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RADIOCHEMICAL DETERMINATION OF ^{226}Ra USING CERENKOV COUNTING

M. S. AL-MASRI,* R. BLACKBURN**

**Department of Radiation Protection and Nuclear Safety, Atomic Energy Commission of Syria, Damascus, P.O. Box 6091 (Syria)*
***Department of Chemistry and Applied Chemistry, University of Salford, Salford (UK)*

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A Cerenkov based method has been developed for the determination of ^{226}Ra via its β-emitting daughters, ^{214}Bi and ^{214}Pb. Radium isotopes are separated from interfering elements by coprecipitation on barium sulphate. The precipitate is dissolved in an alkaline solution of EDTA and the Cerenkov signal produced by the build-up of daughter β-activities is counted after 25 days using the tritium channel of a liquid scintillation counter. To correct for any contribution from the daughters of the radium isotopes ^{224}Ra and ^{228}Ra present in the sample, the barium (radium) sulphate is reprecipitated, dissolved in EDTA, and counted 2 days later. Using this procedure, ^{228}Ra and ^{224}Ra can be determined in the same sample. Cerenkov counting efficiency was found to be 77.25%. A lower limit of detection of 17.4 mBq · l^{-1} (based on 3σ of the background with 500-minute counting time) was achieved. Any liquid scintillation counter can be used. Chemical recoveries in the range 75%–95% were determined gravimetrically. Data from both artificial spiked samples and natural samples are presented.

Due to its long hal-life (1622 y) and its radiological effects[1] ^{226}Ra is the most important isotope to be determined among the naturally occurring nuclides in natural water, including drinking water. The numerous methods for determination of ^{226}Ra have been reviewed.[2] Liquid scintillation methods offer high counting efficiency and ease of sample preparation, and large numbers of sample can be processed, but they suffer from low resolution and high background. Almost all liquid scintillation methods for determination of ^{226}Ra, with few exceptions, are based on determination of its daughter ^{222}Rn. These take advantage of the considerable solubility of radon in organic solvents, including scintillation cocktails. The sample may be kept in a closed container for at least 25 days to establish secular equilibrium with radon, ^{222}Rn being extracted into the scintillator solution and counted after 3 hours.[3,4] Alternatively, small volumes of sample can be mixed directly with the scintillation solution and then counted.[5,6] Radium may be preconcentrated either by using a cation exchange resin,[7] the resin being mixed directly with scintillator, or by coprecipitation as $Ba(Ra)SO_4$ which is subsequently dissolved in EDTA and mixed with scintillator.[8,9] Extractive scintillator methods find little application for ^{226}Ra determination since radium forms few organically–soluble complexes although an extractive scintillator containing the crown ether dicyclohexano-21-crown-7 has been used.[10] ^{226}Ra may be determined via its α-emission by heterogeneous counting after its separation as $RaBaCl_2$[11] or its α-emitting daughter ^{214}Po without separation.[12] Liquid scintillation procedures used for ^{226}Ra suffer from quenching effects and interferences from other isotopes present in the counting vial (e.g., other radium isotopes).

Cerenkov radiation produced when an energetic β-particle enters a medium at a velocity greater than the speed of light in that medium can be detected by the light detection systems used in liquid scintillation spectrometers.[13] Alpha-emissions do not produce Cerenkov radiation, but ^{214}Bi and ^{214}Pb (daughters of ^{226}Ra via ^{222}Rn) do since they emit β-rays with E_{max} of 1.0–3.26 and 0.65–0.98 MeV, respectively, well above the Cerenkov threshold energy (265 keV in water). This effect has been utilized for the determination of ^{222}Rn in water samples, radon being extracted into 20 ml of toluene which is counted 2 hours after extraction.[14] The method can also be used for ^{226}Ra determination but storage and agitation with large volumes of water is required. In the proposed method, the Cerenkov signal produced

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by ^{214}Bi and ^{214}Pb in secular equilibrium with ^{226}Ra, is used for determination of the latter. Radium is separated as $Ba(Ra)SO_4$ from the sample which is dissolved in 15 ml of 0.3M EDTA and the Cerenkov signal counted using the tritium channel of a liquid scintillation counter. Any liquid scintillation counter can be used as there is no need either for pulse shape analysis (PSA) or high resolution. Liquid scintillation cocktails are not involved, and large volumes of sample can be processed. Unlike liquid scintillation counting, the Cerenkov process is unaffected by chemical quenching and has a lower background.

