

Maintaining radioanalytical data quality: The challenges of decommissioning analysis

Phil Warwick, Ian Croudace & Richard Marsh discuss their experiences of the problems with radioanalytical characterisation of decommissioning materials, implications to data quality and some approaches that have been developed to overcome the challenges

The transition of many UK nuclear sites from operational to decommissioning phases has required radioanalytical laboratories to adapt to significantly different technical demands. Previously, emphasis had been on operational support including process control, waste characterisation and health physics / environmental monitoring whereas under decommissioning the demands on the analytical lab have become increasingly diverse. The list of target radionuclides has expanded, and now encompasses a vast and often obscure range of fission and activation products for which routine analysis methods sometimes do not exist.

Despite this, the accurate assessment of such nuclides has become critical for decommissioning waste characterisation due to their long half lives and contribution to the long-term waste repository safety case. Sample activity might originate from contamination or direct irradiation, often over decades. The association of the analyte with the bulk matrix in samples originating from decommissioning further complicates the task of providing robust analysis of radionuclides and is of key importance when considering an appropriate and effective analysis technique.

Long term planning, both in terms of scheduling and sample numbers has become more complex leading to a need for more reactive analytical services working to considerably shorter turn round times. With this shift in operational requirements, it is important to ensure that radioanalytical laboratories maintain a high level of data quality.

The key stages in a typical radioanalytical procedure are summarised in Figure 1. Four key factors may be considered intrinsic to maintaining a high level of analytical data quality:

1. Trained / competent analytical staff
2. Properly validated procedures
3. Suitably calibrated radiometric instrumentation
4. Robust quality control

The availability of appropriately trained radioanalytical chemists has been a concern for laboratories for some time. Training issues are not restricted to decommissioning analysis and are outside the scope of this paper. However, it is noteworthy that no structured training programmes for radiochemical analysts exist. This deficiency must be addressed as part of the overall nuclear skills shortage to ensure suitable experienced radioanalytical staff are available to support the decommissioning programme over its expected duration.

The remaining factors are all affected by the shift to decommissioning analysis and present specific challenges for maintaining radioanalytical data quality.

Testing and validation of procedures

It is of vital importance that the procedure chosen for the analysis is appropriate for the sample type being analysed. Many of the radioanalytical techniques used for waste characterisation are modifications of techniques originally used for process control analysis. However, the sample types encountered in waste characterisation are diverse including soft wastes, metals, plastics, construction materials and oils.

The first potential problem arises in sub-sampling. Radionuclides may be present as a result of contamination on the surface of the matrix or via direct irradiation where the radionuclide may be intimately associated with the bulk material. The radionuclide may be distributed heterogeneously rendering sub-sampling difficult. Liquid samples (such as oils) may contain multiple phases between which the radionuclide may partition and careful sub-sampling is required to obtain representative results.

The nature of the matrix may also make it difficult to thoroughly homogenise the sample prior to sub-sampling. This is a particular issue for mixed wastes where each matrix type may contain differing quantities of a radionuclide and must be sampled proportionally so as to provide a truly representative sub-sample for analysis. The matrix itself may also affect the analytical separation resulting in low chemical recoveries of the radionuclide or interference in the final measurement.

An example of heterogeneity in radionuclide distribution and sample preparation approach impacting on the final measurement was observed for ^3H in metals. Lewis et al [1] observed that ^3H in steels operationally exposed to tritiated water vapour was predominantly confined to the paint and surface oxyhydroxide layer of the metal (Figure 2). Sub-sampling by filing the metal surface would result in significantly higher ^3H activity concentrations being measured compared to a bulk metal sample where the ^3H activity would be diluted by the uncontaminated metal underlying the surface. However, the study also demonstrated that the metal could be effectively decontaminated by removing the surface contaminated layer using shotblasting.

The association of the radionuclide with the matrix may also affect the behaviour of the radionuclide through the separation procedure. It has been shown that the ^3H in reactor bioshield concrete closest to the reactor, which is produced via direct neutron activation of ^6Li in the concrete, is more strongly bound than ^3H arising from tritiated water exposure (Figure 3) [2]. Significantly higher temperatures are required to liberate the strongly-bond ^3H , impacting on the thermal desorption

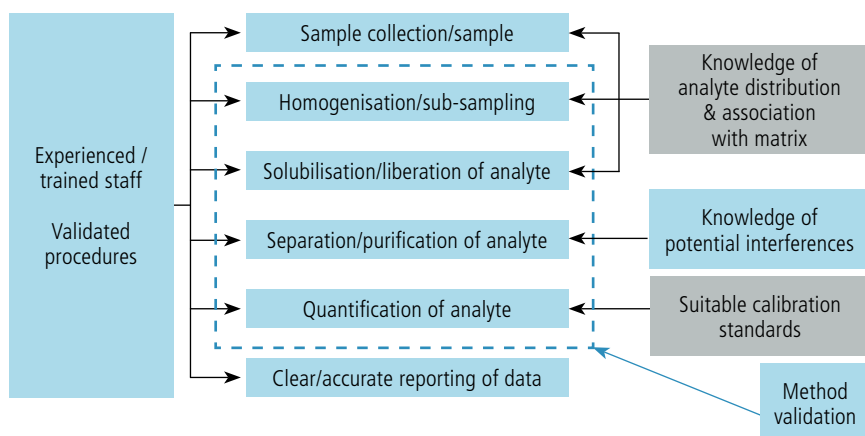


Figure 1: Key stages in a radioanalytical procedure and key factors affecting data quality

techniques used to recover 3H during analysis. A subsequent study has shown that thermal desorption profiles for 3H are highly dependent on the sample type and the origin of the 3H in the materials [3].

