A Method for the Activity Evaluation of Low Energy β – Emitters by Liquid Scintillation Counting Technique

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The method applied to the evaluation of radiation activities implies sample preparation, liquid scintillation cocktail choosing, quench standard curve constructing and implementation, and results verification. We have constructed the quench curve using interpolation method by polynomial spline functions of three degree. In order to evaluate the measurement efficiencies of tritium activity in simulated liquid scintillation cocktail waste samples quench curve have been used. The results have emphasized that the interpolation method is a very accurate analysis method, and it may be applied to the quantification of radioactivity, using a scintillation liquid cocktail compatible with chemical composition of the analyzed sample.

Keywords: tSIE, quench curve, measurement efficiency, interpolation, liquid scintillation counting

Liquid scintillation counting technique is mostly used for the detection and quantification of low energy β – emitters like ^{3}H and ^{14}C. The liquid scintillation process is based on the conversion of the kinetic energy of nuclear emissions into emitted photons. Any factor which reduces the efficiency of the energy transfer or causes the absorption of photons, results in quenching of the sample [1, 2].

One of the spectral analysis methods in Packard's Tri-Carb® liquid scintillation analyzers is to measure quench by the *t*ransformed *S*pectral *I*ndex of the *E*xternal standard – *tSIE*. The measured values of *tSIE* parameter can be used to create the quench standard curve by counting a series of ten standards in which the absolute radioactivity (decays per minute, DPM) per vial is constant and the amount of quench increases from one vial to the other. Once the (*tSIE, Efficiency*) correlation values of the quench standard curve are stored in the instrument computer, they can be used to evaluate the measurement efficiency of β – emitters in waste samples [3 - 8].

Experimental part

The radio-chemical analysis laboratories from Romanian Cernavoda Nuclear Power Plant use the Ultima Gold™ scintillation liquid cocktail to determine the tritium activity, mainly in aqueous samples. After use, these scintillation liquid cocktails become liquid organic radioactive waste. This radioactive waste type represents one of the low and intermediate levels liquid organic radioactive wastes resulting from process system operating and from decontamination and maintenance operations [9 - 11].

To determine tritium content in the liquid organic waste, the Ultima Gold™ XR liquid scintillation cocktail was selected [10], so that a stable homogeneous, colourless, *p*H neutral waste/liquid scintillation cocktail solution to be obtained [1]. Known activity samples were used in order to evaluate the measurement performance of the selected cocktail. The variation of the measurement efficiency reported to the sample loading was studied using analysis methods based on interpolation of quench standard curve by polynomial spline functions of three degree [12].

Known activity samples preparation

A HTO-standard solution with 3.353 MBq activity was diluted with distilled water into a 100 mL flask. 10 mL from this diluted solution were pipetted into another flask and 90 mL distilled water were added, to obtain a HTO-solution with $3.353 \cdot 10^{3}$ Bq/mL activity.

A simulated liquid organic waste with activity of 305.123 Bq/mL was prepared as follows: 4.5 mL HTO-solution of $3.353 \cdot 10^{3}$ Bq/mL activity were pipetted into a 50 mL flask and 45.5 mL Ultima Gold™ scintillation liquid cocktail were added from the dispenser.

An *E* samples series, consisting of five waste/cocktail glass vials labelled on the lid (E_1, E_2, E_3, E_4, E_5), was prepared. The waste volumes were pipetted to the vials in 0.5 mL increments from 1 mL (E_1) to 3 mL (E_5). Then, the Ultima Gold™ XR scintillation liquid cocktail was added from the dispenser so that the waste/cocktail volumes became 20 mL. The vials were closed and shaken for some seconds in order to make homogeneous solutions.

The five vials were visually studied to determine the homogeneity and the colour. Then, the *p*H was measured using a pIONeer 10 pH-meter, with combined electrode, (0…14) *p*H range, ±0.05 *p*H resolution.

After these evaluations, the sample vials were placed into a 2100 TRI-CARBÔ Packard model liquid scintillation analyzer, and each vial was counted for 15 min in a (0...18.6) keV tritium counting window.

Construction of quench standard curve by interpolation method

To construct the (*tSIE*, *Efficiency*) quench standard curve, the *tSIE* parameter and measurement efficiency values were used (table 1). These values are stored in the instrument computer memory, and they have been obtained by measurement of ten ^{3}H labelled standards series.

