Absolute activity measurement of the electron-capture-based radionuclides ^{139}Ce, ^{125}I, ^{192}Ir and ^{65}Zn by liquid scintillation coincidence counting

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Abstract

Four radionuclides with electron-capture-based decay schemes have been directly measured by a liquid scintillation coincidence extrapolation technique. ^{125}I, ^{192}Ir and ^{65}Zn were measured as part of international key comparisons held under the auspices of the International Bureau of Weights and Measures (BIPM). The ^{139}Ce measurements formed part of a regional comparison organized by the Asia Pacific Metrology Programme (APMP). Since ^{139}Ce decays purely by electron-capture, the basic method is described for this radionuclide. Results and difficulties encountered are discussed and uncertainty budgets are presented.
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Keywords: Liquid scintillation coincidence counting; ^{139}Ce; ^{125}I; ^{192}Ir; ^{65}Zn

1. Introduction

Four radionuclides with electron-capture-based decay schemes have been measured using variations of the 4π(LS)e,x-γ coincidence extrapolation technique. Advantages of using liquid scintillation (LS) counting in the 4π-channel are that self-absorption does not occur, leading to Auger electrons being detected with relatively high efficiency; source preparation is easy; and the source geometry is highly reproducible. The latter leads to good reproducibility of the counting efficiency of the X-rays and Auger electrons, which in turn gives rise to consistent results amongst the counting sources. The application of the technique has been reported on previously for ^{201}Tl (Simpson and Meyer, 1994), but little else has been reported in the open literature.

^{125}I, ^{192}Ir and ^{65}Zn were measured as part of international key comparisons held under the auspices of the International Bureau of Weights and Measures (BIPM) and ^{139}Ce was measured as part of a regional comparison organized by the Asia Pacific Metrology Programme (APMP).

Since ^{139}Ce decays purely by electron-capture, the basic method is reviewed for this radionuclide. ^{192}Ir and ^{65}Zn have more complex decay schemes and resulting differences are discussed. For ^{125}I, a modification of the 4π(e,x)-γ coincidence extrapolation technique was investigated to complement widely used methods that are based entirely on K X-ray counting (Taylor, 1967; Eldridge and Crowther, 1964). Results and difficulties encountered are presented.

2. Liquid scintillation coincidence counting

The basic method is reviewed with respect to ^{139}Ce, which decays purely by electron-capture to the 166 keV excited state of ^{139}La. This state de-excites through the emission of conversion electrons and γ-rays. The detection efficiency analysis is based on a counting source being viewed by two phototubes in coincidence, with a single NaI(Tl) crystal detecting the γ-rays. The 4π coincidence count rate from the LS detector is given by (Steyn et al., 1976)

$$N_{4\pi} = N[f + (1-f)PP_S + (1-f)(1-P)\varepsilon_{AX}], \qquad (1)$$

where N is the source activity, f is the conversion electron probability, ε_{AX} is the detection efficiency for the

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electron-capture emissions, P is the probability of the γ-rays interacting with the scintillator solution and P_S is the detection probability of the Compton electrons together with the particles emitted in the electron-capture process (forming a sum pulse). The conversion electrons are detected with 100% efficiency.

The γ-ray count rate given by the NaI detector is

$$N_\gamma = N(1-f)(1-P)\varepsilon_\gamma, \qquad (2)$$

where ε_γ is the efficiency for detecting events in the full-energy peak.

The coincidence count rate is thus

$$N_C = N(1-f)(1-P)\varepsilon_{AX}\varepsilon_\gamma. \qquad (3)$$

Thus ε_{AX} can be determined experimentally by measuring N_C/N_γ. Eq. (1) can then be expressed as

$$\frac{N_{4\pi}N_\gamma}{N_C} = N(1-f)(1-P) + N[f + (1-f)PP_S]\frac{N_\gamma}{N_C}. \qquad (4)$$

When $(N_\gamma/N_C) \to 1$ so will P_S and the source activity is given by the corresponding extrapolated value of $N_{4\pi}N_\gamma/N_C$. As N_γ/N_C is varied, P_S is expected to change due to the fairly low energy of the Compton electron spectrum. If this variation is linear, it is a simple matter to show that the functional form of Eq. (4) is predicted to be linear.

The approach and complexity of the detection efficiency analyses of the other radionuclides investigated here are dependent on the particular decay scheme.

