# Half-live controlled radon/thoron emanation from $MnO_2$ thin films reduces interference betweeen $^{226}Ra$ and $^{224}Ra$ daughter product alpha peaks.

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## Abstract

$MnO_2$ thin films can be used to selectively adsorb radium ions from water samples. The films are thin enough to allow alpha spectrometry at high energy resolution. There are four radium isotopes present in the natural uranium and thorium series. Three of them decay into a radon isotope by alpha particle emission. As a noble gas radon can diffuse out of the thin film. Because of the very different half-lives, this so-called emanation is very different for the three radon isotopes. Almost all of $^{222}Rn$($^{226}Ra$ daughter,$T_{1/2}$ = 3.8 d) can escape before it decays, while $^{220}Rn$ ($^{224}Ra$ daughter,$T_{1/2}$ = 56 s) and $^{219}Rn$ ($^{223}Ra$ daughter,$T_{1/2}$ = 4 s) decay mainly still adsorbed. The differences have an important consequence in the quantification of $^{224}Ra$ in the presence of comparable $^{226}Ra$ concentrations. Due to the strong $^{222}Rn$ ($^{226}Ra$ daughter) emanation, there is almost no spectral interference of $^{222}Rn$ and its daughter products in the energy region of the alpha peaks of $^{224}Ra$ and its daughter products. This is a great advantage over alpha spectrometry with Liquid Scintillation Counting where the strong spectral interference makes separation very difficult and must be calculated from the beta count rate.

**Keywords :** alpha spectrometry, radium, radon, thoron, liquid scintillation counting

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## Introduction

Thermal water from springs and wells in Switzerland are known to have elevated $^{226}Ra$ activity concentrations, up to some 100 mBq/l (Gainon et al. 2007, Gainon 2008). $^{226}Ra$ has been measured by selective adsorption on $MnO_2$ thin films, followed by alpha spectrometry with a Si-detector (Surbeck 1996, Surbeck 2005). $^{228}Ra$ measurements have been made for only a few of these thermal waters. The main reason for this is the long time span of at least several months required for significant buildup of $^{228}Th$ from $^{228}Ra$ (Eikenberg et al. 2001).

A deep geothermal project in Western Switzerland, going 2000-3000 m down into the Aiguilles-Rouges massif, known for abundant uranium and probably thorium mineralizations (Labhart and Rybach 1974), has created new interest in not only $^{226}Ra$, but also $^{228}Ra$ measurements.

The radionuclide concentrations of the water discharched into a publicly accessible water body must comply with the limits of the Swiss Federal Radioprotection Ordinance. Uranium concentrations in the thermal component are expected to be very low, while measurements of existing wells at this site indicate that $^{226}Ra$ and $^{228}Ra$ may rise close to the limits. $^{228}Ra$ is of particular concern because the the limit for $^{228}Ra$ is a factor of 2.5 lower than the limit for $^{226}Ra$.

Therefore uranium, $^{226}Ra$ and $^{228}Ra$ have to be measured in the water discharged to a publicly accessible water body. The limits specified in the ordinance refer to weekly averages.

The results must therefore be available within about a week so that a decision can be made as to whether the discharge point needs to be changed. There is no time to wait for months until a considerable amount of $^{228}$Th has been built up from $^{228}$Ra.

There are procedures published (IAEA 2014, Dinh et al. 2017) that allow for a rapid determination of $^{226}$Ra and $^{228}$Ra in drinking water by Liquid Scintillation Counting (LSC). However alpha spectrometry by LSC suffers from a very strong spectral interference between alphas from the $^{226}$Ra series and alphas from the $^{228}$Ra series. Alphas from $^{222}$Rn and its daughter products have similar energies as the ones from $^{220}$Rn and its daughter products. This makes it difficult to determine $^{224}$Ra as proxy for $^{228}$Ra in the presence of comparable $^{226}$Ra activity concentrations.

In the course of recent measurements with $^{226}$Ra adsorbed on $MnO_2$ thin films it turned out that only a small fraction of the alphas from $^{222}$Rn and its daughter products is visible in the spectra, even after 20 days. It seems that most $^{222}$Rn has left the thin film before decaying.

