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Recent contributions to the rapid screening of radionuclides in emergency responses and nuclear forensics

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Highlights:

- A general overview of current Investigative methods used in nuclear forensics and emergency responses is presented along with a range of new rapid methods.
- Borate fusion is presented as a valuable tool for rapidly dissolving complex samples with one key application being the elimination of matrix absorption effects that can compromise gamma ray spectrometry data.
- A novel, rapid liquid scintillation method is presented that uses multiple quench corrections to allow rapid screening and identification of alpha and beta contaminated water and other samples in emergency situations
- A review of mass spectrometric methods shows their impact on rapid and precise isotopic analysis in the context of nuclear forensics and emergency situations

Abstract

The ability to efficiently identify potential radiological threats or actual radioactive assaults on society and the environment demands a sophisticated and dedicated infrastructure comprising specialised personnel, mobile and fixed laboratories and advanced analytical instrumentation. Most developed countries have such systems but ensuring a long-term and resilient capability is recognised as a perennial challenge. National government laboratories specialising in nuclear forensics play a key role in maintaining capability but these organisations continue to benefit significantly from interdisciplinary and innovative contributions derived from universities and other research institutions. This review provides an insight into the range of technologies used and also provides a broad overview of applied techniques and instrumentation that contribute to rapid screening and analysis in the context of nuclear forensics and radiological emergencies.

Keywords: Homeland security, nuclear forensics, radiological emergencies, rapid radioanalytical methods, radioanalytical skills gaps, universities as innovators

1. Introduction

There is an international threat of nuclear or other radioactive material being used in criminal acts [1,2]. This requires the radioanalytical community to continually develop or improve a range of robust and rapid analytical methods to support investigative and law enforcement agencies. This paper presents a limited review of commonly used methods and some relatively recent approaches that offer practical benefits and enhancements in sensitivity, speed and accuracy in the context of nuclear forensics and radiological emergencies.

Recent non-nuclear acts committed by terrorists have demonstrated their global organisational ability and several countries are justly concerned that radiological acts could follow. That there is an illicit demand for nuclear or other radioactive materials is known by the authorities from attempts to sell such materials [3,4]. The number of successful transactions is imprecisely known and therefore it is difficult to accurately characterize the ‘illicit nuclear market’. Many trafficking incidents are considered amateurish in nature and lacking in planning, resourcing and technical proficiency. There are, however, a few significant cases that are better organised and resourced and involved perpetrators with a track record in trafficking nuclear/radioactive material.

The IAEA has promoted the message that the responsibility for nuclear security matters lies with each member state but that guidance and best practice could be coordinated [5]. It also considers that the identification and inhibition of threats can be most effective through member co-operation and the implementation and development of sophisticated systems. One aspect of this is the IAEA’s Incident and Trafficking Database (ITDB) that was originally established in 1995, and which records incidents of illicit trafficking and other unauthorised activities and events involving nuclear and other radioactive material outside regulatory control. Up to the end of 2014, the ITDB contained a total of 2734 confirmed incidents reported by participating States [1]. Of these, 442 incidents involved *unauthorised possession and related criminal activities*, 714 incidents involved reported *theft or* *loss* and 1526 incidents involved *other unauthorised activities and events*. In the remaining 86 cases, a category could not be assigned due to insufficient reported information.

Nuclear forensics as a technical discipline has been emerging for over two decades [6] and is concerned with characterising various nuclear materials and interpreting the resulting data. It uses a broad array of advanced physical, chemical and isotopic procedures to characterise sampled or seized nuclear and related materials (Figure 1). The insights gained are used to control suspected trafficking activities, to deter nuclear terrorism and to verify that international treaties (e.g. Non-Proliferation Treaty) are being upheld.

Many of the methods used in nuclear forensics can also be profitably employed during the tracking of intentional or unintentional releases of nuclear or radioactive materials into the environment. For example, deliberate contamination of drinking water supplies with radioactive substances would be likely to have significant health, social, and economic impacts. This scenario was addressed in a recent multidisciplinary EU-funded study (SecurEau 2008-12) that focused on developing rapid methods for potential CBRN attacks (chemical, biological, or radioactive or nuclear) on water supplies. One of the most rapid of the radiometric methods developed and discussed later involved a novel Liquid Scintillation technique that applied spectral analysis to identify pure beta and alpha emitters in waters, biofilms and pipeline deposits within one hour [7,8].

The ability to reliably monitor and identify illegal activities [e.g. those involving fissionable materials (pre-detonation and post-detonation) and radiological emergencies] requires constant vigilance, effective globally distributed monitoring systems (e.g. CTBTO), specialist national laboratories, innovative investigative approaches and a cohort of highly skilled specialists. Within the last 20 years a gamut of techniques and systematic investigative approaches has been developed by the nuclear forensic communities [9–13]. Regulatory and nuclear forensic agencies not only require sensitive, accurate and precise analytical techniques to undertake their work effectively, but also a supply of suitably skilled specialists working in well-funded centres [14]. As argued by the National Research Council Committee on Nuclear Forensics (2010) [15], without suitable and sustained support, there is a danger of developing a skills/capability gap (Box 1) that would impact on resilience and the ability to be adequately prepared for radiological threats. Expertise and training offered by well-equipped universities and other research institutions (e.g. those specialising in geochemistry, isotope geochemistry, radioanalytical chemistry etc.) can play a short-term mitigating role in filling these gaps.

