Analysis results of the spectra received via e-mail from [redacted] on the 11th of November, 2019

The analysis and the report below was prepared by

[redacted]

e-mail: [redacted]

Two ^{57}Fe Mössbauer spectra were obtained in the body of the e-mail (the corresponding data are listed at the end of this report). One is the spectrum of α-Fe measured in order to facilitate the calibration of the velocity axis of the second spectrum, which latter is referred to here as "Fe/TRGO" nanocomposite sample on the basis of the corresponding samples previously investigated as part of the work

[1] Tuček, J. et al. Air-stable superparamagnetic metal nanoparticles entrapped in graphene oxide matrix. *Nat. Commun.* **7**:12879 (doi: 10.1038/ncomms12879) (2016).

The as-received original data were transformed to a column of data in order to make them suitable for loading in the spectral analysis program. The analysis was performed by the latest released version (4.0i) of the MossWinn program.

Both spectra were unfolded, and consisted spectral data in 1024 channels. These original data are shown in Figure 1. The optimal folding point as determined on the basis of the spectrum of α-Fe was found to be at the 510.5 channel. Folding of both spectra were performed accordingly and identically, by complementing the obtained (510) folded data with 2 zeroed (and subsequently ignored) channels at the beginning of each of the datasets. The folded data thus obtained are shown in Figure 2. The uncertainty (±1 × standard deviation) of count values are emphasized by vertical bars on Figure 3 for the unfolded as well as for the folded version of the spectrum of Fe/TRGO.

Both the unfolded and the folded spectra were calibrated and fitted separately. Analysis of the spectrum of α-Fe was performed by assuming triangular velocity waveform and that the first (and last) channels in the unfolded spectrum data belong to negative source velocities (source moving away from the absorber), which appeared to be supported by the data. During the calibration fitting of the unfolded and folded α-Fe spectra the use of ^{57}Co(Rh) source was assumed, which is also mentioned on page 10 of ref. [1]. The fit of the unfolded spectrum preferred 0.1 mm/s as the isomer shift of the applied source wrt. that of α-Fe, so this value was assumed during calibration of the velocity axis (instead of 0.114 mm/s that is the default value in the program). The calibrated unfolded and calibrated folded spectra are shown in Figure 4 and Figure 5, respectively.

In line with the analysis of the corresponding spectra as given in ref. [1] as well as in the associated supplementary material, the spectrum of Fe/TRGO was fitted with a singlet and a doublet component in the thin-absorber approximation limit. The fitted curves are shown in Figure 6, while the corresponding analysis results are listed in Table 1, together with the associated results taken from Supplementary Table 2 of ref. [1].

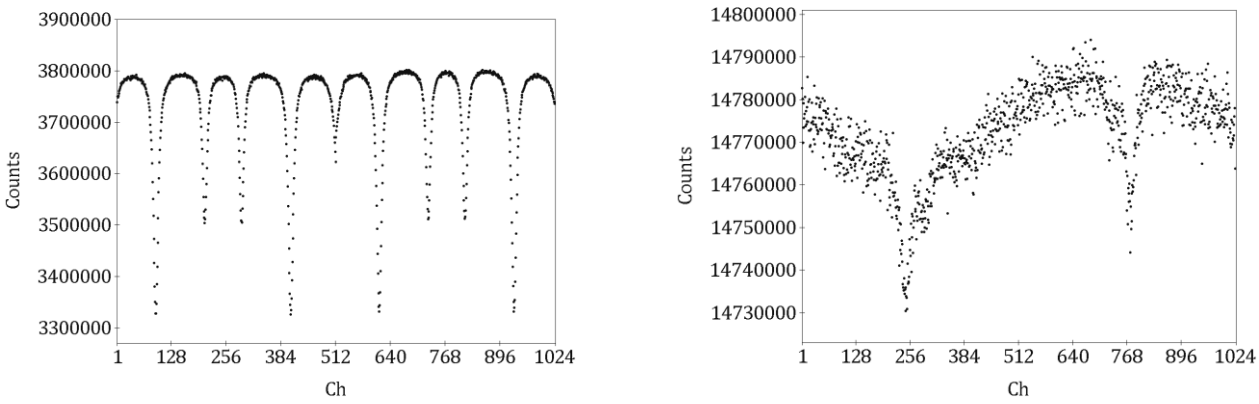

Figure 1. Figures of the as-received spectra: the spectrum of α-Fe (left) and that of Fe/TRGO (right).

