

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON MOLECULAR STRUCTURE
AND SPECTROSCOPY

NOMENCLATURE AND CONVENTIONS
FOR REPORTING MÖSSBAUER
SPECTROSCOPIC DATA

(RECOMMENDATIONS 1975)

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INTRODUCTION

These Recommendations are in considerable measure based on a report of the *ad hoc* Panel on Mössbauer Data of the Numerical Data Advisory Board of the Division of Chemistry and Chemical Technology of the National Research Council, U.S.A. (Chairman, Professor J. J. Zuckerman), which took into account several earlier documents, especially the National Bureau of Standards (U.S.A.) Special Publication 260-13 and the report of the Mössbauer Spectroscopy Task Group of Committee E-4 (Metallography) of the American Society for Testing and Materials (Chairman, Professor R. H. Herber).

The Recommendations incorporate modifications suggested by the present and immediate past Chairman of Commission I.1 (Professor D. H. Whiffen and Dr. M. A. Paul), the Chairman of Commission I.5 (Professor N. Sheppard), Professor N. N. Greenwood (consulted by Commission 1.5) and a number of other scientists who wrote to make specific suggestions.

A. PROPOSED CONVENTIONS FOR THE
REPORTING OF MÖSSBAUER DATA

I. Text

The text should include information about:

(a) the method of sample mounting, sample thickness, sample confinement, and appropriate composition data for alloys, solid solutions or frozen solution samples;

(b) the form of the absorber (single crystal, polycrystalline powder, inert matrix if used, evaporated film, rolled foil, isotopic enrichment, etc.);

(c) the apparatus and detector used and comments about the associated electronics (e.g. single channel window, escape peak measurements, solid-state detector characteristics, etc.) if unusual; data acquisition time if unusual;

(d) the geometry of the experiment (transmission, scattering, in-beam, angular dependence, etc.);

(e) the critical absorbers or filters, if used;

(f) the method of data reduction (e.g. visual, by computer, etc.) and curve-fitting procedure: (See Notes A-1 and A-2);

(g) the isomer shift convention used or the isomer shift of a standard (reference) absorber. Positive velocities are defined as source approaching absorber. Sufficient details concerning the isomer shift standard should be included to

facilitate interlaboratory comparison of data (See Note A-3 and Table); and

(h) an estimate of systematic and statistical errors of the quoted parameters.

II. Numerical or tabulated data

Information collected and summarized in tabular form should include:

(a) the chemical state of source matrix and absorber;

(b) the temperature of source and absorber and the constancy of these parameters over the length of the data acquisition period;

(c) values of the parameters required to characterize the features in the Mössbauer spectrum (given in mm/s, cm/s or other appropriate units (See IIIB)) with estimated errors;

(d) the isomer shift reference point with respect to which the position parameters are reported;

(e) the observed line-widths defined as the full-width at half maximum peak-height;

(f) the line intensities or (relative) areas of each component of the hyperfine interaction spectrum observed, when pertinent.

III. Figures illustrating spectra

Scientific communications in which Mössbauer effect measurements constitute a primary or significant source of experimental information should include an illustration of at least one spectrum (i.e. % transmission or absorption or counting rate vs an energy parameter) to indicate the quality of the data. Such figures should include the following information features:

(a) a horizontal axis normally scaled in velocity or frequency units (e.g. mm/s or MHz. Channel number or analyzer address-values should not be used for this purpose); (see Note A-4)

(b) a vertical axis normally scaled in counts per channel or related units; (See Note A-5)

(c) an indication, for at least one data point, of the statistical counting error limits; (See Note A-6)

(d) individual data points (rather than a smoothed curve alone) should be shown. Computed fits should be indicated in such a way that they are clearly distinguishable from the experimental points.

B. MANUAL OF TERMINOLOGY, SYMBOLS, AND
UNITS FOR MÖSSBAUER SPECTROSCOPY

The symbols for physical quantities are in italics. If the units selected by the experimenter are not SI units, they should be defined in the text.

† *Titular Members*: N. Sheppard (Chairman), M. A. Elyashévich (Vice-Chairman), F. A. Miller (Secretary), E. D. Becker, J. H. Beynon, E. Fluck, A. Hadni, G. Zerbi, *Associate Members*: G. Herzberg, B. Jeżowska-Trzebiatowska, Y. Morino, S. Nagakura, C. N. R. Rao, Sir Harold Thompson, D. W. Turner.

