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RECOMMENDED METHODS FOR THE  
PURIFICATION OF SOLVENTS AND  
TESTS FOR IMPURITIES

1-PROPANOL, 2-PROPANOL, AND  
2-METHYL-2-PROPANOL

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# Recommended methods for the purification of solvents and tests for impurities: 1-propanol, 2-propanol, and 2-methyl-2-propanol

**Abstract** - Specifications for commercially available solvents, the relevant physicochemical properties, and key solvent properties are given for the three water-soluble 3- and 4- carbon alcohols. The procedures for their purification include the removal of water and of organic contaminants. Methods for the determination of these and of metal impurities in the alcohols are presented.

## INTRODUCTION

The water-soluble 3- and 4- carbon alcohols: 1-propanol, 2-propanol (isopropyl alcohol), and 2-methyl-2-propanol (t-butyl alcohol, trimethyl carbinol) have some applications in the studies of solvent effects on electrolytes. Together with methanol and ethanol they form a set of solvents in which the hydrogen atoms of water and of the methyl group of methanol are systematically substituted with methyl groups. This, in turn, permits a systematic study of inductive effects in the solvent on ion solvation, with general implications in electrochemistry.

The three alcohols dealt with in the present report are manufactured commercially by hydration of the pertinent olefinic hydrocarbons. Hydration of propene produces 1-propanol; dissolution of propene in sulfuric acid and subsequent hydrolysis of the sulfate esters produces 2-propanol; and hydration of 2-methylpropene in dilute sulfuric acid produces 2-methyl-2-propanol. Distillation of ternary heteroazeotropes is used to remove the water from the initially obtained alcohol-water azeotropes (72% alcohol in the case of 1-propanol, 92% alcohol in the case of 2-propanol). The major impurities in the high grade commercial solvents are the lower alcohols - allyl alcohol (2-propen-1-ol) was in the past a troublesome impurity in 1-propanol - oxidation products such as aldehydes and ketones, and, of course, water. The American Chemical Society's publication "Reagent Chemicals" (ref. 1) has specifications only of 2-propanol and 2-methyl-2-propanol, but the specifications of several manufacturers, see Tables 1, 2, and 3, present the levels of purity to be expected for the best commercial solvents.

The physical and thermodynamic properties of these solvents have recently been critically reviewed (ref. 2). Selected other properties are given in books dealing with organic solvents (ref. 3), with ion solvation (ref. 4), and elsewhere. Values for selected properties of the alcohols dealt with here are presented in Table 4.

Whereas the two isomeric propanols have low freezing temperatures, and are similar in this respect to methanol and ethanol, 2-methyl-2-propanol freezes just above room temperature, i.e., just above the standard temperature of 298.15 K for reported thermodynamic data. It was, therefore, proposed as a cryoscopic solvent (refs. 11, 12), although its practical utilization for this purpose is beset with difficulties, due to its marked hygroscopic nature.

The two propanols and 2-methyl-2-propanol are relatively innocuous solvents: 1-propanol has less irritating effects than most other industrial solvents, whereas 2-propanol and 2-methyl-2-propanol have only slight irritating and narcotic effects when inhaled. The threshold limits are 200 ppm or 490 mg m<sup>-3</sup> for 1-propanol, 400 ppm for 2-propanol, and 100 ppm or 300 mg m<sup>-3</sup> for 2-methyl-2-propanol, and no ill effects are observable for non-prolonged skin contact (ref. 3).

## STRUCTURE OF THE LIQUIDS

The two propanols and 2-methyl-2-propanol are extensively associated through hydrogen bonding like the lower two alcohols, methanol and ethanol (ref. 13). For 2-methyl-2-propanol the structure of the liquid was actually investigated by means of X-ray diffraction (ref. 14). Each molecule was found to be hydrogen bonded to two neighboring molecules, on the average, in a chain-like structure, but a complete description of the structure could not be given.

