



Complete dissolution of solid matrices using automated borate fusion in support of nuclear decommissioning and production of reference materials

E. Braysher^{1,2} · B. Russell¹ · S. Woods¹ · M. García-Miranda¹ · P. Ivanov¹ · B. Bouchard³ · D. Read^{1,2}

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Abstract

Accurate measurement of natural and anthropogenic radionuclide concentrations is of critical importance to end users in the nuclear sector to ensure correct classification prior to storage, recycling, reprocessing or disposal. Uncertainties in the characterisation of solid matrices and materials could lead to safety, quality and financial implications. Robust sample preparation methods are vital, in particular effective sample digestion, as under-estimated chemical yield recovery results in a corresponding under-estimation of activity levels. Borate fusion has been proven to effectively digest a range of complex sample matrices in the geosciences but is not used routinely elsewhere. In this study, we describe an automated procedure for borate fusion of multiple matrices encountered in nuclear decommissioning, containing diverse radionuclides over a range of activity concentrations. The impact of digestion flux, sample mass and sample to flux ratios are described, as well as the subsequent separation and measurement techniques. The results contribute to accurate and precise measurement of radionuclides in various matrices, as well as to characterisation of reference materials, providing greater confidence in nuclear industry programmes worldwide.

Keywords Fusion · Dissolution · Radionuclide · Decommissioning · Reference material · Characterisation

Introduction

There are currently 438 nuclear power plants in operation worldwide, with a further 149 that are, or soon will be, undergoing decommissioning [1]. Only 13 nuclear power plants have been completely decommissioned worldwide, and lengthy timescales are required to complete the process, meaning technical experience is limited. Given that significant decommissioning activities are either planned or underway in many countries, quality assurance in anthropogenic radionuclide measurements must be ensured. Building on the foundations of nuclear metrology with new reference standards, methods and instruments will improve the safety

and cost efficiency of the decommissioning process [2]. All nuclear sites contain large quantities of hazardous materials with a wide variety of radionuclides in different matrices including concrete, steel, graphite and plastics. In the UK alone, the Nuclear Decommissioning Authority (NDA) has estimated that by 2150, a total of 4.8×10^7 m³ packaged radioactive wastes in 12 different matrices will require disposal via various routes, depending on the activity level [3, 4].

Naturally occurring radioactive material (NORM) is a second key area of consideration, and is a by-product of multiple industries, as highlighted in the Environmental Permitting Regulations 2018 (UK) and the Euratom Basic Safety Standards of the European Commission (EU) [5, 6]. The matrix of a NORM residue varies significantly depending on its industry of origin, and the activity concentrations of naturally occurring radionuclides (isotopes from the ²³⁸U, ²³⁵U and ²³²Th decay chains) can be enhanced through certain anthropogenic processes. Industries that undertake such processes need to adhere to regulations surrounding the storage, handling and disposal of such material.

Effective sample digestion is of critical importance for accurate radionuclide characterisation, as the effectiveness

✉ E. Braysher
emma.braysher@npl.co.uk

¹ National Physical Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, UK

² University of Surrey, Stag Hill, Guildford, Surrey GU2 7XH, UK

³ Katanax systems inc., Quebec, QC G2C 1X1, Canada

of the dissolution has direct effects on the resultant data. This applies to both the characterisation of NORM and decommissioning materials. Additionally, the accurate characterisation of radionuclides is reliant on measurement of certified reference materials (CRM) that ensure quality control and metrological traceability through method validation and calibration of instruments [7]. Owing to the wide range of sample types across industrial sectors, the current lack of CRM is a significant constraint [2, 7–12].

Depending on the sample matrix and the nature of the radionuclide(s) present, some approaches cannot guarantee total dissolution of a sample. If radionuclides are in a refractory matrix, they will not be removed fully without complete digestion [13]. For example, naturally occurring uranium and thorium are often associated with silicate minerals [14–16], where incomplete dissolution would lead to uranium and thorium yield not being representative. Conversely, in some cases, complete dissolution of a sample is not necessary if it can be demonstrated that the element of interest can be quantitatively leached from the sample. This has been proven to be the case for a number of radionuclides (including ^{90}Sr , ^{135}Cs and ^{137}Cs) in certain coal fly ash, soils, cements and sediments [17–19].

Acid leaching typically involves the addition of HNO_3 or HCl ; the use of HF is routine for silicates but is avoided wherever possible due to safety concerns (potential for severe skin burns and eye damage) [20]. The sample size that can be leached is high (up to 100 g has been reported) [17, 19–23], which is advantageous for low activity samples. Leaching is a rapid and straightforward approach in terms of the chemicals and equipment required. Some matrices, such as those containing silicates, phosphates or refractory oxides require harsher conditions for complete digestion. Hydrofluoric acid is effective in decomposing silicates [20, 24, 25]; however, the risks of working with HF and the volatility of fluorides in uranium-containing samples must be considered. Examples of incomplete dissolution techniques for a range of matrices are shown in Table 1.

Following a recent Performance Evaluation Program by the US Department of Energy, Maxwell et al. [27] described how approximately 80% of participating laboratories failed to accurately determine uranium isotopes in soil samples due to incomplete dissolution of refractory particles using acid leaching methods. Laboratories that did not utilize total dissolution methods typically reported ^{234}U and ^{238}U results with approximately –60% bias, even when using HF . Further study showed that using a sodium hydroxide fusion method on soil samples allowed an accurate determination of the MAPEP soil, with an 86% chemical yield from the procedure.

Wang et al. [28] reported a sequential method for determination of actinides and ^{90}Sr in soil. An acid leaching process involving HNO_3 and H_2O_2 was carried out, with activities of ^{238}Pu , ^{230}Th , ^{90}Sr , ^{241}Am and ^{238}U determined using liquid scintillation counting and alpha spectrometry. The recoveries ranged from 40–80%, with the lowest values seen for ^{241}Am . It was noted that the acid leach used did not effectively digest refractory particles present in the sample, and it was suggested that sodium hydroxide fusion may be more effective for this purpose [27].