Experimental

Materials and equipment: ^{226}Ra standard solution was supplied by Amersham International and ^{228}Ra and ^{224}Ra samples were prepared from an aged ^{232}Th sample (in excess of 30 years). Carrier solutions and other reagents utilized A.R. grade materials and deionized water. All counting operations were carried out using a Packard Tricarb 1900 CA liquid scintillation analyzer.

The method: Variation of the count rates with time of three radium isotopes; ^{224}Ra, ^{228}Ra and ^{226}Ra separated as barium (radium) sulphate and counted in EDTA solutions is shown in Fig. 1. The count rate, C_1, after about 25 days is entirely due to ^{228}Ac (the daughter of ^{228}Ra) and ^{214}Bi and ^{214}Pb, the daughters of ^{226}Ra. If the barium (radium) sulphate is reprecipitated and counted (C_2) after a period of time t (days) where ^{228}Ra is in secular equilibrium with its daughter ^{228}Ac, the count rate is all due to ^{228}Ac and build-up of ^{226}Ra daughters. From the difference between the count rates, the build-up of ^{226}Ra daughter activities can be measured and then ^{226}Ra activity can be determined. ^{226}Ra activity is determined from the following expression:

$$^{226}Ra\ (Bq \cdot l^{-1}) = (C_1 - C_2)/Y_{226} \cdot R \cdot e^{-0.693/t_{1/2}} \qquad (1)$$

where C_1, C_2 – count rate, counts $\cdot s^{-1}$,
Y_{226} – Cerenkov counting efficiency of ^{226}Ra daughters (^{214}Bi and ^{214}Pb) in secular equilibrium
R – chemical recovery of radium determined gravimetry using standard barium carrier solution,
t – time after second coprecipitation (days),
$t_{1/2}$ – half-life of ^{222}Rn, days.

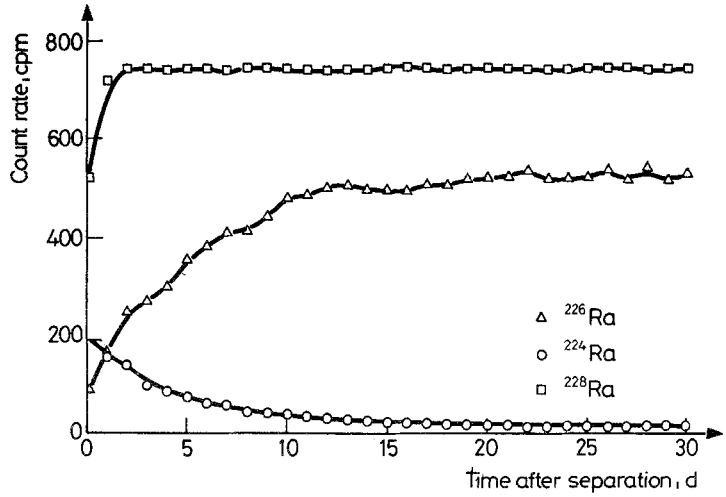

Fig. 1. Ingrowth and decay of Cerenkov signal

Separation procedure: The radium barium sulphate method is widely used for separation of radium from other elements[15,16] but the procedure described here is slightly modified:

(1) 1 ml of lead carrier (30 mg/ml, nitrate solution), and 1 ml of barium (5 mg/ml chloride solution, standardized) is added per 1 l of water sample which is then heated to boiling,

(2) 20 ml of 9M H_2SO_4 is added to the sample while it is stirred. The sample is heated further for 10 minutes and then left aside for 4 hours. The supernatant is discarded and the $PbSO_4$–$BaSO_4$ precipitate is washed twice with 0.1M H_2SO_4 and dissolved with 15 ml of basic solution of EDTA (0.3M), the sample being heated to assist dissolution,

(3) 1 ml of ammonium sulphate (200 mg/ml) is added to the sample while it is stirred and acetic acid (glacial) is added dropwise until precipitation begins when a further 2 ml is added. The sample is digested for 5 minutes,

(4) the precipitate is washed twice with cold water and then transferred to a clean beaker for drying. The weight of $BaSO_4$ is measured to determine the chemical recovery,

(5) the precipitate is dissolved in 15 ml of EDTA and after 20 days storage the count rate C_1 is measured for 200 minutes using the tritium channel of a liquid scintillation counter,

(6) the sample is transferred quantitatively to a 5 ml beaker where barium sulphate is reprecipitated as described in points (3) and (4) and after 2 days the sample is counted again, C_2.

