



An application of LSC method for the measurement of gross alpha and beta activities in spiked water and drinking water samples

Gaye Özgür Çakal,
Rufiyet Güven,
Haluk Yücel

Abstract. In this study, after the pulse shape calibration of a liquid scintillation counting (LSC) spectrometer (Quantulus 1220), the efficiency was determined depending on sample quenching parameters. Then, gross alpha and beta activities in two spiked water samples obtained from International Atomic Energy Agency (IAEA) were used for the validation of the ASTM D7283-06 method, which is a standard test method for alpha and beta activity in water by LSC. Later, the drinking water samples (35 tap water and 9 bottled water) obtained from different districts of Ankara, Turkey, were measured. The maximum gross alpha activities are measured to be 0.08 Bq/L for tap waters and 0.13 Bq/L for bottled waters, whereas the maximum gross beta activities are found to be 0.18 Bq/L for tap waters and 0.16 Bq/L for bottled waters. These results indicate that these drinking water samples are below the required limits, which are 0.1 Bq/L for alpha emitting radionuclides and 1 Bq/L for beta emitting radionuclides. As a result, gross alpha and beta activities in drinking water of Ankara were determined accurately by this validated LSC method. It is also worth noting that LSC is a rapid and accurate method for the determination of gross alpha and beta activities without requiring a tedious sample preparation.

Key words: alpha activity • beta activity • drinking water • liquid scintillation counting (LSC) • pulse shape analysis (PSA) calibration • quench

Introduction

The measurement of radioactivity in water samples is essential for the monitoring of drinking water in view of public health. Gross alpha and beta analyses method is particularly applied to drinking waters. These analyses are used to decide whether further radionuclide analysis is needed or not. If the activities were found to be higher, the radionuclide type and concentration should be determined.

The radiological quality of drinking water is controlled by national and international organizations. According to Environmental Protection Agency (US EPA) (2009), the maximum concentration level (MCL) of gross alpha activity of drinking water is 0.56 Bq/L (15 pCi/L). The activity concentrations of gross alpha and beta were determined as 0.5 Bq/L and 1 Bq/L, respectively, according to World Health Organization (WHO) (2011). European Union in 1998 accepted gross alpha and beta limits as 0.1 and 1 Bq/L, respectively. In Turkey, the EU limits are also adopted according to the national regulations.

In recent years, liquid scintillation counting (LSC) spectrometry is commonly used for the measurement of alpha and beta emitters in environmental samples even if these radionuclides have low activities. Among the known techniques, LSC is preferably used to measure low level radioactivity

G. Ö. Çakal[✉], R. Güven, H. Yücel
Institute of Nuclear Sciences,
Ankara University,
06100, Tandoğan, Ankara, Turkey,
Tel.: +90 532 467 9151, Fax: +90 312 215 3307,
E-mail: gcakal@ankara.edu.tr

Received: 24 September 2014
Accepted: 20 May 2015

since it provides accurate results due to the background reduction features of the instrument. Thus, this results in an improvement in the minimum detectable activity (MDA). LSC also has numerous advantages, such as high efficiencies of detection, simple sample preparation and data processing.

Before counting gross alpha and beta activities in LSC, pulse shape analysis (PSA) is performed to find the optimum PSA value [1–7]. PSA is a separation technique which depends on the method that takes the tail charge of the scintillation pulse into account and compares it with the total charge. Different settings of PSA level categorizes the pulses according to their lengths as long (alpha-like) or short (beta-like) pulse. Typically, increase of the pulse setting locates the pulses into longer ones or alpha category. PSA calibration is done to find out the optimum setting where there is equal and minimum spillover of alpha pulses into the beta MCA and beta pulses into alpha MCA. The main disadvantage during these calibrations is the change of particle energies due to alpha-beta spillover. Real samples may contain alpha-beta emitters at a wide range of varying particle energies. Beta spillover increases with particle energies, but alpha spillover decreases. With increasing quenching high energy beta particles spillover more compared to the low energy ones at the same PSA. *Vice versa* is true for high energy alpha particles. So, quench corrections should be done before the analysis. It is desired to make alpha-beta calibrations with compatible standards, having the average nuclide energies similar to real samples [8].

In this study, PSA and efficiency calibrations together with quench correction were done in the LSC system to determine gross alpha and beta activities of spiked waters, tap and bottled drinking waters according to ASTM D7283-06 [9].

