Determination of ^{222}Rn in fresh water: development of a robust method of analysis by alpha/beta separation liquid scintillation spectrometry

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Abstract

Liquid scintillation spectrometry is used widely for determining ^{222}Rn in natural waters; however, the benefits of α/β separation have not been fully explored. The extractants toluene and Ultima Gold F were compared, and both performed well for a range of extreme waters. A robust method for calibrating extraction and counting efficiencies has been developed. Detection limits are 20 mBq l^{-1} (toluene) and 16 mBq l^{-1} (UGF) for a 60 minute count and 600-ml sample, halving the required sample volume.

1. Introduction

Radon-222 is a naturally occurring, radioactive, noble gas, produced in rocks and soil from the decay of ^{238}U via ^{226}Ra. It can diffuse from mineral grains into pore spaces, and dissolve in any water occupying those pore spaces. As a result, most groundwater is enriched in ^{222}Rn, relative to surface water and, therefore, groundwater inputs to surface waters can be readily identified from their characteristic ^{222}Rn signatures. Consequently, ^{222}Rn has been widely employed as a tracer of ground water – surface water interactions (Ellins *et al.*, 1990; Hamada and Komae, 1998; Genereux *et al.*, 1993; Cook *et al.*, 2003).

^{222}Rn decays to a series of short-lived α- and β-emitting radionuclides.

Nuclide: ^{222}Rn (α) $\rightarrow$ ^{218}Po (α) $\rightarrow$ ^{214}Pb (β) $\rightarrow$ ^{214}Bi (β) $\rightarrow$ ^{214}Po (α) $\rightarrow$ ^{210}Pb (β)

Half-life: 3.82 days 3.11 min 26.8 min 19.9 min 1.6×10^{-4} sec 22.3 y

The four daughters to ^{214}Po equilibrate with ^{222}Rn within 4 hours. Therefore, most analytical techniques actually determine either all 5 radionuclides or the three α emitters.

The most popular techniques for the determination of ^{222}Rn in water are: (i) stripping radon from the sample by a carrier gas and analysis using a Lucas cell (emanation methods); and (ii) extracting radon into an organic solvent and counting by liquid scintillation spectrometry (LSS). Emanation methods are widely used in the study of low-level ^{222}Rn concentrations (*e.g.* in seawater and surface waters (Ellins *et al.*, 1990; Cable *et al.*, 1996; Hussain *et al.*, 1999; Elsinger and Moore, 1983; Colman and Armstrong, 1987), as lower backgrounds and less restricted sample sizes result in lower detection limits than LSS methods. Nonetheless, LSS methods are still frequently chosen because the methodology is simpler and sample throughput is greater with less analyst input.

The development of robust LSS analytical methods for ^{222}Rn determination in fresh water has frequently been driven by public health concerns, focussing on the analysis of drinking water

derived from groundwater sources, such as private wells. The regulatory limit for drinking water is relatively high (11 Bq l^{-1} for the most stringent controls in the U.S.A.) (Newton *et al.*, 2001). Therefore, the standard ASTM method for ^{222}Rn analysis in drinking water involves extracting 10 ml water into a scintillation cocktail and measurement by LSS (ASTM, 1998). This method has been studied in detail, and the extractant, instrumentation, vials and sampling methods have all been optimised (Prichard and Gesell, 1977; Kinner *et al.*, 1991; Vitz, 1991; Prichard *et al.*, 1992; Spaulding and Noakes, 1993; Zouridakis *et al.*, 2002; Escobar *et al.*, 1996).

In comparison with groundwaters, ^{222}Rn concentrations in surface waters are low, and hydrological studies require greater precision than monitoring applications. Therefore, for hydrological surveys it is necessary to analyse larger volumes and / or improve the sensitivity of the technique. Most methods are based on that of Horiuchi and Murakami (1981) in which a toluene-based cocktail is used to extract radon from 1 litre water. The best detection limits have been achieved by extracting a 1 litre sample twice, resulting in a detection limit of 0.02 Bq l^{-1} (Hoehn and von Gunten, 1989).

Since the first development of this technique, there have been two major advances in the field of liquid scintillation. Firstly, many modern LS spectrometers utilize pulse shape discrimination (PSD) to separate α and β events into different multi-channel analyzers (MCAs). Secondly, a new generation of LS cocktails has been developed; these utilize different solvents than traditional cocktails, and are deemed environmentally "safe". Some of these new cocktails have been formulated to optimize counter performance when using PSD. These developments have the potential to improve detection limits for ^{222}Rn analysis, but to date have only been applied in piecemeal fashion.

Alpha / beta separation can reduce the detection limits for ^{222}Rn, as the majority of the background falls into the β window. A number of authors have examined the benefits of α/β separation to ^{222}Rn

analysis, however most of the detailed studies have focused on the small volume method (Prichard *et al.*, 1992; Spaulding and Noakes, 1993; Escobar *et al.*, 1996). It is necessary to optimize the α/β separation by adjusting the PSD setting until the misclassification of events is minimized, using a pure α and β emitters. Pates *et al.* (1998) demonstrated that it is essential to use the same radionuclide for standardization as is being analyzed, as the energy distribution of the spectrum can affect the optimum PSD setting. However, ^{222}Rn daughters rapidly grow in following separation, making it impossible to use a pure ^{222}Rn standard solution.

To overcome this problem, Spaulding and Noakes (1993) showed that ^{222}Rn standards in equilibrium with their daughters could be used to optimize the α/β separation. Theoretically, at the optimum PSD setting the ratio between the count rates in the α and β MCAs should be 3α:2β, and the counting efficiency in the α MCA reaches a plateau. This approach has been adopted generally in small volume methods, whereby the PSD function is optimized by adding a ^{226}Ra tracer to a vial containing 10 ml water and 10 ml cocktail, and after a month of ingrowth proceeding with the normal extraction (Prichard *et al.*, 1992; Spaulding and Noakes, 1993; Escobar *et al.*, 1996). Studies using the large volume method have also employed α/β separation to improve performance,(Cook *et al.*, 2003; Freyer *et al.*, 1997; Bem *et al.*, 1994) but only two have discussed instrument calibration and both used "generic" α and β emitters.(Freyer *et al.*, 1997; Bem *et al.*, 1994) Therefore, the first problem that needs to be resolved is to find a more robust method for optimizing α/β separation for the large volume method.

