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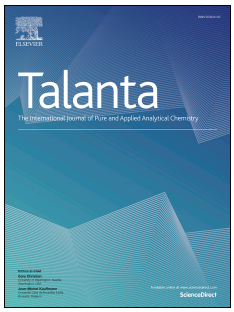

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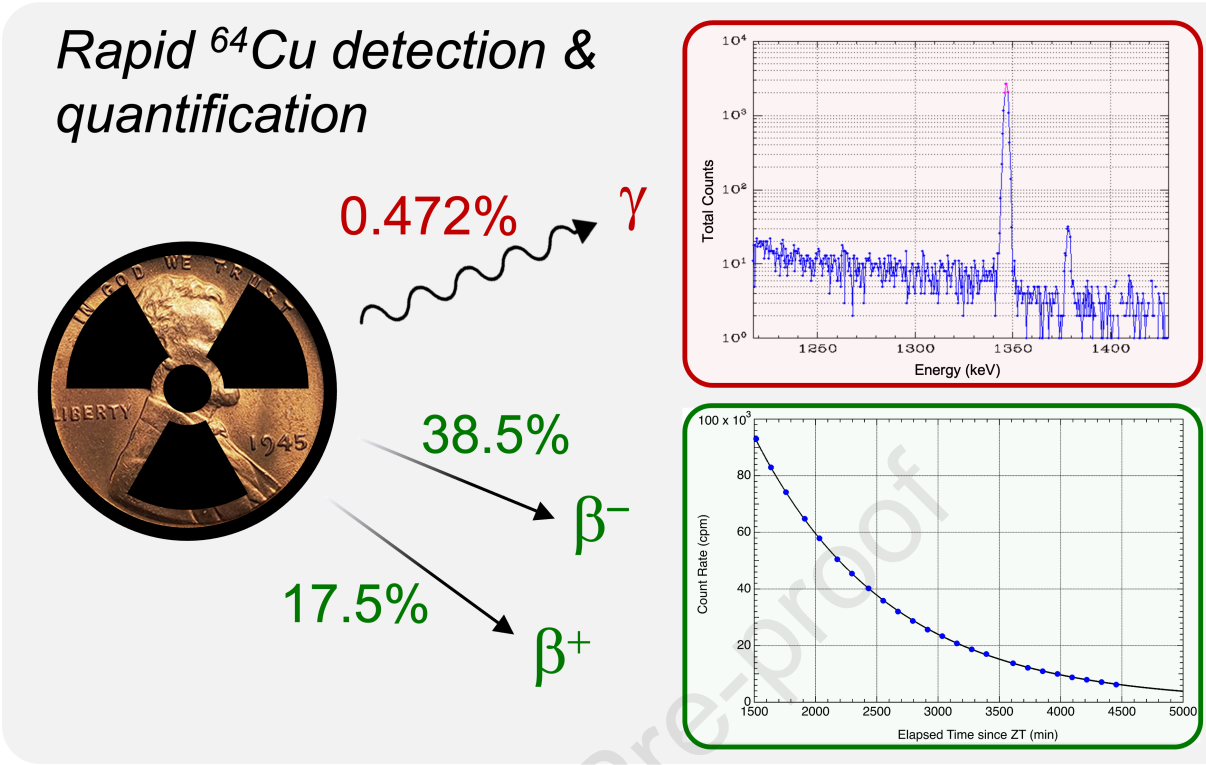

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A New Method for Quantifying ^{64}Cu in Nuclear Debris Samples

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Abstract: Quantifying ^{64}Cu in post-detonation nuclear debris samples can provide important diagnostic information regarding the structural materials used within a nuclear device. However, this task is challenging due to the weak gamma emissions associated with the decay of ^{64}Cu, its short half-life (12.701 h), and the presence of interfering fission product radioisotopes. Large quantities of debris sample are generally needed to accurately quantify ^{64}Cu, which can be problematic in sample-limited scenarios where other radiometric analyses are required. Herein, we present a new method for the separation ^{64}Cu from solutions of mixed fission products and demonstrate the quantification of its activity through use of gas-flow proportional beta counting. The new method was validated through a series of rigorous tests and was shown to improve the detection limit of ^{64}Cu by over two orders of magnitude (from 2.5×10^6 to 1.3×10^4 atoms/sample for 100 min measurements).

