Calibration and Validation of a Proportional Counter for Determining Beta Emitters*

Marko ŠTROK**, Urška REPINC** and Borut SMODIŠ**

**Department of Environmental Sciences, Jožef Stefan Institute
Jamova 39, SI-1000 Ljubljana, Slovenia
E-mail: Marko.Strok@ijs.si

Abstract

Calibration of recently installed proportional counter at the Hot Cells Facility of the Jožef Stefan Institute was performed. Instrument was calibrated for determination of total beta activity, Sr–90 and Pb–210. Detection efficiencies for K–40, Sr–90, Y–90, Pb–210 and Bi–210 were determined, allowing for more accurate determination of the particular nuclide as a single K–40 efficiency. In addition, self-absorption curves for different surface densities for the nuclides mentioned were derived. Two empirical equations for faster and more accurate determination of Sr–90 and Pb–210 were derived. These two equations consider differences in surface density and in-growth of Y–90 and Bi–210, respectively. The detection efficiencies obtained ranged from 10 to 52 %, depending on the nuclide, surface density and chemical compositions of the salts used or precipitates obtained following radiochemical separation in the experiment. As a performance test of derived empirical equation for the determination of detection efficiency for Pb–210, specific activity of Pb–210 in IAEA 385 and IAEA 414 intercomparison materials were determined. All procedures and formulae developed include calculation of minimal detectable activities and uncertainty budgets for the determinations concerned.

Key words: Proportional Counter, Detection Efficiency, Beta Emitters, Total Beta Activity, Sr–90, Pb–210

1. Introduction

Accurate and fast determination of different beta emitters in various samples is very important for monitoring of possible releases of these nuclides into the environment. Part of this determination is also related to proper and accurate calibration of a proportional counter, which in general includes determination of background of the proportional counter and determination of detection efficiency.

In this work we focused on the determination of detection efficiency. The detection efficiency for beta emitters depends on the type of the nuclide, the type of precipitate and surface density. According to that we must prepare and measure calibration standards for determining detection efficiency in the same manner as we prepare and measure samples.

The preparation of standards and samples is not a problem with respect to the type of the nuclide and type of precipitate. But on the other hand it is very difficult to achieve the same surface density for the standards and samples, because we cannot always achieve the same chemical yield for radiochemical separation procedure. The best way to overcome this problem is to measure detection efficiencies for different surface densities and to construct a self-absorption curve and find an equation, which will describe dependence of the detection efficiency on the surface density. After that we can apply this equation to calculate detection

efficiencies for different surface densities of the prepared samples.

Determination of Sr–90 and Pb–210, having beta emitting daughters Y–90 and Bi–210, respectively, represents another difficulty. In this case, activity and also the detection efficiency grows up after radiochemical separation so long as they achieve secular radioactive equilibrium. For Y–90 this time is approximately 14 days and for Bi–210 approximately 30 days.

Usual procedures for the determination of Sr–90 involve its measurement in secular radioactive equilibrium with Y–90 [1] or separation of Y–90 from Sr–90 followed by Y–90 measurement [2]. These procedures usually neglect the effect of surface density because it is expected that samples have the same surface densities as the standard. But in laboratory practice it is very difficult to obtain the same surface densities for both the sample and standard. It is also assumed that the effect of surface density, because of high-energy beta particles from Y–90, can be neglected. Pb–210 is usually determined with a proportional counter by measuring its daughter nuclide Bi–210 [3].

