Direct Determination of Volatile Compounds in Spirit Drinks by Gas Chromatography

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ABSTRACT: A way of direct determination of volatile compounds in spirit drinks by gas chromatography is proposed by using ethanol as internal standard in gas chromatographic analysis of volatile compounds in spirit drinks for routine tests. This method provides determination of volatile compound concentrations in spirit drinks expressed directly in milligrams per liter of absolute alcohol without measuring the alcohol content of the analyzed sample. Theoretical background of the method shows the opportunity to use it in any tested laboratories all over the world and to ascertain in its efficiency and simplicity. The method was approved in control laboratories of Wine and Distillery Plant "Chashniki" (Belarus) and Branch of Joint Stock Company "Rosspirtprom" Wine and Distillery Plant "Cheboksary" (Russia). The experimental results of method validation in the Laboratory of Analytical Research from Research Institute for Nuclear Problems of Belarusian State University are presented.

KEYWORDS: spirit drinks, ethanol, internal standard, volatile compounds, gas chromatography

■ INTRODUCTION

The aim of this Article is to improve on existing methods and enhancement of the reliability of measuring concentrations of volatile compounds in alcohol production that is a considerable part of the food industry all over the world.

Acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, isobutyl alcohol, n-butanol, and isoamyl alcohol are the main volatile compounds that should be determined in spirit drinks according to the standards and regulations.[1−9] Concentrations of these compounds expressed in milligrams per liter (mg/L) of absolute alcohol (AA) are traditionally calculated using the Internal Standard (IS) method.[1−5] Some researchers[10−13] use 4-methyl-2-pentanol or 2-octanol as IS. Other researchers use 2-pentanol,[14,15] 1-octanol,[16] or 4-nonanol[17] as IS. Yet introduction of internal standard compound in low dose (about some ppm (10^{-4} %)) is not a simple task, and it requires highly qualified laboratory technicians. For this reason, the method of External Standard (ES) is used.[6−9,18,19] In both methods, to obtain quantitative values of impurities per liter of absolute alcohol, it is also necessary to determine alcohol strength by volume (% v/v) of the analyzed sample.[1−9]

To increase the accuracy of measurements and obviate the need for the IS addition, we proposed to use the major component (solvent) as an internal standard in the gas-chromatographic determination of impurities.[20,21] As ethanol is the main component in spirit products, it can be and should be used as internal standard in direct determination of volatile compounds in alcohol drinks by gas chromatography.

In searching the IS for quantitation, it is preferred that its concentration be in the same range as that of the analyte. Here, we have a totally opposite situation: the ppm range for the analyte versus >15% for ethanol. One of the main requirements

to the IS is maintaining the linearity of detector response to both the analyte and the IS throughout the range of their measured concentrations.[22] At present, practically all manufacturers produce gas chromatographs (GC) with a wide linear dynamic range of flame ionization detectors (FID), which is generally greater than 10^7. Signals coming from impurity compounds and from the main component, ethanol, are registered without any distortions.

Examination of spirit drinks in this case consists of the traditional procedure of determination of the detector relative response factors (RRF) of analyzed impurities relative to ethanol in standard solution for the given detector. These coefficients are used for calculation of concentrations of impurities. It is important to note that for modern devices, RRF can be tabulated.[23] So, the aim of this Article is further theoretical development and experimental verification of the proposed ethanol-IS method. Experimental results presented here were obtained in the Laboratory of Analytical Research of the Research Institute for Nuclear Problems of Belarusian State University (INP) (Minsk, Belarus).

■ MATERIALS AND METHODS

Theoretical Background. In the ES method, chromatograph calibration includes measuring of the detector response factors, RF_i for every analyzed compound in a sample with the help of standard solutions. Numerical values of these factors RF_i are calculated from the chromatographic data for standard solutions with known concentrations of analyzed compounds and may be expressed by the equation:

$$RF_i = \frac{C_i^{st}(sol)}{A_i^{st}} \tag{1}$$

where A_i^{st} is the peak area in pA·s and $C_i^{st}(sol)$ is the concentration in milligram per liter of standard solution.

The concentration C_i for each compound in the analyzed sample is calculated from the following formula:

$$C_i(sol) = RF_i \cdot A_i \tag{2}$$

where A_i is the peak area of the ith compound in the analyzed sample.

