

# COMPARISON OF LSC AND ALPHA SPECTROMETRY METHODS APPLIED TO ENVIRONMENTAL SAMPLES

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**ABSTRACT.** A comparison of the procedures for detecting  $^{222}\text{Rn}$  in water used at the Laboratory of Environmental Radioactivity of the University of Extremadura (UEX-Spain) and at the Laboratoire Physique des Radiations of the University of Luxembourg (LPR-Luxembourg) has been performed. The liquid scintillation counting (LSC) technique was applied by both laboratories. In addition, the activity concentrations for  $^{234,238}\text{U}$ ,  $^{226}\text{Ra}$ , and  $^{210}\text{Pb}$  in water samples from 6 different spa sources were determined. The analyses were performed using various well-established procedures at UEX and LPR for detecting these radionuclides. The good agreement found in the results allowed for the validation of instrumentation and procedures. Furthermore, great disequilibria between the U-series radionuclides existing in the spa waters have been observed.

## INTRODUCTION

Most of the environmental radioactivity laboratories have well-established and tested radiochemical methods. The methods are checked in order to assure the accuracy of methods and results and adequate operation of the equipment. Intercomparisons between laboratories are an efficient way to accomplish this check. Several techniques have been described in the literature for the determination of uranium, radium, radon, and lead in the environment (Salonen 1988; Schönhofer 1992; Pérez Sánchez et al. 2003). The determination of the activity concentration of these nuclides in groundwater resources is important in order to understand the mobilization mechanisms and to study the hydrogeological behavior of the uranium series. Moreover, in public spa resorts, measurements of natural radionuclides are needed to avoid health risks for the population. In this paper, liquid scintillation counting (LSC) procedures for determining  $^{222}\text{Rn}$  in water from 2 laboratories are compared: the Laboratory of the University of Extremadura (UEX) in Spain, and the Laboratoire des Physique des Radiations (LPR) in Luxembourg. Instrumentation, types of cocktails and vials, and measurement conditions used at each laboratory are studied. Radiochemical procedures for several U-series radionuclides are also revised. To achieve these goals, 6 groundwater samples from different Spanish spas have been analyzed in both laboratories.

## INSTRUMENTS AND METHODS

### LSC Methods for $^{222}\text{Rn}$ in Water

Radon has a relatively high solubility in water and is also very soluble in organic solutions, with values of 0.225, 1, and 12.5  $\text{cm}^3 \text{g}^{-1}$ , for water, air, and toluene at 20 °C, respectively (Prichard and Gessell 1977). Several direct techniques, such as liquid and solid scintillation methods, have been applied for Rn determination in water. Chereji (1992) presented a comparison between a toluene-based liquid scintillator procedure and a solid zinc sulfide (Ag activated) scintillator. Also, indirect techniques based on the measurement of  $^{222}\text{Rn}$  decay products by gamma spectrometry have been applied (Martín-Sánchez et al. 1995). LSC is one of the most widely used techniques due to the easy and quick sample preparation and because it is very suitable for determining the activity concentrations of this radionuclide. LSC has been used by many authors (Salonen 1988; Schönhofer 1992; Chafupnik and Lebecka 1992), although several differences exist among the procedures, depending on the characteristics of the equipment and the elements used.

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At the UEx laboratory, samples were measured in an ultra low-level Quantulus 1220™ (Wallac Oy) spectrometer. The equipment is situated in the basement of the physics building, in an isolated room and with an annual average temperature of  $\sim 17$  °C. Two types of cocktails were used: Radons® (Etrac Lab., Inc.) and Radonex (a toluene-based cocktail with PPO [6 g] and dimethyl-POPOP [0.1 g] made in the laboratory). Standards were prepared with a  $^{226}\text{Ra}$  solution of  $226 \pm 4$  Bq/mL from CIEMAT (Spain), checked at the laboratory. The types of vials used were 20-mL polyethylene vials because they presented better energy resolution (Galán-López et al. 2004). The measuring time was 200 min. The procedures were compared with a gamma spectrometric method, and the results revealed a  $<5\%$  difference between LSC and gamma spectrometry (Galán-López et al. 2003).

At LPR, the experimental device used was a 1414 Guardian™ (PerkinElmer), situated in a room with an air conditioning system. The equipment was calibrated with  $^{222}\text{Rn}$  standards prepared in different scintillation cocktails and different water-cocktail ratios for a range of Rn activities, from 1.45 Bq (0.10 Bq/mL) to 58.12 Bq (4151 Bq/L), in 22-mL glass vials. The Rn-in-water concentrations were prepared with the Rn generator (Czech Metrological Institute) placed in the basement of the building. The Rn generator consists of a  $^{226}\text{Ra}$  source producing  $^{222}\text{Rn}$ , fixed in a specially designed system. Measurements of the  $^{222}\text{Rn}$  standards permitted the optimization of the PSA value (alpha-beta discrimination system) in the 1414 Guardian and the best water-cocktail ratio. The measuring time was 30 min.