In our case the detection efficiencies were determined based on empirical equation that allows for accurate determination of Sr–90 over a whole in-growth period of Y–90 and for different surface densities. With this improvement we can define the detection efficiency for Sr–90 independently of time elapsed after the radiochemical separation of Y–90 and independently of the surface density. Equations (1) to (4) describes the detection efficiency where $\varepsilon_{\text{Sr}-90+\text{Y}-90}$ is total detection efficiency, $\varepsilon_{\text{Sr}-90}$ is detection efficiency for Sr–90, $\varepsilon_{\text{Y}-90}$ is detection efficiency for Y–90, $\lambda_{\text{Y}-90}$ is decay constant for Y–90, $t_{2,\text{Sr}-90}$ is the time elapsed from the separation of Sr–90, $N_{\text{Sr}-90+\text{Y}-90}$ is number of counts for Sr-90 and Y-90, $A_{\text{Sr}-90}$ is the activity of Sr-90 in the standard, t_{m} is measuring time of the standard, $N_{\text{Sr}-90}$ is number of counts for Sr-90 and $N_{\text{Y}-90}$ is number of counts for Y-90.

$$\varepsilon_{\text{Sr}-90+\text{Y}-90} = \varepsilon_{\text{Sr}-90} + \varepsilon_{\text{Y}-90}\left(1 - \exp\left(-\lambda_{\text{Y}-90}t_{2,\text{Sr}-90}\right)\right) \tag{1}$$

$$\varepsilon_{\text{Sr-90+Y-90}} = \frac{N_{\text{Sr-90+Y-90}}}{A_{\text{Sr-90}}t_{\text{m}}} \tag{2}$$

$$\varepsilon_{\text{Sr-90}} = \frac{N_{\text{Sr-90}}}{A_{\text{Sr-90}}t_{\text{m}}} \tag{3}$$

$$\varepsilon_{\text{Y-90}} = \frac{N_{\text{Y-90}}}{A_{\text{Sr-90}}t_{\text{m}}} \tag{4}$$

If we substitute $\varepsilon_{\text{Sr}-90}$ and $\varepsilon_{\text{Y}-90}$ in Eq. (1) with empirical equations for self-absorption curves, we obtain Eq. (7), which allows for the determination of Sr–90 detection efficiency for different surface densities and for various times elapsed from the separation. Empirical equation for the Pb–210 detection efficiency is derived in the same manner.

Performance test of derived empirical equation for the determination of detection efficiency for Pb–210 was also performed. Specific activities of Pb–210 in IAEA 385 and IAEA 414 intercomparison materials were determined. IAEA 385 is Irish Sea sediment material and IAEA 414 is mixed fish material from Irish and the North Sea. In this determination, detection efficiencies for Pb–210 were calculated with the derived Eq. (8). Performance test contained measurements of specific activity of Pb–210 in different times after radiochemical separation. Measured specific activities were plotted versus time after radiochemical separation and compared with the information value.

2. Experimental

2.1 Proportional Counter

A Canberra Tennelec LB4100-W low background gas flow proportional counter having eight proportional detectors in two drawers was used. As a counting gas, mixture of 90 % argon and 10 % methane was used.

2.2 Detection Efficiency for K–40

KCl was weighted onto stainless steel planchets using an analytical balance. KCl was dispersed onto planchets by adding small amount of acetone to achieve homogenous deposit of KCl. When the acetone was evaporated, KCl was mounted with the glue and the detection efficiency was measured with proportional counter. This procedure was applied for different surface densities. Self-absorption curve was fitted to the experimental data with program CurveExpert 1.3.

2.3 Detection Efficiency for Sr–90 and Y–90

Detection efficiency for Sr–90 and Y–90 was determined by two methods, differing in the way of separation of Sr–90 from Y–90. The first procedure involved extraction process and the second procedure precipitation. These two procedures were applied to ensure that separation process of Sr–90 from Y–90 was really selective.

The extraction procedure involved addition of different amounts of 20 mg/mL Sr carrier to the standard Sr–90/Y–90 solution in order to achieve different surface densities of $SrCO_3$. To these solutions 15 mL of 0.15 mol/L HNO_3 were added and then Y–90 extracted with 15 mL of 0.2 mol/L dibutylphosphate in chlorophorm. The time of this extraction was the separation time of Sr–90 from Y–90. The water phase was stored. The organic phase was washed three more times by adding 10 mL of 0.15 mol/L HNO_3 and the organic phase discarded. The water phases were filtered through filter paper and then 0.2 g $(NH_4)_2CO_3$ and NH_4OH were added to make the solution alkaline. This solution was heated on a hot plate to accomplish precipitation of $SrCO_3$.

