


A comparative study of ^{226}Ra determination using total counting and alpha spectrometry in environmental water samples

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Abstract The quick determination of natural radionuclides is very important in emergency situations, supporting decisions of environmental contamination prevention. A quick methodology for determination of the ^{226}Ra was applied in water samples and the results were compared to those obtained by the conventional method. The technique is based on the microprecipitation of radio barium sulfate and subsequent quantification of ^{226}Ra by alpha spectrometry. The procedure used presented high chemical recoveries and good sensitivity. The main advantage is to obtain the results in 3 days.

Keywords ^{226}Ra Isotope · Total counting · Alpha spectrometry · Water sample

Introduction

The early determination of ^{226}Ra is very important in emergency situations where decisions of environmental contamination prevention are necessary. Therefore, a quick method for the determination of this radionuclide is of great relevance [1].

The measurement of radium isotopes in environmental samples is important for public health reasons [2]. All

isotopes of this element disintegrate by alpha decay, except the ^{228}Ra (which disintegrates by beta decay). ^{226}Ra occurs as a relatively long-lived ($t_{1/2}$: 1622 years) isotope, formed from the radioactive decay in the ^{238}U natural series. It is one of the most radiotoxic of the naturally occurring radioisotopes. It belongs to the series of alkaline earth elements and has a behavior similar to calcium. When Ra radioisotopes are ingested, they tend to concentrate in the bones, cells, and/or tissues [3, 4].

Some natural radionuclides are found in water or soils and their concentrations can vary widely. From the radiological protection point of view, studies indicate that concentrations of ^{226}Ra may represent a threat to human or animal health, hence the importance of Ra determination [5, 6].

A number of effective preconcentration procedures has been described for determination of ^{226}Ra , including MnO_2 adsorption, $\text{Ba}(\text{Ra})\text{SO}_4$ coprecipitation, cation-exchange resin adsorption, and Radium Rad Disc adsorption. However, $\text{Ba}(\text{Ra})\text{SO}_4$ coprecipitation is mostly used, as described by Godoy [7, 8]. In this method, the ^{226}Ra activity concentration is determined by gross alpha and beta counting in a gas flow proportional counter of ultra-low background, for about 30 days after the purification and coprecipitation of the sample with $\text{Ba}(\text{Ra})\text{SO}_4$ [8]. This time interval is necessary to obtain the radioactive equilibrium between ^{226}Ra and ^{222}Rn decay products [9].

Another technique for determination of ^{226}Ra is the gamma spectrometry in hyper-pure germanium detectors (HPGe). This radionuclide emits a measurable 186 keV gamma line with intensity of 4 %. However, this energy suffers the interference of another natural radionuclide, 185.7 keV line of ^{235}U , so that ^{226}Ra has to be identified by its decay products ^{214}Pb and ^{214}Bi . In liquid matrices this technique is not feasible due to the low sensitivity and interference related to the type of array [10].

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The counting of α/β liquid scintillation counting (LSC) technique can provide high detection efficiencies for α -particle radiation. It can be used for determination of ^{226}Ra without much difficulty, but the α -background count rates of LSC optimized for α/β discrimination are still too high to allow the determination of ^{222}Rn supported by ^{226}Ra in low activity concentrations. In fact, the LSC method can carry out quantitative analyses at high ^{226}Ra activity and be more useful as a screening technique for qualitative analyses at low Ra activity [7].

A fast method for ^{226}Ra determination is performed by alpha spectrometry, after radiochemical separation and followed by microprecipitation of radio barium sulfate, where the ^{133}Ba tracer is added to establish the chemical recovery analysis and quantified by gamma spectrometry [11].

The micro-precipitation method following alpha spectrometry quantification is easy to carry out and requires only short processing times. A coprecipitation method using BaSO_4 provides very good yields and sources of sufficient qualities when appropriate conditions are used. However, the presence of very large amounts of barium may lead to spectral degradation. The ^{226}Ra peaks are usually sufficiently isolated for easy evaluation or almost direct determination by simple integration [1].

Hosseini and Fathivand [12] studied the measurement of ^{224}Ra and ^{226}Ra contents in micro-precipitate samples that were determined by alpha spectrometry and total alpha counting measurement methods. They showed that, in theory, 15 days after filtration, the radioactive equilibrium should be about 93.5 % for total alpha counting, but they found it to be about 83 %. It seems that the vacuum process forces part of radon gas out of the filter, which then compromises the equilibrium. In order to verify this idea, after radioactive equilibrium had been achieved in the precipitate, the filter was fully covered by a thin aluminum foil. They also showed that it is possible to prepare a micro-precipitate of radium in sulfate form from various environmental and food samples, and measure it immediately after the filtration process, without waiting to achieve radioactive equilibrium between radium and its daughter products. It is also a fast method to measure radium in different kinds of samples [12].