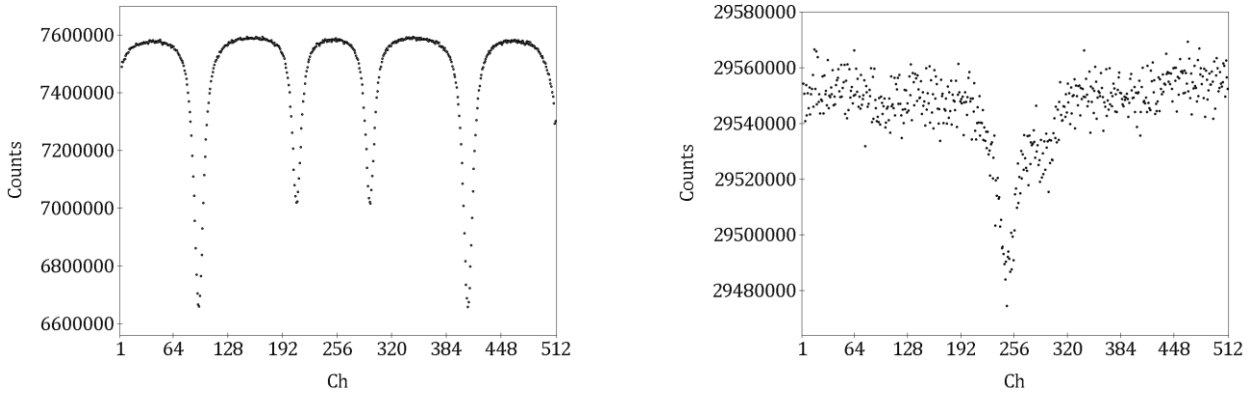

Figure 2. Figures of the folded spectra: the spectrum of α-Fe (left) and that of Fe/TRGO (right).

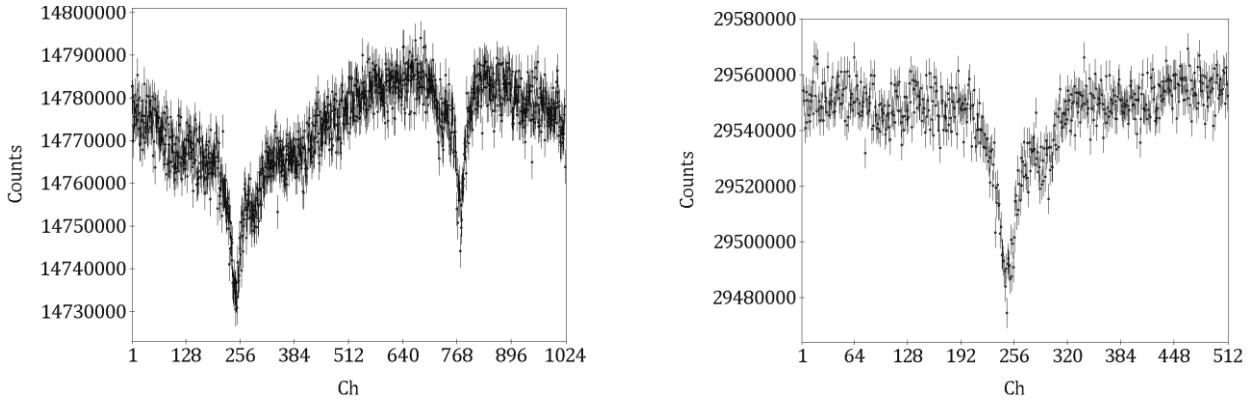

Figure 3. Unfolded (left) and folded (right) spectrum of Fe/TRGO with vertical bars indicating the standard deviation (±σ) of the count values in accordance with the Poisson distribution of counts.

