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The implications of particle energy and acidic media on gross alpha and gross beta determination using liquid scintillation

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ABSTRACT

The interaction of humans with radioactivity present in the environment from natural and artificial sources necessitates an evaluation of its risk on human health. Gross alpha and gross beta activities can provide a rapid evaluation of the radioactive content of a sample and can be simultaneously determined by using liquid scintillation counters. However, calibration of the liquid scintillation counter is required and is affected by many factors, such as particle energy and the acidity of the media. This study investigates what effect the particle energy used for calibration has on misclassification and how to account for this misclassification in routine measurements.

The variability in measurement produced by the final pH, as well as any acids used in sample treatment, was also studied. These results showed that the most commonly used acid for these types of analyses, HNO_3, produced a high amount of misclassifications at very low pH. The results improved when HCl was used to adjust the sample to low pH.

1. Introduction

The presence of radioactivity in the environment is caused mainly by naturally occurring radionuclides and cosmic radiation, although there is also a contribution from artificial sources. Unnatural sources include the fallout from nuclear tests and accidents and human activities, such as nuclear power plants and NORM industries.

Radionuclides are present in all aspects of the environment, soils, water, biota and air, and the continuous interactions of humans with the environment makes it necessary to evaluate the risk of radionuclides on human health.

Radioactivity in water can reach humans and the environment through many different mechanisms because it is a resource that is directly consumed, used in food processing and used in many industries (Mas et al., 2007). Many countries have drinking water regulations (European Council, 1998; USEPA, 2000), although according to the World Health Organisation (2008) the exposure to radioactivity through water is small.

Radioactivity monitoring requires adequate representative parameters that can be easily determined and simple methods that are easy to apply to a wide range of samples. For many applications, the determination of gross alpha and gross beta activity provides a rapid evaluation of the radioactive content of a sample and can be used to decide whether specific radionuclide determinations requiring longer and more expensive analyses are necessary. According to World Health Organisation guidelines (2008), water is considered adequate for human consumption when the gross alpha activity concentration is below 0.5 Bq l^{-1} and the gross beta activity concentration is below 1 Bq l^{-1}. When the values are higher, the determination of specific radionuclides should be carried out. Countries may have different threshold values for these two parameters, as in the case of Spain, where the limit is 0.1 Bq l^{-1} for gross alpha activity and 1 Bq l^{-1} for gross beta activity (Spain, 2003).

Liquid scintillation counting is an adequate technique for these analyses, due to the existence of ultra-low level detectors equipped with pulse-shape discrimination devices that allow the simultaneous determination of alpha and beta emitters. However, simultaneous determination requires calibration of the equipment to establish an adequate value for the pulse-shape discrimination parameter. This calibration is performed by individual measurement of the misclassification produced by pure alpha and pure beta emitters in order to find the point where the sum of both misclassification values achieves its minimum. The two main factors affecting calibration are quenching produced by the matrix and the energies of the radionuclides chosen. Since the sample is mixed with the scintillation cocktail, any substance present in the sample might interfere with the scintillation and other light emission processes. This effect has been studied using diverse chemical agents (DeVol et al., 2007; Palomo et al., 2011; Pujol and Sanchez-Cabeza, 1997; Rodríguez Barquero and Grau Carles, 1998; Villa et al., 2003), and Pates et al.

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(1998) proved that the quenching mechanism depends on the agent used. An alternative to quenching curves is to develop methods that guarantee the quenching values will be constant, for example, by acidifying the sample to a constant pH value, which simplifies the quantification and uncertainty reporting (Rusconi et al., 2006; Zapata-García et al., 2009).

The energies of the emitters used for the calibration also affect the response of the equipment. Many studies assumed that only beta energies should be considered because the beta energy range is much wider than the alpha energy range (Pates et al., 1998; Yang, 1996). More recent work provided evidence that alpha energies also influence the alpha/beta misclassifications (Salonen, 2006b). The most common radionuclides for calibration are ^{241}Am and ^{90}Sr/^{90}Y. However, some authors use other alpha radionuclides, such as ^{230}Th, ^{226}Ra, natural U and ^{210}Pb and other beta radionuclides such as ^{137}Cs, ^{40}K, ^{32}P or ^{36}Cl (Forte et al., 2007; Pujol and Sanchez-Cabeza, 1997; Salonen, 2006a; Wong et al., 2005). In a previous paper (Zapata-García and Llauradó, 2009), the performance of the *Laboratori de Radiologia Ambiental (Environmental Radiology Laboratory, LRA)* method was applied to synthetic and real samples. Despite good validation results, the method showed problems when testing water with high natural radioactivity content. This deficiency was probably due to the difference between the emission energies of the natural alpha emitters and the ^{241}Am used for calibration. One of the objectives of this paper is to study the effect that alpha energy has on misclassification and how this should be accounted for in routine methods where the energies of the emitters in a sample are unknown.

