TRISKEM INFOS

TRISKEM SHARING INNOVATION

Determination of Ra in environmental samples

Especially regulatory bodies show increasing interest in the analysis of radium isotopes, and of Ra-226 in particular; main reason being concerns about the dose contribution of naturally occurring radium as well as about their potential misuse in improvised devices. There is thus strong interest in their routine analysis (e.g. within the context of drinking water monitoring) as well as in their analysis in the context of emergency situations making the development of facile, rapid and sensitive method necessary - for water samples as well as for environmental samples.

Whereas for environmental samples, especially solid ones, rapid methods including rapid sample preparation are of high interest [5] for water samples the main focus lays on obtaining low detection limits using facile methods with preferably low hands-on time [1- 3].

MnO_2 Resin allows fast concentration and separation of Radium from large volume water samples at pH values between 4 and 8 even in presence of high amounts of Ca [1], it could even be shown [2] that a minimum amount of Ca needs to be present in the sample in order to obtain high chemical yields. Burnett et al. have shown that MnO_2 shows sufficiently similar retention of Ba and Ra to allow for the use of Ba-133 as internal standard for Ra in water samples given that the flow rate during the Ra concentration does not exceed 20 mL/min [1].

The MnO_2 Resin is for example used with LN Resin and DGA, Normal resin in a method developed by Sherrod Maxwell [2]. It is used to pre-concentrate Ra from 1 to 1.5L water samples, with 1.25 g/L of MnO_2 Resin being used per water sample. The sample is initially stabilized at pH 6-7 and 25 mg Ca are added per liter. The sample is then loaded onto MnO_2 Resin with a flow rate of about 15 mL/min. Ra is eluted with 15mL 4M HCl/1.5% H_2O_2. In case Ra-228 is to be determined from…

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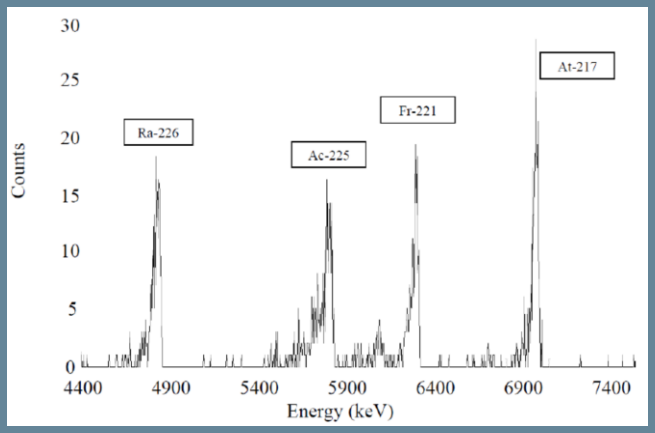

Fig. 1 : Alpha spectrum of an environmental sample obtained by micropecipitation with $BaSO_4$ after chemichal separation (Ra-225 used internal standard) [5]

EDITO

Dear customers,

The last few months have shown the necessity and importance of rapid methods, including rapid sample treatment. Rapid methods are not only of importance during emergency situations, but also in the aftermath when fast decisions on the treatment e.g. of waste, food or debris need to be taken. In order to take these decisions on the basis of a solid knowledge of the situation it is crucial to obtain a sufficient amount of reliable results in a short delay. This is also reflected by the increased interest of regulatory bodies in the development of rapid methods as well as by the increased number of publications on this field.

This issue of the TrisKem Info and next one will mainly focus on rapid methods for the determination of radionuclides in various environmental samples. The current issue will deal with the determination of Ra isotopes, especially Ra-226, in environmental samples with a focus on rapid and facile methods.

We are happy to announce the arrival of some new products, a new MnO2-PAN resin and a line of solid phase extraction products and accessories for the concentration and separation of organic analytes and pollutants.

Michaela Langer
TRISKEM CEO

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Tips and Tricks

- **$BaSO_4$ microprecipitation**

$BaSO_4$ microprecipitation is a very useful technique for preparing Ra samples for alpha spectrometry. However the Ba seeding suspension frequently employed (e.g. Eichrom method RAW04) is not facile to prepare.

