



Influence of Ba concentration on Ra and ^{210}Pb extraction from aqueous samples using EMPORE[®] radium RAD disks

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Abstract

The separation procedure for Ra isotopes and ^{210}Pb from water using the EMPORE[™] radium RAD disks is very quick and convenient. However, higher levels of the chemically similar Ba in the water at least partly prohibit the uptake of Ra and ^{210}Pb , hampering the correct determination of these radionuclides. This investigation shows that the decrease of extraction yield in dependence of the Ba mass is much slower for Ra than for ^{210}Pb : With a Ba content ≤ 1 mg in the water sample, ^{226}Ra could be separated completely, ^{210}Pb , however, showed a decreasing recovery already at 0.1 mg Ba addition.

Keywords Radium RAD disk · Ra and ^{210}Pb recovery · Ba content of water samples

Introduction

The naturally occurring radium isotope ^{226}Ra , member of the ^{238}U decay series, has always been one of the most important radionuclides in environmental surveys and public health studies. Concerning public health, the ingestion of the α -emitting ^{226}Ra via foodstuff and especially via drinking water was—and still is—of major concern. The measurement of ^{226}Ra in water samples usually was done via its daughter products: after sealing the sample for about 2 weeks, ^{222}Rn together with its short-lived progeny ^{218}Po and ^{214}Po (both also α -emitters) have grown into radioactive equilibrium and were easily measurable by different methods, as e.g. in a Lucas cell, in an ionisation chamber or by liquid scintillation counting (LSC). On the other hand, the radiotoxicity of the β -emitting ^{228}Ra , a ^{232}Th progeny, has long been underestimated. Moreover, as the betas of ^{228}Ra have rather low maximum energies of 39.0 keV (60%) and 14.5 keV (40%), the cumbersome standard procedure for its determination was to separate its daughter product ^{228}Ac (maximum β -energy of 2.1 MeV) and to measure it instantly because of its short half-life of 6.13 h.

The determination of radium isotopes in aqueous samples has become very convenient since radium RAD disks

(EMPORE[™]) have been available: the acidified sample is sucked through a 47 mm diameter PTFE membrane holding chromatographic particles containing a 21-crown-7-ether, and the Ra isotopes (as well as ^{210}Pb , a radionuclide also important in view of radiation protection when investigating drinking water) are held back in the membrane. The EDTA solution used to eluate these radionuclides is then mixed with a scintillation cocktail and subsequently measured by LSC (liquid scintillation counting) (see e.g. [1–3] and literature cited there). For a sample volume of 1–1.5 L and a counting time of 1000 min the LLD value (lower limit of detection, i.e. 3σ of the background) for ^{226}Ra is 0.7 mBq per sample. For the beta-emitters ^{228}Ra and ^{210}Pb the LLD is 4 and 2 mBq per sample, respectively [1].

The LSC method usually does not allow the addition of α - or β -emitting spikes due to poor energy resolution. Therefore, repeated extraction of sub-samples from different tap waters with known amounts of the respective isotopes added were used to determine the chemical yield. Using 7 mL alkaline (pH = 10) 0.25 M EDTA solution for the elution step, yields of 95–100% were obtained for Ra isotopes and ^{210}Pb [2]. When an additional γ - or ICP-MS measurement is possible, ^{133}Ba or a minor amount of stable Ba can be used as a tracer for Ra, as Ba and Ra have similar chemical characteristics and ionic radii [4–8].

The RAD disks have a very large capacity for radium, but the quantitative maximum value has never been determined. Smith et al. (1997) were able to load 74 Bq of ^{226}Ra onto a smaller radium RAD disk (25 mm diameter),

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larger quantities could not be investigated due to laboratory-imposed activity limits [5]. But based on this result it was clear, that capacity of Ra uptake would not be a problem when investigating drinking waters or mineral waters.

Scarpitta and Miller [4] and Smith et al. [5] also investigated the potential interference of different mono- and bi-valent cations with Ra uptake. When the sample is acidified to only 0.1 M HNO₃, 1 mg of lithium, magnesium or calcium dissolved in the sample do not lessen the radium uptake to the membrane. However, 1 mg of sodium decreases the Ra uptake to 87%, while 1 mg of ammonium or potassium lower the Ra uptake to 15 and 7%, respectively. When the sample is acidified to 2 M HNO₃, the decrease of Ra uptake is diminished: the effect of 1 mg sodium is negligible, while 1 mg of ammonium or potassium lower the Ra uptake to 49 and 45%, respectively. 0.1 mg of potassium, ammonium, sodium or strontium have no influence on the Ra uptake also at lower (0.1 M) acidity. Special emphasis was given to barium: at lower acidity (0.1 M HNO₃) a mass of 1 mg showed no influence, while 10 mg reduced the Ra uptake to 84%. From 2 M HNO₃ samples the reduction was again lower: 97% and 45% Ra uptake for 1 mg and 10 mg barium mass, respectively. In contradiction to Smith et al. [5], Schönhofer and Wallner [1] could not find any retention of uranium, thorium, polonium or plutonium on the RAD disk.

