Ultra-low background mass spectrometry for rare-event searches

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ABSTRACT

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) allows for rapid, high-sensitivity determination of trace impurities, notably the primordial radioisotopes $^{238}\text{U}$ and $^{232}\text{Th}$, in candidate materials for low-background rare-event search experiments. We describe the setup and characterisation of a dedicated low-background screening facility at University College London where we operate an Agilent 7900 ICP-MS. The impact of reagent and carrier gas purity is evaluated and we show that twice-distilled ROMIL-SpA™-grade nitric acid and zero-grade Ar gas delivers similar sensitivity to ROMIL-UpA™-grade acid and research-grade gas. A straightforward procedure for sample digestion and analysis of materials with U/Th concentrations down to 10 ppt g/g is presented. This includes the use of $^{231}\text{U}$ and $^{230}\text{Th}$ spikes to correct for signal loss from a range of sources and verification of $^{238}\text{U}$ and $^{232}\text{Th}$ recovery through digestion and analysis of a certified reference material with a complex sample matrix. Finally, we demonstrate assays and present results from two sample preparation and assay methods: a high-sensitivity measurement of ultra-pure Ti using open digestion techniques, and a closed vessel microwave digestion of a nickel-chromium-alloy using a multi-acid mixture.

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1. Introduction

Rare event search experiments such as those seeking interactions from galactic dark matter scattering or evidence of neutrino-less double beta decay ($\nu\beta\beta$) require construction from intrinsically radio-pure materials to limit radiogenic backgrounds. Experiments must conduct radio-assay campaigns to select materials and to accurately characterise residual radioactivity for the experiment’s background model against which any observed excess will be evaluated and statistical confidence ascribed. The radioactive isotopes $^{238}\text{U}$ and $^{232}\text{Th}$ and their decay-chain progeny are of particular concern, contributing the bulk of the $\gamma$-ray, $\alpha$-particle, and, via spontaneous fission and ($\alpha$, $n$) reactions, neutron-induced backgrounds.

Comprehensive radio-assay campaigns now increasingly deploy multiple techniques to build a high-precision background model, and to meet sample throughput requirements during the experiment’s construction phase. Mass spectrometry techniques such as ICP-MS can be used to directly measure trace quantities of $^{238}\text{U}$ and $^{232}\text{Th}$, delivering assays from small samples that are digested and screened with turnaround times on the order of 1–2 days. ICP-MS can achieve part-per-trillion (ppt) g/g level sensitivity to $^{238}\text{U}$ and $^{232}\text{Th}$ when sample preparation protocols with stringent cleanliness constraints are used to limit contamination [1–3]. Gamma-spectroscopy is used to assay larger samples, including finished components, over several weeks to determine the activities of the decay chain daughters [4]. Other techniques such as Glow-Discharge Mass Spectrometry (GD-MS) and Neutron Activation Analysis (NAA) may also be used for some materials not well-suited to either ICP-MS or gamma-spectroscopy.

Here we present results from a new ICP-MS facility at University College London (UCL) constructed to perform radio-assays in support of rare-event searches, such as the ‘Generation-2’ LUX-ZEPLIN (LZ) dark matter Experiment [5]. In Section 2 we give an overview of the UCL ICP-MS facility and investigate the impact of reagent and Ar gas purity on achievable sensitivity. Then, in Section 3, we describe a straightforward procedure for routine and fast-turnaround of materials with U/Th concentrations down to 10 ppt g/g. We present detection limits for different vessel cleaning protocols and describe the use of $^{230}\text{Th}$ and $^{235}\text{U}$ spikes for signal loss correction. A certified reference material representing a realistic sample matrix is processed to verify overall U/Th signal recovery. Finally, in Section 4 we present results from an open digestion of ultra-pure Ti and a closed vessel digestion of a nickel-chromium-alloy requiring multi-acid digestion.

