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NOVEL METHOD FOR DIRECT DETERMINATION OF THE VOLATILE COMPOUNDS IN ALCOHOL PRODUCTS

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Abstract
The method "Ethanol as Internal Standard" for direct correct determination of volatile compounds including ethanol in alcohol production is discussed. To simplify the validation of the method in the testing laboratory practice on-line calculator AlcoDrinks was developed and located on the Internet at http://inp.bsu.by/calculator/vcalc.html. It was theoretically grounded and experimentally demonstrated the possibility to validate the proposed method on the basis of experimental data obtained in the laboratory during the tests in accordance with the Commission Regulation (EC) No 2870/2000.

Аннотация
Представлен анализ метрологических характеристик метода прямого корректного определения летучих соединений, в том числе этанола, в спиртосодержащей продукции. Для упрощения валидации метода в практике испытательных лабораторий разработан и размещен в свободном доступе http://inp.bsu.by/calculator/vcalc.html калькулятор AlcoDrinks. Теоретически обосновано и экспериментально продемонстрирована возможность валидации предложенного метода на основе экспериментальных данных, полученных в лаборатории во время испытаний в соответствии с Регламентом Комиссии (ЕС) № 2870/2000.

Introduction

In accordance with the Commission Regulation (EC) No 2870/2000 [1], the official methods of the Association of Official Analytical Chemists (AOAC) [2] and the official methods of International Organisation of Vine and Wine (OIV) [3] determination of volatile compounds in the alcohol production is performed on gas chromatographs. Analysis of the quantitative content of volatile compounds is carried out by the internal standard (IS) method. To represent measured values of the concentrations of analyzed volatile compounds according to [1–3] in mg/l of anhydrous ethanol (Absolute Alcohol - AA) one should perform an additional procedure of measuring the volume ethanol content in the test sample.

The procedure of determination of the volumetric ethanol content is intended for a sample of least 200 ml [1]. It should also be noted that when testing alcohol-containing products with a noticeable volume content of volatile compounds (more than 0.2% by volume), the usage of international alcoholometry water-ethanol tables [4] does not provide the required accuracy in determining the volume ethanol content of 0.1% by volume, since data tables are created only for binary water-ethanol solutions [4]. So, this is a so-called problem of "real" and "apparent" alcoholic strength. The cited above problems are solved in the method "Ethanol as internal standard" proposed in [5-6]. The YouTube channel was created in order to simplify the method validation procedure and subse-

quent implementation of the method in the practice of testing and research laboratories https://www.youtube.com/channel/UCXgL2c__KG3m7lW1oxOGqtQ.

The theoretical basis of the method "Ethanol as Internal Standard"

In accordance with the requirements of ISO/IEC 17025 [7] method must be validated before its application in practice of testing laboratories. To facilitate the implementation of the proposed method in the laboratory practice we propose an algorithm of its validation on the basis of experimental data obtained during routine tests of alcohol products, in accordance with international standards [1–3]. It is important to notice that no additional measurements more than indicated in [1] are required, because in this case the measured chromatograms of prepared in accordance with [1] standard solutions can be calculated in accordance with the proposed new method [5-6] and with the traditional method [1]. Calculated in both cases values of relative bias of measured values of concentrations of volatile compounds have to be checked for compliance with the requirements of Paragraphs 8.4 and 10 [1].

Description of validation algorithm

Validation was performed in accordance with Commission Regulation (EC) No 2870/2000 [1]. Standard solutions "C", "0,1", "0,5", "1,0", "2,0" were prepared by gravimetric method in strong accordance with [1].

Results of the test of standard solution "C" are used to determine the values of relative response factors *RRF*, prepared according to Paragraph 5.14.3 [1].

The test results of standard solutions "0.1", "0.5", "1.0", "2.0" are used to determine the approximation coefficients R^2, that characterize the detector response linearity over the operating range of concentrations of studied quantities of volatile compounds.

In the case of using ethanol as internal standard the values of coefficients RRF_i^{Eth} of *i*-th analyzed compound relatively ethanol can be summarized as follows

$$RRF_i^{Eth} = \frac{C_i^{st}(mg/l(AA))}{A_i^{st}} / \frac{\rho_{Eth}(mg/l(AA))}{A_{Eth}^{st}}, \quad (1)$$

where A_i^{st} and A_{Eth}^{st} are the values of response, for example, areas under the peaks, of the *i*-th test compound and ethanol in measured standard solution "C", $C_i^{st}(mg/l(AA))$ is a concentration of the *i*-th test compound in mg/l (AA), $\rho_{Eth}(mg/l(AA))$ = 789,300 mg/l is the ethanol density.

