РЕФЕРЕНТНЫЙ МЕТОД ОПРЕДЕЛЕНИЯ КОЛИЧЕСТВЕННОГО СОДЕРЖАНИЯ ЛЕТУЧИХ КОМПОНЕНТОВ, ВКЛЮЧАЯ МЕТИЛОВЫЙ СПИРТ, В АЛКОГОЛЬНОЙ ПРОДУКЦИИ

Межгосударственные и международные стандарты по определению летучих компонентов в алкогольной продукции

GB/T 11858-2009
GB/T 15038-2008
GB/T 10781-2021

BIS IS 3752:2005(R2009)

Commission Regulation (EC) No. 2870/2000

AOAC Official Methods 972.10/11, 2005

Norma Mexicana NMX-V-005-NORMEX-2018

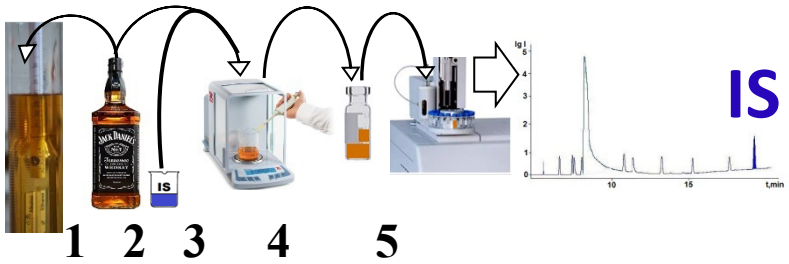
ГОСТ 30536
ГОСТ 31684
ГОСТ 33833
ГОСТ 33834
ГОСТ 33408
ГОСТ 32013
ГОСТ 31811
ГОСТ 14138
ГОСТ 32039
ГОСТ 12280
ГОСТ 13194
ГОСТ 32070
ГОСТ 32036
ГОСТ 10749.3
ГОСТ 10749.6
ГОСТ 10749.13
ГОСТ 10749.14
ГОСТ Р 57893
ГОСТ Р 52363
ГОСТ Р 51999
ГОСТ Р 55878
ГОСТ Р 57893
СТБ ГОСТ Р 51698

Все перечисленные государственные стандарты гармонизированы с Регламентом **(ЕС) 2870/2000** и используют традиционный метод внутреннего стандарта

В государствах **ЕАЭС** действует одновременно более 20 стандартов, использующих метод внешнего стандарта

Идея… с большой выдержкой

Сегодня: **Традиционный метод внутреннего стандарта. Китай, Индия, ЕС, США, Мексика и др.**



В соответствии с традиционным методом внутреннего стандарта концентрация *i*-го компонента в размерности мг/кг определяется по следующей формуле:

$$C_i\,(\text{мг/кг}) = RRF_i^{IS} \cdot \frac{A_i}{A_{IS}} \cdot C_{IS}\,(\text{мг/кг})$$

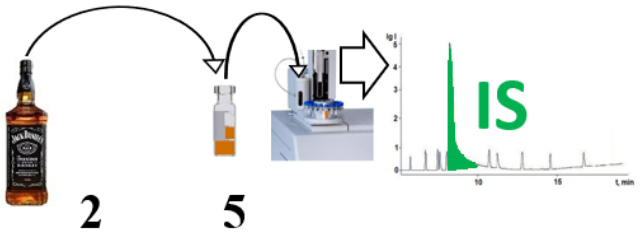
Значения относительных коэффициентов отклика детектора на исследуемый летучий компонент относительно отклика на выбранный внутренний стандарт вычисляют по следующей формуле:

$$RRF_i^{IS} = \frac{C_i^{calibr}\,(\text{мг/кг})}{C_{IS}^{calibr}\,(\text{мг/кг})} \cdot \frac{A_{IS}^{calibr}}{A_i^{calibr}}$$

Для вычисления концентрации компонента, выраженной в **мг/л безводного спирта**, необходимо измерить плотность образца и определить его крепость (объемное содержание этанола):

$$C_i\,(\text{мг/ л безводного спирта}) = \frac{C_i\,(\text{мг/кг}) \cdot \rho_{образец}\,(\text{кг/л}) \cdot 100\ \%}{"крепость"\,(\%, \text{об.})}$$

Завтра: **Инновационный подход**
Этанол в качестве внутреннего стандарта



В соответствии с методом "Этанол в качестве внутреннего стандарта" концентрация *i*-го компонента в размерности мг/л безводного спирта определяется по следующей формуле

$$C_i\,(\text{мг/л безводного спирта}) = RRF_i^{Eth} \cdot \frac{A_i}{A_{Eth}} \cdot \rho_{Eth}\,(\text{мг/л})$$

