

## APPLICATION OF LIQUID-LIQUID EXTRACTION AND RadSpectraDec SOFTWARE IN LS $\alpha$ SPECTROMETRY

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**ABSTRACT.** We developed a new approach for analyzing complex  $\alpha$ -emitting radionuclide mixtures. The approach is based on liquid-liquid extraction using appropriate extractive liquid scintillation (LS) cocktails, followed by LS counting (LSC), and processing of spectra using RadSpectraDec software. This software fits the sample spectrum with a linear combination of spectra from individual radionuclides that have been measured previously. Using extraction with liquid complexing agents and counting via a LS counter, it was possible to increase the relative resolution of scintillation  $\alpha$  peaks to 9–10%, which is sufficient for the RadSpectraDec program. This approach was successfully applied to the analysis of real environmental and technological samples, and good results have been obtained. The limitations of this approach are also considered.

### INTRODUCTION

Liquid scintillation (LS) spectrometry is today one of the most attractive and sensitive techniques for measuring radioactivity because LS spectrometry can detect practically all types of radiation with high efficiency. However, LS spectrometry has some restrictions, such as limitations with processing experimental spectra and poor resolution of the scintillation  $\alpha$  peaks, which complicates the discrimination of  $\alpha$ -emitting radionuclides with similar energies.

To increase the abilities of LS spectrometry, we recently proposed an approach for simultaneously identifying and quantifying the components of complex environmental and technological radionuclide mixtures with unknown composition (Belanov et al. 1997, 1998; Kashirin et al. 2000; Malinovsky et al. 2002). This approach is based on RadSpectraDec software and a previously created spectra library. However, the relative resolution of the LS  $\alpha$  peaks obtained using traditional LS counters (15%) was insufficient for correctly analyzing complex mixtures of  $\alpha$  emitters using the RadSpectraDec program.

To minimize the quenching effects and to produce the best energy resolution during LS counting (LSC), we used liquid-liquid extraction of the  $\alpha$ -emitting radionuclides via extractive LS cocktails. It was then possible to increase the relative resolution to 9–10%. These values are sufficient for accurately analyzing spectra from mixtures of  $\alpha$  emitters using RadSpectraDec.

### METHODS

#### Reagents

All chemicals were analytical grade; the LS cocktail Insta-Fluor was acquired from PerkinElmer (USA). The following extracting agents were used: bis(2-ethylhexyl)phosphoric acid (HDEHP) and tri-*n*-octylphosphinoxid (TOPO), both obtained from Merck, Inc.; P,P'-di(2-ethylhexyl)metane-diphosphonic acid (DIPEX<sup>®</sup>), obtained from Eichrom Industries, Inc.; and mono-isooctyl ester of methylphosphonic acid (MIOMP), obtained from the Institute of Organic Chemistry (Russian Academy of Science). The extractive scintillators ALPHAEX<sup>®</sup>, URAEX<sup>®</sup>, THOREX<sup>®</sup>, POLEX<sup>®</sup>, and RADAEX<sup>®</sup> were obtained from East Tennessee Radiometric/Analytical Chemicals (ETRAC), Inc.

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### Radioisotopes

Standard radioactive solutions of  $^{147}\text{Sm}$ ,  $^{148}\text{Gd}$ ,  $^{226}\text{Ra}$ ,  $^{236}\text{Pu}$ ,  $^{237}\text{Pu}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{232}\text{U}$ ,  $^{233}\text{U}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$ ,  $^{236}\text{U}$ ,  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ ,  $^{243}\text{Am}$ , and  $^{244}\text{Cm}$  were obtained from the All-Russian Scientific Research Institute of Metrology (Russia) with purities in activity of ~95–97%.

### Equipment

A Tri-Carb 2550 TR/AB LS analyzer (PerkinElmer) was used in this study. All measurements were carried out with low-diffusion polyethylene vials.