A study by Hubley et al. [29] investigated field-deployable dissolution techniques as a method to decrease response time following a nuclear event. It was acknowledged that many refractory matrices required HF for complete digestion, but open vessel acid digestions were limited because of the low boiling points of HNO_3 and HF (120 °C and 112 °C, respectively), meaning microwave digestion with pressure vessels were often used. Such microwave digestion systems are not generally field-deployable, have limited sample throughput and sample size (0.5–1 g), and require extensive training and specialized laboratory facilities. It was concluded that a more convenient approach to dissolution techniques for nuclear fallout samples was required. It was also stated that there is not a single chemical dissolution technique capable of handling all types of refractory matrices that could be encountered in nuclear fallout, especially

Table 1 Examples of incomplete dissolution methods

Sample type	Element of interest	Sample size (g)	Acid	Reference
NIST freshwater lake sediment standard reference material	Caesium	2	<i>Aqua regia</i>	Karam et al. [26]
Coal fly ash	Aluminium	50	H_2SO_4	Wu et al. [17]
Litter, lichen, and soil	Caesium	2–4	HNO_3	Zheng et al. [22]
IAEA-375 soil reference material	Caesium	Up to 10	HNO_3	Zheng et al. [21]
Soil and sediment	Plutonium/Americium	Up to 100	HNO_3 , HCl	Environmental Measurements Laboratory [23]
Soil, sediment and cement	Strontium	0.5	<i>Aqua regia</i>	Russell et al. [18]
Irish Sea marine sediment	Caesium	5	<i>Aqua regia</i>	Russell et al. [19]

as a bulk sample must be completely digested or dissolved in order to minimize potential elemental and isotopic bias.

A number of complete dissolution techniques have been successfully developed (Table 2). Such techniques transfer the entire sample into solution. Of the available techniques, fusion-based digestion is a versatile and commonly applied procedure in the geological sciences. Fusion uses high temperatures (600–1200 °C) to heat and dissolve samples in a solvent or flux. Automation of fusion has addressed the safety issues associated with manually adding and removing crucibles from a furnace; however, there are also disadvantages and challenges associated with fusion approaches. Fusion is generally more labour-intensive than leaching, with lower sample sizes (typically 0.5–5 g [1, 10, 30, 31]). Large quantities of the flux relative to the sample size are generally required to decompose most matrices, often several times the sample weight [10, 30]. Furthermore, the aqueous solutions resulting from the fusions can have a high salt content, which may lead to difficulties in subsequent steps of the analysis such as chromatographic separation. The high temperatures associated with some fusion processes also means that volatile radionuclides (e.g. ^3H , ^{14}C , ^{36}Cl and ^{129}I) must be selectively removed beforehand, for example using a furnace system to volatilise samples, with volatile radionuclides subsequently trapped in aqueous solution, whilst the solid sample is retained for subsequent digestion [7, 32].

Sodium hydroxide (NaOH) fusion has been shown to be effective for silicates, carbonates and metals [33]. The Environmental Protection Agency guide for environmental remediation following radiological incidents outlines the method for sodium hydroxide fusion of concrete and brick matrices prior to analysis [34]; the method takes 1 hour for a batch of $20 \times 1\text{--}1.5$ g samples. Zirconium crucibles are used in the NaOH fusion process, at a furnace temperature of 600 °C [34]. Sodium hydroxide fusion has also been applied to 1–2 g soil samples prior to separation and alpha spectrometry analysis of uranium and thorium at the Savannah River National Laboratory (SRNL) [27]. This work was carried out after incomplete dissolution of refractory particles by acid digestion was reported in a recent inter-comparison exercise. Total dissolution of refractory particles was achieved by NaOH fusion in zirconium crucibles. Here, the soil samples were heated in a furnace at 600 °C for 30 min, and then a further 15–20 min after adding the NaOH flux.

Molten ammonium bifluoride (NH_4HF_2) has been proven to be effective for the decomposition of inorganic solid matrices. Actinides, as well as a mixture of alkaline elements, rare earth elements (REE), and transition metals have been measured following digestion by inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) [35]. A study by Hubley et al. [36] evaluated ammonium bifluoride

fusion for a range of geological reference materials with varying levels of silicates. The method was evaluated for its potential use in post-detonation nuclear forensics. Sample sizes of 50 mg and 500 mg of NH_4HF_2 were weighed out and heated at 230 °C for 10, 30, and 180 min. Concentrated HNO_3 was added to the flux mixture prior to elemental analysis using ICP-MS. Total dissolution time was reduced to < 3 h through method optimisation, with high recoveries (91–109%) measured for ^{242}Pu and ^{236}U . It was concluded that ammonium bifluoride fusion was a potential method for dissolution of post-detonation nuclear debris, with advantages over traditional acid digestion methods including reduced procedural time and not having to directly handle HF.

Sodium peroxide fusion (Na_2O_2) has been used extensively for the determination of trace amounts of noble metals, especially platinum group elements [37, 38], and plutonium [39, 40]. A study by Galindo et al. [14] demonstrated, by measuring a number of reference materials, that peroxide fusion achieved complete destruction of mineral lattices and improved the determination of the true activity of actinides in solid samples in comparison to acid leaching. One gram of ashed sample was added to a zirconium crucible with NaOH pellets and heated to 350 °C in a furnace. Once molten, Na_2O_2 pellets were added and heated at 600 °C for 30 min. After cooling, the flux mixture was diluted in hot water and the hydroxide precipitate was separated from the supernatant by centrifugation, from which the actinides were extracted by co-precipitation. Alpha spectrometry measured uranium recoveries of up to 89%, whilst leaching using HCl gave inconsistent results and uranium recoveries up to three times lower than the true value.

Digesting a sample using fluxless fusion can be advantageous in preparing glass beads for X-ray fluorescence (XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in terms of speed of preparation, homogenization, conservation of sample and long-term sample stability. On the other hand, some elements can be lost due to volatilization as a result of the elevated temperatures required. A novel fluxless fusion method was successfully applied by Reading et al. [41] in which geochemical reference materials, uranium ores and uranium ore concentrates were digested for analysis by LA-ICP-MS. In the procedure, synthetic enstatite (MgSiO_3) was added to 1.5 g samples at a 9:1 ratio to aid glass bead formation on an iridium strip resistance heater in an argon-purged chamber. Samples were heated to 1500 °C and fused for 1 min. The method refined existing analytical methods for nuclear forensics to support special investigative and law enforcement agencies.

