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Applied Radiation and Isotopes 52 (2000) 319–323

Applied Radiation and Isotopes

www.elsevier.com/locate/apradiso

Influence of radioactive impurities on SIR measurements

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Accepted 2 July 1999

Abstract

The correction usually applied to an SIR measurement in the presence of a gamma-ray emitting impurity is presented and explained. The method of calibration of a Ge(Li) spectrometer is briefly described. It is used to look for impurities when SIR measurements show inconsistencies. An example is presented where a ^{103}Ru impurity was discovered in a ^{99}Mo solution. The correction applied compensates for the decrease of around 0.2% per day observed in the SIR measurements of this ^{99}Mo ampoule.

1. Introduction

The SIR (International Reference System for activity measurements of γ-ray emitting nuclides) was started in 1976 at the BIPM as a complement to the international comparisons of activity measurements organized by Section II of the CCRI (Comité Consultatif des Rayonnements Ionisants). The participating national metrological institutes (NMIs) submit SIR glass ampoules containing their standardized solutions of radionuclides to the BIPM where the current produced by these samples in a 4π-ionization well chamber is compared with the current obtained with one of the five radium reference sources. A detailed description of the SIR is presented in Rytz (1978, 1983). The simplicity and rapidity of the measurements as well as the long-term stability of the ionization chamber has allowed the comparison of hundreds of radioactive solutions over more than 20 years. In addition, the NMIs may participate at any time. However, the SIR cannot replace international comparisons that allow a review of the measurement methods of a given radionuclide. The SIR and the CCRI international comparisons were recently designated in the Mutual Recognition Agreement (BIPM, 1999) to be the tools for establishing the degrees of equivalence of NMIs in the field of radioactivity measurements.

The presence of γ-ray emitting impurities in a solution must be taken into account in an SIR measurement. The correction method in use at the BIPM for some 20 years, based on the impurity measurement of the participating NMI, is described in the first part of this paper and its influence on the SIR results is discussed. In the second part, the γ-ray spectrometry system recently calibrated at the BIPM is presented and its complementarity to the NMIs measurements is stressed.

2. The correction for γ-ray emitting impurities in the SIR

An SIR measurement of a radioactive solution having an activity A at the reference date t_r, both given by the participating NMI, is expressed in terms of an equivalent activity A_e. This corresponds to the activity of the solution that would produce the same ionization current as the reference ^{226}Ra source number 5 at a fixed date t_0 (Rytz, 1983; Schrader, 1997). Therefore

$$A_e = A \cdot e^{-\lambda(t_m - t_r)} \cdot \frac{F_j \cdot (I_{Ra} - I_f)/e^{-\lambda_{Ra}(t_m - t_0)}}{(I - I_f)/C}, \quad (1)$$

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PII: S0969-8043(99)00172-4

where I_{Ra} and I are the ionization currents produced by the radium source number j and the ampoule, respectively; here I_f is the background current, F_j is the ratio of currents of radium source no. 5 to no. j, λ_{Ra} and λ are the decay constants of ^{226}Ra and of the measured nuclide respectively, t_m is the date of the SIR measurement and C is the correction factor for γ-ray emitting impurities (see below).

This way of presenting the measurements is very convenient: for a given radionuclide, all the ampoules measured should ideally give the same equivalent activity. The inverse of the latter is indeed proportional to the efficiency of the ionization chamber for this radionuclide (Schrader, 1997; Reher et al., 1998). In consequence, the A_e values of the SIR allow us to compare the NMIs measurements for a given radionuclide, assuming the accuracy of the factors in Eq. (1), especially the correction for impurities.

