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Measurement of ^{63}Ni and ^{59}Ni by accelerator mass spectrometry using characteristic projectile X-rays

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Abstract

The long-lived isotopes of nickel (^{59}Ni, ^{63}Ni) have current and potential use in a number of applications including cosmic radiation studies, biomedical tracing, characterization of low-level radioactive wastes, and neutron dosimetry. Methods are being developed at LLNL for the routine detection of these isotopes by AMS. One intended application is in Hiroshima dosimetry. The reaction ^{63}Cu(n,p)^{63}Ni has been identified as one of a small number of reactions which might be used for the direct determination of the fast neutron fluence emitted by the Hiroshima bomb. AMS measurement of ^{63}Ni ($t_{1/2}$ = 100 y) requires the chemical removal of ^{63}Cu, which is a stable isobar of ^{63}Ni. Following the electrochemical separation of Ni from gram-sized copper samples, the Cu concentration is further lowered to $< 2 \times 10^{-8}$ (Cu/Ni) using the reaction of Ni with carbon monoxide to form the gas $Ni(CO)_4$. The $Ni(CO)_4$ is thermally decomposed directly in sample holders for measurement by AMS. After analysis in the AMS spectrometer, the ions are identified using characteristic projectile X-rays, allowing further rejection of remaining ^{63}Cu. In a demonstration experiment, ^{63}Ni was measured in Cu wires (2–20 g) which had been exposed to neutrons from a ^{252}Cf source. We successfully measured ^{63}Ni at levels necessary for the measurement of Cu samples exposed near the Hiroshima hypocenter. For the demonstration samples, the Cu content was chemically reduced by a factor of 10^{12} with quantitative retention of ^{63}Ni. Detection sensitivity (3σ) was ~ 20 fg ^{63}Ni in 1 mg Ni carrier ($^{63}\text{Ni}/\text{Ni} \approx 2 \times 10^{-11}$). Significant improvements in sensitivity are expected with planned incremental changes in the methods. Preliminary results indicate that a similar sensitivity is achievable for ^{59}Ni ($t_{1/2} = 10^5$ y). Initial work has been undertaken on the application of this isotope as a biomedical tracer in living systems.

1. Introduction

The long-lived isotopes of nickel have current and potential use in a number of applications including biomedical tracing, cosmic radiation studies, characterization of low-level radioactive wastes, and neutron dosimetry. The present work was undertaken to explore the sensitivity that could be achieved for the detection of these isotopes by accelerator mass spectrometry (AMS) using the available facilities at Lawrence Livermore National Laboratory.

The first goal was to demonstrate the feasibility of measuring ^{63}Ni ($t_{1/2}$ = 100 y) produced in copper samples via the ^{63}Cu(n,p)^{63}Ni reaction. The intended application, part of a collaborative effort discussed also in Refs. [1,2], is a determination of the fast neutron fluence produced by the Hiroshima bomb, which would address significant discrepancies in Hiroshima dosimetry [1,3–6]. Resolution of these discrepancies has important implications for radiation protection standards [7] and estimates of radiation induced cancer risk [8], both of which are largely based on data on the Hiroshima and Nagasaki survivors.

A second aim of this work was to develop the longer-lived isotope ^{59}Ni ($t_{1/2} = 1.1 \times 10^5$ y) as a tracer for bioscience applications. These experiments commonly use ^{63}Ni as the tracer with detection by liquid scintillation counting. Given the long half-life of ^{59}Ni and the sensitivity of AMS, experiments using ^{59}Ni could potentially be performed using 1000 times less radioactivity than similar experiments using ^{63}Ni.