In both laboratories, sample preparation was done following the method of Prichard and Gesell (1977). This method comprises mixing of the water sample with the scintillator in a vial, shaking vigorously for several minutes, and waiting for 3–4 hr before measurement in order to reach secular equilibrium between  $^{222}\text{Rn}$  and its daughters. For both laboratories, the procedures used were established by varying the values of the  $\alpha$ - $\beta$  pulses discriminator, counting window, total recovery (including counting efficiency and extraction capability of cocktails), and water-cocktail ratio, and then selecting those values giving the best results for the minimum detectable activity (MDA) function (Currie 1968) and the figure of merit (FM) value.

### **Radiochemical Procedures for $^{238,234}\text{U}$ , $^{226}\text{Ra}$ , and $^{210}\text{Pb}$**

#### *Uranium*

At UEx, a procedure was used for coprecipitation of uranium and thorium with iron hydroxide. Samples were collected in 25-L polyethylene containers and acidified to pH 2–3 with nitric acid. At the laboratory, a  $^{232}\text{U}$  tracer and a  $\text{Fe}^{3+}$  carrier were added to a 5-L sample of filtered water. Iron and actinides were coprecipitated by adding ammonia. After 24 hr, iron was extracted with diisopropyl-ether (DIE). This process was repeated 3 times, each time discarding the organic phase. The residue was dissolved in  $\text{HNO}_3$ , and TBP was added to the solution. After shaking in a conventional decantation funnel, the aqueous phase was discarded, and thorium traces were eliminated from TBP by adding xylene and 1.5N HCl. The solution containing the uranium was evaporated to a few mL and 500  $\mu\text{L}$  of 0.3M  $\text{Na}_2\text{SO}_4$  was added. The solution was then evaporated to dryness and dissolved in 300  $\mu\text{L}$  of  $\text{H}_2\text{SO}_4$  and 4 mL of distilled water. Before electrodeposition, pH between 2.1–2.4 is adjusted by adding  $\text{NH}_4\text{OH}$ . The solution was then electrodeposited onto a stainless steel disc. The activity concentration was measured by alpha spectrometry with 450-mm<sup>2</sup> active area PIPS detectors. The spectrometer was calibrated with a mixed standard source of  $^{233}\text{U}$ ,  $^{239/240}\text{Pu}$ , and  $^{241}\text{Am}$ . The counting time was about  $8 \times 10^5$  s, and the overall efficiency of the procedure was  $\sim 20\%$ .

At LPR, for uranium isotopes, a similar method was used based on the coprecipitation of actinides with iron as hydroxides. In this case, 500 mL of filtered sample was sampled, and the tracers for all

natural radionuclides to be estimated were added. For uranium, this was  $^{232}\text{U}$  as a tracer and  $\text{Fe}^{3+}$  as a carrier. The sample was stirred for 20 min at a constant ambient temperature. Actinides were coprecipitated by adding  $\text{NH}_4\text{OH}$  until a pH of 9–10 was reached. After 1 hr, samples were centrifuged, and the precipitate was diluted in 3M  $\text{HNO}_3$ . The solution was passed through UTEVA resins, following the Eichrom Technologies procedure for uranium determination. A Canberra alpha spectrometry system of 4 PIPS detectors with a 900-mm<sup>2</sup> active area was used. The detectors were calibrated with a standard source of  $^{234/238}\text{U}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Am}$  (Analytics Production). The counting efficiency was ~21%.

#### Radium

In the UEx, the  $^{226}\text{Ra}$  activity concentrations were determined following the procedure proposed by Aceña Barrenechea and Crespo Vazquez (1988) based on coprecipitation with  $\text{Ba}_2\text{SO}_4$ .  $^{133}\text{Ba}$  was used as tracer to determine the radiochemical yield by gamma spectrometry. The extraction of actinides was made with tributylphosphat (TBP). Finally, the solution was converted into a Ba-Ra sulfate, filtered using a 0.45- $\mu\text{m}$  Millipore membrane, and counted in the alpha spectrometer. The counting efficiency was about 15%, and the chemical yield was about 45%.