The value of concentration of the *i*-th compound when using ethanol as IS is defined by the next expression

$$C_i(mg/l(AA)) = RRF_i^{Eth} \cdot \frac{A_i}{A_{Eth}} \cdot \rho_{Eth}(mg/l(AA)), \quad (2)$$

where A_i and A_{Eth} are values of the areas under the peaks, of *i*-th compound and ethanol when measuring the test sample.

In the case of using 1-pentanol as IS, values of the coefficients RRF_i^{Pnt} of *i*-th analyzed compound relatively 1-pentanol can be summarized as follows

$$RRF_i^{Pnt} = \frac{C_i^{st}(mg/kg)}{A_i^{st}} / \frac{C_{Pnt}^{st}(mg/kg)}{A_{Pnt}^{st}}, \quad (3)$$

where A_i^{st} и A_{Pnt}^{st} are values response, for example, areas under the peaks, of *i*-th test compound and ethanol solution in the measurement standard solution "C", $C_i^{st}(mg/kg)$ is a concentration of the *i*-th compound of the test in mg/kg of the solution, $C_{Pnt}(mg/kg)$ is the 1-pentanol concentration in mg/kg of solution.

Concentration value of *i*-th analyzed compound using pentanol as IS is defined by the following formula:

$$C_i\,(mg/kg) = RRF_i^{Pnt} \cdot \frac{A_i}{A_{Pnt}} \cdot C_{Pnt}(mg/kg), \tag{4}$$

where A_i and A_{Pnt} are values of the areas under the peaks of *i*-th compound and 1-pentanol when measuring the test sample.

Presentation of concentration values of examined compounds $C_i\,(mg/kg)$ in the required dimension mg/l (AA) [1] is performed according to the following formula

$$C_i\,(mg/l(AA)) = C_i\,(mg/l) \cdot \rho_{sample}(mg/l) / strength(\%(v/v)), \tag{5}$$

where $\rho_{sample}(mg/l)$ is a density of the test sample in mg/l. $strength(\%(v/v))$ is a volumetric content of ethanol (strength) in the test sample, expressed as a percentage.

Let us define estimations of relative uncertainty of concentrations of analyzed volatile compounds, determined by the new method according to (2) and according to the traditional internal standard method by (5) as the following two formulas:

$$\frac{u(C_i)}{C_i} = \sqrt{\left(\frac{u(RRF_{i(Eth)})}{RRF_{i(Eth)}}\right)^2 + \left(\frac{u(A_i)}{A_i}\right)^2 + \left(\frac{u(A_{Eth})}{A_{Eth}}\right)^2} \tag{6}$$

and

$$\frac{u^*(C_i)}{C_i} = \sqrt{\left(\frac{u(RRF_{i(Pnt)})}{RRF_{i(Pnt)}}\right)^2 + \left(\frac{u(A_i)}{A_i}\right)^2 + \left(\frac{u(A_{Pnt})}{A_{Pnt}}\right)^2 + \left(\frac{u(C_{Pnt})}{C_{Pnt}}\right)^2 + \left(\frac{u(\rho_{sample})}{\rho_{sample}}\right)^2 + \left(\frac{u(strength(\%,vol)}{strength(\%,vol)}\right)^2} \tag{7}$$

where $u(RRF_{i(Eth)})$ and $u(RRF_{i(Pnt)})$ are the uncertainties of RRF_i^{Eth} and RRF_i^{Pnt}, respectively, $u(A_i)$, $u(A_{Pnt})$ and $u(A_{Eth})$, $u(A_{Pnt})$ are the uncertainties of the measured detector response for i-th component, 1-pentanol and ethanol respectively, $u(C_{Pnt})$, $u(\rho_{sample})$ and $u(strength(\%,vol)$ are the uncertainties of the concentration of 1-pentanol, of the sample density and of the sample strength respectively.

