Validation of Radioanalytical Techniques for Nuclear Waste Characterisation

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Waste characterisation associated with nuclear site decommissioning relies on radiochemical analysis of a diverse range of sample types, requiring extensive validation of analytical techniques using matrix-matched materials. The absence of relevant reference materials has hindered robust method development and validation. The paper discusses how method validation in support of nuclear waste characterisation can be achieved without using reference materials. The key stages in an analytical procedure are evaluated and a multi-stage approach is proposed with the ultimate aim of determining an operational envelope for an analytical procedure.

Keywords: Decommissioning, Radioactive waste characterisation, Validation, Radioanalytical techniques

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1. Introduction

The requirement for radionuclide characterisation in support of nuclear decommissioning has resulted in a diverse range of material types requiring analysis. Sample types including ion exchange resins, concretes, desiccants, graphite, plastics, ferrous and non-ferrous metals, insulating material, sludges with varying and often undefined compositions and oils pose a significant challenge to the radioanalytical laboratory [1]. To underpin data quality, the laboratory must confirm that the technique selected for analysis is fit for purpose and all techniques must be validated to confirm this. The validation process is designed to assess the performance of the technique in terms of analytical accuracy, precision, sensitivity and robustness and to compare these parameters with the required performance targets. Historically, the validation assessment has relied on the analysis of reference materials of known composition. Reference materials consist of the analyte at a known concentration associated with a specific matrix that can be used to evaluate the entire analytical separation and measurement process including the efficiency of sample dissolution, chemical separation and measurement accuracy. A number of international programmes have historically supplied characterised reference material representing a range of matrices. However, such programmes have focussed on either environmental reference materials or on very specific sample types for a particular application. With the new demands arising from nuclear decommissioning and the associated range of material types prevalent, the existing range of reference materials do not reflect the matrices now being encountered. A limited number of reference materials have been developed to support nuclear waste characterisation (e.g. [2]) and there are plans for developing more representative reference standards [3]. However, it is improbable that a full range of reference materials covering all potential combinations of radionuclide and matrix could practically be produced. Even for a single matrix there are likely to be variations in composition and associations of the analyte

with the matrix depending on the origin of the sample that could potentially impact on the analytical technique. The lack of appropriate reference materials has been identified as a significant risk to delivery of robust method validation [4]. A new overarching approach to method validation is therefore required. One proposed approach is to consider the component stages of the analytical technique and to evaluate each stage separately, assessing the key risk factors that would impact on each stage. Such an approach does not require certified reference materials and provides a more flexible validation procedure that can be applied to any analyte and sample type, taking into account variations in sample composition that may occur even within a single matrix type. By considering sample dissolution and analyte separation independently, matrix-relevant solution standards can be prepared that are more representative of the materials encountered and which can be used to evaluate the separation stages of an analytical process. Independent verification of sample dissolution efficiency can be performed through a combination of supporting research on analyte chemistry and likely association with matrices and experimentally-determined leaching efficiencies using operationally-exposed samples. The approach also permits sample types to be grouped resulting in a more cost-effective validation programme. Where available, reference materials can still be utilised as an additional verification stage and to support the more generic approach proposed.

