

SIMULTANEOUS DETERMINATION OF ALPHA AND BETA EMITTERS BY LIQUID SCINTILLATION COUNTING

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ABSTRACT. The necessity for quickly detecting and assessing alpha and beta emitters in the environment, in nuclear fuel processes, and in storage waste has caused an increase in analyses of gross α (sum of all α emitters in the sample) and gross β (sum of all β emitters in the sample) activity. In fact, these analyses have been the most popular method for measuring radioactivity. Scintillation counting allows for the detection and quantification of α - and β -emitting radionuclides in an accurate and reproducible way without self-absorption problems. Optimization of α/β separation is achieved by using pulse-shape discrimination (PSD), calibrated by quantifying event misclassification at any given setting for pure α and β emitters. We studied α/β separation for different scintillant/vial combinations. We observed that both the optimum PSD level and total interference value were dependent upon the sample quenching. Thus, we propose a procedure for analyzing gross α and β activity in radioactive waste streams, such as ion exchange resins and evaporator concentrates, from Spanish nuclear power plants. The samples were prepared using standard solutions of radionuclides that are normally present in these types of samples. The results are compared with those obtained by other techniques, such as proportional counting.

INTRODUCTION

The necessity for quickly detecting and assessing alpha and beta emitters in the environment (natural water, marine samples, and soils), in nuclear fuel processors, and in storage waste has caused an increase in analyses of gross α (sum of α emitters in the sample) and gross β (sum of β emitters in the sample) activity. In fact, these are the most frequent analyses used to determine radioactivity.

The liquid scintillation counting (LSC) technique allows for the detection and quantification of α - and β -emitting radionuclides in an accurate and reproducible way without self-absorption problems. LSC does not suffer from self-absorption because the sample has been dissolved homogeneously in a mixture consisting of a solvent (usually an organic solvent) and an organic fluorescent scintillator.

Despite these advantages, LSC for α measurement has not been used frequently until now because of the interference from β and gamma radiation in the α assessment. In addition, the counting systems were not made to discriminate between α and β -gamma emitters. Recently, however, a new pulse-analysis technique (pulse-decay analysis [PDA]) has been introduced to discriminate α from β pulses. PDA is applied when it is necessary to calculate gross α and β activity without separating β radionuclides from α radionuclides in the matrix, thus saving time. The results of the PDA technique depend upon accurate calibration of the pulse-shape discrimination (PSD) function.

An optimum pulse-decay time discriminator (PDD) setting is required to minimize the misclassification of α events as β events and vice versa. Yang (1996) found that the optimum PDD setting was independent of the β emitter used in the calibration; however, Pujol and Sanchez-Cabeza (1997) and Pates (1998) observed that the percentage of misclassification changed with the E_{\max} of the β emitter used.

Other parameters affect the optimum PDD as well, such as the type of scintillation cocktail, quenching, and the type of quencher; all of these parameters have been studied in this paper. Once the parameters are optimized and fixed, results may be achieved for the simultaneous determination of the gross α and β activity.

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The aim of this work is to propose a procedure for analyzing gross α and β activity in radioactive waste streams, such as ion exchange resins and evaporator concentrates, from Spanish nuclear power plants. For this reason, the analyzed samples have been prepared using standard solutions of radionuclides that are normally present in the kinds of samples studied. The results are compared with those obtained by other techniques, such as proportional counting.

EXPERIMENTAL

Equipment

- Liquid scintillation (LS) analyzer, model Tri-Carb 2750 TR/LL (PerkinElmer, USA) with α/β discrimination and 60% detection efficiency for ^3H , 95% for ^{14}C . The analyzer is equipped with a spectra analysis program.
- Gas proportional counter with anticoincidence system and detection efficiency for $^{90}\text{Sr}/^{90}\text{Y}$ in equilibrium of 40%.

Reagents

- LS cocktails: Ultima Gold™ AB (Packard, USA), Ultima Gold LLT (Packard), OptiPhase HiSafe 3 (PerkinElmer).
- Standard solutions supplied by Amersham (United Kingdom): ^{241}Am (3.79×10^2 Bq/mL), $^{90}\text{Sr}/^{90}\text{Y}$ (4.02×10^2 Bq/mL at 30/06/1995), ^{55}Fe (5.83×10^3 Bq/mL at 01/06/2005), ^{63}Ni (2.32×10^1 Bq/mL at 01/10/1990), ^{137}Cs (2.58×10^2 Bq/mL at 17/06/1999), ^{60}Co (9.03×10^2 Bq/mL at 14/09/2005).

