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СТАНДАРТНЫЕ ОБРАЗЦЫ В ИЗМЕРЕНИЯХ И ТЕХНОЛОГИЯХ

REFERENCE MATERIALS IN MEASUREMENT AND TECHNOLOGY

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DEVELOPMENT OF REFERENCE MATERIALS OF VOLATILE COMPOUNDS IN ALCOHOL PRODUCTION

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The standards for quality and safety control of alcohol production [1-5] prescribe determination of the following volatile compounds: acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, isobutyl alcohol, n-butanol, isoamyl alcohol. Results of the analysis are expressed in milligrams per liter (mg/L) of absolute alcohol (AA). In the CIS, the analysis is performed by External Standard (ES) method. In all other countries the analysis is calculated by the Internal Standard (IS) method. 1-pentanol and 2-pentanol are most commonly used as IS. This method ensures high data reliability. However, the procedure of introducing of an internal standard substance in the sample at the level of some ppm requires a high level of laboratory technicians, performing analyses. It was proposed [6-8] to use ethanol as IS for the analysis of alcohol production. The concentration of ethanol in this production can vary from 96% to 15%. The concentration of impurities lies within the range from 30% for the intermediate alcohol production to units of ppm in rectified alcohol. As a result, the signals from ethanol and from impurities should be registered in a linear range [9]. Nowadays, the testing laboratories are equipped with modern instrumentation for the analysis of alcohol-containing production. These current-technology gas chromatographs have a linear range of registration of seven orders of magnitude that fully obeys the above requirement. Analysis of alcohol production in this case consists in the traditional procedure of finding the relative ratios of the detector response (*Relative Response Factors - RRF*) of analysed impurities with respect to ethanol by standard solutions and then the subsequent use of these coefficients in the calculation of concentration of impurities. It should be noted that for modern chromatographs coefficients *RRF* are enough stable and can be tabulated.

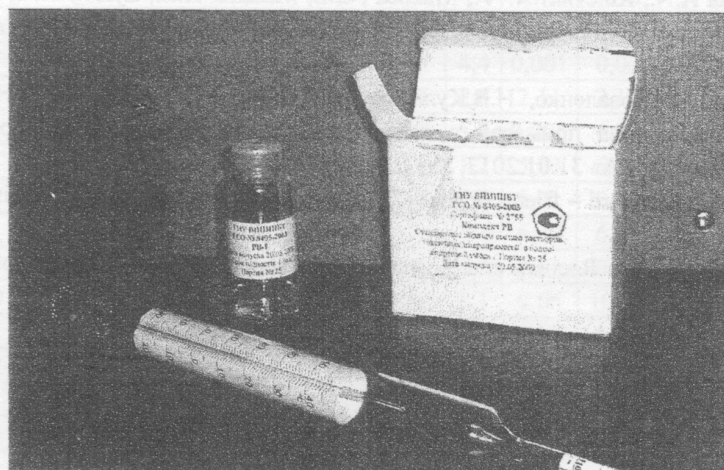


Figure 1. Hydrometer ASP-1 and GSO-8405 in a 15 ml vial

In the CIS, determination of the real alcohol strength by volume in alcohol production, in practice, usually is carried out with a hydrometer or pycnometer according to GOST 3639-79. However, this method can be only applied to binary water-ethanol mixtures. Using a pycnometer or a hydrometer one can directly measure the value of density of the tested solution due to the concentration of an anhydrous alcohol-containing part of the sample and the concentration of water [10]. Having significant concentrations of organic compounds in some alcohol production, such as alcohol and distillery waste production, this leads to the significant contribution of these compounds in density of alcohol-containing sample. As a result, the direct calculation of the real alcohol strength by volume (of ethanol) in accordance with GOST 3639-79 for

such alcohol production gives the value of the total content of all spirits or so-called «visible» strength. The latter may differ significantly from the real one. Using incorrectly calculated real alcohol strength by volume also leads to incorrect results of determining the quantities of volatile organic components in the alcohol-containing production according to GOST R 52363-2005, expressed in milligrams per liter of absolute alcohol.

Let us note that to measure the real alcohol strength by volume of reference materials GSO-8405 in 15 ml vial according to GOST 3639-79 with a hydrometer ASP-1 is not possible. Simply, the working submersible volume of this hydrometer exceeds 100 ml. As a consequence, the reference materials GSO 8405 (see photo of them together with a hydrometer ASP-1 in Fig. 1) can not be used as reference materials for verifying the correctness of the measurements performed in accordance with GOST R 51698-2000. Thus, they can not match the status of state certified reference materials.