Scarpitta and Miller [4] also found out, that with 0.25 M basic EDTA solution not only Ra and Pb, but also Sr and Ba can at least partly be eluted from the membrane: they give a recovery of 85% for Sr and 20% for Ba.

In the papers investigating interferences with other ions [4, 5], mostly “artificial” water, i.e. deionized water with deliberately added salts, or tap waters from public water pipelines were used. When investigating waters with high ionic load such as brines or flowback wastewaters, Nelson et al. [9] compared different methods of Ra determinations, among them also the radium RAD disk method, which proved false probably due to high Ba²⁺ concentrations (among other abundant ions).

For drinking waters (tap water or mineral waters) in the EU the maximum permissible Ba concentration is 1.0 mg/L or 1 ppm (Commission Directive 2003/40/EC) [10], so false Ra results due to high Ba concentrations should not occur. There are, however, mineral waters which clearly exceed this limit [11–13]. Therefore, it was found worthwhile to re-investigate the Ra recovery in dependence of the Ba concentration in the water sample. As the used ²²⁶Ra-solution was purchased already in the 1990s a certain amount of ²¹⁰Pb (half-life 22.3 years) has since then grown in, enabling to present not only Ra, but also ²¹⁰Pb recoveries in the presence of higher Ba levels.

Experimental

This paper describes the extraction of Ra isotopes and ²¹⁰Pb from “normal” water, i.e. tap water containing a known amount of different ions, as many investigations with radioprotection background deal with drinking water or mineral water. The Viennese tap water originates from large mountain springs in the Rax and Schneeberg region in southern Lower Austria and Styria, and from the Hochschwab region (Styria). These areas are dominated by calcareous sedimentary rock, so the most abundant dissolved elements are Ca (49–73 mg/L) and Mg (13–18 mg/L), while the Pb concentration is below 0.001 mg/L.

Following the instructions given by the manufacturer of the EMPORE® radium RAD disks [14], ²²⁶Ra (together with ²¹⁰Pb) was extracted from 1.2 L 2 M HNO₃ solution, consisting of 166 mL HNO₃ conc. (65%) and 1034 mL tap water. The RAD disk was placed on a glass filter plate (diameter 50 mm, porosity 100–160 microns) in a 250 mL filtration attachment (Schott/Duran™) on top of a vacuum flask with a capacity of 1 or 1.5 L. The vacuum flask was connected to a water-jet vacuum pump.

To check the reproducibility of the whole procedure, in a first step the averaged ²²⁶Ra and ²¹⁰Pb yield of 6 identical samples was determined by sucking the sample containing 970 mBq (± 5%) of ²²⁶Ra with moderate speed (1L in about 30 min) through a radium RAD disk, where ²²⁶Ra and its ingrown progeny ²¹⁰Pb are bound to the crown ether immobilised on the membrane. The radionuclides were eluted with 5 mL alkaline (pH = 10) 0.25 M EDTA solution. The elution step was repeated, as 5 mL is a rather low amount compared to the membrane surface, and so the first elution probably will not be complete with regard to ²²⁶Ra and ²¹⁰Pb recovery (see also [15]). On the other hand, a larger amount of elutant is not advisable due to the fact, that 5 mL of 0.25 M EDTA is the maximum amount miscible with 16 mL of the scintillation cocktail OptiPhase HiSafe® 3 (Perkin Elmer) [16].

Both the first as well as the second elution samples were measured with a Hidex 300 SL counter (Hidex™, Finland), using pulse shape analysis for distinguishing between α- and β-counts (the scintillation cocktail AquaLight® by Hidex, optimised for α/β-separation, unfortunately can only be mixed with smaller amounts of 0.25 M alkaline EDTA). Counting times were between 4000 and 9000 s.