TABLE 1. Examples of specification of commercially available 1-propanol

	Merck <sup>a</sup>	Fluka <sup>b</sup>	Baker <sup>c</sup>	B.D.H. <sup>d</sup>
<u>Impurity</u>	<u>Maximal content in ppm</u>			
Free acid, as C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	100	10		20
Free base				5
Methanol, ethanol	500	1000		10
2-propanol	500	1000		500
Aldehydes, as C <sub>2</sub> H <sub>5</sub> CHO	100	50		
Ketones, as CH <sub>3</sub> COCH <sub>3</sub>	100	500		20
Water	500	1000	1000	1500
Nonvolatile substances	10	10	100	10
Carbonizable substances	pass test <sup>e</sup>			
Chloride, sulfate				1
Light metals (Na)		5		0.25
Heavy metals (except Fe)	0.1	0.1		0.05
Fe	0.1	0.5		0.05
<u>Other specifications</u>				
Boiling range <sup>f</sup> , °C		1	2	2
% Transmittance <sup>g</sup>				
at 210 nm		10		
at 240 nm		79		
at 300 nm		95		

<sup>a</sup>GR grade from 1984 catalog and Merck Standards for guaranteed purity reagent.

<sup>b</sup>Fluka specifications for puriss p.a. reagent.

<sup>c</sup>J.T. Baker specifications for "Baker Analyzed" reagent.

<sup>d</sup>B.D.H. "Aristar" specifications.

<sup>e</sup>No darkening after 20 min. when 0.4 mL of solvent is added to 3.6 mL of 70% sulfuric acid.

<sup>f</sup>Bracketing the normal boiling temperature.

<sup>g</sup>Minimal light transmittance in 1 cm light-path cells.

TABLE 2. Examples of specifications for commercially available 2-propanol

	ACS <sup>h</sup>	Merck <sup>a</sup>	Fluka <sup>b</sup>	Baker <sup>c</sup>	B.D.H. <sup>d</sup>
<u>Impurity</u>	<u>Maximal Content in ppm</u>				
Free acid, as C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H		20	20		20
Free base					5
Methanol		1000			
Aldehydes (as CH <sub>2</sub> O)		30			
Ketones, as CH <sub>3</sub> COCH <sub>3</sub>		100			10
Water	2000	1000	500	300	1000
Nonvolatile substances	10	10	100	3	10
Carbonizable substances	pass test pass test				
Chloride, sulfate					1
Light metals			0.5		0.2
Heavy metals (except Fe)		0.01	0.05		0.0005
Fe		0.1	0.05		0.05
<u>Other specifications</u>					
Boiling range <sup>f</sup> , °C	1		2	1	1
% Transmittance <sup>g</sup>					
at 210 nm	10	25		10	40
at 220 nm	40	55	35	40	65
at 230 nm	63	75	75	63	80
at 240 nm			90		88
at 250 nm	}83	95	95	}83	95
at ≥ 260 nm	91	98		91	98

<sup>a</sup> to <sup>g</sup>: see Table 1; <sup>h</sup>Ref. 1.

TABLE 3. Examples of specifications for commercially available 2-methyl-2-propanol

	ACS <sup>e</sup>	Merck <sup>a</sup>	Fluka <sup>b</sup>	Baker <sup>c</sup>	B.D.H. <sup>d</sup>
<u>Impurity</u>	<u>Maximal content in ppm</u>				
Free acid	30	10			30
Free base	10				
Ketones					100
Water		1000	1500		5000
Nonvolatile substances	50	10	100	50	10
Heavy metals (except Fe)		0.1	0.1		0.5
Fe			0.5		0.5
<u>Other specifications</u>					
Melting range <sup>g</sup> , °C	0.7	1.0	1.5	1.5	1.5
Boiling range <sup>f</sup> , °C	1.0		1.0		1.0

a - d, f: see Table 1; e Ref. 1;

g Below the melting temperature of the pure substance.

