

# DETERMINATION OF $^{226}\text{Ra}$ , $^{228}\text{Ra}$ AND $^{224}\text{Ra}$ IN WATER AND AQUEOUS SOLUTIONS BY LIQUID SCINTILLATION COUNTING

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**ABSTRACT.** We developed a technique for radium measurement in water samples and aqueous solutions using a Quantulus 1220™ liquid scintillation spectrometer. Radium is extracted from water by co-precipitation with barium. The precipitate is mixed with a gelling scintillator and measured twice over several days. The activity of different radium isotopes is calculated from count rates of alpha and beta particles at different time intervals after preparation. The following detection limits were achieved:  $^{226}\text{Ra} = 3 \text{ Bq m}^{-3}$ ;  $^{228}\text{Ra} = 20 \text{ Bq m}^{-3}$ ;  $^{224}\text{Ra} = 10 \text{ Bq m}^{-3}$  (water samples of  $1 \text{ dm}^3$  volume and counting time 1 h). Compared with other methods of radium determination, the main advantage is low detection limits for all isotopes of radium, including  $^{228}\text{Ra}$ .

## INTRODUCTION

Natural saline waters with very high  $^{226}\text{Ra}$  concentrations (up to  $390 \text{ kBq m}^{-3}$ ) occur in the Upper Silesian Coal Basin (Tomza & Lebecka 1981); however,  $^{226}\text{Ra}$  concentrations may vary by three or more orders of magnitude. Other Ra isotopes,  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$ , members of the thorium series, also occur here.  $^{226}\text{Ra}$  and  $^{224}\text{Ra}$  emit alpha particles;  $^{228}\text{Ra}$  emits low-energy beta particles.

The role of these isotopes in human radiation exposure makes their determinations important. The recommended annual limit of intake (ALI<sub>o</sub>) of  $^{226}\text{Ra}$  is  $7 \times 10^4 \text{ Bq}$ , of  $^{224}\text{Ra}$  is  $3 \times 10^5 \text{ Bq}$  and of  $^{228}\text{Ra}$  is  $9 \times 10^4 \text{ Bq}$  (ICRP 1980). Polish regulations (MGIe 1989) require monitoring of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  concentrations in mine effluents, river waters, public water supplies and wells. Concentrations of  $^{226}\text{Ra}$  higher than  $0.7 \text{ kBq m}^{-3}$  (PAA 1989) are considered liquid radioactive wastes. In addition, environmental samples, including vegetation, are often measured.

Radioactive waters and deposits may contaminate plants, soils and river beds. The method developed here enables determination of Ra isotope concentrations in water samples and in aqueous solutions. Liquid scintillation (LS) is the practical technique for more than 1000 samples per year.

## METHODS

The basic concept of simultaneous determination of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$  follows the method of Goldin (1961), Tomza (1983) and Chalupnik and Lebecka (1990). Ra is co-precipitated with a Ba carrier and Pb, and the precipitate is dissolved in EDTA. Ra is then separated from Pb by co-precipitation of Ra and Ba as sulfates at  $\text{pH} = 4.5$ . The Ba and Ra sulfate precipitate is mixed with a gelling scintillation cocktail, which we used to ensure that the precipitation is suspended uniformly in the whole volume of the scintillation cocktail. We did not dissolve the precipitate because it required too much solvent, more than the capacity of the scintillation vial. The detailed procedure follows (see also Lebecka *et al.* 1992):

1. To the water sample ( $1 \text{ dm}^3$ ), we added  $10 \text{ cm}^3$  of 1 N citric acid,  $10 \text{ cm}^3$  6 N ammonia,  $1 \text{ cm}^3$  1 N  $\text{Pb}(\text{NO}_3)_2$  and  $20 \text{ cm}^3$  0.1 N  $\text{BaCl}_2$ .
2. We heated the sample to boiling, added methyl-orange indicator and dropped in  $\text{H}_2\text{SO}_4$  solution (in the ratio 1:1) until the color changed, and added two drops of  $\text{H}_2\text{SO}_4$ .
3. After several hours, we decanted the supernatant and transferred the precipitate into centrifuge vials. We centrifuged and rinsed the precipitate with water until the pH reached 7.
4. We added  $60 \text{ cm}^3$  of 0.125 M sodium EDTA and  $9 \text{ cm}^3$  6 N  $\text{NH}_3$ , heated the samples in a

water bath, stirring until the precipitate was dissolved; if necessary, an additional portion of EDTA and  $\text{NH}_3$  was added.

