

# THE ETDCR METHOD OF STANDARDIZING $^{55}\text{Fe}$ AND $^{54}\text{Mn}$

RYSZARD BRODA and KRZYSZTOF POCHWALSKI

The Radioisotope Research Centre, 05-400 Otwock/Świerk, Poland

**ABSTRACT.** The enhanced triple-to-double coincidence ratio (ETDCR) method was designed to determine radioactive concentration of solutions by using a triple liquid scintillation detector. The method is based on the counting efficiency calculation from the triple-to-double coincidence counts ratio. We describe ETDCR measurements of electron capture nuclides using  $^{55}\text{Fe}$  and  $^{54}\text{Mn}$  as examples. The energies of Auger electrons and X photons of these nuclides are similar; conclusions deduced from the measurement of one nuclide may be then, to a certain degree, applied to both. The results of  $^{55}\text{Fe}$  and  $^{54}\text{Mn}$  measurements by the ETDCR method have been compared to  $^{54}\text{Mn}$  results, obtained by the  $4\pi(\text{e,X})$ - $\gamma$  coincidence method, as well as with results of both nuclides' HPGe spectrometric detector measurements.

## INTRODUCTION

The first version of the triple-to-double coincidence ratio (TDCR) method, was published in 1979 (Pochwalski & Radoszewski 1979). A triple photomultiplier liquid scintillation detector enabled simultaneous counting of two types of coincidence pulses, triple coincidence ( $N_T$ ) pulses and sum of three double coincidence ( $N_D$ ) pulses, characterized by different counting efficiencies. The ratio,  $K = N_T/N_D$ , served to represent the counting efficiency of the source. For beta emitters, the K value could roughly approximate the D channel counting efficiency, and the source activity could be obtained by a simple extrapolation, particularly for maximum  $\beta$  energy higher than 150 keV. For emitters with semi-mono-energetically shaped scintillation spectra, the linear extrapolation was no longer possible, and activity determination was not so simple.  $^{55}\text{Fe}$  is an example of this type of emitter. In the case of two distinctly separated energy peaks spectra, *e.g.*, those produced by  $^{131}\text{Cs}$  radiation, the problem is much more complicated. Here we present the possibility of standardizing simple spectrum electron-capture radionuclides.

## METHODS

Both  $^{55}\text{Fe}$  and  $^{54}\text{Mn}$  decay by electron capture; both emit Auger electrons and X-rays of low, comparable energy. In liquid scintillation counting (LSC) of these nuclides, only K-shell radiation ( $\sim 5$  keV) is considered, because L-shell radiation energy ( $\sim 0.6$  keV) is too low for detection. Problems in LSC counting of both nuclides are similar; observations made while counting one may be applicable to the other.  $^{55}\text{Fe}$  is difficult to measure due to its low energy (5 keV). However,  $^{54}\text{Mn}$  emitting gamma quanta of 835 keV is measurable *via* coincidence methods and may be used for comparison with  $^{55}\text{Fe}$ . Table 1 shows predominant, K-shell data of the disintegration rate of the two radionuclides from tables of Lagoutine, Coursol and Legrand (1986) and probabilities of photon interaction with the used LS cocktail, calculated according to Berger and Hubbell (1987) and Becker, Lamé and Vallée (1986).

We use the enhanced triple-to-double coincidence ratio (ETDCR) method (Pochwalski, Broda & Radoszewski 1988; Broda, Pochwalski & Radoszewski 1988; Broda & Pochwalski 1992) to standardize the radioactive concentration of solutions in a triple coincidence LS detector. This is an absolute method, for which no standard or auxiliary source is needed. The method consists of simultaneous counting of five different kinds of coincidence pulses: three double-coincidence  $N_{AB}$ ,  $N_{BC}$ ,  $N_{CA}$ , triple-coincidence  $N_{ABC}$  ( $N_T$ ) and a logical sum of the three double-coincidence, including triple-coincidence  $N_{AB+BC+CA}$  ( $N_D$ ), pulses. The pulses are counted (i) times, each at different counting efficiency, which is modified by the voltage reduction of the detector photomultiplier fo-