TABLE 4. Selected properties of 1-, 2-, and 2-methyl-2-propanols

Property	1-Propanol	2-Propanol	2-Methyl- 2-propanol	Ref.
Molar mass, $M/\text{kg mol}^{-1}$	0.060097	0.060097	0.0074124	
Freezing temperature, $t_m/^\circ\text{C}$	-126.2	-87.9	25.7	2
Boiling temperature, $t_b/^\circ\text{C}$ , at 0.101325 MPa	97.20	82.26	82.42	2
Flash point, $t_{fl}/^\circ\text{C}$	25	12	11	3
Density, $\rho/\text{kg dm}^{-3}$ , at 25°C	0.79975	0.78126	0.7812 <sup>a</sup>	2
Thermal expansivity, isobaric, $\alpha_p/K^{-1}$ , at 25°C	$1.007 \times 10^{-3}$	$1.082 \times 10^{-3}$	$1.39 \times 10^{-3a}$	3
Compressibility, isothermal	$9.70 \times 10^{-10}$	$11.29 \times 10^{-10}$	$10.82 \times 10^{-10a}$	5
Surface tension, $\gamma/N \text{ m}^{-1}$ , at 25°C	0.0233	0.0212	0.0201 <sup>a</sup>	3
Dynamic viscosity, $\eta/\text{Pa}\cdot\text{s}$ , at 25°C	1.956	2.073	5.12 <sup>a</sup>	3
Vapor pressure, $p/\text{kPa}$ , at 25°C	2.79	6.03	5.60 <sup>a</sup>	2
Enthalpy of vaporization, $\Delta H^V/\text{kJ mol}^{-1}$ , at 25°C	47.53	45.40	46.61 <sup>a</sup>	2
	at $t_b$	41.76	39.79	2
Standard molar entropy, $S^\circ/\text{JK}^{-1} \text{ mol}^{-1}$ , at 25°C	194.6	180.6	192.9 <sup>a</sup>	2
Molar heat capacity, $c_p/\text{JK}^{-1} \text{ mol}^{-1}$ , at 25°C	141.0	150.9	220.1 <sup>a</sup>	2
Relative permittivity, $\epsilon$ , at 25°C	20.33	19.92	12.47 <sup>a</sup>	3
Angular dipole correlation parameter, $g$ , at 25°C	0.88	3.08	2.24	4 <sup>f</sup>
Solubility parameter, $\delta/\text{J}^{1/2} \text{ cm}^{-3/2}$	24.4	23.7	21.6	4 <sup>f</sup>
Volume susceptibility, $\chi_v/\text{cm}^3 \text{ mol}^{-1}$ , at 25°C	$-45.2 \times 10^{-6}$	$-46.7 \times 10^{-6}$	$-57.4 \times 10^{-6a}$	4
Refractive index, $n_D$ , at 25°C	1.38370	1.3752	1.3852 <sup>a</sup>	2
Electrolytic conductivity, $\kappa/\text{S cm}^{-1}$ , at 25°C	$9.17 \times 10^{-9b}$	$5.8 \times 10^{-8}$	$2.66 \times 10^{-8c}$	3
Dipole moment, $\mu/D$ <sup>d</sup>	3.09	1.66	1.66	3
Polarizability $\alpha/\text{m}^3 \cdot \text{molecule}$	$6.96 \times 10^{-30}$	$6.98 \times 10^{-30}$	$8.82 \times 10^{-30}$	4 <sup>f</sup>
Polarity index, Reichardt, $E_T/\text{kcal mol}^{-1}$ <sup>e</sup>	50.7	48.6	43.9	6
Polarity index, Kosower, $Z/\text{kcal mol}^{-1}$ <sup>e</sup>	78.3	76.2	71.3	7
Acceptor number, Gutmann, $\Delta N$		33.5		8
Donor number, Gutmann, $\Delta N/\text{kcal mol}^{-1}$ <sup>e</sup>	30	35	42	9
Polarity index Taft, $\pi^*$	0.52	0.48	0.41	10
Polarity power Taft, hydrogen bond donor, $\alpha$	0.78	0.76	0.68	10

<sup>a</sup> Supercooled at 25°C;

<sup>b</sup> at 18°C;

<sup>c</sup> at 27°C;

<sup>d</sup>  $D = 3.33564 \times 10^{-30} \text{ C}\cdot\text{m}$ ;

<sup>e</sup> 1 kcal = 4.184 kJ;

<sup>f</sup> calculated from other data in this Table.