Keywords: Copper-64, separation, nuclear forensics, beta counting

Introduction

The radiochemical analysis of pre-detonation nuclear materials and post-detonation nuclear debris can reveal the identity and provenance of illicit nuclear materials, devices, or accidents. Such analysis is critical to the nuclear deterrence mission, particularly when considering the possibility of nuclear terrorism; the ability and readiness of national laboratory scientists to determine the origin of a nuclear weapon through analysis of debris ensures international accountability for nuclear events and/or material/device trafficking.[1-3] The rapid measurement of radioisotopes in nuclear debris samples is a key capability of post-detonation nuclear forensic analyses and can provide information about the sources and types of materials involved in a detonation and/or accident.[1, 4-10] Radioactive activation products are of particular interest since these can form from neutron capture reactions on commonly used structural materials like steel and copper.[3-6, 9-11]

The measurement of activation products in samples with relevance to post-detonation nuclear forensics poses several challenges. First, nuclear debris samples could contain significant

amounts of entrained environmental matrix, including soil, rock, or fused glassy debris, presenting diverse potential sample characteristics that make purification and analysis difficult.[5, 7-10, 12, 13] Secondly, the isotopes of interest may be present as minor components relative to other radioactive isotopes like fission products. In particular, many short-lived gamma- and beta-emitting fission product radioisotopes can cause interferences when trying to measure other radioisotope constituents in a sample. In many cases, chemical purification is beneficial to remove radiometric interferences and accurately quantify an isotope.

A number of activation product isotopes could be produced in a nuclear accident, reactor or nuclear detonation, making them useful attribution signatures.[10, 14, 15] For example, the radioisotope ^{64}Cu is an activation product that forms from neutron capture reactions (n,γ) occurring on stable ^{63}Cu (Equation 1).[15-17] Measurements of ^{64}Cu in nuclear debris samples are particularly challenging due to the short half-life of the isotope ($t_{1/2}$ = 12.701 h) and its low gamma-ray emission probability.[17, 18] ^{64}Cu decays by both electron capture (61.5%) and beta emission (38.5%) (Equations 2 and 3).[19-21] The electron capture decay mode emits a positron (β^+) with a 17.5% intensity and a gamma-ray at 1345.7 keV with a 0.472% intensity.[17, 18]

$$^{63}Cu \xrightarrow{n,\gamma} {}^{64}Cu \quad (1)$$

$$^{64}Cu \xrightarrow[12.7h]{\varepsilon\ (61.5\%)} {}^{64}Ni \quad (2)$$

$$^{64}Cu \xrightarrow[12.7h]{\beta\ (38.5\%)} {}^{64}Zn \quad (3)$$

Although analytical chemists have attempted use the far more intense annihilation gamma emission at 511 keV (35.0%) to quantify ^{64}Cu in instrumental neutron activation analysis (INAA) via either conventional gamma analysis[22, 23] or γγ coincidence counting techniques,[24] this gamma feature is not unique to ^{64}Cu, thus complicating its analysis. These methods therefore require a detailed knowledge of matrix composition prior to the INAA irradiation in order for correction factors for the resulting radioisotopes to be calculated accurately. However, this level of sample knowledge prior to measurement is unrealistic in nuclear forensics scenarios wherein vast numbers and quantities of interfering radionuclides are present in unknown quantities.

This paper describes a new method for the purification of copper from nuclear debris samples and subsequent measurement by gas proportional beta decay counting. The method rapidly provides effective decontamination against fission products and matrix, enabling measurement of the short-lived ^{64}Cu isotope. The final sample is mounted as a solid precipitate with a fixed diameter geometry and can be determined by gamma-ray spectrometry or beta decay counting. The procedure can be used to effectively measure ^{64}Cu in a range of different sample types and provides enhanced detection sensitivity for this challenging isotope.

Experimental

Materials

Metal carrier solutions (Cu, Ag, Fe, and La) were purchased from Spex CertiPrep as 10 mg/ml solutions and used as received. Optima™ grade hydrochloric acid (HCl), optima grade nitric acid (HNO_3), concentrated ammonium hydroxide (NH_4OH) solution, and potassium

thiocyanate (KSCN) were purchased from Fisher Scientific. Hydroxylamine hydrochloride ($H_2NOH•HCl$), sodium nitrite ($NaNO_2$), and sodium hydroxide (NaOH) solution (50% by mass) were purchased from Sigma Aldrich. Ethanol (200 proof) was purchased from Pharmco by Greenfield Global. None of the aforementioned reagents required further purification. Environmental reference materials (BCR-2, obsidian, Peruvian soil) were dissolved according to previously reported procedures.[25] Atlantic seawater standard was purchased from Ocean Scientific International Ltd (OSIL).

Los Alamos Neutron Science Center (LANSCE) Irradiation #1

A copper metal target (0.2480 g) encapsuled in an aluminum capsule was irradiated at the Los Alamos Neutron Science Center (LANSCE) on October 17th, 2022. At the LANSCE facility, a large (~15 kg) depleted uranium spallation target was bombarded by the 800 MeV proton accelerator beam, producing a spallation neutron field by which the target was irradiated (see Figure S1 for the calculated neutron flux plot). Approximately five hours after the irradiation, the copper target was dissolved in 8 M HNO_3 (2 mL), and the solution was heated to soft dryness, dissolved in HCl (2 mL), and then again heated to soft dryness. The resultant solids were dissolved in water (24.6 g) and transferred to a tared Teflon bottle. This solution of irradiated copper was used for subsequent experiments.

