

Application Note

Alpha/Beta

ABA-002

Rapid Method For Alpha Counting With Extractive Scintillator And Pulse Decay Analysis

by Yang Dazhu and Zhu Yongjun
Institute of Nuclear Energy Technology, Tsinghua University
P.O. Box 1021 Beijing (China)
S. Mobius School of Nuclear Technology Nuclear Research Centre
Postfach 3640 7500 Karlsruhe (FRG)

Abstract

A rapid method for alpha counting with liquid scintillation is presented. The interference of beta and gamma radiation with the determination of alpha emitting nuclides by liquid scintillation counting was examined. An extractive scintillator cocktail, TOPO-PPO-naphthalene-toluene, has been developed for transferring actinide elements into the organic scintillator and separating the undesirable materials as well as most beta emitters. Pulse Decay Analysis (PDA) was applied for the discrimination of beta radiation. The influence of cocktail composition on PDA has been studied and compared with that of a commercial cocktail. An analytical procedure was suggested for the rapid determination of actinide elements U, Pu, Am, and Cm in the nuclear fuel cycle or in environmental samples.

Introduction

It is well known that there are always some difficulties along with alpha counting because of sample self-absorption. Long procedures of chemical separation and sample preparation are often needed. They are quite complicated, time consuming, and not suitable for rapid determination of alpha emitters.

Liquid scintillation techniques allow counting (detection and quantification) of alpha and beta radiation in ways that are usually more accurate and reproducible and are often easier than other methods. Because the radionuclides are in a homogeneous solution of an appropriate

organic scintillator, there is no risk of sample self-absorption and the counting efficiency for alpha radiation is nearly 100%. The sample preparation for liquid scintillation counting is also much simpler and more rapid than other methods. During the last twenty years, liquid scintillation counting has gained more and more interest for the determination of beta emitting nuclides in various samples. However, the liquid scintillation technique for alpha counting has not been widely used for several reasons. One of them is the interference of beta and gamma radiation with the determination of alpha radiation in liquid scintillation counting. Some work has been reported on the improvement of equipment and the development of analytical methods.¹⁻¹⁵ Solvent extraction techniques have been demonstrated^{7,11,14,15} to be rapid, simple, and convenient preliminary methods for preconcentration and separation of alpha emitting nuclides from other undesirable materials, such as acids or salts, as well as some beta and gamma emitting nuclides. Development has been made in the application of Pulse Decay Analysis (PDA) in a liquid scintillation system.^{11,15-19}

In this experiment, the interference of beta and gamma emitting nuclides with the determination of alpha emitting nuclides by liquid scintillation counting was examined. Extractive scintillators have been developed for transferring actinide elements into organic scintillator and separating most of the beta emitters. The application of PDA is discussed. The influence of cocktail composition on PDA has been studied and compared with that of the commercial cocktail Insta-Gel (Packard In-



Packard
A Packard BioScience Company

Packard Instrument Company 800 Research Parkway Meriden, CT 06450

Tel: 203-639-2598 1-800-323-1891 Fax: 203-639-2172

Web site: <http://www.packardinstrument.com> E-mail: webmaster@packardinstrument.com



strument Company). An analytical procedure is suggested for the rapid determination of actinide elements U, Pu, Am, and Cm in the nuclear fuel cycle or in environmental samples.

Experimental

Equipment

A Packard Tri-Carb 2200CA Time-Resolved Liquid Scintillation Analyzer with Pulse Decay Analysis (PDA) and Multichannel Analyzer (MCA) was used for this study.

Reagents

The scintillators used: Insta-Gel produced by Packard Instrument Company; 2-(4-t-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (B-PBD); 2,5-diphenyloxazole (PPO); 2,5-bis-(5-tert-butylbenzoxazolyl) thiophene (BBOT); naphthalene. The extractants used: Tributylphosphate (TBP); trioctylphosphine oxide (TOPO); octyl-(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO); di-(2-ethylhexyl)-phosphate (HDEHP); triisooctylamine (TiOA); tricapryl methylammonium chloride (Aliquot 336); 2-thenoyltrifluoroacetone (TTA). The nuclides used were ^{241}Am , ^{210}Po , ^{137}Cs , $^{144}\text{Ce}/^{144}\text{Pr}$, $^{90}\text{Sr}/^{90}\text{Y}$, $^{106}\text{Ru}/^{106}\text{Rh}$, and $^{95}\text{Zr}/^{95}\text{Nb}$, and were provided by the Amersham Company, England, or the Nuclear Research Centre, Karlsruhe, FRG.

