

# ADSORPTION CORRECTION IN $^{45}\text{Ca}$ and $^{89}\text{Sr}$ ACTIVITY DETERMINATION BY LIQUID SCINTILLATION COUNTING

LEONOR RODRÍGUEZ BARQUERO and J. M. LOS ARCOS

Instituto de Investigación Básica, Metrología de Radiaciones, Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), E-28040 Madrid, Spain

**ABSTRACT.** The adsorption of some  $^{45}\text{Ca}$ - and  $^{89}\text{Sr}$ -labeled compounds on the walls of glass vials may seriously affect liquid scintillation counting (LSC) measurements; several corrective procedures are usually applied to mitigate this effect. This work presents the activity determinations of  $^{45}\text{Ca}$  and  $^{89}\text{Sr}$ , in adsorbed samples, using a simple correction model that accounts for both the counting efficiency of the solution and that of the adsorbed fraction, the latter being determined through a series of measurements performed after consecutively emptying and refilling the vial with fresh scintillator. We applied the procedure to  $^{45}\text{CaCl}_2$ ,  $^{45}\text{Ca}$ -HDEHP and  $^{89}\text{SrCl}_2$  samples in glass vials with 10 ml of Insta-Gel® and controlled adsorption varying between 0 and 20%, with no need for special treatment or calibration curves other than the conventional quench correction. An optimized version of this method allowed recovery of the original activities, with uncertainty typically around 2% for the full set of samples, and less than 1% when only a few vials, with similar adsorption, were processed in a batch over enough time to acquire meaningful statistics.

## INTRODUCTION

The adsorption of  $^{45}\text{Ca}$  and  $^{89}\text{Sr}$  compounds on the walls of glass vials may lead to significant errors in the liquid scintillation counting (LSC) radioassay of these isotopes, which have applications in agriculture, physiology and environment fields. It is possible to minimize adsorption effects by selecting appropriate chemical forms, treating vial walls with silicone (Petroff, Nair & Turner 1964), saturating the adsorption sites with other ions, or changing electrical properties of surfaces by lowering pH. These measures require extra chemical steps (Hardcastle, Hannappel & Fuller 1967; Litt & Carter 1970; Tykva & Podracká 1975; Blanusa 1975; Rucker 1991; Terlikowska & Radoszewski 1992), which may lower counting efficiency. A different approach is based on the correction of the apparent count rate either by time-behavior fitting (Tykva 1980) or by estimating the adsorption degree through an empirical calibration curve (Wigfield 1974; Wigfield & Srinivasan 1974; Wigfield 1976).

We present here the LSC activity determination of  $^{45}\text{Ca}$  and  $^{89}\text{Sr}$  in adsorbed samples by means of a simple correction model (Los Arcos & Rodríguez, ms.) developed to account for both the counting efficiency of the solution and that of the adsorbed fraction. We describe operational procedures and results obtained from several sets of samples with adsorption degree varying between 0 and 20%.

## CALCULATION MODEL

Whenever an activity,  $A$ , is incorporated into an LSC vial where adsorption takes place, the observed count rate,  $F_1$ , satisfies

$$F_1 = A_p \epsilon_{pf} + A_{dl} \epsilon_{dl} \quad (1)$$

where  $A_p$  is the activity adsorbed on the walls,  $A_{dl}$  is the volume activity remaining in the scintillator solution,  $\epsilon_{pf}$  is the counting efficiency for the adsorbed fraction in the presence of scintillator, and  $\epsilon_{dl}$  is the counting efficiency for the volume activity, so that the original activity,  $A$ , is ( $A = A_p + A_{dl}$ ).