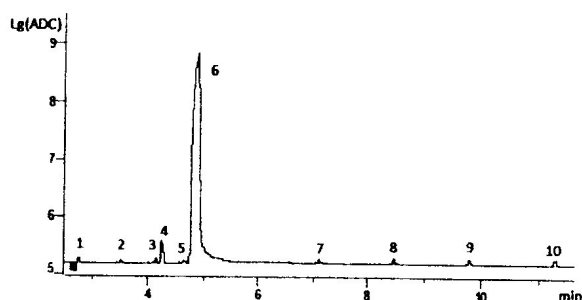


Fig. 2. Typical chromatogram of the standard water-ethanol solution (4% and 96%).

- 1 - acetaldehyde, 2 - methyl acetate, 3 - ethyl acetate, 4 - methanol, 5 - 2-propanol, 6 - ethanol, 7 - 1-propanol, 8 - isobutyl alcohol, 9 - n-butanol, 10 - isoamyl alcohol

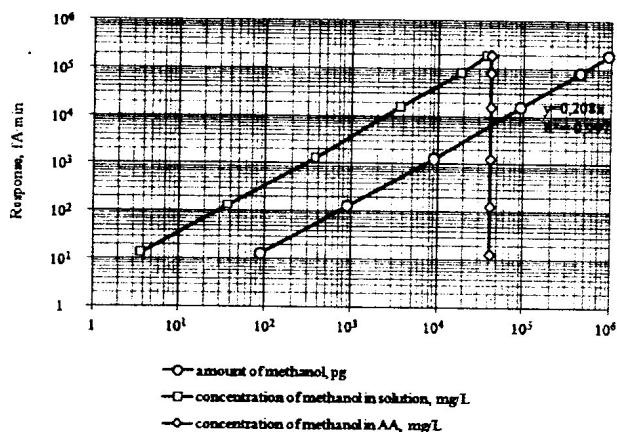


Fig. 3. The dependence of the detector response and the value of measured concentration for methanol

Let us define [6-8] values of volatile organic compounds in waterless parts of the sample. Then the correct calculation of the measured value of sample density in accordance with GOST 3639-79 allows to determine accurately the content of ethanol in alcohol-containing product [6-8].

To evaluate the metrology parameters of the proposed method, it was planned and carried out a series of exercises. Accuracy was estimated by precision factors (standard deviation of repeatability and standard deviation of intermediate precision) and accuracy rates (laboratory bias). Design of exercises and analysis of results on the evaluation of intermediate precision were carried out in accordance with ISO 5725-2-2002. Correctness (laboratory bias) was calculated according to ISO 5725-4-2002.

Analyses on method validation were carried out in the Laboratory of Analytical Research from Research Institute for Nuclear Problems of Belarusian State University on gas chromatograph Crystal-5000 equipped with FID. All individual standard compounds were purchased from Sigma-Fluka-Aldrich (Germany). The standard solutions for calibration and sample solutions were prepared by adding the individual standard compounds to the ethanol-water mixture (96:4) by gravimetric method.

A typical chromatogram of standard solutions used is represented on a logarithmic scale in Fig. 2. Eight standard ethanol-water (96:4) solutions of volatile compounds (SS-1 – SS-8) were prepared gravimetrically according to ASTM D 4307 recommendations. The initial standard solution SS-1 was prepared by adding the individual compounds to high-grade ethanol. A 100-ml glass-stoppered and «KERN ABS 220-4» analytical balance with a margin error measurements not worse than 0,2 mg were used for preparation of the initial standard solution, SS-1, with a mass concentration of methanol of 20000 mg/L (AA) and a mass concentration of all other defined components of 2000 mg/L (AA). Fifty millilitres of rectified ethyl alcohol from food raw materials «Kryshtal super - luxury» (Minsk-Kristall Winery and Distillery Plant, Belarus) was added into the flask and weighed. Then 2,5 ml of methanol and 0,25 ml of each of the other individual compounds were added into the flask. The exact weight of each added compound was recorded. Then rectified ethyl alcohol was added up to the label. In calculations, it was considered that the following impurities were present in the initial ethanol (rectified ethyl alcohol): acetaldehyde – 0,162 mg/L (AA); methanol – 2,53 mg/L (AA); 2-propanol – 1,35 mg/L. Subsequent standard solutions, SS-2 – SS-8, were prepared by adding SS-1 to high-grade ethanol in the following ratios: for SS-2 – 1 part SS-1 to 3 parts ethanol, for SS-3 – the ratio was 1:19; for SS-4 – 1:200; for SS-4 – 3:1000; for SS-6 – 1:4000; and for

SS-7 – 1:10000. The solution SS-8 was obtained by dilution of solution SS-3 with ethanol in proportion 1:100.

