Contents

1. Introduction

1.1. The Liquid Scintillation Process

Liquid Scintillation Counting (LSC) or Spectrometry (LSS) is a measuring technique which is especially suitable for difficult to measure radionuclides like pure β-emitters. It is the method of choice for the determination of low energetic β-emitters like ^{3}H ($E_{\beta max}$ = 18 keV), ^{14}C ($E_{\beta max}$ = 156 keV), ^{35}S ($E_{\beta max}$ = 167 keV) and ^{63}Ni ($E_{\beta max}$ = 67 keV) for more than sixty years.
Due to the measurement as liquid solution under 4π-geometry, nearly without absorption and self-absorption, it is possible to determine low energetic β-emitters with high counting efficiencies. However, liquid scintillation technology is capable to detect all processes emitting light photons, both, directly and indirectly. Therefore, the method is also applicable for high energetic β-emitters, electron capture nuclides and α-emitters as present in recent decommissioning activities. Solid scintillator microspheres as well were added to this technique as they use the same equipment and facilities.

In liquid scintillation LS, organic aromatic compounds are dissolved in a suitable solvent, known as scintillation cocktails, instead of solid crystals. Scintillators applied are based on electronic transitions from organic aromatic molecules with symmetric properties and π-electrons in resonance.
The energy of the in-coming radiation is preferably transferred to the solvent molecules by electronic excitation before being migrated radiation free and trapped finally by the scintillator molecules. Commercially available scintillation cocktails additionally transfer the energy from the primary to a secondary scintillator (wave length shifter) emitting photons with a wave length of 400 to 420 nm (prompt fluorescence). They hit the photocathodes (mostly two in opposite direction in coincidence or more recently three in angular arrangement) and liberate electrons effectively. Amplified, they create an electrical pulse with a pulse height being proportional to the energy of the decaying particle. Thus, in contrast to proportional counting, LSC presents a semi-spectrometric method. By applying upto three energy windows, the spectra can be unfolded comparable to γ-spectrometry.
The mechanism of energy transfer for the production of photons is presented below (fig. 1).

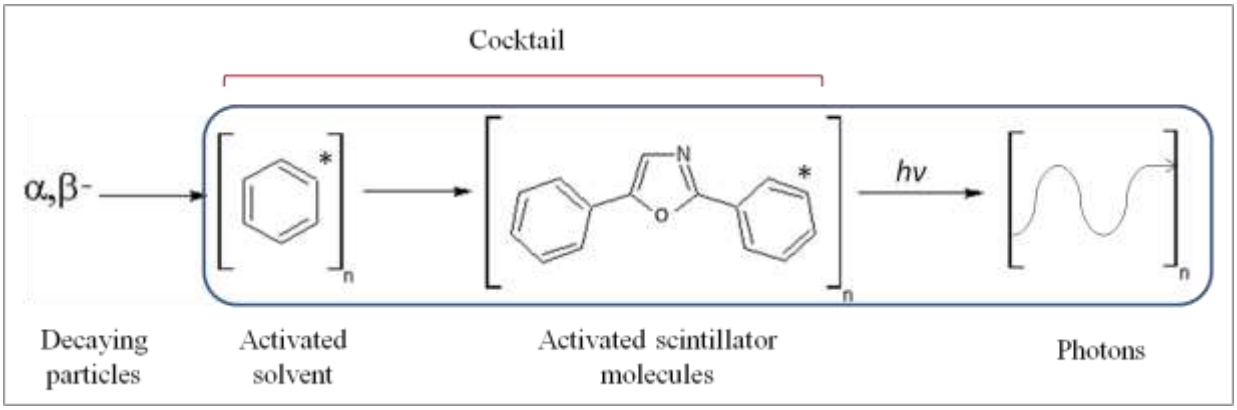


Figure 1: Mechanism of energy transfer in LS

Due to the intimate contact between sample and scintillator molecules as homogeneous solution, the measuring efficiency in Liquid Scintillation is extremely high. α-particles as well as medium and high-energetic β-emitters are detected with 95 to 100% efficiency practically quantitative. Electron capture nuclides as present in decommissioning activities (^{55}Fe, ^{41}Ca) are measured upto 40% mainly by their Auger electron emissions, if higher than 1 keV.

A survey of typical efficiency values is given in table 1.

Table 1: Typical counting efficiencies for various radionuclides by LS

Nuclide		Efficiency [%]
Low energetic β-emitters	^{3}H (19 keV) ^{210}Pb (17 keV) ^{241}Pu (20 keV)	70 to 80 *
	^{63}Ni (64 keV)	80 to 90
	^{14}C (156 keV)	90 to 95
	^{35}S (167 keV)	90 to 95
High energetic β-emitters		95 to 100
Cerenkov radiation	^{32}P (1.7 MeV)	50*
	^{89}Sr (1.5MeV)	45*
Electron capture nuclides (^{55}Fe, ^{41}Ca)		20 to 40*
α-emitters (^{226}Ra + progenies, Actinides)		100
γ-emission (for Eγ>430 keV)		1 to 5

* Lower values for devices with single photomultiplier PM due to luminescence discrimination in the lower spectral part

If suitable calibration standards and TDCR are unavailable, a good approach for the efficiency is 100% for α-emitters without α/β-discrimination and 95% for medium and high energetic β-emitters for unquenched samples in an open energy window. Lower counting efficiencies compared to the theoretical values arise from quenching, but can as well be caused by pulse height discrimination settings and pulse shape discrimination (PSD) when counting in an optimized α-channel.
γ-radiation and X-rays like neutrons do not carry charge and therefore do not ionize directly. However, they interact with liquid scintillators mostly via formation of Compton electrons. Their energy will be absorbed by the scintillation medium like electrons through fluor excitation and emission of visible light.
More recently (LSC2020 Conference) Liquid Scintillation has been reported for neutron and neutrino detection. Even though no primary ionization is available, neutrons may be detected through recoil protons in H-containing scintillators or as thermal ones through ^{10}B(n,α)^{7}Li reaction in Boron containing scintillation cocktails. Applications have been suggested for future fusion facilities [LIU et al. 2021]. The two mechanisms of fluor excitation via recoil protons or Compton electron energy absorption forms the basis for the pulse shape discrimination of neutrons from γ-radiation (see chapter 1.4.1.).

There are presently several neutrino experiments in the world using liquid scintillators for catching neutrinos and detecting them. However, large facilities are necessary [DING et al. 2021], similar to the unique experimental confirmation of the existence of the neutrino using liquid scintillation detectors in 1956 (for details see L'Annunziata [L'ANNUNZIATA 2020/1 pp 716].

With respect to sensitivity Liquid Scintillation is a competitive method even to mass spectrometry for radionuclides with half-lives less than 100 years like ^{3}H, ^{241}Pu and $^{89,90}Sr$.

1.2. Quenching

One major issue in liquid scintillation spectrometry is quenching. Quenching is defined as the irreversible absorption of decay energy or photons during the energy transfer process from the decaying particle to the photocathode. Quenching shifts the whole pulse height spectrum towards lower energies. It consequently results in the reduction of the counting efficiency for radionuclides with continuous energy spectrum like β-emitters (fig. 2).

The main causes for quenching include:
1) Chemical quench: The photoemission is reduced by substances taking over the excitation energy of solvent molecules without transferring them to the scintillator. Chemical quenching prevents the energy transfer from decay particle to the scintillator. It is in practice the most frequent kind of quenching.
2) Color quench: The number of photons produced may be diminished by light absorption from dyestuffs or turbidity. Color quenching hinders the transfer of the pre-formed photons from the primary to the secondary scintillator and from the secondary scintillator to the photocathode. It is the kind of quenching in Cerenkov Counting.

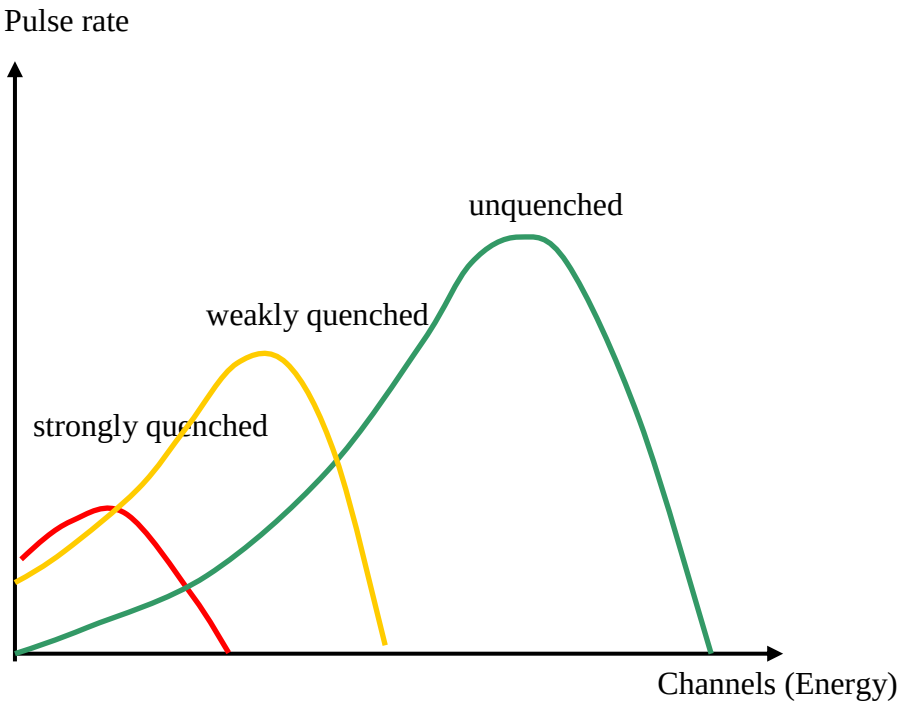


Figure 2: Pulse height spectrum of samples with different degree of quenching

Quenching for β-emitters reduces the counting efficiency. As the degree of quenching cannot be recognized directly, suitable corrections must be applied for quantitative activity determination of the sample. More details on the quenching mechanism can be found in [MOEBIUS and MOEBIUS 2012].

Current methods for quench correction are:

- Internal standardization
- External standardization
- Channel ratio method
- CIEMAT-NIST method
- TDCR
- Shift of the centre of gravity of the spectrum
- Shift of the inflexion point of the Compton edge (H-number)
- Comparison with standard samples ("Instant DPM" method)

The channel ratio method represents a universal method for quench correction. It does not depend on external standardization and can therefore be used in mobile instrumentations. The recently commercially applied TDCR method allows quench correction without standard and external source, but affords devices with three photomultiplier PM tubes.

➢ Internal standardization

The ratio between the difference in the count rate of the sample before and after the addition of a known amount of standard of the same isotope and its activity is a measure for the counting efficiency ε. As sample and standard are affected equally by quenching, the activity of the original sample can be calculated through:

$$\varepsilon = \frac{R_2 - R_1}{A_S}$$

where

R_1 = Net rate of sample
R_2 = Net rate of sample plus standard
A_S = Activity of standard added

Internal standardization is a universal method which allows as well quench correction in heterogeneous and turbid samples.

➢ Channel Ratio method

For the channel ratio method the sample is measured in two different energy regions of the pulse height spectrum (fig. 3).

While channel 1 only detects the high energetic pulses, channel 2 measures the whole spectrum. With increasing quenching, the number of pulses in the high energy channel 1 is much more reduced than the total count rate in channel 2. Thus, the ratio of the count rates varies and is a characteristic measure for the degree of quenching. A calibration curve for the channel ratio versus the corresponding efficiency is plotted by preparing a set of standard samples with different quenching. The detailed procedure for this universal correction method is described in 2.1.1.

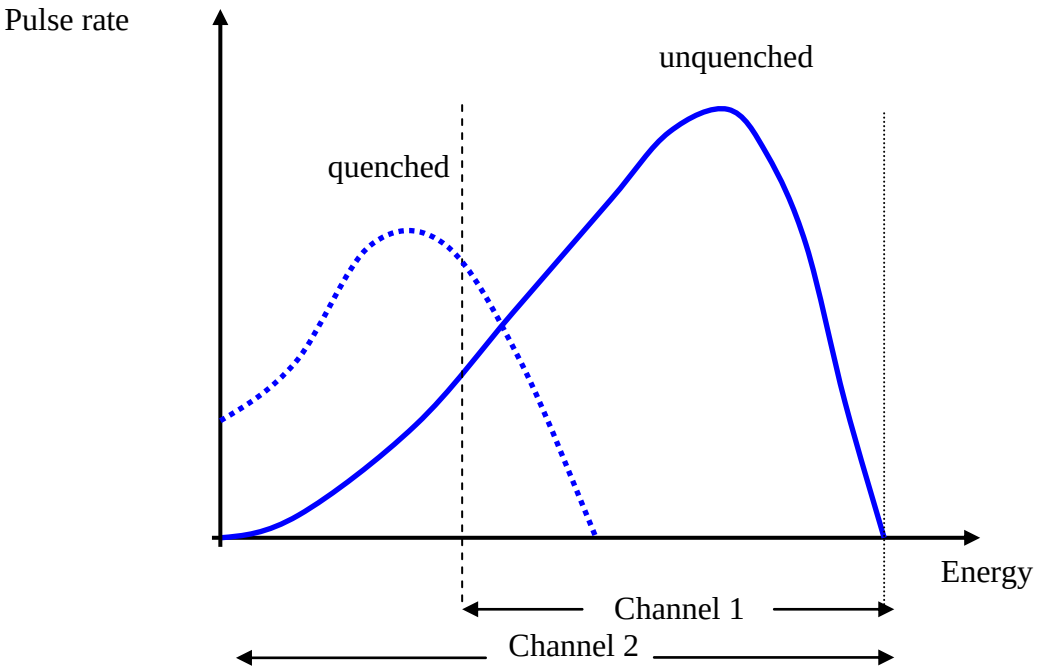


Figure 3: Channel setting for the channel ratio method

- CIEMAT-NIST method

The CIEMAT-NIST method is based on mathematical models, which apply the fact that the distribution of the produced photoelectrons from a secondary electron multiplier is known (Poisson distribution). For β-emitters the continuous β-spectrum has to be calculated. The unknown free parameter on geometry and counting conditions is determined by measurements of a tracer nuclide (mostly Tritium) under equal experimental conditions. It only needs a single calibration measurement and determines the efficiency relative to the standard.

- TDCR method

The TDCR method (Triple to Double Coincidence Ratio), as originally introduced by Broda [BRODA et al. 1988], is nowadays the mostly applied method for quench correction. It does not need any external source or standard. It is an absolute (primary) method, at least for pure β–emitters, but requires three photomultipliers ABC for the determination of the TDCR value as free parameter. The introduction of three photomultipliers in coincidence additionally allows a nearly luminescence free counting. Devices using this option are commercially available (HIDEX 300/600 SL) or have been compiled by various metrological institutes (e.g. PSB). They have been successfully used for various applications (see LSC2017 Conference in Copenhagen and LSC2020 Conference in Shenzhen) and present nowadays an established technique [BRODA et al. 2007]. The method is therefore described more detailed in a separate chapter(1.4.5.).

1.3. Cerenkov Counting

Cerenkov radiation results from a charged particle, when traversing a light transparent polar medium (e.g. water) with a velocity being higher than the phase velocity of light in this medium. This causes local electronic polarization of the dielectric molecules, which release electromagnetic radiation when returning to the ground state. For β-emitters in aqueous solution, a minimum energy of 262 keV is necessary. A reasonable efficiency is accessible for β-maximum energies exceeding 1 MeV (fig. 4). Cerenkov radiation does not require a scintillator and can be counted in a commercial LSC. It can be detected in any medium (acidic or alkaline) and is not subject to chemical quenching. Further advantages of Cerenkov counting are the possibility to apply larger sample volumes and the absence of organic waste. Drawbacks include a strong color quenching and lower counting efficiencies.

Due to the limitation of the Cerenkov effect to higher β-energies, small amounts of high energetic radionuclides may be determined in presence of α- and much higher amounts of low energetic β-emitters. However, strong γ-emissions can contribute to the Cerenkov counting efficiency, as being capable of producing Compton electrons above the threshold energy of Eγ>430 keV [TAYEB et al. 2014]. Consequently, the measured and calculated values for ^{40}K and ^{210}Pb/^{210}Bi are above the average ones for pure β-emitters.

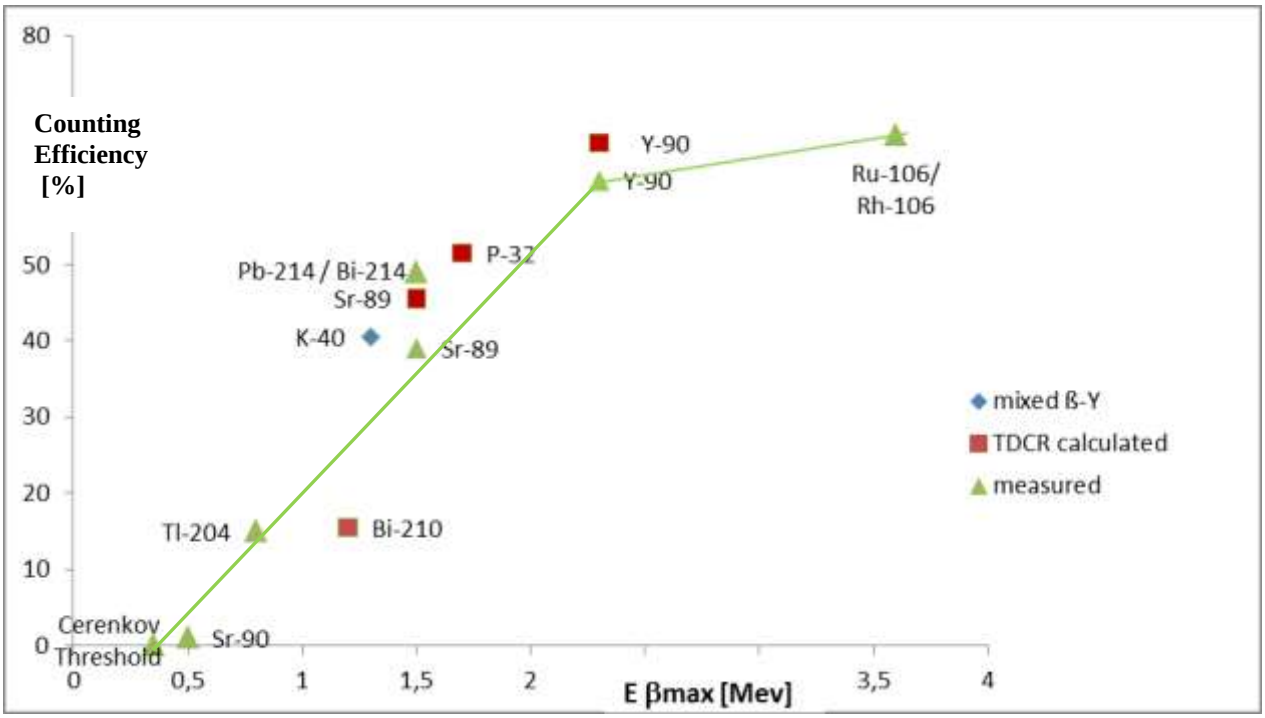


Figure 4: Cerenkov counting efficiency vs β-energy
(calculated for TDCR [TAYEB et al. 2014] and measured by Beckman LS 6000LL [MÖBIUS and MÖBIUS 2008])

Measured values of Cerenkov detection efficiency for HIDEX 300SL instrument were reported recently as of 73.1% for ^{90}Y, 52.4% for ^{32}P, 44.6% for ^{89}Sr and 14.6% for ^{210}Bi

[YANG et al 2021] and 54% for ^{212}Bi [WANG et al. 2022]. TriCarb and Triathler equipment give lower values [L'ANNUNZIATA 2020/2, p 457].
In Radon containing water samples, Cerenkov radiation resulting from ^{214}Bi with an $E_{\beta max}$ of 1.5 MeV and to a smaller extent from ^{214}Pb with an $E_{\beta max}$ of 0.7 MeV can be used for its determination.

Cerenkov counting has recently been applied successfully in combination with TDCR counting. Color quenching can automatically be corrected and no internal or external calibration therefore is needed, which might alter the sample and would cancel one of the main advantages of the Cerenkov counting technique.

1.4. Separation of α- and β/γ-Radiation

The high specific ionization density of α-radiation causes an incomplete energy transfer to the scintillation molecules in a liquid solution. The line spectrum of α-emitters is shifted to lower channel numbers and the whole spectrum becomes broader. Consequently, the energy spectrum of α-emitters appears in the region of medium and high energetic β-emitters (fig. 13).
Thus, a mixture of radionuclides results in a complex spectrum.

