SEPARATION AND MEASUREMENT TECHNIQUES FOR THE DETERMINATION OF ^{228}Th, ^{230}Th AND ^{232}Th IN VARIOUS MATRICES

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Abstract — Three analytical techniques are presented which are used at PSI for determination of U and Th isotopes (^{234}U, ^{235}U, ^{238}U, ^{228}Th, ^{230}Th, ^{232}Th) in different materials, i.e. environmental samples (soils, minerals) and dental ceramics as well as in urine for *in vitro* monitoring of potentially exposed workers. Depending on the sample quantity available and/or required detection limits the measurements are performed either directly via gamma spectrometry or via alpha particle counting with preceding separation chemistry. The separation methods applied are based on either extraction chromatography or on sorption of U and Th on actinide selective resin. Following sample digestion, chemical yield spike additions (^{232}U, ^{229}Th or ^{228}Th), chemical purification and electro-depositional source preparation, alpha particle measurement is carried out using low-level alpha spectrometry. This technique allows detection limits of less than 0.2 mBq per counting source if the assay lasts over a few days and is therefore suitable for determination of trace quantities of short-lived ^{228}Th that can be hardly detected by means of mass spectrometric techniques.

INTRODUCTION

Measurement of Th isotopes in workplace materials or in the frame of radionuclide incorporation programmes require use of analytical techniques and instruments that are able reliably to determine quantities of Th isotopes at trace levels. While mass spectrometric methods (ICP-MS, MCICP-MS, TIMS etc.) have been demonstrated to determine precisely traces of the primordial nuclides ^{232}Th and ^{238}U in human body fluids at levels of a few ng (10^{-9} g) and even less[1,2], radionuclide counting via α spectrometry is still the most suitable technique for detecting the more short-lived Th-isotopes ^{228}Th and ^{230}Th down to activities of 0.2 mBq, which corresponds to quantities of 10^{-17} g (for ^{228}Th) and 10^{-13} g (for ^{230}Th), respectively. Determination of these short-lived Th isotopes is of particular concern if the ^{232}Th decay series is in a state of disequilibrium and, furthermore, because the ^{228}Th/^{232}Th and ^{230}Th/^{232}Th ratios may be very helpful to distinguish between artificially and naturally incorporated Th at the workplace[3,4].

INSTRUMENTS AND METHODS

Radiochemical procedures and α spectrometric measurements

This section introduces two fast radiochemical procedures for separation of U and Th isotopes (i) from environmental samples such as soil or grass for routine radionuclide immission monitoring or minerals (e.g. monazite, allanite, speleothem) that are taken as raw materials for the Th reprocessing industry as well as for geochemical dating of young Pleistocene rocks and (ii) for measurement of actinides in urinary excretions of workers potentially exposed to alpha particle emitting radionuclides in the workplace.

After separation of U and Th from the matrices (details on separation techniques below) α particle counting is performed using semiconductor α spectrometers equipped with partially depleted, high-purity, silicon surface barrier detectors (system α-Analyst, Canberra-Eurisis SA). Setting defined energy windows and adding artificial tracer isotopes to the samples (e.g. ^{229}Th, ^{232}U), the activity concentrations of U and Th are simply obtained by peak area comparison of the measured isotopes to the added spike, for instance for determination of ^{230}Th,

$$A_{230} = (I_{230}/I_{229})A_{229} \qquad (1)$$

where A_{230} and A_{229} are the activities of ^{230}Th and ^{229}Th in the sample and added spike, respectively, and I_{230}/I_{229} is the ratio of total registered impulses from sample and spike isotopes. Equation 1 indicates that knowledge of parameters such as detector efficiency, chemical recovery or counting time may not be necessary if the spectrum analysis is carried out relative to a spike. Clearly, this simplification is only true provided that certain assumptions can be justified; these are that (a) the spectra of the two nuclides do not overlap or interfere, (b) each nuclide decays by 100% alpha emission, (c) the detection efficiency of the counter is independent of the alpha particle energy, (d) the efficiencies of emission of the alpha particles from the source are independent of the alpha particle energy, (e) the spike nuclide is in the same chemical form as the sample when the two are mixed and finally (f) background scatter is negligible. For geological samples older than 20 years, i.e. with

