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Uncertainty budget for determinations of mean isomer shift from Mössbauer spectra

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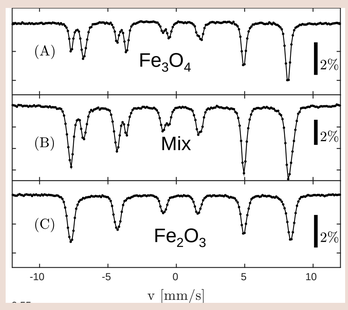
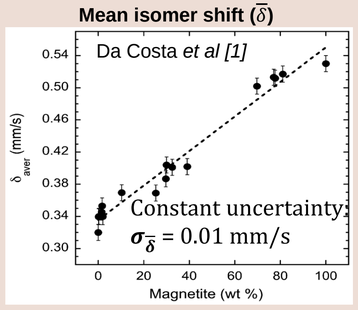
Introduction and Motivation

Mössbauer spectroscopy is one of the few methods which is able to distinguish between magnetite (Fe_3O_4) and maghemite (Fe_2O_3), eg.

1. The presence or absence of characteristic lines
2. Area ratio of spectral components
3. **Mean isomer shift ($\overline{\delta} = \sum_n^N A_n \delta_n / A$)**

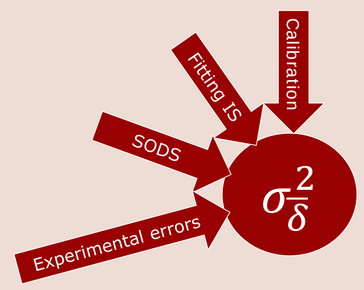




The uncertainty of the mean isomer shift ($\sigma_{\overline{\delta}}$) can be divided up into four uncorrelated contributions:

1) **The calibration (σ_{cal}),**
2) **Correction of Second order Doppler shift ($\sigma_{\Delta\delta}$)**
3) **The fitting of the spectrum (σ_{fit}),**
4) **Experimental errors (σ_{err}).**

$$\sigma_{\overline{\delta}}^2 = \sigma_{\mathrm{cal}}^2 + \sigma_{\mathrm{fit}}^2 + \sigma_{\Delta\delta}^2 + \sigma_{\mathrm{err}}^2$$



1. Calibration, σ_{cal}

Channel-velocity calibration is performed by fitting

$$c_n = \frac{E_n}{k} + c_0 \quad \text{for } 1 \le n \le 6$$

$$c_n = \frac{-E_{13-n}}{k} + c_0 + \frac{c_f}{2} \quad \text{for } 7 \le n \le 12$$

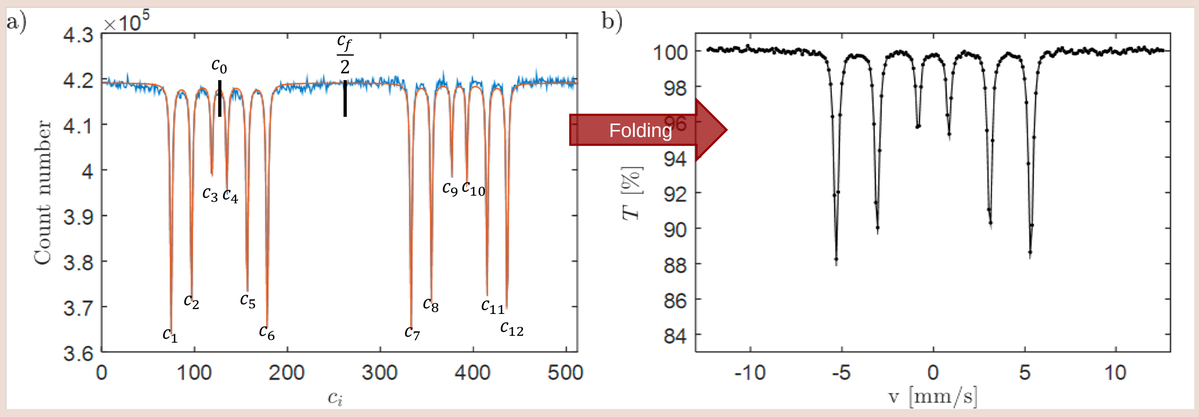
to all twelve peaks in the unfolded α-Fe foil reference spectrum (fig 1a) using the energy of nth line in the reference spectrum (E_n).

