Measurement of krypton-85 in water by absorption in polycarbonates

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ABSTRACT

This article describes a method for quantitative measurements of ^{85}Kr in water by absorption in polycarbonates. The method is based on exposure of polycarbonate samples in water and uses the high absorption ability to noble gases of some polycarbonates like Makrofol® and Makrolon® for sampling ^{85}Kr from the water. After the exposure, the radiation emitted from the samples is measured by gross beta counting or gamma spectrometry. The results from the conducted experiments demonstrate a very good linear correlation between the measured signal and the activity concentration of ^{85}Kr in the water. A possible practical application of the method is to monitor ^{85}Kr concentration in water in at-reactor pools and wet spent fuel storage facilities.

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1. Introduction

Krypton-85 (half-life 10.75 y) is a radioactive noble gas produced by fission of nuclear fuel. Most of the ^{85}Kr produced during reactor operation is released in the atmosphere when the fuel is being reprocessed [1]. However, small amounts of its overall production leak from the fuel elements during fuel operation and storage. Krypton-85 is a key reported radionuclide for discharges to the atmosphere from nuclear power reactors and reprocessing plants [2]. During operation and storage of the nuclear fuel ^{85}Kr is first released in the water surrounding the fuel elements. Technologically, these releases are used as an indicator for quick detection of failed fuel in on-line sipping tests [3]. As the concentration of ^{85}Kr in the water surrounding the fuel is related to fuel status, methods for measurement of ^{85}Kr in water are of practical interest. The objective of this article is to present an easy-to-use and cheap method for the measurement of ^{85}Kr concentrations in water. The method is applicable for regular monitoring of ^{85}Kr concentrations in at-reactor pools and spent fuel storage facilities. It has the advantage of being simple to implement and allows simultaneous monitoring at a large number of points in nuclear facilities.

In recent years, the remarkable ability of Makrofol® and other equivalent polycarbonates to absorb noble gases has been successfully used to measure activity concentrations of ^{85}Kr [4], ^{133}Xe [4] and ^{222}Rn [5] in air. Lately, the absorption in Makrofol

has been used for the measurement of ^{222}Rn in water [6]. In this article we present results from experiments in which polycarbonate species of Makrofol® or Makrolon®[1] are exposed to water with ^{85}Kr dissolved in it. The absorption ability of the polycarbonates is used for sampling ^{85}Kr from the water. After the exposure, the polycarbonates are measured by gross beta counting or gamma spectrometry.

2. Experimental

In the conducted experiments identical polycarbonate samples are exposed in 0.7 L gas-washing bottles to water with different activity concentration of ^{85}Kr. Two rectangular plates (3.5 cm × 4.5 cm) of Makrofol (with thickness 0.25 and 0.7 mm) are placed in each bottle, together with 50 g of Makrolon (equivalent to Makrofol material) grains. The grains used in this experiment have the shape of small elliptic cylinders of height 2.65 mm and semi-axes 1.78 and 1.17 mm. Different activity concentrations of ^{85}Kr in the bottles are achieved by two approaches. In the first approach ^{85}Kr is dissolved in water by means of a closed circuit in which air with high activity of source-supplied ^{85}Kr is slowly blown through the water. Later, the bottles are filled with that water and krypton-free distilled water in different proportions. In the second approach each bottle is filled with distilled water. Air with ^{85}Kr is slowly blown through each bottle, where different activity of ^{85}Kr is used for different bottles and the blowing time is kept the

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same. As a result, various ^{85}Kr concentrations in the bottles are obtained. The bottles are then hermetically sealed. Special attention is paid to ensure that after the sealing each bottle is entirely filled with water without residual air in it. The activity concentration of ^{85}Kr in the water in each gas-washing bottle is determined after the exposure by gamma spectrometry with HPGe detector (ORTEC, relative efficiency of 24.9% and 1.9 keV resolution for the 1332 keV line of ^{60}Co) in geometry "Marinelli" beaker 450 cm^3 (the 514 keV gamma-line of ^{85}Kr is used for the

analysis). Among eleven different activity concentrations six are prepared by the first approach (three in the range 200–500 Bq L^{-1} and three in the range 5–10 kBq L^{-1}, see Fig. 1 or Fig. 2) and five by the second approach (these are in the range 800–3000 Bq L^{-1}). The exposure time in the experiments is 330 h.

3. Results and discussion

The rectangular plates are measured immediately after the exposure with low-level beta counting system (5 min counting time). The net counting rate due to the absorbed ^{85}Kr in each piece is determined. Fig. 1 shows the correlation between the net counting rate from polycarbonates in different bottles and the measured activity concentration of ^{85}Kr in the water. The polycarbonate grains are measured with HPGe detector in geometry "cylinder" (50 cm^3, centered on the detector cap). The 514 keV gamma-line of ^{85}Kr is used. The quantity of interest in these measurements is the specific activity of ^{85}Kr absorbed in the grains (i.e. the activity of absorbed ^{85}Kr per unit mass of the grains). Fig. 2 shows the correlation between the specific activity of the grains and the measured activity concentration of ^{85}Kr in the water, in which the grains are exposed.

As it can be seen from Figs. 1 and 2, there is a very good correlation between the measured signal from the polycarbonate specimens and the activity concentration of ^{85}Kr in the water for both beta measurements and gamma spectrometry. Therefore, we conclude that quantitative measurements by this method are possible.

