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Attenuation of Background Molecular Ions and Determination of Isotope Ratios by Inductively Coupled Plasma Mass Spectrometry at Cool Plasma Condition

Chang Joon Park

Inorgan. Anal. Lab., Korea Research Institute of Standards and Science, Taejeon 305-600, Korea

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Isotope ratios of K, Ca, Cr and Fe are measured at cool plasma condition generated using high carrier flow rate and relatively low RF power of 900 W. Background molecular ions are suppressed to below 100 counts which give isobaric interference to the analytes. The background ions show different attenuation characteristics at increased carrier flow rate and hence for each element different carrier flow rate should be used to measure isotope ratios without isobaric interference. Isotope ratios are measured at both scan and peak-hopping modes and compared with certified or accepted ratios. The measured isotope ratios show some mass discrimination against low mass due to low ion energy induced from a copper shield to eliminate capacitive coupling of plasma with load coil.

Introduction

Thermal ionization mass spectrometry (TIMS) has been used extensively in the geological, nuclear, and analytical sciences for isotope ratio measurements. In 1982 a new technique, inductively coupled plasma mass spectrometry (ICP-MS), was introduced to analysts. ICP-MS is now taking the place of TIMS in many fields of isotope ratio measurements. ICP-MS offers a number of advantages over TIMS in spite of relatively poor precision (about 0.2%) of isotope ratio measurements.¹ Most importantly, sample throughput is rapid. ICP-MS requires typically 1-5 min measurement time and involves less sample pretreatment, while TIMS requires long measurement time of about 1 hour per sample and prolonged sample pretreatment. Thus ICP-MS is an important analytical tool for isotope ratio measurement when many samples have to be analyzed rapidly.

For almost six years after introduction of the first commercial ICP-MS, measurements of isotope ratios of K, Ca, Cr, and Fe had been considered impossible because of huge background peaks in the mass range 39-57.^{2,3} Various methods have been attempted to attenuate background peaks giving isobaric interference to the elements. An electrothermal vaporizer (ETV) was used as an alternative sample introduction device to reduce especially ⁴⁰ArO peak for determination of Fe.⁴⁻⁷ With the ETV, solvent was completely eliminated during drying step and dry salts were subsequently vaporized into the plasma so that ⁴⁰ArO intensity could be reduced to around 1000 counts per second (cps). It was, however, difficult to measure isotope ratios with precision better than 1%, because the ETV, in principle, generated transient signals lasting only 2-3 seconds. Furth-

ermore, it was not easy to get accurate isotope ratios due to the presence of background intensity around 1000 cps. Addition of foreign gases such as N₂, H₂, CH₄, and Xe to the plasma or carrier argon line was also attempted to suppress the ⁴⁰ArO background peak.⁸⁻¹⁰ These foreign gases are known to scavenge oxygen in the plasma by gas-phase collisions. It was also not easy to implement this technique because the plasma became unstable when the foreign gases were introduced into the plasma.

In 1986, Gray published his work on reduction of plasma potential with various load coil geometries.¹¹ He used a screen shield to cut off capacitive coupling between the load coil and plasma, and thereby to reduce plasma potential. He also reported that plasma generated with the screen shield gave unfavorably higher oxide ratios than that with normal load coil. In 1988, Jiang *et al.* reported that K isotope ratios could be measured with ICP-MS at cool plasma condition generated using low forward power and high carrier flow rate.¹² At the cool plasma condition, they could reduce ³⁸ArH and ⁴⁰ArH background peaks to below 100 cps. They added a special note that their Elan 250 ICP-MS with center-tapped load coil generated little or no electrical discharge at the interface so that ³⁸ArH and ⁴⁰ArH background peaks could be suppressed, and that the same result could not be obtained with other ICP-MS instruments with normal load coil due to the electrical discharge at the interface.

Based on the ideas of Gray's shield coil to reduce electrical discharge and Jiang's cool plasma to suppress argon molecular ions, new commercial ICP-MS instruments were introduced which could determine low ppt levels of K, Ca, Cr, and Fe by attenuation of fundamental background ions.

