Co-precipitation approach to measure amount of $^{238}$U in copper to sub-ppt level using ICP-MS

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Abstract

Inductively coupled plasma mass (ICP-MS) spectroscopy is widely used for screening materials of low background detectors in dark matter and double beta decay searches due to its high sensitivity to trace $^{238}$U and $^{232}$Th. This work describes a novel co-precipitation approach to measure the amount of $^{238}$U in high-purity copper to sub-ppt level. Such an approach allows the pre-concentration of U and removal of the matrix, by selecting a proper precipitator to co-precipitate with $^{238}$U and using excess ammonia water to separate the uranium hydroxide from copper by forming water-soluble tetra-amminecopper (II). The isotope dilution method and standard addition method were both used to mitigate the matrix effect and cross-check each other. The latter was also used to measure the recovery efficiency of $^{238}$U by using $^{233}$U as the tracer. The method detection limit (MDL) reached $\sim$0.1 pg $^{238}$U/g Cu for both methods while the recovery efficiency of uranium robustly remains 65%–85%. Various sources of interference in the ICP-MS analysis were thoroughly evaluated, and the contamination from reagents were found to be the dominant factor that affected the MDL. Further purification will allow significant improvements in the MDL. This co-precipitate approach can be easily extended to measure $^{232}$Th by using $^{229}$Th as the tracer.

Keywords: ultra-low radioactivity, ICP-MS, co-precipitation, uranium

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1 Introduction

Experiments searching for neutrino-less double beta decay (NDBD) have a stringent requirement on the natural radioactivity in the detector materials, particularly $^{238}$U and $^{232}$Th. The capability to detect ultra-trace amounts of $^{238}$U and $^{232}$Th allows careful assessment of the backgrounds, and thus is important to the planned NDBD experiments [1, 2, 3, 4]. In addition to NDBD experiments, many neutrino experiments or dark matter experiments also require ultra-low-radioactivity materials for the detector construction. The highly sensitive methodologies known to date include neutron activation analysis and inductively coupled plasma mass spectroscopy (ICP-MS) [5]. ICP-MS analysis is relatively quick and typically has an intrinsic detection limit better than parts-per-trillion (ppt or pg/g) for a large number of elements, particularly uranium and thorium.

ICP-MS analysis is optimized for aqueous samples, e.g., it is commonly used to measure uranium and thorium in water samples [6, 7]. However, the drawback of using this technique to detect ultra-trace elements is the need for arduous pre-treatment of the samples. Acid digestion is typically used to deal with the solid materials, and the tolerable total dissolved salts (TDSs) in the matrix for ICP-MS analysis is $< 0.1\%$. The pre-treatment inevitably needs additional reagents and chemical separation processing to reduce TDSs or concentrated U and Th. It may consequently introduce contamination and result in worse detection limits [8, 9, 10]. Thus the pre-treatment approach must be scrupulously designed and carried out.

Electrochemical techniques, precipitation, and ion exchange are widely used methods used to separate the matrix and analyte [11]. Recently, an anion exchange method was reported in [12] that achieved detection limits of $10^{-2}$ pg/g level for both $^{238}$U and $^{232}$Th in copper samples. With anion exchange, this method effectively concentrated analytes and simultaneously removed an unwanted sample matrix. The radio-assay to ultra-trace U and Th is extremely challenging. Development of other convenient methods with different pre-treatments is highly desired and would benefit future experiments. It is well known that Cu has the complex ability to form water-soluble compounds in excess ammonia water, whereas U will precipitate. However, ultra-trace U or Th in solutions are too diluted to be separated by conventional methods. The co-precipitation approach is feasible in this case. Furthermore, to achieve a sub-ppt-level detection limit, it is critical to scrupulously perform sample preparation, and qualify the cleanness of labware and the purity of reagents. Calibration of the recovery efficiencies of U or Th during the pre-treatment is also essential, and the typical way is to use $^{233}$U or $^{229}$Th as a tracer. We have obtained $^{233}$U and $^{229}$Th standard solutions, but only the former is qualified to have sufficiently low contamination with respect to the target element. Hence, in this work, we present the $^{238}$U measurement to demonstrate this approach, but it should be pointed out that the method is also applicable to the $^{232}$Th measurement.
The rest of this paper is organized as follows: In Sec. 2, the experimental details to detect the ultra-trace amount of $^{238}$U in copper is introduced, highlighting the pre-treatment process with a co-precipitator and tracer. The various sources of interference in the ICP-MS analysis are discussed in Sec. 3. Two separate analyses with the standard addition method and the isotope dilution method are presented in Sec. 4, and they give a consistent detection limit. Finally, we summarize this work and discuss its prospects in Sec. 5.

