

## WHAT IS THE TRUE KRAMERS-KRONIG TRANSFORM?

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The results of Kramers-Kronig transformation obtained from three different software packages (Omnic, Perkin Elmer, and Kluger Nielsen) are discussed. Although identical testing input data (reflectance spectra of yttria-aluminosilicate glasses) were used for the calculations of absorption spectra, the transformations yield qualitatively different results. As the exact algorithms used in commercially available software are unknown to us, it is not possible to give sufficient explanation of described phenomenon. The main aim of the present contribution is to call the attention to this problem and to initiate discussion among the spectroscopists community.

Keywords: Kramers-Kronig transformation, Infrared reflectance spectra, Absorption spectra

## INTRODUCTION

The Kramers - Kronig (KK) [1, 2] transformation, known in the field of reflectance spectrometry also as Robinson-Price [3, 4] analysis is a powerful tool enabling a calculation of absorption spectra in cases where only reflectance spectra can be measured. In principle, the Kramers-Kronig Transform is a numerical method for obtaining the absorbance and refractive index data from reflectance spectra. The complex reflectance spectrum is mathematically decomposed into two separate spectra - extinction coefficient and refractive index spectrum. These are also called K and N spectra. The extinction coefficient spectrum can be then used to calculate the absorption spectrum [5].

The real ( $n$  = refractive index) and imaginary ( $k$  = extinction) parts of the complex index of refraction are calculated from the reflectance spectrum using the following formulas:

$$n(\nu) = \frac{1 - R(\nu)}{1 + R(\nu) - 2\sqrt{R(\nu)} \cos(\theta(\nu))} \quad (1)$$

$$k(\nu) = \frac{-2\sqrt{R(\nu)} \cos(\theta(\nu))}{1 + R(\nu) - 2\sqrt{R(\nu)} \cos(\theta(\nu))}, \quad (2)$$

where  $R$  is the reflectance,  $n$  - wavenumber,  $\theta$  - phase shift angle of the sample

For a given wavenumber, the phase shift is calculated using the equation (3):

$$\theta(\nu_m) = \frac{2 \nu_m}{\pi} \int_0^{\infty} \frac{\ln\sqrt{R(\nu)} d\nu}{\nu^2 - \nu_m^2} \quad (3)$$

The KK Transform algorithm assumes that the reflectance spectra are measured at incidence angles close to zero. Calculating the integral presents two problems. First, in practice, the spectrum is obtained over a finite range, so that approximations are required at either end. Second, there is a pole at  $\nu = \nu_m$ , which also requires an approximation. In order to overcome these problems a Fourier transform is applied to solve the integral. [6, 8]

Application of the method in the past was significantly restricted by its numerical complexity. Therefore, the fully described program source codes (mainly in FORTRAN) were published in specialised journal [4]. Availability of commercial spectrometers with an on-line computer control and data processing led to routine application of the method. Corresponding software, enabling the performance of "one-click" Kramers-Kronig transformation, is usually implemented in the standard spectral data processing package supplied by the producer of a spectrometer. To an end user, details of an applied numerical scheme are usually not available. Due to a complexity of the numerical solution of the problem, the absorption spectra calculated by various software packages may be different, depending on *a priori* unpredictable specific features of input reflectance spectrum. The aim of present paper is to illustrate the differences found among the KK-transforms calculated using two commercially available software packages supplied by renowned producers of spectrometric technique, i.e. Nicolet Omnic v. 3.1 (denoted in following text as OM) and Perkin Elmer Spectrum for Windows v. 1.40 (PE) and by the well documented FORTRAN program of Klucker and Nielsen (KN) [4], and to call the attention to this problem. At the same time we would like to point out the inconsistencies, which arose when different software packages were used, and focus the paper as

warning against mechanical application of the method without deeper knowledge.

## EXPERIMENTAL

The reflectance spectra used as input data for the calculations were measured using a Nicolet Magna 750 Fourier-transformed infra-red spectrometer (FTIR). Four glasses with various compositions corresponding to glassy phases usually occurring at grain boundaries of silicon nitride-based ceramics were used in our study. [9] The compositions are given in table 1. The glasses were prepared by mixing the appropriate quantities of high purity reagents Al<sub>2</sub>O<sub>3</sub> (99,9 %), Y<sub>2</sub>O<sub>3</sub> (PIDC, USA grade 4N-99,99 %), SiO<sub>2</sub> (pure, Reachim, St. Petersburg), CaCO<sub>3</sub> (p.a., Lachema, Brno) and FeO (p.a. Lachema, Brno), to yield 100 g of glass. The powders were dry-mixed and melted in a 10% RhPt crucible in air in an electric furnace and held for 5 h at the melting temperatures between 1570 - 1630°C. The homogeneity of glass was ensured by repeated fritting and hand mixing in the course of melting. The melt was poured onto a stainless steel plate. The samples were subsequently annealed in a muffle furnace for 4 h at 800 - 850°C. After annealing, the samples were cooled down to room temperature in the furnace.