For the Hiroshima measurements, sensitivity requirements are determined by the expected activation level and by the limited quantity of available samples. For copper samples exposed near the hypocenter of the Hiroshima blast, the current (1996) ^{63}Ni activity is expected to be $\sim 1.3\text{–}1.5 \times 10^7$ ^{63}Ni atoms per gram of copper (= 1.5 fg g^{-1} = 3 mBq g^{-1}) [2,3,6]. These estimates are based on the 1986 Hiroshima dosimetry analysis, DS86 [9], and account for decay of the ^{63}Ni in the intervening years. ^{63}Ni is a weak beta-emitter (endpoint energy 67 keV) and, for reasonable sample sizes ($\sim$ 10 g Cu), this activity is near

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the limit achievable by low-level beta counting [6,10]. AMS has the potential for similar or higher sensitivity for the detection of ^{63}Ni. This can be seen for instance in measurements of the longer lived ^{59}Ni in meteorites, in which detection limits of a few fg per sample were obtained [11–13]. For the Hiroshima measurements, AMS offers the advantages that there are no interferences from other radiations which might be present and that measurements take on the order of tens of minutes, instead of hours or days as with low-level counting.

As with many AMS isotopes, the primary interference for AMS measurements of ^{63}Ni and ^{59}Ni comes from stable atomic isobars: ^{63}Cu in the case of ^{63}Ni, and ^{59}Co in the case of ^{59}Ni. Both of these have high natural abundances (69 and 100%, respectively) and readily produce negative ions. Since atomic isobar pairs (e.g., ^{63}Ni/^{63}Cu) cannot be separated electromagnetically, these interferences cannot be removed using the spectrometer alone. Reduction of these interferences to acceptable levels therefore depends firstly on the chemical removal of the interfering element during sample preparation, and secondly on the use of an ion detection technique that allows for additional, post-spectrometer rejection of the interference.

For the Hiroshima measurements, isobaric interference presents a particularly pathological problem. For these samples, there are expected to be 15 orders of magnitude more ^{63}Cu than ^{63}Ni in the initial samples. This places stringent demands on the chemical separation, which must provide the majority of the copper rejection (approximately 12 orders of magnitude), while quantitatively retaining the small quantity of ^{63}Ni. Bioscience tracer experiments using ^{59}Ni will not have this same extreme requirement for removal of bulk material – Co concentrations in biological samples are typically in the low ppm range – however, the requirements for final sample purification in both cases are still substantial. To reach femtogram sensitivity for AMS measurements at LLNL, these isobars must be chemically reduced to picogram levels (i.e., Cu/Ni and Co/Ni ratios $\sim 10^{-8}$, assuming 1 mg stable Ni carrier).

For the measurement of ^{63}Ni in copper samples, three steps were used for the successive elimination of ^{63}Cu. In-situ produced ^{63}Ni was extracted from gram-sized copper samples using electrodissolution of the samples combined with simultaneous controlled electrodeposition of the dissolved copper. Dissolved trace Ni and ^{63}Ni from the sample remain in solution during this process, and mix with additional stable Ni which is added as a carrier. The electrochemistry is described in detail in the accompanying paper by Marchetti et al. [2]. Further purification and sample preparation was accomplished by reacting the nickel with carbon monoxide to form the volatile compound nickel tetracarbonyl, which was subsequently thermally decomposed directly in sample holders, avoiding the need for additional handling of the sample after purification. For the post-spectrometer rejection of remaining ^{63}Cu, ions were detected and identified using the characteristic X-rays emitted as the ions pass through a thin foil [14]. Also crucial to the method development was the reduction of instrumental background associated with copper in the AMS ion source.

To evaluate the ^{63}Ni methods on realistic samples, a demonstration experiment was performed in which two sets of copper wires were irradiated with neutrons from a ^{252}Cf fission source. For these demonstration samples, the fast neutron fluences corresponded to ~ 1 and ~ 10 times the DS86 fluence for a location 1 m above the ground and 100 m from the hypocenter. This experiment is described in greater detail by Marchetti et al. [2].

In our preliminary work on ^{59}Ni, the nickel carbonyl step appears to be sufficient to reduce trace cobalt levels – as anticipated for biological samples – to $\sim 1 \times 10^{-8}$. In other respects, the methods used for ^{59}Ni are essentially identical to those developed for ^{63}Ni.