2. Factors affecting an analytical procedure

A radioanalytical technique can be broadly divided into four key stages

(i) Sample preparation (storage, homogenisation, subsampling, drying / igniting).
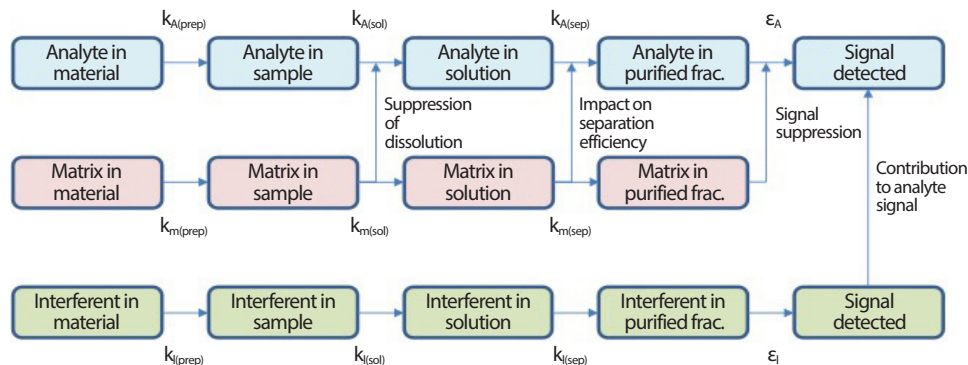(ii) Sample dissolution (acid or alkaline leaching, total digestion, fusion).

Fig. 1. Interaction of analyte, matrix and interferences and impact on analyte separation / detection.

(iii) Analyte isolation / purification (separation of the analyte from the matrix elements and potential chemical and radionuclide interferences.

(iv) Quantification of the analyte.

All four stages must be assessed to demonstrate the overall performance of the technique and the impact that sample composition may have on the efficiency of each stage (Fig. 1). Of these, stages 2, 3 and to some extent 4 have typically relied on reference materials. However, it is possible to validate each of the stages individually without using a reference material and to provide the necessary data to demonstrate the performance of the technique as a whole.

3. Sampling / sample storage / preparation– $k_{(prep)}$

Procedures for sample collection, storage and preparation must maintain the integrity of the sample matrix and minimise potential analyte loss through volatilisation or precipitation / adsorption to sampling equipment / containers. In addition, knowledge of the impact of storage conditions on sample / analyte stability over time is required to assess whether a sample may have been compromised prior to receipt at the laboratory. Although volatilisation-based techniques can offer an efficient means of radionuclide

extraction, uncontrolled losses during sampling and storage can result in significant errors in the analytical measurement. The degree of volatility will depend on the radionuclide and its association with the matrix which in turn will depend on the radionuclide origin (e.g. contamination or in-situ production via activation) and matrix composition. Radionuclides prone to loss via volatilisation include ^{3}H, ^{14}C, ^{99}Tc, ^{106}Ru and ^{129}I. Of these, ^{3}H has been identified as being particularly prone to volatilisation during collection and storage of decommissioning samples [5]. However, in concretes and metals, ^{3}H produced in situ via neutron activation of the matrix is relatively non-volatile compared with ^{3}H arising from surface contamination of the matrix [6,7]. Loss of volatile radionuclides from solid samples is effectively minimised through refrigeration or freezing of the sample [5]. For aqueous samples, precipitation and adsorption onto containers can be minimised through effective pH control. However, there are limited data on the stability of radionuclides in decommissioning wastes over time.

Sample heterogeneity can pose a significant challenge in representatively sampling a material. For solid samples, radionuclides may be present as surface contamination and as such the measured activity concentration will be highly dependent on the quantity of underlying non-active matrix that is co-sampled with the contamination layer. This is particularly noted for metals where contamination is unlikely to penetrate the surface and for painted items where the

Table 1. Radionuclide association with matrices

Readily acid leachable radionuclides	Readily alkali leachable radionuclides	Radionuclides that may be present associated with matrix		Radionuclides that may be present in a intrinsically insoluble chemical form
		Radionuclide	Matrix	
^{55}Fe (c)	^{36}Cl (c)	^{3}H (a)	Bioshield concrete	U(nat)
^{63}Ni (c)	^{129}I	^{14}C (a)	Graphite	Th
^{90}Sr		^{36}Cl (a)	Graphite	Pu
^{99}Tc		^{41}Ca / ^{45}Ca (a)	Bioshield concrete	
^{147}Pm		^{55}Fe (a)	Ferrous metals	
^{151}Sm		^{63}Ni (a)	Steels	
^{210}Po		^{113m}Cd	Cadmium	
^{241}Am (c)				

(a) – nuclide produced in situ due to irradiation of the matrix
(c) – nuclide originating from contamination of the matrix

contamination may be associated predominantly with the paint layer. For aqueous samples, radionuclide partitioning is highly probable between aqueous and particulate phases.