Dissolution of the analyte is typically the first stage in a radioanalytical separation with the choice of technique being dependent on the radionuclide, sample provenance and host matrix. Leachability of a radionuclide from decommissioning wastes may differ from that previously assumed. For example, ^{241}Am is usually regarded as being leachable using mineral acids. In a review of ^{241}Am separation techniques [4] it was noted that HNO_3 or aqua regia (a 3:1 mixture of HCl and HNO_3) were usually sufficient to quantitatively leach ^{241}Am from soils and sediments. However, for an operationally contaminated undefined 'debris' sample, total dissolution using HF was required to quantitatively recover the ^{241}Am with only 33% being liberated using aqua regia alone.

Thorough testing of a procedure is vital to demonstrate that it is 'fit-for-purpose'. However, given the range of matrices that may be encountered and the differences observed even for a single radionuclide / matrix as a result of its exposure history, it is not feasible to validate all procedures for all sample types. In addition, there is a lack of certified reference materials reflecting the types of materials encountered that may be employed to validate the method. Alternatively spiking an uncontaminated matrix with a solution of the relevant radionuclide may be considered. However, although this will allow an assessment of the effect of the matrix on the effectiveness of analyte separation, it will not identify any issues relating to radionuclide association with the matrix or interference from other radionuclides that may be present in a waste with a complex radionuclide fingerprint.

Calibration of radiometric instrumentation

Following chemical separation of the analyte, the radionuclide activity must be determined using a suitably calibrated instrument. Generally, instrument calibration is achieved by assessing the instruments response to a known / certified activity of the radionuclide in matrix-matched standards. However, in decommissioning waste characterisation, radionuclides are often requested for analysis where no certified reference standard of that radionuclide exists. Such radionuclides include ^{41}Ca , ^{79}Se , ^{93}Zr , ^{113}mCd and ^{151}Sm which are of significance in certain waste forms but which have not been routinely measured in the past. Of these, most are beta or electron capture radionuclides and can be effectively measured using liquid scintillation counting (LSC).

To overcome this lack of calibration standards, proxy radionuclides of comparable energies have been used for calibration. However, using a Monte-Carlo based empirical approach to determine liquid scintillation efficiencies, it has been shown [5] that significant differences in instrument response are observed for radionuclide pairs with comparable beta energies (Figure 4).

The Ciemat-NIST approach has now been successfully applied to the routine analysis of radionuclides where no certified standards are available including ^{41}Ca in bioshield concrete (Figure 5) [6], and ^{113}mCd in irradiated Cd shields [7]. For ^{41}Ca , comparison of data arising from LSC and accelerator mass spectrometry (AMS) are in good agreement but deviate from predicted values demonstrating the important role of direct measurement. For ^{113}mCd , comparison of results determined by LSC and gamma spectrometry (via a low abundance gamma emission) showed a discrepancy between the two datasets which has subsequently been attributed to an inaccuracy in the published gamma emission probability [8] highlighting some of the problems encountered in analysing such unusual radionuclides and the strength of the liquid scintillation calibration procedure.

Quality control

Ongoing satisfactory performance of a radioanalytical method is assessed through the analysis of quality control standards of known radionuclide activity concentrations. However, as with method validation, the lack of representative standards limits the usefulness of such quality control measurements. Again, there is a requirement for the supply of standards that more closely reflect the matrices, radionuclides and chemical forms encountered in decommissioning samples. Although it would be impossible to produce standards covering the full range of decommissioning samples encountered, the currently available reference materials are too far removed, being mainly of environmental origin. The preparation and characterisation of more representative standards is therefore a high priority in the industry.

Conclusion

The shift from radioanalytical measurement in support of operating nuclear facilities to that associated with decommissioning has presented significant challenges to radioanalytical laboratories. The diversity of sample matrices, the requirement to analyse less commonly encountered radionuclides and the variability of radionuclide association with the matrix can all impact on the performance of a radioanalytical technique and potentially affect the quality of data generated.

