Specific features of dielcometric water determination in alcohols used in synthesis and analysis of functional materials

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Water determination procedures have been developed for ethanol, methanol, and isopropanol using a special dielcometric cell. Metrological characteristics of titrimetric (under visual detection of end point) and dielcometric methods of water determination in those alcohols have been compared. The combination of both methods has been shown to provide a highly reliable analysis of alcohols at both very low and very high water content. The procedures can be used in extraction/dielcometric and extraction/titrimetric water determination in functional materials.

Разработаны методики определения влажности этанола, метанола и изопропанола при помощи специальной диэлькометрической ячейки. Проведен сравнительный анализ метрологических характеристик титриметрического (с визуальным детектированием конечной точки титрования) и диэлькометрического методов определения влажности этих спиртов. Показано, что сочетание обоих методов позволяет с высокой степенью надежности анализировать как очень сухие, так и очень влажные спирты. Эти методики могут быть использованы при экстракционно-диэлькометрическом или экстракционно-титриметрическом определении воды в функциональных материалах.

The development of novel materials selectively absorbing light in visible or IR spectral regions is among the most topical problems in the modern materials science. Such materials are used widely in IR radiation detection, in manufacturing of biological and chemical sensors, colorants (e.g., SiO_2–SiO_2/Au nanoparticles) [1]. To synthesize such materials using the sol-gel technique, the thoroughly dehydrated monobasic alcohols, as a rule those containing 1 to 3 carbon atoms, are necessary as the media.

Water is a permanent and often undesirable impurity in essentially all reagents used to manufacture various functional materials [2], that is why its content should be monitored. In most cases, the water content control methods are based on its extraction out of the material under analysis with an appropriate organic solvent [3], usually with an absolute alcohol. To that end, the water content in the alcohol should be controlled both prior to and after the extraction. The K.Fischer method used widely for that purpose, in spite of its high specificity and sensitivity, has some limitations and drawbacks, including its toxicity, necessity of daily determination of the reagent titer, time-consuming titration process [4]. The dielcometric method based on measurement of dielectric constants (ε) of organic water solutions is free of the above-mentioned drawbacks. Since most organic substances have considerably lower dielectric constants than water, it is expedient to use calibrating curves [5] and thus to increase the determination accuracy as compared to the K.Fischer method. However, as ε is a func-

tion of temperature, the measuring cell should be thermostated.

The aim of this work was to develop the dielcometric procedures for water concentration determination in alcohols used as extracting agents and media in the synthesis of dispersed materials.

Methanol (Merck, special purity grade), ethanol and isopropanol (both Synbias, chemical purity grade) were dehydrated using the standard technique (refluxing with calcium metal). The Fischer reagent, standard water solution in methanol, and the background dye (methylene blue) solution were prepared according to [6]. The titration with visual indication of the end point was carried out in an apparatus providing the reagent and sample protection against atmospheric humidity [7]. The dielcometric measurements were carried out using a E7-12 digital device (the measurement frequency 1 MHz, the signal amplitude 0.25 V; made in Belarus) in a home-made cell [8] placed in a TC-100/TC-65 dry air thermostat (made in Russia). The data obtained were processed according to [9] at the confidence probability 0.95. The following notations were used: n, the number of individual parallel measurements for a specific sample; f, the number of degrees of freedom; $\overline{C} \pm \Delta C$, the water concentration determined in the specific sample. The estimations of sampling dispersions were used preestablished from the multiple analysis results of samples with various water contents. The mentioned sampling dispersion values are better estimations of corresponding general dispersions than those obtained using small volume samplings [10]. The validity was checked using an independent method (the Fischer one). The t-criterion was used for comparison of the mean values from two samplings when the sampling dispersions differed insignificantly in the F-criterion; otherwise, the q-criterion (Duncan) [9].
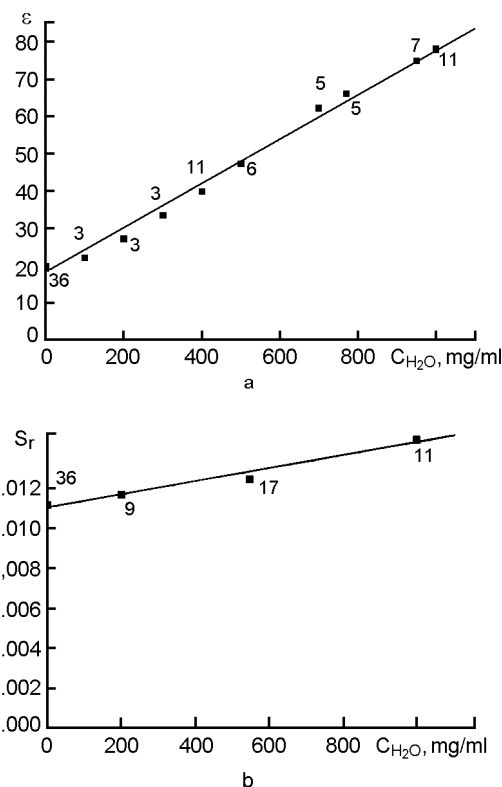

Fig. 1. Concentration dependences of ε (a, $R = 0.997$) and S_r (b, $R = 0.987$) for the dielcometric water determination in isopropanol at 20°C. The numbers near the experimental points indicate the number of freedom degrees.