### PROCEDURE

To create a radionuclide spectra library with reduced quenching and improved resolution, the  $\alpha$ -emitting radionuclides  $^{147}\text{Sm}$ ,  $^{148}\text{Gd}$ ,  $^{237}\text{Np}$ ,  $^{244}\text{Cm}$ ,  $^{232}\text{Th}$ , and isotopes of U and Pu were extracted with 0.2M HDEHP or 0.2M DIPEX solutions in Insta-Fluor LS cocktail from the appropriate acidic media. The LS extracting scintillator POLEX was used for  $^{210}\text{Po}$  extraction, and the  $^{226}\text{Ra}$  source was prepared using extraction with RADAEX reagent from an alkaline medium. Before measurement, each sample was bubbled with dry, oxygen-free argon. After measurement on the Tri-Carb LS counter, an appropriate quantity of  $\text{CCl}_4$  as a chemical quenching agent was added to the each sample. The library of spectra includes 5 to 10 levels of quenching for each  $\alpha$  emitter. All spectra are normalized and combined into groups of channels using the registered algorithm.

The synthetic radionuclide mixtures were prepared from standard radioactive solutions using liquid-liquid extraction. Samples for LSC were prepared from real environmental liquids or technological samples by extraction with 0.2M solutions of extracting agents in Insta-Fluor LS cocktail, either directly from their aliquots or after preliminary concentration using evaporation. The LSC samples from solid specimens were prepared in a similar manner after leaching and transformation into a colorless solution before the extraction stage. To increase the speed of extraction, samples were mixed for 2 min in an ultrasonic bath and then shaken for 5 min. After that, organic and water phases were separated by centrifugation for 10 min at 3000 rpm. The best radiochemical recovery for individual radionuclides was obtained using a double extraction procedure. Separated organic phases were combined and mixed with 15 mL of Insta-Fluor cocktail; bubbled with dry, oxygen-free argon for 3 to 5 min; and then measured using a Tri-Carb 2550 TR/AB spectrometer. The spectra obtained were processed using RadSpectraDec software.

### RESULTS AND DISCUSSION

Discriminating  $\alpha$  peaks is difficult in LS spectrometry because of LSC's intrinsic poor resolution, caused by the interaction of the particle with the scintillator and by the high level of chemical quenching due to the mixing of water or acid solutions with water-compatible scintillation cocktails. It is already known that extraction techniques, with the help of liquid organic reagents, may be very useful for fast and effective concentration of radionuclides from water solutions into small volumes of the organic phase (McDowell and McDowell 1993; McDowell 1996; Dacheux and Aupiais 1997; Dacheux et al. 2000). The concentration factor can reach 150, and, in some cases, the time-consuming evaporation stage can be eliminated.

In order to facilitate and speed up the sample preparation for LSC, to minimize the quenching effects, and to improve the energy resolution, we used liquid-liquid extraction of  $\alpha$  emitters under the appropriate conditions by scintillating-extractive cocktails, which contained HDEHP, DIPEX, MIOMP, and TOPO as extractive molecules and Insta-Fluor as an organic sample-compatible LS

cocktail. Mixing 1–2 mL of 0.2M solutions of this extracting agent with 15 mL of the xylene-based Insta-Fluor cocktail followed by argon bubbling produced practically unquenched homogeneous samples, allowing us to improve the relative resolution of the scintillation  $\alpha$  peaks to 9–10%. The simultaneous determination of alpha emitters in complex mixtures was realized with the assistance of a specially developed spectra processing software, RadSpectraDec, which realizes the deconvolution of LS spectra by recursive minimization of a function representing the difference between a model spectrum and the experimental spectrum, taking into account the quench level. Examples are given of spectra processed by the RadSpectraDec program after extracting synthetic mixtures of U isotopes and  $^{244}\text{Cm}/^{241}\text{Am}$  with different activities. The data obtained are presented in Table 1 and Figures 1 and 2. Extraction of U isotopes was performed using a 0.2M solution of HDEHP in Insta-Fluor cocktail (or ALPHAEX extractive scintillator) from 1M  $\text{HNO}_3$ ; extraction of Cm/Am was realized from 0.005M  $\text{HNO}_3$  with the same extracting agents.

Table 1 Results of the analysis of U isotopes and Cm/Am mixtures after HDEHP (ALPHAEX) extraction using RadSpectraDec.

