

Precision and interlaboratory reproducibility of measurements of the Mössbauer effect in minerals

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Abstract

Although the technique of Mössbauer spectroscopy is now 25-years old and widely used, little empirical work has been done to determine its accuracy in measurements on minerals. To solve this deficiency, two mineral standards (a grunerite and an almandine/andradite garnet mix) have been selected. Precision of the technique was measured through five different sets of experiments seeking to analyze the reproducibility of measurements on a single sample mount, on several identical mounts of the same sample, and on a set of mounts with different sample concentrations, run times, and background counts. The two mineral standards were analyzed by other scientists at seven different laboratories; their data were also fit by the MIT program. The standard deviation of multiple measurements on the MIT apparatus is better than 0.016 mm/sec for isomer shift, 0.060 mm/sec or better for quadrupole splitting, and 1.02% on individual peak area data. The standard deviation of interlaboratory measurements on the same minerals is slightly better because only ideal run conditions were used: 0.006 mm/sec for isomer shift, 0.023 mm/sec for quadrupole splitting, and 1.44% on individual peak area data. Probable errors on different aliquots of the same sample are approximately ± 0.02 mm/sec for isomer shift and quadrupole splittings, and $\pm 1.5\%$ on area data for well-resolved peaks.

Introduction

Since 1967, over 814 papers have been published in the geological literature which apply the Mössbauer effect in ^{57}Fe to interpretations of mineral crystal chemistry (Fig. 1). Numerous other papers have made reference to Mössbauer measurements for $\text{Fe}^{3+}/\text{Fe}^{2+}$ determinations or structural Fe site occupancy information, to the extent that the technique has become one of the many commonly used analytical tools available to geochemists and mineralogists.

However, the technique of Mössbauer spectroscopy is still relatively young; Rudolph Mössbauer published his first papers only 26-years ago (Mössbauer, 1958). In the first 10–15 years after Mössbauer's discovery, Mössbauer spectrometers were literally home-built from scratch in chemistry, physics, and mineralogy laboratories around the world, with a wide array of geometries, standards, and electronic configurations. Because the experimental apparatus and methodology for Mössbauer work were customized for each lab, there was little consistency in the type of source used or the method by which spectral data were processed. By the 1970's, commercial Mössbauer apparatus became widely available, but many workers continued to maintain and update their original equipment. Today each Mössbauer laboratory has its

own distinctive experimental apparatus, computing facility, and philosophy for recording, measuring, and reporting its results (for example, Mitrofanov et al., 1977; Graham et al., 1977; LeFever, 1979; and Fultz and Morris, 1978).

Over the years there have been some attempts to standardize the type of calibration procedures (Herber, 1971) and the method of reporting results (Zuckerman et al., 1972); these have been received with varying degrees of success. The predominant trend has been for each lab (and subsequent generations of graduate students and colleagues) to develop its own philosophy on optimization of experimental technique and curve-fitting. A few attempts at interlaboratory standardization (e.g., Minai and Tominaga, 1982) or comparison of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios against wet chemistry (Whipple, 1973 and 1974; Bancroft et al., 1977) have given inconsistent results, although agreement between different Mössbauer labs is consistently better than between Mössbauer and wet chemical labs.

Fortunately, several workers in the field have devoted great effort toward a statistical evaluation of the technique. The literature prescribes the optimal sample concentration and thickness (Hafemeister and Shera, 1966; Ure and Flinn, 1971; Shenoy et al., 1974), the relative merits of fitting techniques (Lin and Preston, 1974),

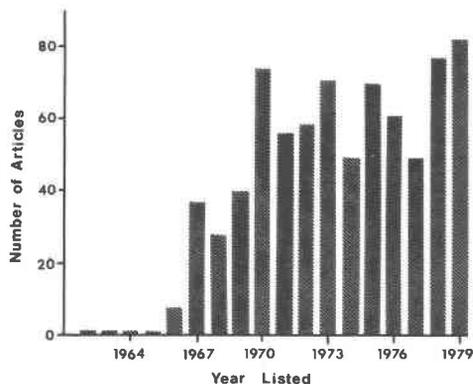


Fig. 1. Publications with MOSSBAUER as a keyword from the Georef Database, search performed August, 1982.

methodology for quantitative site population estimates (Bancroft, 1967; 1969/1970), and even a unique criterion for evaluating Mössbauer curve fits (Ruby, 1973). Both Law (1973) and Dollase (1975) have given thorough, excellent reviews of the statistical limitations of the technique.

However, the practical problems of the technique have rarely been published. While it may be useful to know the optimal iron concentration for a Mössbauer experiment, it is perhaps far more important to the worker with, say, a limited quantity of lunar sample to know how far he can deviate from the ideal value and still have worthwhile results. Is it really necessary to weigh all samples out carefully? A similar problem involves the duration of the experiment. In these days of careful cost monitoring, what is the minimum length of run-time for which optimal results can be obtained? Finally, it may sometimes become necessary to compare or tabulate the Mössbauer results of Lab A with Lab B. How valid are such comparisons?

Five years and 94 Mössbauer spectra ago, this study was undertaken to resolve these many questions. The results reported here represent empirical guidelines for Mössbauer spectroscopy labs based on experimental, not theoretical, calculations. Data on two minerals designated as standards are tabulated for each of seven Mössbauer labs which ran them. The conclusions reached here represent a realistic overview of the state of the art of mineralogical applications of Mössbauer spectroscopy.

Background

Since the subject of statistical limitations of Mössbauer spectroscopy has been covered elsewhere in great detail, a replicate discussion will be passed over. There are a number of books and articles which give a general background on the theory and applications of the Mössbauer effect; a partial list might include Fluck, 1967; Wertheim, 1967; Spijkerman, 1968; Greenwood, 1970; Greenwood and Gibb, 1971; Bancroft, 1973; and Marfunin, 1979. Two handbooks from the Mössbauer Effect Data Center (1984a and b) give thorough summaries of both data

and references on mineralogical studies. However, for the presentation of experimental results which follows, it is useful to review briefly the major parameters by which Mössbauer spectra are evaluated:

Isomer Shift, IS or δ , (also called chemical shift in some papers) arises from the difference in *s*-electron density at the nuclei of the radioactive source and the absorbing iron nuclei in the sample or absorber (Fig. 2). For example, Fe⁵⁷ in Pd (formed by electron capture from ⁵⁷Co) emitting nuclear gamma rays to Fe⁵⁷ in a Pd absorber gives rise to zero isomer shift. But when Fe⁵⁷ is in a different chemical environment from that of the emitter, the resultant difference of *s*-electron density at the nucleus produces a finite δ . Isomer shift is affected by oxidation state, coordination number, spin state of iron atoms, and ligand-type coordinated to iron cations, and may be augmented by a second-order Doppler shift, which is temperature dependent. Since isomer shift depends heavily on a calibration standard, it is often deceptive to compare values from various published papers. In this paper, all values will be cited with respect to the mid-point of the metallic α -iron foil spectrum, by applying the following adjustments to the values reported for alternative standards, as suggested by the Mössbauer Effect Data Center (Gettys and Stevens, 1981): Cr, -0.154; stainless steel, -0.09; Rh; +0.106; Pd, +0.177; and Cu, +0.225 (figures quoted for isomer shift values in mm/sec relative to α -Fe).

Quadrupole Splitting, QS or Δ , arises from an electric field gradient (EFG) at the nucleus, which produces two or more energy levels when nuclear charge distributions are non-spherical (i.e., $I \geq 1$). Both electronic structure of the Fe atom and the arrangement of the ligands around it contribute to the EFG. Asymmetry of the (localized) electronic configuration dominates the symmetry of the ligand environment, such that any departures from "perfect" cubic symmetry will cause the absorbing ion to experience a different electronic environment,

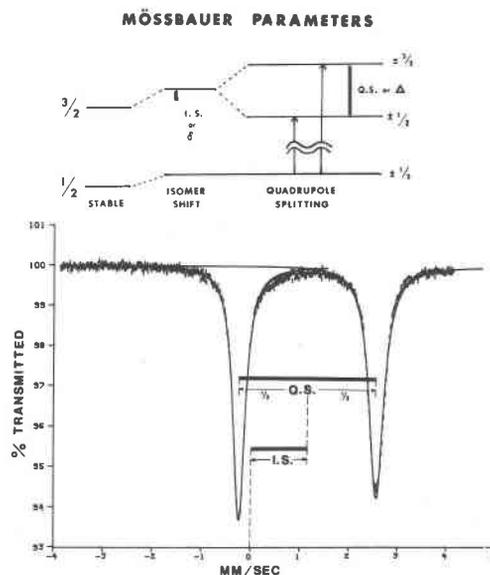


Fig. 2. Graphical representation of Mössbauer parameters, shown on an energy level diagram and a typical (in this case, olivine) spectrum.

which changes the quadrupole splitting (see Fig. 2). QS also depends on iron valency, spin state and relative site ordering; Figure 3 shows a plot of IS vs. QS for common minerals. Note that these data are for oxygen environments only; non-oxygen environments, such as sulfides, tend to follow similar trends with somewhat different parameters. The relationship seen in Figure 3 arises from the dependence of QS on the radial expectation function $\langle r^{-3} \rangle t_{2g}$, and shows how the shielding by d electrons affects IS.