¹³⁻¹⁵ K, Ca, and Fe are important elements in various metabolic and physiological processes of human body and also in semiconductor industry where the analytes are routinely determined by external calibration method. To the best of the author's knowledge, however, isotope ratio measurements with the new ICP-MS instrument have never been reported since Jiang *et al.* reported measurement of K isotope ratio at cool plasma condition in 1988. In this work, an ICP-MS instrument with the same kind of shield coil was employed to reduce plasma potential and carrier flow rate was increased to abnormally high values to suppress the background ions. Optimum operating conditions were investigated to measure isotope ratios of K, Ca, Cr and Fe.

Experimental

Instrumentation. The ICP-MS instrument employed in this work was an EMS200 (Younglin, Anyang, Korea). Schematic diagram of the ICP-MS is shown in Figure 1. Instrument components and typical operating conditions are given in Table 1. An off-axis ion lens was used in this instrument where its quadrupole and interface centers were 8 mm apart. Ions exiting the quadrupole filter were deflected 90° into the mouth of a discrete dynode electron multiplier (AFP562A, ETP Scientific, Auburn, MA, USA). For sample introduction, a concentric nebulizer (TR-30-C1, Meinhard, Santa Ana, CA, USA) and a Scott-type spray chamber were used with a peristaltic pump (Minipuls 3, Gilson, Villiers-le-Bel, France) to control the sample uptake rate. Plasma was ignited with a copper shield (1.5 cm × 6.3 cm) inserted between torch and load coil to eliminate capacitive coupling of the plasma with the coil. Carrier flow rate was then increased upto 1.38 L/min at 900 W to suppress background molecular ions. The shield should not be grounded during ignition. Otherwise the shield will burn out immediately upon ignition. After ignition, torch box was moved toward the interface to ground the shield through a copper rod (0.4 cm in diameter) mounted on the interface.

Reagents. Isotopic reference materials of B and Cr were purchased from National Institute of Standards and technology (Gaithersburg, MD, USA) and that of Fe was bought from Institute for Reference Materials and Measurements (Geel, Belgium). For K and Ca, no isotopic reference materials were available and hence 10-100 ppb stan-

Table 1. Instrument components and typical operating conditions

Component	Operating Conditions
ICP generator	Forward Power: 900 W
ICP-16	Reflected Power: <2 W
RF Plasma Products	Frequency: 40.68 MHz
Plasma torch	
Precision Glassblowing	Argon flow rates:
	Plasma: 15 L/min
	Auxiliary: 0.5 L/min
	Carrier: 1.12 L/min for Cr
	1.28 L/min for Ca, Fe
	1.38 L/min for K
Interface	
Sampler orifice (aluminium): 1 mm	
Skimmer orifice (aluminium): 0.7 mm	Sampling depth: 12 mm
Vacuum	
Interface: Rotary (2020A, Alcatel)	Operating Pressures
2nd: Turbo (5402CP, Alcatel)	Interface: 1.5 torr
3rd: Turbo (5408CP, Alcatel)	2nd: 5×10^{-4} torr
	3rd: 2×10^{-6} torr
Mass Filter	
16 mm pole, 220 mm long	
300W, 2.1MHz, Extrel 150QC	
Prefilter	
16 mm pole, 40 mm long	
Laboratory construction	
Detector	
AF 562A, ETP	Deflector: +230V
	Bias: -2.6 kV

ard solutions prepared by serial dilutions of stock standard solutions made from pure metals. Working solutions at 1% HNO₃ were made with deionized water from a Milli-Q system (Millipore, Bedford, MA, USA) and electronic grade HNO₃ from DongWoo Pure Chemicals (Iksan, Korea).

Results and Discussion

Optimization. Figure 2 shows background mass spectrum obtained at cool plasma condition (900W, 1.28 L/min).

