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DETERMINATION OF WATER IN FURFURAL BY INFRARED SPECTROSCOPY

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The IR absorption band at 5250 cm^{-1} is used to determine 0–5% water in furfural. The accuracy of the determination is not less than 5%. The method is suitable for any kind of furfural. The analytical results are unaffected by the presence of formic, acetic, and pyromucic acids, and methanol and ethanol.

Furfural is quite an unstable compound. Storage leads to auto-oxidation reactions, and formation and accumulation of peroxides, acids, and resins, and the optical density alters. According to contemporary views regarding the mechanism of auto-oxidation [1], water should also accumulate in the furfural. Even carefully purified furfural contains a small amount of impurities, i.e., it usually behaves as a multicomponent system of complex composition.

The wetness of furfural is an important characteristic quality. Several methods differing in principle have been put forward for determining the moisture [2]: azeotropic distillation of the water, manometric, refractometric, and other methods. However, the first is very laborious, the carbide method is complex and insufficiently sensitive, while the refractometric method can be used only on freshly distilled furfural of high purity. The results obtained by the last two methods are affected by peroxides and particularly by acids.

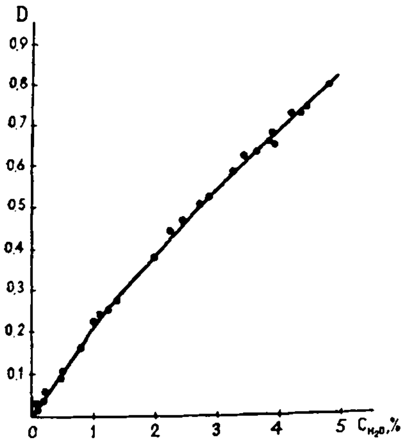

Fig. 1. Calibration curve for determining water in furfural.

IR spectroscopy is being extensively used to determine moisture in organic compounds. It is characterized by a high selectivity, and can be applied to complex multicomponent systems. 0.1–10% water in organic compounds can be determined by utilizing the water absorption bands at 1595, 3700, and 5200 cm^{-1} [3, 4]. Despite the universal applicability and selectivity of IR spectroscopy, an individual approach to each compound investigated is frequently necessary.

The compound vibration band at 5250 cm^{-1} was chosen for analyzing furfural, as a number of technical difficulties in carrying out the analysis disappear in that region. The spectra were determined with a single beam IKS-12 IR spectrometer, with a glass cell, and absorbing layer 1.5 mm thick. The water concentration range was 0.01–5.00%. The upper limit was determined by the solubility of water in furfural, which is temperature-dependent, so that when the water concentration was over 4.5%, attention had to be paid to the question of the homogeneity of the sample. If water separated from the furfural (turbidity), the sample could be slightly warmed, or diluted with a known amount of drier (0–2%) furfural, containing a known amount of water.

Filling the comparison cell with dry furfural greatly complicates the analysis, as drying furfural is laborious, and the results unreliable. Furfural changes appreciably when stored for a short time, and water can accumulate in it. The continuous absorption of furfural is increased. It is considerably simpler and more reliable to use a base line method in carrying out the analysis.

A calibration plot (Fig. 1) was constructed using standard samples prepared by introducing a known amount of water into furfural which had been carefully purified by Khol'kin's method [5], and twice redistilled in a vacuum. Dilution and determination of spectra were carried out immediately after distillation. It was shown that the plot for twice distilled furfural can be used for any furfural, whether commercial, oxidized, or even black and containing a lot of resin. The testing was done as follows: the water content of the specimen of furfural was determined by an IKS-12, a known amount of water then added, the total concentration calculated, and the analysis run again. Table 1 gives some of the experimental data, and from there it can be seen that the calculated moisture is in quite satisfactory agreement with that found spectroscopically. The relative error of a determination does not exceed 5%, i.e., is within the limits of accuracy of the instrument.

Furfural is difficult to dry without altering it. To check the absence of systematic error, samples prepared by mixing two specimens of different moisture content (as determined by IR spectroscopy) were prepared, and analyzed. Table 2 gives the results of the tests.