The conversion of results from milligram per liter of solution to milligram per liter of absolute alcohol for the sample is implemented in the following way:

$$C_i = C_i(sol) \cdot \frac{100}{strength} \tag{3}$$

Here, "strength" is the alcoholic strength by volume of spirit sample expressed in %, v/v.

The ES method is very sensitive to the instability of a GC system. To avoid the irreproducibility of the GC system, the IS method is applied, where the GC calibration includes measuring of relative detector response factors RRF_i for every analyzed compound relative to IS. Numerical values of RRF_i are calculated from the chromatographic data for standard solutions with known concentrations of analyzed compounds and IS. They may be expressed by the following equation:

$$RRF_i = RF_i / RF_{IS} = \frac{C_i^{st}(sol)}{A_i^{st}} \Big/ \frac{C_{IS}^{st}(sol)}{A_{IS}^{st}} = \frac{A_{IS}^{st} \cdot C_i^{st}(sol)}{A_i^{st} \cdot C_{IS}^{st}(sol)} \tag{4}$$

where RF_{IS} is the detector response of the internal standard component. A_i^{st} and A_{IS}^{st} are the peak areas of the ith compounds and IS, respectively, for a standard solution. $C_i^{st}(sol)$ and $C_{IS}^{st}(sol)$ are the concentrations of the ith compound and IS, respectively, expressed in milligram per liter of solution.

The concentration C_i of the ith sample compound in milligram per liter of absolute alcohol is expressed as follows:[1−3]

$$C_i = RRF_i \times \frac{A_i}{A_{IS}} \times C_{IS}(sample) \times \frac{100}{strength} \tag{5}$$

where A_i and A_{IS} are the peak areas for the ith compound and IS, respectively, for the analyzed sample, $C_{IS}(sol)$ is the IS concentration, and "strength" is the alcohol concentration in the solution, expressed in % volume.

In the case of ethanol-IS, we propose to rearrange eqs 4 and 5:

$$RRF_i = \frac{A_{IS}^{st}}{A_i^{st}} \Big/ \frac{C_{Et}^{st}}{C_i^{st}} = \frac{A_{IS}^{st} \cdot C_i^{st}}{A_i^{st} \cdot \rho_{Et}} \tag{6}$$

where A_{Et}^{st} and A_{Et} are the peak areas of ethanol in the standard solution and the analyzed sample, respectively. C_i^{st} and C_{IS} are the concentrations of the ith compound and IS, expressed in milligram per liter of absolute alcohol, and $\rho_{Et} = 789\,300$ mg/L is the known density of ethanol.

The concentration C_i of the ith sample compound relative to absolute alcohol then has the form:

$$C_i = RRF_i \cdot \frac{A_i}{A_{Et}} \cdot \rho_{Et} \tag{7}$$

Substitution of RRF_i from eq 6 into eq 7 gives the final expression for the concentration C_i of the ith component:

$$C_i = RRF_i \cdot \frac{A_i}{A_{Et}} \cdot \rho_{Et} = C_i^{st} \cdot \frac{A_{Et}^{st}}{A_i^{st}} \cdot \frac{A_i}{A_{Et}} \tag{8}$$

It is important to note that the density of ethyl alcohol does not appear in the final expressions 8, and one does not need to determine the strength of the sample using the ethanol-IS method.

When defining the calibration characteristics of a device that are averaged over some measurements of standard solutions with known content of component compound, one can write the expression for coefficients RRF_i^{Et} in the form:

$$RRF_i^{Et} = \frac{\sum_{l=1}^{N} \sum_{j=1}^{M} (S_{ilj}^{st} / S_{Etlj}^{st}) \cdot (C_{ilj}^{st} / C_{Etlj}^{st})}{M \cdot \sum_{l=1}^{N} \sum_{j=1}^{N} (S_{ilj}^{st} / S_{Etlj}^{st})^2}$$

$$= \frac{1}{\rho_{Et}} \cdot \frac{\sum_{l=1}^{N} \sum_{j=1}^{M} (S_{ilj}^{st} / S_{Etlj}^{st}) \cdot C_{ilj}^{st}}{M \cdot \sum_{l=1}^{N} \sum_{j=1}^{N} (S_{ilj}^{st} / S_{Etlj}^{st})^2} \tag{9}$$

where C_{ilj}^{st} and C_{Etlj}^{st} are the concentrations of the ith compound and ethanol of the lth level of the calibration compound, respectively; S_{ilj}^{st} and S_{Etlj}^{st} are the areas of the ith compound and ethanol of lth level of the calibration compound, respectively. N is the number of calibration compounds. M is the number of measurements of each calibration compound.