Borate fusion has been proven to be effective for opening out a wide range of sample types. The analysis of ceramics and geological samples with these fluxes is long established. Borate fluxes will rapidly dissolve most

Table 2 Examples of total dissolution methods

Dissolution method	Rationale	Sample type	Element(s) of interest	Sample size (g)	Furnace temperature, digestion time	Digestion vessel	Measurement technique	Recovery (%)	Reference
NaOH fusion	Alkaline flux beneficial for acidic samples	Soil	Uranium and thorium	1–2	600 °C, 45–50 min	Zirconium crucible	Gamma spectrometry, liquid scintillation counting	86–91	Maxwell et al. [27]
		Concrete and brick	Americium, plutonium, strontium, radium, and uranium	1–1.5	600 °C, 1 h	Zirconium crucible		–	U.S. Environmental Protection Agency [34]
Bifluoride fusion	HF useful breakdown of Si–O bonds and metal oxides	Geological reference materials	Plutonium and uranium	0.05	230 °C, 10, 30, and 180 min	PFA tube	ICP-MS	80–120	Hubley et al. [36]
Borate fusion	Versatile	Soils	Plutonium and uranium	< 1	1200 °C, 30 min	Pt–Au dish	Alpha spectrometry, TIMS	–	Croudace et al. [15]
		Irish Sea marine sediment	Caesium	5	950 °C, 10 min	Pt–Au crucible	ICP-MS	100	Russell et al. [19]
		Soil	Uranium	2	800 °C, 10–15 min	Carbon crucible	Alpha spectrometry	70–90	Dirican et al. [42]
Na ₂ O ₂ fusion	Alkaline flux beneficial for acidic samples	Sediment and soil	Actinides	1	600 °C, 30 min	Zirconium crucible	Alpha spectrometry	89	Galindo et al. [14]
Fluxless fusion	Rapid, produces homogenous and stable samples (high temperatures can lead to loss of volatile analytes)	Geochemical reference materials, uranium ores and uranium ore concentrates	REE	1.5	1500 °C, 1 min	Iridium strip	LA-ICP-MS	–	Reading et al. [41]

silicates, carbonates, sulphates, oxides etc. into aqueous form at low-to-moderate sample to flux ratios [15]. For XRF analysis, the molten flux is poured into a mould to produce a solid bead with a flat, polished surface. The homogeneity and lack of defects in the glass is vital for quantitative XRF analysis [43].

Lithium borate fusion was first used in a radioanalytical context by Croudace et al. [15]. The study compared different techniques for the digestion of soils for plutonium and uranium determination as part of an environmental monitoring programme that required high sample throughput. The HF method was intended to ensure complete dissolution of any PuO_2 present in soils and other matrices, where leaching was shown to be insufficient. Microwave digestion methods including various mineral acids were shown to be effective but can only be used for relatively small samples sizes (up to 1 g). It was found that the problems associated with the partial dissolution of Pu during leaching could be overcome via a complete dissolution of the sample by fusion with an appropriate flux. Borate fusion was chosen due to issues with other fusion techniques (i.e. potassium hydroxide, sodium hydroxide, potassium fluoride and potassium pyrosulphate), including reduced efficiency with certain marine sample compositions because of chloride attack on the Pt sample vessel. The development of the lithium borate fusion procedure allowed the rapid and effective determination of uranium and plutonium activities in soil and other environmental samples. For each sample, 5 g of soil was mixed with 7 g flux in platinum-gold crucibles, and heated at 1200 °C for 30 min. This novel procedure allowed seven hundred environmental samples to be processed over a 10-week period in support of an investigation for an alleged nuclear weapons incident [15].

A study by Russell et al. [19] investigated a range of techniques for the digestion of Sellafield-contaminated Irish Sea marine sediment prior to separation and ICP-MS measurement of ^{135}Cs and ^{137}Cs . Complete chemical yield recovery was achieved by lithium borate fusion, compared to 78% recovery using *aqua regia* acid leaching, which could not completely recover caesium retained in the interlayer of clay-rich sediment. Using the same acid leaching technique, a 100% recovery of ^{241}Am , which shows no such affinity for clay minerals, was evidence for this partial retention mechanism. A separate study determined borate fusion to be the preferred technique for ashed soil samples prior to the alpha spectrometric analysis of uranium [42]. For the fusion process, HF was added to aid with the dissolution of silicates, then sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and boric acid (H_3BO_3) were added to the sample in a carbon crucible, which was heated to 800 °C for 10–15 min. Recoveries of 70–90% were achieved, compared to 60–75% for HNO_3/HCl acid leaching. The fusion method was also faster than acid leaching and required less

preparation time, although the impurity levels were higher as a result of the more complex sample matrix.

This paper describes the development of automated borate fusion procedures for complete dissolution of a range of sample matrices in relation to reference material production, NORM characterisation and nuclear decommissioning. While other fusion techniques may be able to digest similar sample types, borate fusion was chosen due to its flexibility and scope for increasing sample size. Varying flux types, sample to flux ratios, digestion times, furnace temperatures, post-dissolution treatments and measurement techniques are presented depending on the nature of the sample matrix and the radionuclide(s) of interest. The flux type varied depending on the sample matrix, as the solubility of the sample in the flux is key for successful dissolution, while the sample to flux ratio and furnace temperature proved important when digesting a higher mass of starting sample (> 1 g). The results show the benefits of complete sample digestion and the flexibility of the technique.

Methodology

Instrumentation

A Katanax K2 Prime (SPEX) was used throughout. The instrument has 5 sample holder positions, with digestions carried out using either 30 mL straight-walled 95% Pt-5% Au crucibles, or graphite crucibles (SPEX) dependant on the flux used. The mass of sample, flux and reagents added was recorded on a 2-figure balance (Mettler Toledo).

Following digestion, the flux was typically poured into 25% (v/v) HNO_3 in 150 mL PTFE beakers (Fisher Scientific). Samples were transferred to a hot plate with a magnetic stirrer (Accentus) to speed up dissolution of the flux material. Filtering of samples was carried out prior to radiochemical separation and/or measurement using a vacuum filtration rig, and 0.22 μm Millipore filter papers.

Mass spectrometry

Measurement of stable elements and long-lived radionuclides (^{90}Sr , ^{151}Sm , U, Th and Pu isotopes) was carried out using a tandem inductively coupled plasma mass spectrometer (ICP-MS/MS) (Agilent 8800). The instrument is equipped with two quadrupole mass filters separated by a collision-reaction cell and was fitted with a quartz double-pass spray chamber and a MicroMist nebuliser (Glass Expansion) and nickel sample and skimmer cones (Crawford Scientific). The instrument was tuned using a 1 ppb multi-element solution to assess sensitivity, uncertainty, oxide and doubly-charged ion formation and peak axes. A semi-quantitative scan was run to determine the approximate

composition of the sample based on a 1-point multi-element calibration. The scan operated in single quad mode (only one mass filter operating) with helium gas in the cell for removal of polyatomic interferences formed by reactions of matrix elements with gases in the plasma. A fully quantitative scan, in single quad mode, was also run for radionuclide-specific measurements. Matrix-matched calibration standards were prepared for all stable and radioactive isotopes measured, with indium or bismuth run as internal standards to correct for instrument drift.