This was the motivation for the work presented here: to investigate in more detail what happens to the radium daughter products after the mothers are adsorbed onto the $MnO_2$ thin film. For example, is there an optimal time window for measuring $^{224}$Ra as a proxy for $^{228}$Ra ? According to Elsinger and Moor 1983, Szabo et al. 2012 and Nguyen Dinh et al. 2017 $^{224}$Ra and $^{228}$Ra are strongly correlated.

First results of this research have been presented as poster P 20 at the International Symposium on Geofluids, 7-9 July 2021, virtual event, Budapest, Hungary. (Budapest 2021)

**Materials and methods**

Two different stock solutions were prepared by leaching IAEA RGU-1 and IAEA RGTh-1 respectively. RGU-1 ($^{238}$U : 4.9 Bq / g) and RGTh-1 ($^{232}$Th: 3.3 Bq / g) are finely ground solid reference materials. To 10 g of the reference materials 200 ml deionized water and 5 g $Na_2EDTA$ were added. The solution was then stirred vigorously for 4 hours hours and then allowed to stand for at least two days to allow the solid particles to settle.

The leaching resulted in the following activity concentrations of the stock solutions :
U-stock solution : $^{226}$Ra : approx. 25 mBq/ml.
Th-stock solution : $^{228}$Ra, $^{224}$Ra : approx. 35 mBq/ml.
These values were derived from results obtained with the test solutions.

To prepare the test solutions, 2 ml stock solution, passed through a 0.45 μm syringe filter was added to 98 ml deionized water in a 100-ml Teflon beaker. 20 mg $Na_2EDTA$ was added to keep radium in solution and and 30 mg $NaHCO_3$ to allow for formation of neutral or negatively charged uranyl carbonate complexes. Neutral or negatively charged species are not expected to adsorb on $MnO_2$.

Ra-NucfilmDiscs (Nucfilm GmbH) with an active diameter of 26 mm were exposed to the stirred test solutions for 6 h at room temperature (about 20 C). After drying in air, the exposed discs were measured with a 400 $mm^2$ Si detector module (SARAD MOD 01/03-400) at ambient pressure, where the distance between the disc surface and the detector surface was

5 mm. With this geometry, the counting efficiency, i.e., the fraction of alpha particles leaving and hitting the thin film detector in the direction of the detector, is (20 +/-1) %. Calibration was performed by measuring a $^{230}$Th standard with a diameter of 20 mm at various distances between the source and the detector and using a Monte Carlo simulation to extrapolate to the actual geometry used above.

Ra-NucfilmDiscs are also available from Triskem International (Triskem 2023), but for this work only discs from Nucfilm GmbH were used.

Measuring at ambient pressure avoids contamination of the detector by nuclides ejected from the sample surface by alpha recoil.

The output of the detector module, a near-Gaussian pulse with a FWHM of approx. 7 μs is fed to a 12 bit ADC via a peak-hold circuit. 500 channels are used for the energy range from 2'000 keV to 10'000 keV, giving about 16 keV/channel.
An additional sample (P201) was taken from a well supplying hot water to a thermal spa in Western Switzerland. Previous measurements have shown it to contain comparable activity concentrations of $^{226}$Ra and $^{228}$Ra, respectively, on the order of 100 mBq/l.