Sample Preparation

The samples used for parameter optimization, which is required to determine the optimum PDD and therefore minimize the misclassification of α events as β events and vice versa, were prepared by using different types of vials (polyethylene and low-potassium glass vials) and different standard solutions in 3M HCl. We then mixed the solutions with the different LS cocktails.

RESULTS AND DISCUSSION

Optimization of the Alpha/Beta Separation

Optimization of the α/β separation was achieved by separately measuring ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ standards and determining the total interference between both spectra for different PDD. As the composition of these samples is unknown, we chose $^{90}\text{Sr}/^{90}\text{Y}$ ($E_{\text{max}} = 546$ and 2280 keV, respectively) as β emitters and ^{241}Am as the α emitter because their spectras provide a higher overlap, and they present the most difficult case for the samples analyzed in this paper.

Measurements were made in vials of different materials using different volumes and types of scintillation cocktails. Because samples prepared for LSC could present variable quenching, it was necessary to study its effect on the optimum PDD parameter by adding small amounts of quencher (3M HCl and a 2:1 mixture of acetone: CCl_4).

Parameters to be Fixed

To obtain the best conditions for measuring gross α and β activity in a mixture, we studied the effect of the vial materials and the volume and type of scintillation cocktail.

Material of the Vials

Table 1 shows the spillover and efficiency percentages obtained with 3 different cocktails with the same relation between the volume of the cocktail and vial capacity in low-level ^{40}K glass and polyethylene vials.

Table 1 Influence of vial type in determining gross α and β activity.

Scintillation cocktail	Material of vials	Spillover (%)	Efficiency (%)	tSIE
Ultima Gold AB	Polyethylene	4.00	99.5 \pm 3.5	553
		3.89	99.5 \pm 3.2	
	Glass	1.98	96.7 \pm 0.2	625
		1.91	94.0 \pm 0.4	
Ultima Gold LLT	Polyethylene	3.61	98.0 \pm 1.3	533
		3.53	98.5 \pm 1.4	
	Glass	1.74	97.4 \pm 0.2	583
		1.80	99.5 \pm 1.3	
OptiPhase HiSafe 3	Polyethylene	2.36	98.5 \pm 1.3	515
		1.65	99.0 \pm 0.8	
	Glass	1.91	97.3 \pm 0.2	547
		1.87	98.8 \pm 0.3	

Although the efficiency obtained was very good in all the cases, when the polyethylene vial was used the percentage of misclassification was higher than when the glass vial was used. For this reason, the glass vial was chosen as the best option.

Volume of Scintillation Cocktail

Table 2 shows the results obtained from glass vials with different volumes and types of LS cocktails. The samples were prepared by evaporation of the aqueous phase and dissolution with 0.1 mL of acid solution. This volume was kept constant in all the studies performed.

Although misclassification is not the lowest in the case of the 10-mL sample, the difference with the best volume (in 2 of 3 cases) is minimum, and quenching is lower at this volume.

Effect of the Quenching

The influence of quenching in α/β separation was studied using 2 quenching agents: a 1:2 mixture of CCl_4 :acetone and 3M HCl. The study was performed in glass vials with 10 mL of scintillation cocktail to which the corresponding standards for ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ and small amounts of quencher were added.

To measure each quenched sample, the corresponding optimum PDD and efficiency were determined. The cross-over plot was determined automatically for each quenched sample using 10 mL of scintillation cocktail and a glass vial.

Effect of the Quenching Agent in the Spillover

Figures 1 to 6 show spillovers as a function of tSIE for 3 LS cocktails using CCl_4 :acetone at a ratio of 1:2 and 3M HCl as quenchers.

Table 2 Influence of volume of scintillation cocktail in determining gross α and gross β activity in a low-level ^{40}K glass vial.