For both emergency response and nuclear forensics investigations, comprehensive physical, chemical and radiological characterisation of materials are required to inform emergency response strategies, assess risk and provide evidence for subsequent investigations. Generally, characterisation of any material will be staged and will commence with rapid non-destructive, non-contact, testing followed by more time-consuming in-depth studies typically involving destructive testing of sub-samples (Figure 1). The requirement for robust and complex datasets to be produced in a time-constrained manner places unique demands on the sample preparation, separation and measurement approaches required for the in-depth characterisation stages. This review provides a general insight into laboratory-based radioanalytical procedures used in nuclear forensic and emergency situations. It also presents a number of recent analytical procedures developed by our group that contribute to the speed of analysis at key stages in the characterisation process.

2. Rapid and quantitative methods for digesting solid samples

Suspicious seized solid samples of security concern usually need to be dissolved after initial non-destructive investigation and prior to more sensitive and targeted analysis (e.g. mass spectrometry). A range of possible dissolution methods exist (Table 1). The choice will be guided by early compositional information gathered about the suspect material. Some materials will dissolve easily or with persistence in mineral acid media and may benefit from microwave-induced heating in closed PTFE or PFA vessels. Other samples such as silicates, oxides, phosphates and sulphates in soils, sediment, rocks and minerals can be resistant to acid digestion procedures and will succumb following a fusion approach where ‘minerals’ are opened-out. Perhaps the most effective and attractive of the fusion methods is borate fusion where most minerals readily dissolve when blended with a flux and heated (Box 2 and Table 2).

Borate fusion, using lithium borates, was first established in the late 1960s [18] as a means of fusing natural and industrial materials for subsequent XRF analysis. Expansion in the use of the procedure accompanied the development of automated wavelength dispersive X-ray fluorescence spectrometry (WDXRF) and contributed to a general advance in major and trace element geochemistry (e.g. through analysis of numerous samples collected from the International Ocean Drilling Project). It was quickly recognised that most geological rocks and minerals could be readily dissolved in lithium borate fluxes, using either platinum or graphite crucibles. The resulting homogeneous glasses could be measured directly for 50 or more elements by WDXRF analysis. With the advent of inductively coupled plasma spectrometry (ICP-OES and ICP-MS), lithium borate fusions were also used to dissolve samples and the melts were poured directly into dilute acid or water to rapidly fragment the quenched glass. Fragmentation enhanced the speed of subsequent acid dissolution and allowed measurement using ICP instruments. Another approach was to apply laser ablation directly to the borate glass disk to acquire chemical information, even down to low trace element concentrations [19]

Given the beneficial characteristics of borate fusion (speed, safety and ability to dissolve a broad range of materials) and its established use in the geochemical field, it is surprising that it was not applied in radioanalytical chemistry until the work by Croudace and co-workers in 1996 [20]. A likely reason is that most radioanalytical practitioners were chemists who traditionally used classical solution methods (acids, bases) or alkali carbonate or fluoride fluxes to digest samples, both of which were non-ideal. The first reported routine application of borate fusion in radioanalytical sample preparation related to a 1996 research project that demanded high precision and rapid isotopic analysis of U and Pu. The ability to digest, chemically purify and measure 800 soil and QC samples by mass spectrometry within a 3-month period is a testament to the effectiveness of borate fusion. This was a complex and high public profile investigation of an alleged nuclear weapon incident (Feb 1958) at the former USAF airbase at Greenham Common near Newbury in the UK. It was alleged that the ground had become contaminated and a broad ranging soil sampling program was established to assess the veracity of the claims. Prior to this work, radioanalytical specialists would traditionally have used one or more sample digestion approaches to extract U and Pu (and other elements with radioactive species) from soils. The traditional methods were slow and often potentially hazardous using hydrofluoric acid attacks or fusions with alkali fluorides, carbonates and peroxides. The 1996 study demonstrated the impressive benefits of using borate fusion in the rapid digestion of solid materials. Subsequently the lithium tetraborate method has been routinely used by the originators in routine environmental radioactivity and nuclear forensic investigations [28–34].

3. Overcoming matrix attenuation in gamma spectrometric measurements

Upon discovery or seizure of illicitly trafficked nuclear materials, the unknown specimen should be measured via gamma spectrometry within 24-hours to gain a rapid but preliminary understanding of the radiological composition and concentration. The measurement of low energy gamma photons (40-200 keV) in potentially heterogeneous sample matrices containing high-density particles, such as uranium ore concentrate (UOC or yellowcake), can result in under or overestimated activity concentrations. This is because of photon self-attenuation and the inability to correctly adjust photon detection efficiencies based on sample mean density as a result of the heterogeneous sample matrix. For U-ore and UOC, dense U-bearing minerals of variable grain size are supported within a lighter bulk matrix comprising trace minerals and/or chemical residues (analogous to a nugget effect) [33]. The extent of photon attenuation observed in reference materials is proportional to the grain size and concentration of the dense U phases. With high grain size and concentration, the probability of a transmitting photon undergoing attenuation within such a grain is increased. Other experimental [35–38] and theoretical [39–41] approaches have successfully been applied to overcome or correct for photon attenuation but they are not applicable to nuclear forensic investigations and highly heterogeneous matrices due to impracticalities, assumptions or time consuming requirements.

Lithium tetraborate flux was used to rapidly and efficiently dissolve and digest a set of complex and heterogeneous compounds resulting in an aqueous sample with a predictable and consistent geometry / density identical to aqueous calibration standards [33]. This procedure removes the requirement for attenuation correction factors deduced from direct transmission style experiments and no proxy radionuclides are used. Additionally, no prior knowledge about the chemical, physical and radiological composition of the sample is required. To demonstrate the importance of this technique, three certified reference materials (CRMs) for U, CUP-1 (0.128 wt% U), BL-5 (7.09 wt% U) and CUP-2 (75.42 wt% U) were characterised in their as supplied form (direct measurement) and after lithium borate fusion (fused measurement) using HPGe well-type gamma spectrometers (figure 2). The total sample used was 0.5 g and was found to be adequate for the measurement of low U concentration samples such as ores. Where UOC or high radioactivity samples are suspected, lower sample mass could be used but the associated uncertainty would increase. The entire procedure is extremely rapid as the preparation requires approximately 20 h and the measurement time is 1 h.

