig. 1 Examples of the calculation of ion orbits in electrostatic ion lens systems. Initial ion energy: 6 eV.

ment;¹¹ some of these are shown in Fig. 1. In this calculation, the effect of the space charge and optical baffle plate placed in the center axis of the first element were not considered, though 6 eV was assumed for the initial kinetic energy of ions. Because of these simplifications, the calculated optimum lens voltages did not necessarily agree with actually determined ones. The calculation of ion orbits, however, visualized the effect of lens voltages on the ion orbits and gave rough estimates of the optimum lens voltages.

2.3 Sample introduction

The ICPs used for ICP-MS are almost the same as those for ICP-AES. Therefore, all the sample introduction methods which have been employed in the ICP-AES may be used in the ICP-MS. Electro-thermal heating of graphite furnace or metal filament^{12,13}, volatile hydride or oxide generation¹⁴, connection to gas or liquid chromatographs¹⁵, arc vaporization of powder samples^{16,17}, and laser ablation of steel and copper samples¹⁸ were already explored.

Although pneumatic nebulization of sample solutions is a common practice in ICP-MS as in ICP-AES, direct introduction of solid samples is attractive in many cases. For some materials, such as ceramics and polymers, dissolution is difficult and time consuming, contamination from the reagents is not negligible, and also molecular ion species related to mineral acids used to decompose the samples may interfere with analyte peaks in the mass spectra. The quadrupole mass

spectrometer can be scanned over the whole mass range in less than 20 ms. The capability of the rapid sweep allows a simultaneous multielement analysis even with transient sample vapors such as those in the electrothermal heating and laser ablation methods.

3 Analytical performance

3-1 Detection limits

In Table 1, the detection limits of various elements reported by Gray¹⁹ are shown. These values were obtained for single ion monitoring using 10 s integrations for signal and blank. Detection limits for ICP-AES²⁰ and flame atomic absorption (FAAS)²¹ are also shown in Table 1 for comparison. Detection limits reported recently by some of the manufacturers of ICP-MS instruments are about an order of magnitude better than the values listed in Table 1. Instrumental refinements which are not open to the public may contribute to such improvements of detection limits.

As shown in Table 1, the detection limits obtainable by ICP-MS are two to three orders of magnitude lower than those for ICP-AES. Relatively small differences in sensitivity among the elements are also an important figure of merit in ICP-MS. To achieve the measurements at these low concentration levels, however, elaborate sample preparation procedures should be employed to prevent the contamination from reagents, containers or air.

3-2 Interference from background ions

Background ICP mass spectra, which are obtained

Table 1 Comparison of detection limits

Element	Detection limits/ng ml ⁻¹		
	ICP-MS ¹⁹	ICP-AES ²⁰	FAAS ²¹
Ag	0.03	7	2
As	0.04	50	100
Au	0.06	20	20
B	0.4	5	2500
Cd	0.06	2	1
Co	0.05	6	10
Cr	0.06	6	3
Ge	0.02	40	1000
Hg	0.02	20	500
La	0.05	10	2000
Li	0.1	900	0.6
Mg	0.7	0.1	0.1
Mn	0.1	1	2
Mo	0.04	8	30
Pb	0.05	40	20
Sn	0.06	100	20
Te	0.08	40	90
Th	0.02	60	—
U	0.03	200	30000
W	0.05	30	3000
Zn	0.2	2	2

when pure water is introduced, are relatively simple, as shown in Fig. 2. There are only a few obvious peaks, such as O⁺, OH⁺, OH₂⁺, Ar⁺ and ArH⁺. Hydrocarbon peaks commonly observed with an electron impact ionization source are absent in the ICP mass spectra. When the sensitivity is raised to detect trace elements, however, the background is not necessarily simple. For example, oxygen has three isotopes of 16 (natural abundance 97.76%), 17 (0.04%) and 18 (0.20%), and argon has three isotopes of 36 (0.34%), 38 (0.06%) and 40 (99.6%). Therefore, 7 ArO⁺ ion peaks from 52 to 58 amu are generated by the combination of these isotopes. These ion peaks interfere with the detection of ⁵²Cr⁺, ⁵⁵Mn⁺, ⁵⁶Fe⁺ and ⁵⁸Ni⁺.

