LIQUID SCINTILLATION

- MEASURING PROCEDURES, NEW DEVELOPMENTS -

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The results of this book are based on literature compilations and experimental investigations to the best of our knowledge. The authors explicitly point out that in the implementation of the proposals and recommendations of this book the individual circumstances should be taken into account. "Good Laboratory Practice" and the state of the art in analytical quality management is a prerequisite for the reliability of analytical results.

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PREFACE

This handbook on Liquid Scintillation (LS) presents a compilation of the most important radioanalytical procedures applying this modern measuring technology. It serves as a manual for the determination of radioisotopes by LS. New developments in this context are described with emphasis on our research work on natural radionuclides published recently in two other handbooks and in the Proceedings of the "International Conferences on Liquid Scintillation Spectrometry” LSC 2001, 2005, 2008, 2010 and 2013.

Several radioanalytical procedures for the environmental survey have been published in Germany and worldwide. However, only a few of them really concern the liquid scintillation technology – wrongfully. Liquid Scintillation Spectrometry (LSS) presents an effective, efficient and universal method for the measurement of radionuclides, especially with the recent developments of extractive sample preparation, α/β–Pulse Shape Discrimination and TDCR for absolute counting. It avoids a tedious and time-consuming sample preparation.

Modern LSS is presented in the first part of the handbook together with a summary of practical equipment calibration techniques. Measuring procedures include to a major part natural radionuclides like Radon and Radium. Additional emphasis is dedicated to radionuclides from nuclear fission activities, like Sr-isotopes by LS and Cerenkov counting. Analytical methods include also Fe-, Ni- and Ca-isotopes as present in decommissioning activities. Due to the present importance a chapter on procedures for NORM has been introduced.

Quality assurance aspects like method validation with uncertainty budget and error analysis are discussed in the last part. A comprehensive literature survey facilitates further studies.

The request of the “LSC-Handbuch” edited in 2008 in German language, and recently in 2012 in English, as well as the high interest from participants of international training activities for IAEA, KIT Karlsruhe, SPERA and OAP was the motivation for DGFS e.V. to publish these measuring procedures.

As constitutional aim of the German Society for Liquid Scintillation Spectrometry DGFS e.V. the authors wish that this handbook would further spread the modern and future prospective methodology of Liquid Scintillation Spectrometry.

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Summary

The most important radioanalytical procedures for Liquid Scintillation (LS) as a modern measuring technology are compiled in a practice-oriented way. The methods cover α/β-discrimination, extractive scintillation for both natural radionuclides as well as activation/fission nuclides resulting from the nuclear fuel cycle.

Following an introduction of the present state of the art of LS technology, calibration procedures like quench correction, α/β–pulse shape discrimination and working procedures for dual and multi labeled samples are presented.

The measuring procedures of the main part include natural radionuclides with special emphasis on rapid methods for Radon, ^{226,228}Ra and ^{210}Pb in water samples, satisfying the worldwide request for drinking water analysis. An excursion to NORM materials in phosphogypsum and in the oil and gas industries follows.

Procedures for the determination of radionuclides in the nuclear fuel cycle address to ^{89,90}Sr fission nuclides, from conventional to recent TDCR Cerenkov counting (^{89}Sr and ^{90}Y), but includes as well ^{241}Pu as low β-energy built up product. The determination of ^{55}Fe, ^{63}Ni and ^{41,45}Ca isotopes as EC and low energetic β-emitting activation products in decommissioning activities includes their comprehensive sample preparation.

The part on Radiation Protection covers effluent measurements for Tritium and Radiocarbon as well as laboratory contamination control.

The last chapter of this manual is dedicated to quality assurance aspects as the calculation of lower limits of detection and the uncertainty budget.

A comprehensive literature survey facilitates this handbook to apply further studies on modern Liquid Scintillation Spectrometry.

Contents

2.2.1.5. Radium by Derived Radium RAD Disk Method

Introduction

This method is suitable for all Radium isotopes (^{226}Ra, ^{228}Ra and ^{224}Ra).
The decay and ingrowth properties of ^{226}Ra and its occurrence is desribed in chapter 2.2.1.4. in detail.

^{228}Ra is a low energetic β-emitter with 39 keV maximum energy (56%), but also possesses a 15.5 keV component of lower intensity (35%) [MAGILL 1999]. It is normally present in much lower concentrations compared to ^{226}Ra. However, in water reservoirs of Thorium containing geological formations such as e.g. Wismut area, Saxonia, Kerala/South India, Sri Lanka, South Thailand, Bahia/North Brazil or in the south of Madagascar, it has been found in much higher concentrations compared to ^{226}Ra.