The *Linewidth*, Γ , of a Mössbauer line is generally taken to be the sum of the natural source and absorber linewidths; experimentally, this is the full width at half peak height of the Mössbauer peak. It can be defined theoretically as the linewidth arising from the Heisenburg Uncertainty Principle:

$$\Gamma_0 = \frac{\hbar \cdot \ln 2}{t_{1/2}}$$

In a Mössbauer experiment the natural linewidth *observable* can be defined as:

$$W_0 = \frac{2c\hbar \cdot \ln 2}{E\gamma t_{1/2}}$$

where \hbar is $h/2\pi$, E_γ is the energy of the gamma transition, and $t_{1/2}$ is the half-life of the excited nuclear level (Stevens, 1981a). For ^{57}Fe the theoretical value of Γ_0 , as calculated from "lifetime data," is 0.1940(3) mm/sec (Stevens, 1981b).

The best Mössbauer source materials are those which emit a monochromatic line with a width close to the theoretical value and have a substantial recoil free fraction; ^{57}Co in Pt (0.22 mm/sec) and Pd and Rh (0.23 mm/sec) are commonly used. The linewidth of a metallic iron spectrum when measured with such sources gives a "lower limit" for experimentally-determined linewidths of approximately 0.24 mm/sec; the added width between theory and experiment is probably due to nearest

neighbor interactions and defects, residual mechanical vibrations, and the "cosine smearing effect" (Spijkerman et al., 1965) which can broaden and shift the line. In crystalline silicates, which come close to the lower limit, Fe^{2+} peaks range from 0.27–0.28 mm/sec, while Fe^{3+} peaks (0.28–0.35 mm/sec) are often slightly broader (Bancroft, 1973). Deviations from these values may result from several causes: next nearest neighbor effects, electronic relaxation (Morup and Both, 1975), thickness distortion (Ruby, 1973), and multiple, superposed peaks (Whipple, 1981).

It is also instructive to review the *statistical parameters* commonly used to evaluate Mössbauer fits. Chi-squared (χ^2) is generally defined as

$$\text{Chi-squared} = \chi^2 = \frac{1}{N - n} \sum_{i=1}^N \left(\frac{Y_C(I) - Y_D(I)}{\sqrt{Y_D(I)}} \right)^2$$

where N is the number of points to be fitted, n is the number of parameters to be fitted ($N - n$ is sometimes referred to as the number of degrees of freedom), $Y_C(I)$ are the calculated values for the curve, and $Y_D(I)$ are the data points. The optimum value for χ^2 is one; or one times the number of degrees of freedom as presented here. χ^2 can be said to represent the likelihood that the calculated curve represents the data within its errors (note the $\sqrt{Y_D(I)}$ term in the expression, which approximates the standard deviation of each point). However, good values of χ^2 can be very misleading because they may represent fits with large error bars on the data. To get around this problem, a statistical parameter was needed which had the capability to normalize the data with respect to the number of counts in the experiment. The parameter of *Misfit* was derived by Ruby (1973) to provide a comparative goodness-of-fit criterion which could evaluate different spectra irrespective of the magnitude of their baselines. Misfit is defined by two other criteria:

$$\text{Distance, } D = \sum_{i=1}^N \left[\left(\frac{Y_C(I) - Y_D(I)}{\sqrt{Y_D(I)}} \right)^2 - 1 \right],$$

which is the distance between the calculated and the experimental results (discrepancy of the fit); and

$$\text{Signal, } S = \sum_{i=1}^N \left[\left(\frac{Y_C(I) - Y_D(I)}{\sqrt{Y_D(I)}} \right)^2 \right],$$

which measures the difference between the experimental data $Y_D(I)$ and the baseline Y_0 . Misfit, defined as the ratio D/S , is optimal when it is close to zero; i.e., a Misfit value close to zero is essentially the same as a chi-squared close to one.

Misfit is an extremely useful parameter in Mössbauer experiments because it is sensitive to more than the magnitude of the baseline. The numerator, D , is similar to χ^2 in that it deals with the difference between the calculated curve and the experimental results. However, the denominator, S , is a reflection of (and directly proportional to) the duration and counting rate of the experiment, the number of channels over

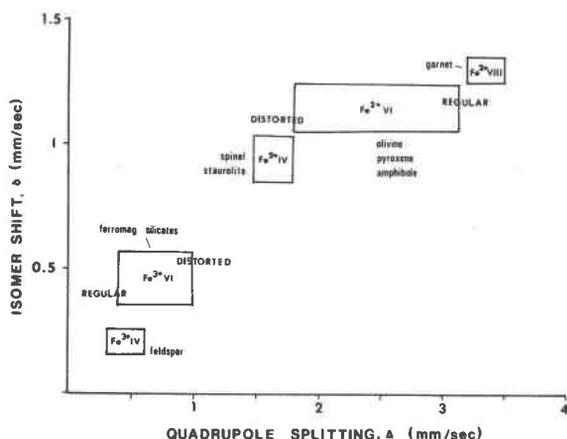


Fig. 3. Plot of isomer shift versus quadrupole splitting for common minerals, based on commonly accepted values (Roger Burns, personal communication).

which a peak is observed, and the square of the observed effect. These characteristics enable the experimenter who calculates Misfit to separate the effects of pure counting statistics (like χ^2) from the actual experimental errors of the experiment (which will be discussed at length). Derivations and further information (including several examples) on Misfit use can be found in Ruby (1973).

For the purposes of this study it is also useful to describe the basic statistical terms which will be used to compare different results. The mean is defined as an arithmetic average or the sum of all the observations divided by the number of observations. It is usually represented by the symbol \bar{X} .

The variance gives an *averaged* squared deviation from the mean. It can be used effectively for comparisons; its square root, the standard deviation, is even more useful because it is in the units of the measurements of the data.

In this study, the sample variance, s^2 , is computed using

$$s^2 = \frac{\sum_{i=1}^n X_i^2 - n \bar{X}^2}{n - 1},$$

where X_i is the observation, \bar{X} is the sample mean, and n is the number of observations. Standard deviation, or s , is defined as the square root of s^2 . Groups of data having the largest s or s^2 values will have the greatest spread among the values of the different measurements. A complete explanation can be found in statistics texts (e.g., Spiegel, 1961; Davis, 1973; or Taylor, 1982).

Finally, for completeness it is useful to briefly describe a typical experimental set-up, as shown in Figure 4. The source of nuclear gamma rays (commonly ^{57}Co in a Pd or Rh matrix for Fe Mössbauer spectroscopy) is attached to an oscillator (or to both ends of an oscillator, as pictured). The doppler velocity of the source is varied by (generally) a linear motor; commonly used "constant acceleration" drives sweep linearly through a range of velocities from negative (as the source moves away from the spectrometer) to positive speeds. The resultant velocity/time profile has a characteristic zig-zag pattern.

The recoil-free gamma rays which are emitted from the source span an array of energies of 14.4 ± 0.001 keV (Stevens, 1981b).

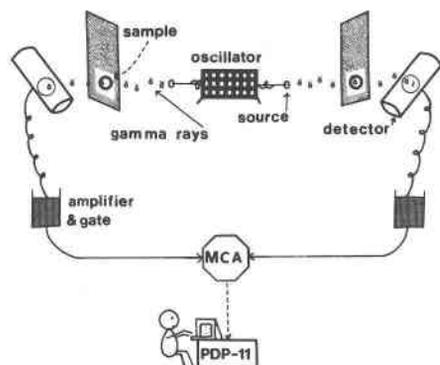


Fig. 4. Schematic of a typical Mössbauer apparatus, showing gamma rays generated by the source mounted on the oscillator, passing through the sample, and being detected, gated, processed, and finally stored in a multichannel analyzer. Data may then be processed by computer.

They pass through the sample, where they may be absorbed by ^{57}Fe isotopes having comparable nuclear energy level separations. Some of the gamma rays pass unabsorbed (depending on sample thickness and density) through the sample, to be registered on a detector. The pulses recorded by the detector pass through a pre-amplifier, linear amplifier, and a linear gate (or single channel analyzer) to select the 14.4 keV energy range. Counts are stored as they are received in each channel in turn of a 256, 512, or 1024 channel (common increments) multi-channel analyzer. The isomer shift zero is standardized (usually) against the midpoint of an iron foil spectrum; the known positions of the iron foil peaks are used to determine the number of mm/sec/channel.

Data are accumulated in the multi-channel analyzer for a time period depending on source strength and the relative Fe concentration versus the bulk weight of specimen. Other calibration standards, such as sodium nitroprusside ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$) or stainless steel, are sometimes used when a high degree of precision over a smaller velocity range is desired. Each standard has a distinctive isomer shift relative to metallic iron; simple corrections can be used to make comparisons between experiments using different standards. Run time varies from hours to days depending on the judgment of the experimenter. Data in counts per channel (i.e., finite velocity increment) are then transferred to the computer and processed by any one of a number of curve fitting and/or deconvolution programs, ranging in complexity from simple triangle fitting programs to such complex programs as the Gauss non-linear regression algorithm of Stone et al. (1971).

Experimental method

This study is divided into two parts: intra- and interlaboratory comparisons. The intralaboratory work was aimed at determining the optimum run characteristics for the experimental apparatus in the Mössbauer Spectroscopy Lab at MIT. Once these were defined, the same grunerite sample was run ten times under identical conditions to test precision, and ten aliquots of the same sample were run to test for homogeneity of this standard mineral.

The interlaboratory work was performed voluntarily at seven different labs chosen randomly from twelve. Participants, institutions, and spectrometers are listed in Table 1. Dr. Wayne Dollase generously ran one of the standards three times with different run durations to test his spectrometer for electronic stability.