Methods for the discrimination between α- and β/γ-radiation apply the pulse height and/or the pulse shape discrimination. This includes scintillator solutions as well as a solid state, either as crystalline materials or as plastic scintillators.

1.4.1. Scintillator Solutions (Pulse Shape Discrimination)

The method of **Pulse Shape Discrimination PSD** makes use of the different time duration of α- and β/γ-pulses for their separation.
When the light photons, being created by the scintillation process, are analyzed in dependence on decay time, two different regions can be observed. The main part of the light emission shows a fast exponential decay in the nanoseconds range, while the other component, because of annihilation of triplet states, is delayed and shows a slower pulse decay in the range of tenth of microseconds. The distribution of these two components depends on the specific ionization and therefore on the type of radiation. The higher the ionization density of the particle, the higher is the part of the triplet transitions as slow component. Therefore, for α-radiation the slow component dominates, while for β- and γ-radiation the fast component is preferred.
The electronic Pulse Shape Discrimination makes use of setting time ramps for α-particles, registering only the 30 to 40 ns longer α-component in separate channels (fig. 5). A proper PSD-level may be optimized by visualization of the pulses using a multi channel analyzer. Even though the method has been published already in 1986 [McDowell 1986], [McDowell and McDowell 1991, 1994], counters with satisfying results and β-interferences in the α-channel of less than 0.1% are commercially available only in the last two decades. Pulses in liquid scintillator solutions are analyzed both by pulse duration (pulse shape) and by pulse height (spectrum shape).
The practical performance of α/β-discrimination in LS-counters varies slightly according to the manufacturer.

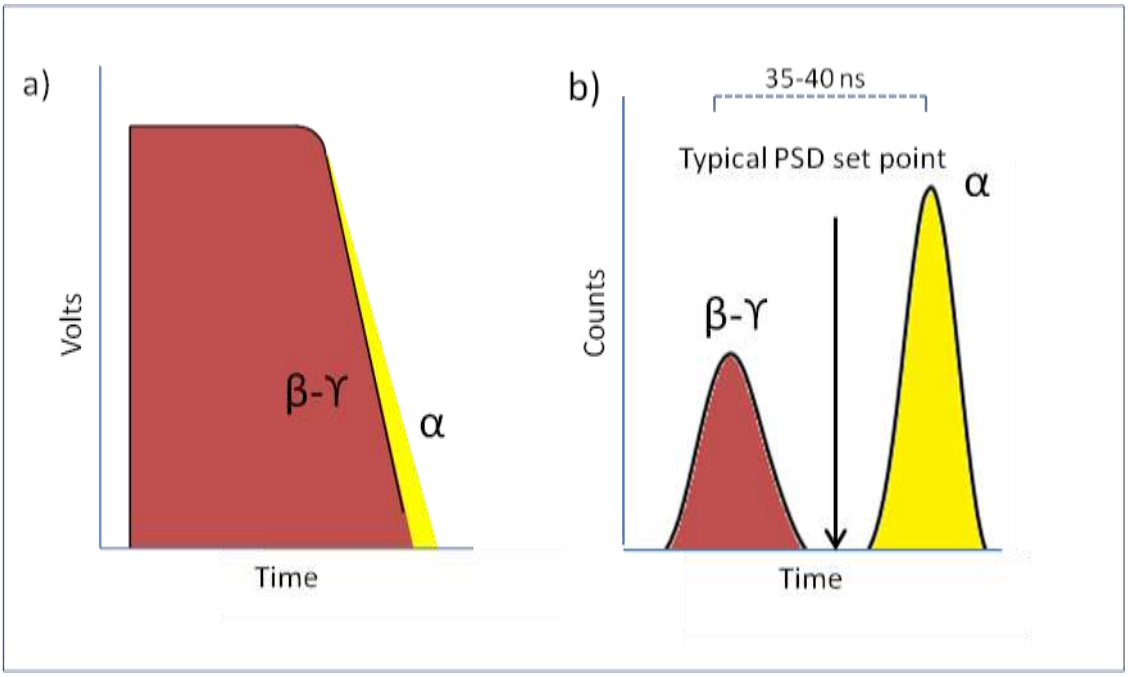


Figure 5: Time duration of pulses for α– and β/γ–signals and representation in a MCA

The time duration of pulses (vertical scale in fig. 6) is plot versus pulse height / energy in figure 6. Thus, α-pulses appear in the upper part of the graph in an energy region of medium to high energy β-emitters. A Pulse Length Index PLI as time ramp is set for α/β discrimination for HIDEX LS equipments (Triathler and 300/600 SL) in that way, that β/γ-pulses do not interfere in the α-channel (fig. 6, pulse duration PLI series 22).
The counter calibration procedure for α/β-discrimination in Triathler as example is outlined in chapter 2.1.3.

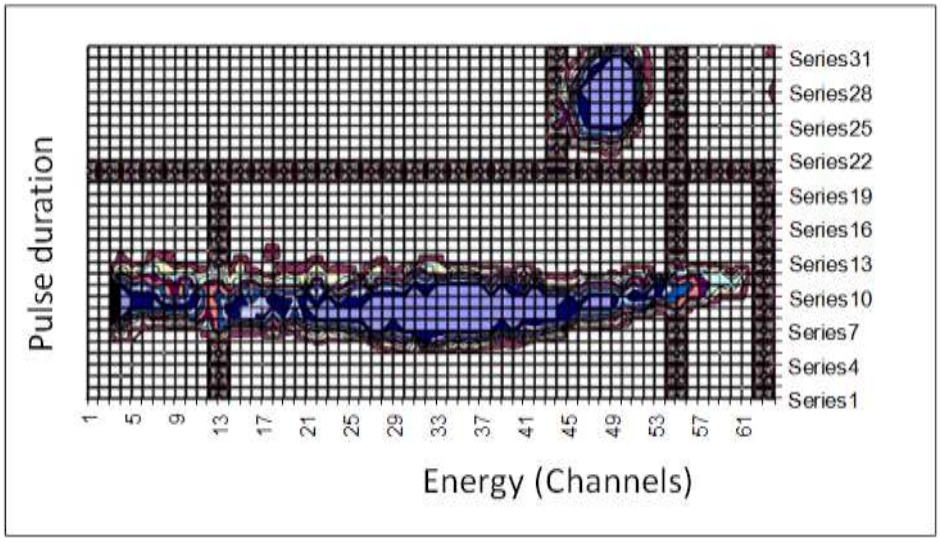


Figure 6: Pulse length vs pulse height spectrum of ^{226}Ra (α–emitter) together with ^{90}Sr/^{90}Y (low/high energy β-emitter) in organic phase (x-axis x 16 = channel number, y-axis x 32 = PLI = Pulse Length Index, Triathler, RADAEX, 0.5 mL in plastic counting vial)

A good α/β-discrimination implies that the pulses are not affected neither by the scintillation cocktail and counting vial, nor by quenching effects or through the registering electronically device.
The time duration of α-pulses in organic scintillation cocktails like BetaPlate Scint™, MaxiLight™ or Extractive Scintillators is comprehensively longer compared to aqueous systems. This leads to a decisive better α/β-discrimination. Organic phases in combination with scrached glass, PE and Teflon vials provide the best separation results (fig. 6 and 7).
According to our measurements less than 0.1% of all high energetic ^{32}P-pulses interfere in the α-channel of Triathler equipment compared to 1% in aqueous phases. Luminescence and low energetic β-emitters practically do not interfere in organic phases. A background of less than 1 count per hour in an optimized α-channel with respect to energy region and Pulse Length Index for BetaPlate Scint in a mini-vial of 8 mL or less has been found.

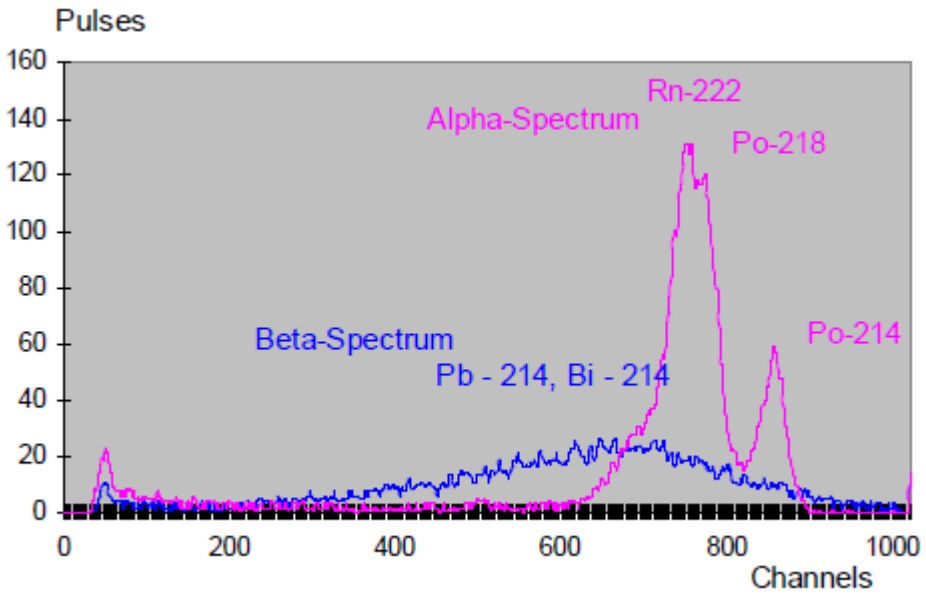


Figure 7: α/β-PSD spectrum of an organic Rn containing sample in scratched glass vial (Triathler)

With aqueous gel phases only a poor α/β-PSD separation is achievable (fig. 18, page 49).
From 8 different gelating cocktails measured in the Triathler device, we have found the best results for Ultima Gold™ AB, OptiPhase HiSafe™ 3 and AquaLight™ in a ratio of 8 mL water to 12 mL cocktail (see also [SALONEN 1993]).
The quality of α/β-PSD in aqueous phases is highly influenced by quenching from higher salt content or from EDTA-containing solutions (section 2.2.1.5.). This allows only a low ratio of aqueous analyte to cocktail. A maximum of 6 mL could be mixed with 16 mL OptiPhase HiSafe 3 in order to form a clear gel. Milky opaque emulsions do not allow any α/β-separation capability.

1.4.2. Solid Scintillators (Pulse Height Discrimination)

Solid Scintillators are available as caps, powder or in columns. Solid Scintillator Caps, commercially purchased as ReadyCaps (Beckman Instruments) and LumaCaps (Packard Instruments), have been introduced in the 90th to reduce the waste problems arising from scintillation cocktails. These are small cylinder crucibles, which are coated with yttrium silicate on the bottom. The analyte as a solution of 200 µL is pipetted onto the surface bottom and dried. The small cylinder is placed in a 20 mL LS counting vial and measured in the dry state. We could show [MÖBIUS and RAMAMONJISOA 1993/3, 1995/1, 1995/2], that α-spectra in solid scintillators are less shifted to lower energies because of the higher scintillator density in solid materials. It therefore may be applied for α/β–discrimination via pulse height analysis without PSD. Even with a surplus ratio of β (^{90}Sr/^{90}Y) : α (^{210}Po) of 1000 : 1, we have not found any remarkable interferences in the α-energy region (fig. 8b,c).

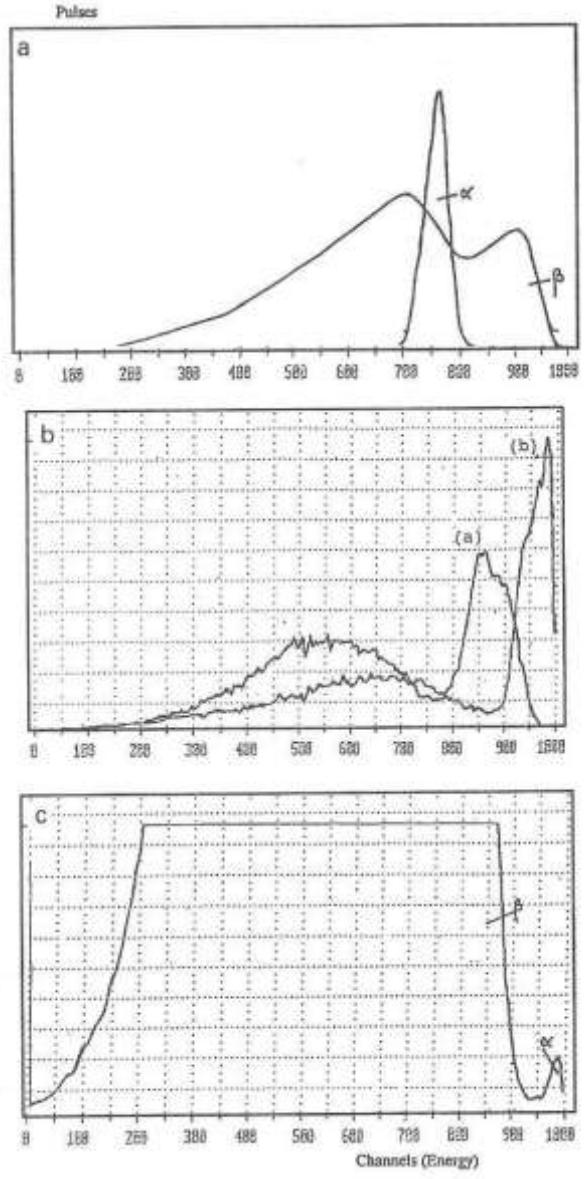


Figure 8:
Spectrum of a mixture of α (^{210}Po) and β (^{90}Sr/^{90}Y)
[MÖBIUS ET AL.1995/1]

a) in liquid scintillator (Ultima Gold XR)
activity ratio 1 : 1

b) in ReadyCaps (a) and LumaCaps (b)
activity ratio 1 : 1

c) in LumaCaps
activity ratio 1 : 1000

From the energy spectrum, illustrated in figure 8c, it can be seen, that interferences from β-emitters in the α-channel from 950 to 1000 (LumaCaps) are < 0.01% for a total α-counting efficiency of 50% and thus can be neglected [MÖBIUS et al.1995/1].
However, the degree of shift for α-particles varied significantly according to the thickness of the Yttrium silicate coating of each batch. The effect was therefore not further investigated.

Solid scintillator materials as Solid Scintillator Microspheres both as powder or in columns have been reported for radionuclide extraction and measurement in the recent decade (see chapter 3.). They allow the fast and efficient analysis of α- and β-emitters. More recently as well their α/β-separation capabilities have been shown.
Solid Scintillation in the form of plastic scintillators may be considered as solid solutions of one or more organic scintillation fluors in translucent plastic. Their design is either the integral plastic scintillator of one whole piece, or as several thousand plastic scintillation fibers (each in 25 – 60 μm in diameter) as individual light pipes bundled together into only a few mm diameter [L'ANNUNZIATA 2020/2, pp 567]. Their feasibility for α/β PSD seems to resemble to those of liquid scintillators.
A plastic scintillator with enhanced α/β-PSD capabilities has recently been reported for the analysis of ^{222}Rn by Hamel [HAMEL 2021]. The high quantity of biphenyl in the plastic scintillator leads to the decent α/β-discrimination.

1.5. Triple to Double Coincidence Ratio Method TDCR

While in traditional LS counters one or two Photomultiplier Tubes PMT are integrated as detectors, an enhanced counting geometry with three PMTs (120^0 angles to each other, fig. 9) and two different coincidence outputs has been commercially provided in 2008 (HIDEX 300/600 SL). This enables higher counting efficiencies, automated quench correction by triple to double coincidence ratio (TDCR), and luminescence free counting [HAASLAHTI 2010].

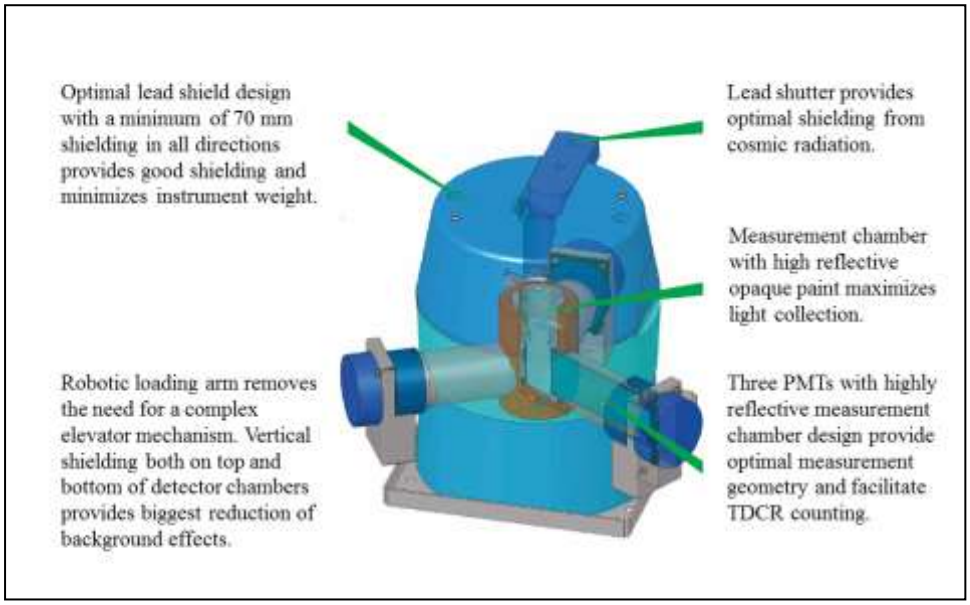
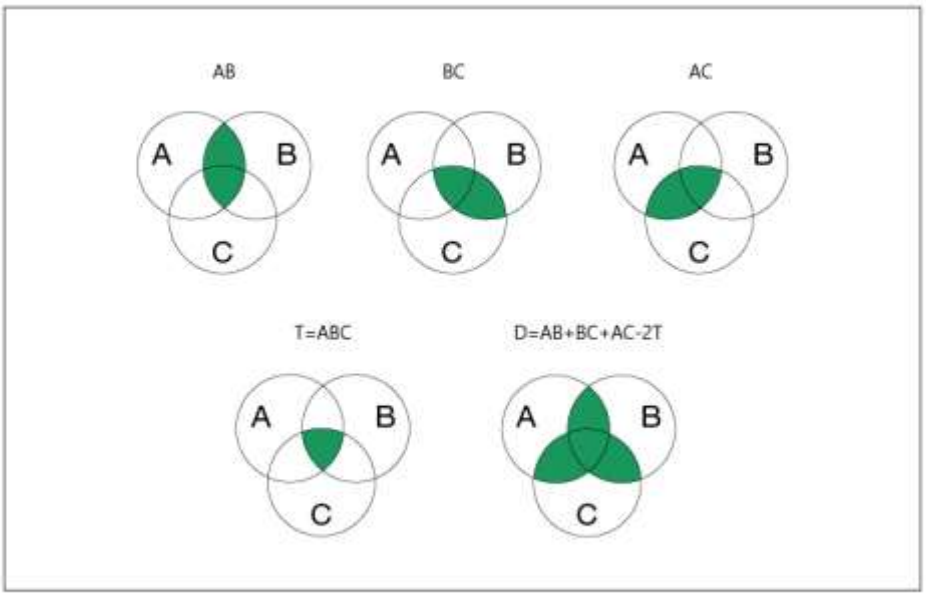


Figure 9: Instrumentation of HIDEX 300 SL TDCR LS counter (Courtesy of HIDEX, Turku)

The TDCR method has originally been developed for the direct determination of the absolute activities of β^- and EC decaying radionuclides in liquid scintillator medium. Instruments on a homemade basis were used by various metrological laboratories already since 1988 for radionuclide standardization [MALONDA AND COURSEY 1988]. TDCR combines theoretical calculations of the counting efficiency and fitting to experimental data. It is a direct counting efficiency determining factor. As triple coincidences are more affected by chemical and color quench than double coincidences, the level of quench is directly related to TDCR. However, the knowledge of the radionuclide decay scheme data is precondition. This is used to calculate the counting efficiency based on a physical and statistical model of the interactions of β-particles, Auger- and Compton-electrons with scintillation cocktails. A detailed mathematical description of the theory and praxis of TDCR can be found in [BRODA et al. 2007], [NÄHLE AND KOSSERT 2011], [CASSETTE 2011] and [L'ANNUNZIATA 2020/1 pp 682]. A more simplified explanation is given below.