Results and discussion

Cerenkov radiation produced by ^{214}Bi and ^{214}Pb is measured in order to determine ^{226}Ra activity. This is a modification of the method described by GODOY[17] in which ^{228}Ra and ^{224}Ra are determined using Cerenkov counting, ^{226}Ra being regarded as an interference. In order to achieve good results using this method, two steps are required. First, a separation of radium from other interfering elements; any separation method can be used but coloured salts should be avoided since Cerenkov light is colour quenched. Separation using the barium (radium) sulphate precipitation technique is the best since high chemical recovery can be achieved and monitored gravimetrically and the precipitate is easily recrystallized to allow a quick separation from other elements. The second requirement is that two counting steps be performed in order to correct for ^{224}Ra and ^{228}Ra daughters. If ^{224}Ra is absent from the

Table 1
Cerenkov counting efficiency of ^{214}Bi and ^{214}Pb in EDTA

Counting condition	Counting efficiency,* %
Plastic vial stored at 18 °C	77.25 ± 0.96
Plastic vial stored at 3 °C	90.12 ± 0.29
Glass vial stored at 18 °C	111.62 ± 0.42

*Mean of five samples $\pm 1\sigma$.

original sample, the recrystallisation step is not necessary, the sample simply being counted twice, at two days and one month after separation. For samples containing only ^{226}Ra, the samples need only be counted once one month after separation.

In this method, ^{214}Bi and ^{214}Pb are Cerenkov counted in EDTA solution. The actual counting efficiency was difficult to determine since the absolute radon activity present in the EDTA soolution is not known since some radon may escape. Cerenkov counting efficiency of ^{214}Bi and ^{214}Pb determined under different conditions is shown in Table 1. The higher value observed at low temperature is due to the increased solubility of radon. Glass vials gave higher counting efficiency since permeation through the vial walls is zero. In general, this counting efficiency is high compared with other methods, e.g.,

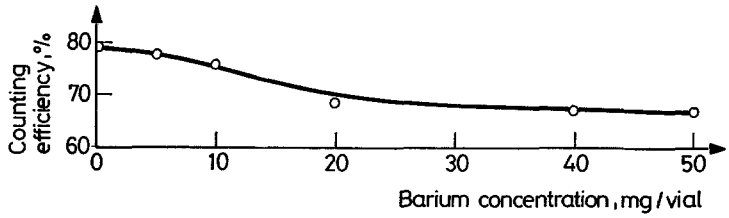

Fig. 2. Effect of barium concentration on Cerenkov efficiency

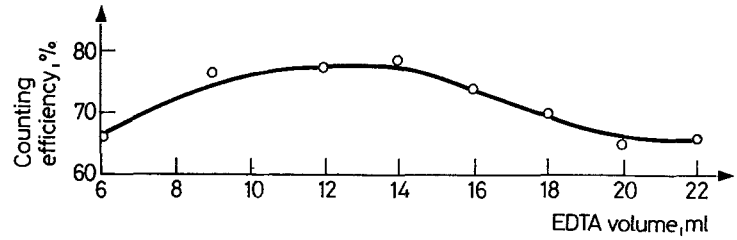

Fig. 3. Effect of EDTA volume on Cerenkov counting efficiency

α-spectrometry. Cerenkov counting efficiency was also determined using a wide range of ^{226}Ra activities, and a value of (73.66 ± 1.93)% was obtained. Variation of Cerenkov counting efficiency with concentration of barium used as a carrier is shown in Fig. 2. An unexpected relationship was observed where an increase in reagent concentration should increase the counting efficiency[18] but in this case the counting efficiency has decreased. Barium ions may act in two different ways; increase in concentration increases refractive index and the counting efficiency but may decrease radon solubility in the solution. The latter effect seems to be more effective in this case. Detection of Cerenkov light is sensitive to sample volume, increasing slightly with volume.[13] Figure 3 shows the expected effect up to a sample volume of 15 ml and a small unexpected decrease thereafter.