2. Laboratory overview

The UCL ICP-MS facility was installed and commissioned in a newly constructed ISO Class 6 cleanroom in late 2015. The primary instrument is an Agilent 7900 ICP-MS with an instrument sensitivity to U and Th.
down to \(10^{-15} - 10^{-14} \text{ g/g (1–10 parts-per-quadrillion (ppq) g/g). The ICP-MS is fitted with an integrated auto-sampler for high-speed discrete sample uptake with a low-flow, Peltier-cooled sample introduction system. High-purity Ar (N5.5 or N5.0), He and H₂ (N6.0) are introduced to the system as carrier, collision and reaction gases, respectively. The system octopole can provide species discrimination through interference removal by running in either the He collision or H₂ reaction gas mode. The system is fitted with an inert sample introduction kit that includes a PFA nebuliser, spray chamber and torch connector, platinum sampling and skimmer cones and a plasma torch with quartz outer body and sapphire injector. This allows up to 20% (v/v)¹ acid concentration in the sample introduced to the ICP-MS, including hydrofluoric acid (HF).

The limiting factor in realising reproducible high throughput ppt sensitivity is clean, standardised sample preparation requiring dedicated digestion apparatus and well developed procedures, including the use of ultra-pure acids to avoid contamination of samples. The facility has the relevant infrastructure to provide this, including: sample preparation in separate ISO Class 5 laminar flow unit (LUF), sample digestion with the Milestone ETHOS-UP closed vessel microwave digestion system with SK-15 high pressure reactor, Milestone sub-boiling point acid distillation (subCLEAN) and reflux cleaning (traceCLEAN) systems and an ELGA PURELAB flex ultra-pure de-ionised (DI) water supply (18.2 MΩ cm, <5 parts-per-billion (ppb) total organic carbon). Finally, a Pyro-260 microwave ashing system allows for the digestion of materials such as PTFE that are resistant to most acids, including HF.

For most assays we follow material-by-material digestion routines available for the ETHOS-UP and SK-15 high pressure reactor. These specify the acid combinations and microwave heating profiles needed to achieve complete digestion. Where these do not exist, custom routines for non-standard materials have been developed based on existing routines and in partnership with Milestone and U.K. supplier Analytix Ltd. Typically nitric acid (HNO₃) is used to digest organic material, hydrofluoric acid (HF) for decomposing silicates and metals such as Ti that are resistant to oxidising acids, and hydrochloric acid (HCl) for Fe-based alloys. When fitted with the SK-15 high pressure reactor the ETHOS-UP can simultaneously digest up to 15 samples (with the same chemistry) each in their own 100 mL TFM vessels. TFM is a chemically modified form of PTFE with excellent properties for trace analysis: high chemical resistance, low-trace metal impurities, high melting point and an extremely smooth surface for decontamination and cleaning.

### 2.1. Reagent purity

The purity of acids and other reagents used for digestion, vessel-cleaning and preparation of calibration standards is critical for the limit of detection achievable when assaying a material. For standard cleaning of vessels and digestion of samples with > ppb U/Th concentrations we use ROMIL-SpA² Super Purity Acids (SpA). These are cost effective acids produced using sub-boiling point distillation and are typically certified to <100 ppt ²³²Th and ²³³Th per gram of reagent. For lower detection limits and sub-ppb materials we use ROMIL-UpA³MAcids and reagents which are produced through multiple re-distillation and are typically certified to <0.1 ppt ²³²Th and ²³³Th.

Table 1 compares measured background equivalent concentrations (BEC) for nitric acid process blanks made with ROMIL-SpA and ROMIL-UpA acids as well as for ROMIL-SpA nitric acid that was subsequently twice-distilled using the in-house subCLEAN distillation system. Inferred concentrations for undiluted HNO₃ are consistent with the manufacturer’s stated typical concentrations: <100 ppt U/Th for SpA and <0.1 ppt U/Th for UpA. We find that twice-distilled SpA is consistent with the UpA background concentration for ²³²Th and approaches that for ²³³U. Based on these results we now use twice-distilled SpA-grade nitric acid for most digestions unless ultimate detection limits are required. In addition, twice-distilled SpA can be used in cleaning procedures requiring larger quantities of reagents where UpA-grade acid is prohibitively costly.