Washington State University (WSU) Irradiation #1

A copper metal target (0.05014 g) was contained in acid-leached polyethylene vial with a heat-welded cap and irradiated for 144 minutes at the Washington State University Reactor facility on June 26th, 2023 (see Figure S2 for the calculated neutron spectrum). A highly enriched uranium (HEU) metal target (93% enriched in ^{235}U) was simultaneously irradiated in a low-sodium glass ampule sealed inside a second low-sodium glass ampule. Approximately two days following the irradiation, the copper target was dissolved in 8 M HNO_3 (5 mL) and the solution was heated to soft dryness. The resulting residue was dissolved in 4 M HNO_3 and quantitatively transferred to a pre-tared Teflon bottle using additional 4 M HNO_3 (22.3 g total). This solution of irradiated copper was used for all subsequent experiments. One day after the irradiation the HEU was dissolved in 7.5 M HNO_3, heated to near-dryness, and reconstituted in 3 M HNO_3.

LANSCE Irradiation #2

A copper metal target (0.1993 g) encapsulated in aluminum and an HEU metal target (0.4138 g, 93.2% enriched in ^{235}U), also encapsulated in aluminum, were irradiated at the LANSCE facility on October 30th, 2023. For this irradiation, a tungsten spallation target (1.0203 kg) was bombarded by the 800 MeV proton accelerator beam, producing a spallation neutron field (see Figure S3 for the calculated neutron flux plot) to which the targets were exposed for two hours. Approximately one day after the irradiation, the copper target was dissolved in 8 M HNO_3 (5 mL). Following complete dissolution, deionized water (5 mL) was added to the solution, which was then quantitatively transferred to a pre-tared Teflon bottle using 4 M HNO_4 (21.9 g total). This solution of irradiated copper was used for all subsequent experiments. The HEU was dissolved according to established procedure.[25]

Sample purification procedure #1

1. Copper carrier (20 mg) was added to a sample, and the mixture was evaporated to dryness by heating. Concentrated HCl (1 mL) was added to the residue, which was again evaporated to dryness.
2. The resulting residue was redissolved in deionized water (10 mL).
3. Six drops of 1 M HCl were added to the solution, followed by 5.0 mL of a 0.1 M solution of potassium thiocyanate in water, and 2.2 mL of a solution of hydroxylamine hydrochloride in water (10 mg/mL). The mixture was heated on a hotplate (set to 175 ^{o}C) for 30 minutes, resulting in the formation of copper(I) thiocyanate (CuSCN) as a white precipitate.
4. The sample was centrifuged (3,500 rpm, 3 minutes) before decanting the supernatant decanted into a fresh glass cone. The white solid was set aside. An additional 2.5 mL of 0.1 M potassium thiocyanate solution and 1.1 mL of hydroxylamine solution was added to the supernatant, which was heated for 30 minutes to test for additional precipitation (possible in the presence of large quantities of environmental matrix). If additional precipitation was observed, the supernatant was discarded, and the two white solids were combined and washed with water (5 mL). Vigorous stirring is necessary to fully remove entrained contaminants. The sample was centrifuged, and the washings were discarded.
5. The white solid was redissolved by dropwise addition of concentrated HNO_3 (0.25 mL). In the presence of large quantities of environmental matrix, heating to boiling was necessary to fully leach copper back into solution. The sample was then diluted with water (10 mL) to form a pale blue solution.
6. Silver carrier (3 drops of a 10 mg/mL solution) was added followed by concentrated HCl (1-2 drops) to precipitate silver chloride (AgCl). The sample was centrifuged, the supernatant transferred to a glass cone. The AgCl precipitate was discarded.
7. Lanthanum carrier (3 drops of a 10 mg/mL solution) was added to the solution, along with iron carrier (3 drops of a 10 mg/mL solution). Concentrated ammonium hydroxide (NH_4OH) solution (30%) was added dropwise with stirring until formation of a precipitate was observed, then an additional 3 – 5 drops were added. The sample was centrifuged, and additional lanthanum and iron carriers (3 drops each) were added to the supernatant. The sample was stirred, centrifuged, and the supernatant was transferred to a fresh glass cone and the precipitates were discarded.
8. 5.0 ml of a 0.1 M solution of potassium thiocyanate in water was added to the resulting blue copper solution, and then 2.2 mL of a solution of hydroxylamine hydrochloride in water (10 mg/mL) was added, resulting in the immediate formation of CuSCN as a white precipitate.
9. The sample was centrifuged, the supernatant discarded, and the white solid washed with water (5 mL). Vigorous stirring is necessary to fully remove entrained contaminants. The sample was centrifuged, and the washings were discarded.
10. The white solid was redissolved by dropwise addition of concentrated HNO_3 (0.25 mL).
11. The sample was diluted with water (10 mL) to form a pale blue solution. Three drops of xylenol blue indicator solution were added to the sample. A NaOH solution (3 M in water) was added dropwise with stirring until the solution turned peach/yellow.
12. A saturated solution of sodium nitrite ($NaNO_2$) in water (0.5 mL) was added to the sample, resulting in formation of a green solution. The solution was allowed to stand at room temperature for 2 minutes.