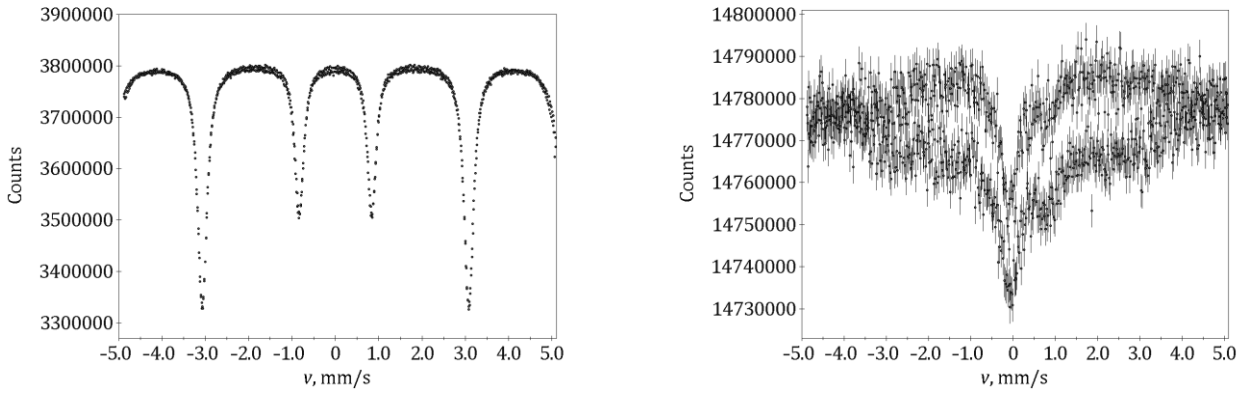

Figure 4. The *unfolded* spectra after calibration of their velocity axis: spectrum of α-Fe (left) and that of Fe/TRGO (right). Note that the two corresponding parts of the unfolded spectra (Figure 1) are now overlaid on the top of each other.

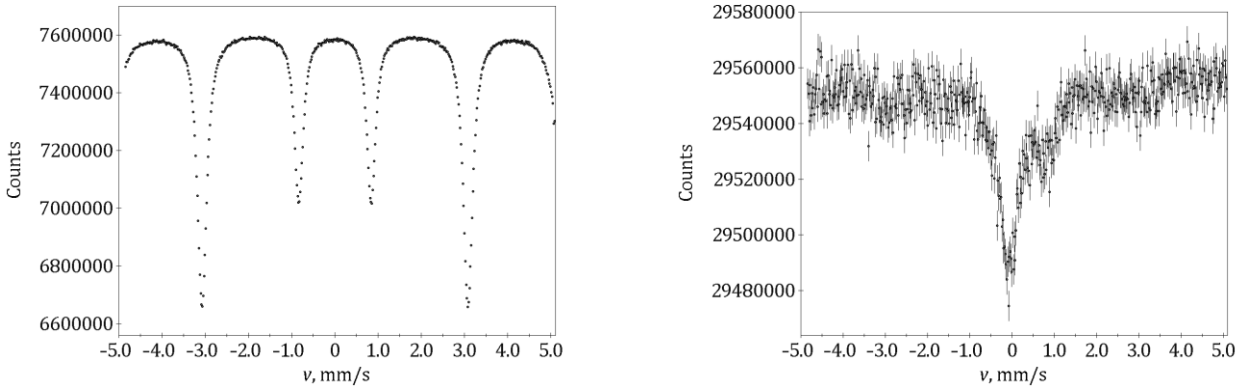

Figure 5. The *folded* spectra after calibration of their velocity axis: spectrum of α-Fe (left) and that of Fe/TRGO (right).

