



Calibration and optimization of alpha-beta separation procedures for determination of radium/radon in single- and two-phase liquid scintillation systems

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Abstract

Liquid scintillation alpha beta discrimination technique based on pulse shape analysis (PSA) was evaluated for determination of ^{226}Ra and ^{222}Rn in water samples. In view of the significance of calibration, for the reliable and precise determination of ^{226}Ra and ^{222}Rn concentrations in water samples, calibration procedures were standardized for single and two phase systems using Quantulus 1220 liquid scintillation counter. PSA optimization and efficiency calibrations were performed using ^{226}Ra standard rather than conventionally used pure alpha and beta standards and substantiated by measuring the activity concentrations of ^{226}Ra and ^{222}Rn in the spiked water samples.

Keywords ^{226}Ra and ^{222}Rn in water · Quantulus 1220 liquid scintillation counter · Pulse shape analysis (PSA) · Single and two phase counting systems

Introduction

Liquid scintillation counting (LSC) is a preferred analytical method for quantification of beta as well as alpha emitters in water samples due to ease of sample preparation, no self absorption effects and nearly 100% counting efficiencies for alpha. Radon (^{222}Rn) and radium (^{226}Ra) are probably the most commonly assayed isotopes by α/β LSC [1]. LSC provides a very simple and time saving method that avoids the need for any chemical separation for the determination of both ^{222}Rn and ^{226}Ra in water [2].

^{226}Ra originates from the natural decay series of ^{238}U and is a long-lived radionuclide ($t_{1/2}$ – 1600 years) that decays by emitting alpha particles with energies of 4.60 and 4.78 MeV to ^{222}Rn , accompanied with an γ emission of 186.2 keV (3.59%). The interest in the determination of ^{226}Ra comes not only from the radiation protection

concern, but also from its application as environmental tracer [3]. LSC is extensively used for determination of ^{226}Ra by measuring its alpha emitting daughters, ^{222}Rn , ^{218}Po , ^{214}Po or beta-emitting daughters ^{214}Bi and ^{214}Pb , after attaining secular equilibrium. However, the detection limit by measuring alpha emitters is much better than that of beta emitters, because of the low background in the alpha counting region and the high counting efficiency (> 95%) [3]. Moreover, ^{214}Po may be used alone to quantify the ^{226}Ra or ^{222}Rn , as it forms a distinct, well separated peak from composite peak of ^{226}Ra , ^{222}Rn and ^{218}Po [4, 5].

The LSC method for direct determination of radium involves procedures in which either water sample is mixed with a immiscible organic cocktail (such as toluene) to form a two phase system [6] where ^{226}Ra can be measured via ^{222}Rn and its progeny [5, 7] or by mixing water in equal proportions with miscible cocktail to form a homogeneous (single phase) or semi-homogeneous sample in a scintillation vial [8].

In view of significance of calibration for the reliable and precise determination of radium concentrations in water samples, alpha beta discrimination procedures were standardized for both, the single and two phase systems using Quantulus 1220 liquid scintillation counter (LSC) coupled

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with pulse shape analysis (PSA) circuitry. Quantulus LSC, enables discrimination of alpha and beta events, using PSA technique which is based on the fact that alpha-induced pulses decay more slowly than beta induced pulses [9]. Usually, according to sample type, composition, type of vial and scintillation cocktail used, the PSA has to be set for each one to achieve the optimum separation of alpha and beta particle spectra [10].

Usually to optimize the PSA setting, a pure alpha (^{214}Am) and a pure beta standards (^{36}Cl or $^{90}\text{Sr}/^{90}\text{Y}$) are measured independently and scanned at various PSA levels. In view of the fact that the most accurate results are obtained when both PSA calibration and measurements of actual samples are carried out with identical radionuclide energies, there is a reasonable assumption that ^{226}Ra standard as alpha emitter could better fit into PSA adjustment instead of ^{241}Am for ^{222}Rn determination experiments [11, 12]. This was the reason to believe that ^{226}Ra would be the ideal alpha standard and its beta progeny as beta standard source for calibrating LSC. However, Stojković reported in her work the limitations while working with ^{226}Ra as an alpha standard [12]. ^{241}Am along with $^{90}\text{Sr}/^{90}\text{Y}$ gave much lower spillover (< 5%) [13], on the contrary, when ^{226}Ra was used as mixed α/β standard for PSA calibration, beta spillover was observed to be $\sim 30\%$. Therefore a thorough study was conducted to review the calibration procedure using ^{226}Ra as mixed α/β standard so that the anomalies reported in the earlier studies would be addressed in detail. The objective of the study was to examine the effect of quenching on the LSC calibration and to standardize alpha beta discrimination procedures for single and two phase counting systems for radium/radon measurements in water samples.