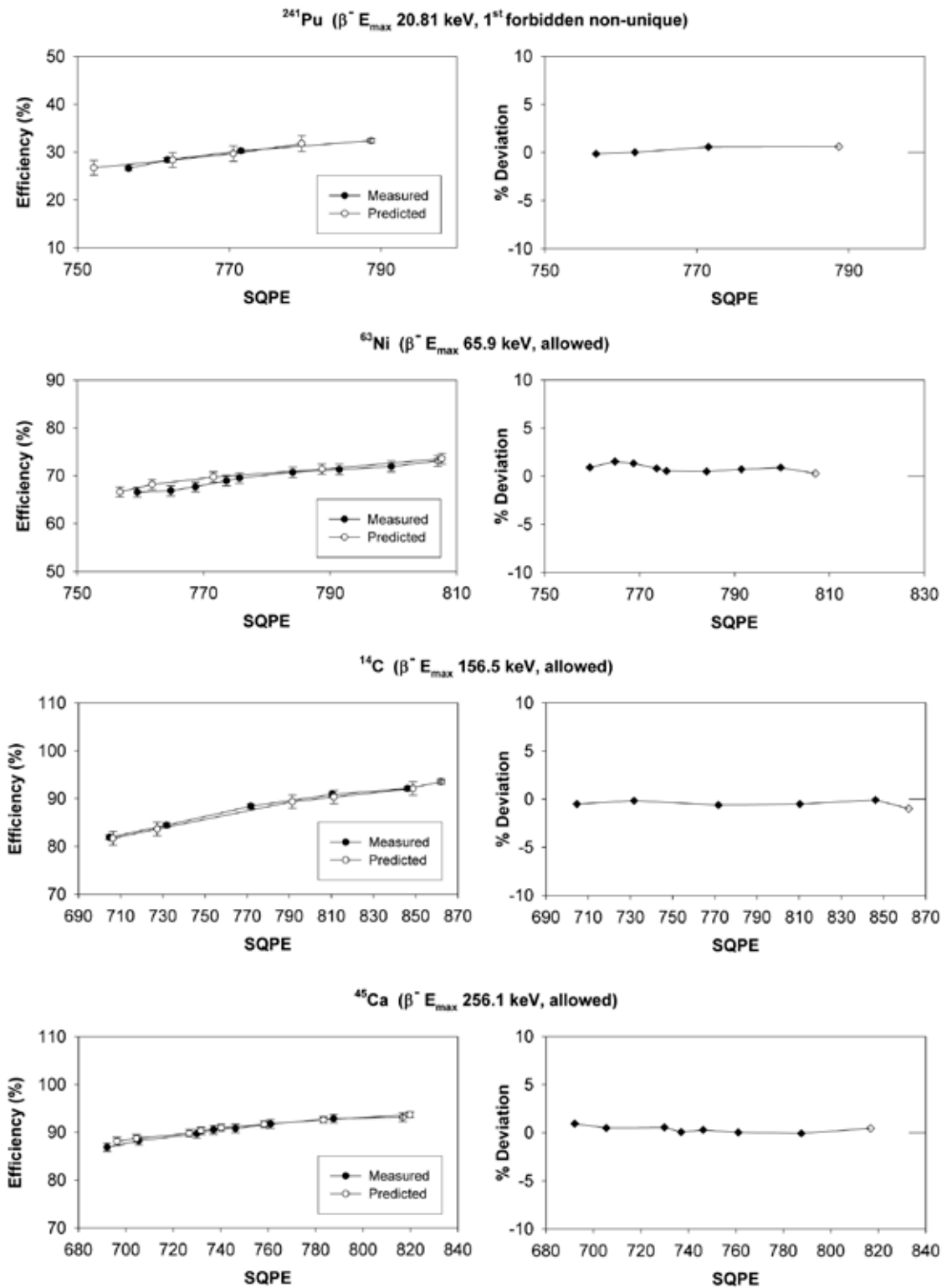


Figure 4: Discrepancies between liquid scintillation efficiencies for target radionuclides and potential proxy calibration radionuclides (reproduced from [5])

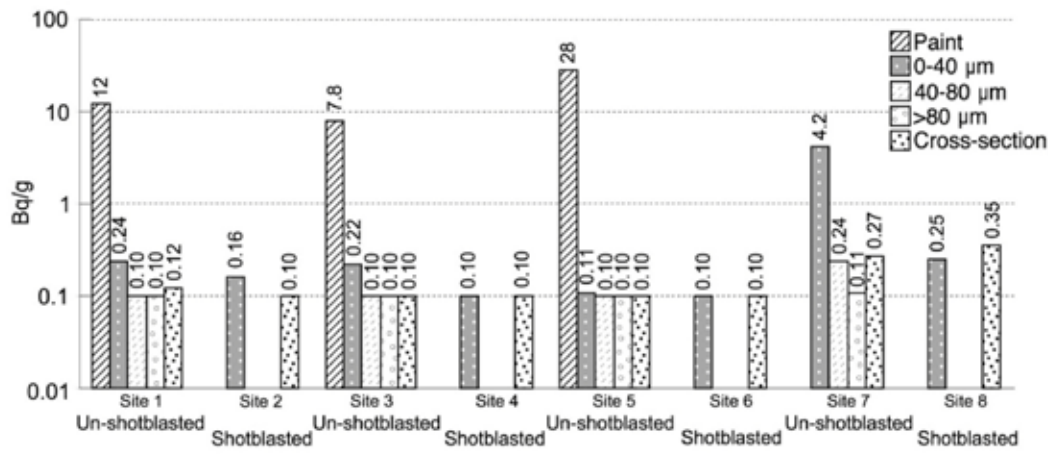


Figure 2: Distribution of ^3H in operationally exposed steels pre and post shotblasting (reproduced from [1])

