

Determination of long-lived radionuclides in water by alpha spectrometry

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Abstract. This study consists of two parts. The first part deals with the prevention of the silicon detectors contamination for low-level alpha spectrometry by recoil nuclides, which is a serious problem in the measurement of alpha emitters. In this order, we describe the production of the thin formvar films as stopper foils for recoil nuclei. In the second part, analysis of ²²⁶Ra using alpha spectrometry is presented. The requirement for the determination of radium has become a matter of interest in public health due to its hazardous nature with respect to internal exposure. A fast and simple procedure based on sorption of Ra on MnO₂ coated discs which can be used directly for α -spectrometry without the need of further separation and preparation methods is described. The measurements were performed with an ORTEC SOLOIST alpha spectrometer with PIPS detector. Using this method a very good resolution of the alpha spectra was obtained (~23 keV). The reproducibility of the sorption uptake behavior was investigated using samples prepared from a standard radium solution.

Keywords: recoil contamination, formvar, radium, MnO₂ discs, α -spectrometry.

Introduction. Quantification and identification of alpha particle emitting radionuclides with long half-life finds application in many fields such as nuclear decay data measurements, monitoring environmental radioactivity, environmental remediation and decontamination, geological studies, characterization of nuclear waste and radioactive waste management (Hou & Roos 2008). Thus the determination of these radionuclides has become of great importance, especially in water samples (Jobbagy et al 2010), in geological and biological samples (Lee et al 1999), the medical evidence, nuclear materials and radioactive waste (Sill 1987). Radionuclides are an important class of environmental contaminants such for determining their activity and their isotopic composition in different matrices are necessary analytical methods with good precision. In the past years, the field of alpha spectrometry has taken on growing importance in such diverse fields. Alpha spectrometry permits the analyst to identify and quantify alpha-emitting radionuclides from the energy and intensity of the peaks in the acquired alpha-spectra (Bojanowski et al 2005). Alpha spectrometry is characterized by good isotope separation, uniform detector efficiency and very low background. It allows precise measurements at low activities, and easy calibration with yield tracers. This method is an extremely useful and sensitive for detection of alpha-emitting nuclides.

A common problem that specialized laboratories face is contamination of the silicon detectors. This contamination can take place when daughter nuclei from the source surface may escape and accumulate at the detector surface giving rise to peaks in the background spectrum due to their subsequent radioactive decay (van der Wijk 1987). It is important to realize that even α -emitting nuclides ejected by alpha recoil can contribute to alpha background if they subsequently decay to alpha emitters. For example, the direct daughter of ²²⁹Th is ²²⁵Ra which decays by α -emission to α -

producing daughter ^{225}Ac . This unwanted contamination leads to decreased measurement sensitivity causing a degradation of the limit of detection (Vainblat et al 2004). The resulting solution to this problem is periodic replacement of expensively detectors or the prevention of contamination. The effect of detector contamination can be minimized by controlling the chamber gas pressure (Martin & Hancock 2004) or by using a catcher film between the alpha source and the detector (Inn et al 2008). We describe here the production and the use of formvar films as stopper film to reduce recoil contamination of alpha surface detectors.

After preparation of protective formvar films, setting up in this way the method to prevent contamination of detector, we made measurements of alpha spectrometry for determination of radionuclides in environmental samples, respectively we determined radium from aqueous samples.

The determination of radium isotopes in aqueous solutions is of primary importance to human health since these nuclides partially concentrates on human bones by replacing calcium, increasing in this way the internal radiation dose which can cause serious health problems (Eikenberg 2001). The analysis of Ra isotopes is furthermore highly suitable for geochemical applications because the isotopes ^{228}Ra and ^{226}Ra can be used for dating various materials that have been formed in recent times up to a few thousands of years ago. Radium dating provides information on questions of recent climate changes, evolution of volcanic rocks and sediments or growth histories of minerals in the marine environment (Eikenberg et al 2001). Due to the reasons described above, there is a growing interest in the development of improved methods for the detection of radium in aqueous solutions. The principals advantages of α -spectrometry over other techniques is that all α -emitting radium nuclides can be determined directly, there is no need to wait for equilibration, therefore, analysis can be performed in a timely manner, the technique is capable of giving good detection limits on small water and solid samples (Lawrie et al 2000). There are several ways of achieving alpha spectrometric sources such as electrodeposition, microprecipitation, adsorption on manganese dioxide-coated disc.