Results and Discussion

Interference of beta and gamma radiation with alpha counting.

The liquid scintillation counter is a universal instrument and can be used for measuring beta and gamma radiation as well as alpha radiation. Because beta and gamma radiation produce about ten times more light for the same amount of energy absorbed in a liquid scintillator than alpha radiation does, *i.e.*, beta radiation with a maximum energy of 0.5 MeV produces the same amount of light as does alpha radiation with an energy of about 5 MeV, it results in a serious overlap of alpha and some energetic beta spectra. The identification and analysis of beta and alpha spectra by Pulse Height Analysis (PHA) can only be used for beta radiation with low energy, such as ^3H (0.0186 MeV), ^{14}C (0.156 MeV), and ^{241}Pu (0.021 MeV). For beta radiation with higher energy, *e.g.*, ^{90}Y (2.27 MeV), ^{106}Rh (3.55 MeV), and ^{144}Pr (2.99 MeV), there will be serious overlaps of the spectra of beta and alpha radiation and they cannot be separated by PHA.

Some important radioactive nuclides that are present in the nuclear fuel cycle are summarized in Table 1. Some of the spectra of the nuclides measured by liquid scintillation analyzer are demonstrated in Figure 1. If the short-cooling samples are dealt with, the main beta ac-

tivity will be from $^{95}\text{Zr}/^{95}\text{Nb}$, $^{106}\text{Ru}/^{106}\text{Rh}$, and $^{144}\text{Ce}/^{144}\text{Pr}$. But for long-cooling samples, the main activity will be from $^{90}\text{Sr}/^{90}\text{Y}$ and $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$. Some of the beta emitters have low energy, *e.g.*, ^{147}Pm (0.233 MeV), ^{95}Nb (0.160 MeV), ^{106}Ru (0.036 MeV), and ^{144}Ce (0.347 MeV), which can be discriminated by PHA. However, ^{106}Rh , the daughter of ^{106}Ru , has high energy, 2.0-3.55 MeV; and ^{144}Pr , the daughter of ^{144}Ce , also has a high energy, 2.99 MeV. ^{106}Rh and ^{144}Pr cannot be discriminated by PHA and will interfere with alpha counting. Chemical separation and/or pulse decay analysis have to be introduced for the determination of alpha emitters in the samples with such energetic beta emitters.

