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^{222}Rn Determination in Water and Brine Samples Using Liquid Scintillation Spectrometry

Oliveira[a] T. C., Monteiro[b] R. P. G., Moreira[b] R. M. and Oliveira[a] A. H.

[a] Departamento de Engenharia Nuclear, UFMG/DEN, 31270-901, Belo Horizonte, Minas Gerais, Brazil

[b] Centro de Desenvolvimento da Tecnologia Nuclear, CDTN/CNEN, 31270-901, Belo Horizonte, Minas Gerais Brazil

oliveiratco2010@gmail.com (Oliveira T. C.)

ABSTRACT

Liquid scintillation spectrometry (LSC) is the most common technique used for ^{222}Rn determination in environmental aqueous sample. In this study, the performance of water-miscible (Ultima Gold AB) and immiscible (Optiscint) liquid scintillation cocktails has been compared for water and brine samples. ^{241}Am, ^{90}Sr and ^{226}Ra standard solutions were used for LSC calibration. ^{214}Po region was defined as better for both cocktails. Counting efficiency of 76 % and optimum PSA level of 95 for Ultima Gold AB cocktail, and counting efficiency of 82 % and optimum PSA level of 85 for Optiscint cocktail were obtained. Both cocktails showed similar results when applied for determining ^{222}Rn activity in water and brine samples. However, the Optiscint is recommended due to its quenching resistance. Limit of detection of 0.08 and 0.06 Bq l^{-1} were obtained for water samples using a sample:cocktail ratio of 10:12 mL for Ultima Gold AB (UGAB) and Optiscint (OPSC) cocktails, respectively. Limit of detection of 0.08 and 0.04 Bq l^{-1} were obtained for brine samples using a sample:cocktail ratio of 8:12 mL for Ultima Gold AB and Optiscint cocktails, respectively.

Keywords: Radon, LSC, Water samples, Brine samples

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1. INTRODUCTION

Radon, ^{222}Rn, is a radioactive noble gas that occurs as natural isotope derived from ^{238}U radioactive decay series. Radon is an alpha-particle emitter (5.48 MeV) with a half-life of 3.8 days and decays to a series of short-lived daughter products (^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po). ^{222}Rn concentrations are quite lower in surface waters, whereas values in groundwater can be many orders of magnitude greater [1, 2, 3].

Radon is an important natural partitioning tracer [1], mainly in oil reservoirs. Information about the reservoir structure may be obtained by produced water composition which is a salty brine generated during the oil production. The salts content is usually higher than the seawater salinity and varies widely between fields or even within the same field.

Liquid scintillation spectrometry (LSC) is a technique widely utilized for radon determination in water [2, 3, 4]. A lower limit of detection (LLD) of 1 Bq l^{-1} is sufficient for these surveys in most cases, easily achieved through LSC [5]. The two main advantages of this technique are the high α counting efficiency and a simple sample preparation.

This solvent is nonflammable, biodegradable, safer to use and enables good alpha/beta discrimination. The first cocktail, Ultima Gold AB, is aqueous-miscible and specifically designed for alpha/beta discrimination while the second one, Optiscint, is suitable for all organic samples.

The analyses have been carried to verify the performance of two DIN based (di-isopropylnaphthalene) liquid scintillation cocktails for radon determination and its behavior in saline samples.

2. MATERIALS AND METHODS

Measurements were carried out in a low background liquid scintillation spectrometer Quantulus 1220 from Perkin Elmer equipped with an anticoincidence guard counter. Polyethylene vials, Ultima Gold AB and Optiscint cocktails were supplied by Perkin Elmer.

^{226}Ra standard solution (activity 2.18 ±0.66 Bq mL^{-1}) was used to spectrometer calibration. This solution was prepared by gravimetrical dilution of ^{226}Ra standard reference material [6]. Total α emission (^{222}Rn, ^{218}Po and ^{214}Po) and high α emitter (^{214}Po) regions were defined for radon determination. Window channels regions have been defined analyzing the efficiency in total α and ^{214}Po regions.