When sample solutions contain hydrochloric or sulfuric acid, the related ions such as Cl⁺, ClO⁺ and ArCl⁺, or S⁺, SO⁺ and SO₂⁺ appear. Since both chlorine and sulfur have their isotopes, each of these species appears with several peaks of isotopes or their combinations. Fortunately, nitric acid gives almost no additional peak to the blank ICP mass spectra. Therefore, sample solutions should be prepared with nitric acid if possible. Tables of major background species for nitric, hydrochloric and sulfuric acids are compiled by Tan and Horlick.²²

3-3 Effect of plasma operating parameters

Variations of ion signals as a function of rf power,

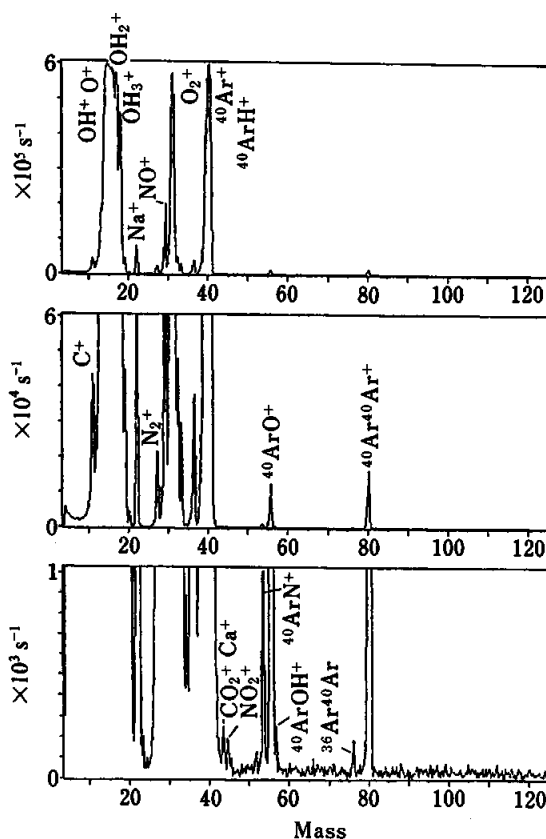


Fig. 2 Blank spectra of ICP-MS. The middle and bottom frames are scale-expanded 10 and 100 times, respectively.

flow rate of nebulizer and auxiliary gas, and sampling depth (distance between the sampler orifice and the load coil) were first reported in detail by Horlick *et al.*²³ They found that the nebulizer gas flow rate and the power were the key ICP parameters in ICP-MS, although ion signals were dependent also on sampling depth and auxiliary gas flow rate.

Vaughan and Horlick²⁴ showed that the ratio of doubly to singly charged ions for Ba decreased with increasing nebulizer gas flow rate and decreasing power. They also reported that the ratio of oxide to singly charged ions for Ba increased with increasing nebulizer gas flow rate and decreasing power. The behavior of these ratios seems reasonable if the

variation of axial plasma temperature²⁵ with the plasma parameters is considered.

On the contrary, Olivares and Houk⁶, using their instrument, reported that the ratio of doubly to singly charged ions for Th increased with increasing nebulizer gas flow rate and decreasing power. Similar behavior of the ratios for U, Th and Ce was observed by Gray.¹⁹ Olivares and Houk⁶, however, obtained similar behavior of the ratio of oxide to singly charged ions for Th to that reported by Vaughan and Horlick²⁴ for Ba.

Variations of La^+ , La^{2+} and their ratio as a function of nebulizer gas flow rate and power obtained with our earlier instrument¹¹ are shown in Fig. 3. Although ion intensities are very low because of the inappropriate

