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Testing of the velocity driving system in Mössbauer spectrometers using reference absorbers

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Abstract

Application of thin reference absorbers namely α-Fe foil, sodium nitroprusside, potassium ferricyanide and potassium ferrocyanide for testing and control of the velocity driving system in the high-quality and -sensitivity Mössbauer spectrometers is demonstrated. The deviation of the absorption line from Lorentzian shape may be considered as indicator of the velocity driving system being out-of-tune. Such an estimation of the differential nonlinearity of the velocity ranges is much more sensitive than that by laser interferometer. This testing and control of the velocity driving system provide the measurements of high-quality and precision Mössbauer spectra and avoid getting the poor spectra with obtaining artifact results.

Keywords Mössbauer spectrometers · Reference absorbers · Testing and control of the velocity driving system

1 Introduction

The velocity driving system is one the most important parts of Mössbauer spectrometers. The quality of this system, including velocity errors, nonlinearity, instability, etc., is responsible for the quality of measured Mössbauer spectra. Therefore, it keeps the velocity driving system under permanent control to exclude measuring incorrect spectra and observing artifacts. In some cases, the laser interferometers were suggested and used for velocity calibration and control (see, e.g., [1–4]). However, this control appeared not to be very good, especially for Mössbauer spectrometers with a high velocity resolution, i.e., with a higher discretization of the velocity reference signal (e.g., 2^{10}, 2^{11}, 2^{12}).

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These spectrometers have velocity driving systems with better precision and sensitivity as compared with conventional spectrometers with discretization of 2^8 or 2^9. An example of the higher nonlinearity of the velocity signal for the high velocity resolution spectrometer being not detectable by laser interferometer can be found in [5]. This led to artifacts, namely the incorrect Mössbauer spectra of bcc α-Fe were interpreted by the authors of [5] as a result of non-zero quadrupole interaction. However, there is another way to check and correct the nonlinearity of the velocity signal using special procedure described recently in [6]. In this case the discretization of the velocity reference signal as well as the velocity mode are not important and can modify the procedure only. Therefore, if there is no chance to adjust the velocity driving system and decrease the nonlinearity of velocity, this procedure can be used to correct the measured spectra.

The most traditional way is the use of the reference absorbers not only for calibration of the velocity scale but also for the control of the velocity driving system. For instance, in some cases the reference absorbers have already been used for the control of the velocity driving system in Mössbauer spectrometers (see, e.g., [7–10]). For this reason, reference absorbers were also used for comparing velocity driving systems in different spectrometers [11]. To continue this approach we used several thin reference absorbers such as α-Fe foils, sodium nitroprusside $Na_2[Fe(CN)_5NO]$ (SNP), potassium ferricyanide $K_3[Fe(CN)_6]$ (PFC(III)) and potassium ferrocyanide $K_4[Fe(CN)_6]\cdot 3H_2O$ (PFC(II)) to demonstrate how these absorbers can help in the control of the velocity driving system in the high velocity resolution spectrometer SM-2201 and in the revealing velocity errors to exclude wrong results and artifacts.

2 Experimental

Mainly an α-Fe foil of ~7 μm thickness was used for measurements in a large velocity range. Powdered samples of SNP, PFC(III) and PFC(II) were glued on iron-free aluminum foils (diameter of ~2 cm) with sample thicknesses in the range ~1 – ~16 mg Fe/cm^2 for SNP and ~ 5 mg Fe/cm^2 for both PFC(III) and PFC(II). These absorbers were used for measurements in a small velocity range. Additionally, a sample with a mixture of SNP, PFC(III) and PFC(II) powders (MIX) with weights ~63 mg (~14.4 mg Fe), ~42 mg (~7.2 mg Fe) and ~18 mg (~2.4 mg Fe), respectively, was prepared and glued on aluminum foil. The average sample thickness was ~8 mg Fe/cm^2 with the ratio of the iron fractions of ~6 SNP: ~3 PFC(III): ~1 PFC(II). It should be noted that the used glue was based on ethanol and, therefore, the mixture of glue with powdered sample was homogeneous. However, ethanol evaporation from the surface is random that is why the dried sample surface had a tiny relief and microbubbles (Fig. 1). Nevertheless, this did not lead to significant variations of the sample thickness. It was earlier shown that the line widths of the 295 K Mössbauer spectra of PFC(II) of ~5 mg Fe/cm^2 in the powdered form and glued were the same: 0.258 ± 0.002 mm/s and 0.257 ± 0.002 mm/s, respectively [12].

