QUESTION OF THE EFFECT OF THE BACKGROUND AND THE OVERLAPPING OF ABSORPTION BANDS ON THE ACCURACY OF QUANTITATIVE INFRARED SPECTRAL ANALYSIS

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UDC 535.34

Infrared spectroscopy is extensively employed in analytical laboratories for the solution of problems encountered in the quantitative analysis of multicomponent mixtures. Moreover, in order to determine the amounts of components in mixtures, a large number of techniques have been developed both for the manual [1] and for the digital computer treatment [2-6] of the spectrograms.

At the same time, however, the effect of the degree of overlapping of the absorption bands on the accuracy and the sensitivity of the analysis has still not been sufficiently studied. As a rule, it is noted that the greater the number of components contained in the mixture and the more similar their absorption spectra, the lower the accuracy.

In [7] this fact is explained in terms of errors in the measurement of the magnitudes of the absorption coefficients for the components. When doing this, it is assumed that the Burger–Lambert–Beer law is observed.

It is pointed out in [8] that the accuracy of the analysis of complex mixtures depends on the form of the absorption bands of the components but, at the same time, no quantitative estimate of this effect is given.

We are proposing a simple technique for taking account of the effect of the background and the overlapping of absorption bands on the accuracy of infrared spectral analysis.

As is well known, infrared spectra are recorded both on instruments with an optical null system and on instruments with electrical compensation, using the transmission scale, since it is the ratio of the intensities of the radiation which has passed through the sample and that which was incident upon it ($T = I/I_0$) which is measured. In the case of mixtures with overlapping absorption bands, a contour is recorded on the transmission scale which is the sum of the absorption bands of the components of the mixture. Hence, the transmission of the components of the mixture is summed while the optical density is the additive quantity in spectrophotometry.

It seems to us that it is necessary to seek the cause of the reduction in the accuracy of the analysis of multicomponent systems in the nonlinearity of the transmission scale which manifests itself when there are overlapping absorption bands.

This supposition was checked with the help of conventional wire grids which are employed as neutral filters of differing degrees of transparency. The use of grids for this purpose has been described in [1, 9].

The transmission of each grid individually and of combinations of two and three grids (see Fig. 1) were measured on a UR-20 spectrophotometer at one and the same wave number and under constant recording conditions. For a system consisting of two grids, the metering of the nonlinearity in the transmission scale is shown in Fig. 1, using grids 1 and 2 as the example. For a single grid, the 0-100% transmission scale is equal to $T_0 = 100\%$. In the case of a combination of grids, the 0-100% transmission scale for the second grid in the presence of the first grid is by now T_1. It follows that it is necessary to introduce a correction coefficient equal to $\alpha_1 = T_1/T_0 = 0.511$ to allow for the absorption of the second grid in the presence of the first grid and the corrected magnitude of the absorption due to the second grid (A_2^*) will be equal to $A_2^* = \alpha_1 \cdot A_2 = 0.511 \cdot 35.9\% = 18.4\%$. In this case the corrected value for the absorption of the combination of grids 1 and 2 will be equal to $A_{1+2}^* = A_1 + A_2^* = 67.3\%$, whence the value $D_{1+2}^* = 1.117$.

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 30. No. 2, pp. 349-352, February, 1979. Original article submitted May 16, 1977; revision submitted April 17, 1978.

0021-9037/79/3002-0243$07.50

TABLE 1. Results of Measurements and the Calculation of the Values of D for Combinations of Grids