In the present paper a simple and rapid procedure which was introduced by Surbeck (1995) based on adsorption of Ra onto MnO_2 -coated discs is proposed to carry out the determination of radium in water samples.

Material and Method

Production of the formvar films to prevent recoil contamination

To prevent the recoil contamination we placed thin formvar foils (polyvinyl formaldehyde, $\text{C}_{10}\text{H}_{18}\text{O}_{12}$ purchased from Sigma – Aldrich Co. Germany) between source and detector to stop recoil nuclei. Such foils are used in experimental nuclear physics e.g. for selective transmission of particles (van der Wijk 1987). The films are made using a simple process, by depositing the formvar on glass, stripping the foil from glass, and capturing it with a foil frame.

The preparation process was the following: a 30 g/L formvar solution is prepared in a solvent mixture of chloroform: dichloroethane = 2:3 under stirring at 30°C and stored in a tightly sealed glass vessel to prevent evaporation. A cleaned piece of thin optical glass is firmly fixed in a dip coater. The layers deposit is made by immersing the glass successively in the formvar solution. The solvent readily evaporates from the solution and a thin polyvinyl formaldehyde layer of high homogeneity sticks to the glass surface. Before stripping the foils from the glass the layers are cut into the desired size using a razor blade. For recovering the film the glass is lowered into water under an angle of about 45°. The foil easily releases from the glass, starts floating and can be picked up with a foil frame. Gently lift the frame vertically out of the water and the film is dried on the support frame at room temperature.

Radium determination

Preparation of MnO₂-coated discs. Determination of ²²⁶Ra was carried out by adsorption of Ra on MnO₂-coated discs prepared as follows: discs of a polyvinyl polymer based substrate of 35mm in diameter were washed successively with ethanol, hydrochloric acid and isopropyl alcohol. After this cleaning process they were immersed under stirring in a KMnO₄ solution at 70 °C which causes coating of the disc with a thin MnO₂-layer. Then discs were then washed with distilled water, dried in air and further used in the radium sorption experiments. All discs were prepared according to this procedure.

Description of the analytical procedure. The flow chart of the analytical procedure used for analyses of radium is given in Figure 1. In a typical ²²⁶Ra sorption on a thin film experiment the MnO₂ coated discs were dipped in a glass beaker containing the sample. In our experiments we used samples containing known activity of radium prepared from a radium standard solution. All experiments were carried out taking 50 ml of sample. The amphoteric behavior of manganese dioxide enables to control the adsorption of radium on its surface by regulating the pH conditions. Taking into account this behavior a pH value of 7.5 was selected to ensure a good adsorption of radium. Sorption of radium is performed at room temperature over about 24 h. An exposure time of about 24 hours is sufficient for almost complete sorption of Ra onto the MnO₂-layer of the disc. Following the sorption step, samples were washed with distilled water and left to dry at room temperature. Radium was determined directly by measuring the completely dried disc with α -spectrometer.

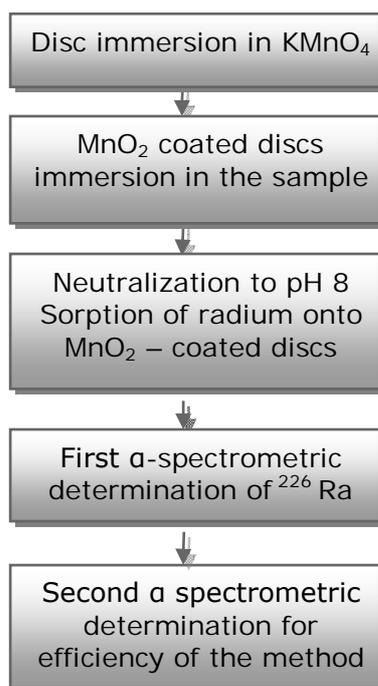


Figure 1. The flow chart of the analytical procedure used for radium analyses.

The measurements were performed with an ORTEC SOLOIST alpha spectrometer with PIPS detector (1200mm² size), the resolution of the detector is 19 keV and the data acquisition was made by ASPEC-927 Dual Multichannel.

Results and Discussion

The use of formvar films as stopper films for recoil nucleus

Contamination of the detector of an alpha spectrometry system can pose severe problems due to the increase of the background and the resulting deterioration of the

minimum detection levels. When an alpha particle passes through a thin foil, the foil on average has "a stopping power" for the particle due to the interactions with the atoms in the foil. This stopping power can be conveniently quantified in terms of the alpha particle energy loss in this foil for a given length of the attenuating material. So the stopping power of the foil varies with the energy of the particles interacting in the foil. Some loose more energy in the foil and some loose less.