5. After the self-cooling of the solution, the Ba and Ra sulfates were precipitated again using glacial acetic acid (6 cm per each portion of EDTA and  $\text{NH}_3$  described above (the date and the time of the precipitation was noted).
6. We centrifuged the samples and rinsed them with water, transferred the precipitate into the scintillation vials, again centrifuged, mixed with water (total volume of sample with water was  $6 \text{ cm}^3$ ), added  $10 \text{ cm}^3$  of gelling scintillator and agitated the solution.

Measurements were performed using a low-background Wallac Quantulus 1220<sup>TM</sup> LS spectrometer which had heavy Pb shielding, low radioactivity of selected construction materials and Pb, an anticoincidence guard, a sophisticated spectrum analyzer and a pulse-shape analyzer, which enables distinguishing  $\alpha$  and  $\beta$  particles.

TABLE 1. Ra Chains in a Prepared Sample

$^{226}\text{Ra}$ chain			$^{228}\text{Ra}$ chain			$^{224}\text{Ra}$ chain		
$^{226}\text{Ra}$	1620 yr	$\alpha$	$^{228}\text{Ra}$	5.7 yr	$\beta$	$^{224}\text{Ra}$	3.63 d	$\alpha$
	↓			↓			↓	
$^{222}\text{Rn}$	3.83 d	$\alpha$	$^{228}\text{Ac}$	6.1 h	$\beta$	$^{220}\text{Rn}$	55 s	$\alpha$
	↓						↓	
$^{218}\text{Po}$	3.05 m	$\alpha$				$^{216}\text{Po}$	0.15 s	$\alpha$
	↓						↓	
$^{214}\text{Pb}$	26.9 m	$\beta$				$^{212}\text{Pb}$	10.6 h	$\beta$
	↓						↓	
$^{214}\text{Bi}$	19.7 m	$\beta$				$^{212}\text{Bi}$	60.6 m	$\alpha, \beta$
	↓						↓	
$^{214}\text{Po}$	164 $\mu\text{s}$	$\alpha$				$^{212}\text{Po}$	300 ns	$\alpha$
							↓	
						$^{208}\text{Tl}$	3.1 m	$\beta$
							↓	
						$^{208}\text{Pb}$		

After radiochemical separation, three independent Ra chains, headed by  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$  are present in the sample; Table 1 lists the members of each chain. Figure 1 shows the changes of total activity (alpha + beta) of each chain after chemical separation of Ra.  $^{224}\text{Ra}$  and its daughters reach maximum activity 24–40 h after separation.  $^{224}\text{Ra}$  decays with  $t_{1/2} = 3.6 \text{ d}$ ; thus, after 26 d, only  $^{226}\text{Ra}$  with its daughters, and  $^{228}\text{Ra}$  with  $^{228}\text{Ac}$ , remain to any extent in the sample.

Both  $^{228}\text{Ra}$  and  $^{228}\text{Ac}$  are  $\beta$  emitters;  $^{228}\text{Ra}$  emits low-energy  $\beta$  particles ( $E_{\beta\text{max}} = 55 \text{ keV}$ ), whereas  $^{228}\text{Ac}$  emits  $\beta$  particles with higher energy ( $E_{\beta\text{max}} = 1.3 \text{ MeV}$ ).  $^{226}\text{Ra}$ ,  $^{222}\text{Rn}$ ,  $^{218}\text{Po}$  and  $^{214}\text{Po}$  are  $\alpha$

