

# Radon in Water Measurements Based on Thin Film Adsorption

Heinz Surbeck\* and Jean-Louis Andrey

Federal Office of Public Health, Environmental Radioactivity Survey  
3, ch. du Musee, CH-1700 Fribourg, Switzerland

## ABSTRACT

Radium adsorbing  $\text{MnO}_2$  thin films developed for water analysis show to adsorb radon daughters as well. A 12  $\mu\text{m}$  polyethylene-terephthalate foil is covered on the water side with a  $\text{MnO}_2$  film. On the opposite side a semiconductor detector counts on-line during adsorption alpha particles passing through the foil.  $^{218}\text{Po}$  and  $^{214}\text{Po}$  are well separated in the alpha spectrum measured that way. We get that all radon daughters are adsorbed equally well, but that  $^{214}\text{Bi}$  produced from adsorbed  $^{214}\text{Pb}$  desorbs quickly. Detection efficiency for this type of on-line radon in water measurement can be up to 10 counts/h per Bq/l.

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\*) heinz.surbeck@mbox.bag.admin.ch

## INTRODUCTION

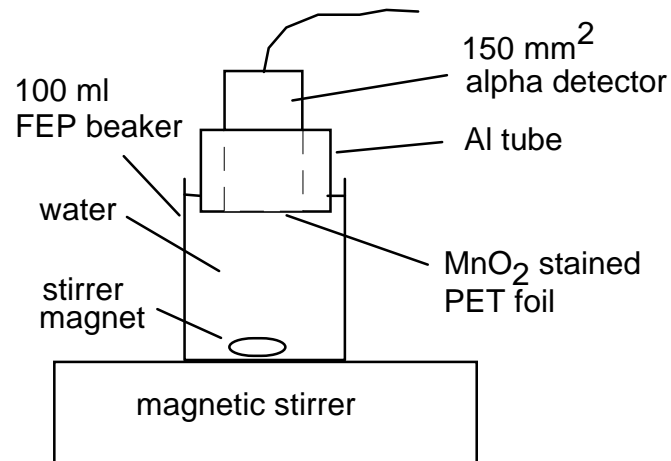
Radium adsorbing thin films have been developed in our lab to make radium determination in aqueous samples easy <sup>1</sup>. The films are formed on a polyamide substrate by exposing it to a hot  $\text{KMnO}_4$  solution. A 20 mm x 20 mm sheet stained on both sides adsorbs within 6 h nearly 100% of the radium present in a 100 ml sample. After exposition the disk is dried and measured with a semiconductor alpha detector. The films are thin enough to allow for high resolution alpha spectrometry. When analyzing samples with elevated radon levels it turned out that also radon daughters are adsorbed with a high efficiency.  $^{214}\text{Po}$  is well visible on films exposed to this sort of samples whereas  $^{218}\text{Po}$  shows only as traces. We first had no intention to use this effect for radon-in-water measurements, but when we started to monitor radium adsorption on-line it popped up that this may be a simple method to monitor radon levels in water. Radium adsorption is measured on-line by placing an alpha detector behind a thin stained polymer foil in contact with the water. The foil thickness is currently 12  $\mu\text{m}$ . This still allows for some spectrometry. During these radium adsorption experiments we frequently noted high counts in the  $^{214}\text{Po}$  energy window. These count rates were far too high to be from adsorbed radium and clearly were due to adsorbed radon daughters. We thus decided to have a closer look at the radon daughter adsorption. It turned out that all radon daughters are adsorbed well. Transfer from solution to thin film happens with a rate that corresponds to a half life of about 40 min. Steady state concentration for  $^{214}\text{Po}$  (in equilibrium with  $^{214}\text{Bi}$ ) on the film is about 10% of the activity contained in a 100ml sample.  $^{218}\text{Po}$  is at a far lower level because of its large decay rate compared to the adsorption rate. With a 150  $\text{mm}^2$  detector placed at some mm from the foil one gets about 1 count/h in the  $^{214}\text{Po}$  window for every Bq/l of  $^{214}\text{Po}$  in the 100 ml sample. With a larger detector and a larger sample volume 10 counts/h per Bq/l may be realistic. It's clearly not a method to detect fast changes at low levels, but it's a simple method to monitor radon daughter product variations at the 10 Bq/l level with a temporal resolution of an hour. With an intermittent flow through the measurement cell one can determine not only radon daughters but also radon. This may be of some interest to determine residence time of groundwater in a water distribution system. Radon daughters are normally not in equilibrium with radon in freshly pumped groundwater and build up during transport and storage.