Sample drying / ignition can result in the loss of volatile radionuclides. Freeze drying can minimise the loss of certain volatile radionuclides but quantitative data are not available. Sample ignition can also render certain radionuclides less soluble. Hou [8] noted that recoveries of both ^{55}Fe and ^{63}Ni decreased significantly if irradiated graphite samples were heated for short periods at 1100℃ or for extended periods (>6 hrs) at lower temperatures (800℃).

4. Dissolution efficiency, k$_{(sol)}$

4.1 Factors affecting dissolution efficiency

In the majority of radioanalytical techniques, a dissolution stage is required to solubilise the analyte and provide a solution suitable for subsequent separation stages. Typically, the dissolution stage involves either an acid leach of the solid sample (typically using HNO$_3$, HCl or a combination of these acids), total dissolution (whereby the entire matrix of the sample is dissolved, often using HClO$_4$ and / or HF) or a total fusion technique whereby the sample is intimately mixed with a flux and heated to produce a homogeneous melt. Organic-rich matrices such as ion exchange resins can be decomposed using oxidants such as Fenton's Reagent (a mixture of H$_2$O$_2$ and Fe^{2+}). For certain radionuclides (notably ^{36}Cl and ^{129}I) an alkaline digest or alkaline fusion is used to solubilise the radionuclide and prevent its loss by volatilisation. A summary of dissolution approaches for radionuclide analysis in decommissioning materials was reported by Croudace et al [9].

The choice of dissolution technique will be dependent on the analyte, the composition of the matrix and the origin of the radionuclide (Table 1). For fission products, the nuclide is most likely to be present as a result of contamination of the material and therefore loosely associated with the matrix. The one exception would be for materials that may contain U and produce fission products in situ following neutron irradiation of the material.

For activation products, the radionuclide may have been formed in situ as a result of irradiation of the matrix and as such may be more strongly bound within the matrix requiring a total dissolution technique to quantitatively liberate

Table 2. Review of literature on dissolution techniques

Matrix	Sub type	Radionuclide source	Radionuclide	Partial	Total dissolution		Notes	Reference
				Leach	Digest	Fusion		
Concrete	Bioshield / barite concrete	Activation	^{3}H	H_2O			Poor recovery compared with combustion	[6]
			^{55}Fe $^{\&}$ ^{63}Ni	aqua regia			92% recovery compared with total dissolution	[8]
			^{3}H, ^{14}C		H_2SO_4 HNO_3 $HClO_4$		Not effective compared with combustion	[10]
			^{55}Fe $^{\&}$ ^{63}Ni			NaOH / Na_2CO_3	Effective	[8]
			^{41}Ca			$LiBO_2$	Effective	[11]
	Structural concrete	Contamination	^{3}H	H_2O			Results comparable with combustion	[6]
		Spiked tracer	^{90}Sr, Pu / U			$LiBO_2$	Not an operationally-exposed sample	[12]
Graphite	Reactor graphite	Activation	^{3}H, ^{14}C		H_2SO_4 HNO_3 $HClO_4$		Data compared well with combustion	[10]
			^{55}Fe $^{\&}$ ^{63}Ni	aqua regia			Low recovery compared with total digestion techniques	[8]
			^{55}Fe $^{\&}$ ^{63}Ni		H_2SO_4 HNO_3 $HClO_4$		Good recovery comparable with ashing / digestion	[8]
			^{55}Fe $^{\&}$ ^{63}Ni		Ashing, HCl		Residue digested in HCl + $HClO_4$ to treat persistent residues. Good recovery comparable with acid digestion	[8]
	Unexposed	Spiked tracer	^{90}Sr, Pu / U		H_2SO_4 HNO_3		Sealed vessel microwave digestion used Not an operationally-exposed sample	[12]
Ferrous metal	Steel	Irradiated						
	Steel	Spiked tracer	^{90}Sr, Pu / U		aqua regia		Not an operationally-exposed sample	[12]
Non-ferrous metals	Cadmium	Irradiated	^{113m}Cd		HNO_3		Effective	[13]
	Lead	Irradiated	^{55}Fe $^{\&}$ ^{63}Ni		8M HNO_3		Effective	[8]
	Aluminium	Irradiated	^{55}Fe $^{\&}$ ^{63}Ni		9M HCl		Effective	[8]