1 Unless stated otherwise v/v indicates a dilution by volume of reagent at standard concentration, in this case 69% HNO₃, with de-ionised water.

### 2.2. Ar gas supply

In analysis mode the ICP-MS consumes up to 20 litres per minute of argon gas, one 50 l. 200 bar cylinder for every 8 h of running.² Given the importance of Ar gas purity for ultra-trace analysis and the potential costs associated with the high-turnaround we have compared the performance of the ICP-MS with two different grades of bottled gas: N5.0/zero-grade (min. 99.999%) and N5.5/research-grade (min. 99.9995%), where the cost of research-grade is significantly higher, between 5 and 10 times that of zero-grade from our supplier.

Table 2 shows the ²³²Th and ²³⁸U BECs for a 5% (v/v) HNO₃ acid blank for both zero- and research-grade argon. Two sets of acid blanks were prepared, a first using unconditioned labware (virgin PP DigiTubes and 1 L Nalgene containers) that was simply rinsed with DI water prior to use and a second set where all labware was first leached in 10% HNO₃ for 24 h prior to use. Switching to blanks prepared using pre-conditioned labware halved the BECs down to 7.1 ppq ²³²Th and 5.9 ppq ²³³Th when using research-grade argon. Zero-grade argon shows a few ppq increase with respect to research-grade although results are almost within measurement errors.

Switching to zero-grade did not cause deterioration in the CPS/ppm instrument response or the level of oxides and doubly charged species during tuning; in this case (¹⁹⁵Ce⁺⁺, ¹⁹⁶Ce⁺⁺⁺) and (⁷⁰⁷Ce⁺⁺, ¹⁹⁶Ce⁺⁺⁺). Given this and the sub-dominate blank rate increment we conclude zero-grade argon is sufficient for most routine samples where ²³²Th and ²³³U are the analytes of interest.

### 3. Procedures and analysis

With a focus on high-throughput and fast-turnaround of time-critical assays, straightforward cleaning, sample preparation and analysis procedures have been developed for materials with U/Th concentrations in the 10 ppb to 1 ppb range: Samples are microwave-digested in pre-cleaned TFM vessels using ultra-high purity acids. They are then diluted, without further chemical treatment, into disposable 50 mL polypropylene (PP) vessels ready for ICP-MS analysis. Fractional recoveries of

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¹ A liquid argon supply was considered but was less cost effective due to wastage during periods of downtime.

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For a differential measurement. If this is not possible the average of three mL TFM vessel on an analytical balance – located in the Class 5 LFU – prepared.

completed in a single day.

full assay including digestion, ICP-MS measurement and analysis can be becoming important.

For digestions with UpA-grade reagents desorption of impurities in the few ppt g/g of 230Th and 238U spikes added prior to digestion are used to correct for 230Th and 232Th and 238U signal loss from a range of sources. In particular, this enables accurate analysis of samples with high total dissolved solids (TDS) where the instrument response degrades throughout the run. A full assay including digestion, ICP-MS measurement and analysis can be completed in a single day.

For a typical material three samples and three process blanks are prepared. Where possible, samples are weighed directly into the 100 mL TFM vessel on an analytical balance – located in the Class 5 LFU – for a differential measurement. If this is not possible the average of three separate measurements is taken before and after addition of the sample. For a 0.1 g sample this results in a systematic uncertainty of between 2% and 4%. If applicable, 230Th and 238U spike solution is then pipetted into the vessel where the amount added is determined as a differential measurement with a fractional error <0.2%. The digestion vessel is then transferred to the fume cupboard where reagents are added.

