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Advancement of isotope separation for the production of reference standards

K. P. Carney · J. J. Horkley · C. A. McGrath ·
A. J. Edwards · J. E. Davies · G. C. Knighton ·
J. D. Sommers · J. J. Giglio

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Abstract Idaho National Laboratory (INL) operates a mass separator that is currently producing high purity isotopes for use as internal standards for high precision isotope dilution mass spectrometry (IDMS). In 2008, INL began the revival of the vintage 1970s era instrument. Advancements thus far include the successful upgrading and development of system components such as the vacuum system, power supplies, ion-producing components, and beam detection equipment. Progress has been made in the separation and collection of isotopic species including those of Ar, Kr, Xe, Sr, and Ba. Particular focuses on ion source improvements and developments have proven successful with demonstrated output beam currents of over 10 µA ^{138}Ba and 350 nA ^{134}Ba from a natural abundance Ba source charge (~2.4 % ^{134}Ba). In order to increase production and collection of relatively high quantities (mg levels) of pure isotopes, several improvements have been made in ion source designs, source material introduction, and ion detection and collection. These improvements have produced isotopes of high purity (>98 %) and in quantities in the tens of micrograms per run. The instrument and results for pure isotope production for IDMS standards will be presented.

Keywords Isotope dilution mass spectrometry · Mass separator · Barium isotopes

Introduction

Isotope dilution mass spectrometry (IDMS) is one of the most accurate and precise methods in use for quantitative chemical analysis [1–3]. The application of IDMS can provide measurement with uncertainties below 1 %, thus making it an excellent method for reference material characterization and trace element determinations [2, 4]. The premise of IDMS is to determine an unknown isotopic concentration from a high precision isotope ratio measurement using an isotope spike with well known isotope abundance and concentration. The unknown solution is mixed with a spike solution, the ratio of the unknown relative to the spike is measured and the unknown concentration is determined from the spike concentration, abundance of the isotopes in the sample and spike and measured ratio. Typically, the spike is a material with a certified isotope abundance and concentration, and does not

K. P. Carney · J. J. Horkley (✉) · C. A. McGrath ·
J. E. Davies · G. C. Knighton
Idaho National Laboratory, PO Box 1625, MS-6180, Idaho Falls,
ID 83415-6150, USA
e-mail: jared.horkley@inl.gov

K. P. Carney
e-mail: kevin.carney@inl.gov

C. A. McGrath
e-mail: christopher.mcgrath@inl.gov

J. E. Davies
e-mail: jacob.davies@inl.gov

G. C. Knighton
e-mail: gaven.knighton@inl.gov

A. J. Edwards
Idaho National Laboratory, PO Box 1625, MS-3740, Idaho Falls,
ID 83415-6150, USA
e-mail: andrew.edwards@inl.gov

J. D. Sommers · J. J. Giglio
Idaho National Laboratory, PO Box 1625, MS-6150, Idaho Falls,
ID 83415-6150, USA
e-mail: james.sommers@inl.gov