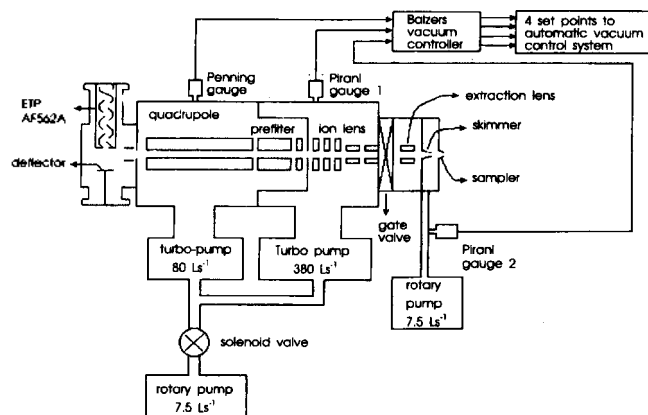


Figure 1. Schematic diagram of ICP-MS instrument.

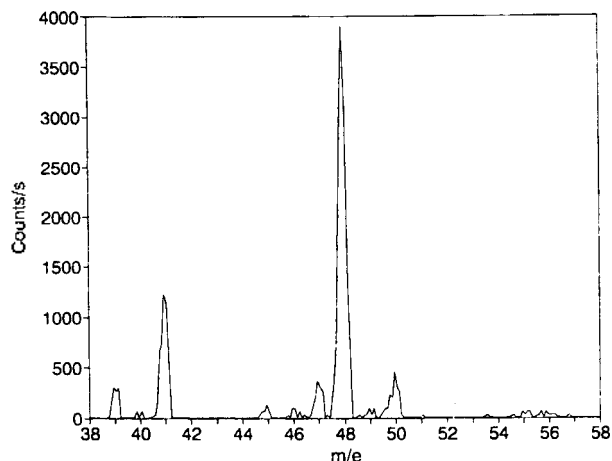


Figure 2. Background mass spectrum at 900 W and 1.28 L/min.

As indicated in Figure 2, Ca isotopes (^{40}Ca , ^{42}Ca , ^{44}Ca) and Fe isotopes (^{54}Fe , ^{56}Fe , ^{57}Fe) are free from isobaric interference at this condition, while K isotopes (^{39}K , ^{41}K) and ^{50}Cr are interfered with background molecular ions. The background ion intensity at mass 50 is greater than that of ^{40}ArN at mass 54. This suggests that the background ion at mass 50 should not be ^{36}ArN because natural abundance of

^{36}Ar is much smaller than that of ^{40}Ar . Considering that hydrides are more easily generated at cool plasma condition, the background ion appearing at mass 50 is believed to be H_2O_3 . It can be also found from Figure 2 that each element may have different optimum carrier flow rate where its isotopic ratios can be measured without isobaric interference.

Figure 3(a)-(c) shows variation of background ion responses at 900W as carrier flow rate is increased from 1.0 to 1.38 L/min. Figure 3(a) shows that ^{40}Ar and ^{40}ArO responses at carrier flow rate of 1.28 L/min go down to below 1/10,000 of their initial values, and that ^{40}ArH is reduced to below 1/10,000 at much higher carrier flow rate of 1.38 L/min. It can be concluded from Figure 3(a) that carrier flow rate should be set to above 1.28 L/min for measurement of Ca and Fe isotope ratios, and to above 1.38 L/min for K isotope ratio. Figure 3(b) shows intensities of three background ions giving isobaric interference to Cr isotopes (^{50}Cr , ^{52}Cr , ^{53}Cr). All the three ion intensities in Figure 3(b) go down to below 100 cps at carrier flow rate of about 1.12 L/min. When the carrier flow rate is further increased, ^{36}ArO and $^{36}\text{ArOH}$ ion intensities keep going down, but H_2O_3 ion response shows the opposite direction. Thus the optimum carrier flow rate was set to 1.12 L/min for measurement of Cr isotope ratios. Figure 3(c) shows responses of three background ions ^{40}ArN , ^{40}ArO and $^{40}\text{ArOH}$ which give isobaric interference to Fe isotopes (^{54}Fe , ^{56}Fe , ^{57}Fe). The background ion intensities in Figure 3(c) go down to below 100 cps at carrier flow rate of 1.28 L/min. For measurement of Fe isotope ratios, 1.28 L/min was chosen as an optimum carrier flow rate because sensitivity of Fe isotopes also went down when the carrier flow rate was further increased to get background intensities well below 100 cps. Figure 4 shows variation of ^{40}ArO intensity at three different RF powers (900, 1000, 1100W). As can be expected from the fact that more energy is input into the plasma at higher RF powers, the response curves in Figure 4 indicate that higher RF powers require increased carrier flow rates to reduce the background ion intensities to below 100 cps. Figure 5 shows time variations of ^{40}Ar and ^{40}ArO background ion intensities obtained at 900W and 1.28 L/min for 10 minutes. The background ions show stable intensities with only a few spikes jumping above 100 cps. If the copper shield is poorly grounded, many spikes jumping above even 1000 cps could appear which can prohibit isotope ratio