Name	Symbol	SI unit	Suggested decimal multiple or sub-multiple SI units for Mössbauer data	Definition and comment
Isomer shift	δ	m/s	mm/s ($=10^{-3}$ m/s)	Measure of the energy difference between the source (E_s) and the absorber (E_a) transition. The measured Doppler velocity shift, δ , is related to the energy difference by $E_a - E_s = \delta E_\gamma / c$ (where E_γ is the Mössbauer gamma energy and c is the speed of light in vacuum) (See Note B-1a, B-1b).
Nuclear quadrupole moment (spectroscopic)	eQ	C m ²	C cm ² ($=10^{-4}$ C m ²)	A parameter which describes the effective shape of the equivalent ellipsoid of the nuclear charge distribution, $Q > 0$ for prolate (e.g. ⁵⁷ Fe, ¹⁹⁷ Au); $Q < 0$ for oblate (e.g. ¹¹⁹ Sn, ¹²⁹ I) nuclei
Electric Field Gradient (EFG) tensor		V/m ²	V/cm ² ($=10^4$ V/m ²)	A second rank tensor describing the electric field gradient specified by η and V_{zz} ; in addition the Euler angles may be required specifying the orientation of the tensor principal axes. (See below) (See Note B-3)
Principal component of EFG	$-V_{zz}$	V/m ²	V/cm ² ($=10^4$ V/m ²)	$(\partial^2 V / \partial z^2) = eq$ (e is the proton charge, $ V_{zz} $ is the largest component of the diagonalized EFG)
Quadrupole coupling constant	$e^2 q Q / h$	Hz	MHz ($=10^6$ Hz)	Product of V_{zz} / h and the nuclear quadrupole moment, eQ . (See Note B-1b)
Quadrupole splitting	Δ	m/s	mm/s ($=10^{-3}$ m/s)	The measured Doppler velocity difference between the two peaks seen in quadrupole split spectra from nuclides such as ⁵⁷ Fe and ¹¹⁹ Sn. Its value is related to the quadrupole coupling constant as $\Delta = 1/2(c/E_\gamma)e^2 q Q \sqrt{(1 + \eta^2/3)}$ (See Note B-2)
Asymmetry parameter	η			$= (V_{xx} - V_{yy}) / V_{zz}$
Line width	Γ_{exp}	m/s	mm/s ($=10^{-3}$ m/s)	Full width at half maximum of the observed resonance line(s)
Natural line width	Γ_{nat}	m/s	mm/s ($=10^{-3}$ m/s)	Theoretical value of the full width at half maximum of the nuclear transition, usually calculated from lifetime data
Resonance effect magnitude	ϵ			Ratio of the difference in the transmitted or scattered intensity at resonance maximum and off-resonance, relative to the intensity off-resonance. (See Note B-4)
Recoil-free fraction	f			The fraction of all Mössbauer gamma rays of the transition which are emitted (f_s) or absorbed (f_a) without significant recoil energy loss. (See Note B-5)
Mössbauer thickness	t			The effective thickness of a source (t_s) or absorber (t_a) in the optical path. (See Note B-6)
Resonance cross-section	σ_0	m ²	barn ($=10^{-28}$ m ²)	The cross-section for resonant absorption of the Mössbauer transition gamma ray (See Note B-7)
Magnetic flux density	B	T = Wb/m ²		Magnetic flux density at the nucleus (from experiment) in those cases in which the magnetic hyperfine interaction can be described by an effective field. In other cases the vector components of the magnetic hyperfine interaction should be reported if possible. (See Note B-8)
Vibrational anisotropy	ϵ_m			When the vibrational anisotropy tensor ($\langle x_i^2 \rangle$) is axially symmetric $\epsilon_m = (1/\lambda^2)(\langle x_{\parallel}^2 \rangle - \langle x_{\perp}^2 \rangle)$ where $\langle x_{\parallel}^2 \rangle$ and $\langle x_{\perp}^2 \rangle$ are the mean square vibrational amplitudes of the Mössbauer nucleus parallel and perpendicular to the cylindrical symmetry axis through the Mössbauer atom, and λ is the wavelength of the Mössbauer radiation divided by 2π
Intensity asymmetry (Gol'danskii-Karyagin asymmetry)	A			For a randomly oriented sample with $\eta = 0$ and for $1/2 \rightarrow 3/2$ magnetic dipole transitions, this is the ratio of the area under the π transition peak to the area under the σ transition peak $A = \frac{\int_0^\pi e^{-\epsilon_m \cos^2 \theta} (1 + \cos^2 \theta) \sin \theta d\theta}{\int_0^\pi e^{-\epsilon_m \cos^2 \theta} \left(\frac{5}{3} - \cos^2 \theta\right) \sin \theta d\theta}$ and is independent of sample orientation. (See Note B-9)

NOTES

(A-1). If data are analyzed by computer, a brief description of the program should be given to identify the algorithm used. The number of constraints should be specified, (e.g. equal line-widths or intensities, etc.) and a measure of the goodness of fit should be indicated.