The room-temperature Mössbauer spectra of the reference absorbers were measured using an automated precision Mössbauer spectrometric system, built on the base of two SM-2201 spectrometers, with a saw-tooth shape velocity reference signal formed by the digital-analog converter using discretization of 2^{12} (quantification of the velocity reference signal using 4096 steps). Details and characteristics of these spectrometers as well as their advances were described in [11, 13–15]. The (1.8–1.0) × 10^9 Bq ^{57}Co in rhodium matrix sources (Ritverc GmbH, St. Petersburg) were used at room temperature. The Mössbauer

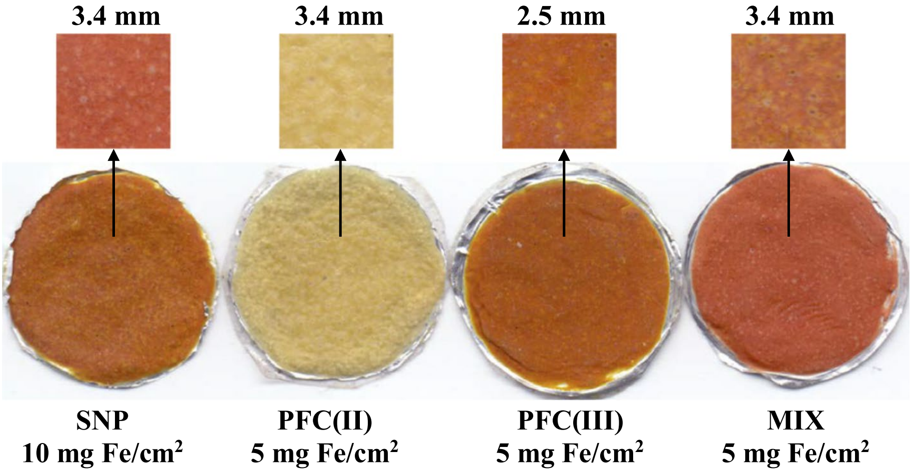

Fig. 1 Samples of reference absorbers with enlarged microphotographs of their surfaces

spectra were measured in transmission geometry with moving absorber at 295 K and recorded in 4096 channels.

Mössbauer spectra were computer fitted using the UNIVEM-MS program (Research Institute of Physics, Southern Federal University, Russian Federation) by the least squares procedure with a Lorentzian line shape. The spectral parameters such as isomer shift δ, quadrupole splitting ΔE_Q (taken to be equal to 2ε, where ε is the quadrupole shift for magnetically split spectra), magnetic hyperfine field H_{eff}, line width Γ, relative subspectrum (component) area A, and statistical quality of the fit χ^2, were determined. An instrumental (systematic) error for each spectrum point was taken to be ±0.5 channel (the velocity scale), the instrumental (systematic) error for the hyperfine parameters was taken to be ±1 channel in mm/s or kOe. If an error calculated with the fitting procedure (fitting error) for these parameters exceeded the instrumental (systematic) error, the larger error was used instead. Criteria of the best fit were the differential (residual) spectrum, the value of χ^2, and physical meaning of parameters. Values of δ are given relative to α-Fe at 295 K.

3 Results and Discussion

The effect of the effective thickness on the Mössbauer spectrum line shape and width is well known (see, e.g., [16–18]). Therefore, first we checked the line broadening and shape in a series of Mössbauer spectra of SNP samples with the thickness in the range ~1 – ~16 mg Fe/cm^2. The selected Mössbauer spectra of SNP and the line broadening vs. sample thickness are shown in Fig. 2. The results demonstrate that the deviation of the line shape from Lorentzian can be seen in the spectrum of SNP sample with ~16 mg Fe/cm^2 only while two different slopes of the line broadening with increase of the sample thickness can be observed: (i) from ~1 to ~10 mg Fe/cm^2 and (ii) from ~13 to ~16 mg Fe/cm^2. These facts indicate that we can use samples of the reference absorbers with a thickness up to ~10 mg Fe/cm^2 for the Mössbauer spectra measurements which line shapes should be Lorentzian and narrow for the well-adjusted velocity driving system.