Значения относительных коэффициентов отклика детектора на исследуемый летучий компонент относительно отклика на этанол вычисляют по следующей формуле:

$$RRF_i^{Eth} = \frac{C_i^{calibr}\,(\text{мг/л безводного спирта})}{\rho_{Eth}\,(\text{мг/л})} \cdot \frac{A_{Eth}^{calibr}}{A_i^{calibr}}$$

1. Нет необходимости добавлять какой-либо внутренний стандарт в образец.
2. Этанол всегда присутствует в алкогольной продукции и его концентрация в **мг/л безводного спирта** всегда известна со 100 % гарантией и равна плотности этанола $\rho_{Eth} = 789300$ мг/л.

Сделано

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20. Improved document Indian Standard 3572-2005, https://elab.bsu.by/download.php?id=315
21. Improved document Norma Mexicana NMX-V-005-NORMEX-2013 https://elab.bsu.by/download.php?id=311
22. Improved document National standards of People's Republic of China GB/T 15038 https://elab.bsu.by/download.php?id=309
23 and GB/T 11858 https://elab.bsu.by/download.php?id=307
24. Improved document AOAC Official Method 972.10 (USA), https://elab.bsu.by/download.php?id=306
25. Improved document AOAC Official Method 972.11 (USA), https://elab.bsu.by/download.php?id=305
26. Improved document ГОСТ 30536-2013 https://elab.bsu.by/download.php?id=314
27. Improved document СТБ ГОСТ Р-2001 https://elab.bsu.by/download.php?id=313

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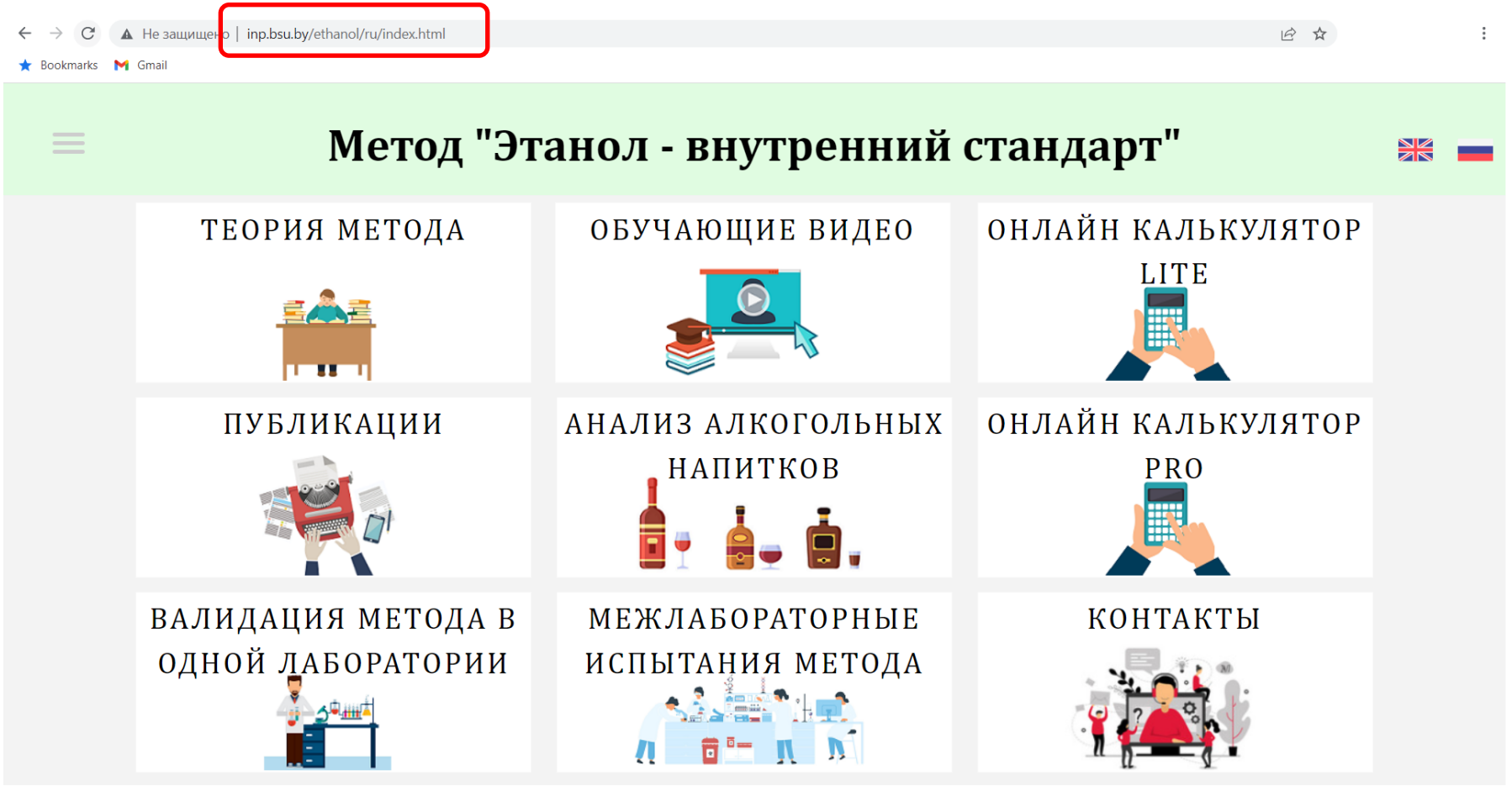
Не защищено | inp.bsu.by/ethanol/ru/index.html
Bookmarks
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Метод "Этанол - внутренний стандарт"
ТЕОРИЯ МЕТОДА
ОБУЧАЮЩИЕ ВИДЕО
ОНЛАЙН КАЛЬКУЛЯТОР LITE
ПУБЛИКАЦИИ
АНАЛИЗ АЛКОГОЛЬНЫХ НАПИТКОВ
ОНЛАЙН КАЛЬКУЛЯТОР PRO
ВАЛИДАЦИЯ МЕТОДА В ОДНОЙ ЛАБОРАТОРИИ
МЕЖЛАБОРАТОРНЫЕ ИСПЫТАНИЯ МЕТОДА
КОНТАКТЫ

