

Optimization Method to Determine Gross Alpha-Beta in Water Samples Using Liquid Scintillation Counter

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ABSTRACT

Liquid scintillation counting (LSC) is an adequate nuclear technique to determine radioactivity levels, as verified by this study for the determination of the gross alpha and beta activities of aqueous samples because of its simplicity and low associated cost comparison with other techniques. This paper discusses a new approach to the monitoring of gross alpha and gross beta activities in water. The method consists of using pulse decay discrimination (PDD) liquid scintillation counting LSC of 2 ml of the sample after conditioning with 12 ml of AB-Ultima Gold LSC cocktail, and PDD 139 condition. Different factors that affected on the counting efficiency were studied such as quench reaction, volume of sample, and type of vial. The gross alpha and gross beta particle activity measurement using ^{40}K and ^{243}Am with different activities concentration for efficiency determination. The calculated detection limits were 0.07 Bq/l and 0.12 Bq/l for gross alpha and gross beta respectively for 500 min measurements of samples produced by concentration of one liter of water.

Keywords: Water; LSC; Pulse Decay Discrimination; Alpha; Beta

1. Introduction

The presence of radioactivity in the environment is caused by naturally occurring radionuclides and cosmic radiation but also by artificial radionuclides, which have been incorporated due to fallout from nuclear accidents and nuclear weapons testing [1]. Levels of naturally occurring radionuclides in the environment are known and in some locations where the levels are high due to the presence of natural radionuclides in the soil, the dose associated to natural sources is much higher than that from artificial sources. However controls for that contribution are not required, except for the case of drinking water, for which many countries have regulations [1]. Many guidance levels have been published to regulate the radiological content of water. In 1998, the European Council Directive 98/83/CE on the quality of water for human consumption was issued [2], which included parameter levels for total dose (0.1 mSv/yr) and tritium content (100 Bq/l). This directive was devised on the basis of previous recommendations made by the World Health Organization [3], which proposed individual radionuclide measurement when gross alpha and gross beta activities are over a screening threshold level (0.5 Bq/l for gross alpha, 1 Bq/l for gross beta). This directive was enforced in Spanish legislation in 2003 [4], which in-

cluded criteria of the European Directive but also parameter values for gross alpha (0.1 Bq/l) and gross beta excluding ^{40}K (1 Bq/l).

The liquid scintillation process is based on the conversion of a part of the kinetic energy of alpha/beta/gamma radiation into photons. The photons are counted and related to the concentration of alpha/beta/gamma emitter. The principal use of liquid scintillation counting was the assay of low energy beta emitting nuclides. Alpha emitters could be counted by liquid scintillation counting was also known for long time [5].

Analysis of decay times of fluorescence in the scintillators was of great theoretical interest [6,7]. These studies led to scintillation Pulse Shape Analysis [PSA] or Pulse Shape Discrimination [PSD] or Pulse Decay Discrimination [PDD] technique in the field of liquid scintillation counting. Pulse shape analysis allows to recognize types of particles or photons and therefore to count a chosen particle e.g. alpha particle in the presence of other radiation. The intensity of photons from a scintillation event as a function of time can be divided into at least two components, fast or prompt and slow or delayed. The prompt component has a decay time of a few nanoseconds, equal to the fluorescence lifetime of the fluorescing species. The slow component has a decay time of about 200 - 300 ns. Kallmann *et al.* [8] have suggested that

relatively slow ion recombination processes in the scintillator might be the indirect cause of slow components. An alternate suggestion by Harrison [9] was that some molecules are initially excited to long lived (10^{-7} S) triplet states and they give rise to slow components. There was an opinion that the intensity of each (prompt and delayed) component is governed by characteristics of ingredients of the scintillator solution. Voltz *et al.* [10] maintained that delayed component is due exclusively to solvent triplets annihilating and eventual production of delayed solute fluorescence. Spurny [11] suggested that delayed fluorescence is caused by mutual annihilation of solute triplets. Ludwig *et al.* [12] have proposed that the delayed component is due to time lag of ion recombination. Berlman *et al.* [13] have studied the effect of liquid scintillation solutions on pulse shape discrimination. They have concluded that quaternary scintillators (solvent containing 3 solutes) are most effective for pulse shape discrimination.

The pulse shape analysis technique can be used to detect recoil protons, alpha particles, fission fragments or other charged particles with high specific ionization in the presence of electron or vice versa [14].