it. Some radionuclides may also require a more aggressive dissolution technique to render them soluble due to their chemical form even if they are not strongly associated to sample matrix (e.g. Pu if present as the refractory PuO_2).

Some information exists in the literature relating to sample dissolution (Table 2). It is therefore possible to use this information to assess the suitability of a proposed dissolution technique. In addition, dissolution of radionuclides formed in situ by irradiation of the matrix can be assessed by determining the dissolution efficiency of the corresponding stable element. For example, the dissolution efficiency of [55]Fe in an irradiated ferrous metal can be assessed by measuring the proportion of stable Fe that is recovered during the dissolution process. Such an approach is not appropriate for radionuclides which are present as a result of contamination where the contaminant radionuclide can exhibit substantially different behaviour compared with stable element analogues in the bulk matrix. In general, it could be assumed that a total dissolution-based technique would quantitatively solubilise all radionuclides and only the potential loss of the radionuclide due to volatility would need to be assessed.

4.2 Concrete

For structural concretes, radionuclide contamination arises from operational exposure to a contaminated atmosphere / fluid and is likely to be surface bound or adsorbed to mineral phases. In general, leaching of the sample should be sufficient to recover such surface contamination. Pu in bioshield concretes (where the Pu is most likely derived from contamination rather than being formed in situ) has been shown to be leachable and sequential extraction studies have suggested that the majority of the Pu is associated with carbonate and Fe/Mn oxyhydroxide phases [14]. Such phases would be readily dissolved via acid leaching.

For irradiated concretes (e.g. bioshield concretes), in addition to contamination, radionuclides such as ^{3}H, ^{14}C, [41]Ca, [55]Fe, [63]Ni and [152]Eu may be formed in-situ and can be

intimately associated with the component mineral phases rendering them less accessible to leaching. Hou [10] compared combustion and H_2SO_4:HNO_3:$HClO_4$ acid digestion techniques for the determination of ^{3}H and ^{14}C in bioshield concretes. Acid digestion data biased low compared with the combustion technique suggesting non-quantitative digestion / analyte recovery. Tritium is produced in-situ via neutron capture of minerogenic [6]Li and is strongly bound within mineral phases within the concrete. To liberate radionuclides from such phases, a total digestion procedure is required. These observations are consistent with Kim et al [6] who demonstrated that ^{3}H produced in–situ via neutron activation was non-leachable with water whereas ^{3}H arising from deposition / contamination was readily leachable. However, Hou [8] demonstrated that a significant proportion of activation-derived [55]Fe and [63]Ni can be leached from bioshield concretes when compared with NaOH / Na_2CO_3 fusion suggesting, that [55]Fe and [63]Ni are associated with a more readily soluble phase. Fusion using lithium borate has also been used to achieve complete dissolution of the concrete matrix and has been applied to the analysis of [41]Ca [11] Pu, U and ^{90}Sr in concretes [12].