The dielectric constant of the sample under analysis is an additive quantity at constant temperature and in the absence of chemical interaction between the components [11]. The measurements were made in the medium frequency range (1 MHz) where both low-frequency and high-frequency dispersions of dielectric constant are absent in the systems being studied [8].

The ε dependences on water concentration (C, mg/mL) for methanol, ethanol, and isopropanol are described satisfactorily by linear equation

Table 1. Coefficients in equations for concentration dependences of dielectric constant and relative standard deviation for various alcohols

Alcohol	t °C	ε				S_r			
		a	$\pm\Delta a$	b	$\pm\Delta b$	a'	$\pm\Delta a'$	b'	$\pm\Delta b'$
Methanol	18	34.3	0.1	0.0481	0.0004	0.00289	$6 \cdot 10^{-5}$	$3.1 \cdot 10^{-6}$	$1 \cdot 10^{-7}$
Ethanol	20	24.2	0.2	0.0568	0.0003	–	–	–	–
Ethanol	27	23.3	0.1	0.0529	0.0004	0.0035	0.0008	$1.8 \cdot 10^{-5}$	$2 \cdot 10^{-6}$
Isopropanol	20	18.4	0.5	0.059	0.001	0.0110	0.0002	$3.3 \cdot 10^{-6}$	$0.4 \cdot 10^{-6}$

$$\varepsilon = a + bC, \quad \varepsilon = f(C). \qquad (1)$$

The corresponding regression factors are presented in Table 1; the dependence for isopropanol is shown also in Fig. 1a.

Using the analytical archive data, the sampling standard deviations of the dielcometric water determination were estimated for a wide water concentration ranges in methanol (0.214 to 1000 mg/mL), ethanol (0.128 to 1000 mg/mL) and isopropanol (0.08 to 1000 mg/mL). The concentration dependences of S_r agree well with similar dependences presented in [12] and are described satisfactorily by the linear equation (2):

$$S_r = a' + b'C, \qquad (2)$$

where C is the water concentration in the alcohol.

For subsequent statistical estimations, S_r values corresponding to the pre-specified C ones were found proceeding from the established linear dependences. According to the linear relation statistics [9], the numbers of freedom degrees for the found S_r estimations are equal to $N-2$, where N is the total number of experiments used to determine the parameters of straight line (2). The coefficients for experimental $S_r = f(C)$ dependences for dielcometric water determination in the studied alcohols are presented in Table 1 (the dependence for isopropanol is shown in Fig. 1b).)

The concentration dependence of S_r is as a rule linear in the S_r-1/C coordinates. Perhaps the unusual shape of the standard deviation dependence on concentration (2) derived by us (its linearity in the S_r-C coordinates) is defined by the peculiarities of the dielectric cell capacity by the bridge method using the LCR digital device. Since the measured capacity value is proportional to ε, that capacity increases in parallel with the water concentration, the capacity measurement error growing in parallel with the sample conductivity. In the cases when S_r increases in parallel with the concentration of the component to be determined, the determination limit should be estimated for both minimum and maximum component concentration. In this case, the upper limit of the concentration is estimated as the maximum concentration value to which the random error $S_r = 0.3$ answers that is maximum admissible for a quantitative analytical procedure [13]. Since at the dielcometric water determination in alcohols containing
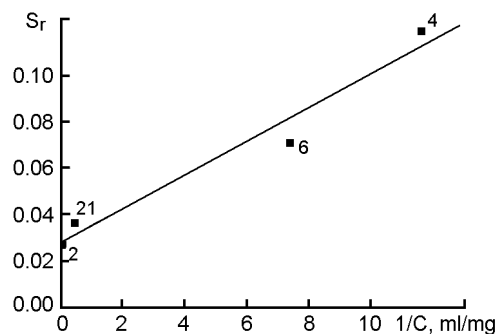

Fig. 2. Concentration dependences of S_r for the titrimetric water determination in isopropanol using the K.Fischer method. $R = 0.983$.

0 to 1000 mg/mL of water, the S_r varies within limits of 0.003 to 0.006 for methanol, of 0.004 to 0.02 for ethanol [8], and of 0.011 to 0.015 for isopropanol (i.e., $S_r<$ at the maximum water content), the developed procedure can be asserted to provide a highly reliable water determination in alcohols containing water in high concentrations. The lower determinable concentration limit for the dielcometric method was estimated in accordance with IUPAC guidelines [14]. To that end, the standard deviation value for the average measured result of difference analytical signal (S_b) for nearly blank samples (in our case, for nearly water-free alcohols) was found from the confidence interval ($\pm\Delta b$) values for angular coefficients (Table 1). The difference analytical signal exceeding S_b by a factor of 6 corresponds to the reliable detection limit C_{lim} [1] that is easy to calculate using the dependence (2) and data from Table 1.