Efficient α/β separation is highly dependent on using an appropriate cocktail, with the correct combination of solvent and fluors.(Pates *et al.*, 1993) Although it has been shown that the new generation of cocktail solvents (*e.g.* di-isopropylnaphthalene (DIN), phenyl-ortho-xylylethane (PXE), linear alkylbenzenes (LAB)) are suitable for Rn extraction,(Kinner *et al.*, 1991; Prichard *et al.*, 1992; Spaulding and Noakes, 1993; Zouridakis *et al.*, 2002) there has been a general reluctance

to move towards cocktails designed for α/β separation in Rn analysis. Large volume methods still favour mineral oil and toluene-based cocktails, often using in-house formulations.(Hamada and Komae, 1998; Cook *et al.*, 2003; Freyer *et al.*, 1997) One study used pure toluene to extract Rn and then mixed it with Ultima Gold modified by the addition of naphthalene to improve PSD performance.(Bem *et al.*, 1994) However, Ultima Gold, while a modern cocktail, does not have particularly good α/β separation performance on its own.(Pates *et al.*, 1993) So the next problem is to investigate whether using a cocktail designed for α/β separation can improve detection limits for [222]Rn analysis. Ultima Gold LLT and Ultima Gold F (Perkin Elmer Life Sciences) are DIN-based cocktails formulated with efficient α/β separation in mind (manufacturer's literature) and, thus, are good candidates for further investigation. Ultima Gold F is water-immiscible and could potentially replace more hazardous toluene-based cocktails for Rn extraction.

Finally, the determination of extraction efficiency has not been discussed in the literature for large volume methods. Calibration of the small volume method is relatively straightforward, as extraction and counting are carried out in the same vial. For the large volume method, there are more problems. A solution of known [222]Rn concentration is needed, which can be obtained by equilibrating a [226]Ra solution over a period of approximately 1 month in the sample container. However, although sample containers can be readily found that are gas-tight for the sampling conditions (*i.e.* extractant added soon after sampling), no-one has demonstrated the same is true for longer periods. Additionally, the extractant cannot be added to the standard solution during the equilibration period, as Rn has been shown to diffuse readily into organic solvents.(Escobar *et al.*, 1996) Therefore, the final aspect to be addressed is how to ensure that the standard extraction efficiency is representative of that achieved during sample analysis.

In this work, we examine the potential for α/β separation LSS combined with specially designed cocktails to lower detection limits for [222]Rn. Furthermore, we have addressed some of the

problematic issues of method calibration that do not arise for small volume ^{222}Rn analysis methods, and propose a robust method for the routine determination ^{222}Rn analysis of fresh waters.

2. Experimental

2.1 Apparatus

All samples were counted by LSS, using a Packard Tri-Carb 3170 TR/SL, which uses PSD for α/β separation. Additionally, background is reduced by the presence of a quasi-active guard of bismuth germanate (BGO), which surrounds the counting chamber. Gamma counting was performed on an EG&G Ortec n-type high-purity germanium (HPGe) detector. Samples were held in a reproducible position in relation to the detector by means of a sample holder.

2.2 Reagents

2.2.1 Liquid scintillation vials

In all instances, vials were 20 ml low-potassium glass vials with aluminium foil lined caps (Perkin Elmer). In other LS applications, plastic vials are often preferred for their lower background characteristics and better energy resolution; however, vials used in ^{222}Rn analysis have to be gas-tight. The properties of Teflon-lined plastic vials have been studied; Salonen (1993) found that of all the vials tested, only glass vials were gas tight, whereas Escobar *et al.* (1996) found that Teflon-lined plastic vials were resistant to leaking. Nonetheless, no great advantage in terms of detection limits has been demonstrated for the plastic vials.(Escobar *et al.*, 1996) Therefore, we decided to use glass vials here, as they appear more reliable in this aspect.

2.2.2 Cocktails

All cocktails are supplied by Perkin Elmer. The cocktails used in this work are Ultima Gold LLT (UGLLT) and Ultima Gold F (UGF). The two cocktails employ the same solvent (DIN) and fluors, but UGF contains no surfactants and is immiscible with water. Pure toluene (reagent grade) was

used as an extractant in this work, and prior to counting it was mixed with UGLLT, following the system of Bem *et al.* (1994) This approach was used in preference to adding fluors directly to the toluene,(Horiuchi and Murakame, 1981) because the fluors in UGLLT have been optimised for α/β separation.

2.2.3 Tracer solutions

Throughout this work, a [226]Ra tracer solution was used to create standards. The specific activity of the tracer was 238.3 ± 5.4 Bq g^{-1} in 0.1 M HNO$_3$. Either 100 μl (~ 20 Bq) or 50 μl (~ 10 Bq) was dispensed gravimetrically for each standard.

2.2.4 Glass bottles

The bottles used throughout for [222]Rn extractions are borosilicate glass bottles, with a nominal capacity of 500 ml. The actual capacity is approximately 610 ml. The cap is made of high-density polypropylene. These bottles were chosen in preference to the narrow-necked bottles with ground glass stoppers favoured in other studies,(Freyer *et al.*, 1997) as field areas are frequently remote, and delicate glassware can be broken easily.

2.3 Calibration of instrumentation: γ-spectrometer

It is not necessary to determine the absolute counting efficiency and absolute extraction efficiency for routine applications. However, for method development, we wanted to examine the effect of the different extractants on counting and extraction efficiencies separately. For LS calibration, samples containing [222]Rn but not [226]Ra can be achieved by solvent extraction. However, the extraction procedure is not quantitative. Therefore, γ-spectrometry was used to determine independently the activity of [222]Rn in the LS vials.

To determine the detection efficiency of the γ-spectrometer, three vials containing 15 ml toluene + 5 ml UGLLT and three vials containing 20 ml UGF were spiked with a known activity of ^{226}Ra (~ 20 Bq per vial). The vials were left to equilibrate for at least 1 month, then analysed by γ-spectrometry for approximately 60 minutes each. Rather than determining the absolute γ detection efficiency for each photopeak, an overall counting efficiency was determined by summing the counts in three of the photopeaks for ^{222}Rn daughters, namely ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV) and comparing this count rate to the added activity.

2.4 Calibration of instrumentation: LS spectrometer

In simple terms, PSD separates α and β events by timing the electronic pulses generated by each radioactive decay in the scintillation vial. The longer the pulse the more likely it is to have been caused by an α event.(Pates *et al.*, 1993) The optimum separation between α and β events can be found by varying a time-gate parameter, called the pulse decay discriminator (PDD). Events longer than the PDD are classified as α events and shorter events are classified as β events.