2. Methods

2.1. Sample purification

2.1.1. Background

Using controlled potential electrodeposition, it is theoretically possible to reduce Cu/Ni ratios to well below 1×10^{-8} while preserving nickel in solution [2]. Experimentally, we have made measurements by AMS and graphite furnace atomic absorption which indicate that these levels may be achievable. However, a significant disadvantage to this approach is that the resulting sample form is Ni^{2+} in aqueous solution. For AMS measurements, the sample must be converted to a solid form, either Ni or NiO. Conversion of the aqueous Ni^{2+} to solid form requires further handling and the addition of reagents, all of which contribute to contamination. For example, even the addition of milliliter quantities of the purest commercially available reagents, such as double sub-boiling distilled acids, ammonia, or even water, can introduce tens of picograms of copper. Beakers and other labware can also present a problem, especially if conversion of the sample involves heating or acids. Copper can be leached at picogram quantities from teflon, even after pre-treatment by boiling in concentrated nitric acid. Finally, we do not have regular access to clean room facilities, so there is the ever-present problem of uncontrollable contamination through room dust or other pathways.

Other approaches were also explored for further purification of the sample. These included anion exchange resin (Dowex 1-8X, Biorad Laboratories), precipitation of nickel with dimethylglyoxime (DMG), and the use of a resin column in which DMG is bound to the resin (Eichrom Industries, Inc.). As with the electrodeposition, these techniques result in Ni^{2+} in aqueous solution. We made several AMS tests on each of these techniques as well as the electrochemical separation. Starting solution for these tests consisted of ultrapure nickel powder (Alpha Aesar, Johnson Mathey Catalog Company) dissolved in a minimum (~ 3 ml per g Ni) of double sub-boiling distilled concentrated nitric acid (Seastar Chemicals Inc.), diluted to ~ 5 mg Ni per ml using distilled deionized water. Following treatment, Ni^{2+} was converted to $Ni(NO_3)_2$ by gentle evaporation with a heat lamp in a teflon beaker with a nitrogen flow. The resulting nickel nitrate was placed in a borosilicate test tube and converted to NiO by flame heating. The resulting Ni/NiO was analyzed for Cu using AMS.

Each of these treatments resulted in samples with Cu/Ni ratios in the 10^{-5} to 10^{-6} range. These levels are 2 to 3 orders of magnitude above the required level, showed significant variability, and were clearly higher than the untreated solution (after conversion to NiO), which yielded $\sim 1\text{–}5 \times 10^{-7}$. For comparison, the original nickel powder consistently gave a Cu/Ni ratio of $\leq 2 \times 10^{-8}$, which appears to be near the current instrumental background of the AMS ion source. Based on these tests, we decided to pursue a purification/sample preparation technique based on the formation of the volatile compound $Ni(CO)_4$.

2.1.2. $Ni(CO)_4$ generation

CAUTION: Nickel tetracarbonyl is a highly toxic gas and should be handled with caution. See, for instance, Ref. [15].

The reaction of nickel with carbon monoxide to form nickel tetracarbonyl is a standard technique for the production of highly purified nickel metal [16]. The method presented here is largely an adaptation of earlier studies in which $Ni(CO)_4$ generation was used for the preconcentration and detection of trace quantities of nickel in solution [17–21].

Following the electrochemical removal of gross copper from wire samples [2], the sample (13 ml) contains ^{63}Ni in 1 M nitric acid, as well as trace stable nickel from the wire and 1 mg stable nickel added as carrier. Concentrated aqueous ammonia is added dropwise to this solution until the pH is 10–11. By complexing the Ni, ammonia prevents the formation of $Ni(OH)_2$ precipitate which is otherwise favored under basic conditions for our relatively large Ni concentrations. For $Ni(CO)_4$ generation, the solution is transferred to the reactor cell, which consists of a 50 ml pear-shaped borosilicate boiling flask with three ground-glass joints in the top for the gas inlet and outlet and for introduction of the BH_4^- solution. The gas inlet ends with a coarse frit (pore size 40–60 μm) which was fully submersed in the solution.

