DIFFERENTIAL SPECTROSCOPY FEATURES OF FURFURAL IN THE 320–400 nm REGION

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Application of differential spectrophotometry to furfural enables the presence in it of foreign compounds, especially the products of its autoxidation, and also their nature to be established by a spectral comparison of the sample investigated with pure furfural. The special feature of the spectrum is that the position of the characteristic maximum formed in the presence of various substances changes according to the thickness of the layer investigated: $\lambda_{max} = 15.9 \log l + \lambda_0$. The establishment of these properties enables the method to be used for the study of different amounts of impurities in furfural by varying the layer thickness. The method is simple in use and possesses a high sensitivity.

To study the kinetics of the accumulation of colored substances in furfural during its autooxidation, the spectrophotometry of furfural without a solvent at a layer thickness of 1 cm with an aqueous standard is frequently used [1, 2]. Under these conditions, descending spectral curves are obtained in the 360–700 nm region which shift in the direction of long wavelengths as the quality of the furfural deteriorates. In this way it is possible to obtain some information on the change in the content of colored products; however, it is impossible to say anything at all about their nature in view of the absence of any extrema on the absorption curves.

We have used the differential spectrophotometry of furfural in the 320–400 nm region. The main features of this method are the use as a standard of chemically pure furfural and a considerable decrease in the working thickness of the cell—less than 1 mm. As a result, the spectrum of furfural itself is eliminated differentially from the spectrum of the sample under investigation, and the decrease in the working layer (l) permits the maximum possible coverage of the spectrum in the direction of the ultraviolet (boundary 320 nm) without using a solvent. The differential method enables additional information to be obtained on the nature and amount of the substances present in furfural and in the solvent spectra were taken on an SF-4 instrument with an an incandescent lamp in quartz cells, in which the thickness of the layer investigated varied from 0.06 to 1.01 mm.

As the standard of comparison we used spectrally pure furfural which was prepared in the following way. Fresh reagent furfural from the Krasnodarsk chemical combine was subjected to two vacuum distillations in an atmosphere of pure nitrogen. The fractions with bp 43° C (5 mm) were collected. The furfural so obtained was transferred into the cell of the instrument in an atmosphere of nitrogen. Such a standard can be kept for 2–3 hr. In studying autoxidation it is possible to use as standard the initial furfural [3], which can be stored without appreciable changes in a refrigerator at 3–5° C for 10–12 days.

Figure 1 shows the spectra of furfural with natural and artificial additions taken against different standards: distilled water (a) and purified furfural (b). The

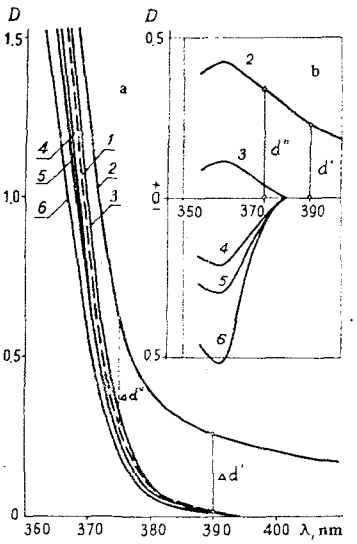


Fig. 1. Spectrum of furfural at a cell thickness l = 0.22 mm; a) against water; b) against standard furfural; 1) standard; 2) oxidized. The following were added to the furfural: 3) sodium chloride; 4) 4% of water; 5) 10% of ethanol; 6) 30% of benzene.

dissolution of water, ethanol, and benzene leads to a fall in the descending branch of the furfural spectrum (a, curves 4, 5, and 6). In examining these samples against standard furfural, spectra are obtained with negative values of the absorption [4] (Fig. 1, b). If autoxidized furfural containing colored substances is photometered, curve 2 (Fig. 1, a) is obtained, which is displaced upwards and to the right. The more the furfural is oxidized, the greater is its density in the visible part of the spectrum with respect to water. Under these conditions differential spectra are obtained with positive absorptions (Fig. 1, b, curves 2 and 3) with maxima at the same wavelengths as the negative spectra.