The correction for the contribution of impurities to the ionization current is calculated from the relative impurity contents ($R_k = A_k/A$, where A_k is the activity of the impurity k at the reference date t_r) given by the NMI and corrected for decay and from the efficiency of the chamber for the main radionuclide and for the impurities (Schrader, 1997). These efficiencies are given by the inverse of the equivalent activities as stated above. Therefore

$$C = 1 + \sum_k \frac{A_k}{A} \cdot \frac{\overline{A_e}}{\overline{A_{e,k}}} \cdot \frac{e^{-\lambda_k \cdot (t_m - t_r)}}{e^{-\lambda \cdot (t_m - t_r)}}$$

$$= 1 + \sum_k R_k \cdot \frac{\overline{A_e}}{\overline{A_{e,k}}} \cdot e^{-(\lambda_k - \lambda) \cdot (t_m - t_r)}, \quad (2)$$

where λ_k is the decay constant of the impurity k and $\overline{A_e}$, $\overline{A_{e,k}}$ are the equivalent activities of the main radionuclide and of the impurity k, respectively. When available, these equivalent activity values are taken as the mean or the median of the SIR results previously obtained for the corresponding nuclide. However, if no SIR data are available for the impurity and/or the main radionuclide, $\overline{A_e}$ and $\overline{A_{e,k}}$ are evaluated from the efficiency curve of the ionization chamber and the decay scheme of the nuclide (Rytz, 1983; Rytz and Müller, 1984; Schrader, 1997). The influence of an impurity may be amplified by more than an order of magnitude by the factor $\overline{A_e}/\overline{A_{e,k}}$. In consequence, even impurities presenting an R_k as small as 1×10^{-4} may have a non-negligible effect on the SIR result.

Let T and T_k be the half lives corresponding to λ and λ_k and let us consider the case where $T_k > T$:

- the correction C increases exponentially with time;
- if R_k is not accurately evaluated or if an impurity has not been detected, the factor C will be incorrect and the resulting error in A_e increases exponentially with time;
- the correction C is minimal when $t_m = t_r$ (usually, the SIR measurement is not made prior to the reference date t_r of the ampoule). The uncertainty of the SIR measurement is then also minimized. It is not advisable, however, to define the reference date t_r too far from the time of standardization of the solution at the NMI. This is because R_k increases with time, as do both the correction for impurities and the uncertainty on the SIR measurement.

When $T_k \ll T$, the best is to wait for the complete decay of the impurity before making the SIR measurement. Finally, if $T_k \leq T$ there is little to be gained by waiting as the impurity correction decreases very slowly.

For a short half life radionuclide, the equivalent activity is often remeasured at different dates. If the resulting A_e values show a trend, this may be due to an inaccurate correction for impurities and/or an incorrect half life. As many parameters are involved, it is often difficult to identify unequivocally the cause of the trend. An independent measurement of the relative impurity content using the BIPM Ge(Li) spectrometer may help to solve the problem.

3. Gamma-ray spectrometry at the BIPM

The calibration method of the BIPM Ge(Li) detector (10% relative efficiency[1]) is described briefly; further details are in Michotte (1999). The measured energy resolution (FWHM) at 1.33 MeV of this detector is 2.3 keV. The full widths at 1/10th and 1/50th of the maximum height are equal to 2.0 × FWHM and 3.3 × FWHM, respectively.

3.1. Source-detector geometry

The Ge(Li) detector has been calibrated using SIR ampoules placed at 20 or 50 cm above the detector in a U-shaped lucite holder which is fixed on a lucite tripod placed on the outer cap of the detector. Small differences in shape and thickness of the ampoule base were observed by Rytz (1983), although the ampoules were (and still are) from the same batch. This induces measurable changes in the attenuation of the γ-ray flux by the glass, especially at low γ energy. The relative standard uncertainty of activity measurements arising from these variations has been evaluated experimentally, giving 2×10^{-3} at 1.2 MeV and 5×10^{-3} at 60 keV. Other sources of uncertainty are the filling height and the density of the radioactive solution, which may

[1] Full-energy peak efficiency relative to a 3″ × 3″ NaI(Tl) cylindrical detector, at 1.33 MeV and a source-to-detector distance of 25 cm.