This precipitate was then transferred to a plastic centrifuge beaker and centrifuged. Supernatant was discarded. The precipitate was washed with deionized water and again centrifuged. Supernatant was discarded and the precipitate quantitatively transferred to a plastic tube with aluminium planchet on the bottom. 2 mL of ethanol was added to the tube and then centrifuged. Supernatant was discarded, the precipitate deposited on planchet and dried up under a heating lamp. So prepared precipitates were weighted on an analytical balance to determine chemical yield of the procedure and then measured in the proportional counter over a whole in-growth period of Y–90.

The precipitation procedure involved the same quantities of Sr carrier and standard Sr–90/Y–90 solution as for the extraction method. 10 mL of deionized water was added to the standards and heated on a hot plate. Then 1 mL of 10 mg/mL Ba carrier and 1 ml of 5 mg/mL Fe carrier were added. After $Fe(OH)_3$ coagulated, solution was filtered through a filter paper. Precipitate was discarded and time of filtration was registered as a separation time of Sr–90 from Y–90. 1 mL of concentrated CH_3COOH, 2 mL 25% NH_3 acetate and 1 mL of saturated $(NH_4)_2CrO_4$ solution were added to the filtrate. Then the solution was heated for 10 min on a hot plate and filtered through a filter paper. The $BaCrO_4$ precipitate was discarded. To the filtrate 0.2 g of $(NH_4)_2CO_3$ and NH_4OH were added to achieve alkalinity. This solution was heated on a hot plate to accomplish precipitation of $SrCO_3$.

The precipitate was centrifuged, washed, dried up, weighted and measured in the proportional counter in the same way as in the extraction procedure.

The experimental data obtained from extraction and precipitation procedures were plotted versus time after separation and fitted with the CurveExpert 1.3 program to the Eq. (1) in order to determine detection efficiencies for Sr–90 at the time of separation and for

Y–90 at the time when Y–90 was in secular equilibrium with Sr–90. These detection efficiencies were plotted to the different surface densities obtained and fitted with the CurveExpert 1.3 to obtain the self-absorption equations for Sr–90 and Y–90. These self-absorption equations were inserted into Eq. (1), replacing the detection efficiencies for Sr–90 and Y–90. As result the empirical equation describing the detection efficiency for Sr–90 was obtained, which is function of the $SrCO_3$ surface density and the time elapsed after the Y–90 separation.

2.4 Detection Efficiency for Pb–210 and Bi–210

Different amounts of $PbCl_2$ were added to the standard solution of Pb–210/Bi–210 to achieve different surface densities of $PbSO_4$. Then HNO_3 and H_2O_2 were added and evaporated. Sample was dissolved in HCl. Pb was separated on a Sr Resin column and again evaporated and dissolved in H_2O. Then the sample was precipitated with sulfuric acid to form $PbSO_4$. This precipitate was quantitatively transferred into a plastic tube having an aluminium planchet on the bottom; 2 mL of ethanol was added and then centrifuged. Supernatant was discarded. The precipitate, deposited on the planchet, was dried up under a heating lamp. So prepared precipitates were weighted on an analytical balance to determine chemical yield of the separation and then measured in the proportional counter over a whole in-growth period of Bi–210.

Experimental data was processed in the same way as for Sr–90, yielding the empirical equation for the detection efficiency for Pb–210 as function of the $PbSO_4$ surface density and the time elapsed after the separation from Bi–210.