J. J. Giglio
e-mail: jeffrey.giglio@inl.gov

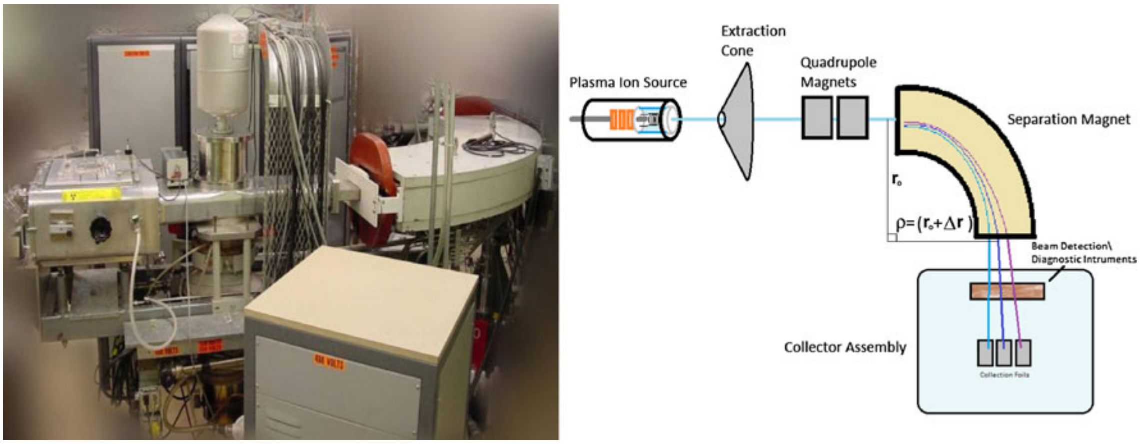

Fig. 1 Mass separator collector and magnet (*left*) and schematic (*right*)

have isotopes that are found in the unknown or if present the confounding isotopes are at low concentrations. For Ba assay, a commercially available certified ^{134}Ba standard (Isoflex USA) can be acquired, however, only the abundance of ^{134}Ba is certified at 88.1 % ± 0.4 %. The isotopes of ^{135}Ba, ^{136}Ba, ^{137}Ba and ^{138}Ba at abundances of 5.36, 1.12, 1.07 and 4.26 % respectively, are stated without uncertainties; the ^{132}Ba and ^{130}Ba have no stated abundances. Similarly, Oak Ridge National Laboratory Isotopes Division provides an 84 % enriched ^{134}Ba material, but it is not certified, and like the Isoflex standard has ^{135}Ba, ^{137}Ba and ^{138}Ba at significant abundances. This is clearly not ideal, as all isotopes should have stated uncertainties and certified concentrations. The spike should consist of a single isotope of the element to be measured and be absent from the sample, thus decreasing the corrections required that add to the uncertainty in the determination. For this work, the separation of and production of ^{134}Ba with an isotopic abundance greater than 99 % is a preliminary objective for the operation of the Idaho National Laboratory (INL) mass separator with the goals of providing a certified pure ^{134}Ba spike.

Experimental

The separator has three major components: a magnet, an ion source coupled to a quadrupole electrostatic ion focusing lens, and a collection/detection system that consists of six Faraday cup detectors, a 2-D spatial profile monitor and a moving wire detector that monitors beam resolution. The magnet is a 5 kg, 59 inch radius, 90° sector type manufactured by Scanditronix. This is sometimes referred to as a Scandinavian instrument, and was commonly used from the 1940s through the 1960s [5–8].

The system vacuum is maintained with three turbomolecular pumps equipped with “oil-free” scroll pumps that provide a combined pumping speed of approximately 1,250 l/s. Vacuum pressures in the range of 4.0×10^{-5} Pa are achieved routinely. Several new power supplies (Amptek) were installed to operate the ion source components: the filament operates at 20 V and 30 A; the oven operates at 10 V and 60 A; and the anode operates at 150 V and 4 A. The high voltage acceleration and extraction supplies have a range from 0–60 to 0–50 kV, respectively. A photograph showing the magnet and a basic layout of the separator is provided in Fig. 1.

The ion beam detection/collection system was designed to optimize beam collection onto target foils that could be easily installed and removed for harvesting isotopes while providing simultaneous detection of each ion beam [9]. The linear dispersion of ions in the mass range of 130–138 is approximately 1 amu/cm; the mass resolution is approximately 1320. High purity isotopes can be produced in that range. A challenge faced subsequently is the rigor in maintaining high isotopic purity (>99 %) in the end product [10]. Because of this, special attention is given not only to ion beam optimization for high resolution, but also to careful product handling after the isotopes are separated onto target foils in the collector end of the separator.