(A-2). If measurements of very high accuracy are reported and the discussion of the reality of small effects is an important part of the work, then the following items should be included:

1. the functional form and all parameters used in fitting (i.e. the constraints should be clearly stated);
2. the treatment of the background (e.g. assumed energy independent, experimentally subtracted, etc.);
3. the relative weighting of abscissa and ordinate (e.g. equal weighting);
4. a measure of the statistical reliability;
5. the number of replications and the agreement between these if applicable;
6. an estimate of systematic errors as primary results.

(A-3). The table in the adjacent column contains a list of materials which have been proposed and are being used for isomer shift standards. The proposals are partly based on the tabulation by R. L. Cohen and G. M. Kalvius [*Nucl. Instr. Methods* **86**, 209 (1970)]. That article also discusses some criteria in the choice of materials for isomer shift standards, and provides an extensive list of references.

(A-4). Constant acceleration spectrometers to be used for work in the mm/s range can be calibrated with respect to velocity using either metallic iron foil of at least 99.99% purity (e.g. N.B.S. Standard Reference Material SRM 1541 or equivalent) or an optical method based on interferometric or Moiré pattern techniques. The ground state (g_0) and excited state (g_1) splitting in metallic iron have been reported. [See, for example, the values quoted in J. G. Stevens and R. S. Preston, *Mössbauer Effect Data Index, Covering the 1970 Literature*, (edited by J. G. Stevens and V. E. Stevens), p. 16. IFI/Plenum, New York (1972), and in other references cited therein. (See also J. J. Spijkerman, J. R. DeVoe and J. C. Travis, N.B.S. Spec. Pub. 260-20, Washington, D.C. 1972 and C. E. Violet and D. N. Pipkorn, *J. Appl. Phys.* **42**, 4339 (1971)]. The temperature dependence of g_0 can be estimated from data quoted in the J. I. Budnick, L. J. Bruner, P. J. Blume and B. L. Boyd, *J. Appl. Phys.* **32**, 1205 (1961), and R. S. Preston, S. S. Hanna and J. Heberle, *Phys. Rev.* **128**, 2207 (1962). [See R. H. Herber in *Mössbauer Effect Methodology*. Vol. 6, (Edited by I. Gruverman) Plenum Press, New York (1971)]. In the absence of independent linearity measurements, a quadrupole split doublet should not be used to effect velocity calibration of spectrometers.

(A-5). It has become customary to display data obtained in transmission geometry with the resonance maximum 'down' and scattering data with the resonance maximum 'up'. In either case sufficient data should be shown far enough from the resonance peaks to establish the non-resonant base line.

(A-6). In most instances (where the data are uncorrected counting results), the standard deviation (i.e.: the square root of the second moment of the distribution) is given by $N^{1/2}$, where N is the number of counts scaled per

Element	Material	Element	Material
K	KCl	Eu	{EuS EuF ₃
Fe	{ α Fe ^a Na ₂ [Fe(CN) ₅ NO]·2H ₂ O ^a	Gd	GdAl ₂
Zn	ZnS	Dy	Dy
Ge	Ge	Er	Er
Kr	Kr (Solid)	Yb	YbAl ₂
Ru	K ₄ [Ru(CN) ₆]·3H ₂ O ^b	W	W
Sn	SnO ₂ ^c	Os	K ₄ [Os(CN) ₆]
	BaSnO ₃ ^c	Ir	Ir
Sb	InSb	Pt	Pt
Te	SnTe ^d	Au	Au
I	CsI	Np	NpAl ₂
Xe	Xe (Solid)		
Sm	SmF ₂		

^aBoth of these materials are in wide use. The spectrum of disodium pentacyanonitrosiferate(2-)dihydrate does not have unresolved hyperfine structure, footnote (b) of R. L. Cohen and G. M. Kalvius [*Nucl. Instr. Methods* **86**, 209 (1970)] misinterpreted the EFG results of R. W. Grant, R. M. Housley and U. Gonsler [*Phys. Rev.* **178**, 523 (1969)]. In view of the reported line spacing anomaly in Fe metal, [J. J. Spijkerman, J. C. Travis, D. N. Pipkorn and C. E. Violet, *Phys. Rev. Lett.* **26**, 323 (1971)], very precise results reported with respect to Fe should specify which lines are being used as a references.

^bThe small size of the effect in this compound may make ruthenium metal also useful as a secondary, or working, standard despite its unresolved quadrupole splitting.

^cThese compounds present minor materials problems which should not interfere with their effective use. Barium stannate has been well established to be a cubic perovskite at room temperature [A. J. Smith and A. J. E. Welch, *Acta Cryst.* **13**, 653 (1970)], but must be made by the ceramic process, and may very well undergo a crystallographic distortion at low temperatures. Much of the older Mössbauer literature reports ¹¹⁹Sn isomer shift data with respect to SnO₂ which has a small quadrupole splitting usually observed as line broadening. Such data are directly comparable to those reported with respect to BaSnO₃ (both at room temperature) within an experimental uncertainty to ± 0.02 mm/s.