A mixture of CO and helium (1:1) is bubbled through the reactor at 80–100 std ml/min each. The system is first purged to clear the lines and saturate the solution with CO. After purging, a solution of $NaBH_4$ (0.5% m/V in water and adjusted to pH 10 with concentrated ammonia solution) is added at a rate of ~ 1 ml/min using a peristaltic pump. Evolved $Ni(CO)_4$ is carried to a liquid nitrogen trap in the CO/He flow. For samples containing 1 mg Ni, the conversion of Ni to $Ni(CO)_4$ is typically complete after ~ 5 min of BH_4^- flow. Quantitative conversion can be verified visually for every sample – as little as ~ 25 μg unconverted Ni results in a noticeably cloudy, gray suspension of Ni in the reactor. In most cases the solution is clear following the procedure. We have also verified completion of the Ni conversion for several samples by measuring the remaining Ni spectrophotometrically, as described in Ref. [2].

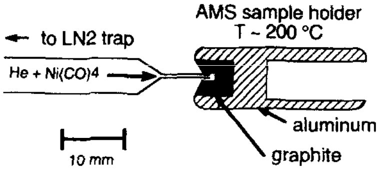

Fig. 1. Thermal decomposition of $Ni(CO)_4$ in target holder. $Ni(CO)_4$ is carried in helium to the sample holder, where it is thermally decomposed to Ni. Ultrapure graphite is used for the sample holder to reduce instrumental backgrounds from Cu and Co.

The cold trap consists of a borosilicate U-tube immersed in liquid nitrogen. Glass beads, treated with dichlorodimethylsilane solution to prevent adsorption of $Ni(CO)_4$, are placed in the trap to increase surface area. The primary purpose of the trap is to separate the $Ni(CO)_4$ from the CO, which would otherwise thermally decompose with the $Ni(CO)_4$, diluting the Ni in an excess of graphite [18]. The addition of helium prevents condensation of CO in the cold trap [18]. The trap also collects aerosols which have the potential to carry dissolved or suspended copper to the final sample holder.

For the thermal decomposition step the CO flow is stopped and the He flow is reduced to ~ 20 ml/min. The AMS target holder, heated to ~ 200°C, is positioned over a thin glass tube which is the exit from the gas line (Fig. 1). The cold trap is then allowed to warm to room temperature. As the $Ni(CO)_4$ evaporates, it is carried in the He flow to the target holder where it thermally decomposes to Ni and CO, coating the inside of the target holder. After the trap reaches room temperature, the He flow is continued for several minutes to thoroughly flush the trap.

For safety reasons, the traps are always placed in an oven and heated to > 200°C before removal from the fume hood. The other glassware and tubing sections are rinsed thoroughly with concentrated nitric acid before removal from the hood. These steps were established to prevent the possible introduction of adsorbed $Ni(CO)_4$ into the room air.

2.2. AMS measurements

2.2.1. Spectrometer

The AMS measurements are performed using the 10 MV FN tandem accelerator at the Center for Accelerator

Mass Spectrometry at Lawrence Livermore National Laboratory [22]. For ^{63}Ni and ^{59}Ni measurements, a characteristic X-ray detector (described below) is used for post-spectrometer ion detection and identification, replacing the standard gas ionization detector which is used for lighter isotopes. Technical details are: terminal voltage 9.0 MV; foil stripping; charge state Ni^{10+}; ion energy 99 MeV. Stripping efficiency to the 10 + charge state was measured to be ~ 22% The stable isotope $^{58}\mathrm{Ni}^{10+}$ (68% natural abundance) is measured in a Faraday cup located off-axis between the high-energy analyzing magnets. To extend sample lifetime and reduce accelerator loading and detector count rate, the ion source is run at a reduced output. Analyzed $^{58}\mathrm{Ni}^{-}$ currents are typically ~ 10 μA for pressed Ni powder samples, and average 3–5 μA for samples produced by $\mathrm{Ni(CO)_4}$ generation. Currents are approximately 3–5 times higher with full source output.