From the linear regression the covariance matrix is obtained:

$$\boldsymbol{\Sigma}_{\boldsymbol{c_0,k}} = \begin{bmatrix} \sigma_{c_0}^2 & \sigma_{c_0,k} \\ \sigma_{c_0,k} & \sigma_k^2 \end{bmatrix}$$

Uncertainty in the isomer shift is:

$$\boldsymbol{\sigma_{cal}} = \sqrt{\frac{\overline{\boldsymbol{\delta}}^2}{\boldsymbol{k}^2} \cdot \boldsymbol{\sigma_k^2} + \boldsymbol{k}^2 \cdot \boldsymbol{\sigma_{c_0}^2} - 2\, \boldsymbol{k\overline{\delta}}\, \boldsymbol{\sigma_{k,c_0}}}$$



Results

- $\boldsymbol{\Sigma}_{\boldsymbol{c_0,k}} = \begin{bmatrix} 1.3 \cdot 10^{-3} & 2.7 \cdot 10^{-23} \\ 2.7 \cdot 10^{-23} & 2.8 \cdot 10^{-10} \end{bmatrix}$
- Uncertainty for $\overline{\delta} = 0$ is $\sigma_{\mathrm{cal}} = 0.0017$ mm/s.

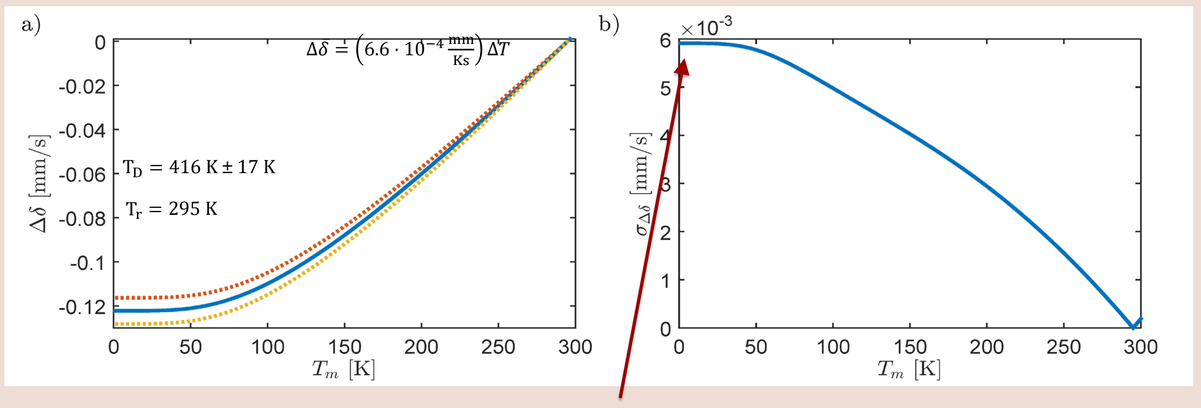
2. Correction for SODS

When the sample is measured at temperature (T_{m}) different from the temperature of reference compounds (T_{r}), the second order Doppler shift (SODS) describe the correction needed ($\Delta\delta$):

$$\Delta\delta = \frac{-9k_B}{2mc}\left[T_{\mathrm{r}}\left(\frac{T_{\mathrm{r}}}{T_{\mathrm{D}}}\right)^3 \int_0^{T_{\mathrm{D}}/T_{\mathrm{r}}} \frac{x^3}{e^x - 1}\,\mathrm{d}x - T_{\mathrm{m}}\left(\frac{T_{\mathrm{m}}}{T_{\mathrm{D}}}\right)^3 \int_0^{T_{\mathrm{D}}/T_{\mathrm{m}}} \frac{x^3}{e^x - 1}\,\mathrm{d}x\right]$$