^dSnTe of exactly 1:1 stoichiometry is difficult to prepare. At low temperatures there is evidence for line broadening in the ¹¹⁹Sn resonance spectrum due to unresolved hyperfine interactions. The transition temperature varies with composition. This material should only be used as a standard at temperatures where no unresolved hfs is present.

velocity point. For corrected data (i.e. when background or other non-resonant effects are subtracted from the raw data), the error propagated should be computed by normal statistical methods which are briefly described in the text or figure legend. Fiducial marks bracketing the data point to show the magnitude of the standard deviation are often useful in indicating the spread of the data.

(B-1a). The centre of a Mössbauer spectrum is defined as the Doppler-velocity at which the resonance maximum is (or would be) observed when all magnetic dipole, electric quadrupole, etc. hyperfine interactions are (or would be) absent. The contribution of the second order Doppler shift (δ_T) should be indicated, if possible. The isomer shift (δ) is the sum of this term and the chemical isomer shift (δ_C).

(B-1b). The SI unit of energy for both isomer shift and quadrupole coupling constant should be J, as also for Δ . The measured quantity is the velocity (m/s) which can be converted to energy as appropriate.

(B-2). Quadrupole splittings are frequently reported in megahertz, especially when direct comparison with NMR or NQR data can be effected (e.g. in the case of ^{129}I). If such units are used in conjunction with data derived from Doppler shift measurements, the conversion factors should be stated.

(B-3). The sum $(V_{xx} + V_{yy} + V_{zz}) = 0$ regardless of the choice of axes. In the absence of magnetic hyperfine interaction, principal axes are chosen so that the off-diagonal matrix elements vanish, $V_{ij} = 0$ ($i, j = x, y, z$; $i \neq j$) and are defined such that

$$|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|, \text{ so that } 0 \leq \eta \leq 1.$$

$$(EFG)_{ij} = -(\partial^2 V / \partial x_i \partial x_j) \quad x_i, x_j = x, y, z.$$

(B-4). This parameter is calculated from the relationship $\epsilon = [I(\infty) - I(0)]/I(\infty)$, where $I(0)$ is the counting rate (or transmission or scattering intensity) at the resonance maximum, and $I(\infty)$ is the corresponding rate at a velocity at which the resonance effect is negligible. If corrections for non-resonant gamma- or X-rays, or other base-line corrections, have been made in evaluating I , these should be stated.

(B-5). The recoil-free fraction can be related to the expectation value of the mean square displacement of the Mössbauer atom by the relationship

$$f = \exp(-k^2 \langle x^2 \rangle)$$

where k is the wave number of the Mössbauer gamma ray and x is the displacement taken along the optical axis.

(B-6). The t parameter is usually calculated for a thin absorber from the relationship $t = n\sigma_0 a f$, in which n is the number of Mössbauer element atoms per unit area in the optical path, σ_0 is the cross-section for recoilless scatter-

ing, a is the fractional abundance of the Mössbauer transition active nuclides, and f is the recoil-free fraction (*vide supra*).





(B-7). This parameter is usually calculated from the relationship

$$\sigma_0 = (h^2 c^2 / 2\pi) E_\gamma^{-2} (1 + \alpha_T)^{-1} (1 + 2I_e)(1 + 2I_g)^{-1}.$$

Where E_γ is the transition energy; I_e and I_g are the excited and ground state spins, respectively; and α_T is the total internal conversion coefficient of the Mössbauer transition.

(B-8). 1 Tesla (10 kG) equals 1 Wb/m².

(B-9). For ^{57}Fe and ^{119}Sn the following table summarizes the conventions which relate the shape of the equivalent ellipsoid of electronic charge surrounding the nucleus, the sign of V_{zz} , the sign of the excited state nuclear quadrupole moment, $Q_{3/2}$, the sign of the quadrupole coupling constant $e^2 q Q / h$, the doublet intensity ratio R (defined as the area ratio of the more positive velocity peak divided by that of the more negative velocity peak in the absence of a magnetic hyperfine interaction), and the angular dependence ratio A for the σ ($\Delta m = 0, \pm 1$) and π ($\Delta m = \pm 1$) transitions for the axially symmetric case:

	^{57}Fe		^{119}Sn	
shape				
	prolate	oblate	prolate	oblate
V_{zz}	-	+	-	+
$Q_{3/2}$	+	+	-	-
$e^2 q Q$	-	+	+	-
	$E_{3/2} < E_{1/2}$	$E_{3/2} > E_{1/2}$	$E_{3/2} > E_{1/2}$	$E_{3/2} < E_{1/2}$
R	$\sigma/\pi (= A^{-1})$	$\pi/\sigma (= A)$	$\pi/\sigma (= A)$	$\sigma/\pi (= A^{-1})$