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REALISATION OF RADIONUCLIDES ACTIVITY UNIT USING THE LIQUID SCINTILLATION COUNTING (LSC)

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Abstract. *Registration of the effects of interaction of the radiation emitted after radioactive decay enables determination of activity of a given material expressed in becquerels (Bq). Measurements in a frame of international comparisons of ^{14}C activity using the triple-to-double coincidence ratio (TDCR) method and of ^{177}Lu activity using the 4π(LS)-γ coincidence and anticoincidence method, where the liquid scintillation technique (LSC) was used, were described. Specificity of short-lived radionuclides activity determination was discussed.*

Keywords: radionuclide activity, liquid scintillators, LSC technique

ODTWARZANIE JEDNOSTKI AKTYWNOŚCI RADIONUKLIDÓW ZA POMOCĄ TECHNIKI CIEKŁYCH SCYNTYLATORÓW (LSC)

Streszczenie. *Rejestracja oddziaływania z materią promieniowania emitowanego w czasie rozpadów promieniotwórczych umożliwia określenie aktywności danego materiału w bekerelach (Bq). Omówiono wykonane w trakcie międzynarodowych porównań pomiary aktywności ^{14}C metodą potrójno-podwójnych koincydencji (TDCR) oraz ^{177}Lu metodą 4π(LS)-γ koincydencji i antykoincydencji, w których zastosowana jest technika ciekłych scyntylatorów (LSC). Omówiono specyfikę pomiaru aktywności radionuklidów krótkożyciowych*.

Słowa kluczowe: aktywność radionuklidu, ciekłe scyntylatory, technika LSC

Introduction

Radioactivity is the phenomenon of spontaneous decay of unstable atomic nuclei with time. Physical quantity related to this is the activity defined as the number of nuclei decaying in a given sample per unit time, or in other words - the decay rate of a radionuclide. As a result of the process various elementary particles (alpha particles, beta particles, gamma-ray photons, Auger electrons or X-ray photons), depending on mode of decay, are emitted. The idea of activity measurement is to register effects of interaction with matter of the above particles. Excellent and detailed description of various methods and detectors developed for activity measurement gave L'Annunziata [7]. Special role in radionuclide standardization plays the liquid scintillation counting (LSC) technique. Its theoretical and practical aspects were described e.g. by Broda et al. [3]. In LSC detector light pulses created in liquid scintillator by ionizing radiation are registered by photomultipliers (PMTs) and output pulses are counted.

The aim of this work is to present application of the LSC technique for activity measurements in the Laboratory of Radioactivity Standards (LRS), National Centre for Nuclear Research Radioisotope Centre POLATOM in Świerk. Only two direct measurement methods are described. Results of the ^{14}C (pure β-emitter) solution activity determination using the triple-to-double coincidence ratio (TDCR) method and the ^{177}Lu (β-γ emitter) solution activity - using the 4π(LS)-γ coincidence and anticoincidence method [5] obtained in a frame of two international comparisons are presented. The purpose of this paper is also to describe application of the last method for standardization of short-lived radionuclides, applied in nuclear medicine, underlining special measurement problems related to short time of measurement.

Credibility of radionuclide activity measurements in the LRS and usefulness of standard radioactive solutions produced in the laboratory are indicated.

1. Determination of the activity unit

The unit of activity in the International System of Units (SI) is the becquerel (Bq). The activity of a sample equals 1 Bq when the decay rate is one per second. Realization of the activity unit means to determine the activity of a given sample. Specificity of the activity measurement is connected with decreasing of the sample activity in time with the half-life specific for a given radionuclide, so an exact date and time of activity determination must be given. The activity remaining after time t from the moment t_o is described by the well-known expression:

$$A = A_o e^{-\lambda t} \mathrm{A} = \mathrm{A_o} \mathrm{e}^{-\lambda \tau_{½}} \quad (1)$$

where

$$\lambda = \ln 2 / \tau_{½} \quad (2)$$

is the decay constant, A_o is the activity at the moment t_o and $\tau_{½}$ is the radionuclide half-life.

2. Radioactivity measurements using LSC

2.1. Liquid scintillation counting

The LSC technique enables quantitative measurement of the activity of radioactive solution mixed with liquid scintillation cocktails [3]. Its main advantage is relatively simple sample preparation and high detection efficiency, practically 100% for α particles and close to 100% for high energy β particles.