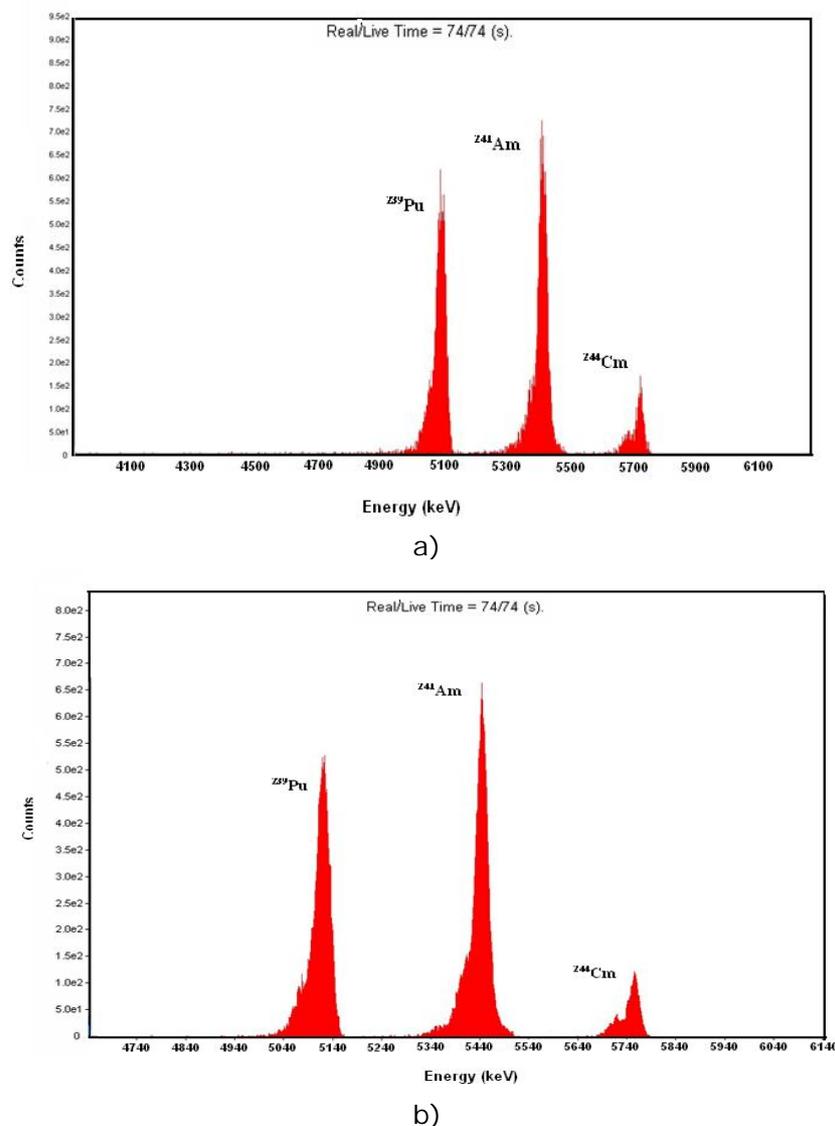


Figure 2. The spectrum of an alpha standard source containing ^{241}Am , ^{244}Cm and ^{239}Pu (Radiochemical Centre Armesham) a) with no stopper foil; b) with formvar stopper foil.

Figure 2 displays the spectra of an alpha standard source containing ^{241}Am , ^{244}Cm and ^{239}Pu without no stopper foil and with a formvar stopper foil. The resolution is the main parameter that deteriorates due to stopper films, but by using a thin formvar film the resolution will not be affected to a great extent as it can be seen in Figure 2. A loss in resolution of only 2-3 keV FWHM was observed.

An additional advantage of using protective films is the possibility to place the source closer to the detector, improving in this way the efficiency. Keeping the background as low as possible will ensure that the best possible detection limits can be achieved. Thus, by using these protective films, one can significantly reduce recoil while losing very little in terms of performance.

