

The Measurement of Isotope Ratios using a JMS-D300 Mass Spectrometer

By

Masako SHIMA

Department of Physical Sciences, National Science Museum, Tokyo.

Abstract

The JMS-D300 mass spectrometer, virtual image ion optics machine, originally designed for identification of organic materials, has been modified to that for determination of isotopic ratios of elements.

The reason, why it is necessary to alter JMS-D300, has been explained connecting with the present purpose, mainly cosmochronological studies, of measuring isotopes.

Improvements has been performed more or less to all parts such as ion source, analyzer tube, collector system, magnetic scan system and vacuum system, of JMS-D300.

By means of actual isotopic measurements of K, Ca and Cr, performance of the modification was examined and results were described in detail.

In present status, fundamental points such as source assembly alignment, sensitivity, resolution, magnetic scan system and collector system are almost completely satisfactory for measurement of normal isotopic ratios of elements. However, for measurements of trace amount of samples, and of a very small peak between large peaks and for much accurate and precise measurements, it is necessary to make further improvements.

1. Introduction

Several mass spectrometers for isotope analysis have been manufactured commercially, and some of them are excellent for precise measurements of isotopic ratios of certain elements. These are, however, normally single focussing, so that their resolution is limited and can only be increased by increasing the physical dimensions of the instrument. This procedure sacrifices sensitivity.

On the other hand, recent developments in the mass spectrometry of organic materials have led to compact mass spectrometers with high resolution. One of these, the JMS-D300 designed by MATSUDA (1968) and MATSUDA *et al.* (1974), and constructed by JEOL Ltd., is well known for its special feature of virtual image double focussing geometry which gives very high resolution without sacrifice of sensitivity.

Because of the completely different purposes of mass spectrometry designed for identification of organic materials and isotopic measurements of elements the two sorts of instrument cannot be readily used for the other purpose. It was considered worthwhile however to modify the JMS-D300 mass spectrometer in order to be able to use it for isotopic ratio measurements.

2. Why high resolution and high sensitivity

In the previous section the author has emphasized high resolution and high sensitivity as necessary features. The reasons for this are itemized in below.

2.1. *Determination of cosmic-ray-produced stable nuclides (other than rare gases) in meteorites.*

Because the production of cosmic-ray-produced nuclides is limited, only trace amount (10^{-13} to 10^{-9} g) of each nuclide is available for each determination. Further, extremely small peaks, such as ^{40}K and ^{46}Ca (1/10,000 and 3/100,000 of the main peaks, ^{39}K and ^{40}Ca , respectively) between large adjacent peaks must be measured accurately. Another problem arises also in measuring such trace amounts of samples. Hydrocarbon ions appear with almost the same m/e as elemental ions. For example, for $m/e=43$, traces of C_3H_7^+ , produced from unavoidable contaminants in the source, interfere with $^{43}\text{Ca}^+$ measurements. For separation of such peaks, one must have a high resolution mass spectrometer.

2.2. *Determination of exact solidification ages of iron meteorites using ^{187}Re – ^{187}Os pair.*

Several methods for determining solidification ages such as ^{40}K – ^{40}Ar (^{40}K – ^{40}Ca), ^{87}Rb – ^{87}Sr , ^{147}Sm – ^{143}Nd , ^{176}Lu – ^{176}Hf and Pb – Pb (^{235}U , ^{235}U , $^{232}\text{Th} \rightarrow ^{206,207,208}\text{Pb} + ^4\text{He}$) are proposed. These methods are used not only to measure solidification ages but also to postulate eras of accretion of the solar nebula to meteorites, the earth, the planets etc. following the formation processes of these objects. Owing to the lithophilic natures of parent elements above, these methods are impossible to apply to the determination of the solidification ages of iron meteorites. In other words, solidification ages of iron meteorites determined so far are, in the strict sense, ages of silicate or sulphide inclusions, not ages of the iron meteorites themselves. By contrast, ^{187}Re – ^{187}Os is the only pair that can be used to determine solidification ages of iron meteorites because rhenium is the only siderophile parent nuclide with proper half-life (4.35×10^{10} years). However the daughter element osmium has unique chemical and physical properties. For example, all known osmium compounds are easy to evaporate at very low temperatures and then decompose to metal. Once the metal is formed it is almost impossible to vaporize it. For measuring isotopes of elements by mass spectrometry it is necessary to have an appropriate concentration of vapor in the ion source. For this reason a new ionization technique must be developed for the mass spectrometry of osmium, such as field ionization or electron impact with a special ionization chamber.