Optimum PSA level for Ultima Gold AB cocktail was selected for minimizing the interferences of α emitters in the β window and vice-versa [7]. Radioactive standard solutions of ^{241}Am [8] and ^{90}Sr [9] were used for optimization of α/β separation, i.e., setting the pulse shape analyzer (PSA) at an adequate value. Optimum PSA level for Optiscint cocktail was determined using ^{226}Ra standard solution, thereby analyzing the variation of efficiency in function of PSA [2].

Sample channels ratio (SCR) was used to assess whether the PSA level has been adjusted correctly for radon. It indicates interferences by count rates registered in different regions. The theoretical value of ^{214}Po region/total α regions (^{222}Rn, ^{218}Po and ^{214}Po) count rates is 0.33, when considering α particle efficiency of approximately 100 %. Experimentally the SCR value is slightly lower than the theoretical value due to the lower efficiency of ^{214}Po compared with others alphas [10].

Tap water samples collected at CDTN/CNEN were analyzed for radon determination using both cocktails. The sample was prepared by collected water with a glass pipette directly into a vial containing the cocktail. No pipette filler was used to avoid suction and ^{222}Rn release. The sample/cocktail ratio for water sample was 10/12 mL for both cocktails. Due to the salts content in brine samples, the sample/cocktail ratio was 8/12, which is usually applied to saline water as seawater samples.

In order to verify the salinity effect in radon determination using LSC, high brine samples (40 to 120 g L^{-1}) were prepared using "pro analysis" grade reagents. Among the ions present in brine samples of Campos Basin, Na^+ (30 %), K^+ (1 %), Mg^{2+} (3.7 %), Cl^- (55 %) and $SO4^{-2}$ (7.7 %) were considered the most important [11].

After sampling, the vial was agitated approximately one minute. It was kept in a dark chamber and under refrigeration for radon equilibration with its short-lived daughters and counted 3-4 h later [5].

Total counting time was divided in three cycles of two repetitions of 20 minutes for each sample. Prepared samples were counted again after about 25-30 days in order to evaluate the supported radon activity and presence of interferences due to α emitter nuclides. Background was determined counting 10 mL of distilled water and 12 mL of cocktail. For calibration, a blank was established by N_2 bubbling through a ^{226}Ra standard solution (1 Bq) during about 4 hours in order to know the contributions of ^{226}Ra and ^{210}Po in α spectrum. The standard:cocktail samples of both cocktails were kept under refrigeration over 25-30 days prior to determination of radon counting efficiency [12].

Radon activity was calculated using the Equation 1.

$$At = \frac{C_\alpha^s - \mathrm{C}_\alpha^{\mathrm{Bg}}}{EFA \times V \times 60 \times f} \qquad (1)$$

Where At is the activity of ^{222}Rn at sampling date (Bq L^{-1}), C^s_α is the α counting rate of the sample (cpm), CB^g_α is the α counting rate of the background (cpm), EFA is the α efficiency, V is the sample volume (0.01 L), 60 is the second to minute conversion factor, f - ($e^{-\lambda Rn \cdot te}$) and ($1 - e^{-\lambda Rn \cdot tp}$), for the first and second measurements respectively for no-supported and supported radon determination. Where λ*Rn* is the radon decay constant, *te* and *tp* are the time between sampling and counting for each measure.

Limit of detection was calculated using Equation 2 [13], where t_c is the total counting time (minute).

$$LD(Bq\,L^{-1}) = \frac{2 + 4\sqrt{B_{\alpha}}}{t_c\,E\,X\,6} \qquad (2)$$

The uncertainty in the activity (μ_{At}) was calculated by the Equation 3, considering the uncertainties of the counting (μ_{cpm}), efficiency (μ_{EFA}) and volume of the sample (μ_v).

$$\mu_{At} = A_t\sqrt{\frac{\left(\mu_{cpm}\right)^2}{\left(cpm\right)^2} + \left(\frac{\mu_{EFA}}{EFA}\right)^2} \qquad (3)$$

.