Materials and method

Materials

Two spiked water samples obtained from IAEA (IAEA-TEL-2014-03) and 44 drinking water samples (35 tap water and 9 bottled water) obtained from different districts of Ankara (Turkey) were used in this study. The drinking water samples were prepared for analysis according to the ASTM D7283-06, which is a standard test method for alpha and beta activity in water by liquid scintillation counting. To preserve the samples 1 N HNO₃ was added to obtain pH ≤ 2. The acidification of the samples was done at least 16 hours before the sample preparation, consistent with the standard.

Sample preparation and counting procedure

100 ml of water sample was taken and evaporated to 5 ml on a hot plate in a glass beaker. Background water was also prepared using deionized water. In case of spiked water, 5–35 ml of samples were taken. The residual water was transferred to a tarred glass scin-

tillation vial. The sides of the beaker were washed with a small amount of 0.1 M nitric acid solution, which was also transferred to the vial. The vial was put on a hot plate and the sample was evaporated to dryness. Then, net mass of the residue was recorded. This mass was used as the quench-indicating parameter (QIP). The residue was then dissolved in 5 ml of 0.1 M nitric acid solution on a hot plate without evaporation, while the vial was closed loosely with the cap. After then, 15 ml of scintillation cocktail (Optiphase Hi Safe3) were added to the vial and mixed thoroughly. The samples were counted in Quantulus 1220 (PerkinElmer), liquid scintillation spectrometer, for at least 400 min to measure their gross alpha and gross beta activities.

Calibration sample preparation and LSC system pulse shape analysis calibration

Two standard solutions were prepared in accordance with ASTM D7283-06 standard using ²⁴¹Am and ⁹⁰Sr/⁹⁰Y reference solutions. ²⁴¹Am radionuclide was used as pure alpha, ⁹⁰Sr/⁹⁰Y radionuclide was used as pure beta emitter. 5 ml of these standards solutions, each having approx. 200 Bq activity were put into 20 ml glass vials and mixed with 15 ml of scintillation cocktail (Optiphase Hi Safe3). These standards were counted in LSC for at least 400 min in order to obtain counting statistics with a standard uncertainty of 1% or less at varying discriminator settings, where PSA values ranged between 50 and 140.

Quenched sample preparation and LSC system efficiency calibration

The residue mass was used as the quench-indicating parameter (QIP) and used to represent the dissolved solids in the water sample. To determine the effect of quenching on the efficiency, alpha and beta standard sets together with matrix blank set were prepared. Alpha standard set was prepared to determine the alpha particle detection in alpha region of interest (ROI_α) and alpha particle detection in beta ROI; whereas beta standard set was prepared to determine the beta particle detection in beta ROI (ROI_β) and beta particle detection in alpha ROI. Seven samples containing residue masses between 0 and 200 mg and each having an activity of approx. 200 Bq were prepared. Matrix blank set was prepared in line with the calibration sets by using seven tap water samples containing residue masses between 0 and 200 mg. For each set (alpha/beta/matrix), different amounts of tap water were used and samples were prepared in 20 ml glass vials. 5 ml of deionized water were used to represent 0 (zero) mass standard. ²⁴¹Am alpha and ⁹⁰Sr/⁹⁰Y beta solutions having 200 Bq activities were used for the calibration solutions. These solutions were then mixed with 15 ml of scintillation cocktail (Optiphase Hi Safe3). The vials containing these standards were counted in LSC for at least 400 min using the optimized discriminator setting, where PSA was at 85 channel.

Calibrations in liquid scintillation spectrometer

PSA calibration

In this study, PSA calibration is done by counting the alpha (^{241}Am) and beta ($^{90}\text{Sr}/^{90}\text{Y}$) standard solutions separately at different discriminator settings (PSA values). While counting, the alpha and beta spectra were collected at different parts of the same MCA memory. The misclassification of alpha as beta ($T_\alpha\%$) and beta as alpha ($T_\beta\%$) was calculated using Eqs. (1) and (2). This misclassification values are shown in Fig. 1 depending on PSA values.

$$(1) \quad T_\alpha[\%] = \frac{\text{alpha counts in beta windows}}{\text{total alpha counts}} \times 100$$

$$(2) \quad T_\beta[\%] = \frac{\text{beta counts in alpha windows}}{\text{total beta counts}} \times 100$$

In Fig. 1, alpha to beta spillover and beta to alpha spillover curves are seen. The point at which there is equal and minimum spillover occurs is the crossover point, the optimum PSA setting. At this point, $T_\alpha = T_\beta$, the interference of alpha and beta pulses, which have different heights and shapes, were successfully discriminated. The cross over point was found as 85, for alpha-beta discrimination when the scintillation cocktail, named as Optiphase Hi Safe3 and the ratio of sample to scintillator of 1/3 was used. This PSA parameter was a fixed value throughout the measurements in this study.