Results of measurements on the transmission of grids and combinations of two and three grids on a UR-20 spectrophotometer				Calc. of D^{BLB} accord. to additivity principle	Calc. of D^* with a correction for the nonlinearity of the transmission scale	$D^{BLB}-D$	$D^{BLB}-D^*$
T	D	T	D				
$T_1=51,1\%$	$D_1=0,670$	$T_{1+2}=35,5\%$	$D_{1+2}=1,036$	$D^{BLB}_{1+2}=1,115$	$D^*_{1+2}=1,117$	0,079	—0,002
$T_2=64,1\%$	$D_2=0,445$	$T_{1+3}=27,8\%$	$D_{1+3}=1,280$	$D^{BLB}_{1+3}=1,412$	$D^*_{1+3}=1,414$	0,132	—0,002
$T_3=47,6\%$	$D_3=0,742$	$T_{2+3}=32,9\%$	$D_{2+3}=1,112$	$D^{BLB}_{2+3}=1,187$	$D^*_{2+3}=1,187$	0,075	0
$T_4=45,2\%$	$D_4=0,794$	$T_{5+6}=61,6\%$	$D_{5+6}=0,485$	$D^{BLB}_{5+6}=0,508$	$D^*_{5+6}=0,508$	0,023	0
$T_5=82,0\%$	$D_5=0,198$	$T_{4+5}=39,9\%$	$D_{4+5}=0,918$	$D^{BLB}_{4+5}=0,992$	$D^*_{4+5}=0,993$	0,074	—0,001
$T_6=73,4\%$	$D_6=0,310$	$T_{4+5+7}=22,6\%$	$D_{4+5+7}=1,487$	$D^{BLB}_{4+5+7}=1,679$	$D^*_{4+5+7}=1,672$	0,192	0,005
$T_7=50,3\%$	$D_7=0,687$	$T_{4+6+7}=20,7\%$	$D_{4+6+7}=1,575$	$D^{BLB}_{4+6+7}=1,791$	$D^*_{4+6+7}=1,785$	0,216	0,006
$T_8=63,8\%$	$D_8=0,450$	$T_{4+5+6}=30,9\%$	$D_{4+5+6}=1,174$	$D^{BLB}_{4+5+6}=1,302$	$D^*_{4+5+6}=1,301$	0,128	0,001
		$T_{4+7+8}=18,5\%$	$D_{4+7+8}=1,688$	$D^{BLB}_{4+7+8}=1,931$	$D^*_{4+7+8}=1,925$	0,243	0,006
		$T_{5+6+7}=35,6\%$	$D_{5+6+7}=1,034$	$D^{BLB}_{5+6+7}=1,195$	$D^*_{5+6+7}=1,194$	0,161	0,001

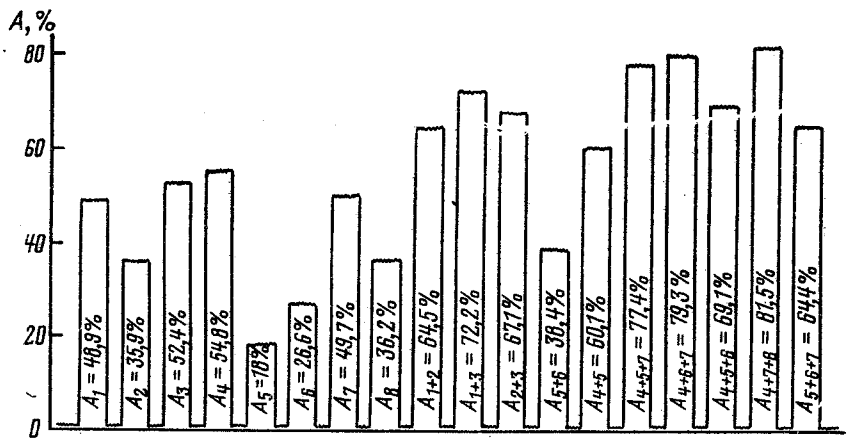

Fig. 1. The absorption of wire grids and combinations of two and three grids.

In a similar manner one may find the correction coefficient for the absorption of the first grid in the presence of the second: $\alpha_2 = T_2/T_0 = 0.641$ and $A_1^* = \alpha_2 \cdot A_1 = 0.641 \cdot 48.9\% = 31.4\%$ whence $A_{1+2}^* = 35.9\% + 31.4\% = 67.3\%$ and $D_{1+2}^* = 1.117$. In the case of a combination of three grids such as, e.g., grids 4, 5, and 6, we obtain $A_{4+5+6}^* = A_4 + \alpha_4 \cdot A_5 + \alpha_4 \cdot \alpha_5 \cdot A_6$. The effect of background absorption may be taken into account in an analogous way.

The values of D* found for each of the combinations of grids with a correction for the nonlinearity of the transmission scale were compared with the values of D and D^{BLB}, where D is the optical density calculated from the value of T measured on a UR-20 spectrophotometer for this combination of grids and D^{BLB} is the optical density calculated according to the principle of additivity of Firordt as the sum of the optical densities of the components of this combination of grids. The results of the calculation are presented in Table 1.

Hence, by allowing for the nonlinearity of the transmission scale, errors in the determination of the concentrations of the components of a mixture which are caused by the overlapping of absorption bands may be eliminated.

In conclusion, the authors express their gratitude to Yu. Ya. Kharitonov for his interest in the work and for discussing the results.

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