emitters, and  $^{218}\text{Po}$  and  $^{218}\text{Bi}$  are also  $\beta$  emitters.  $^{226}\text{Ra}$  concentration can be calculated from results of  $\alpha$  activity measurements after decay of  $^{224}\text{Ra}$ .  $^{228}\text{Ra}$  concentration can be calculated from results of low-energy  $\beta$  activity measurements; however, the result must be corrected for  $\beta$  particles emitted by  $^{226}\text{Ra}$  daughters.  $^{228}\text{Ac}$   $\beta$  particles are more convenient for measurement in the high-energy window, but there is a strong interference of  $\beta$  particles emitted by  $^{226}\text{Ra}$  daughters.

We performed our measurements 24–32 h after preparation and after 28 d following preparation. Figure 1 shows that after *ca.* 28 d from preparation, the  $^{224}\text{Ra}$  remaining is insignificant compared with  $^{226}\text{Ra}$ . The highest activity of  $^{224}\text{Ra}$  and daughters, compared with  $^{226}\text{Ra}$  and daughters, is achieved *ca.* 24 h after preparation.

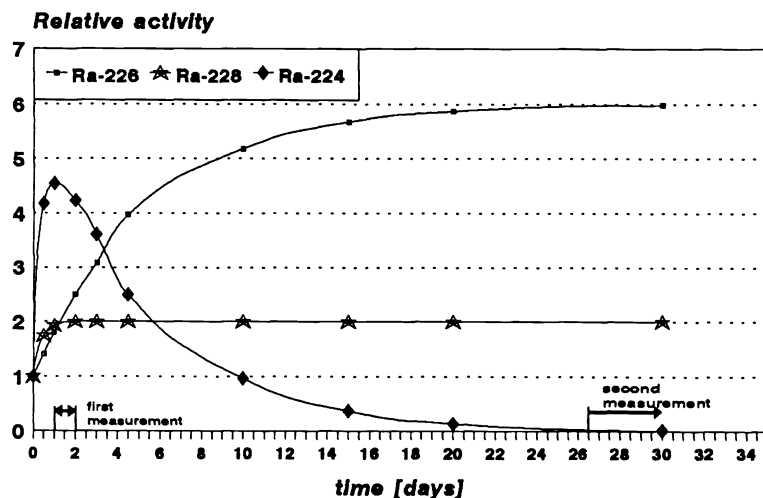


Fig. 1. Changes of activity of radium isotopes in a prepared sample

We chose two windows of the spectrum (as shown in Figs. 2 and 3). Window 1 in the low-energy region of the  $\beta$  spectrum is for calculations of  $^{228}\text{Ra}$  concentration. Window 2, in the upper part of total ( $\alpha + \beta$ ) and  $\alpha$  spectra, is for calculations of  $^{226}\text{Ra}$  concentration and correction of impact between chains. We calculated these correction factors from results of measurements of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  standards. Spectra of  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  standards are shown in Figures 2 and 3. Figure 4 shows spectra of a real water sample ( $0.2 \text{ dm}^3$ ) containing  $^{226}\text{Ra}$  ( $63.4 \text{ Bq dm}^{-3}$ ),  $^{228}\text{Ra}$  ( $30.5 \text{ Bq dm}^{-3}$ ) and  $^{224}\text{Ra}$  after 28 and after 2 d following sample preparation.

Results of two sequential measurements of each sample follow:

1. First measurement: 24–28 h after preparation
  - net  $\beta$  count rate in low-energy window =  $I_{1\beta}^1$
  - net total count rate in high-energy window =  $I_{2T}^1$
  - net  $\alpha$  count rate in high-energy window =  $I_{2\alpha}^1$
2. Second measurement: >28 d after sample preparation
  - net  $\beta$  count rate in low-energy window =  $I_{1\beta}^2$
  - net total count rate in high-energy window =  $I_{2T}^2$
  - net  $\alpha$  count rate in high-energy window =  $I_{2\alpha}^2$

$I_{ja}^i$ , where  $i$  = number of measurement  
 $j$  = number of window  
 $a$  = type of spectrum ( $\alpha$ ,  $\beta$  or total).