2.3. *Determination of the half-life of a long-lived nuclide.*

Longer half-life is more difficult to measure, because, radiation is weaker and production rate of daughter nuclide is much lower. For example, 1 kg of rhenium produces only about 10^{-8} g of ^{187}Os per year. For exact measurement of the half-life of such a nuclide one needs a high quality mass spectrometer. At present the accuracy of the half-life of ^{187}Re is still $\pm 20\%$ or worse. Such uncertainty is useless for measuring solidification ages and for further discussion of the formation of meteorites.

2.4. *Accurate and precise measurements of isotopic ratios of elements especially hard to ionize by the usual surface ionization method.*

Examples of such elements are Ge, Zn and Se. It is important to determine the atomic weights of these elements by a calibrated mass spectrometric method. It seems to be necessary to develop a new ionization technique for the determination of isotopic abundances of these elements.

3. Modification of the JMS-D300 Mass spectrometer

Modification of the JMS-D300 mass spectrometer from an organic analysis to isotopic ratio measurement has been performed as follows.

3.1. *Ion Source.*

A new ion source consisting of a surface ionization assembly with control system has been installed. It is interchangeable with the electron impact ion source assembly originally supplied with the mass spectrometer. The new ion source assembly is similar to that used in JMS-05RB by JEOL Ltd, and can be used with both the single and triple filament techniques. The inside of the ion source can be observed through a glass window at front of mass spectrometer.

3.2. *Analyzer Tube.*

In order to reduce mass discrimination, either the analyzer tube had to be made thicker or the accelerating voltage made higher than in the original instrument. The former option has been chosen by JEOL technical staff. As a result, the magnetic pole gap has been changed from 8.5 mm to 12.0 mm.

3.3. *Method of scanning: Range and Speed.*

For isotopic ratio measurements, it is not necessary to have such as high scan rate as mass 50–500 in 0.3 seconds. Rather it is preferable to have slow repetitive scanning over a small definite mass ranges. The most desirable mode is to only measure the intensity of each peak, so that instead of scanning the spectrometer is switched from peak top to peak top. As a first step towards improvement, the scan speed has been slowed down to 20 or 60 minutes for the whole mass range (0–350) and provision made so that a suitable narrow mass range can be selected.

3.4. *Ion Detection System.*

The modified mass spectrometer is equipped with a faraday cage and electron multiplier for the detection of ion currents. With the faraday cage, 10^{-15} to 10^{-8} ampere of ion current can be measured using a vibrating reed electrometer (type TR-8401 made by Takeda Riken Industry Co. Ltd.) and pen recorder. From the outside of vacuum system, the ion detector can be changed from faraday cage to electron multiplier (Cu-BeO 16 stage, made by Hamamatsu Television Co. Ltd.). The detectable ion current is as low as 10^{-18} ampere or less.

3.5. *Vacuum System.*

Instead of an oil diffusion pump, a turbomolecular pump (OV-TH250VG made by Osaka Vacuum Ltd.) is used for in order to increase the pumping speed in the ion

source cavity. This improves efficiency for exchanging and measuring each sample.

4. Results

The functions of the modified JMS-D300 mass spectrometer, true and actual gain of electron multiplier, linearity of vibrating reed electrometer, performance of collector sensitivity, resolving power, mass fractionation and discrimination, problems of impurities *e.g.* hydrocarbon etc., will be described by using examples measuring isotopic ratios of a couple of elements.

4.1. Gain of electron multiplier.

At present, the real gain of the electron multiplier is about 10^5 , which gives actual gain about 10^3 when using the vibrating reed electrometer with grid leak of $10^{10} \Omega$ for faraday cage and $10^8 \Omega$ for electron multiplier.