Сделано

Алкогольный напиток													
	Виски	Бренди	Ром	Джин	Водка	Граппа	Текила	Кальвадос	Саке	Бурбон	Ракия	Скотч	Этанол 96% об.
Компонент	**Относительное различие в величинах измеренных концентраций , %**												
ацетальдегид	-1.7	0.2	1.2	1.1	0.1	-1.7	1.8	0.1	-1.8	-1.2	-0.6	1.4	-1.6
этилацетат	-1.8	0.1	1.1	1.0	-	-1.7	1.8	0.1	-1.8	-1.3	-0.7	1.3	-
метанол	-1.7	0.2	1.2	1.1	0.1	-1.7	1.9	0.1	-1.8	-1.2	-0.6	1.4	-1.6
2-пропанол	-1.7	0.1	1.2	1.1	0.1	-1.7	1.8	0.1	-	-1.3	-0.6	1.3	-1.6
1-пропанол	-1.7	0.2	1.2	-	-	-1.7	1.8	-	-1.8	-1.2	-0.6	-	-
изобутанол	-1.7	0.1	1.2	-	-	-1.7	1.8	0.1	-1.8	-1.3	-0.6	1.4	-
1-бутанол	-1.7	0.2	1.2	1.1	-	-1.7	1.9	0.1	-1.8	-1.3	-0.7	1.3	-
изоамилол	-1.7	0.2	1.2	1.1	-	-1.7	1.8	0.1	-1.8	-1.2	-0.6	1.3	-

Относительное различие в величинах концентраций, измеренных в соответствии с регламентом ЕС 2870/2000 and в соответствии с предложенным методом не превосходит 2 %.

The study of the matrix effect on the method of direct determination of volatile compounds in a wide range of alcoholic beverages / ***Food Control***, **2021**, doi.org/10.1016/j.foodcont.2020.107528

Сделано

KELLY ET AL.: JOURNAL OF AOAC INTERNATIONAL VOL. 82, NO. 6, 1999 1375

FOOD COMPOSITION AND ADDITIVES

Gas Chromatographic Determination of Volatile Congeners in Spirit Drinks: Interlaboratory Study