Radionuclide composition of the mixtures	Activity (Bq/sample)	
	Actual contents	Obtained contents (RadSpectraDec)
$^{232}\text{U}$	1.0	$0.9 \pm 0.2$
$^{234}\text{U}$	2.5	$2.3 \pm 0.4$
$^{238}\text{U}$	30	$33 \pm 6$
$^{244}\text{Cm}$	5.0	$4.6 \pm 0.9$
$^{241}\text{Am}$	50	$57 \pm 11$

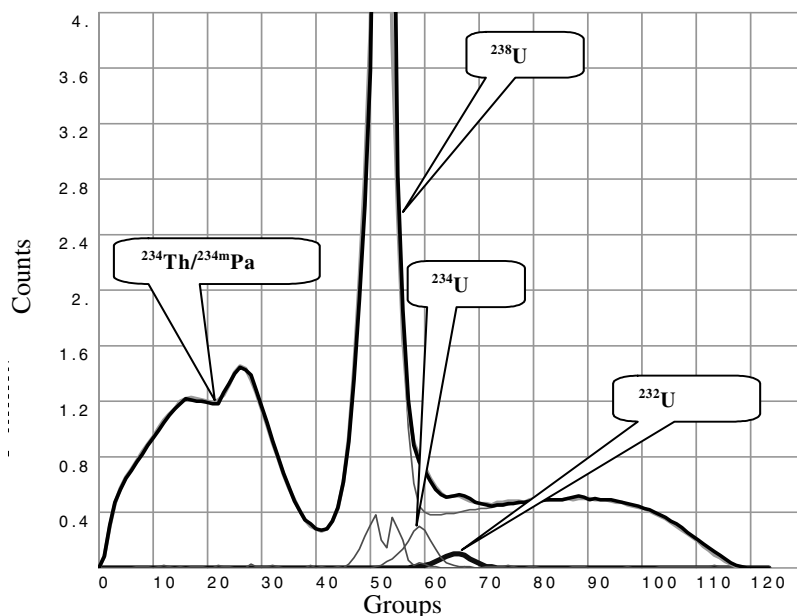


Figure 1 Spectrum decoding (RadSpectraDec program) of a U-isotope mixture after HDEHP (ALPHAEX) extraction from 1M  $\text{HNO}_3$  solution.

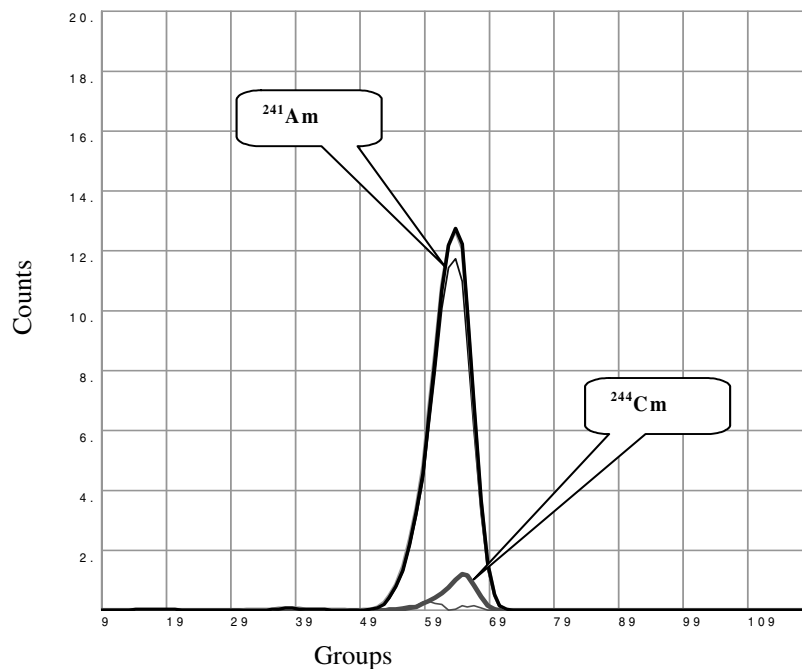


Figure 2 Spectrum decoding (RadSpectraDec program) of a  $^{244}\text{Cm}/^{241}\text{Am}$  mixture after HDEHP (ALPHAEX) extraction from 0.005M  $\text{HNO}_3$  solution.

Because we obtained good results in the model tests, the developed approach was applied to the analysis of real technological and environmental samples. The detection limit of the method is about a few mBq per counting sample for  $\alpha$  emitters.