Approximation coefficients R_i^2 for obtained coefficients RRF_i^{Et} are calculated in accordance with the following formula:

$$R_i^2 = 1 - \frac{\sum_{l=1}^{N} \sum_{j=1}^{M} ((S_{ilj}^{st} / S_{Etlj}^{st}) - RRF_i \cdot (C_{ilj}^{st} / \rho_{Et}))^2}{\sum_{l=1}^{N} \sum_{j=1}^{M} \left((S_{ilj}^{st} / S_{Etlj}^{st}) - \frac{\sum_{l=1}^{N} \sum_{j=1}^{M} (S_{ilj}^{st} / S_{Etlj}^{st})}{N \cdot M} \right)^2} \tag{10}$$

The expression for the concentration of the ith compound can be written as:

$$C_i = \frac{\sum_{l=1}^{N} \sum_{j=1}^{M} (S_{ilj}^{st} / S_{Etlj}^{st}) \cdot C_{ilj}^{st}}{M \cdot \sum_{l=1}^{N} \sum_{j=1}^{N} (S_{ilj}^{st} / S_{Etlj}^{st})^2} \cdot \frac{A_i}{A_{Et}} \tag{11}$$

According to eqs 8 and 11, the concentration C_i of the ith component in the sample is directly expressed in milligram per liter of absolute alcohol, and the additional measurements of the volume content of ethanol in the sample are not required. It should also be mentioned that, in this case, the procedure of the IS introduction into the analyzed sample is not needed, because ethanol is the main component of the sample and is already contained in it. This substantially simplifies the whole measurement procedure as well as improves the reliability of the obtained data.

■ EXPERIMENTAL SECTION

All individual standard compounds were purchased from Sigma-Fluka-Aldrich (Berlin, 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. High-grade ethanol was purchased from Minsk-Kristall Winery and Distillery Plant (Minsk, Belarus). Eight standard ethanol−water (96:4) solutions of volatile compounds (SS-1−SS-8) were prepared gravimetrically according to ASTM D 4307[24] recommendations.

The initial standard solution SS-1 was prepared by adding the individual compounds to high-grade ethanol. A 100 mL volumetric flask and "KERN ABS 220-4" analytical balance with a margin error measurement not worse than 0.2 mg were used for preparation of the initial standard solution, SS-1, with a mass concentration of methanol of 20 000 mg/L of absolute alcohol and a mass concentration of all other defined components of 2000 mg/L of absolute alcohol. Fifty milliliters 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. Next, 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. Rectified ethyl alcohol was then 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 per 1 L of AA; methanol 2.53 mg per 1 L of AA; 2-propanol 1.35 mg per 1 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-5, 3:1000; for SS-6, 1:4000; and

Table 1. Values of Concentration of Analyzed Components in Standard Samples, C_{st}, Experimentally Measured Values of Concentrations C_{exp}, Standard Uncertainty of Concentration $u(C_{st})$, Standard Deviation of Intermediate Precision $S_{(TO)}$, Expressed in milligram per liter of Absolute Alcohol (AA)[a]

