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Determination of ^{210}Pb and ^{226}Ra/^{228}Ra in continental water using HIDEX 300SL LS-spectrometer with TDCR efficiency tracing and optimized α/β-discrimination

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HIGHLIGHTS

- Optimized α/β separation for ^{226}Ra/^{228}Ra LS measurement.
- Evaluation of ^{210}Pb/^{210}Bi, ^{226}Ra/^{222}Rn and ^{228}Ra/^{228}Ra parent progeny in-growth relationships.
- Investigation of β-spectra interferences.

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ABSTRACT

An analytical method for determination of ^{210}Pb, ^{226}Ra and ^{228}Ra is presented based on adsorption on 3M Empore RadDiscs, and measurement applying liquid scintillation spectrometry (LSC) after elution. The LSC measurement was performed with optimized α/β-discrimination and isotope standardization using the triple to double coincidence ratio (TDCR). The consistency of measurement results between radioactive parent–daughter pairs ^{210}Pb/^{210}Bi, ^{226}Ra/^{222}Rn and ^{228}Ra/^{228}Ac was checked in long-term counting experiments and the influence ofinterference of in-growing daughters from ^{226}Ra into the β-spectrum of ^{228}Ra+^{228}Ac was studied as well. Recommendations for optimized LSC ^{228}Ra measurement besides presence of ^{226}Ra are given.

1. Introduction

Methods for determination of the presence of alpha particle emitting radioisotopes in drinking water are essential for evaluating if the water from the corresponding source can be taken for commercial use (Landstetter and Katzelberger, 2010). Besides ^{210}Pb along with the daughter isotope ^{210}Po the radium decay series, i.e. the radium isotopes ^{228}Ra and ^{226}Ra together with several radioactive daughters contribute to the highest dose conversion factors and are therefore subject to several separation and measurement techniques (Möbius et al., 2005, Mosqueda et al., 2008). Application of these techniques with planar source preparation and subsequent high resolution α-spectrometry yield clear resolution between mother and in-growing daughter isotopes (Eikenberg et al., 2001); however the same technique cannot be used for direct determination of low beta energy particle emitting ^{228}Ra. Therefore LSC with optimized α/β separation is one of the most convenient method to measure long lived ^{226}Ra ($T_{1/2}$=1600 years) besides rather short lived ^{228}Ra ($T_{1/2}$=5.7 years) with the latter hardly measurable at environmental levels with other techniques like mass spectrometry (Anderson et al., 1994). Furthermore LSC yields relatively fast results due to high counting sensitivity for both α- and β-emitting radioisotopes and since several samples can be measured in a sequence.

In this article an analytical method for determination of ^{210}Pb, ^{226}Ra and ^{228}Ra is presented based on adsorption 3M Empore RadDiscs in a similar manner as proposed by Möbius et al. (2005). For LSC counting the LS-spectrometer HIDEX 300 SL was used with optimized α/β separation and triple to double coincidence ratio (TDCR) measurement, which enabled determination of the counting efficiency directly. Certified radionuclide solutions (^{210}Pb, ^{226}Ra, ^{228}Ra) were taken for chemical yield evaluation and to prove on the consistency between count rates resulting from parent isotope decay and in-growing daughter radionuclides. Long-term measurements were performed to study the evolution of the following couples: ^{210}Pb/^{210}Bi, ^{226}Ra/^{222}Rn (+several daughters) and ^{228}Ra/^{228}Ac. Finally ^{226}Ra/^{228}Ra mixtures were prepared and measured to investigate the influence of α/β-decaying isotopes from ^{226}Ra decay series on the counting rates of ^{228}Ra/^{228}Ac couple.

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2. Laboratory methods

2.1. Radiochemical separation procedure for determination of ^{210}Pb and ^{226}Ra, ^{228}Ra

To adjust proper counting conditions such as α/β separation and to determine counting efficiencies, NIST or PTB certified radiotracer solution were taken for efficiency determination and window setting of ^{210}Pb and ^{226}Ra with daughter isotopes. To optimize the counting conditions for ^{228}Ra, a certified ^{232}Th solution in secular equilibrium with the daughters ^{228}Ra and ^{228}Th was selected and Ra was separated from Th using extraction chromatography with Triskem *U/TEVA*™ resin. The radium fraction was measured with an independent method (i.e. high resolution γ-spectrometry) to confirm the activity of ^{228}Ra via measurement of ^{228}Ac and to follow up the decay of ^{224}Ra which was no longer supported by the parent isotope ^{228}Th. The measurements using the newly prepared ^{228}Ra-tracer solution were performed for 20–30 days after the removal of ^{228}Th in order to have almost no influence of non-supported ^{224}Ra and ^{228}Th and supported ^{224}Ra, that grows in with a half-life of 1.9 years (i.e. in this time interval $>97\%$ of unsupported ^{224}Ra has decayed and $<3\%$ of ^{228}Th supported ^{224}Ra has grown in).

About 10 Bq per experiment was taken individually from the tracer solutions and transferred into 0.5 l distilled water acidified with HNO_3 to form a 2 M solution. Prior to filtration the 3M Empore RadDisc filter discs were conditioned in the 2 M HNO_3 medium. The spiked water aliquots were then filtrated through the 3M Empore RadDisc filter material and after filtration, Pb was first eluted using 5 ml 0.2 M DHC solution (Diammonium–Hydrogen–Citrate). The subsequent elution of Ra was performed via 6 ml of alkaline (pH 9–10) 0.25 M Na–EDTA–solution. Both fractions were then transferred to LS-vials, mixed with 14 ml OptiPhase Hisafe3 scintillator to a total volume of 20 ml. For routine measurements of environmental water rather large water volumes of 3 l should be taken ideally to determine ^{210}Pb, ^{226}Ra and ^{228}Ra at levels of a few mBq/liter.

