

## Chapter 7

# Low-level Scintillation Counting Method for Determination of U and Ra

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### INTRODUCTION

In uranium mines there are two main types of waste water: one containing predominantly uranium and the other containing predominantly radium. Radiochemical methods for their detection are generally complicated and time-consuming. Their direct determination with the help of nuclear radiation measuring, using classical detectors and methods, is limited by the minimal detectable activity in a given sample volume. Therefore these methods are usually unsuitable for monitoring such radioactive contamination of water.

Provided that the maximal time of determination could be about one hour including sample preparation, it seemed convenient to combine a selective separation method and direct measuring of the separated element. The selective separation and concentration can be performed mainly in two ways: chemically or by ion-exchange. The chemical methods have been described,<sup>1-5</sup> but the best of them,<sup>6,7</sup> so-called EDTA (ethylenediaminetetraacetic acid) method, is also costly and time-consuming. The use of solid adsorbents, cation or anion exchangers, is proposed here as a quick and sufficiently selective method, and when employed in combination with automated sequential sampling and with measuring under definite conditions complies with the requirements of the monitoring.

### CONCENTRATION AND SAMPLE PREPARATION

Radium-226 with its short-lived daughters is adsorbed selectively on strong acid cation exchangers,<sup>8-10</sup> Uranium with its daughters is adsorbed on strong basic anion exchangers.<sup>11-13</sup> Both these elements are also adsorbed on some types of activated biosorbent.<sup>14,15</sup>

In principle, a minimal measurable activity for a chosen type of detector must be adsorbed on these solid adsorbents so that the activity measured ( $A_m$ ) is a function of the nuclide total amount in the adsorbent ( $C_s$ ) and the detector efficiency ( $E_d$ ):

$$A_m = f(C_s, E_d) \quad (1)$$

The  $C_s$  quantity is a function of the nuclide concentration in the liquid phase ( $C_0$ ), the adsorbent bed volume ( $M$ ), its adsorption capacity ( $Q$ ) and the total liquid phase volume passed through the adsorbent ( $V_t$ ):

$$C_s = f(C_0, M, Q, V_t) \quad (2)$$

The total amount depends also on the flow-rate velocity ( $v_f$ ) and other hydrodynamic parameters. In practice, we can express the total volume either as the number of  $\underline{M}$ -volumes ( $\underline{V}_M$ ) passed through the bed volume  $\underline{M}$  or as a function of the flow-rate velocity and duration of the adsorption process ( $\underline{t}_s$ ):

$$\underline{V}_t = \frac{\underline{V}_M}{\underline{M}} (1/\underline{M}) = \frac{v_f}{\underline{M}} \underline{t}_s \tag{3}$$

The total volume is limited by the given breakthrough concentration of the nuclide in the liquid phase on the outflow. Supposing that values  $\underline{E}_d$  and  $\underline{Q}$  are constants and adsorbent volume  $\underline{M}$  is chosen and concentration of the nuclide in the outflow may be neglected, we can express Eqn (1) as follows:

$$\frac{\underline{A}_m}{\underline{A}_0} \sim \frac{\underline{C}_0}{\underline{C}_f} \underline{V}_t = \frac{\underline{C}_0}{\underline{C}_f} \frac{v_f}{\underline{M}} \underline{t}_s \tag{4}$$

where  $\underline{A}_m$  = cpm in chosen  $\underline{M}$ -volume after adsorption;  $\underline{C}_0$  = cpm in a litre of input liquid phase;  $\underline{V}_t$  = total volume of liquid phase passed through the bed in litres.

METHODS OF DETECTION

The volume of the adsorbent  $\underline{M}$  is limited at first by the type of radiation measured. Gamma radiation can be measured with advantage in a well-type NaI-Tl detector in connection with a gamma spectrometer. Then either the photopeak at 187 keV of radium-226 or the photopeaks at 90 and 185 keV of natural uranium can be evaluated.

Direct measuring of the waste water, without a previous concentration process, is possible employing such a detector in minimal concentrations of ng Ra l<sup>-1</sup> or 0.1 g U-nat. l<sup>-1</sup>. Provided that the usual concentrations of examined elements in raw waste water are about 10 pg Ra l<sup>-1</sup> or about mg U-nat. l<sup>-1</sup> and after treatment more than one order lower, it is evident that the concentration factor ( $\underline{F}_c$ ) must be in the order of 10<sup>4</sup> - 10<sup>5</sup>.

