RAPID DETERMINATION OF GROSS ALPHA/BETA ACTIVITY IN MILK USING LIQUID SCINTILATION COUNTER TECHNIQUE

by

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Rapid determination of gross alpha and beta emitters in milk by liquid scintillation counter is discussed. This method is based on direct addition of different types of milk into scintillation cocktail and therefore it is very promising for fast determination of alpha/beta activity due to direct alpha and beta separation, measurement in close 4 geometry and without sample treatment. The selected group of radionuclides was chosen with the respect to military significance, radio-toxicity, and possibility of potential misuse. As model radionuclides ^{241}Am, ^{239}Pu, and ^{90}Sr were selected. The Liquid Scintilation Counter Hidex 300 SL equipped with triple-double-coincidence-ratio technique was used for sample measurement. The aim of the work was focused on comparison of different cocktails produced by Hidex and Perkin Elmer, choosing the best cocktail based on our measurement results and adjustment of its appropriate volume. Furthermore, the optimization of ratio between the volume of scintillation cocktail and the volume of urine was investigated with the respect to the model radionuclides. According to the obtained results, the efficiency for alpha emitters was greater than 85 % and for beta, greater than 95 %. The obtained results allowed this method to be used for rapid determination of gross alpha/beta activity in cases where time is an essence, such as first responders or mass-scale samples, where ordinary means suffer from lack of capacity or simply collapse under the onslaught.

Key words: liquid scintillation, LSC cocktail, milk, americium, plutonium, strontium

INTRODUCTION

Assessment of any major release of radioactivity to the environment, such as NPP accidents or using weapons of mass destruction (WMD), is important for the protection of public health, especially if the released activity can enter the food chain. Such assessment requires a rapid, reliable, and practical measurement technique.

It is generally known that gamma spectrometry, especially low energy gamma spectrometry, is the major technique used for the assay of gamma emitting radionuclides in samples, if a sufficient quantity of a sample is collected. The main disadvantages are problems with overlapping of gamma energy lines, low sensitivity, as well as the self-absorption effect. Both qualitative and quantitative information about gamma emitting nuclides is considered to be the main advantage.

However, for the determination of alpha emitting radionuclides in the environmental samples, the task is much more complicated than for gamma emitting radionuclides. Because of the self-absorption effect of alpha particles by the matrix, complicated sample treatment methods [1, 2], chemical separations and/or extraction step followed by an electrodeposition or (co) precipitation are usually involved [3]. In the event of accidental releases of radioactivity, it is essential for the radiation protection authorities to assess possible contamination in a short time [4]. This method, in comparison with other ways of measurements, is simple, achieves high efficiency and sample throughput and without sample treatment due to direct sample addition which makes it ideal for emergency technique. The main disadvantage is approx. hundred times worse minimum detectable activities (MDA) than using other method [5] based on radiochemical procedures.

In spite of the fact that liquid scintilation counter (LSC) is a laboratory technique, further improvement promises its use as a field technique. From the military point of view, the LSC technique is applicable in the system of stationary and mobile NATO SIRA (sampling and identification of radioactive agent) laboratories [6], where demands on gross alpha and beta analyses are required. The method, in comparison with solid-state alpha spectrometry, is quite simple, effective and relatively without special needs for sample

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treatment. It has also good sensitivity and the measuring time is much shorter than in the case of other methods [7, 8]. Furthermore, a flexibility of LSC is a positive factor as well, as the method is suitable for water/organic solutions, swabs, filters, *etc*. [7-9].

Almost all previously published papers dealing with determination of alpha and beta radionuclides in urine had one thing in common – sample treatment, *e. g*., [10-14] Due to this fact, the purpose of this work was to investigate the possibility of using LSC technique for measurement of simultaneous gross alpha/beta activity of different types of untreated milk samples by direct addition to scintillation cocktail. As model radionuclides ^{241}Am, ^{239}Pu, and ^{90}Sr were selected due to their potential misuse, occurrence in industry and most of all, that they are stated to be military significant radionuclides [6].