4.2. Determination of K isotopic ratios.

Potassium is one of the best elements with which to examine sensitivity, resolution, alignment of the new collector assembly and the linearity of the collector system with both faraday cage and electron multiplier because, as was described in a former section, the extremely small peak of ^{40}K is situated only one mass unit away from both of the large peaks ^{39}K and ^{41}K . The results are shown in Table 1 and Fig. 1. In Table 1, among the literature values so far obtained the best measurement assigned

Table 1. Isotopic ratio of K measured by modified JMS-D300.*

Date, amt. sample method, deviation**	39/41	40/41 ($\times 10^3$)	(40/41 ($\times 10^3$)) normalized***
Feb. 23, '82 10 μg Re single, Faraday Δ (‰)	13.974 ± 0.074 8.47 ± 5.31	1.737 ± 0.052 1.56 ± 30.13	1.730 ± 0.052 -2.48 ± 30.13
Mar. 9, '82 10 μg W single, Faraday Δ (‰)	13.729 ± 0.063 -9.21 ± 4.61	1.762 ± 0.013 15.97 ± 8.15	1.770 ± 0.013 20.8 ± 8.15
Mar. 12, '82 0.1 μg W single, Faraday Δ (‰)	13.935 ± 0.068 5.66 ± 4.90	1.742 ± 0.059 4.44 ± 34.05	1.737 ± 0.059 1.56 ± 34.05
Mar. 12, '82 0.1 μg W single, E.M. Δ (‰)	13.751 ± 0.084 -7.62 ± 6.13	1.709 ± 0.031 -14.6 ± 18.5	1.716 ± 0.031 -10.6 ± 18.5
Apr. 26, '82 0.1 μg Re single, E.M. Δ (‰)	13.564 ± 0.071 -21.12 ± 5.25	1.711 ± 0.044 -13.3 ± 26.0	1.729 ± 0.044 -2.88 ± 26.0
Literature: Garner <i>et al.</i> '75	13.8566 ± 0.0063	1.734 ± 0.006	

* Errors quoted with each value are standard deviation of repeated scan.

** Deviations of each data from literature value listed are expressed as follows:

$$\Delta(\text{‰}) = \{(\text{ratio})_{\text{obs.}} - (\text{ratio})_{\text{lit.}} / (\text{ratio})_{\text{lit.}}\} \times 1000.$$

*** The 39/40 data obtained are normalized to literature's data, 13.8566.

by IUPAC-ICAW-SAIC is also listed. From Fig. 1, it can be seen that the effects of the large peaks on ^{40}K cannot be neglected. Because of the compact size of mass spectrometer enough space was not allowed for the Faraday cage and it was made too shallow. Even when a trace amount of sample was measured by electron multiplier the base line is still lowered on both sides of the ^{40}K peak.

4.3. Determination of Ca isotopic ratios.

Calcium has the largest mass range (40–48, $\sim 20\%$ of its mass number) of any element. Furthermore, ^{46}Ca is the smallest stable isotope compared with its main isotope of ^{40}Ca (3/100,000) among all elements. However, ^{46}Ca is situated 2 mass

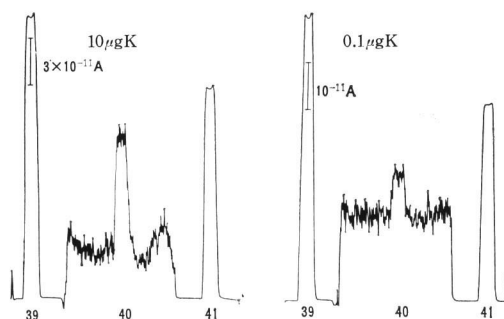


Fig. 1. Examples of K isotopes measured by modified JMS-D300 with Faraday cage.

Table 2. Isotopic ratio of Ca measured by modified JMS-D300.*

Date, methods, etc.	40/44	42/44	43/44	46/44	48/44
Mar. 16, '82	47.302	0.3146	0.06553	0.00151	0.0858
Re triple fil. E.M.	± 0.914	± 0.0042	± 0.00063	± 0.00006	± 0.0014
normalized**	(47.153)	0.3141	0.06543	0.00151	0.0861
$\Delta (\text{‰})^{***}$	$\equiv 0$	6.40	8.75	-5.00	-29.6
Mar. 24, '82	46.078	0.3103	0.06490	0.00190	0.0893
Re single fil. E.M.	± 0.126	± 0.0010	± 0.00036	± 0.00003	± 0.0007
normalized**	(47.153)	0.3139	0.06527	0.00188	0.0873
$\Delta (\text{‰})^{***}$	$\equiv 0$	5.60	6.31	239	-16.1
Mar. 24, '82	—	0.3079	0.06606	0.00154	0.0935
Re single fil. E.M.	—	± 0.0098	± 0.00058	± 0.00009	± 0.0070
normalized**	—	0.3163	0.06693	0.00150	(0.08871)
$\Delta (\text{‰})^{***}$	—	13.5	32.0	-13.2	$\equiv 0$
Literature					
Moore <i>et al.</i> '72	46.480	0.3104	0.0648	0.0017	0.0898
	± 0.087	± 0.0011	± 0.0009	± 0.0005	± 0.0006
Russel <i>et al.</i> '78	47.153	0.31211	0.06486	0.00152	0.08871
	± 0.003	± 0.00002	± 0.00001	± 0.00001	± 0.00002