Following digestion, the content of each vessel is decanted and rinsed into a 50 mL PP vessels (pre-weighted and labelled) using DI water and diluted up to a total volume of 50 mL. The PP vessels are then weighed on the analytical balance to determine overall dilution and sample concentration. If further dilution is needed to reach a sample concentration of 0.296 or because the sample is expected to have a high (> few ppb U/Th content) then a second stage of dilution into a new PP vessel is performed. The samples are then ready to be poured into 6 mL PP vials and loaded into the integrated auto-sampler.

The ICP-MS plasma auto-tune mode is chosen based on the sample type: for samples with high TDS (0.01%–0.2%) the General Purpose mode is used, whereas for low TDS the Low Matrix mode is used. The ICP-MS is then auto-tuned for high mass sensitivity using a tuning solution containing Li, Y, Ti, Co and Ce in 2% HNO3. The samples are then analysed in a single ICP-MS run: for routine analysis we use a batch with external calibrations, whereas for high precision measurements of samples with complex matrices we use the method of standard additions to prepare calibrations in the sample matrix itself. To monitor instrument stability throughout the batch

We apply two levels of cleaning for plastic labware such as the PP and 6 mL auto-sampler vials. Unlike the TFM digestion vessels, they do not come into contact with concentrated acids at elevated temperatures and we have found that using new labware that has simply been rinsed three times with DI water (and left to dry in the LFU if being used for weighing) is sufficient for most purposes as typical U/Th BECs seen in calibrations and samples prepared are below <30 ppq. For samples requiring lower blank rates we leach all labware in 20, 10 or 5% (v/v) SpA nitric acid for 24 h prior to use, where the concentration is matched to account for the expected use. An example of this was shown in Table 2, where we saw a halving of the blank rate for 5% Upa blanks prepared in DigiTubes that were first leached in 10% SpA HNO3 for 24 h.

As they hold concentrated reagents at elevated temperatures contamination from the digestion vessels is of particular concern. Following sample digestion each TFM vessel and lid is rinsed a minimum of three times with DI water and then, after drying, is put through a decontamination microwave programme. For routine cleaning this is a 15 min ramp and 15 min hold at 180 °C with 5 mL of HNO3, SpA-grade and 5 mL of DI water. If a further reduction in blank rate is required the process is repeated with higher purity reagents, longer hold time or by matching the reagents to those being used for the subsequent digestion. For example, for the open vessel digestions of Ti wire in Section 4.1 the vessel cleaning routine included an additional 2 mL of hydrofluoric acid.

We now compare process blank rates for vessels pre-cleaned using different purity HNO3, first with SpA-grade and then with doubly-distilled SpA. Table 3 shows process blank rates measured following closed vessel digestion of 10 mL of Upa-grade nitric acid on a typical microwave routine (15 min ramp and 20 min hold at 210 °C). There is a clear improvement when switching to doubly-distilled SpA with the average blank rates coming down to <5 ppq for 232Th and <10 ppq for 238U. More importantly, the variability of the blank rate reduces significantly with standard deviations going from >10 ppq to <3 ppq.

Taking 3× the standard deviation on the blank rates in Table 3 as a guide to the achievable detection limits and accounting for a hypothetical 500-fold dilution (0.1 g digested sample diluted to 50 mL final solution) this implies detection limits of around 20 ppt g/g for vessels pre-cleaned with SpA HNO3, and below 5 ppt g/g when using vessels cleaned with doubly-distilled SpA.

The reduced blank rates demonstrated with the double-distilled SpA pre-cleaning are at or below instrument detection limits when running the ICP-MS in a General Purpose plasma mode with a standard tune for high-mass sensitivity and stability. It is reported that with a custom

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2 Plus a sacrificial sample in digestion vessel one, the reference vessel with a temperature probe used for microwave process control.

3 To ensure TDS are below the maximum recommended by the manufacturer to avoid significant matrix effects and contamination of sampler and skimmer cones.