Alpha spectrometry

Activities were measured for a range of radionuclides (^{229}Th , ^{232}Th , ^{236}U , ^{238}U) by alpha spectrometry. Sources were prepared by electroplating and counted in an ORTEC Octete Plus α -particle spectrometer with Passivated Implanted Planar Silicon (PIPS) detectors and ORTEC Maestro Multichannel Analyser (MCA) application software. An energy calibration was performed with a ^{241}Am , ^{244}Cm and ^{237}Np source and instrument backgrounds were measured prior to sample measurement. Each source was counted for 350,000 s, with an estimated counting efficiency of 21% based on the solid angle coverage.

Gamma spectrometry

Gamma spectrometry was used for activity measurements of multiple radionuclides (^{226}Ra , ^{232}Th , ^{238}U). A high purity germanium (HPGe) γ -spectrometer was used, with a carbon fibre detector window at a relative efficiency (to a $3'' \times 3''$ NaI(Tl) detector) of 65%. A cylindrical lead shield with a fixed bottom and a movable cover shielded the detector from external γ -ray background. Counting times for each sample were approximately 50,000 s and the detector was calibrated for the individual radionuclides. A calibration curve was also derived based on measurements of an NPL mixed radionuclide solution in the same geometry.

Reagents

The fluxes used were potassium sodium carbonate (analytical grade, Merck), boric acid (99.5%, Acros Organics, melting point 169 °C), sodium nitrate (ultra-pure, Acros Organics, melting point 306 °C), sodium carbonate (99.5%, Acros Organics, melting point 851 °C), potassium iodide (analytical grade, Acros Organics, melting point 680 °C) and lithium fluoride (97%, Acros Organics, melting point 845 °C), with additional lithium bromide (ACROS Organics, melting point 550 °C) used as a non-wetting agent to prevent the sample sticking to the crucibles.

Borate flux mixtures comprised pre-mixed lithium borates (49.75% lithium tetraborate—49.75% lithium metaborate—0.5% lithium bromide, SPEX), lithium tetraborate (pure, SPEX, melting point 917 °C), lithium metaborate (ultra-pure, SPEX, melting point 849 °C). The chemical differences between lithium metaborate (LiBO_2) and lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) (Table 3) affect the digestion procedure. The primary variation is the probability of crystallisation on the cooling of the flux mixture, which is important for XRF analysis, where production of a clear bead is required. Considering the optimum solubility limit for concrete, in terms of making a glass bead for XRF, pure $\text{Li}_2\text{B}_4\text{O}_7$ flux would be optimal due to the alkalinity of the sample benefiting from an acidic flux. On the other hand, the solubility limit for most elements is higher in pure LiBO_2 . As the aim of this work was to achieve total dissolution of elements, rather than a clear bead, the benefits of a pure $\text{Li}_2\text{B}_4\text{O}_7$ flux were considered less important.

Reagent grade nitric acid (Fisher Scientific) was used throughout and diluted in deionised water (18 M Ω cm, <5 ppb Total Organic Carbon) produced from an ELGA Purelabflex water purification system (VeoliaWater) to the required concentration for dissolution of the sample/flux mixture. Polyethylene glycol (PEG, Sigma Aldrich) was prepared at a concentration of 0.2 M and used for precipitation of silicates prior to radiochemical separation. Stable tracers (strontium and calcium) were sourced from Fisher Scientific and active tracers (^{236}U , ^{229}Th , ^{242}Pu , ^{232}U , ^{85}Sr) were prepared in-house.

Table 3 Comparison of lithium metaborate and lithium tetraborate properties

	Chemical formula	Melting point (°C)	Crystallisation on cooling	pH
Lithium metaborate	LiBO_2	849	Lower viscosity, therefore probable crystallisation	Alkaline flux, compatible with highly acidic samples
Lithium tetraborate	$\text{Li}_2\text{B}_4\text{O}_7$	917	Higher viscosity, therefore minimal crystallisation	Light acidic flux, compatible with alkaline samples

Materials

The two main applications were development of reference materials for naturally occurring radioactive materials (NORM), and characterisation of materials for nuclear decommissioning. For NORM, titanium dioxide was obtained from a processing facility in the Czech Republic, tuff was sampled from the Gulf of Naples, Italy, and sand samples originated from the petroleum exploration industry at a variety of locations in Kuwait. The sand samples were taken from depths of 5–25 cm from an area of 175 cm² at the surface. Candidate reference soils prepared by the British Geological Survey (BGS) were also tested for NORM radionuclide content for initial method validation. For decommissioning applications, sediment contaminated by Sellafield discharges was collected from the Wyre Estuary in Cumbria, UK. Soil and concrete samples were provided as part of inter-comparison exercises; a cement sample previously prepared for a NPL proficiency test exercise was also tested. Additional inactive graphite, concrete, soil and sediment samples were spiked with stable and radioactive isotopes of interest for method development.

Experimental

The majority of tests used 0.5 g of sample, with varying flux mixtures and sample to flux ratios. Weighed amounts of sample and flux were added to the crucible and mixed using a plastic stirring rod. The samples were then locked in position on the sample rack. For each sample, a 150 mL PTFE beaker containing approximately 50 mL acid (varied concentration of HCl or HNO₃ depending on the application) was positioned in the holder under the crucible. A PTFE-coated magnetic stirrer was added to the beaker to aid with flux digestion after dispensing.

Once the crucibles and beakers were in position, parameters including the furnace temperature, digestion time, and the speed and extent of crucible rocking could be controlled. The crucibles were automatically taken into the furnace and poured into the PTFE beakers at the end of the procedure. Each heating stage of the process is outlined in Fig. 1. The total time from the sample entering the furnace to the end of the cooling stage is approximately 20 min. It must be noted that a ramp stage is included in each furnace stage to allow it to reach the desired temperature before each timed section of the procedure begins, with each ramping stage adding 1–2 min to the procedure time.