Two mineral standards were selected to be used for this study. Standard "R" is a quartz-grunerite schist from the Luce Lake area, Labrador City, Canada. This well-studied sample (Klein, 1964; Klein and Waldbaum, 1967; Bancroft et al., 1967) was the most iron-rich (95.3% Fe^{2+}) grunerite that I could obtain; it is an especially advantageous standard because of its high iron content (44.99 wt.% FeO), its homogeneity, the simplicity of its spectrum, and the presence of well-resolved peaks. Wet chemical analyses performed at the Smithsonian Institution show that this sample has less than 0.1% Fe_2O_3 , which should not be detectable by the Mössbauer effect. The bulk sample was ground by hand under acetone in an

Table 1. Participants, institutions, and spectrometers in interlaboratory comparison

Wayne A. Dollase Department of Earth and Space Sciences University of California, Los Angeles Los Angeles, CA 90024 USA	homemade, Kankelinite-type, constant acceleration
Roger G. Burns Department of Earth and Planetary Sciences Massachusetts Institute of Technology Cambridge, MA 02139 USA	Austin Science Associates constant acceleration
Frank E. Huggins U.S. Steel Research, MS #98 125 Jamison Lane Monroeville, PA 15146 USA	Nuclear Data ND660 programmable multichannel analyzer with in-house-built drive
Friedrich A. Seifert Mineralogisches Institut Kiel University Olshausenstr. 40, 2300 Kiel West Germany	Elscont MVT20 Drive with Canberra Series 40 MCA
Enver Murad Lehrstuhl für Bodenkunde Technische Universität München D-8050 Freising-Weihenstephan West Germany	Wissel/Halder
Georg Anthauer University of Marburg Institute of Mineralogy Lahnberge, 3550 Marburg West Germany	self-made, Halder drive electro-mechanical Doppler velocity generator, constant acceleration MCA, Halder Electronics, Munich counter, amplifier, power supply: Urtec
Catherine McCammon* Research School of Earth Sciences Australian National University P.O. Box 4 Canberra ACT 2600 Australia	homemade, driven by PDP 11/10 minicomputer, drive signal, linear ramp, and flyback

* Spectra were run by Dr. S. J. Campbell, Department of Solid State Physics, Research School of Physical Sciences

Note: Each participant was randomly assigned a number, ranging from 1-7. To respect the confidentiality of the participants, all references from here on will be to numbers which do not correspond to the order of the list above.

agate mortar, a few grains of magnetite were removed with a hand magnet, and about 80% of the quartz was removed by use of a magnetic separator. Approximately 10% (by volume) quartz and trace amounts of magnetite remained in the batch of standard "R" distributed for interlaboratory comparison.

Standard "A" is a mechanical mixture of two garnets. This mixture was chosen to simulate typical bulk rock Mössbauer measurements, which are commonly performed to determine whole rock $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios on samples containing more than one mineral. Andradite crystals were hand-picked from Harvard University sample 87373 from Val Malenco, Italy; almandine crystals from Fort Wrangell, Alaska were selected from the MIT Teaching Collection. Each garnet was ground by hand, under acetone, and then weighed into individual aliquot vials in the proportion $\text{wt.}\% \text{Fe}_{\text{and}}/\text{wt.}\% \text{Fe}_{\text{alm}} = 0.185$. Participants were asked to use all of the standard material provided, or to take their sampling from a well-homogenized mixture.

Natural mineral standards were chosen in spite of impurities and slight structural defects in order to make the study geochemically (or mineralogically) relevant. Compositions are given in Table 2, and typical fitted Mössbauer spectra are shown in Figures 5 and 6.

Table 2. Compositions of mineral standards

	Standard "R" Grunerite*	Standard "A" Garnet Mix**	
		Almandine	Andradite
SiO ₂	49.01	37.13	35.29
TiO ₂	0.05	0.06	0.00
Al ₂ O ₃	0.00	21.60	0.03
FeO	44.99	31.86	27.74
MnO	0.37	2.37	0.01
MgO	3.17	5.44	0.26
CaO	0.31	1.60	32.93
Na ₂ O	0.04	-	-
K ₂ O	0.00	-	-
Cr ₂ O ₃	-	0.01	0.03
F ₂	1.00	-	-
H ₂ O ⁺	1.28	-	-
H ₂ O ⁻	0.31	-	-
P ₂ O ₅	0.10	-	-
TOTAL:	100.63	100.07	96.29

* from Klein, 1964, p. 966. Microprobe analysis was performed by Jun Ito, Dept. of Geological Sciences, Harvard University. Fe is reported as FeO.

** Garnets were crushed by mortar and pestle and weighed into garnet mix "A" in the proportion $\text{wt.}\% \text{Fe}_{\text{andradite}}/\text{wt.}\% \text{Fe}_{\text{almandine}} = 0.185$. Microprobe analyses of the garnets were made by Karen Kimball on the MIT Dept. of Earth, Atmospheric, and Planetary Sciences Microprobe. Fe is reported as FeO.

Aliquots of each of the two standards were sent to all participants. The format of the accompanying questionnaire was:

General Information Sheet
[Fill this out once for your facility]

Institution where spectrometer is located:
Name and address of person filing this report:
Description of mounting procedure (type of holder, mounting medium, amount of sample, volume of holder, etc.):
Average length of run time:
Source matrix (⁵⁷Co in Pd, Rh, etc.):
Source strength (millicuries):
Distance from sample to source:
Type of spectrometer:
Year purchased:
Number of channels stored for each spectrum:
Calibrations with respect to:
Computer used for processing:
Name of program used for fitting:
Source Program:
Year written/obtained:
Author:
Curve shape used:

RUN SHEET

[Fill out one of these for each run, or send your computer printout]

Sample number:
Temperature:
Number of constraints in final fit:
Type of constraints (list):
Baseline:

Shape of baseline:

Amount of distortion:

Peak #	Peak Parameters			
	Center	Halfwidth	Area	% Gaussian
Positions in mm/sec (if above is in terms of channel numbers)				
Peak Center	Mössbauer Data		Halfwidth	
Peaks	IS	QS		
1-4				
2-3				

Statistics (where applicable)

Misfit:

Chi-squared:

degrees of freedom:

The MIT results were calibrated using the midpoint and peak positions of a 6 μm $\alpha\text{-Fe}$ foil, 99.99% purity, as supplied by New England Nuclear and as specified by the Numerical Data Advisory Board of the National Research Council (1971). Peak positions used were the most recent values supplied by the Mössbauer Effect Data Center: -3.0760 , -0.8379 , 0.8397 , and 3.0760 (John G. Stevens, pers. comm., 1984). Dr. Stevens also pointed out that these values do not depend heavily on the absolute purity of the $\alpha\text{-Fe}$ foil used for calibration; if there is impurity (usually in the form of C) in the foil, it will produce another set of six very weak lines in the spectrum which will not affect the $\alpha\text{-Fe}$ lines. Four hour (500,000 count) calibrations of the spectrometer were carried out once every thirty days, with mineral measurements performed back-to-back in the interim periods. Negligible variation in the position of zero velocity or the velocity gradient of the spectrometer was observed over the thirty day period.

Participants at other laboratories were requested to use similar $\alpha\text{-Fe}$ foils for calibration to insure consistent results. Their individual procedures for calibration were not surveyed; however, subsequent communications have revealed that some labs may not have used the most current Fe peak positions, causing slight deviations in their results (see Discussion).

Results

Work done at MIT

The original aim of this study was to reassess the precision of the Mössbauer technique on a state-of-the-art

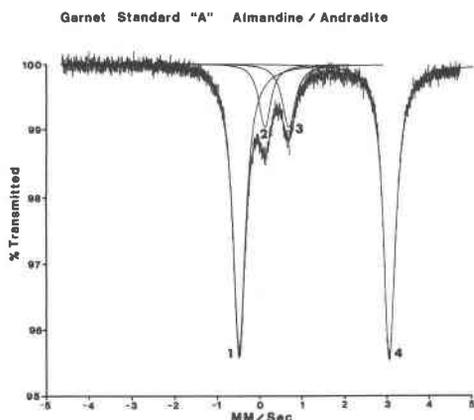


Fig. 5. Fitted Mössbauer spectrum of standard "A", a mixture of almandine and andradite garnet.

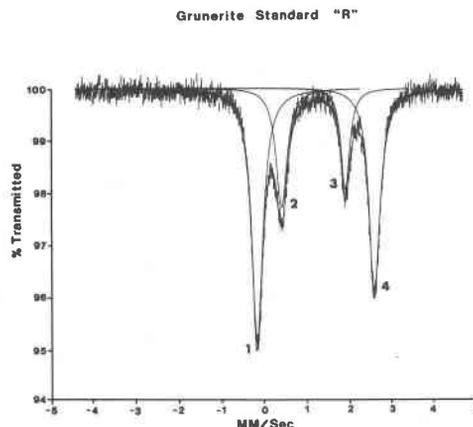


Fig. 6. Fitted Mössbauer spectrum of standard "R", an iron-rich grunerite amphibole, which was used both as intra- and interlaboratory standard.

spectrometer at MIT by using a natural mineral standard. This was pursued through five different sets of experiments, seeking to analyze the reproducibility of measurements on a single sample mount, on several identical mounts of the same sample, and on a set of mounts with different sample concentrations, run times, and background counts. Considerable effort was made to approach the analyses in an unbiased fashion; the following results are presented in the order in which they were determined.

Effects of sample concentration were first studied by running a series of different Fe concentration mounts for identical 24 hour periods, with no control over the number of baseline counts (Table 3).¹ Although a statistical "good fit" was attained for the 20 mg Fe/cm² sample, the predominating trend, as seen in Figures 7a and 7b, was for the best statistics and gamma ray absorbance to occur at a concentration of 5–7 mg Fe/cm², at around 2.5 million baseline counts.