Experimental

Measurements were carried out using Quantulus 1220 LSC. It is specifically designed for the determination of very low activities, using both an anticoincidence active and a passive shield and low background construction Materials [14]. Moreover, Quantulus LSC is equipped with a guard counter that helps to reduce background count rates by providing active shielding against cosmic particles and environmental gamma radiation [15]. It has inclusive spectral analysis capability and two dual programmable multi channel analyzers (MCAs) in which alpha and beta events are stored separately. Pulse shape Analyzer is a software adjustable parameter (PSA parameter) which can vary between 1 and 256 and separates alpha and beta events in different MCAs at an optimal PSA setting. In Quantulus, setting the PSA level by software, it is possible to route beta events into one half of the MCA (SP11)

namely β -MCA and alpha events into other half (SP12) namely α -MCA. Using net count rates in alpha and beta MCAs, spillover of alpha in β -MCA and beta in α -MCA is calculated. When no PSA setting is used, all events are stored in α -MCA (SP12). As PSA values are scanned, some events from α -MCA start registering into the β -MCA. At an optimum PSA setting, alpha and beta events can be discriminated with minimum spillover of beta events in α -MCA and alpha events in β -MCA. The PSA setting at which the spillover is minimum is selected as optimized PSA [13].

In LSC technique, counting efficiencies get affected by an interfering process known as quenching, that results in poor conversion rate of deposited radiation energy to light. To determine absolute sample activity in disintegrations per minute (DPM absolute activity), it is essential to quantify the level of sample quench, and then make the corrections for the reduction in counting efficiencies. In Quantulus 1220, SQP(E), spectral quench parameter of the external standard, denotes the level of sample quenching using ^{152}Eu as an external standard that is inbuilt in the instrument [15].

In the present study, the optimal PSA setting was determined experimentally by measurement of a set of unquenched and quenched calibration standards of ^{226}Ra . ^{226}Ra was used as a mixed α/β calibration standard that was prepared from a standard solution having specific activity 1200 Bq/g and an overall uncertainty of $\pm 3.2\%$. Dilutions were made in 0.1 M HCl to attain the final solution (10 Bq/g) for the calibrations. Two sets of ^{226}Ra standards were prepared, in which the absolute activity (10 Bq) per vial was constant. In the first set, 11 ml of spiked water was mixed with equal amount of immiscible, organic toluene scintillation cocktail in glass vials. Thus vials were filled completely without any air gap for efficient transfer of radon in toluene. The water immiscible toluene based scintillation cocktail was prepared in our lab by adding 120 g of naphthalene and 4 g of PPO (2,5 diphenyl oxazole) to 1 l of Toluene. In the second set, water samples spiked with ^{226}Ra (activity: 10 Bq) was mixed with commercially available di-isopropyl naphthalene (DIN) based Optiphase HiSafe-III scintillation cocktail (12 ml) in glass vials. To the vials in both sets, an incremental amount of quenching agent, nitro-methane was added to obtain the required range of quench. After preparation, the standards and background samples were sealed and stored for 3 weeks in the dark at 10 °C for best stability and for the establishment of equilibrium. During that time, ^{226}Ra attained equilibrium with radon and its short-lived daughters and any indoor radon, which might have entered the vial during the sample preparation, would have decayed completely [16]. After a month, standards were counted for 30 min and sample spectrum was

generated in log scale, counting region (ROI) for alpha events was selected by visual inspection of the spectral peaks can be seen at right of the energy spectrum (Fig. 1). For each quenched ^{226}Ra standard, quench indicating parameter, SQP(E) was noted and optimal PSA setting was determined.

In order to ensure the efficacy of the calibration procedure, series of water samples, spiked with known activity of ^{226}Ra standard solutions with varying levels of quenching was prepared. Quenching was introduced by adding different amounts (10–100 μl) of nitro methane. The ^{226}Ra activity was varied from 50 mBq to 2 Bq in these sets. Two sets were made out of these spiked samples, the samples in the first set, were prepared using miscible cocktail forming single phase system (containing 12 ml cocktail and 8 ml sample) while the samples in another set, were mixed with immiscible organic toluene scintillator in glass vials (contained 11 ml toluene cocktail and 11 ml sample). The sets were preserved for nearly 3 weeks. Later the samples were subjected to counting by following the respective standardized calibration procedures and activity was deduced using the count rate and by applying corresponding alpha efficiencies from the quench calibration plots.

