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Determination of Isotopic Ratios for Ca in Inductively Coupled Plasma Mass Spectrometry (ICPMS) by Removing Water Related Molecules

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Calcium isotopic ratios are precisely measured by removing isobaric interferences originated from water in the plasma. Liquid Ar cryogenic trap combined with membrane desolvator could eliminate backgrounds at m/z 42 and 44. Slow drift of ICP-MS is corrected by the frequent running of the standards. It is found necessary to separate Ca from the sample matrix using Ca oxalate precipitation technique. Currently, the RSD is 0.5-1.0% for 2 minutes of measurement but is expected to be improved if the measurement time is increased. The technique was applied to ^{42}Ca enriched baby fecal samples and successfully determined ^{42}Ca/^{44}Ca ratio changes.

Introduction

Since the development of ICP-MS,[1] it has been established well in the elemental analysis and isotopic ratio measurement of most elements.[2-3] Stable isotopes have been used as tracers to monitor isotopic variations in biology[4] and environmental studies.[5] However, because of large backgrounds from Ar related species, certain elements such as Fe, Ca, and K could not be measured easily. Several different approaches[6-12] have been made to reduce the background in the mass range of 39-57 and measure the isotopic ratios of these important elements precisely.

Taylor *et al.*[6] used an air-acetylene flame as an ion source to determine isotopic ratios for K with a quadrupole mass spectrometer. The detection limit was 2-3 ppb and the ratio of ^{41}K/^{39}/K was measured with 0.5-1% relative standard deviation (RSD). Different ion sources such as helium[7] or nitrogen[8] plasma were also used. However, Helium or Nitrogen plasma/MS technique requires an additional instrument or a large modification such as adding an additional vacuum pump because helium is not easily pumped out. Furthermore, it is not easy to change the plasma source from Ar to another. Some scientists[9,10] attempted to use the scavenger gases such as CH^4 and Xe to the plasma or carrier gas to suppress the ^{40}ArO background for the determination of Fe. Jiang *et al.*[11] used a relatively cool plasma to reduce ArH and was able to alleviate interferences for determination of K isotopes. Park[12] was recently able to reduce molecular backgrounds in the mass range of 39-57 successfully. He used a cool plasma condition and a copper shield to reduce the secondary discharge at the interface. Isotopic ratios of K, Ca, Cr and Fe could be measured precisely but the mass discrimination against low mass was severe. Furthermore, both authors[11,12] mentioned that it might not be possible for a certain ICPMS to reduce the background by using the "cooled" plasma condition. Indeed it was not possible to reduce the background enough to measure the precise isotopic ratio with the model used (Elan 5000) in this research by using the "cooled" condition.

The method developed in this experiment is to use a cryogenic cooling system to remove background produced from water. It does not require any expensive additional apparatus but effectively removes background molecules such as ArO, ArOH and ArH. The elimination of water will greatly alleviate background overlaps because these molecules are mostly produced from the reaction between water and Ar. In the earlier report,[13] it was shown that isotope of Fe, Cu, Li, and Zn could be measured precisely (0.1%) with this technique. In this report, this technique is applied to the measurement of Ca isotope ratio.

Ca is an important biological and environmental element. It has been used in human bodies as a stable isotope tracer? because it is safe compared to radio tracers.[4] The minimal tracer is added because of the high cost of isotope enriched material. Only small dose of stable isotopic tracer is added and its isotopic perturbation should be measured precisely. Ca has several isotopes (mass number 40, 42, 43, 44, 46, 48) and their backgrounds are interfered with ArH_2 (42), CO_2 and N_2O(44), NOH_2O(46) and ArC(48). With cryogenic cooling, backgrounds at 42 and 44 could be sub-

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Table 1. Typical operating conditions of ICP-MS

Plasma power	1000 W
Coolant gas flow	15.0 L/min.
Nebulizer gas flow	1.1 L/min.(USN)
	0.86 L/min. (cross flow)
Aux. gas flow	0.86 L/min.
Detection Mode	peak hopping
Pressure	1.2×10^{-5} torr.
Dwell time	25 msec.
Sweeps/replicate	12
Replicate	10
Time factor	1; 4; 0.3; 2 for 42; 43; 44; 48

stantially reduced. Ca isotope ratios could be precisely measured and this study was applied to the study of biological samples.

Experimental

Instrumentation. A Perkin Elmer ICPMS (Elan Model 5000) was used for the experiment. The operating conditions in this study is listed in Table 1. The mass spectrometer was used in a peak hopping mode. ICP was operated in a typical condition.

