Influence of systematic errors on the spectrophotometric analysis of multicomponent mixtures

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The influence of the height, position, and half-band width of the band of a component unconsidered in the calibration on the precision of the spectrophotometric determination of the other component concentrations in the sample was studied. The concentrations of the components being determined were computed by solving an overdetermined system of linear equations by the method of least squares. The study was performed with a three-component model system, the spectrum of which was approximated by the Lorentz functions.

In our preceding paper [1] we studied the influence of random errors on the precision of the determination of multicomponent mixtures by the method of least squares [2]. In practice we often meet with the problem that the technical product analyzed contains unidentified components that were not considered in the calculation of the calibration data. The occurrence of such components may lead to systematic errors when determining the components taken into account in the calibration. It also influences the values of the elements of the absorbance residues matrix $\mathbf{E}_B$ [3].

The aim of the present work is to show to what extent the component, which was not taken into consideration, influences the accuracy of the determination.

Model system

The influence of systematic errors was studied on a three-component model system, in which the absorption bands were approximated by the Lorentz functions. The constants used are given in Table 1 [1].

In contradistinction of the preceding work [1] no random errors were introduced into the model system and in computing the calibration data the matrices $\mathbf{C}$ and $\mathbf{A}_0$ were used. When computing the concentrations of the components in the sample, the absorbances of the fourth band of the Lorentzian type were added to the column matrix $\mathbf{B}_0$, its position and half-band width being changed at a constant height of this band ($A_{04} = 0.1$). For the maximum of the fourth band the analytical positions $g = 1, 4, 7, \ldots, 31$ were chosen and marked as I, II, III, $\ldots$, XI. The half-band widths varied from 1 to 10 cm^{-1}. By combining these positions and the half-band widths the matrix $\mathbf{B}$ was obtained, which contained 110 rows (and 30 columns).

Results and discussion

The influence of the height of the fourth band on the result of the determination of the particular components was not studied as from the comparison of eqns (7) and (9) mentioned in the preceding paper [1] it ensues that the deviations of the determination are directly proportional to the height of that band.

Dependence of the difference between the computed and the actual concentration of the particular components Δx_j from the position of the absorption band of the 4th component at half-band widths from 1 to 10 cm^{-1} is shown in Figs. 1—3.

From Fig. 1 (component $j = 1$) it can be seen that the maximum value Δx_1 for all half-band widths is next to the position corresponding to the maximum of the 1st band appertaining to component 1. In case the half-band width of the 4th band is equal to that of the 1st band ($\Delta v_{1/2} = 3$ cm^{-1}), the spectrum of the 4th component is identical with that of the 1st one, thus in the computation only the concentration of the 1st component increases, whereas Δx_2 for the 2nd component and Δx_3 for the 3rd one are zero (see Figs. 2 and 3). Similar relations are valid also for the components 2 and 3 and therefore in Fig. 1 in the position V and at $\Delta v_{1/2} = 4$ cm^{-1} and also in the position IX at $\Delta v_{1/2} = 5$ cm^{-1}, $\Delta x_1 = 0$. If $\Delta v_{1/2}(4) < \Delta v_{1/2}(2) = 4$ cm^{-1}, the values for Δx_1 are negative in the position V. On the contrary, at $\Delta v_{1/2}(4) > 4$ cm^{-1} the values of Δx_1 are positive. Near to the position V in Fig. 1 the local minimum
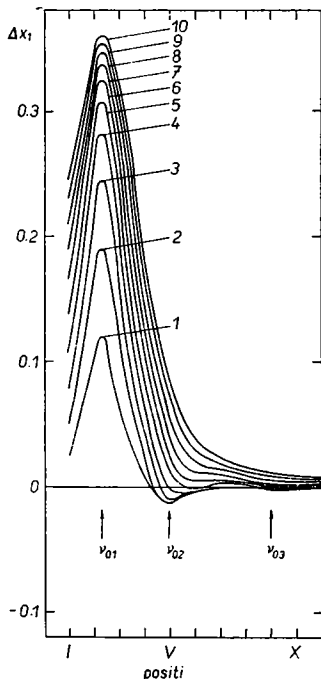