This conclusion was further tested by holding the number of baseline counts constant at 1 million, and allowing time and sample concentration to vary. Results are presented in Table 4. As can be seen in Figures 8a and 8b, the optimal concentration necessary to make χ^2 approach 509 and Misfit approach 0 falls at the concentration of 7 mg Fe/cm².

Effects of run duration and number of background counts on the statistical parameters of the fits were tested after the optimum iron concentration (7 mg Fe/cm²) had been determined. Time and the number of baseline counts

¹ Complete listings of full data for each run (as listed in Tables 3–7, 12, and 13), including run times; baseline counts; Fe concentrations; individual peak positions, widths, and areas; isomer shifts; quadrupole splittings; and error data can be obtained by ordering Document AM-84-256 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, DC 20009. Please remit \$5.00 in advance for the microfiche.

Table 3. 24 hours, counts and concentration varying

Number hours	Baseline counts per channel	Total Fe conc. (mg/cm ²)	% Areas				Isomer Shift (mm/sec)			Quadrupole Splitting (mm/sec)			% Transmitted	χ ²	Misfit
			1	2	3	4	1-4	2-3	1-4	2-3	1-4	2-3			
24	1661501	40	32.27	24.47	14.46	28.80	1.151	1.118	2.905	1.620	93.91	759	0.00101		
24.3	1775161	30	33.24	23.29	14.24	29.23	1.155	1.117	2.929	1.633	92.29	989	0.00111		
24.75	2661504	20	32.26	24.48	14.46	28.80	1.151	1.118	2.905	1.620	90.96	471	-0.00026		
			35.34	24.19	12.89	27.58	1.163	1.137	2.884	1.588	-	875	0.00068		
26.5	2716282	15													
26	3728779	7	35.30	23.93	12.21	28.56	1.161	1.136	2.882	1.573	94.72	780	0.00090		
26.25	3785614	5	35.00	24.08	12.68	28.24	1.167	1.146	2.880	1.585	97.02	553	0.00047		
			35.01	23.45	11.99	29.56	1.166	1.140	2.881	1.576	97.53	472	-0.00054		
26	4208489	3.5	36.21	24.07	12.12	27.59	1.163	1.141	2.885	1.572	97.96	402	-0.00272		
25.5	4529096	2.5	32.46	26.94	12.25	28.35	1.166	1.146	2.887	1.575	99.20	340	-0.02199		
26	5369985	1													
Variance			2.4034	1.1274	1.0439	0.4500	0.0000	0.0001	0.0003	0.0006					
Standard Deviation			1.5503	1.0618	1.0217	0.6708	0.0064	0.0122	0.0165	0.0240					
Mean			34.1211	24.3222	13.0111	28.5233	1.1603	1.1332	2.8931	1.5936					

Table 4. 1 million counts, time and concentration varying

Number hours	Baseline counts per channel	Total Fe conc. (mg/cm ²)	% Areas				Isomer Shift (mm/sec)			Quadrupole Splitting (mm/sec)			% Transmitted	χ ²	Misfit
			1	2	3	4	1-4	2-3	1-4	2-3	1-4	2-3			
18	1145444	40	34.83	19.15	15.39	30.63	1.153	1.082	2.807	1.534	93.23	684	0.00084		
16.5	1198750	30	35.70	18.60	14.13	31.56	1.148	1.084	2.763	1.497	91.53	785	0.00086		
10.5	1101536	20	36.62	18.63	13.77	30.98	1.154	1.100	2.792	1.526	90.59	705	0.00058		
9.75	1116850	15	38.22	18.36	13.72	29.70	1.150	1.094	2.773	1.509	91.91	632	0.00054		
8.5	1072936	10	39.26	17.86	13.11	29.76	1.151	1.097	2.759	1.501	93.80	545	0.00032		
7.5	1073238	7	38.18	18.44	12.61	30.76	1.193	1.130	2.746	1.490	94.87	517	0.00008		
6.67	1042950	5	36.47	18.85	13.08	31.60	1.153	1.089	2.789	1.535	96.57	406	-0.00332		
6.5	1036633	3.5	35.55	20.43	12.59	31.43	1.153	1.090	2.752	1.500	97.31	416	-0.00592		
7.0	1123864	2.5	38.57	18.66	12.63	30.14	1.151	1.086	2.765	1.512	97.38	372	-0.00737		
6.8	1104674	1	31.49	21.28	13.69	33.54	1.157	1.085	2.848	1.587	98.83	403	-0.04891		
Variance			5.2366	1.0796	0.7582	1.2744	0.0002	0.0002	0.0009	0.0008					
Standard Deviation			2.2884	1.0390	0.8708	1.1289	0.0131	0.0140	0.0308	0.0285					
Mean			36.4890	19.0260	13.4720	31.0100	1.1563	1.0937	2.7794	1.5191					

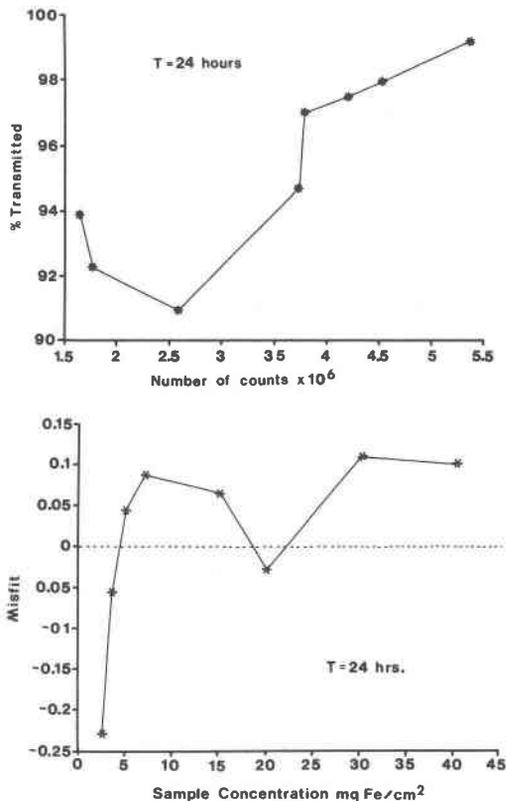


Fig. 7. Plot of number of counts versus % transmission (a) and sample concentration versus Misfit (b) for grunerite runs with $T = 24$ hours.

were allowed to vary (Table 5). Results shown in Figures 9a and 9b amply demonstrate that short run times (based on a gamma ray flux strong enough to supply about 100,000 background counts/hour) give the most desirable values for χ^2 (close to 509) and Misfit (close to 0). This conclusion can be explained by the effects of small instrumental problems, such as the cosine smearing factor (Spijkerman et al., 1965), baseline inconstancies, source problems, non-linear drives, etc., for which Misfit was designed to be sensitive. As will be discussed later, these problems are not unique to the MIT apparatus.

Reproducibility of replicate analyses on a single mount was tested once the optimum run characteristics had been determined (Table 6). Peak positions vary from their respective means by up to ± 0.02 mm/sec; widths vary ± 0.02 mm/sec and areas of individual peaks are within $\pm 1.6\%$. However, isomer shifts are reproducible to within ± 0.012 mm/sec, and quadrupole splittings are generally good to ± 0.016 mm/sec. These figures can be regarded as a realistic lower limit on the experimental reproducibility of the Mössbauer apparatus, as influenced by the MIT lab's electronic stability and computer fitting procedures.

A test of the homogeneity of the standard was undertaken to examine the suitability of the grunerite for

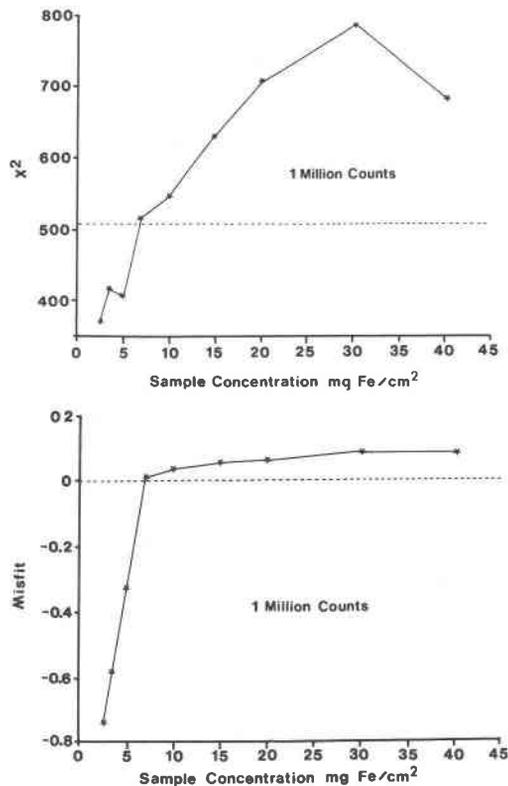


Fig. 8. Plot of sample concentration versus χ^2 (a) and versus Misfit (b) for grunerite runs with one million baseline counts.

interlaboratory calibrations. Results are shown in Table 7. Reproducibilities are ± 0.028 mm/sec for peak positions, ± 0.08 mm/sec for widths, $\pm 2.0\%$ for areas of individual peaks, ± 0.026 mm/sec for isomer shift, and ± 0.11 mm/sec for quadrupole splittings. Although the statistical variance in the Mössbauer parameters of the different aliquots is at least twice that of measurements on the same sample (Table 8), their means are almost identical, and the grunerite was deemed suitable for a standard.