Samples for measurement using LSC technique are prepared in 20 mL high-performance PerkinElmer glass vials filled-in with 10 mL of the scintillation cocktail. The cocktail contains an organic fluors dissolved in a solvent. The Ultima Gold commercial scintillation cocktail - 2,5-diphenyloxazole (PPO) fluor solution in a concentration of about 2–10 g/L dissolved in di-isopropyl-naphtalene (DIN) solvent is applied [3]. Usually, a set of six vials is prepared for measurement in the LRS. From 10 mg to 200 mg of the radioactive solution for standardization is gravimetrically added to each vial. The radionuclidic purity of the solution is controlled using gamma spectrometry method with high purity germanium detector (HPGe). The amount of gamma impurities should be lower than about 0.1% of the main radionuclide activity.

Sample is put into the specified LS-counter and measured using a specified measurement method. Registered counting rate divided by the counting efficiency and by the mass of radioactive solution gives its activity per gram. Correct determination of the detector counting efficiency is challenging but is a requisite of the LSC technique application.

2.2. TDCR method

The TDCR method is a direct measurement method, elaborated in our laboratory over 30 years ago, used for standardization of pure β-emitters and pure electron-capture emitters [4]. The TDCR detector (Fig. 1) contains three PMTs working in coincidence with a symmetric setup at a plane level around an optical chamber where the sample with the liquid scintillator is placed. In the MAC-3 coincidence module the live-time technique with an extendible dead-time is applied [1].

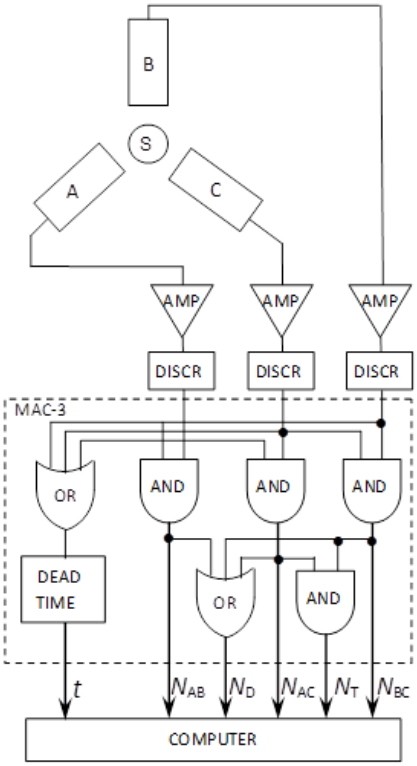

Fig. 1. Simplified scheme of the TDCR counter. A, B, C – photomultipliers, S – sample in liquid scintillator, AMP – amplifiers, DISCR – discriminators, MAC-3 – coincidence and dead time module. Registered counting rates are indicated

Counting rate of three double coincidence pulses (N_{AB}, N_{BC}, N_{AC}), triple coincidence pulses (N_T), logical sum of double coincidence pulses (N_D) and of live-time pulses (t) are registered. The ratio $R = N_T/N_D$ is a characteristic experimental parameter of the TDCR method. The activity value of the measured sample is obtained dividing counting rate value by the TDCR detector counting efficiency, which is calculated numerically as a non-linear function of the R parameter. Calculations are based on the statistical model of phenomena in the liquid scintillator leading to scintillations and pulses registration in the counter [3]. The beta spectrum of a given radionuclide is considered.

Activity measurement of the ^{14}C solution using the TDCR method was performed in a frame of the bilateral comparison with the National Institute of Ionizing Radiation Metrology (ENEA-IMRI) in Italy [2]. ^{14}C disintegrates 100% by beta-minus transition with a maximum β emission energy $E_{\beta max}$ = 156.5 keV and the half-life of $\tau_{1/2}$ = 5700 (30) years.

A set of six sources containing from 135.7 mg to 138.6 mg of radioactive solution mixed with the Ultima Gold liquid scintillator was prepared. Sources were measured in the TDCR [3] and a new TDCRG counter equipped with a digital board with FPGA [11]

Counting rates were registered and background rate was subtracted. A set of 8 counting points at various counting efficiencies was obtained by reducing the PMTs focusing potential. The total measurement time of each sample was 40 min. R parameters were determined. The counting efficiency $\varepsilon_D(R)$ function of D pulses was calculated and activity at each counting point was obtained (Fig. 2).

The arithmetical mean of these values divided by the mass of the solution was taken as the activity per gram of the ^{14}C solution in the sample. Activity per gram of the ^{14}C solution was obtained as the arithmetical mean of all sample results obtained in both TDCR counters. The LRS result was A_{LRS} = 49.93 kBq g^{-1} with a standard uncertainty u_{LRS} = 0.13 kBq g^{-1} (0.25%). Three ready-to-measure sources from the set have been sent to the ENEA-INMRI and then measured using the TDCR method. The ENEA-INMRI reference value was A_{ref} = 49.85 kBq g^{-1} with a standard uncertainty u_{ref} = 0.14 kBq g^{-1} (0.29%).