Table 1

Determination of Water Added to Furfural

Water content of the starting furfural, %	Water added, %	Water found, %		$\Delta C, (C_a - C_p)$, %	$\frac{\Delta C}{C_p} \cdot 100$, %
		C_p calculated	C_a spectroscopic		
Purified furfural					
2.30	1.45	3.75	3.70	−0.05	1.35
1.07	1.04	2.11	2.21	+0.10	4.54
0.80	0.48	1.28	1.32	+0.04	3.03
Commercial furfural (2nd kind)					
0.35	3.93	4.28	4.35	+0.07	1.61
0.35	1.83	2.18	2.20	+0.02	0.91
0.45	0.21	0.66	0.69	+0.03	4.35
0.45	0.42	0.87	0.82	−0.05	6.10
0.45	0.80	1.25	1.23	−0.02	1.63
0.32	2.44	2.76	2.68	−0.08	2.99
0.32	3.86	4.18	4.15	−0.03	0.72
2.68	1.87	4.55	4.60	+0.05	1.09
3.35	1.50	4.85	4.80	−0.05	1.04
Oxidized furfural					
0.51	2.36	2.87	2.92	+0.05	1.72
1.92	0.43	2.35	2.30	−0.05	2.17
1.92	0.96	2.88	2.87	−0.01	0.35
1.77	1.49	3.26	3.30	+0.04	1.21
1.77	0.52	2.29	2.07	−0.12	5.80
Highly oxidized (black) furfural					
2.02	0.50	2.52	2.52	0.00	0.00
0.43	2.80	3.23	3.17	−0.06	1.89
				Mean:	3.10

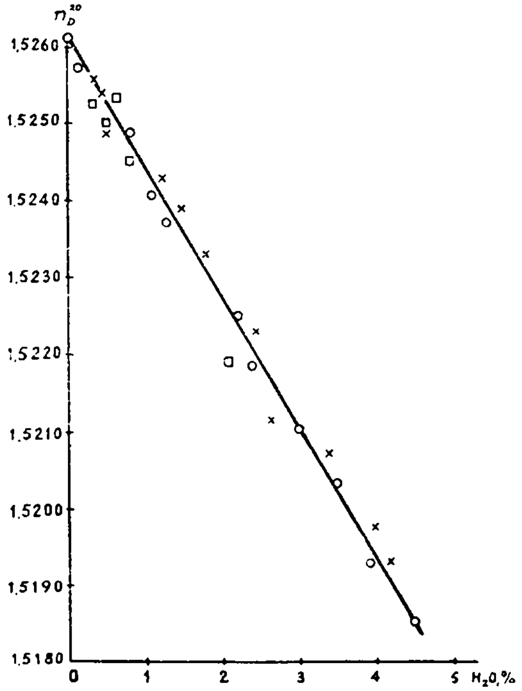

Fig. 2. Change in refractive index as a function of the water content of the furfural.
○—purified; ×—commercial (2nd kind)
□—technical (oxidized) furfural.

The effect of various impurities on the analytical results was checked by adding them. To samples of furfural with known water contents were added known excessive amounts (up to 3%) of formic, acetic or pyromucic acid, or of methanol or ethanol, either alone, or mixed together. In every case it was established that these impurities do not affect the accuracy of the determination of water in furfural.

Table 2

Analysis of Samples Obtained by Mixing

Water content in the starting furfural, %		Furfural taken for mixing, g		Water found in the mixture, %		$\frac{\Delta C \cdot 100}{C_p}$, %
C_1	C_2	Specimen 1	Specimen 2	C_p calculated	Spectroscopic	
			Purified furfural			
0.11	3.50	36.02	32.65	1.72	1.77	2.9
1.37	2.26	53.54	43.29	1.79	1.72	3.9
			Oxidized furfural			
2.28	4.35	50.00	50.00	3.32	3.40	2.4
1.77	3.45	38.05	61.24	2.80	2.76	1.5
0.51	3.30	54.52	47.28	1.81	1.77	2.3

Determinations of the refractive index of the furfural were carried out parallel to the moisture determinations, and the results plotted (Fig. 2). The points for technical furfural are so close to this plot, that one and the same plot can be used for analyzing both pure and technical furfural. However, the predominant clear shift of the points away from the plot indicates that, when analyzing technical furfural, it is better to make a separate plot. Large errors result by using the pure furfural graph for refractometric analysis of oxidized and commercial furfural.

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