If we choose the maximal possible volume of  $\underline{M} = 200$  ml and  $\underline{t}_s$ -value of 20 min, we get the following combinations for radium monitoring as shown in Table 1. Analogous results are obtained for natural uranium monitoring under described conditions (see Table 2).

Table 1.

$\frac{\underline{C}_0}{\underline{C}_s} (\text{Ra})$ pg Ra l <sup>-1</sup>	$\frac{\underline{F}_c}{\underline{C}_s} (\text{MC}_o)^{-1}$	$\underline{V}_t / l$	$\underline{M} / \text{ml}$	$\frac{\underline{a}}{\underline{V}_M} (\text{Mh})^{-1}$	$\underline{t}_s / \text{min}$	$\frac{\underline{C}_s}{\underline{C}_0} (\text{Ra}) /$ pg Ra l <sup>-1</sup>
10	500	100	200	300	100	1000
50	100	20	200	300	20	1000
100	50	10	200	300	10	1000
500	10	2	200	300	2	1000

Table 2.

$\frac{\underline{C}_0}{\underline{C}_s} (\text{U-nat.})$ mg U l <sup>-1</sup>	$\frac{\underline{F}_c}{\underline{C}_s} (\text{MC}_o)^{-1}$	$\underline{V}_t / l$	$\underline{M} / \text{ml}$	$\frac{\underline{a}}{\underline{V}_M} (\text{Mh})^{-1}$	$\underline{t}_s / \text{min}$	$\frac{\underline{C}_s}{\underline{C}_0} (\text{U-nat.})$ mg U l <sup>-1</sup>
0.1	1000	200	200	300	200	20
0.5	200	40	200	300	40	20
1.0	100	20	200	300	20	20
10.0	10	2	200	300	2	20

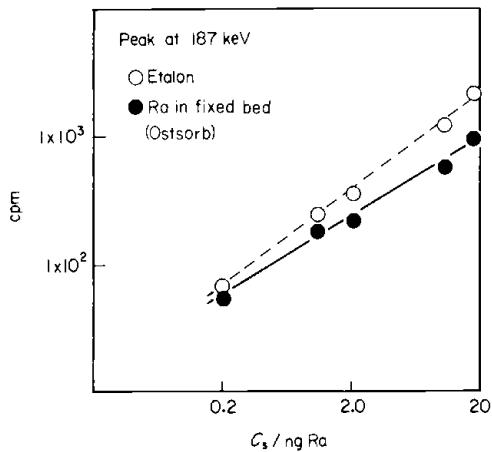


Fig. 1 Calibration of radium ( $M = 200$  ml).

The specific flow-rate velocity ( $a$ ) that could be achieved with the adsorbent tested was  $a = 300 \frac{V_M}{M_t}$ , for example with biosorbent Ostrosorb MV, a product of Spolchemie, Czechoslovakia. This implies that the time limit 20 min may not be satisfied when measuring very low concentrations. Therefore the adsorption time is expressed in both the tables.

#### DISCUSSION

Direct and rapid monitoring of uranium- or radium-contamination of water is very important since these two elements are a hazard to the environment because of their toxicity and very long half-lives. We studied a number of relevant methods described in the literature but they were all either too laborious and therefore time consuming, or unsatisfactory as far as the minimal detectable activity was concerned.

Therefore we have employed the described combination of the separation and combination processes of the element to be detected in a fixed-bed column, modified to be measurable directly in a well-type NaI-Tl detector. The material of this column should be perspex or plastic; the filtration element used is glass wool.

In a fixed-bed column the various ion-exchange resins and biosorbents were tested. The main disadvantage of most ion exchangers was residual activity in the outflow by high specific flow-rates used. The activated biosorbent Ostrosorb MV proved to be the best so far.

The dimensions and geometry of the well-type NaI-Tl crystal are to be chosen according to the radiation energy measured. In the present case the thickness of the well walls and bottom should be about 25 mm and the protective container of the crystal in the well should be thin. In our laboratory the well-type crystals were 120 x 120 mm and 160 x 120 mm, the well volume was 250 ml and its diameter 60 mm. The lead shielding was 70 and 50 mm respectively. The output signal of the detector was evaluated with the help of a 100-channel  $\gamma$  spectrometer (types NKG 315 and NZG 601-Tesla).