If the vial contents are repeatedly poured out, refilled with fresh scintillator and measured after each operation, the consecutive count rates can be written as

$$V_1 = A_p \epsilon_{pv} \quad (2)$$

$$F_2 = (A_p - A_{d2}) \epsilon_{pf} + A_{d2} \epsilon_{d2} \quad (3)$$

$$V_2 = (A_p - A_{d2}) \epsilon_{pv} \quad (4)$$

$$F_3 = (A_p - A_{d2} - A_{d3}) \epsilon_{pf} + A_{d3} \epsilon_{d3} \quad (5)$$

$$V_3 = (A_p - A_{d2} - A_{d3}) \epsilon_{pv} \quad (6)$$

where  $V_i$  is the observed count rate when the vial is empty but the walls are still wet,  $F_i$  is the observed count rate when the vial is filled with scintillator,  $A_{di}$  is the volume activity dissolved in the scintillator solution,  $\epsilon_{di}$  is the counting efficiency of the volume activity, which can be determined by standard methods, and  $\epsilon_{pf}$ ,  $\epsilon_{pv}$ , are the counting efficiencies of the adsorbed fraction when the vial is filled or empty, respectively.

Solving the non-linear system (Eqs. 1–6), the estimate for the adsorption correction factor,  $F_A$ , that transforms the initial count rate,  $F_1$ , into  $A$ , is

$$F_A = \frac{1}{\epsilon_{d1}} \left[ 1 + \frac{\epsilon_{d1} V_1 (F_2 V_3 - V_2 F_3) + \epsilon_{d2} V_1 F_3 (V_2 - V_1) + \epsilon_{d3} V_1 F_2 (V_2 - V_3)}{\epsilon_{d2} F_1 V_3 (V_1 - V_2) + \epsilon_{d3} F_1 V_2 (V_3 - V_2)} \right] \quad (7)$$

One can assume a single-efficiency model, with  $\epsilon_{pf} = \epsilon_{pv} = \epsilon_p$ , and the correction factor becomes

$$F_A = \frac{1}{\epsilon_{d1}} \left[ 1 + \frac{V_1 (F_2 - V_2) \epsilon_{d1} + V_1 (V_2 - V_1) \epsilon_{d2}}{F_1 (V_1 - V_2) \epsilon_{d2}} \right] \quad (8)$$

which requires that the vial is poured out only twice instead of three times.

## METHODS<sup>1</sup>

The LSC measurements were performed with a Wallac Rackbeta 1219 Spectral spectrometer, with two photomultiplier tubes (PMTs) working in summed-coincidence mode and a <sup>226</sup>Ra source for external standard quench correction. We used glass vials with low potassium content; each vial was always filled with 10 ml of Insta-Gel® with a Brand dispenser, accurate to 2%. We prepared the samples with a <sup>3</sup>H-hexadecane standard reference solution, two commercially available aqueous solutions of <sup>45</sup>CaCl<sub>2</sub> and <sup>89</sup>SrCl<sub>2</sub>, and a laboratory-made <sup>45</sup>Ca-HDEHP complex. We added aliquots

<sup>1</sup>Mention of commercial names does not imply recommendation or endorsement by the authors or CIEMAT and is included only for information purposes.

to the scintillator with a pycnometer, and gravimetrically controlled the exact amount of radioactive material with a 0.01 mg-sensitive Mettler balance.

The organic samples were prepared by adding the complex solution directly to the scintillator; we monitored count rate for several days, observing no significant trend after correction for decay. For inorganic samples, variable amounts of inactive carrier,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , were previously incorporated into the scintillator and then, the radioactive solution. Thus, the samples had different degrees of adsorption, depending on the carrier concentration, and we monitored their decay-corrected count rates until they became stable, before applying the adsorption correction procedure. We also measured each sample immediately after preparation, and compared its count rate,  $N_0$ , to subsequent measurements.

## RESULTS

We measured several sets of samples for each radionuclide. Some sets had samples of similar degree of adsorption, whereas others had a wider range of variations, so as to study their influence on the final results. Both the single- and the double-efficiency models were used, respectively, to check their reliability. The LS volume efficiencies,  $\epsilon_{d1}$ ,  $\epsilon_{d2}$ ,  $\epsilon_{d3}$ , were evaluated by the CIEMAT/NIST method (Grau & García-Toraño 1981); we estimated the original activity with the adsorption correction factor,  $F_A$ , from Equations (7)–(8).