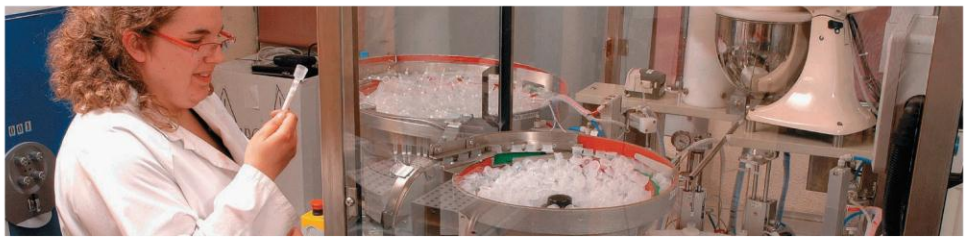
Unfortunately the quality of the alpha spectra is very strongly depending on the quality of this suspension. Maxwell et al. describe a new method without the use of a seeding suspension.

They microprecipitate Ra from 23 mL 1.5M HCl following addition of 3g ammonium sulfate, 50µg of stable Ba and 5 mL of isopropanol. Precipitation tubes are placed in an ice bath and vortexed in the beginning and middle of the icing, and after the tube has been removed from the ice. Samples were ready for counting after filtration over 0.1µm resolve filter and drying of the filter. Fig. 1 shows an example of an alpha spectrum obtained using this method.

- **Cartridges:**

We are now also providing TEVA cartridges from our own production, the cartridges of all our five major resins are thus now produced by TrisKem. You can recognize these cartridges via the color-coded ring.

Figure 3: TrisKem Cartridges



the same sample the solution is left a minimum of 36 hours for Ac-228 ingrowth before being loaded onto 2 stacked cartridges: LN Resin (retention of U and Th) and DGA, Normal Resin (retention of Ac-228). Ac-228 is eluted from DGA Resin with 10 mL 0.5M HCl, then microprecipitated with CeF_3 on a Resolve™ Filter. The Ac yield can be calculated from the Ba-133 yield (MnO_2 concentration step) and the Ac yield (extraction chromatographic separation and the precipitation) obtained gravimetrically via CeF_3 [3]. Ra and Ba are not retained on LN or DGA resin under these conditions and are thus found in the sample load eluate; they can be directly microprecipitated with $BaSO_4$ from this solution.The method has the advantage of allowing simultaneous determination of alpha emitting Ra isotopes and of Ra-228. A similar method, based on the use of DGA only is described in Eichrom method RAW04.

The elution of Ra from the MnO_2 resin with 4M HCl/1.5% H_2O_2 leads to a complete destruction of the MnO_2 layer and thus an elevated amount of Mn in the Ra fraction. This is not a problem when samples are prepared for alpha spectrometry by microprecipitation but can cause problems when Ra-226 is measured by ICP-MS. This issue can be avoided by using a MnO_2-PAN resin (see 'In Brief') instead of the standard MnO_2 resin by that can be quantitatively eluted with 5M HCl without completely destroying the MnO_2 layer thus lowering the amount of Mn in the Ra fraction significantly.

Another possibility for determining Ra-226 in water samples by alpha-spectrometry is the use of Ra selective discs based on a polyamide disc coated with a fine layer of MnO_2 (Ra NucFilm discs [4]). The discs are contacted with the untreated water samples (pH 4 – 8, typical volume = 100 mL) under stirring for 6h. Ra extraction under these conditions is typically greater 90% for water samples having drinking water quality, other types of water samples might also be analyzed, however the adsorption efficiency will depend on the composition of the sample, especially high contents of stable Ba can lead to significantly lower chemical yields due to capacity issues. The dried disc can then be measured with a solid state alpha detector. The energy resolution of the obtained sources is very good as demonstrated in Fig.2.

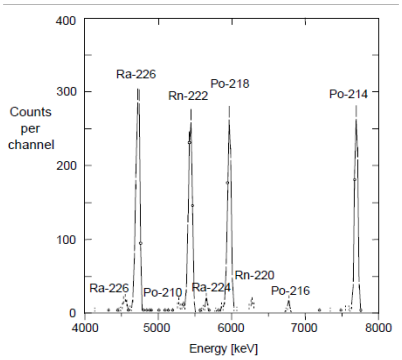
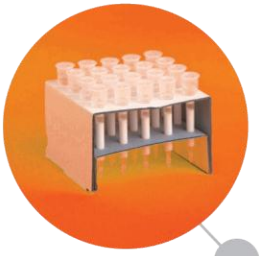


Fig. 2 : Alpha spectrum of a radium adsorbing thin film exposed to a Portuguese mineral water [source: NucFilm GmbH]

High Ba content of samples is not only a problem in case of using Ra NucFilm discs, but also when samples are prepared for alpha spectrometry by $BaSO_4$ microprecipitation or electrodeposition [5] and also in case of Ra-226 measurement via ICP-MS due to isobaric interference of polyatomic $^{88}Sr^{138}Ba$ [5]. Environmental samples or samples derived from decommissioning potentially contain elevated amounts of Ba, accordingly Ba needs to be removed from the sample upfront to counting sample preparation thus making the use of Ba-133 as



internal standard impossible.