Results and discussion

The spectra of ^{226}Ra in equilibrium with its alpha and beta progeny, that grew a month later sample preparation, are illustrated in Fig. 1. The alpha spectrum presents ^{226}Ra and its short lived daughters ^{222}Rn , ^{218}Po and ^{214}Po while beta spectrum shows a continuum comprising ^{214}Pb , ^{214}Bi and

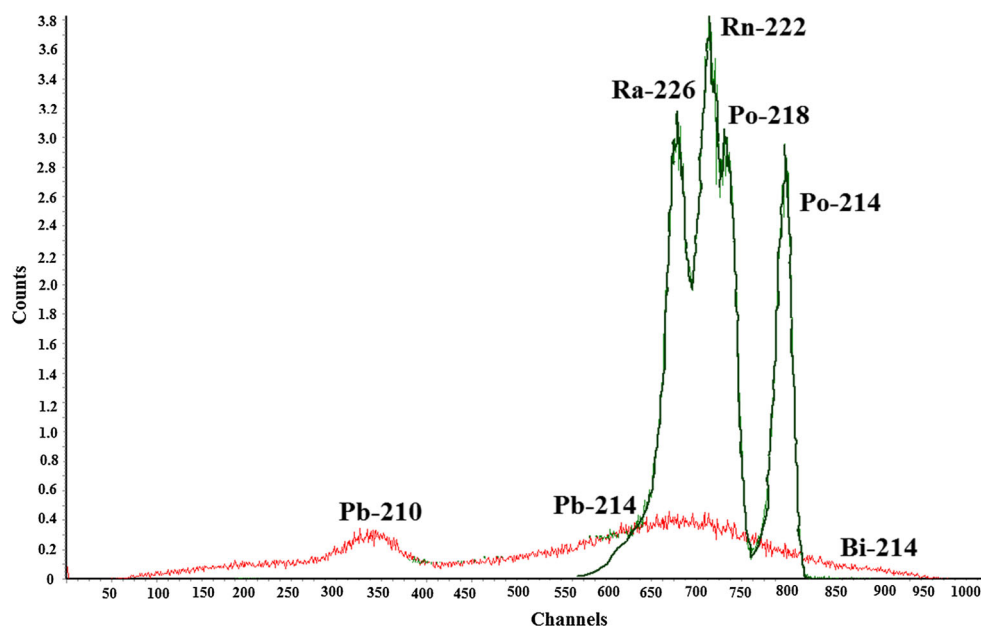
^{210}Pb . Since ^{226}Ra standard that we used was older, a low energy beta emitter ^{210}Pb is also seen in the spectrum. Similar ^{210}Pb peak was reported by Salonen in her study while studying ^{226}Ra spectrum [16].

The x axis in Fig. 1 represents the logarithmic pulse height in terms of channels and Y axis represents counts per channel. As the pulse height depends on many factors such as type of cocktail, vials and sample quenching, LSC has to be calibrated for each of these factors [8].

Criteria for optimization of PSA setting

Theoretically for ^{226}Ra , after accomplishment of equilibrium, the gross counting efficiencies in a single phase homogeneous system (with Optiphase HiSafe-III scintillation cocktail) should be 600%. This includes counting efficiencies of alpha (^{226}Ra , ^{222}Rn , ^{218}Po and ^{214}Po each having 100% efficiency—total 400%) and beta (^{214}Pb and ^{214}Bi —total 200%). Consequently the theoretical α/β ratio should be 2. Whereas for two phase heterogeneous system (with toluene scintillation cocktail specific to ^{222}Rn), the α/β ratio is 1.5 (total 300% alpha counting efficiency, each alpha daughter nuclides, ^{222}Rn , ^{218}Po and ^{214}Po having 100% and beta counting efficiency 200%). However the observed alpha efficiency in case of ^{226}Ra standard did not match with the theoretical one (400%) and hence the α/β ratio, as the distinct ^{214}Po alpha, practically imparted lower efficiency than expected (100% efficiency). The lower efficiency in ^{214}Po region is attributed to very short half-life of ^{214}Po ($T_{1/2} = 164 \mu\text{s}$) and ionization quenching due to very high alpha energy (7.68 MeV) as reported by Salonen [2, 4]. Additionally, if the guard counter in Quantulus LSC is on, it eliminates a proportion of the ^{214}Po

Fig. 1 Spectra of ^{226}Ra in equilibrium with its alpha and beta daughters



counts, since it detects some high energy ^{214}Bi gamma radiation, at the same time as the Quantulus detection system registers the presence of ^{214}Po alphas [4]. Also another reason for reduced alpha efficiencies can be attributed to radon gas partitioning between sample and air in liquid scintillation vial [17, 18]. Therefore, not all alpha emissions are counted with the same efficiency which leads to somewhat wrong calibration [12]. To avoid these inaccuracies in the calibration procedures while using radium source as mixed α/β calibration standard, we followed a unique criteria for optimization of PSA setting as suggested by Spaulding and Noakes and Salonen which are very specific and apt especially for ^{226}Ra standard. Salonen recommended α/β ratio that was obtained from the count rate of α and β in specific counting windows as a key factor for PSA optimization [2] and should agree with theoretical value (α/β ratio- 2 for single phase and 1.5 for dual phase counting systems as reported in literature) while Spaulding and Noakes suggested plotting alpha MCA count rate versus PSA for determination of a optimized PSA range when working with mixed α/β calibration standard [19].