The interpolation method by polynomial spline functions of three degree (cubic spline functions) was chosen,

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Table 1
(tSIE, EFFICIENCY) CORRELATION VALUES FOR QUENCH SET OF ^{3}H

Quench standard number	1	2	3	4	5	6	7	8	9	10
tSIE	1070	786	607	459	362	272	209	168	134	104
Efficiency [%]	68.0	62.5	56.3	48.7	41.7	33.3	25.2	19.5	14.3	9.71

Table 2
VISUAL INSPECTION RESULTS AND *p*H MEASUREMENT VALUES FOR WASTE / LIQUID SCINTILLATION COCKTAIL SAMPLES

Sample code	Volumetric ratio waste/cocktail [mL:mL]	Homogeneous	Colour	pH value
E_1	3.0:17.0	Mixable	Colourless	6.40
E_2	2.5:17.5	Mixable	Colourless	6.39
E_3	2.0:18.0	Mixable	Colourless	6.37
E_4	1.5:18.5	Mixable	Colourless	6.35
E_5	1.0:19.0	Mixable	Colourless	6.34

because it accomplished transitions of the functions in inner nodes, eliminating oscillations which appear through the use of Lagrange polynomials [13]. The latter ones accomplish a global interpolation, on the whole interval, as opposed to cubic polynomial spline functions which achieve an interpolation on polynomial pieces.

The polynomials which approximate the theoretical interpolation function for the ten standards series are represented in (1).

$$Eff_i = p_{i1}\cdot(tSIE_i)^3 + p_{i2}\cdot(tSIE_i)^2 + p_{i3}\cdot(tSIE_i) + p_{i4} \quad (1)$$

where:

Eff_i = measurement efficiency for the interval of indexes *i*;

$p_{i1} \cdots p_{i4}$ = polynomial interpolation coefficients, (*i* = 1, 2, …, 9);

$tSIE_i$ = *t*ransformed *S*pectral *I*ndex of the *E*xternal standard of indexes *i*.

Nine interpolation polynomials of three degree, each of them with four coefficients (total of 36 coefficients), were obtained using the equation (1). The 36 polynomial interpolation coefficients were calculated with MATLAB® software application [14].

To plot the quench standard curve, the *SplineTool*© software application [15] was set with the *tSIE* parameter and measurement efficiency values.

Quench standard curve utilization

To calculate the values of measurement efficiency for the *E* samples series, an interpolation can be achieved both inside of initial intervals (interpolation) and outside the initial intervals (extrapolation) using determined spline functions.

The *tSIE* parameter values acquired by spectral analyzer were set using MATLAB® software application [14] in order to get the measurement efficiency values from the quench standard curve.

The interpolated measurement efficiency values were used for plotting the (*Efficiency, Sample loading*) curve.

The values of activities for the *E* samples series are defined by equation (2).

$$A_{measured} = \frac{CPM}{Eff \cdot 60} \quad (2)$$

where:

$A_{measured}$ = activity of the measured sample [Bq/sample];

CPM = number of counts (pulses) per minute accumulated in the energetic region of interest for ^{3}H (0…18.6) keV, [cpm];

Eff = measurement efficiency;

60 = conversion factor from minutes to seconds.

Determination of percentage relative deviation of tritium activity in radioactive samples

The percentage relative deviation of tritium activity in the *E* samples series was calculated using the equation (3).

$$RD_A = \left|\frac{A_{measured} - A_{calculated}}{A_{calculated}}\right| \cdot 100[\%] \quad (3)$$

where:

RD_A = relative deviation of tritium activity [%];

$A_{measured}$ = activity of the sample according to equation (2) [Bq/sample];

$A_{calculated}$ = calculated activity using the activity value (305.123 Bq/mL) of simulated radioactive waste [Bq/sample].

Results and discussion

E samples series values

The results obtained after visual inspection and *p*H measurement for the *E* samples series are presented in table 2.

The *E* samples series complies with homogeneous and colour criteria, and the *p*H values are placed into the limits of a neutral solution.

The Ultima Gold™ XR liquid scintillation cocktail was selected for the evaluation of measurement efficiencies because this cocktail is compatible with chemical composition of the analyzed sample.

The acquired values for *CPM*, *tSIE*, *2S%* (measuring statistical precision of sample) from the spectral analyzer are shown in table 3.