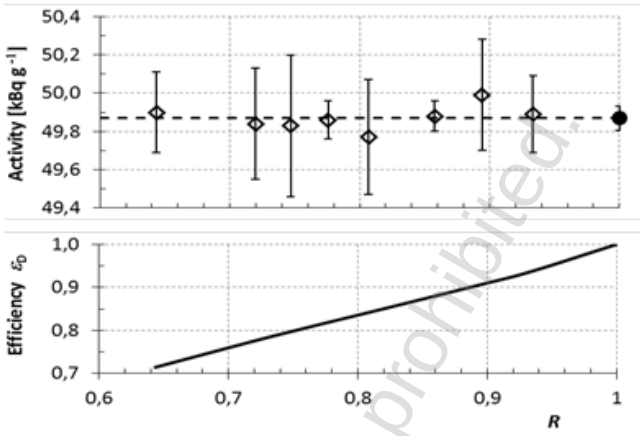

Fig. 2. Results of one ^{14}C sample measurement using the TDCR method. The ionization quenching parameter value of kB = 0.010 cm MeV^{-1} was used in calculation [3]. Black circle represents the final activity per gram value of the ^{14}C solution in the sample. Solid line – numerically calculated counting efficiency $\varepsilon_D(R)$

2.3. 4π(LS)-γ coincidence and anticoincidence method

The 4π(LS)-γ coincidence and anticoincidence method is a direct method used for standardization of β-γ emitters. The detector contains two PMTs working in coincidence and the liquid scintillator in so called beta channel and two PMTs with NaI(Tl) crystals working in the sum mode in the gamma channel [5]. The beta and gamma channels are working in coincidence. PMTs are mounted at a plane level around an optical chamber where the sample in the liquid scintillator is placed (Fig. 3).

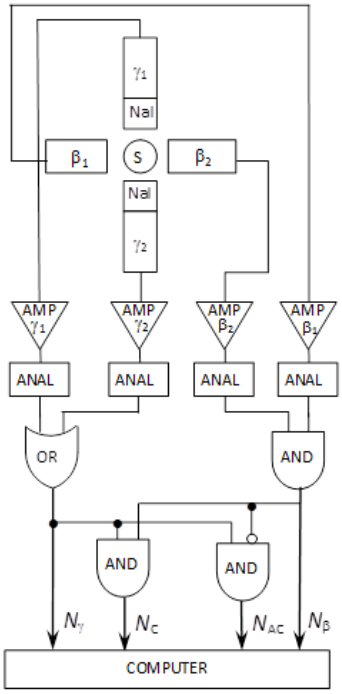

Fig. 3. Simplified scheme of the 4π(LS)-γ coincidence and anticoincidence counter. β_1, β_2 – PMTs in beta channel, γ_1, γ_2 – PMTs with NaI(Tl) crystals in gamma channel, AMP – amplifiers, ANAL – one-channel analyzers, S – sample in liquid scintillator. Registered counting rates are indicated

Before the β-γ emitter activity measurement the energy range of gamma spectrum is selected. The selection influences the value of γ photons counting efficiency, φ, in the beta channel. The efficiency φ serves as the method parameter.

Counting rates of gamma channel pulses (N_γ), beta channel coincidence pulses (N_β), coincidence between beta and gamma channels pulses (N_C) and anticoincidence between beta and gamma channels pulses (N_{AC}) are registered. The counting efficiency is changed by high voltage applied to PMTs in beta

channel and a set of counting points is obtained. The beta channel counting efficiency is calculated as $\varepsilon_\beta = N_C/N_\gamma$ at each counting point. The disintegration rate in the sample, N_o, is defined by the formula:

$$\frac{N_\beta N_\gamma}{N_C} = N_o\left[1+\frac{1-\varepsilon_\beta}{\varepsilon_\beta}\varphi\right] \quad (3)$$

or

$$\frac{N_\beta N_\gamma}{N_\gamma - N_{AC}} = N_o\left[1+\frac{1-\varepsilon_\beta}{\varepsilon_\beta}\varphi\right] \quad (4)$$

The linear extrapolation of $N_\beta N_\gamma/N_C$ or $N_\beta N_\gamma/(N_\gamma - N_{AC})$ as a function of $(1-\varepsilon_\beta)/\varepsilon_\beta$ to $\varepsilon_\beta = 1$ determines N_o.