Table 1. Chemical compositions of tested glasses (mol %).

glass	Chemical composition (mol %)				
	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	FeO
YAG Si	14.2	23.6	62.2	0	0
YASiCa	10.4	17.4	62.2	10	0
YAGSiCa	12.0	20.1	52.9	15	0
YAGSiFe	13.5	22.4	59.1	0	5

The reflectance spectra were measured on the natural glass surface in the range of wavenumbers from 4000 to 400 cm<sup>-1</sup> at nearly normal incidence of radiation beam and with resolution 4 cm<sup>-1</sup>. In order to compare the calculated absorption spectra with real ones, the real absorption spectra of respective samples were measured using the KBr technique with identical experimental settings as for reflectance spectra. The samples were prepared by mixing 200 mg of dried KBr and 3 or 7 mg of glass. The mixture was then pressed at 100 MPa to form transparent pellets. Finally the absorption spectra were roughly estimated using equation (4):

$$A_N(\nu) = \frac{A_7(\nu) - A_3(\nu)}{\Delta m_{7-3}} \times R_f \quad (4)$$

where  $A_N$  is the estimate of normalized absorption spectrum,  $A_7$  - absorption spectra measured on KBr pellet containing approximately 7 mg of glass,  $A_3$  - absorption spectra measured on KBr pellet containing

approximately 3 mg of glass,  $\Delta m_{7-3}$  - the difference of exact weights of glass in both KBr pellets,  $R_f$  - scaling factor (used  $RF = 4000$ ).

This method was applied in order to eliminate the background signal arising from using KBr and to compare the measured spectra quantitatively.

## RESULTS AND DISCUSSION

The typical relations observed among individual transforms together with absorption spectra obtained by KBr technique are summarised on figures 1 - 4. The relative intensities of the two maxima of the complex band observed between 800 - 1200 cm<sup>-1</sup> were used as a measure of equivalency of different KK-transforms.

Spectra measured on KBr pellets are showed only for illustration. It is obvious that due to the interaction of KBr with glass, the KBr spectra can be different from spectra measured on powdered glasses using diffuse reflectance spectroscopy, which is considered to be more suitable technique for glassy samples. In our work, the semiquantitative results obtained by the KBr technique (namely the relative intensities of two bands observed in the wavenumber range 800 - 1300 cm<sup>-1</sup>) were used only to compare qualitatively the real spectra with those generated numerically by various software packages.

Mutual typical relations observed among individual transforms together with absorption spectra obtained by KBr technique are summarised on figures 1 - 4. Figure 1 illustrates the situation where the KN and PE transforms are equivalent, while the OM one is different. On the other hand, equivalent OM and PE with different KN transform are shown on figure 2. The worst case of three mutually different transforms is documented by figure 3. In some cases with more simple peak shapes (figure 4) all the used algorithms yield equivalent results.

As can be seen from the figures 1 - 4, the applied software packages also yield the spectra with a different shape of the baseline in the wavelength range between 1200 and 3000 cm<sup>-1</sup>. While the OM transformation yields a baseline monotonously falling with growing wavelength, the flat baseline in the whole wavelength range is typical for the PE transformation. The KN transformation yields spectra with monotonously growing baseline.

As the exact algorithms used in commercially available software are unknown to us, we are not able to give sufficient explanation of described phenomenon. Therefore, the main aim of the present contribution is to call the attention to this problem and to initiate discussion among the spectroscopists community. At the same time we would like to point out the inconsistencies, which arose when different software packages were used, and focus the paper as warning against mechanical application of the method without deeper knowledge. Mutual comparison of calculated spectra from different sources should be avoided when exact algorithm is not known.

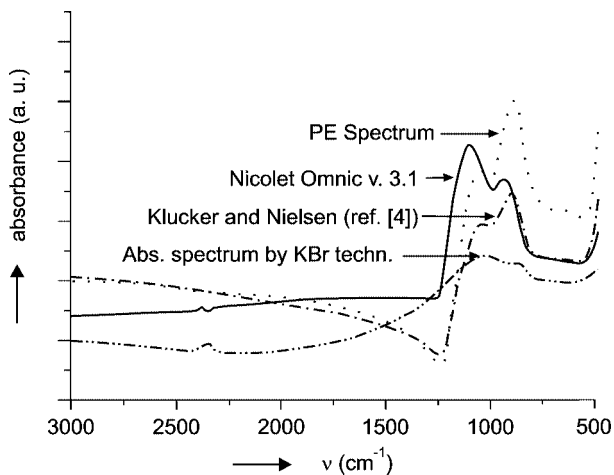


Figure 1. Calculated absorption spectra of the YAGSi sample.

