Alpha spectrometry sample preparation using selectively adsorbing thin films

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

ABSTRACT

Several years ago, Switzerland has introduced limits for natural radionuclides in food, e.g. 1 Bq/l for ^{226}Ra or 10 Bq/l for the sum of ^{238}U and ^{234}U in drinking water. To make enforcement by regional (cantonal) labs more attractive, simplified analytical methods had to be offered, at least for drinking water.

A first step has been the development of radium adsorbing sheets. A 20mm x 20mm large MnO_2 film on a polyamide substrate adsorbs > 80% of the radium present in a 100 ml water sample within 6 hours. The film is thin enough to allow for high resolution alpha spectrometry.

A second step now under way is to produce thin films selectively adsorbing uranium. Actually an ion exchange resin with diphosphonic and sulfonic acid groups is used for this purpose. Although not yet very thin, these films make possible energy resolutions far better than with any liquid scintillation alpha spectrometry method. Adsorption efficiencies are > 80% after 20 hours exposition to a 100 ml water sample (20mm x 20mm sheet).

A third step is to have a system that measures radionuclide concentrations in water on-line. A prototype is presented where radionuclides are adsorbed on a film in contact with the water. A Si-detector placed on the other side of the film support counts the alphas passing through.

Paper presented at
ICRM Conference on Low Level Radioactivity Measurement Techniques
18-22nd October 1999, Mol, Belgium

e-mail : heinz.surbeck@mbox.bag.admin.ch

INTRODUCTION

In Switzerland we have limits for radionuclides in food not only for artificial radionuclides but also for naturally occurring ones. Members of the uranium and thorium series are classed according to their radiotoxicity. The first class contains ^{224}Ra, ^{228}Th, ^{234}U, ^{238}U and ^{234}U. The limit for e.g. liquid food for this class is at 10 Bq/l for the sum of all radionuclides in this class. The more radiotoxic nuclides ^{210}Pb, ^{210}Po, ^{226}Ra, ^{228}Ra, ^{230}Th, ^{232}Th and ^{231}Pa are in class 2. The limit for this class is set to 1 Bq/l (for liquid food). The limits for food in general are a factor of 5 higher. For seafood that naturally may contain high ^{210}Po levels and for some other food of minor importance for Swiss consumers higher levels are tolerated.

When considering the most important food, drinking water, fortunately not all the nuclides mentioned are to be determined. Large differences in solubility and natural abundance make that ^{234}U and ^{238}U dominate in class 1. For class 2 these main nuclides are ^{226}Ra and ^{228}Ra. The latter can be easily determined by gamma spectrometry (via ^{228}Ac). There remain 3 alpha emitters to be analysed.

Whereas many environmental radioactivity labs are well equipped with alpha counters they frequently hesitate to do all the painful and expensive classical radiochemistry. To make enforcement by regional (cantonal) labs more attractive, simplified analytical methods had to be offered, at least for drinking water.

The ions of the nuclides to be analysed in general make only a very small part of the total number of ions present in an aqueous sample. One thus needs a method concentrating the ions of interest selectively (Fig.1). Selective extraction can be used with liquid scintillation counting (LSC) or as a first step to make thin films by electrodeposition. Direct selective adsorption on thin films and subsequent measurement with a semiconductor detector is the possibility shown here. One thus avoids time consuming and expensive chemical steps still having a far better energy resolution than with liquid scintillation measurements.