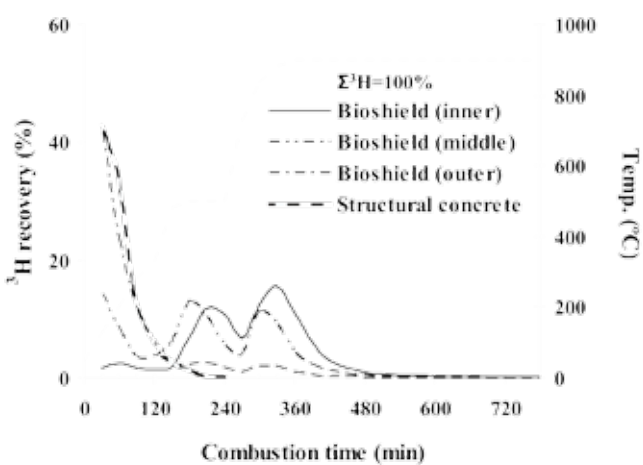


Figure 3: Thermal desorption of ^3H from bioshield concretes compared to structural concretes exposed to HTO (reproduced from [2])

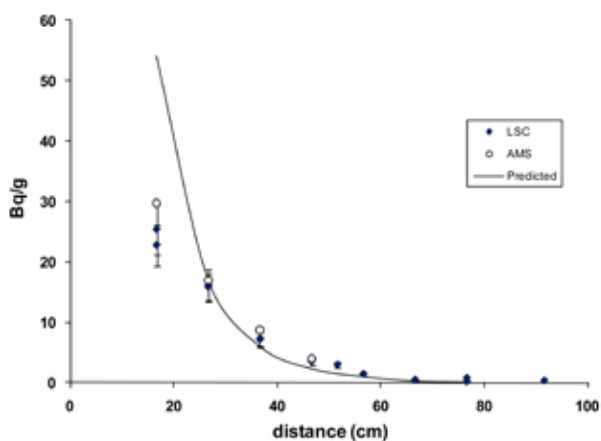


Figure 5: Profile of ^{41}Ca in reactor bioshield concrete

To ensure good data quality, a better understanding of the wastes and radionuclide association is required to ensure that analytical methods are fit for purpose and that sampling strategies will not bias the final results. New methodologies and instrument calibration procedures have had to be developed to cope with the complexities of decommissioning samples.

However, method validation and ongoing quality control have been hindered by the lack of suitable reference materials. Investment in analytical method development, more comprehensive sample characterisation and production of representative reference materials must be an industry priority in order to ensure ongoing data quality in decommissioning analysis. ❄

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Advances in tritium extraction methods to aid efficient waste characterisation

Ian Croudace, Richard Marsh & Phil Warwick discuss their experiences in developing two efficient devices that have become widely used by the industry for extracting tritium prior to its radioanalytical determination

Over the last decade the accelerated decommissioning of nuclear and related facilities in the UK in particular has led to large numbers of samples (>100,000) requiring analysis for a range of radionuclides. Knowledge of the activities of critical radionuclides is required to ultimately guide project managers and health physics professionals on the appropriate treatment of waste or indeed waste sentencing. A broad range of materials commonly requiring consideration include concrete, asbestos, MMMF (man made mineral fibres), wood, desiccants, reactor metal work, graphite and soft wastes such as paper towels, coveralls and gloves. Included in the list of nuclides requiring analysis has been tritium, the only radioactive hydrogen isotope.

The application of tritium is wide-ranging and includes the JET experimental nuclear fusion reactor, thermonuclear weapons, luminous signs and radioactive labelling of specialist organic compounds. It also exists in the environment as a consequence of natural production in the upper atmosphere (cosmogenic tritium), from the legacy of atomic weapons fallout (now mostly decayed [1]) and from the nuclear fuel cycle. The main production routes in the nuclear fuel cycle are via neutron capture by D, Li and B, ternary fission; heavy water reactors (CANDU and the prototype SGHWR at Winfrith) produce significant tritium. The reprocessing of spent nuclear fuel is a significant source of tritium that is normally discharged to coastal seas since it cannot be readily isolated by any cost-effective chemical separation procedure.

It is notable that until recently tritium has required specific measurement because it cannot be reliably linked to a fingerprint owing to its mobility/volatility. When associated with solid materials on a nuclear licensed site (NLS) undergoing decommissioning its control was subject to SoLA (Substances of Low Activity Exemption Order). On this basis, the clearance of materials from NLS prescribed that any solid material with a total substantially insoluble artificial activity of less than 0.4 Bq/g was deemed exempt from control (although it may still be deemed radioactive).

There are advanced plans for the replacement of SoLA which is set to be replaced by a series of nuclide specific exclusion values with limits ranging from 0.01 Bq/g to 10,000 Bq/g (based on values stated in EU RP122 [2] and possibly moving to the IAEA RS-G-1.7 [3] value. Regardless of the system adopted there will still be a need to

characterize decommissioning samples for tritium content to guide waste sentencing.

The purpose of this article is to inform the reader of the developments in the main techniques used to extract tritium from decommissioning and environmental sample matrices prior to analytical characterization.

Tritium extraction and measurement approaches

Direct or in-situ measurements of tritium in solids are complicated by its low energy pure beta emissions ($E_{\text{max}}=18.6\text{keV}$) [4]. Although surface contamination may be assessed via smears or direct instrumental measurement of 'escaping' tritium betas, the significant attenuation by the sample matrix makes determination of total tritium by these methods ambiguous and unreliable. Aqueous leaching has been used to determine bulk activity [5] (figure 1) however the exchange of tritium upon which such methods rely is highly species dependant. Although tritiated water (HTO) could be expected to be leachable, it is unlikely that tritium locked in mineral lattices (formed in-situ by neutron capture) or tritium that is organically bound (OBT) would be quantitatively recovered. It is therefore advisable to extract tritium from the host matrix prior to measurement (figure 2).