TABLE 1. Probability of Particular Scintillation Pulse Formation

Nuclide	Pulse origin	Probability
<sup>55</sup> Fe	K shell	0.861 ± 0.007
<sup>54</sup> Mn	K shell	0.825 } 0.888 ± 0.006
	γ*	

\*We made a correction of +0.002 for γ interaction with the vial walls.

using electrodes. Thus, a measurement of a source as a series of (i) counting points is obtained. Each point consists of the counting rates,  $N_x^i$ , of each type, x, of the coincidence pulses. The counting efficiency at each of the points is related but not equal to the basic efficiency parameter of the ETDCR method,  $K = N_T/N_D$ , which determines the counting efficiency. The ETDCR parameter can be expressed independently of  $N_D$  by

$$K = \left( \frac{N_{AB}}{N_T} + \frac{N_{BC}}{N_T} + \frac{N_{CA}}{N_T} - 2 \right)^{-1} . \quad (1)$$

The theoretical counting efficiency,  $\Phi_x^i$ , and the radioactive concentration,  $N_o^i$ , are calculated at each counting point. The radioactive concentration,  $N_o$ , of the solution is taken as the mean of all counting point radioactive concentrations,  $N_o^i$ , because  $N_o^i$  becomes independent of the counting points when proper counting conditions and calculation parameters are selected.

At each counting point, i, the radioactive concentration of the solution,  $N_o^i$ , can be determined from the counting rates,  $N_x^i$ , the source mass, m, and theoretical counting efficiencies,  $\Phi_x^i$ , by solving a system of four equations

$$N_{AB}^i = N_o^i \Phi_{AB}^i(\varepsilon_A, \varepsilon_B) \quad (2)$$

$$N_{BC}^i = N_o^i \Phi_{BC}^i(\varepsilon_B, \varepsilon_C) \quad (3)$$

$$N_{CA}^i = N_o^i \Phi_{CA}^i(\varepsilon_C, \varepsilon_A) \quad (4)$$

$$N_{ABC}^i = N_o^i \Phi_{ABC}^i(\varepsilon_A, \varepsilon_B, \varepsilon_C) \quad (5)$$

where  $\varepsilon_A$ ,  $\varepsilon_B$  and  $\varepsilon_C$  are the overall phototube efficiencies. Calculation of  $\Phi_x^i$  and  $N_o^i$  is performed by fitting the theoretical to experimental TDCRs, according to Broda and Pochwalski (1992) and Broda (1989). Proper selection of the ionizing quenching constant, kB, the energy conversion factor, L, and the detector light collection efficiency,  $\xi$ , enables us to reduce the dependence of the counting point radioactive concentration,  $N_o^i$ , on the counting efficiency,  $\Phi_x$ , as well as on the ETDCR. The degree of independence of the calculated radioactive concentration on the efficiency value is treated as the criterion of measurement quality. The counting efficiency,  $\Phi_x$ , of each type, x, of pulse of an electron-capture radionuclide is a sum of counting probabilities,  $P_{Ex}^j$ , of all, j, scintillations of intensities,  $I_j$

$$\Phi_x = \sum_j I_j P_{Ex}^j . \quad (6)$$

The  $P_{Ex}$ , which depends on  $\epsilon_A$ ,  $\epsilon_B$  and  $\epsilon_C$ , as well as on the constants,  $kB$ ,  $L$  and  $\xi$ , are shown in Broda, Pochwalski and Radoszewski (1988) for binomial and Poisson photoelectron distribution. For low-energy electron-capture radionuclides, the best fit, in random uncertainty limits, of the calculated  $\Phi_x(K)$  to the experimental efficiency, has been obtained for the negative binomial distribution. However, there is no other reason to apply this distribution. The sum of double coincidences is most efficiently counted, compared to any other coincidence of the system; the  $N_D$  counts and  $\Phi_D$  efficiency are then the most convenient for presenting the results. Figures 1A and 2A show the theoretical efficiencies,  $\Phi_D(K)$ , for <sup>55</sup>Fe and <sup>54</sup>Mn, excluding L-shell radiation, calculated with the negative binomial distribution. When  $K = 1$ , the scintillation probability reaches these values, not unity, as presented in Table 1.

