Microcalorimeter Q-spectroscopy for rapid isotopic analysis of trace actinide samples

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Abstract

We are developing superconducting transition-edge sensor (TES) microcalorimeters that are optimized for rapid isotopic analysis of trace actinide samples by Q-spectroscopy. By designing mechanically robust TESs and simplified detector assembly methods, we have developed a detector for Q-spectroscopy of actinides that can be assembled in minutes. We have characterized the effects of each simplification and present the results. Finally, we show results of isotopic analysis of plutonium samples with Q-spectroscopy detectors and compare the results to mass spectrometry.

Keywords: microcalorimeter, Q spectroscopy, nuclear forensics

Introduction

Microcalorimeter Q-spectroscopy is a powerful tool for isotopic analysis of trace actinide samples^{1,2}. By embedding a radioactive sample in the detector, a calorimetric measurement of the total nuclear decay energy (Q) for individual

decays can be made. Because every decay can be measured, the technique is ideally suited to analysis of trace samples where maximum detector efficiency is necessary. In this paper we present a simplified Q-spectroscopy detector design that is optimized for rapid assembly. The detector can be assembled with simple equipment, and only minimal changes are made to the sample. The material to be analyzed is encapsulated within an absorber, in which the energy of the radioactive decay products is deposited as heat. The absorber is coupled to a superconducting transition-edge sensor, which acts as a very sensitive thermometer to measure the temperature change of the absorber that corresponds to an individual radioactive decay. Microcalorimeter Q-spectroscopy is unaffected by isobaric interferences such as $^{238}\text{Pu}/^{238}\text{U}$ and $^{241}\text{Pu}/^{241}\text{Am}$ that present a challenge for mass spectroscopy. Q-spectroscopy is a non-consumptive measurement technique, unlike mass spectrometry, so samples can be reanalyzed by other means if necessary. Compared to alpha spectrometry, the Q-spectrum shows increased energy peak separation for a given sample. These properties make microcalorimeter Q-spectroscopy uniquely suited to analysis of trace actinide samples.

Robust transition-edge sensors

Previous superconducting transition-edge sensors (TESs) have relied on a fragile silicon nitride membrane to provide thermal isolation of the sensor^{3,4}. We have developed an improved design that uses much more robust silicon springs instead of a silicon nitride membrane (figure 1). The thermal conductance of the silicon springs is designed to match that of the silicon nitride membrane of the

previous design, and so the properties of the sensor are preserved. The silicon-spring TES is well suited to Q-spectroscopy because its mechanical strength simplifies the process of bonding the absorber to the TES. Absorbers can be removed and re-attached to the TES, allowing the TES to be used for the measurement of many different samples. Only an inexpensive absorber foil is required for measurement of a new sample, while the TES can be a semi-permanent part of the spectrometer system.

Figure 1: Robust transition-edge sensor die uses silicon springs instead of a fragile silicon nitride membrane for thermal isolation of the sensor. In the center region that is isolated by the silicon springs, the transition-edge sensor can be seen on the left side, and a bismuth pad for absorber attachment can be seen on the right side.

Absorber preparation

Preparing an absorber for Q-spectroscopy consists of two major steps: deposition of radioactive material, and encapsulation of that material. Gold has

many properties that make it a good choice for an absorber material. As a noble metal, it is compatible with many techniques of radioactive material deposition and encapsulation. Gold is resistant to most chemicals used in the dissolution and electrodeposition of actinides. Its resistance to oxidation and ability to diffuse enable gold foils to be diffusion welded to provide excellent encapsulation of material within an absorber. Fabrication of the absorber is simplified by the malleable and ductile nature of gold. The high conductivity of gold yields good thermal uniformity within the absorber, which contributes to detector performance. Gold has a high atomic number (Z) and is effective in stopping radiation. A 15 μm thick gold foil is sufficient to stop most actinide decay radiation. Although gold has a higher heat capacity than other commonly used microcalorimeter absorber materials like tin, its excellent radiation stopping ability means that gold absorbers can be made small enough to have an acceptably low heat capacity for the detector to retain good energy resolution. Because only a small amount of gold is needed, approximately 2 mg for each absorber, the cost of gold does not present an obstacle to the use of this technique.