In (6) and (7) the first three terms under the square root have the same nature and the same order of magnitude. At the same time in (7) we have more than three terms than in (6). These additional terms are responsible for the uncertainty in determining the concentration of the internal standard, density of the test sample and the volumetric content of ethanol in the sample. The presence of these additional terms in (7) in comparison with (6) indicates a higher uncertainty in determining the concentrations of these components by the traditional method [1-3] than using a new method [5-6].

Experimental

All individual chemical compounds were purchased from Sigma-Fluka-Aldrich (Berlin, Germany). Standard solutions were prepared gravimetrically by adding individual chemical compounds in the ethanol-water solution with a volumetric content of 40% ethanol in accordance with Commission Regulation (EC) No 2870/2000 [1]. Experiments were carried out in the Laboratory of analytical research of the Institute for Nuclear Problems of Belarusian State University. GC methodical parameters are presented in [5]. In order to validate the method in an extended with comparison [1] range of the studied concentrations of volatile compounds standard solution of "A" has been tested as well as prepared standard solution "Min 1,0" with extremely low compound concentrations. The measured chromatograms of standard solutions "A", "C" and "Min 1,0" are presented in Fig. 1–3.

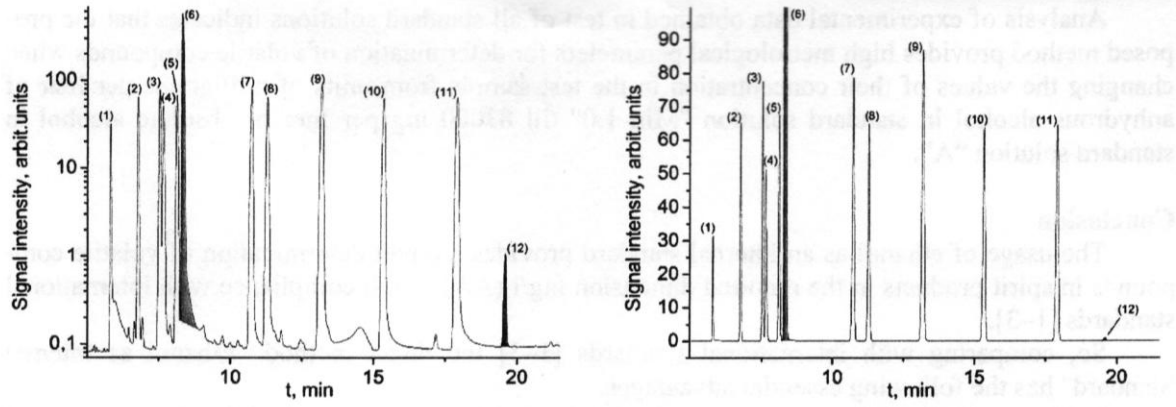

Fig. 1. Type of chromatograms of standard solution "A" with the following compounds: (1) acetaldehyde, (2) methyl, (3) ethyl, (4) methanol, (5) 2-propanol, (6) ethanol, (7) 2-butanol, (8) 1-propanol, (9) isobutanol, (10) n-butanol, (11) isoamilol, (12) 1-pentanol in the logarithmic (left panel) and linear (right panel) range.

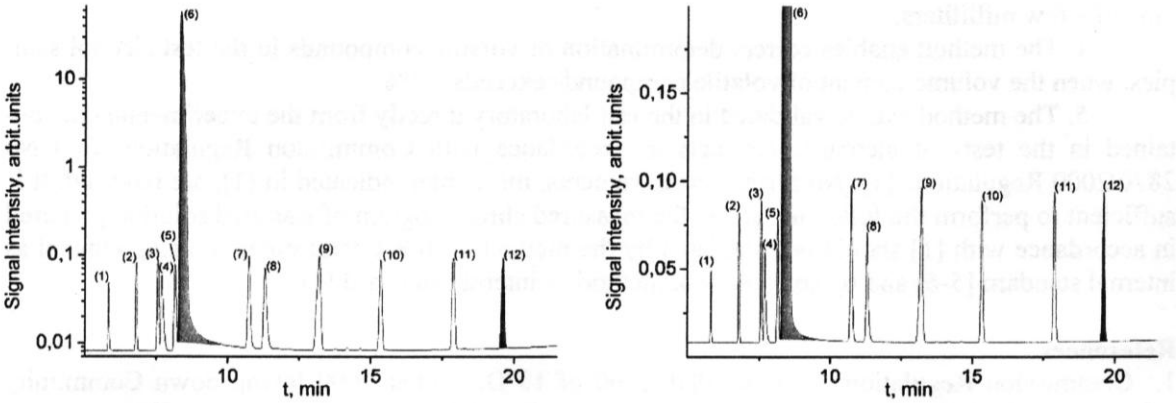

Fig. 2. Chromatogram of a standard solution "C".