4.3 Graphite

Radionuclides including ^{3}H, ^{14}C, [36]Cl, [55]Fe and [63]Ni in graphite arise from neutron activation of the matrix and associated trace contaminants. Hou [8] compared acid leaching with aqua regia, acid digestion using H_2SO_4:HNO_3:$HClO_4$ and ashing / acid digestion with HCl for the recovery of [55]Fe and [63]Ni from irradiated graphites. The recoveries of both [55]Fe and [63]Ni were low for acid leaching compared with total dissolution techniques. Comparison of H_2SO_4:HNO_3:$HClO_4$ acid digestion and combustion techniques for the determination of ^{3}H and ^{14}C in reactor graphite confirmed that there was no significant difference between the two techniques, indicating that the acid digestion procedure was effective at recovering the radionuclides from the graphite matrix [10]. Ignition and dissolution of

the residue in HCl has been used to solubilise graphite prior to radiochemical analysis of gamma emitting radionuclides, actinides, [41]Ca, [55]Fe, [63]Ni, ^{90}Sr, [93]Mo, [93]Zr and [126]Sn. A similar approach was adopted for carbon bricks, although an insoluble residue resulted which required microwave digestion in a mixture of HBF_4, HCl, H_2O_2 and HNO_3 to effect total dissolution [15]. Sealed vessel microwave digestion of graphite using H_2SO_4 / HNO_3 has also been utilised for the analysis of Pu, U and ^{90}Sr in graphite although the approach was not validated on operationally-exposed materials [12].

4.4 Metals

A wide range of metals and metal-alloys are encountered during decommissioning with the choice of dissolution procedure being dictated by the sample composition. These include (but are not limited to) ferrous metals (wrought / cast iron, steels, stainless steels), aluminium, cadmium, copper, lead, Zr alloys and Inconel. Radionuclides may be present either as surface contamination or may be formed by neutron activation of the metal and hence integral with the matrix (Table 1). In general, a total dissolution procedure is favoured to ensure quantitative recovery of the analyte. Ferrous metals such as steels can be dissolved in aqua regia prior to analysis of actinides and [90]Sr [12]. HNO_3 has been used for the dissolution of Cd prior to measurement of neutron-induced [113m]Cd [13]. 8M HNO_3 and 9M HCl have been used to dissolve irradiated lead and aluminium respectively prior to measurement of [55]Fe and [63]Ni [8]. Sodium metal and NaK alloy have been used in fast breeder reactor programmes. Dissolution of these metals must be undertaken with extreme caution given their high reactivity but can be achieved by dissolving small pieces in methanol or, to further reduce reaction rates, propanol.

4.5 Resins / desiccants

Ion exchange resins are routinely used for water circuit purification and therefore activation products tend to be adsorbed to the material. Ignition to decompose organics followed by acid leaching of the residues will effectively recover most transition metal species. Any ^{3}H or ^{14}C would be liberated during the ignition stage and require trapping. Fenton's reagent has also been used to decompose the organic resin and liberate radionuclides prior to separation. High pressure microwave digestion using $AgNO_3$ + HNO_3 has been used to solubilise ion exchange resins prior to [36]Cl analysis [16].

Desiccants, typically alumina used in gas dryers, contain predominantly ^{3}H and [36]Cl (and potentially ^{14}C associated with graphite dust from graphite moderated reactors). Extraction of these radionuclides via volatilisation is preferred but where a radiochemical separation of [36]Cl is required, the desiccant may be digested using a strong alkaline digest under reflux.

4.6 Sludges

The term 'sludge' covers a range of materials associated with nuclear reactor operation and fuel reprocessing and is defined more from their physical properties rather than their chemical composition. Acid digestion using a mixture of HNO_3, HCl and HF has been used to solubilise radionuclides including [126]Sn [17]. Alkaline fusion, using KOH-KNO_3 has been used to solubilise solid fractions of diluted 'feed materials' [18].

4.7 Soft wastes

Soft wastes include gloves, tissues rags, protective clothing etc that become contaminated through contact with loose contamination during routine operations in the nuclear facility. Soft wastes are a particular challenge for sample dissolution as the sample can comprise multiple material types. In general, radionuclides associated with soft wastes are present as surface contamination and not integral to the sample matrix. Contamination may also be highly heterogeneous and care must be taken to ensure

representative sampling prior to digestion. In general, ignition followed by acid leaching is used for recovering acid-soluble radionuclides.