After the samples have been dispensed, the acid and flux mixture was decanted into 250 mL borosilicate glass beakers (Fisher Scientific, UK) containing varied concentration of HCl or HNO₃ depending on the application,

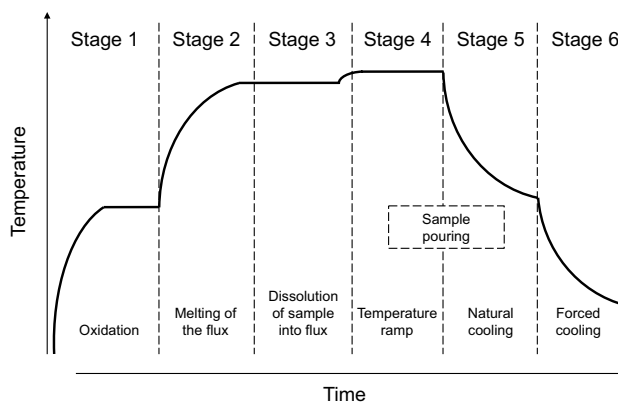


Fig. 1 General outline of automated fusion procedure using (SPEX Katanax) detailing the heating stages (adapted from Claisse and Blanchette [43])

and stirred on a magnetic stirring hot plate set to approximately 60 °C to complete the dissolution of any remaining solid residue; this takes approximately 30 min to 1 h for a 0.5 g sample depending on the sample matrix.

The majority of studies followed digestion with a PEG precipitation to remove silica from the flux mixture that would otherwise block any columns used for chromatographic separation. The samples were left on a hot plate for 1 h to allow the PEG precipitate to form, then left to settle overnight, though a shorter time period of ~2 h was determined to be sufficient. Separation of the PEG precipitate was carried out by centrifuging, followed by vacuum filtration through a 0.22 μm filter. The subsequent chemical separation and/or measurement techniques used depends on the sample matrix and radionuclide(s) of interest.

Results and discussion

The Pt–Au crucibles were generally favoured as, in some cases, graphite crucibles transfer graphite residue into the sample following digestion and sample flux remaining in the crucibles proved difficult to remove. A common occurrence across procedures was for a small bead (~10 mm diameter) to remain on the tip of the crucible after pouring. This could easily be removed using a plastic stirring rod and transferred to the PTFE beaker. Stirring must be carried out following the automated fusion process to ensure complete dissolution of the solid residue.

Table 4 Summary of fusion techniques used for naturally occurring radioactive materials

Sample type	Radionuclides of interest	Tracers	Sample size (g)	Flux mixture	Measurement technique	Recovery (%)
Titanium dioxide	^{226}Ra , ^{238}U , ^{232}Th	^{236}U , ^{229}Th	1	2 g KNaCO_3 1.5 g H_3BO_3	Alpha spectrometry, gamma spectrometry, ICP-MS	9–99*
Sand	^{226}Ra , ^{238}U , ^{232}Th	^{236}U , ^{229}Th	0.5	1.2 g LiBO_2 1.2 g $\text{Li}_2\text{B}_4\text{O}_7$ 0.02 g LiBr	Alpha spectrometry, ICP-MS	51–74*
Tuff	^{226}Ra , ^{238}U , ^{232}Th	^{236}U , ^{229}Th	0.5	1.2 g LiBO_2 1.2 g $\text{Li}_2\text{B}_4\text{O}_7$ 0.02 g LiBr	Alpha spectrometry, ICP-MS	59–83*

*Denotes recovery including separation procedure

Characterisation of reference materials for naturally occurring radioactive materials

The lack of suitable reference materials in the NORM industries is a significant issue [2, 7–12], which also makes initial validation of procedures challenging. Candidate reference soil and sediment materials from British Geological Survey (BGS) were digested using lithium borate fusion and the concentration of ^{232}Th and ^{238}U calculated and compared with the reference values as an initial validation of the method. The main application for NORM measurement was a European Metrology Research Programme (EMRP) titled Metrology for Processing Materials with High Natural Radioactivity (MetroNORM, 2013–2016). This focused on improving validity of measurement for selected naturally occurring radionuclides to more efficiently control occupational exposure to radiation. New candidate reference materials were processed for several industries including residue from titanium dioxide production, tuff used in building products and sand from the petroleum exploration industry. The active samples were characterised by gamma spectrometry prior to sample dissolution. Details of these procedures are outlined in Table 4 [9, 44].

Candidate reference material soils were digested using 1.2 g $\text{Li}_2\text{B}_4\text{O}_7$ and 1.2 g LiBO_2 , with 0.02 g lithium bromide acting as a non-wetting agent. The procedure used a furnace temperature of 1000 °C, prior to dispensing into 100 mL 30% v/v HNO_3 . For the range of soil types, the ^{238}U and ^{232}Th concentrations measured by ICP-MS were in agreement with the reference value range given over concentrations of 0–20 ppb.

Sand and tuff were successfully digested using the same method as the soil. The fusion procedure used for titanium dioxide dissolution was that recommended by Sulcek and Povondra [45]. As titanium dioxide is a more acidic sample, a more alkaline flux was required. Therefore, one gram of sample was dissolved with a flux mix of 4:3 $\text{NaKCO}_3:\text{H}_3\text{BO}_3$, with a flux to sample ratio of 3.5:1. The mixture was heated to 1000 °C in the furnace and then

dissolved in 8 M HCl. This matrix was more challenging to digest compared to the sand and tuff; hence the variation in flux mixture used. Significant residue remained in the crucibles after heating, which was inconvenient for re-use of the equipment for different matrices. Cleaning of the crucibles was achieved by adding flux only and heating in the furnace, followed by an HCl wash.

Titanium dioxide was also dissolved in the pre-mixed $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7/\text{LiBr}$ flux. Care must be taken with this method as titanium dioxide has a relatively low solubility limit in lithium borate flux and also crystallises, forming a cloudy suspension, potentially trapping elements of interest. Crystallisation is encouraged by the thermal shock of pouring the flux mixture into acid and therefore the best strategy is to avoid pouring. This allows the mixture to cool without crystallisation occurring, and the resulting glass can be transferred to acid for dissolution. A large excess of flux is required for this method, with 0.2 g titanium dioxide and 2.5 g flux mixture, as recommended by the instrument manufacturer.