2 Experimental Section

2.1 Instruments, reagents, and labware

All chemical operations and measurements were done in a class 10,000 clean room to suppress environmental contamination, since the concentration of $^{232}$Th and $^{238}$U in dust is typically around the ppm level. The analyses were performed using a ThermoFisher iCAP-Qc Quadrupole ICP-MS instrument with a PFA concentric nebulizer. A collision cell was equipped but not used in this work. The spectrometer was tuned every few months. For 1 pg $^{232}$Th or $^{238}$U per gram solution, the typical counts per second with the ICP-MS device is approximately 700–900. Before measuring the samples, a standard $^{238}$U solution with a ppt-level concentration should be tested for at least 30 min to ensure that the instrument is stable. Between every two samples, ultra-pure HNO$_3$ solution was measured to ensure that the entire system was clean.

The reagents used in this work are listed in Table 1. The water for cleaning and dilution was unexceptionally ultra-pure water. The ammonia water was further purified before use. The ZrCl$_4$ and FeCl$_3$, both of 99.99% purity, were dissolved in ultra-pure water. The $^{233}$U standard solution contains $2.3539(42) \times 10^{-6}$ g ($^{233}$U)/g (solution). The $^{238}$U standard solution was diluted with 5% HNO$_3$.

| Reagents or Labware   | Description                      |
|----------------------|----------------------------------|
| ultra-pure water     | Milli-Q® Reference               |
| nitric acid          | OPTIMA (Fisher Scientific)       |
| ammonia water        | BV-III (BICR $^a$)               |
| ZrCl$_4$, FeCl$_3$   | Sigma-Aldrich                    |
| $^{233}$U standard   | IRMM $^b$                        |
| $^{238}$U standard   | 100 µg·mL$^{-1}$ $^c$             |

$^a$ BICR refers to Beijing Institute of Chemical Reagents.
$^b$ IRMM refers to Institute for Reference Materials and Measurements.
$^c$ From national standard reference material of P.R. China.

The filter units were Millex-LG® sterilizing filter units (Millipore Ireland BV, Carrigtwohill, Co. Cork), which were tested to be compatible with 6 mol·L$^{-1}$ HNO$_3$. The 20-mL
polypropylene syringes were produced in JiangSu, China. All vials, containers, pipette tips, stirring bars, filter units, and syringes were cleaned with Alconox® detergent and rinsed with ultra-pure water at least three times, followed by at least two overnight leaches in 6 mol·L⁻¹ electronic grade HNO₃, followed by rinsing with water. All labware was filled with or immersed in hot 6 mol·L⁻¹ OPTIMA HNO₃ for 20 min prior to use, followed by at least three rinses with water.

2.2 Pre-treatment process

The pre-treatment flow is shown in Fig. 1. The key idea is to form water-soluble Cu ammonia complex with excess NH₃·H₂O, which allows the separation between the bulky Cu and the ²³⁸U and ²³²Th elements that precipitate in such circumstances. The major steps include dissolution, co-precipitation, and filtration. During pre-treatment, the calibration of recovery efficiency is critical and also implemented.

![Flowchart of pre-treatment process.](image)

2.2.1 Dissolution

The copper samples were first soaked in the detergent (Alconox®) aqueous solution for 15 min under ultrasonic conditions, then rinsed and soaked in fresh water for 5 min three times.
under ultrasonic conditions. Finally they were dried with high-purity nitrogen. To remove the surface contaminants, the cleaned copper was etched in fresh 6 mol·L⁻¹ HNO₃ twice until its total weight lost was ~3% by mass. The remaining copper was rinsed with water, dried with nitrogen gas, and completely dissolved by using 8 mol·L⁻¹ HNO₃. A reddish-brown smoke was visible in the beginning of dissolution, which indicates the formation of NO₂:

\[
\text{Cu} + 4\text{HNO}_3 = \text{Cu(NO}_3)_2 + 2\text{NO}_2 \uparrow + 2\text{H}_2\text{O}.
\]

As the acid is consumed over time, the reaction equation becomes:

\[
3\text{Cu} + 8\text{HNO}_3 = 3\text{Cu(NO}_3)_2 + 2\text{NO} \uparrow + 4\text{H}_2\text{O}.
\]

The molar ration of Cu to HNO₃ was chosen to be 1:4 for complete dissolution, and the excess HNO₃ helped to maintain the stability of the copper solution.