The aim of this work was to develop a method for simultaneous determination of gross alpha and gross beta in water samples by LSC was established. Therefore, different parameters affecting on the measurement were studied to provide a rapid results, adequate sensitivity and minimum sample preparation with widely using of chemical needed in order to make it applicable.

2. Experimental

2.1. Apparatus

Liquid scintillation counter, LSC model Packard TRI CARB 3170 TR/SL, which used PSD for α/β separation. The background is reduced by the presence of a guard of bismuth germinate (BGO), which surrounds the counting chamber.

2.2. Standard Solutions Preparation

High purity double deionized water and analytical re-

agents were used through this study in order to achieve the lowest possible minimum detectable activities (MDA). Standard solutions of ^{243}Am prepared with different activities and ^{40}K standard solutions were prepared by dissolving KCl (MERK, 99% Analar) with different weight in de-ionized water for the total efficiency determination depending on the internal standard method. Three different standards solutions were prepared A, B and C. First standard solution (A) was prepared from mixing equal activity of ^{243}Am and ^{40}K which have a reference values for alpha and beta activities about 8 ± 0.1 Bq/l for both. Second standard solution (B) was prepared with lower activity of beta and higher of alpha from mixing ^{243}Am with activity 8 ± 0.1 Bq/l and ^{40}K with activity 1 ± 0.1 Bq/l. A third standard solution (C) was prepared from mixing higher activity of beta ^{40}K 8 ± 0.1 Bq/l and lower activity of alpha ^{243}Am with 1 ± 0.1 Bq/l.

2.3. Procedures

Synthetic samples solutions were prepared by using different volumes of ^{243}Am and ^{40}K standards with de-ionized water to achieve different activity levels, corresponding to the minimum detectable activities MDA of the method, total of 20 spiked water samples were analyzed.

The samples were adjusted pH to 2.5 with concentrated HNO_3 (68%). 100 ml of each sample was evaporated directly in a Liquid scintillation vial a till 10 ml using hotplate with vigorous stirring in order to eliminate radon and to avoiding the salt precipitation. The maximum temperature recommended for polyethylene vials was 80°C . After evaporation the orthophosphoric acid is added to the evaporated samples to dissolve the salts. The treated samples were mixed with a certain amount of Packard AB-Ultima Gold LSC cocktail for starting the measurement. Each sample was counted for 500 min (2×250 min counts). Blanks were prepared by applying the same procedure as for samples taking into consideration the dilution factor [15].

The different factors affecting on the measurement

$$\text{Alpha activity} = \frac{\text{Samples counting on alpha channel} - \text{alpha channel background}}{\text{alpha efficiency} \times \text{sample volume} \times 60} \quad (1)$$

$$\text{Alpha efficiency} = \frac{\text{Alpha standard counting on alpha channel} - \text{alpha channel background}}{\text{alpha standard activity} \times 60} \quad (2)$$

$$\text{Beta efficiency} = \frac{\text{Beta standard counting on alpha channel} - \text{beta channel background}}{\text{beta standard activity} \times 60} \quad (3)$$

$$\text{Beta activity} = \frac{\text{Samples counting on beta channel} - \text{beta channel background}}{\text{beta efficiency} \times \text{sample volume} \times 60} \quad (4)$$

process such as quenching effect by using CCl_4 with different concentration, volume of the sample and vial type (polyethylene or glasses) were studied.

Validation method has been done by analysis IAEA-Cu-2008-04, reference material which contains activity concentration 3.93 and 15.7 Bq/Kg for gross alpha and beta.

The equations, from (1) to (4) were used to calculate the alpha and beta activities and efficiencies.

Minimum detectable activities (MDA's) are calculated as shown in Equation (5).

$$\text{MDA} = \frac{[2.71 + (4.65\text{B}^{1/2})]}{(2.22 \times \text{T} \times \text{E} \times \text{AF} \times \text{V} \times \text{Y})} \quad (5)$$

where:

B = total counts for an appropriate reagent blank;

T = count time in minutes;

E = counting efficiency;

AF = attenuation factor (if applicable);

V = sample volume (if applicable) in liters and;

Y = chemical yield (if applicable).

The equation provides the result in pCi/L [16].

3. Results and Discussion

3.1. Calibration

In order to optimize alpha/beta separation performance, it is essential to determine the correct PDD setting; the optimum setting is the setting where there is equal and minimum spill of alpha pulses into the beta multichannel analyzer, MCA and beta pulses into the alpha MCA [17].