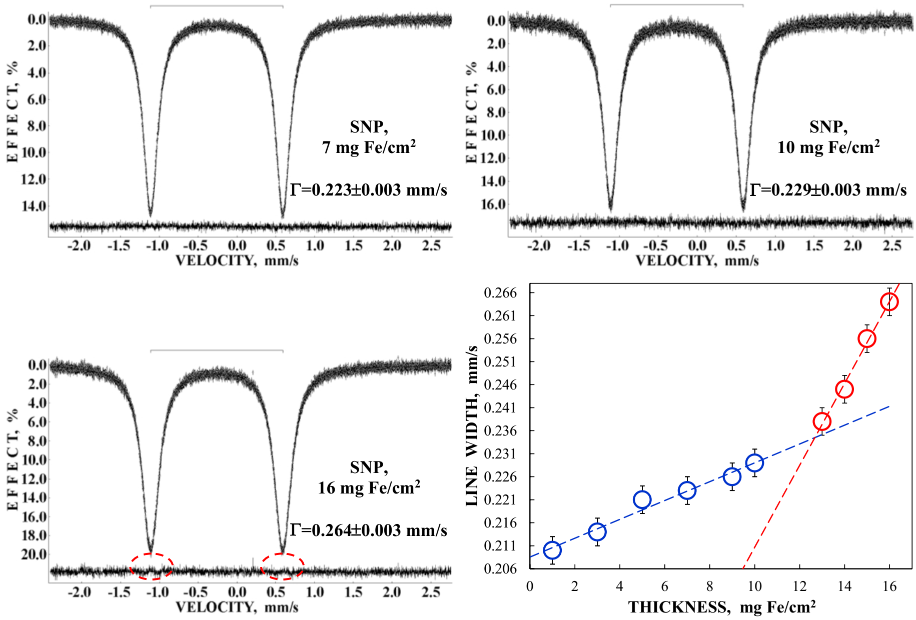

Fig. 2 Selected Mössbauer spectra of SNP samples with different thickness fitted with Lorentzian lines (the differential spectra are shown on the bottom; red dashed ellipsoid lines indicate misfits related to the deviation of spectrum line shape from Lorentzian) and experimental line broadening with thickness increase (blue and red dashed lines indicate two different slopes of the line broadening)

Therefore, deviation of the line shape of the Mössbauer spectrum of thin reference absorber from Lorentzian shape may indicate the necessity to adjust the velocity driving system. For example, the Mössbauer spectra of SNP (5 mg Fe/cm^2) measured with well-adjusted and out-of-tune velocity driving system are shown in Fig. 3.

The line shapes of the spectrum measured with out-of-tune velocity driving system clearly indicate misfits at the differential spectrum with line broadening as compared with the spectrum of the same SNP measured with the well-adjusted velocity driving system. The former spectrum can be better fitted with two rather than one quadrupole doublets, but this result is an artifact because SNP shows one quadrupole doublet in the Mössbauer spectrum.

Estimation of the integral and differential velocity nonlinearity is very important to analyze the quality of the velocity driving system and the measured Mössbauer spectra. Analysis of the differential nonlinearity (DNL) can also be done for velocity ranges using reference absorbers. The Mössbauer spectra of thin α-Fe foil measured with well-adjusted and out-of-tune velocity driving system are shown in Fig. 4. These spectra were fitted using one magnetic sextet and six singlets. The obtained distances between the same absorption peaks for two different fits ($A_{m,n}$ and $B_{m,n}$, respectively, see Fig. 4) can be used for the estimation of the differential velocity nonlinearity by the formula $DNL = |A_{m,n} - B_{m,n}|/A_{m,n}$. The results for two Mössbauer spectra are given in Table 1.