The Hidex 300 SL counter is equipped with three photomultipliers surrounding the sample vial (with angular distances of 120° in the horizontal plane) and with suitable coincidence electronics. For betas the triple to double coincidence rate (TDCR), i.e. the ratio of the number of triple coincidences to the number of double coincidences

(i.e. all coincidences) in a convenient counting window is a good approximation of the counting efficiency [17, 18]; the alpha counting efficiency is 100%. When measuring low β -activities, the background (often having a TDCR value different from the sample TDCR) must be subtracted. Here the number of all coincidence counts and the number of triple coincidence counts of the sample measurement as well as of the background measurement are needed for activity estimation [19]:

$$\text{dpm}_{\text{sample}} = \frac{(\text{cpm}_{\text{tot}} - \text{cpm}_{\text{bg}})^2}{(\text{cpm}_{\text{tot}} * \text{TDCR}_{\text{tot}} - \text{cpm}_{\text{bg}} * \text{TDCR}_{\text{bg}})}$$

dpm_{sample}: disintegrations per minute (sample). cpm_{tot}, cpm_{bg}: counts per minute of (sample + background), counts per minute of background; these counts comprise all accepted coincidences (3-coincidences + 2-coincidences). TDCR_{tot}, TDCR_{bg}: TDCR value of (sample + background)-measurement, TDCR value of background-measurement.

To determine the influence of Ba on the Ra and Pb extraction, again 970 mBq ($\pm 5\%$) ^{226}Ra was added to the respective samples together with an amount of Ba between 0.1 and 40 mg (all samples were prepared in triplets). Concerning the radionuclide uptake, the mass of Ba in the sample (and not the Ba concentration) is crucial. Therefore, in the course of this investigation the amount of sample was reduced from 1200 to 120 mL in order to speed up the separation procedure.

The EMPORE® radium RAD disk can be reused up to nine times without losing its extraction capacity [1]. Whenever a new RAD disk came into use, first a sample without Ba addition was processed before it was re-used with different amounts of Ba added to the samples, then again a last sample without Ba was prepared and measured. This was done to check if Ba is eluted from the sample completely or if a Ba “background” can build up in the membrane, as suggested by Scarpitta and Miller [4].

Results and discussion

The averaged activities of the first elutions from 6 identical water samples were (86.5 ± 5.2) % of the added ^{226}Ra activity, and (94.2 ± 7.1) % of the added ^{210}Pb activity. These percentages must be used to correct measured activities of the respective first elutions, as the second elutions (performed to release leftover ^{226}Ra and ^{210}Pb from the re-usable membrane) usually is discarded when measuring low level water samples with long counting times. The corresponding activities in the second elutions were (13.6 ± 1.7) % for ^{226}Ra and (5.1 ± 3.1) % for ^{210}Pb (in third elutions the corresponding values were in the

order of 1%). The higher yield of ^{210}Pb eluted in the first run compared to ^{226}Ra does not come unexpected, as Fons-Castells et al. (2016) found the same behaviour in elution curves performed in 2 mL steps: in the first 4 mL of elution the percentage of ^{210}Pb was higher than that of ^{226}Ra , later the trend was inverted [15].

The ^{226}Ra and ^{210}Pb results of two Ba free samples per membrane (the first and—even more important—the last sample investigated by using the same membrane) were always within the above given uncertainties of the respective average yields, indicating that also Ba is completely eluted from the disk with two times 5 mL alkaline 0.25 M EDTA solution. This is in contradiction to Scarpitta and Miller (1996), who suggested at least a partial retention of Ba on the disk [4].

Table 1 and Fig. 1 show the influence of Ba added to the water samples with respect to ^{226}Ra and ^{210}Pb yields. As Ba and Ra are chemically similar it must be expected (and has already been shown by different authors) that Ba is also bound to the crown ether in the RAD disk [4, 5]. No statistically relevant difference between respective samples containing the same Ba mass, but different Ba concentrations due to different sample volumes (1200 mL and 120 mL) was found, which reassured the use of a smaller sample volume to shorten the experimental procedure.

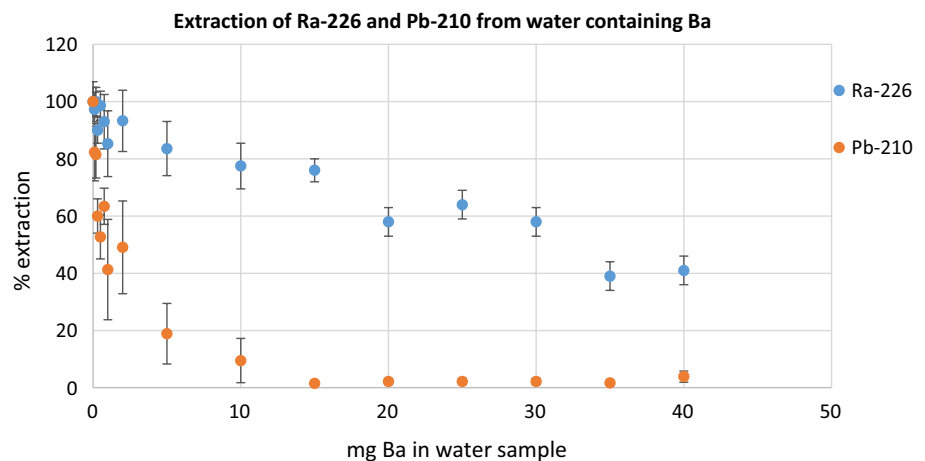
^{226}Ra was completely extracted when Ba additions were ≤ 1 mg, followed by a slow decline of the extraction yield to (41 ± 5) % with 40 mg of Ba present in the water sample. The extraction yield of ^{210}Pb , however, declined

