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Application of MnO_2-coated discs in the case of the measurement of ^{226}Ra with alpha-spectrometric method

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Abstract. Among the naturally occurring isotopes the determination of radium is the most difficult ones. In this work some alpha-spectrometric source preparation methods to determine radium were measured. The aim of our work was to investigate the feasibility of MnO_2-coated discs for radium detection with a semi-conductor PIPS detector. This method based on the sorption of radium onto MnO_2-coated surfaces. Parameters of this method were measured, and efforts were made to solve the incidental problems. In the case of using polyamide discs for base material, the executed experiments were showed that it might be applied to detection of ^{226}Ra, however the resolution was weak. It can be caused by the surface roughness and by the width of the MnO_2 coat. In the consecutive investigates we have these parameters changed. Whereas the surface roughness of MnO_2 cannot be changed more, smooth surfaces could produce in another way, so there were took several surfaces into account, like stainless-steel, nickel, copper and chrome plate. Regarding our results - in the case of optimal width of MnO_2 coat – using MnO_2-coated discs is a simple and effective source preparation method in radium measurement.

1. INTRODUCTION

^{226}Ra is the progeny of the ^{238}U, it is one of the key isotopes among natural radionuclides from the radiation protection point of view. Several researchers are examining modern sample-preparation processes throughout the world. It has several causes: for example the low activity concentration in the environmental samples and the complicated source preparation procedure due to alpha spectrometry The average chemical concentration of ^{226}Ra in environmental samples is about 10^{-14} – 10^{-15} g l^{-1}, therefore the factor of sensitivity is an essential point. To determine the ^{226}Ra concentration was investigated several methods, like gamma-spectrometry [1], alpha-spectrometry [2, 3] and radonemanation method [4]. Despite of the difficultness of source preparation methods, the alpha-spectrometry is the best way to measure radium in environmental samples. Therefore developing these source preparation methods is an important task. The most popular and most simple methods are using selective reagent to concentrate radium isotopes. One of these methods is the utilization of the high selectivity of the α-MnO_2 crystal structure. It has been reported by several investigators that the MnO_2 coated manganese fibres can be used to pre-concentrate radionuclides from large water samples [5] and other researchers applied MnO_2 coated polyamide disks for source preparation [6].

In this work we would like to present our attempts on new methods of the source preparation. Various MnO_2 surfaces were used, for example polished MnO_2 surfaces and thin MnO_2 films.

2. MATERIALS AND METHODS

2.1 Radonemanation method

The sample preconcentration was executed via two methods: evaporating 4 l water sample to 180 ml and coprecipitating the radium content of water sample with MnO_2. In case of the latter method 4 l water sample was neutralized and then $MnCl_2$ and $KMnO_4$ was added into the sample under continuous stirring. It was filtered and the precipitate was dissolved in a mixture of HCl and H_2O_2. The efficiency was determined using ^{133}Ba as a tracer via semi-conductor gamma-spectrometry.

After preconcentration procedure, the remained radon content of the sample was removed with inert N_2 gas, the chamber was closed and the sample was stored for 15-20 days. The radon gas generated from the dissolved radium was then flushed into the Lucas-cell using nitrogen. After 3 h the Lucas-cell was measured with EMI photomultiplier tube.

2.2 Alpha-spectrometric methods

2.2.1 Sample preparation method: microprecipitation of Ba(Ra)SO_4

In this method radium was coprecipitated with barium-sulphate, filtered threw a 0.1 μm pore size polypropylene membrane filter where the resulting insoluble sulphates were retained. This filter was measured with semi-conductor (PIPS) alpha detector.

2.2.2 Sample preparation method: adsorb radium onto MnO_2-coated discs

2.2.2.1 Preparation of MnO_2 film onto different materials: PA66 polyamide discs of 30 mm in diameter were used. At first, the discs were washed with ethanol and deionized water accurately. After this cleaning process they were immersed under stirring in 0.08 M $KMnO_4$ solution at 70±5 °C for an hour which generates a thin MnO_2 layer on discs. The discs were then washed with deionized water and left to dry at room temperature.

In the adaptability study we used ordinarily stainless-steel, nickel and chrome discs too. In these cases the concentration of $KMnO_4$ solution was 0.04 M, the temperature was 80±5 °C and the time of the immersion of discs was 2 hour.

2.2.2.2 Source preparation: This source preparation method is based on the adsorption of radium on MnO_2 coated discs. The process was the following: At first the pH value of the aqueous sample was adjust to between 7 and 8. After it, the discs were dipped into a 200 ml plexi beaker containing the sample. Sorption of radium was performed 48 hours continuous stirring at room temperature. Finally the discs were washed carefully with deionized water and left to dry at room temperature. This was measured with Canberra type semi-conductor (PIPS) alpha detector.

3. RESULTS

On Figure 1. some typical spectra can be seen which were derived from the same test water with known ^{226}Ra measurement using different disc materials. At first we studied the adaptability of different materials as a barrier for MnO_2 coat, because in case of MnO_2 surfaces the executed experiments showed that the method can be applied for the detection of ^{226}Ra, however the resolution is low (Fig. 1.a). It can be caused by the surface roughness and by the width of the MnO_2 coat. Whereas the surface roughness of MnO_2 cannot be smoothened more, we had to find other ways to produce smooth MnO_2 surfaces on other materials, like stainless-steel, nickel and chrome plate.

On Table 1 we summarized the FWHM and efficiency values of measurements in case of using different barrier materials.

Table 1. The FWHM and efficiency values of measurements in case of using different barrier materials.