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^{232}Th/^{228}Th in equilibrium, ^{228}Th can be used as a spike as well and the fraction of ^{228}Th from the sample is then simply obtained by subtracting the peak area of ^{232}Th from the ^{228}Th sum peak. If the sample is not 'under-spiked' this tracer is of advantage because many even–odd actinide isotopes such as ^{229}Th decay via complex excited levels with several discrete alpha emission energies, that partially interfere with alpha peaks of the sample isotopes to be analysed.

For counting of a sample source with an active surface area of 300 mm^2 close to a somewhat larger (450 mm^2) detector, the counting geometry tends towards 2π, and therefore, if the radioassay lasts over a few days, minimum detectable activities (MDAs) of <0.2 mBq (per counting source) are obtained for most of the alpha-emitting isotopes within the actinide group. The evolution of the MDAs for ^{228}Th in urine as an example is shown graphically in Figure 1. Three counting methods are compared: alpha spectrometry and alpha/beta liquid scintillation spectrometry (LSC) following extraction of Th from a 0.5 litre aliquot as well as direct counting of a 1 litre sample using high-resolution low-level gamma spectrometry (and assuming, for simplification, secular equilibrium between ^{228}Th and all progenies). The MDAs in this example (in mBq.l^{-1}) were calculated according to the relations given by Seymour et al[5] as follows:

$$\text{MDA (mBq.l}^{-1}) = \frac{2.71 + 2K\sqrt{2I_0}}{tY_{chem}\epsilon V_{samp}P_w} \quad (2)$$

where: K = 1.65 = statistical value for a confidence interval of 95%, I_0 = total background counts in time t; t = counting time, Y_{chem} = chemical recovery for Th, ϵ = counting or detector efficiency, V_{samp} = sample volume and P_w = transition probability for a gamma ray or an alpha particle in the respective counting win-dow. The set of values used for the calculation of the MDAs for ^{228}Th in urine are given in Table 1. Figure 1 shows clearly that alpha spectrometry yields the lowest MDA values, mainly because the background count rate (I_0/t) is extremely low. Although I_0/t is two orders of magnitude higher for α/β LSC, the MDA is only a factor of three above that obtained with alpha spectrometry and this is because the alpha particle counting efficiency is close to 100% for LSC (i.e. maximum 4π counting geometry). However, deconvolution of a complex Th isotope spectrum (inclusive of daughter and spike isotopes) is less practical with LSC because of the rather poor alpha peak resolution of ≈ 500 keV compared to only 30–60 keV for electroplated counting sources used for alpha spectrometry.

