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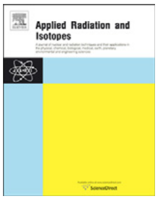

# Evaluation of uncertainty and detection limits in $^{210}$Pb and $^{210}$Po measurement in water by alpha spectrometry using $^{210}$Po spontaneous deposition onto a silver disk

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## ABSTRACT

An easy and accurate method for the determination of $^{210}$Pb and $^{210}$Po in water using $^{210}$Po spontaneous deposition onto a silver disk is proposed and assessed for its detection capabilities according to the ISO Guide for the expression of uncertainty in measurement (GUM) and ISO Standard 11929-7 concerning the evaluation of the characteristic limits for ionizing radiation measurements. The method makes no assumption on the initial values of the activity concentrations of $^{210}$Pb, $^{210}$Bi and $^{210}$Po in the sample to be analyzed, and is based on the alpha spectrometric measurement of $^{210}$Po in two different aliquots: the first one measured five weeks after the sampling date to ensure radioactive equilibrium between $^{210}$Pb and $^{210}$Bi and the second after a sufficient time for the ingrowth of $^{210}$Po from $^{210}$Pb to be significant. As shown, for a recommended time interval of seven months between $^{210}$Po measurements, the applicability of the proposed method is limited to water samples with a $^{226}$Ra to $^{210}$Pb activity ratio $C_{\mathrm{Ra}}/C_{\mathrm{Pb}} \leq 4$, as usual in natural waters. Using sample and background counting times of 24 h and 240 h, respectively, the detection limit of the activity concentration of each radionuclide at the sampling time for a 1 L sample typically varies between 0.7 and 16 mBq L$^{-1}$ for $^{210}$Pb in water samples with an initial activity of $^{210}$Po in the range 0–200 mBq L$^{-1}$, and between 0.6 and 8.5 mBq L$^{-1}$ for $^{210}$Po in water samples with an initial activity of $^{210}$Pb in the same range.

## 1. Introduction

$^{210}$Pb and $^{210}$Po are naturally occurring, relatively long-lived decay products of $^{226}$Ra belonging to the decay series of $^{238}$U. Fig. 1 shows the decay scheme for $^{226}$Ra including half-lives and, for alpha emitters, the major alpha emission energy. All radionuclide data were taken from the NuDat database of the National Nuclear Data Center, Brookhaven National Laboratory, Upton, NY (available online at http://www.nndc.bnl.gov/nudat2/, accessed 26 June 2010).

Because of their widespread distribution in the environment as a result of $^{222}$Rn decay and ulterior deposition, both $^{210}$Pb and $^{210}$Po enter food chains through direct uptake, ingestion or inhalation, clearly playing a meaningful role in human radiation exposure, with ingestion, particularly of seafood and protein-rich meat, being the most important exposure pathway excluding tobacco smoking (Chen et al., 2001; Khater, 2004; Watson, 1985). Actually, $^{210}$Pb and $^{210}$Po are recognized to be the main contributors to the annual effective dose from ingestion of uranium- and thorium-series radionuclides in diet, delivering on average about 8% of the natural radiation dose to the population from internal exposure (UNSCEAR, 2000).

When $^{210}$Pb and $^{210}$Po are in radioactive equilibrium, it is only necessary to measure either the grandparent or the granddaughter. However, this equilibrium between $^{210}$Pb and $^{210}$Po cannot be assumed in natural sources (Bacon et al., 1976; Smith-Briggs et al., 1986; Suriyanarayanan et al., 2008; Yamamoto et al., 2009), which stresses the importance of the simultaneous measurement of both radioisotopes for a more realistic dose assessment, specially in environmental samples from areas where technologically enhanced natural radiation sources such as effluents and tailings from the mining industry, particularly in uraniferous regions, or disposal of products with high $^{226}$Ra content (e.g., phosphogypsum released by the phosphate fertilizer industry) may lead to a significant increase of radiation exposure to people living in those areas (Carvalho, 1995; Martin and Ryan, 2004). In particular, with regard to drinking water, the European Commission Recommendation 2001/928/Euratom (2001) on the protection of the public against exposure to radon in drinking water supplies sets out that where significant concentrations of $^{210}$Pb and $^{210}$Po in water are suspected, on the basis of the results of representative surveys or other reliable information, monitoring of these nuclides should be arranged in

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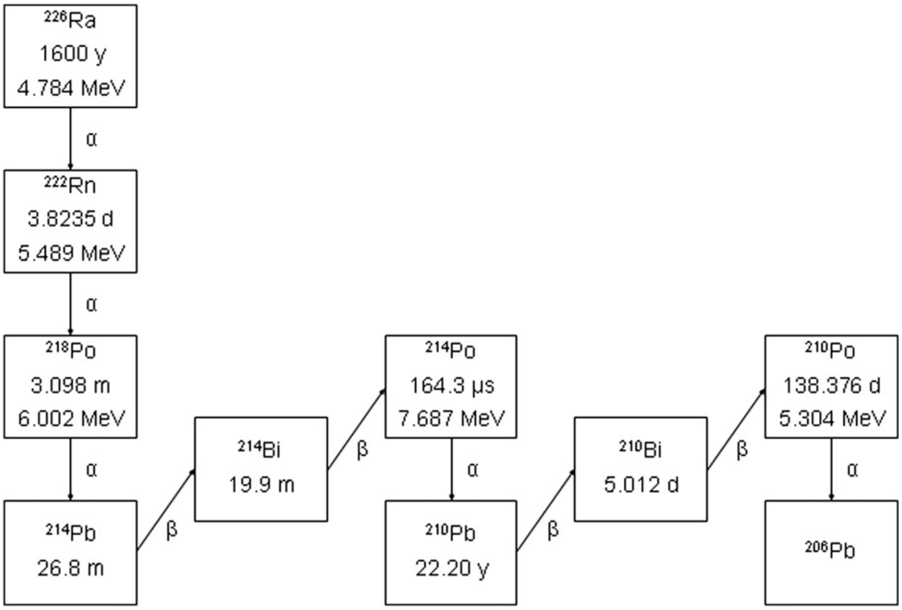

