The production of ultra-high purity single isotopes or tailored isotope mixtures by ICP-MS

M. Liezers^{a,*}, O.T. Farmer III^a, M.P. Dion^a, M.L. Thomas^a, G.C. Eiden^a

^a*Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA, 99352, USA*

Abstract

We report the development and testing of a collector arrangement for quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS) that for the first time has been used to isolate small quantities of highly enriched (>99.99%) single isotopes, with deposition rates >10 ng hr⁻¹. The collector assembly replaces the standard instrument detector allowing for implantation with simultaneous monitoring of the incident ion current. Even under zero bias implant conditions, low energy (<10 eV) ion collection efficiency was observed to be very high 99%. ¹⁵¹Eu ion currents of 0.1–0.5 nA were collected on a simple, planar foil without resorting to any type of cup configuration. Recovery of the enriched isotope from such foils is much simpler than from a more complex cup configuration. High rejection of adjacent mass isotopes was demonstrated by selectively implanting ¹⁶⁷Er, then using laser ablation ICP-MS imaging to confirm the absence of any co-implanted ¹⁶⁶Er or ¹⁶⁸Er. The important analytical possibilities of this new approach to isotope ratio measurement, tracer purification, and radiation measurements are discussed.

Keywords: Isotope Enrichment; ICP-MS; Ion Implantation; Isotope Dilution; Laser Ablation

1. Introduction

Isotope enrichment by mass spectrometry is an old technique proposed as early as the 1920s, but only with the practical isolation of ²³⁵U from ²³⁸U by

*Corresponding author

Email address: martin.liezers@pnnl.gov (M. Liezers)

4 Nier et al. was the method potential realized [1]. Their subsequent demon-
 5 stration that ^{235}U was the principal fissionable isotope of uranium, led to
 6 the mass spectrometry being adopted on a massive scale for the Manhattan
 7 Project [2]. In the following decades, mass spectrometry was entirely dis-
 8 placed for bulk U enrichment in favor of more efficient gaseous diffusion [3]
 9 and gas centrifuge [4] technologies, but has remained in use on a small scale
 10 using Calutron type instruments for the production of enriched isotopes of
 11 other elements excluding U on the mg–g–kg scale. Relatively few of these
 12 instruments are in routine operation so access to the isotopically enriched
 13 product of this type of mass spectrometer (MS) is restricted; principally
 14 owing to their large size and the limited market for enriched isotopes that
 15 remains mostly research based [5, 6]. To produce single isotopes on the gram
 16 scale requires the use of high ion currents, typically μA –mA, and relatively
 17 high operating pressures, $\approx 1 \times 10^{-5}$ mbar. For magnetic sector-based instru-
 18 ments these conditions lead to low abundance sensitivity and limited isotopic
 19 purity - rarely $>99.5\%$. While these large instruments can produce enriched
 20 material at the gram level, most analytical MS measurements performed us-
 21 ing enriched isotopes and tracers display detection limits of femtograms to
 22 picograms, therefore the presence of other unwanted isotopes of that element
 23 in the enriched spike at even nanogram to picogram levels can become a
 24 severe hindrance. In addition, the range of enriched isotopes available and
 25 their purities are fairly restricted and the cost of tailoring isotopic compo-
 26 sition of an element for some specific application is usually cost prohibitive.
 27 In recent years a small number of publications have appeared applying the
 28 same approach to selectively implanting organic molecules by mass spectrom-
 29 etry [7, 8], although preserving their structure and chemical functionality has
 30 remained problematic.

31 In 1996 Hu and Houk [9] reported the deposition rates of the mono-
 32 isotopic element ^{165}Ho onto a graphite target using ICP-MS. They performed
 33 a series of ^{165}Ho depositions at different biases (-10 to -4500 V) applied to the
 34 graphite target, observing significant deposition rates ranging from 2×10^{12} –
 35 5×10^{12} ^{165}Ho ions s^{-1} . This equates to deposition rates of up to 1.4 ng s^{-1}
 36 or nearly $5 \mu\text{g hr}^{-1}$, obtained using an input ^{165}Ho solution concentration
 37 of 1000 ppm. Variations in the ion deposition rate as a function of the ion
 38 kinetic energy were observed and interpreted as changes in the ion stopping
 39 mechanism in the shift from low to high ion kinetic energies. They mention
 40 the idea of creating altered isotopic layers, but no evaluation of isotopic purity
 41 achieved by this approach was subsequently reported and the concept of using