MEASUREMENT METHODOLOGY

The measurements were carried out using Automatic TDCR (triple-double-coincidence-ratio) Liquid Scintillation Counter Hidex 300 SL (Hidex, Finland) with 20 ml glass vials with low concentration of ^{40}K and the upper lid with Teflon seal. Scintillation cocktails were obtained from Hidex – AquaLight and MaxiLight and from Perkin Elmer – Ultima Gold, Ultima Gold AB, Ultima Gold MV, Ultima Gold LLT, InstaGel Plus, InstaGel 2 Plus.

The calibration standards of ^{241}Am – ER3 reference material type (5.258 MBq), ^{90}Sr – ER2 reference material type (116.2 kBq) and ^{239}Pu – ER2 reference material type in solution (45.83 kBq) were used for calibration. The ^{239}Pu reference material contained impurities of ^{240}Pu and ^{241}Pu (beta emitter with E_{max} = = 20.8keV and half-life = 13.2 y decaying to ^{241}Am). The abundance of impurities in the reference material at the time of measurement was 4.98 % for ^{241}Pu and 0.56 % for ^{241}Am. All the radionuclides were obtained from CMI – IIZ Prague (CZ) and converted into 0.1 mol.l^{-1} HNO_3 solution.

In order to investigate deviation, which could have been caused by different milk matrix, three types of milk were studied – a standard UHT treated semi-skimmed milk, human breast-milk and fresh cow milk.

The following technique of optimizing the volume and type of LSC cocktail was used: the 5 ml of different types of milk contaminated by the known activities of studied radionuclides were added into 20 ml vials and filled with LSC cocktails of different volumes (5, 10, and 15 ml), well shaken in order to mix LSC cocktail, and finally, measured in "Alpha/beta separation mode". The time of measurement was set to 300 s. The whole process was five times repeated.

The background was measured in the standard geometry with inserted vials, with LSC cocktail and blank samples. The conditions of measurements were the same as with the previous measurement. The background was measured at the beginning, in the middle and at the end of experiments.

RESULTS AND DISCUSSION

At the beginning, the attention was paid to find a suitable cocktail and the criteria were: excellent efficiency for alpha and beta radionuclides, absence of any types of quenching, clogging and finally good alpha/beta discrimination. The procedure was as follows: 5 ml of milk, contaminated by listed radionuclides of known activities, were added to 20 ml scintillation vial and filled with 15 ml of each of the cocktails. Based on our results (tab. 1), two cocktails were found to fulfil given criteria – AquaLight and Ultima Gold AB. On the contrary, both InstaGels and especially MaxiLight were found to be completely insufficient due to clogging and creation of thick white emulsion (fig. 1). The efficiency of MaxiLight reached up to 10 % for alpha radionuclides and up to 60 % (TDCR = 0,7) for beta particles, which was the worst result from all the cocktails.

Subsequently, the influence of cocktails volume was investigated in order to find proper ratio and some deviation, if any. The volume of cocktails varied from 5 ml to 15 ml, in steps of 5 ml. 5 ml of different types of milk contaminated by listed radionuclides of known activities were added to each volume of scintillation cocktail. The results indicated that even 5 ml of cocktail were sufficient to obtain good efficiency. Further volume enhancing brought only slight efficiency improvement (tab. 2). The optimal volume of scintillation cocktail was set to be 15 ml; thus, the ideal ratio was 1:3 in favour of cocktail. The differences among

Table 1. Comparison of detection efficiencies of selected scintillation cocktails and types of milk