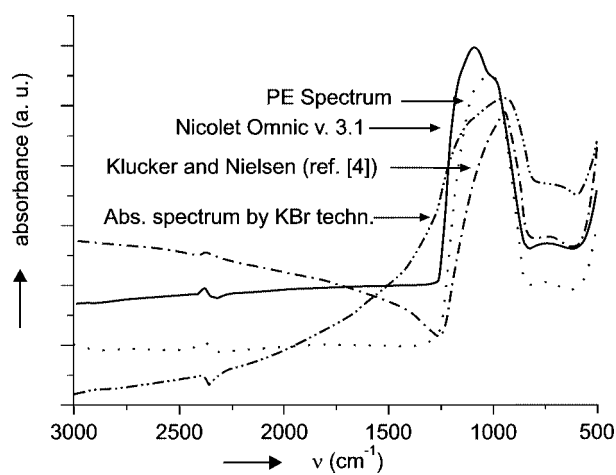


Figure 3. Calculated absorption spectra of the YAGSiCa sample.

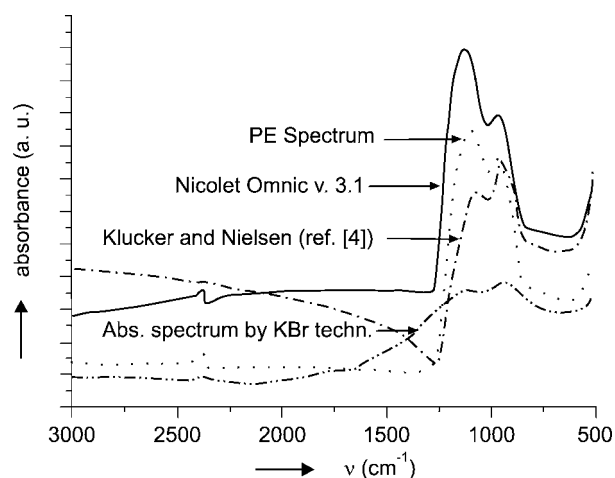


Figure 2. Calculated absorption spectra of the YASiCa sample.

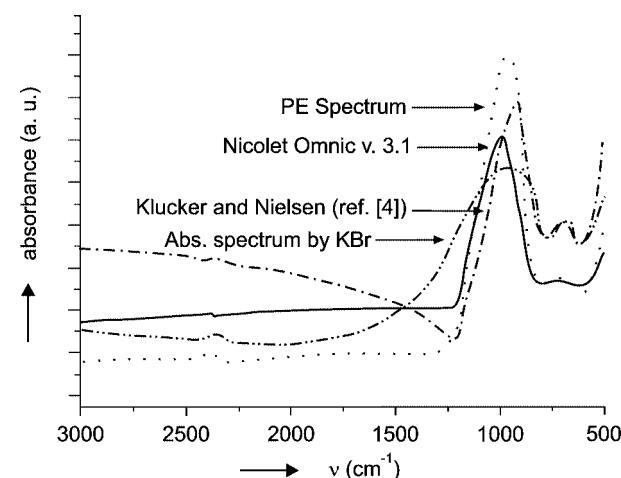


Figure 4. Calculated absorption spectra of the YAGSiFe sample.

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### References

1. Dunken H.H., Stephanowitz R.: *Zeitschrift für Chemie* 23, 353 (1983).
2. Pelikán P., Čeppan M., Liška M.: *Applications of Numerical Methods in Molecular Spectroscopy*, Chap. 5, 9CRC Press, Boca Raton, 1994.
3. Robinson T.S.: *Proc. Phys. Soc., London* 66B, 969 (1953).
4. Klucker R., Nielsen U.: *Comp. Phys. Commun.* 6, 187 (1983).
5. Kronig R.L., Kramers H.A.: *Atti Congr. Intern. Fisici, Como* 2, 545 (1927).
6. Cameron D.G., Jones J.P.: *Computer Programs for Infrared Spectrophotometry XLII-XLVII*, in: NRC Bulletin No. 16, p.6 (1977).
7. Peterson C.W., Knight B.W.: *J. Opt. Soc. Am.* 63, 1238 (1973).
8. Ohta K., Ishida H.: *Applied Spectroscopy* 42, 952 (1988).

9. Lichvár P., Antalík J., Liška M., Šimon P.: *Proc. 14<sup>th</sup> Conf. Thermal. Anal. TERMANAL '97*, p.99, Belušké Slatiny, Slovak Republic 1997.

### ČO JE SPRÁVNA KRAMERSOVA-KRONIGOVA TRANSFORMÁCIA?

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Porovnali sa výsledky výpočtu absorpčných spektier tromi komerčne dostupnými programami (Omnic, Perkin Elmer, Klucker Nielsen) Kramersovej-Kronigovej transformácie. Výpočty sa uskutočnili na testovacom súbore reflexných infračervených spektier yttritých hlinitanokremičitanových skiel. Zistilo sa, že použité programy dávajú kvantitatívne i kvalitatívne odlišné absorpčné spektrá. Vzhľadom k nedostupnosti detailov použitých komerčných softwarov nie je možné bližšie identifikovať príčiny zistených rozdielov. Hlavným zámerom prezentovanej práce je na rozdiely poukázať a vyvolať zodpovedajúcu diskusiu.