The influence of pH on sorption of radium onto MnO₂ coated discs

From literature data it was found that adsorption of radium onto manganese dioxide is decisively influenced by pH value. The effect of pH on ²²⁶Ra sorption on MnO₂ was studied in a previous investigation (Karamanis et al 2006) in the pH range of 2–10, adjusted by adding diluted NaOH or concentrated HNO₃ and their results indicate that the ²²⁶Ra sorption increases with increasing pH and is optimum in the pH range from 4 to 8.5 and decreases thereafter. The range was limited between these limits because of their outside manganese dioxide has a different behavior (Eikenberg 2001). Therefore, at pH values lower than 4, MnO₂-layer may dissolve, and at pH values higher than 8 mineral precipitation (hydroxides and carbonates) can occur. Also OH⁻ groups may be fixed on the surface of manganese dioxide causing the surface complexation reaction of species. This amphoteric behavior of manganese dioxide enables to control the adsorption of radium on its surface by regulating the pH conditions. Taking into account this behavior a pH value of 7.5 was selected to ensure a good adsorption of radium.

The influence of the preparation time of MnO₂ films

In this work we studied the influence of the preparation time of MnO₂ films on adsorption yield of radium. Therefore, to determine the optimal time of preparation of manganese dioxide films we made measurements at different preparation times, maintaining constant the concentration of KMnO₄ solution. In this order this series of experiments was carried for different preparation times, 30, 60, 90 respectively 120 min. On figure 3 is shown the effect of the preparation time of MnO₂ films on adsorption yield of radium. As an optimum for both, spectral resolution and energy intensity, preparation time of MnO₂ films of two hours is recommended for the determination of Ra isotopes. Therefore, in all measurements we used this preparation time.

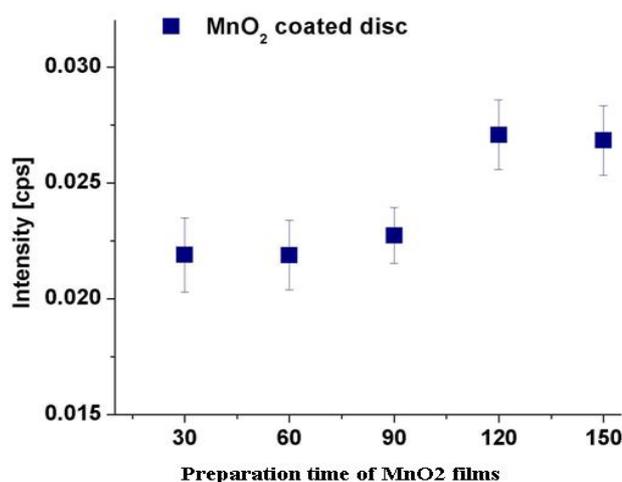


Figure 3. Effect of the preparation time of MnO₂ films on adsorption yield of radium.

The spectrum obtained for two hours preparation time is shown in Figure 4. ²²⁶Ra produces a doublet at 4.602 MeV (5.55%) and 4.785 MeV (94.45%). Also contained in the spectrum are the ²²⁶Ra daughters, ²²²Rn, ²¹⁸Po and ²¹⁴Po.

Analysis of the alpha spectra shows that a very good resolution was obtained (FWHM = 23 keV). So, it was found that this method is suitable to prepare sources to be counted by alpha spectrometry system, since peaks can be isolated very good.

In order to verify the reproducibility of the radium sorption we measured five samples of radium standard solution prepared in the same experimental conditions, respectively same preparation time of manganese dioxide films, same concentration of

potassium permanganate solution and same sorption time from radium solution. On figure 5 are shown the results obtained for these samples and it is clearly indicate almost identical sorption uptake data for the five samples, suggesting a reproducible method.