Scintillation mixture	Scintillation volume (mL)	Spillover (%)	Efficiency (%)	tSIE
Ultima Gold AB	5	2.24	97.0 ± 2.3	578
		2.00	94.2 ± 2.1	
	7	1.81	96.7 ± 1.9	615
		1.72	94.5 ± 1.8	
	10	1.98	96.7 ± 0.2	625
		1.91	94.0 ± 0.4	
	12	2.78	95.6 ± 3.0	608
		2.52	94.5 ± 2.7	
Ultima Gold LLT	5	1.98	97.8 ± 0.4	543
		1.95	99.0 ± 0.8	
	7	1.73	97.8 ± 1.6	577
		1.68	98.9 ± 1.7	
	10	1.74	97.4 ± 0.2	583
		1.80	99.5 ± 1.3	
	12	1.87	97.2 ± 0.5	575
		1.90	99.0 ± 2.0	
OptiPhase HiSafe 3	5	1.44	97.5 ± 1.4	563
		1.04	99.0 ± 1.0	
	7	1.53	97.7 ± 1.5	573
		1.33	98.8 ± 1.3	
	10	1.91	97.3 ± 0.2	547
		1.87	98.8 ± 0.3	
	12	1.68	97.6 ± 1.7	570
		1.72	98.3 ± 1.8	

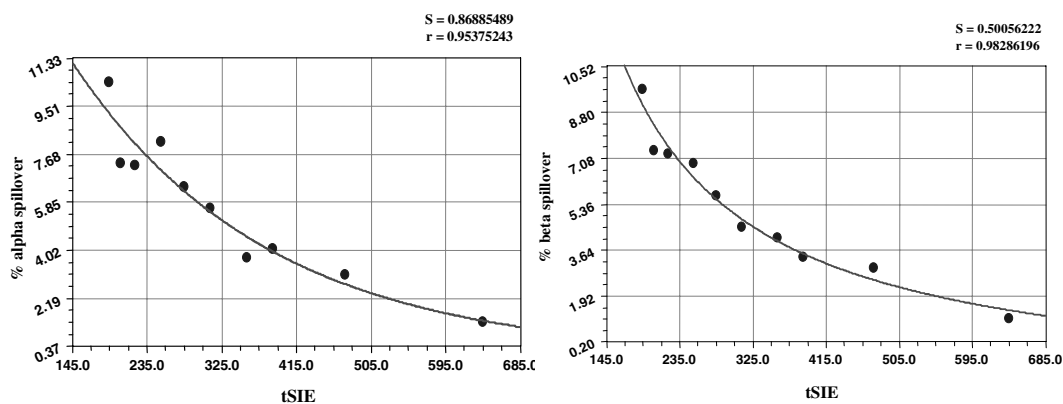


Figure 1 Alpha and beta spillover with different levels of quenching using CCl_4 :acetone 1:2 with Ultima Gold AB

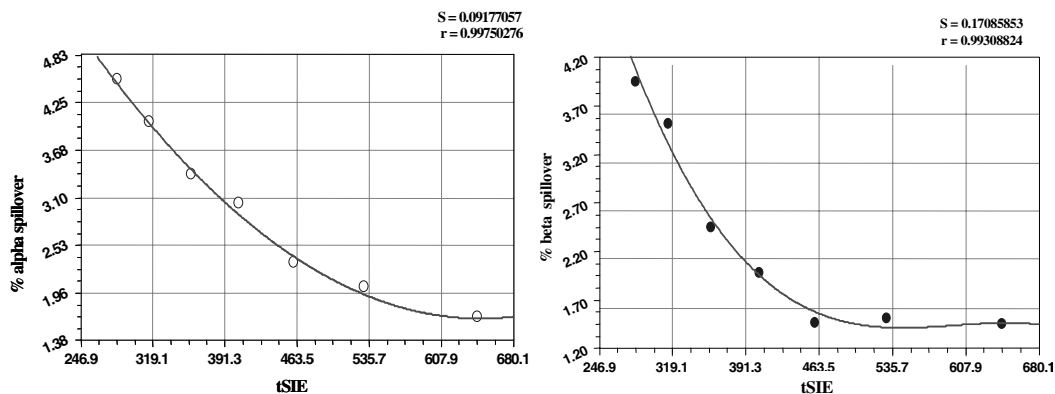


Figure 2 Alpha and beta spillover with different levels of quenching using CCl₄:acetone 1:2 with Ultima Gold LLT