The values of the *tSIE* parameter are high enough to reflect a low quenching degree of the samples and high measurement efficiencies. The measuring statistical precision of the samples has very good values, less than 1% of the *CPM* activity values.

Quench standard curve plotting

The values of the polynomial interpolation coefficients are shown in table 4.

The graphical representation of the (*tSIE, Efficiency*) correlation curve and of the interpolation method errors

Table 3
SAMPLES MEASUREMENT VALUES

Sample code	*CPM* [cpm]	*tSIE*	*2S* [%]
E_1	26987.81	469.821	0.54
E_2	22886.63	472.064	0.59
E_3	18196.78	475.618	0.66
E_4	13541.16	479.109	0.77
E_5	9262.91	481.863	0.93

Table 4
POLYNOMIAL INTERPOLATION COEFFICIENTS VALUES

Polynomial number \ Coefficient degree	1	2	3	4
1	8.64092e-007	-1.17497e-016	0.152222	9.71
2	-3.68366e-006	7.77683e-005	0.154555	14.3
3	2.48203e-006	-0.000297965	0.147069	19.5
4	-1.77435e-006	7.32425e-006	0.135152	25.2
5	9.76268e-007	-0.000328028	0.114948	33.3
6	-1.28727e-007	-6.44354e-005	0.0796264	41.7
7	1.34198e-007	-0.000101895	0.0634923	48.7
8	1.89342e-009	-4.23109e-005	0.0421499	56.3
9	4.84673e-008	-4.12941e-005	0.0271846	62.5

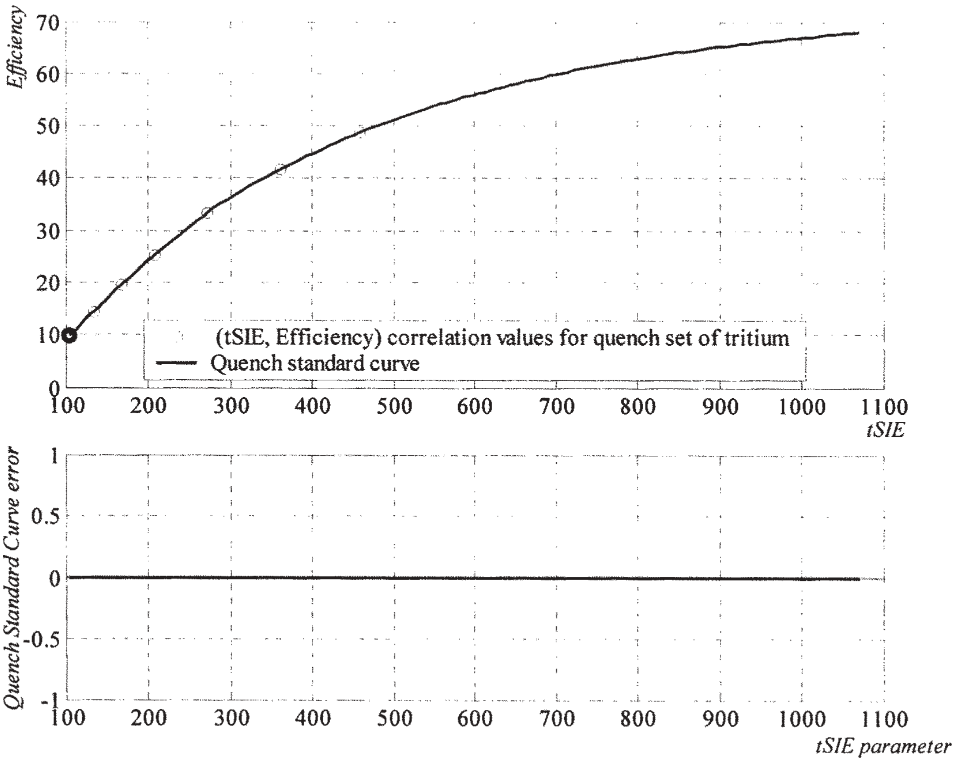

Fig. 1. Plotting of quench standard curve

was obtained using the *SplineTool*© software application [15], and it is depicted in figure 1.

The quench standard curve has neither inflexion points in inner nodes nor oscillations at the ends of the interpolation interval, fact revealed by the zero - values of the errors obtained on the whole interpolation domain.