Determination of PDD required pure alpha and beta standard, for the most accurate results, the standards must be as near identical as possible to the unknown samples in their chemistry, volume, vial type, etc. To arrive the optimum setting each standard counted individually at a range of PDD setting and the percent misclassification of alpha into beta MCA and vice versa are plotted against PDD on the same graph. **Figure 1** represents the typical misclassification plot for ^{36}Cl and ^{241}Am standards for determination the optimum setting that result in minimum misclassification of alpha and beta activity. The obtained calculated data show that 139 is the best setting for the PDD as in **Figure 1**.

When only beta emitters is of interest, a PDD values below the determined value may be used which minimize the misclassification of alpha activity into beta the MCA at the expense of reducing the beta efficiency similarly when alpha emitter is of interest [18].

3.2. Factors Influencing Alpha/Beta Discrimination

3.2.1. Quenching

In this approach, the misclassification is always deter-

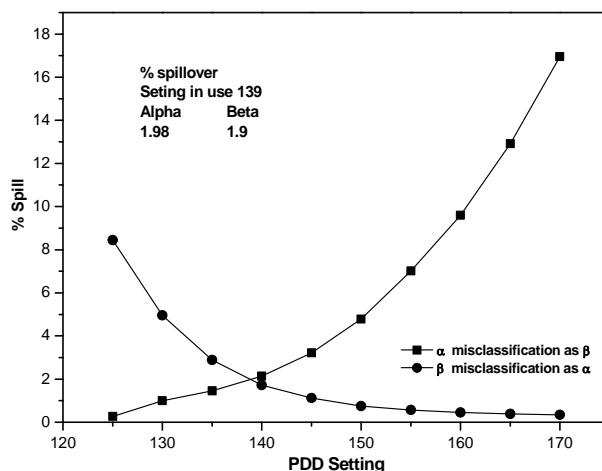


Figure 1. Misclassification for the determination of optimum PDD setting using ^{241}Am and ^{36}Cl standards.

mined at the original PDD setting. By plot the percentage misclassification versus transformer spectral index of the sample, tSIE for single PDD setting. All samples then be counted within a single protocol and a correction for misclassification as a function of quench is applied. The following **Figures 2** and **3** show the effect of quenching tSIE on percent misclassification of alpha and beta events using CCl_4 with different concentrated for quench reaction as in **Table 1**.

From **Table 1** with increasing the concentration of CCl_4 from 0 to 2000 μl the activity determined for ^{243}Am decrease from 557 CPM to 238 CPM and for ^{40}K from 402 CPM to 424 CPM due to the effect of quench.

3.2.2. Materials of Vial

Glass vials and plastic vials were used and it was found that the efficiency obtained was very good in both plastic and glass vials. polyethylene vial used and the background net count was 2 CPM and 9 CPM for alpha and beta respectively and it was lower than the glass vials 3 CPM and 17 CPM. The higher background due to the glass vials containing little amount of ^{40}K in the glass composition. So the plastic vials were chosen as the best option for display lower background as shown in **Table 2** and this agree with other investigators Yu-Yufu *et al.*, (1990) [19] and IAEA, (2010) [20].

3.2.3. Sample Volume

The results obtained from using different volumes of liquid scintillation cocktails, at which the samples were prepared by evaporation of the aqueous phase and residue dissolution with 2 ml, 4 ml of H_3PO_4 2 M acid solution. The volume was kept constant in all the measured samples. Although the different in volumes the best volumes is minimum volume due to the lower quench [21].

Table 1. Alpha and beta activity measurements with different volume of quench solution (CCl₄).

Volume of CCl ₄ Added by (μl)	Am-243 (8 Bq/vial)			K-40 (8 Bq/vial)		
	Alpha CPM	SIS	tSIE	Beta CPM	SIS	tSIE
0	557	384.11	372.12	402	547.96	411.73
100	524	375.85	262.99	402	550.01	290.50
200	492	321.13	221.36	402	541.49	281.03
400	379	269.98	163.68	424	428.00	173.49
500	357	235.29	144.64	406	377.60	145.02
700	351	206.74	120.16	420	318.21	116.78
800	342	200.90	397.28	413	304.01	107.39
1000	310	155.57	94.67	422	270.95	89.79
1500	266	115.70	68.84	409	230.63	74.40
2000	238	97.48	60.89	416	176.27	52.19

SIS = Spectral Index of the Sample; tSIE = Transformed Spectral Index of the External Standard.