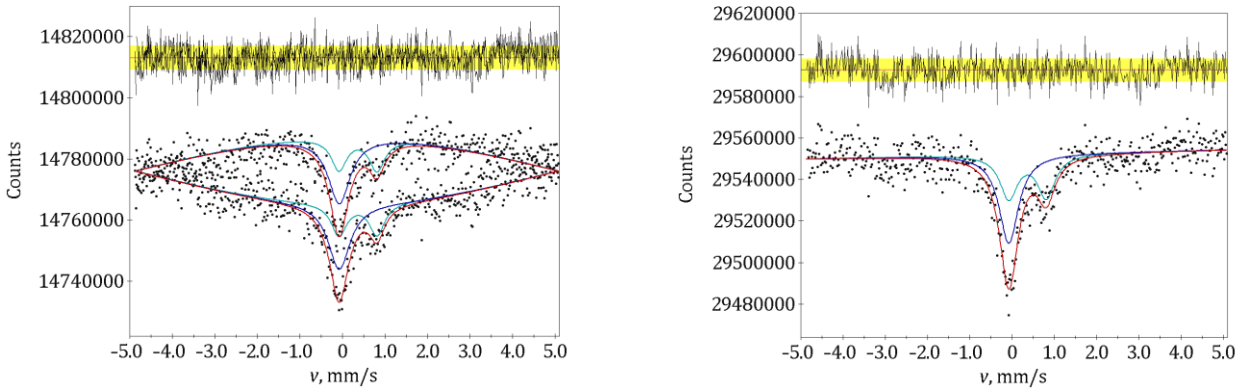

Figure 6. The unfolded (left) and folded (right) ^{57}Fe Mössbauer spectrum of Fe/TRGO, fitted to a singlet and a doublet component. Above the spectra the fit residual is displayed, with the yellow stripe having a height of ~ 2σ.

Table 1. Relevant fit parameter values as obtained from the fit of the folded and the unfolded version of the received spectrum of Fe/TRGO, in comparison with corresponding fit parameter data of Fe(10)/TRGO (one month in air) taken from Supplementary Table 2 of ref. [1]. RA stands for relative spectral area fraction, δ denotes the isomer shift wrt. α-Fe, ΔE_Q is the quadrupole splitting, and W is the Lorentzian (FWHM) line width. Numbers in parentheses denote standard error (1×σ) in the last digit(s) of the corresponding fit parameter values in the case of Fe/TRGO, whereas they refer to the error limits given in Supplementary Table 2 of ref. [1] in the case of Fe(10)/TRGO. In the case of Fe/TRGO the standard errors were estimated by the calculation of the second derivatives of the χ^2 (chi-square) quantity.

Parameters	**Fe/TRGO (folded)**	**Fe/TRGO (unfolded)**	**Fe(10)/TRGO (one month in air, from Supplementary Table 2 of ref. [1])**
Singlet, RA	53.4(7.4)%	59.9(6.1)%	77(1)%
δ, mm s^{-1}	-0.077(36)	-0.074(27)	0.00(1)
W, mm s^{-1}	0.56(9)	0.62(7)	
Doublet, RA	46.6(7.4)%	40.1(6.1)%	23(1)%
δ, mm s^{-1}	0.37(3)	0.37(2)	0.34(1)
ΔE_Q, mm s^{-1}	0.89(7)	0.89(5)	0.72(1)
W, mm s^{-1}	0.51(10)	0.44(7)	