Quench standard curve utilization

The values of interpolated measurement efficiency for the *E* samples series are listed in table 5. The Ultima Gold XR™ scintillation liquid cocktail has exhibited good efficiency values, around 50%, which are higher than typical efficiency of 40% encountered in such measurements [16].

The *Measurement Efficiency* versus *Sample loading* correlation curve is shown in figure 2.

Table 5
INTERPOLATED MEASUREMENT EFFICIENCY

Sample code	E_1	E_2	E_3	E_4	E_5
Efficiency [%]	49.37	49.51	49.73	49.94	50.10

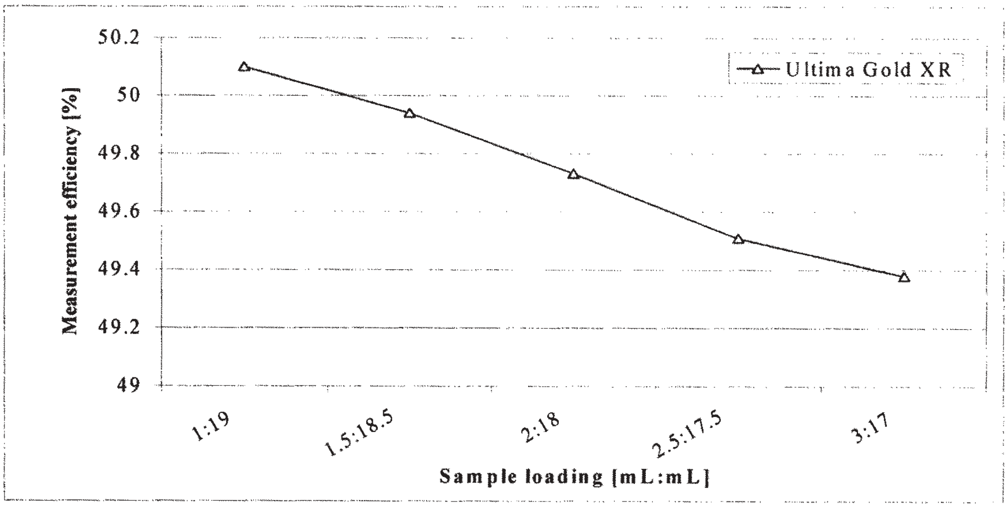

Fig. 2. Measurement efficiency vs. Sample loading correlation curve

Table 6
TRITIUM ACTIVITY VALUES IN *E* SAMPLES SERIES

Sample code	Volumetric ratio waste/cocktail [mL:mL]	Ratio waste/cocktail [%]	$A_{measured}$ [Bq/sample]	$A_{calculated}$ [Bq/sample]	Relative Deviation, RD_A [%]
E_1	3.0:17.0	17.65	911.073	915.369	0.47
E_2	2.5:17.5	14.29	770.437	762.807	1.00
E_3	2.0:18.0	11.11	609.975	610.246	0.04
E_4	1.5:18.5	8.11	452.004	457.684	1.24
E_5	1.0:19.0	5.26	308.147	305.123	0.99

The changes on the sample loading factor did not affect measurement efficiency, the spanning variations of efficiency were less than 1%, regarding the *E* samples series prepared with Ultima Gold™ XR liquid scintillation cocktail.

Percentage relative deviation of tritium activity in E samples series evaluation

The values of $A_{measured}$, $A_{calculated}$, and the RD_A values calculated according to equation (3) are shown in table 6. It is observed a very low variation, less than 1.3 % of $A_{measured}$, in comparison with$A_{calculated}$, for a (5...18) % range of sample loading.

Conclusions

To evaluate the activity of low energy β – emitters by liquid scintillation counting technique, the quench levels are measured (*tSIE*) and these values are used to interpolate the measurement efficiencies from the respective quench standard curve.

The using of polynomial spline functions of three degree in order to construct the quench standard curve represents a very accurate analyze method, and it can be applied to quantification of radioactivity in samples which forms with the scintillation liquid cocktail a stable homogeneous, colourless, *p*H neutral solution.

The Ultima Gold™ XR scintillation liquid cocktail can be used to evaluate the ^3H activity in liquid organic waste generated from radio-chemical analysis laboratories of Cernavoda Nuclear Power Plant.

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