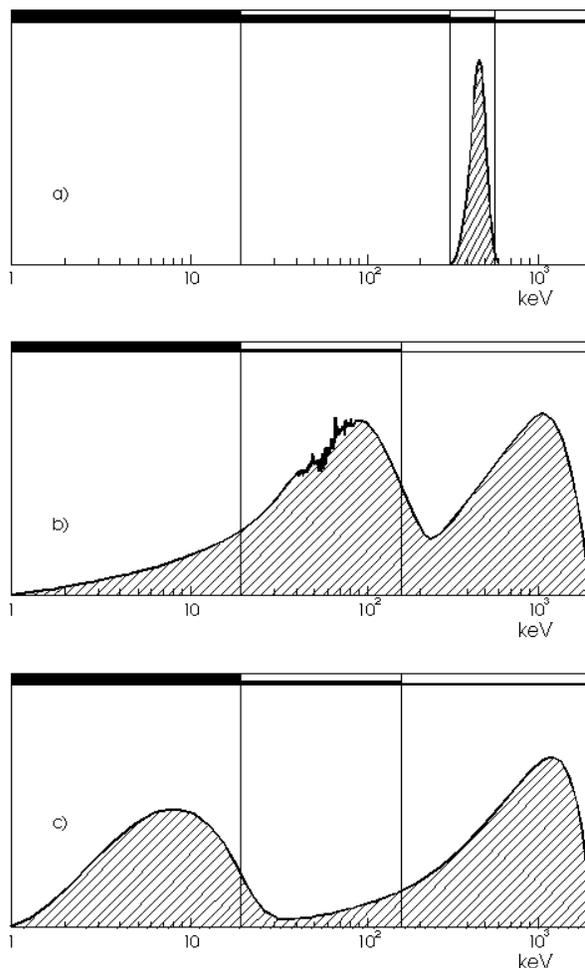


Figure 1.
Spectra of Some Alpha and Beta Emitting Nuclides: a) ^{241}Am ; b) $^{144}\text{Ce}/^{144}\text{Pr}$; c) $^{106}\text{Ru}/^{106}\text{Rh}$.

Nuclide	Half-life	Energy	Relative Activity, %	
			1 year cooling time	6 years cooling time
Sr-89	50.7 d	1.463 (100%)	2	---
Sr-90	28.5 y	0.546 (100%)	1.7	16
Y-90	64.1 h	2.274 (100%)	1.7	16
Y-91	58.6 d	1.545 (99.7%)	3.6	---
Zr-95	64.0 d	0.396 (55%)	6.3	---
		0.360 (43%)		
		0.89 (2%)		
Nb-95	35.1 d	0.160 (>99.9%)	11.8	---
		0.924 (>0.08%)		
Ru-103	39.5 d	0.101 (6.3%)	2	---
		0.214 (89.0%)		
		0.711 (4.4%)		
Rh-103m	56.1 m	(IT)	2	---
Ru-106	368 d	0.036 (100%)	9.6	1.7
Rh-106	30 s	3.55 (68%)	9.6	1.7
		2.4 (12%)		
		3.1 (11%)		
		2.0 (3%)		
Cs-134	2.06 y	0.089 (25%)	4.6	7
		0.415 (3.0%)		
		0.658 (70%)		
Cs-137	30.2 y	0.512 (94.7%)	2.4	23
		1.173 (5.3%)		
Ba-137m	2.554 m	(IT)	2.3	22
Ce-144	185 d	0.347 (100%)	17.5	1
Pr-144	17.3 m	2.99	17.5	1
Pm-147	2.62 y	0.233 (100%)	2.3	5
Eu-154	16 y	0.28 (28%)	0.2	1.4
		0.58 (38%)		
		0.87 (24%)		
		1.86 (10%)		

Table 1.
Some Beta Emitting Nuclides in Nuclear Fuel Cycle.²²

Introduction of PDA

It is known²¹ that fluorescent decay of a scintillation pulse is composed of prompt and delayed components; the amount of light in the delayed component is dependent on the particle or decay type. Alpha particles and neutrons produce more delayed component than electrons originating from beta and gamma radiation (Fig-

ure 2). This means that the pulse length (decay lifetime) of alpha particles is different from that of beta or gamma radiation. Therefore, pulse decay analysis (PDA) provides a useful means for the identification and separation of the light pulse produced by alpha and beta radiation. With the help of PDA, it is possible that the determination of alpha emitting nuclides can be made separately, ignoring the presence of beta and gamma emit-

ting nuclides. For PDA to identify alpha and beta radiation, a pulse decay discriminator (PDD) can be set by the user. The pulse decay analyzer compares the pulse input with the PDD and decides whether it is an alpha-like or a beta-like pulse. The alpha-like pulses are sent to the alpha MCA (Multichannel Analyzer) and beta-like pulses to the beta MCA. In this way, the spectra of alpha and beta can be separated. For a good PDD setting there should be few counts in the beta MCA if a “pure” alpha emitter is measured, and vice versa.