5. Analyte separation – k$_{(sep)}$

The separation stage of the analysis is designed to isolate the analyte from the bulk matrix elements, to remove any elemental or radionuclide interferences and to concentrate the analyte into a form suitable for its measurement. During the dissolution stage, a range of matrix elements will be solubilised along with the analyte and these elements may have an adverse affect on the subsequent separation resulting in low analyte recoveries. Some matrix elements may follow the analyte through the separation stage and interfere with the final measurement (e.g. lanthanides in [241]Am measurement by alpha spectrometry where the alpha spectrum will be severely degraded if lanthanides are present in the measured source). In addition certain radionuclides may co-separate with the analyte resulting in a radiometric interference.

Matrix elements can interfere with the efficiency of analyte separation through a number of mechanisms.

(i) Co-precipitation of the analyte on an unplanned, matrix associated precipitate (loss of analyte).

(ii) Modification of the degree of analyte inclusion, adsorption or occlusion within a planned precipitation stage.

(ii) Specific, direct matrix competition with the analyte on extraction media where the chemical properties of the analyte and interferent are similar.

(iv) Ion-pair formation / complexation with the analyte and subsequent modification of analyte chemistry.

(v) Non-specific matrix competition with the analyte through modification of ionic strength, viscosity and diffusive properties of solution.

(vi) Analyte / matrix co-extraction and incorporation

into final source affecting the source / measurement characteristics.

The range and concentration of matrix elements and radionuclides present in the solution will vary depending on sample type, the mass analysed and the chosen dissolution technique. However for each technique, it is possible to determine typical concentrations in digests based on the solubilisation efficiency, k$_{m(sol)}$, and set upper limits on elemental composition for classes of matrices. Simulant test solution containing elements at these upper concentration limits can then be prepared and spiked with the analytes and interferents of interest and the separation procedure tested using these simulants. The chemical recovery of the analyte, the concentration of matrix elements in the purified fraction and interference decontamination factors can then be determined providing information on the robustness of the technique. Replicate tests would also provide information on the precision of the technique. Where new matrices are encountered, the composition of the digest can be determined to confirm that the elemental concentrations below the values that would adversely affect the separation. It is assumed that the presence of elements at lower concentrations would not result in any adverse effects unless the element forms an intrinsic part of the separation procedure (e.g. where matrix-derived Fe is used to produce Fe(OH)$_3$ precipitates to co-precipitate actinides). Such instances can be identified and where necessary additional carrier added. Interferent separation can be determined using either added tracers or the stable element analogue arising from the matrix where present. Decontamination factors can then be determined and limits on the concentrations of interference species calculated. These data can be used in defining the operational envelope for the analytical procedure.

6. Analyte quantification - ε$_A$

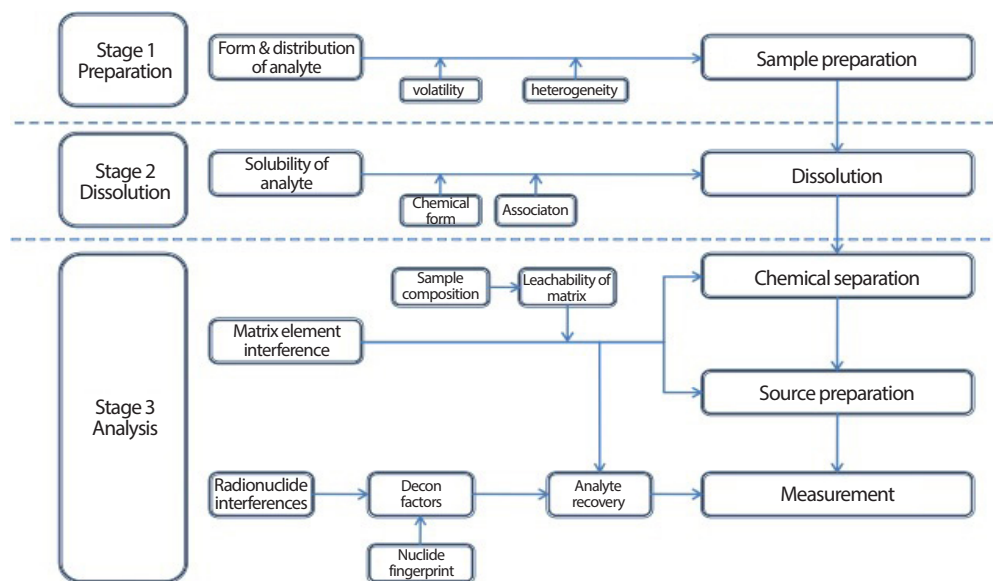The accuracy of the final measurement is often assessed