Table 3

| Blank rate: ppq g/g diluted solution | 230Th | 238U |
|-------------------------------------|-------|-------|
| **Vessel pre-cleaned with SpA** |       |       |
| V1                                 | 3.8 ± 2.2 | 8.2 ± 5.7 |
| V2                                 | 0.4 ± 0.4 | 7.4 ± 2.5 |
| V3                                 | 0.6 ± 0.1 | 9.0 ± 8.4 |
| V4                                 | 3.6 ± 3.5 | 9.1 ± 6.8 |
| Avg. ± Std.Dev.                    | 3.5 ± 2.3 | 8.7 ± 1.1 |

| **Vessel pre-cleaned with distilled-SpA** |       |       |
| V1                                 | 3.8 ± 2.2 | 8.2 ± 5.7 |
| V2                                 | 0.4 ± 0.4 | 7.4 ± 2.5 |
| V3                                 | 0.6 ± 0.1 | 9.0 ± 8.4 |
| V4                                 | 3.6 ± 3.5 | 9.1 ± 6.8 |
| Avg. ± Std.Dev.                    | 3.5 ± 2.3 | 8.7 ± 1.1 |
tuning the Agilent 7900 can achieve >1000 CPS/pppt response with instrument detection limits of 1.3 ppq with BEC of 0.48 ppq for a 238U calibration [6]. In these circumstances further steps to reduce the process blank rate would be motivated, such as using only fluorinated polymers (FEP, PFA) for all labware and the use the traceCLEAN acid steam cleaning system.

3.2. 230Th and 233U spikes

Isotopic reference materials for 230Th and 233U were purchased from the Institute for Reference Materials and Measurements (IRMM)\(^6\) for use as spikes in isotopic dilution analysis. Each reference material was supplied in a glass ampoule containing 5 mL of chemically stable nitric acid and was subsequently diluted using 5% (v/v) UpA nitric acid into pre-conditioned FEP bottles to make ~100 mL stock solutions. These stock solutions are then further diluted as needed to make ~ppb g/g working solutions from which the 1–100 ppt typical spike and calibration solutions are made up.

Tables 4 and 5 show calculated concentrations for the stock, working and a final spike solution based on certified values for the 230Th (IRMM–061 [7]) and 233U (IRMM–051 [8]) spikes, respectively. To confirm the spike concentrations as well as the overall dilution scale the spike solutions were measured using an ICP-MS run with external calibrations (matrix matched) and show good agreement for all isotopes.

The low spike ratios of \(n(231\text{Th})/n(230\text{Th}) < 0.2\%\) and \(n(238\text{U})/n(233\text{U}) < 1\%\) and the proximity of typical low-background materials to instrument detection limits means that for many materials full isotope dilution analysis to determine 232Th and 238U reduces to a simple spike recovery correction.

3.3. 232Th and 238U recovery for IAEA-385 Irish sea sediment CRM

To verify 232Th and 238U recovery in a realistic sample matrix four samples of reference material IAEA-385 [9] were processed for comparison to certified values. IAEA-385 is a powder made from sediment collected from the Irish Sea in 1995 which was sieved and homogenised and then certified for a range of radioelements. Consisting mainly of Si (160 mg/g), Ca (55 mg/g), Al (45 mg/g), Fe (31 mg/g) and K (18 mg/g), it represents a complex matrix requiring multi-acid digestion. The certified values of 33.7 Bq/kg 232Th and 29.0 Bq/kg 238U translate to concentrations of 8.3 ppm and 2.3 ppm respectively.