The fit of the spectra to only two components yields acceptable fit results with the normalized chi-square of the fit being ~ 1.17 and ~ 1.31 in the case of the unfolded and the folded spectrum respectively. The fit results obtained for the folded and the unfolded spectra, as given in Table 1, are consistent with each other if the standard error of the fit parameter values are also taken into account. The parameters obtained for the doublet component are quite typical for Fe^{3+} oxide-hydroxide and hydroxide phases (see, e.g., [2]), but similar values may also be obtained for Fe^{3+} coordination compounds where iron bonds to oxygen of the surrounding ligands (see, e.g., [3]). Compared to the previous results on the Fe(10)/TRGO sample (Table 1), the relative area fraction of the doublet is considerably larger (though the uncertainty of the RA values is substantial) whereas its quadrupole splitting is somewhat larger in the newly measured spectrum. This suggests that the oxidation of iron in the sample has progressed somewhat since 2016. Assuming that the singlet component in the spectrum can still be associated with superparamagnetic α-Fe nanoparticles in accordance with its original interpretation [1], the progression rate of oxidation in the measured sample is rather low, given that the relative spectral area of the singlet is still somewhat above 50% (Table 1) despite the 3 (or more) years passed since the measurement published in ref. [1] was performed. The isomer shift of the singlet component in the spectrum of the recent measurement is somewhat lower than 0 mm/s expected for α-Fe, but the deviation of δ from zero is not more than 2-3× the standard error of the isomer shift, so the deviation may also be due to the statistical uncertainty of fit parameters. The line width of the singlet component is rather large (being ca. 0.6 mm/s), which agrees with the corresponding numerical results included in the document submitted by the author (https://www.prf.upol.cz/fileadmin/userdata/PrF/Aktuality/2019/Priloha_7-nove_grafy.pdf). In order to show that the singlet component still represents superparamagnetic α-Fe nanoparticles, an ^{57}Fe Mössbauer spectroscopy measurement could be performed on the sample at low (5…50 K) temperatures, similarly to what the authors did in the original publication (see Figure 2 in ref. [1]). If the conversion of the singlet component to the typical α-Fe sextet component can be observed in the low-temperature measurement (similarly to Figure 2b and 2c in ref. [1]), then the sample is still intact and the singlet component observed at room temperature still belongs to superparamagnetic α-Fe nanoparticles.

Concerning the present measurement several questions were raised, which are answered below on the basis of the above described results of the fit.

Whether the new measurement supports or contradicts the original findings presented in the paper.

By considering also the statistical uncertainties of the fit parameters, the present measurement does not contradict to the original findings as presented in ref. [1]. The main difference between the present measurement and corresponding results presented in ref. [1], is the increased relative area fraction of the doublet component in the present measurement with respect to the results given in Supplementary Table 2 of ref. [1]. This can indicate that further oxidation of iron in the sample has taken place since the paper was published. This corresponds to the expectations, and does not invalidate the statement about "Air-stable superparamagnetic metal nanoparticles" as given in the title of the publication. Assuming that the sample was kept under air during the past years, and that the singlet component observed in the recent measurement can still be associated with superparamagnetic α-Fe nanoparticles, the sample has displayed quite a high stability against oxidation in my opinion. Namely, stability of iron nanoparticles in the present sample can be contrasted for example with the pyrophoric property of metallic iron nanoparticles (see, e.g., [4]).

Whether the sample contains superparamagnetic iron singlet as stated in paper.

This cannot be decided on the basis of the present measurement alone. The singlet may belong to superparamagnetic iron nanoparticles, but in order to prove this, a low-temperature ^{57}Fe Mossbauer spectroscopy measurement needs to be performed (e.g., at 5 K). If conversion of the singlet spectral area to that of a typical α-Fe sextet can be observed at lower temperatures (as in Figure 2 of ref. [1]), then the answer is yes.

Whether it was possible that the original ratio iron: oxide was roughly 80:20 as stated in the paper.

Yes. (Assuming that the ratio is meant concerning the spectral areas of the corresponding components, or the number of iron atoms in the metal and in the oxide phases.) The higher amount of oxidized iron reflected by the new measurement can be the consequence of the ongoing oxidation of the sample that has slowly progressed in the past 3 years.

Whether there is a measurable amount of alpha-iron sextet in the data or not.

The analysis of the spectrum does not require the assumption of such a sextet component. By subtracting the fitted singlet and doublet component from the folded spectrum, a residual shown in Figure 7 is observed. A hypothetical sextet component of non-superparamagnetic α-Fe is superimposed with red solid line on the residual. In the residual we can observe small dips at velocities where the 2nd (ca. -3 mm/s) and 5th (ca. 3 mm/s) peaks of an α-Fe sextet should appear. This may indicate that a small-amplitude sextet contributes to the spectrum, but the appearance of the dips may also be accidental due to statistical noise. In order to answer this question, a measurement with a higher S/N ratio would be needed. Measuring the spectrum in a wider velocity range could help as well, given that the 1-6 peaks of the sextet (which would appear outside of the velocity range of the present spectrum) should have the highest amplitude.