3. RESULTS AND DISCUSSION

The main settings for Ultima Gold AB and Optiscint cocktails, such as level of PSA, window channel and alpha efficiency, were studied for radon determination.

Optimum PSA value is 95 for Ultima Gold AB cocktail due to in this level the mutual α/β interferences are minimized (Figure 1). ^{226}Ra standard solution was prepared for establishing of alpha efficiency.

Figure 1 - *Optimum PSA value using* ^{241}Am, ^{90}Sr

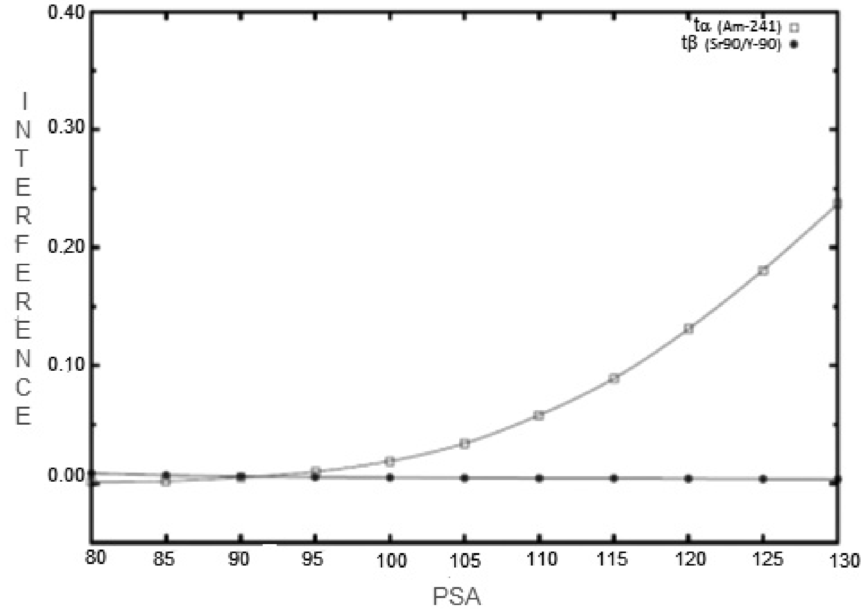


Figure 2 shows its α/β spectra, bubbling with N_2 during 4 hours (the blank spectrum) and after 30 days for ^{226}Ra/^{222}Rn equilibrium. After bubbling only ^{226}Ra and its daughters, ^{210}Po, ^{210}Pb and ^{210}Bi are presents.

It is observed in Figure 3 that total α and ^{214}Po regions correspond to window channels 500-800 and 700-800 respectively. Alpha counting efficiencies were 257 % and 76 % for total α and ^{214}Po regions, respectively. The value of SCR obtained was 0.296, which differs a little of theoretical value (0.33).

Figure 2 - *α/β spectra, sample bubbling with* N_2 *during 4 hours and after 30 days for* ^{226}*Ra/*^{222}*Rn equilibrium*