Efficiency [%]	Semi-skimmed milk		Breast-milk		Fresh cow milk	
	α	β	α	β	α	β
AquaLight	89 3	95 4	86 5	99 2	85 5	98 2
MaxiLight	8 5	57 5	7 5	59 6	7 5	55 6
Ultima Gold MV	57 8	57 8	56 8	56 8	57 7	57 7
Ultima Gold LLT	82 4	98 3	85 5	99 2	81 6	99 2
Ultima Gold AB	89 3	97 3	89 3	96 3	87 4	98 3
Ultima Gold	56 7	99 3	56 6	97 2	54 7	99 4
InstaGel plus	3 3	99 3	2 2	98 2	5 4	98 3
InstaGel 2 plus	2 2	99 2	1 1	97 3	1 1	97 4

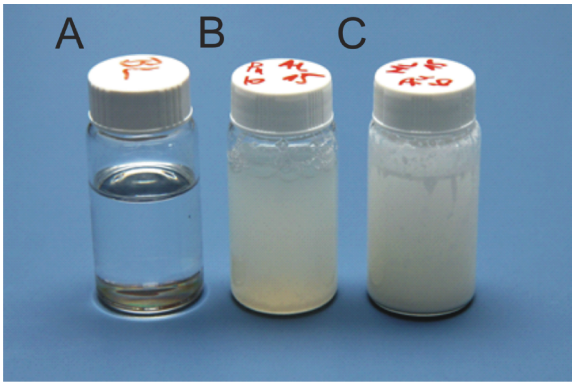

Figure 1. The appearance of scintillation cocktail *(A) blank (clean cocktail without turbidity), (B) milk dissolved in AquaLight (a slightly turbid liquid, no precipitate), (C) milk dissolved in MaxiLight (a highly turbid liquid with precipitate)*

different types of milk were negligible, therefore milk origin and the method of production had no significant effect on measurement efficiency.

After adjusting the volume and its influence to efficiency, all the data were compared, including the purchase price. The most suitable cocktail for direct measurement was AquaLight (Hidex) which was used for further measurements. This cocktail dissolved all types of milk without any problems or distortion, creating a white solution. Surprisingly, this solution had to be transparent for photons, because only a small fraction of photons was quenched. The difference between alpha and beta efficiency was probably caused by imperfect dissolution of milk where alpha radionuclides were bound. Due to a very small mean range of alpha particles in matter, there is no energy transfer to solvent, leading to lower efficiency.

Results of the measurement efficiencies, MDA as well as TDCR, in the selected samples and cocktails, are presented in tab. 3. The spectra of directly measured milk samples using AquaLight cocktail are shown in fig. 2. As TDCR technique deals with quenching, no further calibration was needed. Furthermore, the tray of the instrument greatly saved the

Table 2. The dependence of detection efficiencies for scintillation cocktail volume

Volume of scintillation cocktail [ml]	α efficiency [%] AquaLight	β efficiency [%] AquaLight
5	91	99
10	92	99
15	94	99

Table 3. Observed LSC parameters (efficiency, MDA, TDCR, background counts) for selected radionuclides with an optimal milk to cocktail ratio 1:3

Parameter (AquaLight)	^{241}Am	^{239}Pu	^{90}Sr
Efficiency [%]	94 3	88 4	99 1
MDA [Bql^{-1}]	100	105	450
TDCR	1	1	0.985
Background [s^{-1}]	0.07	0.07	2.45