The influence of the PDD on the efficiency of alpha counting and the discrimination of beta radiation has been studied. The results are given in Table 2. With a low PDD setting, a higher efficiency of alpha counting is achieved, but a poor discrimination of beta radiation is obtained. In contrast, with a high PDD setting, a very good discrimination of beta radiation can be expected, but some of the alpha counting will be lost. By optimizing the PDD setting between 130 and 150, a high efficiency > 99% of alpha counting and a satisfactory discrimination of beta emitter > 99.95% is possible.

Extractive Scintillator

An extractive scintillator cocktail is composed of extractant, scintillators (first scintillator and second scintillator), and solvent.

Extractant

An appropriate extractant for an extractive scintillator system must show good behavior in pulse height analysis (PHA) and pulse decay analysis (PDA), as well as an ability of selective extraction for the nuclides of interest. Good PHA behavior means that the extractant has little quench effect on the light yield produced in the liquid scintillation system and good PDA behavior means that the extractant has little influence on the pulse

decay (the prompt and delayed fluorescent component).

Seven widely used extractants have been examined. Their quench effects on alpha counting in liquid scintillation are shown in Figure 3. The neutral phosphorus-based extractants TBP and TOPO have little quench effect. The other phosphorus-based extractants CMPO and HDEHP have a little more quench effect than TBP and TOPO, but not serious. The nitrogen-based extractants TiOA and Aliquot 336 have some quench effect, but can be used with low concentration and some care. TTA has a very serious quench effect and cannot be used in a liquid scintillation system. The mechanism and the difference of the quench effects of these extractants seem to depend on the structure of the extractants, especially on the position of the oxygen atom in the molecules.

The distribution coefficients of some actinide elements and beta and gamma emitting nuclides are shown in Table 3. U and Pu (IV) can be extracted from nitric acid solution into Toluene containing 0.3 mol/L TOPO with high distribution coefficients. Trivalent Am and Cm can be extracted from 0.1-0.6mol/l nitric acid solution, but distribution coefficients are very low in 4mol/l nitric acid solution. Most beta and gamma emitting nuclides, *e.g.*, Sr. and Cs, cannot be extracted by TOPO, so they can be easily separated from the actinide elements. But some of the beta emitting nuclides, such as Ru, Zr, and Nb, can also be extracted partly by TOPO. The lanthanides and yttrium, which show quite similar extraction behavior to trivalent actinide elements, can hardly be separated from Am and Cm by TOPO. So TOPO is suitable to separate Cs, Sr, and other elements from actinides, in the case of long-cooled samples. It should be noted, however, that some beta emitting nuclides, especially trivalent lanthanides and yttrium may be co-extracted with alpha emitters (Am and Cm) and interfere with the alpha counting.

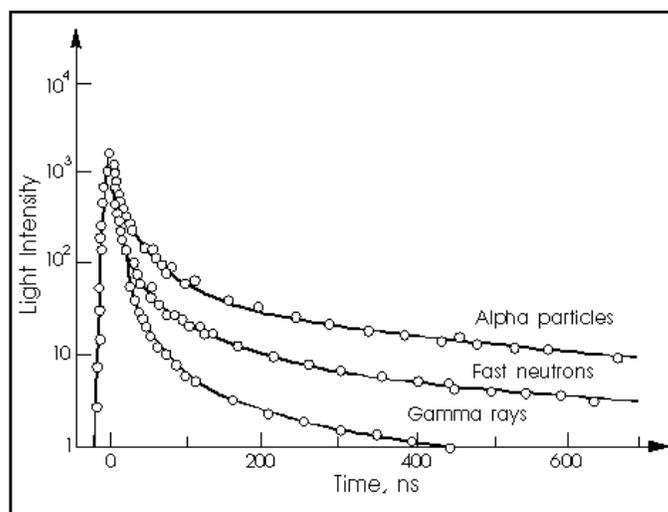


Figure 2.

Scintillation Pulse Shape in Stilbene When Excited by Different Types of Radiation.