The above method was used in the LRS for the ^{177}Lu solution standardization in a frame of international key comparison organized by the National Institute of Standards and Technology (NIST) in USA. In the comparison 11 leading laboratories have participated from the whole world [6].

^{177}Lu disintegrates 100% by beta-minus transition with $E_{\beta max}$ = 498.3 keV to the ground state and with three β^- branches ($E_{\beta max}$ = 177.0 keV, 248.6 keV and 385.4 keV) to three excited level of ^{177}Hf following by γ-ray emission. ^{177}Lu has a relatively short half-life of $\tau_{1/2}$ = 6.65 days.

Radionuclidic purity of the ^{177}Lu solution was checked by gamma spectrometry. A set of 12 sources containing from 6.0 mg to 30.9 mg radioactive solution mixed with the Ultima Gold liquid scintillator was prepared. For each source a set of 6 or 7 counting points at various counting efficiencies was obtained. Two various energy ranges of gamma spectra, thus various φ parameters, were selected. Total measurement time of all sources was 21.5 hours. Counting rates were registered and corrected for a dead-time. Background rate was subtracted.

The disintegration rate N_o of each sample was obtained from linear extrapolation of counting points based on equation (3), then divided by mass of radioactive solution (Fig.4).

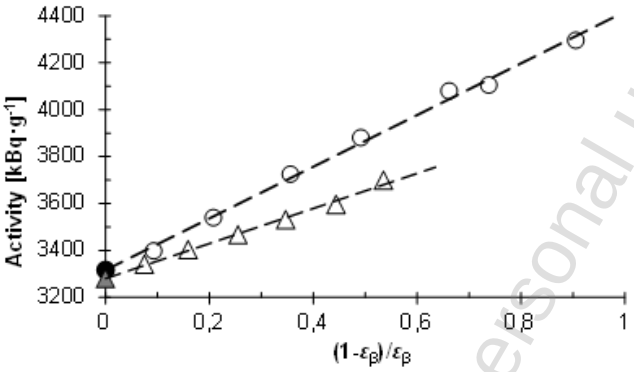

Fig. 4. An example of one ^{177}Lu source standardization using the 4π(LS)-γ coincidence method. Black circles and gray triangles represent activity per gram of the solution determined by linear extrapolations with various parameters φ.

The activity per gram value of the ^{177}Lu solution was taken as the arithmetical mean of all samples resulting A_{LRS} = 3279 kBq g^{-1} with a combined standard uncertainty u_{LSR} = 18 kBq g^{-1} (0.54%).

The key comparison reference value of ^{177}Lu was found to be A_{ref} = 3288 kBq g^{-1} with a standard uncertainty u_{ref} = 4 kBq g^{-1} (0.12%).

2.4. Uncertainty estimation

Uncertainty components, as a relative standard uncertainty for either a Type-A (evaluation by statistical methods) or Type-B (evaluation by other methods) assessment [9], of ^{14}C (Table 1) and ^{177}Lu (Table 2) solution activity measurement were estimated. Standard uncertainty related to the TDCR method itself and counting model, considering TDCR results in various international comparisons, was estimated to be 0.33%. The total combined uncertainties were determined as quadratic sum of all uncertainty components. ^{14}C samples were measured in two various counters, thus the solution standard uncertainty was taken as the mean total combined uncertainties of both counters divided by √2.

Table 1. Uncertainty budget of ^{14}C solution standardization using the TDCR method. Standard uncertainties in percent

Uncertainty component	Type	TDCR counter	TDCRG counter
counting statistics	A	0.04	0.13
weighing	B	0.1	0.1
background	A	0.01	0.03
counting time	B	0.001	0.001
measurement method and model	B	0.33	0.33
total combined uncertainty		0.34	0.37
solution standard uncertainty		0.25	

Table 2. Uncertainty budget of ^{177}Lu solution standardization using the 4π(LS)-γ coincidence and anticoincidence method.

Uncertainty component	Type	Uncertainty (%)
counting statistics	A	0.14
weighing	B	0.12
background	A	0.01
dead time	B	0.01
resolving time	B	0.03
extrapolation method	B	0.50
half-life	B	0.03
impurities	B	0.01
adsorption	B	0.04
total combined uncertainty		0.54

2.5. Degree of equivalence

Employing the convention used in the Bureau International des Poids et Mesures (BIPM) [10], the degree of equivalence of the LRS result, A_{LRS}, with respect to the international comparison reference value, A_{erf}, was determined by a pair of terms: the difference, D_{LRS}, and U_{LRS}, its expanded uncertainty (k = 2), expressed as

$$D_{LRS} = A_{LRS} - A_{ref} \quad (5)$$

$$U_{LRS} = 2\sqrt{u_{LRS}^2 + u_{ref}^2} \quad (6)$$

where u_{LRS} and u_{ref} were standard uncertainties.