An example of the combination of liquid-liquid extraction followed by LSC and spectra processing with RadSpectraDec software is given from the analysis of a soil sample taken from a local radioactive spot at a research institute in Moscow. Screening analysis of this sample was done after acidic digestion followed by frequent evaporation to dryness and then added to a 1M HCl solution. The sample revealed the presence of a complicated mixture of  $\gamma$ -,  $\beta$ - and  $\alpha$ -emitting radionuclides. The total spectrum of the aliquot and its deconvolution is shown in Figure 3. Clearly, the complex mixture of  $\alpha$ -emitting radionuclides presented by Pu, Am, Cm isotopes produces the extensive  $\alpha$  peak, and it was impossible to decode this mixture without additional procedures. To determine the  $\alpha$  emitters, 2 stages of liquid-liquid extraction were carried out. In the first stage, 0.2M HDEHP was used for separating Pu isotopes from 1M  $\text{HNO}_3$  solution with  $^{242}\text{Pu}$  as a tracer to evaluate the extraction recovery. Under these conditions, Pu isotopes migrate in the organic phase (HDEHP–Insta-Fluor), whereas the triple-valent isotopes of Am and Cm remain in the aqueous phase. The spectrum deconvolution for the isotope mixture extracted at this step is presented in Figure 4.

In the second stage, Am and Cm isotopes were separated via extraction by 0.2M HDEHP from the diluted (0.005M)  $\text{HNO}_3$  solution.  $^{148}\text{Gd}$  was used both as a tracer of the radiochemical yield and for correcting the peak shift. The spectrum deconvolution for this step is shown in Figure 5. The concentrations of  $\alpha$  emitters obtained using liquid extraction, LSC, and spectra processing with RadSpectraDec software were in good agreement with results obtained by semiconductor  $\alpha$  spectrometry. However, the former approach, unlike traditional  $\alpha$  spectrometry, provides information about the radioactive pollution in only a few hours. All data obtained are summarized in Table 2.

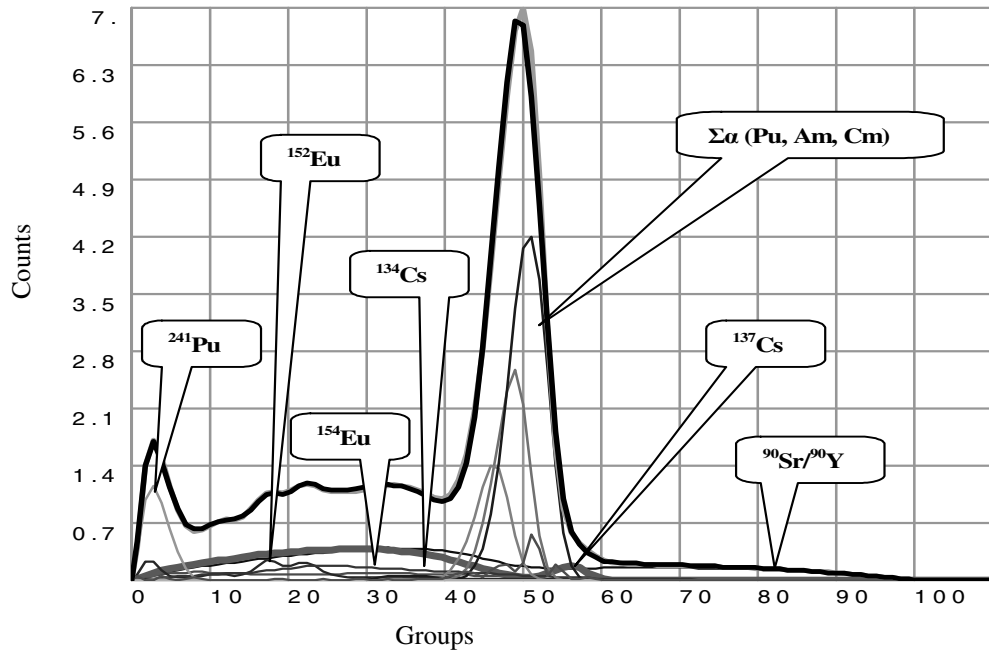


Figure 3 Total LS spectrum of a soil sample from a local radioactive spot using RadSpectraDec