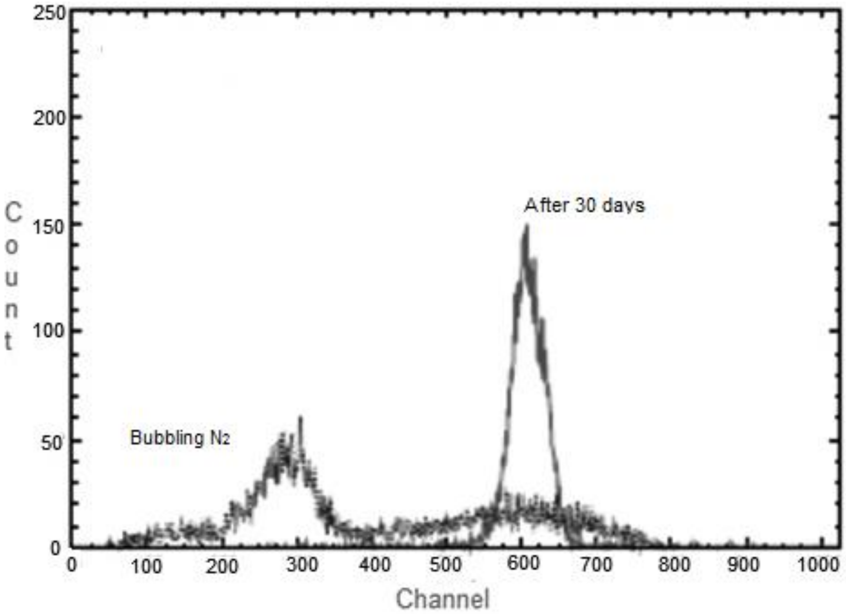
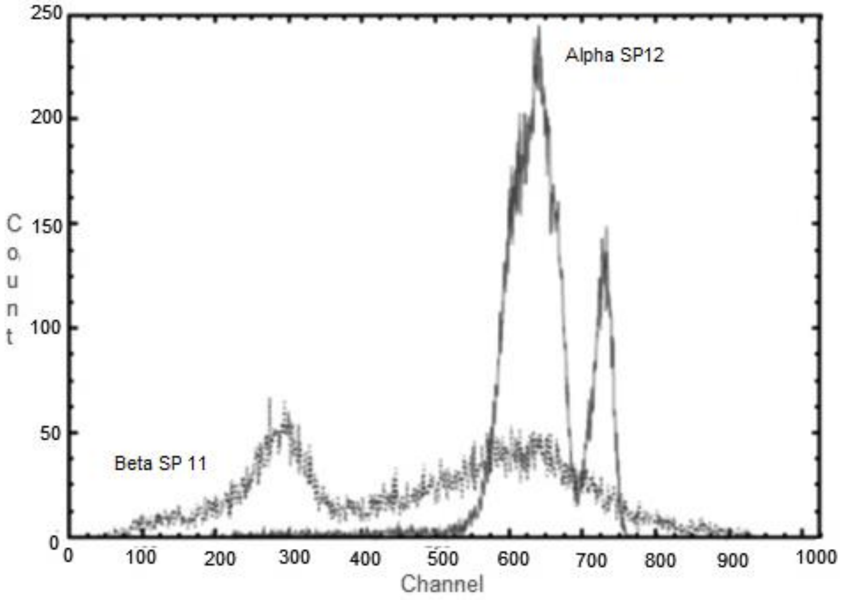


Figure 3 - *^{226}Ra/^{222}Rn equilibrium spectra using Ultima Gold AB and PSA 95*



Due to the Optiscint cocktail being water immiscible, the PSA level was established using ^{226}Ra standard solution. Optimum PSA value was determined by α counting efficiency (range of 65-95 -