At the ^{63}Ni/Ni and ^{59}Ni/Ni levels of interest in this experiment ($> 1 \times 10^{-12}$), only two significant interferences remain after the spectrometer: the atomic isobar (^{63}Cu or ^{59}Co), and stable Ni "tails" (i.e., off-energy or scattered ions which inadvertently match the acceptance of the spectrometer).

2.2.2. Instrumental copper and cobalt background

Three main steps were necessary for the reduction of instrumental ^{63}Cu and ^{59}Co background associated with ambient copper and cobalt in the ion source. These were: fabrication of copper- and cobalt-free AMS target holders; thorough cleaning of the ion source before runs; and the addition of a cryogenic pumping system to the ion source. The target holders consisted of a high-purity graphite plug (99.9995%, obtained from the Johnson Mathey Catalog Co.) pressed into an aluminum casing and machined to the required shape (see Fig. 1). The installation of a cryopump in place of a turbomolecular pump reduced background copper rates by more than a factor of 10, both for empty graphite sample holders and for Ni samples. We speculate that the source of copper observed with the turbopump was organometallic compounds in the turbopump lubricant which have a sufficiently high vapor pressure to reach the samples. An additional precaution taken was the inclusion of an aerosol filter in the sample chamber roughing line. Even with the cryopump, we found that samples left in the sample chamber collect copper with time. Left overnight, with the ion source turned off, copper levels in virgin samples increase by as much as a factor of 50, indicating that there is still room for improvement in the instrumental background.

2.2.3. Projectile X-ray AMS

After analysis in the AMS spectrometer, the ions are detected via X-rays which are emitted as the ions pass through a thin foil [14]. This technique, referred to at LLNL as PXAMS (projectile X-ray AMS), allows the identification of the ions by atomic number. In the present arrangement, a zirconium foil (2.0 mg/cm^2) was used for X-ray production, and the ions were stopped in a thick beryllium foil (0.13 mm). A mylar layer (0.19 mm) was also included to attenuate low energy X-rays. X-rays were detected using a high resolution high-purity germanium (HPGe) detector (Iglet-X, EG&G Ortec; active area 95 mm^2; resolution 150 eV FWHM at 5.9 keV).

The foil material and thickness were not optimized for detection of Ni ions, but were sufficient for these demonstration experiments. The energy of the Ni ions dropped from 99 to ~ 64 MeV while passing through the foil. The X-ray production efficiency (into 4π) was ~ 0.09 Ni K_α X-rays per incident Ni ion. The X-ray yield would be ~ 1.7 times larger for a foil of stopping thickness, however this increase would be offset by increased X-ray attenuation and, more importantly, increased Doppler spreading of the X-ray lines which would reduce the rejection of ^{63}Cu K_α X-rays. For the current setup, the average transmission of Ni K_α X-rays through the foils and mylar was between 0.5 and 0.6. The distance from the Zr foil to the detector was ~ 10 mm, for a detector solid angle of $\sim 0.075 \times 4\pi$ sr. The overall detection efficiency for the system was measured to be 3.5×10^{-3} detected K_α counts per incident ^{63}Ni. This value was consistent with an estimate made using a computer simulation of the setup. An optimized choice of target material and thickness is expected to increase the detection efficiency to 0.01–0.02 K_α counts per incident Ni ion. A thin germanium target on a beryllium backing is currently being fabricated for this purpose.

Detector count rates are ~ 500 Hz for samples with Cu/Ni ratios $\sim 2 \times 10^{-8}$. With an amplifier shaping time of 10 μs, the livetime for most samples was > 90%. Count rates up to 3 kHz showed no measurable effect on the detector gain or line shape.

Examples of the observed X-ray spectra for ^{63}Ni measurements are shown in Fig. 2. A fraction of the Cu counts extend through the Ni region as a low energy tail, so that subtraction of background Cu counts from the Ni sum is necessary for ultimate sensitivity. Ni and Cu counts were extracted using the indicated summing regions. The ^{63}Ni/Ni results and uncertainties were found to be largely insensitive to the exact placement of cuts. The amount of isobar rejection, defined as the ratio of Cu counts in the Cu region to Cu counts in the Ni region (i.e., the "peak-to-tail" ratio), was ~ 310 for the present work. It was found that this ratio can be stable to < 0.5% over periods of hours, and for count rates up to 3 kHz.