Low-level alpha particle counting of environmental samples

Solid samples are first powdered and homogenised to allow sequential analyses on different aliquots. Those samples containing fractions of organic material (such as speleothem) are heated at 500°C overnight in order to oxidise the organic component. A ^{232}U/^{228}Th secular equilibrium spike is added to the sample prior to digestion. Carbonate minerals are dissolved in 3 M HNO$_3$, silicate minerals at moderate temperature on a heating plate in 35% HF (5 ml per g of rock). After evaporation to dryness the last step is repeated two to three times until the silica structure has been decomposed completely. The mineral ash is then dissolved and evaporated again using 5 ml of 7 M HNO$_3$ (3×) and subsequently in a mixture of 300 mg H$_3$BO$_3$ and 10 ml 7 M HNO$_3$ (to remove any remaining fluoric acid quantitatively). The residue is then dissolved in 10 ml of a 1:1 mixture of 3 M HNO$_3$/0.5 M Al(NO$_3$)$_3$ and this solution is rinsed through a conditioned U/TEVA™ extraction chromatography column (Eichrom Biosciences SA, Darien, IL, USA). When the sample solution has been passed through, the column is washed twice with 4 ml of 3 M HNO$_3$. Thorium is eluted with 2×10 ml of 5 M HCl and the uranium fraction is consecutively mobilised with 2×10 ml of 0.02 M HCl. 0.6 ml of 1 M NaHSO$_4$, 0.4 ml of 18 M H$_2$SO$_4$ and 0.6 ml of 9 M HClO$_4$ are then added to each fraction. This solution is taken to dryness and strongly calcinated on a heating plate for about 10 min until all hydrochloric gases have disappeared. After evaporation there should remain a colourless and transparent residue, which is dissolved in 4 ml of de-ionised H$_2$O and finally transferred to an electrolysis cell. This cell is an open liquid scintillation vial from which the bottom has been removed[6]. The vial contains a mounted stainless steel disc (acting as the cathode) in the cup and is placed upside/down into an electrolysis apparatus. 0.6 ml of 1 M NaHSO$_4$/5.2 ml 1M Na$_2$SO$_4$ buffer solution is then added to the sample solution. Electrolysis is performed over 1 h at a current of 1.2 A[6]. A flow chart showing the analytical
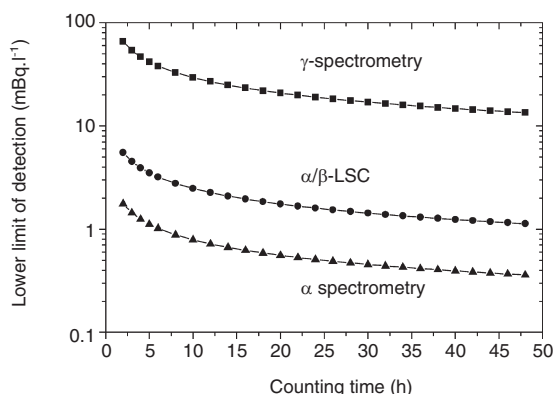

Figure 1. Development of the minimum detectable activity (MDA) for the α-emitters ^{228}Th, ^{230}Th and ^{232}Th extracted from 0.5 litre of urine with time. Three low-level counting methods are compared: (▲) α spectrometry, (●) α/β-LSC and (■) γ spectrometry.

procedure and the resulting α spectra of Th and U isotopes separated from a rock sample are presented in Figures 2 and 3.

Urine bioassay

The extraordinary strong sorption coefficients of Eichrom's product *Actinide Resin*™ for tetra- and hexavalent actinides (with Kd values in the order of 10^7) allows fast procedures to be used for determining Th, U and transuranium elements from complex matrices without the need to carry out preceding pre-concentration steps. This product is used at PSI for screening transuranium alpha-emitting radionuclides in urine in the course of incorporation monitoring or for determining gross alpha activity concentrations in reactor coolant or waste water[7]. *Actinide Resin*™ is also suitable to determine the levels of short-lived Th isotopes (^{230}Th, ^{228}Th) for bioassay monitoring at the workplace[4]. The method is briefly described as follows:

A 0.5 litre urine sample and 100 ml of 14 M HNO_3 are transferred to a glass beaker. A precisely known quantity of a Th spike tracer (i.e. for urinary bioassay about 0.3 mBq of ^{229}Th) is then added to the acidified solution for chemical yield determination. The organic matter in the solution is then partially oxidised under boiling on a heat plate. After cooling to room temperature, 0.2 g *Actinide Resin*™ are added and the solution is stirred for four hours to allow the fixation of the actinides on the resin. The resin containing the sorbed actinides is then extracted from the aqueous solution via filtration and the reagent is stripped from its inert substrate by rinsing the filter with isopropanol (3×5 ml). After evaporation to dryness the reagent is decomposed using a mixture of 7 M HNO_3 (5 ml) and 9 M $HClO_4$ (1 ml). The actinides are now present in few mg of phosphoric acid which can be easily dissolved in 10 ml $NaHSO_4$ (0.1 M)/Na_2SO_4 (0.5 M) buffer solution. This solution is transferred to an electrolysis cell and the actinides are electrodeposited over one hour under a fixed current of 1.2 A (see above) and the radioassay is carried out applying α spectrometry.