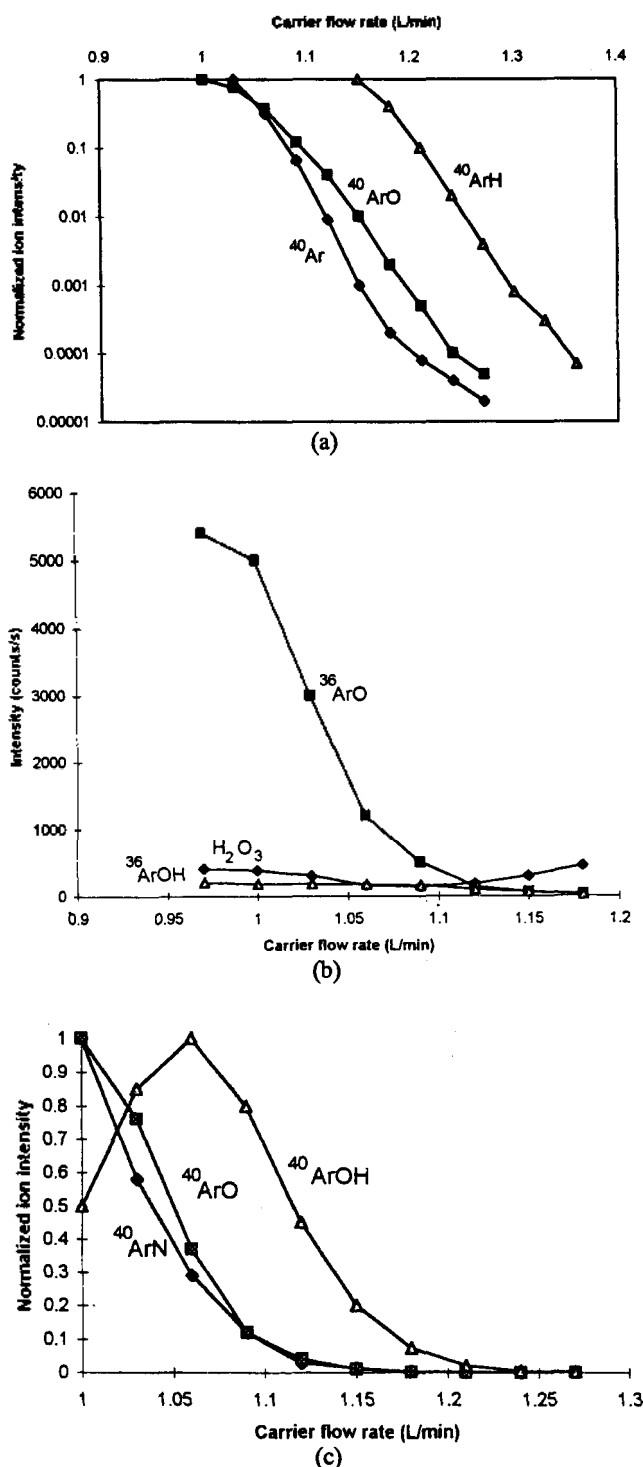


Figure 3. Background ion response vs. carrier flow rate at 900 W: (a) ^{40}Ar , ^{40}ArH , and ^{40}ArO (b) H_2O_3 , ^{36}ArO , and $^{36}\text{ArOH}$ (c) ^{40}ArN , ^{40}ArO , and $^{40}\text{ArOH}$.