### Table 4

| IRMM–061 230Th spike isotope concentrations based on certified values [7] for the various stages of dilution. ICP-MS measured concentrations of the final spike solution using an external 238Th calibration are in good agreement. | 238Th | 232Th |
|---|---|---|
| **Ampoule [ppm]** | 0.569 | 0.00086 |
| Stock [ppb] | 30.77 | 0.047 |
| Working [ppt] | 214.2 | 0.324 |
| Spike [ppt] | 38.49 | 0.058 |
| Mean. [ppt] | 39.2 ± 0.3 | 0.06 ± 0.01 |

### Table 5

| IRMM-051/233U spike isotope concentrations based on certified values [8] for the various stages of dilution. ICP-MS measured concentrations of the final spike solution using an external 238U calibration are in good agreement. | 238U | 235U | 234U | 233U |
|---|---|---|---|---|
| **Ampoule [ppm]** | 2.354 | 0.0221 | 0.0052 | 0.0006 | 0.0197 |
| Stock [ppb] | 142.9 | 1.339 | 0.315 | 0.036 | 1.197 |
| Working [ppt] | 1436 | 13.46 | 3.16 | 0.36 | 12.03 |
| Spike [ppt] | 46.8 | 0.439 | 0.103 | 0.012 | 0.392 |
| Mean. [ppt] | 48.3 ± 0.4 | 0.44 ± 0.04 | 0.1 ± 0.02 | <0.1 | 0.38 ± 0.02 |

### Table 6

ICP-MS analysis of certified reference material IAEA-385, sediment from the Irish sea. Measured ppm g/g values are corrected for sample dilution and include a sub-dominant process blank subtraction (<0.01 ppm). For the final values we take the average and standard deviation of all four samples, convert to Bq/kg and compare with certified values and their 95% confidence intervals [9].

| Sample mass (g) | Sample conc. % | ppm g/g Sea sediment |
|---|---|---|
| 232Th | 238U |
| #1 | 0.092 | 0.0018 | 7.27 ± 0.14 | 2.41 ± 0.02 |
| #2 | 0.180 | 0.0034 | 6.31 ± 0.08 | 2.32 ± 0.02 |
| #3 | 0.176 | 0.0035 | 5.95 ± 0.10 | 2.37 ± 0.02 |
| #4 | 0.188 | 0.0029 | 6.35 ± 0.06 | 2.41 ± 0.04 |
| Avg. | — | — | 6.47 ± 0.56 | 2.38 ± 0.04 |
| Equiv. Bq/kg | 26.3 ± 2.3 | 29.4 ± 0.5 |
| c.f. IAEA certified | 33.7 [32.8–33.9] | 29 [28–30] |

Samples were digested using the ETHOS-UP microwave following a method developed for soil samples with Analytix. Up to 0.2 g of sample was weighed into each TFM vessel and then 8 mL HNO3 (ROMIL SpA) + 2 mL HF (Fisher TraceMetal) + 2 mL H2O2 (Merck Suprapur) was added. The vessels were left for 10 min before running through a modified ETHOS-UP Sea Sediment method (SK – Environmental – 026): 15 min ramp to 200 °C, then hold for 20 min, then fan cool for 40 min. Following digestion the vessel contents were decanted into 50 mL DigiTubes and diluted up to a total volume of 50 mL using de-ionised water, a dilution of around 250. The digested solution was a clear light green/blue liquid. Due to the high > ppm levels of contamination expected a further factor 100 dilution was performed to bring final solution concentrations down to <100 ppt to avoid potential contamination of the sample introduction system and ICP-MS itself. In addition to the four IAEA-385 samples three process blanks were prepared. Samples were not spiked with 230Th and 233U as this would have required a significant quantity of each stock solution, with an associated potential for contamination, to be added to each vessel to yield comparable concentrations to those expected for 232Th and 238U.

Twice diluted samples and process blanks were processed in a single batch with the Agilent 7900 running in General Purpose plasma mode and auto-tuned for high-mass sensitivity. 20, 75, 150 and 300 ppt external calibrations were used yielding instrument sensitivities of 350 CPS/pppt 232Th and 351 CPS/pppt 238U with calibration blank rates <1 ppt. Measured concentrations in ppm g/g IAEA powder are shown in Table 6. These are corrected for sample dilution and include a sub-dominant process blank rate subtraction (<0.01 ppm). Individual results for each sample are shown as well as their average and standard deviation. The equivalent Bq/kg specific activity can be compared to the IAEA certified values (95% confidence intervals in square brackets). For 238U the measured specific activity is within 2% of the certified value whereas for 232Th there is a ~20% deficit indicating a partial recovery.