The measurement result is satisfied if the condition $|D_{LRS}| < U_{LRS}$ is fulfilled. Obtained degree of equivalence for ^{14}C measurement result: D_{LRS} = 0.08 kBq g^{-1}, U_{LRS} = 0.38 kBq g^{-1} and for ^{177}Lu result: D_{LRS} = -9.0 kBq g^{-1}, U_{LRS} = 36.9 kBq g^{-1} showed, that both LRS results of standardization were in excellent agreement with the comparison reference value.

2.6. Standardization of short-lived radionuclides

Short-lived radionuclides are essential for nuclear medicine and radionuclides with half-lives much shorter than one day are used as radiotracers. The use of nuclear medicine increases as these radionuclides become more accessible and they attract the interest of the National Metrology Institutes (NMIs).

Determination of the activity unit of short-lived radionuclides decaying by β^+ transition such as ^{18}F (1.8 h), ^{64}Cu (12.7 h) or ^{68}Ga (67.8 min) applied mainly in positron emission tomography (PET), causes special measurement challenges. General procedure of primary standardization is described in Section 2.3. The radionuclidic purity of an initial solution is checked. The solution, usually with a high total activity, is measured initially in the instrument that should be calibrated, such as ionization chamber, and system response is registered. Then solution is diluted to have radioactive concentration suitable for standardization in the 4π(LS)-γ coincidence and anticoincidence system. A set of samples is prepared. Measurements as short as possible, to achieve number of counts sufficient for reasonable low statistical uncertainty are performed. An exact time of each single measurement act (counting point) is registered. Number of counts registered during single measurement act are corrected for decay and recalculated for the reference time according to equation:

$$N' = \frac{\lambda \Delta t}{1 - e^{-\lambda \Delta t}} e^{\lambda (t_i - t_o)} N_i \quad (7)$$

where: N_i – registered counts in counting point, t_i – time of counting point measurement, t_o – reference time, λ – decay constant, Δt – measurement duration.

Measurement results of a set of samples are computed, activity per gram of the solution is obtained and then the calibration factor for calibrated instrument is calculated. The aim of short-lived radionuclides standardizations performed by LRS is to prepare the standard sources for calibration of dose calibrators used in nuclear medicine departments. In most cases calibrated instrument being the secondary standard (e.g. ionization chamber), traceable to the national standard, is used in the above process

Key comparisons of short-lived radionuclides activity are organized by BIPM to enable traceability to the International Reference System (SIR) [10]. All measurements within comparison are performed on place in participating laboratory/NMI using a Transfer Instrument (SIRTI), developed at the BIPM, based on a transportable well-type NaI(Tl) detector calibrated against the SIR [8]. The instrument enables participation NMIs situated far from the BIPM.

3. Radioactivity standards

The TDCR and the 4π(LS)-γ coincidence and anticoincidence LS-counters, described above, form a part of the primary standard applied and kept in the LRS, established as the national standard of radioactivity unit in Poland [5]. Radioactive solutions standardized in the LRS with reference to this national standard became secondary standards. Peculiarity of these radioactivity standards, underlined in Section 1, is their activity decreasing in time. Standard radioactive solutions are used for calibration of the measurement equipment e.g. ionization chambers, very useful for many users of radioactive materials. Standard solutions are also used in the LRS for manufacture working standards such as liquids closed in sealed ampoules or solid sources in a form of disks, cylinders, capsules, etc. of various dimensions.

4. Conclusions

Application of the LSC technique for activity measurements of ^{14}C and ^{177}Lu solutions using the LSC technique gave credible results. The results were satisfied as in both cases difference, D_{LRS}, between the LRS result and the reference value of international comparison was lower than its expanded uncertainty, U_{LRS}, defined by equation (6). Obtained expanded uncertainties ($k = 2$) of 0.50% and 1.08% for ^{14}C and ^{177}Lu solutions activity respectively were also satisfied.

The LRS participated in many international comparisons and confirmed credibility of activity measurements of many others radionuclides. It was showed that the LRS is able to standardize short-lived radionuclides applied in nuclear medicine using the 4π(LS)-γ coincidence and anticoincidence direct method. It was indicated that the LRS manufactures radioactivity standards with reference to the national standard of radioactivity unit.

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