Interlaboratory comparison

Seven laboratories ran the two mineral standards which were circulated. Each lab had its own distinctive method of sample preparation (Table 9); all were careful to weigh out the appropriate amount of sample to be used. Run characteristics (Table 10) were fairly consistent throughout. As anticipated, each group had its own distinctive fitting procedure (Table 11).

Results of the Mössbauer experiments are shown in Tables 12 and 13. Comparison of variances between the MIT experiments and the corresponding values from different laboratories for standard "R" shows some interesting trends (see Table 8). For peak positions, widths, isomer shifts, and quadrupole splittings, there is only slightly more variance between labs than there is on the

Table 5. 7 mg Fe/cm² with time varying

Number hours	Baseline counts per channel	Total Fe conc. (mg/cm ²)	% Areas					Isomer Shift (mm/sec)			Quadrupole Splitting (mm/sec)	% Transmitted	χ ²	Misfit
			1	2	3	4		1-4	2-3	1-4				
3	293152	7	38.08	16.71	14.36	30.85	1.144	1.060	2.818	1.553	92.72	495	-0.00034	
7	663667	7	37.20	17.27	14.00	31.53	1.140	1.055	2.785	1.531	93.46	503	-0.00008	
10	897661	7	37.73	17.08	13.82	31.37	1.155	1.069	2.796	1.542	92.92	542	0.00023	
12	1075768	7	37.96	16.46	13.84	31.75	1.150	1.071	2.789	1.547	92.76	545	0.00022	
15	1540192	7	37.97	16.76	13.89	31.38	1.146	1.066	2.816	1.561	93.40	592	0.00043	
18	1820108	7	37.36	16.90	14.08	31.66	1.150	1.068	2.807	1.547	93.50	570	0.00026	
21	1986456	7	37.58	16.93	13.83	31.66	1.139	1.061	2.813	1.559	93.45	553	0.00017	
24	2455543	7	37.79	16.59	13.86	31.76	1.143	1.059	2.808	1.556	93.60	707	0.00064	
28	2749269	7	37.66	16.69	14.02	31.63	1.146	1.061	2.819	1.553	93.47	640	0.00036	
33	3356315	7	37.41	16.77	13.75	32.08	1.143	1.060	2.813	1.557	93.53	745	0.00055	
39	3888139	7	37.58	16.76	14.00	31.65	1.142	1.059	2.794	1.544	93.51	807	0.00060	
48	4627081	7	37.31	16.89	14.24	31.56	1.144	1.060	2.801	1.550	93.56	767	0.00043	
60	5971105	7	37.07	17.36	13.77	31.80	1.139	1.061	2.792	1.538	93.55	947	0.00057	
Variance			0.0974	0.0655	0.0338	0.0832	0.0000	0.0000	0.0001	0.0001			0.0001	
Standard Deviation			0.3120	0.2559	0.1838	0.2885	0.0047	0.0047	0.0117	0.0087			0.0087	
Mean			37.5923	16.8592	13.9685	31.5908	1.1447	1.0623	2.8039	1.5492			1.5492	

Table 6. Repeated runs of same sample, same mount

Number hours	Baseline counts per channel	Total Fe conc. (mg/cm ²)	% Areas					Isomer Shift (mm/sec)			Quadrupole Splitting (mm/sec)	% Transmitted	χ ²	Misfit
			1	2	3	4		1-4	2-3	1-4				
12	1155249	7	36.92	17.43	13.90	31.74	1.138	1.060	2.813	1.561	88.71	551	0.00028	
12	1145712	7	37.18	17.33	13.93	31.55	1.141	1.065	2.821	1.577	91.78	543	0.00023	
12	1090119	7	37.15	17.18	13.82	31.86	1.134	1.057	2.800	1.557	93.39	505	-0.00003	
12	1075779	7	37.34	16.95	13.40	32.31	1.150	1.071	2.788	1.547	92.76	528	0.00011	
12	1138450	7	37.10	17.09	13.63	32.17	1.133	1.053	2.797	1.550	93.36	511	0.00001	
12	1091482	7	37.03	17.37	13.56	32.03	1.137	1.057	2.802	1.543	90.99	491	0.00013	
12	1068833	7	36.28	18.04	13.49	32.18	1.135	1.052	2.804	1.550	93.46	531	0.00015	
12	960189	7	35.36	19.07	13.34	32.22	1.140	1.055	2.808	1.554	93.85	580	0.00061	
12	949604	7	34.99	19.44	13.15	32.41	1.143	1.062	2.809	1.551	93.81	538	0.00025	
12	985877	7	36.00	18.23	13.77	32.00	1.145	1.060	2.808	1.546	93.57	592	0.00064	
Variance			0.6972	0.7440	0.0668	0.0713	0.0000	0.0000	0.0001	0.0001			0.0001	
Standard Deviation			0.8350	0.8626	0.2584	0.2670	0.0053	0.0057	0.0090	0.0098			0.0098	
Mean			36.5350	17.8130	13.5990	32.0470	1.1396	1.0592	2.8050	1.5536			1.5536	

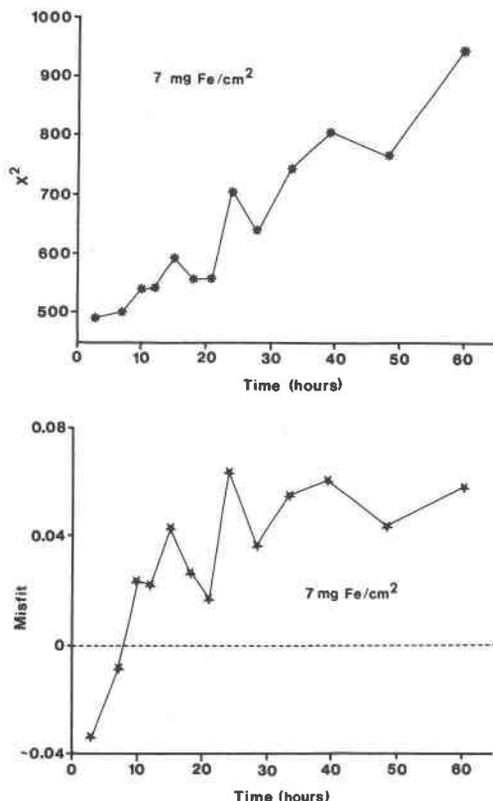


Fig. 9. Plot of time versus χ^2 (a) and versus Misfit (b) for grunerite runs where the sample concentration was held constant at 7 mg Fe/cm².

MIT apparatus alone. However, there is considerably less variance in peak area throughout the MIT experiments, especially when the "Different Laboratory" data set is compared against the most similar MIT data set, "7 mg Fe/cm² with Time Varying." This is probably because the MIT data are all fit with identical curve shapes. To test this hypothesis, raw spectral data were collected from the different labs. Spectra were entered by hand into the MIT computer, to be processed and fit with the MIT curve-fitting program. The results are shown in Tables 8 and 14; as predicted, variance in individual peak areas is somewhat reduced when all spectra are fit to the same curve shape.

Discussion

Optimization of experimental technique

It is not surprising that this study found the optimal sample concentration to be 5–7 mg Fe/cm². However, it is important to be reminded that even small deviations from that value can produce rather drastic increases in the corresponding statistics of the eventual fit. Above the optimal concentration, χ^2 increases (degrades) very

Table 7. 10 aliquots of the same sample; identical run conditions

Number hours	Baseline counts per channel	Total Fe conc. (mg/cm ²)	% Areas				Isomer Shift (mm/sec)			Quadrupole Splitting (mm/sec)			% Transmitted	χ^2	Misfit
			1	2	3	4	1-4	2-3	1-4	2-3	1-4	2-3			
12	1063038	7	34.88	17.46	14.43	33.22	1.180	1.091	2.871	1.589	94.42	506	-0.00003		
12	1054196	7	35.39	16.06	13.70	34.84	1.162	1.072	2.823	1.566	94.68	641	0.00133		
12	962361	7	36.26	15.99	14.90	32.85	1.160	1.067	2.818	1.558	93.93	474	-0.00033		
12	996971	7	35.15	16.40	14.67	33.78	1.174	1.081	2.885	1.594	94.63	536	0.00027		
12	980563	7	34.48	16.91	14.98	33.63	1.166	1.072	2.872	1.585	95.47	495	-0.00022		
12	756641	7	34.40	18.02	14.15	33.42	1.183	1.093	2.936	1.637	94.61	430	-0.00112		
12	1046152	7	33.49	17.58	14.90	34.03	1.185	1.085	2.909	1.614	95.42	517	0.00010		
12	859754	7	32.95	19.18	14.00	33.87	1.197	1.103	2.907	1.606	96.10	501	-0.00019		
12	890532	7	34.69	17.07	13.34	34.90	1.149	1.062	2.747	1.498	95.21	507	-0.00004		
12	1075779	7	37.34	16.95	13.40	32.31	1.150	1.071	2.788	1.547	92.76	528	0.00011		
Variance			1.5963	0.9285	0.3903	0.6500	0.0003	0.0002	0.0036	0.0015					
Standard Deviation			1.2634	0.9636	0.8062	0.8131	0.0158	0.0131	0.0598	0.0393					
Mean			34.9030	17.1620	14.2470	33.6850	1.1706	1.0797	2.8556	1.5794					

Table 8. Standard deviations of Mössbauer parameters* for standard "R"

	Position Peak 1	Width Peak 2	Area Peak 3	I.S. 1-4	I.S. 2-3	Q.S. 1-4	Q.S. 2-3
Repeated Runs, Same Sample, Same Mount	0.0074	0.0152	0.2584	0.0053	0.0057	0.0090	0.0098
Identical Run Conditions, Different Samples	0.0169	0.0468	0.6247	0.0158	0.0131	0.0598	0.0393
7mg Fe/cm with Time Varying	0.0077	0.0063	0.1838	0.0047	0.0047	0.0117	0.0087
24 Hour Runs, Counts and Concentration Varying	0.0140	0.0169	1.0217	0.0064	0.0122	0.0165	0.0240
1 Million Counts, Time and Concentration Varying	0.0226	0.0120	0.8708	0.0131	0.0140	0.0308	0.0285
Different Laboratories	0.0142	0.0241	1.1459	0.0058	0.0057	0.0225	0.0109
Different Laboratories, Same Fitting Program	-	-	0.9564	0.0060	0.0100	0.0144	0.0126

* Note that values for all the different parameters cannot be directly compared, because standard deviation is in the units of the original measurement (mm/sec for all but area, which is given in %).

quickly; for example, at 30 mg Fe/cm² χ^2 is 1.5 to 2 times larger than at 7 mg Fe/cm². The more sensitive parameter of Misfit is also greatly affected by sample concentration.