The procedure involves the measurement of low count rates of nearly empty vials that may affect the numerical accuracy of the solution. This has been compensated by an optimization technique that minimizes the variance of the estimates of the activity concentration, taking into account the information of all the samples in the same set. Figure 1A shows the results corresponding to a 20-sample set of  $^{45}\text{Ca}$ , with adsorption varying between 0% and 15%. The single-efficiency model was enough to recover the true activities within  $\pm 1.5\%$ . We computed the true value from a different set of samples of the same radioactive solution that had been previously treated with inactive carrier to ensure that adsorption was not significant. It is worth noting that, even after the second emptying, the adsorbed samples still keep a residual activity, between 5 and 10 times the background.

Figure 1B shows results corresponding to samples emptied three times. Once again, the double-efficiency model did not bring any significant improvement over the single-efficiency model, and the true activity was estimated within 0.7%. Figure 2 presents the discrepancy between the true and estimated activities as a function of the adsorption correction factor, summarizing the results of sets shown in Figures 1A and 1B and several others. Set C has an average deviation around +1%, whereas Set A is about -0.5%. The upper uncertainty bounds are around 2% for the highly adsorbed samples.

Figure 3 shows the results of a 16-sample set of  $^{89}\text{Sr}$ , which was emptied three times. In this case, although the single-efficiency model no longer works, even at moderate adsorption degrees, the double-efficiency model still works well. This reflects the fact that  $^{89}\text{Sr}$  has an end energy considerably higher than  $^{45}\text{Ca}$ ; thus, the filled/empty conditions lead to different efficiency values for the beta particles emitted by the adsorbed fraction on the wall. The summary of results for several sets of  $^{89}\text{Sr}$  samples, shown in Figure 4, also indicates behavior similar to  $^{45}\text{Ca}$ , with a bias around +1% and discrepancy lower than 2% at high values of the adsorption factor.

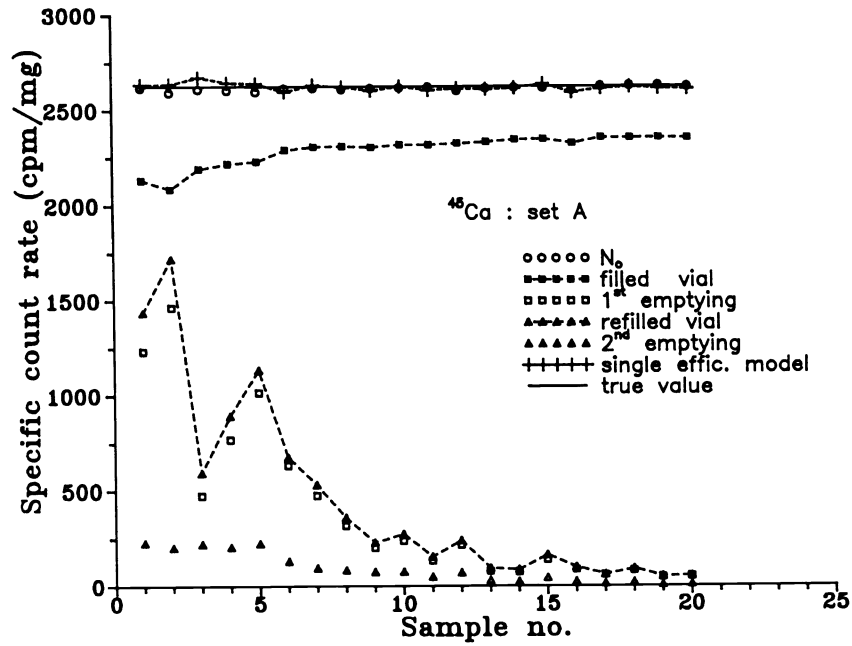


Fig. 1A. Measured count rates and predicted values (single-efficiency model) for  $^{45}\text{Ca}$  samples after two consecutive emptyings