Th isotope measurements via gamma spectrometry

Gamma spectrometry is a highly suitable counting technique for non-destructive Th isotope analysis in solid workplace or environmental materials, provided that the sample quantity is sufficiently high to allow a precise count. At PSI two high-resolution intrinsic p-type coaxial Ge-detectors (Princeton Gamma Tech, PGT, model IGC30) are used for gamma ray counting (FWHM = 1.3 keV at 59 keV, 2.0 keV at 1332 keV). These detectors are characterised by high peak-to-Compton ratios of 60:1 (at the photo peak of ^{60}Co at 1332 keV) and a relative efficiency of 40%. An 8k MCA is used for photo peak separation in an energy range between 0 and 2 MeV (i.e. 0.25 keV/channel). Spectrum analysis and peak deconvolution is performed automatically using Interwinner 4.1 software (Eurisis-Packard).

Gamma ray counting of environmental samples

Typical environmental materials for Th isotope analysis are heavy mineral sands (used as raw materials for the Th producing industry) or soils (for radionuclide immission monitoring). Th isotopes determined by gamma spectrometry are counted indirectly by measuring the dominant photo-peaks of short-lived progeny isotopes, i.e. ^{228}Ac as a measure for ^{228}Ra and ^{232}Th as well as ^{212}Pb and ^{208}Tl (for ^{224}Ra and ^{228}Th). The simplified progenitor/progeny relationships in the ^{232}Th decay series are illustrated in Table 2 with the short-lived isotopes rapidly gaining equilibrium with their precursors (given in brackets).

The third isotope of Th, ^{230}Th, which belongs to the ^{238}U decay series is also easily determined in geological material via gamma spectrometry of ^{226}Ra progeny products (i.e. ^{214}Pb, ^{214}Bi) because for most geological materials it can be assumed realistically that their U and Th series are in radioactive equilibrium. While coarse grained materials (i.e. mineral sand etc.) can be measured directly in calibrated geometry, soil samples (containing large fractions of μm-sized clay minerals) have to be transferred into sealed (air tight) beakers to

Table 1. Compilation of the relevant parameters that are needed for calculating the minimum detectable activity of ^{228}Th in urine. Three analytical methods are compared.

Method	Parameter				
	V_{samp} (litre)	Y_{chem} (%)	I_0/t (cpm)	ϵ (%)	P_w (%)
α spectrometry	0.5	90	0.001	35	100
α/β-LSC	0.5	90	0.1	100	100
γ spectrometry	1	100	0.01	2.5	43*

*Transition probability for the γ-line of ^{212}Pb at 295 keV.

avoid emanation of ^{222}Rn, the precursor of short-lived isotopes that decay to ground state with high photon transition probabilities (i.e. ^{214}Pb at 352 keV, ^{214}Bi at 609 keV).

U and Th radionuclides in dental ceramics

According to the ISO-6872 report[8], dental ceramic products should not be used as teeth implantation if the activity concentrations of ^{238}U and ^{232}Th (and respective decay series isotopes) exceed 1 Bq.g^{-1}. This investigation can be carried out using non-destructive gamma spectrometry. Clearly, ideal for increasing counting statistics would be the use of large quantity samples. However several dental ceramic products include a significant fraction of zirconium oxide and therefore represent high-density materials (density of compacted ZrO powders is typically 2–3 g.cm^{-3}). This means that the photon attenuation for low energetic gamma quanta such as the major line of ^{212}Pb (at 295 keV) becomes so significant for large kg-sized samples that correction for self-absorption results in large uncertainties. However, precise measurement of ^{228}Th progenies alongside ^{228}Ac (as a measure for ^{228}Ra) is of high importance in order to detect disequilibrium between ^{228}Th and ^{228}Ra and therefore to derive a realistic value (or upper limit) for pure α-emitting ^{232}Th. Such a determination of disequilibrium state is necessary for materials such as dental ceramics or Th workplace materials, which may have been chemically processed only a short time ago.