Fig. 1. Dependences of the deviations of the 1st component concentration from the positions of the 4th band maxima at half-band widths $\Delta v_{1/2}(4) = 1-10$ cm^{-1}.
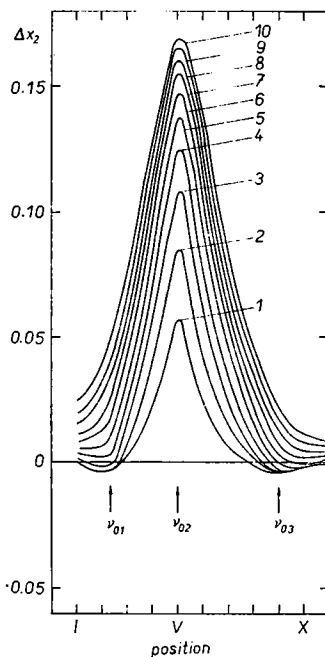
Fig. 2. Dependences of the deviations of the 2nd component concentration from the positions of the 4th band maxima at half-band widths $\Delta v_{1/2}(4) = 1-10$ cm^{-1}.
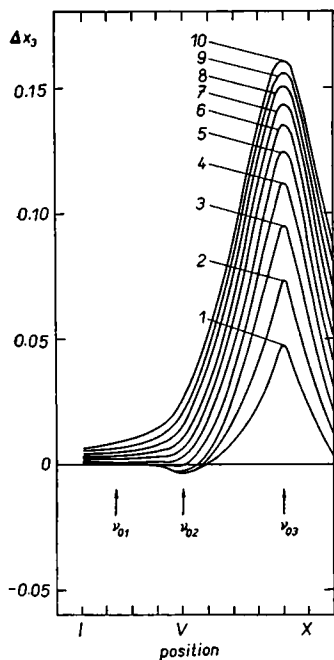
Fig. 3. Dependences of the deviations of the 3rd component concentration from the positions of the 4th band maxima at half-band widths $\Delta\nu_{1/2}(4) = 1-10$ cm^{-1}.
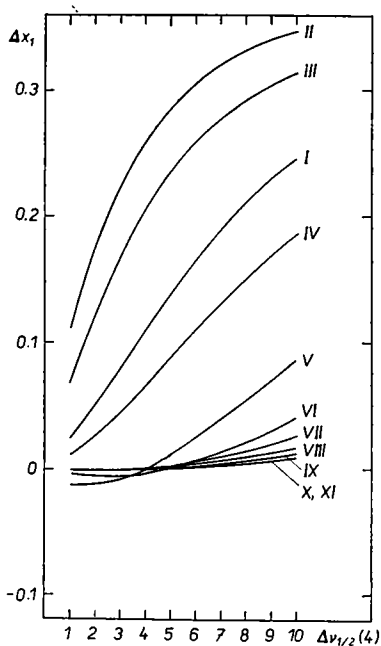
Fig. 4. Dependences of the deviations of the 1st component concentration from the half-band width of the 4th band at its positions I—XI.

Δx_1 can be seen which is shifted by increasing the half-band width of the 4th band and disappears by degrees. The curves take an analogous course even near the position IX but as the absorption band of the 3rd component is farther, the local minimum on the curves is less clean-cut. The curves in Fig. 3 take essentially the same course in contradistinction to Fig. 2 where both minima are distinct.

The dependence of Δx_j on the half-band width of the 4th band in its positions I—XI is shown in Figs. 4—6. It can be seen from these pictures that the errors Δx_j increase with the increase of the half-band width of the 4th band, which presumably is in connection with its area. In the case when between the position of the 4th band maximum and that of the maximum of the component examined there is the absorption band of some other component, this course is affected in the region of the small half-band widths of the 4th band where the minimum may be.

In Figs. 4—6 significant zero values Δx_j can be found similarly as in Figs. 1—3. The value Δx_1 (Fig. 4) is zero in case $\nu_{04} = \nu_{02}$ and at the same time $\Delta\nu_{1/2}(4) = \Delta\nu_{1/2}(2)$ and also when $\nu_{04} = \nu_{03}$ and $\Delta\nu_{1/2}(4) = \Delta\nu_{1/2}(3)$. Analogous points can be found in the dependences Δx_2 and Δx_3 on the half-band widths of the 4th band (Figs. 5 and 6).

The investigation of the influence of systematic errors due to a component unconsidered in the calibration has shown that with the increasing concentration of this
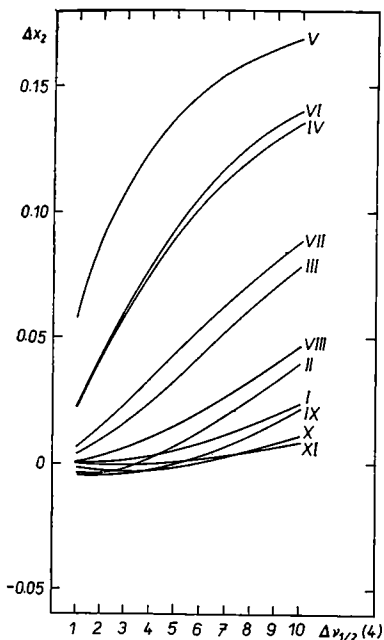
Fig. 5. Dependences of the deviations of the 2nd component concentration from the half-band width of the 4th band at its positions I—XI.
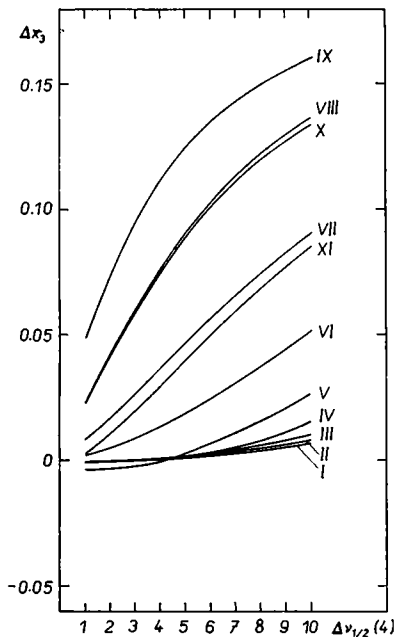
Fig. 6. Dependences of the deviations of the 3rd component concentration from the half-band width of the 4th band at its positions I—XI.

component the error of the determination of other components increases in direct proportion. If the spectrum of some component being determined is similar to that of the component unconsidered in the calibration, the error of the concentration computed is greater. The other components will be laden with a smaller error, which may be also negative. This fact is to be taken into account when requiring a certain precision of the determination of the particular components and, as far as possible, measurings in the region of the spectra should be avoided, where there are the greatest relative deviations of the absorbance values measured and computed back.

References

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