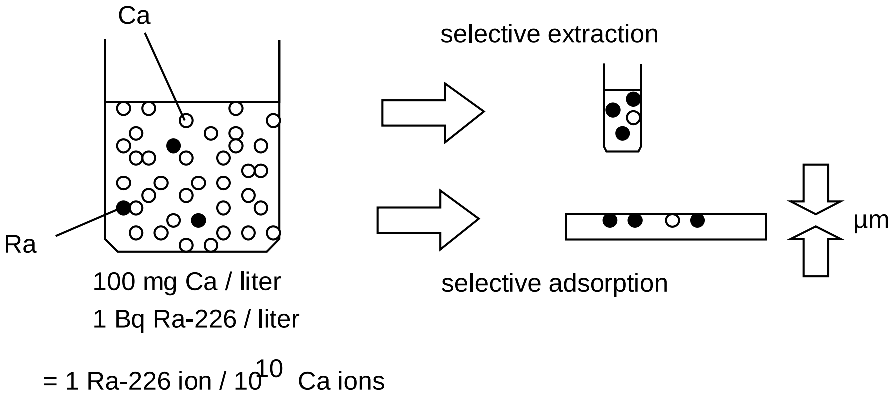

Fig.1 : selective extraction or selective adsorption.

EXPERIMENTAL AND RESULTS

Radium adsorbing thin films

MnO_2 efficiently adsorbs radium even at high Ca concentration. After having improved methods described earlier (Moore and Reid, 1973, Glöbel and Berlich, 1983, Surbeck et al.. 1989, Surbeck, 1995) we now are able to produce selectively adsorbing MnO_2 thin films on polyamide substrates. Exposing a 20mm x 20mm sheet for 6 h to an untreated, stirred 100 ml sample extracts typically more than 80% of the radium. The dried film is then measured with a solid state alpha detector. Energy resolution is nearly as good as for electroplated sources as can be seen in Fig.2. After counting times of one day one typically gets a detection limit of 10 mBq/l for ^{226}Ra.

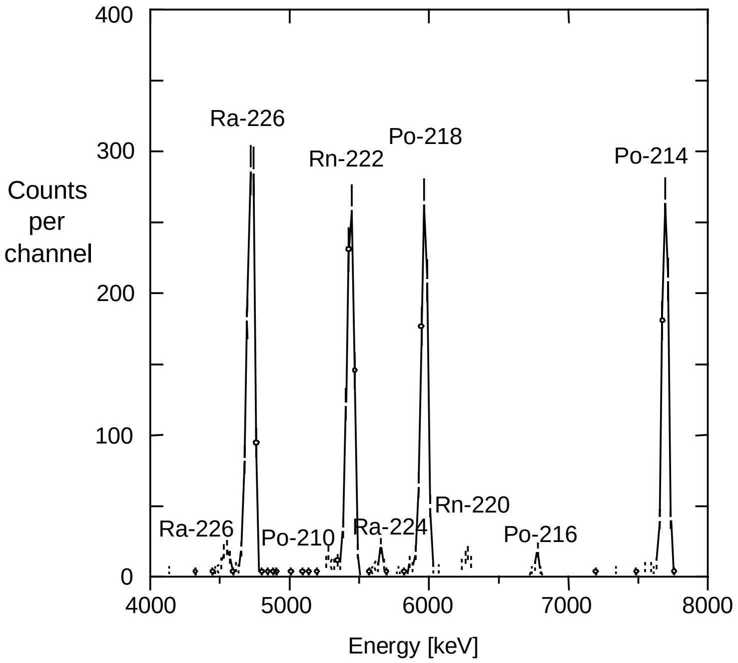

Fig. 2 : Alpha spectrum for a radium adsorbing thin film exposed to a Portuguese mineral water. The water contains about 1200 mBq/l ^{226}Ra, exceeding the Swiss limit. It thus has been banned from the Swiss market.

The films are produced by exposing the polyamide to a hot $KMnO_4$ solution. There are some doubts that the staining on the polyamide is really or only MnO_2. It looks like, but a detailed analysis is still missing.

Adsorption efficiency depends on the sample's chemical composition. Mainly barium (at mg/l levels) competes with radium for the adsorption sites. Exposing at least two films subsequently to the same sample solves the problem. Each film adsorbs the same fraction of radium still present in solution as can be seen for the sample "M" in Fig.3.

For low sample activities (tens of mBq/l) count rates are too low to use this method. In this case a known ^{226}Ra activity (some 10 mBq) is added to the sample before exposing the second film. It is essential to have a low Ba (<< mg/l) ^{226}Ra standard solution.