Fortunately, tritium (regardless of its speciation) can generally be selectively volatilized from most substances using thermal desorption or oxidative decomposition which has the benefit that other nuclide interferences are virtually eliminated. The collected tritium (usually HTO) is normally measured by liquid scintillation counting since the method is able to count the low energy beta emissions with reasonable efficiency.

Thermal decomposition in a purpose designed furnace (e.g. Pyrolyser) is generally the preferred option but where samples are combustible this limits the size of sample that can be determined. In such cases a closed, oxygen-filled pressure vessel approach is preferred (see Hyperbaric Oxidiser, HBO). With both methods the separation of the volatile constituents from the sample matrix serves to reduce or eliminate radionuclide interferences.

The effectiveness of thermal desorption/oxidation for tritium recovery depends on the efficient performance of four key stages:

1. Quantitative liberation of ^3H from the sample matrix

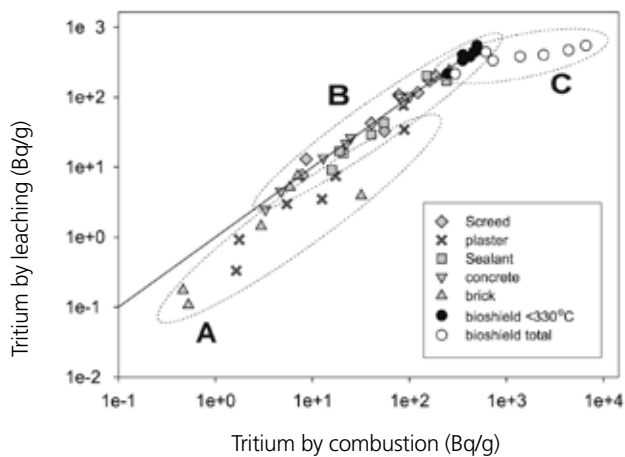


Figure 1: Relationship between ^3H extracted from various construction materials by aqueous leaching and combustion. Zone A, partial ^3H leaching correlating with total ^3H ; zone B, quantitative leaching of ^3H correlating with total ^3H ; zone C, partial leach not correlating with total ^3H (bioshield samples) (reproduced from [5])

2. Quantitative conversion of all ^3H species to HTO
3. Efficient trapping of the liberated ^3H as HTO
4. The effective separation of ^3H from other nuclides in the sample that could interfere with the final quantification of ^3H .

Tritium extraction – thermal decomposition versus simple leaching (Figure 1)

In the past simple aqueous leach tests have been used to assess the level of tritium contamination in a solid sample. However, the weakness of this approach is highlighted by work that shows the comparison of data obtained by leaching ($^3\text{H}_{\text{leach}}$, generally HTO) versus Total- ^3H ($^3\text{H}_{\text{total}}$) determined by combustion. For some sample types exposed to HTO (including structural concrete), the $^3\text{H}_{\text{leach}}$ compares well with the $^3\text{H}_{\text{total}}$ (zone B). Similar results are also observed between leaching and the weakly-bound ^3H component (inferred to be HTO) of bioshield concrete samples.

For some porous materials (brick, plaster and sealant), the $^3\text{H}_{\text{leach}}$ results were lower than the $^3\text{H}_{\text{total}}$ although a correlation still existed between the two measurements (zone A). However, for samples (e.g. activated bioshield concrete) where a significant part of the ^3H was strongly held in mineral lattices [produced via $^6\text{Li}(n,\alpha)^3\text{H}$] then only a poor correlation is seen between the $^3\text{H}_{\text{leach}}$ and the $^3\text{H}_{\text{total}}$ as measured by combustion (zone C).

A minor revolution in tritium extraction – Introduction of the Pyrolyser furnace

Up until 2000 the industry-standard approach for extracting tritium from samples (metal, insulation, oil, concrete, brick, plaster, wood, graphite etc) from nuclear licensed sites was to employ many single-tube furnace systems that, though well-designed, were inefficient and required significant space. The dramatic rising demand for tritium and ^{14}C analysis, stimulated by accelerated decommissioning, required a more efficient device with a smaller footprint.

The solution was the arrival of the Pyrolyser-Trio multi-sample furnace system that allowed for the extraction of six samples at a time and the potential for rapid cool down between runs so that another analytical cycle could be carried out if required. The new generation system has shown that it readily allows 1000+ tritium (and ^{14}C , ^{35}S , ^{36}Cl and ^{129}I) samples per year to be extracted from a single furnace system [6].