42 ICP-MS to create isotopically enriched materials has so far not been actively
43 developed.

44 ICP-MS in its many forms has been widely adopted for both elemental
45 and isotopic analysis with combined ion generation and detection efficiencies
46 currently reaching up to 2–3% for some large magnetic sector instruments
47 under low signal conditions [10, 11]. However, this level of performance is
48 probably not sustainable for mass separated ion currents much above 10nA.
49 For quadrupole ICP-MS the combined ion generation and detection efficiency
50 is usually much lower, <0.01%, but this still equates to incident single isotope
51 ion currents after the quadrupole of ≈ 200 pA or higher using a solution
52 containing 10 ppm of the element where the target isotope displays a modest
53 abundance (25% or higher). While higher elemental concentrations can be
54 introduced into the ICP-MS, nonlinearity will often result due to space-charge
55 limitations occurring within the plasma sampling interface and ion optics. As
56 the bulk of the total ion current (≈ 10 μ A) [12] in these regions is carried by
57 the primary plasma gas ion (Ar^+), argon based molecular ions and various
58 molecular ion combinations of H, C, N and O, these ultimately limit the
59 maximum rate at which an enriched isotope can be accumulated using this
60 approach. The atmospheric ICP ion source is very robust and can turn most
61 elements in the periodic table into positive ions quite efficiently from either
62 solid or liquid aerosols. As a result of this sample introduction flexibility and
63 high sensitivity, ICP-MS instruments have become very widely available.

64 For the most common quadrupole based units the superior abundance
65 sensitivity of the mass filter alone suggests they can achieve far higher levels
66 of isotopic purity than Calutrons or gaseous diffusion techniques if ng– μ g
67 quantities of these highly enriched materials is adequate for the target appli-
68 cation. While the production of such small quantities is not without potential
69 isotopic contamination challenges, the amounts of enriched material actually
70 required for tracer spikes in most analytical inorganic mass spectrometry
71 methods can range from pg to μ g, well within practical reach of the ICP-MS
72 production method proposed in this paper. Typical adjacent mass abundance
73 sensitivity specifications for a quadrupole ICP-MS based on 0.8 amu peak
74 width is <1 ppm on the low mass side of the peak and <0.5 ppm on the
75 high mass side. Expressed another way <1 cps would be detected at M-1
76 when the count rate on mass M is 1×10^6 cps and <0.5 cps at M+1. Abun-
77 dant sensitivity at masses ± 2 amu or further away are extremely difficult to
78 measure but should be <<0.01 ppm and, unlike magnetic sector mass analyz-
79 ers, quadrupole mass filters display no significant degradation in abundance

sensitivity even at relatively high operating pressures up to 5×10^{-5} mbar.

In this paper we describe the design of an isotope collection assembly for a quadrupole ICP-MS and results obtained in the production of nanogram quantities of highly enriched ($\approx 99.99\%$) ^{151}Eu isotope from a diluted Eu standard with a natural Eu isotopic distribution. The results include: incident ion current measurement, implant efficiency, isotopic purity, and (Laser Ablation) LA-ICP-MS imaging of the ^{151}Eu distribution on a copper foil substrate. The adjacent mass rejection of ^{166}Er and ^{168}Er from ^{167}Er is also demonstrated and the exciting new potential applications of this bench top approach of isotope enrichment are discussed.

2. Implant Design

The work we describe was performed using a model PQ-Excell (VG Elemental Ltd, Winsford, England) quadrupole ICP-MS with no major modifications made to the ICP ion source, plasma-sampling interface, primary ion optics, and quadrupole mass filter. The instrument employed a simultaneous pulse counting/analog multiplier model AF-214 (SGE Inc., Austin, TX, USA) and the initial enriched isotope collector design made to mimic the basic shape and the exact length of the electron multiplier to allow for easy substitution. The main body of the collector was machined from PEEK (PolyEther Ether Ketone) with a simple hollow copper cup attached to the end. The 11.0 mm aperture of the copper cup was set to match the grounded front aperture of the multiplier with a cup depth of 20.0 mm. While the shape of the collector resembles a Faraday cup, no suppressor grid or other electrodes were employed in front of the cup to reduce potential electron or ion scattering losses. Subsequent experiments demonstrated that electron and/or ion scattering loss for the elements studied were $< 5\%$, suggesting the cup geometry was unnecessary because high implant yields were obtained using a thin (0.05 mm) planar copper foil (30 mm x 24 mm) placed over the cup aperture. The use of the planar foil geometry simplified chemical recovery of the enriched isotope and reduced potential isotopic contamination by minimizing the weight of the substrate. Laser ablation imaging subsequently also confirmed the implant region was well defined and centrally located within the dimensions of the cup aperture allowing the use of an even smaller implant foil with dimensions of 10 mm x 10 mm. As a result all the implant experiments reported were conducted using electrically conductive adhesive backed copper foil (1181 3/4X18, 3M/Interconnect Solutions, USA), that is

116 normally used for general radio frequency screening applications. The ad-
117 hesive backing also serves to hold the collection foil in place in the vertical
118 collector orientation. The presence of rare earths including Eu were detected
119 in the copper foil by LA-ICP-MS, but the low background levels (low ng
120 gram⁻¹) contributed only a minute level of background isotopic contamina-
121 tion.