The spectra of ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ reference solutions used in PSA calibration were acquired in order to observe the alpha and beta spectra at PSA = 85, Fig. 2. Alpha spectra were evaluated between 400 and 900 channels, whereas beta spectra were evaluated between 250 and 1023 channels of LSC system in order to exclude low energy betas such as ^3H ($E_{\beta\text{max}} = 18.591 \text{ keV}$ (100%)), ^{210}Pb ($E_{\beta\text{max}} = 63.5 \text{ keV}$ (100%)) and ^{14}C ($E_{\beta\text{max}} = 156.476 \text{ keV}$ (100%)) [10]. For instance, in this selected channel range ^{40}K ($E_{\beta\text{max}} = 1.31 \text{ MeV}$ (89%), 1.51 MeV (11%), $\bar{E}_\beta = 0.522 \text{ MeV}$) and ^{137}Cs ($E_{\beta\text{max}} = 1.175 \text{ MeV}$ (5%), 0.510 MeV (95%), $\bar{E}_\beta = 0.186 \text{ MeV}$) are included [11]. In fact, this is deemed as a deviation from the ASTM-D7283 standard because the standard recommends the beta energy range as 0–2000 keV for ROI selection corresponding to 5–1023 channel.

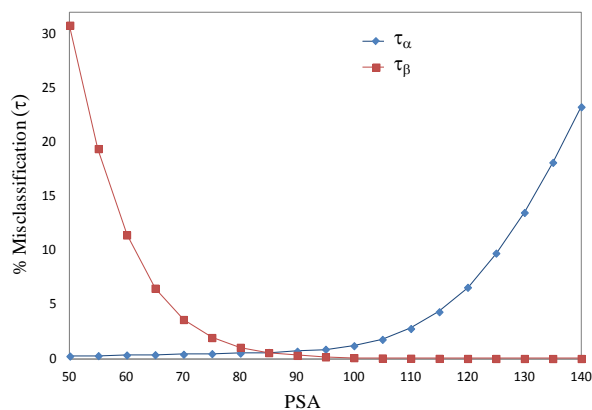


Fig. 1. PSA calibration of liquid scintillation spectrometer.

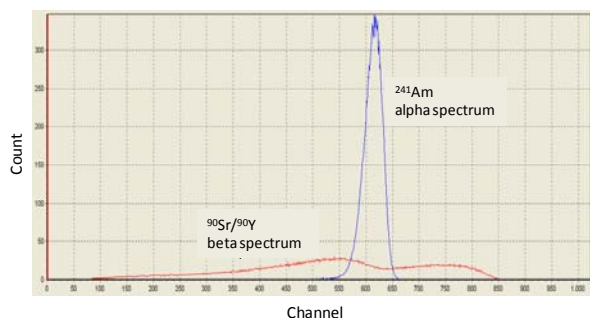


Fig. 2. The spectra of ^{241}Am and $^{90}\text{Sr}/^{90}\text{Y}$ reference solutions at PSA = 85.

In this study, low energy beta emitting radionuclides having mean energies below 60 keV were excluded due to the abovementioned explanations.

As seen from the spectra in Fig. 2, there are two peaks in the beta spectrum, which are due to ^{90}Sr ($\bar{E}_{\beta\text{max}} = 0.546 \text{ MeV}$ (100%)) and ^{90}Y ($\bar{E}_{\beta\text{max}} = 2.28 \text{ MeV}$ (100%)), respectively. This is the fact that the beta particle has a zigzag path and a continuous energy spectrum, when compared to that of an alpha particle with a relatively heavy mass and greater charge. Beta particle pulses are normally much smaller than those induced by alpha particles of equivalent kinetic energy and will also cover a broader range of amplitude because of the spread in the beta particle energies and the variations in possible paths in the medium [12]. However, only one alpha peak is seen in the spectrum for ^{241}Am radionuclide ($E_{\alpha 1} = 5.443 \text{ MeV}$ (13.23%) and $E_{\alpha 1} = 5.486 \text{ MeV}$ (84.45%) due to LSC system energy resolution. This is because the alpha particles are monoenergetic and they have short ranges in the medium. Thus, they are slightly deflected in the material and have smooth paths.