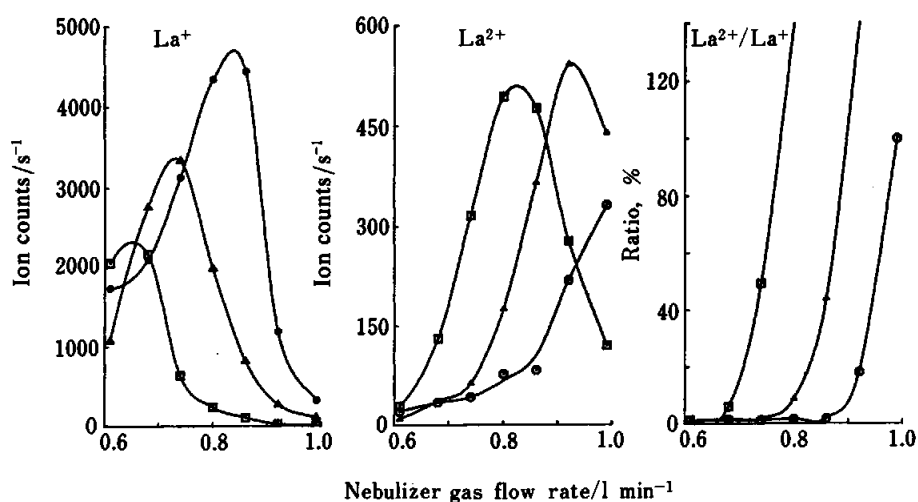


Fig. 3 Variation of intensities and ratios of singly and doubly charged ions of lanthanum as a function of nebulizer gas flow rate.

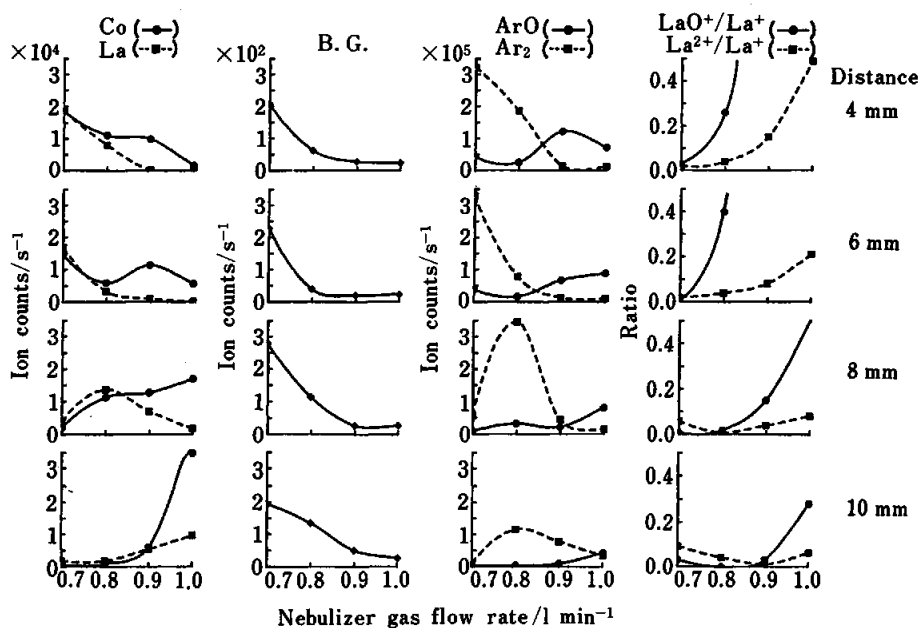


Fig. 4 Variation of ion signals as a function of nebulizer gas flow rate.

detector and other instrumental parameters²⁶, the effects of plasma operating conditions are clearly observed. Note that the ratio of doubly to singly charged ions increases with increasing nebulizer gas flow rate and decreasing power. Such behavior is similar to that reported by Olivares and Houk⁶ and Gray¹⁹, but contrary to that reported by Vaughan and Horlick.²⁴ The contradiction may be caused by the different grounding of the load coil, as described in the previous section. Presumably, a residual discharge persists at the sampler orifice in the laboratory-made instruments, especially at higher nebulizer gas flow rate and at lower power.

Variations of several ion signals, as well as background as a function of nebulizer gas flow rate obtained with our recently modified instrument²⁷, are shown in Fig. 4. The behavior of ion signals and their ratios is further complicated by varying the sampling depth. The optimum operating conditions for nebulizer gas flow rate, rf power and sampling depth correlate to each other: this is an important point to remember.

3-4 Effect of concomitant elements

a) Spectral interferences

Although ICP mass spectra are far more simple than ICP emission spectra, serious spectral interferences are often encountered because of the limited freedom of spectral line selection. For example, nickel has 5 isotopes of 58 (abundance 67.7%), 60 (26.2%), 61 (1.25%), 62 (3.66%) and 64 (1.16%). The $^{58}\text{Fe}^+$ and $^{44}\text{CaO}^+$ will interfere with the peaks of $^{58}\text{Ni}^+$ and $^{60}\text{Ni}^+$, respectively. Therefore, only minor peaks of nickel isotopes can be used for its determination in the presence of iron and calcium. The interference tables prepared by Vaughan and Horlick²⁴ are convenient to consult for the potential of such spectral interferences. A computerized reference manual for spectral data and interferences in ICP-MS was also proposed by the same authors.²⁸ Similar computer programs are provided as an accessory from the manufacturers of most commercial instruments for ICP-MS.

b) Non-spectroscopic interferences

In ICP-AES, the minimal non-spectroscopic interferences (matrix effects) are one of the most important advantages. Although the same advantage was expected in the early stage of the development, more severe matrix effects have been reported by several authors in ICP-MS.