Samples were introduced with a commercial ultrasonic nebulizer (USN) and desolvation system (Model U-5000, Cetac Technologies, Inc. Omaha, Nebraska). An argon cryogenic desolvation and membrane desolvator was added after USN. Aerosols were completely dried with argon cryogenic trap and the vapor carried by the sample gas was almost none. Membrane desolvator was not essential but it helped to prolong the running time of the argon cryogenic trap. Flaky ice was formed at the trap region and blocked the path of aerosol after about 4 hours of running time while membrane desolvator could prolong it to 8 hours. Liquid nitrogen is cheaper than argon to use. However, due to its lower boiling point than argon, Ar plasma gas can be liquified in liquid nitrogen trap.

Reagent and Samples. Fecal samples (0.2-0.5 gr) were ashed in the muffle furnace overnight using platinum crucibles. The furnace temperature was set at below 500 °C. Feces were collected from the babies fed by an isotope or isotopes enriched milk. Sample collection procedure was entirely controlled by the hospital (Univ. of MO, Columbia) and no detailed information about the isotopes was given prior to the research. Ashed samples were dissolved with 10 mL of conc. HNO_3. It was diluted to 1/10 or 1/100 if necessary. To separate Ca, 1.0 mL of 2.5% ammonium oxalate (reagent grade, Aldrich Chem. Co., WI, U.S.A) was added to 10 mL of sample. Precipitates were collected after three times of 5 minutes of centrifuging plus washing. Finally, it was dissolved in 50 mL of 1% HNO_3. High purity nitric acid (Optima grade, Fisher Scientific) and high purity Ca standard (reagent grade, Aldrich Chem. Co., WI, U.S.A) was used.

Result and Discussion

The background counts at m/z 42, 43 and 44 were examined to measure the amount of background caused by water (Table 2). Dry plasma represents background counts when no aerosol is introduced. Cross flow and ultrasonic nebulizer (USN) show that the background counts obtained when a cross flow nebulizer and USN are used, respectively. USN was equipped with a water cooled condenser. Consequently, the values of USN should be lower than those of cross flow. However, compared with dry plasma, it is evident that water was not completely removed with water condenser alone. USNC (USN combined with cryogenic condenser) dramatically reduced the values at m/z 42 and 44. Counts at mass 42 (ArH_2^+) was almost the same as that of dry argon.

Table 2. The effect of cryogenic desolvation at backgrounds (unit; cps)

m/z	42	43	44	48
Dry plasma	830	1020	4090	1000
Cross flow neb.	37620	2600	30720	390
USN	5200	540	23300	1800
USNC	910	540	8500	1700

USNC; Ultrasonic nebulizer with cryogenic desolvator

Mass 44 (CO_2 and N_2O) showed highest background even at dry plasma condition. When a cross flow nebulizer was used, background counts increased about 10 times compared with dry plasma. Obviously, water was an important factor for mass 44 and was not completely removed even with cryogenic trap. It is suspected that mass 44 was affected both from aerosol and environment. Thus, the background count is high and fluctuating. There were little changes in mass 43 and 48.

In determination of precise isotopic ratios, dead time should be corrected.[14,15] It is very small and can be omitted in a usual trace elemental analysis. For Elan 5000 model used in this study, the dead time is near 4.0×10^{-8} sec and used for the correction of counting using the following equation

$$R_c=R_0/(1-R_0\,\tau)$$

where R_0 and R_c are the observed and corrected counting rates (sec^{-1}) and τ is the dead time (sec).

In ICP-MS, one of the largest error is from counting statistics. As is well known, the standard deviation of a measurement is $\sqrt{N}$ when N is the total number of counts accumulated. Thus, one has to accumulate at least 106 to get a single measurement RSD of 0.1%. If two isotope ratio is counted, the total RSD is $\sqrt{(N_1+N_2)/N_1N_2}$, where N_1 and N_2 are the total counts for each isotopes. If one designs to get 0.1% RSD of two isotope ratio, two million counts should be accumulated for each isotope.

Isotope ratio in ICPMS shows a slow drift which depends on mass difference. For example, Ca^{42} and Ca^{44} has $\Delta M/M$= 0.05 which can be a significant source of error in the precise determination of isotope ratio. Figure 1 demonstrates that $^{42}Ca/^{44}Ca$ shows a drift with time. Since each run takes about 10 minutes, the time span is 1.5 hour. There are several ways to correct for the drift. In this experiment, reference Ca solution was run before and after each sample.