To date, we have focused on deposition of radioactive material that starts in an acid solution. An acid solution is a form that enables convenient handling and the option of chemical separation of contaminants. A deposit can be made quickly and easily by drying a drop of acid solution. The dried drop method produces a non-uniform metal salt deposit that has a maximum thickness comparable to the decay radiation path lengths (figure 2). The measured Q-spectrum for a dried drop deposit shows two energy peaks for a single isotope (figure 3, left). We attribute this energy

95 peak splitting to energy thermalization that differs between the metal salt deposit
96 and the gold absorber¹.

97 Radioactive material in solution can also be electrodeposited⁵. The Q-
98 spectrum of an electroplated deposit shows one energy peak per isotope (figure 3,
99 right). This is consistent with the above explanation of energy peak splitting. An
100 electrodeposited sample is thin compared to the path length of the decay radiation,
101 so that gold is the dominant environment in which decay radiation is absorbed.
102 However, electrodeposition is a much more difficult and time-consuming procedure
103 than droplet drying. Additionally, the electrodeposition process is known to change
104 the elemental composition of a sample due to the variation in electrochemical
105 potentials of deposition among different actinides in the solution. For
106 electrodeposition to be useful for analysis of samples that contain multiple
107 actinides, tracers must be added to characterize and correct for this problem. These
108 complications discourage the use of electrodeposition in the preparation of samples
109 for rapid isotopic analysis of mixed actinide samples by Q spectroscopy.

110 We have investigated the possibility of improving the measured Q spectra of
111 dried drop deposits by mechanical manipulation (“kneading”) of the absorber to
112 fracture salt crystals in the deposit and increase its homogeneity. Starting with a
113 dried drop deposit within a folded gold foil, the foil was then folded twice more to
114 form a square that was one-quarter of its original size. A vise was used to press the
115 foil so that it deformed to approximately its original size. The folding and pressing
116 procedure was repeated three times to ensure that the deposit was homogenized.
117 Results are presented in the following section.

118

119 Figure 2: Dried drop of sample

120 020414, $^{240}\text{Pu}/^{239}\text{Pu}$ in nitric acid

121 solution on gold absorber foil. The

122 material is concentrated around the

123 perimeter of the deposit in salt crystals

124 that measure 5-15 μm .

125

126

127

128 Figure 3: (Left) Measured Q-spectrum of a sample made by drying a drop of

129 ^{238}Pu in nitric acid solution. Two energy peaks are observed for ^{238}Pu . (Right)

130 Measured Q-spectrum of an electrodeposited ^{238}Pu sample shows a single energy

131 peak.

Encapsulation of radioactive material by diffusion bonding within gold foils has been used to produce Q-spectroscopy absorbers with good results^{1,2,6,7}. While this technique yields good encapsulation, there are some drawbacks that reduce its utility for a practical analytical technique. A typical procedure reported in the literature for diffusion bonding is to clamp the gold foils together and heat for 16 hours at 400 °C⁶. The long time requirement is unsuitable for rapid analysis of samples. We have found that good bonding can be achieved with shorter times, as low as one hour, when the clamping pressure is sufficient to slightly deform the gold foils. This shorter time requirement may be acceptable for an analytical technique. However, the high temperature required to enable a reasonable rate of gold diffusion risks changing the composition of the sample. For example, plutonium metal and compounds such as plutonium nitrate are expected to convert to plutonium dioxide when heated in air to 400 °C⁸. A future goal of this research is to use microcalorimeter Q spectroscopy to measure the isotopic composition of an unprocessed actinide-containing single particle. When measuring an as-collected particle, it is advantageous to preserve its chemical form for future analysis by other methods, so a room-temperature encapsulation method is useful.

We have shown that folding a gold foil in half to cover the radioactive deposit provides sufficient encapsulation for a Q-spectroscopy measurement. The top and bottom layers of the foil do not need to be bonded together. The high thermal conductivity of the gold allows the absorber to thermalize quickly enough that a quantity of energy deposited in either the top or bottom layer of the absorber will produce the same signal in the TES. This simple folding method can be done in

under a minute at room temperature, and is suitable for a rapid analytical technique where only minimal changes to the sample can be tolerated.