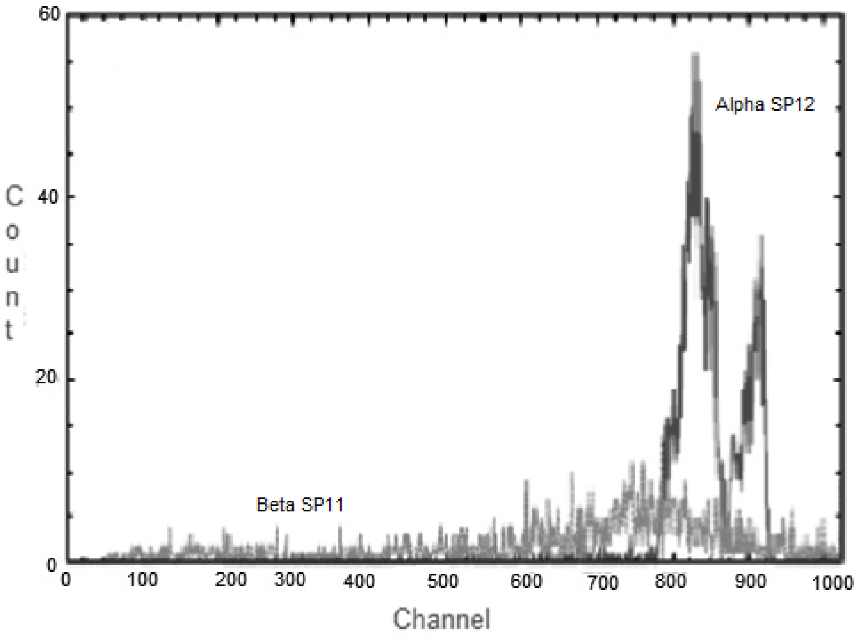
Table 1). The medium value of 85 was defined as the optimum PSA level with an alpha efficiency of 348 % and 82 % for total α and ^{214}Po regions, respectively. Although the PSA level of 85 had been properly defined, the value of SCR obtained was 0.237 which differs significantly of theoretical value (0.33) at the 95% confidence level. In addition, a higher efficiency than 300 % was observed in total α counting region. This is indicative of interference on α counting that needs to be investigated.

Table 1 - Optimum PSA value using Optscint cocktail

PSA	Total α efficiency	^{214}Po efficiency	SQP(E)
55	3.627	0.667	938 ± 3
65	3.570	0.814	940 ± 3
75	3.480	0.820	938 ± 6
85	3.482	0.824	939 ± 5
95	3.453	0.819	937 ± 6
105	3.266	0.693	940 ± 3
115	2.908	0.285	937 ± 6

The increase of the efficiency in total α region can be due to beta spillover or ^{210}Po which is an alpha emitter with energy of 5.30 MeV and is also soluble in the organic phase. This radionuclide is contained in ^{226}Ra standard solution that was not purification recently. The α/β spectra of ^{226}Ra standard solution at PSA 85 shows in the Figure 4. It was observed that total α and ^{214}Po regions correspond to window channels 750-950 and 900-950 respectively.

Figure 4 - *^{226}Ra spectra using Optscint and PSA 85*



In order to evaluate the ^{210}Po interference was prepared a vial containing ^{210}Pb standard solution (1 Bq) in equilibrium with ^{210}Po which was compared with a ^{226}Ra standard solution (1 Bq) using Optiscint cocktail. Figure 5 shows ^{210}Po spectra interference in total *α* region.

The results indicate that ^{222}Rn content must be calculated from ^{214}Po region for both cocktail. For Ultima Gold AB cocktail, due to the possible interference of alpha emitters as ^{226}Ra, ^{210}Po and ^{238}U and for Optiscint cocktail, due to interference in total α region. Furthermore, the background count rate in ^{214}Po is lower than for total α region and thus a lower limit of detection can be achieved. The main parameters for radon determination in water using both cocktail are shown in Table 2.

Figure 5 – *Alpha spectra of ^{226}Ra and ^{210}Po standard solution using Optscint and PSA 85*