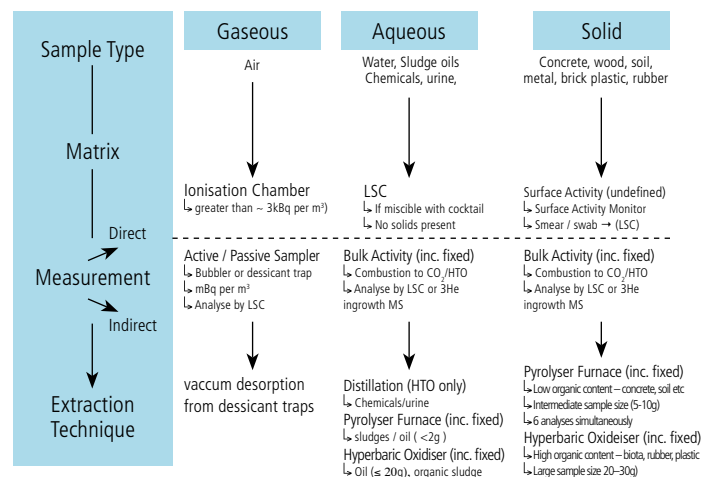


Figure 2. Summary of tritium analysis methods and techniques for tritium extraction from different sample matrices. 'Fixed' refers to both non-exchangeable organically bound tritium and lattice bound tritium

The Pyrolyser-Trio (Raddec Ltd, Southampton, UK) was designed to simultaneously extract $^3\text{H}_{\text{total}}$ (and ^{14}C) from virtually any type of nuclear and environmental sample (figure 3).

The standard methodology consists of placing weighed samples into silica glass boats that are then inserted into their own silica work-tube (1m long) containing 10g of platinumised alumina catalyst. A laminar flow of air or oxygen is passed over the sample while it is progressively ramped in temperature typically from 50-900°C over a period of about 3 hours. This controlled oxidation ensures that decomposition is slow and does not lead to any pressure excursions as the sample components decompose and liberate CO_2 , hydrocarbons, water etc. The oxidized combustion products (water/HTO and CO_2) are collected in bubblers from which sub-samples are taken for LSC measurement.

Hyperbaric Oxidiser (HBO)

The Hyperbaric Oxidiser (HBO, figure 5) represents a significant refinement of earlier technologies that have now largely disappeared from the marketplace. It is in effect a specially designed bomb calorimeter and was developed to provide a tritium extraction device that would complement the Pyrolyser. It is a closed-system oxidative combustion device that uses pressurised oxygen (typically 20 bar) to promote the rapid and complete oxidation of samples (generally combustible samples). The pressure vessel is a 5 litre heavy gauge stainless steel (316L) cylinder fitted with a hinged door to enable easy loading of samples. The hinged door incorporates a novel locking mechanism with three interlocks to ensure safe operation. An ignition system initiates combustion and the significant excess of oxygen ensures a very rapid and effective combustion of a wide range of combustible samples from tritium contaminated oil, rubbers, plastics, paper, wood, vegetation, wet fish, sea-weed etc. The oxidizing environment ensures the complete conversion of most suitable materials to CO_2 and HTO from samples as large as 40g.

The HBO system incorporates a range of temperature and pressure sensors that are integrated into a software monitoring system (National Instruments LabVIEW) to log the combustion process by way of vessel and gas temperatures and pressure. The complete combustion of a sample takes approximately one minute after which the combustion products ($^{14}\text{CO}_2/\text{CO}_2$ and water/HTO) are quantitatively collected using

GAU - Radioanalytical

National Oceanography Centre, Southampton
SO14 3ZH United Kingdom

Tel: +44 (0) 23 8059 2780
Fax: +44 (0) 23 8059 6450

Mob: 07739 898344
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Figure 3: Pyrolyser-Trio combustion furnace for extraction of total tritium



Figure 4: Two images of the Hyperbaric Oxidiser. A – pre-production evaluation configuration, B – production configuration

an integrated gas collection system. The semi-automated gas handling system, with vacuum purge, collects water and CO₂ into separate traps which are then available for analysis by LSC or ³He in-growth mass spectrometry.

The HBO is particularly suited to the extraction of tritium from combustible matrices such as paper, wood, rubbers, plastics and oils, which frequently are only incompletely oxidized when processed using the Pyrolyser, especially at masses above 1-2 g. The ability to completely oxidise large sample masses, (thus generating large volumes of analyte for LSC) is advantageous when investigating heterogeneous decommissioning (e.g. soft wastes) and low activity environmental samples (biota).

The effectiveness of the HBO has been validated through gravimetric recovery and HTO/OBT recovery trials (figure 6), indicating that yields of in excess of 95% are readily achievable with an associated propagated method uncertainty of better than 10% (2 sigma).

Applications of the Pyrolyser and HBO

Tritium commonly exists on sites as tritiated water (HTO), but also potentially as HT and organically-bound ³H. Since HT and HTO are both volatile then plant and buildings are likely to become contaminated with time and will become intimately incorporated into the fabric of construction and other exposed materials via physical absorption, diffusion and isotope exchange. The amount of ³H incorporation depends on such factors as the concentration and form of tritium, the length of exposure, and other physical conditions such as the ambient humidity, pressure and temperature. The nature and composition of surfaces can also control the extent and distribution of tritium in exposed materials (painted or porous materials).

Waste characterization for decommissioning

Systematic investigations of the distribution of tritium in the concrete of fuel ponds, bioshields, graphite, insulation, desiccants, pump oils, metals, wood etc are regularly carried out during decommissioning programmes as such information is used to guide waste management. For example scabbling of contaminated concrete surfaces or shot-blasting of metal can be a useful waste minimisation strategy.