The partial recovery of 232Th could be due to a number of factors such as the formation of insoluble fluoride species formed by the reaction of Th and hydrofluoric acid or the over-dilution of the digested samples such that 232Th is no longer stable in the solution. Further measurements with a boric acid (H3BO3) complexation step and with judiciously chosen 233Th and 235U spikes would likely resolve the source of partial recovery. For now an additional 20% systematic uncertainty is assumed for 232Th measurements.

4. Results for typical low-background materials

To illustrate both a high-sensitivity assay using open digestion and a more routine material requiring closed-vessel digestion in a multi-acid mixture we present results for two low-background materials that were assayed as part of the LZ materials screening campaign: an open vessel digestion of small drilling burrs taken from a slab of ultra-low background Ti and a closed-vessel digestion of a nickel-chromium- alloy wire.

\(^6\) Located in Geel, Belgium.

\(^7\) Leached for 48 h in 20% (v/v) SpA nitric acid.
4.1. Open digestion: ultra-pure Ti chips

TIMET HN3469 is a single 15 000 kg slab of ultra-radiopure ASTM Grade 1 titanium procured to make the LZ cryostat following an extensive radio-assay campaign [10]. A sample of ~2 g of burrs drilled from a test coupon, taken from the middle of TIMET HN3469, were provided for rapid ICP-MS analysis for the purposes of quality control. For this coupon the inferred values of $^{238}\text{U}$ and $^{232}\text{Th}$ as determined through gamma-spectroscopy measurements with high purity germanium (HPGe) detectors were $^{238}\text{U} = 2.8 \pm 0.15 \text{ mBq/kg}$ and $^{232}\text{Th} < 0.2 \text{ mBq/kg}$. The small sample mass, low activity and fast turnaround makes this a canonical use-case for ICP-MS.

Prior to digestion samples were sonicated twice in high-purity IPA (Fisher Chemical Optima grade >99.9%), rinsed in DI water and then etched in a 2% (v/v) HF and 2% (v/v) HNO$_3$ solution. The etching process consumed around 30% of the mass, after which samples were rinsed in DI water and left to dry overnight in the ISO Class 5 LFU. At each stage a small amount of the sample was set aside to gauge the effectiveness of each step. Four samples with masses between 0.1 and 0.2 g were prepared for digestion: samples #1 and #2 had been both cleaned and etched, sample #3 was only cleaned and sample #4 was neither cleaned nor etched.

Samples were weighed into open TFM vessels (pre-cleaned in the ETHOS-UP with SpA-grade HNO$_3$) and spiked with ~1.5 mL of 50 ppt $^{230}\text{Th}$ and $^{234}\text{U}$ solution, to give ~0.75 ppt in diluted samples. In addition to the sample vessels three process blanks were prepared and spiked. To digest, 10 mL of a ~10% (v/v) HF and ~10% (v/v) HNO$_3$ mixture was added to each vessel. The vessels were left for an hour (visually, samples were dissolved within 5 min) prior to a two-stage dilution with DI water to bring the total sample concentration to below 0.2%, the maximum recommended TDS for the ICP-MS. For both etching and digestion only ROMIL UpA-grade HF and doubly-distilled SpA HNO$_3$ were used.