Detection efficiency calibration

For gross alpha and beta measurement in liquid scintillation spectrometer, the efficiency calibration was done to determine alpha particle detection efficiency in ROI $_\alpha$, $\epsilon_{\alpha\alpha}$; alpha particle detection efficiency in beta region of interest (ROI $_\beta$), $\epsilon_{\alpha\beta}$; beta particle detection efficiency in ROI $_\beta$, $\epsilon_{\beta\beta}$, and beta particle detection efficiency in ROI $_\alpha$, $\epsilon_{\beta\alpha}$.

The alpha and beta standard sets together with the matrix blank set were measured at PSA = 85 for at least 400 min and spectrum analyses were performed. The spectra obtained from LSC are given in Figs. 3 and 4 for alpha and beta standard sets, respectively.

As seen from Figs. 3 and 4, the sample residue mass, which was used as the quenching agent, affected the view of the spectra. As the sample residue mass was increased, there were losses from the energy and counts as expected. Thus, the spectra shifted left causing efficiency losses. Four detection efficiencies, $\epsilon_{\alpha\alpha}$, $\epsilon_{\alpha\beta}$, $\epsilon_{\beta\beta}$ and $\epsilon_{\beta\alpha}$, were calculated by using the count rates obtained from the alpha and beta blank sets (Figs. 3 and 4) and matrix blank set at different residue masses. For alpha calibration vials, $\epsilon_{\alpha\alpha}$, $\epsilon_{\alpha\beta}$ and for beta calibration vials $\epsilon_{\beta\beta}$, $\epsilon_{\beta\alpha}$ were calculated.

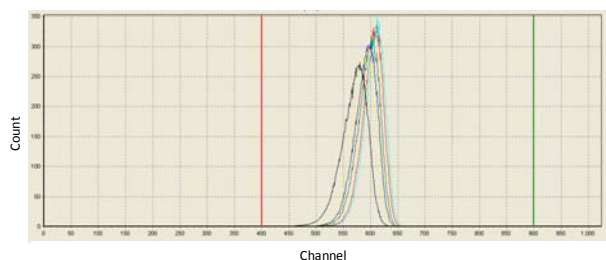


Fig. 3. Spectra of alpha standard set having different quench levels obtained in liquid scintillation spectrometer.

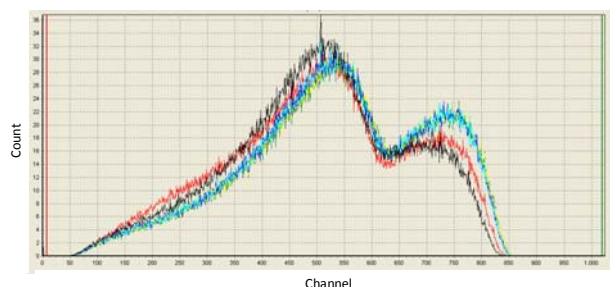


Fig. 4. Spectra of beta standard set having different quench levels obtained in liquid scintillation spectrometer.

As in Figs. 5–8, the variation of alpha and beta efficiency depending on sample residue masses were fitted to a polynomial. In gross alpha and beta measurement, by using these fits, the efficiency values were calculated for the sample residue mass.

Results and discussion

Ideally, the water samples should be prepared similar to a standard, that is, same volume, composition, turbidity and cocktail and vial type [13]. Since real samples have different quench levels compared to

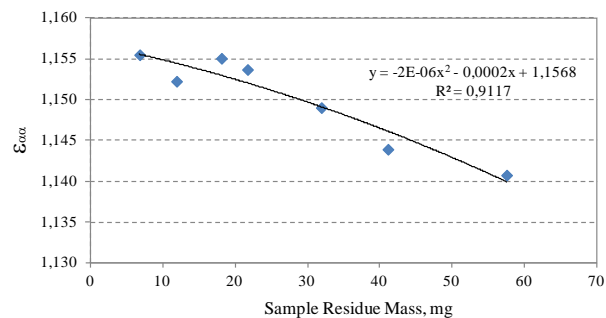


Fig. 5. The alpha particle detection efficiency as a function of sample residue mass in ROI_α.

