be done with the cut-off window width in the case of FFT. The smoothing optimization criteria are discussed in [5].

The smoothed spectra were used in calculation of the multivariate calibration models using the PLS regression method. An example of their application for the XRF determination of sulphur in black coal [6] is shown in Fig.3. It should be noted, that application of the smoothed spectra can improve root mean square error of crossvalidation (RMSECV) by about 50%. However, in some other cases of the multivariate calibration very small or no improvement in the model performance was observed. Hence, further research is to be performed to explain when and why smoothing of the raw data can improve performance of the multivariate calibration model.

References

DIRECT DETERMINATION OF ABSORBER THICKNESS FROM MÖSSBAUER SPECTRUM

W. Starosta

The shape of Mössbauer spectrum in transmission geometry is given by the expression:

$$ n(E_a) = \frac{2\Delta E_a}{\Gamma_a - \omega} \left( \frac{t_a}{2} \right)^2 \exp \left( - \frac{t_a}{2} \right)^2 \left( E - E_a \right)^2 \left( \frac{t_a}{2} \right)^2 $$

(1)

which is also called the transmission integral (TI). In this expression $\Gamma_a$, $\Delta E_a$ are energy line halfwidths of source and absorber, respectively, $t_a$ - peak positions and effective thicknesses of the i-th line of absorber and $E_a = E_0(1+v/c)$ - energy of source quantu. Due to difficulties connected with obtaining a compact expression for TI, several methods for determining the shape of spectrum of absorber are applied, e.g. numerical integrations of TI, Fourier or Voigt based deconvolution method, approximation of exponent by Lorentz terms with width and amplitude depending on absorber thickness, or at last approximation by Lorentz function with the condition of "thin absorber". Each of these approaches have some disadvantages. Numerical integration is time consuming, especially if such a method is to be incorporated into the best parameters fitting routine. Fourier transform generally needs a knowledge of the halfwidth of source line. Two other methods need some calibrations if contents of Mössbauer nuclei are to be determined from the spectrum. Besides of that the conception of "thin absorber" requires some definition which can be drawn only on the basis of knowledge of spectrum distortion introduced by finite absorber thickness. All these problems could be avoided when a new formula recently obtained by the author is applied. Using it a direct determination of effective absorber thicknesses is possible.

The formula has been obtained using the following representation for Lorentz terms

$$ \frac{t_a}{a} \left( \frac{t_a}{2} \right)^2 \left( E - E_a \right)^2 \left( \frac{t_a}{2} \right)^2 \left( E - E_a \right)^2 \left( \frac{t_a}{2} \right)^2 $$

(2)

here $i = \sqrt{-1}$, and using the expansion of exponent containing the Lorentz terms in the form:

$$ \exp \left( - \frac{t_a}{2} \right)^2 \left( \frac{t_a}{2} \right)^2 \left( E - E_a \right)^2 \left( \frac{t_a}{2} \right)^2 \left( E - E_a \right)^2 \left( \frac{t_a}{2} \right)^2 $$

(3)

here $I_m$ - Bessel modified function of m-th order.

Applying the known theorem concerning calculation of an integral in complex plane by the residuals method, the TI can be expressed as a sum of residuals in poles in upper half-plane. Finally, the TI is given by infinite series in the form:

$$ n(E_a) = 1.0 + \sum_{k=1}^{\infty} \left( \frac{t_a}{2} \right)^2 \left( E - E_a \right)^2 \left( \frac{t_a}{2} \right)^2 \left( E - E_a \right)^2 \left( \frac{t_a}{2} \right)^2 $$

(4)

where:

$$ L_k(E_a) = \sum_{p=1}^{\infty} A_{kp} (a_{kp} - 1.0), $$

$$ a_{kp} = \frac{E_a - E_k + \frac{1}{2} (\Gamma_a - \Gamma_k)}{E_a - E_k + \frac{1}{2} (\Gamma_a + \Gamma_k)} $$

Formula (4) can be easily calculated using a personal computer if the calculations on complex type data are involved.

In order to check the validity of the formula, calculations of the effective thickness of Armco absorber have been performed for 6 µm iron ARMCO foil supplied by Amersham for the calibrations of spectrometer. In the calculations, the halfwidth of the absorber line was assumed to be constant and equal to table value of iron $^{57}$Fe nuclide halfwidth. The value of 2.76 has been obtained for the effective thickness of absorber in fair agreement with 2.80 as calculated for our Armco foil using the table nuclear data for iron $^{57}$Fe. For the halfwidth of source line the value of 0.134 mm/s has been obtained. A larger value of halfwidth for the source line can be explained as due to self absorption of Mössbauer resonant radiation.

The obtained results show that the direct determination of the absorber effective thickness can be done using our exact formula for TI and the nuclear
data for iron $^{57}$Fe nuclide. At present, the validity of the formula is under study as applied to the contents determination of iron containing minerals (pyrite, clay minerals) in coals and for aluminosilicates. It is expected that the application of this formula will be helpful in removing thickness distortion effects in the Mössbauer spectrum and for more accurate determination of physical parameters of the absorber, particularly in the case when spectra lines are overlapping.