13. NaOH (10 M solution in water) was added dropwise until the solution turned blue, and then 1 additional drop was added to precipitate blue copper(II) hydroxide ($Cu(OH)_2$). The sample was centrifuged, and the supernatant discarded.
14. The $Cu(OH)_2$ pellet was washed with water (5 mL), and the resulting supernatant was discarded. NOTE: vigorous stirring during the washing step is necessary for removing entrained contaminants.
15. The blue $Cu(OH)_2$ pellet was dissolved in concentrated HCl (0.25 mL).

Steps 11 – 15 were repeated 2 times (3 times total) before proceeding to step 16.

16. The sample was evaporated to soft dryness with heating and was then dissolved in water (10 mL).
17. *Step 3* was repeated to form CuSCN.
18. The white CuSCN precipitate was washed with water (5 mL), centrifuged, and the resulting supernatant was discarded.
19. The precipitate was suspended in ethanol (5 mL) and was collected by vacuum filtration onto a pre-tared Whatman Type 42 Filter paper (using a Fisher Scientific filtering chimney to achieve a 25 mm diameter spread of the precipitate). The solid was dried by heating at 100 ^{o}C (10 minutes), cooled to room temperature, and weighed. Three drops of a solution of rubber cement (0.5 g in 20 mL toluene) were added to the sample, which was dried at 100 °C. The sample was then mounted on a stainless steel planchet and covered with type A mylar for gamma/beta counting.

Sample purification procedure #2 (improved procedure)

Step 7 in the "Sample purification procedure #1" was replaced with the following sub-steps:

7.1. Lanthanum carrier (3 drops of a 10 mg/mL solution) was added to the sample, along with iron carrier (3 drops of a 10 mg/mL solution). Concentrated ammonium hydroxide (NH_4OH) solution (30%) was added dropwise with stirring until formation of a precipitate was observed, then an additional 3 – 5 drops were added. The sample was centrifuged, and the supernatant was transferred to a fresh Falcon tube.
7.2. The precipitate was washed with water (3 mL), centrifuged, and the supernatant was combined with the supernatant from *step 7*. The precipitate was discarded.
7.3. Lanthanum carrier (3 drops of a 10 mg/mL solution) and iron carrier (3 drops of a 10 mg/mL solution) were added to the combined solution, resulting in the immediate formation of precipitate. Concentrated HCl was added dropwise with stirring until the precipitate redissolved.
7.4. Concentrated NH_4OH was added dropwise with stirring until the formation of a precipitate was observed, then an additional 3 – 5 drops were added. The sample was centrifuged, and the supernatant was transferred to a fresh Falcon tube.
7.5. The precipitate was washed with water (3 mL), centrifuged, and the supernatant was combined with the supernatant from *step 7.4* for continuation of the procedure at *step 8*. The precipitate was discarded.

Counting

The activity of ^{64}Cu in solution and solid samples was determined by gamma-ray spectrometry using a high-purity germanium detector (a p-type detector with a 53% relative efficiency). The gamma-ray line at 1345.7 keV (0.472% intensity) was used to calculate the total activity in the sample, which was then decay corrected to a reference time that corresponded to the end of the irradiation. From the measured and decay-corrected activity the number of atoms of ^{64}Cu in the samples was then calculated using the decay constant λ (9.0964×10^{-4} min^{-1}). A second high-purity germanium detector (p-type 119% relative efficiency) was used for determining the limit of detection for ^{64}Cu. Activities at the end of the irradiation (end of bombardment or EOB) were calculated according to published methods.[25] See ESI for more specific details on the calculations.

Copper sample activities were determined by beta decay counting on Los Alamos National Laboratory (LANL) counter #14, a propane-filled gas proportional beta counter with a thin titanium window. The beta decay data were fit using the CLSQ program to calculate the activity of ^{64}Cu (in units of counts per minute, cpm) at the reference time (the irradiation stop time) according to a previously published method.[26]

ICP-MS analysis of samples

Following gravimetric yielding of the samples, the copper(I) thiocyanate disk was carefully tapped into a fresh beaker. The material was wetted with minimal water (*ca.* 1 mL), and then concentrated HNO_3 (2 mL) was added slowly to oxidize and dissolve the solid. The resulting blue solution was transferred to a pre-tared Falcon tube. The beaker was washed with several portions of water, which were combined with the solution in the Falcon tube. The filter paper was then transferred to the beaker, and HNO_3 was added to dissolve residual copper(I) thiocyanate. The resulting solution was transferred to the Falcon tube. Five additional portions of water (3 mL) were sequentially added to the beaker to ensure quantitative removal of Cu from the filter paper, and were combined with the Falcon tube solution. Successive dilutions of the solution were undertaken until the final Cu concentration was *ca.* 6 ng/g.