The sample is measured in all three PMT simultaneously:



The three double coincidence counts (D) AB, BC and AC and the triple coincidence (T) ABC are determined. The ratio of triple to the logical sum of double coincidence counts is calculated according to

$$TDCR = \frac{T}{\sum D + T} = \frac{\text{Triple Counts}}{\text{All Counts}} = a * \varepsilon$$

For **pure β-emitters** TDCR is directly proportional to the overall efficiency ε or even equal for low or medium quenched samples, both chemical and color quench.
At higher quench levels, double counts drop faster than triple counts. These deviations of TDCR from the counting efficiency ε of up to +-15% can be eliminated by corrective equations e.g.

$$\varepsilon = [TDCR + a\,(1-TDCR)^{b} * (9\,TDCR^{2} / 1+2\,TDCR)^{2} - TDCR]^{c}$$ [HAASLAHTI et al. 2017]

where a, b and c are coefficients depending on radioisotope and cocktail used.
For low activities the TDCR values must be corrected as well for background (see 2.3.4.) [HIDEX Technical note DOC 513-008]. For the correct application of the TDCR method optimized settings of the coincidence time, threshold and bias voltage are crucial [WANKE et al. 2012].

The TDCR technique can be extended also to monoenergetic electrons as from **electron capture nuclides.** During the process of EC, a gap in the inner electron shell is created, which is filled up by the transition of outer electrons. The resulting characteristic X-rays are either emitted or are converted into Auger-electrons from the outer shell. These Auger-electrons as

far as above 1 keV, activate the scintillator medium and create a low energy pulse. The low counting efficiencies between 15 and 45% is subject to a high degree of quenching. Thus, the efficient TDCR quench correction is valuable for the practical LS application.
However, as the decay spectra are not continuous due to the contribution of two or more separated group of scintillation energy from conversion electrons and γ-quanta, there can be more than one counting efficiencies corresponding to a given TDCR value. For radionuclides with known decay scheme, like ^{55}Fe and ^{41}Ca, the activity A can be calculated by the probability for logical double coincidences TDCR through

$$A = \frac{27\,(TDCR)^2}{(1 + 2 * TDCR)^3 * K}$$

where K is the transition probability of the Auger-electrons resulting from the conversion of characteristic X rays [KOSSERT 2010], [OIKARI 2012]. The contribution of photons from additional γ- and X-ray transitions (^{40}K) to the electron spectra has to be considered as well. In case of ^{55}Fe, the combined factor K is 0.869. Otherwise a correlation of counting efficiencies vs TDCR value with a set of standards to correct for quenching has to be established. A counting efficiency of about 45% for ^{55}Fe and some 20% for ^{41}Ca has been found (see fig. 32, p113).
Diffusive vials like polyethylene or frosted glass of 20 mL volume, filled with 12 to 15 mL, generally give the highest counting efficiency and are preferable for TDCR counting.

For **Cerenkov** counting the counting efficiencies can also be calculated through TDCR and the known energy spectrum of Cerenkov electrons (Maxwell equations) [KOSSERT 2010]. It hence leaves the sample unaltered in contrast to classical internal standardization.

Even though the TDCR correction has been reported as effective for color quenching, an asymmetry in the detector geometry and the anisotropy of Cerenkov light propagation, which depend on measuring conditions and instrument, has generally to be taken into account. Therefore an experimental fitting is recommended for more accurate activity analysis. An empirical natural logarithm correction curve in TDCR Cerenkov counting has been described recently [ZIEMEK et al. 2022/1], [Yang et al. 2021] and [DAI et al. 2021] as

$$\varepsilon_{Cerenkov} = a * \ln(TDCR_{net}) + b$$

whith a has a given value for a and known average β-energy.
It combines the theoretical calculations with experimental calibration curves from quench standard sets. Experimental quench curves with TDCR are quite generic and do not need to be redone unlike with the conventional quench methods.
For HIDEX 300SL equipment the variable parameters have been determined for frequently used Cerenkov radionuclides according to table 2 [YANG et al 2021].

Cerenkov TDCR measurements can be applied for rapid screening of high energy β-emitters in the presence of lower ones for environmental applications.
Hence the method is a perfect choice for discrimination between ^{89}Sr and ^{90}Sr (procedure 2.3.4.), for ^{90}Sr determination via the higher energy β-emitting daughter ^{90}Y (procedure 2.3.3.), or for ^{212}Bi from ^{212}Pb, when the state of equilibrium is known (procedure 2.2.1.8.).

Table 2: Correlation between Cerenkov efficiency and average β-energy for HIDEX 300SL(L) TDCR LS-counter (20 mL samples) [YANG et al. 2021], [DAI et al. 2021[1)]] and [WANG et al. 2022]

Nuclide	β-maximum Energy [MeV]	Average β-Energy [keV][1)]	a	b
Y-90	2.3	933.6	0.465	0.866
P-32	1.7	695,0	0.309	0.665
Sr-89	1.5	584.6	0,287	0.610
K-40	1.3	560.6	0.254	0.595
Bi-210	1.2	389.0	0.107	0.256
Bi-212	2.3	NN	0.431	0.742
Ac-228	1.2, 2.1	351.9	0.183	0.349
Cl-36	0.7	251.3	0.065	0.192

Applications of TDCR furthermore have been reported for environmental and biological samples, environmental monitoring and tracking, radiocarbon dating, waste characterization and nuclear medicine e.g. for
- ^{3}H, ^{210}Pb, ^{228}Ra, ^{99}Tc, ^{89}Sr and ^{90}Sr in environmental water samples
- ^{241}Pu, ^{90}Sr, ^{63}Ni in radionuclide waste and decommissioning
- ^{51}Cr, ^{90}Sr, ^{32}P in various biological samples.

For further literature see L'Annunziata [L'ANNUNZIATA 2020/2 pp 59].

Three PMT detectors, additionally, enable high counting efficiencies with minimum interferences from luminescence (fig. 10). This facilitates the immediate measurement of even high luminescent samples including bio-oils, without need for dark adaption (see procedure 2.2.2.1.).

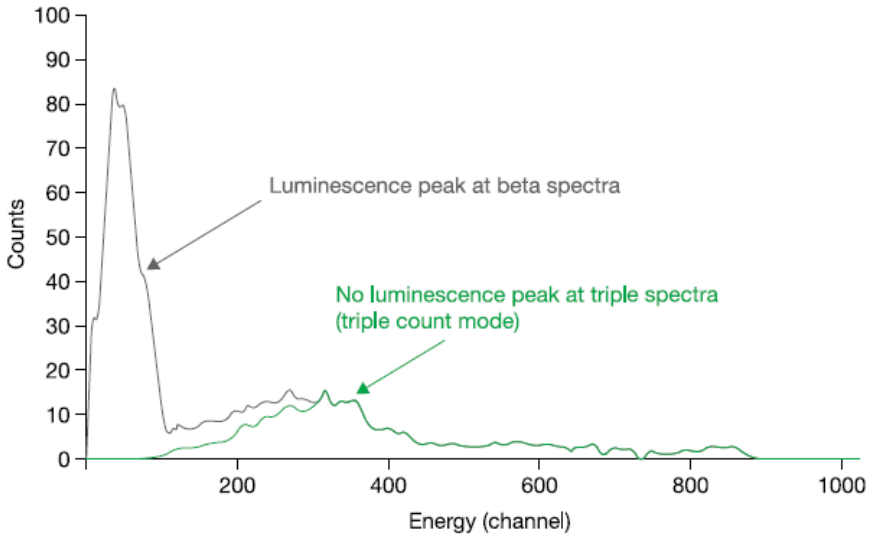


Figure 10: Comparison of spectra by direct detection of bio-oil samples with triple and double count mode
(10 mL oil-samples were mixed with 10 mL MaxiLight cocktail) [HIDEX 2016]

1.6. Miniaturization of LS Devices

Liquid Scintillation (LS) is a universal and efficient measuring method, but nevertheless a simple one. However, it lacked for long time from the availability of mobile instrumentation and low cost equipment. The latter aspect is of importance for spreading this relative novel technology with respect to the limited budget of educational institutions, especially in developing countries.
The first approach has been solved through the availability of HIDEX Triathler mobile equipment with only one photomultiplier tube and less than 10 kg of weight. It comprises a powerful α/β-PSD unit and is thus the method of choice not only for the analysis of Radon and daughter nuclides in air and water un the environment (see procedures 2.2.1.2. and 2.2.1.3.).
Portable TDCR counters were developed in the last two decades as well at LNHB (France), PTB (Germany) and other metrological institutions in the framework of the European Metrofission Project [CASSETTE et al. 2013].

More recently the design and performance of a mobile miniature TDCR counting system incorporating only the necessary components has been described [MITEV et al. 2017]. Three miniature PM tubes and compact optical Teflon chambers, made by flexible 3D printing and digital electronics devices, have been reported. The customized equipments by LNHB (Paris) and NIM (China) are down to 15 cm in diameter and 10 cm in height for 20 mL vial and are powered with 1 Watt by PC USB port. Such mini TDCR devices offer possibilities for onsite activity standardization of short lived radionuclides, as used for medical PET applications (^{18}F, ^{11}C, ^{15}O). The present state of miniaturized equipments has been surveyed by Cassette in LSC2020 [CASSETTE 2021].

We have reacently compiled a low cost simple LS arrangement from widely available materials for use in nuclear educational training. It cannot substitute more sensitive commercial equipments with automatic sample changer and α/β–discrimination, but can promote LS in education in developing countries with limited financial support to a broader group of future users. The set up consists of a recycled photomultiplier tube (PMT) and a widely used nuclear analyzer (Berthold 2040) as central unit. The crucial step arises from the necessity of total light shielding of the PMT during manual sample changing. The arrangement can be seen from figure 11.

Materials and Equipment:

- Scaler/Timer with HV supply (right), preferable with log scale and low entrance level (e.g. Berthold 2040)
- PMT recycled e.g. from defect NaI scintillation counter tubes or disposed LS unit; the scintillation detector is uncapped and rearranged for LS counting with light shielding (fig. 11, left)
- Light reflecting tube (Al) e.g. Garden Ground Socket Set as PM tube holder (left)
- Large rubber stopcock and black crimson for light shielding

Make sure to previously shut-down HV when changing samples manually!

The instrumentation was adjusted for optimum counting conditions and calibrated for measurement. We found it suitable for quantifying α–, high and medium energy β–radiation down to 0.2 MeV maximum energy with limited sensitivity, due to the relatively high background.

Figure 11: Simple self-made LS arrangement [MOEBIUS et al. 2017]

Such customized mobile equipment was compiled at the University of Antsiranana in Madagascar and was successfully applied for LS measurements within radioisotope training for science students. Data of on site Rn and Ra in water measurements have been published [MOEBIUS et al. 2017].

1.7. Cocktails and Sample Preparation

Cocktails:
The LSC cocktail is essential and necessary for analysis. Therefore a proper cocktail selection is a crucial step in sample preparation. The overall performance of a scintillation cocktail is usually assessed by parameters like counting efficiency, sample load capacity, α/β discrimination, quench resistance, sample stability, intrinsic background contribution and sample compatibility. A variety of scintillation cocktails for all kind of applications (aqueous, organic, gelating, filter materials, etc.) are commercially available with modifying scintillator composition and solvents [VASILE et al. 2022]. Cocktails must contain one or more phosphors and an organic solvent containing π-electrons for radiation free energy transfer. Emulsifying or water accepting cocktails contain a mixture of detergents that ensure the coherence of aqueous samples.

The "Bray"-solution as effective and frequently used classical cocktail consists of 120 g naphthalene, 4 g PPO (2,5-diphenyloxazole), 0.1 g POPOP (1,4-bis-2-(5-phenyloxazolyl)-benzene), being filled up to 1 Liter with dioxane or toluene.
Nowadays user friendly and environmental safer cocktails with di-isopropyl-naphtalene (DIN) as solvent are available. Linear alkylbenzenes and/or alcohol ethoxylate (AE) instead of nonyl phenol ethoxylate (NPE) as emusilfier are preferred. These 'safe cocktails' with DIN are heavily inflammable, environmental friendly, biologically degradable and allow as well an excellent α/β-PSD.
An incomplete compilation of frequently used cocktails is given in table 3. A comprehensive review on cocktails and their applications can be found in L'Annunziata [L'ANNUNZIATA 2020/1 PP 803].

Recently NPE-free cocktails were studied with regard to loading capacity in clay water and urine samples for their selection in routine measurements [VASILE et al. 2022].
NPO 2-(1-Naphtyl)-5-phenyloxazole without secondary cocktail, Diisopropylnaphtalene as solvent and a detergent mixture was suggested as ideal composition for water accepting scintillation cocktails [RAJCHL et al. 2022]. For the application of polysilane as efficient and environmentally friendly liquid scintillator see [PU et al. 2022].

Kind of Vial and Volume:
Counting efficiency and quality of the α/β-discrimination depend not only on cocktail composition, but also on kind of counting vial and size.
We have investigated sample volumes of 20 mL and 10 mL in standard vials, 8 mL and 6 mL in mini-vials as well as 2 mL and 0.5 mL in Eppendorf plastic mini-vials for α/β-discrimination using Triathler (HIDEX). The best energy resolution and α/β-discrimination have been achieved with the latter ones in the provided adapters. The lowest limit of detection has been found for 8 mL sample volume in diffused (scratched) mini-vials. Plastic and sand blasted glass vials show a diffuse light and are preferable compared to normal glass vials (commercially available as "froasted scratched vials" e.g. by HIDEX Oy, Turku or FCI, Mainz).
For the commercially available TDCR counter HIDEX 300SL a volume of 12 to 15 mL in 20 mL PE vial has been reported to result the highest counting efficiency [OLFERT et al. 2014]. Kind of counting vial influences as well the reliability of TDCR. Diffusive vials (polyethylene

or froasted glass) are preferred as they do not show reflexions of the internal light and consequently do not give a deviation from the Poisson distribution.
Table 3 presents a compilation of frequently used scintillation cocktails.

Table 3: Compilation of frequently used scintillation cocktails (incomplete)

Purpose	Safe Cocktails/(NPE free)	Classical Cocktails
Aqueous Samples - High Sample Volume - pH < 6	Ultima Gold XR[1)] Ultima Gold AB[1)] (AquaLight[2)]) AquaLight Beta[2)] AquaSafe500Plus[3)] Gold Star LT2[4)] (ProSafe[+4)])	Insta-Gel XF[1)] Insta-Gel Plus[1)]
Organic Cocktails	BetaPlate Scint[1)] Ultima Gold F[1)] MaxiLight[2)] Quicksafe N[3)] (Gold Star O[4)]) Pro-Scint Rn[4)]	Toluene Scint (Bray) Insta Fluor Plus[1)]
High Ionic Strength Samples pH < 6	OptiPhase HiSafe III[1)] (Quicksafe A[3)])	
Low Level Samples	Ultima Gold LLT[1)] AquaLightLL[2)] (Gold Star Quanta[4)])	
Oxidizer and Pyrolyzer	Optisorb-S[1)] Oxisolve C-400[3)] Carbon Count[4)] Tritium Count[4)]	
Filter Samples	(Ultima Gold MV[1)]) (ProSafe FC[+4)]) Filter count[1)]	
Biological Samples (Urine, Plasma, Blood)	(AquaLight AB[2)]) (ProSafe[+4)]) (ProSafe TS[+4)])	

[1)]PerkinElmer [2)]HIDEX [3)]Zinsser [4)]Meridian

1.8. Extraction for Radionuclide Separation and Enrichment

Solvent Extraction in chemistry is a classical method for sample separation and enrichment. The fundamentals and the extractive behaviour of important radionuclides are outlined in [MOEBIUS and MOEBIUS 2012].

Extractive agents for radionuclide separation are nowadays available in the form of Extraction Chromatographic Columns (EICHROM, TrisKem) (see table 5), selective Disk Filter Materials (3M Empore), as Extractive Scintillators in liquid form (ETRAC, 3M EMPORE) (table 4) and as Plastic Scintillator Microspheres (University of Barcelona, TrisKem) (table 10, page 160).

The method of Plastic Scintillator Microspheres is described in more detail in chapter 3..

A comprehensive part of analytical procedures, which are presented in this Handbook (e.g. for Ra, Rn, U, Sr, Ni, Fe and Pu) applies solvent extraction as central separation step.

In **Extractive Scintillators,** a selective extractant is mixed together with a scintillation cocktail. The Extractive Scintillator is contacted before the measurement with the aqueous analyte phase and takes over the function of separating and/or enriching of radionuclides. Sample preparation for radionuclide separation and measurement is done in one single analytical step.

A combination of different extractive scintillators allows rapid procedures for the determination of Actinides in nuclear plants [BICKEL et al. 1992], [LAURIA et al. 1987], [MÖBIUS and YANG 1989] and [YANG et al. 1990, 1991]. Procedures applying Extractive Scintillators for the natural radionuclides Rn, Ra, Pb and Po in aqueous environmental samples are outlined in more detail in our "Handbook of LSS" [MOEBIUS and MOEBIUS 2012], see also [MÖBIUS et al. 1993/1-3] and [YANG et al. 1991]. Commercially available Extractive Scintillators are compiled in table 4.

Extractive scintillators as organic cocktails combine the advantage of allowing additionally a good α/β-PSD-discrimination (fig. 7, 15, 16).

An analytical procedure for the determination of U-isotopes on a HDEHP based extractive scintillator is described in chapter 2.2.1.9..

Table 4: Commercially available extractive scintillators (ETRAC Knoxville/3M EMPORE)

Trade Mark	**Extractive Agent (Element extracted)**
ALPHAEX	0.1 M HDEHP (Actinides)
POLEX	0.1 M TOPO (Po)
RADAEX	0.1 M 2-methyl-2-heptylnonanoic acid (HMHN) + 0.05 M dicyclohexano-21-crown-7 (DC21C7) (Ra)
STRONEX	Crown ether-18 (DC18C7) (Sr)
URAEX, THOREX	0.3 M TOA (from 1 M sulfate at pH 2) (Th and U)
RADONS	Organic cocktail (Rn)

Since more than twenty years, also selective **Filter Disks** for different radionuclides are commercially available. Bonded silica sorbents are known to be commonly used for the solid phase extraction of analytes from complex sample matrices. A variety of functional groups, such as crown ethers, can be bonded to the silica surface to provide selective interactions.

Strontium and Radium RAD Disks have been introduced for the determination of radioactive Strontium and Radium in aqueous samples (see procedures 2.2.1.5. and 2.3.1.).
However, Lead is as well retained by both filters and can be analyzed separately by its slightly different complexing properties, as shown in chapter 2.2.1.6. . For Technetium RAD Disks see chapter 2.3.6..

Extraction Chromatography on columns was first introduced in the 1970s, but it has found now a broader application ever since materials as powder or in prepared columns are available. It contains a selective organic extractant on an inert support. They are commercially available (EICHROM Ind./ TrisKem Int.) and can be used from a variety of sample matrices [HORWITZ et al. 1992]. Among the various available products (table 5), the Strontium SPEC is probably the mostly applied column.

Table 5: Commercially available extraction chromatographic columns (EICHROM / TrisKem) (not comprehensive)

Extractants	Resins	Applications
DTCH18C6/octanol	SR SPEC	Strontium
DTCH18C6/isodecanol	PB	Lead and polonium
CMPO/TBP	TRU	Actinides, Fe
	RE	Rare Earths
Aliquat 336	TEVA	Actinides (IV) and Tc
DPPP	UTEVA	Uranium (VI)
Dipex	Actinide	Total alpha
DMG	Ni	Ni
Crownether	TK101	Pb, Ra, Sr
Tertiary amine	TK201	Tc (neutral, acidic)
Polyethylene glycol	TK202	Tc (alkaline)
TOPO	TK200	Actinides (Pu, Th, U)
	TK300	Cs
Long chained alcohol	TK400	Fe

Additionally, **Plastic Scintillator Microspheres** PSm since 2010 (LSC2013 Conference Barcelona) are an often applied alternative. A plastic scintillation resin (PSresin) is a plastic scintillation microsphere coated with a selective extractant. The method is introduced in a separate chapter 3. in more detail. It is described for the determination of Sr, Pb in various matrices (3.2.1.), Tc (3.2.2.1.), Pu (3.2.2.2.), Po-210 (3.2.2.3.), Cl-36/I-129 (3.2.2.4.) and Gross Alpha (3.2.3.). PSresins are now commercially available (e.g. TK TcScint, TrisKem Int.). They can directly be measured as cartridge after previous removal of liquid phase. For a more comprehensive description of Plastic Scintillators see [HAMEL 2021], [TARANCON et al. 2017], [GARCIA 2022] and the detailed literature citied in chapter 3..

The time consuming extraction chromatographic methods, and handling of generally strong acids for elution, can be avoided by **automation**. An instrument for the simultaneous application of upto 6 mobile phase reagents and 8 samples simultaneously is commercially available by HIDEX, Turku (Q-ARE 100plus)) [LEHMUSVUORI 2021]. It can be used for various sizes of prepared and self-packed columns from 1 to 20 mL.