To strongly mineralised sparkling waters some Na_2EDTA is added to complex calcium. This prevents precipitation when CO_2 is lost. There is no visible effect of this complexation on radium adsorption efficiency (up to 1g/l Na_2EDTA added).

Apart from radium, ^{210}Po is also adsorbed with a high efficiency. Uranium adsorption is low. In general, less than 5% of the ^{238}U or ^{234}U activity are adsorbed, but there are large variations in this adsorption efficiency. These variations may be due to differences in the chemical form in which uranium is present (Langmuir 1978). CO_2 forms quite stable anionic or neutral complexes with the cationic uranyl (UO_2^{++}). As the MnO_2 film seems to act like a cation exchanger this complexed uranium fraction is probably not adsorbed. Lowering the pH to below 4 would help to destroy these complexes, but at this pH the MnO_2 film adsorbs neither uranium nor radium.

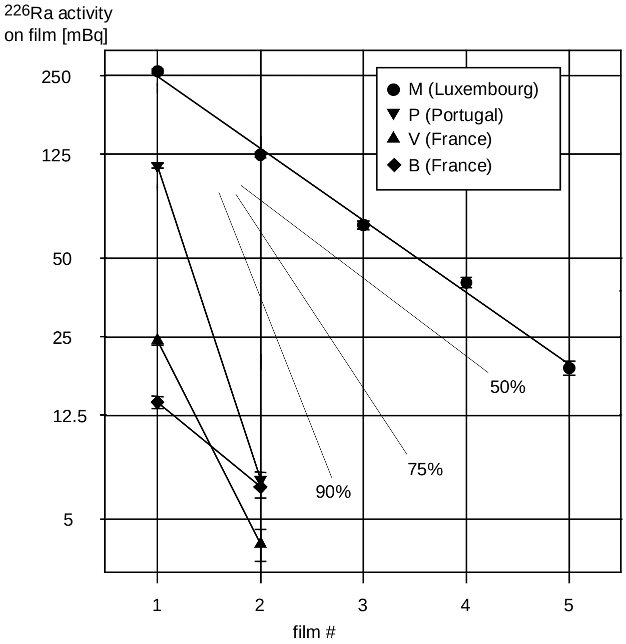

Fig. 3: Determining adsorption efficiency by subsequently exposing radium adsorbing filmsto the same sample. Sample volume : 80 ml, sheets : 20mm x 20mm Polyamid 66, covered on both sides with MnO_2 , exposition time : 6 h per film. Samples are mineral waters from several European countries. Error bars are $\pm 1\sigma$ counting statistics. Dashed lines : slopes for 50%, 75% and 90% adsorption efficiency.

Even at the good energy resolution with these MnO_2 films, ^{234}U alpha energies are too close to the ^{226}Ra energies to be resolved. Unfortunately one can't use the well separated ^{238}U lines to correct for the ^{234}U contribution to the ^{226}Ra line. ^{234}U and ^{238}U are rarely in equilibrium in drinking water samples. To correct for this contribution one has to measure the $^{234}U/^{238}U$ ratio by some other method. This need and the fact that uranium adsorption on MnO_2 turned out to be low and very variable has led us to look for a thin film adsorbing uranium far better than radium. In addition the film has to work at low pH to avoid uranyl complexation.

Uranium adsorbing thin films

A commercially available cation exchanger containing diphosphonate and sulfonate groups showed to have the required selectivity for uranium (Horwitz et al., 1993). Radium adsorption is very low and the resin is intended for low pH applications. This resin thus would be the ideal material for uranium adsorbing thin films. Unfortunately it is only available as beads. To produce nevertheless some sort of thin film we grind the dried beads to a fine powder. This powder is then fixed with a binder to a flat substrate. Polishing removes part of the binder covering the grains thus exposing them to the surface. By this procedure films with an active thickness on the order of 10 µm can be made.