Determination of region of interest (ROI)

We slightly modified the method suggested by Salonen for optimization of PSA setting, by selecting alpha counting window as ROI that excludes distinct ^{214}Po alpha peak. As illustrated in Fig. 1, alpha spectrum of ^{226}Ra with its alpha active daughters (^{222}Rn and ^{218}Po) form a merged alpha peak that spreads over a counting region comprising 640–760 channels while a distinctive ^{214}Po peak can be observed in 760–830 channels.

For deriving α/β ratio, instead of considering the entire counting region that was spread over 640–830 channels, Region of interest (ROI) was set at channels 640–760, where ^{226}Ra , ^{222}Rn and ^{218}Po alpha peaks lie. By selecting this ROI, we could get nearly 280% alpha counting efficiency, thus the inconvenience due to lower counting efficiencies in ^{214}Po window was avoided. The problem becomes worst on higher quench levels, as alpha efficiency in the ^{214}Po region was found to be declined as per the level of quench (Fig. 2) that would alter the α/β ratio to a great extent and would have posed difficulties in calibration. Thus by selecting the ROI that excludes ^{214}Po region, for single phase homogeneous counting system, the desired α/β ratio was 1.5 (considering three alphas and two betas), whereas for two phase heterogeneous system, the desired α/β ratio was 1.0 (considering two alphas and two betas).

It is noteworthy to remember that ROI should be selected according to spectral peak positions as it changes according to the degree of quenching in the sample. Sanchez-Cabeza et al. [20] therefore compensated for the alpha peak shift, as the result of sample quenching, by defining

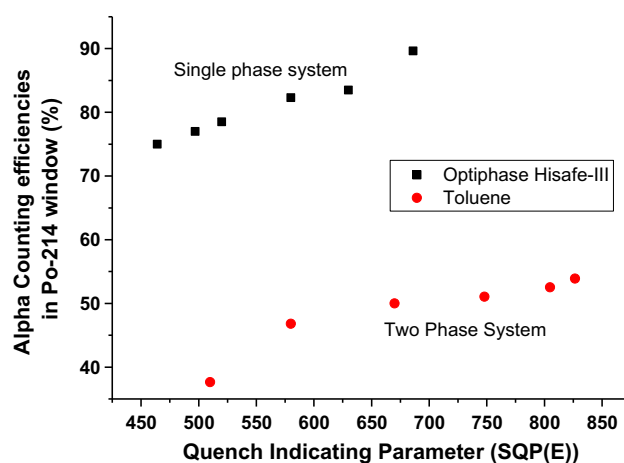


Fig. 2 Alpha counting efficiencies in ^{214}Po counting window in single phase and two phase sample systems

counting windows with a fixed width (channels) but a variable position in the spectrum for instance a wide alpha window of 120 channels and a ^{214}Po window of 70 channels. By adopting the modified method in which ROI setting excludes the ^{214}Po counting region, we could nullify the dependency of α/β ratio on the sample quenching.

Variation in counting efficiencies and α/β ratio at different PSA settings

Alpha counting efficiencies when plotted against different PSA settings as shown in Fig. 3, it was observed that at lower PSA settings, all the events (alpha as well as beta) were registered in alpha MCA. Hence up to PSA 60, the gross alpha efficiency exceeded the maximum value of 300% due to the spill over of beta events in α MCA. As PSA levels were scanned, some beta events started getting registered in beta MCA until an optimized setting was

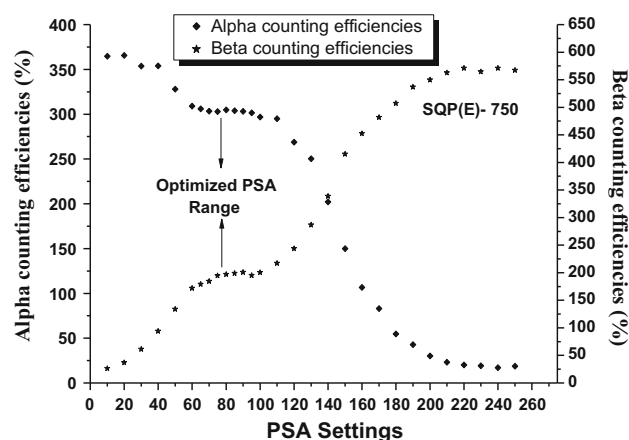


Fig. 3 Variation in alpha and beta counting efficiencies when mixed α/β ^{226}Ra standard was counted on different PSA settings

reached, where essentially all beta events were excluded from α MCA and a plateau appeared in the mid-region.