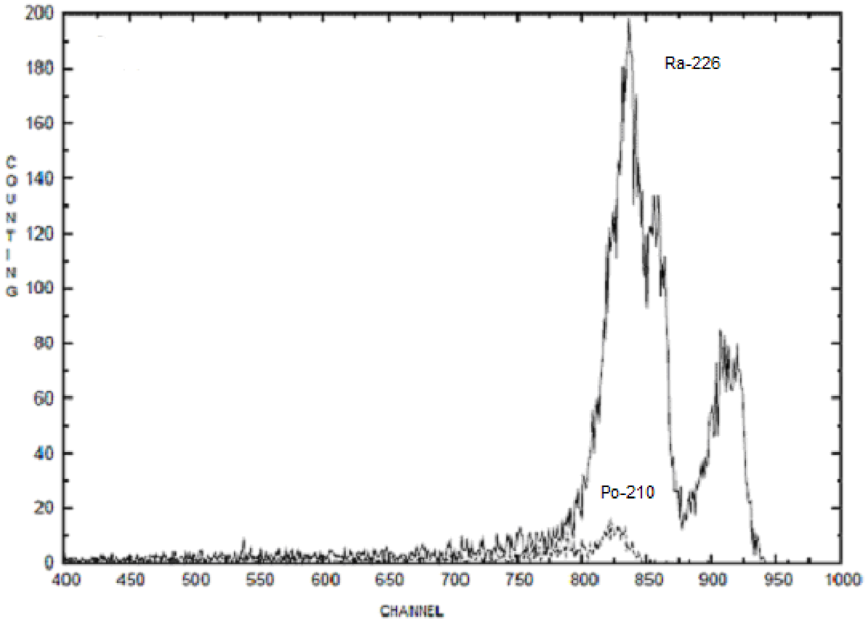


Table 2 – Main parameters for Ultima Gold AB and Optiscint cocktails

Parameter	Ultima Gold AB	Optscint
PSA	95	85
^{214}Po region	700-800	900-950
^{214}Po efficiency	76 %	80 %
Detection limit	0.08 Bq L^{-1}	0.06 Bq L^{-1}

Both cocktails were applied to radon determination in tap water collected at CDTN/CNEN. Table 3 shows some results obtained in triplicate. Similar values of ^{222}Rn activity were observed for both cocktails. This examples show the good repeatability of the methods. The counting of the samples after 30 days not indicated the presence of the supported radon.

Table 3 – ^{222}Rn results using Ultima Gold AB and Optscint cocktails

Cocktail	**α Total Bq L^{-1}**	**^{214}Po Bq L^{-1}**	**SQP(E)**
Ultima Gold AB	0.2 ± 0.18	0.2 ± 0.17	775 ± 2
	0.3 ± 0.26	0.3 ± 0.25	765 ± 3
	0.1 ± 0.10	0.1 ± 0.10	763 ± 3
Optscint	0.3 ± 0.17	0.4 ± 0.3	919 ± 2
	0.3 ± 0.18	0.4 ± 0.3	921 ± 4
	0.3 ± 0.18	0.4 ± 0.3	913 ± 8

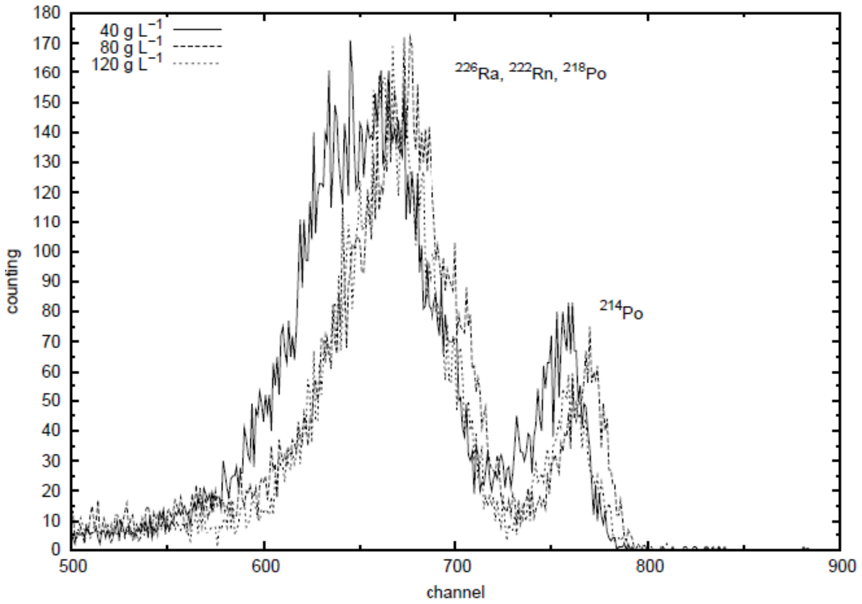
Salinity effect in radon determination shows in Table 4. It was observed a phase separation and a non-transparent emulsion for all samples when Ultima Gold AB cocktail was used. Then, a decrease in counting efficiency is expected due to the inhomogeneous distribution. However, the decrease in radon counting efficiency was significant only for high salts concentration.