A more important application of this type of adsorption experiments may be to study adsorption dynamics. There is clear evidence for a different chemical behavior of nuclides that had time to "cool down" after production from their mother nuclide with respect to those freshly produced.

## EXPERIMENTAL

Exposing polyamide (PA66) to a hot  $\text{KMnO}_4$  aqueous solution produces a thin ( $\mu\text{m}$ ) staining that looks like  $\text{MnO}_2$ . Its exact composition is not known but it seems to work like an ion exchanger releasing K when adsorbing divalent cations. PA66 is not available as a thin foil so we tried to stain other foils. The thinnest foils still watertight and mechanically stable we could get are made from polyethylene-terephthalate (PET). Unfortunately they are not attacked even by hot  $\text{KMnO}_4$  solutions. So far the only foil that showed to be stainable is a 12 to 15  $\mu\text{m}$  thick PET foil containing small Al particles evenly distributed in the volume <sup>2</sup>.

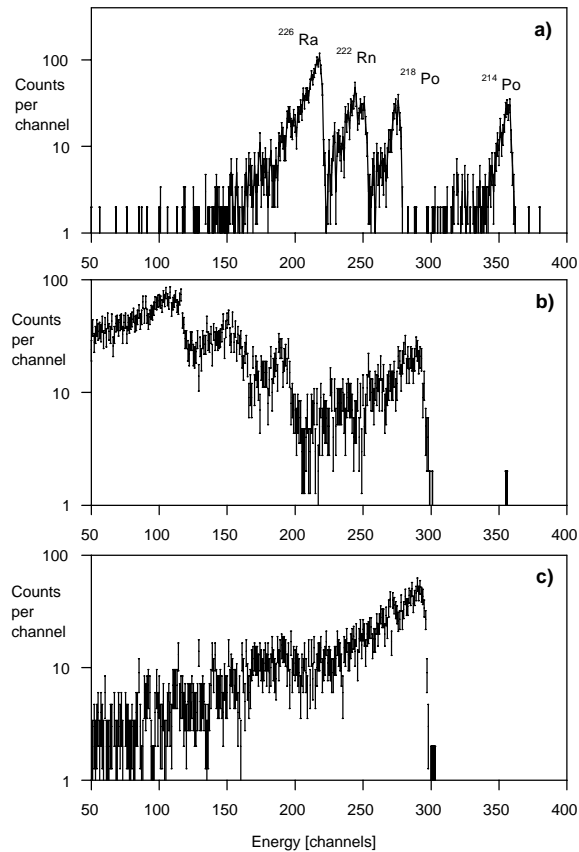
An experimental setup to determine radon daughter adsorption on this foil is shown in Fig 1.



**Fig. 1** : experimental setup. The detector/preamplifier module used is a MOD 01-03/150 from SARAD <sup>3</sup>. The PET foil is stained on its entire surface (app. 15 cm<sup>2</sup>).