2.5 Determination of Pb–210 Specific Activity

For the determination of Pb–210 specific activity in an IAEA intercomparison sample, $PbCl_2$ carrier was added to the sample and sample was digested in HNO_3 and H_2O_2. After digestion, HNO_3 and H_2O_2 were evaporated and the sample was dissolved in HCl. Pb was separated on the Sr Resin column and again evaporated and dissolved in H_2O. Then this sample was precipitated with sulfuric acid to form $PbSO_4$. This precipitate was quantitatively transferred into a plastic tube having an aluminium planchet on the bottom; 2 mL of ethanol was added and then centrifuged. Supernatant was discarded. The precipitate, deposited on the planchet, was dried up under a heating lamp. So prepared precipitate was weighted on an analytical balance to determine chemical yield of the separation and then measured in the proportional counter over a whole in-growth period of Bi–210.

Specific activity was calculated with the help of Eq. (5). In this equation a_S is specific activity of the sample, R_S is count rate the sample, R_B is background count rate, m_S is mass of the sample, $\varepsilon_{Pb-210+Bi-210}$ is from Eq. (8) calculated total detection efficiency and η_S is chemical recovery of the sample.

$$a_S = \frac{R_S - R_B}{m_S \varepsilon_{Pb\text{-}210+Bi\text{-}210} \eta_S} \tag{5}$$

3 Results and Discussion

3.1 Detection Efficiency for K–40

Detection efficiency and self-absorption curve derived from experimental data for K–40 is shown in Fig. 1. Surface densities from 10 mg/cm^2 to 235 mg/cm^2 were considered. Detection efficiency ranged from 47 % for the lowest surface density to 18 % for the greatest surface density. Equation (6) shows plotted self-absorption curve that was calculated by the CurveExpert 1.3. In this equation ε_{K-40} is detection efficiency of K–40 and

$\rho_{A,\text{KCl}}$ is surface density of the KCl. Good agreement between the experimental results and the derived self-absorption curve can be observed.

$$\varepsilon_{\text{K}-40} = 0.4215\left(0.1804 + \exp\left(-0.0060\rho_{A,\text{KCl}}\right)\right) \tag{6}$$
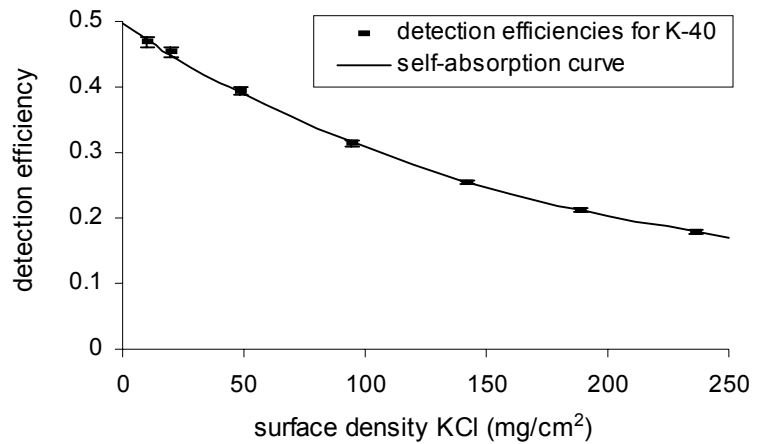

Fig. 1   Detection efficiency for K–40 in KCl and self-absorption curve

3.2 Detection Efficiency for Sr–90 and Y–90

Detection efficiencies for Sr–90 and Y–90 and self-absorption curves obtained by the CurveExpert 1.3 program are presented in Fig. 2. Surface densities ranged from 10 mg/cm^2 to 72 mg/cm^2. Detection efficiency for Sr–90 ranged from 32 % for the smallest surface density to 17 % for the greatest one. The detection efficiency for Y–90 ranged from 52 % to 44 %. Equation (7) represents the empirical equation for the determination of total detection efficiency as function of the SrCO$_3$ surface density and the time elapsed after the separation from Y–90.