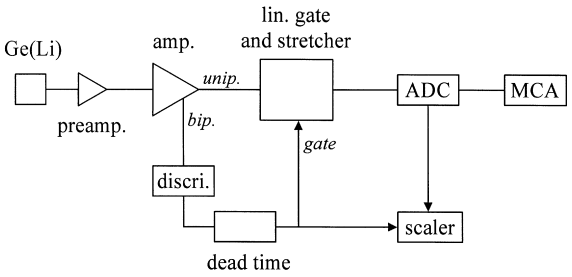

Fig. 1. Block diagram of the electronics of the Ge(Li) spectrometer.

vary among the ampoules. To account for this, a correction factor is evaluated in the approximation of large source-to-detector distances (D). In most cases the correction is less than 5×10^{-3} in relative terms. However, it may reach 1.5% for low energy γ-ray emitters in a high-density solution.

3.2. Electronics

The block diagram of the electronics is presented in Fig. 1. The dead time is determined by the module after the low-level discriminator that generates a gate signal G controlling the digital conversion of the linear unipolar pulses at the stage of the Linear-Gate-and-Stretcher module (LGS). The dead-time module (Bréonce, 1981) inserts a non-extended dead time by impeding the transmission of logic signals during the time chosen. The latter is sufficiently long (51 μs) to allow a complete conversion of the linear pulse before accepting another event. The dead-time correction is evaluated afterwards using the known formula for a non-extended dead time (NCRP, 1985). If the gate signal is present, the LGS converts the linear pulses from the amplifier into square linear pulses which are then analyzed by a Wilkinson/100 MHz Analog-to-Digital-Converter (ADC Canberra 8701). The advantage of the LGS, in comparison with Canberra ADCs, is that in the absence of a gate signal G the input pulse is not stretched, thus avoiding the generation of additional dead time and pulse loss.

3.3. Pile-up and true coincidence summing corrections

The pile-up correction factor has been measured by the two-source method, i.e. by using an additional source beside the detector to induce pile up (e.g. Debertin and Helmer, 1988). For a given count rate, the measured correction shows a dependence on the γ-ray energy.

The true coincidence summing is evaluated by the KORSUM FORTRAN program developed at the PTB and considering the SIR ampoules as point sources. This correction is only used for $D = 20$ cm where it can reach as much as 6×10^{-3} in rare cases, for example ^{56}Co.

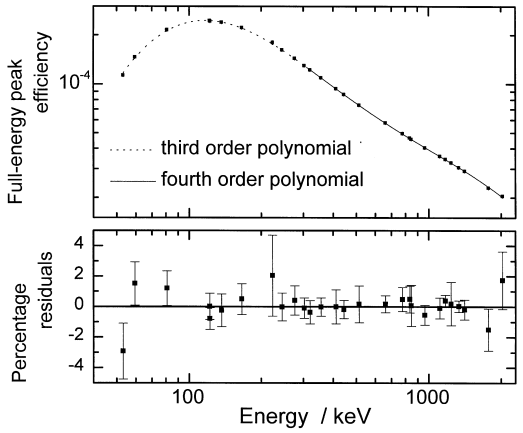

Fig. 2. Efficiency curve and residuals of the Ge(Li) detector for an ampoule-to-detector distance of 50 cm. Eleven radionuclides in SIR ampoules were used.

3.4. Peak integration method

The peak area is evaluated by a simple summation of the channel contents in an interval around the peak. The continuum under the peak is presumed to be linear. The width of the summation intervals is a multiple of the FWHM for the integration of both the peak and the continuum.

3.5. Efficiency curve

As far as possible, ampoules that have given an equivalent activity in good agreement with the international mean value were selected for the calibration. The logarithm of the measured full-energy peak efficiencies are plotted against the logarithm of the γ energy and fitted to a third (fourth) order polynomial at low (high) energy, respectively. The resulting efficiency curve for $D = 50$ cm and the residuals are shown in Fig. 2.