Fig. 2. Critical information for multi-stage validation of an analytical procedure.

through the use of reference materials. However, accuracy can also be readily assessed through participation in proficiency tests and through the analysis of stimulant solutions spiked with a traceable standardised solution of the analyte. For alpha spectrometry, the correlation between the reference solution of the analyte and the tracer provides independent confirmation of the accuracy of the measurement. For liquid scintillation analysis, alternative calibration approaches (such as Ciemat NIST method) can be used to independently confirm instrument calibration. The impact of isobaric / radiometric interferences can also be assessed. The presence of such interferences can be evaluated through a review of the sample composition and likely co-associated radionuclides. An upper limit on the concentrations of interferences can be determined using data on the degree of solubilisation, $k_{I(sol)}$, of the interference during sample dissolution and the degree of separation, $k_{I(sep)}$, during analyte purification. Representative sources containing the interferent can then be prepared and the contribution of the interferent, ε_I, to analyte measurement can be assessed. Assessment of measurement accuracy in the absence of a matrix-matched reference material is therefore readily

achievable. Such data can be used in conjunction with data on the separation to define an operational envelope for a measurement

7. The validation approach

The following stages are proposed for the assessment of the suitability of a procedure for radioactive waste characterisation (Fig. 2).

(i) Collation of information to provide a scientifically underpinned assessment of expected method performance and potential impact of matrix elements.

(ii) Assessment of radionuclide volatility and distribution within the matrix to inform sample storage and preparation strategy.

(iii) Assessment of the chemical composition of the sample and the recovery of matrix elements during the dissolution stage to provide data on the composition of the solution presented to the chemical separation stages.

(iv) Identification of potential isobaric or radiometric interferences arising from the matrix or associated radionuclides.

(v) Assessment of the robustness of the separation technique over a defined range of leachate compositions in order to define an operational envelope for the technique. This stage will assess the impact of matrix elements on the separation efficiency and determine the degree of separation of the analyte from potential interferences. Use of experimental design can be utilised to reduce the number of tests required.

(vi) Assessment of measurement performance and the impact of isobaric / radiometric interferences.

8. Conclusions

The diversity of matrices requiring analysis in support of nuclear waste characterisation poses a significant challenge to the radioanalytical laboratory. Careful consideration of the key stages in an analytical procedure and knowledge of the material being characterised is critical in evaluating the performance of a technique. In the absence of matrix-relevant reference materials, much of the method validation can be achieved using simulants that reflect the composition of the sample that is being presented to the separation and measurement stages of the procedure. However, validation of the sample preparation and dissolution stages is more complex. Knowledge of sample composition and analyte association is critical. In particular, radionuclide association will be highly dependent not only on the type of material but also the origin of the radionuclide within that material and this must be carefully evaluated during the validation process. In practice, a multi stage approach to method validation is required to ensure that the impact of sample type on analytical measurement is fully understood. In achieving this, an operational envelope for the procedure can be defined in terms of matrix composition, sample mass and radionuclide activity concentrations

and this can be used to assess the suitability of the procedure for samples submitted for analysis.

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