PSD has the major advantage for ^{222}Rn analysis of substantially reducing the background. Typical open window (0-2000 keV) backgrounds for this instrument without PSD are ~ 20 cpm. With PSD, the background is reduced to ~ 2.5 cpm for the α MCA, and by optimising the counting window, it can be reduced still further. As this background reduction is achieved with limited effects on counting efficiency, the detection limit is significantly reduced.

The approach of Spaulding and Noakes (1993) has been adapted here for the large volume method. ^{226}Ra standard solutions were made up by filling 500 ml glass bottles to the brim with de-ionised (DI) water. Either 25 or 35 ml water was removed from the bottle, depending on which extractant was to be used. A known activity of ^{226}Ra tracer solution (~ 20 Bq per bottle) was dispensed into

each bottle. The extractant (either 20 ml toluene or 30 ml UGF) was added to the bottle, which was tightly capped and left to equilibrate for at least 30 days. Each standard was made up in triplicate.

After 30 days, the bottles were shaken thoroughly for 1 minute each by hand, ensuring that the extractant was well dispersed throughout the water. The bottles were then left for approximately 2 hours for the layers to separate. Vials were prepared for counting by removing either 10 ml toluene or 20 ml UGF from each bottle. The extractant was transferred carefully to a scintillation vial containing 10 ml UGLLT, and the vials were shaken thoroughly. Background vials were made up containing either 10 ml toluene + 10 ml UGLLT or 20 ml UGF. This procedure was used to prepare sample and background vials for all the experiments that follow, unless stated otherwise.

After allowing the ^{222}Rn daughters to equilibrate for at least 4 hours, the vials (standards and backgrounds) were counted by γ spectrometry, for 60 minutes each, to determine the absolute ^{222}Rn activity in each. They were then counted by LSS, over a range of PDDs, to ascertain the optimum setting. The count time was 10 minutes per sample at each setting. Once the optimum PDD was known, the LSS counting efficiency was determined for that setting.

2.5 Extraction efficiency: theoretical

The radon partition coefficient between water and toluene is 50 at room temperature, (Prichard and Gesell, 1977) and for Opti-Fluor O it is 48.(Zouridakis *et al.*, 2002) Opti-Fluor O is an LAB-based cocktail, whereas Ultima Gold F is a DIN-based cocktail. There are no radon partition data available for this solvent, but it is assumed to behave similarly to toluene and LAB. Assuming partition coefficients of 1:50:4 for water:toluene:air and 1:48:4 for water:DIN:air, the effects of sample volume, air volume, extractant volume, and the impact of repeated extractions were investigated.

2.6 Extraction efficiency: experimental

The challenge here was to design a system whereby a solution of known ^{222}Rn activity could be subjected to an extraction under the same conditions as environmental samples. The simplest method to obtain a ^{222}Rn solution of known activity is to seal a ^{226}Ra solution in the sampling bottles and leave it for approximately 1 month to reach radioactive equilibrium. Rn is known to diffuse readily into organic solvents,(Escobar *et al.*, 1996) therefore the extractant cannot be added at the beginning of the equilibration period. Consequently, there is enhanced potential for the ^{222}Rn to diffuse out of the bottles. Therefore, it was necessary to determine the ^{222}Rn concentration in the water prior to extraction to check for losses.

^{226}Ra standard solutions were made up by filling 500 ml glass bottles to the brim with DI water and 5ml removed. A known amount of ^{226}Ra tracer solution (~ 20 Bq per bottle) was dispensed into each bottle, which was tightly capped and left to equilibrate for at least 30 days.

The ^{222}Rn activity was determined using the ASTM method,(ASTM, 1998) in duplicate or triplicate; 10 ml water was carefully transferred from each bottle into a vial containing 10 ml UGF using a glass bulb pipette. One background was made up for every 4 samples, consisting of 10 ml DI water and 10 ml UGF. Standards were made up in the same way as background vials, except that ~ 20 Bq ^{226}Ra tracer solution was also added, and the vials were left to equilibrate for 30 days. All the vials were shaken, and counted at the optimum PDD after equilibrating for 4 hours in the counter.

Either 20 ml toluene or 30 ml UGF was added to the ^{226}Ra standard solutions, which were then capped and shaken for different times as follows: (i) 1 minute by hand; (ii) 5 minutes by hand; (iii) the extractant was dispersed by hand, then placed in an end-over-end shaker for 10 minutes; (iv) the extractant was dispersed by hand, then placed in an end-over-end shaker for 20 minutes. Each

shaking time was tested in triplicate. Vials were prepared for counting as described above. After equilibrating for 4 hours, the vials were counted by LSS, and the extraction efficiency determined.

The reproducibility of the toluene extractions using 20 minutes shaking in an end-over-end shaker was evaluated by repeating this experiment on 5 separate occasions over a period of 6 months. On each occasion, the batch of standards ranged in number between 3 and 9, with 24 ^{226}Ra standards being analysed in total.

2.7 Extraction of radium and sample stability

The ^{222}Rn standards from the above experiments were counted regularly, at the optimum PDD, for 30 days following their extraction (a total of 15 toluene standards, 15 UGF standards and 5 backgrounds for each extractant). Both the count rate and the tSIE were assessed for stability. The tSIE is the transformed Spectral Index of the External standard, and is a measure of quenching (see below). Variations in the tSIE indicate that the sample is unstable over the counting period, due to evaporation or degradation of the cocktail, for example.

The count rate should decay according to the half-life of ^{222}Rn ($t_{1/2} = 3.82$ days). Deviations from this line could be caused by two factors. ^{226}Ra extracted alongside ^{222}Rn will cause the apparent decay constant to be too low. Alternatively, if the vials leak ^{222}Rn over the counting period, decay will appear to be too rapid, and the apparent decay constant will be too high. It is possible that both of these effects will occur, negating each other. However, the presence of ^{226}Ra in the vial will be detected as an enhanced background once all the unsupported ^{222}Rn has decayed away (*i.e.* after > 10 half-lives).