$$\begin{aligned}
\varepsilon_{\text{Sr}-90+\text{Y}-90} &= 0.3449\left(0.0854 + \exp\left(-0.0159\rho_{A,\text{SrCO3}}\right)\right) \\
&+ 0.1881\left(1.8751 + \exp\left(-0.0130\rho_{A,\text{SrCO3}}\right)\right) \\
&\cdot \left(1 - \exp\left(-\lambda_{\text{Y}-90}t_{2,\text{Sr}-90}\right)\right)
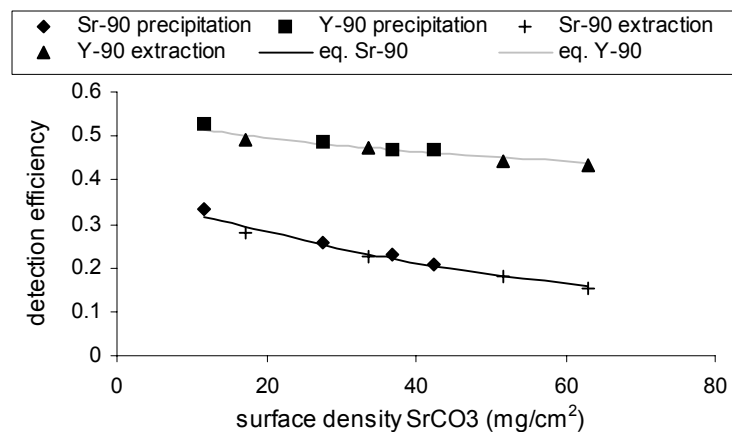\end{aligned} \tag{7}$$

Fig. 2   Detection efficiencies for Sr–90 and Y–90 versus surface density of SrCO$_3$

Figures 3 and 4 present in-growth of Y–90 from Sr–90 indicated as increase in the total detection efficiency. The curves in the figures are derived from Eq. (7) and show good agreement with the experimental data. By comparing detection efficiencies for Sr–90 and Y–90 for the precipitation and extraction procedures, it is evident that the detection efficiencies for the precipitation procedure are slightly higher than for the extraction one, as evident from Fig. 2. Accordingly, the curves derived from Eq. (7) in Fig. 3 are below the experimental data and in Fig. 4 above the experimental data.
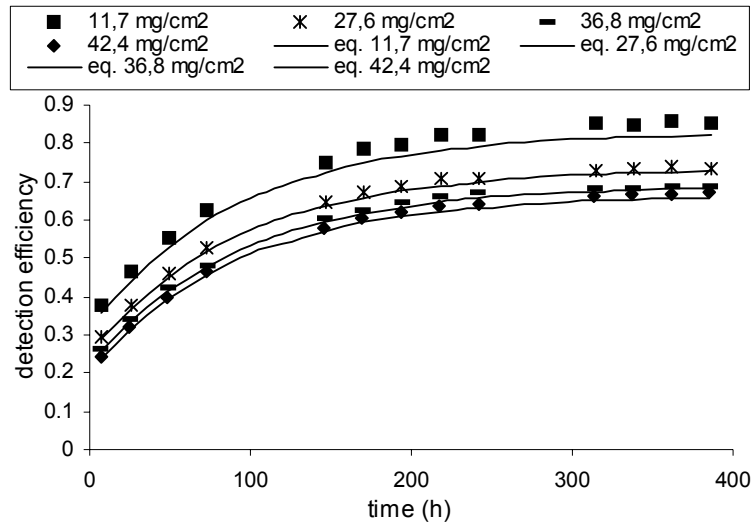
Fig. 3　In-growth of total detection efficiency for different surface densities of $SrCO_3$; precipitation
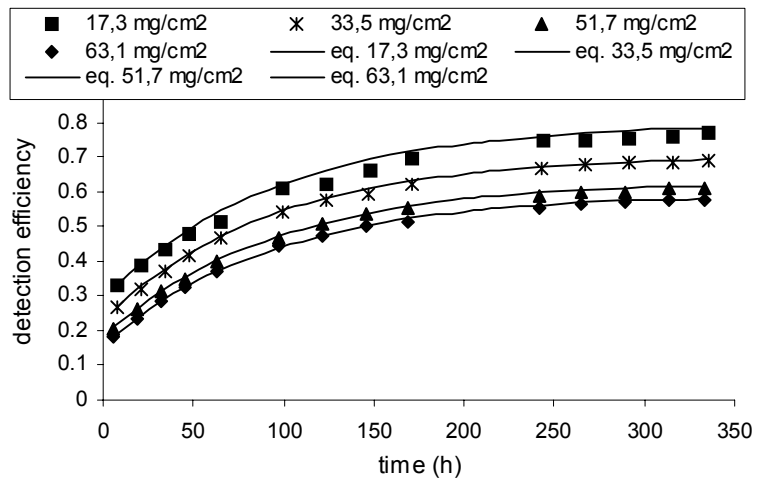
Fig. 4　In-growth of total detection efficiency for different surface densities of $SrCO_3$; extraction