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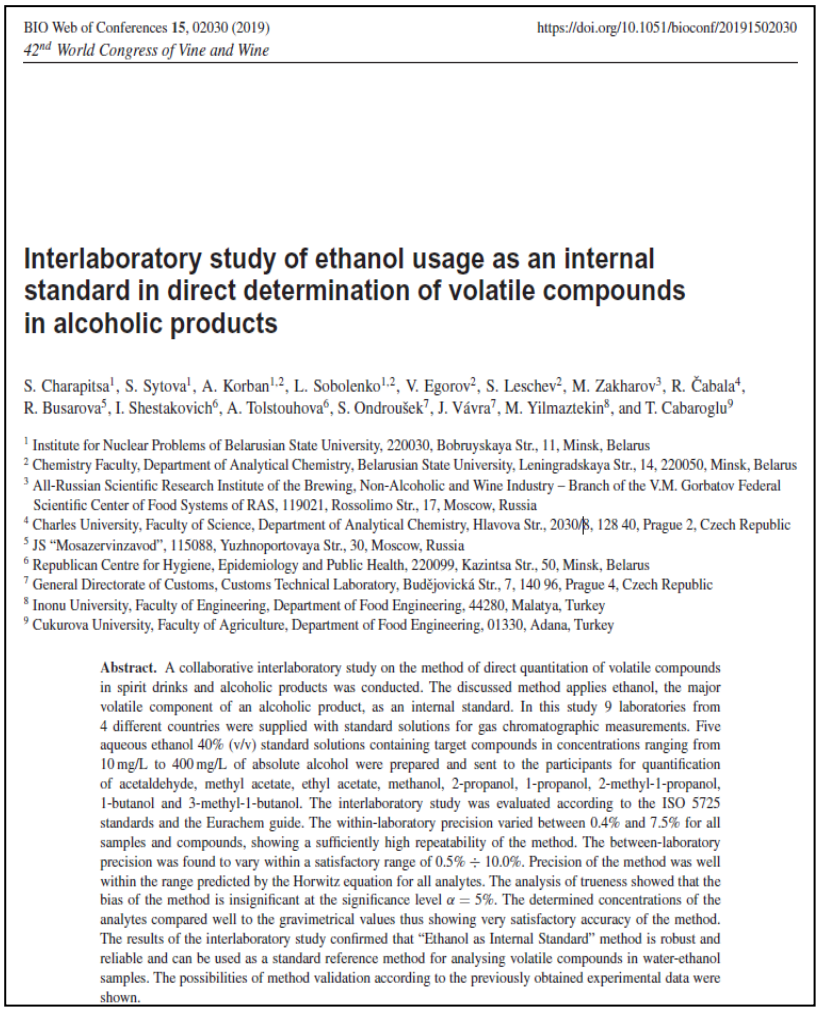
An interlaboratory study of a gas chromatographic (GC) method for the determination of volatile congeners in spirit drinks was conducted; 31 laboratories from 8 countries took part in the study. The method uses GC with flame ionization detection and incorporates several quality control measures which permit the choice of chromatographic system and conditions to be selected by the user. Spirit drink samples were prepared and sent to participants as 10 blind duplicate or split-level test materials for the determination of 1,1-diethoxyethane (acetal), 2-methylbutan-1-ol (active amyl alcohol), 3-methylbutan-1-ol (isoamyl alcohol), methanol (methyl alcohol), ethyl ethanoate (ethyl acetate), butan-1-ol (*n*-butanol), butan-2-ol (sec-butanol), 2-methylpropan-1-ol (isobutyl alcohol), propan-1-ol (*n*-propanol), and ethanal (acetaldehyde). The precision of the method for 9 of the 10 analytes was well

(2) that will prescribe methods of analysis to be used to monitor compliance with 1576/89.

Congeners are volatile substances formed along with ethanol during fermentation and maturation of spirit drinks and can be used to provide both qualitative and quantitative information for labelling purposes. In addition proposed European legislation specifically defines the volatile congener component of volatile substances as comprising the sum of: ethanal (acetaldehyde) and the ethanal fraction contained in 1,1-diethoxyethane (acetal) expressed as ethanal, and the sum of propan-1-ol (*n*-propanol), 2-methylpropan-1-ol (isobutyl alcohol), butan-1-ol (*n*-butanol), butan-2-ol (sec-butanol), 2-methylbutan-1-ol (active amyl alcohol) and 3-methylbutan-1-ol (isoamyl alcohol). Regulation 1576/89



BIO Web of Conferences **15**, 02030 (2019) https://doi.org/10.1051/bioconf/20191502030
42nd World Congress of Vine and Wine

Interlaboratory study of ethanol usage as an internal standard in direct determination of volatile compounds in alcoholic products