Analysis of diluted sample solutions was performed using high-resolution inductively coupled plasma mass spectrometry (ICP-MS, Thermo Element XR). Prior to analyses, instrument tune settings, detector linearity, and individual analyte mass offsets were calibrated. Concentrations were determined through external calibration using a set of five Cu standard solutions with concentrations between 0.83 and 11.3 ng/g. Stable Cu masses (63 and 65) were monitored in low resolution with a 10% mass window (see ESI for additional parameters).

Results and discussion

Stable copper consists of two isotopes, ^{63}Cu (69.15% abundance) and ^{65}Cu (30.85% abundance),[27] and neutron capture reactions on ^{63}Cu form the isotope ^{64}Cu.[15, 16] The short-lived isotope ^{64}Cu ($t_{1/2}$ = 12.7 h) decays by two different modes (Equations 2 and 3, Figure 1): electron capture (61.5% probability) produces ^{64}Ni, and beta decay (β^-, 38.5% probability) produces ^{64}Zn.[18] Positrons and beta particles are emitted from the two different modes with decay emission intensities of 17.5% and 38.5%, respectively.[18] The electron capture decay mode emits a gamma ray at 1345.7 keV (0.472% intensity), but no other gamma rays are produced with any significant intensity.[18] Given the complicated decay scheme of ^{64}Cu and the very low probability of gamma-

ray emission, we aimed to develop a flexible measurement method that would allow for quantification of ^{64}Cu by either gamma-ray spectrometry or beta decay counting.

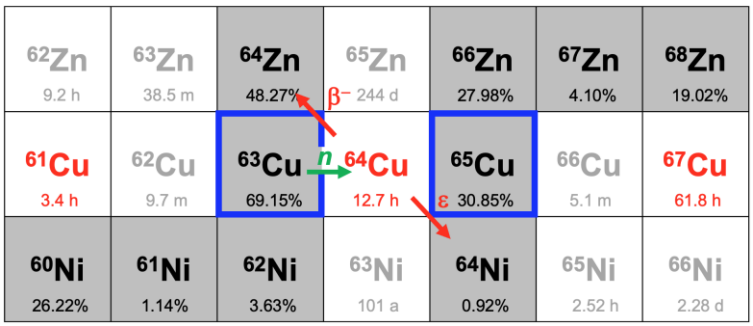

Figure 1. Isotopes of copper. Stable copper isotopes are boxed in blue, and copper radioisotopes with appreciable half-lives are highlighted in red. Natural abundances are tabulated below the isotopic symbol for stable isotopes (gray boxes), and half-lives are tabulated for radioisotopes (white boxes).

Purification of Cu from mixed fission products

An effective chemical purification is required to remove other radioisotopes and entrained environmental constituents from the samples prior to measurement. We developed a purification procedure that involves addition of stable copper carrier to the sample, followed by selective precipitation steps to remove other stable elements and radioisotope interferences. The procedure employs precipitation of copper(I) thiocyanate from aqueous solution. This step provides excellent decontamination from many other transition metals whose thiocyanate salts are water soluble.[28, 29] Scavenging steps with lanthanum hydroxide and iron hydroxide co-precipitation remove radioactive interferences including ^{95,97}Zr, ^{147}Nd, ^{141,143}Ce, and ^{140}La.[30, 31] Radioactive ^{111}Ag is removed by silver chloride precipitation.[32] Subsequent precipitation of copper(II) hydroxide in the presence of sodium nitrite provides decontamination against radioactive fission product isotopes of ruthenium (^{103}Ru and ^{106}Ru); in the presence of sodium nitrite, ruthenium forms nitrito- nitroso-complexes[33, 34] which are soluble in basic solution.[35] Finally, copper is precipitated as copper(I) thiocyanate, collected by filtration, and weighed to determine the chemical yield gravimetrically. Typical yields for the full procedure range from 40-55%.

The ability of the new chemical purification procedure to remove fission product interferences was tested. A sample was prepared containing a solution of fission products (1.6×10^{12} fissions, produced from a sample of HEU irradiated concomitantly with copper in the WSU irradiation) and added stable copper carrier, but no radioactive copper. The sample was purified according to the sample purification procedure #1 (*experimental*), and the final copper sample was examined by gamma-ray spectrometry to assess which, if any, radioisotopes remained. A small amount of ^{95}Zr (~300 dpm) was detected, corresponding to a decontamination factor of 9.6×10^2 for this isotope. Approximate minimum decontamination factors could be calculated for several other fission products, where the decontamination factor represents the ratio of ingoing analyte to the amount of analyte remaining after the chemical purification. The decontamination factors are shown in Table 1 and indicate an effective removal of a variety of fission product interferences. To address the issue of ^{95}Zr contamination, the purification procedure was altered and then tested again with a second sample containing a mixture of fission products (2.0×10^{12} fissions) and