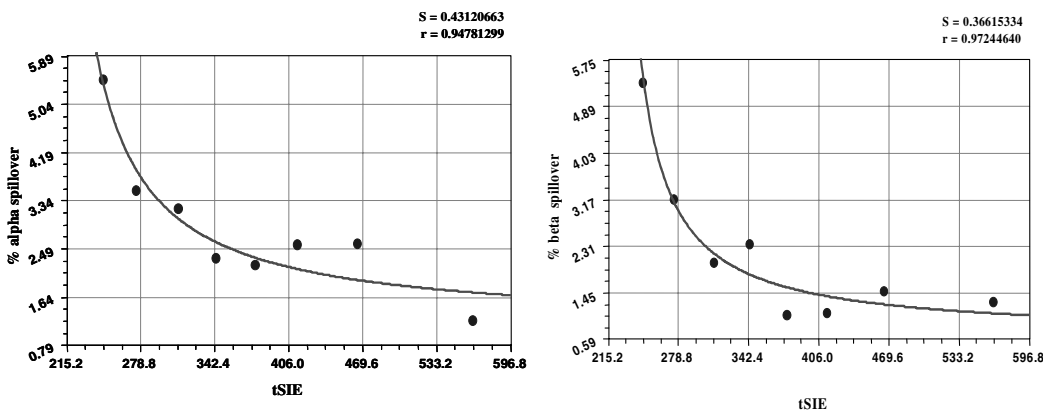


Figure 3 Alpha and beta spillover with different levels of quenching using CCl₄:acetone 1:2 with OptiPhase HiSafe 3

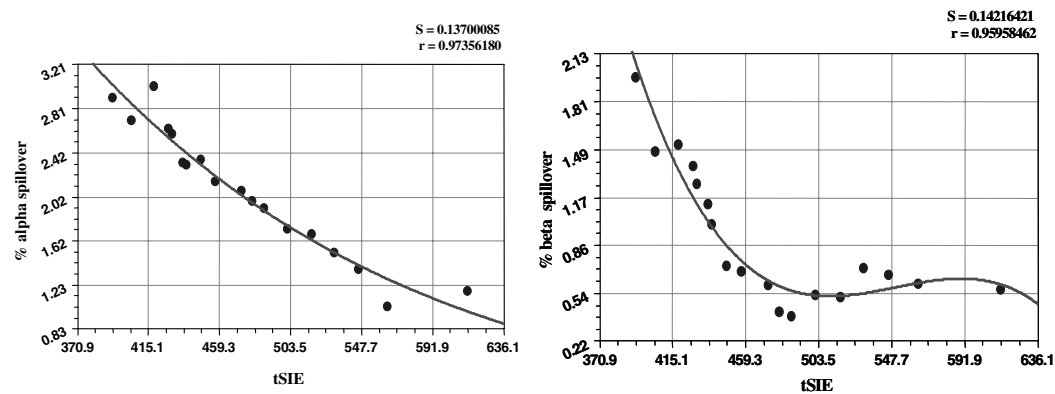


Figure 4 Alpha and beta spillover with different levels of quenching using 3M HCl with Ultima Gold AB

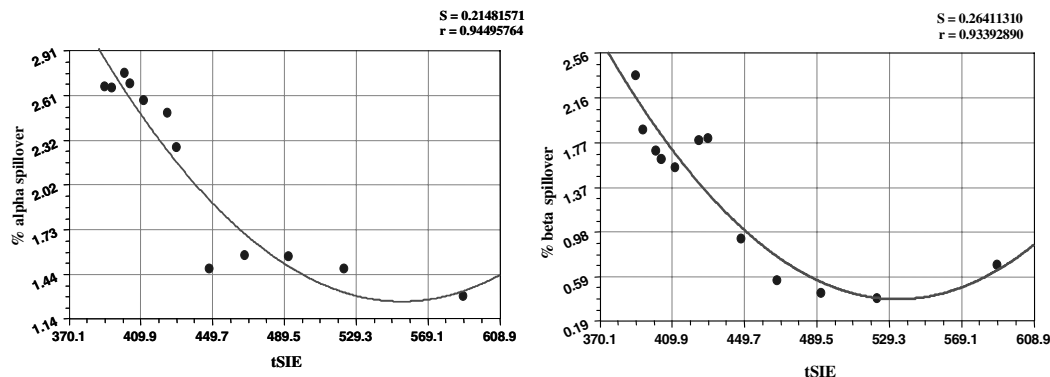


Figure 5 Alpha and beta spillover with different levels of quenching using 3M HCl with Ultima Gold LLT