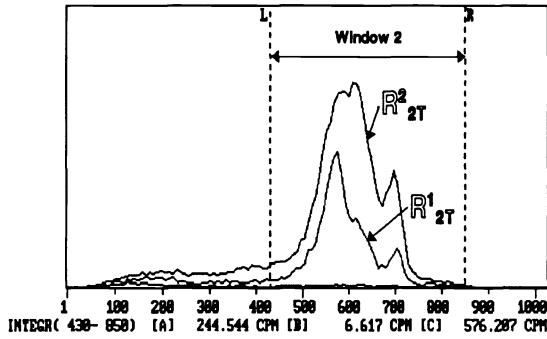


Fig. 2A. Total spectra of  $^{226}\text{Ra}$  standard

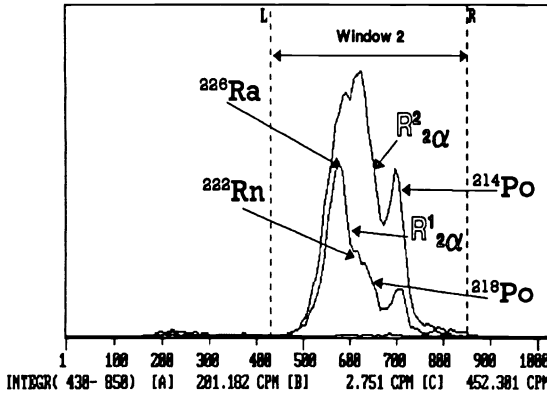


Fig. 2B.  $\alpha$  spectra of  $^{226}\text{Ra}$  standard

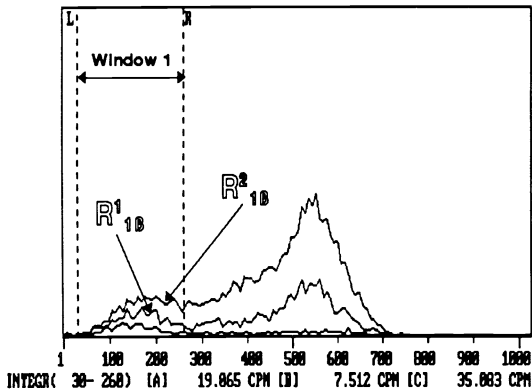


Fig. 2C.  $\beta$  spectra of  $^{226}\text{Ra}$  standard

Of course, background count rates must be subtracted. The spectra of  $^{228}\text{Ra} + ^{224}\text{Ra}$  standard are denoted as  $T_{ja}^i$ , whereas spectra of the  $^{226}\text{Ra}$  standard are denoted as  $R_{ja}^i$ . Figures 2A–C show the spectra of total,  $\alpha$  and  $\beta$  activity for the  $^{226}\text{Ra}$  standard and Figures 3A–C for the  $^{228}\text{Ra} + ^{224}\text{Ra}$  standard.

On the basis of measurements of the  $^{226}\text{Ra}$  standards, we calculated the following coefficients

$$K_1 = R_{1\beta}^2 / R_{2T}^2 (\approx 0.03) . \quad (1)$$

Part of the  $^{226}\text{Ra}$ -daughters' count rate in the low-energy  $\beta$  window is divided by the total count rate in the high-energy window