122 Preceding implantation, the surface of the copper foil was cleaned with a
123 mildly abrasive cleaning pad, thoroughly rinsed in a flow stream of 18 MΩ
124 deionized water, rinsed with high purity isopropyl alcohol and finally dried
125 in a flow stream of argon or nitrogen gas. The foil was then cut to length
126 and mounted on the implant assembly before being inserted into the ICP-
127 MS. No degradation of the base ($<1 \times 10^{-7}$ mbar) or operating ($\approx 8 \times 10^{-7}$
128 mbar) pressures of the ICP-MS was observed using these materials. Electrical
129 connection to the implant was made using one of the three existing high
130 voltage coaxial feed-thrus normally used to supply the multiplier voltages.
131 Figure 1 is a photograph of the prototype collector assembly with a copper foil
132 affixed to the collector. Once inserted into the vacuum chamber the implant
133 foil was located within 1 mm of the quadrupole exit lens aperture (6.0 mm
134 diameter) to minimize the effects of ion beam spread. Other modifications
135 included widening the bias range of the quadrupole exit lens to ± 500 V
136 and relocating the multiplier preamp board that has to remain attached to
137 the internal instrument controller for the ICP-MS software to operate mass
138 control of the quadrupole normally. The quadrupole peak width was set to
139 standard instrument settings of 0.8 amu at 5% peak height, that yields an
140 abundance sensitivity of <1 ppm at M-1 and <0.5 ppm at M+1. Typical
141 quadrupole pole bias settings were in the range 0 to -2 V. When operating the
142 isotope collecting foil at ground potential, ion implant current measurements
143 were made using a model 6517B electrometer (Keithley Instruments Inc.,
144 Cleveland, OH, USA).

145 3. Implant Operation

146 All elemental solutions employed in this work were prepared from high
147 purity single element 1000 ppm concentration standards (Inorganic Ventures,
148 Christiansburg, VA, USA). These elemental standards are used in routine
149 elemental analysis and all display natural isotopic abundances. All standard
150 dilutions were prepared by weight using a 2% HNO₃ diluent prepared from

Figure 1: A photograph of the prototype ion collector assembly mounted on the ICP-MS detector flange.

high purity concentrated HNO_3 (Optima Grade, Fisher Scientific, Canada) and high purity $18.2 \text{ M}\Omega$ deionized water.

Preliminary implant measurements were conducted using 10 ml of a 10 ppm solution of Eu prepared as described previously. The Eu solution was aspirated in the ICP-MS using the standard liquid sample introduction system, comprising a concentric nebulizer and a Peltier cooled impact bead spray chamber held at 3°C . The ICP operating power was set to 1350 W. As the sample introduction system displays a relatively low efficiency with only $\approx 0.02 \text{ g min}^{-1}$ of solution actually entering the plasma with an uptake rate of 0.3 ml min^{-1} the waste can be effectively recycled without any loss in analyte concentration, ensuring several hours of continuous operation consuming only small volumes (5–10 ml) of solution. Re-cycling the solution in this way improves overall efficiency. High efficiency nebulization methods are widely available that employ more aggressive desolvation methods, but the solution sample can only be passed once through these systems as the waste produced is analyte depleted $\approx 10\%$ compared to the input stock concentration.

Measured collector-implant noise current with the ICP-MS in operate state and the quadrupole mass set to 220 amu was $< +0.05 \text{ pA}$. When set to the mass of ^{151}Eu the implant ion current attained a maximum steady-state value of $+160 \text{ pA}$ after some minor re-optimization of the ion lenses. In general, maximum ion current was achieved with plasma conditions and ion lens settings very similar to those employed for routine high sensitivity analysis using the electron multiplier. It was observed that the quadrupole exit lens yielded maximum ion current with a bias voltage of -30 V , and ion