In the PSA range 70–100, alpha and beta events were precisely discriminated and a plateau of almost constant efficiency was observed. Further beyond the plateau region, due to alpha spill over in beta MCA, alpha efficiencies were found to decline steeply at higher PSA settings. Unlike alpha, gross beta counting efficiency increased steeply until it reached a plateau. Later the plateau region, at higher PSA settings, a steady rise in beta counting efficiency was observed due to alpha spill over in beta MCA.

In the present study in order to choose the optimum PSA setting within the plateau, we used α/β ratio as the decisive factor. The α/β ratio at various PSA settings for single phase homogeneous counting system is illustrated in Fig. 4. At a plateau region, that covers a range of PSA settings from 70 to 100, a constant value of α/β ratio (~ 1.5) was obtained.

^{226}Ra spectra at various PSA settings

In view of the fact that ^{226}Ra standard itself was used for calibration, which has both alpha and beta progenies, PSA discriminator setting played a major role in providing exact spectra separation. At lower PSA settings, all alpha as well as beta events get registered in alpha MCA as illustrated in Fig. 5a where a prominent alpha (with highest beta spillover) and minor beta spectrum can be seen (at the left end). As PSA levels were scanned, some of the beta events started registering in beta MCA. At optimized PSA setting, a well separated alpha and beta spectra with specific, well

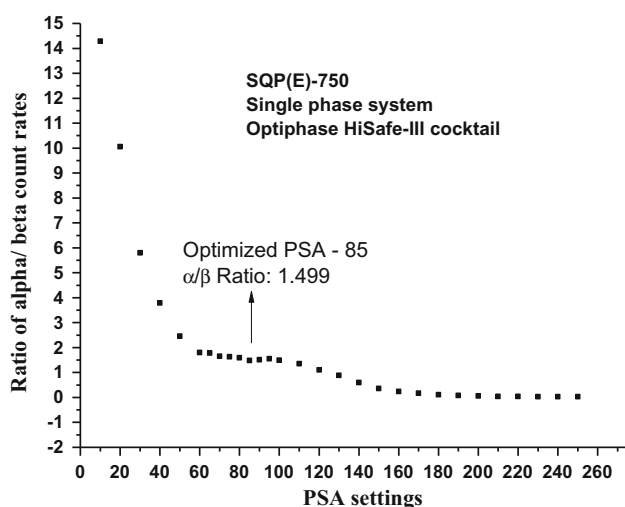


Fig. 4 Ratio of α/β count rates at various PSA levels, as one of the criteria to optimize the PSA level setting

known peaks for alpha and beta progeny were obtained (Fig. 5b). Further at PSA 150, alpha events started registering in beta MCA and beta spectrum was seen influenced significantly by the same (Fig. 5c). At the extreme end of the PSA setting range (220–250), a very vague alpha and prominent beta (with highest alpha spillover) spectra were seen as shown in Fig. 5d.

The calibration plots that correlate PSA settings at different quench levels are illustrated in Figs. 6 and 7 while Figs. 8 and 9 show corresponding alpha and beta counting efficiencies at the optimized PSA settings for single and two phase counting systems respectively.

The standardized calibration procedures for determination of ^{222}Rn and ^{226}Ra activities in water samples were verified by measuring the activity concentrations of the spiked samples (^{226}Ra) and comparing them with the known referred values (50 mBq to 2 Bq). Activity (Bq) in prepared spiked sample was calculated using the following formula

$$\text{Activity concentration} = \frac{(\text{Gross cpm} - \text{bkg.cpm})}{(60 * V * E)}$$

where E is the alpha counting efficiency corresponding to the quench indicating parameter $\text{SQP}(E)$ and V is the volume of the spiked standard. Excellent reproducibility with utmost $\pm 3\%$ deviation from the reference activity was obtained over a wide range of quenching. The minimum detectable activity (MDA) was evaluated using Currie Formula [21].

$$\text{MDA} = L_d / (E * V * T)$$

where $L_d = 2.71 + 4.66\sqrt{B * T}$ and B , E , V and T are background count rate (cpm), counting efficiency, sample volume and counting time (500 min.) respectively. MDA of 45 mBq l^{-1} was achieved specifically for radon in two phase counting system (11 ml deionised water was added to the 11 ml toluene cocktail in glass vial) for a counting time of 500 min with the following variables $B = 0.06 \text{ cpm}$ (counting region: 645–745 channels), $E = 190\%$, $V = 11 \text{ ml}$ and $T = 500 \text{ min}$ with $\text{SQP}(E) = 800$ and corresponding $\text{PSA} = 60$. MDA for single phase counting system with Optiphase HiSafe-III scintillation cocktail achieved was 39 mBq l^{-1} with variables $B = 0.05 \text{ cpm}$ (counting region 450–610 channels), $E = 280\%$, $V = 8 \text{ ml}$ and $T = 500 \text{ min}$ with $\text{SQP}(E) = 685$ and corresponding $\text{PSA} = 55$. MDA can be improved further by employing Teflon instead of glass vials and by pre-concentration of water samples for estimation of ^{226}Ra .