Similarly, duration of runs is a very critical parameter. Samples which were run for just one million counts seem to give Misfit values closest to zero; above that χ^2 increases by at least 10% for every million counts. Shorter runs produce decaying Misfit values. These conclusions may seem to contradict one of the common assumptions in counting statistics: the idea that more counts will produce better χ^2 values. Unfortunately this assumption is not true in cases where electronics and drive systems are involved; for Mössbauer spectroscopy, more time means a chance for long term electronic drift (due to a combination of instability in the electronics and mechanical instability) to have a greater influence on runs. Use of a laser interferometer (e.g., Cosgrove and Collins, 1971 or Otterloo et al., 1983) might partly offset long-term instabilities, and thus allow longer runs. However, the addition of an interferometer to the drive mechanism monopolizes one half of the spectrometer, such that only one mineral spectrum (instead of the usual two) can be run at a time. Such a loss of productivity is

probably not worth the increase in stability, except in cases where major fluctuations are suspected. Therefore, it is generally necessary to strike a compromise between having a long enough run to accumulate sufficient counts to adequately define the spectrum, and having a short enough run to avoid electronic drift. On the MIT equipment, runs which last 1 million counts seem to make the best compromise. That corresponds to about six hours exposure of a mineral to a 95 mCi source.

When this result was defined, it seemed logical to see if others had a similar problem with instability. Wayne Dollase ran our standard "R" for run times corresponding to 2, 4, and 6 million background counts on the UCLA spectrometer. He reported the following results (Dollase, pers. comm., March, 1983):

1. The weighted peak location precision calculated from the least-squares fit is: 0.0012 mm/sec, 0.0010 and 0.0008 for the 2, 4, and 6 million count spectra, respectively. However, the mean reproducibility of the four peaks on the three spectra is 0.013 mm/sec and thus isomer shifts and quadrupole splitting probable errors are approximately ± 0.02 mm/sec. This large difference between precision and actual reproducibility is due to a systematic offset of random magnitude (0.01–0.02) from spectrum to spectrum caused by the nature of the electronics and drive systems. Because of this poorer reproducibility, one could not expect to see more accurate peak locations in higher count spectra.

2. Peak width and Lorentzian/Gaussian peak shape fractions show reproducibility of 0.01–0.02 mm/sec and 1%, respectively. Higher background-count spectra are expected to show slightly broader peaks and slightly greater Gaussian components due to short term drift but this effect seems negligible in the case of these three spectra.

3. Area fractions have a mean reproducibility of 0.2% which is probably fortuitous as experience suggests that probable errors in area are about 1% for such spectra. Least-squares fitting errors are 0.1–0.2%.

4. The goodness of fit indicators reflect the differences in total background counts. The value of chi-squared increases with background count as would be expected

Table 9. Methods of sample preparation

1.	Pellets pressed between aluminum foil, with volume adjustable (3–5 mg Fe/cm ²); sample diameter approximately 1/2 inch.
2.	At 0° rotation, sample in plastic compression holder with 1.5 cm diameter sample hole; sample diluted in ~50 mg of cubic boron nitride: 17 mg "R", 20 mg "A". At 54.7° rotation, samples dispersed in lucite (78 mg "R", 110 mg "A" to 1000 mg lucite) in disks of 3.2 cm diameter.
3.	Buehler transoptic powder (200 mg) used as mounting medium; 18.6 mg "R", 26.7 mg "A", in lead or aluminum 1.3 cm ² sample holder.
4.	Samples ground in agate mortar and mixed with sugar, mounted in 2 cm ² cylindrical plexiglass holders with quantities adjusted to concentrations of 3 mg Fe/cm ² .
5.	Samples mixed with warm vaseline in polyethylene "cap" (a flat, circular disk of ~1" diameter x 3/16" height). Sample density of 0.16 mg ⁵⁷ Fe/cm ² for "R" and "A".
6.	Samples ground with sugar and acetone and mounted in 5 mm thick plexiglass holders with 1" diameter holes for sample. Sample held in place by clear cello tape. Concentrations adjusted to 7–10 mg Fe/cm ² .
7.	Sample mixed with boron nitride powder, mounted between two mylar disks (average thickness 0.12 mm) and mounted in brass sample holder. Area of sample = 1.43 cm ² , thickness of sample (excluding mylar disks) = 0.60 mm; 24.69 mg "R": 131.32 mg BN; 30.40 mg "A" = 124.33 mg BN used.

Table 10. Run characteristics*

Lab Number	1	2	3	4	5	6	7
Average run time, in hours	10-16	8-23	48	48	44	8	20-24
Source matrix	Rh	Pd	Rh	Rh	Pd	Rh	Rh
Source strength, in mCi	20	~100	20	30	15	100	35
Distance from sample to source, in cm	20	~9 -11**	15	7	20	10	3
# channels	1024	512	1024	1024	256	512	256 or 512

* All results were calibrated with respect to metallic iron.

** Distances from detector to source were given as 13.5-19 cm.

due to the small systematic inadequacies of the calculated model (as caused by spectrometer nonlinearity and drift, sample saturation, chemical inhomogeneities, etc.). Note, however, that MISFIT decreases to very low values for high background count spectra demonstrating their increased quality.

Note that on the UCLA spectrometer, Misfit does not appear to get larger with longer run times. This suggests that the UCLA system has much less long term drift. However, two of their % Misfit values are an order of magnitude higher than the corresponding values observed in the MIT data (see Table 15). Because it yields consistently lower Misfit values, the MIT fitting program probably gives better fits over a wide range of background counts, in spite of long term drift. This point serves to highlight the uniqueness of each spectrometer set-up and fitting program and to emphasize that each apparatus probably has its own criteria for optimization.

It is also necessary to consider what the optimal sample concentration might be for non-silicates. Results for a pyrite and a ferberite (FeWO_4) sample are shown in Figures 10 and 11. Sulfur-bearing samples appear to have

a lower optimum concentration around 2 mg Fe/cm^2 ; the tungsten-bearing ferberite probably requires more sample for experimental optimization.

Interlaboratory comparison

It is obvious from even a cursory inspection of Table 8 that the variance in Mössbauer parameters is somewhat greater for the array of different laboratories than for measurements made at a single lab. Given that the variation does exist, it is important to consider three questions: (1) Are the variations significant? (2) What are the probable causes of this variation? (3) What can be done to reduce such variation? The answers to these questions are of vital importance to both experimenters and users of Mössbauer data.

The question of significance is fairly easily answered. The different results can be compared rigorously through use of common statistical tests. The T test, which is used to test hypotheses about the equivalency of two samples, evaluates the likelihood of mean values falling within a sample-based distribution. The F test determines equality of variances based on the theoretical F distribution of all possible pairs of sample variances in a random sampling of a normal population (Davis, 1973).

To perform these tests, two populations are needed. Rather than combining all the MIT measurements, one

Table 11. Fitting procedures used*

1. MOSSFIT program, obtained in 1974 from Geophysical Laboratory, Washington, DC. Runs on PDP 11 computer using Lorentzian line shapes.
2. AMOSS program, originally from Carnegie-Mellon University (P. Flynn et al.), extensively modified for use by surveyed institution. Runs on TSI-11 or PDP-11/34A with 28K memory, fitting 100% Lorentzian line shapes.
3. MOESFIT program, obtained from B. J. Evans, Ann Arbor, in 1978, modified by Runge in 1978 and by Nagel in 1982. Runs on Telefunken TR 440 computer, fitting Lorentzian curve shapes.
4. NORMOS program (based on MOSFIT, Argonne National Laboratory with subroutines written in the Physics Department of the surveyed institution), written in 1978 by G. Shenoy, B. Dunlap, F. E. Wagner, and W. Koch. Runs on CDC Cyber 175 using Lorentzian line shapes.
5. MOSFIT program written by the survey participant in 1970. Runs on IBM 3033, using a Gaussian-broadened Lorentzian curve shape.
6. STONE program written by A. J. Stone in 1970, modified for PDP-11/34 computer by K. Parkin and users at the surveyed institution. Uses Lorentzian line shapes.
7. DCPFIT program written in 1975 by D. C. Price. Runs on Univac 1100/82 computer fitting pseudo-Lorentzian line shapes.