At LPR,  $^{226}\text{Ra}$  was analyzed by 2 methods. The first one, after elimination of the actinides in the step of uranium determination, was based on the coprecipitation of radium as barium-radium sulfate, followed by carbonization and then conversion into Ba-Ra chloride diluted in 2 mL of water (Tosheva et al. 2003). The activity concentration was determined by LSC, using 18 mL of OptiPhase HiSafe 3 scintillation cocktail and measured for 60 min using the Guardian. The counting efficiency of  $^{214}\text{Po}$  was  $95 \pm 3\%$  in alpha-beta counting mode when  $^{214}\text{Po}$  was in equilibrium with  $^{226}\text{Ra}$ . This method was slightly modified by the neutralization of one of the active surfaces with plastic glue. Then, 0.5 mg of NaEDTA and 2 mL of 1M  $\text{K}_2\text{CO}_3$  were added to allow only available  $\text{Ra}^{2+}$  to undergo surface complexation and to eliminate  $\text{CO}_2$ . These modifications improved the absorption of radium, and the adsorption of uranium or thorium on the disks was avoided. The alpha-spectrometric measurements were performed for 2 days.

#### Lead

$^{210}\text{Pb}$  was determined by a simple procedure developed in the UEx laboratory (Pérez Sánchez et al. 2003). Samples were collected in polyethylene containers; after filtration,  $\text{Fe}^{3+}$  and  $\text{Pb}^{2+}$  carriers and a  $^{209}\text{Po}$  tracer were added. After stirring and waiting 24 hr for equilibrium, iron, lead, and actinides were coprecipitated by adding ammonia. The solution was mineralized by heating with  $\text{H}_2\text{O}_2$  and evaporated to dryness. The residue was dissolved again with concentrated HCl. The  $^{210}\text{Pb}$  determination was made by solvent extraction of a lead bromide complex into ALIQUAT-336 in toluene. Samples and backgrounds were counted with the Quantulus 1220 for 400 min. The LS counter was calibrated using aliquots of a  $^{210}\text{Pb}$  standard solution in equilibrium with its daughters. A  $^{210}\text{Bi}$  standard source was prepared for the determination of the ratio of the counting rate in the  $^{210}\text{Pb}$  window. For  $^{210}\text{Bi}$  standards, the separation was made using the SrSpec crown ether resin (Pérez Sánchez et al. 2003). The lead chemical recovery was obtained by gravimetry. The counting efficiency for  $^{210}\text{Pb}$  was calculated from a source in secular equilibrium with  $^{210}\text{Bi}$ , taking into account the ratio in the  $^{210}\text{Pb}$  window, was about  $63 \pm 5\%$ .

In the LPR,  $^{210}\text{Pb}$  was estimated through  $^{210}\text{Po}$  following the method proposed by Tosheva et al. (2003), assuming equilibrium. (The time elapsed from sampling to analysis must be chosen accordingly.)  $^{210}\text{Po}$  was adsorbed on a 35-mm-diameter homemade copper disk for 6 hr at a constant controlled temperature of 60 °C and then measured by alpha spectrometry using  $^{208}\text{Po}$  as a tracer. The

water volume used for analysis was 500 mL, and the procedure was performed before the uranium-radium separations. The counting efficiency in the optimized  $^{210}\text{Pb}$  window was  $90 \pm 4\%$ , and the chemical yield was 86%.

## RESULTS AND DISCUSSION

In Table 1, some of the calibration results for the procedures of LSC for radon-in-water used in both laboratories are shown. The water volumes chosen ranged between 10 and 12 mL (by applying the lowest MDA and highest FM criteria). The best recovery results were found with the commercial cocktail Optiscint HiSafe, with an efficiency of about 100%, and for the water-cocktail ratio 10:12. Recoveries were good using other commercial cocktails as well. Ultima Gold™ F is routinely used in the LPR laboratory, and the optimization of sample-cocktail ratio was previously done. The homemade cocktail, Radonex, although it presented the lowest recovery value, has the advantage of a very low cost. The MDA results in both laboratories are in the range of the  $^{222}\text{Rn}$  activity concentrations found in environmental samples. The MDAs reached by the UEx laboratory are 1 order of magnitude better than those from LPR. The main reason for this is the difference between the background levels of the 2 LS counters used; the Quantulus 1220 has a much thicker asymmetrical lead shield than the Guardian. The shield encloses the 2 principal photomultiplier tubes (PMTs) and the electronic instrumentation that permits it to achieve measurements of ultra low-level background (as shown in Table 1). The results obtained in the calibrations of the equipment and in optimizing scintillation cocktails and vials led us to conclude that the methods performed could be applied to environmental groundwater samples.

Table 1 Comparison of the measurement characteristics for LSC procedures used at both laboratories [Environmental Radioactivity Laboratory of the Universidad de Extremadura (UEx) and the Laboratoire Physique des Radiations (LPR)] for measuring radon in water. Background level, total recovery (including extraction efficiency), MDA, and FM are referred to the counting window selected for each equipment. Sample volume is optimally found by applying the minimal MDA and the maximum FM criteria.