Indirect information on the self-association of the alcohols is obtainable from the consideration of their thermodynamic and other properties. The angular correlation factor  $g$ , (see Table 4), is considerably higher than unity for the second and tertiary alcohols 2-propanol and 2-methyl-2-propanol, as is expected for liquids highly associated in a chain-like manner. Contrary to expectation, however,  $g = 0.88$  only for 1-propanol, which can be construed as indicating an antiparallel-type of association. The high values of Trouton's constant,  $13.3 < \Delta S/R < 13.6$  for all three alcohols (compared with an average of  $10.7 \pm 0.7$  for non-associated liquids), confirms the extensive self-association attributed to them (ref. 4). A recent evaluation of the vapor pressures and molar volumes of the alcohols, compared with isostructural hydrocarbons, also confirmed their extensive association and the scarcity of "free" OH-groups in them (ref. 15).

### KEY SOLVENT PROPERTIES

The three alcohols dealt with here, 1-propanol, 2-propanol, and 2-methyl-2-propanol, are miscible with water in all proportions at room temperature. They are highly polar solvents but with only moderately high solubility parameters  $\delta$  (see Table 4), so that many non-polar substances dissolve in them. Indeed, even aliphatic hydrocarbons, such as n-hexane, are completely miscible with them.

On the other hand, these alcohols are not particularly good solvents for many electrolytes, especially those with high lattice energies.

The two propanols and 2-methyl-2-propanol are hydrogen bond donors as protic solvents but have also moderately pronounced electron-pair donation capabilities. Therefore they solvate both anions and cations, but with the bulkier ones the solvation numbers are expected to be low. Their solvating power for ions is considerably less than that of water, the standard molar Gibbs free energies of transfer of 1:1 electrolytes from water to these alcohols being in the range of 30 to 50 kJ mol<sup>-1</sup>. Still, iodides on the one hand and lithium salts on the other are fairly soluble. The solubilities of several salts in 1-propanol and 2-propanol are presented in Table 5. The solubilities of only a few salts in 2-methyl-2-propanol have been reported. These include (in mol/dm<sup>3</sup> at 298.15K): (CH<sub>3</sub>)<sub>4</sub>NCl 0.0181, [(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>]<sub>3</sub>(C<sub>4</sub>H<sub>9</sub>)-NB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> 8x10<sup>-6</sup> (ref. 19), and KCN 0.0015 (ref. 20).

TABLE 5. Molar solubilities of some alkali metal-, ammonium- and tetra-alkylammonium salts in 1-propanol (1-PrOH) and 2-propanol (2-PrOH), mol/dm<sup>3</sup>, (at 298.15 K, ref. 16, unless otherwise noted)

	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Me <sub>4</sub> N <sup>+</sup>	Bu <sub>4</sub> N <sup>+</sup>
Cl <sup>-</sup> /1-PrOH	3.82 <sup>ab</sup>	0.00188	0.00065	0.00099	0.00276	0.0214		
2-PrOH		0.0127 <sup>a</sup>	0.00028 <sup>c</sup>				0.180 <sup>d</sup>	
Br <sup>-</sup> /1-PrOH		0.0353 <sup>a</sup>	0.00211	0.00220	0.00225	0.0431	0.00714	v.s.
2-PrOH		0.0099 <sup>a</sup>	0.00081 <sup>c</sup>					
I <sup>-</sup> /1-PrOH	3.55 <sup>ab</sup>	1.32	0.0214	0.0537		0.180	0.00057	0.335
2-PrOH			0.0087 <sup>c</sup>					
ClO <sub>4</sub> <sup>-</sup> /1-PrOH	5.78	0.297		0.00046	0.00020 <sup>a</sup>	0.0263	0.00024	0.0777
2-PrOH								
Ph <sub>4</sub> B <sup>-e</sup> /1-PrOH		0.840					0.00011	
2-PrOH			0.0001 <sup>d</sup>					

<sup>a</sup>Ref. 17; <sup>b</sup>Molal solubility (mol/kg solvent); <sup>c</sup>Ref. 18; <sup>d</sup>Ref. 19; <sup>e</sup>Ph<sub>4</sub>B<sup>-e</sup> ≡ (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B<sup>-</sup>.