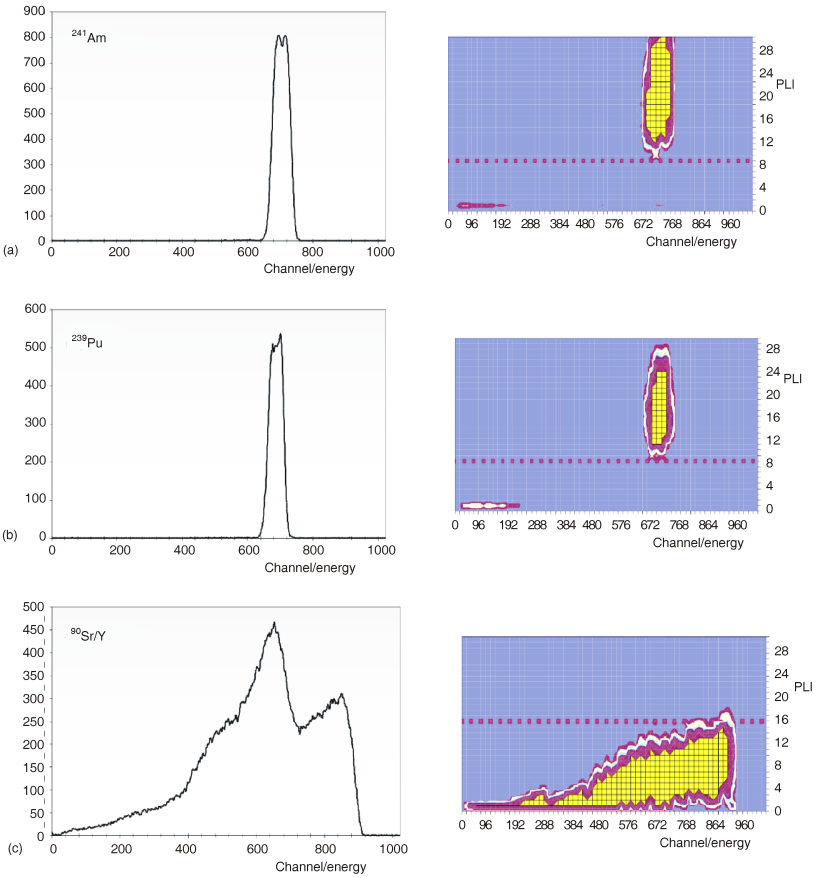

Figure 2. XY spectra and 2-D spectra for selected radionuclides, 5 ml of milk and 15 ml of AquaLight; the colour Z-axis count scale and α/β separation discrimination line; (the horizontal line which divides the graph is called pulse length index "PLI" and the pulses above are registered as alpha, the ones below as beta).

measurement time of large sample series in comparison with Triathler counter. It is clearly seen that by this method very high efficiencies of all radionuclides, exceeding 90 %, were achieved. The highest values of efficiencies were obtained for ^{241}Am and ^{90}Sr, which were 94 3 % and even 99 1 %, respectively.

CONCLUSION

The obtained results show that described LSC method is fast and effective for determination of gross alpha and beta activity of milk samples, as no further (pre)treatment of samples is needed. The main advantage of this method is that it is: virtually freed from sample preparation, fast measurement technique, connected with high efficiency and last but not the least, relatively high sensitivity of measurement. Another advantage of this method and the technique used is: when chemical or colour quenching appeared, at some degree, the TDCR technique is capable of its correction, especially when handling with beta radionuclides.

AUTHORS' CONTRIBUTIONS

The idea for the study was put forward by D. Sas. The measurements and the theoretical calculations were carried out by D. Sas and J. Janda. The data were evaluated and interpreted by J. Janda.