2.2.4. ^{63}Ni and ^{59}Ni standards

A series of ^{63}Ni/Ni standard solutions was prepared by successive dilution of a NIST-traceable ^{63}Ni standard solution (Du Pont Radiopharmaceutical Division) in Ni atomic absorption (AA) standard solution. The quoted relative uncertainty in the activity of the standard was ± 4.7%. The AA standard (VWR Scientific) contained 0.998 mg Ni/ml

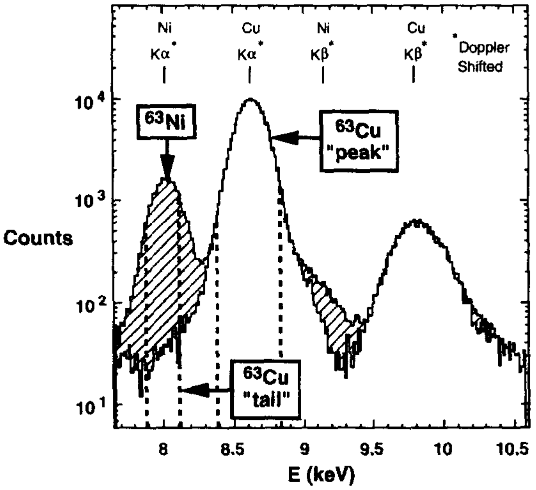

Fig. 2. Measured X-ray spectra for ^{63}Ni. A fraction of the Cu counts (the Cu "tail") must be subtracted from the measured Ni counts. The Cu "peak-to-tail" ratio is ~ 310 for the indicated summing regions (dashed lines). The spectra are from a standard (^{63}Ni/Ni = 1×10^{-8}) and an empty target holder (therefore removing contributions from stable Ni ions). The spectra have been scaled to have equal counts in the Cu peak.

in weak nitric acid. The ^{63}Ni activity was converted to a number of ^{63}Ni atoms using the half-life ($t_{1/2} = 100.1 \pm 2.0$ y) measured by Barnes et al. [23]. The AMS standards were prepared by successive dilutions of the stock solution in AA standard. The dilutions were performed gravimetrically, yielding uncertainties of ~ 2% relative to the calibrated solutions. The ^{63}Ni/Ni ratios for the standards were 1.00×10^{-8}, 0.99×10^{-9}, and 0.98×10^{-10}. AMS blanks were made using the AA Ni standard directly. The standards and blanks were processed using $Ni(CO)_4$ generation as described above.

Standards for ^{59}Ni were prepared in a similar manner. The ^{59}Ni source (Analytics, Inc.) was calibrated for the supplier by the Department des Application et de la Metrologie des Rayonnements Ionisants (DAMRI), Paris. The quoted relative uncertainty was ±3.0%. The ^{59}Ni activity was converted to a number of ^{59}Ni atoms using the half-life ($t_{1/2} = 1.08 \pm 0.13 \times 10^5$ y) measured by Rühm et al. [24].

3. Results

3.1. $Ni(CO)_4$ generation

Carbonyl generation has proved to be an effective method for the separation of Cu from Ni, allowing us to regularly lower Cu/Ni ratios to less than $\sim 4 \times 10^{-8}$, which appears to be near the instrumental background associated with Cu in the ion source. The cleanest samples have shown Cu/Ni ratios of $< 2 \times 10^{-8}$. Samples which were deliberately spiked with ~ 1 mg Cu^{2+} (Cu/Ni ≈ 1) before carbonyl generation showed no increase in final copper over other samples, demonstrating a removal of copper by nearly 8 orders of magnitude. In addition, there was no apparent drop in conversion of Ni to $Ni(CO)_4$ for these samples, even though the reactor cell became fully opaque with Cu^0 after the addition of BH_4^-. The very high separation of Cu significantly eased the requirements for the electrochemistry. In addition, no special preparation of the glassware was necessary (other than silanizing the glass beads) and reagent grade chemicals were used throughout. Since the purified sample was deposited directly in the target holder, there was no need for clean room facilities.