175 current was effectively reduced to background noise levels if the exit lens
 176 bias voltage was set to +20 V, indicating the typical ion energy of most
 177 ions exiting the quadrupole is $<+10$ eV. Based on the measured implant
 178 current, the average number of incident ^{151}Eu ions was calculated to be:
 179 $1.60 \times 10^{-10} / 1.602 \times 10^{-19}$ (electron charge) that equals 9.99×10^8 ions s^{-1} .
 180 When the incident ion flux is normalized for the natural abundance of ^{151}Eu
 181 and to a solution concentration of 1ppm, there was good agreement with the
 182 typical instrument mid-high mass sensitivity observed for a mono-isotopic
 183 element with the standard electron multiplier ion detection system of $\approx 2 \times 10^8$
 184 cps ppm $^{-1}$. The expected accumulation rate of ^{151}Eu would then be given
 185 by: $(I_S \times A_R) / N_A$. Where I_S is the number of incident ions per second,
 186 A_R is the Relative Atomic Weight and N_A is the Avogadro Constant. For an
 187 ^{151}Eu ion current of 160 pA this equates to a deposition rate of 2.5×10^{-13} g
 188 s^{-1} , or 0.9 ng hr^{-1} from the input solution concentration of 10 ppm.

189 The implant incident ion current response was measured over a range of
 190 elemental concentrations (0–1000 ppm) and for a range of elements at very
 191 low and mid – high mass regions. Figure 2 shows the ion current response
 192 for a) ^{10}B and b) ^{151}Eu as a function of elemental concentration, the ^{10}B ion
 193 current response differs quite markedly from that of ^{151}Eu . The ^{10}B ion cur-
 194 rent response remained linear up to 1000 ppm concentration, although the
 195 magnitude of the ion current is about an order of magnitude lower than that
 196 observed for ^{151}Eu . In part this can be explained by the lower abundance of
 197 ^{10}B (19.8%), its relatively high ionization potential and the reduced sensitiv-
 198 ity displayed by ICP-MS towards low-mass elements caused by the processes
 199 of collisional scattering and space charge repulsion in the plasma sampling
 200 interface and ion optics before the quadrupole. As a result even using a
 201 solution containing 1000 ppm B, the deposition rate would only be ≈ 0.16
 202 ng hour^{-1} for ^{10}B . Aspirating more complex mixtures of different elements
 203 affects the onset at which non-linearity in the current response versus con-
 204 centration occurs, particularly for low mass elements, but describing these
 205 effects is outside the primary focus of this particular publication. ^{151}Eu ion
 206 current increases linearly with concentration up to 100 ppm, but then grad-
 207 ually tapers off and does not reach an asymptotic value at 1000 ppm. The
 208 current linearity limit for ^{151}Eu was in the range 1–2 nA, although at 1000
 209 ppm the ion current reached 5.8 nA, which equates to a deposition rate of
 210 32.7 ng hr^{-1} . Increased Eu ion currents up to 10 nA were obtained by retun-
 211 ing the ion optics under the higher ion current conditions, offsetting some of
 212 the space charge effects responsible for limiting the ion current.

Figure 2: Incident ion current response for (a) ^{10}B and (b) ^{151}Eu as a function of element input concentration (ppm).

213 4. Experimental Results

214 4.1. Imaging the isotopically enriched ^{151}Eu

215 The first experiment undertaken was to establish that a high degree of iso-
 216 topic isolation could be achieved by quadrupole ICP-MS on a simple copper
 217 foil target. During this first experimental run with a clean copper foil sub-
 218 strate ^{151}Eu was implanted from a solution of 10 ppm Eu for 250 minutes.
 219 The total accumulated implant charge measured by the electrometer over
 220 this period was 1.40×10^{-6} C, which equates to a nominal mass of 2.19 ng
 221 of ^{151}Eu . The ICP-MS was switched into standby state, followed by venting
 222 to remove the implant assembly and the copper foil target. The implanted
 223 target was transferred to a laser ablation cell with the intention of imaging
 224 the distributions of both the ^{151}Eu and ^{153}Eu isotopes. The ablation was
 225 performed using a model 266Macro (Merchantek Inc., CA, USA) coupled to
 226 a model X2 quadrupole ICP-MS (ThermoFisher Inc., Winsford, England).
 227 Laser wavelength was 266 nm, ablation fluence of 4.5 J cm^{-2} , repetition rate
 228 10 Hz, spot size $100 \mu\text{m}$ and scan speed $50 \mu\text{m s}^{-1}$. The laser was set to
 229 ablate across the implant as a series (25) of horizontal line scans 24 mm long
 230 with a line spacing of $500 \mu\text{m}$, while the ICP-MS recorded the response at
 231 masses 151 and 153 in time resolved analysis mode. The ICP-MS data was
 232 exported into Microsoft Excel and compiled into a three dimensional x-y plot
 233 with the analyte intensity plotted on the vertical axis.