Table 2. Influence of vial type in determining gross alpha and beta activity.

Sample	Time count (min)	Background net count (Polyethylene vials)				Background net count (Glass vials)			
		Beta CPMA	Alpha CPMA	SIS	tSIE	Beta CPMA	Alpha CPMA	SIS	tSIE
1		8	2	462.39	307.18	16	3	383.83	254.18
2		9	2	444.06	249.12	17	3	400.72	257.94
3	250	9	2	527.67	226.85	17	3	344.17	263.83
4		9	2	462.54	256.11	17	3	380.24	255.15
5		9	3	493.60	254.3	17	3	400.02	245.96

CPMA = Count per minute for beta; CPMA = Count per minute for alpha.

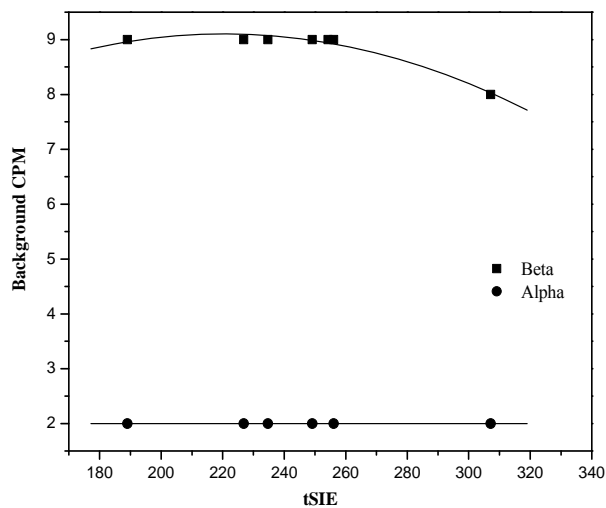


Figure 2. Alpha and beta background count rate as a function of transformer spectral index (tSIE) for polyethylene LSC vials.

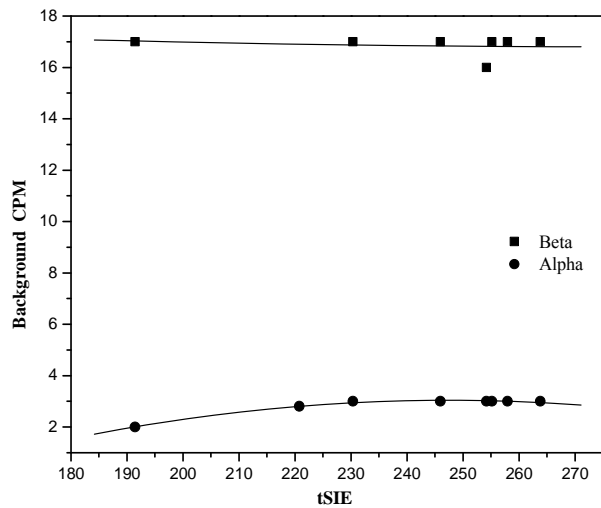


Figure 3. Alpha and beta background count rate as a function of transformer spectral index (tSIE) for glass LSC vials.

4. Accuracy of Measurement with Varying α/β Ratios

A set of standards containing varying quantities and ra-

tios of Alpha and Beta was measured to assess the accuracy.

Table 3 and **Figures 4-6** summarize the results that obtained from LSC after counting both higher and lower

Table 3. Efficiencies calculated for standard solutions contain different ratio from alpha and beta.

Samples	Reference activity Bq/vial		Measurement activity CPM		Measurement activity Bq/vial		Efficiency	
	Beta	Alpha	Beta	Alpha	Beta	Alpha	Beta	Alpha
STANDARD SOLUTIONS FOR LOW ACTIVITY CONC. ²⁴³Am & ⁴⁰K								
1) Equal Activity Alpha = Beta	8.18 ± 0.1	8.18 ± 0.1	462	457	7.7	7.61	0.94	0.93
2) Lower Activity Beta/ Higher Activity Alpha	1.02 ± 0.1	8.18 ± 0.1	57	487	0.95	9.12	0.92	0.99
3) Higher Activity Beta/ Lower Activity Alpha	8.18 ± 0.1	1.02 ± 0.1	467	52	7.78	0.87	0.95	0.84
STANDARD SOLUTIONS FOR HIGH ACTIVITY CONC. ²⁴¹Am & ³⁶Cl								
4) Alpha- ²⁴¹ Am	-	833.3 ± 16.6	-	47724	-	833	-	0.96
5) Beta- ³⁶ Cl	833.3 ± 16.6	-	47268	-	833	-	0.94	-
6) ²⁴¹ Am- ³⁶ Cl	416.6 ± 8	416.6 ± 8	24024	23973	400	399	0.96	0.958