Ion source advancements

There are several variations in ion source designs found throughout the literature [11–13]. The ion sources used at INL over the past year are hybrids based on a modification to a Colutron Q-100 effusion type ion source. The source is shown in Fig. 2, and utilizes a graphite oven heating element to heat a boron nitride sample holder (4 mm diameter, 20 mm length). This component is mounted external to the quartz-walled plasma chamber that contains the filament and a second sample holder made from tantalum (4.9 mm diameter, 25 mm length). The internal sample holder has small inlet and discharge hole (0.5 mm) for the

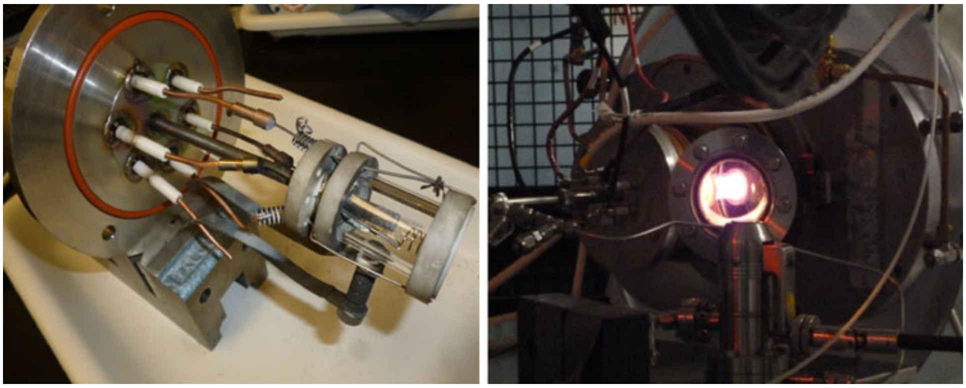

Fig. 2 Modified Colutron Q-100 with external oven chamber, tantalum charge holder, and custom o-ring flange

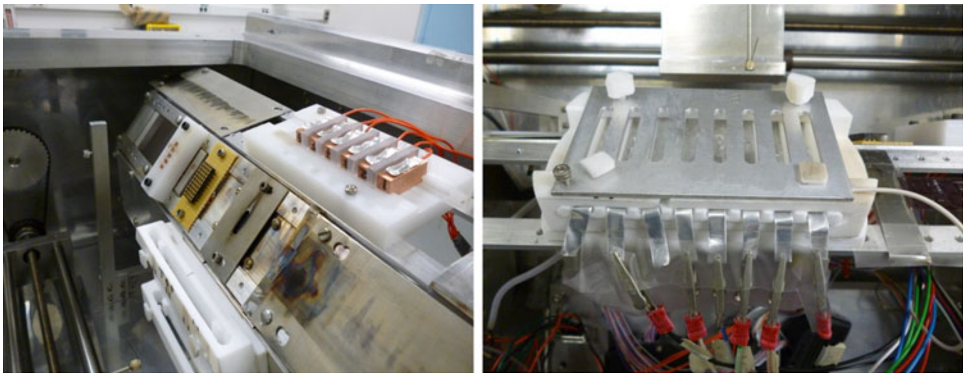

Fig. 3 Collector arrangement: (1) Five cup vertical positioning array, (2) 50 pin/cup beam profiling monitor (3) 6-isotope collector with removable collection foils (*left*) and Teflon-mounted collector setup with aluminum screen and removable collection foils (*right*)

introduction of gases into the ionization region. Combined, the holders have an approximate volume of 0.7 cm^2. The Conflat flange typically used for the Q-100 was replaced with a Viton gasket-sealed flange with copper electrical feed-throughs that can easily be installed and removed. This source design is simple and has modular components that are easily replaced. It provides expected beam currents, run times, and accommodates a wide composition of source materials. The source successfully vaporized Ba metal and has attained temperatures that vaporized barium oxide and strontium chloride. The source also provides sufficient heat to chemically react mixtures of aluminum and BaO, $Ba(CO_3)_2$, or $Ba(NO_3)_3$, that reduce the Ba to form elemental Ba vapor and Al_2O_3. Direct vaporization of Ba metal provides the longest most stable runs and will be discussed in further detail.