no. st. sol.	acetaldehyde						methyl acetate						ethyl acetate						methanol						2-propanol						1-propanol						isobutyl alcohol						n-butanol						isoamyl alcohol					
	C_{st} mg/L	$u(C_{st})$ mg/L	C_{exp} mg/L	$S_{(TO)}$ mg/L	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %	C_{st}	$u(C_{st})$	C_{exp}	$S_{(TO)}$	Δ %	u %
1	1.23	0.024	1.23	0.07	−0.1	6.1	1.08	0.001	1.08	0.04	−0.5	3.5	1.13	0.002	1.10	0.05	−2.3	5.2	13.39	0.376	12.82	0.22	−4.2	5.4	2.45	0.20	2.55	0.07	4.0	9.6	1.13	0.001	1.15	0.07	1.8	6.3	1.08	0.001	1.08	0.05	−0.3	4.4	1.08	0.001	1.07	0.07	−0.7	6.3	1.12	0.001	1.08	0.06	−3.8	7.0
2	2.25	0.025	2.26	0.09	0.2	4.3	2.11	0.005	1.99	0.08	−5.4	6.7	2.20	0.005	2.08	0.07	−5.8	6.7	23.72	0.382	22.29	0.14	−6.0	6.3	3.50	0.20	3.58	0.10	2.2	3.8	2.21	0.005	2.30	0.10	3.8	5.8	2.11	0.005	2.17	0.09	2.6	5.3	2.11	0.005	2.19	0.13	4.0	7.5	2.19	0.005	2.11	0.13	−3.5	7.1
3	5.16	0.03	5.10	0.10	−1.0	2.2	5.04	0.01	4.90	0.08	−2.9	3.3	5.27	0.01	5.08	0.11	−3.5	4.1	53.15	0.38	51.28	0.19	−3.5	3.6	6.49	0.20	6.55	0.08	1.0	6.8	5.29	0.01	5.36	0.13	1.4	2.9	5.05	0.01	5.11	0.10	1.2	2.3	5.03	0.01	5.15	0.11	2.3	3.3	5.22	0.01	5.24	0.17	0.4	3.4
4	6.44	0.03	6.25	0.11	−2.9	3.4	6.34	0.01	5.75	0.11	−9.2	9.4	6.62	0.01	6.16	0.07	−7.0	7.0	66.17	0.38	59.71	1.01	−9.8	9.9	7.81	0.20	7.53	0.08	−3.5	4.5	6.65	0.01	6.41	0.16	−3.6	4.3	6.34	0.01	6.12	0.09	−3.6	3.9	6.32	0.01	6.14	0.12	−2.9	3.5	6.57	0.01	6.30	0.19	−4.0	5.0
5	9.75	0.03	9.81	0.31	0.7	3.4	9.68	0.01	9.56	0.26	−1.2	3.0	10.11	0.01	10.01	0.22	−1.0	2.4	99.70	0.39	99.78	0.55	0.1	0.7	11.21	0.20	11.50	0.10	2.7	2.7	10.15	0.01	10.51	0.16	3.5	3.8	9.69	0.01	9.98	0.13	3.1	3.4	9.66	0.01	10.07	0.12	4.3	3.1	10.03	0.01	10.38	0.13	3.5	3.7
6	96.65	0.15	94.06	1.44	−2.7	3.1	97.38	0.12	95.68	1.77	−1.7	2.6	101.8	0.13	101.1	1.57	−0.7	1.7	980.5	0.85	990.3	1.86	1.0	1.0	100.5	0.23	101.2	0.31	0.7	0.7	102.2	0.12	103.3	0.17	1.1	1.1	97.47	0.12	98.97	0.25	1.5	1.6	97.18	0.13	99.28	0.20	2.2	2.2	100.9	0.12	103.6	0.38	2.7	2.7
7	506.0	0.98	486.8	5.79	−3.8	4.0	510.5	0.90	491.6	12.5	−3.7	4.5	533.5	0.96	520.7	9.93	−2.4	3.1	5129	7.46	5124	11.8	−0.1	0.3	521.3	0.90	515.6	0.57	−1.1	1.1	535.6	0.90	530.8	0.55	−0.9	0.9	511.0	0.88	507.0	0.95	−0.8	0.8	509.5	0.93	506.0	1.82	−0.7	0.8	529.1	0.90	526.2	2.50	−0.5	0.7
8	2085	2.77	2080	20.9	−0.2	1.1	2104	2.25	2113	10.1	0.4	0.7	2198	2.46	2202	5.29	0.2	0.3	21128	11.05	21130	20.0	0.0	0.1	2144	2.08	2139	5.04	−0.2	0.2	2207	2.10	2206	2.28	−0.1	0.2	2106	2.14	2107	3.61	0.1	0.2	2099	2.43	2104	6.81	0.2	0.2	2180	2.12	2187	11.0	0.3	0.6

[a] The relative bias Δ between the experimentally measured values C_{exp} and the values of concentrations C_{st}, assigned by preparation of standard solution by gravimetric method, as well as the relative standard uncertainty u are expressed as a percent.

for SS-7, 1:10 000. The solution SS-8 was obtained by dilution of 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.