It follows from Fig. 1a, that the presence of foreign substances leads to a change in the curvature of the descending branch of the furfural spectrum. In one case with an increase in the optical density (curves 2 and 3), the curvature decreases; in another case with a decrease in the optical density (sample investigated

more transparent than the standard), the curvature increases. Change in the curvature takes place irregularly: at one wavelength the absorption rises (or falls) to a greater extent and at another wavelength to a smaller extent. Thus, the difference in the optical densities of samples 1 and 2 at λ 390 nm is Δd = 0.22,

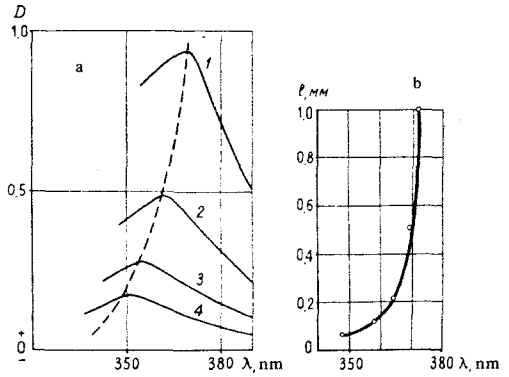


Fig. 2. a) Differential spectra of oxidized furfural and various layer thicknesses in the cells (l, mm); 1) 0.51; 2) 0.22; 3) 0.11; 4) 0.06. b) Dependence of the position of the maximum of the absorption curve on the layer thickness.

and at 375 nm it is Δd = 0.34. A similar pattern is observed when spectra 1 and 3 or 1 and 4 are compared, and so on.

When the furfural under investigation is examined against the standard material, the changes introduced into the spectrum by the dissolution of various substances in it appear clearly. In this case furfural is a solvent with a high optical density, the spectrum of which is almost completely eliminated by mutual absorption and in converted into a straight line coinciding with the axis of abscissas. Under these conditions the presence of impurities appears in the form of positive or negative spectra with characteristic maxima in the 320–370 nm region (Fig. 1, b).

The correctness of the ideas put forward is confirmed by a quantitative comparison of the spectrum of furfural against water and the differential spectrum of the same sample against standard furfural. The differences between the standard and oxidized furfural (Fig. 1, a, b, curves 1 and 2) taken at two arbitrary points (λ' = 390 and λ" = 375 nm), Δd' = d' = 0.22 ± 0.01 and Δd" = d" = 0.34 ± 0.01 are identical for the differential spectrum and for the spectrum of furfural against water. A similar situation is observed for all other points of these spectra as well. However, such a comparison with an aqueous standard is possible only when the difference in the spectra being compared is sufficiently large. For example, for 1 and 3 or 1 and 4 it is extremely difficult to determine the difference quantitatively. The method of differential spectra does not have the disadvantages mentioned. It is extremely sensitive and substantially simpler in performance, and without any additional operations whatever gives a direct answer to the question of changes in the optical characteristics of the furfural under investigation.

However, when the differential method is used in investigations of furfural (and possibly with other compounds as well) it is necessary to know some of its characteristics. Thus, a change in the working layer of the cell leads to a shift in the maximum of the spectrum, i.e., there is a definite nonobservance of the Lambert-Beer law. The necessity in individual cases for working at different thicknesses of the working layer has forced us to consider this phenomenon in more detail. Fig. 2, a, shows the differential spectra of oxidized furfural at l = 0.51–0.06 nm. The regular increase in the optical density with an increase in the thickness of the layer investigated can be seen. In addition to this, it can be seen that the characteristics of the spectrum change—the maximum shifts in the longer-wave direction. The shift is particularly appreciable at l < 0.2 mm (curves 3 and 4). Under these conditions, the curve of the maxima (Fig. 2, b) turns sharply in the short-wave direction. The difference in the position of the maxima for cells with l from 0.06 to 0.51 mm is fairly considerable, amounting to 21 mm.