copper carrier. In the altered procedure, the supernatant containing copper was re-acidified following the precipitation/removal of the La/Fe hydrolysis products. This modified procedure (sample purification procedure #2, *experimental*) allows for equilibration of the Fe/La carriers with radioisotopes in solution prior to the second precipitation. Our hypothesis was that ^{95}Zr co-precipitates with La/Fe, and that fully equilibrating the solution prior to the second precipitation would enhance its removal from the sample. Indeed, no ^{95}Zr was observed in the gamma-ray spectrum of the sample following purification. Beta decay counts showed that the sample contained activity below the counter detection limit of 1.8 cpm, and the minimum ^{95}Zr decontamination factor for this experiment was calculated to be 4.4×10^3 for ^{95}Zr, which represents an improvement of at least 4× from the initial procedure.

Table 1. Minimum decontamination factors determined for several fission products for the copper purification procedures. Bolded values represent the largest decontamination factor across the two experiments. Minimum decontamination factors were derived from calculated detection limits (see ESI). *The value for ^{95}Zr in Sample #1 represents the measured decontamination factor, as opposed to a minimum decontamination factor.

Isotope	**Decontamination Factor: Sample #1**	**Decontamination Factor: Sample #2**
Number of added fissions	1.6E+12	2.0E11
^{89}Sr	9.7E+00	**9.4E+03**
^{91}Y	2.6E+02	**1.1E+04**
^{95}Zr	9.6E+02*	**4.4E+03**
^{99}Mo	**7.5E+03**	4.3E+03
^{103}Ru	**9.5E+04**	3.4E+03
^{111}Ag	**9.9E+01**	7.3E+01
^{132}Te	**1.8E+05**	2.8E+03
^{140}Ba	**9.3E+04**	4.4E+04
^{141}Ce	**1.4E+05**	7.5E+03
^{143}Ce	**9.1E+03**	1.5E+02
^{144}Ce	**4.5E+03**	3.2E+03
^{147}Nd	**4.2E+04**	6.2E+03
^{153}Sm	**6.0E+02**	1.9E+01

Testing the Cu purification method in the presence of external matrices

Additional experiments were performed to validate the ability of the copper purification procedure to remove entrained environmental constituents. In the first, a matrix of dissolved

obsidian was added to stable copper carrier to simulate a fused glassy debris sample. We found that the procedure allowed for consistent recovery of copper in a carrier only blank as well with samples containing up to ~660 mg (defined by the initial mass of the rock prior to dissolution) of the obsidian (Figure 2, red triangles). Other types of environmental matrices were also evaluated, including rock, soil, and seawater. Stable copper carrier was added to dissolved portions of the NIST standard reference material 4355 Peruvian soil and the USGS Columbia River Basalt reference material BCR-2 (*ca.* 100, 250, 400 mg aliquots of each) and the samples were purified. Sufficient and consistent yields (>50%) were obtained for each material, with no decrease in yield observed upon increasing the mass of added matrix (Figure 2, green triangles and blue squares). For the seawater, two samples containing 10.47 g and 10.33 g of the Ocean Scientific International Ltd (OSIL) Atlantic Seawater standard were combined with stable copper carrier, purified, and the final copper thiocyanate precipitates were obtained in similar yields (52.1% and 57.9% respectively). Purities of the final mount forms were tested for the samples containing the largest quantities of added matrix (for each matrix standard). The purified copper(I) thiocyanate products were gravimetrically yielded, dissolved, and diluted to concentrations of *ca.* 6 ng/g before being analyzed for copper content via inductively coupled plasma mass spectrometry (ICP-MS). Importantly, the concentrations predicted from the gravimetric yields matched the observed concentrations of the samples within experimental error (Table S1), indicating that suitable purification from matrix elements was achieved for all samples.