## RESULTS

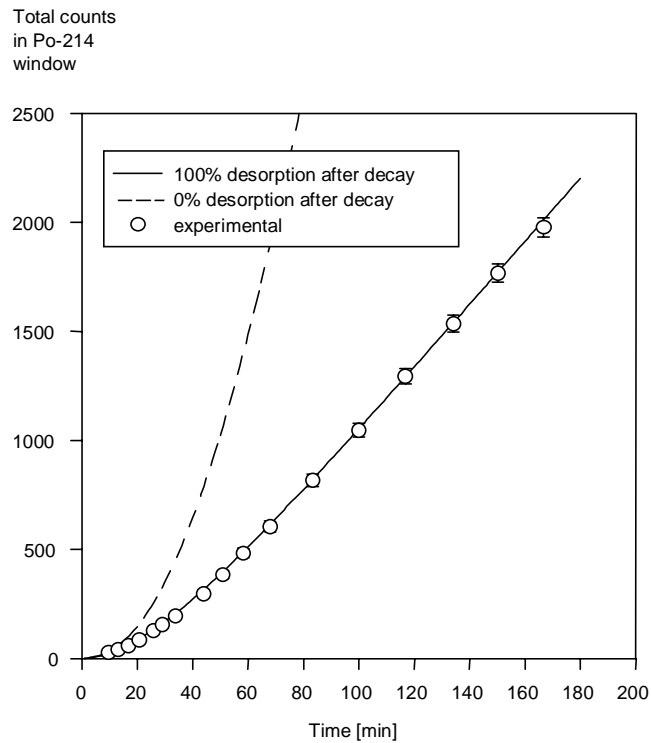
Figure 2 shows how alpha spectra are degraded when the particles have to pass our PET foil. A thin  $^{226}\text{Ra}$  source produced by adsorbing radium on a  $\text{MnO}_2$  film is placed in air at a distance of about 3 mm from the detector surface (spectrum a). Spectrum b) has been acquired with the 12 to 15  $\mu\text{m}$  PET foil placed between the source and the detector. There is a considerable shift in detected energy and a serious tailing, but radon daughters are still well separated.



**Fig. 2 :** a) alpha spectrum for a 20mm x 20mm  $^{226}\text{Ra}$  source at 3 mm in front of the detector, b) alpha spectrum for the same source with our 12 to 15  $\mu\text{m}$  PET foil placed between source and detector, c) alpha spectrum taken with the experimental setup in Fig.1 with about 50 Bq  $^{222}\text{Rn}$  in the water sample. Integration time 10'000 s, started just after filling in the water.

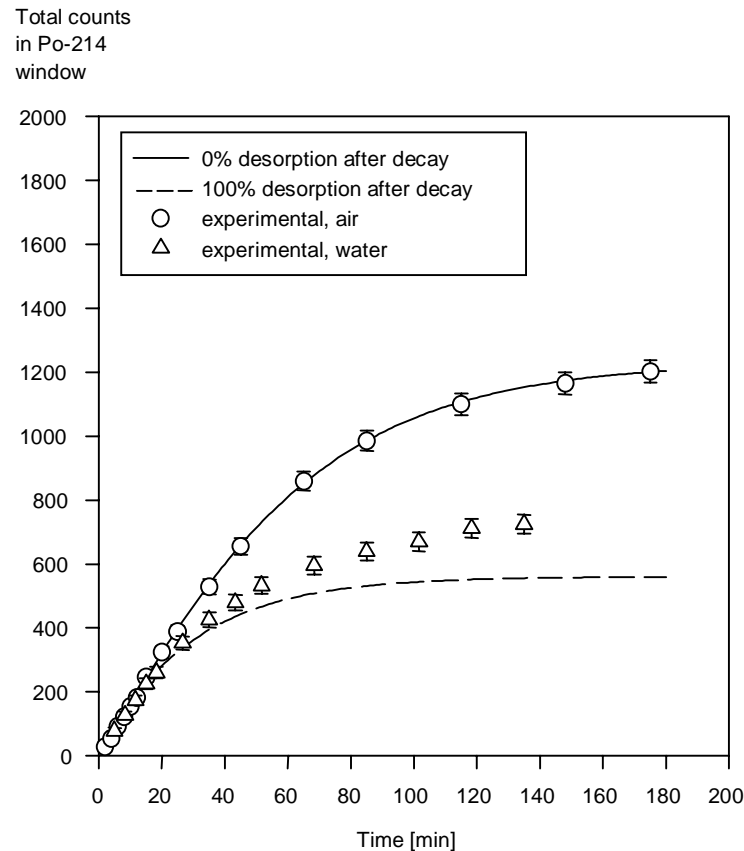
Error bars are +/- 1 sigma counting errors.