Direct measurement of the low-grade U-ore reference material CUP-1 gives ^{210}Pb and ^{234}Th activity concentration of 78 ± 10% and 94 ± 10% respectively of its certified value. The higher energy ^{235}U and ^{226}Ra measured activity concentrations agree with certified values within uncertainty. In the fused form, measured ^{210}Pb and ^{234}Th are 95 ± 10% and 98 ± 8% respectively of the certified value. For the UOC analogue CUP-2, the directly measured ^{234}Th activity concentration is 7 ± 1% of the certified activity concentration whereas after fusion, this value is 100 ± 2% of the certified value. Additionally, directly measured ^{234m}Pa (1001 keV) in CUP-2 was 91 ± 5% of the certified value indicating that even high-energy gamma photons are being measurably attenuated.

Gamma spectrometry is used in nuclear forensic analysis as offers a non-destructive capability thereby preserving the recovered sample for other testing. Although the borate fusion procedure is a destructive technique, the sample mass required is very small resulting in the majority of the sample being preserved for future analyses and requirements. Additionally, the resulting fused sample can be used for mass spectrometric / radiochemical measurements without the requirement of further sub-sampling and digestion thus increasing the speed in which other analytical techniques can be implemented as part of the nuclear forensics characterisation.

4. Rapid radionuclide screening including identification and quantification

Following an actual or suspected assault on a water supply, rapid identification and quantification of contaminants is critical to assessing the risk to the public and remediation actions required. The EU Framework 7 project – Secureau [7] considered CBRN assaults on drinking water supplies. As part of this programme, our group was tasked with the development of rapid techniques for the identification and quantification of radionuclide contaminants. Such a screening technique must be capable of detecting alpha and beta emitting radionuclides and must be sensitive to low energy beta emitters. Most techniques used for routine analysis of radionuclides in drinking waters either are incapable of detecting alpha, high energy beta and low energy beta emitting radionuclides or do not provide spectrometric information necessary for radionuclide identification. Liquid scintillation analysis (LSA) was identified as the only radiometric technique capable of fulfilling this role. The technique exhibits detection efficiencies approaching 100% for alpha and high energy beta emitting radionuclides and good efficiencies even for low energy beta emitters such as ^{3}H (18.6 keV) and ^{14}C (156 keV). Alpha and beta emissions can be distinguished if required using pulse shape analysis techniques. In addition liquid scintillation analysis provides spectrometric information that is critical for radionuclide identification.

Radionuclide identification by LSA is complicated by the effect of quenching on peak position. Theoretically, the maximum energy of emission (E_{max}) is diagnostic of the nuclide present. However, quenching effectively shifts the beta spectrum to lower energies, with the degree of quench being dependent on the sample composition. To overcome this, a multiple quench correction approach was developed to permit radionuclide identification irrespective of quench conditions [8]. Two quench parameters, the internal quench parameter (which is dependent on emission energy and quench level) and the external quench parameter (which is dependent on quench level only), were measured along with the sample activity. The quench parameters were combined to provide a factor that is related only to emission energy and is independent of quench. This factor was then used to determine the decay energy of the emission and hence the identity of the radionuclide present. Once the decay energy is known, the measured sample count rates can be corrected for detection efficiency to provide activity estimates. An additional factor, termed the peak shape factor was developed to measure the asymmetry of the peak and to distinguish between alpha and beta emitting radionuclides as well as providing an indication of the presence of multiple radionuclides (Figure 3). Internal quench parameters (SQPI(x)) are determined from the sample spectrum and are quoted in terms of the spectrum channel number below which a defined percentage area (x) of the spectrum lies. The peak shape factor (PSF) is the ratio of the SQPI values calculated for 95% of the spectrum and 50% of the spectrum (PSF = SQPI(95)/SQPI(50)). Deconvolving of alpha and beta emitting radionuclides can be achieved using other approaches but this requires specific signal processing capability that is not available on all commercial liquid scintillation counters and which is also dependent on quench.

The novel approach was demonstrated to be effective at identifying and quantifying radionuclides in a range of drinking waters with [Ca+Mg] ranging from 0 - 230 mg L^{-1}. The approach is rapid, providing data within 60 minutes of sample receipt and is capable of quantifying alpha and beta emitting radionuclides down to at least 10% of the emergency drinking water action levels. The approach was also demonstrated as effective for the screening of radionuclide contamination in Fe-rich (up to 64 wt % Fe), Mn-rich (5.7 wt % Mn and 42 wt % Fe) and CO_3^{2-}—rich (35 wt % Ca) pipeline scales. Both developments relate to advances in data processing rather than instrumental development and can therefore be implemented using existing, commercially-available hardware.