Following digestion, an aliquot was taken for ICP-MS measurement and the ^{232}Th and ^{238}U compared to initial gamma spectrometry values. Good agreement was seen for ^{238}U in all matrices, with gamma spectrometry and ICP-MS activities of < 34 Bq/g and 26 ± 4 Bq/g for sand, 426 ± 92 Bq/g and 464 ± 45 Bq/g for tuff, and < 21 Bq/g and 6 ± 1 Bq/g for TiO_2 , respectively. For ^{232}Th , there was good agreement for sand, with both techniques calculating activities of 7 ± 1 Bq/g. For tuff, the ICP-MS activity (484 ± 70 Bq/g) was higher than for gamma spectrometry (350 ± 10 Bq/g), whilst for TiO_2 , the ICP-MS activity was 3 orders of magnitude lower than for gamma spectrometry, with alpha spectrometry showing similar values to ICP-MS following chemical separation.

For the TiO_2 , the lower activities measured by ICP-MS was likely due to the significant residue remaining in the crucible following the $\text{NaKCO}_3:\text{H}_3\text{BO}_3$ digestion method. Whilst there was good agreement for the low activity sand samples, for the tuff, the higher values measured by ICP-MS

Table 5 Summary of fusion techniques used for nuclear decommissioning

Sample type	Radionuclides of interest	Tracers	Sample size (g)	Flux mixture	Measurement technique	Recovery (%)
Concrete	^{239}Pu , ^{236}U , ^{90}Sr	^{242}Pu , ^{232}U , ^{85}Sr	0.5	2 g pre-mixed $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7/\text{LiBr}$	Alpha spectrometry, gamma spectrometry	40–95*
Graphite	^{90}Sr , ^{93}Zr , ^{151}Sm , ^{236}U	^{88}Sr , ^{90}Zr , ^{147}Sm , ^{238}U	2–5	2 g pre-mixed $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7/\text{LiBr}$	ICP-MS	75–95*
Concrete	^{41}Ca	Stable Ca	0.5	2 g pre-mixed $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7/\text{LiBr}$	ICP-MS	100
Soil	^{90}Sr	Stable Sr	0.5	0.2 g NaNO_3 0.2 g Na_2CO_3 2.0 g LiBO_2 0.1 g KI	ICP-MS	92–100
Cement	^{90}Sr	Stable Sr	0.5	3.0 g LiBO_2 1.5 g $\text{Li}_2\text{B}_4\text{O}_7$ 0.25 g LiBr 0.01 g LiF	ICP-MS	82–96
Sediment	^{90}Sr	Stable Sr	0.5	0.2 g NaNO_3 0.2 g Na_2CO_3 2.0 g LiBO_2 0.1 g KI	ICP-MS	85–100

*Denotes recovery including separation procedure

may be due to ^{232}Th being indirectly measured by gamma spectrometry, compared to direct measurement by ICP-MS. Additionally, or one or more polyatomic interferences may have increased the ICP-MS background. Despite the discrepancy, it is worth noting that there was no evidence of loss of tuff from the borate fusion stage.

For all samples, digestion was followed by PEG precipitation, and then extraction chromatography separation, and measurement of ^{238}U and ^{232}Th by alpha spectrometry and ICP-MS. Recoveries were calculated based on gamma spectrometry values prior to dissolution. The recoveries following chemical separation were 51–74% for sand and 59–83% for tuff, with the lowest recoveries for ^{232}Th [9]. For TiO_2 the recoveries were more varied, ranging from 9% for ^{232}Th up to 99% for ^{238}U . The difference in flux mixture is thought to have impacted performance of the extraction chromatography resin, which is relatively sensitive to changes in sample matrix, thus leading to the low ^{232}Th recoveries. The materials characterised were determined to be suitable for candidate reference materials with activities ranging from 1–400 mBq g^{-1} .

Characterisation of materials for nuclear decommissioning

An outline of the fusion techniques used for nuclear decommissioning samples is shown in Table 5. A selection of samples from decommissioning sites were digested and their recoveries quantified.

Fission and activation products in concrete and graphite

The EMRP project titled Metrology for Decommissioning Nuclear Facilities (MetroDECOM, 2014–2017) focused on the improvement of accuracy and reliability of measurements to assist in more reliable decision-making concerning disposal of low-level wastes from the nuclear sector. The follow-on project (MetroDECOM II, 2017–2020) aims to ensure safe disposal of radioactive waste from decommissioning nuclear sites [46]. Both projects have a focus on developing rapid, automated and in situ measurements for decommissioning, delivering reliable and accurate results, including development of less hazardous dissolution techniques for fission and activation products in decommissioning materials [47].

For initial proof of capability, concrete (0.5 g) was spiked with stable analogues of radionuclides of interest (10 ppm Sm and Zr), which was then mixed and dried prior to lithium borate fusion. The concrete was mixed with 2 g pre-mixed lithium borate flux, and the fusion was followed by PEG precipitation and extraction chromatography separation using TBP resin (Triskem International). The samples were diluted by a factor of 100 prior to measurement to account for the high matrix content of the digested flux. ICP-MS was used to determine recoveries from the dissolution and chemical separation process, achieving a Zr yield of 40% and a Sm yield of 95% with uncertainties of 5–6%. The dissolution procedure was then applied to the measurement of actinides (U, Pu and Th in the mBq/g range) and stable elements in

Sellafield-contaminated concrete, as part of characterisation prior to distribution for a proficiency test exercise.

The dissolution of graphite matrices is discussed in detail elsewhere [30]. In short, stable graphite samples of up to 5 g were dispensed into Pt–Au (95–5%) crucibles. The samples were ashed overnight at 800 °C prior to digestion. Two grams of pre-mixed lithium borate flux was added and the material was digested at 1000 °C for 10 min and dissolved in 5 M HNO₃. The quantity of flux was not adjusted to the mass of sample, as the graphite was present as a residue following ashing. There was no residual material after the fusion indicating that all graphite was successfully digested. Measurement of stable isotopes present in graphite by ICP-MS showed a directly proportional increase in concentration with sample mass, validating the digestion technique. Digestion was followed by an iron hydroxide precipitation and TBP resin separation, with stable Sm and Eu tracer recoveries of > 95%. The benefit of this approach is that the use of strongly oxidising perchloric acid for dissolution was avoided. This work was taken forwards for quantitative measurement of ¹⁵¹Sm-contaminated graphite by ICP-MS/MS [48], achieving detection limits two orders of magnitude below the exemption level of 1000 Bq g⁻¹ [49].