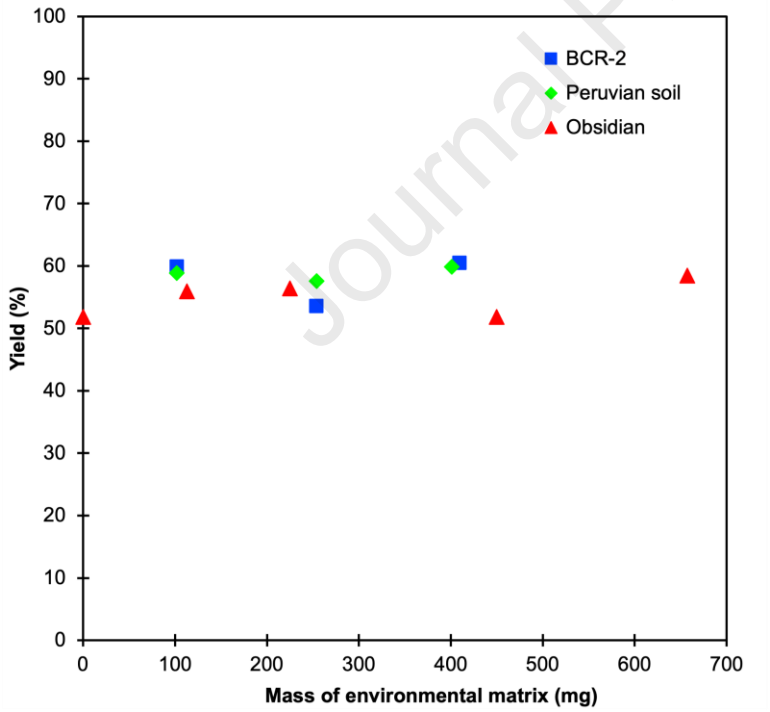

Figure 2. Impact of environmental matrix mass on copper recovery from the copper purification procedure.

Determination of self-absorption correction for beta counting

With an effective chemical purification demonstrated, subsequent efforts focused on establishing a beta counting calibration for ^{64}Cu. Due to the high detection efficiency of beta decay counting, we hypothesized that beta decay counting would be a sensitive measurement technique, providing a low detection limit and a means to conserve sample.

For beta particles, appreciable self-absorption and scattering of the radiation occurs within the sample itself and must be considered when making quantitative measurements.[36-42] The extent of self-absorption is a function of sample mass, with decreasing self-absorption occurring in thinner samples.[36-42] A common approach is to empirically determine an absorption correction function that can be used to predict and correct for beta self-absorption in a sample; this type of empirical correction applies to a specific detector and sample geometry. All samples were prepared in a standard geometry: a 16 mm diameter solid precipitate spread, mounted on a stainless steel planchette and covered with type A mylar.

To determine an absorption correction function for ^{64}Cu, we measured the beta decay rates for fifteen samples having a fixed ratio of ^{64}Cu activity to stable copper mass. The samples ranged in mass from 4.88 to 40.92 mg, and the observed count rate decreased as a function of increasing mass, consistent with self-absorption. From these data, the self-absorption was calculated for each sample and normalized to a typical sample mass of 20 mg (A = 1) (Figure 3). An absorption correction function can be determined from a fit to the experimental data. In this case, the data were fit to a linear function, which is shown in equation 4. Measurements in the low mass region (typically less than 4 – 5 mg) should be avoided due to the greater uncertainties associated with small masses as well as the greater uncertainty associated with the extent of the self-absorption in this region.

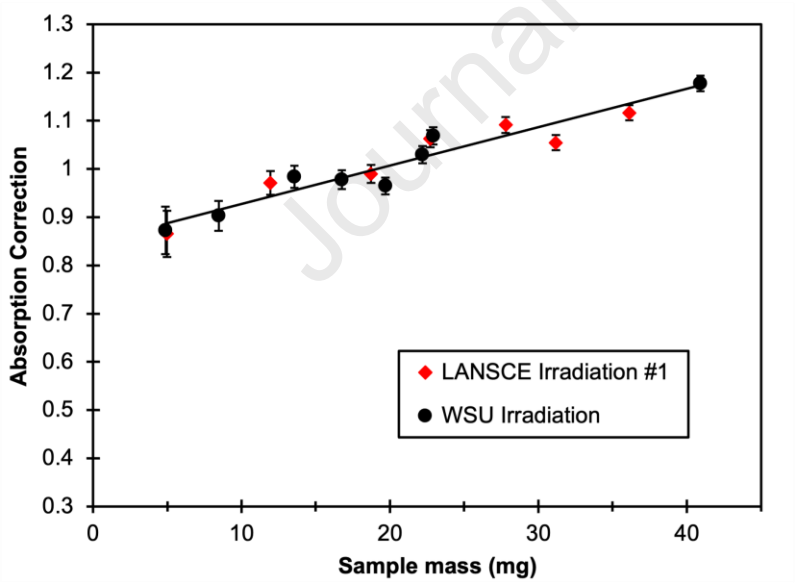

Figure 3. Absorption correction function determined for ^{64}Cu.

$$y = 7.97 \times 10^{-3}x + 8.48 \times 10^{-1} \quad (4)$$

Relating beta counts to atoms ^{64}Cu: *k*-factor determination

Sixteen samples spanning three separate irradiation experiments were prepared for beta decay counting from irradiated copper target samples. The samples were measured by gamma-ray spectrometry using a high-purity germanium detector to quantify the amount of ^{64}Cu in each sample. The very short-lived isotope ^{61}Cu was also detected and quantified in the samples from the LANSCE Irradiation #1, as only about 10 hours had elapsed between the end of the irradiation and sample counting. Beta decay data were collected as a series of one-minute counts over a period of several days following sample preparation, with 8 – 12 counts collected for each sample per day, and the observed activity of ^{64}Cu (in units of cpm) at the reference time (the irradiation stop time) was determined through standard procedure (see *experimental*), followed by application of a self-absorption correction (see above). The measured activities of ^{64}Cu from gamma spectrometry were used to calculate a calibration factor, or *k*-factor, for the beta decay counting, where the *k*-factor relates the observed cpm of the isotope of interest to the total number of atoms present in the sample (equations 5 and 6). Table 2 provides the *k*-factors determined for sixteen different samples; the average value was used for subsequent determinations. The *k*-factor is specific to the particular gas proportional counter and the counting geometry used in these experiments.