The uncertainty is calculated using propagation of uncertainty:

$$\sigma_{\Delta\delta} = \left|\frac{\partial\Delta\delta}{\partial T_{\mathrm{D}}}\right| \sigma_{T_{\mathrm{D}}} = \left|3\frac{\Delta\delta}{T_{\mathrm{D}}} + \frac{9k_B}{2mc}\left(\frac{1}{e^{T_{\mathrm{D}}/T_{\mathrm{r}}} - 1} - \frac{1}{e^{T_{\mathrm{D}}/T_{\mathrm{m}}} - 1}\right)\right| \sigma_{T_D}$$



- The SODS correction adds an uncertainty of up to 0.006 mm/s to the total uncertainty of $\overline{\delta}$.
- At high temperatures the mean isomer correction is approximately linear.
  - Uncertainty in the temperature (σ_{T}).

Uncertainty Propagation → $\sigma_{\Delta\overline{\delta}} = \left(6.6 \cdot 10^{-4}\,\frac{\mathrm{mm}}{\mathrm{Ks}}\right) \sigma_{\mathrm{T}}$

  - Seasonal or day/night temperature changes can induce uncertainties in $\overline{\delta}$

3. Fitting of spectrum, σ_{fit}

1. Spectrum S_i fitted to model $f(v_i, \boldsymbol{p})$ by minimizing:

$$\chi^2 = \sum_i (f_i(\boldsymbol{p}))^2 \text{ where } f_i(\boldsymbol{p}) = \frac{S_i - f(v_i, \boldsymbol{p})}{\sigma_{S_i}}$$

Fitted parameters ($\boldsymbol{p}$) consist of the areas ($\boldsymbol{A}_n$) and isomer shifts (δ_n) of the N spectral components.

2. The covariance matrix of fitting parameters :

$$\boldsymbol{\Sigma}_{\mathbf{p}} = \left(\boldsymbol{J}(\boldsymbol{p}^*)^T \boldsymbol{J}(\boldsymbol{p}^*)\right)^{-1}, \qquad \boldsymbol{J}(\boldsymbol{p}) = \begin{bmatrix} \frac{\partial f_1(\boldsymbol{p})}{\partial A_1} & \cdots & \frac{\partial f_1(\boldsymbol{p})}{\partial \delta_N} \\ \vdots & \ddots & \vdots \\ \frac{\partial f_n(\boldsymbol{p})}{\partial A_1} & \cdots & \frac{\partial f_n(\boldsymbol{p})}{\partial \delta_N} \end{bmatrix}$$

3. Uncertainty of mean isomer shift is calculated by propagation of uncertainties:

$$\sigma_{\mathrm{fit}}^2 = \boldsymbol{J}_{\overline{\delta}} \boldsymbol{\Sigma}_{\mathbf{p}} \boldsymbol{J}_{\overline{\delta}}^{\mathbf{T}}$$

$$\boldsymbol{J}_{\overline{\delta}} = \left[\frac{\partial\overline{\delta}}{\partial A_1} \cdots \frac{\partial\overline{\delta}}{\partial A_N} \quad \frac{\partial\overline{\delta}}{\partial c_1} \cdots \frac{\partial\overline{\delta}}{\partial c_N}\right] = \left[\frac{\delta_i - \overline{\delta}}{A} \cdots \frac{\delta_N - \overline{\delta}}{A} \quad \frac{A_1}{A} \cdots \frac{A_N}{A}\right]$$