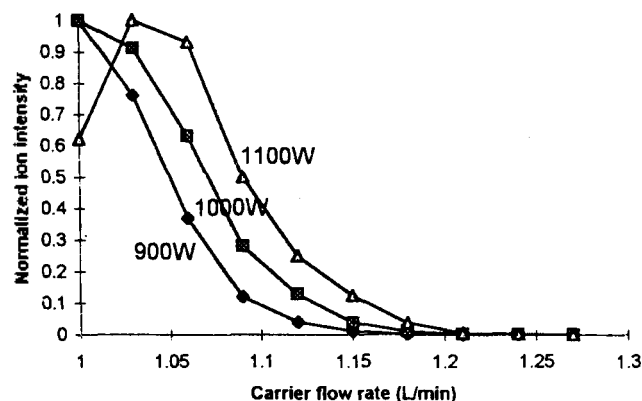


Figure 4. ^{40}ArO ion response vs. carrier flow rate at three different RF powers.

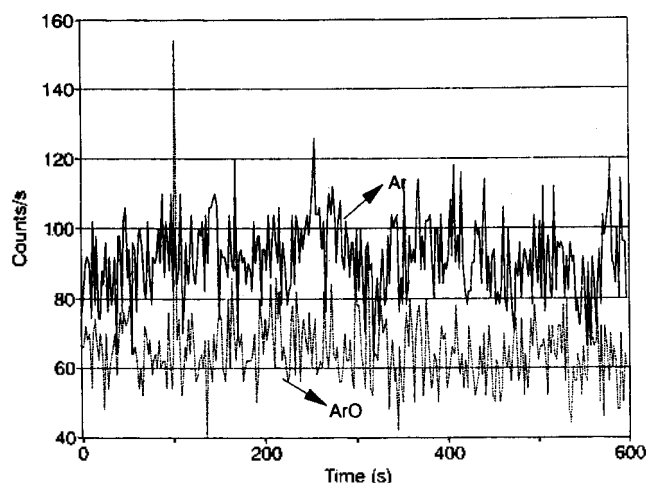


Figure 5. Time variation of ^{40}Ar and ^{40}ArO ion intensities at 900 W and 1.28 L/min.

measurements.

Isotope Ratios. Figure 6(a)-(c) shows mass spectrum of K, Ca, Cr and Fe isotopes obtained at cool plasma condition with different carrier flow rates (Table 1). Mass spectra shown in Figure 6(a) and (b) were obtained using 100 ppb K and Ca standard solutions respectively. Mass spectrum in Figure 6(c) was obtained using 10 ppb Cr and 10 ppb Fe isotopic standard solutions. In Figure 6 (a)-(c), analyte isotope peaks are observed with clean background. Isotope ratios of the analytes were measured at two measurement modes of peak-hopping and scan. The isotope ratios were automatically corrected for dead time in EMS200 software by equation 1.¹⁶

$$n = m / (1 - m \tau) \quad (1)$$

where n is true count rate; m is observed count rate; and τ is dead time. Since dead time of the ICP-MS instrument employed in this work is about 20 ns, the error due to the dead time effect would be only 1% even at a high count rate of 500,000. Corrected isotope ratios are given in Table 2 with accepted or certified ratios. Since the same dwell time had to be allocated to all the isotopes in scan mode, precision of isotope ratios measured in scan mode came out to be worse than that of isotope ratios measured in peak-hopping mode where longer dwell time could be assigned to isotopes of lower abundance. Among the isotope ratios measured in the peak-hopping mode, better precision was achieved when sweep number was increased. This result can be explained by pulse counting statistics where uncertainty of measuring counts of an isotope is given by the square root of integrated counts. Precision of isotope ratio measurement is therefore estimated by the relative combined uncertainty given by¹⁷