3.3 Detection efficiency for Pb–210 and Bi–210

Detection efficiencies for Pb–210 and Bi–210 versus surface density are presented in Fig. 5. Self-absorption curves, obtained by the program CurveExpert 1.3, are also shown in the figure. Surface densities ranged from 2.7 mg/cm^2 to 21 mg/cm^2. The detection efficiency for Pb–210 ranged from 13 % for the lowest surface density to 11 % for the greatest. The detection efficiency for Bi–210 ranged from 36 % to 20 %. Equation (8) shows the empirical equation for the total detection efficiency ($\varepsilon_{Pb–210,Bi–210}$) as function of

the surface density ($\rho_{A,\text{PbSO4}}$) and the time elapsed after separation from Bi–210 ($t_{2,\text{Pb–210}}$). This equation was also obtained by the program CurveExpert 1.3.

$$\begin{aligned}
\varepsilon_{\text{Pb–210+Bi–210}} &= 0.0492\left(1.8007 + \exp\left(-0.0373\rho_{A,\text{PbSO4}}\right)\right) \\
&+ 0.2648\left(0.7469 + \exp\left(-0.1811\rho_{A,\text{PbSO4}}\right)\right) \\
&\cdot\left(1 - \exp\left(-\lambda_{\text{Bi–210}}t_{2,\text{Pb–210}}\right)\right)
\end{aligned} \tag{8}$$
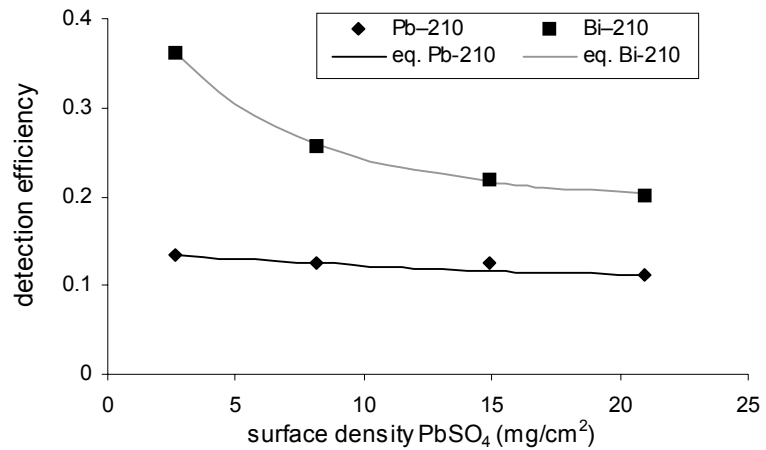
Fig. 5   Detection efficiencies for Pb–210 and Bi–210 versus surface density of PbSO$_4$