Calculated concentrations C_{st} and standard uncertainties $u(C_{st})$ of analyzed volatile compounds in the prepared standard solutions are presented in Table 1. Here are the experimentally measured values of concentrations C_{exp} , the values of standard deviation of intermediate precision $S_{(t)}$, expressed in mg per litre of absolute alcohol. The relative bias Δ between the experimentally measured values C_{exp} and the values of concentrations C_{st} , assigned by preparation of the standard solution by gravimetric method, as well as the relative standard uncertainty u are expressed as a percent. The analysis of the experimental data presented in Table 1 shows that the value of relative uncertainty u in the determination of the impurity concentration in experiments in the whole range of concentrations for all eight examined impurities does not exceed 10%.

Experimental data for methanol is presented in Fig. 3. For the rest of the components we have similar graphs. There are three lines in Fig. 3. The first one is the detector response versus the amount of the compound. The second and the third ones are the detector response versus the concentration of the compound, expressed in mg/L of solution and in mg/L (AA). A corresponding linear dependence $y = a \cdot x$ with correlation coefficient R^2 , ranging from 0.996 to 0.999, is added in figure. One can see that even after dilution with water in the ratio 1:999, the difference between the measured concentrations of all compounds and their values calculated using the gravimetric method does not exceed 7.7%. It is evident that, when the sample is diluted with water in 1000 times, proposed method gives good results because of the concentration of test component based on 1 liter of absolute alcohol is obtained constant even when the range of the detector response for methanol and ethanol is equal to 10 000 times.

Thousands of analytical and testing laboratories all over the world carry out gas chromatographic analysis of volatile compounds in spirit drinks. Their employees may validate our new method in actual practice, making sure its simplicity, accessibility and effectiveness in everyday practice. The obtained results show the possibility of developing a new international standard of measurement procedure, which will allow to increase the data accuracy and will considerably simplify the measurement procedure.

Results of validation of the proposed new method for the analysis and the project of production on its basis the reference materials of volatile compounds in the alcohol and alcohol-containing production, expressed in milligrams per liter of absolute alcohol, were presented at the Visiting Session of the General Meeting of Association of Analytical Centers «Analytica» the April 17, 2013 in Moscow. It was admitted expedient to take place in 3-4 quarters of 2013 inter-laboratory comparative tests of the new analytical method. Association of Analytical Centers «Analytica» is ready to act as a data provider of these comparative tests.

Results of validation of the cited new method of analysis allow us to propose to produce reference materials of volatile compounds in alcohol production with certified values of concentrations of the testing components, expressed in mg/L (AA), as it is required in all state and interstate standards. Implementation in practice of the method of direct determination of the volatile compounds of alcohol production would solve many existing problems. In particular, this removes the fundamental limits on the minimum size of a standard sample and increases the reliability of the results as well as simplifies the routine work of staff of testing laboratories.

We propose to produce reference materials containing the following volatile compounds: acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, isobutyl alcohol, n-butanol, isoamyl alcohol. For all compounds except methanol the ranges of concentration are the following: 0.7 – 2000 mg/L. Methanol concentration covers the range 3.0 – 20000 mg/L. All this corresponds to the possible concentrations of compounds in real samples and ensures correct device calibration in a wide range of measured concentrations.

Table. Comparison of calculated values of the mass concentrations of the test components and their standard uncertainties for the standard solutions with the experimentally measured values