The Ba/Ra separation can be performed using Sr resin [5, 6]. When loading from 3M HNO_3 Ba is retained on the resin whereas Ra is breaking through with the sample loading solution.

In such cases it is possible to use Ra-225 (originating from a Th-229 standard solution) as internal standard as suggested e.g. by Maxwell et al. [5]. The author describes a rapid method for the determination of Ra-226 in environmental samples such as air filters, vegetation (5g), concrete, brick and soil (each 1g) allowing for obtaining results within one day. The described method was further adapted, and applied, to 150 mL water samples by the same author. Figure 4 shows the sample preparation schemes. The rapid method is based on a fast sample preparation of the solid samples by mineralization in a furnace followed by wet ashing and a fusion with NaOH in a Zr crucible.

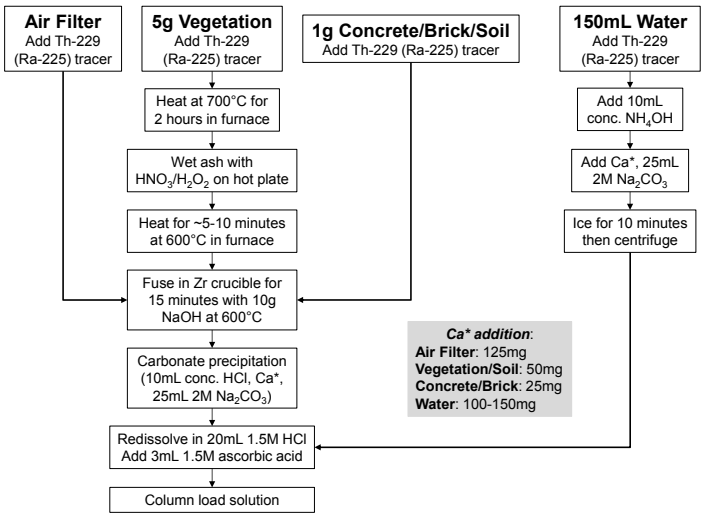


Fig.4: Sample preparation environmental samples [5]

Due to the high matrix load of the fused samples it is necessary to dissolve the fusion in an acidic solution since part of the matrix, especially Fe(III), would start precipitating at pH 7 resulting in a partial loss of Ra.

Accordingly it is not possibly to use a MnO_2 resin for matrix removal. The authors suggest matrix removal via a $CaCO_3$ co-precipitation (after adjustment of the Ca content of the sample) followed by a cation exchange step for Ca removal. Samples potentially containing elevated amounts of Ba (e.g. concrete) are purified using SR resin for Ba removal. The final purification of the Ra fraction is achieved on a LN resin column that eliminates Ac, Ca and rest of the matrix. Figure 5 summarizes the separation steps. The alpha spectrometry source was prepared by microprecipitation in the presence of isopropanol without using a seeding suspension.

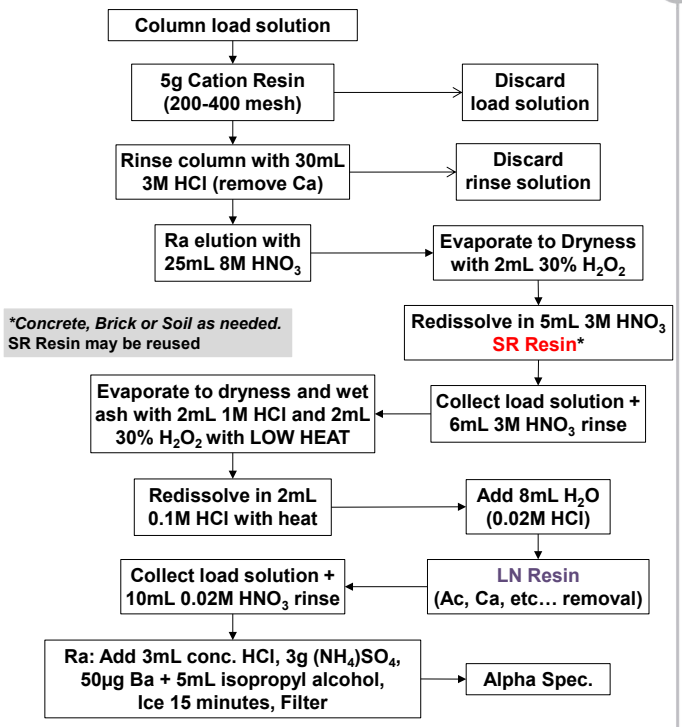


Figure 5: Separation scheme environmental samples [5]

Fig 2. shows a typical alpha spectrum obtained using this method. Table 1 summarizes some results obtained by Maxwell et al. for various spiked matrices [5].