**Fig. 1.** $^{226}$Ra decay scheme.

conjunction with the monitoring of other natural radionuclides required by European Council Directive 98/83/EC (1998) on the quality of water intended for human consumption.

There is widespread information in the scientific literature concerning the measurement of $^{210}$Po in different kinds of natural sources (air, rainwater, freshwater, seawater, soils, sediments, foodstuffs, vegetation, etc.) through a wide range of analytical techniques for sample preparation, $^{210}$Po purification when needed, and determination of $^{210}$Po, mostly via its spontaneous deposition onto metal disks, being silver disks the generally preferred choice (Matthews et al., 2007). Nevertheless, many environmental surveys are reported in which $^{210}$Po measurements are not accompanied by that of its grandparent, $^{210}$Pb, although knowledge of $^{210}$Pb activity is necessary for an accurate determination of the $^{210}$Po activity at the sampling time since $^{210}$Pb is a continuous source of $^{210}$Po. Consequently, to accurately assess the $^{210}$Po content at the sampling time as well as at equilibrium, $^{210}$Pb should also be determined either directly by gamma-ray spectrometry (Dovlete et al., 1996) or liquid scintillation counting (Kim et al., 2008), or indirectly by gas-flow proportional counting (Peck and Smith, 2000), Cerenkov photon counting (Al-Masri et al., 1997) or alpha spectrometric measurement of $^{210}$Po ingrown from $^{210}$Pb (Häsänen, 1977; Miura et al., 1999).

The method presented here is an improved and more rigorous version of that suggested by García-Orellana and García-León (2002), because no assumption is made on the initial values of the concentrations of $^{210}$Pb, $^{210}$Bi and $^{210}$Po in the sample to be analyzed and a more elaborate and precise evaluation of uncertainty and detection limits is accomplished. It is based on the determination of $^{210}$Pb and $^{210}$Po activity concentrations in water at the sampling time by carrying out two alpha spectrometric measurements of $^{210}$Po in two different aliquots: the first one five weeks after the sampling date for radioactive equilibrium between $^{210}$Pb and $^{210}$Bi to be reached and the second after a sufficient time for the ingrowth of $^{210}$Po from $^{210}$Pb to be significant. Both measurements are made after spontaneous deposition of $^{210}$Po onto a silver disk by a slight modification of the standard procedure (Flynn, 1968), using $^{209}$Po as the yield determinant tracer.

Unlike the classical method that uses two $^{210}$Po depositions from the same aliquot, the proposed method has the advantage that it avoids interferences of the polonium isotope employed as a yield tracer in the two depositions in the measured $^{210}$Po activity, as well as other possible error sources in the radiochemical procedure such as those derived from $^{210}$Pb and $^{210}$Po remaining in the solution after the first polonium deposition (Vesterbacka and Ikäheimonen, 2005). The aim of this paper is focused on the quality assessment of the measuring method by evaluating the uncertainty and the characteristic limits of measurement (decision threshold and detection limit) for each radionuclide according to the ISO Guide for the expression of uncertainty in measurement (GUM) (1995) and ISO Standard 11929-7 (2005). Following Currie's basic formulation (Currie, 1968), the decision threshold of a measurand, also called "decision level" or "critical level", is the primary measurement result above which the probability for a false decision that the physical effect quantified by the measurand is present in the analyzed sample (error of the first kind) is at most equal to a given value $\alpha$. It must be carefully distinguished from the detection limit, which is the smallest true value of the measurand for which a false decision that the physical effect it quantifies is not present in the sample to be measured (error of the second kind) may occur at most with a given probability $\beta$. Accordingly, the detection limit represents the smallest true value of the measurand which is detectable by a given measuring procedure, and then allows a decision on whether or not the measuring procedure is suitable for the intended measurement purposes.

## 2. Materials and methods

When a water sample is appropriately de-emanated, e.g., by bubbling nitrogen or "radon-poor" air through it, to avoid the build-up of $^{210}$Pb from $^{222}$Rn originally dissolved in water, and adsorption effects on the walls of the storage container may be disregarded by storing the sample in 0.1–1.0 M HCl in a glass container (Katzlberger et al., 2001; Suganuma and Hataye, 1981; Vesterbacka and Ikäheimonen, 2005) , the $^{210}$Po activity concentration in the sample after a time $t$ since the sampling date long enough to ensure radioactive equilibrium between $^{210}$Pb and $^{210}$Bi can be approximated by the function

$$C_{\mathrm{Po}}(t) = C_{\mathrm{Po}} e^{-\lambda_{\mathrm{Po}} t} + \frac{\lambda_{\mathrm{Po}}}{\lambda_{\mathrm{Po}} - \lambda_{\mathrm{Pb}}} C_{\mathrm{Pb}} (e^{-\lambda_{\mathrm{Pb}} t} - e^{-\lambda_{\mathrm{Po}} t}) \quad (1)$$