Environmental assessments

Tritium has been discharged into the marine environment from reprocessing plants, nuclear power stations and radiopharmaceutical facilities over the last sixty years. Being able to assess the impact of such discharges is important for Regulators and other Agencies. One example of such a study was the Severn Estuary research project that investigated the interaction of OBT with marine sediment. An unexpected finding of the study was that the more-hydrophobic OBT compounds were retained by sediment and that a record of the discharge could be found in a systematically sampled sediment core (Figure 4). Reprocessing plants have introduced the largest activities of tritium (mostly as HTO) into the marine environment and tracking its dispersion and possible accumulation in biota is of ongoing interest. The HBO is currently being applied to the investigation of tritium accumulation in biota in the English Channel.

Speciation studies

The design and high efficiency of the Pyrolyser readily enables useful information to be obtained on the chemical association of tritium in materials by serially collecting the tritiated off-gas at different stages during the thermal decomposition of the sample. The chemical form of the tritium can be inferred from the temperature(s) at which it is liberated. HTO is liberated at temperatures up to 100°C whereas water

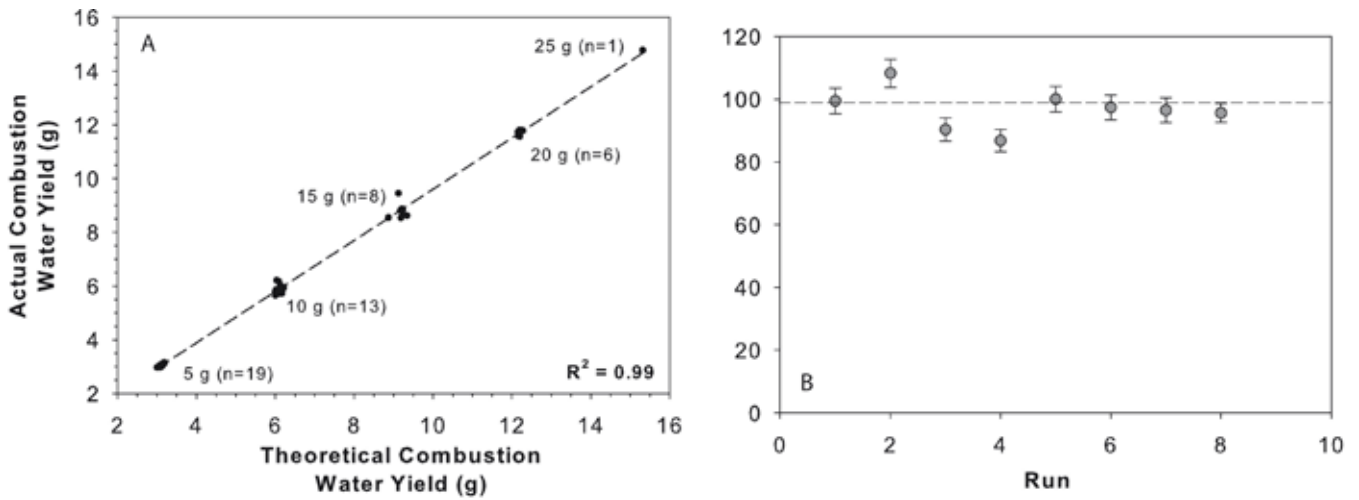


Figure 5: A – gravimetric recovery of the HBO expressed in terms of the actual versus theoretical mass of water recovered from the combustion of varying masses of cellulose, B – HBO recovery of activity from ³H-thymidine (OBT) labeled samples (10g in mass)