The equilibrium conditions with its progenies are substantially more complex. According to

$$ {}^{228}\mathrm{Ra} \xrightarrow[5.7\mathrm{a}]{\beta^-} {}^{228}\mathrm{Ac} \xrightarrow[6.1\mathrm{h}]{\beta^-} {}^{228}\mathrm{Th} \xrightarrow[1.9\mathrm{a}]{\alpha} {}^{224}\mathrm{Ra} \longrightarrow $$

$$\begin{tikzcd}
 & & & & & {}^{212}\mathrm{Po} \arrow[dr, "\alpha\ 0.3\,\mu\mathrm{s}"] & \\
{}^{224}\mathrm{Ra} \arrow[r, "\alpha", "3.6\mathrm{d}"'] & {}^{220}\mathrm{Rn} \arrow[r, "\alpha", "56\mathrm{s}"'] & {}^{216}\mathrm{Po} \arrow[r, "\alpha", "0.15\mathrm{s}"'] & {}^{212}\mathrm{Pb} \arrow[r, "\beta^-", "10.6\mathrm{h}"'] & {}^{212}\mathrm{Bi} \arrow[ur, "\beta^-\ 61\mathrm{m}"] \arrow[dr, "\alpha", "25\mathrm{m}"'] & & {}^{208}\underline{\mathrm{Pb}} \\
 & & & & & {}^{208}\mathrm{Tl} \arrow[ur, "\beta^-", "3\mathrm{m}"'] &
\end{tikzcd}$$

^{228}Ra forms a variety of α-emitting daughter nuclides.
Its determination of is more challenging because of its low energetic β-radiation and the influences of the short-lived α- and high energetic β-emitting daughter nuclides.
^{228}Ra with $3\mathrm{x}10^{-5}$ Sv/Bq [MAGILL 1999] (ICRP-68 recommends $6.7\mathrm{x}10^{-7}$ Sv/Bq) is estimated as radiobiological more hazardous due to the various α-emitting daughter nuclides in partial equilibrium. In order to limit the effective dose to 0.1 mSv/a, a maximum value of 20 mBq/L in drinking and mineral water for small children should not be exceeded.

The method described here is applicable to all Radium isotopes. It makes use of selective extraction disks and the complexing properties of Radium with EDTA.
Solid Phase Extraction Disks are commercially available for Ra, Sr, Cs and Tc from 3M EMPORE Company (St. Paul, USA) (fig. 14c). Radium RAD Disk filters are made of thin membranes which selectively extract Radium and Lead because of their ionic size. 21-crown-7-ether as extractive agent (see fig. 21) is bound onto a stable inert material of poly-tetrafluoro-ethylene (PTFE). Water samples are extracted through the filter disk and eluted with EDTA [SMITH et al. 1997]. According to the recommendations by 3M, the solution should be stored air-tight for equilibration of ^{226}Ra with ^{222}Rn. After 20 to 30 days ^{222}Rn can be flushed into a ZnS cell and is determined through its α-scintillations.

For ^{228}Ra determination, the loaded filter is stored for 1 to 20 hours. The ingrowing ^{228}Ac is then eluted from the filter by diluted HNO_3, evaporated on a plate and measured in a proportional counter [EPA 1980].
The main advantage of the Radium selective filter is the enrichment of Radium from water samples of up to 3 to 5 L volume. The procedure prescribed by the manufacturer [3 M EMPORE 1998] is unsuitable for fast results and in-situ analysis because of the long storage time and the laboratory intensive solid scintillation measurement.

Following our investigations [Möbius et al. 2002], we recommend a simplified and rapid modification. After filtration Radium is eluted drop wise with a small amount of alkaline EDTA. After the addition of a gelating cocktail (OptiPhase HiSafe III), the eluate is measured directly in an α/β-LS spectrometer. ^{226}Ra can be quantified in the α-channel and ^{228}Ra simultaneously in the β-channel (fig. 16).
We have also used the method for in-situ water analysis with a filter cartridge (fig. 14 b). The sample is filtered into a syringe, eluted immediately and measured with the mobile HIDEX Triathler instrument.