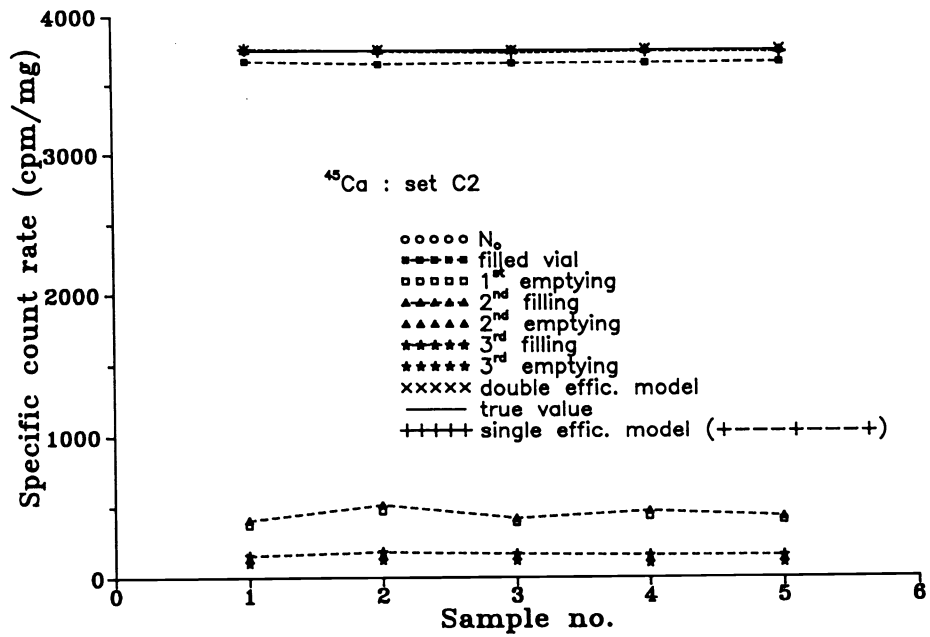


Fig. 1B. Measured count rates and predicted values (single- and double-efficiency models) for  $^{45}\text{Ca}$  samples after three consecutive emptyings

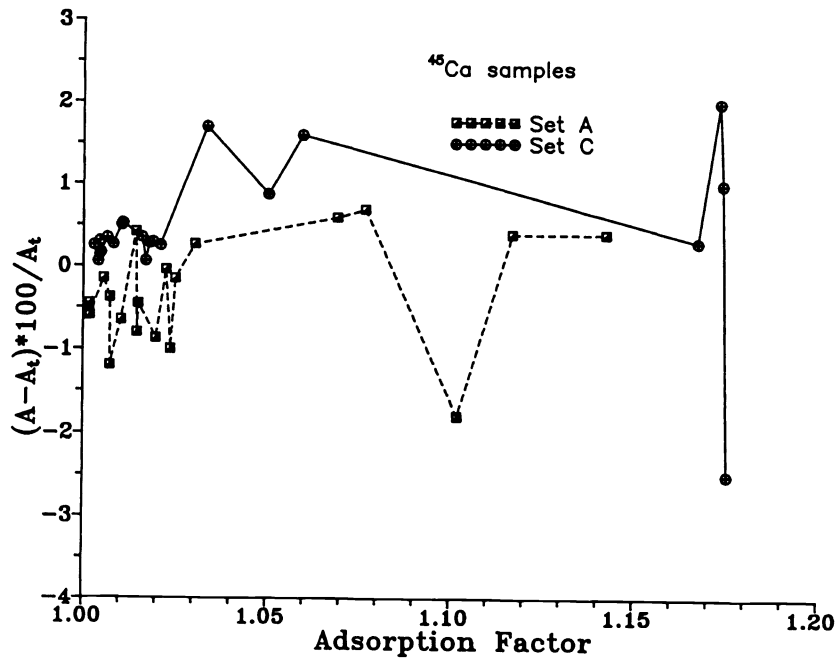


Fig. 2. Relative discrepancy (%) between true and estimated activity as a function of the adsorption correction factor,  $F_A$