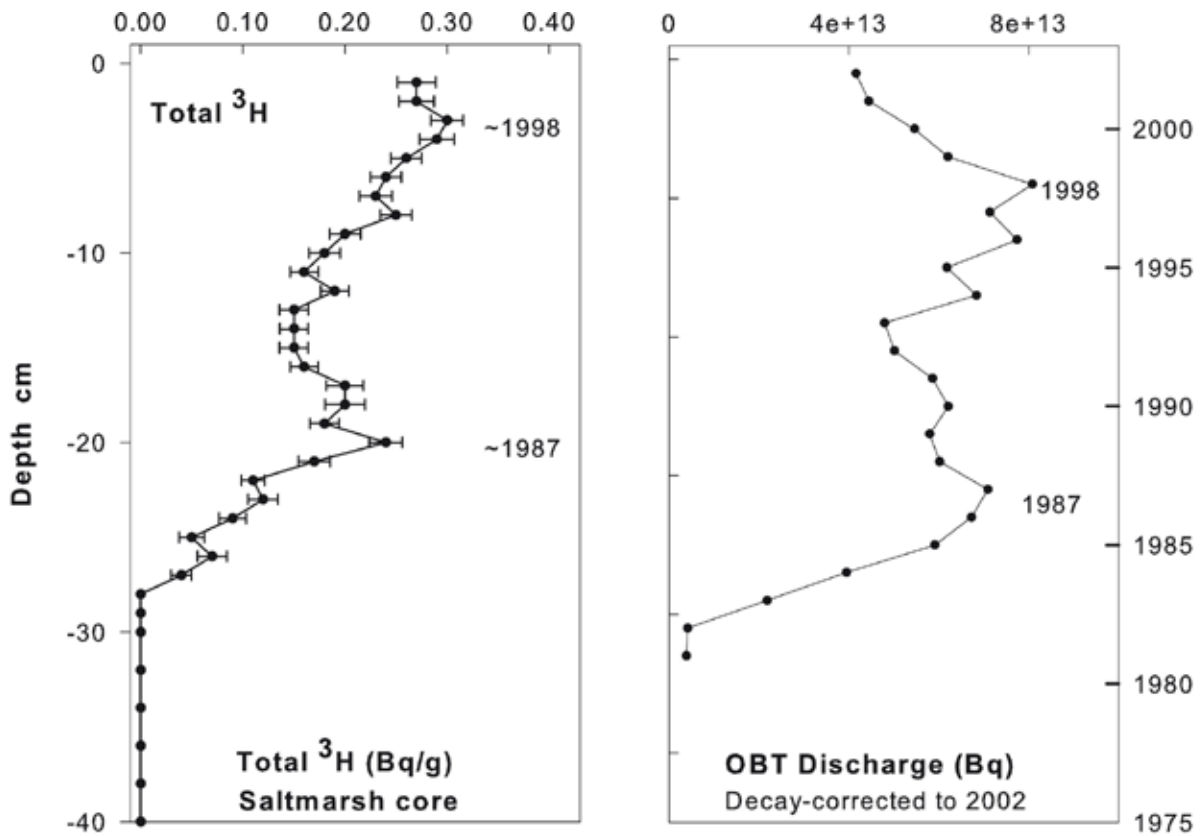


Figure 6: Correlation of total tritium activity measured in a Severn Estuary sediment core and decay corrected OBT discharge (reproduced from [8])


of crystallization is lost at the appropriate temperature of the hydrated compound (e.g. in cements and concretes). Later losses at about 300–400°C are associated with the decomposition of hydrated oxide phases (e.g. from hydrated oxides trapped along grain boundaries of metals). Temperatures from 600°C up to 900°C are required to liberate tritium trapped in the crystal lattices of graphite and clay minerals.

Extraction of other volatile radionuclides

The volatilization of isotopes of H, C, S, Cl and I are liberated from most materials by thermal decomposition and the Pyrolyser is routinely used to trap these products. ^{129}I for example is regularly extracted from environmental samples using the Pyrolyser prior to AMS measurements by the Xi'an AMS Centre [7].

Conclusions

The rapid progress of nuclear decommissioning in both the UK and further afield has required the development and enhancement of techniques for the quantitative extraction of tritium (and other volatile radionuclides) from a diverse spectrum of sample matrices. The techniques needed to be capable of dealing with samples having potentially variable tritium speciation.

This article introduces the key elements of the two main developments that led to improvements in the accurate and effective analysis of tritium. The Pyrolyser System is suited to the extraction of tritium from the majority of decommissioning related wastes and was designed for flexibility and efficiency. It has been applied to the extraction of many tens of thousands of samples in the UK alone (e.g. Magnox and UKAEA sites). Each instrument allows for the extraction of tritium from six separate samples at a time as well as enabling tritium speciation studies. More recently, the Hyperbaric Oxidiser has been developed to readily and quantitatively extract tritium from samples that were more difficult to deal with when using the Pyrolyser because of their higher combustibility (biota, wood, paper, plastics, oils). 

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Ian Croudace (BSc, PhD, MRSC)

is Director of GAU-Radioanalytical, which he founded in 1988, which is a successful University of Southampton Industrial Advisory Unit. Annually the GAU undertakes approximately 300 contracts for various parts of the nuclear industry as well as servicing ten or so research contracts in the field of radioanalytical chemistry. Ian obtained

his PhD in geochemistry from the University of Birmingham and subsequently undertook post-doctoral research at the University of Paris VI and at the French Centre d'Etude Nucleaires, before arriving at Southampton in 1983. He has 35 years' research and consultancy experience and has more than 110 scientific publications. He is a specialist in gamma spectrometry, neutron activation analysis, X-ray fluorescence analysis and analytical geochemistry. He has co-designed a commercially successful micro-XRF system for sediment core investigation as well as designing and proving two tritium and C-14 extraction systems (with Phil Warwick).



Phillip Warwick (BSc, PhD, CChem, FRSC)

is the deputy Director of GAU-Radioanalytical and its Principal Radiochemist. He is Chairman of the RSC Radiochemistry Group. He previously managed the Environmental and Biological Chemistry laboratory for the Atomic Energy Authority at Winfrith. He is a specialist in radio-analytical chemistry, has over 20

years research and consultancy experience in environmental radiochemistry and obtained his doctorate at the University of Southampton. He has published over 50 papers in the scientific literature. He was also contractor project manager for the Environment Agency's environmental radioactivity monitoring programme 2000–2002). Phillip co-developed the successful Pyrolyser system for tritium and C-14 analysis. Responsible for Radioanalytical Training for various clients in the nuclear sector with interests in radioanalytical chemistry.



Richard Marsh (BSc, MSci, PhD)

carried out doctoral research into novel methods of tritium analysis in support of decommissioning at the University of Southampton. His PhD was funded through an AWE Outreach award co-supervised by Croudace, Warwick and Dr Richard Greenwood at AWE. Richard helped to develop and test the Hyperbaric Oxidiser (HBO). He has

also worked on testing and development of solid scintillators for low-energy beta detection as a potential alternative to LSC for certain sample types.