The primary drawback to carbonyl generation is the loss of sample at the point of thermal decomposition. This loss is caused partly by the escape of some $Ni(CO)_4$ without decomposition, and partly by sub-optimal distribution of the deposited Ni in the holder, such that it is poorly placed for ionization in the AMS ion source. These losses are to some extent unavoidable without abandoning the direct decomposition in the target holder. Because AMS is an isotope ratio measurement, these losses have a minimal effect on the accuracy of the results, but they do significantly limit sample lifetimes.

To roughly quantify the loss of Ni in the decomposition step, sample lifetimes for $Ni(CO)_4$ generated samples were compared to samples prepared from 1 mg of Ni powder packed directly into the holder. The powder samples produced ion currents which were typically a factor of 2 higher and lasted 4–8 times longer than typical carbonyl generated samples. As we have developed our methods, maximum currents and sample lifetimes steadily increased, however there is still a large degree of sample-to-sample variability. Additional modifications in the physical apparatus are planned which we expect will improve the efficiency and reliability of the process.

3.2. Applicability of ^{63}Ni AMS for Hiroshima fast neutron dosimetry

A proof-of-principle experiment was performed in which copper wires were irradiated with neutrons from a ^{252}Cf source and the resulting ^{63}Ni activation was measured by AMS. This experiment is described in detail in Ref. [2]. Two different activation levels were used, corresponding to ~ 1 and ~ 10 times the DS86 fluence for a location 1 m above the ground and 100 m from the hypocenter, and samples of varying total Cu mass were analyzed. Good agreement was obtained between measured and expected values. For a 20 g sample irradiated with 1 times the DS86 fluence, the expected ^{63}Ni content was 49 fg, and the measured value was 54 ± 11 fg. Linearity was also observed between samples with different masses and neutron fluences, demonstrating the accuracy and reproducibility of the method. A weighted linear fit to the measured values produced a slope of 1.07 ± 0.05.

The results of this demonstration experiment illustrate the level of sensitivity that can be expected for real Hiroshima samples. At the time of the experiment, a minimum detection limit (3σ) of 20–30 fg was obtained. Since this experiment, modifications of the methods have improved the limit to ~ 15 fg (1.4×10^8 atoms), sufficient to allow a 3σ measurement of a 20 g copper sample exposed near the Hiroshima hypocenter, assuming the DS86 fluence. Since the discrepancy described by Straume et al. [3]. indicates a possible fast neutron fluence of 5–10 times the DS86 value, implying 7–14 fg ^{63}Ni per g Cu, meaningful measurements could be made with samples as small as 2–5 g.

The present detection limit, which corresponds to ~ 30 mBq, approaches the limit achievable with low-level decay counting (see, for instance, Refs. [6,10]). The advantages of AMS are that measurements are made in minutes or tens of minutes, rather than hours or days, the method is insensitive to other radiations which might be present, and the backgrounds are well understood and well quantified. Finally, because AMS and decay counting are based on completely independent physical processes, they can be applied as complimentary techniques, greatly increasing the meaning of the final results.

3.3. Preliminary development of ^{59}Ni as a tracer in biological systems

The techniques developed for the detection of ^{63}Ni have been directly applicable to the detection of ^{59}Ni, and have resulted in similar detection sensitivity. Instrumental cobalt background in the ion source is overall lower and more consistent than the copper background, and the combination of source cleaning, graphite target holders, and the use of carbonyl generation for final sample preparation consistently results in Co/Ni ratios ~ $2\text{–}4 \times 10^{-8}$; ratios $< 1 \times 10^{-8}$ are frequently observed. Carbonyl generation is not as effective for the removal of large (mg) quantities of Co as it is for Cu. Tests with Co spikes indicate that the transfer of Co from the sample solution to the AMS target is ~ 1×10^{-3} (as compared to $< 2 \times 10^{-8}$ for Cu). However, Co concentrations in biological samples are typically in the low ppm range, so this is expected to be sufficient for this application. In addition, anion exchange columns are effective for the removal of larger quantities of Co, and can be used for pre-processing.