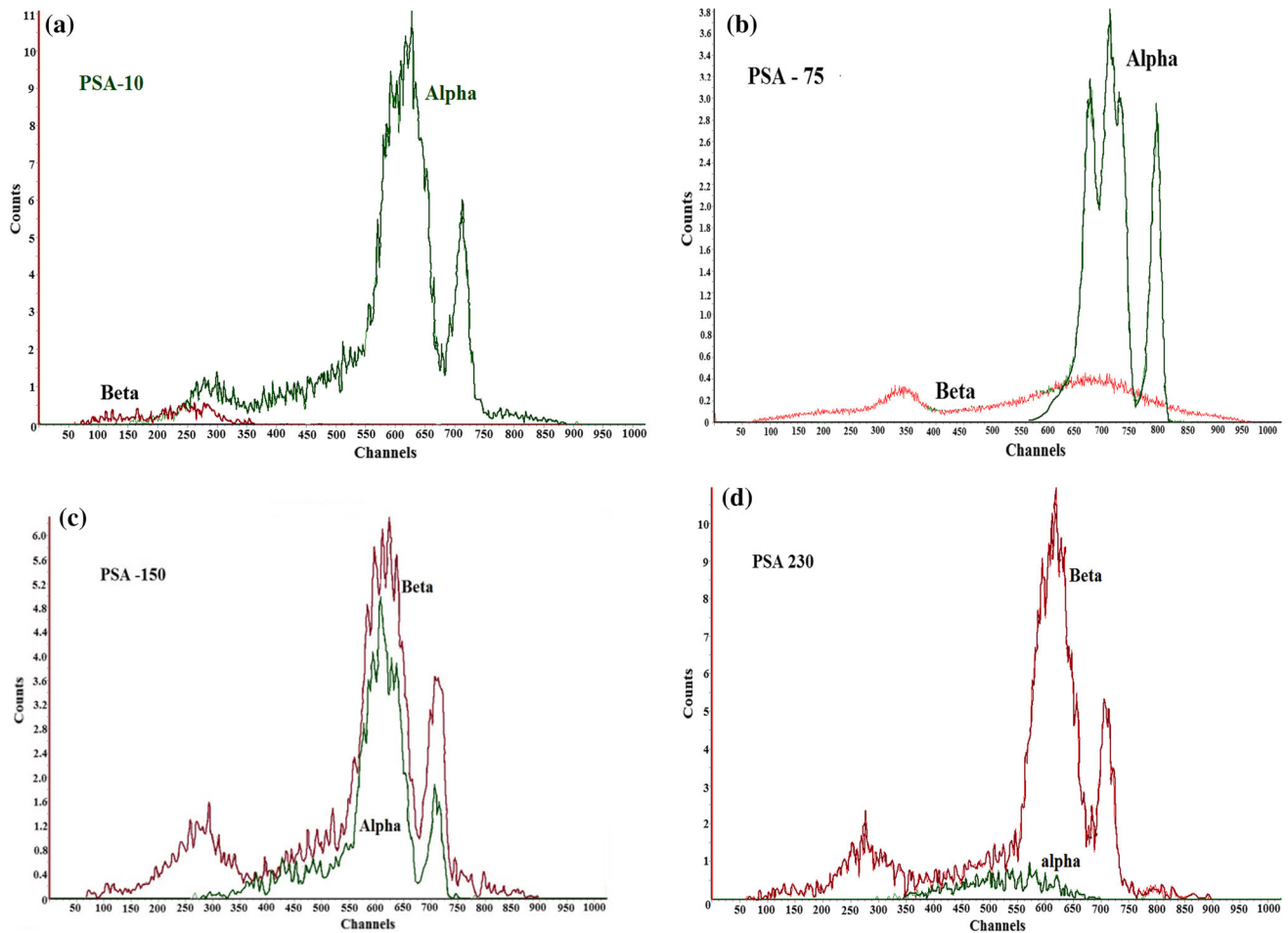


Fig. 5 Alpha and beta spectra of ^{226}Ra in equilibrium with its progeny at different PSA settings