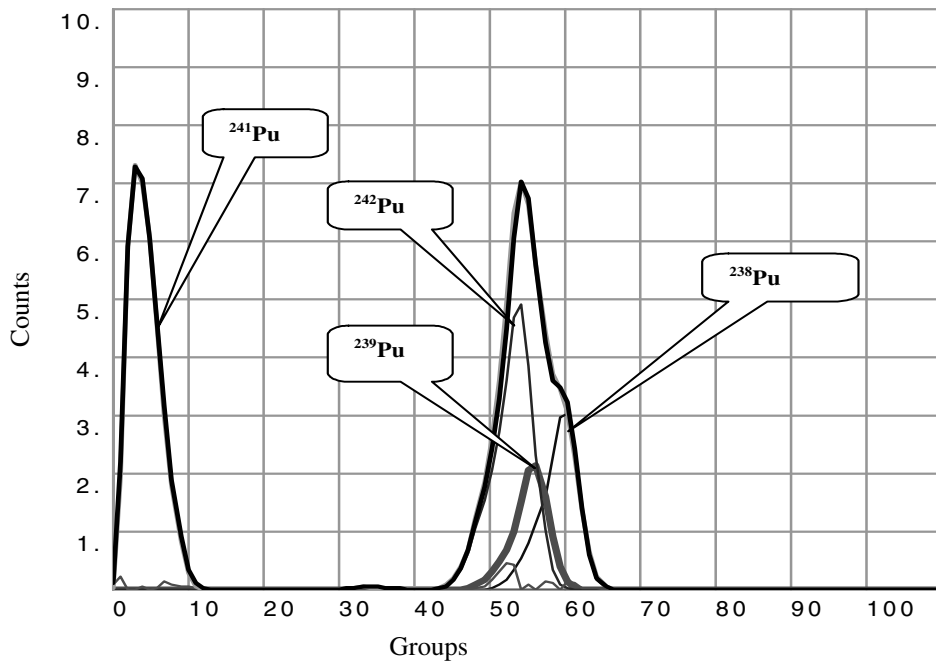


Figure 4 Spectrum deconvolution of the Pu fraction using RadSpectraDec ( $^{242}\text{Pu}$  tracer)

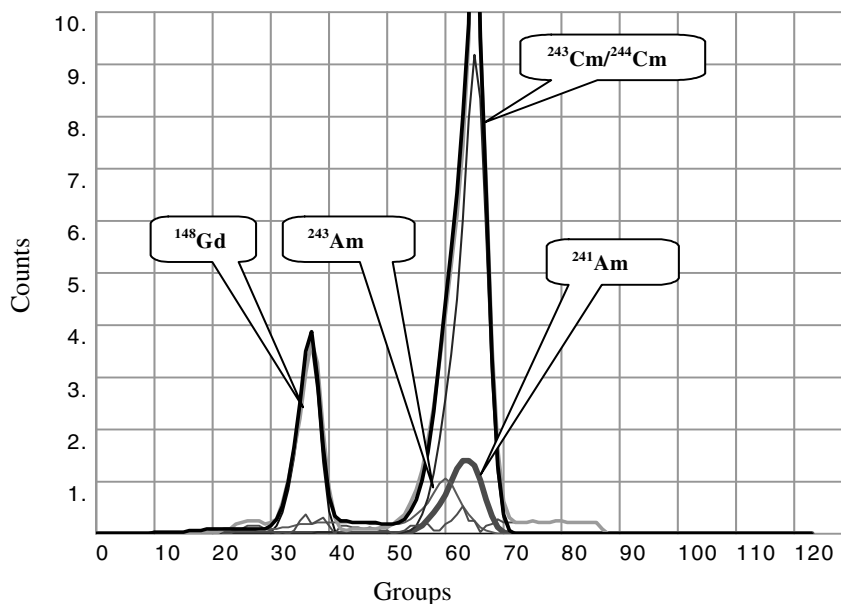
Figure 5 Spectrum deconvolution of Am/Cm fraction using RadSpectraDec ( $^{148}\text{Gd}$  tracer)

Table 2 Results of comparative analysis of the radioactive soil sample.