Table 4 – Salinity effect in radon determination using Ultima Gold AB and Optscint cocktails

Cocktail	**Salinity (g L^{-1})**	**Efficiency (%)**	**Background (cpm)**	**SQP(E)**	**LLD (Bq L^{-1})**
Ultima Gold AB	40	87	0.05	795	0.04
	80	86	0.02	795	0.03
	120	61	0.10	790	0.08
Optiscint	40	68	0.02	944	0.04
	80	68		937	
	120	64		942	

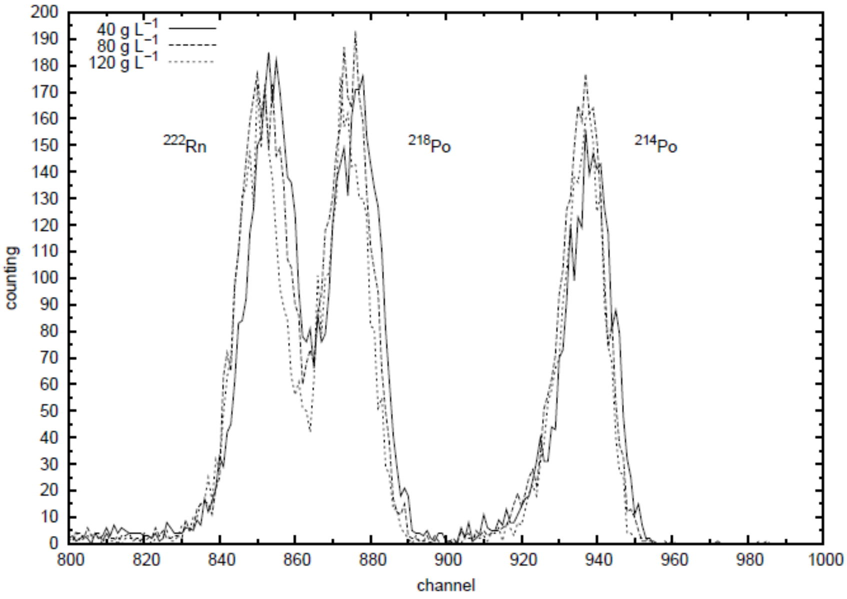
We consider that decrease using the Ultima Gold AB cocktail occurred mainly due to the physical quenching. The poor resolution observed in sample spectra (Figure 6) is typical of quenching presence.

Figure 6 – *Alpha spectra of ^{226}Ra standard using Ultima Gold cocktail AB for brine samples*



On other hand, Optiscint cocktail showed high SQP (E) quenching parameter that was evidenced by good resolution presented to all samples (Figure 7). Lower counting efficiency compared to Ultima Gold AB cocktail is due to the partitioning radon between the organic and aqueous phases into vial.

Figure 7 – *Alpha spectra of* ^{226}*Ra standard using Optiscint cocktail for brine samples*



4. CONCLUSION

Two methods for radon determination in water using water-miscible and immiscible liquid scintillation cocktails, Ultima Gold AB and Optscint, respectively, showed similar results. Both cocktails were recommended to radon determination in water but Optiscint cocktail is more recommended for the brine samples due to its quenching resistance. The same calibration procedure for efficiency determination, i.e., N_2 bubbling for standard solution blank establishment, is recommended for both cocktails. ^{214}Po region should be chosen for radon activity calculation due to minimize the interferences of other radionuclides and beta spillover. In order to improve the understanding the interferences in alpha region using Optiscint, new assay should be performed.

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