3.6. Test measurements

To test the accuracy of the present calibration, several SIR ampoules were measured (^{22}Na, ^{56}Co, ^{99}Mo, ^{109}Cd, ^{131}I, ^{139}Ce, ^{152}Eu, ^{153}Sm, ^{169}Yb, ^{201}Tl) including their impurity content if relevant and the results compared with those given by the participating NMI. Most of these new measurements are in agreement within 1 or 2 standard uncertainties with the NMI values (see Michotte, 1999 and for the impurities, see Table 1). A typical uncertainty budget of an activity

Table 1
Relative impurity contents as measured with the Ge(Li) detector and as given by the NMI, together with their ratio. The standard uncertainties are given in brackets

Radionuclide	Impurity	R_k from Ge(Li) (10^{-3})	R_k from NMI (10^{-3})	Ratio Ge(Li)/NMI
^{56}Co	^{57}Co	9.49 (11)	9.21 (6)	1.031 (13)
	^{58}Co	4.3 (2)	4.2 (1)	1.02 (5)
^{56}Co	^{57}Co	10.90 (7)	11.00 (20)	0.991 (19)
	^{58}Co	5.2 (5)	5.02 (13)	1.03 (10)
^{109}Cd	^{65}Zn	0.046 (7)	0.047 (5)	0.98 (18)
^{152}Eu	^{154}Eu	3.1 (2)	3.0 (3)	1.04 (13)
^{153}Sm	^{154}Eu	0.37 (1)	0.34 (2)	1.09 (7)
	^{156}Eu	0.93 (3)	1.26 (9)	0.74 (6)
^{201}Tl	^{202}Tl	6.01 (16)	6.00 (10)	1.00 (3)
^{201}Tl	^{202}Tl	8.11 (12)	7.6 (6)	1.07 (9)

measurement with the Ge(Li) detector is given in Table 2.

4. Example

A solution of ^{99}Mo ($T = 65.92 \pm 0.10$ h) measured at an NMI using their pressurized 4π-ionization chamber was submitted to the SIR, with no impurity notified. The equivalent activity was measured at the BIPM at the reference date of the solution and additional measurements were made over a period of three weeks. As shown in the upper part of Fig. 3, the results show a strong decrease that could be explained if the true half life of ^{99}Mo is 66.6 h (a value in agreement with measurements made in the seventies) or if an impurity is present in the solution. The Ge(Li) spectrometer allowed clear identification of a γ ray at 497 keV corresponding to ^{103}Ru ($T = 39.255 \pm 0.015$ d), yielding $R_k = (2.78 \pm 0.04) \times 10^{-4}$ as seen in the lower part of Fig. 3. This impurity was probably hidden by the high activity of ^{99}Mo ($A(t_r) = 73.3$ MBq) when the impurity check was performed by the NMI and consequently not notified to the SIR. The present R_k value has been used to evaluate the correction factors C using Eq. (2) and the corrected A_e values obtained no longer depend on time (circles in Fig. 3). The SIR result registered in the SIR database is the initial measurement for which the correction C is negligible. Nevertheless, if the SIR measurements had suffered a delay of one week for any reason, then the effect of ^{103}Ru would have required a correction.

5. Discussion and conclusion

The example given above is an easy case as most parameters (e.g. half life, efficiency of the SIR chamber) are well known for both the main radionuclide and the impurity. Other examples are ^{201}Tl containing a ^{202}Tl impurity, or ^{153}Sm containing some ^{154}Eu and ^{156}Eu. The latter case is complex as both the decay scheme of ^{153}Sm and the efficiency of the chamber for ^{156}Eu are not well known. The discrepancy observed between two SIR measurements separated by an interval of a few days is most likely the result of an inaccurate value of the product ($R_{156} \cdot A_e / A_{e,156}$), where the subscript 156 refers to ^{156}Eu. In this case, a relative difference of 1×10^{-2} in the SIR result for ^{153}Sm is observed depending on which R_{156} value