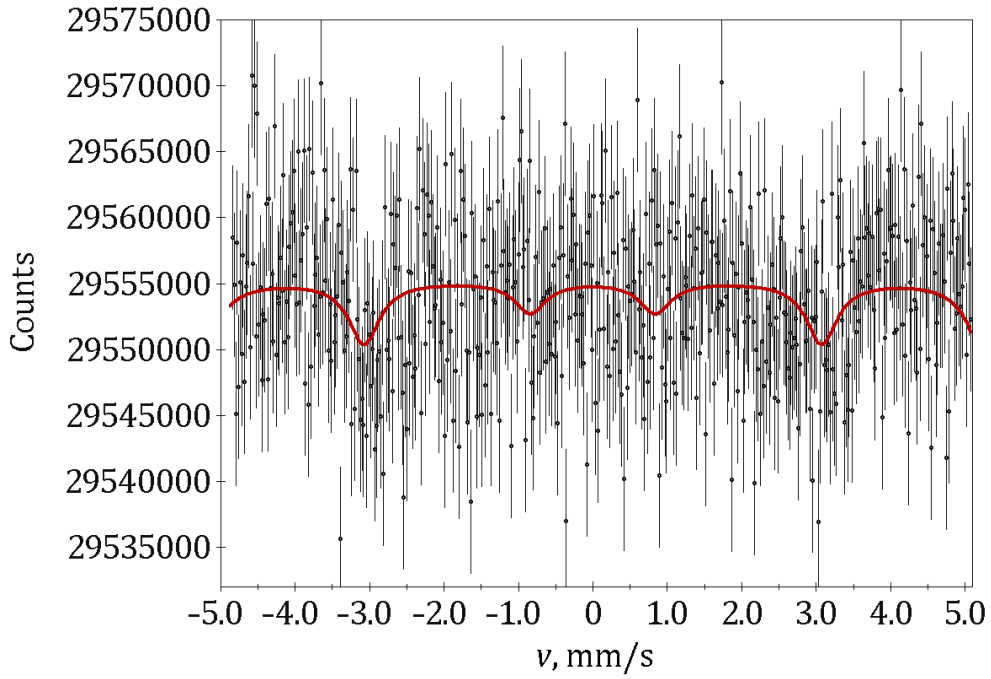

Figure 7. Spectrum residual after subtracting the fitted singlet and doublet components from the folded spectrum. Red solid line indicates the position of absorption peaks of a hypothetical sextet component belonging to non-superparamagnetic α-Fe (isomer shift = 0 mm/s, hyperfine magnetic field = 33T).

Whether the value of y-axis is important for the findings of the study (reported transmittance is 0.7% in Figure 2a and only 0.2% in the provided data and newly measured data - data without y-scale from correction fits both).

The findings of ref. [1] were supported by the obtained Mössbauer fit parameters, among others by the *relative area fractions* of the different spectral components, as given in Supplementary Tables 1 and 2, whereas the transmission data reflected by the y-axes of Mossbauer measurements were not directly needed to support the conclusions. In this sense, the transmission values measured on the y-axis were not important in the findings of the study. As explained below, the *A*(%) amplitude of an absorption peak, as measured in percentage of the baseline transmission value along the y-axis, depends on various experimental conditions applied during the measurement. If these conditions were different during two measurements (as it is often the case) deriving relevant conclusions on the basis of the direct comparison of the *A*(%) values in the two spectra may be unfeasible. It is therefore quite common in Mossbauer work that the corresponding information is directly not utilized to derive conclusions, which latter can usually be well supported by considering only the *relative area fractions* (along with other Mössbauer parameters) of spectral components, similarly to the case of ref. [1].

Whether the change in transmittance could have been done by data manipulation in order to obtain easier acceptance in the journal, or whether you would expect it to be just overlooked mistake that does not change the validity of the findings.