A background count rate of (12.00 ± 0.347) counts · min^{-1} was determined; using 3σ of the background and 500-minute counting time, this corresponds to a lower limit of detection value (LLD) of 17.4 mBq · l^{-1}. This value is lower than those for liquid scintillation methods based on radon measurement,[3–7] but higher than those using pulse shape analysis (PSA).[10,11]

Barium sulphate has a known tendency to coprecipitate species other than radium isotopes, e.g., uranium and thorium.[18] This is especially likely to occur if an amount of barium carrier greater than 5 mg is used. ^{238}U and ^{234}Th may coprecipitate with barium sulphate and Cerenkov radiation due to their short-lived daughter ^{234m}Pa ($t_{1/2}$ = 1.17 min) may be produced. Another thorium isotope which may produce interference is ^{228}Th which decays to give β-emitters such as ^{212}Bi and ^{212}Pb via ^{224}Ra. These interferences may be removed by reprecipitating the barium (radium) sulphate with acetic acid; it is recommended to use not more than 5 mg of barium.

Two types of spiked samples were examined. One contained only ^{226}Ra and the other contained ^{224}Ra and ^{228}Ra along with ^{226}Ra. Table 2 shows some of the data. No significant difference of accuracy was observed for the two types of samples, suggesting that there are no interferences from other radium isotopes. Some negative values of accuracy were observed, possibly due to radon escape from the plastic counting vial. A mean recovery of (85.90 ± 7.73)% was observed for ^{226}Ra.

The method can be used for determination of ^{224}Ra and ^{228}Ra where the following procedure can be used:

Table 2
Spiked water samples

^{226}Ra added activity, mBq · l^{-1}	^{226}Ra measured activity, mBq · l^{-1}	Chemical recovery, %	Accuracy,* %
No interferences			
54	55	87.31	1.13
109	111	84.10	1.44
219	210	74.56	–3.94
764	733	97.34	–4.09
873	918	94.33	5.14
1091	1131	91.63	3.86
With interferences			
219	231	77.82	5.48
764	721	87.63	–5.57
873	808	79.20	–7.40
982	988	86.15	0.61
1091	1060	94.26	–2.84

$$*\text{Accuracy (\%)} = \frac{(\text{Measured activity} - \text{Added activity})}{\text{Added activity}} \times 100.$$

Table 3
Some environmental ^{226}Ra activities

Location	Type of water	^{226}Ra,* mBq · l^{-1}	
		Cerenkov counting**	Liquid scintillation counting
Coniston	Lake	9.91 ± 1.12	7.04 ± 0.03
Windermere	Lake	–	6.85 ± 0.74
Yewdale Beck	Stream	11.69 ± 1.34	12.81 ± 2.39
Red Dell Beck	Stream	–	10.00 ± 0.02
Coniston	Spring	13.61 ± 1.05	12.15 ± 2.22
Shap Wells Hotel	Well	12.18 ± 0.81	13.65 ± 1.51

*Mean of two samples ± 1σ.
**Two-liter samples.

Radium isotopes are separated by coprecipitation on barium sulphate which is dissolved in 15 ml of EDTA solution and the Cerenkov signal produced by the build-up of ^{224}Ra daughter β-activities (^{212}Bi and ^{212}Pb) is counted directly for ^{224}Ra determination. For ^{228}Ra determination, the barium (radium) sulphate is reprecipitated after storage time of 25 days, dissolved in EDTA, and counted 2 days later.

Data obtained from application of the method to determination of ^{226}Ra in some natural waters are shown in Table 3 and compared with results from a liquid scintillation method.[11]

Conclusion

^{226}Ra activity can be quantitatively measured by Cerenkov counting via its β-emitting daughters ^{214}Bi and ^{214}Pb. Interferences from other radium isotopes can be easily avoided giving the method an advantage over liquid scintillation. This method also allows determination of ^{228}Ra and ^{224}Ra provided standard solutions of ^{228}Ra and ^{224}Ra are available. High counting efficiency and chemical recovery can be achieved. The method can be used for any type of sample which ultimately can be obtained in aqueous form. As in the case of most liquid scintillation methods a disadvantage is the delay time (about one month) required to establish secular equilibrium.

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