3. Activity measurements

In all cases, counting sources were prepared in custom made flat-faced cylindrical glass vials, each being viewed in turn by two RCA 8850 phototubes coupled in coincidence. The escaping γ-rays were detected with a $75\,\mathrm{mm} \times 75\,\mathrm{mm}$ NaI(Tl) crystal. Conventional analogue pulse processing was used, with slow logic signals fed into a locally designed and built coincidence unit (Simpson and Meyer, 1988) and routed through to a 32-channel scaler, enabling up to 15 datum points to be collected simultaneously (Simpson and van Oordt, 1997). To ensure the detection of the low energy X-rays and Auger electrons, the lowest threshold in the 4π-channel was set below the single electron peak. The counting efficiency was varied by setting additional discrimination levels among the first few monopeaks, counting integrally above these thresholds. In this way all electron-capture events contribute to the counting, thereby eliminating the need of a correction for losses as reported by Funck and Larsen (1983) for a proportional counter. Suitable γ-window settings were set for each radionuclide as described below.

The recorded counts were corrected for background, afterpulsing and rate-dependent effects due to the coincidence resolving time ($0.48 \pm 0.01\,\mu$s) and the inherent non-extending deadtime (Simpson, 1991), which was in the range 1.07–1.39 μs depending on the threshold settings. The

afterpulse correction for the lowest threshold setting was measured as 0.81% (^{65}Zn), 0.44% (^{192}Ir), 0.23% (^{125}I) and 0.15% (^{139}Ce). In most cases data in the form $N_{4\pi}N_\gamma/N_C$ vs. N_γ/N_C were generated from the corrected counts.

3.1. ^{139}Ce

The ^{139}Ce solution was received from the coordinating laboratory for measurement within the framework of a regional key comparison. Four accurately weighed sources were prepared from the solution by mixing in 12 ml of liquid scintillator (Quicksafe A from ZINSSER ANALY-TIC) to which 12.5 ml/l of a carrier solution comprising 1 g/l CeCl$_3 \cdot$7H$_2$O in 1 M HCl had been added to minimize adsorption to the glass vials.

Three separate windows were set in the γ-channel (166 keV photopeak; spanning a range from the K X-ray peak to the photopeak; and the iodine escape peak and photopeak), providing three different sets of data for each source. Thirteen bias levels were set in the 4π-channel and all levels were counted simultaneously in integral mode, giving 13 data points for each γ-window. Fig. 1 shows typical sets of data from one of the sources. The source activity was obtained from an extrapolation of the data to $N_\gamma/N_C = 1$ using a function that mimics a linear fit at the higher efficiencies coupled to a second-order fit at lower efficiencies (Miyahara et al., 1986). Since all the sets gave the same extrapolated value within counting statistics, an average value was taken. At the present time the results of the comparison are confidential, but the present activity value agrees well with a preliminary analysis of the submissions of the other participants. The uncertainty estimates are given in Table 1.
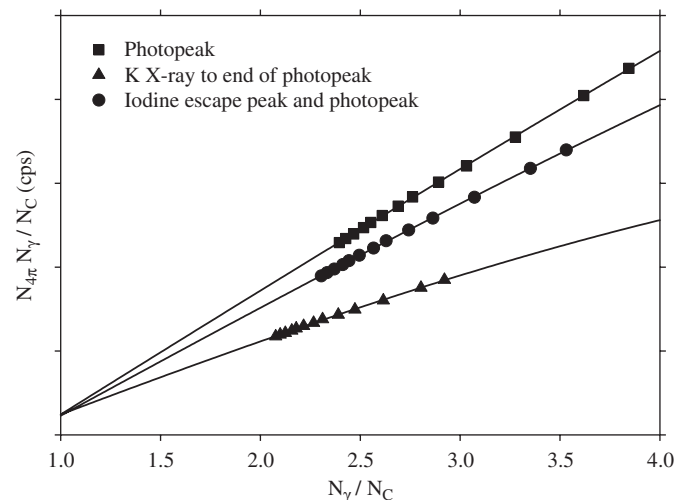

Fig. 1. A series of 4π count rates, $N_{4\pi}$, from a ^{139}Ce source expressed as the inverse of the counting efficiency for various γ-window settings, where N_γ is the γ-channel rate and N_C the coincidence rate. The lines are fits to the data sets using a third-order polynomial with the second-order coefficient set to zero.

Table 1
Standard uncertainty budgets for each of the radionuclides measured, in percentage of the respective activity concentrations

Component	Relative standard uncertainty multiplied by a sensitivity factor (%)			
	^{139}Ce	^{125}I	^{192}Ir	^{65}Zn
Counting statistics	0.09	0.32	0.06	0.11
Weighing	0.015	0.05	0.02	0.02
Dead time	0.05	0.09	0.004	0.006
Coincidence resolving time	<0.01	0.007	<0.001	<0.001
Satellite pulses	0.30	0.03	0.05	0.06
Background	0.01	0.05	0.05	0.10
Adsorption	0.002	—	—	—
Impurities	—	—	—	<0.012
Half life	0.002	—	0.02	0.025
Extrapolation of efficiency curve	0.42	0.40	0.03	0.26
γ-efficiency gate	—	—	0.18	—
Combined uncertainty (in quadrature)	0.53	0.53	0.21	0.31

3.2. ^{192}Ir

The original ^{192}Ir solution received from the BIPM was used to prepare six sources by dissolving accurately weighed aliquots in 12 ml of Quicksafe A liquid scintillator to which 1 ml/l 3 M HCl had been added.