Table 1 Percentages of ^{226}Ra and ^{210}Pb (corrected percentages of the first elutions) separated from water samples containing different amounts of Ba

Ba (mg)	% Ra eluted	% ^{210}Pb eluted
0	100 \pm 5	100 \pm 7
0.1	97 \pm 6	82 \pm 10
0.2	100 \pm 5	82 \pm 8
0.3	90 \pm 5	60 \pm 6
0.5	99 \pm 5	53 \pm 8
0.75	93 \pm 10	63 \pm 6
1	85 \pm 12	41 \pm 17
2	93 \pm 11	49 \pm 16
5	84 \pm 10	19 \pm 11
10	78 \pm 8	10 \pm 8
15	76 \pm 4	1.5 \pm 0.8
20	58 \pm 5	2.2 \pm 1.1
25	64 \pm 5	2.2 \pm 1.1
30	58 \pm 5	2.2 \pm 1.1
35	39 \pm 5	1.7 \pm 0.9
40	41 \pm 5	4 \pm 2

The given errors are 1 σ -errors of the respective average values

Fig. 1 ^{226}Ra and ^{210}Pb extraction yields (corrected yields of the first elutions) as a function of the Ba content in the water samples



much faster: with 1 mg of Ba added, only (41 ± 17) % of the ^{210}Pb could be separated from the sample. With more than 10 g Ba added, the extraction yield was below 10%. This large difference between ^{226}Ra and ^{210}Pb extraction yields came unexpected and has not, to the best of my knowledge, been described in the literature so far.

From these findings can also be concluded, that for aqueous samples the presence or the addition of ≤ 0.5 mg stable Ba for Ra yield determination is possible without a consequential yield shift of the Ra result. But a corresponding ^{210}Pb result certainly will be affected and must therefore be corrected. Yield determination for Ba free samples via measurement of added stable Ba by ICP-MS is possible for both Ra and ^{210}Pb , as in this case the added Ba masses are clearly lower: in most cases they are in the order of a few tens of micrograms per sample (see e.g. [8]).

Conclusions

The extraction yields of ^{226}Ra and ^{210}Pb using EMPORE® radium RAD disks were investigated in the presence of competitive Ba ions in the water samples. With a Ba content ≤ 1 mg per sample, ^{226}Ra could be separated completely, while larger Ba amounts caused a slow decline of the ^{226}Ra recovery. ^{210}Pb , however, showed a decreasing recovery already at 0.1 mg Ba addition. At 10 mg Ba addition only (10 ± 8) % of ^{210}Pb was recovered, in comparison to (78 ± 8) % of ^{226}Ra .

These findings are important with regard to drinking water investigations. As in the EU the maximum permissible Ba concentration in drinking water (tap waters and mineral waters) is 1.0 mg/L, the ^{226}Ra (and of course also ^{228}Ra) determination using radium RAD disks will continue as a convenient and precise method for waters already verified by the authorities with regard to Ba. Even for the small number of mineral waters with elevated Ba levels of a few mg/L the

extraction yield for Ra isotopes will be ≥ 85 %. However, a simultaneous determination of the ^{210}Pb activity can only be preliminary and must be evaluated sceptically as long as information about the corresponding Ba content is not available.

When investigating non-verified waters, the above given results indicate that a measurement (e.g. by ICP-MS) of the sample's Ba concentration is highly recommended. If the derived Ba masses are in the order of milligrams per sample, they can be used to correct the measured Ra values. A sound correction of the corresponding ^{210}Pb values, however, is only possible as long as the sample's Ba mass is ≤ 1 mg, as larger Ba masses cause very large (≥ 40 %) uncertainties of the corrected ^{210}Pb results.

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Declarations

Conflict of interest No conflict of interest to declare.

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