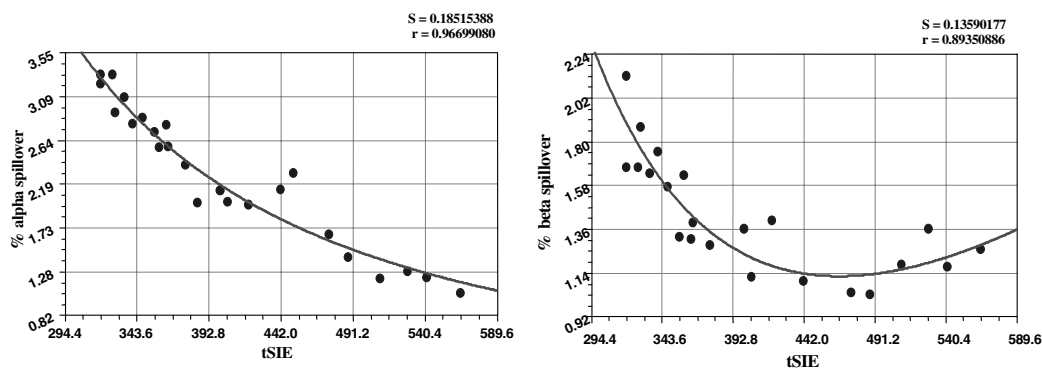


Figure 6 Alpha and beta spillover with different levels of quenching using 3M HCl with OptiPhase HiSafe 3

The main conclusions observed in this study are the following:

- Spillover α and β increase when the quench increases, but not in the same way as with the 2 quenching agents.
- When using 3M HCl, the quench obtained is lower than when the organic mixture is used for the same volume of quencher.
- In the 3 cocktails studied, the spillover is lower when 3M HCl is used as the quenching agent.
- In general, with low quenching, Ultima Gold AB cocktail has the lowest spillover, but its high quenching behavior is the worst of the 3 cocktails. The other 2 cocktails exhibit similar behavior.

Effect of the Quenching in PDD

The data in Figures 7–9 show the difference between the optimum PDD calculated with 2 different quenching agents. For 3M HCl, the range of tSIE is lower due to the formation of 2 phases with a high volume of acid.

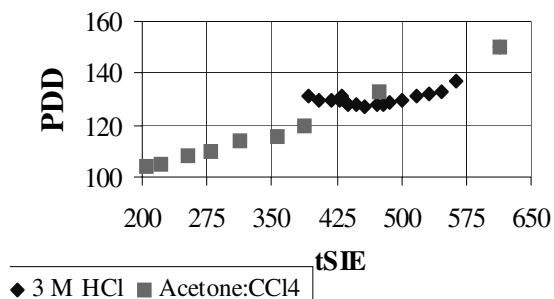


Figure 7 PDD vs tSIE using 2 different quenchers and Ultima Gold AB.

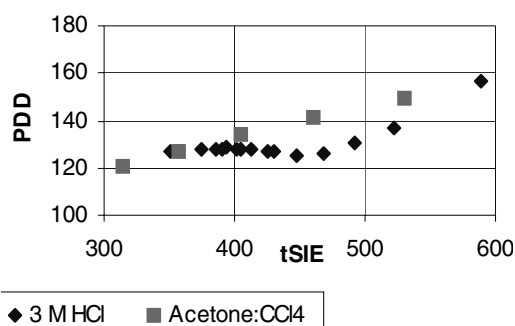


Figure 8 PDD vs tSIE using 2 different quenchers and Ultima Gold LLT.

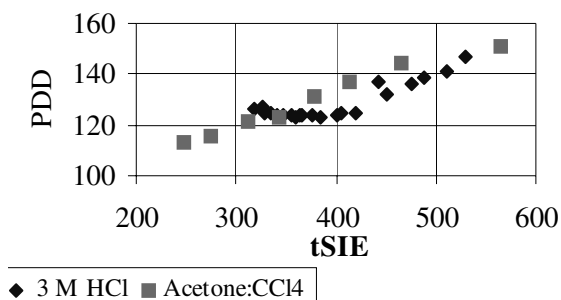


Figure 9 PDD vs tSIE using 2 different quenchers and OptiPhase HiSafe 3.

In the 3 cases, and when 3M HCl is used as quenching agent and the tSIE is at a certain level (500, 468, and 420 for Ultima Gold AB, Ultima Gold LLT, and OptiPhase HiSafe 3, respectively), there is no appreciable change in the optimum PDD. When using CCl₄:acetone 1:2 as the quenching agent, the increased quench produces a noticeably lower value in the optimum PDD.

The difference between the behavior of the 2 quenching agents for the optimum PDD can be calculated because the carbon tetrachloride produces a change in the triplet state, creating a shorter pulse and thus decreasing the PDD. The relative difference between pulse types is reduced immediately, thereby increasing misclassification.