$$k_{^{64}Cu} = \frac{atoms_{^{64}Cu}}{cpm_{^{64}Cu}} \tag{5}$$

$$^{64}Cu\ (atoms/sample) = measured\ cpm_{^{64}Cu} \times k_{^{64}Cu} \tag{6}$$

Table 2. *k*-factor determined for ^{64}Cu for beta counter 14.

Sample	Irradiation	Atoms ^{64}Cu/cpm
1	LANSCE #1	7.27×10^3
2	LANSCE #1	7.39×10^3
3	LANSCE #1	6.99×10^3
4	LANSCE #1	7.23×10^3
5	WSU	7.15×10^3
6	WSU	7.24×10^3
7	WSU	7.07×10^3
8	WSU	7.34×10^3
9	WSU	6.97×10^3
10	WSU	7.78×10^3
11	WSU	8.00×10^3
12	WSU	7.65×10^3
13	LANSCE #2	7.23×10^3
14	LANSCE #2	7.27×10^3
15	LANSCE #2	7.15×10^3
16	LANSCE #2	6.61×10^3
	Average	$\mathbf{7.27 \times 10^3}$
	Uncertainty	**4.56%**

Validation of the method: samples containing ^{64}Cu and mixed fission products

The new measurement method was applied to two samples containing ^{64}Cu and a mixture of fission products produced in the LANSCE Irradiation #2. Specifically, two solutions of radioactive copper produced from the irradiated copper metal target were mixed with two solutions containing a mixture of fission products (1.8×10^{10} total fissions, produced from a solution of dissolved HEU irradiated at the same time as the copper target). The two samples each had known quantities of added ^{64}Cu, $6.2(2) \times 10^{8}$ atoms/g of solution, as determined by gamma-ray spectrometry of separate samples prepared from the irradiated target. The two samples were purified according to the new procedure, mounted in the standardized geometry, and measurements were performed by gas-flow proportional beta counting. Each measurement was within error of the known ^{64}Cu content, with an average value of $2.2(1) \times 10^{8}$ atoms/g of ^{64}Cu solution (Table 3). These experiments showcase the readiness of this new method for application in quantifying ^{64}Cu contained in fresh post-detonation nuclear debris.

Table 3. Quantification results for ^{64}Cu solution combined with mixed fission products generated in the LANSCE Irradiation #2.

Sample	Atoms/g ^{64}Cu solution
1	6.27E+08
2	6.13E+08
Average	6.20E+08
Known value	6.19E+08

As discussed earlier, ^{64}Cu can be difficult to measure since its most intense gamma emission (1345.7 keV) is extremely weak (intensity = 0.472%).[17] A relatively large quantity of ^{64}Cu must therefore be present to reliably detect and quantify this radionuclide by gamma spectrometry. Specifically, using the most efficient gamma spectrometer at our disposal (a high-purity germanium detector with a 119% relative efficiency), a ^{64}Cu detection limit of 2.5×10^{6} atoms/sample was calculated for a 100-minute measurement time.[43] In contrast, a detection limit of 1.3×10^{4} atoms/sample was calculated for the beta counter employed in this study using the same counting time.[43] The new purification/quantification method reported herein therefore provides an improvement in ^{64}Cu detection by more than two orders of magnitude, allowing for quantitative analysis of weak samples and/or conservation of material in sample-limited nuclear forensics scenarios.

Conclusions

The rapid analysis of radioisotopes in complex sample types that would result from a nuclear accident or detonation is a central focus of contemporary technical nuclear forensics programs.[1-10] However, a major challenge in the measurement of radioactive structural activation products in nuclear debris samples is that the isotopes of interest may be present in low concentrations relative to fission products. This challenge is exacerbated in the case of ^{64}Cu due to the low probability of gamma emission during its radio decay (0.472%).[17] The method described

herein mitigates this challenge by producing samples of ^{64}Cu of suitable purity for quantification by beta decay counting, thus allowing for a far lower limit of detection for this radioisotope (by >2 orders of magnitude). The method was found to be effective in the presence of both fission products (up to 1.6×10^{12} total fissions) and considerable quantities of environmental matrices (rock, soil, or seawater). Ultimately, ^{64}Cu quantification was demonstrated in the presence of mixed fission products, thus validating the method for use in analyzing post-detonation nuclear debris.

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CRediT authorship contribution statement

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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