Lab Hardware and Gas Chromatographic Conditions. Analyses were carried out in the Laboratory of Analytical Research from Research Institute for Nuclear Problems of Belarusian State University on gas chromatograph Crystal-5000 (JSC SDB Chromatec, Yoshkar-Ola, Russia) equipped with FID, a split/splitless injector, liquid autosampler, Unichrom software (New Analytical Systems Ltd., Minsk, Belarus), capillary column Rt-Wax, 60 m × 0.53 mm, phase thickness 1 μm (Restek, Bellefonte, PA). The oven temperature was: the initial isotherm at 75 °C (9 min), raised to 155 °C at a rate of 7 °C/min, with final isotherm of 155 °C (2.6 min). The carrier gas was nitrogen; the gas flow was 2.44 mL/min; the injector temperature was 160 °C; the detector temperature was 200 °C; the injector volume was 0.5 μL; and the split ratio was 1:20. This high split ratio was chosen to achieve good separation between the 2-propanol and ethanol peaks.

■ RESULTS AND DISCUSSION

Once the gas chromatographic conditions were optimized, the satisfactory separation under these conditions was achieved. A typical chromatogram of the used solutions is presented in Figure 1. To show the dominant ethanol compound and other
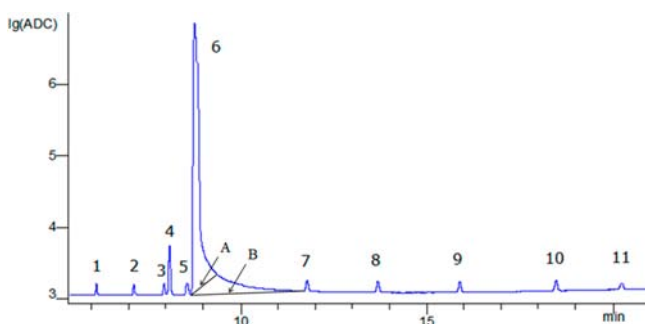

Figure 1. Typical chromatogram of the standard ethanol−water (40:60) solution. (1) acetaldehyde, (2) methyl acetate, (3) ethyl acetate, (4) methanol, (5) 2-propanol, (6) ethanol, (7) 1-propanol, (8) isobutyl alcohol, (9) n-butanol, (10) isoamyl alcohol, (11) 1-pentanol.

minor compounds simultaneously, the logarithmic scale of the response signal was chosen in Figure 2. In these figures, one can see peaks of the following volatile compounds: acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, ethanol, 1-propanol, isobutyl alcohol, n-butanol, isoamyl alcohol, and 1-pentanol. The last compound was added in examined solution to compare experimental results obtained by traditional IS method and our proposed method.

In the presented chromatograms, it is obvious that the ethanol peak has a long tail. A computer software data system implements the peak integration with the help of the second derivative of the chromatogram. The points of inflection or local maxima of the second derivative of the chromatogram above the thresholds are the start and the end points of the integration domain. The baseline profile of the ethanol peak, automatically drawn by the computer software, is marked by the letter A. A forced baseline profile of the ethanol peak stretched up to the beginning of the subsequent peak of 1-propanol is marked by the letter B. The relative difference between the ethanol peak areas in both cases does not exceed 0.01% in all measured chromatograms. So, ethanol peak tailing does not have a significant influence on the results.
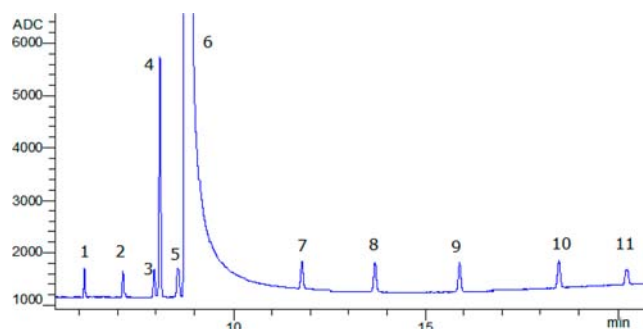

Figure 2. The same chromatogram as in Figure 1, but linear scale of response signal is chosen.

Let us illustrate this in the following data. In the considered experiments, the characteristic value of the peak area of ethanol in case A was equal to 63 387 ADC·min or 6045.1 pA·min, while in case B, the characteristic value of the peak area of ethanol was 63 392 ADC·min or 6045.6 pA·min, respectively. As a consequence, the apparent "tail" of the peak of ethanol does not make a significant contribution to the final results of calculations of the examined concentrations.