When placing the stained foil, mounted in front of the detector, in contact with water containing radon daughters in equilibrium with radon, radon daughters start to be adsorbed on the  $\text{MnO}_2$ . How the spectrum looks like after 10'000 s acquisition time can be seen in figure 2 c).  $^{214}\text{Po}$  is clearly visible, but hardly any  $^{218}\text{Po}$ . Buildup of total counts in the  $^{214}\text{Po}$  energy window is shown in figure 3.



**Fig. 3** : total counts in  $^{214}\text{Po}$  energy window vs. exposition time. Integration started after having filled the beaker with water containing about 50 Bq  $^{222}\text{Rn}$ . Error bars are +/- 1 sigma counting errors. *Solid line* : model assuming complete  $^{214}\text{Bi}$  desorption after being produced from adsorbed  $^{214}\text{Pb}$ . *Dashed line* : model assuming no desorption.

The water sample contains about 50 Bq of  $^{222}\text{Rn}$ . After 10'000 s the water is removed and the acquisition restarted. The resulting buildup of total counts in the  $^{214}\text{Po}$  window is shown in figure 4 ("experimental, air"). The second data set in figure 4 ("experimental, water") results from a modified experimental protocol. Using the same radon concentration as before, the water is replaced after 10'000 s by radon free water.