The calibration curves for radium and natural uranium are presented in Figs 1 and 2 and Tables 3 and 4 respectively. They are both in a good agreement with the theory described above.

The same method of sample concentration, if non-selective electrodes are employed, is suitable for monitoring the total activity level in various waste water.

If no high  $\gamma$ -energy emitters are present in the sample, the employment of liquid scintillation detectors is advantageous. The minimal detectable activity for

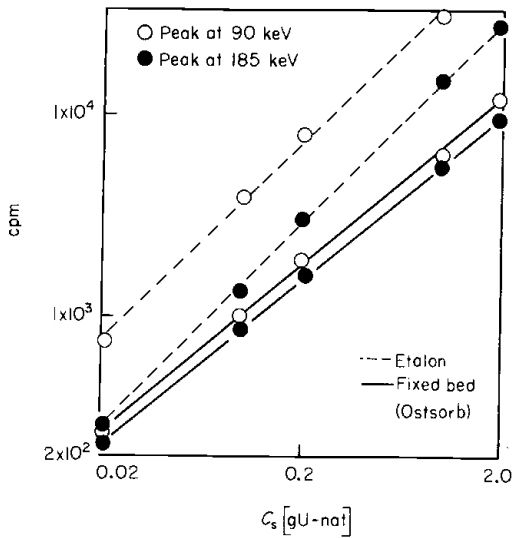


Fig. 2 Calibration of U-nat. ( $M = 200$  ml).

Table 3.

$\frac{C_s}{S}$ (Ra)	$\frac{A_m}{m}$ (cpm $\pm 2\sigma$ )		
	ng Ra	Standard	Fixed bed
0.2	62 $\pm$ 7	55 $\pm$ 6	
1.0	208 $\pm$ 18	162 $\pm$ 17	
2.0	345 $\pm$ 28	224 $\pm$ 23	
10.0	1190 $\pm$ 36	686 $\pm$ 32	
20.0	2388 $\pm$ 54	1024 $\pm$ 58	
Background	142 $\pm$ 12	123 $\pm$ 12	

Table 4.

$\frac{C_s}{S}$ (U-nat.)	$\frac{A_m}{m}$ (cpm $\pm 2\sigma$ )			
	Peak at 90 keV		Peak at 185 keV	
	Standard	Fixed bed	Standard	Fixed bed
g U-nat.				
0.02	788 $\pm$ 15	262 $\pm$ 24	281 $\pm$ 12	224 $\pm$ 16
0.1	3946 $\pm$ 22	1033 $\pm$ 33	1361 $\pm$ 28	970 $\pm$ 31
0.2	8332 $\pm$ 34	1952 $\pm$ 58	3050 $\pm$ 44	1745 $\pm$ 44
1.0	32473 $\pm$ 59	6785 $\pm$ 132	14875 $\pm$ 116	5747 $\pm$ 102
2.0	62202 $\pm$ 108	12734 $\pm$ 324	28020 $\pm$ 284	10714 $\pm$ 363
Background	420 $\pm$ 22	394 $\pm$ 34	143 $\pm$ 12	123 $\pm$ 12

Standard: 200 ml of standardized Ra-solution only;  
 Fixed bed: 200 ml of solid adsorbent granules with adsorbed Ra + residual liquid phase in interstitial space (adsorbent used: Ostsorb  $M_V$ -Mn).

$\alpha$  - ,  $\beta$ - and weak  $\gamma$ -emitters is about 50 pCi l<sup>-1</sup>, i.e. about 2 Bq l<sup>-1</sup> using liquid scintillators in dioxane or aromatic hydrocarbons bases (for example SLE 31-Spolana or Instagel-Packard Inst.).

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## DISCUSSION

G.A. SUTTON: I would be interested to learn how you measure the 90 keV natural uranium peak over what I believe to be a large Compton continuum. I can see that the 185 keV peak is relatively easy but in my experience it is very difficult to measure the low-energy peak with any great accuracy.

H. PROCHAZKA: The ratio of the peaks is constant because of the constant ratio of U-238/U-235 in natural uranium. The Compton continuum is about 70% in this case (due to U-235) in the 90 keV-peak (the 90 keV  $\gamma$ -line is in reality from thorium UX-1).