It has been established before [8] that the concentration dependences of standard deviations for titrimetric water determination in the alcohols under study using the Fischer reagent are described satisfactorily by linear equations, namely, $S_r = 0.009 + 0.026\ (1/C_w)$ for methanol, $S_r = 0.05 + 0.0043\ (1/C_w)$ for ethanol, respectively. In this work, the concentration S_r dependence for titrimetric water determination in isopropanol (at water concentrations of 0.06 to 83.1 mg/mL) is shown to correspond the linear equation $S_r = 0.028(\pm0.007) + 0.0073(0.001)(1/C_w)$, see Fig. 2.

The lower concentration limit at titrimetric water determination in alcohols using the Fischer method was estimated by extrapolating the above concentration dependences to $S_r = 0.3$ [13]. In Table 2, shown are the estimated limiting potential for

Table 2. Comparison of water determination limits (C_{lim}) in alcohols using the dielcometric method and K.Fischer titration

No.	Sample	Water determination method	C_{lim}, mg/mL
1	Ethanol ($t = 20°$C)	Dielcometry	0.09
		Titration	0.02
2	Methanol ($t = 18°$C)	Dielcometry	0.12
		Titration	0.09
3	Isopropanol ($t = 20°$C)	Dielcometry	0.51
		Titration	0.03

Table 3. Comparison of water determination results by K.Fischer titration and dielcometry in alcohol samples

No.	Sample	Water determination method	Found, $\overline{C}\pm\Delta C$, mg/mL	n	S ($f = 10$)	Comparison of both averages in the Duncan criterion q (using the archive data)[**]
1	Ethanol ($t = 20°$C)	Titration	519±19	10	26	0.33<2.91 = q ($P = 0.95$
		Dielcometry	522±6	8	7	
2	Ethanol ($t = 27°$C)	Titration	283±10	10	14	2.74<2.83 = q ($P = 0.95$
		Dielcometry	281±2	6	2	
3	Methanol ($t = 18°$C)	Titration	43.4±0.3	10	0.4	2.74<2.83 = q ($P = 0.95$
		Dielcometry	43.3±0.1	6	0.1	
4	Isopropanol ($t = 20°$C)	Titration	22.0±0.4	10	0.6	1.14<2.80 = q ($P = 0.95$
		Dielcometry	22.1±0.3	6	0.2	

[*]The table presents the data with a smaller number of significant digits than those used to estimate the confidence intervals and to check the statistical hypotheses according to F-, t-, q- criteria.
[**]Dispersions are compared using F-criterion.
Sample No.1: 14.89>2.97 = F ($P = 0.95$, $f_1 = f_2 = 10$);
Sample No.2: 40.13>2.97 = F ($P = 0.95$, $f_1 = f_2 = 10$);
Sample No.3: 10.12>2.97 = F ($P = 0.95$, $f_1 = f_2 = 10$);
Sample No.4: 6.49>2.97 = F ($P = 0.95$, $f_1 = f_2 = 10$).

titrimetric Fischer method and dielcometric one. As is seen, the calculated lower limits for the dielcometric method are somewhat higher than for the titrimetric determination. For methanol and ethanol, the lower determination limits for both methods are of the same order while for isopropanol, that limit for dielcometric method exceeds that for titrimetric one more than by one decimal order.

At the other hand, when titrating 1 mL of alcohol containing, e.g., 17.5 mg/mL water with concentrated Fischer reagent with titer of 3.5 mg/mL, the volume of one burette for the Fischer reagent (5 mL) is consumed. Since both the decrease of the sample aliquot and increase of the Fischer reagent volume for the titration results in an increased analysis error, it is inexpedient to analyze the samples with higher water concentration using the titrimetric method. The dielcometric method is free of such limitations, because it provides, as it has been shown above, a high accuracy of water determination in alcohols at water concentrations up to 100 %.

The calibration of dielcometric determinations against the Fischer method has shown that the water content found by both methods differs insignificantly from the introduced one in the q-criterion, see Table 3.

Thus, the analytical procedures have been developed for water determination in methanol, ethanol, and isopropanol, that can be used for analytical control of functional materials. Metrological characteristics of titrimetric and dielcometric water concentration measurements in those alcohols have been compared.

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Особливості діелькометричного визначення води у спиртах, що використовуються для синтезу та аналізу функціональних матеріалів

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Розроблено методики визначення вологості етанолу, метанолу та ізопропанолу з застосуванням спеціальної діелькометричної комірки. Проведено порівняльний аналіз метрологічних характеристик титриметричного (з візуальним детектуванням кінцевої точки титрування) та діелькометричного методів визначення вологості цих спиртів. Показано, що комбінація обох методів дозволяє з високою надійністю аналізувати як дуже сухі, так і дуже вологі спирти. Ці методики можуть бути застосовані при екстракційно-діелькометричному або екстракційно-титриметричному визначенні води у функціональних матеріалах.