Radionuclide composition	Activity (Bq/sample)	
	LS spectrometry, RadSpectraDec software	Semiconductor $\alpha$ spectrometry
<b>Pu fraction</b>		
$^{238}\text{Pu}$	$750 \pm 150$	$890 \pm 44$
$^{239}\text{Pu}$	$640 \pm 128$	$500 \pm 50$
$^{241}\text{Pu}$	$1200 \pm 120$	—
<b>Am/Cm fraction</b>		
$^{241}\text{Am}$	$1400 \pm 420$	$1500 \pm 150$
$^{243}\text{Am}/^{239}\text{Np}$	$830 \pm 250$	$1100 \pm 80$
$^{243}\text{Cm}/^{244}\text{Cm}$	$280 \pm 84$	$370 \pm 25$

It must be noted that unexpected shifts of the spectra (in comparison with the created analytical database) may occur in the real mixtures of  $\alpha$ -emitting radionuclides. These shifts may cause the RadSpectraDec software to incorrectly identify the  $\alpha$  emitters. We used “exotic” radionuclides, such as  $^{147}\text{Sm}$  (E-2.25 MeV) or  $^{148}\text{Gd}$  (E-3.18 MeV), for correcting the peak location and quenching value (Kashirin et al. 2003).

The following example presents a fast analysis of radioactive borosilicate glass (synrock). A few years ago, synrock containing a set of various radionuclides was produced in SIA Radon to study waste containment, but unfortunately the radionuclide composition information was lost. We were asked to determine the radionuclide composition of this glass as soon as possible. In this case, a 2-stage extraction via appropriate liquid complexing agents was performed for separating  $\alpha$  emitters.

In the first stage, the glass was completely dissolved using an acid mixture (HF + HNO<sub>3</sub>), followed by frequent evaporation to dryness. An aliquot was measured on a LS spectrometer and results were processed by RadSpectraDec. It was clear that the main activity of the synrock was due to <sup>137</sup>Cs (4.7 × 10<sup>6</sup> Bq/kg), <sup>90</sup>Sr (1.3 × 10<sup>4</sup> Bq/kg), <sup>60</sup>Co (8.7 × 10<sup>3</sup> Bq/kg), and <sup>134</sup>Cs (3.6 × 10<sup>3</sup> Bq/kg). The total spectrum of the aliquot and its deconvolution is shown in Figure 6.

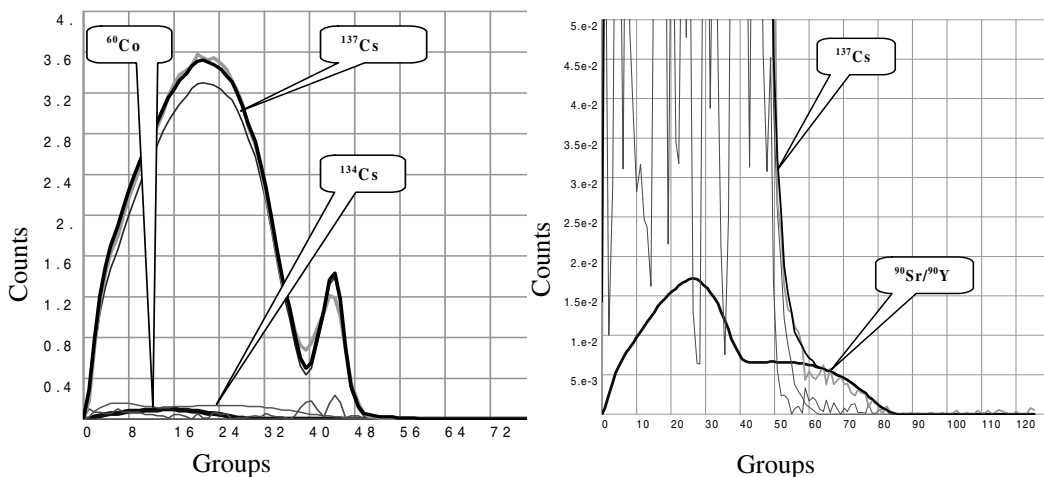


Figure 6 Total LS spectrum of the radioactive glass and its analysis by RadSpectraDec under low (on left) and high (on right) sensitivities.