### 2.2.2 Recovery efficiency calibration

Recovery efficiency is an important indicator used to evaluate the effectiveness of pretreatment and must be obtained. To evaluate the ²³⁸U recovery efficiency during the pretreatment process, ²³³U can be used as a tracer. Because ²³³U does not naturally exist, its recovery efficiency can be determined easily. As an isotope of uranium, ²³³U has the most similar chemical properties as ²³⁸U. If the ²³³U content is at the same level as ²³⁸U in the solution, their recovery efficiencies are expected to be the same. In addition, it is possible to use the isotope dilution method with ²³³U.

Our tests showed that when ²³⁸U in aqueous solution is at 10⁻⁹ g/g (ppb) level, the ²³⁸U recovery efficiency can be >90% by using the normal precipitation method with ammonia water. However, if the ²³⁸U content is at 10⁻¹² g/g (ppt) level or lower, the ²³⁸U recovery efficiency decreases to almost zero, and thus the co-precipitator must be introduced.

### 2.2.3 Co-precipitation

The co-precipitation approach is widely used in radiochemistry to separate elements that are too diluted to be separated by conventional methods. All metal elements that do not precipitate in ammonia water, such as Ag, Cu, Zn and Mg, cannot be chosen as co-precipitator. Fe and Zr ions are found to be more suitable candidates. The ²³³U recovery efficiency for blanks (see Sec. 2.2.5) was measured to be 71%±4% with ZrCl₄ as co-precipitator and 48%±2% with FeCl₃ as co-precipitator, respectively; thus, ZrCl₄ was chosen for this assay.

As shown in Fig. 1, the quantitative ²³³U standard solution and ZrCl₄ solution are first added into the Cu(NO₃)₂ solution. Then, water is added in advance to dissolve the copper ammonia complex formed later. Third, the ammonia water is added slowly under stirring and the Cu²⁺ ions start to precipitate:

\[
[\text{Cu(H}_2\text{O)}_6]^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 ↓ + 6\text{H}_2\text{O}.
\]
The ions of elemental Th, U, and Zr precipitate as well. When adding excess ammonia water to the Cu(NO$_3$)$_2$ solution, the Cu(OH)$_2$ precipitates start to disappear gradually:

$$\text{Cu(OH)}_2 + 4\text{NH}_3 + 2\text{H}_2\text{O} \rightarrow [\text{Cu(NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 2\text{OH}^-.$$

The solution turns dark blue due to the formation of water-soluble tetra-amminecopper (II) in excess ammonia water, whereas the precipitates due to Th, U, and Zr ions still exist. In this process, one molar Cu needs four molar HNO$_3$ and six molar NH$_3$·H$_2$O. More ammonia water and ZrCl$_4$ may improve the recovery of metal ions, but the impurities in these two reagents will degrade the detection limits of ICP-MS analysis. Thus, less ammonia water or ZrCl$_4$ is preferred.

### 2.2.4 Filtration

The mixture after co-precipitation can be separated by filtration with syringe-operated filter units. The trace amount of the precipitates from U ions will be adsorbed on the zirconium hydroxide and intercepted by the filter. Then, the precipitates inside the filter unit are washed by warm 6 mol·L$^{-1}$ HNO$_3$ after rinsing with a small amount of diluted ammonia water and pure water. The eluent is collected and heated to remove excess acid until the residual liquid is less than 0.4 g. The last step is to dilute the residual liquid with 5% HNO$_3$ to a certain amount. The final solution is ready for ICP-MS analysis, and called Cu-sample in the following context.

### 2.2.5 Blanks

Instrumental analysis is essential to determine the detection limit when any pre-treatment is involved. The typical way is to prepare the blank solution (called blank in the following context), which should be prepared by following exactly the same procedure as that for the sample, but without the sample. For instance, the starter solution for the Cu-sample is a certain amount of Cu(NO$_3$)$_2$ solution; thus, the starter solution for the blank is the equivalent amount of nitric acid to make that Cu(NO$_3$)$_2$ solution. The contamination introduced from air, vessels, water, and reagents can be estimated by blank measurements.