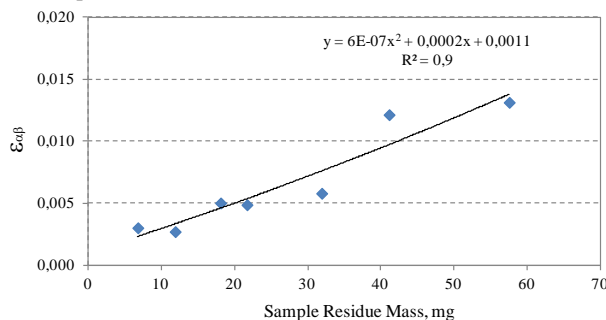


Fig. 6. The alpha particle detection efficiency as a function of sample residue mass in ROI_β.

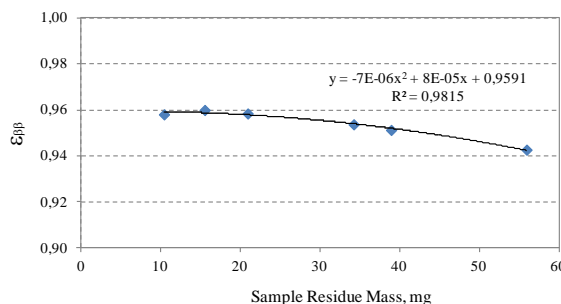


Fig. 7. The beta particle detection efficiency as a function of sample residue mass in ROI_β.

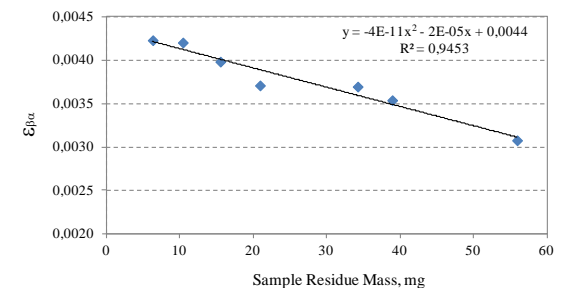


Fig. 8. The beta particle detection efficiency as a function of sample residue mass in ROI_α.

standards, the quenching of the standards should be modified to represent real samples. As an example, a tap water sample spectra is shown in Fig. 9. As there was sample quenching, spillover correction were done.

The percentage spillover factors are shown in Fig. 10 as a function of sample residue masses. From Fig. 10, optimum residue mass was found as 20 mg, at which the spillover factors equate. While performing gross alpha and beta analysis, the samples were prepared from the water volumes which will give approximately this residue mass. Percentage spillover

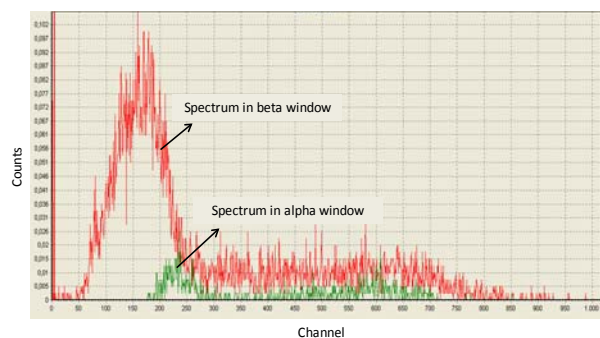


Fig. 9. Tap water sample (M-35) spectra obtained in liquid scintillation spectrometer.

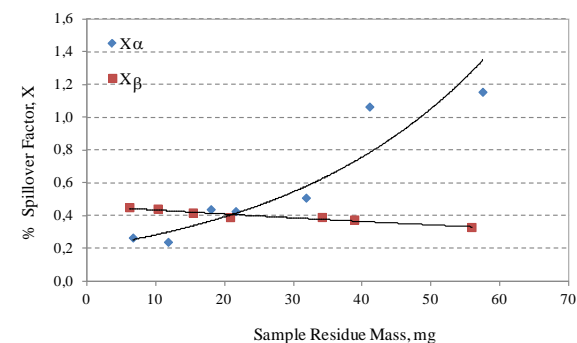


Fig. 10. Percentage alpha and beta spillover factors as a function of sample residue mass.