5. Analyte separation techniques

Chemical separation of the analyte from the bulk matrix and potential interferences is critical to alpha spectrometric and beta radionuclide analysis as well as for mass spectrometric determination of radionuclides. Traditionally, such separations have been achieved using solvent extraction, precipitation or ion-exchange based techniques. Extraction chromatographic materials potentially offer more specific separation whilst retaining the benefits associated with chromatographic separation. Development of novel extraction chromatographic materials has permitted targeted separation of the analyte, simplifying separation schemes and reducing analysis times. A range of extractants including simple complexants, ion-selective macrocyclic complexants (e.g. crown ethers, cryptands, calixarenes), chelating agents and liquid ion exchangers have been used. In general, materials are based on an extractant / solvent coated onto an inert support although covalent bonding of the extractant to the support has also been reported. Commercially-available resins have been developed for the targeted purification of Ni, Sr, Sn, Pb, Tc, lanthanides and actinides and have been utilised in safeguards / nuclear forensics applications [42–49]. Higginson *et al* (2015) [50] reported the development and characterisation of a soft N-donor ligand extractant for the separation of ^{241}Am from matrix elements including rare earth elements, specifically for nuclear forensics applications. Our group has developed and characterised extraction chromatographic materials based on ketones (DIBK) for the isolation of ^{55}Fe [51], amines for the separation of ^{99}Tc [52] and calixarene-based materials for the isolation of ^{135}Cs prior to ICP-MS measurement [53]. In all cases high specificity for the target analyte was demonstrated. For ^{135}Cs, the calixarene (Bob-CalixC6) was used to effectively separate ^{135}Cs from the isobaric interference ^{135}Ba (6.59% natural abundance), achieving separation factors > 2500. Caesium was eluted from the column in 0.05M HNO_3. This acid strength can be aspirated directly into an ICP-MS, avoiding the need for further evaporation of the sample prior to ICP-MS, reducing analysis times and eliminating the potential for contamination. Direct assay of the analyte adsorbed onto an extractant has been applied for the measurement of rare earth elements in U ore concentrates by LA-ICP-MS [54]. Combining the extraction chromatographic functionality with scintillant detection into a single solid-phase material offers further simplification of the analytical scheme, reduction in analysis times and potential reduction in waste generation.

6. Mass spectrometric developments for rapid screening of radionuclides

Measurement of a number of radionuclides by radiometric techniques is extremely challenging and labour-intensive, and in some cases may not be possible. The advances in mass spectrometric techniques (particularly ICP-MS) has increased the number of nuclides detectable and in many cases the sensitivities achievable, expanding measurement capabilities in the field of nuclear forensics. Initially, ICP-MS focussed on detection of single longer lived radionuclides where the low specific activities favoured an atom-counting technique e.g. ^{238}U, ^{235}Th, ^{99}Tc, and ^{237}Np. As the technique has advanced, the capabilities have expanded to include the detection of long lived, low abundance radionuclides including ^{93}Zr, ^{135}Cs and ^{59}Ni; quantification of shorter-lived radionuclides such as ^{90}Sr, significantly reducing the analytical time for such analyses [55]; and measurement of isotopic ratios e.g. ^{135}Cs/^{137}Cs [56,57], ^{239}Pu/^{240}Pu [58] ^{236}U/^{238}U [59], and ^{127}I/^{129}I [60,61]. This has significant implications in the field of nuclear forensics, enabling the user to determine the source of nuclear contamination.

ICP-MS offers a significantly reduced measurement time and higher sample throughput compared to alpha and beta counting techniques for longer-lived radionuclides, with a count time of several minutes per sample. Following sample digestion, ICP-MS can be used as a rapid screening technique to determine the bulk sample composition and identify radionuclides of interest. Following chemical separation, multiple radionuclides can be determined within a single sample run. A major consideration is the extent of interference removal required, primarily the elimination of isobaric, polyatomic and tailing interferences. The instrumental setup will influence the extent of chemical separation required prior to sample introduction, and the sensitivity and detection limits achievable (Table 2). The flexibility of sample introduction has led to significant advances in radionuclide measurement capabilities by ICP-MS. A number of variables must be considered including the sample uptake rate, instrumental sensitivity, hydride and oxide formation rate, and the efficiency of sample washout to avoid cross-contamination.

Quadrupole instruments without a collision or reaction cell have limited ability to remove interferences, and are reliant on chemical separation and/or sample introduction-based separation to remove interferences. An example of a recent instrumental development in quadrupole ICP-MS is the Agilent 7900 with an Ultra High Matrix Introduction (UHMI) system that allows direct analysis of sample with up to 25 % TDS, potentially reducing the sample preparation time required prior to analysis. Alternatively, the Agilent 8800 Triple Quad ICP-MS/MS (ICP-QQQ) consists of a quadrupole positioned either side of a collision-reaction cell (termed the octopole reaction system, ORS), which leads to greater control over the ions entering the cell compared to previous generation reaction cell instruments, and improves the abundance sensitivity to a theoretical value of 10^{-14}. This setup has been proven to be advantageous to measurement of several isotopic ratios, including $^{135}Cs/^{137}Cs$ [56], $^{129}I/^{127}I$ [61], and $^{236}U/^{238}U$ [59].

Sector field instruments have limited ability to remove interferences, as even at high resolution the majority of isobaric and polyatomic interferences cannot be resolved. Operating at medium or high resolution reduces the instrument sensitivity, but has been proven to improve the detection limit because of the enhancement in abundance sensitivity and polyatomic interference removal [55,62,63]. Generally, radionuclide measurements by sector field measurements (such as the Thermo Scientific Element 2XR) are performed in low resolution mode and combined with extensive chemical separation and efficient sample introduction to achieve very high sensitivity and detection limits in the fg/g range [32,53,58,64]. Further to this, multi-collector instruments are fitted with multiple detectors, which increases beam usage efficiency compared to single collector instruments, as there is no need to cycle a number of small ion beams through a single detector [65,66]. This enables highly accurate measurement of isotopic ratios (~0.001 %) [65,66]. In order to achieve accurate isotopic ratio values, the instrumental mass bias and response of each detector must be monitored, most commonly by measuring a standard of known isotope ratio and determining a mass bias factor, using an element with a similar mass and ionisation efficiency to the nuclide of interest.