Uranium adsorption on these films is considerably slower than radium adsorption on MnO_2 films. It takes about 20h until equilibrium is reached (4h to 50% equilibrium). After 20h a 20mm x 20mm sheet exposed to an acidified, stirred 100ml sample has taken up more than 80% of the uranium. pH is adjusted with formic acid to about 2.5. After drying the exposed sheet is measured with a solid state alpha detector. As shown in Fig.4 energy resolution is by far not as good as for the MnO_2 films. However it is better than achievable with liquid scintillation alpha spectrometry. For a 100 ml sample and counting times of one day one gets a detection limit of typically 10 mBq/l.

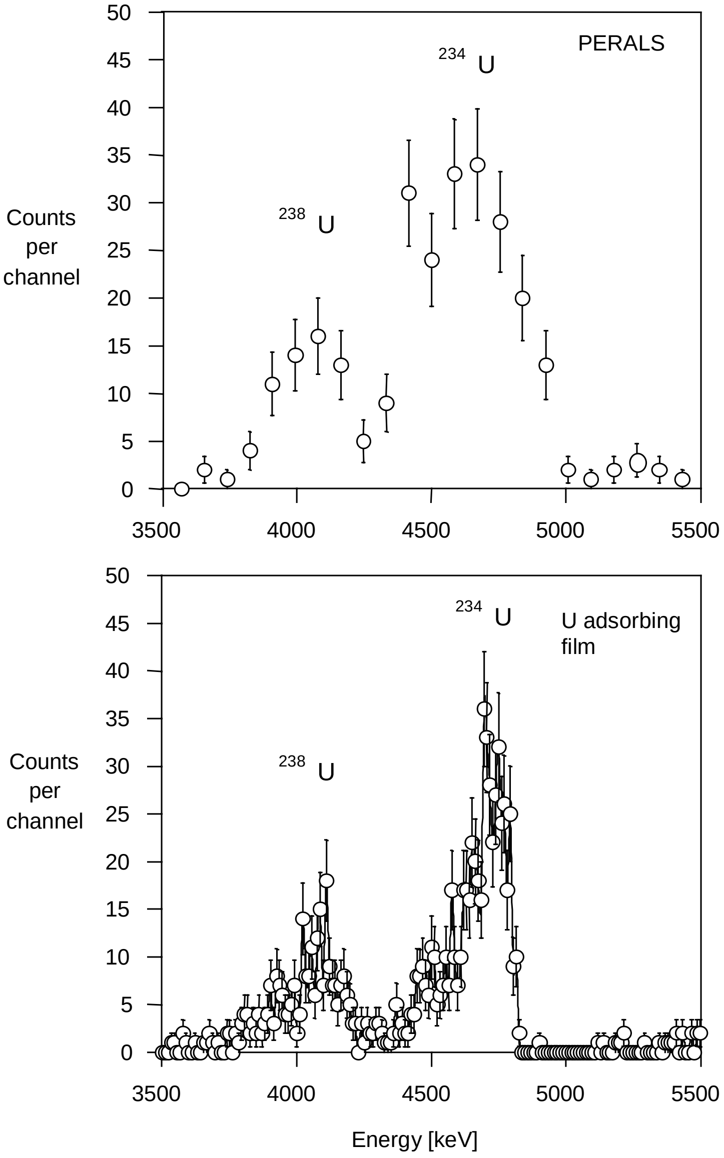

Fig. 4 : Comparing alpha spectra obtained either with LSC or with the method using uranium adsorbing films . Spectra are for the same French mineral water ("Badoit", produced 1996) and for the same counting time (20'000 s). The water contains about 1 Bq/l ^{238}U and about 2 Bq/l ^{234}U. *Upper spectrum* : 50 ml sample acidified to pH 2.5 , boiled, evacuated and released with argon, 2.5 ml "ALPHAEX"- scintillator added to 10 ml of this solution , shaken for 2 min., 1ml of the scintillator measured with a PERALS-Spektrometer (McDowell and McDowell, 1994). *Lower spectrum* : 100 ml sample acidified to pH 2.5, a 25mm x 25mm uranium adsorbing film exposed for 20h (stirred), dried and then measured with a 900 mm^2 Si-surface-barrier alpha detector, detector-sample distance approx.. 10 mm. Error bars are ±1σ- counting statistics.