As mentioned above, the key feature of the method is that it uses the high absorption ability of polycarbonates for sampling ^{85}Kr from the water. During the exposure, the activity of ^{85}Kr in the polycarbonate increases from zero (at the beginning of the exposure) and the profile of this increase depends on the sorption process. During the desorption process, which takes place after the end of exposure, the activity of ^{85}Kr in the polycarbonate decreases due to decay and outgasing. Therefore, the kinetics of the sorption and desorption processes must be taken into account to achieve favorable conditions for the practical applications of the method. A theoretical and experimental study of the processes of sorption and desorption of radioactive noble gases in polycarbonates is given in Ref. [7], where a theoretical model for the time dependence of the activity of ^{85}Kr in the polycarbonates has been proposed and validated. This model is used hereafter to calculate the time dependence of ^{85}Kr concentration in the polycarbonates during the exposure and measurement steps. Fig. 3 shows the calculated relative activity increase vs. exposure time for polycarbonate plates of different thicknesses exposed in water with constant ^{85}Kr concentration. The curves in Fig. 3 demonstrate that the activity profile depends on the plate thickness and the sorption process is faster for thinner plates. The activity of ^{85}Kr in the polycarbonate increases monotonously to the maximum reachable activity (A_{max}). From practical point of view this means that for a given plate thickness exposure times greater than the corresponding time for reaching A_{max} will not improve the performance of the method. The curves in Fig. 4 demonstrate the decrease in the activity in the plates after the end of exposure (it is assumed that the maximal krypton activity in the plate is reached during the sorption process). Evidently, the decrease is faster for thinner plates and gets much slower for thicker ones. Hence, if the method is applied with thin plates, they have to be measured shortly after the exposure. Thicker plates are more suitable in the cases when the measurement cannot be performed immediately after the exposure or if larger measurement times are necessary. In general, precise quantitative measurements by the proposed method are possible, provided
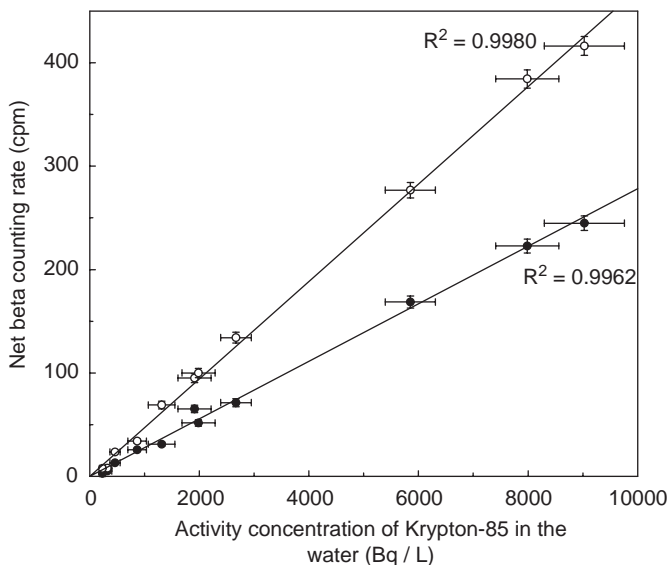
Fig. 1. Correlation between the measured net beta counting rate and the activity concentration of ^{85}Kr in the water for plate Makrofol samples of thickness 0.25 (●) and 0.7 mm (○). The error bars indicate the overall estimated uncertainties. The solid lines represent linear fit of the data $y = ax + b$. The parameters a and b are: $a = (2.78 \pm 0.17) \times 10^{-2}$ cmp Bq^{-1} L, $b = -0.47 \pm 2.43$ cpm and $a = (4.71 \pm 0.24) \times 10^{-2}$ cpm Bq^{-1} L, $b = 0.99 \pm 2.96$ cpm for samples of thickness 0.25 and 0.7 mm, respectively. The uncertainties of the parameters and the error bars in the figure are given at the level of one standard deviation.
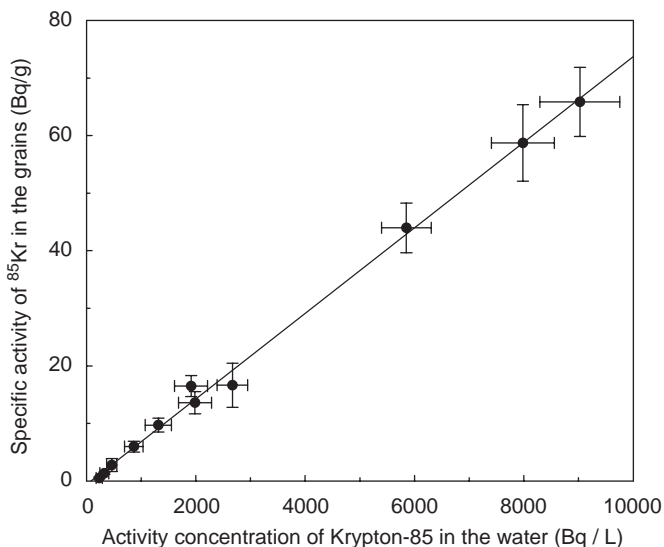
Fig. 2. Correlation between the specific activity of ^{85}Kr in the grains and the activity concentration of ^{85}Kr in the water. The solid line represents linear fit of the data $y = ax + b$, where $a = (7.43 \pm 0.45) \times 10^{-3}$ Bq g^{-1} Bq^{-1} L and $b = (-0.60 \pm 0.60) \times 10^{-2}$ Bq g^{-1}. The uncertainties of the parameters and the error bars in the figure are given at the level of one standard deviation.