Thermal ionisation mass spectrometry (TIMS) is a realistic alternative to ICP-MS and has some benefits (high source stability leading to high precision measurements) but also has some negative features (longer filament preparation time, filament burnout). The TIMS technique was well established before the advent of ICP-MS but is undoubtedly being progressively replaced by double focussing, sector field plasma-based methods. Accelerator mass spectrometry (AMS) and resonance ionisation mass spectrometry (RIMS) are both highly sensitive techniques that offer superior sensitivity to ICP-MS. They have a place in nuclear forensics but exist in fewer highly specialised and expensive facilities. They are likely to be used if readily available or in otherwise exceptional circumstances.

7. Conclusion

The ability to investigate radioactivity assaults requires a broad and multi-disciplinary technical capability that includes appropriately skilled personnel, a range of instrumental and analytical approaches and laboratory infrastructure (mobile and fixed). International co-operation is also a key requirement to ensure the spread of good practice and to share know-how given a limited pool of talent. Building greater resilience within the nuclear forensics and radioanalytical sector is largely stimulated within the existing national laboratories. However, as is shown in this review, other organisations like universities with specialisms in radioanalytical science, geochemistry, photonics and mass spectrometry can also play a beneficial role. As demonstrated, such centres of excellence frequently contribute innovative analytical solutions and skilled scientists that are fit for the nuclear forensics community.

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Phillip Warwick is the deputy Director of GAU-Radioanalytical and a Professorial Fellow at the University of Southampton. He previously managed the Winfrith Environmental and Biological Chemistry laboratory for the Atomic Energy Authority. He has over 25 years research and consultancy experience and has published more than 55 papers in environmental and analytical radiochemistry and nuclear waste characterisation. He has been the chair of the Radiochemistry

Group of the Royal Society of Chemistry and is a member of the Analyst Informal Working Group and Cross Industry Assay Working Group. With Ian Croudace, he has worked extensively on the development of mass spectrometric techniques for radionuclide analysis and has applied this to several high profile nuclear and environmental forensics research projects. Both are currently evaluating the radioanalytical potential of the Agilent 8080 ICP-MS/MS instrument.

David Reading received his MSci in Geology from The University of Southampton in 2011. He continued with a PhD in the field of nuclear forensics funded by AWE Plc with Ian Croudace and Phil Warwick as advisors. His project focused on the development of novel sample preparation methods for uranium ores and uranium ore concentrates prior to radiometric and high precision mass spectrometric determinations (REE, U isotopes). The research has created a range of analytical tools to identify geolocation criteria for UOCs and U ores. David's work has led to five drafted publications with one being published as an Elsevier featured article in Analytica Chimica Acta.

Ben Russell completed his PhD at the University of Southampton in 2014 with Ian Croudace and Phil Warwick as advisors. He investigated the application of sector field inductively coupled plasma mass spectrometry (ICP-SFMS) for level nuclear waste characterisation, focussing on radiocaesium isotopes and strontium-90. The project combined novel and efficient chemical separation techniques with high sensitivity ICP-SFMS quantification, resulting in three lead-author peer-reviewed papers and with a significant invited review paper in draft. Ben now works in the radioactivity group at the National Physical Laboratory, London, with his primary role being to assess the radioanalytical capability of a novel ICP-MS/MS instrument.