Beam diagnostics and collection

Beam collection/detection and diagnostic equipment includes several Faraday cup arrays that are used to determine ion beam shape and spatial dimensions, intensity, and isotopic dispersion (Fig. 3). The detectors are mounted on a rotating hexagonal assembly that permits three faces to rotate into the focal plane position. Mounted on individual faces are six Faraday cup detectors each with independent analog meter readout and dedicated 12-bit A/D convertor (Keithley Instruments) for real time data acquisition. A single Faraday cup detector coupled to a separate meter is mounted on a separate face. Masses of interest are focused onto respective Faraday cups by adjusting the magnet current to scan the isotopes across a single Faraday cup detector. Next to this detector is a spatial beam profile monitor. The 2-D beam profile monitoring consists of a 50 pin, 5 × 10 matrix of Faraday cup array detectors and is used to optimize beam focus. The single Faraday cup detector and 2-D monitor are shown in Fig. 3. A scanning wire beam profile monitor is used to maximize peak shape/resolution and monitor magnet drift.

The six simultaneous Faraday cup collector assemblies are mounted to a Teflon base plate (Fig. 3) that can easily be removed for pre-cleaning in an acid bath. An aluminum mask positioned in front of the foils aids to segregate particular isotopes on individual foils (Fig. 3). This mask reduces cross contamination and provides electron suppression to reduce fraudulent current.

High purity (99.9999 %) aluminum foils (Alfa Aesar) are cleaned by soaking in 6–8 m Optima® nitric acid, then mounted in a sliding “well”. This design provides easy installation and removal with minimal foil handling. Before collection, the ion beam is optimized using a quadrupole focusing lens, a vertical steering component,

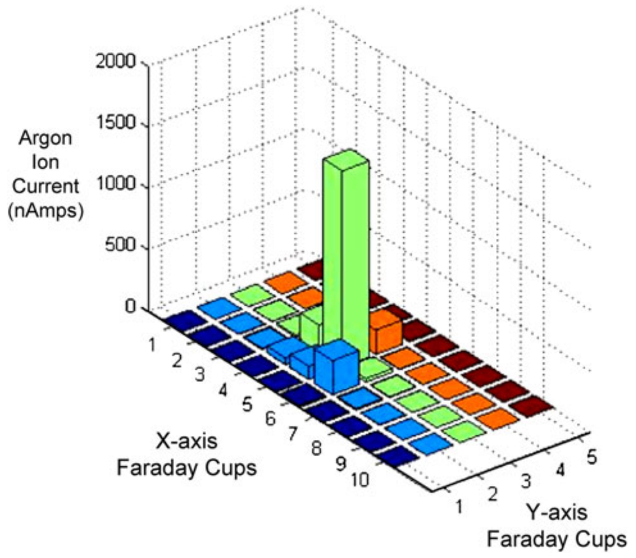

Fig. 4 Graph showing the beam 2-D spatial profile. Profile monitor base (*x* and *y-axis*) is ~13 × 25 mm. *Z-axis* represents argon ion beam current in nA

and by adjusting acceleration and extraction voltages. These operating voltages typically range from 35–40 to 5–10 kV, respectively. To aid in maintaining focus consistency between tests, a viewport was also installed on the ion source mounting flange so the source can be aligned with the extractor prior to startup. After a collection the foils are removed and soaked in 6 m nitric acid in order to leach the deposited isotope from the surface. An aliquot is taken from the nitric acid/product solution and analyzed by ICP-MS for total isotopic concentration and purity.

Results

Stable ion currents with the modified source design have exceeded 10 µA for run times greater than 20 h. Peak currents have exceeded 15 µA; however, at peak currents exceeding approximately 30 µA, the beam width broadens significantly. This degrades the instrument resolution and isotopic purity. This observation is consistent with published results [14].

Beam focus is important to ensure that each separated ion beam is collected within the area of each Faraday cup collector. A plot showing the focus of the ^{138}Ba beam current monitored with the 2-D beam spatial profile monitor is provided in Fig. 4. The majority of the beam resides in an area approximately 3 × 3 mm^2; that approximates the area of each Faraday cup collector.