To confirm the characteristics found, in another variant we carried out the spectrophotometry of freshly-distilled furfural in which 1–4% of water had been dissolved. The addition of water led to a decrease in the optical density of the furfural in the 320–380 nm section. As a result, a negative spectrum was obtained. Each sample was subjected to spectrophotometry at different layer thicknesses. Two groups of the spectra are shown in Fig. 3, a and b. As in the

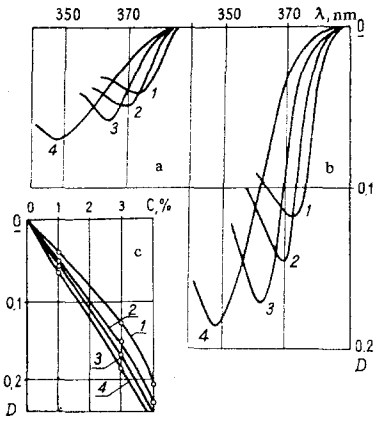


Fig. 3. Differential spectra after the dissolution of water in furfural: a) 1%; b) 3%; c) dependence of the negative optical density on the concentration of water in the furfural (l, mm): 1) 1.01; 2) 0.51; 3) 0.22; 4) 0.66.

preceding case, a change in the characteristics of the differential spectra is observed. With an increase in the thickness of the working layer in the cells, there is a shift in the maxima of the spectra in the long-wave direction. Fig. 3, c shows that at constant thickness of the cell the change in the negative optical density is proportional to the concentration of water in the sample and takes place in accordance with the Lambert-Beer law. The graph of the position of the negative maxima

as a function of the layer thickness is identical with the l-λ_{max} curve (Fig. 2, b), i.e., with the change in the maxima of the positive spectra.

Besides water, various organic and inorganic substances were added to the furfural (benzene, glacial acetic acid, sodium or potassium chloride, anhydrous alkalis, etc.). In all cases positive or negative differential spectra were obtained, the maxima of which regularly shifted with a change in the thickness of the cells.

From a comparison of graphs a, b, and c (Fig. 3), it can be seen that $-D_{max}$ increases not with an increase but with a decrease in the thickness of the photometered layer. At first sight, this appears anomalous, but it must not be forgotten that we are considering differential spectra with negative values of the absorption. Generally the standard is more transparent (lighter) than the sample under investigation. In this case, conversely, anhydrous furfural (the standard) is "darker" than furfural containing water.

Symbols: 1) D_1 represents the positive density of a sample against the standard at cell thickness l_1, D_2 at $l_2, \ldots$, D_n at l_n; 2) D'_1 represents the negative absorption of a sample against the same standard at l_1, D'_2 at l_2, and D'_n at l_n, where $l_n > l_{n-1} \ldots > l_2 > l_1$ (Fig. 4).

The standard upon which the instrument is adjusted is lighter than the sample under investigation in the first case, while it is darker in the second case, and therefore on spectrophotometry the positions of the cell and the sample must be changed, i.e., the density of the standard relative to the sample investigated must actually be recorded. However, in both cases the sign of the absorption is considered only with respect to the standard. Consequently, in the second case negative values (–D') are obtained. However, the absolute magnitude of the optical density increases with an increase in the thickness of the cell ($l_1 \rightarrow l_n$) both for the positive and for the negative spectra. With a change in the thickness of the layer observed by $+\Delta l$, the

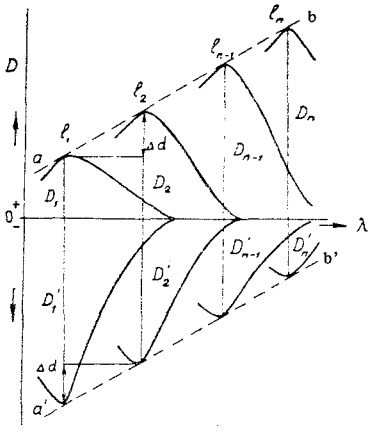


Fig. 4. Change in D_{max} of the differential spectra as a function of l at $l_n > l_{n-1} \ldots > l_2 > l_1$.