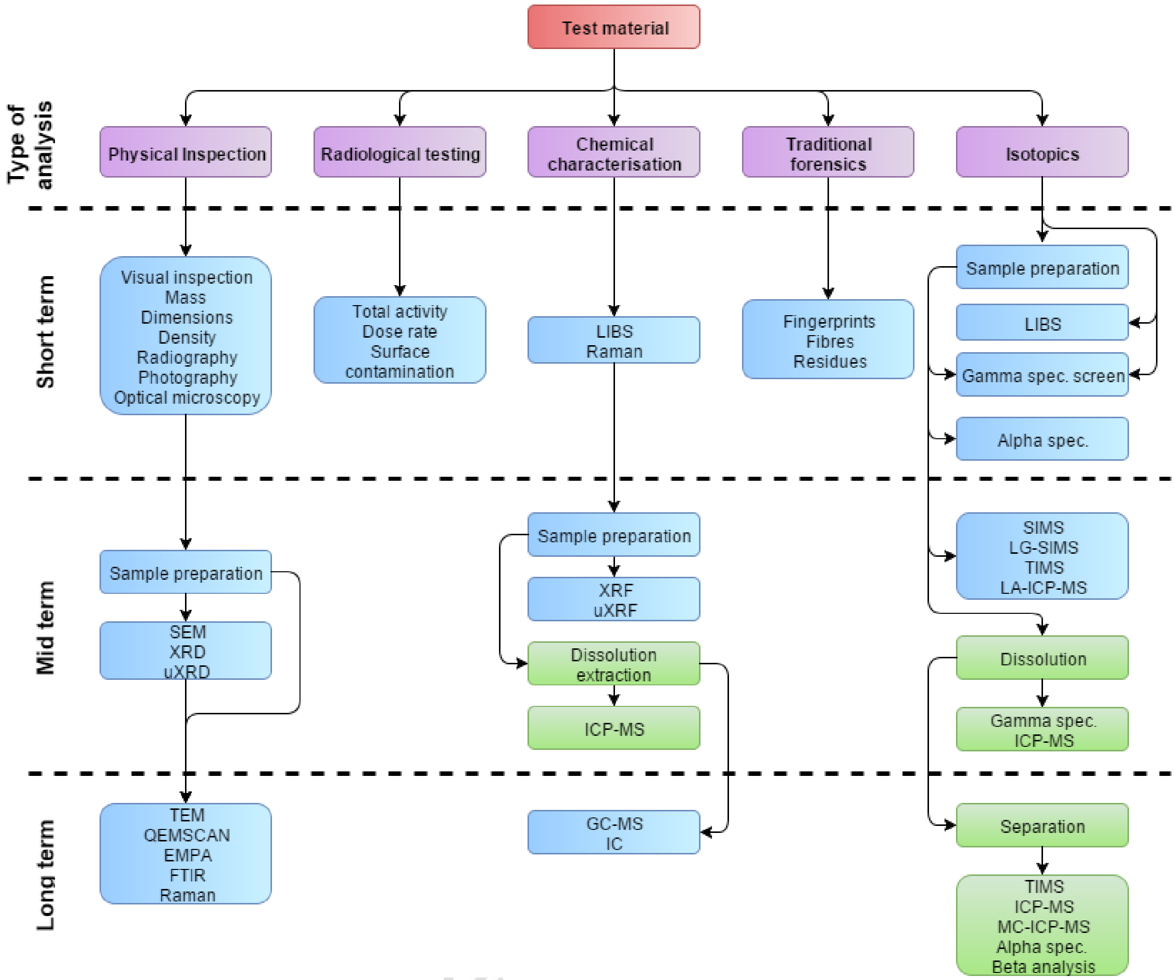

Figure 1: Summary of analytical sequences and methods used when investigating nuclear / radioactive suspect materials in the context of nuclear forensics or emergencies. Techniques shown in green coloured boxes are the focus of this paper. Adapted, and further developed, from Hutcheon et al 2013 and Mayer et al 2005 [16,17]

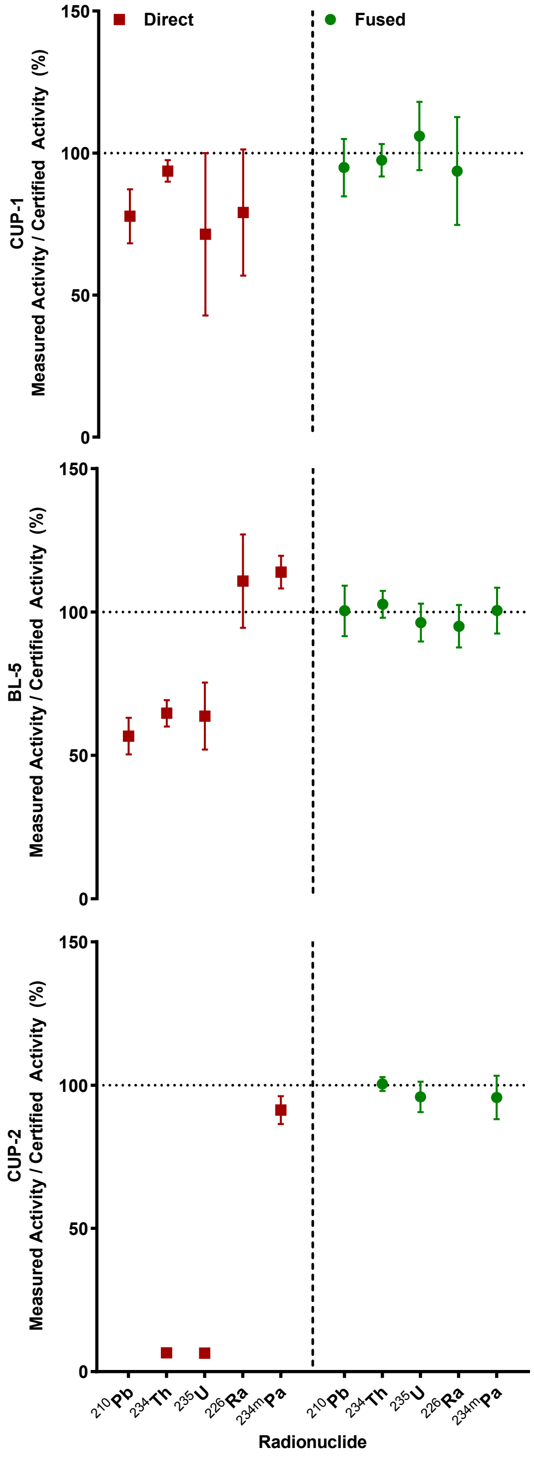

Figure2: Activity concentrations for natural uranium radionuclides of direct and fused reference materials using certified activities. Missing data are due to activity concentrations being below LOD. Uncertainty = 2σ. Adapted from Reading et al. 2015 [33].