2. Measuring Procedures

2.1. Instrument Calibration Procedures

2.1.1. Quench Correction Curves

2.1.2. Dual Labeling

2.1.3. Calibration for α/β-Discrimination

2.2. Natural Radionuclides

2.2.1. Aqueous Samples

2.2.1.1. Gross Alpha/Beta Survey in Drinking Water

2.2.1.2. Radon by Extraction

2.2.1.3. Radon by Gel Counting

2.2.1.4. Ra-226 through Radon Emanation

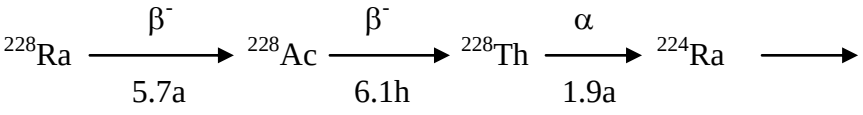
2.2.1.5. Radium by Derived Radium RAD Disk Method

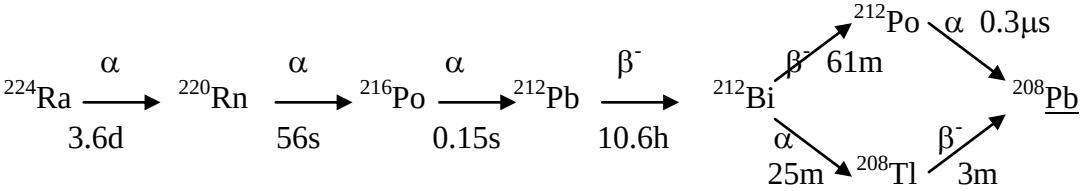
Introduction

This method has been developed by us and is suitable for all Radium isotopes (^{226}Ra, ^{228}Ra and ^{224}Ra). It is evaluated more comprehensively as it presents as well the central step of the following procedures.
The decay and ingrowth properties of ^{226}Ra and its occurrence are described in 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}Ra forms a variety of α-emitting daughter nuclides.
Its determination is more challenging because of its low energetic β-radiation and the influences of the short-lived α- and high energy β-emitting daughter nuclides.
^{228}Ra with $3x10^{-5}$ Sv/Bq [MAGILL 1999] (ICRP-68 recommends $6.7x10^{-7}$ 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. 19). 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. 26b) 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 further determined through its α-scintillations.

For ^{228}Ra determination, the loaded filter should be 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 (3M 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 dropwise with a small amount of alkaline EDTA. After addition of a gelating cocktail (OptiPhase HiSafe III), the eluate is measured directly in a α/β-LS spectrometer. ^{226}Ra can be quantified in the α-channel and ^{228}Ra simultaneously in the β-channel (fig. 21).
We have used the method as well for in-situ water analysis with a filter cartridge (fig. 19 b). The sample is filtered into a syringe, eluted immediately and measured with the mobile HIDEX Triathler instrument.

Figure 19: RAD Disk filter
(a) Filtering apparatus (up left) (b) Filter cartridge with Radium filter (up right)
(c) Filter material (enlarged) (down)

Materials and Equipment

- Radium RAD Disk filter (3M Empore)
- HNO_3 (conc., 2 M, 0.5 M)
- 0.25 M 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 2 M (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.
(4) 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.
(5) ^{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 0.25 M 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

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

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
$f(t) = 1 / 3(1-\exp-(t_1/T_{1/2}\ (^{222}Rn)) * \ln 2)$

For 3 h storage, 1 h measuring time and $T_{1/2}$ (^{222}Rn) = 3.8 d
f(t) results to 1.027.
The factor 3 stands for altogether 3α-nuclides for ^{222}Rn and progenies.

Detection Limit (MDA) for EDTA Gel measurement by PSD:
^{226}Ra 5 mBq/L, ^{228}Ra 40 mBq/L (LL-LS counter)
Total Analysis Uncertainty: 6.7% (see also chapter 4.3.)
.
The total uncertainty budget is mainly due to the uncertainty of the extraction yield and the influence of the α/β-PSD on the counting efficiency.
Because of the poor α/β-PSD of the EDTA gel phase the detection limit for ^{226}Ra determination is limited to 5 mBq/L.

For **improved sensitivity** (factor of 50) ^{226}Ra can be quantified through Rn ingrowth after storage (see modification) according to

$$A_C = \frac{R_N * 1000}{\varepsilon * V} * f_{t1} * f_{t2} \quad [Bq/L]$$

with $f_{t1} = 1 / \exp-(t_1/T_{1/2}(^{222}Rn)) * \ln 2$
and $f_{t2} = 1 / 1 - \exp-(t_2/T_{1/2}(^{222}Rn)) * \ln 2$

R_0 = Background 0.5 count per hour
ε = Measuring effiviency 300% (^{222}Rn, ^{218}Po, ^{214}Po)
V = Sample volume (3 L)
f_{t1} = Correction factor for Rn decay (time between extraction and mean counting time)
f_{t2} = Correction factor in case of unequilibrium
t_1 = Storage time
t_2 = Ingrowth time

Detection Limit (MDA) for modified method: ^{226}Ra 0.1 mBq/L

^{224}Ra interferes the measurement because of the formation of several α-emitting daughter products. We therefore recommend a storage of 2 to 3 weeks until ^{224}Ra has completely been

decayed. We have shown that Bi, Po, Th and U do not disturb, however, Pb-isotopes as well as Ba, Sr and K are retained quantitatively (>90%) from 2 M HNO_3 solution. The presence of Barium in higher concentration reduces the Ra extraction considerably. 3M EMPORE recommends a maximum of 1 ppm for Pb and Ba and 2 ppm for Sr when using 1 L water sample.

Detailed results for Rn and Ra analysis from the workshop along with the LSC2001 Conference can be found in "LSC-Handbuch" page 71 [MÖBIUS and MÖBIUS 2008].

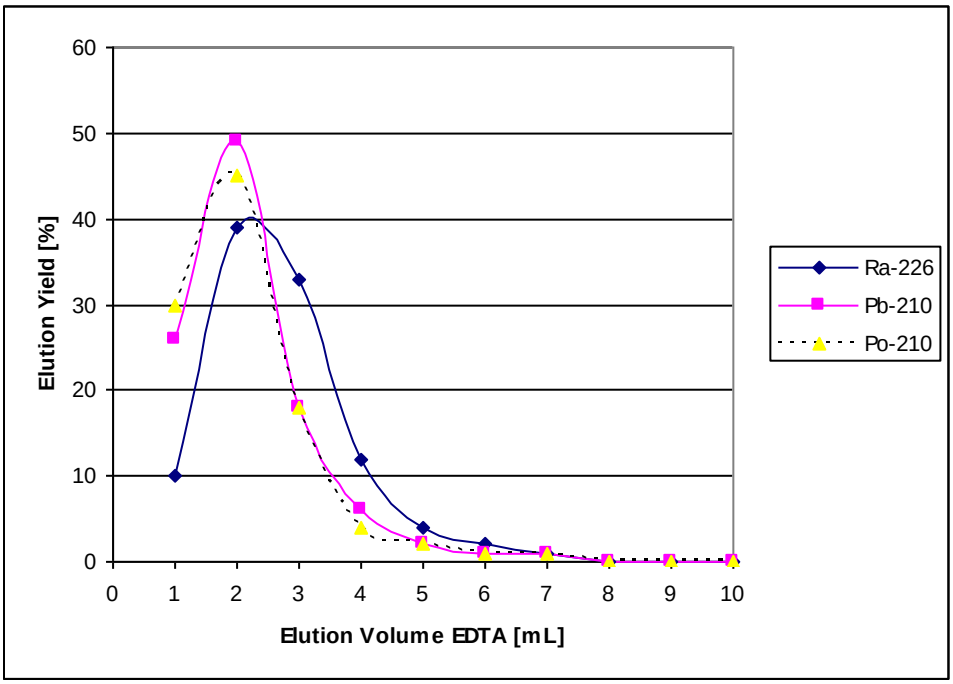
Elution Behavior

Our investigations concerning the elution behavior of different radionuclides on Radium RAD Disk filters have shown that:

- With 6 mL 0.25 M alkaline EDTA, more than 95% of Radium could be eluted drop wise. Pb-isotopes (^{210}Pb), in contrast to ^{210}Po and ^{210}Bi, are also retained quantitatively on the filter; they are eluted as well in alkaline EDTA quantitatively within the first 6 mL (fig. 20).
- Radium shows a higher affinity on RAD Disk filters compared to Lead as can be seen from figure 20. By using 0.2 M alkaline DHC (di-hydrogen citrate) or neutral EDTA as weaker eluent, the elution of ^{226}Ra is less effective than ^{210}Pb. Consequently, interferences from Pb-isotopes may be eliminated by elution with 5 mL of 0.2 M DHC in the first step. Stripping of Pb-isotopes with 6 ml DHC reduces the yield for Radium by approx. 5% (fig. 20b).
- Ingrowing radionuclides from elements which are not retained on the filter may be separated by diluted HNO_3 at any time. This concerns ^{228}Ac as daughter of ^{228}Ra, as well as ^{222}Rn, ^{218}Po, ^{214}Bi and ^{214}Po as daughter nuclides of ^{226}Ra, and additionally ^{212}Bi as daughter of ^{212}Pb. Rn-isotopes exhale during filtration and do not interfere in contrast to RADAEX as extractive scintillator. ^{214}Pb and its direct daughters ^{214}Bi and ^{214}Po decay after 3 hours storage. ^{228}Ra may be selectively determined through the elution of ingrowing ^{228}Ac after storage (fig. 21).

For the measurement of the EDTA eluate, we recommend a quench resistant gelating cocktail like OptiPhase HiSafe III. With the latter a maximum of 5 to 6 mL EDTA eluate with 16 ml cocktail can be mixed to become a clear gel. Larger volumes of EDTA result in an opaque solution with high quenching and inefficient α/β-PSD separation. In presence of ^{210}Pb we recommend the modification described below under 2.2.1.6..

Daughter ingrowth from ^{226}Ra has to be taken into account if separation and measurement are not done in timely conformity.



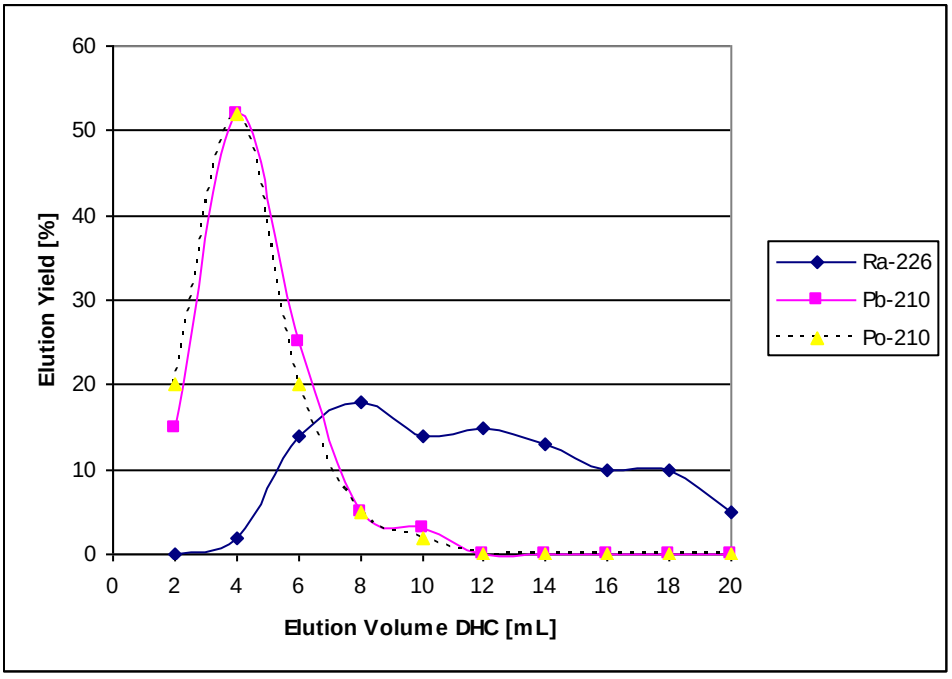


Figure 20: Elution behavior of ^{226}Ra, ^{210}Pb and ^{210}Po on Radium RAD Disk filter
(a) With 0.25 M EDTA alkaline (upper)
(b) With 0.2 M DHC (lower)

2.2.1.6. Simultaneous Determination of Ra-226/228 and Pb-210 Using Radium RAD Disk and TDCR

Introduction

Naturally occurring $^{210}Pb^{2+}$ can be found in altered water samples with originally high Radon concentrations. The maximum concentration in drinking water is 70 mBq/L in order not to exceed 0.1 mSv/a for small children assuming regular water consumption.

A simple tool to estimate the ^{210}Pb concentration in water is LS measurement after enrichment and separation on Radium RAD Disk filters. The method makes use of the fact that Lead is quantitatively extracted together with Radium into crown-ether 21 and is thus retained on the filter. Lead may be quantitatively eluted with small amounts of DHC, while Radium isotopes still remain on the filter to more than 90%. The method in detail is described in chapter 2.2.1.5. After filtration and washing, ^{210}Pb is eluted dropwise with 5 mL 0.2 M DHC (fig. 21). The measurement is done after homogenization with 16 mL OptiPhase HiSafe III in a low energetic β-channel. The relatively high detection limit value of 50 mBq/L for the single PM Triathler device is due to the high luminescence background in the low energetic β-area, but could be improved with a multi PMT low level counter, especially when using TDCR.
^{210}Pb can also be determined through the measurement of the high energetic β-emitting daughter ^{210}Bi by Cerenkov counting, when equilibrium can be assumed.
Recently, Fons-Castells [FONS-CASTELLS et al. 2017] confirmed our previous findings.

Materials and Equipment

- 0.5 M HNO_3
- 0.2 M DHC
- 0.25 M EDTA alkaline
- RAD Disk filter (3M Empore)
- OptiPhase HiSafe III
- Gelating cocktail

Procedure

(modified method with Radium RAD Disk in presence of Pb-isotopes, see figure 21)

(1) 3 L of the 2 M HNO_3 acidified water sample are sucked through a preconditioned Radium RAD Disk filter.
(2) After washing the filter with 10 mL 0.5 M HNO_3 and 10 mL H_2O, ^{210}Pb is eluted dropwise with 5 mL 0.2 M DHC.
(3) The filter is washed with further 10 mL H_2O. ^{226}Ra-isotopes are then eluted from the filter twice with 5 mL 0.25 M EDTA.
(4) Each fraction is mixed with 16 ml OptiPhase HiSafe III and measured with TDCR after 3 hours storage.

Quench correction using β-standards for ^{210}Pb may be neglected if the TDCR technique is applied.

Evaluation

The activity concentration of ^{210}Pb is calculated according to

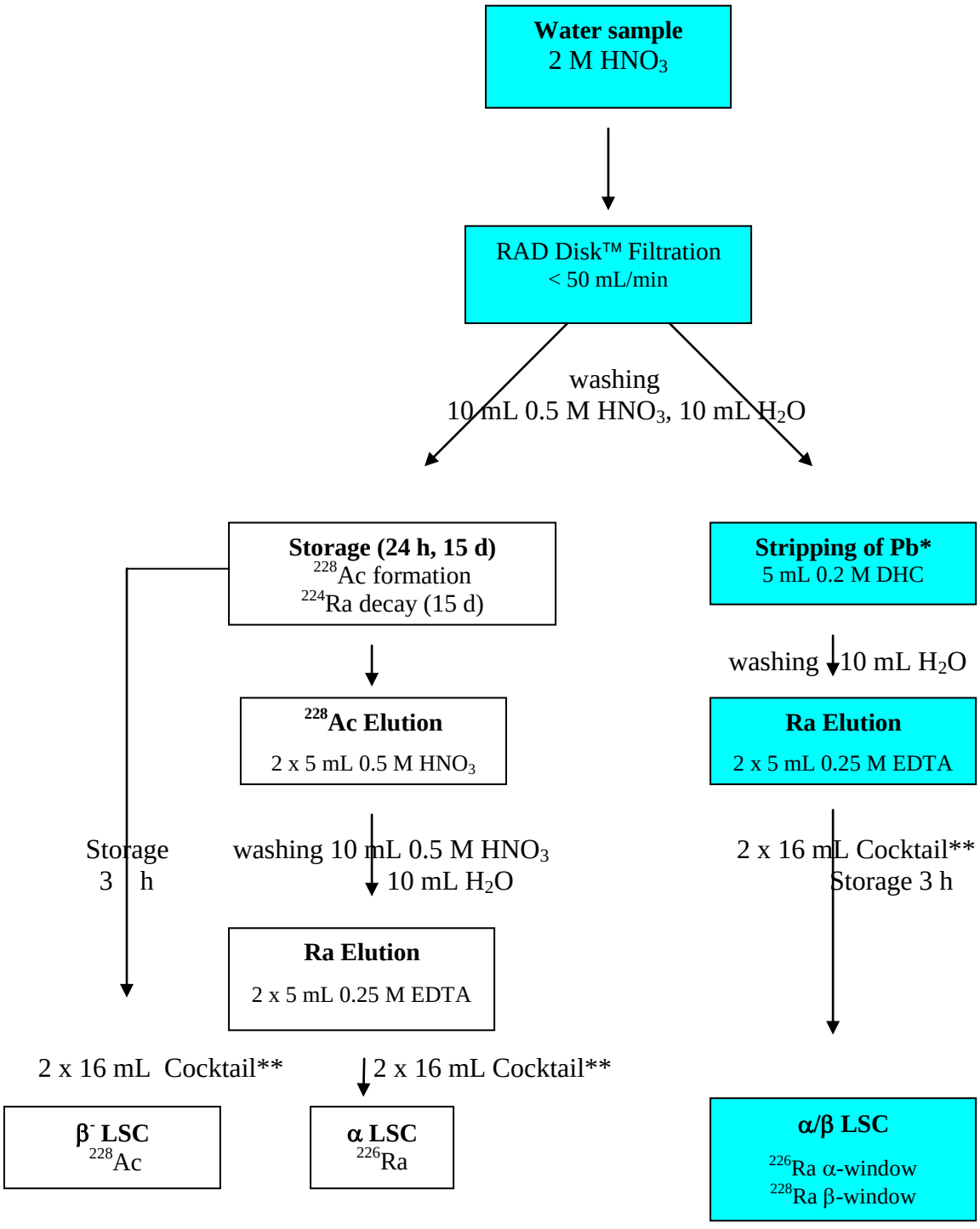
$$A_C = \frac{R_N * 1000}{\varepsilon * \eta * V} \quad [Bq/L]$$

whereas

R_N = Net rate (cps)
ε = Measuring efficiency (95% for ^{226}Ra and 60% for ^{210}Pb)
η = Elution yield (95%)
V = Sample volume (3 L)

Detection Limit (MDA): ^{226}Ra 5 mBq/L,
^{210}Pb 70 mBq/L (Triathler) and 10 mBq/L (LL LS counter)
Total Analysis Uncertainty: for ^{226}Ra 8% and
for ^{210}Pb 15% (due to the calibration uncertainty)

As alternative to the direct measurement, ^{228}Ra may be quantified by ingrowth of ^{228}Ac after a storage time of 24 hours ($T_{1/2}$ (^{228}Ra) = 6.13 hours), or after 15 days, when ^{224}Ra with its complex daughter nuclides has fully been decayed (fig. 21 left side). This modification is more time consuming and unsuitable for in-situ analysis, however, allows a considerably lower limit of detection and a higher counting efficiency compared to direct ^{228}Ra measurement because of the high β-energy of ^{228}Ac.



* can be omitted in absence of Pb-isotopes
** OptiPhase HiSafe III

Figure 21: Modified Radium RAD Disk filter method for rapid determination of ^{226}Ra, ^{228}Ra and ^{210}Pb

2.2.1.6. Simultaneous Determination of Ra-226/228 and Pb-210 Using Radium RAD Disk and TDCR

2.2.1.7. Quick Method for Key Nuclides in Drinking Water

2.2.1.8 TDCR Cerenkov Counting in Medical α-Therapy (Ra-224/Bi-212)

2.2.1.9. Uranium Isotopes by Extractive Scintillation

2.2.1.10. Tritium by Distillation

2.2.1.11. Sea Water Samples

2.2.1.12. LL H-3 in Sea Water by Electrolytic Enrichment

Tritium in water samples may be determined directly after purification by distillation in the effluents of nuclear plants or to ensure Tritium levels of <5 Bq/L according to procedure 2.2.1.10.. However, for environmental samples like surface and sea water the Tritium activity concentration is generally below the lower limit of detection of LS counters. This calls for an additional enrichment process. Electrolytic enrichment has been described for an enrichment factor of 10 to 20, thus reducing the detection limit to <1 TU (about 0.1 Bq/L). It can be used for low level (LL) H-3 in freshwater, precipitation [NAJMAN et al. 2024] and s well sea water with vast amount of salt, when distillation before head is applied.
The procedure is based on the selective isotope enrichment using electrolysis.
Because of their higher binding energies, THO molecules are less decomposed to H_2 and O_2 than H_2O or DHO (T = Tritium, D = Deuterium). The slightly alkaline water sample in a conventional electrolysis cell is reduced to about 5% of the initial volume by decomposition, resulting to an enrichment of Tritium to more than 90% in the remaining water. The concentrated sample is further purified by distillation and counted by LS after addition of a low level cocktail. The electrolysis efficiency of the cell is checked by occasional spiking with a certified tritiated (HTO) water solution.
The procedure below describes a LL ^3H analysis in seawater by electrolytic enrichment, but can be applied as well for ground and drinking water samples. It includes the steps:

(1) Sample pretreatment by water distillation, reducing impurities and interfering radionuclides
(2) Electrolytic enrichment of water sample
(3) Neutralization and second distillation
(4) Measurement by LSC

Applying the solid polymer electrolytic film technology without need of Na_2O_2 addition, step (3) has been omitted. For a 700 mL sea water sample and optimization of the channel range for Tritium, the detection limit has further been reduced to 0.45 TU (about 0.045 Bq/L) [ZHANG et al. 2023], [KIM 2024].