2.8 Quenching

The presence of impurities in an LS sample can result in quenching, *i.e.* a reduction in the counting efficiency. Traditional LS applications, such as the determination of ^{14}C in biological samples, have overcome this problem by generating quench correction curves. However, with the advent of modern LS spectrometers, quench correction is problematic and needs to be applied with care.(Pates *et al.*, 1998) The best solution is that samples and standards should all be quenched to the same degree (*i.e.* have the same tSIE). The solvent extraction approach to LS sample preparation is generally less prone to variable quenching problems than samples prepared using water miscible cocktails and aqueous samples. However, the highly variable nature of natural waters means that this effect needs to be investigated.

Three water samples were chosen to provide a range of water types, including extreme end-members. Dissolved organic matter and dissolved ions were evaluated by measuring the absorbance at 340 nm and the conductivity respectively. For each water type, triplicate samples were prepared for each extractant (bottles were filled to the brim, then either 25 ml or 35 ml removed, for toluene and UGF extractions respectively). Either 20 ml toluene or 30 ml UGF was added to the water samples which were then spiked with a known activity of ^{226}Ra (~ 10 Bq), and capped. The samples were left to equilibrate for 30 days, after which they were shaken for 20 minutes in an end-over-end shaker, after initial dispersion of the solvent by hand. The samples were then treated as detailed above.

2.9 Field evaluation

The reliability of the method was tested under field conditions. These experiments focussed on the toluene extractant, as it had proved the more robust to quenching (see below). A series of experiments were carried out using water pumped from a borehole located on the Sherwood Sandstone aquifer in Shropshire, U.K. These experiments aimed to evaluate the accuracy of the

method, by comparing it with another well-established method, and to assess points in the analysis vulnerable to ^{222}Rn loss from the samples.

In each experiment, a large container was filled with approximately 50 litres water. Samples were collected either by gently submerging the 500 ml glass bottle and capping it under water or by drawing 10 ml water into a gas-tight syringe. The small volume samples were then injected directly into a pre-weighed vial containing 10ml UGF, following the ASTM method.(ASTM, 1998) The vials were re-weighed prior to counting to determine the exact volume of water analysed. In all cases, to avoid bias due to loss of ^{222}Rn from the bulk sample during sub-sampling, samples were allocated to treatment groups sequentially.

Several studies advocate adding the extractant to the sample container prior to sampling, in order to minimise losses during transit and processing.(Hoehn and von Gunten, 1989; Freyer *et al.*, 1997) However, toluene in particular is a hazardous chemical, and the potential for bottle breakage in the field is high. With this in mind, we wanted to determine if significant radon losses occurred either during transit or when processing the samples on return to the laboratory.

The first experiment was designed to detect losses of ^{222}Rn from the samples during transit. Batches of 8 samples were extracted with delays of 22, 27, 44 and 49 hours from time of sampling. The second experiment was to assess the effect of removing the bottle caps to add toluene. Batches of 5 samples were treated as follows: Group 1 were treated individually, minimising the time the caps were off the bottles; Group 2 were treated as a batch; Group 3 were left to stand with the caps off for 10 mins in the fume hood before toluene was added; and Group 4 were left to stand with the caps off for 30 mins in a fume hood before toluene was added.

This experiment was repeated with Groups 1 and 2 being treated in the same manner as above, but Groups 3 and 4 were treated differently. Group 3 were processed as a batch, but following shaking and separation of the toluene, the caps were removed from the bottles, which were left to stand in the fume cupboard for 10 min before the aliquot was removed for analysis. Group 4 were treated in the same way, but the bottles were left to stand for 20 min.

Finally, the large volume method developed here was compared with the small volume ASTM method.(ASTM, 1998) Samples were collected alternately using the small and large volume techniques in the following sequence: 5 small, 4 large, 5 small, etc. until 25 small volume and 20 large volume samples were collected.

3. Results and discussion

3.1 Calibration of instrumentation: γ-spectrometer

The mean γ counting efficiency was 2.221 ± 0.047 %. There was no significant difference between the vials containing toluene and UGLLT and those containing UGF.

3.2 Calibration of instrumentation: LS spectrometer

After extraction, the LS vials were counted by γ spectrometry. Given the counting efficiencies quoted above, the ^{222}Rn activity in each vial was determined, and decay corrected to the time of extraction. The mean ^{222}Rn activities were 4.904 ± 0.027 Bq per vial for the toluene extraction, and 8.05 ± 0.61 Bq per vial for the UGF extraction. The uncertainties quoted are the standard deviations of triplicate samples. The exact ^{222}Rn activity in each vial was used for subsequent calculations.

The vials were then counted by LSS over a range of PDD settings from 90 to 230. The α window was determined by visual examination of the LS spectrum (Fig. 1), and was chosen to include the entire α "peak". Although there are 3 α emitters in each sample, with distinct energies, LSS does

not have sufficient energy resolution to resolve each α emitter into a single peak. For the following discussion, the α region of interest (ROI) means the α window in the α MCA. The α window was 200 – 800 keV for the toluene samples and 400 – 1100 keV for the UGF samples. The different windows were the result of the UGF samples being less quenched than the toluene samples, as shown by tSIEs of approximately 855 and 590 respectively. Quenching causes the spectrum to be shifted to lower energy. Unfortunately, this instrument automatically assigns events with energies > 1000 keV to the β MCA. Without this cutoff, the α counting efficiencies for the UGF samples would have been higher, and detection limits lower.

For each setting, the percentage of counts recorded in the α ROI as a function of the total recorded counts was calculated (% alpha) and the background for the α ROI was determined. Based on these parameters, the optimum PDD was found to be 180 and 160 for UGF and toluene respectively (Fig. 2). The background data show relatively high uncertainties, as a result of the short count times used. Real samples would be counted for longer and the uncertainties would be lower. Repeated counts showed the background to be 0.96 ± 0.30 cpm for toluene, and 0.98 ± 0.17 cpm for UGF. Counting efficiencies were determined using:

$$E_\alpha = \frac{C_\alpha}{A_{Rn}} \qquad\qquad (1)$$

where E_α is the counting efficiency for the α ROI, C_α is the count rate in the α ROI (in cpm) and A_{Rn} is the activity of ^{222}Rn in the vial as determined by γ spectrometry (in dpm). The counting efficiencies were found to be 262 ± 11 % and 294 ± 11 % for UGF and toluene respectively, at their optimum PDDs. The toluene counting efficiency reflects the approximately 100% detection of ^{222}Rn and its two α-emitting daughters. The counting efficiency for UGF is lower than would be expected, due to the automatic rejection of all events with energies > 1000 keV, as discussed above.