2.2. Liquid scintillation measurement procedure

LS-counting was performed using a HIDEX 300 SL equipped with triple to double coincidence (TDCR) signal measurement and pulse length index processing (PLI) electronics for optimized α/β separation (important for simultaneous measurement of ^{226}Ra besides ^{228}Ra). In contrast to the two classical photomultiplier counting systems that require coincidence signals for background noise suppression, the system used here in addition measures coincidences between all three photomultipliers. TDCR values of all α-particle emitting radioisotope were always found to be 1.00, i.e. all photons produced by the α-particle scintillation process were registered as triple coincidences and double coincidences resulting in a TDCR of 1.0 which means 100% counting efficiency (Fig. 1). Furthermore this figure shows the relationship between measured TDCR and efficiency calculated from the certified tracer solutions with a slope of 1.0 between TDCR and efficiency. For ^{210}Pb the TDCR and efficiency was found to be identical, i.e. high efficiency of 0.94 due to the additional generation of conversion electrons during β-decay. For this decay mode only 20% of the beta radiation decays into the ground state, while 80% remains in an excited state at an energy level of 46.5 keV. For this level only 4% is transferred via gamma emission to the ground state, while the residing excitation energy is transmitted to electrons. For pure beta decaying ^{228}Ra a slight difference can be noted between efficiency and TDCR (i.e. 0.49 vs 0.52), which is however within counting uncertainty.

The α/β-separation of the Ra-isotopes was achieved at 100% because two parameters can be used for discrimination, that are (i) PLI-setting (i.e. difference between the electronic pulse raise and the decay time) and (ii) differences between the particle

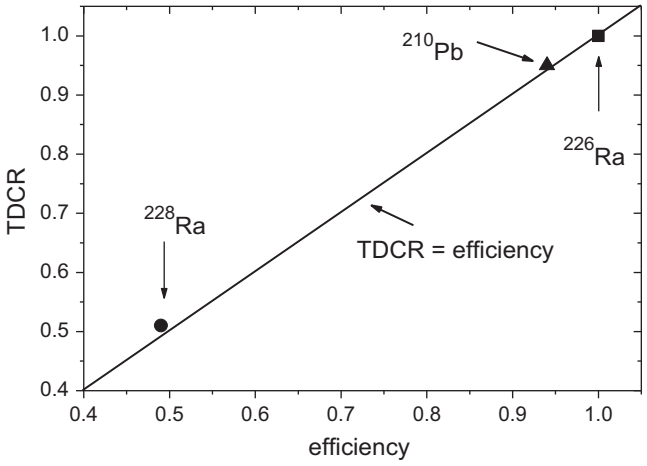

Fig. 1. Measured TDCR values vs. efficiency for three isotopes investigated.

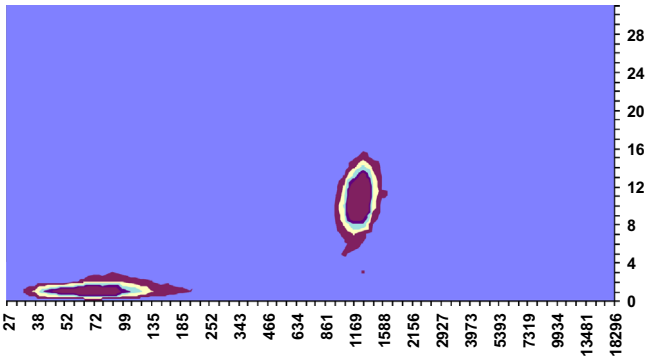

Fig. 2. Pulse length index (PLI) values (*y*-axis) illustrated for pure alpha (^{226}Ra) and beta (^{228}Ra+^{228}Ac) emitters in a two dimensional illustration with the channel number on the *x*-axis.

emission energies, i.e. for the above described cocktail composition the α-emission energies on LS-scale are always above 1 MeV while β-particle emitting radioisotopes from the ^{226}Ra and ^{228}Ra decay series are measured below 1 MeV on LS-scale (see below). The PLI regions for α- and β-pulses from ^{226}Ra/^{228}Ra mixed spike solution measured a few hours after separation is illustrated in Fig. 2 with the channel number (or energy) on the *x*-axis and the PLI-value on the *y*-axis. It is clearly indicated that PLI-values as well as the energy regions are highly different between α- and β-emitting isotopes (i.e. for ^{228}Ra+^{228}Ac, PLI below 4 and for ^{226}Ra above 4). α- and β-spectra obtained for a PLI-setting of 4 are shown in Fig. 3 (α-spectrum of ^{226}Ra+daughters) and Fig. 4 (β-spectrum of ^{228}Ra and ^{228}Ac). Two situations are shown in these figures: one for a 1 h lasting count performed 2 h after chemical separation and one for the same cocktail measured 10 h after separation, therefore with a higher fraction of daughter isotopes. It is obvious that there are almost zero registered α-pulses below 1000 keV and vice versa no β-counts above 1000 keV. Measurements performed under the above described conditions with pure ^{226}Ra and pure ^{228}Ra+^{228}Ac containing cocktails yielded spill-over fractions of β in α (^{228}Ra+^{228}Ac) or α in β (^{226}Ra) of less than 0.1% for both cases.

3. Results and discussion

3.1. Counting conditions and progeny-progenitor isotope relationships

Since pure β^--emission goes along with the emission of an antineutrino, β-spectra are continuously shaped, i.e. ranging from