The significant differences in DNL values for corresponding velocity ranges are clearly seen for the well-adjusted and out-of-tune velocity driving system. Moreover, in the latter case, the fit of the Mössbauer spectrum of α-Fe foil using magnetic sextet demonstrates big misfits in the differential spectrum. This is an indication of the large differential nonlinearity of the out-of-tune velocity driving system. Ignoring this fact in [5] lead to an artifact

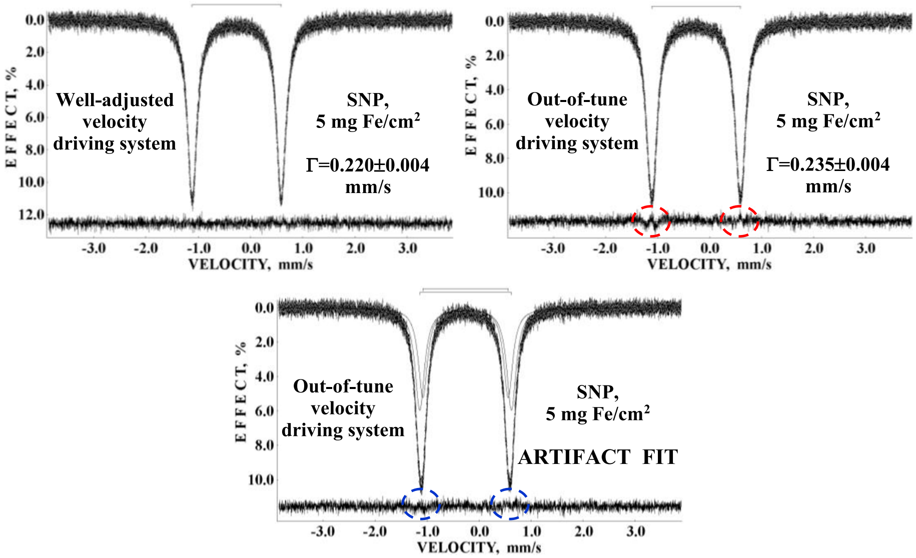

Fig. 3 Mössbauer spectra of SNP measured with well-adjusted and out-of-tune velocity driving system and their fits including artifact fit. The differential spectra are shown on the bottom. Red and blue ellipsoid dashed lines indicate different misfits

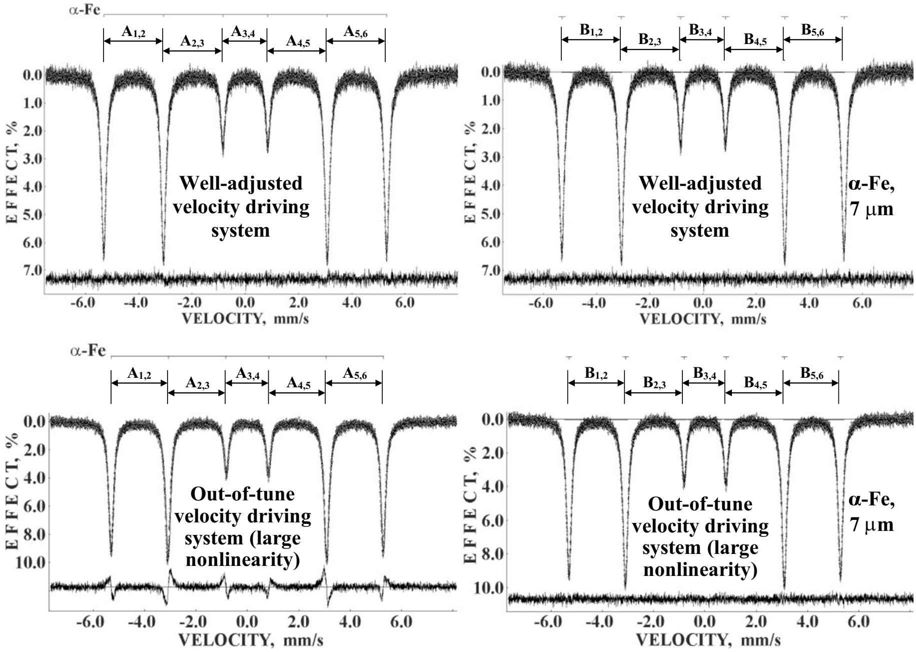

Fig. 4 Estimation of the differential nonlinearity of the well-adjusted and out-of-tune velocity driving system using reference absorber α-Fe foil with a thickness of 7 μm. The differential spectra are shown on the bottom. $A_{m,n}$ and $B_{m,n}$ are the distances between corresponding peaks fitted using one magnetic sextet (left panel) and six singlets (right panel)