$$\text{Precision of isotope ratio } a/b = (1/a + 1/b)^{1/2} \times 100 \quad (2)$$

where a and b are integrated counts of the two isotopes. It can be seen from Tables 2 that the measured ratios are generally lower than the accepted or certified ratios. In Table 3, two B isotope ratios are compared which were measured at the same carrier flow rate of 0.95 L/min but with different coil configuration. Table 3 shows that B isotope ratio

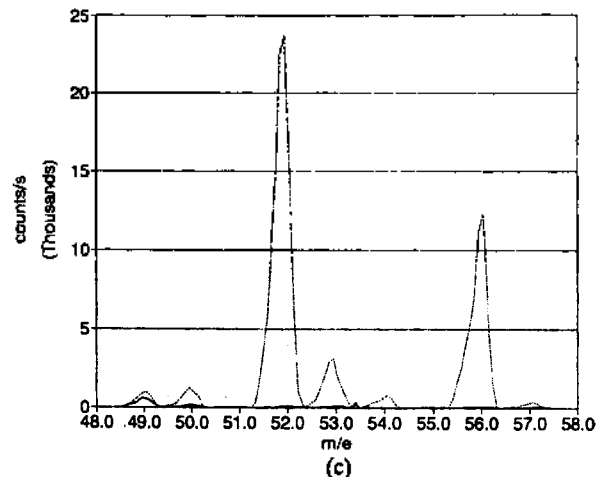
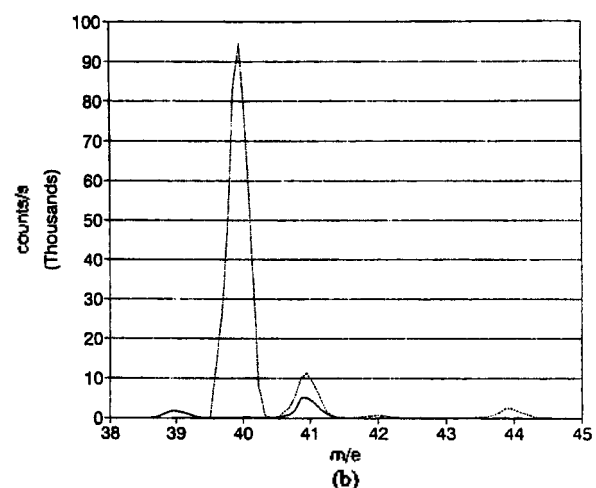
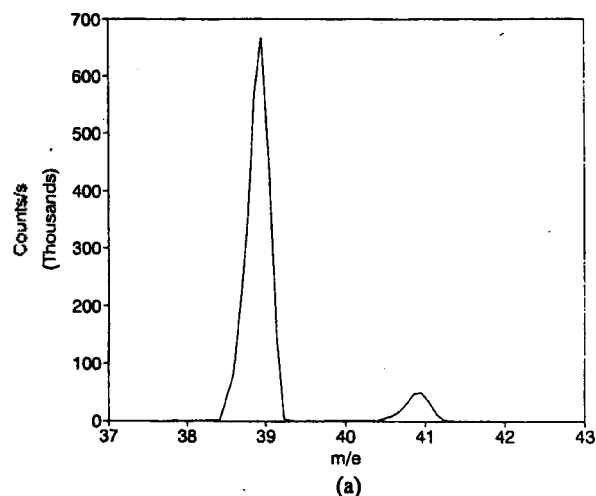


Figure 6. Mass spectrum of isotopes of interest at 900 W: (a) 100 ppb K at 1.38 L/min (b) 100 ppb Ca at 1.28 L/min (solid line: blank, dotted line: 100 ppb Ca) (c) 10 ppb Cr at 1.12 L/min and 10 ppb Fe at 1.28 L/min (solid line: blank, dotted line: 10 ppb Cr, Fe).