Three <sup>55</sup>Fe and <sup>54</sup>Mn sources of each radionuclide were prepared in glass vials in a scintillator of 10 ml toluene solution of 10 g liter<sup>-1</sup> of butyl-PBD and 0.3 g liter<sup>-1</sup> of bis-MSB. To avoid quenching by water, the Fe and Mn aqueous solutions were transformed into dehydrated organic complexes with TOPO before mixing with the scintillator. Three sources from each solution of both radionuclides were prepared on Mylar foil for comparative measurements by using an HPGe spectrometric detector.

**RESULTS**

Figures 1 and 2 show theoretical curves,  $\Phi_D(K)$ , best fitted to experimental points for both nuclides, the experimental efficiencies,  $N_D^i(K)/N_o$ , and radioactive concentration,  $N_o^i$ . The photoelectron negative binomial distribution was used in calculations with

$$\begin{aligned}
 kB &= 0.013 \pm 0.002 \text{ g MeV}^{-1} \text{ cm}^{-2} \\
 L\xi &= 0.025 \pm 0.001
 \end{aligned}
 \tag{7}$$

as in Broda, Pochwalski and Radoszewski (1988). Tables 2 and 3 show the calculated radioactive concentrations,  $N_o$ , and uncertainties. The random and systematic uncertainties at 99% confidence level are presented here. The systematic uncertainty includes decay data uncertainties according to the tables of Lagoutine, Coursol and Legrand (1986).

TABLE 2. Results of <sup>55</sup>Fe Measurements

Method of measurement	$N_o$ (kBq g <sup>-1</sup> )	Random (%)	Systematic (%)	Overall (%)
ETDCR	547.4	± 0.3	± 1.5	± 1.5
HPGe	555.3	± 0.9	± 2.9	± 3.0

TABLE 3. Results of <sup>54</sup>Mn Measurements

Method of measurement	$N_o$ (kBq g <sup>-1</sup> )	Random (%)	Systematic (%)	Overall (%)
ETDCR	1009	± 0.4	± 1.5	± 1.6
HPGe	992	± 0.5	± 0.8	± 0.9
4π(e,x)-γ	1003	± 0.8	± 0.1	± 0.8