The progression of a disequilibrium situation in the ^{232}Th series with time following fractionation between Th and Ra (with a complete removal of Ra, i.e. boundary condition Ra(0) t=0) is given in Figure 4. The figure indicates that as soon as ^{228}Ra has been separated, the level of ^{228}Th starts to reduce relative to ^{232}Th. However, ingrowth of ^{228}Ra with time slows down the decrease of ^{228}Th and after about 4 years the subsequent relative activity of ^{228}Th passes through a minimum and then turns into a transient equilibrium with its progenitor ^{228}Ra (until equilibrium is obtained again in the decay series after about 30 years). In principle the state of disequilibrium between ^{228}Th and ^{228}Ra could be
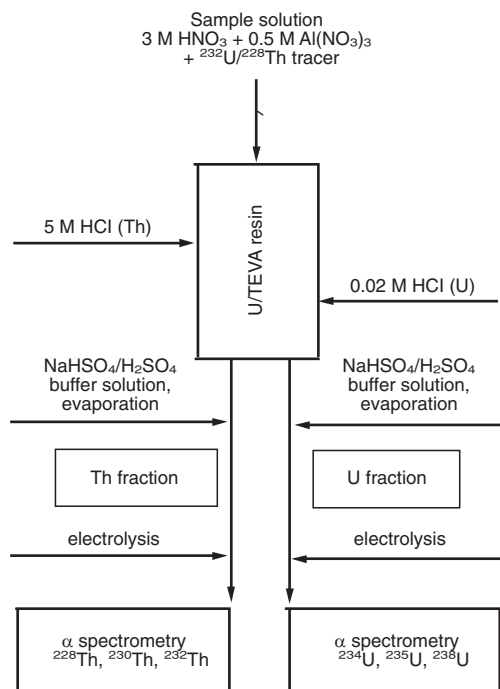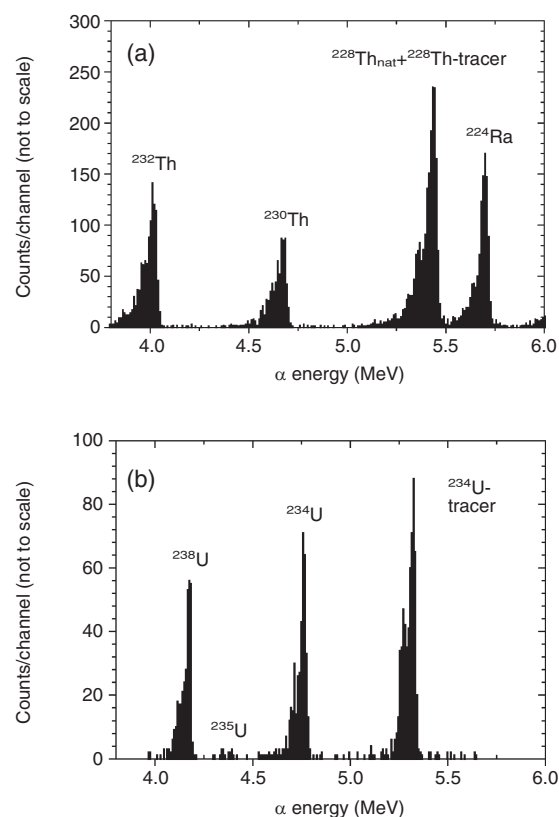
Figure 3. Alpha spectrum of Th isotopes (a) and U isotopes (b) in the energy range between 3.5 and 6 MeV following extraction chromatography on U/TEVA resin and electrodeposition on stainless steel planchets.

Table 2. Simplified illustration of the progenitor/progeny sequences within the ^{232}Th decay series.

^{232}Th→^{228}Ra(^{228}Ac)→^{228}Th(^{212}Pb,^{208}Tl)

Figure 2. Flow chart showing the separation procedure for determination of Th isotopes in solid materials.
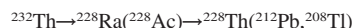
used to calculate the activity of ^{232}Th, however, the initial boundary condition of ^{228}Ra at t=0 cannot be known in a sample with unknown history. Nevertheless, the upper limit for the activity of ^{232}Th can be estimated to be no more than a factor of 2 higher than that of ^{228}Th regardless of the moment of chemical processing of the Th-containing material. Therefore to measure ^{228}Th precisely, small 50 ml samples are counted in well-calibrated geometry and for a 12 h count on a 40% relative efficiency gamma detector an MDA of 0.002 Bq.g^{-1} results for ^{228}Th.