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Abstract. A collaborative interlaboratory study on the method of direct quantitation of volatile compounds in spirit drinks and alcoholic products was conducted. The discussed method applies ethanol, the major volatile component of an alcoholic product, as an internal standard. In this study 9 laboratories from 4 different countries were supplied with standard solutions for gas chromatographic measurements. Five aqueous ethanol 40% (v/v) standard solutions containing target compounds in concentrations ranging from 10 mg/L to 400 mg/L of absolute alcohol were prepared and sent to the participants for quantification of acetaldehyde, methyl acetate, ethyl acetate, methanol, 2-propanol, 1-propanol, 2-methyl-1-propanol, 1-butanol and 3-methyl-1-butanol. The interlaboratory study was evaluated according to the ISO 5725 standards and the Eurachem guide. The within-laboratory precision varied between 0.4% and 7.5% for all samples and compounds, showing a sufficiently high repeatability of the method. The between-laboratory precision was found to vary within a satisfactory range of 0.5% ÷ 10.0%. Precision of the method was well within the range predicted by the Horwitz equation for all analytes. The analysis of trueness showed that the bias of the method is insignificant at the significance level $\alpha = 5\%$. The determined concentrations of the analytes compared well to the gravimetrical values thus showing very satisfactory accuracy of the method. The results of the interlaboratory study confirmed that "Ethanol as Internal Standard" method is robust and reliable and can be used as a standard reference method for analysing volatile compounds in water-ethanol samples. The possibilities of method validation according to the previously obtained experimental data were shown.

8 стран **31 лаборатория** **42 соавтора**

4 страны **9 лабораторий** **15 соавторов**

Результаты межлабораторных с международным участием испытаний метода были представлены в виде устного доклада и опубликованы (**doi.org/10.1051/bioconf/20191502030**) в трудах 42-го Международного конгресса международной межправительственной организации виноделия и виноградарства (МОВВ - OIV), 15-19 июля 2019 г., Женева, Швейцария (www.OIV2019.ch).

Сделано

Проект

МЕЖГОСУДАРСТВЕННЫЙ СОВЕТ ПО СТАНДАРТИЗАЦИИ, МЕТРОЛОГИИ И СЕРТИФИКАЦИИ
(МГС)
INTERSTATE COUNCIL FOR STANDARDIZATION, METROLOGY AND CERTIFICATION
(ISC)

МЕЖГОСУДАРСТВЕННЫЙ СТАНДАРТ

ГОСТ 00001— 2023

ПРОДУКЦИЯ СПИРТОСОДЕРЖАЩАЯ

Определение метилового спирта методом газовой хроматографии

Издание официальное

Москва
Стандартинформ
2023

Проект

МЕЖГОСУДАРСТВЕННЫЙ СОВЕТ ПО СТАНДАРТИЗАЦИИ, МЕТРОЛОГИИ И СЕРТИФИКАЦИИ
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INTERSTATE COUNCIL FOR STANDARDIZATION, METROLOGY AND CERTIFICATION
(ISC)

МЕЖГОСУДАРСТВЕННЫЙ СТАНДАРТ

ГОСТ 00002— 2023

ПРОДУКЦИЯ СПИРТОСОДЕРЖАЩАЯ

Определение альдегидов, эфиров и спиртов методом газовой хроматографии

Издание официальное

Москва
Стандартинформ
2023

OIV-MA-BS-BS-14 / EC2870/2000 (10 principal volatile substances) becomes simpler, faster, easier, cheaper, trust and robust

OIV-MA-BS-14

Determination of the principal volatile substances of spirit drinks of viti-vinicultural origin

Type II method

1. Scope
This method is suitable for the determination of the following compounds by gas chromatography in spirit drinks of viti-vinicultural origin: ethanal (acetaldehyde), both free and total (obtained from the sum of ethanal and the fraction of ethanal contained in 1,1-diéthoxyéthane), ethyl ethanoate (ethyl acetate), 1,1-diethoxyethane (acetal), methanol (methyl alcohol), butan-2-ol (sec-butanol), propan-1-ol (n-propanol), 2-methylpropan-1-ol (isobutyl alcohol), butan-1-ol (n-butanol), 2-methylbutan-1-ol (active amyl alcohol), 3-methylbutan-1-ol (isoamyl alcohol).

2. Normative References
ISO 3696:1987 Water for analytical laboratory use - Specifications and test methods.

3. Definition
Congeners are volatile substances formed along with ethanol duringfermentation, distillation and maturation of spirit drinks.

4. Principle
Congeners in spirit drinks are determined by direct injection of the spirit drink, or appropriately diluted spirit drink, or its distillate, into a gas chromatography (GC) system. ~~A suitable internal standard is added to the spirit drink prior to injection.~~ The ethanol contained in the analyzed alcoholic product is used as an internal standard.
The congeners are separated by temperature programming on a suitable column

and are detected using a flame ionisation detector (FID). The concentration of each congener is determined with respect to the internal standard from response factors, which are obtained during calibration under the same chromatographic conditions as those of the spirit drink analysis.
Note: The concentrations of the analytes are expressed as grams per 100 litres of absolute ~~alcohol; the alcoholic strength of the product must be determined prior to analysis~~. It is not necessary to determine the alcohol strength of the product prior to analysis.