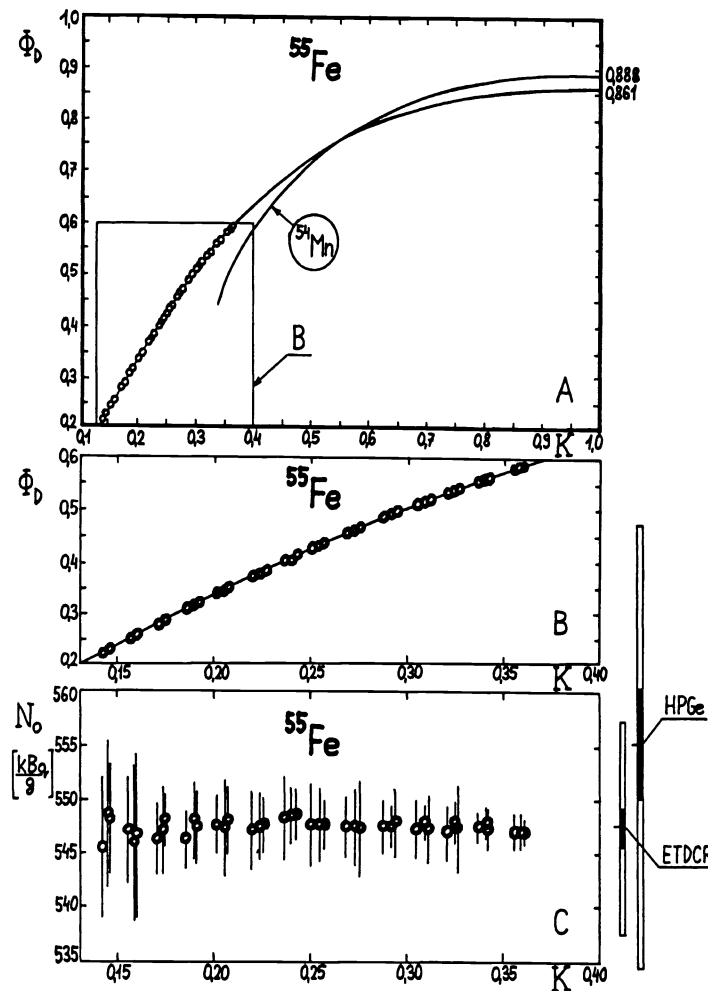


Fig. 1. The results of measurements of the  $^{55}\text{Fe}$  source set. A, B. Theoretical efficiency function,  $\Phi_D(K)$ , (—) and the experimental efficiency (o). For comparison, a  $^{54}\text{Mn}$  curve and maximum counting probability values at  $K=1$  are shown. C. The counting point radioactive concentration,  $N_{0i}$ , as a function of the K ratio and the solution radioactive concentration,  $N_0$ , with random and systematic uncertainties, determined by ETDCR LSC and HPGe spectrometry.

Chylinski (1992) separately standardized  $^{54}\text{Mn}$  solution by the  $4\pi$  (e,X) LS- $\gamma$  coincidence method.  $^{54}\text{Mn}$  mylar foil sources were measured with a 72-cm<sup>3</sup> coaxial HPGe detector (Kempisty 1991), and  $^{55}\text{Fe}$  mylar foil sources were measured with a 3-cm<sup>2</sup> detection surface, 1-cm-thick planar HPGe detector (Kempisty 1990). For  $^{55}\text{Fe}$ , the systematic uncertainty of the K-shell LSC detection efficiency, based on X-rays and Auger electrons detection, is much lower than the systematic uncertainty of the K-shell spectrometric detector efficiency based on X-ray detection only. The results of radioactive concentration measurements of the  $^{55}\text{Fe}$  and  $^{54}\text{Mn}$  solutions, obtained by using different measurement methods, are consistent within the uncertainty limits. The detector figure of merit per one phototube is:

$$\eta_0 = \frac{L\xi\varepsilon}{h\bar{\nu}} \tag{8}$$

where  $\varepsilon$  is the overall efficiency of the phototube, and  $h\bar{\nu}$  is a mean energy of emitted photon. The maximum counting efficiency,  $\Phi_D$ , and, related to it, the K values for both nuclides are shown in Table 4. Figure of merit values are similar because the same cocktail was used. The counting efficiency and ETDCR do not differ much, as expected, because of the similarity of the decay data.