Materials and Equipment

- Gelating LL cocktail (e.g. Ultima Gold LLT)
- PE LS vial (20 mL)
- Electrolysis cell (250 mL)
- Rotary evaporator
- Certified HTO solution (e.g. Analytics)
- $Na_2S_2O_3$ (Sodium thiosulphate)
- $PbCl_2$ (Lead chloride)

Procedure [MADRUGA et al. 2009], [GOMES et al. 2017]

(1) After addition of 0.5 g of $Na_2S_2O_3$ and 1 g of Na_2CO_3, 500 mL water sample are distilled (rotary evaporator). In case the conductivity is >2 µS/cm, the distillation process should be repeated.
(2) To an aliquot of 250 mL, 1 g of Na_2O_2 (formation of NaOH as electrolyte) are added. The electrolytic process is performed at stabilized current and cooling at 0 to 4°C until the water volume is reduced to about 15 to 20 mL (about 600 A, 5 to 7 days).
(3) The remaining water sample is neutralized by adding $PbCl_2$ and newly distilled.
(4) An aliquot of 8 mL of the distillate is mixed with 12 mL scintillation cocktail in a 20 mL PE vial and measured for 300 min.
.

Evaluation

The activity concentration A_c of each sample is calculated by

$$A_c\ (Bq/L) = \frac{R_N\ (cpm)}{60 * \varepsilon * V * EF}$$

with V as volume of sample in vial (8 mL=0.008 L).
The detection efficiency ε is determined by internal standardization or more easily by TDCR. The enrichment factor EF is the recovering efficiency RE multiplied by the initial weight of the sample W_i divided by the final weight W_f. The isotopic separation performance is characterized by spiking the cell from time to time with a HTO water standard to determine the recovering efficiency (initial/final ^3H concentration in the electrolytic sample).

$$EF = RE * W_i / W_f$$

Electrolysis cells generally handle samples of 150 to 250 mL and result in an enrichment factor of 15 to 30 with a recovering factor of about 90%.

Detection Limit (MDA): 0.1 Bq/L
Total Analysis Uncertainty: 5%

2.2.2. Organic Samples

2.2.2.1. Radiocarbon in Biobased Products (Fuel)

2.2.2.2. Sample Preparation by Combustion

2.3. Radionuclides from Nuclear Fission Activities

2.3.1. Strontium by Strontium RAD Disk

2.3.2. Sr-90 and Pb-210 by Extraction Chromatography

2.3.3. Sr-90/Y-90 by LSC and Cerenkov Counting (TDCR)

2.3.4. Rapid Method for Sr Isotopes (Sr-89/Sr-90) by TDCR Cerenkov

(according to [FRENZEL,WISSER et al. 2013] and [HIDEX]

Introduction

In samples shortly collected from nuclear facilities or its surrounding environment, both ^{89}Sr and ^{90}Sr/^{90}Y might be present. Measurements of 3 β^--decaying nuclides (Sr-89/Sr-90/Y-90) by classical LSC require the setup of 3 counting windows with comprehensive quench correction. Figure 29 shows the spectra of ^{89}Sr, ^{90}Sr and ^{90}Y in the application where the measurement is based on using two LSC windows.

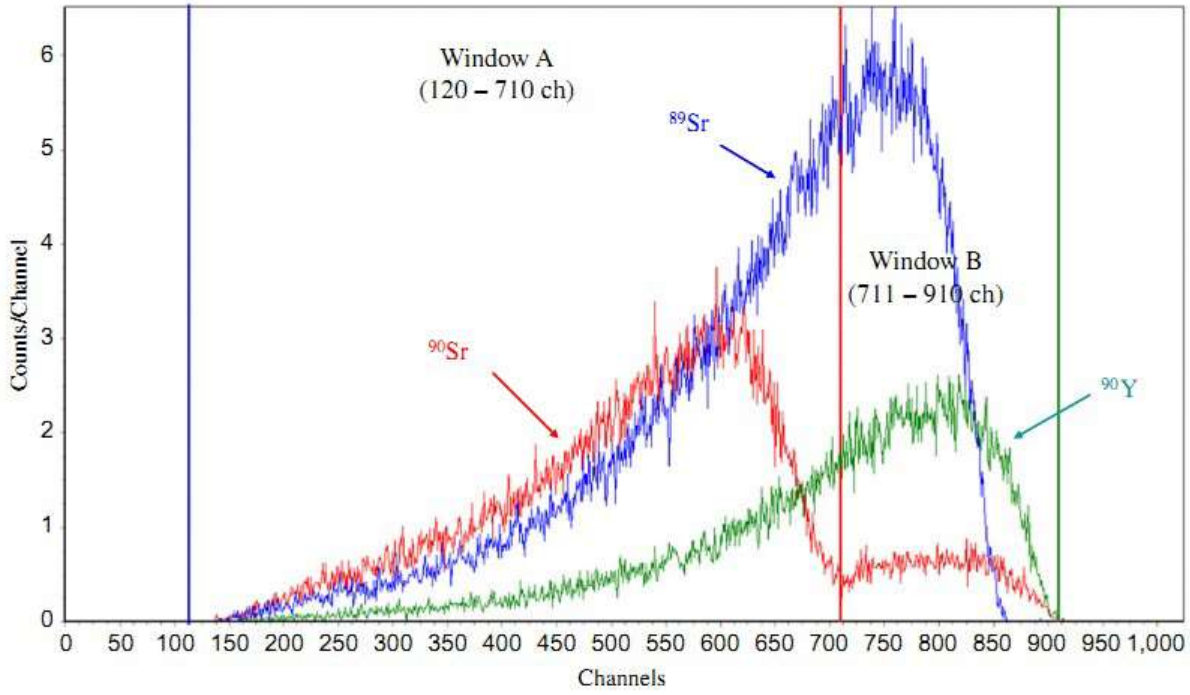


Figure 29: LSC spectra of ^{89}Sr, ^{90}Sr (with a small contribution of ^{90}Y) and ^{90}Y [HOU 2018]

Applying Cerenkov counting facilitates the measuring procedure for the determination of Strontium isotopes, as the high energetic radionuclides Sr-89 and Y-90 can be measured in aqueous solutions in nearly absence (<1%) of the low energy β^--emitter Sr-90.

$$^{89}\mathrm{Sr} \xrightarrow[50.5\ \mathrm{d}]{\beta^- (1.5\ \mathrm{MeV})} {}^{89}\mathrm{Y}\ (\mathrm{stable})$$

$$^{90}\mathrm{Sr} \xrightarrow[28.5\ \mathrm{a}]{\beta^- (0.5\ \mathrm{MeV})} {}^{90}\mathrm{Y} \xrightarrow[64.1\ \mathrm{h}]{\beta^- (2.3\ \mathrm{MeV})} {}^{90}\mathrm{Zr}\ (\mathrm{stable})$$

This simplifies the measurement to only Cerenkov counting and subsequent LS counting [OLFERT et al. 2014], [FRENZEL et al. 2013], [TAYEB et al. 2014] and [ZIEMEK et al. 2022]. When additionally TDCR is applied, no calibration is required and even colored samples can be measured.

This rapid procedure for ^{89}Sr and ^{90}Sr has recently been extended to the bioassay for ^{90}Sr and is routinely used by IAEA for urine samples [CAPOTE-CUELLAR et al. 2015] (see 2.4.5.). It can be applied for soil samples in emergency situations after digestion by fusion, followed by coprecipitation and extraction chromatography [PITOIS 2017]. The main advantage is not requiring any calibration.

As no significant waiting times after sample preparation are required this procedure can be classified as rapid analysis method. Thus, it can be applied for the determination of ^{89}Sr/^{90}Sr in case of a nuclear accident when the activity ratio of ^{89}Sr/^{90}Sr is higher than 100:1. The prompt availability of results with deviation of less 10% and 5 min counting time allows the competent authorities and radiation protection experts a fast reaction.

For sample preparation the use of a rapid extraction chromatographic separation using Sr SPEC columns in an automated apparatus (HIDEX, Q-ARE 100plus) [LEHMUSVUORI 2021] is recommended for rapid and reproducible results.

Materials and Equipment

- TDCR Liquid Scintillation Counter (HIDEX 300SL)
- High-performance LS cocktail (e.g. AquaLight)
- Plastic LSC vials

Procedure

The measurements have to be carried out directly after the radiochemical separation to avoid additional ingrowth of ^{90}Y, which negatively affects the TDCR-Cerenkov and LSC measurements.

(1) After Sr extraction from sample, measure 8 mL of the liquid in a plastic vial, using the TDCR Cerenkov mode for ^{89}Sr (energy window 1-25 keV)
(2) Add 12 mL of a high-performance LS cocktail (e.g. AquaLight); mix well and remeasure in an open energy window in TDCR Scintillation mode for ^{89,90}Sr (1-2000 keV)

Evaluation

In order to obtain the activity of ^{90}Sr, the result of the TDCR Cerenkov measurement has to be subtracted from the result of the second measurement (with LS cocktail) according to:

$$R_x(H_2O) = R(Sr\text{-}89)$$
$$R_x(Scint) = R(Sr\text{-}89) + R(Sr\text{-}90)$$

$$A(Sr\text{-}89) = \frac{R_X(H_2O)}{\varepsilon(Sr\text{-}89) \text{ in } H_2O}$$

$$A(\text{Sr-90}) = \frac{R(\text{Sr-90})}{\varepsilon(\text{Sr-90}) \text{ in Scint.}}$$

$$R(\text{Sr-90}) = R_X(\text{Scint.}) - A(\text{Sr-89}) * \varepsilon(\text{Sr-89}) \text{ in Scint.}$$

with ε (Sr-89) in $H_2O = TDCR_{corr} * 0.6672 + 0.0828$ [FRENZEL et al. 2013]

with $TDCR_{corr} = (CPM_{Cer} * TDCR_{Cer} - CPM_{back} * TDCR_{back}) / (CPM_{Cer} - CPM_{back})$.

ε (Sr-90) in H_2O <1%
ε (Sr-89) in Scint. = TDCR value of measurement with scintillator
ε (Sr-90) in Scint. = TDCR value of measurement with scintillator.

A more recent empirical correction curve for Cerenkov TDCR values recommends
ε (Sr-89) in $H_2O = 0.287 * \ln(TDCR_{corr}) + 0.610$ [YANG et al 2021] (see table 2).

The counting efficiencies obtained with HIDEX 300 SL for the TDCR-LSC measurement of ^{90}Sr and ^{89}Sr were above 97%. The counting efficiencies for ^{89}Sr and ^{90}Y by TDCR-Cerenkov-Counting were 45 and 73% respectively [WANG et al. 2022].

Of course the Sr isotopes may be determined as well without TDCR mode. However, quench correction and calibration is recommended according to chapter 2.1.1.

Detection Limit (MDA): about 25 mBq per sample
(10 h counting time, R_0 =50 cpm for standard model instrument),
but depends on sample preparation methods
Total Analysis Uncertainty: 5% and
<10% for 5 min counting time in emergency situations

^{90}Sr by ingrowth of ^{90}Y:

For low activity samples with high ^{89}Sr/^{90}Sr activity ratios, ^{90}Sr is preferably determinded through measurement of the ingrown ^{90}Y. In this case Sr in the sample solution is first separated onto the Spec column, and then allowed ingrowth of ^{90}Y on the column for 1 to 2 days. The ingrown ^{90}Y is then eluted from the column using 8 M HNO_3 for Cerenkov counting. ^{89}Sr and ^{90}Sr are eluted afterwards using water or diluted HNO_3 (0.05 M) and measured by LS. However, because of the storage time it cannot be considered anymore as rapid method.
When using the Y-90 ingrowth for Sr-90 quantification in presence of Sr-89, its decay during measurement has to be considered (fig. 28), according to

$A_{total} = A(^{89}Sr) + A(^{90}Sr)$
$= A_0(^{89}Sr) * \exp -(t/50.5d) * \ln 2 + A_0(^{90}Sr) * (1 - \exp -(t/2.7d) * \ln 2$

and in equilibrium condition (>25 d)

$A_{total} = A_0(^{89}Sr) * \exp -(t/50.5d) * \ln 2 + A(^{90}Sr)$

$A(^{90}Sr) = A_{total} - A_0(^{89}Sr) * \exp -(t/50.5d) * \ln 2$

where
t = time difference between measurement directly after separation and after equilibration
and
$A_0(^{89}Sr)$ = Activity after separation

For more calculation details see [BMU 2000/2].

2.3.5. Strontium in Milk

2.3.6. Tc by Technetium RAD Disk

2.3.7. Quality Control of Eluate from a Tc-99m/Mo-99 Generator [HOU 2017]

Introduction

The widespread use of short lived radiopharmaceuticals in PET (Positron Emission Tomography) or as generator nuclides like ^{99m}Tc/^{99}Mo requests for good quality specifications. While the radiochemical purity is usually determined by thin layer chromatography, γ-spectrometry is mostly used for radionuclide purity analysis. However, it cannot detect specifically PET nuclides like ^{18}Fe-FDG as they only emit positrons making them indistinguishable from each other as well as from other pure β^--emitters or EC nuclides. γ-spectrometry additionally lacks in high-count rate annihilation radiation spectrum, especially if the γ-line in question lies below 511 keV.
The modern regulatory guidelines call for very high purities (minimum 99.9%) of the product [PHARMACOPOEIA 2017]. This includes longer lived contaminants without γ-emissions like the low energy β-emitter ^{3}H from ^{18}O (p,T) ^{16}O and ^{55}Fe as EC nuclide from nuclear reactions in the target foil for PET nuclides. For ^{99m}Tc diagnostics this concerns ^{99}Mo as leakage and the β-emitter ^{99}Tc as long lived daughter nuclide, which is enriched in urine, saliva and hospital residues.
Besides the high counting efficiency and simple sample preparation, Liquid Scintillation detects β, X- and γ–ray secondary electrons, conversion and Auger electrons, Cerenkov radiation as well as α–nuclides. The method even may distinguish between α- and β-nuclides, and through Cerenkov mode as well between low- and high energetic β-emitters in a semi spectrometric way. By applying the TDCR mode it results directly in decays without calibration and quench correction, and thus eliminates sources of errors.
A comprehensive sequentially analytical method was developed by Hou for simultaneous determination of radionuclidic impurities in ^{99m}Tc eluate. It was used for quality control of ^{99}Mo/^{99m}Tc generators with respect to ^{99}Mo, ^{131}I, ^{103}Ru, γ-emitters, ^{89}Sr, ^{90}Sr and total α-emitters [HOU 2017].

In the following, two LS procedures are described for quality control QC of a ^{99m}Tc/^{99}Mo generator using TDCR Liquid Scintillation and Cerenkov counting. Especially the method of half-life determination becomes a universal excellent way to identify the radionuclide purity of any given radiopharmaceutical (procedure 1), especially when TDCR Liquid Scintillation is used as measuring method [JENSEN and JORGENSEN 2017]. Procedure 2 makes use of column chromatography of various radionuclides fpllowed by LS measurement for QC [HOU 2017]. Procedure 3 covers the activity control of effluents from medical institutions, where Tc generators are in use.

1) QC of ^{99m}Tc eluate via half-life determination

Materials and Equipment
- TDCR Liquid Scintillation Counter (HIDEX 300SL)
- High-performance LS cocktail for α/β PSD (e.g. AquaLight)
- Plastic LSC vials 20 ml

Procedure
(1) Elute the ^{99m}Tc sample with 6 ml 0.9% NaCl solution (t_o)
(2) Add 14 ml of cocktail, mix and measure by LS counting (fix mean counting time)
(3) Repeat measurements in 15 to 30 min intervals until a constant counting decrease of 66 h (^{99}Mo) or constant background rate is reached (^{99m}Tc fully decayed).
(4) Plot the net count rates vs mean counting time on semi logarithmic paper (evaluation see below)

2) QC of ^{99m}Tc eluate via chromatographic separation [HOU 2017]

This method concerns especially Tc generators produced by fission of Uranium. Impurities not detectable by γ-spectrometry include ^{89,90}Sr and pure α- and β-emitting impurities.

Materials
- Anion exchange column (AG1x4, 50-100 mesh)
- Sr SPEC column (TrisKem)

Procedure
(1) The eluate from the Tc generator as 0.1 M HCl – 0.9% NaCl solution is loaded on a 2 ml anion exchange column (AG1x4) and washed with 2 ml 0.1 M HCl.
(2) To half of eluent and wash, 10 ml cocktail (AquaLight) are added (mix well). The gelated solution is measured for total α– and β–activity in α/β PSD mode according to 2.2.1.1.
The total β–activity does not include ^{131}I, ^{99}Mo and ^{103}Ru, which are measured directly by γ-spectrometry.
(3) The other half of the solution from (1) is prepared to 8 M HNO_3 and loaded on a 2 ml Sr column. Sr isotopes are eluted with 10 ml 0.05 M HNO_3.
(4) The solution is immediately measured for ^{89}Sr (before ^{90}Y ingrowth) in Cerenkov mode (see 2.3.4.).
(5) The measurement is repeated after some days for ingrowth of ^{90}Y. The ^{90}Sr activity is calculated from the activity increase and ingrowth time (for evaluation see 2.3.4.).

3) Control of effluents for ^{99}Tc

Materials

- H_2O_2 30%
- TK-TCScint column (TrisKem)

Procedure

(1) To up to 200 ml of filtered hospital effluent, some ml of 30% H_2O_2 are added. The solution is heated 1 h at 90°C in order to oxidize all Tc to TcO_4^-.
(2) ^{99}Tc is retained from 100 ml sample on a 2 ml cartridge of Tc PSm resin (TK-TCScint), followed by washing with 2 ml 0.1 M HCl.
(3) The cartridge is placed into a 20 ml LS vial. Scintillation cocktail is added and the vial measured in TDCR scintillation mode for 180 min (counting efficiency about 90%) (see also 3.2.2.1.).