5. Reagents and Materials
Unless otherwise stated, use only reagents of a purity greater than 97 %, purchased from an ISO accredited supplier with a Certificate of Purity, free from other congeners at test dilution (this may be confirmed by injection of individual congener standards at the test dilution using GC conditions as in 6.4) and only water of at least grade 3 as defined in ISO 3696. Acetal and acetaldehyde must be stored in the dark at <5 °C, all other reagents should be stored according to the supplier's instructions.

5.1 Ethanol absolute (CAS 64-17-5)
5.2 Methanol (CAS 67-56-1)
5.3 Propan-1-ol (CAS 71-23-8)
5.4 2-methylpropan-1-ol (CAS 78-33-1)
~~5.5 Acceptable internal standards: pentan-3-ol (CAS 584-02-1), pentan-1-ol (CAS 71-41-0), 4-methylpentan-1-ol (CAS 626-89-1), 4-methylpentan-2-ol (CAS 108-11-2), or methyl nonanoate (CAS 1731-84-6).~~
5.6 2-methylbutan-1-ol (CAS 137-32-6)
5.7 3-methylbutan-1-ol (CAS 123-51-3)
5.8 Ethyl acetate (CAS 141-78-6)
5.9 Butan-1-ol (CAS 71-36-3)
5.10 Butan-2-ol (CAS 78-92-2)
5.11 Acetaldehyde (CAS 75-07-0)
5.12 Acetal (CAS 105-57-7)
5.13 40% v/v ethanol solution
To prepare 400 ml/l ethanol solution pour 400 ml ethanol (5.1) into a 1 litre volumetric flask, make up to volume with distilled water and mix.
5.14 Preparation and storage of standard solutions (procedure suggested for the validated method: the calibration ranges should be adapted to the nature of the different types of products analysed by each laboratory).

All standard solutions must be stored at <5 °C and be prepared freshly on a monthly basis, if necessary. Masses of components and solutions should be recorded to the nearest 0.1 mg.

5.14.1 Standard solution - A
Pipette the following reagents into a 100 ml volumetric flask, containing approximately 60 ml ethanol solution (5.13) to minimise component evaporation, make up to volume with ethanol solution (5.13) and mix thoroughly. Record the weight of the flask, each component added and the total final weight of contents.

Component	Volume (ml)
Methanol (5.2)	3.0
Propan-1-ol (5.3)	3.0
2-methylpropan-1-ol (5.4)	3.0
2-methylbutan-1-ol (5.6)	3.0
3-methylbutan-1-ol (5.7)	3.0
Ethyl acetate (5.8)	3.0
Butan-1-ol (5.9)	3.0
Butan-2-ol (5.10)	3.0
Acetaldehyde (5.11)	3.0
Acetal (5.12)	3.0

NOTE - It is preferable to add acetal and acetaldehyde last in order to minimise losses through evaporation. The solutions may be prepared individually, and the final solution and dilutions prepared subsequently.

~~5.14.2 Standard solution - B~~
~~Pipette 3 ml of pentan-3-ol, or other suitable internal standard, (5.5) into a 100 ml volumetric flask, containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.~~
~~Record the weight of the flask, the weight of pentan-3-ol or other internal standard added and the total final weight of contents.~~

5.14.3 Standard solution - C
Pipette 1 ml solution A (5.14.1) ~~and 1 ml solution B (5.14.2)~~ into a 100 ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

5.14.4 Standard solution - D
In order to maintain analytical continuity and an effective quality control, prepare a quality control standard using the previously prepared standard A (5.14.1) or, preferably, prepare a control standard as indicated for standard A, but using different batches or suppliers of reagents. Pipette 1 ml solution A (5.14.1) into a 100 ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

~~5.14.5 Standard solution - E~~
~~Pipette 10 ml solution B (5.14.2) into a 100 ml volumetric flask containing approximately 80 ml ethanol solution (5.13), make up to volume with ethanol solution (5.13) and mix thoroughly.~~
~~Record the weight of the flask, each component added and the total final weight of contents.~~

5.14.6 Standard solutions used to check the linearity of response of FID
Into separate 100 ml volumetric flasks, containing approximately 80 ml ethanol (5.13), pipette 0, 0.1, 0.5, 1.0, 2.0 ml solution A (5.14.1) ~~and 1 ml solution B (5.14.2)~~, make up to volume with ethanol solution (5.13) and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

5.14.7 QC standard solution
Pipette 9 ml standard solution D (5.14.4) and 1 ml ~~of standard solution E (5.14.5)~~ ***ethanol solution (5.13)*** into a weighing vessel and mix thoroughly.
Record the weight of the flask, each component added and the total final weight of contents.