The results from two tests with Ba metal are provided in Table 1. The individual cups corresponding to each respective mass are listed in the first column, with the isotopic masses measured in each respective cup shown in the successive rows. The expanded uncertainty for the measured quantities shown in Table 1 is on the order of 2 % ($k = 2$). This uncertainty encompasses instrument repeatability and calibration. The results from the ^{132}Ba

Table 1 Separator collection: ICP-MS results showing purity and recovered products

Isotope	Mass Ba collected (ng)							Purity (%)
	^{130}Ba	^{132}Ba	^{134}Ba	^{135}Ba	^{136}Ba	^{137}Ba	^{138}Ba	
Run 1								
Cup								
^{132}Ba	<0.6	*19*	0.6	0.9	0.8	1	6.5	65
^{134}Ba	<0.6	<0.6	*470*	3.7	0.4	<0.6	<1.9	98
^{135}Ba	<0.6	<0.6	4.4	*1,280*	4.3	<0.6	<1.9	99
^{136}Ba	<0.6	<0.6	<0.6	7.3	*1,540*	6.6	5.4	98
^{137}Ba	<0.6	<0.6	<0.6	<0.4	9.1	*2,170*	44.7	97
^{138}Ba	<0.6	<0.6	<0.6	<0.4	<0.1	12.8	*8,857*	99
Run 2								
Solution								
^{130}Ba	*440*	<0.6	1.2	2.8	2.6	3.4	23.4	92
^{132}Ba	<0.6	*440*	1.7	2.7	3.7	<0.6	<1.9	97
^{134}Ba	<0.6	<0.6	*5,130*	111.5	84.3	24.3	97.6	94
^{135}Ba	<0.6	<0.6	24.1	*8,570*	170.3	33.1	70.2	96
^{136}Ba	<0.6	<0.6	2.6	55.1	*7,710*	176.6	242.2	94
^{137}Ba	<0.6	<0.6	0.7	7.2	52	*13,030*	1246.9	90
^{138}Ba	<0.6	<0.6	<0.6	0.7	4	57.7	*25,290*	99

cup show that 19 ng ^{132}Ba were collected and trace quantities of ^{134}Ba, ^{135}Ba, ^{136}Ba and ^{138}Ba are present in a ratio that doesn't correlate with the natural abundance of Ba, indicating that the isotopes were introduced during the separation or handling of the foils. Approximately 470 ng ^{134}Ba were collected on the ^{134}Ba cup with 3.7 ng ^{135}Ba and 0.4 ng ^{136}Ba. The purity of the ^{134}Ba and ^{136}Ba isotopes collected is over 98 %. The ^{135}Ba and ^{138}Ba collected on the respective cups each had purities greater than 99 %. From this data it appears that the contamination of foils due to post-run handling was sporadic, but maintained at acceptable levels; the resultant isotopic purity was on average approximately 95 % and often exceeded 99 %.

In total, about 75 µg of barium isotopes were separated and collected in two runs. From the collected and input masses of Ba, a source efficiency of 0.01 % was estimated, with the majority of Ba being plated to the surface of the source. The ratio of the mass of the major isotope collected on each cup relative to the mass collected on the ^{137}Ba cup roughly approximated the ratios expected for Ba at natural abundance, indicating that self-sputtering of the target material is not evident for masses less than mass ^{137}Ba. The mass collected at the ^{138}Ba cup for each run is markedly depressed relative to the mass expected based on the ^{137}Ba mass. This reflects an alignment problem of this cup relative to isotope spacing (dispersion).

Discussion

The mass separator at INL is providing isotopes with high purity levels around 98–99 %. This purity level is considered satisfactory to produce a high purity isotope standard provided sufficient ^{134}Ba of equivalent purity can be isolated. A goal is to produce greater than 500 µg of enriched ^{134}Ba (>98 %) and to provide an accurate certified abundance and assay value for all measurable isotopes. Advancements in the source have provided the foundation for longer runs with higher throughput and efficiency. Greater mass output and purity are nonetheless the focus of current work. Surfaces on the collector other than foils are being contaminated with scattered product sometimes referred to as "wings", producing significant losses that could be minimized if the beam was better focused [10]. This can also be a source of cross-contamination.

Conclusions

High purity barium isotopes are being produced using a renovated mass separator with purities greater than 98 %. Modifications to a commercially available source resulted in stable ion beam currents for periods exceeding 20 h at currents that provide excellent isotope resolution. Isotope collection and foil handling techniques appear adequate to produce products that would be considered highly useful for IDMS.

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