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Covariance methodology applied to ^{35}S disintegration rate measurements by the CIEMAT/NIST method

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HIGHLIGHTS

- ^{35}S disintegration rate measured in Liquid Scintillator system using CIEMAT/NIST method.
- Covariance methodology applied to the overall uncertainty in the ^{35}S disintegration rate.
- Monte Carlo simulation was applied to determine ^{35}S activity in the $4\pi\beta$(PC)-γ coincidence system.

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ABSTRACT

The Nuclear Metrology Laboratory (LMN) at IPEN is carrying out measurements in a LSC (Liquid Scintillation Counting system), applying the CIEMAT/NIST method. In this context ^{35}S is an important radionuclide for medical applications and it is difficult to be standardized by other primary methods due to low beta ray energy. The CIEMAT/NIST is a standard technique used by most metrology laboratories in order to improve accuracy and speed up beta emitter standardization. The focus of the present work was to apply the covariance methodology for determining the overall uncertainty in the ^{35}S disintegration rate. All partial uncertainties involved in the measurements were considered, taking into account all possible correlations between each pair of them.

1. Introduction

To establish a routine method for standardize beta pure emitters, the Nuclear Metrology Laboratory (LMN) at IPEN is carrying out measurements in a Liquid Scintillation Counting system (LSC), applying the CIEMAT/NIST method, which is a standard technique used by most metrology laboratories. To validate the procedure, the results obtained were compared with measurements using the efficiency tracing technique with the $4\pi\beta$(PC)-γ coincidence system.

The present work describes the covariance methodology applied to the overall uncertainty in the ^{35}S disintegration rate, considering all partial uncertainties involved in the measurements, taking into account all possible correlations between each pair of them. This methodology was applied for measurements for both systems.

The radionuclide selected for this first measurement was ^{35}S because it is widely used in different applications such as nuclear medicine, agriculture and in industry. It decays with a half-life of 87.44 days only by a low energy beta emission with 167.50 keV end-point energy.

In the CIEMA/NIST method a ^{3}H standardized solution was used as tracer due to its very low beta energy. For the $4\pi\beta$(PC)-γ tracing technique the radionuclide ^{60}Co was selected as tracer because it emits beta particles with end-point energy close to those from ^{35}S.

2. Standardization method

2.1. CIEMAT/NIST method

One of the methods used for standardizing beta emitting radioactive solutions by means of a liquid scintillation system is called CIEMAT/NIST (Calhoun et al., 1992). By this method, the curves of experimental efficiency versus quenching parameter (extinction factor) and Factor of Merit (FM) versus calculated efficiency of ^{3}H solution standard, yield the universal curve Factor of Merit (FM) versus quenching parameter. From the universal curve and from the calculated efficiency versus Factor of Merit (FM) of the radionuclide under investigation, it is possible obtain

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the efficiency related to the quenching parameter. These curves were obtained by means of CN2001 code (Günther, 2001).

There are many interpretations for the Factor of Merit (Grau Malonda and Garcia-Torano, 1982), in this paper it is defined as the amount of energy required to produce one photoelectron at the photocathode of the Photo Multiplier Tube (PMT).

2.2. Liquid scintillator counting system

The liquid scintillation system used was a PACKARD TRICAB Mod 2100, consisting of two photomultipliers operating in coincidence. An external source of ^{133}Ba placed near the measurement system is used for determining the quenching parameter, transformed Spectral Index of External Standard (tSIE) which is calculated from the Compton spectrum induced in the scintillation cocktail by the external source (Thomson, 2001). To determine different quenching parameter and therefore different efficiencies, amounts of quenching agent were added to the samples.

The activity for *i*-th quenching parameter is given by:

$$A = \frac{S_i}{\varepsilon_i} \tag{1}$$

where A is the activity, S_i is the counting rate for i-th quenching parameter corrected for decay and background rate; ε_i is the calculated efficiency obtained by the CIEMAT/NIST method for i-th quenching parameter.

The final activity was obtained by the weighted average activity, which was calculated considering the partial uncertainties with their correlation.

2.3. $4\pi\beta$-γ Coincidence measurement

The $4\pi\beta$-γ coincidence system used for measuring the tracer solution and beta pure mixed with tracer solution, consisted of a proportional counter with 4π geometry filled with 0.1 MPa P-10 gas mixture, coupled to a pair of 76 mm × 76 mm NaI(Tl) crystals. The measurements were performed by integral mode for beta detection, cutting off only the electronic noise. The calibrations of tracer and mixed solutions were performed selecting a gamma-ray discrimination window comprising (1173.24+1332.51) keV total absorption energy peaks. The tracer method is described in detail elsewhere (Dias et al., 2006).