3.3 Extraction efficiency: theoretical

Although the presence of air in the bottle reduces transfer of radon to the solvent slightly, it is not a pronounced effect (Fig. 3(a)). More important is the volume of solvent used for extraction, and the proportion of this solvent subsequently counted. The presence of air in the extraction bottle is an important variable as: (i) it is not always possible to exclude all air when sampling; and (ii) having a bottle filled to the brim inevitably leads to loss of extractant and / or water when the bottle is re-capped. Therefore, the protocol adopted for all experiments here was to fill bottles to the brim, and then remove the extractant volume plus 5 ml. A 5 ml air volume does not significantly reduce the extraction efficiency, but may aid reproducibility in other ways.

Some authors advocate doing two extractions, removing a portion of the solvent between extractions.(Hoehn and von Gunten, 1989; Freyer *et al.*, 1997) The benefits of doing this are not pronounced and add considerably to the time taken for analysis (Fig. 3(b)). A greater proportion of the ^{222}Rn in the sample can be analysed simply by increasing the proportion of the extractant analysed. Therefore, only single extractions were investigated experimentally. The UGF extraction has the advantage that no additional cocktail needs to be added prior to counting, and, hence, a greater proportion of the extractant can be analysed.

The effect of varying the sample volume was investigated using a detection limit parameter. The detection limit is a function of the reciprocal of the proportion of radon counted multiplied by the sample volume. Increasing the sample volume up to 500 ml resulted in significant improvement in the "detection limit" (Fig. 3(c)). Beyond that volume, however, gains were small. Overall, it was deemed that 500 ml samples gave the best compromise between detection limits and practicality; larger samples are harder to transport in remote field areas and are more likely to be broken during analysis. Indeed, given the short half-life of ^{222}Rn, the delay between sampling and analysis is likely to have a greater impact than sample volume on minimum detectable activity, for samples > 500 ml.

3.4 Extraction efficiency: experimental

The experimental extraction efficiencies are given in Table 1. Two values are presented for each condition; the % Rn counted is the proportion of ^{222}Rn in the counting vial compared to the sample, whereas % Rn extracted is the proportion in the total volume of extractant used. For both toluene and UGF, 5 minutes shaking by hand produced a similar level of extraction to 20 minutes using the end-over-end shaker. These shaking conditions result in a greater level of extraction than 1 minute shaking by hand, or 10 minutes in the end-over-end shaker, although the 10 minute shaking time is not statistically different for toluene.

Although shaking for 5 minutes by hand gives a slightly greater extraction than using the end-over-end shaker for UGF, overall it is preferable to use the mechanical extraction procedure for both solvents. If large numbers of samples are being analysed, a much greater input of time is required from the analyst if shaking by hand is used. Shaking by hand does not produce sufficiently better results to be justified.

The calculated extraction efficiencies are also presented in Table 1, assuming the same conditions as in the experiment. In both cases, the experimentally derived extraction efficiencies were close to the theoretical values. There are few values for extraction efficiencies in the literature, but they range between 16 and 36% for 1-litre samples, using a range of extractants (mineral oil, DIN and toluene-based cocktails).(Cook *et al.*, 2003; Hoehn and von Gunten, 1989; Purkl and Eisenhauer, 2004) In two cases,(Cook *et al.*, 2003; Hoehn and von Gunten, 1989) an extraction efficiency is not quoted, but can be determined assuming a counting efficiency of 300%. Although this assumption may not be strictly valid, the true counting efficiency is not likely to be greatly different. The current data set fits comfortably in this range.

The data from the 10ml aliquots of water show that the bottles are not 100% Rn proof under these conditions, namely storage for 30 days without an extractant layer. Nonetheless, the bottles showed excellent reproducibility. Of the 24 bottles involved in the experiment, only 4 were greatly different and had experienced greater than expected Rn loss. Data from these bottles was not used in subsequent data analysis. Of the remaining 20 bottles, the mean Rn activity was 75.2 ± 4.1 % of that expected at radioactive equilibrium.

Repeated evaluation of the preferred extraction conditions (20 minutes in an end-over-end shaker) by different analysts over a 6-month period showed that the extraction process was extremely reproducible. The mean extraction efficiencies varied between 25.7 ± 0.3% and 26.9 ± 1.3%. The mean and standard deviation of all 24 standards was 26.1 ± 1.1%, which represents less than 5% uncertainty in the extraction efficiency.

3.5 Extraction of radium and sample stability

The total net count rate (C_1) (*i.e.* $\alpha + \beta$ count rate less their respective backgrounds) from the first count of each vial was decay corrected to the extraction time (C_0). The total net count rate for each subsequent count (C_t) was normalised to C_0, using:

$$N = \frac{C_t}{C_0} \qquad (2)$$

The decay of a radionuclide can be expressed as:

$$A_t = A_0 e^{-\lambda t} \qquad (3)$$

where A_0 is the initial activity (time = 0), A_t is the activity at time = t, λ is the decay constant and t is time. Rearranging gives:

$$\ln\left(\frac{A_t}{A_0}\right) = -\lambda t \qquad (4)$$

ln(N) is equivalent to ln(A_t/A_0), and therefore a plot of ln(N) against time (Figs. 4(a) and (b)) should be a straight line with slope = -λ and intercept on the y-axis = 0.

A best fit line plotted through the data in Figures 4(a) and (b) gives values of λ of 0.181 d^{-1} and 0.180 d^{-1} respectively, both with R^2 values of 0.999. Both these values are in excellent agreement with the accepted literature value, 0.18129 d^{-1}.(Lederer and Shirley, 1978) There is no evidence of ^{222}Rn leaking from the vials over this period, which is supported by other studies using this type of vial.(Escobar *et al.*, 1996; Salonen, 1993)

The vials were counted again after 31 days had elapsed since extraction. The count rates were slightly above background (C_{31} = 3.96 ± 1.23 cpm and 8.65 ± 2.70 cpm for toluene and UGF respectively). This decay time represents approximately 8 half-lives since separation from ^{226}Ra and therefore only about 0.4% of the starting activity should remain. However, given the relatively high activities under consideration, even this minor residual activity makes a significant contribution to the count rate and was therefore further subtracted from the data quoted above. Thus, the total count rate that can be considered as being due to the presence of ^{226}Ra in the vials was 0.35 ± 1.07 cpm and 3.22 ± 2.86 cpm for toluene and UGF respectively.