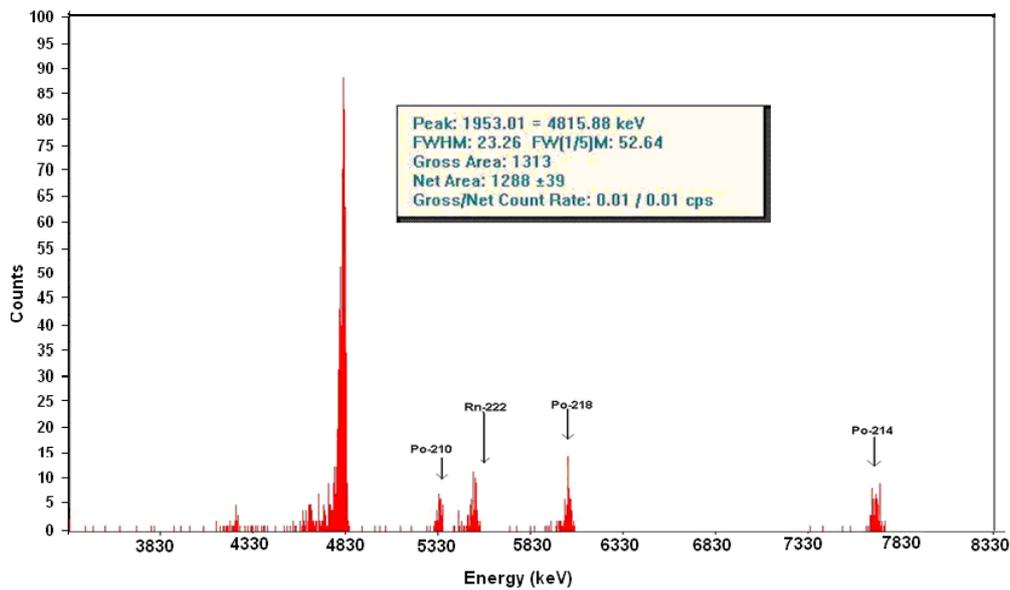


Figure 4. The alpha spectrum obtained for 2 hours preparation time of MnO₂ films.

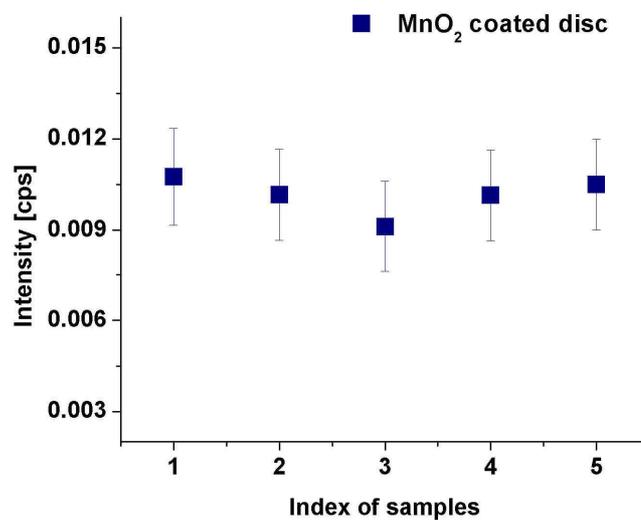


Figure 5. Adsorption yield of Ra on the samples prepared in the same experimental conditions.

In order to verify the percentage of radium adsorption, following these measurements we prepared other MnO₂ coated discs in the same conditions for a second adsorption from the same radium samples. As seen on Figure 6 the obtained values are very low, few of them are lower than our detection limit.

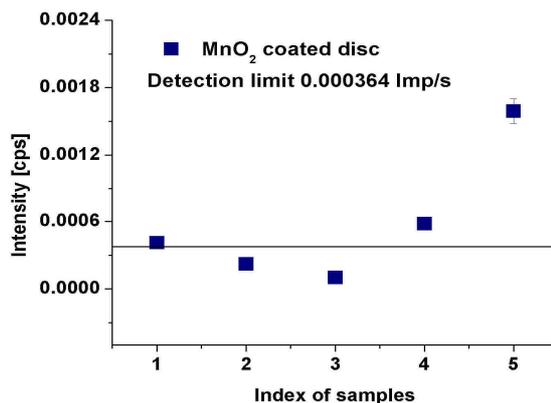


Figure 6. The second adsorption yield of Ra on the MnO₂-coated discs.

As long as chemically similar types of water are analyzed, sorption uptake constants can be determined to calculate the sorption yield or chemical recovery on the sample discs. If, however, further purification steps are included it is recommended to use a spike which is a calibrated standard solutions containing artificially produced isotopes of the element of interest.

Conclusions. High sensitivity is one of the main advantages of alpha spectrometry. This advantage is lost if the detector becomes contaminated. Formvar film has been shown to be a good alternative for prevention of recoil contamination. The process of production of these films is simple and by using this film no significant deterioration of energy resolution will be caused.

The results obtained for radium determination suggest that this method using manganese coated-discs, as a sample preparation method, is quite suitable for determination of radium isotopes from water samples. Due to the thinness of the MnO₂ layer the resolution of the spectra is very good (~23 keV). The reproducibility of the radium sorption uptake behavior was investigated using samples prepared from a standard radium solution and the results obtained indicate almost identical sorption uptake data for the five samples, suggesting a reproducible method.

This method has the potential to be a cheap and fast alternative to other methods available for alpha spectrometry source preparation, therefore future work will focus on radium determination from environmental samples, respectively from mineral water from Romania.

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