$$K_2 = T_{2T}^2 / T_{1\beta}^2 (\approx 2.5) . \quad (2)$$

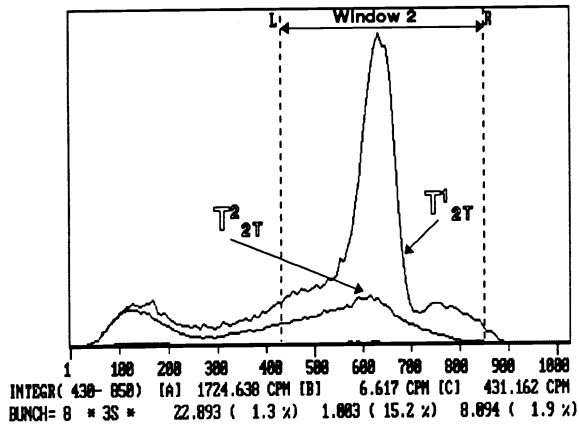


Fig. 3A. Total spectra of  $^{228}\text{Ra}$  standard

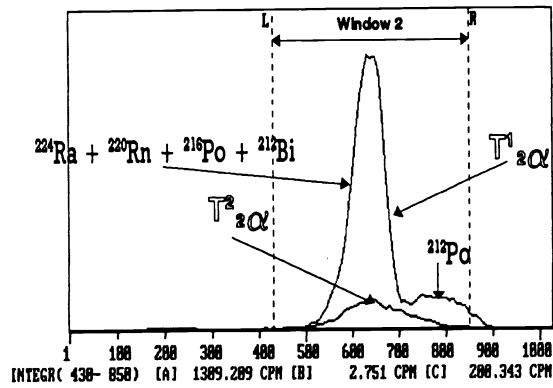


Fig. 3B.  $\alpha$  spectra of  $^{228}\text{Ra}$  standard

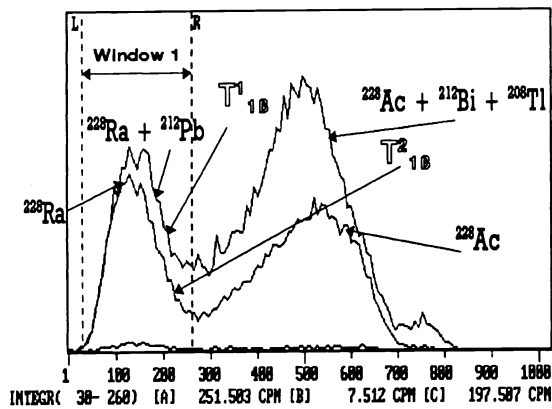


Fig. 3C.  $\beta$  spectra of  $^{228}\text{Ra}$  standard

The  $^{228}\text{Ac}$  count rate in the high-energy window (total counts) is divided by the  $\beta$  count rate of  $^{228}\text{Ra}$  in the low-energy window

$$K_3 = T_{1\beta}^2 / T_{2\alpha}^2 (\approx 0.7) \quad (3)$$

In practice, the discrimination of  $\alpha$  and  $\beta$  particles by pulse-shape analyzer is not perfect. Thus, some  $\beta$  particles are counted as alphas. This is corrected for  $^{228}\text{Ra}$  using results of measurements of  $\beta$  and  $\alpha$  count rates for the  $^{228}\text{Ra}$  standard

$$K_4 = R_{2\alpha}^1 / R_{2\alpha}^2 \quad (4)$$

The growth of  $\alpha$  activity of  $^{226}\text{Ra}$  + daughters can be calculated based on Bateman equations, but because distinguishing  $\alpha$  and  $\beta$  particles is not ideal, it is more convenient and practical to calculate the ingrowth from data of  $^{226}\text{Ra}$  standard measurements.

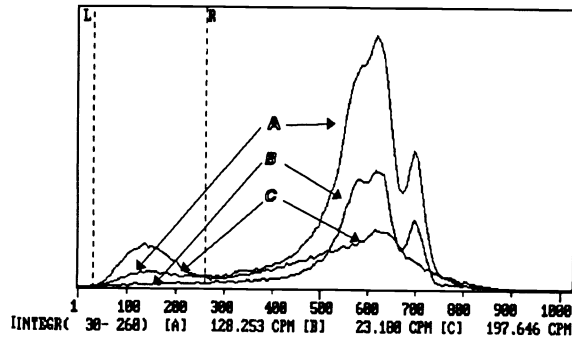


Fig. 4A. Total 28 d; A. Real water sample. B.  $^{226}\text{Ra}$  standard. C.  $^{228}\text{Ra}$  standard