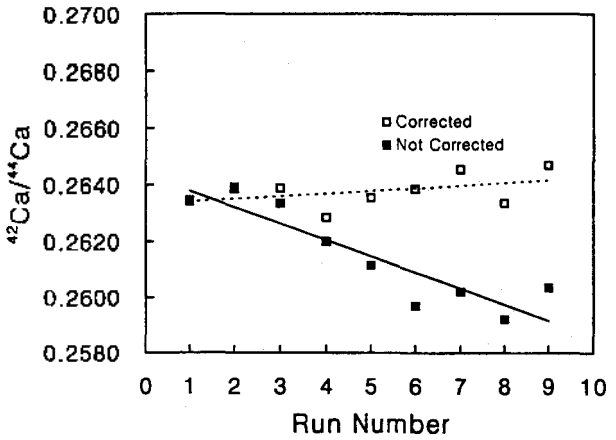

Figure 1. Correction of $^{42}Ca/^{44}Ca$ ratios based on drift in standard $^{42}Ca/^{44}Ca$.

Any changes of ratio in sample were corrected by the known ratio of reference.

Currently, the RSD of $^{42}Ca/^{44}Ca$ is 0.5-1.0%, which is higher than expected. One of the reason is that the time spent for the measurement of two masses was not enough. Even though 10 minutes are used for data collection, the time factor given for 42 and 44 was only a small portion. In the peak hopping mode which is used in the experiment, the time factor for masses 42, 43, 44, and 48 was 1 : 4 : 0.3 : 2 according to their natural abundances. Thus, the time spent in 42 and 44 was less than 20% (2 min.) of the total time. In this particular study, it was not known which isotope/isotopes are enriched from the start. Consequently, it was necessary to examine all the isotopes. If two masses had been chosen with the proper measurement time, the RSD could have been lowered to 0.1%.[13]

Biological samples often contain many different elements that can form molecular ions. Complex matrix can increase isobaric interferences. Also it has been shown[16] that a matrix salt can carry water due to its hygroscopic property. Other interferences such as chemical interferences do not play significant roles because only the isotopic ratio is measured. Calcium can conveniently be separated from matrix by forming calcium oxalate precipitates. Details of the precipitation process are described in the experimental section. The result shows that matrix can interfere in isotopic ratio measurement and needs to be separated. When matrix was not isolated, $^{42}Ca/^{44}Ca$ ratios were consistently lower than the ones separated (Table 3), which means that spectral interferences on mass 44 exist. Molecules such as $^{27}MgOH$ or ^{28}SiO could give positive interferences. However, large salt matrix can carry water even under cryogenic cooling and causes errors too. Consequently, it should be studied if a large matrix concentration would give erroneous results. This type of study was investigated using Na as a matrix because large amount of Na can be easily found in a

Table 3. The effect of matrix on $^{42}Ca/^{44}Ca$ ratios

Sample	Matrix isolated	Matrix unisolated
1	0.1482±0.0021	0.1426±0.0024
2	0.1241±0.0020	0.1202±0.0015
3	0.2977±0.0047	0.2908±0.0053

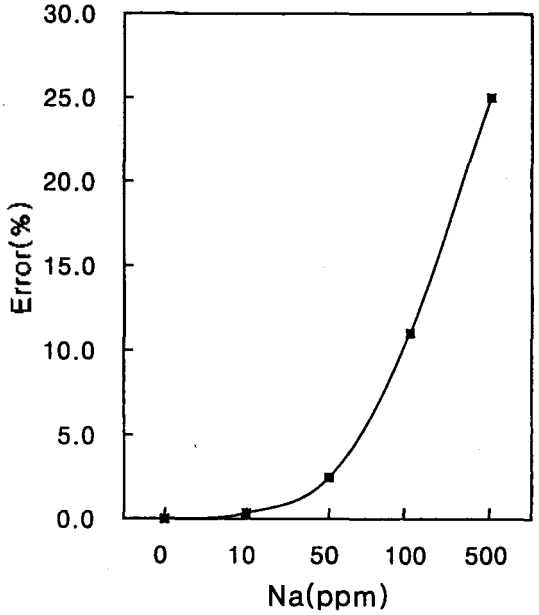

Figure 2. Effect of sodium concentration on $^{42}Ca/^{44}Ca$ ratios.

biological sample. As the concentration of Na was increased, the relative error increased non-linearly (Figure 2) even though Na did not form molecules directly in the mass range 42-44. Thus, it is important to control Na concentration under 10 ppm for the precise measurement of Ca isotope ratio.