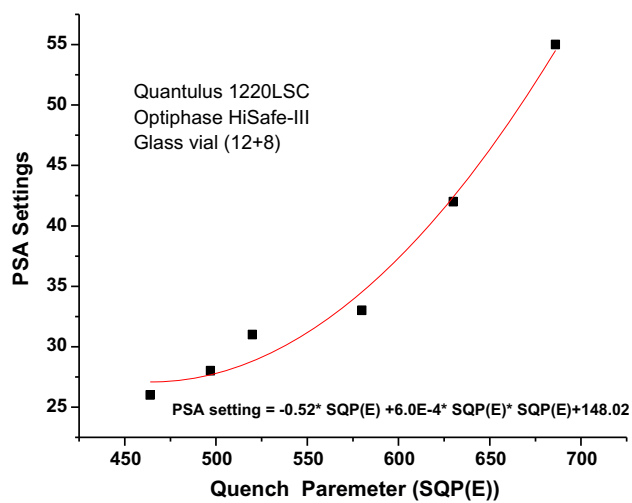


Fig. 6 A calibration plot of PSA settings versus quench indicating parameter (SQP(E)) in single phase system

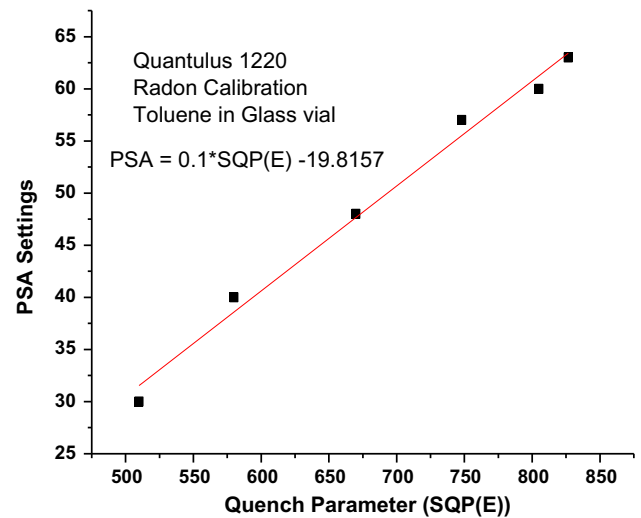


Fig. 7 PSA settings as a function of quench indicating parameter [SQP(E)] in two phase counting system (toluene in glass vial)

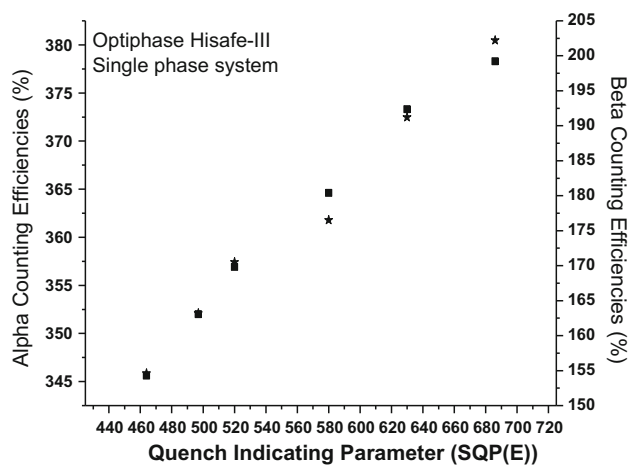


Fig. 8 Alpha and beta counting efficiencies as a function of SQP(E) in single phase sample system

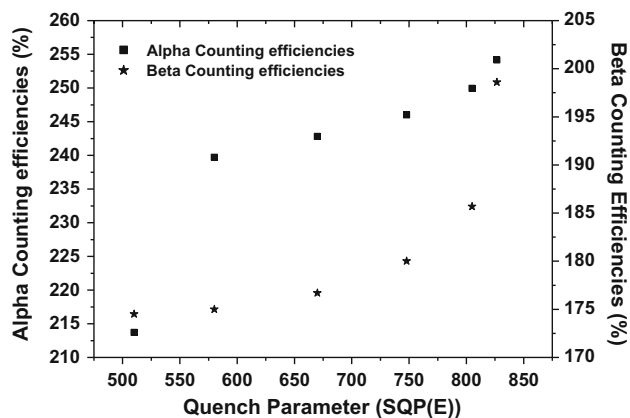


Fig. 9 Alpha and beta counting efficiencies with varying SQP(E) parameter in two phase toluene scintillator system

Conclusions

A method was developed for calibration of LSC and optimization of PSA settings using mixed α/β ^{226}Ra standard for direct determination of radium and radon concentrations in water samples. The effect of quenching on the calibration procedure was studied for one phase homogeneous and two phase heterogeneous counting systems using Quantulus 1220 LSC. In order to choose the optimum PSA setting, α/β ratio was used as the key factor. The calibration procedures specifically standardized for one and two phase counting systems, were established by measuring the alpha activities in spiked water samples and results were found to be within $\pm 3\%$ of the reference activities, over a wide range of quenching. Minimum Detectable Activities (MDA) determined for ^{222}Rn and ^{226}Ra were 45 and 39 mBq l^{-1} respectively. Further, practicability of these proposed calibration procedures will

be checked by analyzing real water samples for determination of ^{226}Ra and ^{222}Rn .