* Errors quoted with each data are standard deviation of repeated scan.

** The original data are normalized to data taken by Russel *et al.*, (1978).

*** Δ values are same as Table 1.

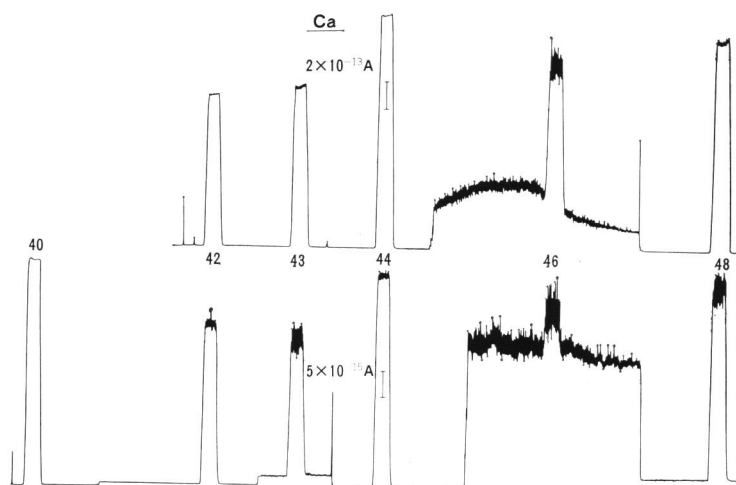


Fig. 2. Examples of Ca isotopes measured by modified JMS-D300 with E.M.

units from the adjacent peaks of ^{44}Ca and ^{48}Ca and 6 mass unit from the main peak of ^{40}Ca . This is again one of the best elements with which to check the performance of the mass spectrometer, *i.e.* source assembly alignment through mass fractionation and discrimination, resolving power and collector assembly alignment and collector system. Results are shown in Table 2 and Fig. 2.

In the Table 2, the most recent literature values of Ca isotopic ratios are also shown. From Table 2, it can be understood how difficult it is to measure Ca isotopic ratios. For ^{46}Ca especially it seems that two values for $^{46}\text{Ca}/^{44}\text{Ca}$ (0.0017 and 0.0015) exist. The present work also obtained two kinds of data: two data of 0.0015 are taken from triple filament technique and the one measured without ^{40}Ca peak, and another data of 0.0019 is from single filament technique. A $^{46}\text{Ca}/^{44}\text{Ca}$ ratio of 0.0015 is rather preferable by the present results, though accepted value by IUPAC-ICAW-SAIC is 0.0017. With the mass spectrometer modified, mass fractionation and discrimination of Ca isotopic measurements were not observed to any great extent. This indicates that the source assembly, ionization chamber, and analyzer parts of this mass spectrometer are satisfactory.

Further, hydrocarbons C_3H_6^+ , $m/e=42$, and C_3H_7^+ , $m/e=43$, which often disturb Ca isotope measurements never appeared. They seem to be separated by the energy focussing feature of the instrument.