On-line measurement during adsorption

Selectively adsorbing thin films have already greatly simplified drinking water analysis. However exposition and measurement are still separated. So the next step has to be to combine both, i.e. to cover an alpha detector with a thin selectively adsorbing film. This unit then can be placed directly into the water sample to be analysed to measure on-line during adsorption. The film has to be thin enough to allow for some energy resolution, it has to be watertight and replaceable. What is shown here is an intermediate step towards this ambitious goal.

When exposing MnO_2 films to water containing radon the subsequent alpha measurement of the dried film clearly shows that radon daughter products are adsorbed as well as radium. It is easier and cheaper to have high (some 100 Bq/l) radon in water concentrations than to have comparable radium concentrations. Therefore first on-line measurements have been carried out with radon daughters adsorbed on MnO_2.

A 12 to 15 µm thick PET foil stained with MnO_2 is placed in contact with the water containing radon. Alpha particles emitted from adsorbed nuclei pass through the foil and are counted with a silicon detector. That way first on-line radon daughter adsorption measurements could be made. Although 12 to 15µm are not very thin, energy resolution is still good enough to discriminate radon daughters.

A detailed description of on-line adsorption measurements and its application for on-line radon in water measurements will be published elsewhere (Surbeck and Andrey, 1999).

FURTHER WORK

Selective adsorption on thin films has shown to be an easy method to concentrate trace amounts of uranium and radium from aqueous solutions. It has the potential to become a cheap alternative to more traditional methods, not only for uranium or radium. Together with industrial partners we will now improve production processes and start to make these films commercially available.

On-line adsorption measurements have shown that “cooled down” radon daughters that have been produced in the water are all well adsorbed. However “hot” nuclides freshly produced on the film from the decay of adsorbed nuclei desorb easily back to the water. It may be worth to continue research to understand this unexpected behaviour of “hot” nuclides.

REFERENCES

McDowell, W.J. and McDowell B.L., (1994) Liquid Scintillation Alpha Spectrometry, CRC Press, , ISBN 0-8493-5288-6.
Extractive scintillators produced by ETRAC, Knoxville, Tennessee, represented by EG&G ORTEC. PERALS-spectrometer produced by ORDELA/ORTEC

Glöbel, B. and Berlich, J., (1983)Eine einfache und schnelle Methode zur Bestimmung von ^{226}Ra in wässrigen Proben, In : Proc. Fachgespräch Ueberwachung der Umweltradioaktivität, 22-24 March 1983, Karlsruhe, Der Bundesminister des Innern.

Horwitz, E.P., Chiarizia, R., Diamond, H., Gatrone, R.C., Alexandratos, S.D., Trochimzuk, A.Q. and Creek, D.W. (1993) Uptake of Metal Ions by a New Chelating Ion Exchange Resin, Solvent Extraction and Ion Exchange, 11, 943. Commercially available as Diphonix from

Eichrom Industries, Darien, Illinois, USA

Langmuir, D., (1978),Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta,42, 547-569

Moore, W.S. and Reid, D.F.,(1973) Extraction of Radium from Natural Waters Using Manganese Impregnated Acrylic Fibers, J. Geophys. Res. 78, 8880-8886

Surbeck H., Piller, G. and Ferreri, G., (1989) Die Suche nach Radonquellen, In : Tagungsbericht "Radon und die Strahlungsbelastung der Lunge", Crameri, R. and Burkart, W. (Eds.), PSI-Bericht Nr.22, Villigen, Switzerland, 1989.

Surbeck, H., (1995) Determination of natural radionuclides in drinking water, a tentative protocol, Sci.Total Environment 173/174, p.91-99, 1995.

Surbeck, H. and Andrey, J.-L., (1999), Proceedings 5th Int. Conf. on Rare Gas Geochemistry, Aug.30-Sep3, Debrecen, Hungary, to be published in J. Radioanalytical and Nuclear Chemistry