In this paper, a modification of the method based on the micro-precipitation of radio barium sulfate and subsequent quantification of ^{226}Ra by alpha spectrometry is described. This method allows for ^{226}Ra determination improvement by quick quantification. The results are compared with those obtained by the conventional method for water samples.

Experimental

Four water samples, prepared by the Institute for Radio-protection and Dosimetry (IRD) for the Brazilian National Intercomparison Program of Radionuclide Assays in

Environmental Samples (PNI), were analyzed: sample A [13], sample B [14], sample C [15], and sample D [16]. Two methods were employed to determine ^{226}Ra in these samples: total counting [8] and alpha spectrometry [11].

Total Counting

For this analysis Ra was purified by radiochemical separation, with Ba^{2+} (20 mg mL^{-1}) used as a carrier to determine loss during the analysis of 1 L of water sample. The radionuclide was coprecipitated as $\text{Ba}(\text{Ra})\text{SO}_4$ using 50 mL of 3 M sulfuric acid, 5 mL of 1 M citric acid with 0.1 % phenol solution and concentrated ammonium hydroxide at pH 6.5, using methyl orange as indicator.

In those circumstances, the Ra isotopes remain coprecipitated as barium sulfate. The supernatant solution was separated from the precipitated $\text{Ba}(\text{Ra})\text{SO}_4$ through centrifugation.

This precipitate was then dissolved with 2 g of EDTA and 5 mL of concentrated ammonium hydroxide. The ^{226}Ra was selectively coprecipitated with addition of 5 mL of 25 mg/mL ammonium sulphate and the adjustment of pH between 4.5 and 5.0 with glacial acetic acid.

The precipitate of $\text{Ba}(\text{Ra})\text{SO}_4$ was filtered through a 0.45 μm Millipore paper and the chemical recovery was obtained by gravimetry.

Once the radioactive equilibrium of ^{226}Ra and its daughter ^{222}Rn (30 days) was achieved, the quantification was performed in the gas flow ultra-low background proportional counter model S5-XLB Tennelec Canberra.

Alpha spectrometry

For this analysis, ^{133}Ba tracer (approximately 6 Bq) was added in 1 L of water sample. After that, 1 mL of 0.2 M KMnO_4 and 1 mL of 3 M MnCl_2 were added, and the pH between 8.0 and 8.5 was adjusted with concentrated ammonium hydroxide. The supernatant solution was then separated from the precipitate by centrifugation. The MnO_2 precipitate was dissolved with 1 mL concentrated hydrochloric acid and 2 mL of 0.5 M hydroxylamine hydrochloride.

Thereafter, the samples were purified with 3 mL of 10 % Titriplex V and suffered a micro-precipitation of Ra with 100 μL of 0.75 mg mL^{-1} Ba, 3 mL of 40 % Na_2SO_4 , three drops of acetic acid, and 200 μL of Ba solution seeding. This solution was prepared with 625 μL of 10 mg Ba and 10 mL 70 % Na_2SO_4 dried in hot flame, then 25 mL of distilled water was added, as well as 25 mL of a saturated solution of Na_2SO_4 .

The solution containing the precipitate (not visible) was filtered through polypropylene filters of 0.1 μm .

Table 1 Results for determination of ²²⁶Ra in water samples

Sample	Real value (Bq L ⁻¹)	Total counting (Bq L ⁻¹)	Alpha spectrometry (Bq L ⁻¹)
A (Aug/2012)	1.410 ± 0.210	1.377 ± 0.051	1.205 ± 0.034
		1.364 ± 0.045	1.333 ± 0.034
		1.423 ± 0.055	–
B (Dec/2012)	0.990 ± 0.150	0.952 ± 0.043	1.080 ± 0.029
		1.040 ± 0.047	1.000 ± 0.042
		0.979 ± 0.044	–
C (April/2013)	0.500 ± 0.075	0.485 ± 0.030	0.453 ± 0.012
		0.473 ± 0.030	0.478 ± 0.013
		0.499 ± 0.032	–
D (Dec/2013)	1.470 ± 0.220	1.491 ± 0.056	1.301 ± 0.035
		1.437 ± 0.053	1.443 ± 0.035
		1.445 ± 0.060	–

After drying (5 min), quantification of ²²⁶Ra was performed by Alpha Spectrometry using a Canberra Alpha Spectrometer model Alpha Analyst, with 12 passivated implanted planar silicon (PIPS) detectors of 450 mm² active area, with counting efficiency of 17–19 %, and Genie 2000 Alpha Analysis software. The chemical recovery analysis was conducted by ¹³³Ba quantification by gamma spectrometry in a Canberra detector model GX4510 with relative efficiency 45 %.