density increases by $+\Delta d$. In the first case, the total absorption rises (straight line ab): $D_2 = D_1 + \Delta d \ldots D_n = D_{n-1} + \Delta d$; and in the second case the negative absorption decreases (straight line a'b'): $-D'_2 = -D'_1 + \Delta d \ldots -D_n = D_{n-1} + \Delta d$. Consequently, in the upper series $D_n > D_{n-1} \ldots > D_2 > D_1$, and in the lower series $D'_1 > D'_2 \ldots > D'_{n-1} > D'_n$. In the limit, D tends

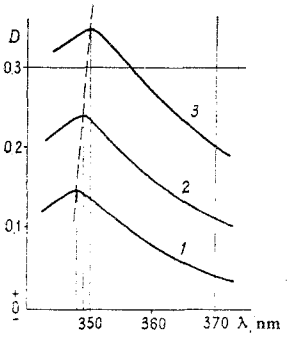


Fig. 5. Position of λ_{max} with a change in the content of oxidation products after heating furfural at 90° C with the passage of air through it: 1) 30 min; 2) 1 hr 30 min; 3) 2 hr 30 min.

to infinity and D' to zero, i.e., at very great layer thicknesses in the cell, when the influence of the "clarifying" additive can be neglected, the optical density of the sample under investigation becomes equal to the density of the standard. If tangents are drawn at the positions of the maxima (D_{max} and D'_{max}), the straight lines ab and a'b' which have the same slope to the axis of abscissas and which show the direction of the change in the optical density with a change in the thickness of the cells, are obtained. The scheme permits the following methodical rule to be put forward: the lower content of impurity in the furfural, the thinner must be the layer investigated in the case of negative spectra and, conversely, if the differential spectra are positive, the thickness of the cell must be as large as possible.

A small shift in the maximum is also observed at constant layer thickness with a change in the concentration of impurity in the furfural. It can be seen from Fig. 5 that in the oxidation of furfural with atmospheric oxygen there is a gradual accumulation of some substance with λ_{max} 349 ± 1 nm.

The general case of the dependence of λ_{max} on l is shown in Fig. 6. This graph of the movement of the peaks is typical for the differential spectra of furfural in the 320–380 nm region. With a change in the concentration of impurity in the furfural, the λ_{max} –l curve undergoes a proportional shift, the magnitude of which generally does not exceed 2 nm for the cases considered. This curve may be represented empirically by the equation [5]:

$$y = a^n .$$

By calculating several variants it has been found that, as applied to the present case,

$$l = a^{\lambda - \lambda_a},$$

where l is the thickness of the working layer in the cell, nm; λ is the wavelength nm; and a is a constant.

By solving the systems of equations, we find:

$$\lambda_0 = \frac{\lambda_2 \lg l_1 - \lambda_1 \lg l_2}{\lg l_1 - \lg l_2}.$$

At l_1 = 1.0 nm, log l_1 = 0, and $\lambda_0 = \lambda_1 = 372 \pm 1$ nm. Thus, λ_0 is a constant determining the position of the

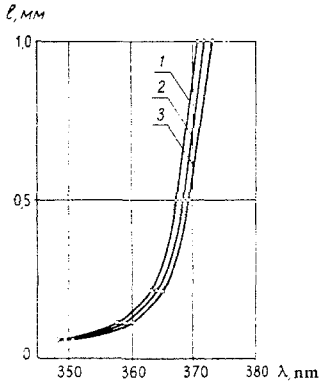


Fig. 6. Change in the l-λ_{max} curve with a change in the concentration (C) of impurities in furfural: 1) C_1; 2) C_2, etc., at $C_n > C_2 > C_1$.

curve on the wavelength scale at 1 = 1 nm. By solving further, we find:

$$l = 1.156^{\lambda - \lambda_0} \text{ or } \lambda = 15.9 \lg l + \lambda_0.$$

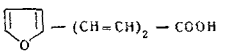
λ_0 is defind for a given concentration of impurities in furfural at l = 1 nm. The calculated shape of the curve agrees well with the experimental curve.