References

- Pates JM, Cook GT, Mackenzie AB (1996) Alpha/beta separation liquid scintillation spectrometry: current trends. In: Cools GT, Harkness DD, Harkness AB, Mackenzie BF, Scott EM (eds) Liquid scintillation spectrometry 1994. Radiocarbon, New York, pp 267–281
- Salonen L (2010) Comparison of two direct LS methods for measuring ^{222}Rn in drinking water using α/β liquid scintillation spectrometry. Appl Radiat Isot 68:1970–1979
- Hou X, Roos P (2008) Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. Anal Chim Acta 608:105–139
- Salonen L, Hukkanen H (1997) Advantages of low background liquid scintillation alpha spectrometry and pulse shape analysis in measuring ^{222}Rn , uranium and ^{226}Ra in ground water samples. J Radioanal Nucl Chem 226(1–2):67–74
- Zelensky AV, Buzinny MG, Los IP (1993) Measurements of ^{226}Ra , ^{222}Rn and Uranium in Ukrainian Groundwater using ultra-low-level liquid scintillation counting. In: Noakes JE, Schonhofer F, Polach HA (eds) Liquid scintillation spectrometry 1992. Radiocarbon, New York, pp 405–411
- ASTM 1998. Standard test method for radon in drinking water. D—5072—98. Annual Book of ASTM Standards, 11.01
- Prichard H, Gesell T (1977) Rapid measurements of ^{222}Rn concentrations in water with a Commercial liquid scintillation counter. Health Phys 33:577–581
- Schönhofer F (1989) Determination of Radon-222 and Radium-226 in mineral water and drinking water e a Survey in Austria. Analyst 114:1345–1347
- Horrocks DL (1970) Pulse shape discrimination with organic liquid scintillator solutions. Appl Spectrosc 24(4):397–404
- Kaiholta L, Oikari T (1989) Some factors affecting alpha particle detection in liquid scintillation counting. In: Ross H (ed) Liquid scintillation counting and organic scintillators. CRC Press, Boca Raton, pp 211–221
- Stojković I, Tenjović B, Nikolov J, Vesković M, Mrđa D, Todorović N (2015) Improvement of measuring methods and instrumentation concerning ^{222}Rn determination in drinking waters—RAD7 and LSC technique comparison. Appl Radiat Isot 98:117–124
- Stojković I, Todorović N, Nikolov J, Tenjović B (2016) PSA discriminator influence on ^{222}Rn efficiency detection in waters by liquid scintillation counting. Appl Radiat Isot 112:80–88
- Bhade SPD, Reddy PJ, Narayanan A, Narayan KK, Babu DAR, Sharma DN (2010) Standardization of calibration procedures for quantification of gross alpha and gross beta activities using liquid scintillation counter. J Radioanal Nucl Chem 284(2):367–375
- Rusconi R, Azzellino A, Bellinzona S, Forte M, Gallini R, Sgorbati G (2004) Assessment of Drinking water radioactivity content by liquid scintillation counting: set up of high sensitivity and emergency procedures. Anal Bioanal Chem 379:247–253
- PerkinElmer Life and Analytical Sciences (2005) Quantulus 1220 ultra low level liquid scintillation spectrometer
- Salonen L (1993) A rapid method for monitoring of uranium and radium in drinking water. Sci Total Environ 130(131):23–25

17. Schubert M, Paschke A, Lieberman E, Burnett WC (2012) Air-water partitioning of ^{222}Rn and its dependence on water temperature and salinity. *Environ Sci Technol* 46:3905–3911
18. Lee KY, Yoon YY, Cho SY, Ko KS, Yum BW (2012) Determination of radon partitioning between groundwater and atmosphere by liquid scintillation counter. *J Radioanal Nucl Chem* 294:27–30
19. Spaulding JD, Noakes JE (1993) Determination of ^{222}Rn in drinking water using an alpha/beta liquid scintillation counter. In: Noakes JE, Schonhofer F, Polach HA (eds) *Liquid scintillation spectrometry 1992*. Radiocarbon, New York, pp 373–381
20. Sanchez-Cabeza JA, Wee Kwong LL, Betti M (2010) Method to determine ^{226}Ra in small sediment samples by ultralow background liquid scintillation. *Anal Chem* 82:6847–6853
21. Currie LA (1968) Limits for qualitative detection and quantitative determination—application to radiochemistry. *Anal Chem* 40:586–593