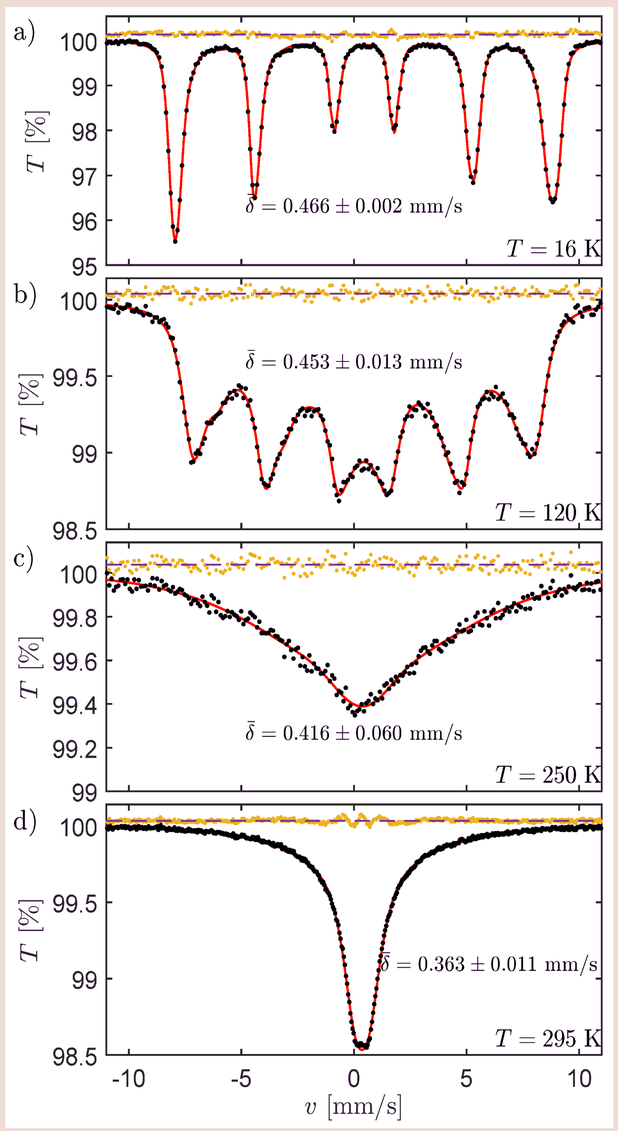
Results

a) Uncertainty of individual components is larger than 0.006 mm/s. Inducing correlations between parameters the uncertainty on $\overline{\delta}$ is 0.002 mm/s.

b-c) Broadening of spectra increase uncertainty.

d) Collapse into the doublet decreases uncertainty.

Multi-core, polystyrene iron oxide nanoparticles. Nominal size 8 nm



4. Discussion and Conclusion

- The experimental error (σ_{err}) is difficult to quantify.
- It is important to have:
  - A flat non-sloping background
  - Sufficient counting statistics.

Dominated by SODS correction — ***Magnetite content***

T [K]	σ_{cal} [mm/s]	σ_{fit} [mm/s]	$\sigma_{\Delta\delta}$ [mm/s]	$\sigma_{\overline{\delta}}$ [mm/s]	w [%]
16	0.0015	0.0015	**0.0059**	0.0063	4 ± 1
120	0.0015	**0.013**	0.0046	0.014	7 ± 6
250	0.0015	**0.0596**	0.0016	0.060	24 ± 28
295	0.0016	**0.0108**	0	0.011	13 ± 5

Insignificant — *Dominated by fitting uncertainty*

High uncertainty due to:
- Broad lines
- Low recoil-free fraction

The values are not equal within the uncertainty budget:
- Uncertainty in temperature not included.
- Possible experimental errors

Conclusion

- The uncertainty is not constant
- The fit introduce uncertainties
  - o Spectrum with narrow lines gives low uncertainty
- Uncertainty in calibration is insignificant
- Correcting using SODS can result in a significant uncertainty
- Temperature uncertainty introduces uncertainty in mean isomer shift

Acknowledgements

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