### 2.2.6 Pre-treatment optimization

For blanks, an equivalent amount of HNO$_3$ for dissolving Cu is used to replace the Cu-solution. The main reaction occurring in the blanks is:

$$\text{HNO}_3 + \text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}.$$

Different molar ratios of nitric acid to ammonia water, $n_{\text{HNO}_3} : n_{\text{NH}_3\text{H}_2\text{O}} = 4:5.8$, 4:6, 4:6.4, 4:6.6, 4:11.5, were tested while keeping the Zr concentration 3.5 ppm after adding all chemicals. The Cu samples were tested under the same Zr concentration, and the molar ratio of Cu...
to ammonia water was chosen to be 1:5.8 and 1:6.4, respectively. No obvious changes were observed in the $^{233}\text{U}$ recovery efficiencies with different pH values. Thus, the molar ratio $n_{\text{Cu}} : n_{\text{HNO}_3} : n_{\text{NH}_3\cdot\text{H}_2\text{O}} = 1 : 4 : 5.8$ was chosen to dissolve Cu and form Cu ammine complex. The pH value of the mixture after adding ammonia water and stirring was monitored, and it was 8.2–9.0 for blanks and 8.5–8.9 for Cu-samples.

The ZrCl$_4$ concentration was optimized accordingly. For blanks, when the Zr concentration during pre-treatment increased from 1.7 ppm to 3.5 ppm, the $^{233}\text{U}$ recovery efficiencies were measured to be 70%±3% and 65%±2%, respectively. For Cu-samples, when Zr concentration was 1.7 ppm, the $^{233}\text{U}$ recovery efficiency was measured to be 64 ±5%. Finally, the Zr concentration for the pre-treatment was chosen to be 1.7 ppm, resulting in 0.026% Zr(NO$_3$)$_4$ left in the blank or Cu-sample.

The reaction between metal ions and NH$_3$·H$_2$O was quick. After adding NH$_3$·H$_2$O, the freshly formed Zr precipitate was left in the solution under stirring to form larger particles, which benefits the following filtration step. Different stirring times from 1 to 3 h were tested, and no difference was observed in the measured $^{233}\text{U}$ recovery efficiencies.

### 3 Interference analysis

After pre-treatment, the zirconium nitrate will remain in the solution for both blanks and Cu-samples. Part of the impurities from Cu or ZrCl$_4$ will also remain in the solution. It is important to evaluate and eliminate the interference to reduce the error. Typically the sources of interferences for ICP-MS analysis include non-mass spectroscopic interferences, spectral interferences, and contamination.

#### 3.1 Non-mass spectroscopic interference

Non-mass spectral interference is also called physical interference, and the most critical one in this work is the matrix effect. For blanks, the main dissolved salts in the solution are Zr(NO$_3$)$_4$ and other metallic nitrates formed by impurities in ZrCl$_4$. For Cu-samples, the main dissolved salts are almost the same as the blanks, except for extra metallic nitrates originating from impurities in the copper. The Zr(NO$_3$)$_4$ content was estimated to be 0.026% by mass. The content of Cu$^{2+}$ ions in the Cu-sample was measured to be approximately $5\times10^{-5}$ g/g, or equivalently 0.015% Cu(NO$_3$)$_2$ by mass. The maximum concentration of metal ions originating from Cu impurities was estimated to be $3\times10^{-5}$ by mass when the purity of Cu is 99.995%. Other metal salts originating from ZrCl$_4$ in Cu-samples and blanks were estimated to be $10^{-6} - 10^{-7}$ by mass. Thus the TDSs in blanks or Cu-samples were <0.1% by mass, which is close to the upper limit of TDSs for ICP-MS measurement [13]. This can be ignored for ordinary analysis, but must be taken into account for the determination of ultra-trace concentrations of analytes.
There are several ways to mitigate or eliminate the matrix effect, such as the internal standard method, standard addition method, argon gas dilution, and chemical separation method. As one of the internal standard methods, the isotopic dilution method allows a relative measurement by adding a known amount of standard (isotopically enriched form of the analyte) to the sample and measuring the ratio of analyte to standard. This can significantly suppress the matrix effect since the analyte and standard are in the same matrix. However, the $^{233}\text{U}$ recovery efficiency after pre-treatment cannot be obtained by using the isotopic dilution method. To obtain the recovery efficiency and cross-check it, the standard addition method can be used to simultaneously determine the efficiencies for both $^{233}\text{U}$ and $^{238}\text{U}$, because the matrix effect for both elements are perfectly matched. The analysis details of these two methods are described in Sec. 4.