Table 1: Results, analysis spiked matrices, corrected for blank Ra-226 content, N=5

Matrix	Chemical yield / %	Obtained result / mBq per sample	Reference value / mBq per sample	Bias to ref. value / %
Vegetables	87.1 (5.7)	72.8 (5.1)	73.8	-1.2
Concrete	84.6 (6.8)	180.6 (8.0)	184.5	-2.1
Brick	86.5 (6.6)	77.8 (4.6)	73.8	5.5
Air filter	76.7 (4.2)	77.1 (6.2)	73.8	4.5
Soil	75.3 (1.9)	184.9 (6.2)	184.5	0.2
Water	91.8 (6.7)	70.9 (3.7)	73.8	-3.9

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If you'd like to unsubscribe from our TrisKem Infos please contact us either by e-mail (*contact@triskem.fr*) or by phone (+33 (0)2 99 05 00 09).

AGENDA

We'll be participating to the following upcoming conferences and are very much looking forward to meeting and discussing with you there!

° NRC8 – 16-21/09/2012, Lake Como (Italy), http://nrc8.mi.infn.it/

° Jahrestagung FV Strahlenschutz – 17-20/09/2012, Karlsruhe (Germany) *http://www.fs-2012.de/*

°7th Russian conference "Radiochemistry-2012", - 15 – 19/10/12, Dimitrovgrad (Russia) *http:/ www.radiochemistry2012.ru /*

° Advances in Liquid Scintillation Spectrometry – 18 – 22/03/13, Barcelona (Spain) *http://www.ub.edu/LSC2013BCN/*

Please note that an international workshop will take place prior to the conference:
« Plastic scintillation in practice »- 15 – 16/03/13, Barcelona (Spain) *www.ub.edu/LSC2013BCN/PS*

You will find an update on our participations to conferences on our website

InBrief:

MnO_2-PAN

TrisKem International is now providing a MnO_2-PAN resin developed by Dr. Šebesta from the Czech Technical University in Prague. It consists of very fine MnO_2 particles and modified polyacrylonitrile (PAN) as binding polymer offering a very stable MnO_2 resin with a very high surface area.
Other than classical MnO_2 resin it can be eluted quantitatively with 5M HCl only without the addition of H_2O_2; the resin is thus not completely destroyed during the elution, accordingly the Ra fraction is containing a significantly lower amount of Mn. Further the MnO_2 is much tighter bound to the resin compared to standard MnO_2 resin eliminating the need of prolonged rinsing of the resin to remove fine particles before its use.
For best results 2 mL of MnO2 PAN resin should be employed per L of aqueous sample (approx. pH 7) and the sample should be loaded at about 15 mL/min. After rinsing the column with deionized water for matrix removal Ra (and Ba) can be eluted with 15 mL 5M HCl at a flow rate of 2 mL/min. Yields under these conditions are > 95% and the breakthrough during load < 1% for water samples of drinking water quality.

Users group meetings

We are planning on having two users' group meetings at the end of this year, one in Germany and one in Italy. We'll send you more detailed information on both UGMs soon. In the meantime, if you have any special wishes concerning the topics to be discussed, or if you'd like to present some of your work please be so kind as to send a short mail to abombard@triskem.fr (Italian UGM) or shappel@triskem.fr (German UGM).

New team member

In order to increase our availability for and to strengthen our contact with you we've decided to reinforce our team with Tatiana Semenova. She's trilingual (Russian, English and French) and will be your main contact when you are situated in Russian spoken countries.

New product line

We are very glad to announce that we will be adding a new product line to our catalogue in the upcoming weeks.
In addition to our current products which are very much focusing on radiochemical and inorganic analysis we will now also offer a line of solid phase extraction (SPE) products and accessories dedicated to the separation of organic analytes and pollutants.
The Cleanert product line contains a number of high quality SPE products that typically find application in the following fields: environmental monitoring, medical/pharmaceutical, food control and cosmetics.
You'll find more detailed information on our website soon.

DO NOT HESITATE TO CONTACT US FOR MORE INFORMATION

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