⁴¹Calcium in concrete

Calcium-41 is present in reactor-shield concrete as a result of neutron activation of stable ⁴⁰Ca. Measurement by liquid scintillation counting or ICP-MS is feasible but requires complete separation of multiple interferences prior to quantification. This must be preceded by effective sample dissolution. Blank concrete samples (0.5 g) were spiked with varying amounts (20–200 mg) of stable calcium to determine the concentration required as a yield tracer, due to unknown amounts of calcium already present in the sample; 50 mg stable calcium was deemed appropriate. After spiking, the concrete was dried and mixed to ensure homogeneity of the spike. The samples were fused with a 1:1 Li₂B₄O₇:LiBO₂ flux at 1000 °C for 10 min. The flux mix was dissolved in 5 M HNO₃, and an aliquot of the dissolved material was taken for ICP-MS/MS measurement, which showed complete recovery of calcium based on the measurement of ⁴⁴Ca. Borate fusion was followed by a multi-stage chemical separation procedure, with recoveries for dissolution and iron hydroxide precipitation of 70–85%.

⁹⁰Strontium in soil, sediment and cement

Lithium borate fusion was investigated along with open vessel acid leaching and microwave leaching for several

decommissioning matrices as part of developing an optimised procedure for digestion and separation of high yield fission product ⁹⁰Sr prior to measurement by ICP-MS/MS [50]. This work was driven by the requirement to develop a rapid and cost-effective method for ⁹⁰Sr measurement for waste deriving from decommissioning activities, to overcome the long procedural times associated with liquid scintillation counting (LSC).

The fusion procedure developed for concrete samples as part of the MetroDECOM II project described previously was successfully applied to cement samples from an NPL proficiency test exercise, characterised for radionuclides including ⁹⁰Sr at approximately 100 Bq/g. A sample of 0.5 g was heated to 1000 °C for 10 min, with the temperature ramping up to 1020 °C for a further 1 min. The flux mixture was dissolved in 50 mL 20% (v/v) HNO₃ followed by PEG precipitation [18]. No residual material remained in the crucibles after fusion, showing that the cement was completely digested. Cement was spiked with both stable strontium and ⁸⁵Sr and evaporated to dryness prior to fusion. The recoveries of the two spikes were in good agreement, with values ranging from 82 to 96%. Following chemical separation, the ⁹⁰Sr activity was below the detection limit for ICP-MS, and was measured by LSC, with a ⁹⁰Sr activity in good agreement with the 100 Bq/g value characterised prior to dissolution when the stable ⁸⁸Sr and ⁸⁵Sr recovery was considered.

Borate fusion offered complete destruction of the samples but was limited by the sample size used, which was problematic for the low activity samples under study. Cement losses from borate fusion were believed to be a result of PEG precipitation, although this was necessary for subsequent chromatographic separation. Microwave leaching also suffered from the limited sample mass that could be digested, whilst acid leaching was favoured as good recoveries (88–100%) were achieved and higher sample masses could be processed (up to 10 g in this study). In this case, due to the high leachability of ⁹⁰Sr, a total dissolution approach was not necessary although borate fusion was still successfully applied.

Soil from an Analytical Laboratories for the Measurement of Environmental Radioactivity (ALMERA) inter-comparison exercise and Sellafield-contaminated sediment samples were digested using a combined carbonate/borate fusion technique that was developed for soil samples as part of an ALMERA network project [18]. The sample size, crucible type and heating procedure were unchanged from those previously described for cement; however, PEG precipitation after digestion was not necessary due to lower silica content. The flux mixture consisted of 0.5 g sample, 0.2 g NaNO₃, 0.2 g Na₂CO₃, 2.0 g LiBO₂ and 0.1 g KI, which makes the flux more alkaline than borates alone, aiding the digestion of more acidic soil samples. Again, stable strontium was used as a tracer; recoveries of 92–100% were achieved for soil and 85–100% for sediment (compared to 86–96% and

68–88% for acid leaching, respectively). The higher recoveries seen for soil over sediment may be due to the fusion procedure being initially developed for soils. Investigation of a wider range of soil and sediment compositions would improve understanding of this [18].

Increasing sample mass

Increasing the sample mass that can be digested is beneficial to the measurement of low-level samples. The experimental approach started by using an existing procedure for borate fusion of cement using 0.5 g sample with a pre-mixed $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7/\text{LiBr}$ flux at a sample to flux ratio of 1:4. At this ratio, the amount of flux used meant that only a modest increase in sample mass could be achieved before the crucible was too full to carry out the procedure. Therefore, a range of sample to flux ratios were investigated. The original procedure involved heating the mixture for a total of 5 min; 4 min at 1000 °C and 1 min at 1020 °C.

Here the pre-mixed lithium metaborate-tetraborate flux was used initially, although further work could explore the effects of this flux mixture on the fusion. Following discussion with the instrument manufacturer, a 1.33:1 sample to flux ratio was initially investigated for a higher mass of concrete samples.

Initially, all assessment of procedures were based on visual inspection of the samples and crucibles. A 1.33:1 sample to flux ratio showed incomplete dissolution of the solid for 0.5–1 g of sample, which was not improved when the heating time was doubled. A 1:1 sample to flux ratio was successfully tested for 0.5–1.5 g of sample, with minimal residue remaining in the crucible. Following this and in order to further increase sample size without the risk of over-filling the crucibles, the rocking angle and speed during digestion was reduced, and the angle and speed that samples were poured out of the crucibles after fusion increased. Sample sizes of 2.0 g and 2.5 g were assessed, but some residue remained in the crucible. This was resolved by a 20 °C temperature increase (initially 1020 °C compared to 1000 °C, followed by 1040 °C compared to 1020 °C), which successfully prevented any residue sticking to the crucible, and change in sample to flux ratio to 1:1.2. This ratio was effectively used up to a sample mass of 5.0 g, however, the higher mass samples required a longer stirring time of several hours following the heating procedure to ensure that the higher sample and flux mixture was dissolved.