The ^{60}Co activity was determined in advance by the $4\pi\beta$(PC)-γ coincidence method. The ^{35}S specific activity, which is usually determined by means of the extrapolation technique applied to the mixed sources, for the present measurement, was obtained by means of the application of ESQUEMA code (Dias et al., 2006).

This code makes use of decay scheme parameters, system geometry and source characteristics. In this way, all detection processes in the coincidence system are simulated, predicting the behavior of the extrapolation curve by the Monte Carlo technique. The detector response curves were obtained by means of the radiation transport code MCNPX (ORNL, 2006).

To determine the final activity N_0 a least square fitting was performed combining experimental and simulated data. The corresponding chi-square was given by

$$\chi^2 = (\vec{y}_{\exp} - N_0 \vec{y}_{MC})^T V^{-1} (\vec{y}_{\exp} - N_0 \vec{y}_{MC}) \tag{2}$$

where: $\vec{y}_{\exp}$ is the experimental vector of $N_\beta N_\gamma / N_c$; $\vec{y}_{MC}$ is the $N_\beta N_\gamma / N_c$ vector calculated by Monte Carlo for unitary activity; N_0 is the specific activity of the radioactive solution; V is the total covariance matrix, including both experimental and calculated uncertainties, and T stands for matrix transposition.

A series of simulated values were calculated for a wide range of beta efficiency parameter in small bin intervals. The $\vec{y}_{MC}$ values used in Eq. (2) correspond to the same efficiency obtained experimentally. In the case of efficiency tracing technique, the tracer activity has been subtracted from $\vec{y}_{\exp}$ before performing the fit.

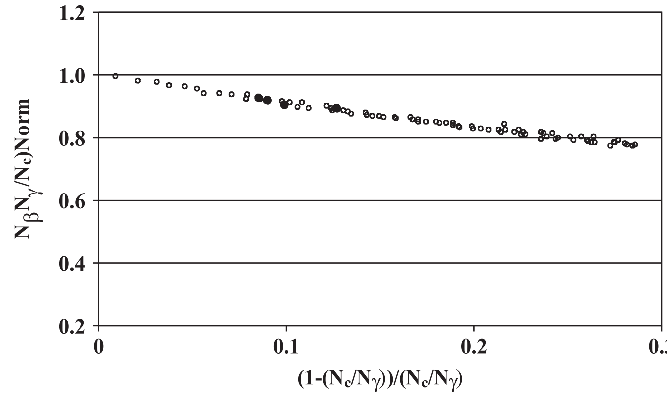

Fig. 1. Normalized Monte Carlo simulation of predicted $N_\beta N_\gamma / N_c$ as a function of efficiency parameter $(1 - N_c/N_\gamma)/(N_c/N_\gamma)$ for ^{35}S (open circles). Black circles correspond to normalized experimental data.

Table 1
Values of activity corrected by Monte Carlo simulation correction factor. The uncertainties correspond to one standard deviation (u=1).

Sample	$(1 - N_c/N_\gamma)/N_c/N_\gamma$	$N_\beta N_\gamma / N_c \times 10^3$ cps	MC correction factor	Activity (kBq/g)
1	0.0996 (9)	167.68 (67)	0.9124 (23)	183.8 (19)
2	0.1273 (12)	165.89 (68)	0.8839 (22)	187.7 (20)
3	0.0859 (10)	172.13 (70)	0.9209 (23)	186.9 (19)
4	0.0904 (7)	170.51 (67)	0.9117 (23)	187.0 (20)

Table 2
Partial uncertainties in the activity of ^{35}S and correlation matrix from $4\pi\beta$-γ tracing technique.

σ_{total}	σ_{stat}	σ_{mass}	σ_{efic}	σ_{dec}	σ_{trac}	σ_{mc}	Correlation matrix			
1.01	0.52	0.36	0.20	0.60	0.40	0.25	1000			
1.06	0.52	0.48	0.20	0.60	0.40	0.25	485	1000		
1.03	0.52	0.40	0.20	0.60	0.40	0.25	497	474	1000	
1.05	0.52	0.40	0.20	0.60	0.40	0.25	489	467	478	1000
	0	0	0	1	1	1				

Table 3
^{35}S activity results from LSC measurements.