Lab	Equipment	Type of cocktail	Counting window (channels)	Sample volume (mL)	Background (cpm)	Efficiency (%)	MDA (Bq/L)	FM (cpm <sup>-1</sup> )
UEx	Quantulus 1220	Radons®	700–950	10	$0.11 \pm 0.02$	$88 \pm 4$	0.2	7.04
		Radonex		10	$0.19 \pm 0.05$	$71 \pm 3$	0.4	2.65
LPR	1414 Guardian	Ultima Gold F	660–950	12	$2.65 \pm 0.21$	$100 \pm 7$	2.0	0.38
		Rn mineral oil		10	$2.91 \pm 0.22$	$93 \pm 2$	2.8	0.30
		Optiscint		10	$2.73 \pm 0.18$	$97 \pm 4$	2.7	0.34
		Hisafe		12	$2.77 \pm 0.18$	$89 \pm 6$	2.3	0.29

The methods for uranium, radium, and lead were applied by each laboratory to 6 environmental samples taken from 5 different spas and a mineral water plant, all of them from the Extremadura (Spain) region. The water samples were collected in 2002, and the radionuclide determinations were then made in the Spanish laboratory. The LPR determinations were made 18 months later. Samples were acidified after sampling and stored. Thus, the time delay between determinations in both laboratories should not change the characteristics of the water conditions.

Table 2 shows the results for the uranium-series radionuclides obtained at the LPR and UEx laboratories. In general, a rather good agreement is found in the results for both laboratories in most of the samples.

Table 2 Results (in mBq/L) for the different U-series radionuclides in the spa waters of Extremadura for the Laboratoire Physique des Radiations (LPR) and for the Environmental Radioactivity Laboratory of the Universidad de Extremadura (UEX).

	$^{238}\text{U}$		$^{234}\text{U}$		$^{226}\text{Ra}$		$^{210}\text{Pb}$		
	LPR	UEX	LPR	UEX	LPR	UEX	LPR	UEX	
					Copre	Ra disk			
Valdefernando	3.10 ± 0.1	2.50 ± 0.1	7.10 ± 0.2	6.50 ± 0.2	87 ± 3	94 ± 7	107 ± 5	51 ± 9	75 ± 6
Alange	2.80 ± 0.2	2.40 ± 0.1	2.30 ± 0.2	1.80 ± 0.1	13 ± 1	—	45 ± 3	120 ± 12	79 ± 6
Riscos	7.40 ± 0.2	5.60 ± 0.2	4.80 ± 0.2	3.60 ± 0.2	61 ± 3	78 ± 7	75 ± 4	73 ± 8	51 ± 3
Trampal	4.72 ± 0.03	0.42 ± 0.03	1.88 ± 0.04	1.16 ± 0.06	15 ± 1	21 ± 1	6 ± 1	4.5 ± 0.4	4.4 ± 0.4
Raposo	8.60 ± 0.2	9.40 ± 0.5	40.0 ± 1	35 ± 2	2.6 ± 0.2	6.6 ± 2.7	—	49 ± 8	14 ± 1
Baños de Montemayor	0.85 ± 0.02	0.43 ± 0.04	0.53 ± 0.04	0.69 ± 0.05	6.2 ± 0.4	—	5.4 ± 0.3	59 ± 6	10 ± 1

For the  $^{238,234}\text{U}$  activity concentrations, a great discrepancy for the Trampal spa-water was found. As not enough water sample remained to repeat the analysis, we assumed that the acidification process of water with  $\text{HNO}_3$  after the sampling could not be correctly completed, and the water characteristics could have changed during storage.

A significant excess of  $^{234}\text{U}$  versus  $^{238}\text{U}$  was found in 4 of the samples. The theory for the disequilibrium is based on the assumption that the  $\alpha$ -particle recoil of  $^{238}\text{U}$  causes the ejection of  $^{234}\text{Th}$  in the mineral whose processes result in the preferential chemical leaching of  $^{234}\text{U}$  into porewater and then to groundwater (Osmond and Cowart 1976).

In the radium procedures used at LPR, the  $^{226}\text{Ra}$  activity concentrations were higher using the Ra adsorbing disks (as explained above). Comparing the results of LPR with those obtained at UEX, the major difference is also found in the Trampal sample. That leads us to suspect a possible modification in the water characteristics during storage. In the Alange spa sample, the value obtained at UEX was 4 times higher; unfortunately, no results with a Ra-adsorbing disk could be done.

The  $^{210}\text{Pb}$  activity concentrations measured by LPR were, with the exception of the Valdefernando sample, higher than the UEX determinations. In order to explain the differences found in the results, more sample exchange to test the methods will be done in future.

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