

# RAPID DETERMINATION OF Ra, Rn, Pb, AND Po IN WATER USING EXTRACTIVE LIQUID SCINTILLATION

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**ABSTRACT.** We present a rapid procedure for successive separation and measurement of radium (<sup>226</sup>Ra) and its decay products in aqueous solutions. The method makes use of extractive scintillators for direct liquid scintillation counting, including di-isopropylketone (DIPK) (Po), trioctylamine (TOA) (Pb), and di-cyclohexano-21-crown-7 (DC21C7) (Ra). Rn is extracted in the first step directly into a toluene-based scintillator. For water samples with low Ra content, we recommend an additional preconcentration step, using cation exchange followed by Ra elution with 3 M HNO<sub>3</sub>. We also describe a method to recover the extractive scintillator cocktail. The general procedure without measurement is done in <2 h, with sensitivities down to 0.1 Bq liter<sup>-1</sup>, if pulse-shape discrimination is used to reject beta and gamma interferences.

## INTRODUCTION

Radium, polonium and radon isotopes contribute most nuclear radiation to humans. <sup>210</sup>Pb (t<sub>1/2</sub> = 22.3 yr) enters the human body through the food chain, where it becomes enriched, thus effecting long-term internal irradiation. Investigators have used several methods to detect these isotopes, for example, by the Lucas method, using scintillation cells or electroplating for alpha radiation, which have proven to be laborious and time-consuming. The fact that liquid scintillation counting (LSC) is applicable to alpha nuclides has been known almost as long as the method is used for low-energy beta emitters. LSC allows easy sample preparation and counting efficiencies up to 100%. However, poor energy resolution, high background and variable interferences from beta and gamma radiation have prevented its successful application. Pulse-height analysis and electronic rejection of β and γ radiation by pulse-shape discrimination (PSD) is currently available. With these methods, background in the α channel is reduced to conditions <0.005 counts per minute (cpm).

Extractive scintillators of different compositions also provide selective separation and measurement of α emitters in a single step. These have been suggested as rapid methods in single (Burnett & Tai 1992; McDowell 1991, 1992; McDowell, Arndsten & Case 1989 and earlier publications) and group separation for actinides (Bickel *et al.* 1992; Möbius & Yang 1989; Yang *et al.* 1990; Yang, Zhu & Möbius 1991) or α emitters in the natural decay series (Möbius, Kamolchote & Roeksbutr 1992). We report here on our study of rapid determination of Ra, Rn, Pb and Po isotopes in water, using extractive LS with and without preconcentration by cation exchange (Ra) and evaporation (Po) (De Oliveira Godoy 1983). Our method can be used for both single and group determination.

## METHODS

We used a Beckman LS 5801 spectrometer for this study. Some samples were remeasured in the low-level Quantulus 1220™ using pulse-shape analysis. The 47-keV X-rays of <sup>210</sup>Pb were analyzed with an intrinsic Ge γ spectrometer. Scintillator cocktails were prepared either from 1–3 g liter<sup>-1</sup> 2,5 diphenyloxazole (PPO) as scintillator, 5–10% naphthalene as energy transfer agent and the corresponding extractant with toluene as solvent. Alternatively, we used Ultima Gold® XR (Packard

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Instruments, Downers Grove, Illinois, USA). All measurements were made in Teflon vials.

Di-isopropylketone (DIPK), trioctylamine (TOA) and trioctylphosphineoxide (TOPO) were from Fluka Chemie AG (Buchs, Switzerland). For Ra extraction, we used RADAEX™ (ETRAC®, Knoxville, Tennessee, USA) as scintillation cocktail. The  $^{210}\text{Po}$  and  $^{226}\text{Ra}$  standard solutions were from Amersham International plc, Cardiff, Wales. For the Rn measurements, we used groundwater from the southern Black Forest (Blasiwald) with high natural radioactivity ( $\sim 1500 \text{ Bq liter}^{-1}$ ) after calibration in an LS counter.

The procedure described below is derived from the method used by Möbius, Kamolchote and Roeksbutr (1992). In the first step, Rn was extracted using a common toluene-based scintillation cocktail. In the final step, Ra was extracted with crown ether and carboxylic acid (see also Burnett & Tai (1992); McDowell (1991)) and measured as homogeneous solution instead of as  $\text{BaSO}_4$  precipitate-in-gel counting. Uranium and thorium do not interfere if present, but can be quantified by an additional separation step into a TOPO-containing extractive scintillator. For further details, see Möbius, Kamolchote and Roeksbutr (1992) and Yang *et al.* (1990). Figure 1 shows the scheme of the overall procedure.

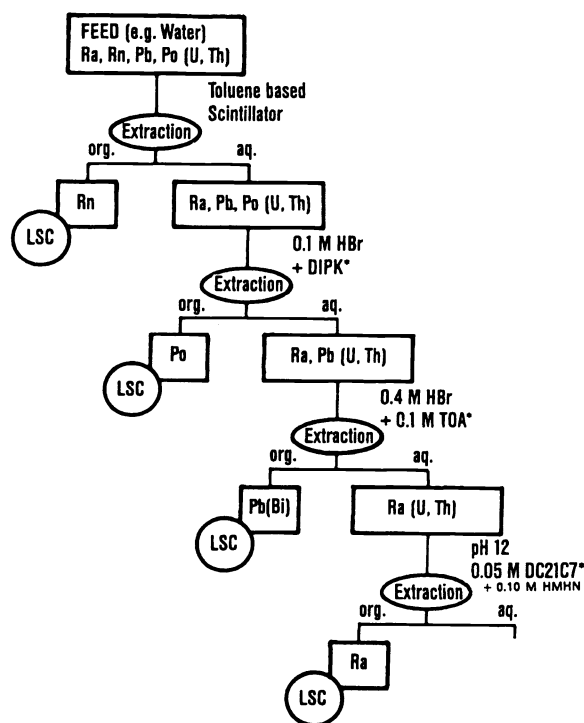


Fig. 1. Procedure for Ra and daughter products in aqueous samples; \* Extractive scintillator containing PPO