The calculated values C_{st} of mass concentration of the standard samples and the values of their standard uncertainties $u(C_{st})$ for all 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 $S_{(TO)}$, expressed in milligram per liter 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.[25]

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%.

Standard solutions SS-5, SS-6, and SS-8 used to draw the calibration curves in Figures 3 and 4 are presented in Table 2.
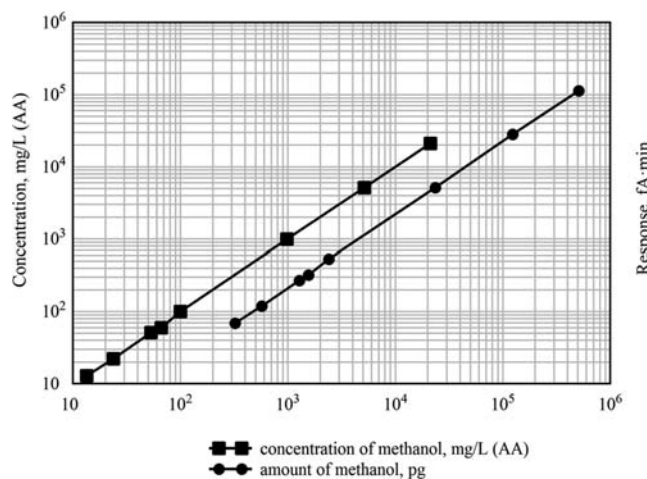

Figure 3. Experimental results on determination of methanol.

The measurement of each standard solution consisted of 15 episodes of two measurements in each series; that is, the measurement of each solution was carried out 30 times. A total of 240 chromatograms were processed.
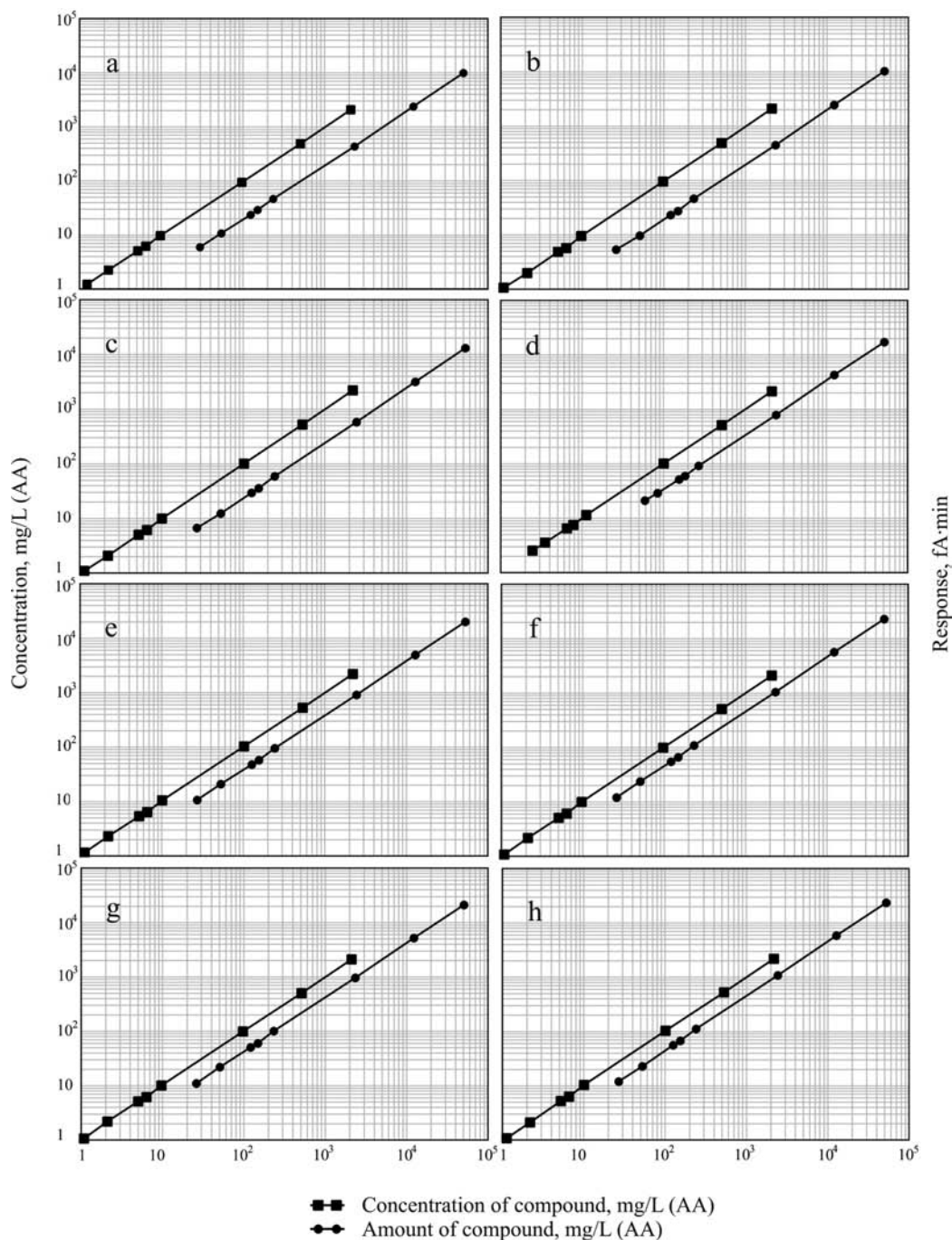
Figure 4. Experimental results on determination of the following compounds: (a) acetaldehyde, (b) methyl acetate, (c) ethyl acetate, (d) 2-propanol, (e) 1-propanol, (f) isobutyl alcohol, (g) n-butanol, and (h) isoamyl alcohol.