* Further information on the various fitting routines is available from this author; to preserve confidentiality referenced papers are not cited here.

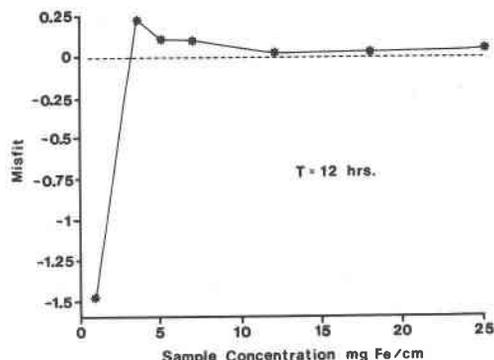


Fig. 10. Plot of sample concentration versus Misfit for pyrite spectra where time was held constant at twelve hours.

Table 12. Mössbauer data on sample R (all unconstrained fits)

Lab No.	Temp. (°K)	Baseline counts per channel	Lab No.	% Area (or χ_{eff})							Isomer Shift (mm/sec)			Quadrupole Splitting (mm/sec)			Misfit	χ^2	Degrees of Freedom
				1	2	3	4	1-4	2-3	1-4	2-3	1-4	2-3	1-4	2-3				
1	300	374600	1	35.65	16.81	13.31	34.22	1.166	1.080	2.797	1.545	0.014	523.5	487					
2	295	3847859	2	35.4	13.5	14.0	37.1	1.158(1)	1.069(1)	2.787(1)	1.544(2)	0.086±0.006	1336	487					
2	295	3491639	2	37.6	15.2	12.6	34.5	1.156(1)	1.067(1)	2.792(1)	1.539(2)	0.048±0.007	751	487					
3	295	1365000	3	34.7	15.8	13.5	36.0	1.158	1.074	2.798	1.545	0.00087	1008	497					
4	295	1141242	4	34.24**	15.76**	15.76**	34.24**	1.151	1.064	2.796	1.537	-	979.5	-					
5	297	4072459(402)	5	35.1(4)	16.6(4)	13.3(4)	35.0(4)	1.163±.01	1.079±.015	2.735±.01	1.515±.01	0.100*	381	241					
6	298	1075779	6	37.34	16.95	13.40	32.31	1.150	1.071	2.788	1.547	0.00011	528	509					
7	298	746459	7	30.75**	13.84**	13.84**	30.75**	1.151	1.069	2.787	1.534	-	243	237					
7	298	2350842	7	33.00**	17.00**	17.00**	33.00**	1.159	1.074	2.799	1.544	-	289	237					
7	298	362213	7	34.81**	15.19**	15.19**	34.81**	1.152	1.068	2.786	1.544	-	520	493					
7	298	1160999	7	33.45**	16.55**	16.55**	33.45**	1.160	1.073	2.800	1.542	-	456	493					
Variance*				2.0819	0.8100	1.3132	1.8765	0.0000	0.0000	0.0005	0.0001	-	-	-					
Standard Deviation				1.4429	0.9000	1.1459	1.3698	0.0058	0.0057	0.0225	0.0109	-	-	-					
Mean				35.2186	15.9886	14.0314	34.3671	1.1573	1.0724	2.7852	1.5385	-	-	-					
2	77	4040139	2	37.1	17.8	12.4	32.8	1.273(1)	1.188(1)	3.120(2)	1.548(2)	0.084±0.009	969	487					

* All statistics were computed using one value (averaged, if necessary) from each lab.

** These workers gave their % areas in terms of area per doublet; these values were halved for purposes of this table (probably a poor assumption, but necessary to enable compilation of statistics).

Table 13. Mössbauer data on sample A (all unconstrained fits)

Lab No.	Temp. (°K)	Baseline counts per channel	Lab No.	% Area (or χ_{eff})							Isomer Shift (mm/sec)			Quadrupole Splitting (mm/sec)			Misfit	χ^2	Degrees of Freedom
				1	2	3	4	1-4	2-3	1-4	2-3	1-4	2-3	1-4	2-3				
1	300	454800	1	40.94	10.11	9.91	39.05	1.296	0.412	3.531	0.550	0.00465	512	487					
2	293	4962630	2	41.7	8.8	8.8	40.7	1.293(1)	0.396(1)	3.517(1)	0.547(3)	0.013±0.004	586	487					
2	293	1519572	2	42.8	8.1	9.2	39.9	1.292(1)	0.399(1)	3.520(1)	0.551(3)	0.017±0.004	633	487					
3	295	1245000	3	42.7	7.6	7.9	41.9	1.291	0.407	3.536	0.553	0.00022	637	497					
4	296	993278	4	40.04**	9.96**	9.96**	40.04**	1.282	0.403	3.534	0.562	-	765	-					
5	297	4266211(615)	5	40.8(4)	10.7(6)	10.3(4)	38.2(4)	1.283±.01	0.396±.015	3.521±.01	0.546±.005	0.125*	705	241					
6	298	1805976	6	41.17	8.65	9.64	40.53	1.291	0.405	3.528	0.559	0.0018	293	499					
7	298	2275546	7	40.37**	9.64**	9.64**	40.37**	1.282	0.400	3.517	0.546	-	247	237					
7	298	2900293	7	40.51**	9.49**	9.49**	40.51**	1.284	0.401	3.520	0.551	-	516	493					
Variance*				0.9172	0.9751	0.6410	1.3817	0.0000	0.0000	0.0001	0.0000	-	-	-					
Standard Deviation				0.9577	0.9875	0.8006	1.1755	0.0056	0.0056	0.0074	0.0059	-	-	-					
Mean				41.1914	9.3750	9.4679	40.0657	1.2884	0.4030	3.5267	0.5525	-	-	-					
2	77	3652275	2	41.5	10.5	7.7	40.2	1.435(1)	0.531(2)	3.675(1)	0.542(4)	0.034±0.005	764	487					

* All statistics were computed using one value (averaged, if necessary) from each lab.

** These workers gave their % areas in terms of area per doublet; these values were halved for purposes of this table (probably a poor assumption, but necessary to enable compilation of statistics).

Table 14. Mössbauer spectra fit with one program

Lab No.	% Area				Isomer Shift (mm/sec)		Quadrupole Splitting (mm/sec)		Misfit	χ^2	Degrees of Freedom
	1	2	3	4	1-4	2-3	1-4	2-3			
1	35.57	16.88	1.380	33.75	1.161	1.076	2.798	1.548	0.000013	515	499
2	37.04	16.02	13.35	33.60	1.153	1.064	2.797	1.541	0.000625	837	487
3	35.54	14.60	14.34	35.52	1.166	1.082	2.798	1.545	0.00106	1106	499
4	32.06	15.31	14.39	38.25	1.159	1.072	2.803	1.541	0.00111	779	495
5*(0)	35.87	12.60	16.15	35.38	1.163	1.093	2.760	1.512	0.00205	1072	243
5(21)	35.37	13.10	16.77	34.77	1.178	1.093	2.730	1.516	0.000627	501	243
6	37.34	16.95	13.40	32.31	1.150	1.071	2.788	1.547	0.000111	528	509
7	37.57	14.62	13.87	33.94	1.153	1.066	2.787	1.533	0.000485	537	497
Variance	3.5222	2.3296	0.9147	3.6892	0.0000	0.0001	0.0002	0.0002			
Standard											
Deviation	1.8768	1.5263	0.9564	1.9207	0.0060	0.0100	0.0144	0.0126			
Mean	35.8557	15.2829	14.1857	34.6786	1.1579	1.0749	2.7901	1.5381			

* Data from lab 5 were originally submitted with a 21% Gaussian line shape component in peak shapes. The MIT program refit the same data with both 0% and 21% Gaussian component. Statistics are computed using only the 0% data.

set of data, the 7 mg Fe/cm² with time and concentration varying data set, were used because those parameters most closely approximate the conditions of the different labs. The T test, which determines equality of means of two groups of samples, is defined as:

$$T = \frac{\bar{X}_1 - \bar{X}_2}{s_p \sqrt{(1/n_1) + (1/n_2)}}$$

where \bar{X}_1 and \bar{X}_2 are the two sample means, n_1 and n_2 are the number of samples in each sample group, and s_p is defined as the square root of:

$$s_p^2 = \frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}$$

If the calculated value of the T test exceeds the selected value of 2.074 for a 2.5% level of significance with 22 degrees of freedom (for data column 1), then the test implies that there is little evidence to suggest that the means are equal.

Similarly, the F test is defined as

$$F = \frac{s_1^2}{s_2^2}$$

where the degrees of freedom equal $n_1 - 1$ for the numerator, and $n_2 - 1$ for the denominator. Again, the

Table 15. Comparison of misfit values on different spectrometers

Background Counts	UCLA Spectrometer	MIT Spectrometer
2×10^6	0.108 (15)%	0.0170 (103)%
4×10^6	0.111 (12)%	0.0601 (83)%
6×10^6	0.043 (5)%	0.0576 (63)%

null hypothesis that the variances are equal will be disproven when the values for the F test in column 2 exceed the critical value of 3.37 for the 2.5% level of significance (see Davis, 1973 or Bevington, 1969).

Results of the statistical evaluation are shown in Table 16. Data columns one and two show results for the MIT data versus different laboratories' data, all fit with different programs. The results suggest that mean values for peak position, isomer shift, and quadrupole splittings are significantly different between the two groups. Note that isomer shift and peak position, which are dependent on foil calibration and source corrections, show the most significant variation in their mean values. Highest values for variance between the two data sets occurs for area data, as might be expected from use of different fitting programs and the incorrect assumption made about equality of peak areas.