High activities of <sup>137</sup>Cs and <sup>90</sup>Sr/<sup>90</sup>Y may mask the  $\alpha$ -emitting radionuclides. Thus, in order to separate the latter, we performed liquid-liquid extraction using 0.2M MIOMP from the 1M HNO<sub>3</sub> solution with <sup>242</sup>Pu as a tracer. To better the peak identification, <sup>148</sup>Gd was added to the organic phases after extraction. The extracting properties of MIOMP are similar to the properties of HDEHP for U, Th, Pu, Am, and Cm isotopes. LSC of the MIOMP organic phase, followed by spectrum deconvolution with RadSpectraDec software, revealed mainly Pu isotopes in the mixture (Figure 7, left side). RadSpectraDec software is unable to discriminate between <sup>241</sup>Pu and tritium, but frequent evaporation of the sample to dryness allows one to remove tritium.

The presence of <sup>241</sup>Pu allowed us to assume that its daughter, <sup>241</sup>Am, may also occur in this synrock. Thus, in order to isolate Am and Cm from the residual 1M HNO<sub>3</sub> solution, the liquid-extracting agent DIPEX was used, which, in contrast to HDEHP, can quantitatively extract triple-valent isotopes under such conditions. <sup>148</sup>Gd was used in this experiment for evaluating the extraction recovery, as well as to accurately locate  $\alpha$  peaks (Figure 7, right side). The data obtained by the 2-stage extraction are summarized in Table 3.

The examples given above show the good prospects for applying this approach for quickly analyzing or screening complicated radionuclide mixtures and for eliminating some expensive, time-consuming stages, such as radiochemical separation and electrodeposition specific to semiconductor  $\alpha$  spectrometry.

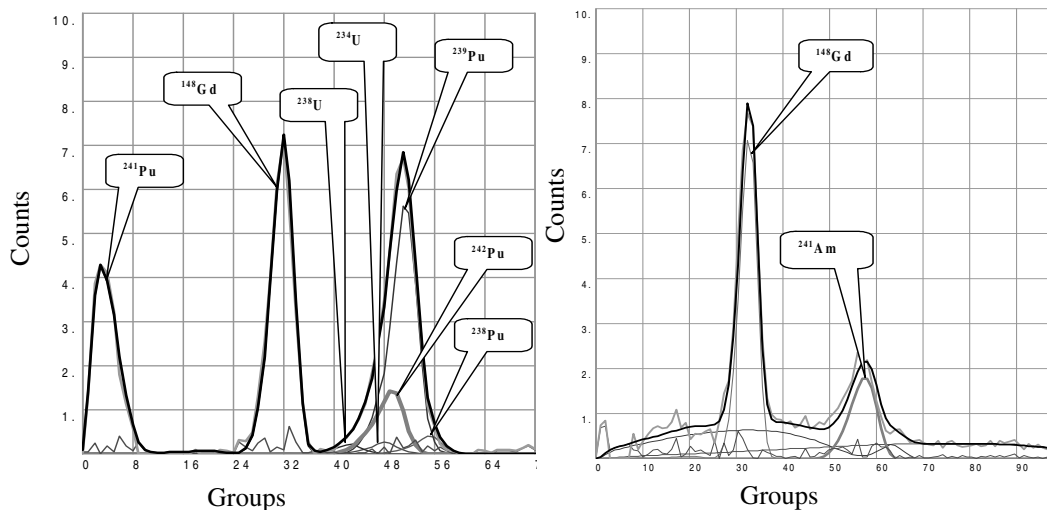


Figure 7 Spectrum deconvolutions of the MIOMP (on left) fraction ( $^{242}\text{Pu}$  tracer for extraction recovery and  $^{148}\text{Gd}$  tracer for quench and shift correction) and the DIPEX (on right) fraction ( $^{148}\text{Gd}$  tracer for recovery and shift correction) using RadSpectraDec.

Table 3 The radionuclide composition of the synrock obtained by extractions and RadSpectraDec processing.