234 Figure 3 shows the spatial distribution of the quadrupole implant of ^{151}Eu
 235 on the copper foil and figure 4 the corresponding image for ^{153}Eu . Compar-

ing the distribution of both isotopes it is clear that ^{153}Eu was very effectively rejected with only trace level counts detected for this isotope; the level observed is consistent with natural Eu background in the copper implant substrate with no discernible structure to its distribution. A single ^{153}Eu inclusion with a maximum intensity of 400 counts was detected, but this is the typically observed behaviour for trace level elements that are not spread through a sample homogeneously when using laser ablation. The far higher level of ^{151}Eu counts ($\approx 1.25 \times 10^5$ cps at peak) confirms only the target isotope was implanted. The implant $^{151}\text{Eu}/^{153}\text{Eu}$ ratio based on total counts (12094177/2928) accumulated in the main ablated area was 4130, suggesting the ^{151}Eu isotopic purity is now 99.976%, as compared with the natural $^{151}\text{Eu}/^{153}\text{Eu}$ isotopic ratio of the starting material of 0.916. For comparison, the isotopic distribution of the starting solution (10 ppm natural Eu) used to prepare the implant was ^{151}Eu 47.81% and for ^{153}Eu 52.19%. Had the accumulation time been extended this would have continued to enhance the ^{151}Eu isotopic purity. The shape of the ^{151}Eu distribution was rather odd, forming an asymmetric bimodal pattern that may be related to the ion beam being horizontally pinched by the asymmetric focusing of the deflection optics just prior to entering the quadrupole. Other researchers imaging ion beams exiting from a quadrupole have reported more star-like distributions that align more closely with the open central axis of the quadrupole and the four gaps between the rods [13, 14]. The other possibility highlighted in the work by Short et al.[15] demonstrated elongation of the exit beam could be caused by ions entering the quadrupole slightly off axis.

4.2. ^{151}Eu implant yield versus accumulated charge

One initial concern with the simple planar foil implant geometry and low energy ions was possible loss of the target isotope ^{151}Eu atoms caused by atoms failing to attach to the implant substrate, despite being neutralized during the initial impact with the foil. Hu and Houk [9] possibly observed this effect for low energy ^{165}Ho ions being implanted onto a graphite target in their ICP-MS experiments. In addition, as no bias was applied to the implants to minimize any measurement errors induced by bias current leakage, it would not be unreasonable to suspect that ^{151}Eu atom attachment to the foil could be both inefficient and weak. As a result while the electrometer would register the neutralizing charge transfer to the incident ion, the measured total charge would over estimate the total ^{151}Eu atoms accumulated during the implant process. To test the efficiency of this process a series of

Figure 3: The laser ablation ICP-MS image of ^{151}Eu on the copper foil after implantation.

Figure 4: The corresponding laser ablation ICP-MS image of ^{153}Eu on the copper foil after implantation of only ^{151}Eu .

implants were prepared for which the total ^{151}Eu accumulated charge deposited on each was accurately measured and the predicted weight of ^{151}Eu calculated from the total accumulated charge. The implants were then dissolved and analyzed by isotope dilution ICP-MS to measure the actual mass of ^{151}Eu deposited on the copper foil target.

After preparing three implants with differing amounts of ^{151}Eu ranging from 2.7–108 ng, estimated from accumulated charge measurement, the adhesive backing on each foil was carefully removed using a cotton swab soaked in iso-propyl alcohol, followed by rinsing in 18.2 M Ω deionized water. The central 11 mm diameter of each copper foil that encompasses the implanted area was removed, taking care not to touch the implanted surface during the process. Each cut out foil (≈ 20 mg) was accurately weighed to 0.01 mg resolution and dissolved in 4 ml of 50% v/v high purity HNO_3 in separate cleaned and tared test tubes. Following dissolution the copper solutions were diluted up to a volume of 10 ml using 18.2 M Ω deionized water and the total weight of each sample stock solution recorded. The $^{151}\text{Eu}/^{153}\text{Eu}$ ratio of all three implant solutions were analyzed both un-spiked and spiked with natural Eu ($^{151}\text{Eu}/^{153}\text{Eu} = 0.915$). The level of the Eu spike added to each of the three solutions was set to match the expected ^{151}Eu level from each of the respective implant solutions after further dilution to reduce the copper concentration to 5 ppm or 10 ppm. Indium was also added as an internal standard. The results of the isotope dilution experiments are summarized in Table 1. The ^{151}Eu yield results suggest that for the combination of Eu with a the copper foil target, implant efficiency is high and measurement of the total charge accumulated is a reliable guide to the weight of the purified isotope attached to the foil target.