Seven fecal samples from a baby fed by an isotope enriched milk were received to test the isotopic changes with time. It was not known which isotope was enriched at the moment the samples were received. After the experiment, it was found that ^{44}Ca was enriched and Figure 3 shows that ^{44}Ca begins to come out after 14 hours from feeding. It is almost depleted after 26 hours but slowly comes out even after 40 hours. It is well demonstrated from this technique that

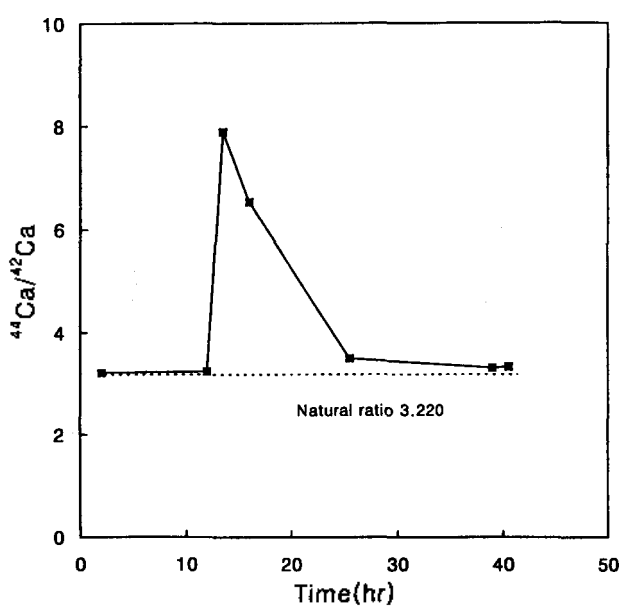

Figure 3. Change of $^{44}Ca/^{42}Ca$ ratios with time in fecal samples of a baby dosed with ^{44}Ca enriched milk.

which isotope is enriched and how it behaves with time in a baby.

Conclusion

In conclusion, Ca isotope ratios could be measured precisely by removing water related isobaric interferences. Liquid Ar cryogenic condenser was used in addition to a conventional condenser and membrane desolvator. Drift was corrected with frequent calibration of standards. The technique was applied to feces from a baby dosed with ^{44}Ca enriched milk. For biological samples, it was found that Na could give an erroneous Ca isotope ratio, and that matrix separation was beneficial for more precise determination of isotopic ratios. Currently, RSD is 0.5-1.0% for the ratio of $^{42}Ca/^{44}Ca$ in 10 minutes of total measurement time. However, it can be improved easily if just two isotopes are monitored with a longer observation time.

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Oxygen Adsorption Process on ZnO Single Crystal

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The adsorption of oxygen on ZnO was monitored by measuring the capacitance of two contacting crystals which have depletion layers originated from the interaction between oxygen and ZnO at 298 K-473 K. An admission of oxygen to the sample induced an irreversible increase in the depth and the amount of adsorbed oxygen was less than 0.001 monolayer in the experimental condition. The relation between pressure of oxygen and variation of the depth was tested from the view point of Langmuir or Freundlich isotherm. Using Hall effect measurement and kinetic experiment, a model equation on the adsorption process was proposed. From the results, it was suggested that oxygen adsorption depended on the rate of electron transfer from ZnO to oxygen while the amount of adsorbed oxygen was kinetically restricted by the height of surface potential barrier.

Introduction

The electron transfer between gas species and semiconductor surface induces a surface layer such as a depletion layer or an accumulation layer depending on their mutual energy levels.[1] The layer characterizes not only chemical and electrical properties of the surface but also catalytic processes. The surface layer theory is often tested on ZnO powder and single crystal because the electron configurations of zinc ion is d^{10} and they have negligible activity compared to the other transition element ions. The properties of the layer which was developed in adsorption process were characterized by potential barrier and carrier density near the surface.[2-6] In general, oxygen was adsorbed on anion vacancy or surface defect by capturing the conduction electron of ZnO.[7] In 1950, Weisz first pointed out the fact that, no matter how impure the sample, the surface coverage is limited to about 10^{-3}-10^{-2} monolayer of equilibrium adsorption when a depletion layer is present.[8] Unfortunately, there is no direct quantitative evidence of the theory until now.

Since the depletion layer has very low concentration of