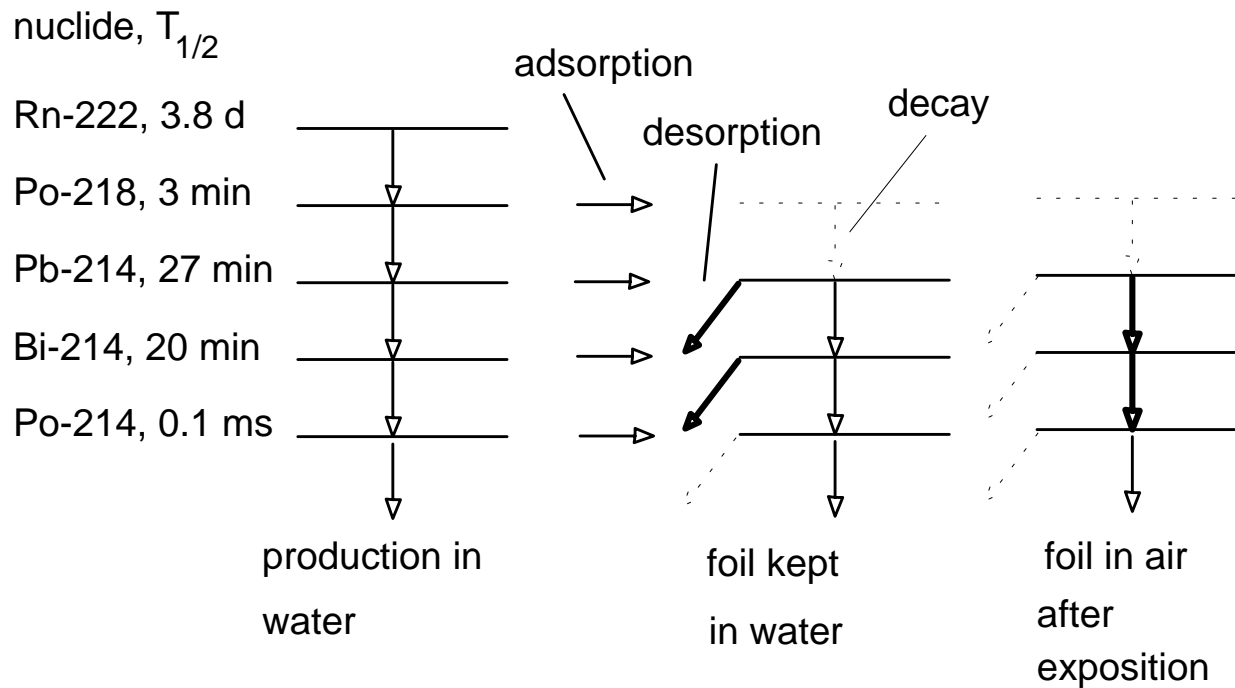


**Fig. 4** : total counts in  $^{214}\text{Po}$  energy window vs. time. For both data sets, the foil has been exposed for 10'000 s to water containing about 50 Bq  $^{222}\text{Rn}$  prior to these measurements. *Circles* : water removed before acquisition started. *Triangles* : radon water replaced by radon free water before acquisition started. *Solid line* : model assuming that  $^{214}\text{Pb}$  as well as  $^{214}\text{Bi}$  stay on the foil after being produced from their respective mother nuclide. *Dashed line* : model assuming that  $^{214}\text{Pb}$  as well as  $^{214}\text{Bi}$  desorb completely from the foil after being produced from their respective mother nuclide. Error bars are +/- 1 sigma counting errors.

## DISCUSSION

From the slope in figure 3 and the known radon concentration one can calculate the radon detection efficiency for this experimental setup. It is around 1 count/h per Bq/l. Steady state adsorbed  $^{214}\text{Po}$  activity is about 10 % of the activity contained in the 100 ml water sample. For  $^{218}\text{Po}$  his figure is around 1%.

More interesting than this steady state is what can be learned about adsorption dynamics from the data in figures 3 and 4. Calculations to fit experimental data are based on the level schematic shown in figure 5.



**Fig. 5** : level schematic used to calculate radon daughter activities.

A good fit can be obtained by assuming that  $^{218}\text{Po}$  and  $^{214}\text{Bi}$  are adsorbed with the same rate ("half live" of 40 min.). Because of its extremely short half live  $^{214}\text{Po}$  is a measure for the adsorbed  $^{214}\text{Bi}$ . After it has been produced from  $^{214}\text{Bi}$  it has no time to diffuse back to the water before it decays. A good fit to the experimental points in figure 3 is only possible if there is either no  $^{214}\text{Pb}$  adsorption or if  $^{214}\text{Bi}$  produced from adsorbed  $^{214}\text{Pb}$  desorbs quickly (solid line in Fig 3). That the latter is true can be seen from the fits in figure 4.  $^{214}\text{Pb}$  is adsorbed as well as  $^{214}\text{Bi}$ . If the foil is kept in the air,  $^{214}\text{Bi}$  produced from  $^{214}\text{Pb}$  stays on the foil ("experimental, air") whereas when in contact with water  $^{214}\text{Bi}$  produced that way desorbs nearly completely ("experimental, water").

To summarize radon daughter adsorption and desorption behavior : "cooled down"  $^{218}\text{Po}$ ,  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  nuclides present in the water are adsorbed with a high efficiency whereas "hot" nuclide resulting from a decay of adsorbed atoms quickly return to the water.  $^{214}\text{Po}$  produced from adsorbed  $^{214}\text{Bi}$  has not enough time to desorb before it decays.

This type of adsorption experiments may be a good way to learn more about chemical differences between "cooled down" and "hot" nuclides.

Back to our radon monitor : with a  $150\text{ mm}^2$  detector placed at some mm from the foil one gets about 1 count/h in the  $^{214}\text{Po}$  window for every Bq/l of  $^{214}\text{Po}$  in the 100 ml sample. With a larger detector, a larger sample volume and a staining limited to the area seen by the detector, 10 to 20 counts/h per Bq/l may be realistic. Its clearly not a method to detect fast changes at low levels, but it's a simple method to monitor radon daughter product variations at the 10 Bq/l level with a temporal resolution of an hour. With an intermittent flow through the measurement cell one can determine not only radon daughters but also radon. This may be of some interest to determine groundwater residence times in a water distribution system. Radon daughters are normally not in equilibrium with radon in freshly pumped groundwater and build up during transport and storage.

## ACKNOWLEDGMENTS

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## REFERENCES

- 1) Surbeck, H., Determination of natural radionuclides in drinking water, a tentative protocol, Sci. Total Environment 173/174, 91-99, 1995
- 2) Sika-Trocal AG, Duding, Switzerland
- 3) Sarad GmbH, Dresden, Germany