Figure 6 shows in-growth of Bi–210 from the Pb–210 indicated as the in-growth of the total detection efficiency. Curves in this figure are derived from Eq. (8) and are in good agreement with the experimental data shown as points.
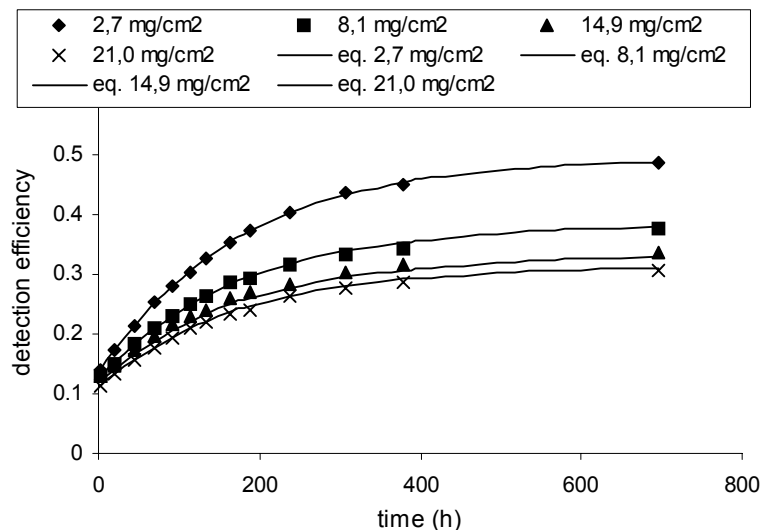

Fig. 6   In-growth of total detection efficiency for different surface densities of PbSO$_4$

3.4 Comparison of detection efficiencies

The results obtained show that beta detection efficiency varies with the surface density and with the type of the precipitate as revealed in Fig. 7. The detection efficiency for Bi–210 in PbSO$_4$ is lower than the one for Sr–90 in SrCO$_3$, although Sr–90 has lower maximum beta energy than Bi–210. This is due to greater molecular mass of the PbSO$_4$.

From Fig. 7 it can be seen that the detection efficiency for Pb–210 is almost independent of the surface density but that is due to the low energy of the beta particles emitted by Pb–210, which are almost completely absorbed in PbSO$_4$ precipitate. Due to that, a detector can detect only the beta particles emitted by Pb–210, which are on the surface of the sample.
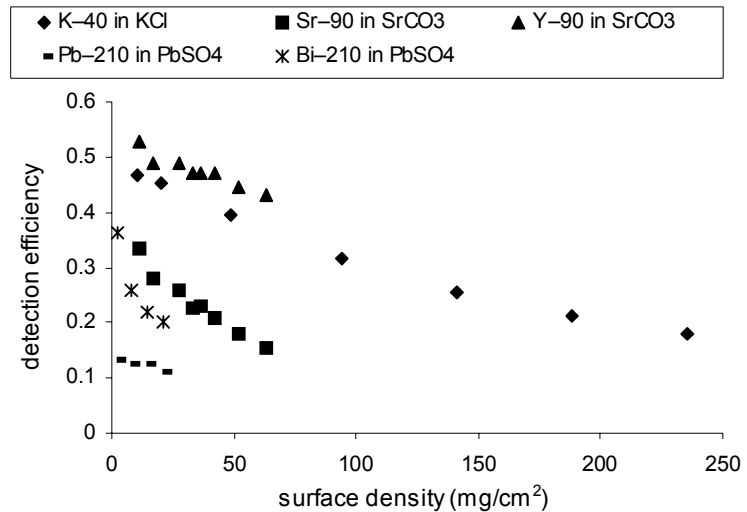