Data columns three and four show results for the same MIT data compared with the different laboratories' data, all fit with the same program. Means of the two sets are

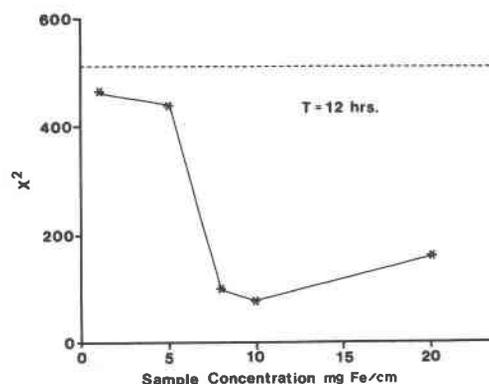


Fig. 11. Plot of sample concentration versus χ^2 for ferberite spectra where time was held constant at twelve hours.

Table 16. Statistical tests for variance in different Mössbauer parameters

Parameter	One Lab (MIT), same program, vs. Different Labs, same program		One Lab (MIT), same program, vs. Different Labs, same program	
	T Test	F Test	T Test	F Test
Peak Position, Peak 1	5.1447	2.2194	-	-
Width, Peak 2	0.6872	12.2826	-	-
Area, Peak 3	1.0844	64.5183	0.8472	27.0980
Isomer Shift, 1-4	5.9235	1.2370	5.4500	1.5872
Isomer Shift, 2-3	4.7606	1.1179	3.8690	4.6136
Quadrupole Splitting, 1-4	2.6232	2.4077	2.3088	1.5109
Quadrupole Splitting, 2-3	2.9057	1.0981	2.3383	2.1179
T test $H_0: \mu_1 = \mu_2$ fails if $T > 2.074$ (95% confidence level)			T test $H_0: \mu_1 = \mu_2$ fails if $T > 2.101$ (95% confidence level)	
F test $H_0: s_1^2 = s_2^2$ fails if $F > 3.37$ (95% confidence level)			F test $H_0: s_1^2 = s_2^2$ fails if $F > 3.73$ (95% confidence level)	

different only for isomer shift data; variance is significantly different only for the area data and one of the isomer shift values. These results suggest that use of a consistent curve-fitting program among all labs might improve reproducibility to a small degree, especially if the apparent discrepancy caused by foil calibrations and source corrections could be corrected. If such a universal fitting program were to be selected, a logical candidate would be MOSSPEC (and its many descendants), originally written by A. J. Stone at Cambridge and developed extensively there by both theoretical and physical chemists (see Stone et al. 1971 or Stone et al., 1984). This program is undoubtedly the most widespread Mössbauer fitting program, due in part to its mention in Bancroft's (1973) book. However, such an improvement would probably not be worth the large amount of time and trouble that would be necessary to implement such a plan.

Next it is useful to discuss the possible causes for imprecision in these data, and to ascertain why the observed variance for all the samples is as high as it is. It is convenient to discuss each suspected cause of error separately:

Counting statistics are the underlying source of error for this type of measurement. However, a simple example can be used to show that this type of error is relatively small when compared to the overall peak areas that are used to determine Fe^{3+}/Fe^{2+} ratios (Whipple, 1973). In a typical spectrum with one million baseline counts, where one standard deviation is 1000 and an average peak height might be 20,000 counts (2% absorption) one standard deviation is 5% of the average peak height. Since a peak's area may cover 20–30 channels, the *area* variation of the peak due to statistics alone is very small. Furthermore, it has been shown that errors due to having too few background counts can be minimized by thorough testing of the individual spectrometer.

Long term drift is also a universal problem in all of the labs tested. It may be responsible for a substantial part of the error in these measurements. However, it can also be

minimized by individual testing and/or laser interferometry.

Inhomogeneity in the standards was tested; variance in these measurements was found to be about the same or worse than the variance between labs. Inhomogeneity may contribute to the errors in these measurements, but it is difficult to separate its effects from the other sources of error.

Sample concentration might cause error; as was seen in the MIT measurements, many of the fit statistics and parameters can change with concentration. However, sample concentration remained essentially constant in the interlaboratory experiments, so that factor cannot be responsible for causing imprecision in those measurements.

Electronic relaxation may cause differences in peak amplitudes, particularly in ferric iron (Goldanskii and Makarov, 1968). However, there was no evidence of amplitude differences in the ferric peaks of the garnet standard spectrum, showing a lack of relaxation effects.

Peak overlap has been shown by Dollase (1975) to be a source of large uncertainty in Mössbauer measurements where peak separation is less than 0.6 times the peak width at half peak height. However, this is not the case for either the grunerite or the garnet standard, both of which have large separations between peaks. In both mineral standards, a slight overlap between the two lower velocity peaks may cause the (2) to rob area from the lowest velocity peak (1), causing the observed inequalities in the areas of the inside doublets (peak 2 and 3). This problem could be corrected by use of area data from a more fully constrained fit, or by using only the higher velocity peaks of the doublets for area ratios. The latter approach is favored by the data given here, which generally show less variance in peak position for the two high velocity peaks.

Real area inequalities in unconstrained fits can affect area data and resultant Fe^{3+}/Fe^{2+} ratios. Whipple (1973) observed that unequal peak areas may be due to the

spectrometer drive moving too rapidly through one region of the spectrum, causing the apparent width of any peaks in that region to decrease. In such cases, it may be important to make adjustments to the drive spring, or to use the other half of a doublet for $\text{Fe}^{3+}/\text{Fe}^{2+}$ calculations. However, in this study all but one of the labs which did unconstrained fits on sample "R" found the lower velocity peak (2) to be 2.30–3.55% larger than its higher velocity mate. Since these results are based on several different spectrometers, drive maladjustment was probably not a cause for this error.

Lack of width constraints has been suggested by Hawthorne (1983) as a possible source of error. However, since there is so little overlapping of peaks it seems unlikely that the lack of width constraints could be causing any of the peaks to borrow width from any others.

Preferred orientation in the samples can be a major cause of peak asymmetry and inequality, particularly with platy minerals. However, all the surveyed labs took the precaution of mixing the samples with some sort of filler/coating to remove preferred orientation, so this is probably not a major source of error either.

Errors in the model, especially how many peaks can be fit, could be suspected as a cause of error, especially since the grunerite spectrum contains contributions from Fe^{2+} in four sites, leading to the potential of four quadrupole split doublets. However, Hawthorne (1981), Bancroft et al. (1967), Hafner and Ghose (1971), and Ghose and Weidner (1972) have all shown that three of those four doublets overlap almost perfectly in the spectra, indicating that fitting a two doublet spectrum is a justifiable model for grunerite. The garnet standard is known to be a mixture of two minerals, each with only one Fe-bearing site; modelling that spectrum with two doublets is probably not a source of error either.

Fe foil calibration values are a fundamental source of error because a spot check revealed that all labs do not use the same values for standard peak position in the iron calibration spectrum. The values listed above as supplied by Dr. Stevens should be universally adopted. Lack of consensus on which values are preferable may contribute to error in Mössbauer measurements, if a given lab deviates significantly from the values that others are using.

Curve-fitting or deconvolution programs are another likely cause of error in these measurements. As discussed above, there is a small reduction in variance when all labs' data are fit with the same program. However, use of a universal curve-fitting program is logistically unfeasible.

This brings us to the third big question for discussion: how can interlaboratory differences best be reconciled? Since it would surely be a hopeless task to try to agree on a single method for curve-fitting/deconvolution, it seems wise to consider other alternatives.

In neutron activation studies it is common practice to

report results of repeated runs on the same sample, and results on standard rocks, in each paper. Mass spectroscopists correct all their values to accepted standards. These standardization procedures are impractical for Mössbauer spectroscopists; the errors in Mössbauer measurements are more complicated than simply adding a certain number to correct for isomer shift or quadrupole splitting. Nor is it really practical, given the time and energy involved, to redo repeated runs on standards and on the samples at hand on a consistent basis. However, on an occasional basis it would be helpful to see published comparisons of the individual research lab's results on the standards compared to the consensus' "mean values." It would also be helpful if each lab could publish its own record for repeated measurements on the same mineral standards, if only infrequently. Such steps would probably go a long way toward reinforcing the credibility and universal acceptance of the Mössbauer technique as an analytical tool.

Conclusions

From the outset, the goal of this work was to reevaluate the analytical precision of the technique of Mössbauer spectroscopy. The results of this prolonged study highlight three major conclusions:

1. The standard deviation of measurements on the MIT apparatus is better than 0.016 mm/sec for isomer shift, 0.060 mm/sec or better for quadrupole splitting data, and 1.02% on area data. These values are for measurements on different aliquots of the same mineral. Repeated measurements on the same sample have considerably better statistics.

2. Optimal precision can be achieved only through careful measurements involving strict control and thorough understanding of the effects of sample concentration, run duration, and baseline counting statistics.

3. The precision of interlaboratory measurements on the same standards is slightly better than that observed for only one lab (0.006 mm/sec for I.S., 0.023 mm/sec for Q.S.; 1.44% on individual peak area data), since only "ideal" run conditions were employed. Mean values for peak position and isomer shift vary significantly between labs, and the highest statistical variance is observed in individual peak area data.

These conclusions then yield some answers to the questions posed earlier in the introduction: samples with small Fe concentrations can be run but the statistics may be affected in the ways predicted in Figures 7 and 8; it is possible (and in fact, often preferable) to minimize run times and still have good results; and it is possible to compare results between labs, provided a common mineral standard has also been analyzed.

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