^{99}Tc elution is best done in an automated extraction apparatus (Q-ARE 100plus, HIDEX Turku) in order to increase the reproducibility and to avoid manual handling.
For urine samples a further sample preparation step in order to reduce the salt concentration is obligatory.
Detection Limit (MDA): 0.1 Bq/L (for 100 mL sample and 180 min counting time)

Evaluation of QC from half-life determination (procedure 1)

The radionuclide impurity P_o of the ^{99m}Tc eluate at the time of elution t_o is calculated from the decay curve graphically (fig. 30). After ^{99m}Tc has been decayed (>66 h) extrapolate the ^{99}Mo dacay values (red) linear to separation time t_o in order to obtain A_0(Mo-99). Extrapolation of the measured decay curve (green) to t_o results A_0(total).
Substract the ^{99}Mo contributions from the corresponding net count rates to obtain the ^{99m}Tc counts (blue values).

$$P_o = \frac{\text{Activity}_{\text{Tc-99m}}(t_o)}{\text{Activity}_{\text{total}}(t_o)} = \frac{A_0(\text{total}) - A_0(\text{Mo-99})}{A_0(\text{total})}$$

The total activity A_{total} at any time t can be calculated according to

$$A_{total} = A_o(\text{Tc-99m}) * \exp\text{-}(t/6h) * \ln 2 + A_o(\text{Mo-99}) * \exp\text{-}(t/66h) * \ln 2$$

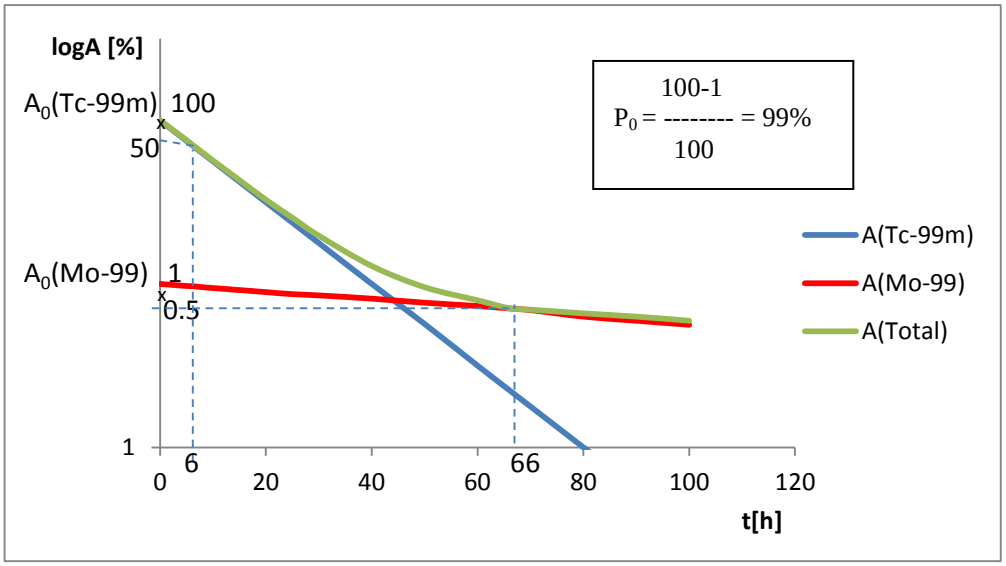


Figure 30: Decay curve of ^{99m}Tc eluate in presence of co-eluted ^{99}Mo

Down to 0.05% impurities can be determined, which is even better than requested by the EU regulations [PHARMACOPOEIA 2017].

2.3.8. Fe-55 by Extraction Chromatography

2.3.9. Ni-63 by Extraction Chromatography

2.3.10. Fe-55 and Ni-63 in Radioactive Waste

2.3.11. Ca Isotopes in Biological Shield

2.3.12. Fe-55 and Ca-41 in Decommissioning Activities by TDCR-LSC

2.3.13. Sample Preparation for Pu-241 Analysis (BioRad)

2.3.14. Pu-241 in Presence of Other Plutonium Isotopes (LS-α-Spectrometry)

2.3.15. Multiple Radionuclide Analysis

2.4. Radiation Protection

2.4.1. Radon in Air

2.4.1.1. Enrichment in Organic Cocktail

2.4.1.2. Adsorption on Active Carbon 'PicoRad'

2.4.2. NORM Samples

2.4.2.1. NORM in Phosphogypsum

2.4.2.2. Rn in Crude Oil and Oil Fractions

2.4.2.3. Radium Isotopes and Pb-210 in Scale, Deposits and Production Water

2.4.3. Off-gas

2.4.3.1. Tritium

2.4.3.2. Radiocarbon

2.4.4. Contamination Control by Swipe Assays (Wipe tests)

Introduction

Wipe tests, also known as wipe or smear tests, are mainly used for contamination and leakage control of surfaces that cannot be measured directly. Recovery of activity from the surface depends on various factors like radioactive compound, property of surface, swap material and pressing force. Swipe Assays should therefore be considered more semi-quantitative. However, there is no practical alternative for low-energy β-emitters, such as H-3, C-14 or Ni-63. In order to get a complete picture of the contamination, direct and indirect controls are usually made one after the other.

Guideline values for the limits of surface contamination are nuclide and country specific (e.g. §57 StrlSchV in Germany), however, action levels are generally recommended for weak β-emitters in restricted areas for radioactivity levels exceeding 20,000 DPM/100 cm^2 and 2000 DPM/100 cm^2 in unrestricted areas, respectively [L'ANNUNZIATA 2020/1]. Guidelines for measurement and evaluation of surface contamination using wipe test samples can be found in DIN ISO 7503 2017-12.

Various methods and devices can be used to study wipe tests. Liquid scintillation counters are generally applicable for determining the gross alpha/beta activity concentration. They usually result in lower detection limits and provide limited spectrometry. They allow at least a picture on radionuclide and if or more of them are present. Swipe assays for α-and β-contamination using LSC is an excellent alternate to proportional counting. For nasal swab analysis in case of internal α-contamination using LSC see [DAI et al. 2012] and [DI PASQUALE 2024].

In our studies Ni-63 as low energy β-emitter resulting from electron capture detectors (ECD) or activated steels [WOLF 2017], and Uranium as α-emitter from Depleted Uranium weapons [IAEA 20001] have been used.

The most common **wipe test materials** are the following
- Glass fiber filter
- Filter Paper
- Cotton swab
- Plastic squares, e.g. polystyrene platelets

Depending on the nature of contamination, each material holds selective advantages. Glass fiber filter, however, are suitable for most applications as they get translucent when moistened with organic cocktails.

There are several possibilities how sample and wipe test material behave when **cocktail** is added (table 9).

Table 9: Behavior of wipe test samples with cocktail and their effects

Possibility	Wipe Material	Sample	Effect to Radionuclides
1	dissolved	dissolved	homogeneous solution
2	dissolved	not dissolved	homogeneous suspension
3	translucent	dissolved or not	reproducible counting geometry
4	unchanged	dissolved completely	homogeneous solution
5	unchanged	dissolved partially	non reproducible geometry
6	unchanged	undissolved	unsuitable

In the best case, sample and/or wipe material dissolve completely (1, 4), because the sample has the same lipophilic properties as the cocktail. An emulsifying cocktail, such as Ultima Gold, is also recommended. To ensure that hydrophilic samples also pass into the cocktail, 2% water should be added. This results in the desired homogeneous liquid, but quenching effects may occur due to the undissolved wipe material itself (4).
If the sample is not dissolved, it remains completely attached to the wipe material. In this case, a cocktail/solvent should dissolve the wipe test material to obtain a homogeneous distribution of the sample in the cocktail and thus avoid self-absorption (2). We recommend polystyrene platelets and organic cocktails; others describe Filter-Count for dissolution of cellulose nitrate/ester wipe materials and Ultima Gold AB as cocktail (ratio 2:1) [DOUGNIAUX et al. 2011]. Some filters become transparent in the cocktail and are therefore also suitable for measurements (3).
In case (5), the sample is partially suspended in the wipe material and is partially dissolved. This can cause inaccurate results and should be avoided. Repeated measurements are recommended. If the measuring rate increases with time, this is an indication that the sample has not yet completely dissolved in the cocktail.
In table 7.21 of L'Annunziata the filter materials and their solubility behaviour in the cocktail are summarized [L'ANNUNZIATA 2020/1].

Glass fiber filters become transparent in the most common cocktails and give the best light output. Frenzel [FRENZEL et al. 2002] described the method of fixing the filters to the inside of a 20 ml glass vial. As the filter is only moistened with some organic cocktail, it is fixed on the inner glass wall in an ideal counting position, especially for Triathler (HIDEX, Turku) measurements (fig. 43). Thus, the medium to be measured is the wipe test itself.

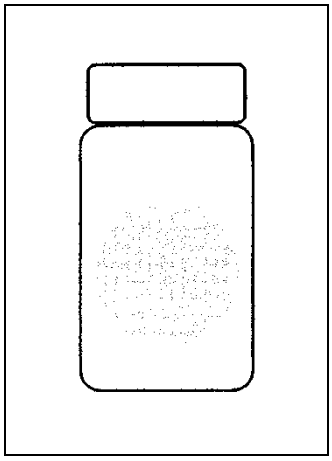


Figure 43: Filter material (25 mm) in 20 mL standard counting vial with 1.5 mL organic cocktail [FRENZEL et al. 2002]

Some laboratories moisten their wipe test materials before taking the sample; some use water, others a mixture of water and ethanol. Moist wipe test materials usually absorb more and the swiping yield is higher than 10%. However, spreading the contamination can occur during sampling.

The counting efficiency and reproducibility of filter papers and glass fiber filters were investigated by us. The filter materials were spiked with a Ni-63 standard solution and dried. The filters were measured both with a α–β Low-Level Counter and by LSC applying external standardization and TDCR, and the results were compared (for experimental details see [Wolf 2017]).
Deviations above 50% were determined for the dried filter paper. Microscopically, paper filters appear as capillary tubes, whereas the glass fiber filters appear as an impermeable virtual network of threads [L´ANNUNCIATA 2020/1]. Thus, it is difficult for the cocktail to dissolve the sample in the capillary tubes of the paper filters after drying the wet wipe test. We therefore do not recommend drying, when using filter paper materials and LSC. LS measuring results for glass fiber filters and moist filter papers did not deviate from the expected activities (<3.9%).
Drying should also be avoided for volatile radionuclides like H-3 and I-isotopes [DIN ISO 7503 2017-12].
Polystyrene platelets have been applied successfully for the surface contamination of Depleted Uranium penetrator (see 2.2.1.9.). After sampling, the wipe material has been dissolved in organic cocktails (procedure b).

We describe below two priviledged swipe assay approaches:
Procedure (a) uses glass fiber filters, which get translucent when moistened with lipophilic cocktails. This is best performed with Triathler equipment, providing both in-situ sampling and analysis.
Procedure (b) applies smear test materials, which are dissolved and result in a homogeneous counting solution (case 1) or suspension (case 2) for optimum yield output and optimized α/β PSD separation in α-assay.

Materials and Equipment

- Polystyrene platelets (4 x 1 x 0.1 cm)
- Glass fiber filter (25 mm; e.g. Whatman GF/A)
- Cellulose nitrate/ester filter (e.g. Millipore/Advantec)
- Organic (lipophilic) cocktail (e.g. Toluene Scint, MaxiLight)
- Filter count (PerkinElmer)
- Ultima Gold AB
- PSD LS counter

Procedure (a)
translucent method (3) [HIDEX 2001]

(1) Using a glass fiber filter, swipe off a surface of about 100 cm^2 with a moderate amount of pressure (dry wipe)
(2) Roll the filter along the inner wall of a glass vial (fig. 43)
(3) Add 1 to 1.5 mL of a lipophilic cocktail (MaxiLight), cap the vial and tilt it, so that the filter is moistened
(4) Using Triathler equipment, insert the vial with filter facing to the adapter opening and measure for 300 seconds

Procedure (b)

homogeneous suspension, case (2) [FRENZEL et al. 2002]:
(1) Use a rectangle polystyrene platelet for sampling (100 cm^2, see (a1))
(2) Dissolve the platelet in a 20 mL plastic vial with 10 mL organic cocktail
(3) Measure the sample for 300 seconds as homogeneous solution with PSD option for α-contamination

Homogeneous solution, case (1) [DOUGNIAUX et al. 2011]:
(1') Alternatively, take a cellulose nitrate/ester filter for sampling (100 cm^2)
(2') Add 14 mL filter count for dissolution, followed by 7 mL Ultima Gold AB as cocktail (ratio 2 : 1)
(3') Measure for 300 seconds in a common LS counter with PSD option for simultaneous α/β-counting.

Evaluation

The activity per unit area Ac is calculated according to the following formula:

$$Ac = \frac{R_M - R_0}{\varepsilon * \eta * 100} \quad [Bq/cm^2]$$

R_M = Measuring rate (cps)
R_0 = Background rate (cps)
ε = Measuring efficiency (approx. 100% for α, 90% for β, less when ^3H is measured)
η = Swiping yield (10% as conservative value)

For α-swipe tests it has been shown that the solution of the dissolved polystyrene platelet shows a clear α/β–separation (fig. 44b), the lowest background in the α-channel (<0.1 cpm) and consequently the lowest limit of detection [FRENZEL 2002].
Classical Toluene Scint („Bray" solution) dissolved the material immediately, while commercially available safe cocktails require a longer overnight storage time.

Detection Limit (MDA) for procedure b:
for α-emitters <0.002 Bq/cm^2
for β-emitters <0.02 Bq/cm^2
The calculations are based on a 2σ standard deviation with a measuring time of 300 seconds and a wiped area of 100 cm^2, considering a conservative swiping yield of 0.1 or 10%.

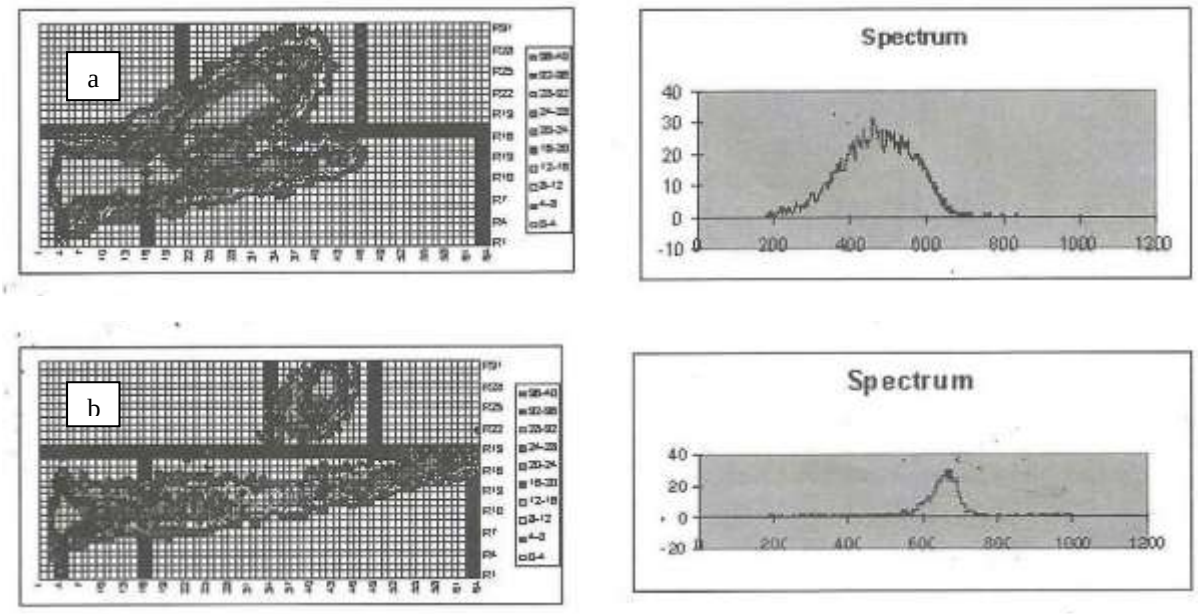


Figure 44: α-pulse height spectrum (right side) and 2D PSD plot (left side) from swipe assay samples of a Depleted Uranium penetrator (see 2.2.1.9.) (HIDEX Triathler)

(a) Glass fiber filter

(b) Polystyrene dissolved in MaxiLight

2.4.5. Urine by TDCR Counting (P-32, Sr/Y-90, Fe-55)

Introduction

Urine bioassay is a suitable method in radiation protection for screening internal contamination in body. For pure α- and β-emitters as well as EC nuclides liquid scintillation is the method of choice for the final measurement. A radiochemical separation procedure avoids interferences from interfering radionuclides if present, but is no more suitable for rapid screening.

A fast radiochemical screening of transuranium radionuclides in urine using DIPEX as actinide extractive resin and low-level α/β LSC has been described by Eikenberg. [EIKENBERG et al. 1999].
The direct analysis of **Fe-55** as EC nuclide using TDCR LS has been reported [GUERIN and DAI 2015]. In presence of interferences, a previous hydroxide precipitation followed by anion exchange chromatography was recommended.

In life science and radiopharmaceutical pure high energetic β-emitters like P-32 and Sr/Y-90 are widely used. In these applications, researchers, medical staff and patients need to be monitored for exposure by possible dose intake as early as possible in order to allow counter measures.
A rapid bioassay method for **Sr-89/90**, reported by Dai [DAI et al. 2013], applies column separation of 20 mL urine on TRU, and further Sr resin for Sr separation and elution with a detection limit of 10 Bq/L for 10 min counting time. The rapid procedure for ^{89}Sr and ^{90}Sr measurement described in 2.3.4. is routinely used for urine samples by IAEA [CAPOTE-CUELLAR et al. 2015].
Removal of deposited **P-32** from the body occurs principally through urine. Hence, bioassay is the preferred individual monitoring technique for radiation workers handling ^{32}P [WANKHEDE et al. 2016]. Here as well, Cerenkov counting holds the advantages of being insensitive to α- and low energy β-emitters, no need to add scintillation cocktail and being free of chemical quenching. Residual color quenching from urine may be quantified and corrected using the TDCR technique.This has been recommended as well in an annex of the ISO (International Standard Organisation) standard method (ISO19361, 2017). Interferences from dietary K-40 contribution can be avoided by previous precipitation of P-32 as Ca phosphate [YOON et al 2014] and/or ammonium-molybdatophophate (AMP) [WANKHEDE et al. 2016]. .

In the rapid screening method presented below [YANG et al. 2020], the color of urine was reduced through simple acidification and oxidation pre-treatment in order to obtain counting efficiencies of >30%. Acetic acid is added finally to decompose the excessive H_2O_2 and thus avoiding increased chemiluminescence. The sample is measured directly by TDCR Cerenkov counting using an empirical formula between TDCR and Cerenkov Counting efficiency for evaluation. A flow diagram of the bioassay procedure for ^{32}P is shown in figure 45.
As chemical separation steps are avoided, other high energetic β-emitters might interfere, when present in higher activities. However, this should not be an issue for incidental urine bioassay.

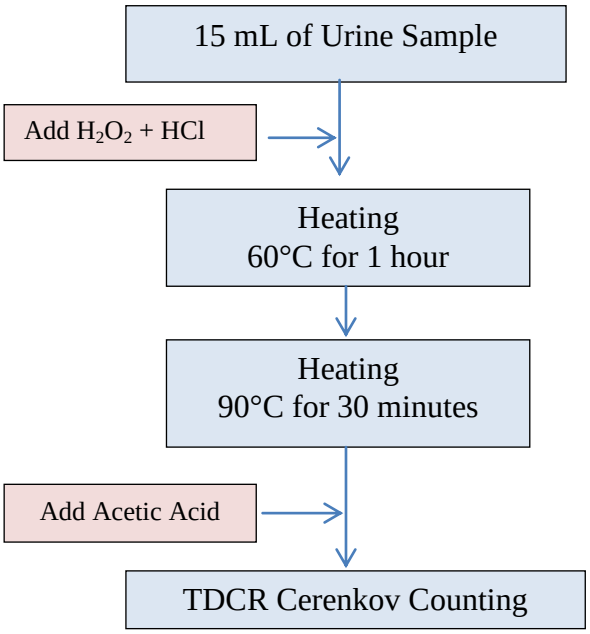


Figure 45: Flow diagram of the bioassay procedure for ^{32}P in urine samples [YANG et al. 2020]

Materials and Equipment

- LSC equipment with TDCR facility e.g. HIDEX 300SL
- 20 mL PE counting vial
- 50 mL centrifuge tube
- Water bath
- 30% H_2O_2
- HCl conc.
- Acetic acid conc.

Procedure

according to [YANG et al. 2020]

(1) 15 mL of the urine sample are transferred into a 50 mL centrifuge tube.
(2) 2 mL of 30% H_2O_2 and 3 mL of concentrated HCl were added.
(3) The sample is heated for 1 h at 60°C in a water bath, followed by heating at 90°C for 30 min.
(4) After addition of 1 mL concentrated acetic acid, the sample is cooled to ambient temperature.
(5) Finally the sample is transferred into a 20 mL PE counting vial and measured for 30 min in the TDCR Cerenkov mode.

Evaluation

The activity concentration of urine is calculated according to

$$A_C = \frac{R_N}{\varepsilon_C * V * \eta} \text{ [Bq/mL]}$$

R_N = Net rate (cps) or $(Dbl_S - Dbl_B)$
ε_C = Counting efficiency of the Cerenkov measurement (^{32}P)
V = Urine sample volume (mL)
η = Chemical revovery (100%)

with
ε_C (^{32}P) = $0.3297 * \ln(TDCR_{net}) + 0.6917$ [YANG et al. 2020]

and

$$TDCR_{net} = \frac{Tpl_S - Tpl_B}{Dbl_S - Dbl_B}$$

where Tpl_S and Dbl_S are triple and double gross count rates of the samples,
and Tpl_B and Dbl_B are triple and double background count rates of the blanks, respectively.

The effect of sample volume on quench correction is reported to be negligible.

Detection Limit (MDA): 10 Bq/L (for 15 mL urine sample, 30 min counting time and LL β-counter)

3. Solid Scintillators and Microspheres

3.1. Introduction

Solid scintillators have been integral to the evolution of scintillation techniques since their inception in the 1950s. Early literature contains reports on this technique using stilbene crystals or dopped polystyrene to transform the energy of the radioactive particles into optical photons. These advancements coincide in time with the discovery of the photomultiplier a highly efficient tool for detecting the scant photons generated during the scintillation process.