On the basis of an analysis of the experimental material that we have obtained, certain considerations can be expressed concerning the causes of the existence of maxima in the differential spectra of furfural in the 320–400 nm region.

The whole of the UV spectrum of furfural in water can be obtained only for its very dilute solutions (10^{-4} mole-%). It has two maxima (228 and 278 nm). With an increase in the concentration of furfural, the absorption rises to such an extent that measurement becomes impossible (Fig. 7, curves 2–4). At the same time, the descending branch of the spectral curve gradually shifts in the long-wave direction. Finally, for furfural without a solvent (curves 4–7), it appears as the visible spectrum of furfural which, however, has no characteristic points. With the changes taking place in furfural on autoxidation, the spectral curve shifts not only to the right but also upwards, which is regarded by a number of authors as an increase in the coloration of the furfural [2] or as an accumulation of resinous substances in it [1]. The dissolution of various organic or inorganic compounds in furfural also causes a change in the position of this curve (Fig. 1, a). Depending on the nature of the additive, it may be either positive (curves 2 and 3) or negative. However, by the usual photometry against water it is very difficult to detect the changes in the spectrum as furfural. The use of purified furfural as standard permits not only the nature of the impurity but, in individual cases, also its quantitative changes, to be established.

Of the substances added to furfural discussed above, the greatest interest is presented by formic acid and water, which are shown up by spectra with negative absorptions, and also by the colored products which increase the optical density of furfural. These substances are formed in furfural, and the study of their dynamics is necessary for a discussion of the process of autoxidation.

On the basis of the spectral characteristics of furan derivatives [6], it may be assumed that one of the substances responsible for absorption in the 320–380 nm region may be the dienic acid I and substances similar to it in structure, the formation of which have been postulated in a discussion of the mechanism of the autoxidation of furfural [7,8] but have not been shown experimentally.



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The deviation from the Lambert-Beer law indicates that the spectra obtained are composite, and the proposed method of differential spectrophotometry enables

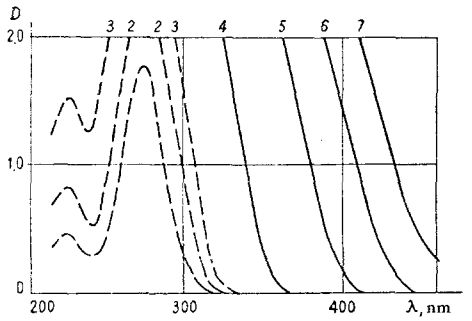

Fig. 7. Spectra of furfural against water. —— Solution in water with concentrations of furfural of: 1) $C_1 < 10^{-3}$%; 2) C_2, and so on, at $C_3 > C_2 > C_1$ and l = const. or $l_3 > l_2 > l_1$, C = const.; ---- furfural without a solvent; 4) l_4; 5) l_5, etc., at $l_7 > l_6 > l_5$, etc., at $l_7 > l_6 > l_5 > l_4$.

information to be obtained on the dynamics of a series of substances with similar natures formed in furfural.

REFERENCES

1. Yu. I. Khol'kin and G. N. Chenyaeva, Investigations of the Field of the Chemistry and Chemical Technology of Wood [in Russian], Moscow, p. 35, 1963.

2. T. E. Goldovskaya, V. G. Kul'nevich, and B. I. Shapovalov, Izv. VUZ. Pishch. tekhnol., 5, 96, 1962.

3. V. G. Kul'nevich and Yu. M. Shapiro, Izv. VUZ. Pishch. tekhnol., **3**, 50, 1967.

4. V. F. Barkovskii and L. I. Khurtova, ZhAKh, **20**, 912, 1965.

5. Handbook of Chemistry, Vol. 1 [in Russian], Goskhmizdat, Moscow-Leningrad, p. 113, 1962.

6. A. Gillam and E. Stern, Introduction to Electronic Absorption [Russian translation], IL, Moscow, p. 111, 1957.

7. I. Marcusson, Ber., **58**, 69, 1925.

8. A. P. Dunlop, The Furans, Vol. **5**, p. 381, 1953.

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