The *A*(%) relative amplitude of an absorption peak, measured in % when the y-axis displays transmission in comparison with the fitted baseline value (the latter being taken as 100%), depends not only on the nature of the

measured material, but also on various experimental conditions such as spectrometer settings, measurement geometry and sample geometry (e.g. absorber thickness), for example. The amplitude values in question are useful mainly in cases when the geometrical factors and spectrometer settings can be kept constant for several subsequent measurements, such that changes in the *A*(%) amplitude values can be interpreted in the context of some physical theories relevant from the point of view of the investigated material. In the case of Figure 2 of ref. [1], for example, one may assume that measurements were done by using the same spectrometer settings as well as the same sample- and measurement geometry, with only the temperature of the sample being changed between subsequent measurements. In such a situation the y-axis scale can be relevant because it enables one to do a meaningful comparison of the different spectra. This can explain why the authors have included the y-axis scale in the case of Figure 2 of ref. [1]. The case of Supplementary Figure 6 of ref. [1] is different, however: here different samples were measured and a longer time may have been passed between the measurement of the fresh sample and that of the aged samples. The measurement conditions, spectrometer settings may have been different in the case of the subsequent measurements, and the samples prepared for the Mossbauer experiment may have also differed somewhat regarding their sample mass and geometrical details, so that a meaningful direct comparison of the A(%) amplitude values of the different spectra could turn out to be unfeasible. (Note that differences among the spectra regarding the *relative area fractions of the individual spectral components* can still be meaningfully interpreted though, even in this case.) In such a situation one may conclude that the y-axis scale is not informative from the point of view of the relevant differences among the spectra, and consequently the y-axis scale of the figures may be omitted deliberately. This may explain the omission of the y-axis scale on the (revised) Supplementary Figure 6 of ref. [1].

References

[1] Jiří Tuček, Zdeněk Sofer, Daniel Bouša, Martin Pumera, Kateřina Holá, Aneta Malá, Kateřina Poláková, Markéta Havrdová, Klára Čépe, Ondřej Tomanec, Radek Zbořil: Air-stable superparamagnetic metal nanoparticles entrapped in graphene oxide matrix. *Nat. Commun.* **7**:12879 (doi: 10.1038/ncomms12879) (2016).

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[4] A. Krietsch, M. Scheid, M. Schmidt, U. Krause: Explosion behaviour of metallic nano powders, *Journal of Loss Prevention in the Process Industries* **36** (2015) 237. (doi: 10.1016/j.jlp.2015.03.016)

[5] https://www.prf.upol.cz/fileadmin/userdata/PrF/Aktuality/2019/Priloha_7-nove_grafy.pdf

The spectral data as received in the body of the e-mail:

New measurement of sample:
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Chorzów, 08-01-2020

Final report for Palacky University Olomouc, Czech Republic

Main goal:

The room-temperature Mössbauer measurements of the original sample in order to test the presence of superparamagnetic iron nanoparticles entrapped in the graphene oxide matrix.

Measurement:

Transmission ^{57}Fe Mössbauer spectrum was recorded using an MS96 Mössbauer spectrometer operating in a constant acceleration mode and equipped with a ^{57}Co:Rh source with activity of ~50mCi. The spectrometer was calibrated at room temperature with 30 μm thick α-Fe foil. The time of the measurement was equal to about 1001 hours, which is more than 41 days. However, the effect was smaller than 0.1% and even after such a long time of the measurement the quality of the spectrum was not very good. The numerical analysis of the Mössbauer spectrum was performed with the use of the MossWinn program.

Results

The Mössbauer spectrum and the fitted components for the investigated sample are presented in Figure 1 and obtained hyperfine parameters for each component are listed in Table 1. The spectrum was fitted as a superposition of three components, which were singlet, doublet and sextet. These three components indicate presence of three iron-containing fractions. The relative area of the singlet is about 16%. The value of isomer shift obtained for this component is close to zero (Table 1) , which indicates presence of the ultrafine α-Fe nanoparticles in the investigated sample, which are in a superparamagnetic state at room temperature. The hyperfine parameters of the doublet are connected with presence of ferric ions in the sample with contribution of ~21%. The third component visible on the Mössbauer spectrum is a sextet with hyperfine magnetic field of 32.6T and contribution of about 63%. This sextet can also correspond to α-Fe but presence of this magnetically ordered phase will be a result of the magnetic blocking of some α-Fe nanoparticles.