Attachment of absorber to TES

Epoxy has been successfully used for attachment of the absorber to the TES for gamma, alpha, and Q-spectroscopy microcalorimeters^{1,2,3,4}. For Q-spectroscopy, the sample is embedded within the absorber, and so a method by which the absorber can be removed from the TES and replaced is useful. We have demonstrated two detector configurations where the absorber can be replaced. The first configuration (figure 4, left) uses a single TES die on which the absorber is mounted with an indium cold-welding method. The TES die has an evaporated bismuth pad on which is placed a small piece of indium powder. At room temperature, the gold absorber and TES die are pressed together with hand pressure with the indium powder between them. The indium deforms and cold-welds to both the bismuth pad and the gold foil. The large amount of deformation in the indium powder ensures that the native indium oxide layer is disrupted to expose indium metal at the bond interfaces. This method of absorber attachment can be completed in under a minute, and has been shown to produce strong, reliable bonds. Indium cold-welding has an important advantage over soldering in that it does not require any flux or controlled atmosphere to create a reliable bond. Because indium and bismuth form an eutectic alloy with a melting temperature of 72 ° C, the absorber can be easily removed by heating the detector to slightly above this temperature on a hot plate and lifting off the absorber.

The second configuration (figure 4, right) uses separate die for the TES and absorber. Gold wire bonds provide a thermal connection between the absorber and the TES. The wire bonds can be easily removed from the TES die by pulling with tweezers, and new wire bonds can be added many times. The two-die configuration is more complex than the single-die detector, but for long-term use it may have an advantage. In the event of imperfect sample encapsulation, the separate absorber die reduces the probability of contamination on the TES die that may cause systematic errors in subsequent measurements.

Figure 4: (Left) The single-die detector configuration has the absorber bonded to a pad on the TES die. (Right) The two-die configuration has a separate absorber die on the left that is thermally connected by gold wire bonds to the TES die on the right.

Results and comparison of detector assembly processes

To compare the effects of different detector assembly processes, we prepared two samples from NIST-traceable standard nitric acid solutions that contain ^{240}Pu and ^{239}Pu in different ratios. Sample 012214 has a $^{240}\text{Pu}/^{239}\text{Pu}$ activity

ratio of approximately 1:4, while sample 020414 has a ratio of approximately 4:1. These samples give two interesting cases to test the ability of Q spectroscopy to measure the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio. For sample 012214, the tail of the low-intensity ^{240}Pu peak overlaps with the high-intensity ^{239}Pu peak. Sample 020414 gives a more challenging scenario where the tail of the high-intensity ^{240}Pu peak overlaps with the low-intensity ^{239}Pu peak.

These samples were deposited by droplet drying onto 2mm x 1mm x 15 μm gold absorber foils that were then used to create three detector variations for each sample. The total quantity of Pu in each sample was 170-350 pg, with a total activity of 0.8-1.7 Bq. The first detector variation, indicated by A and C, is a type that we have previously reported¹. In this type, the deposit was encapsulated in a gold foil that was folded in half, pressed, and diffusion welded for 16 hours at 400 °C. The absorber was then attached to the TES die with Stycast 1266 epoxy. The second detector variation (B and E) is a simplified design that can be assembled in minutes. The dried deposit was encapsulated within a gold foil that was folded in half, with no diffusion welding. The absorber was attached to the TES die by indium cold welding. A final detector variation (C and F) was tested to determine the effects of mechanical manipulation (“kneading”) to break up the dried deposit within the absorber. The absorbers on detectors B and E were removed and kneaded following the procedure reported earlier. They were then reattached to the TES die with an indium cold weld bond to create detectors C and F.