A mixture of α and β emitters, using 3M HCl as quencher, was measured by applying the value of PDD calculated with 3M HCl and the value of PDD calculated with the organic mixture (results in Table 3).

Table 3 Activity obtained using the correct PDD (3M HCl quencher) in the upper cell and the incorrect PDD (organic quencher) in the lower cell.

Cocktail	tSIE	PDD	Activity measured (Bq)	Bias (%)	Activity measured (Bq)	Bias (%)
Ultima Gold AB	498	130	3.25	-11.3	25.78	-9.0
		135	3.17	-13.31	26.28	-7.2
Ultima Gold LLT	485	128	3.35	-8.4	25.2	-11.05
		143	3.15	-16.15	26.33	-7.05
OptiPhase HiSafe 3	458	125	3.13	-14.5	21.12	-25.44
		134	3.05	-16.58	21.32	-24.71

These results indicate that is very important to know the sample medium in order to choose the correct PDD due to the deviations with respect to added activity. The deviations are lower when the activity is measured using the value of PDD calculated with the type of impurity in the sample.

The same sample was measured with 2 levels of quenching using different cocktails. The results obtained (Table 4) indicate that the deviations are lower with a high quenching due to the overlap between α and β spectra.

Table 4 Activity measured for α and β emitters with different levels of quenching.

Cocktail	tSIE	Activity measured (Bq)	Bias (%)	Activity measured (Bq)	Bias (%)
Ultima Gold AB	204	3.9	6.5	25.89	-8.6
	500	3.25	-11.3	25.78	-9.0
Ultima Gold LLT	187	3.72	1.6	25.25	-10.88
	489	3.35	-8.4	25.2	-11.05
OptiPhase HiSafe 3	207	3.53	-3.5	26.03	-8.1
	461	3.13	-14.5	21.12	-25.44

Comparison Between Liquid Scintillation Analyzer and Gas Proportional Counter

Table 5 compares the results from the α and β mixture ($^{90}\text{Sr}/^{90}\text{Y}$, ^{137}Cs , ^{60}Co , ^{55}Fe , ^{63}Ni , and ^{241}Am) obtained via LS analyzer to the results obtained via gas proportional counter. The β mixture contains radionuclides studied in this paper that are normally present in the samples.

Table 5 Comparison of the results obtained via LS counter and gas proportional counter.

Analyzer	Activity added (Bq)	Activity measured (Bq)	Bias (%)	Activity added (Bq)	Activity measured (Bq)	Bias (%)
Ultima Gold AB	3.6	3.05	-15.27	28.46	26.55	-6.73
Ultima Gold LLT	3.6	3.26	-9.4	28.46	26.12	-8.19
OptiPhase HiSafe 3	3.6	3.05	-15.27	28.46	25.25	-11.28
Berthold	3.6	2.95	-18.05	28.46	12.08	-57.55
				12.38		-2.42

We observed that the gross α and β activity obtained is more concordant with the added activity when the measurement is performed by LSC. When the β emitters are analyzed by proportional counter, the low-energy β emitters (^{55}Fe and ^{63}Ni) are not measured, and for that reason a great discrepancy is observed between the activity added and the activity measured. In the upper cell, the result is presented considering the activity of the all radionuclides; in the lower cell, the result is presented without considering the activities of ^{55}Fe and ^{63}Ni .

We conclude that Ultima Gold LLT shows the best behavior for the different conditions used.

REFERENCES

- Pates JM, Cook GT, MacKenzie AB, Passo CJ Jr. 1998. Implications of beta energy and quench level for alpha/beta liquid scintillation spectrometry calibration. *Analyst* 123:2201–7.
- Prichard HM, Venso EA, Dodson CL. 1992. Liquid-scintillation analysis of ^{222}Rn in water by alpha-beta discrimination. *Radioactivity and Radiochemistry* 3(1): 28–36.
- Pujol L, Sanchez-Cabeza J-A. 1997. Role of quenching on alpha/beta separation in liquid scintillation counting for several high capacity cocktails. *Analyst* 122: 383–5.
- Salonen L. 1993. A rapid method for monitoring of uranium and radium in drinking water. *Science of the Total Environment* 130/131:23–35.
- Yang D. 1996. Calibration and quench correction for alpha liquid scintillation analysis. In: Cook GT, Harkness DD, MacKenzie AB, Miller BF, Scott EM, editors. *Liquid Scintillation Spectrometry 1994*. Tucson: Radiocarbon. p 339–44.