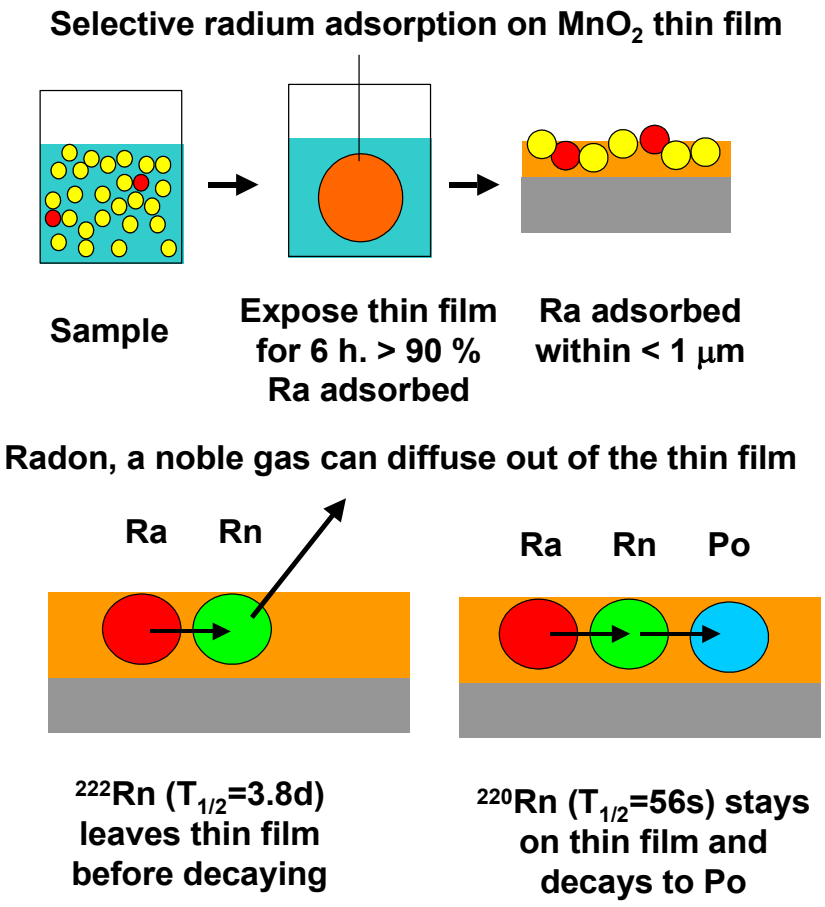



**Fig.1 : Radium adsorption on thin film and radon emanation from thin film.**

## Results

There are four radium isotopes present in the natural uranium and thorium series. Three of them decay into a radon isotope by alpha particle emission. These radon isotopes have very different half-lives, ranging from days to seconds. As a noble gas radon can diffuse out of the thin film. Because of the very different half-lives this so-called emanation is very different for the three radon isotopes. Almost all of $^{222}$Rn($^{226}$Ra daughter,$T_{1/2}$ = 3.8 d) can escape before it decays, while $^{220}$Rn ($^{224}$Ra daughter,$T_{1/2}$ = 56 s, also called thoron) and $^{219}$Rn ($^{223}$Ra daughter,$T_{1/2}$ = 4 s, also called actinon) decay mainly still adsorbed (Fig.1).