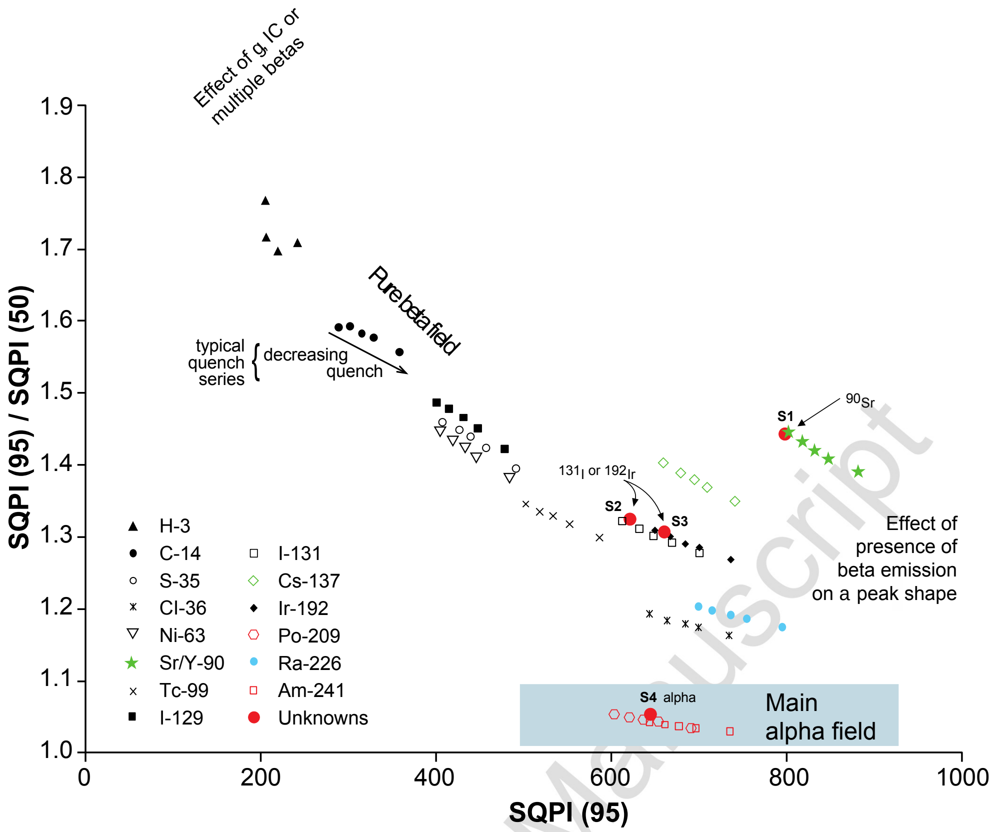

Figure 3: Identification of radionuclides using a peak shape factor (SQPI(95)/SQPI(50)). S1 – S4 represents test samples spiked with an unknown radionuclide that are superimposed on standards data. The radionuclide present in each sample was identified by its position on the plot along with data from the combined internal / external quench ratio. Reproduced with permission from Warwick et al, 2013 [8], Copyright 2013, American Chemical Society.

Table 1: Sample digestion methods available for suspect materials.

Digestion method	**Problems / comments**	**Silicates**	**Oxides**	**Sulphates**	**Carbonates**	**Borates**	**Phosphates**	**Metals ***	**References**
Borate fusion +/- acid digestion	Flexible method with no problems. Effectively digests all materials and is ideal for many elemental and isotopic analysis purposes. High purity lithium borate fluxes used to ensure low analytical blanks. Sample size can vary from 0.1-10 g. Sample:flux ratios from 1:1 upward. Pt-Au crucibles used which are easily cleaned. Typical fusion temperature < 1000-1200 °C.. Possible volatility issues with: Cs, Tc, Ru, I, Hg, Pb Po & Tl.	X	X	X	X			X	[20]
Flux free fusion +/- acid digestion	Small sample volumes treatable. Conducted in inert Ar atmosphere. Typical fusion temperature > 1300 °C. May require addition of SiO_2 and MgO if silicate poor to help glass formation. Possible volatility issues with Cs, Hg, Pb & Tl.	X	X	X	X			X	[21]
HCl, HNO_3	Microwave digestion, heating in PTFE or PFA pressure vessels may be effective. Full recovery of analytes potentially low. Oxidation of sample may be required to prevent volatilisation. Difficult to achieve full dissolution Possible volatility issues with: As, Ge, Po, S, Sb, Se, Tc.				X	X		X	[22]
HF / $HClO_4$ Acid mix	Only small sample masses readily treatable. HF needs to be removed prior to analysis. Insoluble fluoride precipitates in large sample volumes. Perchlorates potentially explosive. Frequently requires the use of HCl and/or HNO_3. Possible volatility issues with: As, B, Ge, Po, Sb, Tc.	X	X		X	X	X	X	[23]
HF / H_2SO_4 Acid mix	Small sample volumes treatable. HF needs to be removed prior to analysis. Many evaporation stages.							X	[22]
Alkali fluoride with pyrosulfate	Hazardous as HF produced; requires treatment with pyrosulfate to remove fluorides. Will attack Pt hardware.	X			X				[24]
$NaCO_3$ fusion	Opens out mineral lattices but requires lengthy treatment. Dissolution of Pt hardware possible. Elevated Pb or Fe(II) will alloy with Pt hardware. Possible volatility issues with: As, Hg, Po, Tc, Tl, Se.	X			X	X		X	[25]
NaOH fusion	Opens out mineral lattices but requires lengthy post fusion treatment. Dissolution of Pt hardware possible.	X			X			X	[26]
Na_2O_2 fusion or sinter with acid digestion	Attack of Pt hardware possible. Typical fusion temperature of 250-500 °C. Small sample volumes treatable. Time intensive procedure to dissolve the alkaline fusion cake. Possible volatility issues with Au & Ru.	X						X	[27]

*Use of oxidants or nitric acid digestion may be required.