Results and discussion

Usually, the ²²⁶Ra is measured by radon emanation by alpha spectrometry. However it is a slow, indirect measurement and the sample handling is difficult since ²²²Rn is

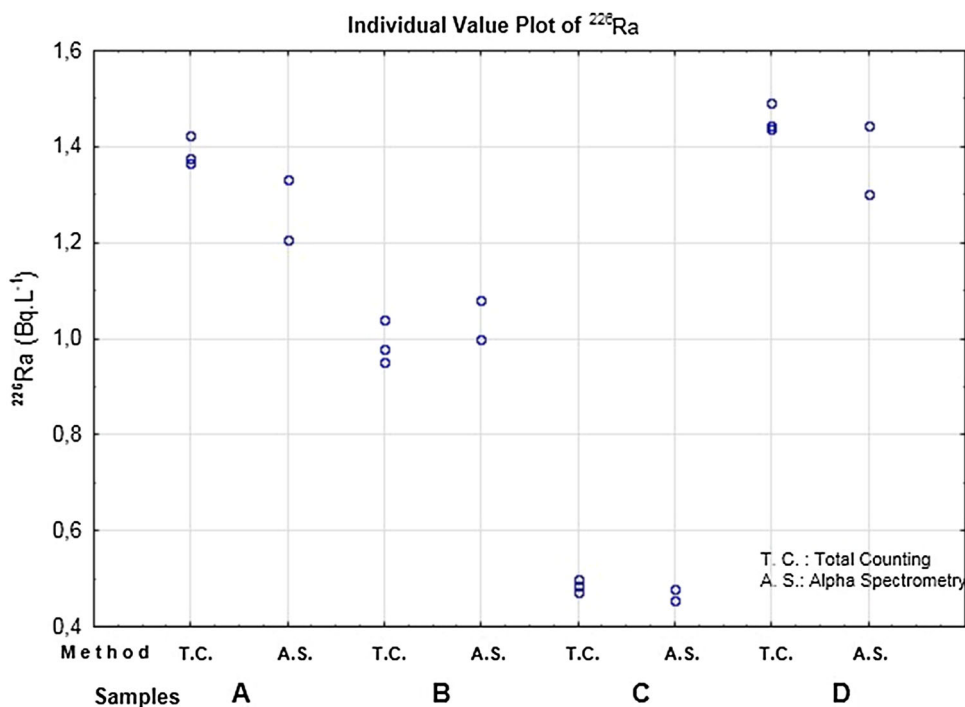
a gas. Therefore, barium sulfate coprecipitation is used to concentrate samples for alpha spectrometry, but it is analyst-dependent [2].

Table 1 presents the results obtained for the environmental samples used in the PNI proficiency test program for the ²²⁶Ra determination using total counting and alpha spectrometry. The box plot of the data set of ²²⁶Ra activity concentration in the PNI samples can be found in Fig. 1.

The chemical recoveries of analyses were between 63 and 89 % for total counting by gravimetry, and between 60 and 93 % for the alpha spectrometry obtained by ¹³³Ba determination by gamma spectrometry. According to this criterion, both methods were effective.

The two methods employed in this study for ²²⁶Ra determination in environmental samples were compared by

Fig. 1 Box plot of the data set of ²²⁶Ra activity concentration in PNI samples



applying analysis of variance ANOVA GLM. Output (unbalanced experiment). This test presented, a statistical probability of approximately 98 %, meaning that both methods fit model well. The analysis of variance presented a p value of 0.117, greater than 0.05. Thus there seen to be no significant difference between the methods used for ^{226}Ra determination.

The determination of both methodologies applied presented good accuracy, precision, and variations within the satisfactory limits for the intercomparison exercise.

The ^{226}Ra determination by total counting however does disadvantage: the need to wait for the radioactive equilibrium between radium and its daughters to be reached. On the other hand, this method presents an advantage, that the ^{228}Ra determination is simultaneous, a beta emitter radionuclide, that presents the same chemical behavior of calcium, that tends to accumulate in the bones when ingested. The ^{228}Ra determination using the quick analysis technique in liquid matrices still been evaluated in studies, with gamma spectrometry or total beta counting.

Conclusions

The quick determination of ^{226}Ra is very relevant and important in emergency or in environmental contamination situations. The method for the determination of this radionuclide by alpha spectrometry can be as fast (3 days), effective and efficient as the total counting, which requires waiting for about 30 days to reach the radiochemical equilibrium between ^{226}Ra and its daughter ^{222}Rn .

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