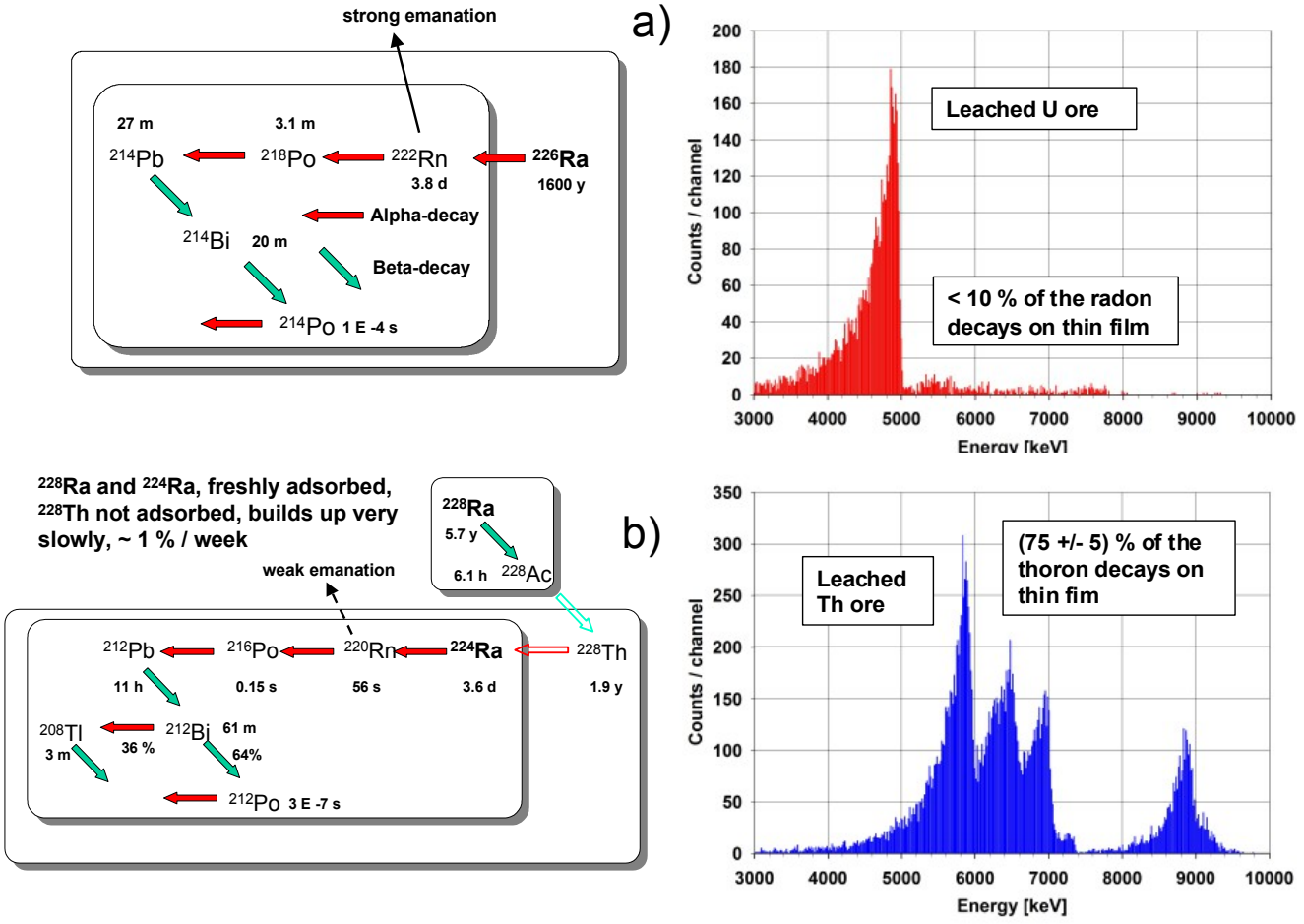
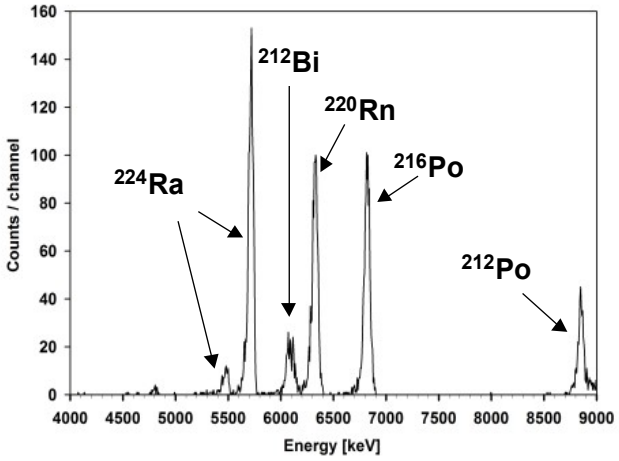



**Fig.2 : a) Alpha spectrum for a U test sample. b) Alpha spectrum for a Th test sample. Both samples are measured at ambient pressure.**

The alpha spectra in Figure 2 clearly show this difference in the emanation factor of radon and thoron, respectively. The diffferences have an important consequence in the quantification of $^{224}$Ra in the presence of comparable $^{226}$Ra concentrations. Because of the strong $^{222}$Rn ($^{226}$Ra daughter) emanation there is almost no spectral interference of $^{222}$Rn and its daughter products in the energy range of the alpha peaks of $^{224}$Ra and its daughter products.

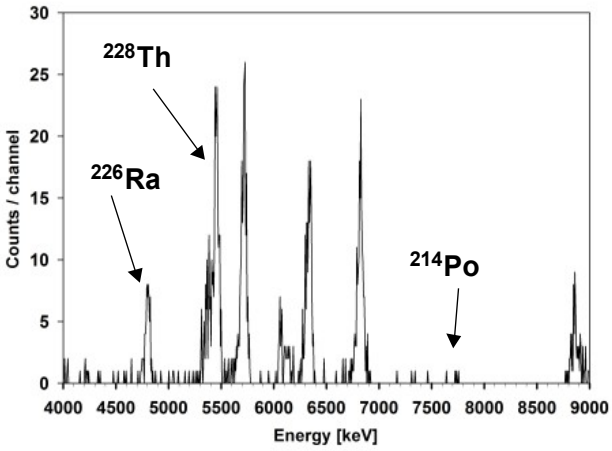
The spectra measured at atmospheric pressure were deconvoluted using PeakFit (V 4.12, SeaSolve Software Inc.) to determine the percentage of radon and thoron that decays on the thin film. In addition, one of the exposed Ra-discs was also measured in vacuum to obtain better energy resolution (Fig. 3).