Pulse Decay Discriminator Setting (PDD)	Am-241, CPM		Ce-144/Pr-144, CPM	
	Alpha MCA 230-600 keV	Beta MCA 230-600 keV	Alpha MCA 230-600 keV	Beta MCA 0-2000 keV
100	1 329	3	274	25 909
110	1 350	3	25	27 054
120	1 348	5	4	27 399
130	1 330	5	6	27 302
140	1 320	18	5	27 386
150	1 231	102	3	27 615
160	1 111	217	2	27 347

5 g/l PPO, 0.3 mol/l TOPO, 10% Naphthalene, glass vials.

Table 2.
Influence of Discriminator Setting on PDA.

The influence of TOPO concentration on PDA is studied. The results are summarized in Table 4. There is no obvious interference of TOPO with pulse decay analysis.

First Scintillator

Three scintillators have been studied. The concentration dependence of the scintillation yield is shown in Figure 4. Because PPO has a high scintillation yield and is cheaper than B-PBD, it was chosen as the scintillator used in this work.

The influence of PPO concentration on PDA is given in Table 5. The low concentration of PPO seems to bring about better results for identification and separation of alpha and beta radiation than high PPO concentrations.

Second Scintillator

Naphthalene was used to improve counting efficiency for low energy beta emitters in dioxane based cocktail. It plays an important part in pulse decay analysis. The influence of the concentration of naphthalene on PDA is given in Table 6. The good identification and separation is not possible without naphthalene in the cocktail. One of the explanations for this function might be the long decay time of naphthalene (96.0 ns), relative to that of PPO (1.4 ns).

Vials

Glass vials and polyethylene vials have been compared. With polyethylene vials, the energy resolution for alpha emitting nuclides is better than with glass vials, but the separation of alpha and beta pulses is worse.

Commercial Cocktail

The commercial cocktail, Insta-Gel, has been tested and compared with extractive scintillator, TOPO-PPO-naphthalene-toluene. Insta-Gel is an original universal LSC cocktail. It excels in the incorporation of water and water soluble samples into the scintillator system, and is equally useful for organic soluble samples. The aqueous or organic sample can be mixed with the cocktail directly. But at the same time, the undesirable materials, including all beta emitters, will also be incorporated into the cocktail and might interfere with alpha counting. In order to obtain optimum performance with pulse decay analysis, it is recommended to add 20% naphthalene into the cocktail. The influence of the PDD setting on the efficiency of alpha counting and the discrimination of beta radiation are given in Table 7. By optimizing the PDD setting between 140 and 150, a high efficiency 98% for alpha counting and a satisfactory discrimination of beta emitters of 99.9% are achieved. Comparing the cocktail with the extractive scintillator cocktail, its sample preparation is simpler than that of the latter, but it cannot pre-concentrate or pre-separate the alpha emitting nuclides. For this reason, the use of an extractive scintillation in conjunction with PDA shows an increase in alpha/beta discrimination performance (see Table 2).

Analytical Procedure for Alpha Counting

A rapid analytical procedure has been suggested for alpha counting and the schedule is shown in Figure 5. The key point of the procedure is the combination of extractive scintillator and the pulse decay analysis technique. The extractive scintillator cocktail is composed of 1-3 g/l PPO, 0.1-0.3 mol/l TOPO, 5-10% naphthalene and

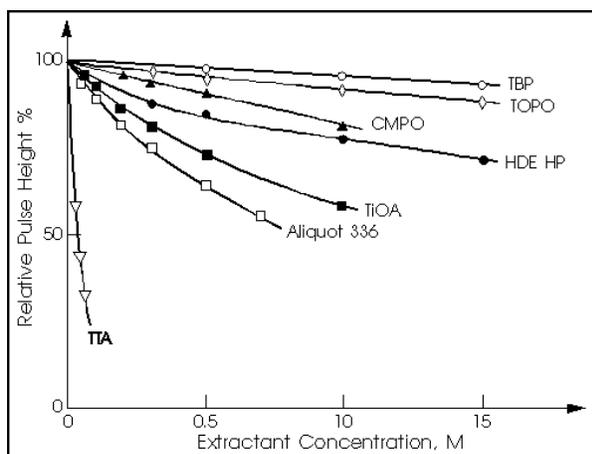


Figure 3.
Quench Effect of Various Extractants.
Nuclide Used Was ²⁴¹Am.