4.3. Study of adjacent mass leakage using Er isotopes

Contamination of the target enriched isotope with those from adjacent masses is of particular concern in mass spectrometry as these isotopic impurities can limit spiking levels and reduce measurement accuracy. Eu has two natural occurring isotopes that are separated by two mass units, therefore contamination mainly originates from trace levels of natural Eu in the copper foil target. To study possible isotopic leakage on adjacent masses i.e. m-1 and m+1, the element Er was selected for implant experiments where the isotope ^{167}Er was implanted on the copper foil target with the intention of rejecting the adjacent Er isotopes ^{166}Er and ^{168}Er . All three isotopes display broadly similar natural abundances (^{166}Er (33.50%), ^{167}Er (22.87%) and

Table 1: A comparison between ^{151}Eu implant weights estimated from total charge measurement versus % yield estimated by isotope dilution (ID) ICP-MS.

Implant	^{151}Eu Implanted (ng) deposited by charge	% Yield measured ID
1	2.762	94.0
2	7.08	110.0
3	108	98.6
	Average	100.8
	SD	8.23
	% Rsd	8.16

^{168}Er (26.97%)), making this a good selectivity demonstration of the isotopic purification potential of this approach.

A solution concentration of 10 ppm Er with a natural isotopic distribution was employed for the implant experiments performed under similar ICP-MS operating conditions used for the Eu implants. Quadrupole mass peak width was 0.8 amu. The measured ^{167}Er ion current was ≈ 95 pA and after 217 minutes the total charge accumulated was $1.01 \mu\text{C}$, that equates to a theoretical mass of 1.75 ng implanted. The ICP-MS was vented and the copper foil target removed from the mount and placed in the ablation cell of the LA-ICP-MS system. An area of 14.78 mm x 14.72 mm of the copper foil target was ablated during the imaging experiments comprised of 60 horizontal ablation lines. Laser spot size was set to $240 \mu\text{m}$, laser ablation fluence to 5 J cm^{-2} , line spacing $250 \mu\text{m}$, laser firing rate 5 Hz with a laser scan rate of $100 \mu\text{m s}^{-1}$. The ICP-MS responses for the isotopes ^{166}Er , ^{167}Er and ^{168}Er were recorded in time resolved analysis mode with a dwell period of 0.5 seconds/isotope during the ablation.

Figures 5, 6 and 7 shows the imaged Er isotopic distributions on the copper foil target for ^{166}Er , ^{167}Er and ^{168}Er respectively. There is no discernible distribution for the Er isotopes ^{166}Er and ^{168}Er on the copper foil target, indicating that both isotopes are very effectively rejected as ions and that there is no sign of these isotopes leaking through the mass spectrometer as neutral atoms co-depositing on the target. The ICP-MS does register some single point spikes for the rejected Er isotopes they are of low intensity < 500 cps maximum and randomly distributed, with an average background of < 10 cps indicating trace contamination of the copper with natural Er. For the selected isotope ^{167}Er , the distribution observed was very similar to that

336 shown earlier for the ^{151}Eu implant, forming an asymmetric bimodal distri-
 337 bution reaching a peak intensity of 300,000 cps, clearly demonstrating that
 338 highly selective isotopic enrichment was achieved. The natural isotope ratios
 339 for Er are $^{167}\text{Er}/^{166}\text{Er} = 0.681$ and for $^{167}\text{Er}/^{168}\text{Er} = 0.854$, in comparison
 340 with implant Er ratios of $^{167}\text{Er}/^{166}\text{Er} = 1682$ and $^{167}\text{Er}/^{168}\text{Er} = 2139$.

341 5. Discussion

342 The experimental results presented demonstrate that micro scale iso-
 343 topic purification can be readily accomplished using moderately sensitive
 344 quadrupole ICP-MS instrumentation. Such equipment is widely available in
 345 any analytical laboratory likely to be performing elemental analysis and iso-
 346 tope ratio measurements by mass spectrometry. The modifications required
 347 to the equipment are simple and the source materials readily available in
 348 the form of solution concentration standards with natural isotopic distri-
 349 butions for most elements. Even the use of the source material in a solid
 350 form is possible using laser ablation and, while not reported in this paper,
 351 ion current measurements have been successfully conducted for specific iso-
 352 topes using that method of sample introduction. This flexibility in sample
 353 introduction methods for most elements allowed by using the ICP ion source
 354 offers considerable benefits over the Calutron or gas diffusion-centrifuge ap-
 355 proaches. For Calutrons the chemical form, even the methods of atomization
 356 and ionization vary according to the element being processed. While for gas
 357 diffusion-centrifuge approaches the element feed must be converted into a
 358 gaseous form that is stable at modest temperatures. The primary limits on
 359 the ICP-MS method are set by the space-charge limit of the ion optics and
 360 instrument sensitivity versus mass response, that favors mid and high masses
 361 over low masses (<40 amu). Even so, the ICP-MS employed in this work dis-
 362 played a linear response for the exit ion beam of the quadrupole up to 2 nA.
 363 That would equate to deposition rates for mid-high mass elements of 6-18 ng
 364 hour $^{-1}$. Potential deposition rates up to 90 ng hour $^{-1}$ would be possible by
 365 operating with ion currents of 10 nA where the quadrupole exit ion current
 366 becomes non-linear with respect to input concentration. However, sustained
 367 operation might become difficult, with problems caused by gradual block-
 368 ing of the skimmer aperture in the plasma-sampling interface. Operating at
 369 these higher ion currents might reduce implant efficiency through sputtering
 370 losses, although this could be overcome by adopting the angled pocket col-
 371 lector design adopted on Calutrons [16, 17]. There may also be an increase