All diluted samples and blanks were processed in a single ICP-MS batch in General Purpose plasma mode and auto-tuned to high-mass sensitivity. External calibrations of 0.2, 1.0 and 20.0 ppt established instrument sensitivities of 238 CPS/ppt $^{238}\text{U}$, 238 CPS/ppt $^{232}\text{Th}$, 272 CPS/ppt $^{235}\text{U}$ and 272 CPS/ppt $^{238}\text{U}$. Results are shown in Table 8. Measured ppb g/g of Ni-Cr-alloy concentrations include a sub-dominant average process blank subtraction and are corrected for the spike recovery in sample #1. Errors on individual sample measurements include the instrument statistical error, uncertainty in the process blank and the error associated with weighing the ~1 g samples. The use of a single spike correction results in an additional 10% systematic error giving final specific activities for $^{232}\text{Th}$ of 4.0 \pm 0.1 (meas.) \pm 0.4 (syst.) \text{ mBq/kg}, and 110.9 \pm 2.1 (meas.) \pm 1.1 (syst.) \text{ mBq/kg} for $^{238}\text{U}$. This measurement demonstrates the precision that can be achieved for samples with relatively high activities. The additional systematic would be eliminated by the use of appropriate quantities of spikes in all samples.

5. Summary and outlook

The UCL ICP-MS rare-event search laboratory serves as a dedicated materials screening facility for the LZ dark matter experiment. The primary instrument is an Agilent 7900 ICP-MS with an instrument sensitivity down to ~10 ppt U/Th and fitted with an inert sample introduction kit to allow direct sampling of solutions with up to 20% acid concentrations, including HF. The ICP-MS is operated inside an ISO Class 6 cleanroom alongside all necessary infrastructure for sample preparation.

Straightforward cleaning, sample preparation and analysis procedures have been developed to allow high-throughput and fast-turnaround of materials with U/Th concentrations down to 10 ppt g/g of sample. These are based on microwave assisted sample digestion in pre-cleaned TFM vessels and then direct ICP-MS measurement of the diluted sample with no further chemical treatment or evaporation steps. We use $^{239}\text{Th}$ and $^{233}\text{U}$ spikes to correct for signal loss from a range of sources, and demonstrate the importance of their use through digestion and assay of a complex sea sediment CRM. These procedures allow a complete assay, including digestion, ICP-MS measurement and analysis, to be completed in a single day.

We have evaluated the impact of reagent purity on U/Th background levels and found that for most routine assays it is possible to use doubly-distilled ROMIL-SpA nitric acid as an almost equivalent and cheap alternative to ultra-pure ROMIL-UpA grade acid. In addition, it was shown that switching ICP-MS Ar carrier gas purity from research-grade (N5.5) to zero-grade (N5.0) causes no significant increase in U/Th background level given current instrument sensitivity and labware cleaning protocols.

Results were presented for two typical low-background materials assayed as part of the LZ materials screening campaign: an open digestion of ultra-pure Ti demonstrating a ~30 ppt g/g $^{232}\text{Th}$ measurement and showing consistency with HPGe results for both Th and U; and a closed vessel digestion of a nickel–chromium-alloy wire requiring a multi-acid mixture as an example of a high-precision measurement of a ppb-level sample. These demonstrate the suitability of the procedures to screen the majority of materials for the current generation low-background experiments. Over 100 assays have been performed for LZ with this facility already as part of the experiment’s construction phase. Results from these measurements will be presented by the collaboration in the future.

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*a Using a Knipex Chrome Vanadium steel wire cutter pre-cleaned with IPA-wipes and DI water.
Looking ahead, future low-background experiments, such as so-called ‘Generation-3’ dark matter, and next generation $0{\nu}\beta\beta$ searches will require backgrounds and consequent radio-assay capability at least an order of magnitude better than present searches. ICP-MS, with both requisite sensitivity to direct $^{232}$Th and $^{238}$U measurements and high throughput, will be a key technique, complementing gamma-spectroscopy, radon emanation, and material surface activity measurements in the radio-assay campaigns of all such future experiments. Moreover, sensitivity can be enhanced further. Improved cleanliness procedures and matrix separation techniques, see for example [11], can be applied to concentrate U/Th and boost $^{232}$Th and $^{238}$U signal to sub-ppt sensitivity.

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