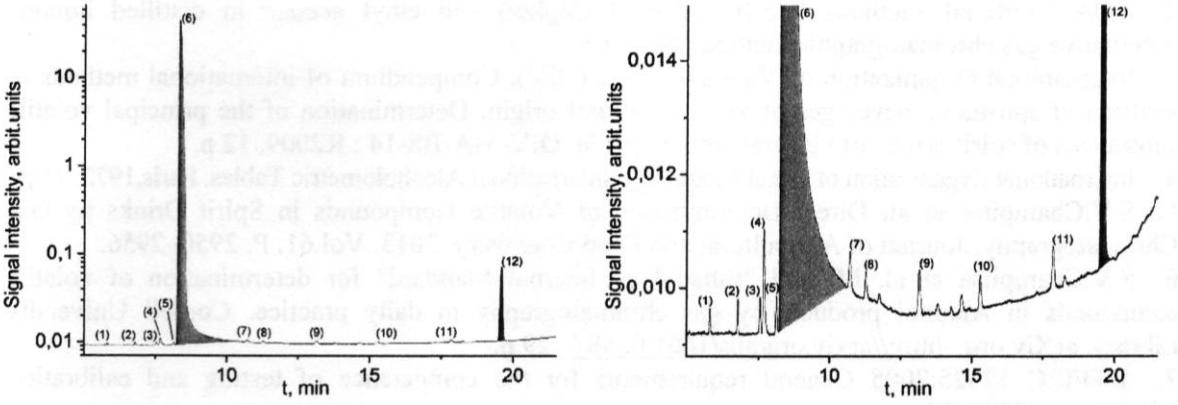

Fig. 3. Chromatogram of a standard solution "Min 1.0".

The values of relative bias $\Delta U_{ethanol}$ calculated from experimental data of tests of standard solution "QC", for all compounds are not greater than 5.2%. At the same time, the magnitude of the relative bias $\Delta U_{pentanol}$ determined using conventional internal standard method [1] reaches values of 6.4%. The values of relative bias $\Delta U_{ethanol}$ calculated from the results of tests of standard solutions "0.1", "0.5", "1.0", "2.0", "Min 1.0" and "A" for all volatile compounds does not exceed 6.4%. At the same time, the value of the relative bias $\Delta U_{pentanol}$ determined using conventional IS method [1] reaches values of 11.2%.

Analysis of experimental data obtained in test of all standard solutions indicates that the proposed method provides high metrological parameters for determination of volatile compounds when changing the values of their concentration in the test sample from units of milligrams per liter of anhydrous alcohol in standard solution "Min 1.0" till 83000 mg per liter of absolute alcohol in standard solution "A".

Conclusion

The usage of ethanol as an internal standard provides a direct determination of volatile compounds in spirit products in the required dimension mg/l (AA) in full compliance with international standards [1–3].

So, comparing with international standards [1–3] the direct method "Ethanol as Internal Standard" has the following essential advantages.

1. The method eliminates the manual procedure of internal standard adding in the prepared standard solutions for calibration of the gas chromatograph and in the test sample.

2. The method provides zero uncertainty of ethanol concentration in the prepared standard solution in dimension mg per liter of anhydrous alcohol.

3. The method makes it possible to use the control (standard) samples with a minimum volume of a few milliliters.

4. The method enables correct determination of volatile compounds in the test alcohol samples, when the volume content of volatile compounds exceeds 0.5%.

5. The method can be validated in the test laboratory directly from the experimental data obtained in the tests of alcoholic products in accordance with Commission Regulation (EC) No 2870/2000 Regulations [1]. No further measurements, more than indicated in [1], are required. It is sufficient to perform the following steps: the measured chromatogram of standard solution prepared in accordance with [1] should be calculated by the method of direct determination using ethanol as internal standard [5-6] and by conventional method of internal standard [1].

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