Figure 5: The laser ablation ICP-MS image of ^{166}Er on the copper foil after implantation of only ^{167}Er .

Figure 6: The laser ablation ICP-MS image of ^{167}Er on the copper foil after implantation.

Figure 7: The laser ablation ICP-MS image of ^{168}Er on the copper foil after implantation of only ^{167}Er .

in the probability of either neutral atoms or ions of unwanted isotopes being co-implanted with the target isotope. These possibly adverse high ion current effects would require further investigation.

Careful measurements of low energy ^{151}Eu ion deposition onto a copper foil demonstrated virtually 100% ion collection efficiency. This may be a result of the fortuitous combination of Eu on Cu, as other workers [9] studying ^{165}Ho ion deposition on graphite observed lower deposition rates for low energy ^{165}Ho ions, compared to those with higher ion energies. Actual Ho ion deposition efficiency could not be estimated as the incident ^{165}Ho ion current was not measured. However the literature results highlight that deposition efficiency for ions of different elements may be quite variable depending on the composition of the implant substrate and ion energy conditions under which implantation takes place. At high ion energies sputtering of deposited material by incoming ions must also be considered as a possible factor in the reduction of ion collection efficiency.

The quadrupole ICP-MS modified for this study dates from the late 1990s, displaying an ion transmission efficiency of $\approx 0.007\%$ for mid-high mass elements, where ICP-MS tends to display the highest sensitivity. Some of the latest bench top ICP-MS instruments display improved efficiencies of $\approx 0.035\%$. While this might seem very poor, the standard aqueous sample introduction systems found on most instruments allow the stock solution to

393 be recycled to exhaustion. So, a 10 ml solution can be made to last 6-8 hours
394 because the amount of aerosol entering the plasma is only 0.02–0.03 g min⁻¹.
395 This effectively allows a 10-fold increase in the amount of an isotope that can
396 be deposited from the same volume compared to only using a single solution
397 pass.

398 During these initial studies the deposition area of the enriched isotope
399 was fairly large (≈ 6 mm x 6 mm) with little obvious focusing observed by
400 varying the bias voltage on the exit lens. Shrinking the deposition area would
401 improve isotopic purity as it would require less of the implant substrate to
402 be processed to recover the purified isotope. While the quadrupole in this
403 spectrometer has rf-only pre-filters, there are no rf-only post filters that could
404 reduce exit aperture divergence in the ion beam that in turn might shrink
405 the deposition area. One could reduce the aperture of the quadrupole exit
406 lens, currently 6 mm in diameter, although this may reduce the ion current
407 hitting the implant. Sufficient space is available within the detector chamber
408 to add additional ion optics to focus the ion beam onto the implant surface.
409 While neither of these potential improvements have been investigated yet,
410 experiments applying a negative bias to the implant have shown the implant
411 area can be reduced, but at the expense of making measurement of the ion
412 current and accumulated charge more difficult, as a result of bias voltage
413 leakage.

414 All the results reported here are focused on enrichment and implantation
415 of one single isotope of an element at a time, as this highlights the single mass
416 limitation of the quadrupole mass filter. The possibility exists of implanting
417 multiple isotopes of an element to create a tailored isotopic distribution suit-
418 able for some specific application like mass bias correction in isotope ratio
419 measurements. For a quadrupole based ICP-MS this is probably best per-
420 formed sequentially, one mass at a time. While mass peak jumping is easily
421 programmed through the software to cover multiple isotopes, if this involves
422 skipping over unwanted isotopes slight transmission of these isotopes will
423 occur scanning both up and back down the mass range, as there is no gating-
424 off of the ion beam during this process in commercial ICP-MS instruments.
425 However, this feature could easily be added by applying a positive high volt-
426 age bias to either a lens or the quadrupole on an instrument designed for
427 this application. The use of magnetic sector multicollector ICP-MS is a pos-
428 sibility to selectively collect multiple isotopes of an element simultaneously,
429 however these remain considerably more expensive and therefore less readily
430 available than quadrupole based ICP-MS. In addition the isotopic purity ob-

Table 2: Certified isotopic distribution of Pu in CRM-131 in 1981.