a)




**Leached Th ore, measured 3 days after exposition, acqusition time 80 ks. $^{220}$Rn and daughter products at (75 +/-5)% of $^{224}$Ra activity.**

b)

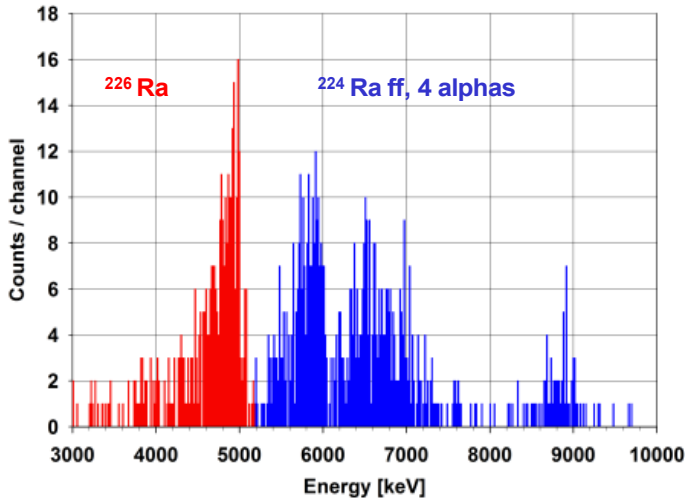



**Same Ra-disc, remeasured 30 days after exposition, acqusition time 240 ks. $^{228}$Th partly built up. $^{222}$Rn and daughter products hardly visible.**

**Fig.3 : Th test sample measured in vacuum. Measured by Philipp Steinmann, Swiss Federal Office of Public Health.**

When measured under atmospheric pressure, the tailing is much larger than when measured in vacuum, but both methods gave comparable percentages of radon and thoron decaying on the thin film. For radon it was < 10%, for thoron it was (75 +/- 5) %.

Figure 4 shows for sample P201 the spectra obtained 5 days after sampling and for the same Ra disc measured again after 630 days. The corrections for decay and buildup were made using the values given in Figures 5 and 6. Figure 5 was calculated using numeric integration (1 minute steps). It shows an example with sample preparation starting 20 h after sampling. It was assumed that stirring during disc exposition removed all $^{220}$Rn and that after drying the disc 25 % of the $^{220}$Rn newly produced by the adsorbed $^{224}$Ra can escape.



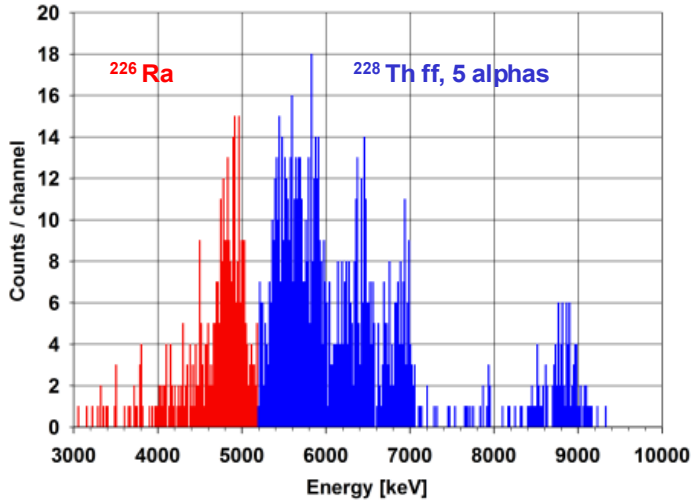

a)

P201 well, 5 days after sampling

Acqusition time : 197 ks

$^{226}$Ra : (100 +/- 10) mBq/l

Initial $^{224}$Ra : (150 +/- 10) mBq/l, corrected for decay




b)