Olivares and Houk²⁹ investigated the suppression of analyte signals by various concomitant salts, reporting that ICP-MS was more susceptible to ionization suppression effects than ICP-AES. The lower the ionization potential of matrix elements, the more severe were the interference effects. They considered these effects from the point of view of the shift in the ionization equilibrium in the plasma.

Kawaguchi *et al.*²⁶ examined more extensively the matrix effects in ICP-MS. In Fig. 5, the effects of

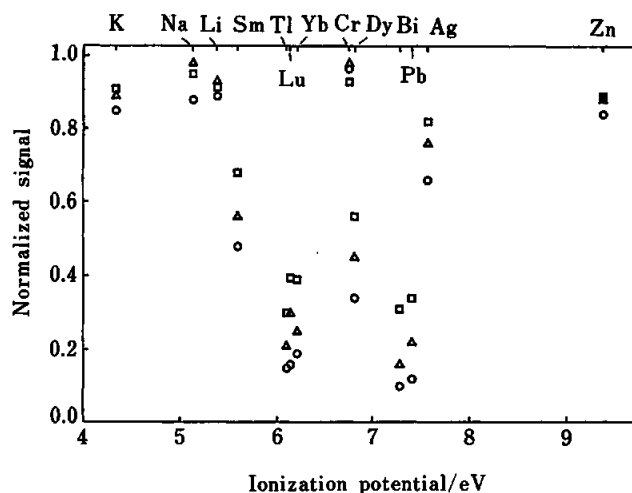


Fig. 5 Variation of suppression effect as a function of ionization potential of matrix elements. Analyte: Co(O), Y(Δ), La($\square$). Concentration: analytes 10^{-5} M, matrix elements 0.01 M.

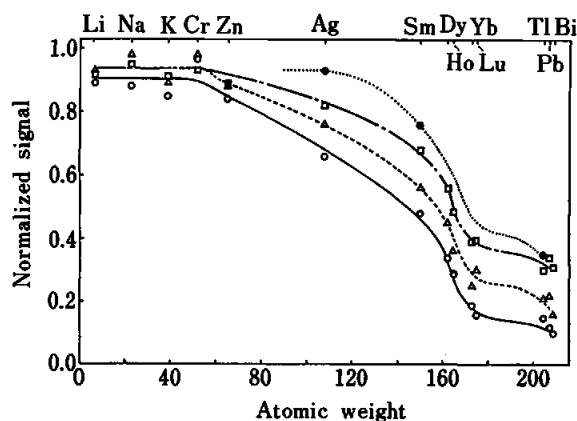


Fig. 6 Variation of suppression effect as a function of atomic weight of matrix elements. Analyte: Co(O), Y(Δ), La($\square$), Bi($\bullet$).

various matrix elements at 0.01 M on the signals of Co^+ , Y^+ , and La^+ are shown as a function of ionization potential of matrix elements. The analyte signals are normalized to those from the samples without matrices. No clear systematic correlation is observed between the suppression effects and the ionization potential. The result suggests that the ionization interference by easily ionizable elements is not the major cause of the suppression effect. On the other hand, when the data shown in Fig. 5 are replotted against atomic weight of matrix elements, a dependence on the atomic weight becomes clear, as shown in Fig. 6. The effect becomes more significant with decreasing atomic weight of analyte. The authors²⁶ considered that the suppression effect arose in the course of ions traveling from the sampling orifice to the mass spectrometer by ion scattering or diffusive effects.

Recently the dependence of the suppression effect on the atomic weight of matrix elements was also reported by Gregoire³⁰ and Tan and Horlick.³¹ As the mechanism of the effect, however, the ambipolar diffusion of ions in the plasma and the effect of space charge in the ion optics were suggested. The enhancement effect by concomitant elements have also been reported by several authors. Interference effects reported by Beauchemin *et al.*³² are especially complicated. In the presence of 0.01 M potassium, for example, analyte signals were enhanced by 40–300% and the enhancement effect continued more than one hour after the sample solution was changed to the one without potassium.