Pu Isotope	238	239	240	241	242	244
Atom %	0.005	0.034	0.677	0.092	1.325	97.867

431 tained from a magnetic sector maybe slightly inferior owing to their usually
 432 poorer abundance sensitivity performance compared to quadrupole based
 433 systems.

434 Isotopic purification of some radioactive tracers is another area where this
 435 approach could make a significant impact. For example ^{244}Pu is widely used
 436 in the quantification of ^{239}Pu and ^{240}Pu , but all ^{244}Pu available contains sig-
 437 nificant traces of all the Pu isotopes from ^{238}Pu to ^{242}Pu . Table 2 highlights
 438 the isotopic distribution of this certified reference material CRM-131 (New
 439 Brunswick Laboratory Argonne, IL, USA). By applying this isotopic purifica-
 440 tion approach it should be possible to achieve ^{244}Pu isotopic purity $>99.999\%$,
 441 greatly reducing the atom % of all the lower mass isotopes given their mass
 442 spacing from the target ^{244}Pu and the additional benefit gained from there
 443 being no natural background for this element in the implant substrate. That
 444 should make recovery of the highly purified ^{244}Pu very straight-forward. This
 445 process could also be applied to other currently unobtainable rare isotopes
 446 like ^{236}Np , that may be present at low levels in some ^{237}Np waste streams
 447 produced during nuclear fuel reprocessing, as no other long-lived isotopic
 448 tracer for accurate quantification of ^{237}Np in environmental samples exists.

449 One final benefit of this isotope selective method that has been described
 450 is its application to improving radiation measurements [18]. As mass spec-
 451 trometry is inherently selective, the technique can effectively be used as a
 452 sample processing tool to isolate some target isotope from unwanted inter-
 453 ferences that may also be present in a sample. Conventionally, this would
 454 require wet chemistry separations, but using ICP-MS as the sample process-
 455 ing tool it should be possible to prepare implants with the target isotope
 456 largely isolated from a sample matrix. The sample could be presented in ei-
 457 ther liquid or solid form. While quantification would be challenging, using
 458 this approach it may be adequate for rapid screening applications where the
 459 presence of a particular isotope may target that sample for further more
 460 rigorous analysis. For α -spectrometry we used the ICP-MS to implant trace
 461 levels of ^{241}Am and compared the α -energy spectrum with those produced by
 462 the standard methods of -sample preparation of electro-deposition and direct
 463 solution stippling [19, 20, 21]. The ICP-MS implanted ^{241}Am α -spectrum dis-

464 played considerable improvement in energy resolution compared to samples
 465 with similar levels of activity produced using the two conventional meth-
 466 ods highlighted. This improvement in energy resolution is attributed to the
 467 purity and low ion energy surface deposition achieved by ICP-MS, whereas
 468 conventional preparation methods partially bury the ^{241}Am atoms with other
 469 impurity atoms. It should also be possible to apply this method of sample
 470 preparation to ultrathin film sources (nm- μm thick) and to enhance aspects
 471 of β and γ radiation measurements.

472 6. Conclusion

473 This work shows for the first time that quadrupole ICP-MS can be mod-
 474 ified to generate small quantities (ng- μg) of a single isotope of an element
 475 with extremely high isotopic purity ($>99.99\%$). High rejection of adjacent
 476 mass isotopes was readily demonstrated with Er. Collection efficiency for Eu
 477 appears to be very high, approaching 100% even using a simple planar cop-
 478 per foil target, based on accumulated charge-isotope dilution measurements.
 479 While overall ion loss from the solution source to the implant substrate are
 480 large, equivalent to $\approx 0.005\%$ ion transmission efficiency, elemental concen-
 481 tration standards are cheap and recycling the waste from the sample intro-
 482 duction system improves efficiency to 0.05–0.5%, at the penalty of extending
 483 deposition time. The use of more sensitive ICP-MS instruments that are cur-
 484 rently available would improve efficiency to $\approx 1\%$ or higher. The potential ap-
 485 plications of this development should be considerable for mass spectrometric
 486 isotope ratio measurements, where highly enriched spikes or tailored isotope
 487 distributions could easily be prepared using this widely available bench top
 488 instrumentation.

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Graphical Abstract

Quadrupole Inductive Coupled Plasma – Mass Spectrometer