The analysis of the experimental data shows that the relative bias Δ between the experimentally measured values C_{exp} and the values of concentrations C_{st} assigned during the preparation by gravimetric method for all analyzed components in the eight analyzed solutions does not exceed 10% and neither does the relative standard uncertainty u.

For illustrative purposes, the experimental data are presented as graphs in Figures 3 and 4 for the following main analyzed components: methanol (Figure 3) and acetaldehyde, methyl acetate, ethyl acetate, 2-propanol, 1-propanol, isobutyl alcohol, n-butanol, and isoamyl alcohol. The figures show linear dependence (square marked) of experimentally measured values of concentration of the analyzed components with respect to the

concentrations assigned during the solution preparation by gravimetric method. These figures show the dependence of the detector signal response on the amount of the substance of the examined component coming directly to the detector (circle marked). Data of prepared solutions SS-1—SS-8 are given as a sequence of points in ascending order concentration from left for solution SS-8 to right for SS-1.

The linearity of the dependences obtained in a wide range of concentrations of the test components indicates that in this range are concentrations of more than 3 orders of magnitude; as expected,[22] the signal from ethanol and the impurities belongs to the linear range. This means that the method can be effectively used for the stated purposes.

Table 2. Values of Relative Response Factors RRF$_i^{Et}$ and Approximation Coefficients R_i^2 Calculated by Equations 9, 10

component	RRF$_i^{Et}$	R_i^2	LOD[a] mg/L (AA)
acetaldehyde	1.627	0.99999	0.26
methyl acetate	1.591	0.99997	0.32
ethyl acetate	1.305	0.99999	0.24
methanol	1.449	0.99999	0.14
2-propanol	0.962	0.99999	0.11
1-propanol	0.852	0.99999	0.11
isobutyl alcohol	0.708	0.99999	0.08
n-butanol	0.772	0.99999	0.07
isoamyl alcohol	0.715	0.99999	0.06

[a]Limit of detection (LOD).

The method was evaluated during the analysis of alcohol-containing byproducts and finished goods in control laboratories of Wine and Distillery Plant "Chashniki" (Belarus) and Branch of Joint Stock Co. "Rosspirtprom" Wine and Distillery Plant "Cheboksary" (Russia) on Kristall2000m gas chromatograph and 6890N (Agilent) chromatograph, respectively, using FFAP 50 m × 0.35 mm × 0.50 mkm capillary columns. The analysis shows that bias between the results of calculation of the values of concentration of microimpurities in finished goods obtained by a traditional method of absolute graduation and by the proposed new method is within 10%.