Table 1 Differential nonlinearity in the velocity ranges between absorption peaks estimated using the α-Fe thin foil Mössbauer spectra

Velocity ranges *m–n* ($A_{m,n}$ or $B_{m,n}$)	1–2	2–3	3–4	4–5	5–6	Velocity driving system
DNL, a.u.	0.19	0.13	0.09	0.19	0.20	Well-adjusted
DNL, a.u.	1.62	2.53	3.44	2.08	1.55	Out-of-tune

obtaining while laser interferometer was unable to detect this large differential nonlinearity. In addition to differential nonlinearity, the other problems with the out-of-tune velocity driving system can be found if the spectrum fit using six singlets with Lorentzian line shape also shows misfits in the differential spectrum.

Similarly, it is possible to estimate the differential nonlinearity of the velocity driving system in the small velocity range using α-Fe (two internal peaks) or SNP plus PFC(III) reference absorbers. The Mössbauer spectrum of α-Fe + PFC(III) measured in the small velocity range with the well-adjusted velocity driving system and fitted using (i) two doublets and (ii) four singlets is shown in Fig. 5. The results for the velocity ranges 1–2 and 3–4 are the following: $DNL_{1-2} = 0.22$ and $DNL_{3-4} = 0.14$. Again, deviations of the absorption line shape from Lorentzian will indicate the necessity to adjust the velocity driving system.

The reference absorber PFC(III) can also be used for testing the zero-velocity region. Sometimes the Mössbauer spectrum of SNP can be well fitted with Lorentzian line and without misfits in the differential spectrum while some deviations in the velocity signal near the zero-velocity point can be detected in the spectrum of PFC(III) by misfits in the differential spectrum and different values of Γ for two peaks in the quadrupole doublet as shown in Fig. 6. This deviation was due to a weak spring fastening while after fixing the fastening, the Mössbauer spectrum of PFC(III) demonstrated quadrupole doublet with Lorentzian line shape and equal Γ vales without misfits (Fig. 6).

In some cases, the thin reference absorbers can be used for checking correctness of rough evaluation of the iron content in different compounds in the mixture using Mössbauer spectroscopy (presuming the equal *f*-factors). For this reason, a mixed sample of SNP + PFC(III) + PFC(II) with known iron fractions in each compound was prepared. The

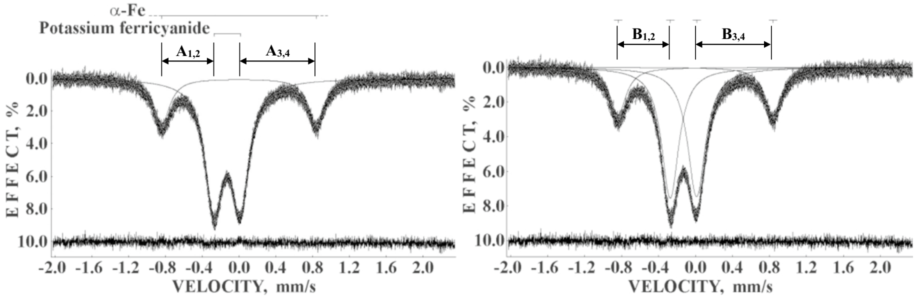

Fig. 5 Estimation of the differential nonlinearity of the well-adjusted velocity driving system in the small velocity range using two fits of the Mössbauer spectrum of α-Fe + PFC(III) reference absorbers. The differential spectra are shown on the bottom