Table 2: Summary of key features of ICP-MS and alternative mass spectrometric techniques

Instrument stage	Strengths	Potential problems
ICP-MS sample introduction		
Solution nebulisation	• Straightforward and potential for low sample uptake rates	• Higher oxide and hydride formation rates, and lower introduction efficiencies compared to other techniques
Desolvating sample introduction	• Reduced hydride and oxide formation • High introduction efficiency • Low sample uptake	• Long washout times • High cost compared to solution nebulisation
Laser ablation	• No sample preparation prior to introduction • Low oxide and hydride formation compared to solution nebulisation	• Lower sensitivity than solution nebulisation • Heterogeneous sample leads to inaccurate measurement
Cold plasma	• Rapid compared to offline chemical separation	• Increased vulnerability to matrix effects, necessitating chemical separation prior to measurement
Glow discharge	• High sample introduction efficiency	• Prior separation required for complex sample matrices
Capillary electrophoresis	• Reduced sample preparation	
Electro thermal vaporisation		
ICP-MS instrument design		
Quadrupole	• Robust • Straightforward preparation	• Lack of instrument-based separation • Inferior instrument detection limit
Collision cell (Thermo iCap-Q)	• Polyatomic interference removal	• No isobaric interference removal • Higher LOD than ICP-SFMS
Dynamic Reaction Cell (Perkin Elmer NexION)	• Isobaric interference removal	• Potential for polyatomic interference formation in the cell • Higher LOD than ICP-SFMS
Triple quadrupole (MS/MS) (Agilent 8800)	• Improved cell chemistry control • High abundance sensitivity	• Lower instrumental sensitivity and instrument LOD than ICP-SFMS
Sector field (single detector) (Thermo Element 2, 2XR) (Nu Attom) (Spectro MS)	• High instrument sensitivity • Low detection limits	• Extensive chemical separation required prior to sample introduction
Sector field (multi-collector) (Thermo Neptune plus) (Nu Plasma II)	• High accuracy isotope ratio measurements	• Extensive chemical separation required prior to sample introduction
Alternative measurement techniques		
TIMS	• Widely applied to radionuclide measurement, particularly precise isotope ratio measurements	• ICP-MS now more widely applied due to its high ionisation efficiency • Longer sample preparation
RIMS and AMS	• High sensitivity	• Time consuming sample preparation • Lack of commercial instrument availability • High instrument cost

BOX 1: Adapted from ***Nuclear Forensics: A capability at risk*** [15].

Likely expanded growth of nuclear technologies and subsequent illegal access to materials (e.g. through conflicts) adds to the risk of unauthorised activities and demands a sustained support for nuclear security infrastructure and nuclear forensics as summarized below.

The status quo in 2010

Organization in the NF field is insufficiently focused and inhibits development of a strategic consensus

Sustainability – in many countries NF capabilities developed in Government laboratories based on nuclear weapons programs that are in a state of decline.

Workforce skills and Infrastructure are in decline and key facilities are old and are not up to modern standards.

Procedures and Tools – many current NF techniques were developed to carry out Cold War missions and do not reflect current technical capabilities.

Recommendations

1. Streamline organizational structures, align authority and responsibility, develop and issue documents.
2. Issue coordinated and integrated implementation plans to improve national NF program capabilities.
3. Build and maintain effective NF workforces at national laboratories and through collaborations with universities and other organizations.
4. Adapt NF to the challenges of real emergency situations, including, for example, conducting more realistic exercises that are unannounced and that challenge regulations and procedures followed in the normal work environment, and implementing lessons learned.
5. National laboratories should optimize procedures and equipment through R&D to meet program requirements. Modelling and simulation should play an increased role in research, development, and planning.
6. The NF community should develop standards and procedures that are rooted in the same underlying principles that guide modern forensic science.
7. Homeland Security agencies should devise and implement plans that enable access to relevant information in databases including classified and proprietary databases—for NF missions.
8. Establish international sharing of information and best practice, subject to safeguards.

BOX 2: Borate fusion

Tools: *Pt-Au crucibles are most frequently used and although initially expensive they are very long-lived and can be used to process several hundred samples before requiring refurbishment or re-manufacture. Graphite crucibles are less costly and can be used effectively for 20 or more fusions.*

Heating: *Electrical furnace or gas burner systems (e.g. propane-oxygen) are used to heat fusion mixtures to approximately 1000 C.*

Borates*: For reasons of chemical purity lithium metaborate and lithium tetraborate are most commonly used. Originally developed for the XRF market these are now also widely applied to ICP-OES or ICP-M.*

Sample: flux: *Mixtures used can vary from 1:2 upward and generally produce a homogeneous melt/glass.*

Effectiveness: *Borate fusions will dissolve virtually any sample within 5-10 minutes. Otherwise intractable minor or accessory minerals are readily rendered soluble following a borate fusion. The majority of chemical elements are retained during the fusion procedure except some volatile elements. The melt can be cast onto a Pt-Au plate to produce a homogeneous glass or it can be cast into water or dilute acid and dissolved within 1-2 hours using stirring or ultrasonic disaggregation.*

Manufacturer of fusion device	**Models**	**Heating method and no. of samples processed per batch**		**Acid digestion capability**
		Gas	**Electric**	
Claisse Canada	LeNeo, TheOx Eagon 2,M4	1-6	1-6	Yes
Breitlander Germany	Autofluxer 2 Autofluxer 4	2 4	na	Yes
Equilab	**Fi** induction heating **F2** induction heating	na	1-2	Yes
Fluxana Germany	Vulcan (XRF/ICP/AES)	1-6	1-6	Yes
Herzog Germany	HAG-M-HF Induction heating	na	1	No
Inititiative Scientific Australia	Beadmaster-4 QP PF	na	1-4 2, 4, 6, 12 5, 10, 15	Yes
Spex Katanax Canada	K1 K2 X-300 ; X-600	na	1 1- 6 1-6	Yes
XRF Scientific Australia	Phoenix II xrFuse-2 xrFuse-6	1-6	1-6	Yes

na – not available as an option.