Example X-ray spectra for ^{59}Ni measurements are shown in Fig. 3. In this case the Ni K_α peak sits between the Co K_α and K_β peaks, resulting in a rejection of Co which is ~ 2 times worse than the rejection of Cu.

We have made a small number of preliminary runs using standards and blanks which were prepared by carbonyl generation. Reproducibility in standards with ^{59}Ni/Ni ratios between 1×10^{-8} and 1×10^{-10} has been ~ 10%, both between standards and over the course of a day. Backgrounds from stable Ni isotopes, as measured by blanks, have been observed in the range $0\text{–}40 \times 10^{-12}$, however on a given day this background appears to be constant at the $\pm 5\text{–}10 \times 10^{-12}$ level. Uncertainties for blanks are typically $\pm 3\text{–}6 \times 10^{-12}$ for ~ 15 min measurement times. More runs with a larger number of blanks and standards will be required to fully understand our systematics. Based on these preliminary runs, our minimum detection limit (3σ) is currently ~ $20\text{–}30 \times 10^{-12}$. This limit corresponds to ~ 25 fg ^{59}Ni, or ~ 50 μBq, for 1 mg of Ni carrier. It is also worth noting that this sensitivity was obtained with Co/Ni ratios a factor of 1000–2000 higher than the ^{59}Ni/Ni ratios, demonstrating the effectiveness of the PXAMS technique.

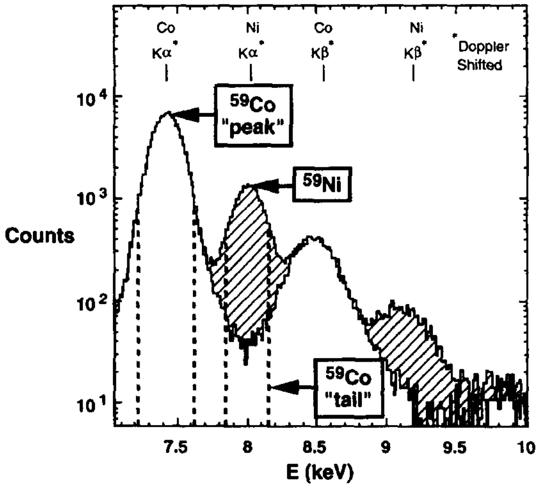

Fig. 3. Measured X-ray spectra for ^{59}Ni. A fraction of the Co counts (the Cu "tail") must be subtracted from the measured Ni counts. The Co "peak-to-tail" ratio is ~ 130 for the indicated summing regions (dashed lines). The spectra are from a standard (^{63}Ni/Ni $= 1 \times 10^{-8}$) and an empty target holder (therefore removing contributions from stable Ni ions). The spectra have been scaled to have equal counts in the Co peak.

For the application of this isotope as a bioscience tracer, we are currently developing protocols for the digestion of biological samples to extract ^{63}Ni and ^{59}Ni, and a proof-of-principle animal study is underway.

4. Conclusions

We have developed methods for the detection of the long-lived isotopes ^{63}Ni and ^{59}Ni using AMS at LLNL. Our detection sensitivity (3σ) is currently ~ 15–30 fg ($1\text{–}3 \times 10^8$ atoms) for each isotope. The sensitivity is currently limited by a combination of sample lifetime, remaining isobaric interference, and background from stable Ni ions which reach the detector. With planned improvements and additional experience, further improvements by a factor of 2–3 are expected. This work will make possible a determination using AMS of the fast neutron fluence from the Hiroshima bomb via the ^{63}Cu(n,p)^{63}Ni reaction in copper samples. Our sensitivity for ^{59}Ni will allow tracer experiments in biological systems using 1000 times less activity than is required for similar experiments using ^{63}Ni.

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