Many methods can be found in the literature that use liquid scintillation for gross alpha/beta determination. Most of them apply a concentration process to the acidified sample before mixing it with the scintillation cocktail (Dávila Rangel et al., 2001; Kleinschmidt, 2004; Ruberu et al., 2008). Concentration eliminates radon and its short-lived daughter isotopes and improves the minimum detectable activity (MDA). Validation of such methodologies is accomplished by analysis of synthetic samples and participation in intercomparison exercises. However, little has been published on the internal variability of these methods.

In this work, the variability produced by pH and the acid used in the treatment of samples was studied. Synthetic samples were analysed by applying the optimised conditions in order to evaluate how any remaining misclassification affected the results when the alpha and beta emitter levels were different.

2. Materials and methods

2.1. Instrumentation

For pH measurements, a Cyberscan pH1100 (Eutech Instruments, Singapore) pH-meter was used. Gross alpha and gross beta activities were measured using a 1220 Quantulus (Wallac, Turku, Finland) ultra low-level analyser, which had a pulse shape discrimination device (pulse shape analyser (PSA)) and an external standard of ^{152}Eu for the measurement of external quench parameters (SQP[E]). Twenty-millilitre polyethylene vials (Perkin Elmer, Waltham, Massachusetts, USA) and an Ultima Gold AB scintillation cocktail (Perkin Elmer) were used.

All vials were maintained inside the counter for at least two hours to allow dark adaptation prior to counting. Standards were measured for 100 minutes and samples for 400 minutes.

Spectra were analysed using EASY View Spectrum Analysis Software. The counting windows were set to channels 550–800 in the alpha spectrum and channels 250–1024 in the beta spectrum. Windows were chosen so that all alpha events in the 4–8 MeV range and all beta events excluding ^{3}H could be detected.

2.2. Reagents and solutions

Double-deionised water was obtained from a Millipore water purification system, and analytical grade reagents were used throughout this study.

Commercial solutions of ^{236}U (Eckert & Ziegler, Valencia, California, USA), ^{241}Am (Amersham, Amersham, Buckinghamshire, UK), ^{90}Sr/^{90}Y (Amersham) and ^{137}Cs (CERCA LEA, Pierrelatte Cedex, France) were used. A ^{40}K standard was prepared by dissolving KCl (MERCK, 99.5% pure) in water until saturation was reached. The ^{40}K activity was then measured using high-resolution gamma spectrometry (Canberra BE 3830-7500SL, resolution 1.73). A ^{90}Sr-free ^{90}Y standard was prepared by precipitating $Y(OH)_3$ with NH_4OH after the addition of a Y_2O_3 carrier. $Y(OH)_3$ was dissolved using HCl (50%, v/v).

2.3. Samples

A total of 20 synthetic samples were prepared for analysis using the different procedures. Solutions were prepared using ^{236}U and ^{90}Sr/^{90}Y as alpha and beta emitters, respectively, at three levels of activity concentration: slightly over the MDA and at concentrations approximately 1 and 2 orders of magnitude over MDA. The alpha and beta activity concentrations for the different samples are shown in Table 1.

A series of real samples with different levels of natural and artificial radionuclides were analysed in the final part of the study for method validation.

2.4. Calibration

The optimum PSA was established by calculating alpha and beta misclassification at different PSA settings. The effect of the beta energy was studied using 3 different beta emitters (^{137}Cs, ^{40}K and ^{90}Y). The effect of the alpha energy was studied using 2 different alpha emitters (^{241}Am and ^{236}U). Once the PSA was established, the evaluations of the misclassification and the

Table 1
The gross alpha and gross beta activity concentrations of the synthetic samples used in the study. Concentrations are expressed in Bq l^{-1}.

Sample	Alpha	Beta	Sample	Alpha	Beta	Sample	Alpha	Beta
A1	4.78E-02	–	AB1	5.98E-02	2.03E-01	AB1*	9.93E-02	7.82E-01
A2	4.80E-01	–	AB2	5.69E-02	2.10E+00	AB2*	9.98E-02	2.43E+00
A3	5.05E+00	–	AB3	5.69E-02	2.10E+01	AB3*	9.80E-02	2.37E+01
B1	–	4.42E-01	AB4	5.61E-01	2.10E-01	AB4*	5.00E-01	7.84E-01
B2	–	8.59E-01	AB5	5.60E-01	2.08E+00	AB5*	4.98E-01	1.94E+00
B3	–	1.70E+01	AB6	5.41E+00	2.05E-01	AB6*	3.08E+00	8.03E-01
			AB7	4.99E+00	1.69E+01	AB7*	3.00E+00	2.34E+01