Taking into account the detection efficiency and the total ^{226}Ra activities from which the ^{222}Rn standards were extracted, it was calculated that 0.006 ± 0.018 % and 0.050 ± 0.044 % of the total ^{226}Ra in the standards was extracted by toluene and UGF, respectively. As these data show, UGF was more variable than toluene in its co-extraction of ^{226}Ra, with up to 0.16 % of the total ^{226}Ra being extracted. On several occasions, it was noted that some water was present in the UGF vials, and the cocktail was much slower in separating from the water after shaking than toluene. Nonetheless, given that ^{226}Ra concentrations are typically from 10 – 1000 times lower than ^{222}Rn

concentrations in natural waters,(Asikainen and Kahlos, 1979; King *et al.*, 1982) even the maximum ^{226}Ra contamination found here is not significant.

Finally, the tSIE of the Rn standards was examined over the 20 days following extraction (Fig. 4c). Both sets of vials showed excellent stability. Indeed, the variation between the first and last counts was less than the variability between vials.

Overall, these data demonstrate that, over the 20 days following extraction of ^{222}Rn: (i) there is no Rn leakage from the vials; (ii) minimal ^{226}Ra is co-extracted from the water; and (iii) there is no significant change in the chemical composition of the cocktail. Thus, the system is sufficiently stable to count samples for at least 5 half-lives following sampling.

3.6 Quenching

The waters tested represent a wide range of composition of natural waters. Roudsey Wood is a stream water rich in dissolved organic matter. Windermere is a soft water, low in dissolved solids and organic matter. Although this method has not been designed for the analysis of seawater, a coastal seawater (Morecambe Bay) was analysed, being analogous to a high salinity groundwater. Both the toluene and UGF extractions performed well in general, with good reproducibility (Table 2).

The toluene extractions were not affected by quenching. In all instances, the tSIEs were close to that of the background samples, and the recoveries were all close to 100 %. The UGF extractions, however, were more sensitive. The recoveries for Roudsey Wood and Windermere samples were low (81 % and 80 % respectively). Furthermore, the tSIEs were low for Roudsey Wood samples, and high for Windermere samples. During the extraction of these samples, it was noted that the cocktail did not separate cleanly from the water and that it took on a slightly milky appearance.

On examination of the spectra, it was evident that the α peaks were shifted relative to the defined ROI. The Roudsey Wood samples were shifted to lower energies, whereas the Windermere samples were shifted to higher energies. In both cases, the net result was a lower proportion of the total counts falling in the α ROI, *i.e.* the counting efficiency was effectively reduced. Although UGF has been shown to be sensitive to quenching, the shift in the α ROI could be taken into account if this type of sample were to be analysed frequently.

3.7 Field evaluation

The results of the field evaluation experiments are summarised in Table 3. Experiment 1 examined differences in the ^{222}Rn activity in water samples processed at a range of times following sampling. There is no statistically significant difference between the groups, and it can be concluded that no ^{222}Rn is lost from the bottles during transit and storage.

The impact of delays between uncapping and re-capping the bottles during sample processing before toluene addition was examined in Experiment 2. Again, there is no statistically significant difference between the groups. These data show that even when the cap is removed for prolonged periods, in excess of times typically used during processing, no significant ^{222}Rn is lost from the water sample.

These experiments demonstrate that there is no analytical reason to add toluene to sample containers prior to sample collection. No significant ^{222}Rn losses occur either during transit or when container lids are removed for toluene addition.

The samples are much more vulnerable to ^{222}Rn loss once the extractant has been added and the samples shaken. Experiment 3 shows a loss of 75% of the ^{222}Rn in the samples after just 10 minutes

without lids; after 20 minutes only 5% of the ^{222}Rn remains. This experiment demonstrates that removing the lids from the sample bottles after shaking is the most critical point in the analysis. Nonetheless, if this step is performed quickly, there is no significant loss of ^{222}Rn during typical sample processing as indicated below.

When the method described here was compared with the standard ASTM method,(ASTM, 1998) there was no significant difference between the means of the samples (Table 3). Therefore, when samples are processed in a timely manner, no significant losses of ^{222}Rn occur.

It can be concluded that the method proposed here is both robust and accurate. The ASTM method is widely adopted by a range of monitoring agencies due to its reliability. The method proposed here is more sensitive and is equally accurate. The reproducibility is excellent, with a 2.3% relative standard deviation for 19 analyses.

3.8 Detection limits

According to Currie (1968) the minimum detectable activity (MDA) for a method is given by:

$$MDA\left(Bq\ l^{-1}\right) = \frac{2.71 + 4.65\sqrt{Bt}}{tE_\alpha XV60} \qquad (5)$$

where B is the background in the α ROI in counts per minute (cpm), t is the count time (minutes), E_α is the counting efficiency for the α ROI (as defined by Equation 1), X is the extraction efficiency and V is the sample volume (litres). Assuming a count time of 60 minutes, sample volume of 580 ml, and the remaining parameters as previously specified, the MDA is 0.020 Bq l^{-1} and 0.016 Bq l^{-1} for toluene and UGF respectively. If the sample volume is increased to 1 litre, the MDA becomes 0.012 Bq l^{-1} and 0.009 Bq l^{-1} for the two extractants, although this value is dependent on the extraction efficiency, which may be lower than for the smaller volume. These values compare favorably with the best literature values 0.02 – 0.05 Bq l^{-1}.(Hoehn and von Gunten, 1989; Freyer *et*

al., 1997) However, the present MDA is achieved with a smaller sample volume (580 ml rather than 1 litre) and a single extraction rather than two. These are important considerations; less time is needed by the analyst and the sample volume is nearly halved, important when working in remote field sites and when sample sizes are limited.

4. Conclusions

It has been shown that the system of extracting radon with pure toluene and then combining it with a cocktail suited for α/β separation (UGLLT) is robust for a wide range of natural fresh waters. The alternative method of extracting with the commercially available cocktail UGF produces slightly better detection limits; however, it is somewhat prone to quenching. The effects of quenching can be accounted for by adjusting the α ROI to take into account the spectral shift, but would need to be examined more closely for the specific samples in question. The detection limits achieved with these extractants and α/β separation LSS are comparable to existing methods, but utilise a substantially smaller sample and require only a single extraction. The extraction can be performed in a mechanical shaker, offering further savings in the analyst's time. Overall, this method provides a fast, simple and reproducible method for the analysis of ^{222}Rn in fresh waters.