Solid scintillators offer the advantage over liquid scintillators due to their adaptability in terms of size and shape for specific analytical purposes. Conversely, the production of pure and homogenous solid materials is a more complex process compared to liquid scintillators where the primary focus is achieving complete mixability among all components, including sample, within a homogenous phase, or, at the very least, a temporally stable single phase. In the preparation of solid scintillators, the initial step involves achieving homogenisation of the raw components, whether in liquid or solid form. Subsequently, the transformation into a homogeneous solid phase becomes imperative to prevent non-reproducible scintillation caused by optical effects or heterogenous mixture of components on both micro and macro scales leading to non-reproducible scintillation.

While liquid scintillators exclusively exist within organic media, solid scintillators exhibit versatility, manifesting in the form of organic crystals, inorganic materials, or plastics. Moreover, solid scintillators take on various formats, including blocks, sheets, particles, and powders. Liquid scintillators shine particularly in their proficiency for analysing β-emitting radionuclides being the main technique for this purpose. In contrast, solid scintillators find widespread applications in diverse fields such as medicine, space industry, security, and environmental monitoring [HAMEL 2021].

One of the main applications of the solid scintillators includes the analysis of α- and β-emitting radionuclides as an alternative to liquid scintillators [TARANCON et al. 2017].

Plastic scintillators share a composition similarity with liquid scintillators, but in solid form. In both, the role of the capturing the energy from radioactive particles is carried out by the solvent, usually a compound containing aromatic rings. In the case of plastic scintillators, the solvent is the polymer itself, typically polystyrene or polyvinyltoluene.

Just like in liquid scintillators, the energy deposited into the polymeric solvent undergoes a series of transfers within the polymer chain, ultimately reaching the fluorescent solutes trapped within the polymer structure. These fluorescence solutes used are the same ones used in LS (e.g. PPO, POPOP). However, as said before, the preparation of plastic scintillators presents its primary challenge. To prevent issues as polymer degradation during polymerization, cracking or fogging, meticulous care must be taken as this defect could lead to colour or optical quenching effects. Moreover, achieving a uniform distribution of the fluorescence solutes within the polymer is required so homogenous polymerization of a homogeneous solution is required. Consequently, precise control of the polymerization temperature becomes crucial [HAMEL 2021].

On the flip side, PS can be prepared into various forms and sizes: blocks, sheets, foils, fibres or microspheres. Additionally, they can be dopped with a variety of substances, enhancing their utility and adaptability for different applications.

For the specific analysis of α- and β-emitting radionuclides, plastic scintillators in form of microspheres is the type of PS most preferred due to its resemblance to liquid scintillators. When using microspheres, the plastic scintillators and the liquid sample, organic or aqueous, are mixed and the liquid sample occupies the interstices between the microspheres. This makes that more liquid can be in close contact with the solid than in films, fibres or blocks. Moreover, the distance between the radionuclide in the solution and the plastic scintillator is reduced in range from micrometres to millimetres depending on the size of the microspheres.

This remarkable feature empowers the detection of not only high energy β-emitters, but also medium and even low energy β-emitters. Furthermore, it enables the detection of α-emitters when distance between radionuclide and scintillators falls below 50 μm, the range of most of α-particles in water.

Utilizing scintillators in the form of microspheres for radionuclide measurements offers some advantages compared to liquid scintillators. The first stems from the fact that plastic scintillator is polymerized rendering it chemically inert and non-volatile. Consequently, it can be stored longer durations without losing its effectiveness. Additionally, the mixture of the radioactive samples and the scintillator does not generate mixed wastes, a waste with hazardous and radioactive properties. Instead, the resulting product from these measurements, a combination of a liquid and a solid, can be treated as radioactive solid waste, simplifying disposal compared to managing mixed waste, which is more challenging [TARANCÓN et al. 2002/1].

The second advantage lies in its ability to facilitate continuous measurements of radioactivity in water without consuming reagents, as is common in liquid scintillation on-line systems. The microspheres of the plastic scintillator are placed within a containment cell, where they are retained, allowing the radioactive liquid to flow through and interact with them, thereby generating the scintillation signal [TARANCÓN et al. 2022].

The final advantage arises from the possibility to modify the surface of the plastic scintillator to add selective extractants. This modified material, called PSresin, can be used to retain the radionuclide of interest but also to measure it in absence of interferences that are not retained. When placed inside a solid-phase extraction cartridge, it serves dual purposes, facilitating the chemical separation and the scintillation measurement. This streamlined procedure eliminates the need for eluting radionuclides from the column and subsequently adjusting the medium to achieve an appropriate mixture of the liquid scintillator and the separated radionuclide solution [BAGÁN et al. 2011].

Plastic scintillation microspheres (PSm) present a viable alternative to LS for the measurement of α and β emitting radionuclides, especially when the goal is to minimize the generation of mixed waste or for emergency purposes, owing to their extended storage capability without degradation. The measurement process involves combining the plastic scintillation microspheres with the water sample in a polyethylene or glass vial, maintaining a ratio of 1.5 g of PSm to 0.625 mL of the water sample. This specific proportion ensures that the water sample effectively fills the interstices between the microsphere maximizing contact and proximity between the radionuclide and the scintillator. To achieve thorough mixing, simply apply a 3-minute vortex at 3500 rpm to the mixture [SANTIAGO et al. 2016].

It is important to note that there exists a correlation between the diameter of the PSm and the detection efficiency of the radionuclides. The detection efficiency diminishes as the PSm

diameter increase. This relationship is attributed to the increased average distance that α- or β-particles must traverse to reach a microsphere as the microsphere's size grows.
It is noteworthy that decrease on the detection efficiency is particularly pronounced for low-energy β-emitters compared to their high-energy counterparts.

Concerning α-emitters, the same correlation holds true. Nevertheless, in this context, it becomes critical to attain a diameter that is either close to or below 50 µm, as this dimension aligns with the range of α-particles in water. With plastic scintillation microspheres (PSm) of this size, the detection efficiency reaches a remarkable 100%, and the resulting spectra features a narrow peak that is slightly broader than what is observed with liquid scintillation (fig. 46).

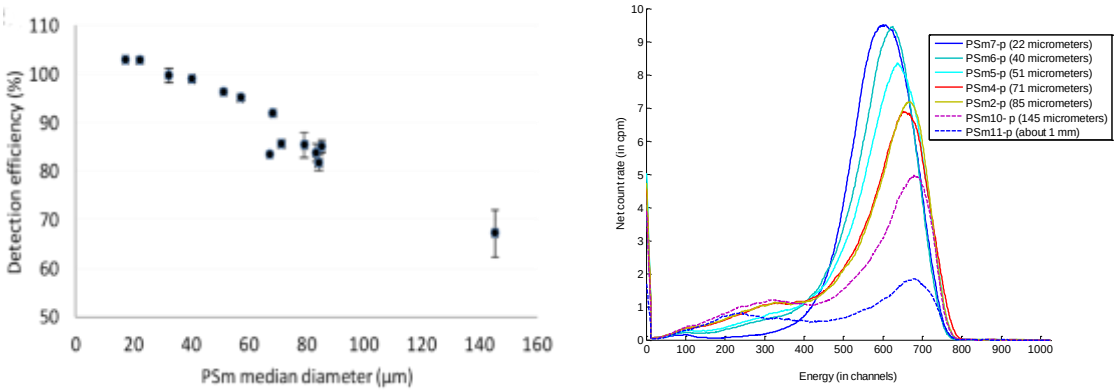


Figure 46: Detection efficiency and spectrum for PSm of different mean diameter for ^{241}Am

3.2. Plastic Scintillation Resins (PSresins)

A plastic scintillation resin (PSresin) is a plastic scintillation microsphere coated with a selective extractant. This coating can be achieved through deposition, employing weak chemical forces for adhesion, or through chemical reactions, where the extractant becomes chemically linked to the polymer's surface. PSresin serves as a novel approach, distinct from classical resins for radionuclide separations offered by Triskem International or Eichrom, as it possesses the unique capability to generate scintillating signals due to the presence of retained radionuclides on its surface. Because the coating is thin, there is no attenuation of the α- or β-particles emitted, ensuring detection efficiencies equal or greater than those described in the previous section.

PSresin can be used in two formats:

- As an integral component of an online scintillation detector: In this configuration, the PSresin is positioned within continuous cell within the scintillation detector, actively accumulating the target radionuclide. As the solution flows through, the count rate increases progressively with the pass of the radionuclide (fig. 47). The resulting profile offers valuable insights into the activity of the radionuclide in the liquid stream.

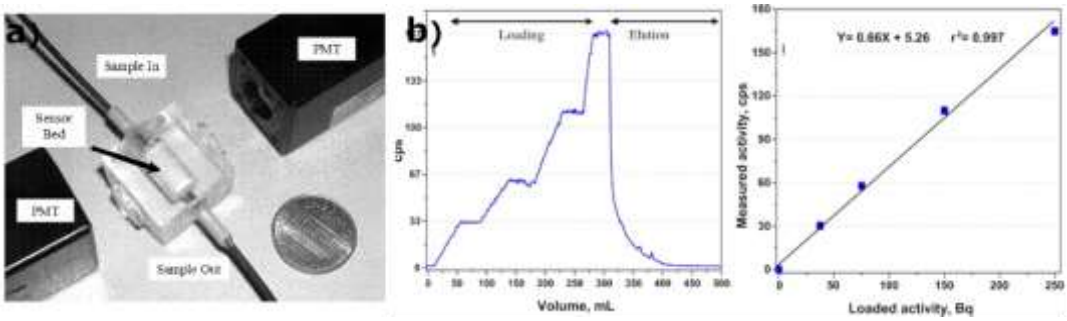


Figure 47: (a) Photograph of a composite bed sensor cell and
(b) the response of the sensor to pertechnetate solutions
(reproduced from [HAMEL 2021])

- As a solid-phase extraction material: To employ PSresin for this purpose, 1 g or 1.5 g of it is loaded onto a 2 mL solid-phase extraction cartridge (fig. 48). After conditioning, the sample is passed through the PSresin, employing either a vacuum box or a peristaltic pump, following a procedure akin to the traditional radionuclide separations with columns. After the sample has passed through and the PSresin is cleaned to remove interferences, the cartridge is placed inside a 20 mL vial and measured in a scintillation counter. The resulting count rate and recovery data facilitate a precise determination of the sample's activity.

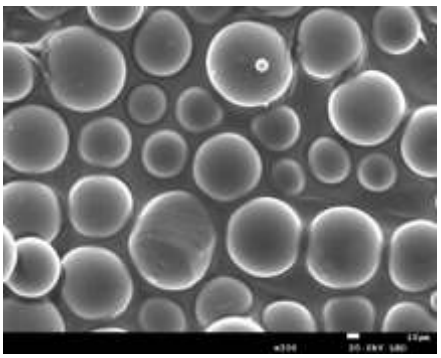


Figure 48: (a) SEM image of a PSresin (b) PSresin-cartridges
(c) vacuum box separation set-up

When employing PSresin as a solid-phase extraction material, it is essential to consider two practical factors to ensure accuracy in the results.

First, the addition of a non-radioactive tracer (carrier) to the sample is necessary to determine the proportion of the target radionuclide retained into the PSresin. This tracer must be non-radioactive to prevent interference with the scintillation signal of the target radionuclide. The yield of the separation can then be calculated based on the quantity of tracer added and the amount of tracer found in the effluent solution obtained after passing the sample through and cleaning the PSresin (equation 1).

$$Yield = \frac{amount\ of\ tracer\ retained}{amount\ of\ tracer\ added} = \frac{amount\ of\ tracer\ added - amount\ of\ tracer\ non-retained}{amount\ of\ tracer\ added} \quad (1)$$

The second aspect to consider is the necessity of emptying the PSresin-cartridge of any residual solution before performing the counting process. The presence of solution residues could potentially interfere by attenuating α- or β-particles, impacting on the detection efficiency. Consequently, after cleaning the PSresin, it should be allowed to pass air for a period of 5 to10 min to thoroughly remove traces of solution in it.

The calibration process for determining the detection efficiency of the PSresin involves measuring standard samples with known activity under the same conditions that later will be applied to the actual samples. This includes maintaining consistent levels of stable tracer. It is crucial that the PSresin cartridges, following the separation of samples, retain their colourless state to eliminate the possibility of colour quenching effects. Therefore, monitoring the quenching parameter of the detector is essential to ensure it yields values akin to those obtained from the standard samples.
Calculation of the sample activity A is done using equation (2)

$$A(Bq/L) = \frac{Sample\ net\ count\ rate\ (cpm)}{yield_{pre} \cdot yield_{PSresin} \cdot eff \cdot V \cdot 60} \quad (2)$$

Where $yield_{pre}$ represents the recovery of the steps previous to the PSresin-cartridge separation, $yield_{PSresin}$ signifies the recovery of the PSresin-cartridge separation, *eff* is the detection efficiency and *V* (in L) is the sample volume.

Numerous examples of PSresin exist. Table 10 below compiles those previously documented in the literature, along with the corresponding target radionuclides, categorized by the medium in which they are applied.

Table 10: List of PSresin described in the literature and the target radionuclide

Extractant	**Target radionuclide**
4,4'(5')-di-t-butylcyclohexano 18-crown-6 in 1-octanol	^{90}Sr [BAGÁN et al. 2011]
	^{210}Pb [LLUCH 2016]
Aliquat·336	^{99}Tc [BARRERA et al. 2016]
	Pu isotopes [TORRES et al. 2022]
	^{36}Cl/^{129}I [LLOPART-BABOT et al.2023]
	^{210}Po
	S^{14}CN^{-} [BAGÁN et al.2012]
bis(3-trimethylsilyl-1-propyl)methandisphosphonic	Actinides [GIMÉNEZ 2021]
	Gross alpha [GIMÉNEZ et al. 2023/1]
TBP in dodecane [VILLARROYA et al. 2019]	^{126}Sn
CMPO in TBP [ROANE and DEVOL 2005]	Uranium
HDEHP in benzene [EGOROV et al. 1999]	^{99}Tc
ethylene glycol methacrylate phosphate [DUVAL et al. 2016/2]	Actinides
N-methyldioctylamine covalently linked [GROGAN and DEVOL 2011]	^{129}I
methylphosphonic acid [DUVAL et al. 2016/1]	Uranium
trioctylamine [SELIMAN et al. 2013]	^{99}Tc

3.2.1. PSresin for Sr-90 and Pb-210

Strontium and Lead exhibit strong affinity to 4,4'(5')-di-t-butylcyclohexano 18-crown-6 extractant, particularly in concentrated nitric media. This affinity is dependent on the solvent used to dissolve the crown ether. Traditional resins employ 1-octanol as the solvent, wherein Pb has exceptionally strong retention in nearly all HNO_3 media, while Sr is primarily retained in highly acidic environments (6-8 M). Alternatively, other solvents, such as ionic liquids or long-chain alcohols, can also be utilized, as happens with the non-scintillating resins (TK100, T101 or TK102) (table 5). When using these solvents, the conditions for separation may vary slightly and, in some instances, even yielding better recoveries.

In the case of the PSresin utilizing 4,4'(5')-di-t-butylcyclohexano 18-crown-6 in 1-octanol, the determination of Strontium must consider the potential presence of ^{210}Pb on the sample as both would become retained. Therefore, when dealing with samples that may contain naturally occurring radionuclides, such as environmental samples, it is imperative to precede the passage of the sample through the PSresin with a chemical separation step for Lead (see also chapter 2.3.2.). Conversely, in cases where ^{210}Pb is absent from the samples (decommissioning, milk, etc) the analysis of radioactive Strontium can be performed without the need for this precipitation step.

To ensure effective Sr retention on the PSresin, the sample medium must be adjusted to 6 or 8 M HNO_3 with the final cleaning step involving the use of 6 M $LiNO_3$. This precaution is necessary because residue of high H^+ concentration can lead to chemiluminescence when counting the PSresin cartridge.

Stable Sr^{2+} serves as tracer for the chemical separation. The quantity of Sr^{2+} added as carrier varies from 1 to 5 mg, depending on the natural Sr content of the sample or its volume. For instance, in milk samples, where Sr^{2+} concentration exceeds 1 mg/L, 5 mg Sr^{2+} is added to ensure accurate yield determination. When Sr^{2+} quantity surpasses 2 mg, it is advisable to employ SPE cartridges containing 1.4 g of PSresin to achieve higher yields.

Procedure

Once the sample is ready for PSresin separation the procedure comprises the following steps:

(1) Condition the Sr-PSresin cartridge with 2 mL of 6 M or 8 M HNO_3.

(2) Load 10 mL of the solution in the Sr-PSresin cartridge at a flow rate of 1 mL/min

(3) Clean the Sr-PSresin cartridge twice with 2 mL of 6 M or 8 M HNO_3

(4) Clean the Sr-PSresin cartridge twice with 2 mL of 6 M $LiNO_3$

(5) Pass air through the Sr-PSresin cartridge for 10 min

(6) Place the Sr-PSresin cartridge into a 20 mL polyethylene vial and measure it immediately after separation to prevent the ingrowth of ^{90}Y

Evaluation

Typical values for recovery yield fall within the range of 70-95%, while detection efficiency typically ranges from 80-90%. Figure 49 displays the spectrum recorded for ^{90}Sr and ^{89}Sr and ^{210}Pb.

Procedures for the determination of ^{90}Sr and/or ^{89}Sr with the Sr-PSresin has been described for water, milk, vegetation, air-filter and solid decommissioning samples.

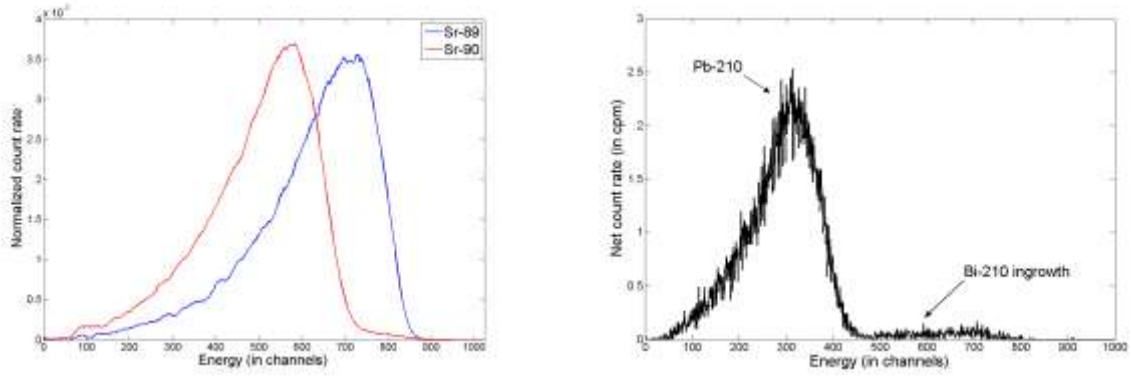


Figure 49: Energy spectra for microspheres (a) $^{89/90}$Sr (b) ^{210}Pb

Sample preparation for ^{90}Sr in water samples at environmental level that may contain ^{210}Pb.

In this type of analysis, Pb is selectively precipitated as $PbIO_3$ in boiling water, as under these conditions, $PbIO_3$ precipitates while $SrIO_3$ remains soluble. The effectiveness of decontamination heavily relies on working at the highest possible temperature [GIMÉNEZ et al. 2023/2].

In a traditional procedure, 1 L of the river water sample is placed in a beaker and spiked with 5 mg each of stable Sr and Pb as tracers. 1 g of Na iodate and 0.41 g of Ca nitrate are added as a precipitating agent. The mixture is boiled for 15 min and centrifuged at 5000 rpm for 5 min or filtered. The resulting supernatant, which contains Sr^{2+}, is carefully separated from the precipitate containing Pb^{2+} through decantation. This process is repeated once, this time adding only stable lead and the precipitating agents.

Subsequently, 0.5 g of ammonium dihydrogen phosphate is introduced to the supernatant and its pH adjusted to 10 by adding NH_4OH. At this point, Sr precipitates. The solution is centrifuged for 5 min; the liquid is decanted while retaining the solid precipitate.

The remaining solid is dissolved with 11.5 mL of 6 M or 8 M HNO_3, and then 10 mL of the solution is passed through the PSresin cartridge. The measurement of the quantity of Sr^{2+} in the loading solution and in the solution eluted allows the calculation of both the yield of the precipitation step and the column separation.

This procedure can be completed in just 6 hours, with 1 hour allocated for counting time achieving a limit of detection of 0.027 Bq/L. The total recovery, encompassing the precipitation step and the column separation, typically falls with the range of 65-85%. Detection efficiency depends on the integration window used. Around 80% in the total window and 50% in the optimum window without interference from ^{210}Pb. Measurement can be performed 21 days later once ^{90}Sr and ^{90}Y are in equilibrium.