Element	Concentration of nitric acid	
	0.5mol/l	4 mol/l
U (VI)	>10e3	>10e3
Pu (IV)	>10e3	>10e3
Am(III)	>10	0.05
Cm(III)	>10	0.04
Cs (I)	<10e-3	<10e-3
Ba(II)	<10e-2	<10e-2
Sk (II)	<10e-3	<10e-3
Y (III)	>10	0.05
Ce (III)	>10	0.04
Pr (III)	>10	0.05
Pm(III)	>10	0.05
Eu (III)	>10	0.1
Zr (IV)	>10e2	70

Table 3.
Distribution of Some Elements in Nuclear
Fuel Cycle-Extraction into TOPO-Toluene

[TOPO], mol/l	Am-241, Bq		Ce-144/Pr-144, Bq	
	Beta-MCA	Alpha-MCA	Beta-MCA	Alpha-MCA
0.1	1.9	27.7	809	0.8
0.3	2.0	27.0	804	1.0
0.5	0.3	26.9	813	1.3

5 g/l PPO, 10% naphthalene, toluene, PDD setting 140, glass vials.

Table 4.
Influence of TOPO Concentration on PDA.

[PPO], g/l	Am-241, Bq		Ce-144/Pr-144, Bq	
	Beta-MCA	Alpha-MCA	Beta-MCA	Alpha-MCA
1	1.6	26.0	727	1.2
2	1.7	23.9	718	0.8
3	1.7	23.5	711	0.9
4	1.5	24.4	730	0.9
5	2.0	24.4	733	3.8

1-5 g/l PPO, 10% naphthalene, 0.3 mol/l TOPO, toluene, PDD setting 140, glass vials.

Table 5.
Influence of PPO Concentration on PDA.

[Naph]	Am-241, CPM		Ce-144/Pr-144, CPM	
	Beta-MCA	Alpha-MCA	Beta-MCA	Alpha-MCA
0%	20.1	8.0	685	0.2
5%	2.8	21.8	675	0.8
10%	2.3	21.5	659	0.7
15%	2.4	22.4	653	0.6
20%	2.0	21.8	649	0.7

0-20% naphthalene, 5 g/l PPO, 0.3 mol/l TOPO, toluene, PDD setting 140, glass vials.

Table 6.
Influence of Naphthalene Concentration on PDA.

Decay Time Disc	Po, CPM		Ce/Pr, CPM	
	Alpha MCA 200-500 CH	Beta MCA 200-500 CH	Alpha MCA 200-500 CH	Beta MCA 200-500 CH
120	43 873	668	172	18 280
130	43 774	710	30	18 843
140	43 750	776	10	19 037
150	43 330	1101	6	19 098
160	41 564	2852	3	19 108
170	35 472	3971	4	19 082

15 ml Insta-Gel, 20% naphthalene, glass vials.

Table 7.

Influence of Pulse Decay Discrimination Setting on PDA.

toluene. With the help of the extractant in the cocktail, the alpha emitting nuclides, especially actinide elements, are transferred into the solution of the organic scintillator and most of the beta emitting nuclides and other undesirable materials are removed. With PDA, the light pulses from the beta emitters can be discriminated, which are co-extracted with alpha emitters in the organic scintillator. In order to determine U/Pu and Am/Cm separately, the concentration of nitric acid is first adjusted to 4 mol/l. Under this condition, U and Pu get into the organic scintillator cocktail, but Am and Cm remain in aqueous phase and are separated from U and Pu. U and Pu in the organic scintillator cocktail are measured in the LSC directly. Then, by adding NH_4OH to adjust to pH 1, Am and Cm can be extracted by TOPO and transferred into the organic scintillator cocktail. This prepared sample is measured in the LSC separately.

The background for alpha is about 0.9 CPM in the whole alpha MCA and 0.1 CPM in the energy region of 5 MeV alpha emitters. The detection limit for ^{239}Pu (5.155 MeV) is 0.5 mBq/sample (1,000 minute counting time, 3 s of background). This procedure can be used as a rapid method for alpha counting in nuclear fuel cycle or environmental samples.