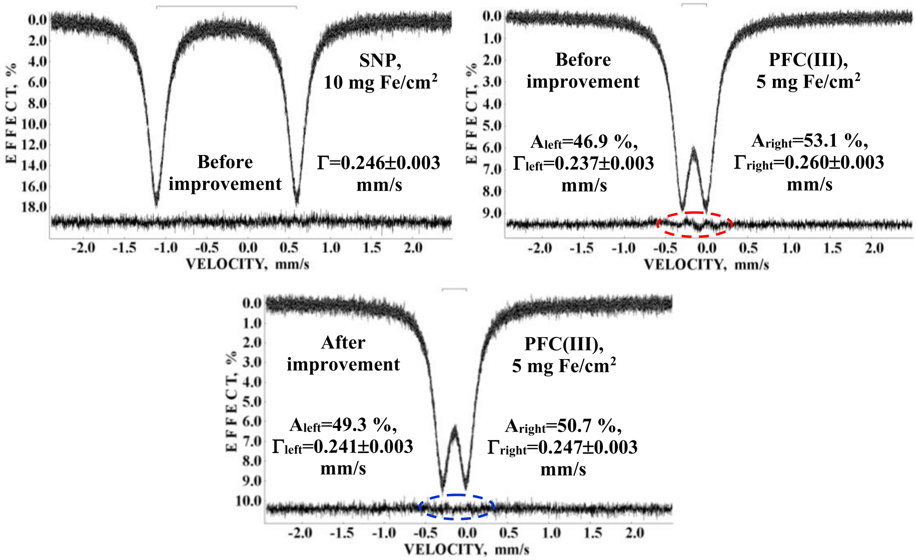

Fig. 6 Testing of the zero-velocity point range using potassium ferricyanide. The Mössbauer spectra of reference absorbers SNP and PFC(III) measured before and after spring fixing. The differential spectra are shown on the bottom. The red and blue dashed ellipsoid lines indicate misfits before spring fixing and their absence after spring fixing

Mössbauer spectrum of this mixed sample is shown in Fig. 7. This spectrum was measured with a statistics of 2.5×10^5 counts per channels and signal-to-noise ratio of 56 and fitted well using two quadrupole doublets belonging to SNP, PFC(III) and one singlet assigned to PFC(II) (parameters are shown in Table 2), with $\chi^2 = 0.983$ and the linear differential spectrum.

The obtained ratio of the relative areas for SNP, PFC(III) and PFC(II) is A_{SNP}: $A_{PFC(III)}$: $A_{PFC(II)} = 6$: 2.7: 1.3. This ratio is similar (within the error) to the ratio of iron fractions in this sample: SNP: PFC(III): PFC(II) = ~6: ~3: ~1.

Fig. 7 Mössbauer spectrum of the MIX sample with mixed reference absorbers SNP, PFC(III) and PFC(II). The differential spectrum is shown on the bottom

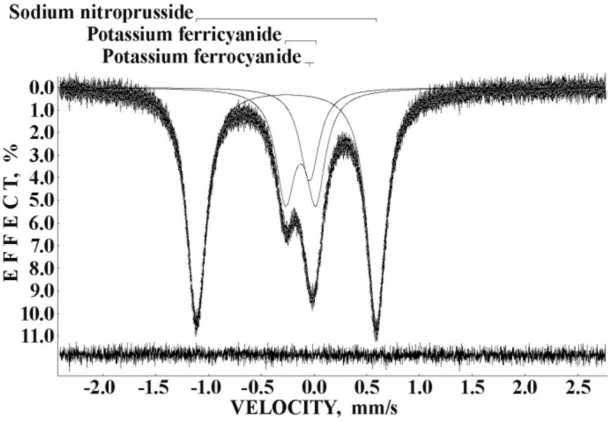

Table 2 Mössbauer parameters for the mixed sample of reference absorbers

Compound	Γ, mm/s	δ, mm/s	ΔE_Q, mm/s	A, % (relative error ≤ 10%)
SNP	0.218 ± 0.003	−0.260 ± 0.001	1.7034 ± 0.001	60.1
PFC(III)	0.218 ± 0.003	−0.126 ± 0.001	0.289 ± 0.002	27.3
PFC(II)	0.226 ± 0.008	−0.044 ± 0.002	–	12.6

4 Conclusion

The high-quality and -sensitivity Mössbauer spectrometers need to be well-adjusted to measure high-quality and high-precision spectra. Therefore, for the testing and control of the velocity driving system, it is useful to measure Mössbauer spectra of thin reference absorbers such as α-Fe foil, SNP, PFC(III) and PFC(II). These spectra will signal about any out-of-tune velocity driving system by deviation of the absorption line shape from Lorentzian as well as about increase of the differential nonlinearity for the velocity ranges and velocity error in the nearest region of the zero-velocity point. This control is much better than the use of laser interferometer and can help to exclude the measuring incorrect Mössbauer spectra and obtaining artifact results.

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