3.2 Spectral interference

Sources of spectral interference include polyatomic interference and isobaric interference. Evaluation of the spectral interference is necessary in this work due to the ultra-low concentration of $^{238}\text{U}$ and the relatively high content of dissolved salts in blanks and Cu-samples. For $^{238}\text{U}$ and $^{233}\text{U}$ measurements, the isobaric interference can be ignored since there is no isobar for these two isotopes. The polyatomic interference is analyzed below.

A polyatomic ion can be formed in the plasma, and it can mimic a monatomic ion with the same mass-to-charge ratio. In the following, $C_{m/z}$ are denoted as the measured counts per second with ICP-MS at a particular mass-to-charge value $m/z$. The ubiquitous types of polyatomic ions, such as $\text{MO}^+$, $\text{MOH}^+$, $\text{MO}^2+$, $\text{MO}_2\text{H}^+$, $\text{M}_2^+$, $\text{M}_2\text{O}^+$, and $\text{MAr}^+$, were taken into account, and such a list could be not complete depending on the possible presence of other elements. The possible polyatomic ions that contribute $C_{233}$ are $^{232}\text{ThH}^+$, $^{201}\text{Hg}^{16}\text{O}^2+$, $^{200}\text{Hg}^{16}\text{O}_2\text{H}^+$, and $^{193}\text{Ir}^{40}\text{Ar}^+$. The concentration of $^{232}\text{Th}$, $^{200}\text{Hg}$, $^{201}\text{Hg}$ and $^{193}\text{Ir}$ in Cu-samples was measured to be approximately $10^{-12}$ g/g level or even lower; thus, the probability of forming these polyatomic ions is quite low. The Cu-samples and blanks without adding $^{233}\text{U}$ were tested to check the interference, and the measured $C_{233}$ was $3.0\pm0.0$, $2.1\pm0.9$, and $0.2\pm0.2$ for Cu-samples, blanks, and 5% HNO$_3$, respectively.

The polyatomic interference on $C_{238}$ cannot be measured directly because $^{238}\text{U}$ is naturally existing and widely distributed. Instead, we divided the possible interference into three groups and theoretically calculated their contributions. Dedicated tests were performed to verify the calculations; the details appear below.

- Group A: $^{119}\text{Sn}^+$, $^{198}\text{Hg}^{40}\text{Ar}^+$, $^{111}\text{Cd}^{16}\text{O}^+$, $^{206}\text{Pb}^{16}\text{O}_2^+$

If any of these polyatomic ions is generated, there will be also contributions to $C_{240}$ if the heaviest atom is replaced with its natural isotope, as shown in Table 2. Because the element with $m/z = 240$ does not naturally exist, non-zero $C_{240}$ observed by ICP-MS should come from the polyatomic interference. For each polyatomic ion in group A,
the ratio of $C_{240}$ to $C_{238}$ is calculated according to the natural abundances. Table 3 shows the measured $C_{m/z}$ with ICP-MS. Taking the maximum $C_{240}$ and the minimum ratio in Table 2, the interference on $C_{238}$ can be conservatively estimated to be $<0.01$ ppt.

- **Group B:** $^{198}$Pt$^{40}$Ar$^+$

Similar estimation can be applied for $^{198}$Pt$^{40}$Ar$^+$. If PtAr$^+$ is generated, the ratios $C_{234}(^{194}$Pt$^{40}$Ar$^+)/C_{238}(^{198}$Pt$^{40}$Ar$^+)$ and $C_{235}(^{195}$Pt$^{40}$Ar$^+)/C_{238}(^{198}$Pt$^{40}$Ar$^+)$ are calculated to be 4.6:1 and 4.7:1, respectively. Using the measured $C_{234}$ and $C_{235}$ in Table 3, the projected contribution of $^{198}$Pt$^{40}$Ar$^+$ to $C_{238}$ would also be $<0.01$ ppt.