### Procedure for Ra and Daughter Nuclides

Extract Rn in a closed system from a 100-ml water sample into 25 ml of a PPO-based scintillator in toluene and measure the organic phase. Adjust the aqueous phase to 0.1 M with respect to HBr. Separate Po in the second extraction step with a DIPK scintillator ( $1\text{--}3 \text{ g liter}^{-1}$  PPO, DIPK) in homogeneous solution and measure immediately (all Po isotopes) and/or after decay of  $^{214}\text{Po}$  and  $^{218}\text{Po}$ . Acidify the aqueous phase to 0.4 M HBr and equilibrate with a TOA-containing scintillation

cocktail (PPO, naphthalene, 0.3 M TOA). Measure the organic phase, which contains Pb isotopes together with  $^{214}\text{Bi}$ . If only the long-lived  $^{210}\text{Pb}$  has to be quantified, store the organic phase 10 h before measurement.

For Ra separation, adjust the aqueous phase with 0.4 M NaOH to pH 12 and extract twice with 5 ml each of RADAEX™ extractive scintillator 2-(4-biphenyl)-6-phenylbenzoxazole (PBBO), naphthalene, 0.05 M dicyclohexano-21-crown-7 (DC21C7), 0.1 M 2-methyl-2-heptyl-nonanoic acid (HMHN)). McDowell, Arndsten and Case (1989) reported that HMHN acts synergistically with DC21C7, and therefore, is a stronger extractant for Ra compared to crown ethers alone. Due to the high cost of crown ethers, the volume of the aqueous phase should be kept small before Ra extraction without exceeding a salt amount  $>0.2$  M. Otherwise, the distribution coefficient for Ra drops markedly. For small Ra concentrations, the separate enrichment step described below is recommended. The time required for the analytical procedure, excluding measurement, is  $<2$  h with counting efficiencies of  $>98\%$  for the  $\alpha$ -emitting nuclides, Rn, Po and Ra, and 80–90% for the  $\beta$  emitters. With distribution coefficients  $>10$  ( $>100$  for Ra in the pH range of 10 to 13), overall recoveries of  $>90\%$  have been achieved. With PSD (Quantulus 1220™) interferences from  $\beta$  and  $\gamma$  emissions are  $<0.01\%$  and a sensitivity to  $10^{-5}$  Bq  $\text{ml}^{-1}$  of feed solution is available for each radionuclide. The procedure can be automated easily.

#### Procedure for Ra After Preconcentration (Fig. 2)

Load a Dowex 50 W  $\times$  8 column of 8-ml resin with 1 liter water sample containing  $^{133}\text{Ba}$  as yield tracer. Complex Ca and Mg, if present, in considerable amounts with an EDTA buffer solution (pH 3). Elute the column with 50 ml 3 M  $\text{HNO}_3$  at 0.5  $\text{ml min}^{-1}$ . Add 5 mg Ba carrier and evaporate to dryness. Dissolve the residue in 2 ml 0.2 M NaOH and 0.4 ml of 1 M  $\text{NaNO}_3$ . Transfer the solution into a small test tube, add 1.2 ml of RADAEX™ extractive scintillator and contact the phases for 2 min on a vibrator. After phase separation, measure 1 ml organic phase in a minivial in a  $\beta$ - $\gamma$ -rejective LS counter. Due to the high cost of extractive scintillators ( $>\$500$  for 100 ml, 1992) and problems in waste disposal, we have used it repeatedly after recycling. We collect the organic phases and strip Ra into 0.5 M  $\text{HNO}_3$ , then wash the organic phase with 0.5 M  $\text{NaNO}_3$ . We did not observe any decrease in extraction efficiency after five recycling steps.

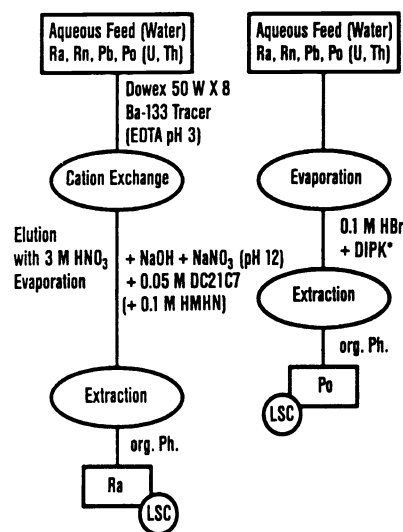


Fig. 2. Procedure for Ra and Po after preconcentration; \*Extractive scintillator containing PPO

## CONCLUSION

Beta-gamma-rejective LS is rapid and efficient for  $\alpha$  emitters. Used with specific extractants as extractive scintillators, it is also selective. Thus, we are on the threshold of replacing time-consuming  $\alpha$  spectrometry using electrochemical deposition. The simple and reproducible chemical steps will be straightforward to automate. By combining various extractive scintillators, the general procedure is easily adapted to the corresponding medium and analytical problem. As the distribution coefficients for common elements are known, interferences can be eliminated by an appropriate software program.

LSC can be even more diversified; it is merely a question of time before it will be combined with modern flow injection analysis (FIA) and ion chromatography (IC). The latter was reported recently for pure  $\beta$  emitters and electron-capture nuclides (Bradbury, Elder & Dunn 1990). Preliminary experiments have been conducted successfully for actinides in the primary coolant of nuclear power plants and natural  $\alpha$  nuclides in environmental water samples. Results are reported elsewhere (Möbius 1993).

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