4.4. Determination of Cr isotopic ratios.

For Cr isotopic ratio measurements, NBS standard, $\text{Cr}(\text{NO}_3)_3$ is available. Chromium isotopic abundances are ideally distributed, that is, the central isotope, mass number 52, is the most abundant, about 10 times higher than the other 3 peaks. Among the other 3 isotopes, 2 are located on the high mass side at adjacent masses and the other isotope, on the low mass side, is 2 mass units away from the main isotope

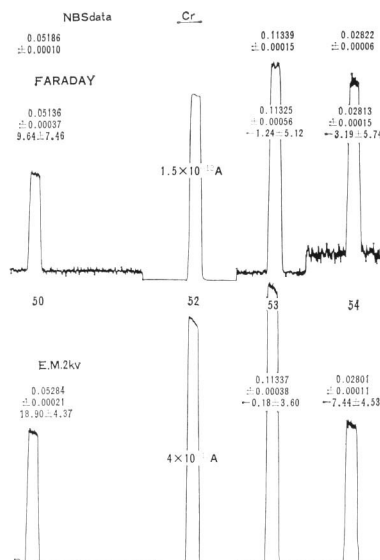


Fig. 3. Examples of Cr isotopes measured by modified JMS-D300. Numbers on each peak are isotopic ratio of each peak versus isotope 52, and Δ value of each ratio against standard values by NBS., which are listed at the top of the figure.

52. This is a convenient distribution for the precise measurement of isotopic ratios. So far only one measurement has been made. The results are shown in Fig. 3, with data calculated from 21 repeated scans, and Δ values from a standard.

5. Conclusion

In all of the studies made so far on the modified JMS-D300 mass spectrometer, the linearity of the electron multiplier and vibrating reed electrometer were found to be almost satisfactory. Impurities such as hydrocarbons could be eliminated in the stage of energy focussing, that is, divergent electrostatic field separate ions from isotopes and from hydrocarbons.

However, the following still need some improvement.

5.1. Ion Source.

In the present work only the surface ionization technique has been examined. Alignment of a triple filament source assembly still involves a couple of problems: Improvement of the materials of filament stem and pinscrews are necessary.

At the begining of this work, before the JMS-D300 was modified, the electron impact ionization technique was also checked. With such experience, one could expect good results using an electron impact source with the machine in its present state but some alternations such as improvement of the ion source temperature control system and minor changes in the ion source cavity may be necessary.

5.2. Collector system.

The most serious problem arose with the faraday cage. Because of the compact size of the JMS-D300, the faraday cage could not be made deeper. In the future electric treatment, such as the addition of an electric shield, or suppressor, for large beams may be considered. Otherwise the analyzer tube must be made thicker to give enough space for a deeper faraday cage just after the magnetic field.

5.3. Scan system.

At present, a constant magnetic scan system is adopted. However the JMS-D300 has already been equipped with a Hall element which controls the magnetic field intensity. Such equipment could be used for a peak switching magnetic scan system in the future.

5.4. Vacuum system.

While the turbomolecular pump appeared to be ideal, clean and fast pumping, an unexpected problem occurred. During surface ionization processes, metals such as W, Re and Ta are heated, especially in triple filament work where the temperature of the ionizing filament rises as high as 2000°C or higher. The vapor of metals evacuated by the pump become a fine condensed metal powder which sinks gradually to the bottom of the pump destroys electric insulation. To avoid this disadvantage it is necessary to add a cold trap between the ion source cavity and turbomolecular pump.

Acknowledgement

Technical improvement work on the JMS-D300 has been carried out by the technical staff of JEOL Ltd. Without their assistance, this work and the following cosmochemical studies on meteorites etc. could not be made.

This work has been financially supported by Grant-In-Aid for Scientific Research in 1980–1982, the Ministry of Education, Science and Culture.

References

- GARNER, E. L., T. J. MURPHY, J. W. GRAMLICH, P. J. PAULSEN and I. L. BARNES, 1975. Absolute isotopic abundance ratios and the atomic weight of a reference sample of potassium. *J. Res. Natl. Bur. Stand. Sect. A*, **79**: 713–725.
- MATSUDA, H., 1968. Mass spectrometer with diverging electric field. *ShitsuryoBunseki (Mass Spectroscopy)*, **16**: 30–36.
- MATSUDA, H., M. NAITO and M. TAKEUCHI, 1974. Advanced virtual image double focussing mass spectrometer. *Advances in Mass Spectrometry*, **16**: 407–412.
- MOORE, L. J. and L. A. MACHLAN, 1972. High accuracy determination of calcium in blood serum by isotope dilution mass spectrometry. *Anal. Chem.*, **44**: 2291–2296.
- RUSSEL, W. A., D. A. PAPANASTASSIOU and T. A. TOMBRELLO, 1978. Ca isotope fractionation on the earth and other solar system materials. *Geochim. Cosmochim. Acta*, **42**: 1075–1090