- **Group C:** $^{205}$Tl$^{16}$O$_2$H$^+

$^{205}$Tl$^{16}$O$_2$H$^+$ is a polyatomic ion with four atoms. The $^{205}$Tl concentration in a blank or Cu-sample is low, and thus the formation of TlO$^+$ is rare, as shown in the lower part of Table 3, where the measured $C_{205}$, $C_{219}$, and $C_{221}$ are corresponding to $^{205}$Tl, $^{203}$Tl$^{16}$O$^+$, and $^{205}$Tl$^{16}$O$^+$, respectively. The possibility of forming four-atomic ions such as $^{205}$Tl$^{16}$O$_2$H$^+$ is much lower than that of forming TlO$^+$, and thus it can be neglected in this assay.

In conclusion, the polyatomic interference on $^{233}$U and $^{238}$U measurements for both blanks and Cu-samples are less than 0.01 ppt. If the uranium in copper is at the 0.1–1-ppt level, such sources of interference can be ignored. Furthermore, they can be effectively subtracted using the blank measurements.

### Table 2: Abundance of metal ions and calculated $C_{240}/C_{238}$ ratio.

| Polyatomic ions | Abundance         | $C_{240}/C_{238}$ |
|-----------------|-------------------|-------------------|
| Sn$^+_2$        | $^{119}$Sn = 8.58% | 14.7:1            |
|                 | $^{120}$Sn = 32.85%|                   |
| Hg$^{40}$Ar$^+$ | $^{198}$Hg = 10.02%| 2.3:1             |
|                 | $^{200}$Hg = 23.13%|                   |
| Cd$^{16}$O$^+$  | $^{111}$Cd = 12.75%| 1.9:1             |
|                 | $^{112}$Cd = 24.0% |                   |
| Pb$^{16}$O$^+_2$| $^{206}$Pb = 24.1%  | 2.2:1             |
|                 | $^{208}$Pb = 52.3%  |                   |

### 3.3 $^{238}$U contaminations from reagents

Table 4 summarizes the analysis of $^{238}$U contamination from various sources, and lists the required amount of reagents to deal with 3.2 g copper. According to the used mass and
Table 3: Measured counts per second at different m/z with ICP-MS.

| Measured C_{m/z} | 5% HNO_3 | Blanks | Cu-samples |
|-------------------|----------|--------|------------|
| C_{240}           | 0.4±0.3  | 4.4±2.5| 3.0±1.8    |
| C_{234}           | 0.2±0.2  | 9.6±4.4| 6.3±3.2    |
| C_{235}           | 1.6±2.3  | 6.8±1.9| 5.6±2.5    |

the measured ^{238}\text{U} content of each reagent, ammonia water contributed the largest contamination, and the ^{233}\text{U} standard contributed the least. ZrCl\textsubscript{4} had the worst purity, but its contribution was not significant due to the tiny amount used. Environmental contamination, due to dust in the air and surface impurities from labware, was estimated by subtracting the reagents’ contribution from the total. Although not listed in Table 4, the ^{232}\text{Th} contamination of nitric acid, ammonia water, and ZrCl\textsubscript{4} were measured to be <0.01, ~0.02, and ~150 ppt, respectively. For future prospects, we expect to further purify the ammonia water and ZrCl\textsubscript{4} and reduce the impurities by a factor of 10 and 100, respectively. Further distillation to nitric acid may result in a factor-of-2 improvement. The environmental contamination will be reduced by at least an order of magnitude with a new class 100 clean laboratory being built. The total contamination after these improvements is projected to be within 0.06 ppt, which will significantly improve the detection limits.