measured with the normal coil is slightly higher than the NIST certified ratio, while that measured with the shield coil is much lower than the certified ratio. This means that the ICP-MS instrument employed in this work shows some mass discrimination against low mass simply due to the

Table 2. Measurement of isotope ratios at peak-hopping and scan modes

Element	Isotope ratio ^a	Peak-hopping			Scan ^b	Accepted or certified ratio
		Sweep number				
		100	200	300		
K	³⁹ K/ ⁴¹ K	13.07 (0.75%)	13.22 (0.41%)	13.14 (0.48%)	³⁹ K: 2 ⁴¹ K: 10	12.77 (0.86%)
	⁴⁰ Ca/ ⁴⁴ Ca	46.03 (0.84%)	45.51 (0.72%)	45.33 (0.78%)	⁴⁰ Ca: 2 ⁴² Ca: 50	42.63 (1.07%)
Ca	⁴² Ca/ ⁴⁴ Ca	0.300 (0.45%)	0.296 (0.54%)	0.299 (0.33%)	⁴⁴ Ca: 10	0.317 (1.43%)
	⁵² Cr/ ⁵³ Cr	8.421 (0.50%)	8.361 (0.28%)	8.423 (0.19%)	⁵² Cr: 2 ⁵³ Cr: 10	8.312 (0.79%)
Cr	⁵⁴ Fe/ ⁵⁷ Fe	2.322 (0.72%)	2.277 (1.08%)	2.375 (0.62%)	⁵⁴ Fe: 5 ⁵⁶ Fe: 2	2.213 (2.90%)
	⁵⁶ Fe/ ⁵⁷ Fe	41.26 (0.83%)	39.47 (0.88%)	40.88 (0.51%)	⁵⁷ Fe: 20	37.78 (3.87%)
Fe						

^a Mean of 5 measurements (RSD). ^b Sweep number=200, Dwell time=2 ms.

Table 3. Measurement of ¹⁰B/¹¹B isotope ratio at two coil configurations

Run	Operating condition	Normal coil	Shield coil
1		0.2564	0.2279
2		0.2559	0.2271
3		0.2562	0.2274
4		0.2565	0.2279
5		0.2554	0.2274
	Mean	0.2560	0.2275
	SD	0.0004	0.0003
	RSD (%)	0.17	0.15

certified ratio: 0.2473. Measurement Mode: peak-hopping. Dwell time: ¹⁰B=12 ms, ¹¹B=3 ms

presence of the copper shield inserted between load coil and torch to reduce plasma potential. Nonose *et al.*¹³ measured average kinetic energies of ions for ICP sources with and without the copper shield. they found that the average kinetic energies were in the range 15-20 eV for the ICP source without the shield, while for the ICP source with the shield, the average kinetic energies were in the range 2-5 eV. Space charge effect is generally attributed to the mass-dependent non-spectroscopic interference in ICP-MS.¹⁸ Due to the space charge effect, isotopes of lower mass have lower efficiency of transmission through the ion lens than those of higher mass. It can be reasonably speculated that the space charge effect may get worse when ion energy becomes lower.

Conclusion

Isotope ratios of K, Ca, Cr and Fe can be easily measur-

ed without isobaric interference by simply increasing carrier flow rate with a copper shield between load coil and torch. The optimum carrier flow rate was different for each element because the various background ions giving isobaric interference to the analytes show different attenuation characteristics at increased carrier flow rates. Peak-hopping mode was superior to scan mode in precision of isotope ratio measurements. The measured isotope ratios show serious mass discrimination against low mass. The mass discrimination effect seems to result from low ion energy induced from the copper shield to eliminate capacitive coupling of plasma with the load coil. The mass discrimination effect may be a unique feature of the ICP-MS instrument with an off-axis ion lens system and it may not appear in other ICP-MS instruments.

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