P201 well, Ra-disc remeasured 630 days after sampling

$^{228}$Th built up to 41 % of initial $^{228}$Ra

Acqusition time : 151 ks

$^{226}$Ra : (112 +/- 12) mBq/l

Initial $^{228}$Ra : (160 +/- 10) mBq/l, calc. from $^{228}$Th and its daughter products

**Fig.4 : Alpha spectra for sample P201 : a) measured 5 days after sampling, b) same disc remeasured after 630 days. Both measurements were done at atmosperic pressure.**

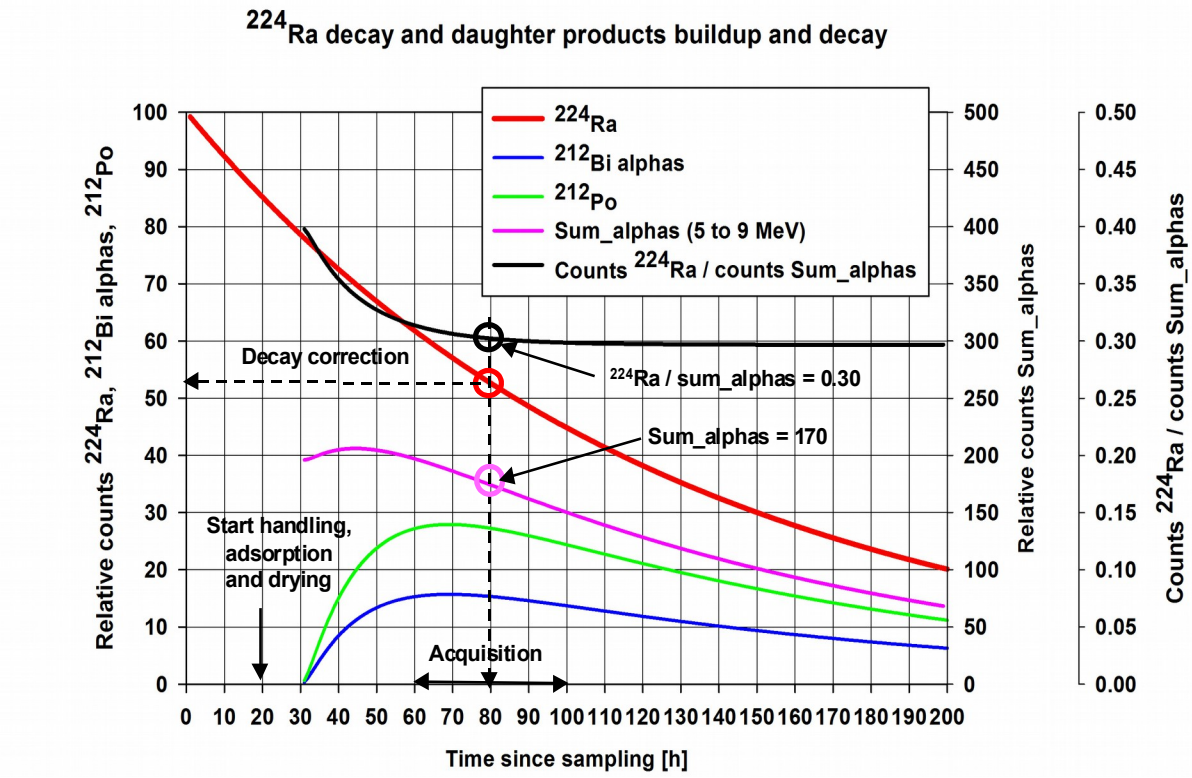



**Fig. 5 : $^{224}$Ra daughter products buildup. Unsupported $^{224}$Ra. Sum alphas : 5.2 to 9 MeV.**

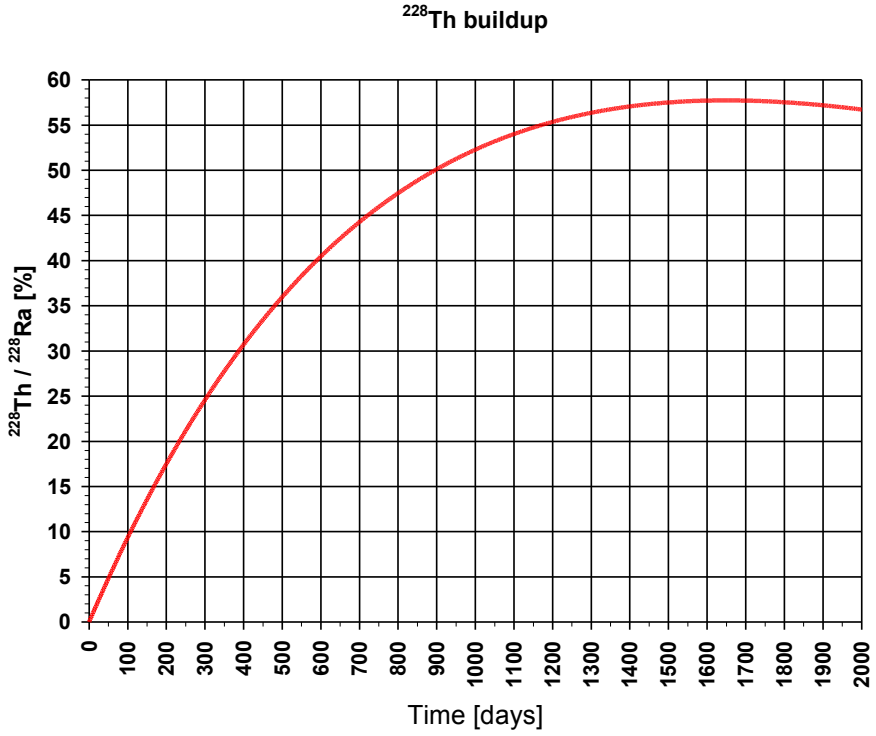



**Fig. 6 : $^{228}$Th buildup. Unsupported $^{228}$Ra.**

## Conclusions

The radium adsorbed on the thin $MnO_2$ layers of the Ra-Nucfilm disc is very close to the surface, at a distance of less than 1 μm. Thus, the noble gases radon, the $^{226}Ra$ daughter product, and thoron, the $^{224}Ra$ daughter product, can diffuse (emanate) out of the thin film. Because of the large differences in the half-lives of these two radon isotopes, the emission factors are very different. Most of the thoron, about 75%, decays on the thin film, while most of the radon, more than 90%, leaves it before it decays.

Because of the strong radon emanation there is almost no spectral interference between radon and thoron daughter products. This is a great advantage over alpha spectrometry with LSC, where the strong spectral interference makes separation very difficult. The separation of the $^{226}Ra$ contribution and the $^{224}Ra$ contribution respectively must be calculated from the beta counts (Dinh et al. 2017).