6. Apparatus and Equipment
6.1 Apparatus capable of measuring the density and alcoholic strength.
6.2 Analytical balance, capable of measuring to four decimal places.
6.3 A temperature programmed gas chromatograph fitted with a flame ionisation detector and integrator or other data handling system capable of measuring peak areas.
6.4 Gas chromatographic column(s), capable of separating the analytes such that the minimum resolution between the individual components (other than 2-methylbutan-1-ol and 3-methylbutan-1-ol) is, as a guide, at least 1.3, if a simple visual examination of the chromatogram is not sufficient.

NOTE - The following columns and GC conditions are given as suitable examples:

1 A retention gap 1 m x 0.32 mm i.d. connected to a CP-WAX 57 CB column 50 m x 0.32 mm i.d. 0.2 µm film thickness (stabilised polyethylene glycol) followed by a Carbowax 400 column 50 m x 0.32 mm i.d. 0.2 µm film thickness. (Columns are connected using press-fit connectors.)

Carrier gas and pressure:	Helium (135 kPa)
Column temperature: hold at 70 C for 25 min.	35 °C for 17 min., 35 °C to 70 °C at 12 °C/min.,
Injector temperature:	150 °C
Detector temperature:	250 °C
Injection volume:	1 µl, split 20 to 100:1

2 A retention gap 1 m x 0.32 mm i.d. connected to a CP-WAX 57 CB column 50 m x 0.32 mm i.d. 0.2 µm film thickness (stabilised polyethylene glycol). (Retention gap is connected using a press-fit connector.)

Carrier gas and pressure:	Helium (65 kPa)
Column temperature: 110 °C to 190 °C at 30 °C/min.,	35 °C for 10 min., 35 °C to 110 °C at 5 °C/min., hold at 190 °C for 2 min.
Injector temperature:	260 °C
Detector temperature:	300 °C
Injection volume:	1 µl, split 55:1

3 A packed column (5% CW 20M, Carbopak B), 2 m x 2 mm i.d.

Column temperature: hold at 140 °C for 5 min., 140 °C to 150 °C at 5 °C/min., hold at 150 °C for 3 min.	65 °C for 4 min., 65 °C to 140 °C at 10 °C/min.,
Injector temperature:	65 °C
Detector temperature:	200 °C
Injection volume:	1 µl

7. Sampling and Samples.
7.1 Laboratory sample
On receipt, the alcoholic strength of each sample is measured (6.1).

8. Procedure (used for the validated method, and given as an example; the exact procedure, and in particular the calibration range, should be adapted to the nature of the spirit drinks analysed and to the procedures validated by each laboratory)
8.1 Test portion
~~8.1.1 Weigh an appropriate sealed weighing vessel and record the weight.~~
~~8.1.2 Pipette 9 ml laboratory sample into the vessel and record the weight (M_{SAMPLE}).~~
~~8.1.3 Add 1 ml of standard solution E (5.14.5) and record the weight (M_{IS}).~~
~~8.1.4 Shake the test material vigorously (at least 20 inversions). Samples must be stored at less than 5 °C prior to analysis in order to minimise any volatile losses.~~
~~***8.1.1 Put laboratory sample into 2 mL chromatographic vial for analysis.***~~
8.2 Blank test
~~8.2.1 Using a four decimal place balance (6.2), weigh an appropriate sealed weighing vessel and record the weight.~~
~~8.2.2 Pipette 9 ml 400 ml/l ethanol solution (5.13) into the vessel and record the weight.~~
~~8.2.3 Add 1 ml of standard solution E (5.14.5) and record the weight.~~
~~8.2.4 Shake the test material vigorously (at least 20 inversions). Samples must be stored at less than 5 °C prior to analysis in order to minimise any volatile losses.~~
~~***8.2.1 Put ethanol solution (5.13) into 2 mL chromatographic vial for analysis.***~~
8.3 Preliminary test

Inject standard solution C (5.14.3) to ensure that all of the analytes are separated with a minimum resolution of 1.3 (except 2-methylbutan-1-ol and 3-methylbutan-1-ol).