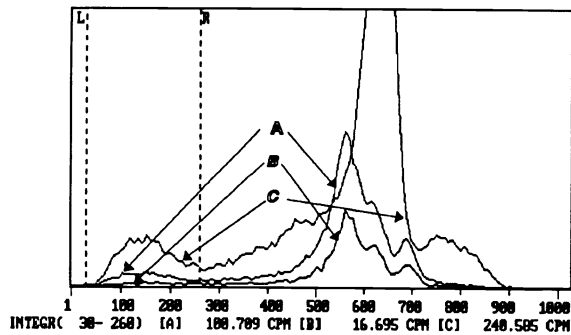


Fig. 4B. Total  $\alpha + \beta$ , 2 d; A. Real water sample. B.  $^{226}\text{Ra}$  standard. C.  $^{228}\text{Ra}$  standard

The results of each sample measurement must be corrected first, using the coefficients defined above. After such correction, one can calculate activities of  $^{226}\text{Ra}$  isotopes.

$$\begin{aligned} &^{228}\text{Ra} \\ I_{1\beta}^2 \text{corr} &= [I_{1\beta}^2 - K_1 \times I_{2\gamma}^2] / [1 - K_1 \times K_2] \\ C_{228} &= I_{1\beta}^2 \text{corr} \times A_{228} / [V \times T_{1\beta}^2] \end{aligned}$$

$$\begin{aligned} &^{226}\text{Ra} \\ I_{2\alpha}^2 \text{corr} &= I_{2\alpha}^2 - K_3 \times I_{1\beta}^2 \text{corr} \\ C_{226} &= I_{2\alpha}^2 \text{corr} \times A_{226} / [V \times R_{2\alpha}^2] \end{aligned}$$

$$\begin{aligned} &^{224}\text{Ra} \\ I_{2\alpha}^1 \text{corr} &= I_{2\alpha}^1 - K_3 \times I_{1\beta}^2 \text{corr} - K_4 \times I_{2\alpha}^2 \text{corr} \\ C_{224} &= I_{2\alpha}^1 \text{corr} \times A_{224} / [V \times T_{2\alpha}^1 \text{corr}] \end{aligned}$$

where

V	= sample volume
$A_{226}$	= activity of $^{226}\text{Ra}$ standard
$A_{228} = A_{224}$	= activity of $^{228}\text{Ra}$ and $^{224}\text{Ra}$ standards
$I_{\text{corr}}^i$	= count rate after correction of impact between chains
$C_{226}$ , $C_{228}$ and $C_{224}$	= concentrations of $^{226}\text{Ra}$ , $^{228}\text{Ra}$ and $^{224}\text{Ra}$ in the measured sample.

From these equations, one can calculate concentrations of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$ .

Low backgrounds allow high detection sensitivity. For a sample prepared from 1 liter of water, and with two 1-h measurements, the following limits of detection (LLD), calculated according to Currie (1968) at confidence level 0.95 can be achieved:

$$\begin{aligned} ^{228}\text{Ra} &= 20 \text{ Bq m}^{-3} \\ ^{224}\text{Ra} &= 10 \text{ Bq m}^{-3} \\ ^{226}\text{Ra} &= 3 \text{ Bq m}^{-3}. \end{aligned}$$

Further, our sample preparation procedure enables simultaneous determination of  $^{210}\text{Pb}$  in water samples or aqueous solutions (Lebecka & Chalupnik 1990; Lebecka *et al.* 1992).

## CONCLUSION

We have presented a method for the simultaneous measurement of three Ra isotopes,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  and  $^{224}\text{Ra}$  in water samples and aqueous solutions using radiochemical preparation and a low-background Quantulus 1220<sup>TM</sup> LS spectrometer with  $\alpha/\beta$  discrimination. We performed measurements with low LLD for the isotopes,  $^{228}\text{Ra} = 20 \text{ Bq m}^{-3}$ ,  $^{224}\text{Ra} = 10 \text{ Bq m}^{-3}$  and  $^{226}\text{Ra} = 3 \text{ Bq m}^{-3}$ .

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