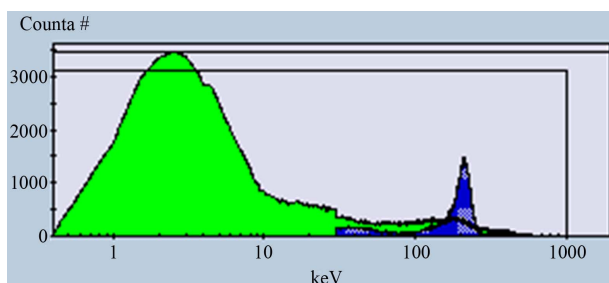


Figure 4. Alpha and beta spectra of sample measured at PDD 139 when the activity of alpha equals the activity of beta (A).

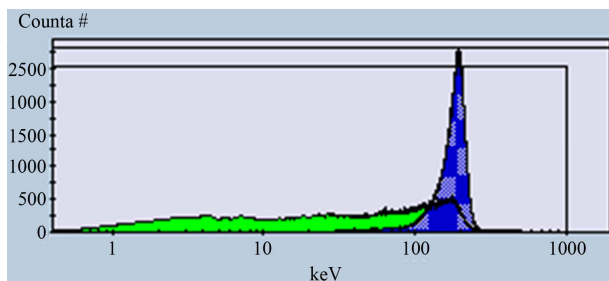


Figure 5. Alpha and beta spectra of sample measured at PDD 139 when the activity of alpha higher than the activity of beta (B).

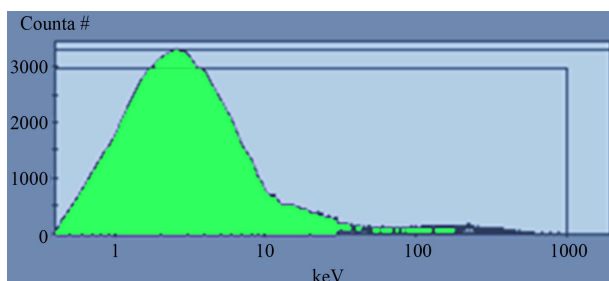


Figure 6. Alpha and beta spectra of sample measured at PDD 139 when the activity of beta higher than the activity of alpha (C).

activity concentration with different ratio depending on the using internal standard method.

The efficiencies calculated for low activity standard solutions from (²⁴³Am) alpha and (⁴⁰K) beta with different ratio. For the equal activity concentration 1) 8.181 ± 0.1 Bq/l the efficiencies reached 93% and 94% for alpha and beta respectively. While the efficiencies calculated for solution 2) contain lower activity of beta and higher of alpha reached 99% for alpha and 92% for beta and in case of higher activity of beta and lower alpha 3) the efficiencies about 84% for alpha and 95% for beta. The efficiencies calculated for high activity concentration 833.3 ± 16.6 Bq/l for standard solutions contain (²⁴¹Am) alpha 4) and (³⁶Cl) beta 5) reached 96% for pure alpha and 94% for pure beta and for equal activity concentration 6) the efficiencies about 95% and 96% for alpha and beta respectively.

The validation of the results were done by analysis certified reference material IAEA-Cu-2008-04, the obtained results were within acceptable values for alpha 3.44 Bq/kg and 14.7 Bq/kg for beta

5. Conclusions

Liquid scintillation counting LSC with the simple time resolved counter was an adequate nuclear technique to determined gross alpha and beta activities of water samples. The results confirm the validity of the method for fast and inexpensive procedure beside the simplicity of sample preparation.

The LSC with discriminator setting for alpha/beta counting obtained in this study is 139 with 1.98:1.90 percentage ratio of alpha/beta spillover. The lower background counts (2 to 9 CPM) obtained in case of using polyethylene vial and count time 500 min (2×250 min), the efficiencies calculated reached >90% for both alpha and beta. The minimum detectable activities were 0.07

Bq/l for gross alpha and 0.12 Bq/l for gross beta. These values meet the guidelines required by world health organization WHO 2008 [22].

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