5. Acknowledgements

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Figures

Fig. 1: Liquid scintillation spectra at the optimum PDD for ^{222}Rn extracted into (a) toluene (PDD = 160) and (b) Ultima Gold F (PDD = 180). The α spectrum is white, and the β spectrum shaded. The α region of interest (ROI) is indicated. All α counts with energies > 1000 keV are allocated to the β MCA.
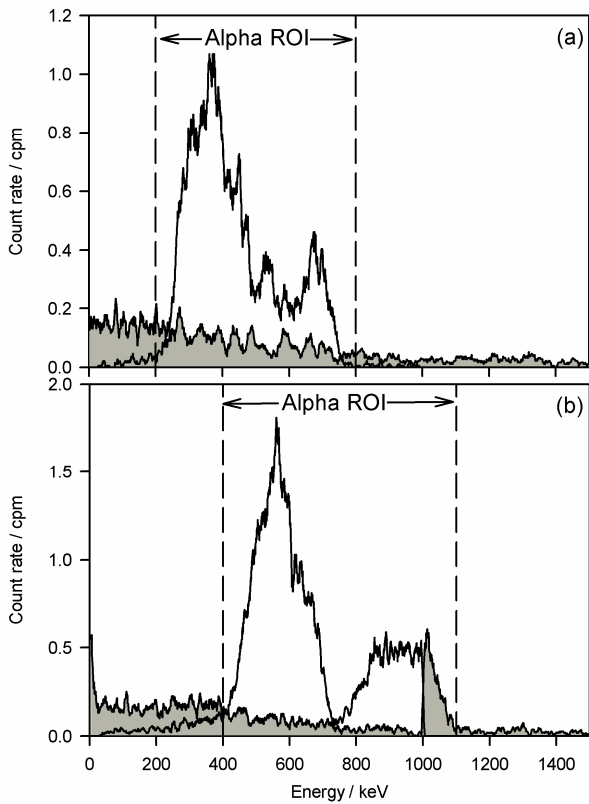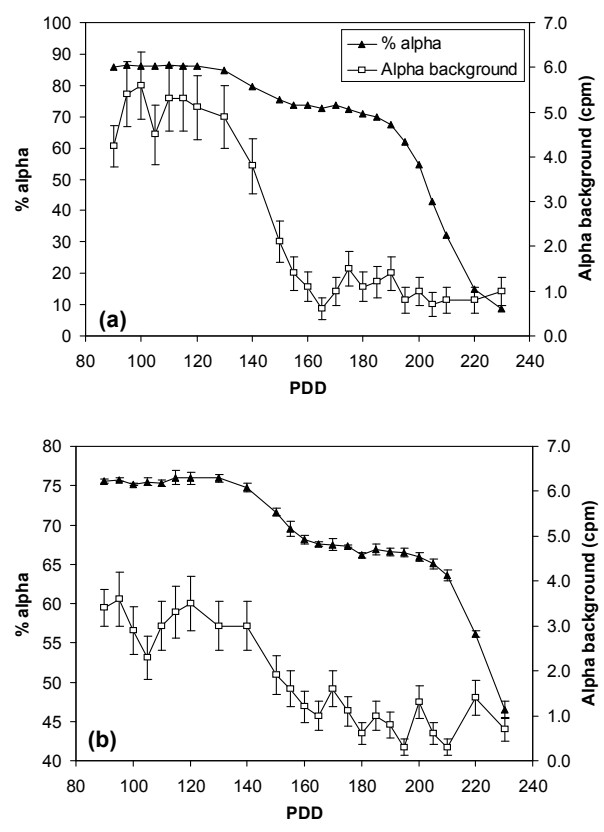
Fig. 2: Alpha background and % events recorded in the α region of interest (α window of the α MCA) for (a) toluene and (b) Ultima Gold F as a function of pulse decay discriminator (PDD) setting.
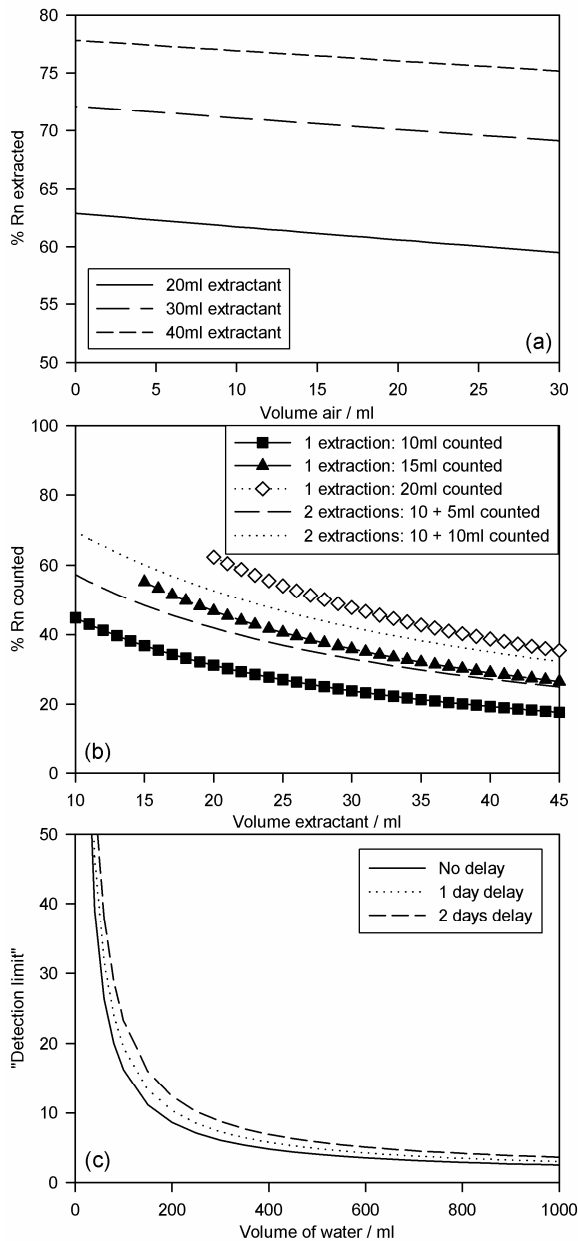
Fig. 3: The effect of varying extraction conditions on the extraction of radon. In all cases, the extractant:air:water partition coefficients are assumed to be 50:4:1, and the total volume is assumed to be 610 ml (unless otherwise specified): (a) the effect of air volume on the extraction efficiency; (b) the effect of extractant volume and number of extractions on extraction efficiency, assuming an air volume of 5 ml; (c) the effect of time and sample volume on "detection limit" (see text for details of calculation), assuming 5 ml air volume, 30 ml extractant volume and 20 ml extractant being counted.
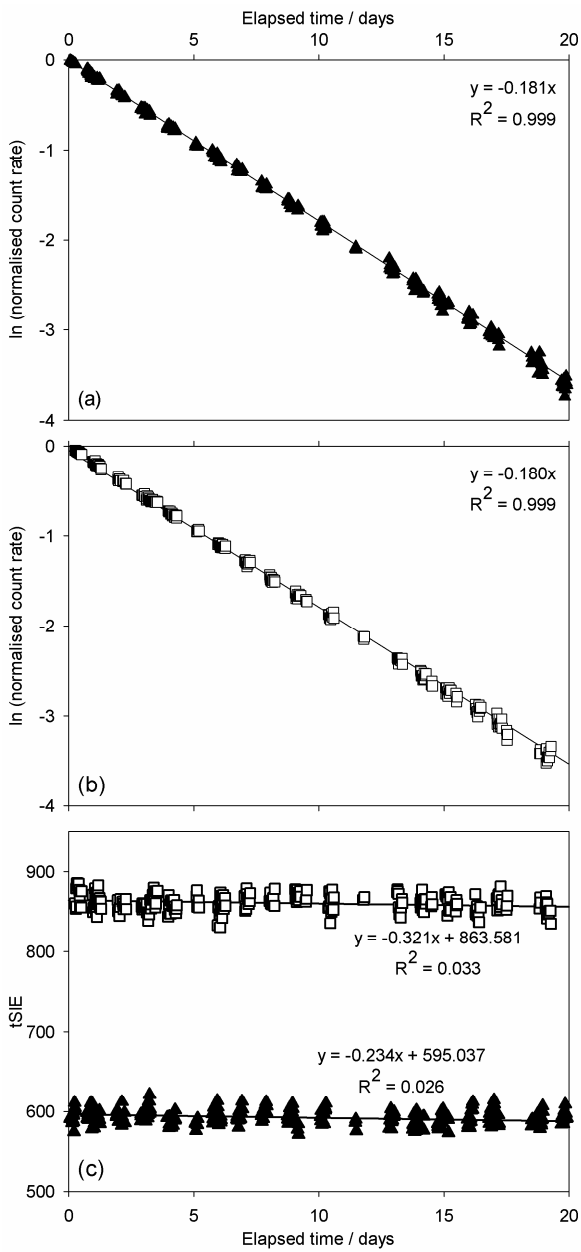
Fig. 4: Stability of vials containing extracted ^{222}Rn over a 20 day period: (a) toluene extractions, (b) Ultima Gold F extractions. The total net count rate for each vial has been normalised to its own theoretical starting count rate, based on the net count rate at the first count. (c) The variability in the tSIE.