Table 4: Analysis of ^{238}\text{U} contamination. For each reagent, measured ^{238}\text{U} contamination and required amount to deal with 3.2 g copper is listed. Fractions represent relative contributions of each source in this assay. Significant improvement can be expected with future purifications.

| Sources                          | ^{238}\text{U} contamination (ppt) |
|----------------------------------|-----------------------------------|
|                                  | this assay | projection |
| HNO\textsubscript{3} (67%, 18.4 g)| <0.01 \textsuperscript{a} (16%)  | 0.005      |
| NH\textsubscript{3} \cdot H\textsubscript{2}O (25%, 19.5 g) | ~0.034 (59%) | 0.003 |
| ZrCl\textsubscript{4} (0.001 g) | ~130 (12%) | 1          |
| ^{233}\text{U} standard (1 g)   | ~0.014 (1%) | 0.014      |
| environmental and labware        | 0.04 (12%) | 0.004      |
| total                            | 0.35      | 0.056      |

\textsuperscript{a} Quoted from OPTIMA specification.
4 Results and discussion

The method detection limit (MDL) is defined as the minimum measured concentration of a substance that can be reported with 99% confidence so that the measured concentration is distinguishable from the method blank results. In this work, the MDL was obtained by following the U.S. Environmental Protection Agency (EPA) process [14]. The blanks with a matrix similar to that of the Cu-samples were prepared by following the procedures in Sec. 2.2, and then measured with two independent methods as a cross-check, namely the isotope dilution method (IDM) and standard addition method (SAM). As discussed in Sec. 2.2.2, $^{233}$U was used to calibrate the recovery efficiency during pre-treatment, and the SAM and IDM shared the same premise that the recovery of $^{233}$U and $^{238}$U are the same.

4.1 Isotope dilution method

Isotope dilution analysis is known as an important analytical technique for the quantification of mass-spectrometric data [15]. It is a relative approach and only involves the measurement of isotopes of the same element, thus eliminating differences in chemical behavior. If the isotopes are mixed homogeneously, their ratio is expected not to change during the entire analytical procedure, including sample preparation, analyte separation, and enrichment. In addition, the matrix effect and instability of ICP-MS have exactly the same influence on each isotope; thus, they have negligible impact on the result. In this work, a known quantity of Cu-HNO$_3$ solution (for Cu-sample) or corresponding HNO$_3$ (for blank) was mixed homogeneously with a known amount of $^{233}$U standard, and several parallel samples were prepared and measured.

For isotope dilution analysis, the measured signal ratio of $^{238}$U to $^{233}$U was used to calculate the $^{238}$U introduced during the pre-treatment of each gram of Cu:

$$ R = \frac{n_{238} + n'_{238}}{n'_{233}} $$

where $R$ is the measured ratio of $^{238}$U to $^{233}$U, $n_{238}$ is the total $^{238}$U not originating from the tracer solution, and $n'_{238}$ and $n'_{233}$ are the total $^{238}$U and $^{233}$U from the tracer solution, respectively. Note that $^{233}$U does not exist naturally, so it does not appear in the denominator. Given the measured $R$ and the known $n'_{233}$ and $n'_{238}$, $n_{238}$ can be easily calculated. In this assay, for Cu-samples, $n_{238}$ was the total amount of $^{238}$U originating from Cu and introduced during the pre-treatment, while, for blanks, $n_{238}$ was only the amount of $^{238}$U introduced during the pre-treatment.

The isotope dilution method measures the ratio of $^{238}$U to $^{233}$U in blanks or Cu-samples, and thus it is necessary to quantify the recovery efficiency of $^{233}$U because it is an important indicator used to evaluate the effectiveness of the pre-treatment method. The standard addition method was chosen to quantify the recovery efficiency, instead of the commonly used external standard method due to the possible matrix effects mentioned in Sec. 3.1.
4.2 Standard addition method

As discussed in Sec. 3.1, the Cu-samples or blanks in this assay contained certain impurities that may cause a matrix effect. If using the external standard method, the calibration curve built with pure standard solutions may result in incorrect data. Thus, the standard addition method (also see [15]), as one of the internal standard methods, was applied to solve the matrix effect by adding the standard to the samples to match the matrix.

A series of $^{233}$U and $^{238}$U standards with different concentrations was prepared in advance. The blank or Cu-sample after pre-treatment was equally divided into four or five sub-samples, typically 1 g for each sub-sample. Then, 0.2-g standard solutions with different concentrations of $^{233}$U and $^{238}$U were added to the parallel sub-samples of blanks or Cu-samples. The final mixtures, namely the test samples, were injected into the ICP-MS instrument for analysis. Figure 2 shows an example of the blank data. A linear function was used to fit the measured signals (in counts-per-second unit) versus different added $^{233}$U or $^{238}$U contents in the test samples, respectively, and the ratio of the intercept to the slope represented the concentration of $^{233}$U or $^{238}$U in the first test sample in which the concentration of added $^{233}$U or $^{238}$U was zero. Therefore, the concentrations of $^{233}$U and $^{238}$U in the blanks could be obtained. The recovery efficiency of $^{233}$U was determined and used to extrapolate the overall $^{238}$U contamination when dealing each gram of raw Cu.