The sample preparation and instrument parameters for automated borate fusion of up to 5.0 g are described in Tables 6 and 7, respectively. The primary difference between the modified and original method is the reduced sample to flux ratio, which uses a lower mass of flux mixture reagents and allows a larger mass of sample in the crucibles. An increased mass of non-wetting agent from 0.01 to 0.3 g

Table 6 Comparison of sample preparation for the original and modified procedure for lithium borate fusion of concrete

Procedure	Original (0.5 g)	Modified (up to 5 g)
Mass of concrete (g)	0.50	3.00
Flux: sample	1:4	1:1.2
Mass of flux (g)	2.00	3.50
Mass of non-wetting agent (g)	0.01	0.3
Dilution	50 mL 5 M HNO_3	50 mL 5 M HNO_3

Table 7 Comparison of instrumental parameters for the original (0.5 g) and modified (3.0 g) procedure for lithium borate fusion of concrete

Procedure	Original	Modified
Heating	Stage 3: 1000 °C, 4 min	Stage 3: 1020 °C, 5 min
	Stage 4: 1020 °C, 1 min	Stage 4: 1040 °C, 1 min
Rocking	Stage 3: 90%* 20°	Stage 3: 20% 5°
	Stage 4: 25% 5°	Stage 4: 20% 5°
Pouring	55% 120°	70% 130°

*Refers to the % of the maximum rocking and pouring speeds

was also added to prevent the mixture sticking to the crucibles. The rocking angle and speed was reduced to ensure no spillage from the crucibles. Finally, the temperature was slightly increased in addition to the pouring angle and speed to reduce residue in the crucible.

The original procedure saw the flux mixture poured into glass beakers containing 50 mL 5 M HNO_3 and stirred on a hotplate until total dissolution is achieved. The solubility limit of lithium borate flux was considered and on scaling up the sample size, a larger volume of acid was required for total dissolution (100 mL). While the scale-up here was suitable for the acid types and amounts used, the incompatibility



Fig. 2 PTFE beakers and Pt–Au crucibles containing the digested concrete samples (1–5 g left to right) in 5 M HNO_3 nitric acid

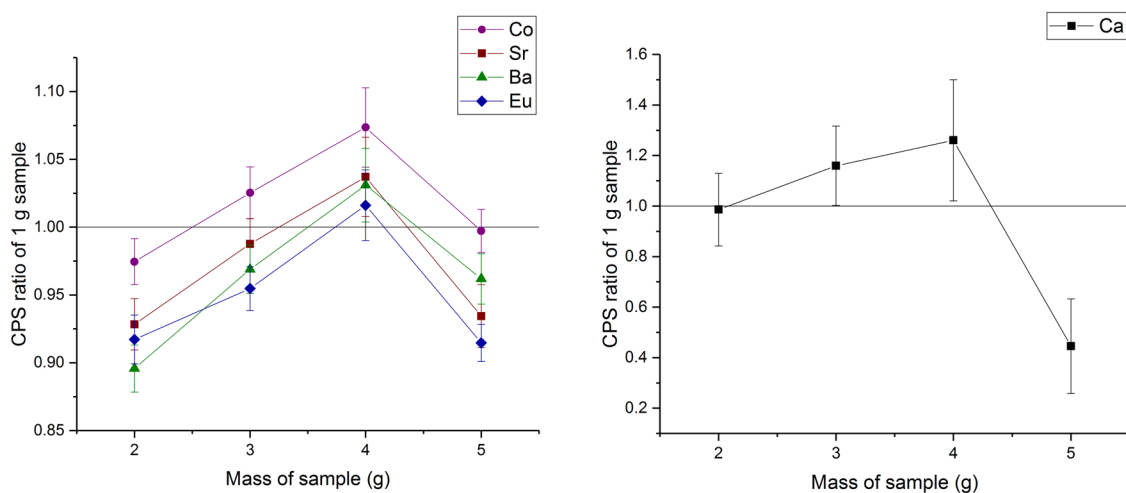


Fig. 3 Ratio of cobalt, strontium, barium and europium (left) and calcium (right) counts for increasing sample mass as a ratio of 1 g sample. Error bars represent the mean of 3 repeats of the relative standard deviation calculated by the ICP-MS

of lithium bromide non-wetting agent with acidic solutions must be noted. The direct pouring of a fusion mixture containing high quantities of a halogen-based non-wetting agent into a dilute acid solution could potentially result in an explosive reaction. The reaction is dependent on the halogen compound and the type and concentration of acid. The parameters described in Table 6 worked safely and effectively, but special care must be taken as there is no set limit of the safe amount of lithium bromide to use.

The effectiveness of the optimised procedure was tested by investigating the stable element composition using ICP-MS. Sample masses from 1 g to 5 g in 1 g increments were run (from left to right in sample positions, Fig. 2), with flux solution used as a blank. To ensure the optimised method was successful for up to 5.0 g sample, the flux mixtures at each mass were run in triplicate and spiked with a series of stable analogues of selected radionuclides of interest in concrete (^{41}Ca , ^{60}Co , ^{90}Sr , ^{133}Ba , ^{152}Eu). Matrix-matched standards were prepared by spiking blank samples (flux only) with various concentrations of the elements of interest, as the high matrix content reduced instrument sensitivity compared to clean element standards. Additionally, indium-115 was measured as an internal standard to monitor instrument drift and reduced ion transmission due to matrix deposition in the instrument. Data was analysed to show the ratio of the spike that was detected for each sample mass against the 1 g sample. Procedural blanks (flux only) were also prepared for all sample masses in order to correct for the presence of any of the elements tested in the flux components.

For cobalt, strontium, barium and europium, the count ratios relative to the 1.0 g sample showed good agreement over the mass range investigated, with ratios between 0.85 and 1.10 (Fig. 3). Increased variation was observed for calcium, particularly for fusion of 5 g of concrete, where the

ratio relative to 1 g was significantly lower than 1. Potential reasons for this include the high calcium content of the concrete prior to spiking, and the low abundance of the isotopes measured (0.135% and 2.086% for ^{43}Ca and ^{44}Ca , respectively) resulting in a higher measurement uncertainty. Single-factor ANOVA testing was carried out for between-element variance and between-mass variance. Results showed that there is no significant variance between masses, suggesting that the yield recovery for each mass was the same as for the 1 g sample and differences seen are due to chance. A significant difference was found, however, for different elements, which was as expected.

Conclusion

Fusion procedures have proven effective for the analysis of a range of radionuclides in solid matrices including titanium dioxide, sand, tuff, sediment, soil, cement, graphite and concrete. Flux type and furnace parameters have been optimised for multiple applications to enable successful dissolution prior to chemical separation and quantification. Additionally, an optimised procedure for borate fusion of up to 5.0 g of concrete was achieved by modifying the sample to flux ratio and furnace operating parameters. This was validated through measurement of spikes of stable elements by ICP-MS. This will allow analysis of higher sample masses, which is advantageous for high sample throughput and measurement of low activity samples. The work will support the significant NORM and nuclear decommissioning activities envisaged in the near future, as well as in the development of reference materials that provide the underpinning metrology to such programmes.

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