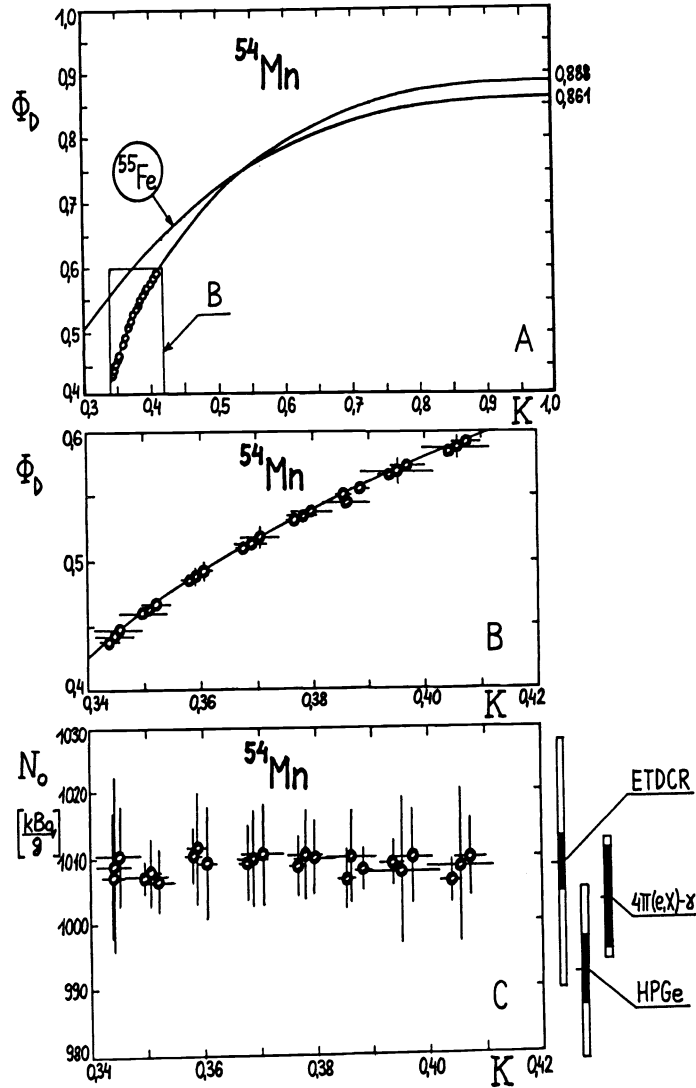


Fig. 2. Results of measurements of the <sup>54</sup>Mn source set. A, B. Theoretical efficiency function,  $\Phi_D(K)$ , (—) and experimental efficiency (o). For comparison, a <sup>55</sup>Fe curve and maximum counting probability values at K=1 are shown. C. The counting point radioactive concentration,  $N_0^1$ , as a function of the K ratio and the solution radioactive concentration,  $N_0$ , with random and systematic uncertainties determined by ETDCR LSC, HPGe spectrometry and  $4\pi(e,X)-\gamma$  coincidence methods.

TABLE 4. Characteristic Detection Parameters

Nuclide	$\eta_0$ (electrons/keV)	$\Phi_D$	K
$^{55}\text{Fe}$	$1.01 \pm 0.04$	$0.58 \pm 0.01$	$0.36 \pm 0.01$
$^{54}\text{Mn}$	$1.07 \pm 0.04$	$0.59 \pm 0.02$	$0.41 \pm 0.01$

### CONCLUSION

Using the ETDCR method, we made a series of measurements at different counting efficiencies, intending to find the best fit of the  $\Phi_D(K)$  function. The counting efficiency was modified during measurement by reducing the focusing electrodes voltage of the photomultipliers. Thus, photoelectron collection deteriorates, the statistical distribution of photoelectrons arriving at the first dynodes broadens, and simple models, such as Poisson or binomial distributions, become poor approximations to photoelectron energy distributions. A facultative type of photoelectron distribution can be applied to calculate radioactive concentration of higher energy emitters, counted at higher counting efficiencies; its influence upon results is insignificant. For low-energy electron-capture nuclides, the slope of  $\Phi_D(K)$  depends considerably, and the radioactive concentration depends little, on the type of photoelectron distribution used in calculations. For  $^{55}\text{Fe}$  and  $^{54}\text{Mn}$ , maximum  $N_0$  difference is no greater than 6%. The best fit was obtained for the negative binomial distribution. The consistency in the results of both nuclides confirm each other, in a sense, because of the similarity of their decay data. Thus, using the ETDCR method for standardizing low-energy electron-capture emitters seems to be useful.

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