The authors wish to thank DAAD (Deutscher Akademischer Austauschdienst) for the financial support and Mr. Meier, Nuclear Research Centre Karlsruhe, for the use of the LSC instrument and valuable discussion, and especially Prof. Keller, Director of the School of Nuclear Technology, who supported the work generously.

References

1. D. Horrocks, Rev. Sci. Instrum., 35 (1964) 334.
2. D. L. Horrocks, M. H. Studier, Anal. Chem., 36 (1964) 2077.
3. K. Flynn, L. Glendenin, E. Steinsers, P. Wrisht, Nucl. Instrum. Methods, 27 (1964) 13.
4. H. Ihle, M. Karayannis, P. Murrenhoff, Liquid Scintillation Counting of Alpha Emitters, in: Proc. Sympos. on

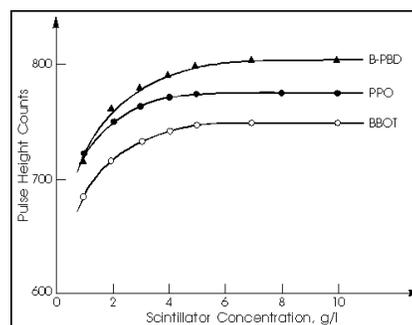


Figure 4.

Pulse-height Produced by Three Scintillators as a Function of Scintillator Concentration. Nuclide Used Was ^{241}Am .

Radioisotope Sample Measurement Techniques, IAEA, Vienna, 1965, p. 483.

5. A. Linderbaum, C. Judd, Radiation Res., 37 (1969) 131.
6. W. J. McDowell, Liquid Scintillation Counting Techniques for the Higher Actinides, in: Organic Scintillator and Liquid Scintillation Counting, D. L. Horrocks and C. T. Peng (Eds), Academic Press, New York, 1971, p. 937.
7. W. J. McDowell, C. F. Coleman, Combined Solvent Extraction - Liquid Scintillation Method for Radioassay of Alpha Emitters, in: Proc. Intern. Solvent Extraction Conference, London, 1974.
8. J. H. Thorngate, W. J. McDowell, D. J. Christian, Health Phys., 27 (1974) 132.
9. J. W. McKlveen, W. R. Johnson, Health Phys., 28 (1975) 5.
10. J. W. McKlveen, W. J. McDowell, Nuclear Technol., 28 (1976) 159.
11. W. J. McDowell, Alpha Liquid Scintillation Counting; Past, Present, and Future, in: Liquid Scintillation Counting: Recent Applications and Developments, C. T. Peng, D. L. Horrocks and E. L. Alpen (Eds), Academic Press, New York, 1980, p. 315.
12. Y. Baba, J. Radioanal. Chem. 79, (1983) 83.
13. J. W. McKlveen, W. J. McDowell, Nucl. Instrum. Methods Phys. Res., Sect. A, 223 (1983) 372.
14. J. W. McDowell, G. N. Case, Separation and Methods for Alpha Assay by Liquid Scintillation, in: Chemical Aspects of Nuclear Methods of Analysis, IAEA-TECDOC-350, Vienna, 1985, p. 33.
15. W. J. McDowell, Alpha Counting and Spectrometry Using Liquid Scintillation Methods, Report NAS-NS-3116, 1986.
16. J. H. Thorngate, W. J. McDowell, D. J. Christian, Health Phys., 27 (1974) 123.
17. J. H. Thorngate, D. J. Christian, Health Phys., 33 (1977) 443.
18. J. H. Thorngate, Health Phys., 34 (1978) 103.
19. L. K. B. Wallace, 1219 Spectra Master, Product Information Package, 1987.
20. L. M. Bollinger, G. E. Thomas, Rev. Sci. Instr., 32 (1964) 1044.

21. D. L. Horrocks, Application of Liquid Scintillation Counting, Academic Press, New York, 1974.
22. M. Benedict, T. H. Pigford, H. W. Levi, Nuclear Chemical Engineering, McGraw-Hill, London, 1981.