To sum up, my measurement supports the original finding in Tucek et al, Nature Communication (2016) 7, 12879 (DOI: 10.1038/ncomms12879) and the related correction (DOI: 10.1038/s41467-019-10702-2). I take into account that the sample is about six years old and stored in a lab with air access, which can significantly influence contributions of iron-containing fractions.

Table 1. The Mössbauer hyperfine parameters of the investigated sample. Is – isomer shift, Qs – quadrupole splitting, H – hyperfine magnetic field, A – real area fraction of subspectra, FWHM – full line width at half maximum.

Component	Is (mm/s)	Qs (mm/s)	H (T)	A (%)	FWHM (mm/s)
Singlet	-0.018 ± 0.019	-	-	15.98	0.55
Doublet	0.276 ± 0.026	0.876 ± 0.039	-	21.18	
Sextet	0.113 ± 0.008	-	32.60 ± 0.09	62.84	

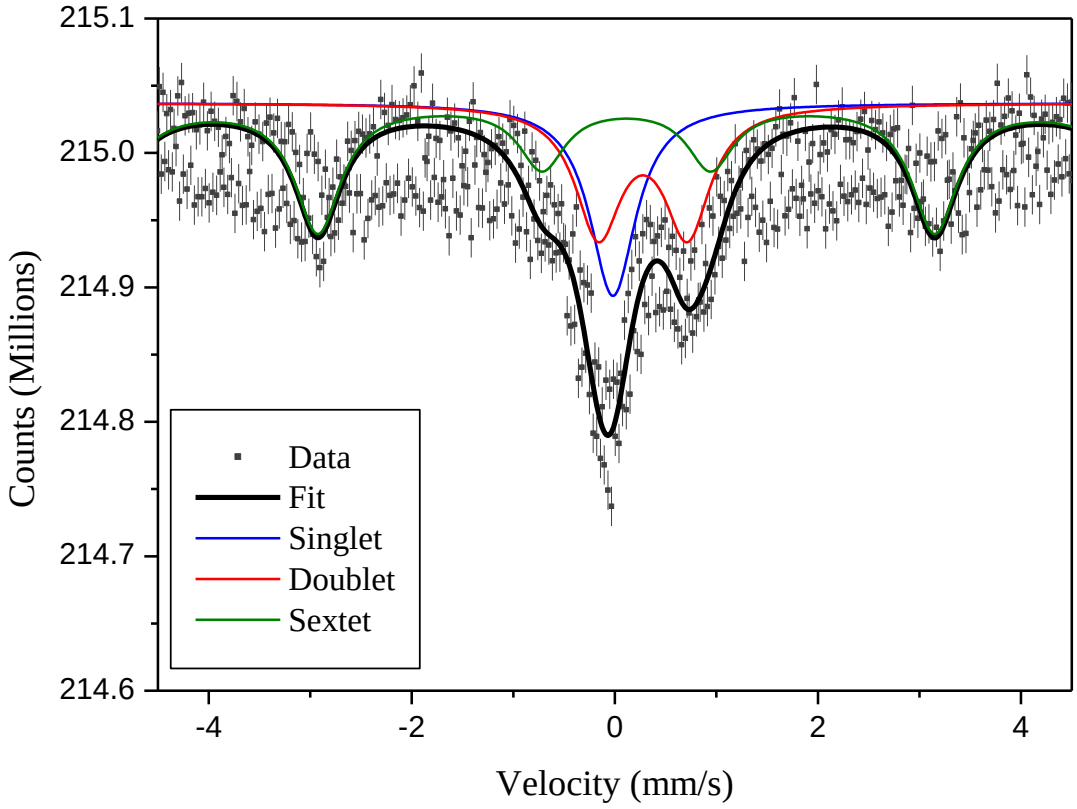

Figure 1. The room-temperature Mössbauer spectrum of the investigated sample. The fitted subspectra are presented on the spectrum.

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