More problematic is the gamma measurement of ^{238}U via progeny isotopes in potential disequilibrium samples. In contrast to minerals, short–lived ^{226}Ra pro-

genies cannot be used because of the rather long half-life of the preceding ^{230}Th. (76,000 y). The most appropriate isotope for such high-density materials is ^{234}Pa^{m} with a transition probability of only 0.75% (at 1001 keV). With the parameters listed above this leads to a MDA for ^{238}U of 0.06 Bq.g^{-1}, i.e. a value, which is still more than one order of magnitude below the upper tolerance level recommended in ISO-6872[8] (i.e. 1 Bq.g^{-1}).

CONCLUSIONS AND RECOMMENDATIONS

Different separation and counting methods are applied at PSI for Th analysis in various matrices. For measurement of complex Th and progeny isotopes it is concluded that semi-conductor, high-resolution alpha and gamma spectrometry are the most suitable counting techniques. If trace levels of short-lived Th isotopes (^{230}Th and ^{228}Th) are of concern, α particle counting following chemical purification is still the most sensitive procedure, while mass spectrometry is considerably more sensitive for detection of traces of primordial ^{232}Th.
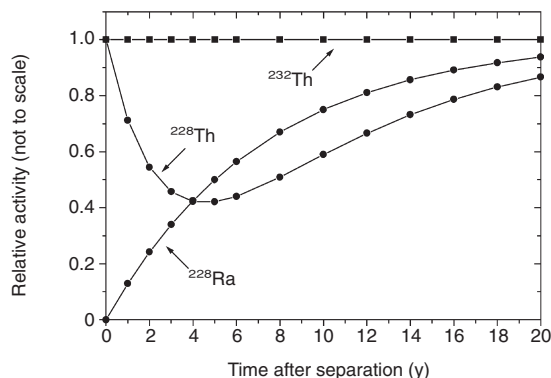

Figure 4. Evolution of a disequilibrium in the ^{232}Th series with time after quantitative removal of radium (^{228}Ra).

REFERENCES

1. Karpas, Z., Halics, L., Roiz, J., Marco, R., Katorza, E., Lorber, A. and Goldbart, Z. *ICP-MS as a Simple, Rapid and Inexpensive Method for Determination of Uranium in Urine: Comparison with LIF*. Health Phys. **71**, 879–885 (1996).
2. Roth, P., Werner, E., Wendler, I. and Schrammel, P. *Variation of Natural ^{232}Th Excretion in Non-exposed Persons*. J. Radioanal. Nucl. Chem. **226**, 285–287 (1997).
3. Naumann, M., Hänisch, K. and Hartmann, M. *Levels of Natural Radionuclides in Human Excreta in the Berlin Area*. Radiat. Prot. Dosim. **79**, 197–200 (1998).
4. Eikenberg, J., Vezzu, G., Zumsteg, I. and Fern, M. J. *Th Isotope Relationships in Human Diet and Excreta*. Radioact. Radiochem. **10**(3), 31–40 (1999).
5. Seymour, R., Sergent, F., Knight, K. and Kyker, B. *Impact of Sensitivity and Throughput on Optimum Selection of a Low-background Alpha/Beta Gross Counting System*. Radioact. Radiochem. **3**, 14–27 (1992).
6. Bajo, S. and Eikenberg, J. *Elektrodeposition of Actinides for α-spectrometry*. J. Radioanal. Nucl. Radiochem. **3**, 745–751 (1999).
7. Eikenberg, J., Ruethi, M., Bajo, S., Zumsteg, I., Fern, M. J. and Passo, C. J. *Fast Radiochemical Screening of Transuranium Nuclides in Urine using Actinide Extractive Resin and Low Level α/β-LSC*. Radioact. Radiochem. **10**(3), 19–30 (1999).
8. ISO (International Organization for Standardization) *Dental Ceramic, Amendment 1*. ISO Reference Number 6872:1995/Amd.1:1997 (1997).