Although it is generally recognized that the matrix effects in ICP-MS are more serious than the analogous effects in ICP-AES, the extent and the trends of the effects depend on the type of instruments and their operating conditions. Apparently more work is necessary to delineate possible causes and sources of the matrix effects.

4 Applications

Since commercial ICP-MS instruments became available, many papers on the application to analysis of real samples have been reported. Although this technique is quite sensitive to most of the elements, prior chemical separations are often required in the analysis of real samples because of the interferences by concomitant elements as described above.

Trace elements in geological samples^{32–34} were determined directly following acid digestion without separation or preconcentration. The influence of polyatomic interference was investigated extensively.³⁴ Lichte *et al.*³⁵ made corrections mathematically for isobaric interferences from oxide ions and other diatomic and triatomic ions in the determination of rare-earth elements. They used cadmium as an internal standard to compensate for drifts in sensitivity.

In the analysis of nickel base alloys³⁶, the determination of trace elements was severely limited owing to the interference of metal oxide ions. Archaeological native silver³⁷ was analyzed by preparing sample solutions with 50 µg g⁻¹ of total dissolved solid to eliminate any suppression effect of the matrix. In the determination of trace metals in river water³⁸, 15 elements were determined directly, while 5 elements required a preconcentration prior to analysis. Cobalt, nickel, cadmium and lead in the samples were collected on a silica-immobilized 8-hydroxyquinoline columns and stripped with a 1 M HCl/0.1 M HNO₃ acid mixture, while arsenic was concentrated by evaporating water to dryness followed by a dissolution of the residue in 0.1 M HNO₃. In the determination of traces of uranium and thorium in gold³⁹, the latter was removed by an ion exchanger column to avoid interferences of AuCl⁺ and AuAr⁺ ions.

One of the attractive features of ICP-MS is the capability of isotope ratio determinations on a multielement basis. The isotope ratio determinations were utilized for the human metabolic or bioavailability studies^{40,41} and the dating of geological samples.¹³ Application of isotope dilution method in ICP-MS will also be developed in various fields. McLaren *et al.*⁴² developed an isotope dilution ICP-MS for the determination of 11 trace elements in the marine sediment reference materials. Results for strontium, molybdenum, tin, thallium, uranium and lead were in very good agreement with the accepted values, while results for chromium and zinc were too low, because of interferences by chlorine-containing molecular ions. Non-saline, natural water samples were analyzed for nickel, copper, strontium, cadmium, barium, thallium and lead by isotope dilution ICP-MS without preconcentration.⁴³ Computational correction methods were developed for interferences resulting from elemental and molecular isobars such as Sn, CaO and CaOH.

5 Conclusion

This new method of analysis has already found numerous applications in actual analytical problems of various fields. Especially in the semiconductor manufacturing industries, attention is paid to the detection capability of ICP-MS for uranium and thorium. Although many points remain to be investigated in both instrumental and analytical problems, the number of fields where ICP-MS plays an important role will grow rapidly.

References

1. R. S. Houk, V. A. Fassel, G. D. Flesch, H. J. Svec, A. L. Gray and C. E. Taylor, *Anal. Chem.*, **52**, 2283 (1980).
2. A. L. Gray, *Analyst* [London], **100**, 289 (1975).
3. A. R. Date, *Trends Anal. Chem.*, **2**, 225 (1983).
4. R. S. Houk, *Anal. Chem.*, **58**, 97A (1986).
5. D. J. Douglas and J. B. French, *Spectrochim. Acta*, **41B**, 197 (1986).
6. J. A. Olivares and R. S. Houk, *Anal. Chem.*, **57**, 2674 (1985).
7. H. Kawaguchi, K. Asada and A. Mizuike, *Mikrochim. Acta* [Wien], in press.
8. R. S. Houk, V. A. Fassel and B. R. LaFreniere, *Appl. Spectrosc.*, **40**, 94 (1986).
9. H. P. Longerich, B. J. Fryer, D. F. Strong and C. J. Kantipuly, *Spectrochim. Acta*, **42B**, 75 (1987).
10. G. P. Ruth III and J. M. Bazan, *Spectrochim. Acta*, **42B**, 49 (1987).
11. H. Kawaguchi, T. Tanaka, T. Nakamura and A. Mizuike, *Bunseki Kagaku*, **36**, 271 (1987).
12. D. W. Boofner, M. Powell, R. L. A. Sing and E. D. Salin, *Anal. Chem.*, **58**, 975 (1986).
13. C. J. Park, J. C. VanLoon and P. Arrowsmith, *Anal. Chem.*, **59**, 2191 (1987).
14. G. P. Ruth III, J. M. Bazan and A. R. Date, *Anal.*