REFERENCES

[1] Janda, J., Microwave Digestion of Hardly Dissoluble Samples, *J. Radioanal. Nucl. Chem., 290* (2011), 3, pp. 637-642
[2] Janda, J., *et al*., Rapid Dissolution of Biological Samples Using Microwave Digestion for Determination of Radionuclide Contamination by Liquid Scintillation, *J. Radioanal. Nucl. Chem., 293* (2012), 1, pp. 223-229
[3] Janda. J., et al., Electrodeposition of Selected Alpha-Emitting Radionuclides from Oxalate-Ammonium Sulfate Electrolyte and Measured by Means of Solid-State Alpha Spectrometry, *J. Radioanal. Nucl. Chem., 286* (2010), 3, pp. 687-691
[4] Yang, D., *et al*., Rapid Method for a-Counting with Extractive Scintillator and Pulse Shape Analysis, *J. Radioanal. Nucl. Chem., 147* (1991), 1, pp. 177-189
[5] Eikenberg, J., *et al*., Rapid Procedure for Screening Transuranium Nuclides in Urine Using Actinide Resin and Low Level a/b-LSC, *Radioact. Radiochem., 10* (1999), 3, pp. 19-30
[6] ***, Standardization Agreement – STANAG 4590, Sampling and Identification of Radiological Agents (SIRA), NATO, Brussels, 2000
[7] Lannunziata, M. F., Handbook of Radioactivity Analysis, 3nd ed., Elsevier, New York, USA, 2012, 566-596
[8] Ross, H., *et al*., Liquid Scintillation Counting and Organic Scintillators, Lewis Publishers, Chelsea, Mich., USA, 2001
[9] Lee, M. H., *et al*., Measurement of ^{90}Sr in Aqueous Samples Using Liquid Scintillation Counting with Full Spectrum DPM Method, *Appl. Radiat. Isot*., *57* (2002), 2, pp. 257-263
[10] Bem, H., *et al*., Rapid Method for the Determination of Strontium-90 in Powdered Milk, *J. Radioanal. Nucl. Chem., 14* (1991), 7, pp. 263-268
[11] Spasova, Y., *et al*., European Measurement Comparison of ^{137}Cs, ^{40}K, and ^{90}Sr in Milk Powder, *J. Radioanal. Nucl. Chem., 277* (2008), 1, pp. 211-215
[12] Chung, K. H., *et al*., Rapid Determination of Radiostrontium in Milk Using Automated Radionuclides Separator and Liquid Scintillation Counter, *J. Radioanal. Nucl. Chem., 304* (2015), 1, pp. 293-300
[13] Douglas, M., *et al*., Liquid Scintillation Counting of Environmental Radionuclides: A Review of the Impact of Background Reduction, *J. Radioanal. Nucl. Chem., 307* (2016), 3, pp. 2495-2504
[14] Lin, Z., *et al*., Rapid and Simultaneous Detection of Alpha/Beta Radioactivity in Food by Solid Phase Extraction Liquid Scintillation Counting, *J. Radioanal. Nucl. Chem*., *307* (2016), 3, pp. 1987-1994

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БРЗО ОДРЕЂИВАЊЕ УКУПНЕ АЛФА И БЕТА АКТИВНОСТИ У МЛЕКУ ПРИМЕНОМ ТЕЧНОГ СЦИНТИЛАЦИОНОГ БРОЈАЧА

У овом раду разматрано је брзо одређивање укупне алфа и бета активности у млеку употребом течног сцинтилационог бројача. Метода је заснована на директном додавању различитих врста млека сцинтилационом коктелу, те има могућност брзог одређивања алфа и бета активности услед директног раздвајања алфа и бета честица, мерења у геометрији блиској 4 и без потребе за третирањем узорка. Радионуклиди су бирани на основу војне употребе, радиотоксичности и потенцијалне злоупотребе. Као модели одабрани су радионуклиди ^{241}Am, ^{239}Pu и ^{90}Sr, а за мерења је коришћен LSC Hidex 300 SL са "трипл-дабл" коинцидентном техником.

Циљ овог рада је усмерен на поређење различитих коктела произведених од стране Hidex-а и Perkin Elmer-а, за избор најбољег на основу резултата наших мерења и на подешавање прикладне запремине коктела. Даље, оптимизован је однос између запремине сцинтилационог коктела и запремине урина у зависности од изабраних модела радионуклида. На основу добијених резултата, ефикасност за алфа емитере је већа од 85 %, а за бета емитере већа од 95 %. Добијени резултати омогућавају примену ове методе за брзо одређивање укупне алфа и бета активности у случајевима када је време од значаја, на пример, код ванредних догађаја, или када су у питању узорци великих размера – када уобичајена средства немају довољно капацитета или отказују.

Кључне речи: течни сцинтилатор, LSC коктел, млеко, америцијум, плутонијум, стронцијум