Results for these measurements are shown in tables 1 and 2, with corresponding spectra in figure 5. Measurement times range from 16-28 hours. All

of these spectra show two energy peaks per isotope, which is consistent with previous measurements of dried drop deposits. Each spectrum was fit with four two-tailed Bortels functions to account for the two peaks for each of the two isotopes⁹. For each spectrum, the four peak functions were constrained to have equal resolution and tailing parameters, as well as equal peak separation and intensity ratios for the two peaks from each isotope. The low values of reduced χ^2 for the fits indicate that although split Q-peaks from dried drop deposits add complexity to the spectrum, the entire spectrum can be well-described by the fit functions and isotopic analysis can be performed. The $^{240}\text{Pu}/^{239}\text{Pu}$ ratios measured by Q spectroscopy were within 3.5% of the mass spectrometry results for sample 012214. Sample 020414 was expected to be a more difficult case to measure by Q spectroscopy because tail of the high-intensity ^{240}Pu peak overlaps with the low-intensity ^{239}Pu peak. For this sample, the measured $^{240}\text{Pu}/^{239}\text{Pu}$ ratios deviate from the mass spectrometry result by up to 10.8%. Further work is required to understand the systematics of this analysis.

Kneading the absorber to break up the dried deposit (detector variations C and F) appears to have a very significant effect on the energy resolution and the distribution of counts in the peaks for each isotope. The energy resolutions determined from the Gaussian component FWHM of the Bortels fit for detectors C and F, 1.08 and 1.06 keV respectively, are the best that we have observed for Q-spectroscopy detectors. Comparing spectra B and C, and E and F, kneading the absorber appears to shift counts to the higher energy peak for each isotope. We attribute this change to the fact that kneading fractures large salt crystals in the

deposit, and increases the fraction of decay events where energy is absorbed and thermalized in the gold foil of the absorber instead of the dried deposit.

Table 1: Sample 012214 Measurement Results

ID	Absorber Attachment	Deposit Encapsulation	Measured Time (hr)	Gaussian FWHM (keV)	Fit χ^2_{red}	Mass Spec. m_{240}/m_{239}	Q Spec. m_{240}/m_{239}	Δ (%)
A	Epoxy	Diffusion weld	16.0	2.14	2.2	0.08690 (45)	0.0839 (13)	-3.5
B	Indium	Folded foil	19.8	2.44	1.3	0.08690 (45)	0.0844 (16)	-2.9
C	Indium	Kneaded foil	20.0	1.08	1.5	0.08690 (45)	0.0873 (16)	0.5

Table 2: Sample 020414 Measurement Results

ID	Absorber Attachment	Deposit Encapsulation	Measured Time (hr)	Gaussian FWHM (keV)	Fit χ^2_{red}	Mass Spec. m_{240}/m_{239}	Q Spec. m_{240}/m_{239}	Δ (%)
D	Epoxy	Diffusion weld	28.0	2.21	3.1	1.2053 (15)	1.195 (23)	-0.9
E	Indium	Folded foil	19.8	2.54	1.0	1.2053 (15)	1.109 (36)	-8.0
F	Indium	Kneaded foil	20.0	1.06	1.9	1.2053 (15)	1.336 (32)	10.8

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248 Figure 5: Measured Q spectra of $^{240}\text{Pu}/^{239}\text{Pu}$ samples 012214 (A, B, C) and 020414

249 (D, E, F) with different detector assembly methods. Each spectrum is fit with four

250 Bortels functions to account for the two observed energy peaks for each isotope. A

251 black line indicates the total fit function, with the ^{239}Pu component in red and ^{240}Pu

252 component in blue. Details are listed in tables 1 and 2.

Conclusions and future work

We have studied different detector assembly processes in order to develop microcalorimeter detectors for rapid isotopic analysis of actinide samples by Q spectroscopy. We have developed a simplified detector design that can be assembled in minutes and shown that it can be used to determine the $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio of a sample. Experiments on mechanical manipulation, or kneading, of absorbers with dried drop deposits have shown very promising results. Future experiments will continue to investigate the concept of reducing grain size in a dried drop deposit to eliminate observed peak splitting and optimize Q spectroscopy measurement results. We also plan to test the ability of microcalorimeter Q spectroscopy to measure single particles rather than samples from solution, with the ultimate goal of determining the isotopic composition of an as-collected, unprocessed actinide-containing single particle.

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