Fraction	Radionuclide composition	Activity (Bq/kg)
U/Pu (MIOMP)	$^{234}\text{U}$	$500 \pm 200$
	$^{234}\text{U}$	$400 \pm 200$
	$^{238}\text{Pu}$	$800 \pm 200$
	$^{239}\text{Pu}$	$12,000 \pm 1200$
	$^{241}\text{Pu}$	$14,000 \pm 1400$
Am/Cm (DIPEX)	$^{242}\text{Pu}$	$900 \pm 200$
	$^{241}\text{Am}$	$4900 \pm 500$

## CONCLUSION

Our approach of combining liquid-liquid extraction, LS spectrometry, and spectrum deconvolution by RadSpectraDec software, makes it possible to identify and quantify  $\alpha$ -emitting radionuclides in complex mixtures. The method was tested with both synthetic mixtures and real samples, and satisfactory results were obtained in comparison with traditional  $\alpha$  spectrometry and X-ray analysis. However, despite the fact that the LS relative resolution of  $\alpha$  peaks is only  $\sim 10\%$  in some cases, the method is sufficient for spectra processing with the RadSpectraDec program. In order to obtain the best results, chemical separation is required. For example, the software is not able to distinguish radionuclides with similar energies, such as  $^{241}\text{Am}$  and  $^{238}\text{Pu}$  or  $^{226}\text{Ra}$  and  $^{234}\text{U}$ . This is the main limitation of RadSpectraDec. Using specific liquid-liquid extractants allows for separating practically all groups of isotopes (Ra, Th, Pu, U, Am, Cm) from complex mixtures. Thus, the use of LS spectrometry followed by RadSpectraDec spectrum processing considerably facilitates and accelerates analysis and can successfully compete with semiconductor  $\alpha$  spectrometry.



## REFERENCES

- Belanov SV, Kashirin IA, Malinovskiy SV, Egorova ME, Efimov KM, Tikhomirov VA, Sobolev AI. 1997. The method of identifying radionuclides with the use of a liquid scintillation counter. RF Patent 2 120 646.
- Belanov SV, Kashirin IA, Malinovskiy SV, Ermakov AI, Efimov KM, Tikhomirov VA, Sobolev AI. 1998. The method of identifying radionuclides with the use of a liquid scintillation counter. RF Patent 98 106 407.
- Dacheux N, Aupiais J. 1997. Determination of uranium, thorium, plutonium, americium and curium ultratraces by photon electron rejecting  $\alpha$  liquid scintillation. *Analytical Chemistry* 69:2275–82.
- Dacheux N, Aupiais J, Courson O, Aubert C. 2000. Comparison and improvement of the determinations of actinide low activities using several  $\alpha$  liquid scintillation spectrometers. *Analytical Chemistry* 72:3150–7.
- Kashirin IA, Ermakov AI, Malinovskiy SV, Belanov SV, Sapozhnikov YuA, Efimov KM, Tikhomirov VA, Sobolev AI. 2000. Liquid scintillation determination of low level components in complex mixtures of radionuclides. *Applied Radiation and Isotopes* 53:303–8.
- Kashirin IA, Ermakov AI, Malinovskiy SV. 2003. LSC: from the routine counter to the real spectrometer. In: Warwick P, editor. Proceedings, 9th International Symposium on Environmental Radiochemical Analysis. Maidstone, UK, 18–20 September 2002. *Environmental Radiochemical Analysis II*:174–84.
- Malinovskiy SV, Kashirin IA, Ermakov AI, Tikhomirov VA, Belanov SV, Sobolev AI. 2002. Mathematical aspects of decoding complex spectra applied to liquid scintillation spectrometry. In: Möbius S, Noakes JE, Schönhofer F, editors. *LSC 2001, Advances in Liquid Scintillation Spectrometry*. Tucson: Radiocarbon. p 127–35.
- McDowell WJ, McDowell BL. 1993. The growth of a radioanalytical method: alpha liquid scintillation spectrometry. In: Noakes JE, Schönhofer F, Polach HA, editors. *Liquid Scintillation Spectrometry 1992*. Tucson: Radiocarbon. p 193–200.
- McDowell WJ. 1996. Recent applications of PERALS<sup>®</sup> spectrometry. In Cook GT, Harkness DD, MacKenzie AB, Miller BF, Scott EM, editors. *Liquid Scintillation Spectrometry 1994*. Tucson: Radiocarbon. p 327–37.