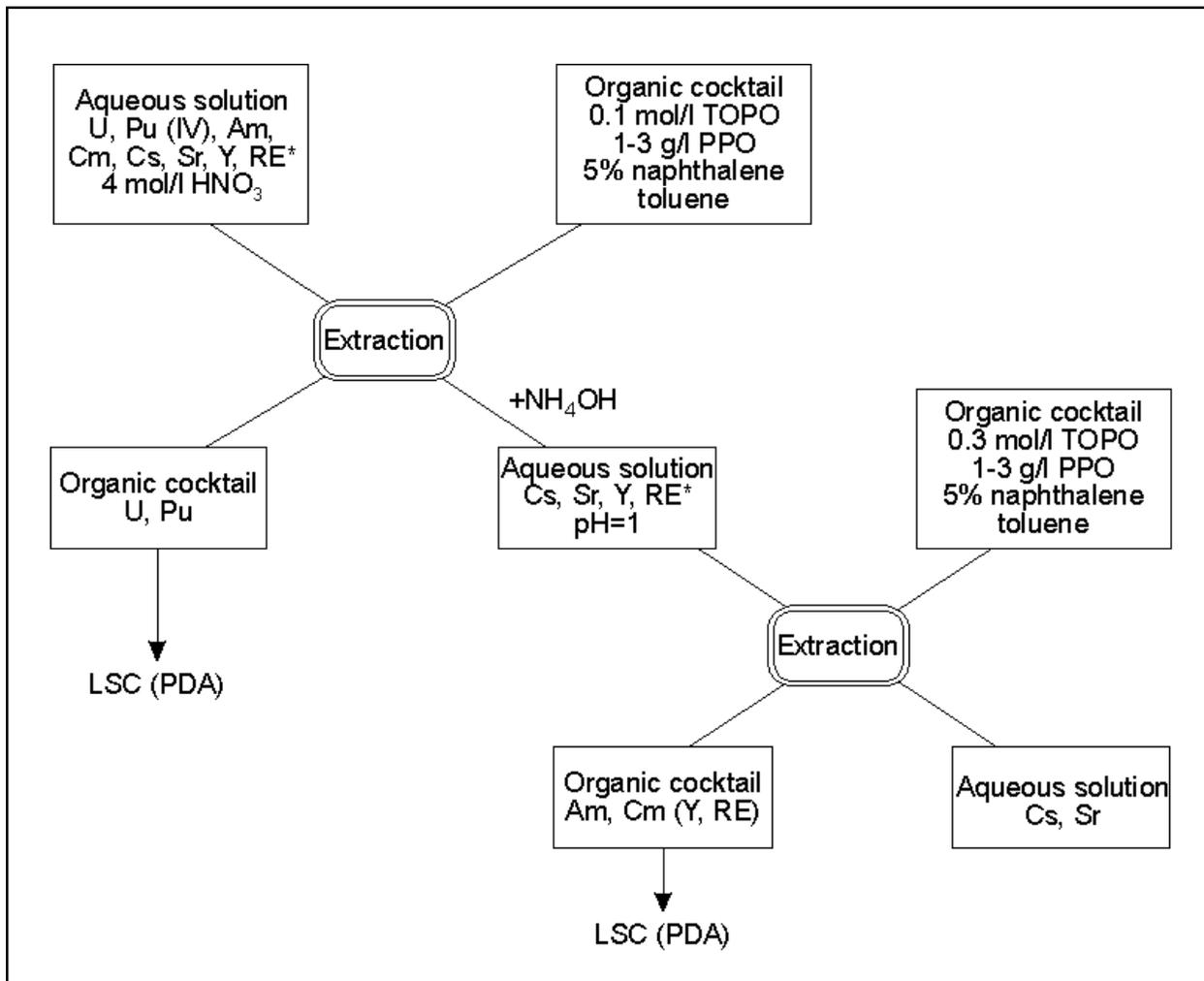


Figure 5.
Analytical Scheme.