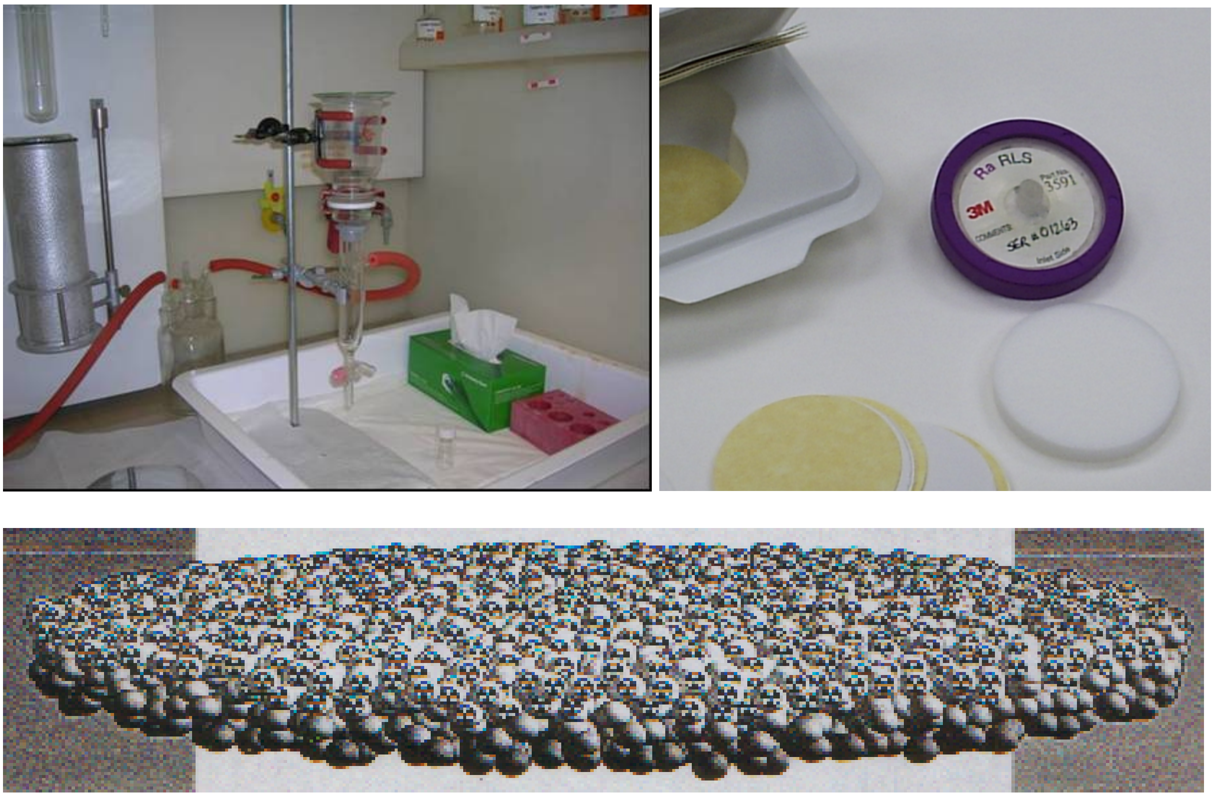

Figure 14: RAD Filter Disk
(a) Filtering apparatus (b) Filter cartridge with Radium filter
(c) Filter material (enlarged)

Materials and Equipment

- Radium RAD DiskFilter (3M Empore, FCI Consulting & Instruments)
- HNO_3 (conc. 2M, 0.5M)
- 0.25M EDTA solution alkaline

- OptiPhase HiSafe III
- Filtering apparatus (for 48mm filter diameter) with recipient
- Sucking finger (50 mL)

Procedure [MÖBIUS et al. 2002]

(1) 3 L water sample are acidified with concentrated HNO_3 to 2M (130 mL 12 M HNO_3 per Liter of water).
(2) After preconditioning of the Radium RAD Disk with 20 mL 2 M HNO_3 the water sample is extracted by filtration (< 50 mL/min).
(3) The filter is washed with 10 mL 0.5 M HNO_3, with further 10 mL distilled water and then sucked sharply.
(4) The Radium isotopes are eluted from the filter by drop wise addition of 5 ml 0.25 M alkaline EDTA (twice for quality control!) and collected in a small recipient.
(5) The 5 mL sample is mixed with 16 mL of OptiPhase HiSafe III cocktail in a glass vial (clear gel!) and is stored for 3 hours (decay of ^{214}Pb) before measurement.
(6) ^{226}Ra is quantified from the α-PSD-channel and ^{228}Ra from the low energetic β-channel.

Remark: Do not run the filter dry during extraction!

Modified Procedure for better sensitivity

(1') The Radium isotopes are eluted dropwise with 12 mL 0.25M EDTA alkaline and then covered with 9 mL organic cocktail (BetaPlate Scint or Toluene Scint).
(2') The vial is closed and stored with the cover downwards in a refrigerator.
(3') After equilibration with ^{222}Rn (minimum 20 days) the vial is shaken vigorously (time t_0), stored for another 3 hours and then measured in the α-channel.

Evaluation

Measurement of the EDTA eluate directly:

The activity concentration A_C of the water sample is calculated by

$$\boxed{A_C = \frac{R_N * 1000}{\varepsilon * \eta * V} * f(t) \qquad [\mathrm{Bq/L}]}$$

whereas

R_N = Net rate (cps)
ε = Measuring efficiency (90 to 100 % for ^{226}Ra)
η = Elution yield (95 to 100 % under optimized conditions)
V = Sample volume (3 L)
f(t) = Correction factor for ^{222}Rn ingrowth between elution and measurement in case of ^{226}Ra
$f(t) = 1 / 3(1-\exp-(t_1/T_{1/2}\ ^{222}\mathrm{Rn}) * \ln 2))$