Due to the comparatively low relative permittivities of the alcohols under discussion (see Table 4), all electrolytes are expected to be extensively ion-paired in these solvents: at concentrations above a few millimolar. Some electrolytes, such as the hydrohalic acids or those among the salts presented in Table 5 that have been mentioned above, are sufficiently soluble to be affected by this association. The ion pairing is manifested in such properties of the electrolyte solutions as the conductivities (see, e.g., ref. 19), the activity coefficients (ref. 21) and the apparent molar volumes (ref. 22).

The solubility products of the silver halides AgX are of interest, since the silver-silver halide couple is often used as a reference electrode. The values of  $pK_{-sp} = -\log[Ag^+][X^-]$  on the molar scale is 298.15 K are shown in Table 6.

TABLE 6. The  $pK_{sp}$  values of silver halides at 298.15K

Solvent	AgCl	AgBr	AgI
H <sub>2</sub> O	9.753 <sup>a</sup>	12.27 <sup>a</sup>	16.07 <sup>a</sup>
1-propanol	14.36±0.06 <sup>b</sup>	16.24±0.10 <sup>b</sup>	19.38±0.10 <sup>b</sup> (19.54±0.05 <sup>c</sup> )
2-propanol			19.99±0.08 <sup>c</sup>
2-methyl-2-propanol			

<sup>a</sup>From the standard Gibbs free energies of formation of the salts and ions (ref. 23);

<sup>b</sup>J. Nedoma, *Chem. Listy*, **65**, 71 (1971);

<sup>c</sup>N.A. Kazaryan, L.N. Bukova, and N.S. Chernova, *Zh. Obshch. Khim.*, **47**, 969 (1977).

TABLE 7. The Acidity and basicity of the alcohols at 298.15 K

Constant	1-propanol	2-propanol	2-methyl-2-propanol
$-pK_a$ (ion product)	19.32 <sup>a</sup>	20.50 <sup>a</sup>	28.5 <sup>b</sup>
$\log \frac{K}{K_w}(\text{ROH} + \text{H}_3\text{O}^+ = \text{ROH}_2^+ + \text{H}_2\text{O})$		0.74 <sup>c</sup>	0.80 <sup>c</sup>

<sup>a</sup>Ref. 21

<sup>b</sup>I.M. Kolthoff and M.K. Chantooni, Jr., *Anal. Chem.*, **51**, 1301 (1979);

<sup>c</sup>W. Reeve, C.M. Erikson, and P.F. Aluotto, *Can. J. Chem.*, **57**, 2747 (1979).

The alcohols dealt with here are weaker acids than water. Values of the autoionization constant,  $pK_{a1} = -\log[\text{ROH}_2^+][\text{RO}^-]$ , and of the acidity relative to water  $\log \frac{K}{K_w}(\text{ROH} + \text{H}_3\text{O}^+ = \text{ROH}_2^+ + \text{H}_2\text{O})$  on the molar scale at 298.1 K are recorded in Table 7.

## PURIFICATION OF 1-PROPANOL

In the past 2-propen-1-ol (allyl alcohol) was a major contaminant in commercial 1-propanol, and its removal was by bromination and fractional distillation. The propionaldehyde also formed in the bromination was removed by the formation of the 2,4-dinitrophenylhydrazone (ref. 24). Another major impurity, 2-butanol, was removed by means of fractional distillation (ref. 25). In currently available 1-propanol of the highest grades these impurities are no longer of importance, see Table 1. For electrochemical purposes water is practically the only obnoxious impurity. The solvent purified as described below should also meet the standards demanded for conductivity (ref. 26), thermodynamic (ref. 25) and density (ref. 24) measurements.

### Procedure I (removal of water)

- Step 1. Reflux for 4 hr over freshly ignited calcium oxide (ref. 27), or 2 h over magnesium ribbon, activated by iodine (refs. 24, 28).
- Step 2. Fractionally distill twice with a glass column packed with glass rings having at least 50 theoretical plates (ref. 29) or a length of 1.2 m (ref. 25). Collect the middle fraction within a boiling range of 0.2 K (ref. 25).
- Step 3. Store over calcium hydride under nitrogen (ref. 29). The purity determined gas-chromatographically of 1-propanol dried essentially in this manner was 99.94% (ref. 29). The nature of the remaining impurities (methanol, ethanol, 2-propanol, water) was not reported, but it may be suspected that of the 600 ppm impurities a major fraction is still water.
- Step 4. For further drying, down to 20 ppm water, passage through a column of pre-dried (3 h at 300°C in a current of nitrogen) molecular sieves of type-A in the potassium form was reported to be effective (ref. 30).