Tables:

Table 1: Comparison of the extraction efficiency for different shaking times and extractants. Toluene samples were counted at PDD = 160; Ultima Gold F samples were counted at a PDD = 180. The data presented are the mean ± standard deviation of triplicate samples.

	Toluene		Ultima Gold F	
Shaking conditions	% Rn extracted	% Rn counted	% Rn extracted	% Rn counted
Theoretical	62	31	71	47
1 minute by hand	38.3 ± 1.3	19.15 ± 0.66	49.9 ± 4.4	33.2 ± 3.0
5 minutes by hand	47.4 ± 4.5	23.7 ± 2.2	56.7 ± 4.1	37.8 ± 2.7
10 minutes, end-over-end shaker	46.4 ± 3.3	23.2 ± 1.6	47.4 ± 2.2	31.6 ± 1.4
20 minutes, end-over-end shaker	51.3 ± 4.1	25.6 ± 2.1	54.3 ± 2.2	36.2 ± 1.4

Table 2 Performance of the two extractants for a range of water samples. The recovery is the percentage of measured ^{222}Rn compared to the activity of ^{226}Ra added to the sample. Data are the mean and standard deviation of triplicate samples.

Water	pH	Conductivity (μS cm^{-1})	Absorbance at 340 nm	Toluene Recovery (%)	Toluene tSIE	Ultima Gold F Recovery (%)	Ultima Gold F tSIE
Roudsey Wood	6.50	241	1.410	93 ± 3	586 ± 2	81 ± 6	773 ± 74
Windermere	7.04	103	0.017	94 ± 4	591 ± 16	80 ± 3	917 ± 26
Morecambe Bay	7.40	3830	0.009	106 ± 7	595 ± 7	98 ± 5	830 ± 10
Background	--	--	--	--	583 ± 11	--	817 ± 8

Table 3 Results of the field evaluation experiments. Data are the mean and standard deviation of replicate samples.

Experiment 1			Experiment 2			Experiment 3			Experiment 4		
Time delay	^{222}Rn activity (Bq l^{-1})	N	Condition[a]	^{222}Rn activity (Bq l^{-1})	N	Condition[b]	^{222}Rn activity (Bq l^{-1})	N	Method	^{222}Rn activity (Bq l^{-1})	N
22 hours	9.27 ± 0.29	9	1	8.71 ± 0.18	5	1	11.22 ± 0.20	4	ASTM method[10]	8.58 ± 0.45	25
27 hours	9.23 ± 0.28	8	2	8.59 ± 0.08	4	2	11.28 ± 0.18	4	This method	8.74 ± 0.20	19
44 hours	9.14 ± 0.22	8	3	8.76 ± 0.27	5	3	2.89 ± 0.06	4			
49 hours	9.44 ± 0.29	8	4	8.87 ± 0.16	5	4	0.54 ± 0.02	4			

a Condition 1: Samples prepared and extracted individually; Condition 2: Samples prepared and extracted as a batch; Condition 3: Samples prepared as a batch, then left to stand in the fume cupboard for 10 minutes without lids before toluene was added; Condition 4: as Condition 3, but samples left to stand for 30 minutes.

b Condition 1: Samples prepared and extracted individually; Condition 2: Samples prepared and extracted as a batch; Condition 3: Samples prepared as a batch, then left to stand in the fume cupboard for 10 minutes without lids after toluene added and extraction performed; Condition 4: as Condition 3, but samples left to stand for 20 minutes.