Similar efficiency formulae given in Reher et al. (1992) for a proportional counter are applicable to the LS system. Although it can be shown that the activity is given by an extrapolation with $N_\gamma/N_C = 1$, the complex decay scheme makes it difficult to predict the functional form. Various γ-window settings were investigated, giving rise to a number of counting sets as follows:

Counting set 1: γ-window encompassing the 201–308 keV photopeaks (linear fit).
Counting set 2: γ-window incorporating the 604 and 612 keV photopeaks (second-order polynomial fit).
Counting set 3: γ-window $\geqslant 296$ keV photopeaks (third-order polynomial fit).
Counting set 4: γ-window incorporating the 296 and 308 keV photopeaks (second-order polynomial fit using the 10 highest efficiency points).

Data from one of the sources with these settings is illustrated in Fig. 2. It is of interest to note that with counting set 4 it was necessary to increase the 4π-channel amplification considerably to obtain a 4π-efficiency comparable with the other sets and also a reliable extrapolation. With the same settings as used with the other sets, the measured efficiency was much lower, the extrapolation leading to an apparently low activity value (the dotted line in Fig. 2). For reporting purposes counting set 1 was selected due to the linear efficiency function and because the γ-window included γ peaks corresponding to both the electron-capture and β branches. The other data sets were used to give an estimate of systematic effects due to different γ-window settings. The activity specified was 204.77 ± 0.43 kBq/g on the comparison reference date 1
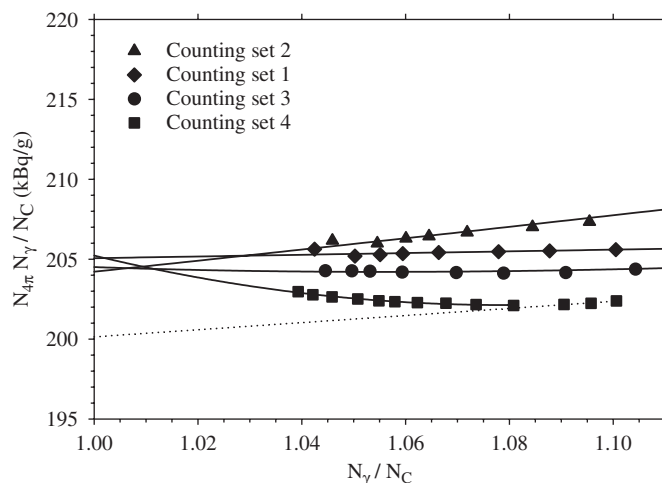

Fig. 2. A series of 4π count rates, $N_{4\pi}$, from an ^{192}Ir source expressed as the inverse of the counting efficiency, where N_γ is the γ-channel rate and N_C the coincidence rate. The data were divided by the source mass for display purposes and only the high-efficiency points are shown. The γ-windows used are described in the text, as are the polynomial fits to the data.

December 2002, 0 h UTC, with the uncertainty budget shown in Table 1. The present value is in good agreement with those of the other participants, most using non-LS techniques (Ratel and Michotte, 2004).

3.3. ^{65}Zn

The master ^{65}Zn solution received from the BIPM was used to prepare eight sources by dissolving accurately weighed aliquots in 12 ml of pure Quicksafe A liquid scintillator.

The detection efficiency formulation for ^{65}Zn can be easily derived from the expressions given in Simpson and Morris (2004), showing that an extrapolation to an efficiency of unity gives the activity. Three separate γ-settings were utilized, one over the 1115.5 keV photopeak
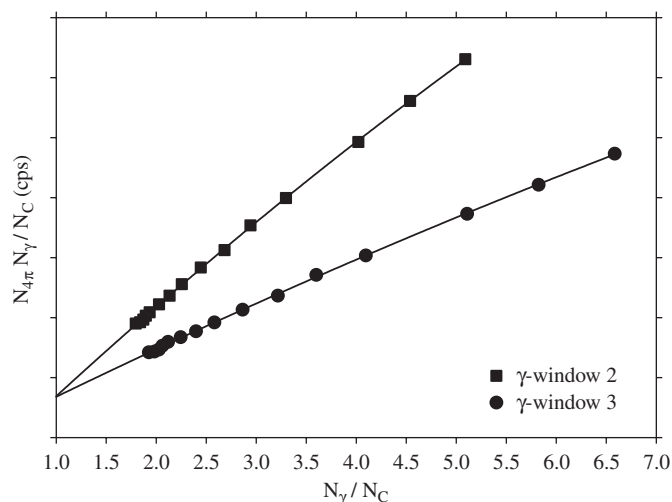
Fig. 3. Two sets of 4π count rates, $N_{4\pi}$, from a ^{65}Zn source expressed as the inverse of the counting efficiency, where N_γ is the γ-channel rate and N_C the coincidence rate. The lines are second-order polynomial fits to the data.