№ of solution	acetaldehyde			methyl			ethyl			methanol		
	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %
1	1,23	1,23	-0,1	1,08	1,08	-0,5	1,13	1,10	-2,3	13,39	12,82	-4,2
	0,024	0,07	6,1	0,001	0,04	3,5	0,002	0,05	5,2	0,376	0,22	5,4
2	2,25	2,26	0,2	2,11	1,99	-5,4	2,20	2,08	-5,8	23,72	22,29	-6,0
	0,025	0,09	4,3	0,005	0,08	6,7	0,005	0,07	6,7	0,382	0,14	6,3
3	5,16	5,10	-1,0	5,04	4,90	-2,9	5,27	5,08	-3,5	53,15	51,28	-3,5
	0,03	0,10	2,2	0,01	0,08	3,3	0,01	0,11	4,1	0,38	0,19	3,6
4	6,44	6,25	-2,9	6,34	5,75	-9,2	6,62	6,16	-7,0	66,17	59,71	-9,8
	0,03	0,11	3,4	0,01	0,11	9,4	0,01	0,07	7,0	0,38	1,01	9,9
5	9,75	9,81	0,7	9,68	9,56	-1,2	10,11	10,01	-1,0	99,70	99,78	0,1
	0,03	0,31	3,4	0,01	0,26	3,0	0,01	0,22	2,4	0,39	0,55	0,7
6	96,65	94,06	-2,7	97,38	95,68	-1,7	101,8	101,1	-0,7	980,5	990,3	1,0
	0,15	1,44	3,1	0,12	1,77	2,6	0,13	1,57	1,7	0,85	1,86	1,0
7	506,0	486,8	-3,8	510,5	491,6	-3,7	533,5	520,7	-2,4	5129	5124	-0,1
	0,98	5,79	4,0	0,90	12,5	4,5	0,96	9,93	3,1	7,46	11,8	0,3
8	2085	2080	-0,2	2104	2113	0,4	2198	2202	0,2	21128	21130	0,0
	2,77	20,9	1,1	2,25	10,1	0,7	2,46	5,29	0,3	11,05	20,0	0,1

№ of solution	2-propanol			1-propanol			isobutyl alcohol			n-butanol			isoamyl alcohol		
	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %	C_{st} , $u(C_{st})$, mg/L	C_{exp} , $S_{(TO)}$, mg/L	Δ , u , %
1	2,45	2,55	4,0	1,13	1,15	1,8	1,08	1,08	-0,3	1,08	1,07	-0,7	1,12	1,08	-3,8
	0,20	0,07	9,6	0,001	0,07	6,3	0,001	0,05	4,4	0,001	0,07	6,3	0,001	0,06	7,0
2	3,50	3,58	2,2	2,21	2,30	3,8	2,11	2,17	2,6	2,11	2,19	4,0	2,19	2,11	-3,5
	0,20	0,10	6,8	0,005	0,10	5,8	0,005	0,09	5,3	0,005	0,13	7,5	0,005	0,13	7,1
3	6,49	6,55	1,0	5,29	5,36	1,4	5,05	5,11	1,2	5,03	5,15	2,3	5,22	5,24	0,4
	0,20	0,08	3,5	0,01	0,13	2,9	0,01	0,10	2,3	0,01	0,11	3,3	0,01	0,17	3,4
4	7,81	7,53	-3,5	6,65	6,41	-3,6	6,34	6,12	-3,6	6,32	6,14	-2,9	6,57	6,30	-4,0
	0,20	0,08	4,5	0,01	0,16	4,3	0,01	0,09	3,9	0,01	0,12	3,5	0,01	0,19	5,0
5	11,21	11,50	2,7	10,15	10,51	3,5	9,69	9,98	3,1	9,66	10,07	4,3	10,03	10,38	3,5
	0,20	0,10	3,4	0,01	0,16	3,8	0,01	0,13	3,4	0,01	0,12	4,5	0,01	0,13	3,7
6	100,5	101,2	0,7	102,2	103,3	1,1	97,47	98,97	1,5	97,18	99,28	2,2	100,9	103,6	2,7
	0,23	0,31	0,8	0,12	0,17	1,1	0,12	0,25	1,6	0,13	0,20	2,2	0,12	0,38	2,7
7	521,3	515,6	-1,1	535,6	530,8	-0,9	511,0	507,0	-0,8	509,5	506,0	-0,7	529,1	526,2	-0,5
	0,90	0,57	1,1	0,90	0,55	0,9	0,88	0,95	0,8	0,93	1,82	0,8	0,90	2,50	0,7
8	2144	2139	-0,2	2207	2206	-0,1	2106	2107	0,1	2099	2104	0,2	2180	2187	0,3
	2,08	5,04	0,3	2,10	2,28	0,2	2,14	3,61	0,2	2,43	6,81	0,4	2,12	11,0	0,6

The novelty of proposed approach consists in the originality of measuring and processing the experimental data. The main feature here is the use of ethanol as an internal standard that allows to receive the results in mg/L (AA).

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