Table 2
Uncertainty budget of an activity measurement with the Ge(Li) detector

Source of uncertainty	Relative uncertainty	Comment
Dead time	$< 3 \times 10^{-4}$	for count rates < 5000 s^{-1}
Pile up	$3–6 \times 10^{-3}$	for count rates < 1500 s^{-1}
True coincidence summing	1×10^{-3}	if relevant
Full-energy peak efficiency	$3–10 \times 10^{-3}$	for E_γ between 100 keV and 1.5 MeV
Self attenuation of the solution	1×10^{-3}	
Attenuation by the ampoule base	$1–5 \times 10^{-3}$	depending on gamma energy
Ampoule position	1×10^{-3}	
Long term drift of the efficiency	6×10^{-3}	for $E_\gamma > 1$ MeV, 1 year after calibration
Decay correction and γ-emission probability		depends on the nuclide decay scheme

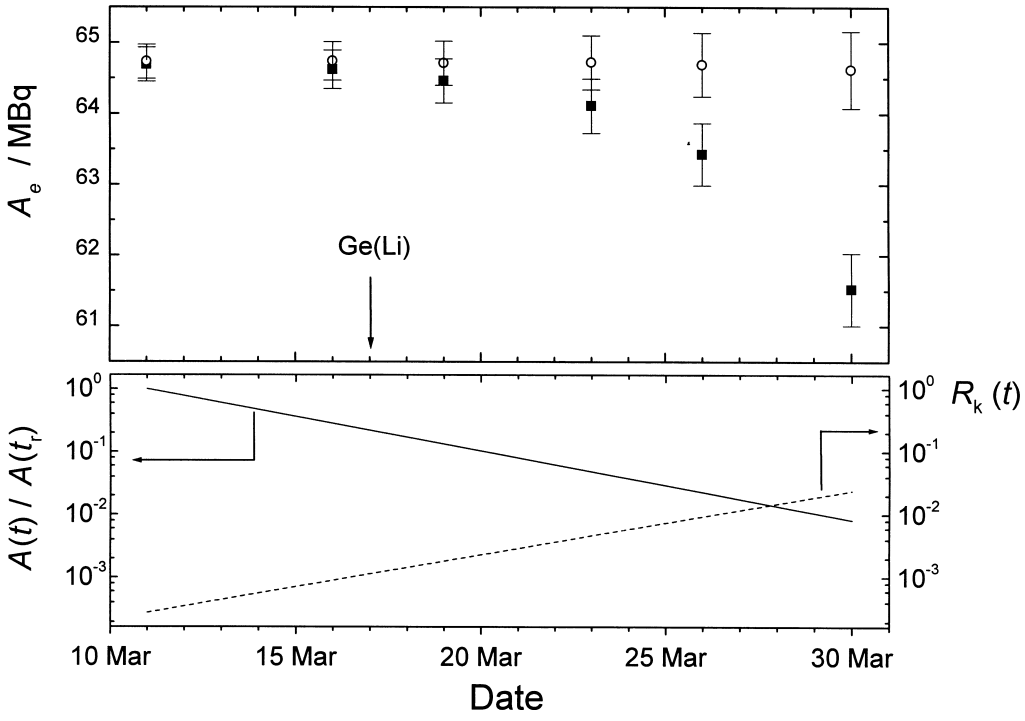

Fig. 3. (Top) Squares: equivalent activities for an ampoule of ^{99}Mo as determined using the NMI standardization. Circles: idem but corrected for the ^{103}Ru impurity measured with the BIPM Ge(Li) spectrometer. (Bottom) Activity of the ^{99}Mo ampoule normalized to unity at the reference date (full line). Relative impurity content of ^{103}Ru (dashed line).

is used (NMI or Ge(Li)). The combination of the NMI, Ge(Li) and SIR measurements should identify whether the problem arises from the R_{156} value or from the ratio $A_e/A_{e,156}$. The analysis is in progress.

In conclusion, the influence of γ-ray emitting impurities on SIR measurements has been underemphasized until now. The calibrated Ge(Li) spectrometer of the BIPM demonstrates that impurities can be the cause of significant discrepancies in the SIR results and should help to eliminate this problem.

Acknowledgements

The author wishes to thank M. Nonis and C. Colas for their technical assistance, K. Debertin for providing the KORSUM program and, the LPRI γ-spectrometry group, L. Lucas (NIST), G. Ratel and J.W. Müller for valuable discussions.

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