Fig. 7   Detection efficiencies versus surface density

3.5 Determination of Pb–210 Specific Activity

Figures 8 and 9 present performance test results involving the derived empirical equation for determination of detection efficiency for Pb–210. These two figures show Pb–210 specific activities obtained for the two IAEA intercomparison materials versus time after radiochemical separation. It is noticeable that in both cases uncertainties decrease with time after radiochemical separation due to in-growth of Bi–210 from Pb–210; the increase in count rate causes reduction of uncertainty. All results except the first ones are in good agreement with the information values. Greater deviation from the information values in the first and second measurement after radiochemical separation is due to the relatively low count rate at the beginning of in-growth of Bi–210.
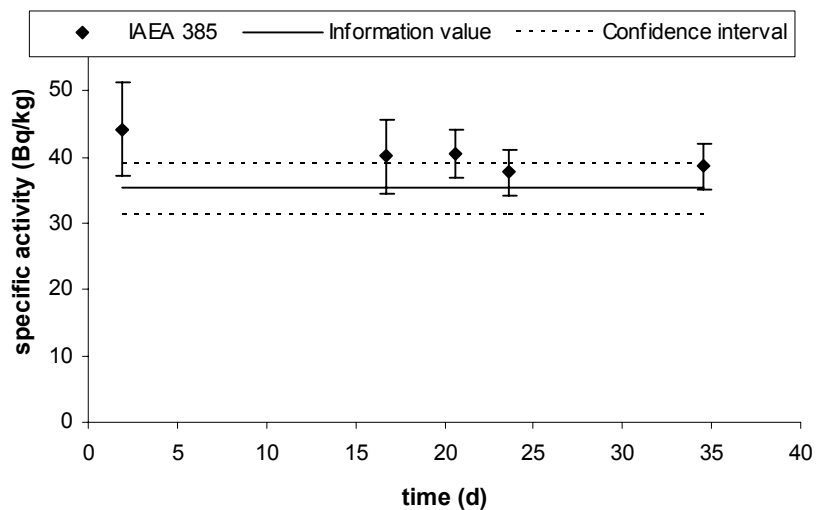

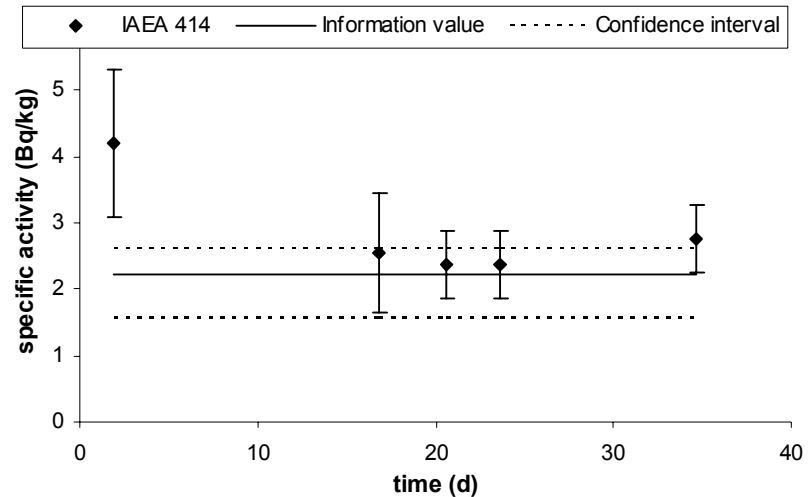Fig. 8   Pb–210 specific activity of IAEA 385

Fig. 9   Pb–210 specific activity of IAEA 414

4. Conclusion

All the obtained self-absorption curves and empirical equations follow well experimental results. The derived empirical equations offer possibility for accurate and faster determination of beta emitters, having beta-emitting daughters that come into secular radioactive equilibrium with their parents. The main advantage of using these empirical equations are the facts that one does not need to wait for achieving secular radioactive equilibrium (approximately 14 days for Sr–90 and approximately 30 days for Pb–210) and worry if the surface density of the sample is the same as the one for the standard. The performance test showed that calculation of detection efficiencies with help of the derived empirical equation is a suitable and very helpful method, which improves accuracy and flexibility in the determination of Pb–210 or Sr–90 using a proportional counter.

Acknowledgement

References

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