Sample preparation for $^{90}Sr/^{89}Sr$ in milk samples for emergency response.

For this type of samples, a preliminary step involves the separation of greater amounts of inactive Calcium. For details see procedure 2.3.5. "Strontium in Milk". A fast procedure for $^{90}Sr/^{89}Sr$ for emergency response includes a preliminary precipitation of the fats and the proteins followed by oxalate precipitation and can be found in [SÁEZ-MUÑOZ et al. 2018].

Sample preparation $^{90}Sr/^{89}Sr$ in aerosol samples.

When analysing aerosol filters, a rapid calcination step is performed, lasting 30 min at 450°C, within 250 mL porcelain crucibles [SÁEZ-MUÑOZ et al. 2019]. After calcination, the resulting ashes are completely dissolved through a two-step microwave digestion process: First using a mixture of 8 mL of HNO_3, 2 mL of HCl and 2 mL of H_2O_2; then, a second with 2 mL of HF. Following this, the sample is evaporated to dryness to remove HF, and the remaining residue is dissolved in diluted nitric acid. In case any residue persists, it is filtered using a 0.1 μm (pore size) filter. 5 mg of Sr^{2+} carrier and 50 mg of Ca^{2+} are added to improve the oxalates precipitation. After heating, 2 g of oxalic acid is introduced, and the mixture is stirred for 5 min. Subsequently, the pH is adjusted to 2–3 with the addition of ammonia. The resulting precipitate is centrifuged at 4200 rpm for 5 min and dissolved in 10 mL 6 M HNO_3 with the aid of a hot water bath to facilitate dissolution. Following this point, an aliquot of the solution is passed through the PSresin-cartridge and treated as explained before.

This comprehensive procedure, including sample treatment, PSresin cartridge separation and measurement, can be completed in just 8 hours. It achieves a detection limit of 0.03 Bq/filter and yields a total recovery of approximately 90%.

A sample preparation procedure described for $^{90}Sr/^{89}Sr$ in vegetation samples closely resembles that used for aerosol samples [SÁEZ-MUÑOZ et al. 2019].

Concrete samples from decommissioning activities present the challenge of being very complex as more radionuclides are present (see procedure 2.3.10./11.).

3.2.2. Aliquat-336 PSresin for Tc-99, Pu Isotopes, Cl-36

3.2.2.1. Tc-99 in Water Samples

3.2.2.2. Pu Isotopes in Water Samples

3.2.2.3. Po-210 in Water Samples

3.2.2.4. Cl-36 and I-129 in Decommissioning Samples

4. Quality Assurance and Uncertainty Budget

Quality assurance in analysis is a critical aspect that guarantees the quality of the results obtained by the method used. That means, the methods proposed had to be validated extensively during its development, in order to assure the validity of the results, determine its quality parameters, but also to detect potential sources of error. Moreover, during the application of the validated methods, regular checks have to be done in order to assure the trueness of the results reported. Some of the common actions, performed in the quality assurance of analytical methods, are: periodic analysis of control samples, participation in interlaboratory exercises and proficiency tests, analysis of reference certificate materials, methods comparison, analysis of blank samples and to check of instrumental stability.

Two of the most relevant quality parameters that have to be taken into consideration, are limit of detection and uncertainty budget. Limit of detection defines the capacity of the method and which activity levels can be measured. Analysis of uncertainties associated to the analysis provides a measure of dispersion of the values, which could be reasonably attributed to the measurand. It helps understanding the method and detecting sources of errors.

In this sense, uncertainty analysis and determination of sources of errors, given for the procedures described in this Handbook, have been identified and quantified according to the recommendations made by IAEA [DE REGGE and FEJGELJ 2004], EURACHEM [EURACHEM 2012] and the Guide of Uncertainty [JCGM 2008] for the total uncertainty budget.

For additional quality assurance of the analytical methods for Rn and Ra, described above and developed by us, we have organized intercomparison runs adjacent to the International Conference on "Advances in Liquid Scintillation Spectrometry" LSC 2001. The results from our LS methods have been validated with data from the classical ones. Details on the intercomparison measurements can be found in [MÖBIUS and SALONEN 2002] and in “LSC-Handbuch” [MOEBIUS and MOEBIUS 2008].

The methods for the determination of Radium via Radon emanation (procedure 2.2.1.4.) as well as by means of Radium RAD Disk filters (procedure 2.2.1.5.) are validated below in detail. Lower Limits of Detection LLD are calculated explicitely and are presented as general examples.

4.1. Uncertainty Budget in LS Spectrometry

The identification and quantification of uncertainty components are critical parts of any measurement. Results without uncertainty budget are incomplete and only of low value. Even when previous chapters have shown, that LS is an effective and sensitive counting method, a number of possible variables have to be considered. They are partly also correlated amoung each other, see figure 53 for example. This applies to classical laboratory operations, but also to the calculation models for the efficiency (TDCR, CIEMAT-NIST, etc).

For the determination of natural radionuclides in air and water, LS avoids a complicated and time intensive sample preparation and consequently faults from electrolytic deposition like in α-spectrometry. Errors during sample conservation, as well as during transport to the laboratory are avoided when used as in-situ method with mobile devices. Thus, the total uncertainty of the procedure remains restricted to sampling and the measurement itself.

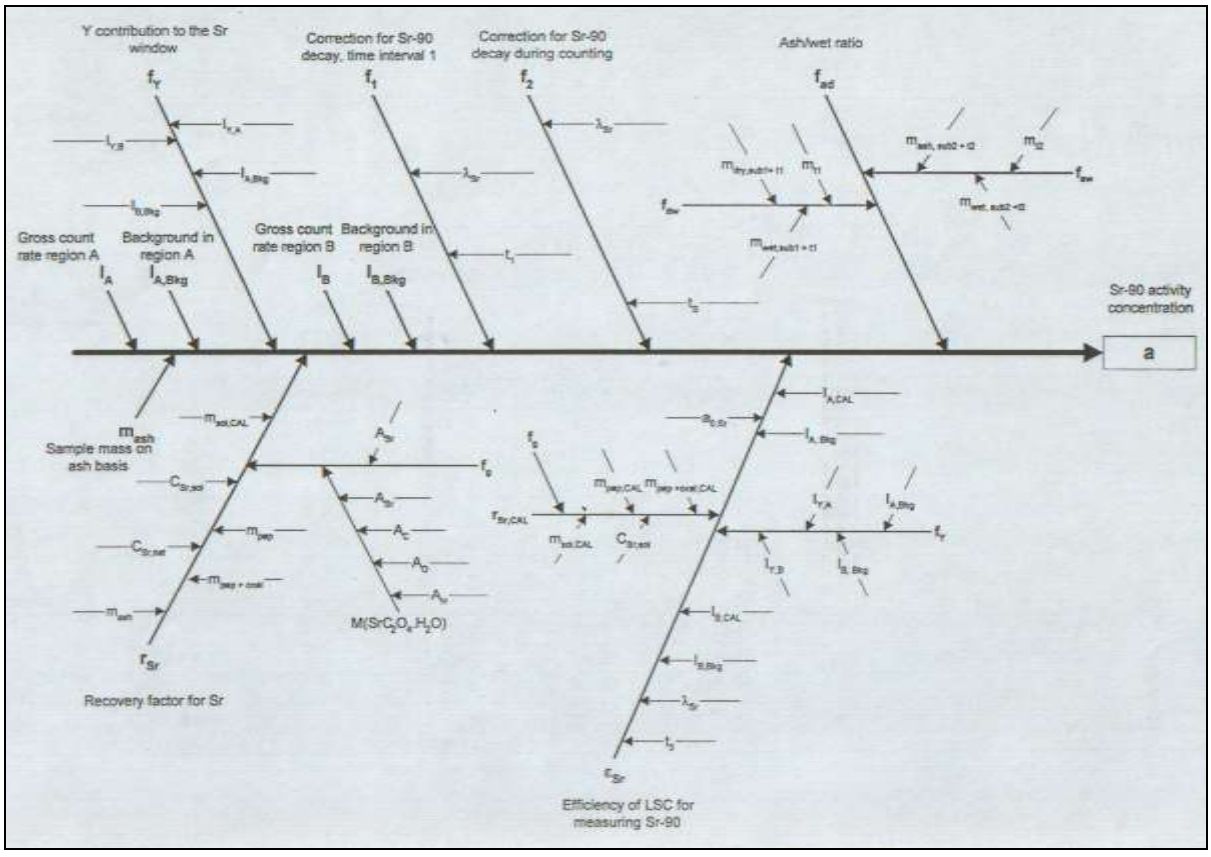


Figure 53: Cause and effect diagram for the determination of the activity concentration: Example of ^{90}Sr via LSC [MORENO et al. 1999]

When chemical separation steps are part of the sample treatment, uncertainty in the calculation of the yield has to be taken into consideration. Yield calculation can be based on mass determination, addition of internal standards and/or OES or ICP-OES measurements.

For the uncertainty budget of methods based on liquid scintillation counting, the following main parameters have to be considered for calculation. Values of relative standard uncertainty

depend on the quality of the materials and the amount of the component. Some of the common parameters have been found to be

- uncertainty of weighing / volume of standards (pipetting error)	± 1%
- uncertainty of weighing / volume of sample	± 1%
- uncertainty of weighing for calibration of the balance	< 0.5%
- uncertainty of cocktail volume	
through weighing	± 0.5%
through volume measurement	± 2%
- decay data of standards	± 2%
- decay data of samples	± 1%
- activity of the standards	± 1 - 2%
- chemical recoveries	± 1 - 5%
- statistical deviation of sample (2σ)	< 1%
- statistical deviation of standard (2σ)	< 1%
- statistical deviation of background (2σ)	< 1 %
- measuring efficiency in dependence of quenching (a)	± 2.5%
- measuring efficiency in dependence of α/β-PSD (b)	
in organic phase	± 1%
in aqueous phase	± 3 – 5%
- measuring efficiency in dependence of channel setting (c)	± 1.5%
- measuring efficiency (sum of single uncertainties a – c)	± 3% (5%)

However, it should be taken into account, that the uncertainty associated to these variables depends on the value itself. Therefore for low weights, low count rates or low recoveries higher uncertainties should be expected. On the other hand, some parameters, even having high relative standard uncertainties, may have a low impact in the combined uncertainty. This concerns the background in the case of samples highly above the limit of detection or the chemical recoveries when they are close to 100%.

The steps that should be followed, when doing an estimation of the uncertainty, are:

1. Specify the measurand and how to calculate it
2. Identify sources of uncertainty and list it
3. Quantify the uncertainty associated to each component
4. Calculate combined uncertainty

The quantification of the uncertainty associated to each component can be done on the basis of previous data, repetition of experiments, data from producers or through approximations. In this sense two type of uncertainty evaluations are identified:

- Type A: method of evaluation based on statistical evaluation of a series of observations
- Type B: method of evaluation based on a pool of comparatively reliable information

Combined uncertainty is calculated using the law of propagation of errors. For simplicity reasons, the uncertainties here are considered as being independent from each other.

$$u(y) = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial y}{\partial x}\right)^2 * u(x_i)^2} = \sqrt{\sum_{i=1}^{n} (c_i)^2 * u(x_i)^2}$$

where, u(y) (or U) is the combined uncertainty, $u(x_i)$ are the individual Type A or Type B uncertainties and c_i are the sensitivity factors.

Thus, the uncertainty for the LS measurement in general has been calculated to be 4 to 6% according to the conditions.

Recently, Montecarlo simulation has been introduced as a way of calculating individual or combined uncertainties. Although this is a method of high complexity, there are some applications, like the "quench" package [Cassette 2016], that could be of help to determine the uncertainty associated to quench correction in liquid scintillation.

More detailed studies of uncertainty evaluation for various analytical procedures can be found in [MORENO et al. 1999] regarding Strontium determination by LS, in [Forte et al. 2006] about α- and β-indices in water, and in [DE REGGE and FAJGELJ 2004] and [MARLAP 2004] for general hints for the uncertainty consideration.

Single components of the standard uncertainty have been quantified as follows:

- Uncertainty of weighing: by multiple weighing and manufacturer information
- Volume of pipetting: by multiple pipetting, weighing and manufacturer information
- Decay data: according to the literature data
- Counting statistical deviation: $(R)^{1/2}$
- Measuring efficiency: by using a standard solution and performing several replicate measurements under identical performance for the standard solution and the measuring sample
- Measuring efficiency in dependence of quenching: through quench correction curve.
- Recovery: by considering the combined uncertainty of the factors that affect its determination (i.e. weighting, solubility, pipetting, calibration curve in atomic absorption or ICP measurements, standards)
- Standard solutions: manufacturer information

For the total uncertainty budget, faults from sampling and sample preparation as main source of error have to be taken into consideration, if these faults cannot be avoided or correctly quantified.
In the case of ^{222}Rn measurements, 5% have been considered for losses during liquid/liquid extraction, when using a geometry of 8 mL water sample and 12 mL cocktail. Radon losses can considerably be higher, if the total volume of the liquid phase is less than 20 mL.

Incorrect calibrations, like not taking into account glass or plastic vials or the dependency on cocktail, can result in errors of up to 20%. When quench correction for low and medium quenched samples is neglected up to 30% error for low energy β-emitters and up to 15% for medium and high energy β-emitters might result. This error can be diminished, when TDCR with three PM tubes is used (less than 5% for ^{3}H and medium quenched samples). Errors caused from wrong α/β-PSD measurement are due to not considering quenching effects on PLI level adjustment (e.g. different salt content) or to differences between radionuclides used in the calibration (e.g. ^{90}Sr and ^{241}Am) and the radionuclide in the sample. In this case, a 2 or 3 dimensional visualization plot will help recognizing and prevent faults.

Further uncertainties result from handling radionuclides forming secular (e.g. ^{226}Ra and ^{222}Rn), or transient (^{232}U as standard) radioactive equilibrium. A careful ingrowth correction is necessary for correct results (see 2.2.1.4.). In case of using ^{232}U as standard solution (e.g. for isotope dilution analysis), a regular separation from ingrowing daughter nuclides is precondition (fig. 54). On the other hand, when chemical separation is performed, ingrowth of daughter radionuclides should be avoided by counting the samples just after separation or by correction through the estimation of its contribution to the counting window (fig. 55).

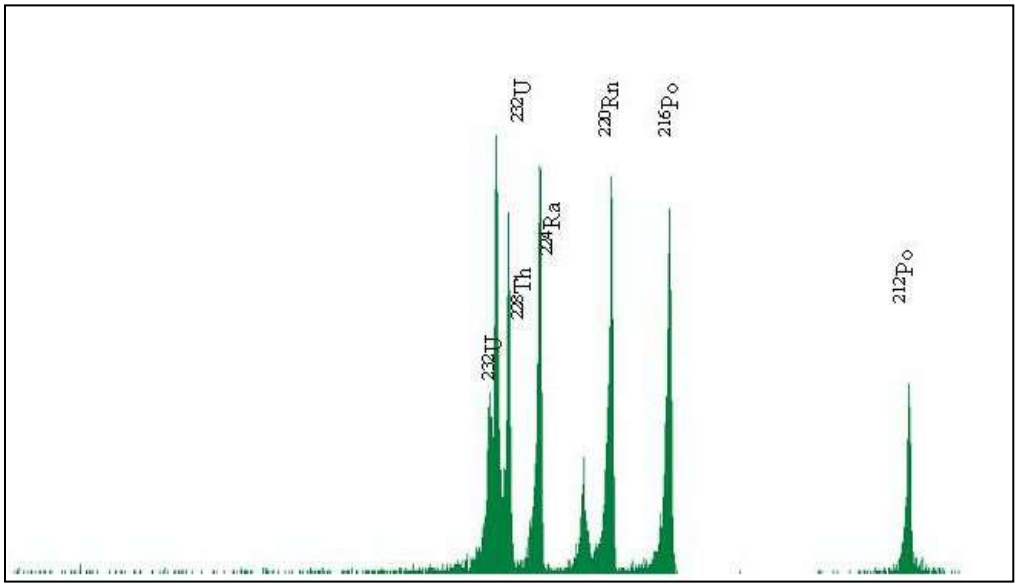


Figure 54: α-spectrum of ^{232}U standard solution with daughters [MOEBIUS T. 2008]

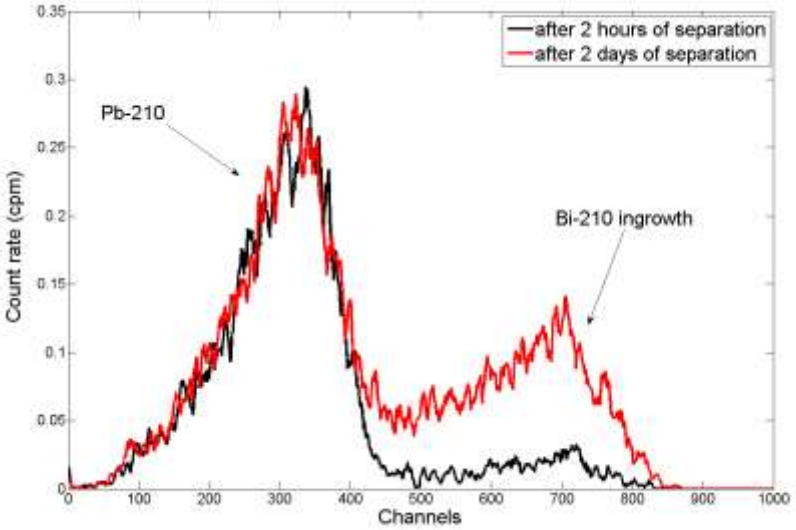


Figure 55: Spectrum of a ^{210}Pb standard solution measured with a PSresin 2 hours and 2 days after separation (i.e. ^{210}Bi ingrowth)

4.2. Lower Limit of Detection

4.3. Method Evaluation and Validation

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Annex 3: Recent International Conferences on Advances in Liquid Scintillation Spectrometry

LSC 1992: Vienna, F. Schönhofer

LSC 1994: Glasgow, G. Scott

LSC 2001: Karlsruhe, S. Möbius

LSC 2005: Katowize, S. Chalupnik

LSC 2008: Davos, J. Eikenberg

LSC 2010: Paris, P. Cassette

LSC 2013: Barcelona, J.F. Garcia

LSC 2017: Copenhagen, X. Hou (http://lsc2017.nutech.dtu.dk)

LSC 2020 : Shenzhen 2021, R. Shuangchen (http://lsc2020.swust.edu.cn; https://cloud.yiyum.com/?sid=1374&mid=362&v=100)

LSC 2024: Portsmouth UK, P. Warwick https://lsc2024.co.uk/programme/ https://store.southampton.ac.uk/conferences-and-events/school-of-ocean-and-earth-science/events

Annex 4: DGFS Poster LSC2020 Shenzhen

Karlsruhe Institute of Technology

German Society for Liquid Scintillation DGFS e.V.

20 Years DGFS Society for Liquid Scintillation – New Developments

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DGFS Key Objects

- Development and exchange of experiences in modern Liquid Scintillation (LS) to a broader community
- Development and improvement of analytical procedures with special emphasis on natural radionuclides, gross α / β, Ra and Rn isotopes, NORM (see various LSC Conference Proceedings)
- Academical education and training in Liquid Scintillation: International Training Courses Karlsruhe (Germany), Rio de Janeiro (Brazil), Bangkok (Thailand), Brisbane (Australia) and Antsiranana (Madagascar)

LS Analytical Procedures (1)

- Quick method for key nuclides in drinking water (Rn-222, Ra-226/8, Pb-210, H-3, gross α/β) pp55(1)
- RAD Disk based methods and plastic scintillator microspheres for Ra and Sr-isotopes, Pb-210 and Tc-99
- Artificial radionuclides in the nuclear fuel cycle (Fe-55 and Ca-41 in decommissioning activities by TDCR) pp93(1)
- Tritium analysis in pipes after oxidation for KATRIN neutrino mass experiment (new)
- Pb-210 Black Powder deposits from pipelines after leaching (e.g. Nord Stream) pp119(1) (new)
- Radiocarbon in biobased products (e.g. fuel) pp64(1)
- Simple self-made LS arrangement for training pp22(1)

and others

Literature

(1) Moebius S., Erat S., Mayer K., Moebius R., Moebius T., Santiago L., Tarancon A., Wendel J., Wisser S.

Liquid Scintillation – Measuring Procedures, New Developments – 2nd extended Ed. 2018, DGFS e.V. German Society for Liquid Scintillation Spectrometry and KIT Karlsruhe Institute of Technology, 2018 Karlsruhe

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