Table 1. Gross alpha and beta activities of spiked water samples

Sample code	Activities [Bq/L]		IAEA Proficiency Test* Activities [Bq/L]	
	Alpha	Beta	Alpha	Beta
IAEA-01	35.49 ± 1.90	116.51 ± 5.52	34 ± 13	101 ± 36
IAEA-03	84.12 ± 3.36	131.18 ± 5.96	Known activity control sample	

* IAEA-TEL-2014-03.

Table 2. Gross alpha and beta activities of tap water samples

Sample code	Activities [Bq/L]	
	Alpha	Beta
M-1	< MDC _α	0.15 ± 0.06
M-2	< MDC _α	0.14 ± 0.06
M-3	< MDC _α	< MDC _β
M-4	< MDC _α	0.15 ± 0.06
M-5	< MDC _α	0.12 ± 0.06
M-6	< MDC _α	< MDC _β
M-7	< MDC _α	0.14 ± 0.06
M-8	< MDC _α	< MDC _β
M-9	< MDC _α	0.13 ± 0.06
M-10	< MDC _α	< MDC _β
M-11	< MDC _α	< MDC _β
M-12	< MDC _α	0.15 ± 0.06
M-13	< MDC _α	< MDC _β
M-14	< MDC _α	< MDC _β
M-15	< MDC _α	< MDC _β
M-16	< MDC _α	0.15 ± 0.06
M-17	< MDC _α	< MDC _β
M-18	< MDC _α	< MDC _β
M-19	< MDC _α	< MDC _β
M-20	< MDC _α	< MDC _β
M-21	< MDC _α	< MDC _β
M-22	< MDC _α	0.18 ± 0.07
M-23	< MDC _α	< MDC _β
M-24	< MDC _α	< MDC _β
M-25	< MDC _α	< MDC _β
M-26	< MDC _α	< MDC _β
M-27	< MDC _α	< MDC _β
M-28	< MDC _α	< MDC _β
M-29	< MDC _α	< MDC _β
M-30	< MDC _α	< MDC _β
M-31	< MDC _α	0.13 ± 0.02
M-32	< MDC _α	< MDC _β
M-33	< MDC _α	< MDC _β
M-34	< MDC _α	< MDC _β
M-35	0.08 ± 0.01	0.13 ± 0.02

Table 3. Gross alpha and beta activities of bottled water samples

Sample code	Activities [Bq/L]	
	Alpha	Beta
T-1	< MDC _α	< MDC _β
T-2	0.03 ± 0.01	< MDC _β
T-3	0.07 ± 0.01	< MDC _β
T-4	< MDC _α	< MDC _β
T-5	0.03 ± 0.01	< MDC _β
T-6	< MDC _α	0.16 ± 0.03
T-7	< MDC _α	< MDC _β
T-8	0.13 ± 0.01	< MDC _β
T-9	0.12 ± 0.01	< MDC _β

factors were calculated as a function of the sample residue mass, which were used during the alpha and beta activities.

In the present LSC system, the minimum detectable concentrations (MDC) of the activity are calculated based on the background count rate, B [cpm] in the selected channel window as follows:

$$(3) \text{ MDC [Bq/L]} = 16.7 \times \frac{\left[3.29 \cdot \sqrt{B \cdot t_s \cdot \left(1 + \frac{t_s}{t_b} \right)} + 3 \right]}{t_s \cdot \varepsilon \cdot V}$$

where 16.7 is a conversion factor from count per minute [cpm] to activity [Bq] and from sample volume in mL into L. t_s is sample count time [min], t_b is background count time [min], ε is counting efficiency [cpm/dpm] and V is sample volume [mL].

The minimum detectable concentrations were found to be $\text{MDC}_\alpha = 0.02$ Bq/L for alpha measurements, and $\text{MDC}_\beta = 0.11$ Bq/L for beta measurements. The gross alpha and beta activities for spiked waters are given in Table 1, tap waters in Table 2 and bottled waters in Table 3.

As seen in Table 2, gross alpha and beta activities of tap water samples were mostly below the limit values. Even, nearly all of the gross alpha activities were below MDC_α value. As the activities were found to be low, lower count statistics was attained. Due to this reason, the uncertainties of activity concentrations were found to be higher, that is, in order of max. 30–50%. These uncertainties can be expected for the very low activities in water samples. Besides, the gross alpha and beta activities of bottled water samples, Table 3, were also found to be below the allowed limits.