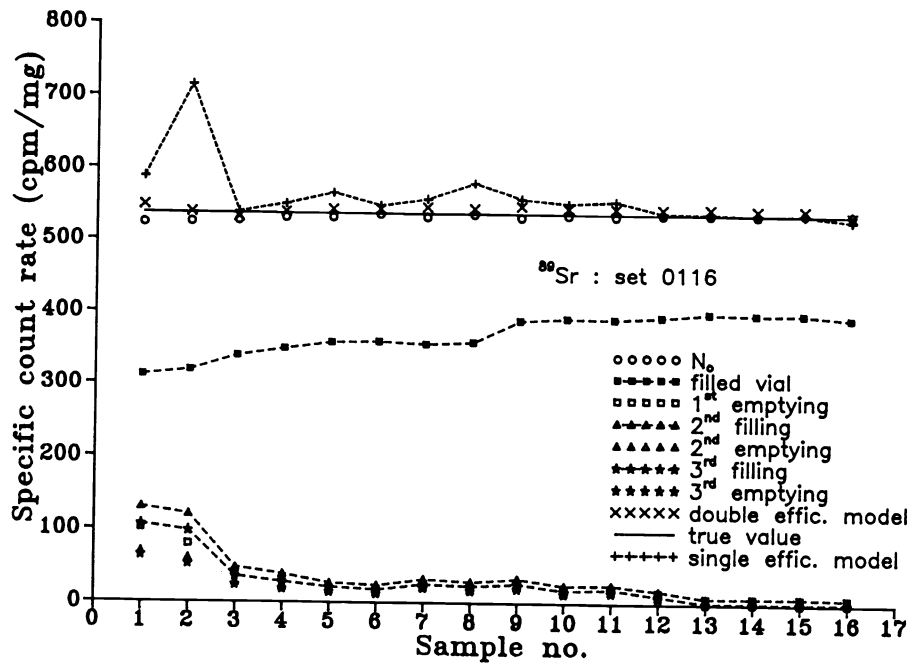


Fig. 3. Measured count rates and predicted values (single- and double- efficiency models) for <sup>89</sup>Sr samples after 2 or 3 consecutive emptyings

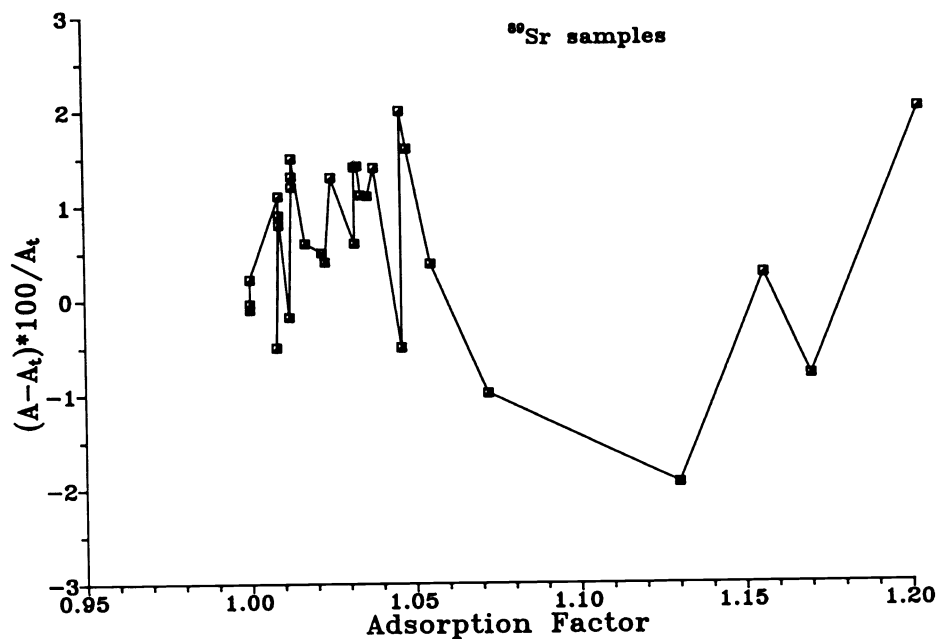


Fig. 4. Relative discrepancy (%) between true and estimated activity as a function of the adsorption correction factor,  $F_A$

## CONCLUSIONS

The single/double-wall-efficiency model provides a useful method of detecting adsorption through a simple cycle of emptying and filling operations, without using other chemicals. It also allows evaluation and correction for the degree of adsorption in terms of the adsorption correction factor,  $F_A$ . This can be estimated directly from the measurement cycle, without calibration curves, and has been successfully applied to the recovery of adsorbed samples of  $^{45}\text{Ca}$  and  $^{89}\text{Sr}$  with 2% uncertainties at adsorption up to 20%.

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