Using the Ra-disc method $^{224}Ra$ can be easily determined even in the presence of a comparable $^{226}Ra$ activity concentration. One can define a region of interest (ROI) starting above the $^{226}Ra$ peak and extending up to just above the $^{212}Po$ peak. Since 75% of the thoron decays on the disk, this gives good statistics. Due to tailing, there is about 7% spillover from the above ROI to the $^{226}Ra$ ROI.

At least for the P201 sample (Fig.4) $^{224}Ra$ is a good proxy for $^{228}Ra$. There is no need to wait for months for $^{228}Th$ buildup. As figure 5 shows the optimal time window for the measurement is within a few days after sampling. $^{228}Th$ buildup can be neglected, as it builds up with only about 1 % per 10 days.

All discs used have been produced by Nucfilm GmbH. Radon emanation from discs produced by Triskem seems to be lower (Jobbagy et al. 2021). This difference may be due to a different $MnO_2$ film thickness, but more likely to the fact that Jobbagy used a $^{226}Ra$ solution with a 4 orders of magnitude higher activity concentration than the one used for these experiments. In addition Jobbagy's solution contained a high Ba carrier concentration. Barium competes with radium for the $MnO_2$ adsorption sites. Both, a very high Ra concentration and the Ba carrier may lead to a deposition deeper down in the $MnO_2$ thin film, reducing the emanation considerably.

## Acknowledgements

The author would like to thank Philipp Steinmann ( Swiss Federal Office of Public Health) for vacuum measurements and a critical review..

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