Conclusions

In this study, PSA and efficiency calibrations together with quench correction were done in a LSC system to determine gross alpha and beta activities of spiked waters, tap and bottled drinking waters according to ASTM D7283-06.

- It was observed that the efficiencies changed somehow depending on the quenching agent, in this case sample residue mass.
- For the validation of ASTM standard method using a LSC system, the activity results are measured as 35.49 ± 1.90 Bq/L for alpha activity and 116.51 ± 5.52 Bq/L for beta activity in spiked water samples of IAEA-01. They are consistent with the proficiency test results of IAEA-TEL-2014-03.
- The measured gross alpha and beta activities in drinking waters are found to be below the required limits.

Acknowledgments. This study was supported by Ankara University via project no. 12A4045001 and 12A4045002.

References

1. Warwick, P. E., & Croudace, I. W. (2002). Measurement of gross alpha and beta activities in acid leachates using alpha-beta discriminating liquid scintillation counting. In S. Möbius, J. Noakes & F. Schönhofer (Eds), Proceedings of the International Conference LSC 2001 Advances in Liquid Scintillation Spectrometry, 7–11 May 2001 (pp. 75–82). Karlsruhe, Germany.
2. Rusconi, R., Forte, M., Caresana, M., Bellinzona, S., Cazzaniga, M. T., & Sgorbati, G. (2006). The evaluation of uncertainty in low-level LSC measurements of water samples. *Appl. Radiat. Isot.*, *64*, 1124–1129.
3. Sanchez-Cabeza, J. A., Pujol, L., Merino, J., Leon, L., Molero, J., Vidal-Quadras, A., Schell, W. R., & Mitchell, P. I. (1992). Optimization and calibration of a low-background liquid scintillation counter for the simultaneous determination of alpha and beta emitters in aqueous samples. In J. E. Noakes, F. Schönhofer & H. A. Polach (Eds), Proceedings of the International Conference LSC 2001 Advances in Liquid Scintillation Spectrometry, 14–18 September 1992 (pp. 43–50). Vienna, Austria.
4. Zapata-Garcia, D., Laurado, M., & Rauret, G. (2012). The implications of particle energy and acidic media on gross alpha and beta determination using liquid scintillation. *Appl. Radiat. Isot.*, *70*, 705–711.
5. Todorovic, N., Nikolov, J., Tenjovic, B., Bikit, I., & Veskovic, M. (2012). Establishment of a method for measurement of gross alpha/beta activities in water from Vojvodina region. *Radiat. Meas.*, *47*, 1053–1059.
6. Lin, C. -F., Wang, J. -J., Huang, J. -C., Yeh, C. -H., Yuan, M. -C., & Chang, B. -J. (2012). Evaluating practicability of an LSC method for routine monitoring gross alpha and beta activities in water samples in Taiwan. *Appl. Radiat. Isot.*, *70*, 1981–1984.
7. Abdellah, W. M. (2013). Optimization method to determine gross alpha-beta in water samples using liquid scintillation counter. *J. Water Res. Prot.*, *5*, 900–905.
8. Salonen, L., Kaihola, L., Carter, B., & Cook, G. T. (2012). Environmental liquid scintillation analysis. In M. F. L'Annunziata, *Handbook of radioactivity analysis*, 3rd ed. (pp. 626–693). USA: Elsevier.
9. ASTM. (2006). ASTM Standard Test Method for Alpha and Beta Activity in Water by Liquid Scintillation Counting. West Conshohocken, PA. (ASTM D7283-06).
10. Nucleide. (2015). LARA database, laraweb.free.fr (last accessible date: 24.02.2015).
11. Kleinschmidt, R. I. (2004). Gross alpha and beta activity analysis in water – a routine laboratory method using liquid scintillation analysis. *Appl. Radiat. Isot.*, *61*, 333–338.
12. Knoll, G. F. (2000). *Radiation detection and measurement*, 3rd ed. (pp. 185). New York: John Wiley and Sons.
13. Palomo, M., Villa, M., Casacuberta, N., Penalver, A., Borrull, F., & Aguilar, C. (2011). Evaluation of different parameters affecting the liquid scintillation spectrometry measurement of gross alpha and beta index in water samples. *Appl. Radiat. Isot.*, *69*, 1274–1281.