- Chem.*, **59**, 984 (1987).
15. N. S. Chong and R. S. Houk, *Appl. Spectrosc.*, **41**, 66 (1987).
 16. S. J. Jiang and R. S. Houk, *Anal. Chem.*, **58**, 1739 (1986).
 17. S. J. Jiang and R. S. Houk, *Spectrochim. Acta*, **42B**, 93 (1987).
 18. P. Arrowsmith, *Anal. Chem.*, **59**, 1437 (1987).
 19. A. L. Gray, *Spectrochim. Acta*, **41B**, 151 (1986).
 20. R. K. Winge, V. J. Peterson and V. A. Fassel, *Appl. Spectrosc.*, **33**, 206 (1979).
 21. G. F. Kirkbright and M. Sargent: "Atomic Absorption and Fluorescence Spectrometry", Academic Press, New York (1974).
 22. S. H. Tan and G. Horlick, *Appl. Spectrosc.*, **40**, 445 (1986).
 23. G. Horlick, S. H. Tan, M. A. Vaughan and C. A. Rose, *Spectrochim. Acta*, **40B**, 1555 (1985).
 24. M. A. Vaughan and G. Horlick, *Appl. Spectrosc.*, **40**, 434 (1986).
 25. H. Kawaguchi, T. Ito and A. Mizuike, *Spectrochim. Acta*, **36B**, 615 (1981).
 26. H. Kawaguchi, T. Tanaka, T. Nakamura, M. Morishita and A. Mizuike, *Anal. Sci.*, **3**, 305 (1987).
 27. H. Kawaguchi, T. Tanaka and A. Mizuike, *Spectrochim. Acta*, in press.
 28. M. A. Vaughan and G. Horlick, *Appl. Spectrosc.*, **41**, 523 (1987).
 29. J. A. Olivares and R. S. Houk, *Anal. Chem.*, **58**, 20 (1986).
 30. D. C. Gregoire, *Appl. Spectrosc.*, **41**, 897 (1987).
 31. S. H. Tan and G. Horlick, *J. Anal. Atom. Spectrosc.*, **2**, 745 (1987).
 32. D. Beauchemin, J. W. McLaren and S. S. Berman, *Spectrochim. Acta*, **42B**, 467 (1987).
 33. A. R. Date and D. Hutchison, *Spectrochim. Acta*, **41B**, 175 (1986).
 34. A. R. Date, Y. Y. Cheung and M. E. Stuart, *Spectrochim. Acta*, **42B**, 3 (1987).
 35. F. E. Lichte, A. L. Meier and J. G. Crock, *Anal. Chem.*, **59**, 1150 (1987).
 36. C. N. McLeod, A. R. Date and Y. Y. Cheung, *Spectrochim. Acta*, **41B**, 169 (1986).
 37. H. P. Longerrich, B. J. Fryer and D. F. Strong, *Spectrochim. Acta*, **42B**, 101 (1987).
 38. D. Beauchemin, J. W. McLaren, A. P. Mykytiuk and S. S. Berman, *Anal. Chem.*, **59**, 778 (1987).
 39. K. Ito, S. Kuboyama, H. Oguro, T. Kagaya and T. Shimamura, *Bunseki Kagaku*, **37**, 25 (1988).
 40. B. T. G. Ting and M. Jaughorbani, *Anal. Chem.*, **58**, 1334 (1986).
 41. R. E. Serfass, J. J. Thompson and R. S. Houk, *Anal. Chim. Acta*, **188**, 73 (1986).
 42. J. W. McLaren, D. Beauchemin and S. S. Berman, *Anal. Chem.*, **59**, 610 (1987).
 43. J. R. Garbarino and H. E. Taylor, *Anal. Chem.*, **59**, 1568 (1987).

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