![Figure 2: Measured signals vs different $^{233}$U (solid circles) and $^{238}$U (open circles) concentrations in one of the blanks by using the standard addition method; error bars are standard deviations of parallel samples. Linear function fits showed good linearities for both $^{233}$U and $^{238}$U.](image)

4.3 MDL results

Eight re-duplicative blanks were processed and measured, and Table 5 shows that a method detection limit of $\sim$0.1 ppt is consistently achievable for the two different quantitative meth-
ods. The measured $^{238}$U contents versus the $^{233}$U recovery efficiencies are shown in Fig. 3, and no obvious dependency was observed, indicating the robustness of the pre-treatment and analysis.

Table 5: Method detection limit (MDL) for $^{238}$U in copper obtained by measuring eight reduplicative blanks. SD denotes standard deviation, and MDL is calculated as $2.998 \times \text{SD}$ [14]. Two quantitative methods, standard addition method (SAM) and isotope dilution method (IDM), were used to cross-check each other. $^{233}$U recovery efficiencies obtained by SAM are also listed.

| Blank No. | meas. by SAM (ppt) | meas. by IDM (ppt) | $\epsilon^{(233}\text{U})$ |
|-----------|--------------------|--------------------|-------------------|
| 1         | 0.3206             | 0.4162             | 76.0%             |
| 2         | 0.4010             | 0.3768             | 71.0%             |
| 3         | 0.3543             | 0.3438             | 67.0%             |
| 4         | 0.3116             | 0.3325             | 84.0%             |
| 5         | 0.3623             | 0.3505             | 81.0%             |
| 6         | 0.3143             | 0.3333             | 72.3%             |
| 7         | 0.3572             | 0.3608             | 65.6%             |
| 8         | 0.4001             | 0.4125             | 64.7%             |
| average   | 0.3527             | 0.3658             | 72.2%             |
| SD        | 0.0356             | 0.0333             | -                 |
| MDL       | 0.107              | 0.099              | -                 |

Figure 3: Measured $^{238}$U vs the different $^{233}$U recovery efficiencies. No obvious dependency was found.
5 Summary

A novel co-precipitation method was developed to determine the trace or ultra-trace amount of $^{238}$U in high-purity copper, and the current MDL could achieve 0.1 ppt. The matrix effect could be effectively suppressed by using the isotope dilution method or standard addition method. The interference for ICP-MS was evaluated to be lower than 0.01 ppt and thus could be ignored for this assay. The $^{232}$Th in copper could be determined by using exactly the same method and $^{229}$Th as the tracer. Preliminary tests achieved a similar MDL and recovery efficiency for $^{232}$Th.

Several efforts are in progress to further improve the MDL. The cleanliness of the pretreatment lab will be improved to class 100. A more rigorous validation procedure is being developed to verify the surface cleanliness of the vessels and filter units. Further purification of ammonia water has been undertaken and preliminary tests have shown that the purity can be improved by an order of magnitude. Further purification of ZrCl$_4$ should be able to realize at least a 2-order-of-magnitude improvement by using an ion exchange resin column or co-precipitation. An alternative option is to find other co-precipitators that can have higher purity or can be purified easily. Nevertheless, along with the above improvements, the sources of polyatomic interference will become a major factor that affects MDL. The collision cell incorporated into the ICP-MS setup can be used to suppress such effects. Collision reaction cell technology is one of the major breakthroughs to obviate the polyatomic or isobaric interference for ICP-MS measurement based on ion-molecule chemistry. The ions entering the multipole (quadrupole, hexapole or octupole) system will collide or react with the collision gas, such as H$_2$ or He. Then, the polyatomic ions can be changed into interference-free substances, or the elements to be measured can be turned into other ions that will not cause interference. Ultimately, the proposed method promises to improve the MDL of $^{238}$U and $^{232}$Th in copper by an order of magnitude. Methods determining the $^{238}$U and $^{232}$Th in, e.g., other metals, quartz, and silicon, will be developed in the future as well.

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