## PURIFICATION OF 2-PROPANOL

The purification of 2-propanol follows substantially the same procedure as described above for 1-propanol (see also refs. 28-32). No special impurities have been reported, and the specifications in Table 2 pertain to a somewhat purer solvent of the highest grade commercially available than those in Table 1 for 1-propanol. The solvent resulting after Step 3 contains only 400 ppm of total impurities (ref. 29). Drying with  $K^+$  A-type molecular sieves in Step 4 is expected to reduce the water content to the same level as for 1-propanol (ref. 30).

## PURIFICATION OF 2-METHYL-2-PROPANOL

The purification of 2-methyl-2-propanol differs from that of the propanols described above in that additionally to fractional distillation purification by recrystallization is also possible. The high degree of purity required for the use of 2-methyl-2-propanol as a cryoscopic solvent (refs. 11, 12) is very difficult to obtain, due to the hygroscopicity of the substance. One tenth of a mole % of impurity (mainly water) reduces the freezing point by 0.1056 K (ref. 29) from that of the purest material ever produced and recorded (ref. 33): 298.813 K. The latter could be attained only after fractional recrystallization in a sealed vessel, without exposure to the atmosphere, and by keeping the substance over calcium hydride.

For all other purposes, 2-methyl-2-propanol can be purified by the same procedure presented above for 1-propanol. The variant drying method of distilling over sodium (ref. 31) or calcium (ref. 34) did not produce a material with as high a freezing point as the solvent purified according to the method in ref. 29, which is substantially the same as recommended here for 1-propanol (Steps 1 to 3). The variant of refluxing the solvent for 24 h over calcium hydride, distilling, and redistilling of the central fraction from benzoic acid was found (ref. 3) to reduce the acidity to  $< 2$  ppm and the water content to  $< 50$  ppm.

## DETERMINATION OF THE IMPURITIES

Metal impurities in the alcohols are determined by flame spectrophotometry for the light ones ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ , see ref. 36) and by atomic absorption (eventually after preconcentration by slow evaporation, see ref. 37) for the heavy metals. Flameless atomic absorption with a graphite furnace and a tantalum boat, anodic stripping voltammetry and cathode ray polarography (ref. 38), or X-ray fluorescence after preconcentration of the metal impurities, as in the recommendations for methanol and ethanol (ref. 13), can also be used for the present set of alcohols.

Organic impurities are commonly determined by gas chromatography. The generally applicable procedure calls for a stationary phase made of 67% polyethylene glycol 400 and 33% bis-(2-ethylhexyl) sebacate, applied at 15% on silanized kieselguhr, a working temperature of 60°C, and a flame ionization detector (ref. 38) or tetrakis(N-2-hydroxyethylene diamine), applied at 10% on Celite, and a working temperature of 75°C (ref. 29). Other stationary phases and conditions have also been described for the gas-chromatographic determination of organic impurities (refs. 39,40). Carbonyl-group containing impurities, i.e., aldehydes and ketones, can be determined by direct current polarography (ref. 38). Certain alcohol impurities can be detected by means of a color change from yellow to orange or red, when 0.3 mL 2M NaOH + 1.2 mL diazotized sulfanilic acid are added to 1 mL of the alcohol to be examined. The method detects  $\geq 0.1\%$  1-propanol in 2-propanol and  $\geq 0.08\%$  1-butanol or  $\geq 0.8\%$  2-methyl-1-propanol in 2-methyl-2-propanol (ref. 41).

Water as an impurity in the alcohols is generally determined by Karl-Fischer titration. Sensitivities of 5 ppm for the coulometric implementation of this method were claimed (ref. 42). Low concentrations of water (even traces) were said to be determinable by the measurement of the UV absorption peak of the Dimroth and Reichardt betain 30 (ref. 6), the wavelength of which depends on the water content of the alcohol according to a calibration formula, given explicitly for 2-methyl-2-propanol, but said, with changed parameters, to apply also to the other solvents (ref. 43).

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