Fig. 4. A set of ^{125}I 4π count rates, X, plotted as a function of the counting efficiency, C/G, where G is the γ-channel rate and C the coincidence rate. The line is a second-order polynomial fit to the data.

(window mode), a gate set just below the 1115.5 keV photopeak (window 2, counted integrally) and one set just above the 511 keV photopeak (window 3, counted integrally). The integral-mode data sets from one of the sources are illustrated in Fig. 3, the window-mode set being very similar to window 2. Sources 1–4 were counted with γ-window 1 and sources 5–8 with γ-windows 2 and 3. All 12 extrapolated values gave similar results and an average was taken as the specified activity concentration. The value agrees well with a preliminary analysis of the comparison results, being confidential at the time of writing.

3.4. ^{125}I

A complete derivation of the LS efficiency formulae for ^{125}I is available in Simpson and Meyer (1989). In this treatment the γ-window is set to select only the true-coincidence sum events to ensure the detection of a K X-ray, X_1, associated with the initial electron-capture process. Thus, the $4\pi-X$ coincidences between X_1 and its related Auger electrons is sampled to obtain the 4π efficiency.

The ^{125}I solutions studied were received from the BIPM for measurement within the frameworks of both the earlier 1988 (Ratel, 1995; Ratel and Michotte, 2003) and recent 2004 international comparisons. In 1988 seven sources were prepared from a 2.045 times weaker dilution using 12 ml of liquid scintillator (Instagel from Packard) containing 3 ml/l 3 M HCl. For the 2004 comparison, a number of sources were prepared in both Instagel and Quicksafe A. Because of the low count rate expected experimentally in the γ-window, the source masses were such that the 4π count rates were high (typically 25000 s^{-1}) so as to get a reasonable rate for the sum peak events (34 s^{-1}).
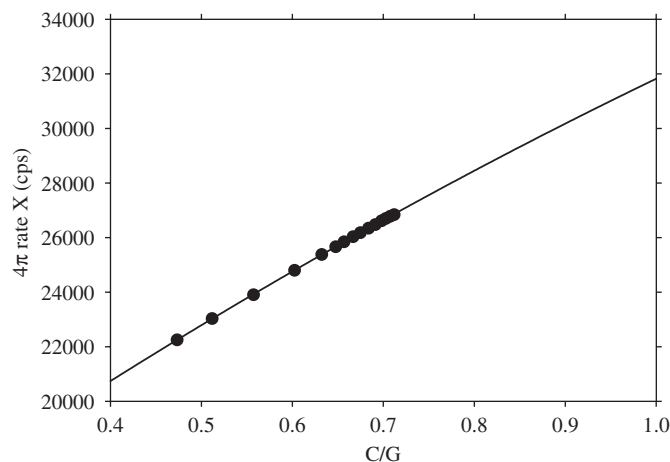
In the 1988 comparison the result obtained by the LS method was higher than that given by the Taylor method (Taylor, 1967) by 0.78%, the activity concentration being 1448 ± 8 kBq/g. The uncertainty estimates are given in Table 1. Fig. 4 shows a typical data set, where the maximum efficiency obtained was about 0.71, being essentially the detection efficiency for L Auger electrons. A less successful result was obtained in the 2004 comparison, the activity extracted being higher than the Taylor method by about 6%. It was noted that there was poorer separation between the single and sum peaks, the poorer resolution possibly leading to additional counts in the sum peak. This supposition is substantiated by the fact that the maximum efficiency obtained was only 0.67, considerably lower than previously. This observation is undergoing further investigation.

4. Conclusions

The coincidence extrapolation method with a liquid scintillation counter in the 4π-channel is a viable technique for the absolute activity measurement of electron-capture-based radionuclides. An advantage is that because there is no self-absorption effect in the sources, all low-energy emissions contribute to the measured counting efficiency. The efficiency data can generally be fitted with a linear function, particularly in the high-efficiency region, or by a low-order polynomial expression, giving rise to reliable extrapolated activity values.

The application of the method to ^{125}I is more difficult due to the requirement of a proper background correction to the sum peak area. It is surmised that a NaI detector with improved resolution that better separates the sum peak will reduce the discrepancy observed in the more recent activity measurement.

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