Vial no.	CCl_4	Efficiency (%)	tSIE	Activity (kBq g^{-1})
01	0	91.23 (31)	544	182.9 (22)
02	10	87.98 (32)	383	183.9 (22)
03	20	84.25 (27)	278	185.5 (18)
04	30	79.56 (36)	206	187.6 (24)
05	40	75.45 (24)	163	186.1 (28)
06	50	74.67 (31)	156	187.8 (29)
07	150	74.55 (20)	155	186.3 (47)

3. Source preparation

3.1. LSC

The samples for liquid scintillation counting were prepared in glass vials with low potassium concentration. Known aliquots of

Table 4
Partial uncertainties in the activity of ^{35}S and correlation matrix measured in the LSC.

$\sigma_{ef.\ S.}$	$\sigma_{stat.}$	σ_{mas}	$\sigma_{ef.\ H3}$	σ_{dec}	σ_{act}	σ_{quen}	Correlation matrix						
0.34	0.04	0.29	0.23	0.41	0.65	0.78	1000						
0.36	0.08	0.29	0.23	0.41	0.65	0.76	503	1000					
0.32	0.11	0.29	0.23	0.41	0.65	0.35	616	617	1000				
0.45	0.25	0.29	0.23	0.41	0.65	0.82	469	470	576	1000			
0.32	0.08	0.29	0.23	0.41	0.65	1.19	404	404	496	377	1000		
0.42	0.09	0.29	0.23	0.41	0.65	1.25	386	386	473	361	310	1000	
0.27	0.88	0.29	0.23	0.41	0.65	2.18	241	241	296	225	194	185	1000
0	0	1	1	1	1	0							

Ultima Gold liquid scintillator and radioactive material were mixed and stirred to obtain a homogeneous solution. For the present measurements, seven samples of ^{3}H and ^{35}S were prepared with different amounts of CCl_4 solution used as carrier, in order to obtain different quenching parameters and therefore different efficiencies.

3.2. $4\pi\beta$(PC)-γ

Two types of radioactive sources to be measured in the $4\pi\beta$-γ system were prepared: pure ^{60}Co and ^{35}S+^{60}Co mixed sources.These sources were prepared by dropping known aliquots of the solution on a 20 μg cm^{-2} thick Collodion film. This film had been previously coated with a 10 μg cm^{-2} gold layer in order to turn the film conductive. The masses of radioactive material used for LSC system and for $4\pi\beta$-γ system measurements were accurately determined by the pycnometer technique in a Sartorius MC 21S balance.

4. Covariance methodology

Covariance methodology makes use of a covariance matrix, which is a form of representation of the uncertainties in the parameters involved yielding the overall uncertainty together with information about the existing level of correlation among the parameter uncertainties (Smith, 1991).

The covariance matrix is given by

$$V_{xij} = \sum_{1}^{L} E_{il} E_{jl} C_{ijl} \tag{3}$$

where E_{il} *e* E_{j1} are the partial uncertainties of parameters used for obtaining the final disintegration rate and C_{ij1} are the corresponding correlation coefficients, having values between −1 and +1.

5. Results and discussion

5.1. $4\pi\beta$-γ Measurements

In Fig. 1 the Monte Carlo simulation of predicted $N_\beta N_\gamma/N_c$ curve as a function of efficiency parameter $(1\text{-}N_c/N_\gamma)/N_c/N_\gamma$ for ^{35}S is shown as open circles. The experimental values are presented as close circles. The curve was normalized to the average activity.

The sources activities were determined applying the correction factor obtained from the simulation curve and are presented in Table 1. A list of all partial uncertainties involved in the tracer technique activity determination are listed in Table 2, together with the correlation coefficients which are shown at the bottom of the table. In this table the correlation matrix is also given. These partial uncertainties are related to ^{60}Co activity, statistical counting, decay correction, radioactive source mass and Monte Carlo simulation.

Table 5
Comparison between experimental values of the activity obtained with the two methods. The uncertainties correspond to one standard deviation (u=1).

Method	Activity (kBq g^{-1})
CIEMAT/NIST	(185.22 ± 0.1.70)
$4\pi\beta$-γ Tracing technique	(186.17 ± 1.51)

5.2. LSC Measurements

In Table 3, the average activity for ^{35}S, obtained from three sequential runs, is shown. The amount of carrier, the quenching parameter (tSIE) and the average efficiencies obtained by the application of CIEMAT/NIST method are also shown.

In Table 4 all partial uncertainties involved in the measurements, taking into account all possible correlations between each pair of them. The correlation matrix is also presented in this table. The correlation factor of each uncertainty is shown in the bottom of this table.

Table 5 shows the comparison between the activities obtained with the CIEMAT/NIST method and the $4\pi\beta$-γ tracing technique showing good agreement between these two techniques.

6. Conclusion

The results from the two primary methods are in good agreement within the experimental uncertainties, demonstrating the feasibility of using the LSC system for ^{35}S standardization on a routine basis.

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