Type of disc	FWHM (keV)	Efficiency (%)
Polyamide	112.1	7.89
Stainless-steel	65.1	4.2
Nickel	60.2	0.1
Chrome	72.1	0.69

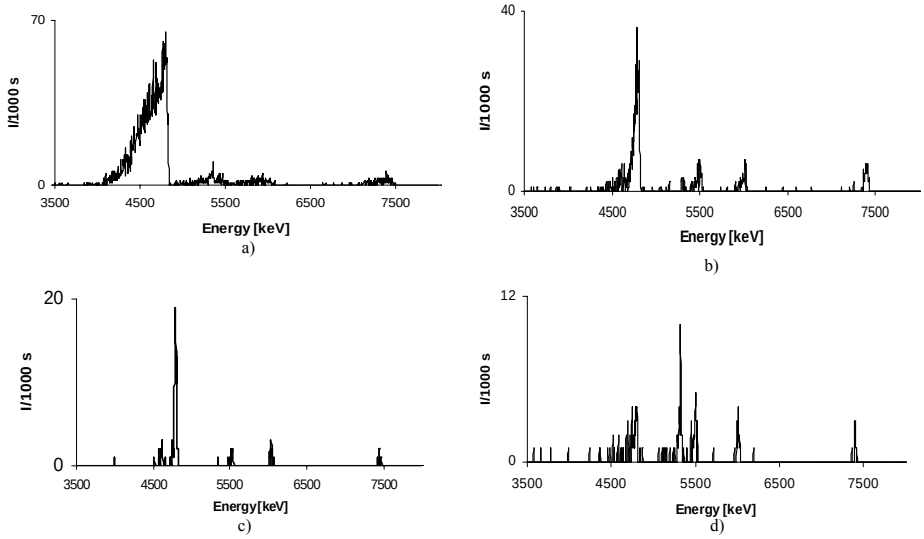

Figure 1. Some typical spectra from water sample with known ^{226}Ra activity in case of applying a) polyamide b) stainless-steel c) nickel and d) chrome disc.

On Table 1. it can be seen that the use of stainless-steel, nickel or chrome barrier result less sum efficiency then using polyamide disc. Although the resolution was better in case of stainless-steel, nickel and chrome barrier, the sum efficiency was smaller. Against the worse efficiency – thanks for the good resolution – stainless-steel discs could be used as a barrier for environmental samples. But the adaptability of using this barrier in case of particular samples more investigation is necessary.

Finally we found that polyamide and stainless-steel discs - with correct wide of MnO_2 coat - can be used for the determination of radium activity concentration.

Following this measurement we compared our previous mentioned methods with alpha-spectrometric method. To compare our applied methods for radium measurement we used 6 test water samples with different ^{226}Ra activity concentrations in a quite wide range (5-50 mBq/l) to get to know the adaptability scale of our methods. Figure 2. shows the results of this comparing investigation. It can be seen that the results can be compared in each cases in a quite wide activity range.

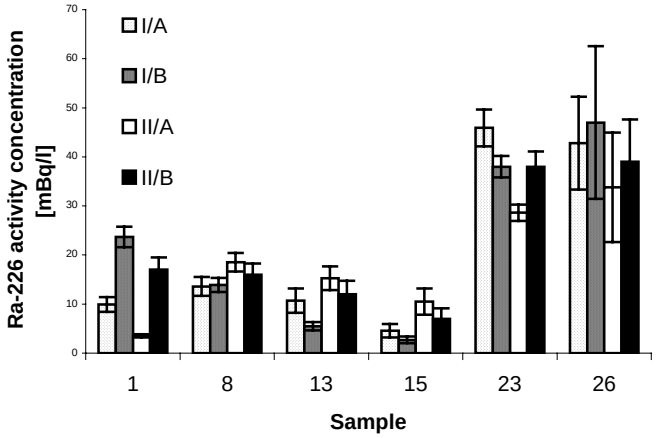

Figure 2. Results of our comparing investigation: determination of ^{226}Ra content of water samples with different methods.

Finally the time demand of the applied methods was compared. Table 2. shows these values.

Table 2. Time demand of our applied measurements for ^{226}Ra measurement.

Method	Sample preparation	Duration of complete analysis [d]	Measurement time [s]	Yield tracer
radonemanation	evaporating	25	2000	
	coprecipitating with MnO_2	22	2000	^{133}Ba
Alpha spectrometry	microprecipitation with $Ba(Ra)SO_4$	3	80000	^{133}Ba
	sorption of Ra onto MnO_2 coated PA disc	3-4	2x80000	inner standard
	sorption of Ra onto MnO_2 coated stainless-steel disc	3-4	2x80000	inner standard

In case of alpha spectrometry the duration of the whole measurement is much more less than in case of the radonemanation method. Although the radonemanation method is cheaper than any kind of alpha spectrometry, in routine analysis time-consume and simplicity are the determinant factors.

4. CONCLUSION

Comparing the new ^{226}Ra determining alpha-spectrometry examinations the efficiency of the sources on polished metal surfaces greatly drops behind the efficiency of the MnO_2-coated polyamide plate applied first by Surbeck and his colleagues. Conversely, due the thinness of the MnO_2 layer and its surface quality the resolution is very good (actually, it has reached the maximum resolution of the detector). The disadvantage of the polyamide disc process is also present by the source preparation method, as it can only be used within restricted chemical conditions (narrow pH range, dependence on other ions present). Even so, they can be satisfactorily used for the ^{226}Ra alpha-spectrometry measurement of drinking waters.

Comparing the time needed and the efficiency of our applied methods, alpha-spectrometry needs more less time, and the efficiency is quite the same. Comparing our two applied alpha-spectrometric methods – microprecipitation with $Ba(Ra)SO_4$ and sorption of radium onto MnO_2-coated PA disc – the latter method needs more less practice.

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