Let us compare the efficiency of well-known traditional analytical methods with the method of using ethanol as internal standard proposed in this Article. These experiments were carried out in the Laboratory of Analytical Research from Research Institute for Nuclear Problems of BSU on gas chromatograph Crystal-5000. Three solutions with different concentrations of volatile compounds were prepared by gravimetric method. 1-Pentanol was added in all three solutions. These initial concentrations are given in Table 3. We then compared experimentally measured concentrations of volatile compounds in solutions obtained by three methods: 1-pentanol as traditional IS; the ES method; and the method of using ethanol as internal standard, with the initial concentrations

according to the gravimetric method. All results including relative bias are in Table 3. It is evident that the obtained results using the three methods well agreed.

In conclusion, theoretical consideration and the results of experimental investigation on the determination of metrological characteristics of impurity concentration in alcohol drinks and spirit products by the method of using ethanol as internal standard are presented. The values of relative standard uncertainty in the whole range of concentrations of main volatile compounds do not exceed 10%.

It is important to note that in direct determination of volatile compounds in milligram per liter of absolute alcohol there are no hard conditions on volume of examined sample of alcohol product for determination of ethanol volatile contain.

The obtained results show the possibility of developing a new international standard of measurement procedure, which will allow increasing the data accuracy and will simplify the measurement procedure considerably. Thousands of testing laboratories all over the world carry out gas chromatographic analysis of volatile compounds in spirit drinks. They may validate this new method in actual practice, using detailed formulas proposed in this Article. It is important to note that there is no need to perform any additional measurements. This method could be tested while performing current measurements with existing instrumentation. As the alcohol industry is an important part of the food industry in the world, the proposed method can be easily implemented in daily practice of analytical and testing laboratories.

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Notes

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Table 3. Comparison of Experimentally Measured Concentrations of Volatile Compounds in Solutions Obtained by Three Methods: 1-Pentanol as IS; the ES Method; and the Method of Using Ethanol as IS with Initial Concentrations According to Gravimetric Method

	concentration, mg/L (AA)														
	acetaldehyde			methyl acetate			ethyl acetate			methanol			2-propanol		
gravimetric method	2.22	56.2	1096	2.29	57.8	1128	2.17	54.9	1070	25.0	556	10 774	3.69	54.1	1025
1-pentanol as IS	2.55	58.5	1201	2.48	61.8	1211	2.42	57.1	1181	26.8	568	11 766	3.91	53.6	1078
relative bias, %	14.9	4.1	9.5	8.4	6.9	7.4	11.7	4.0	10.3	7.4	2.2	9.2	5.9	0.2	−0.9
ES relative bias, %	2.38	57.4	1129	2.32	60.7	1139	2.26	56.0	1110	25.0	557	11 066	3.72	53.7	1035
	7.2	2.2	3.0	1.2	4.9	1.0	4.2	2.1	3.7	0.3	0.3	2.7	0.9	−0.7	0.9
ethanol as IS	2.36	57.3	1163	2.3	60.5	1173	2.24	55.9	1144	24.8	556	11 396	3.69	53.6	1066
relative bias, %	6.2	1.9	6.0	0.2	4.7	4.1	3.2	1.9	6.8	−0.7	0.1	5.8	−0.1	−0.9	4.0

	concentration, mg/L (AA)														
	1-propanol			isobutyl alcohol			n-butanol			isoamyl alcohol			1-pentanol		
gravimetric method	2.08	52.8	1029	2.06	52.3	1020	2.11	53.5	1044	2.11	53.5	1044	27.1	27.1	27.1
1-pentanol as IS	2.17	52.5	1076	2.35	51.6	1052	2.35	54.3	1104	2.16	52.6	1103	27.1	27.1	27.1
relative bias, %	4.2	−0.6	4.6	13.8	−1.4	3.2	11.2	1.4	5.8	2.5	−1.8	5.7			
ES relative bias, %	2.06	52.6	1033	2.28	52.7	1031	2.24	54.4	1060	2.06	52.7	1059	26.8	28.2	28.1
	−0.8	−0.4	0.4	10.5	0.8	1.1	6.1	1.6	1.5	−2.3	−1.7	1.4	−1.1	4.0	3.6
ethanol as IS	2.04	52.5	1064	2.26	52.6	1062	2.22	54.3	1091	2.04	52.5	1090	25.9	27.4	28.2
relative bias, %	−1.7	−0.6	3.4	9.5	0.6	4.1	5.0	1.4	4.5	−3.2	−1.9	4.4	−4.6	1.2	4.0

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