8.4 Calibration
The calibration should be checked using the following procedure. Ensure that the response is linear by successively analysing in triplicate each of the linearity standard solutions (5.14.6) ~~containing internal standard (IS)~~. From the integrator peak areas for each injection calculate the ratio R for each congener and plot a graph of R versus the concentration ratio of congener to internal standard (***ethanol***), C. A linear plot should be obtained, with a correlation coefficient of at least 0.99.

$$R = \frac{\text{Peak area of congener}}{\text{Peak area of IS}}$$

$$C = \frac{\text{Concentration of congener } (\mu g/g)}{\text{Concentration of IS } (\mu g/g)}$$

$$R = \frac{\text{Peak area of congener}}{\text{Peak area of ethanol}}$$

$$C = \frac{\text{Concentration of congener (g/100 L of anhydrous ethanol)}}{\text{Concentration of ethanol (78927 g/100 L)}}$$

8.5 Determination
Inject standard solution C (5.14.3) and 2 QC standard solutions (5.14.7). Follow with unknown samples (prepared according to 8.1 and 8.2) inserting one QC standard every 10 samples to ensure analytical stability. Inject one standard solution C (5.14.3) after every 5 samples.

9. Calculation
An automated system of data handling can be used, provided the data can be checked using the principles described in the method below and to good gas-chromatographic practice (calculation of response factors and/or establishment of calibration curves).
Measure peak areas for congener and internal standard ***(ethanol)*** peaks.

9.1 Response factor calculation.
From the chromatogram of the injection of standard solution C (5.14.3), calculate response factors for each congener using equation (1).

$$\text{(1) R response factor} = \frac{\text{Peak area of IS}}{\text{Peak area of congener}} \times \frac{\text{Conc. congener } (\mu g/g)}{\text{Conc. IS } (\mu g/g)}$$

where:
~~IS = internal Standard~~
~~Conc. congener = concentration of congener in solution C (5.14.3)~~
~~Conc. IS = concentration of internal standard in solution C (5.14.3).~~

$$\text{(1) Response factor} = \frac{\text{Peak area of ethanol}}{\text{Peak area of congener}} \times \frac{\text{Concentration of congener (g/100 L of anhydrous ethanol)}}{\text{Concentration of ethanol (78927 g/100 L)}}$$

9.2 Sample analysis
Using equation (2) below, calculate the concentration of each congener in the samples.

(2) Congener concentrations, ~~(µg/g)~~ ***(g/100 L)***=

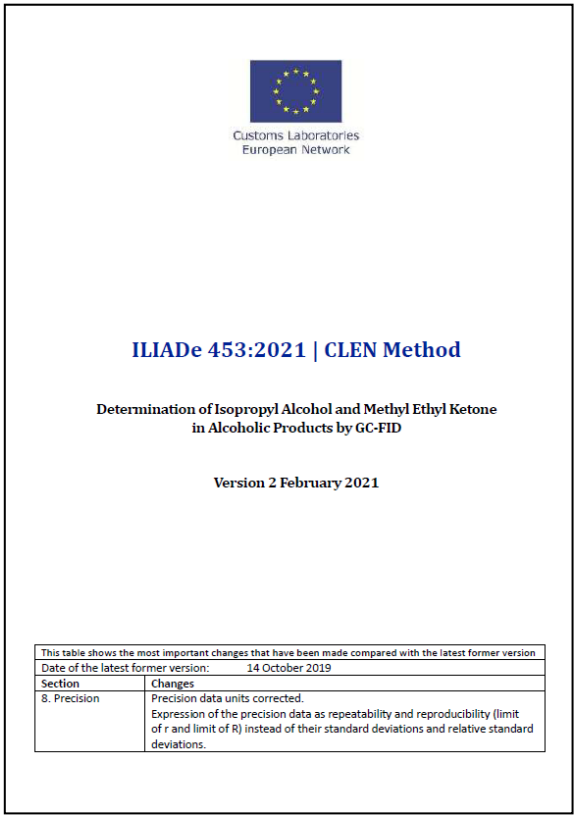
$$\frac{\text{Peak area of congener}}{\text{Peak area of IS}} \times \frac{M_{IS}(g)}{M_{SAMPLE}(g)} \times \text{Conc. IS } (\mu g/g) \times RF$$

where:
~~M_{SAMPLE} = weight of sample (8.1.2);~~
~~M_{IS} = weight of internal standard (8.1.3);~~
~~Conc. IS = concentration of internal standard in solution E (5.14.5);~~
~~RF = response factor calculated using equation 1.~~

$$\frac{\text{Peak area of congener}}{\text{Peak area of ethanol}} \times \text{Concentration of ethanol (78927 g/100 L)} \times RF$$

9.3 Quality control standard solution analysis
Using equation (3) below, calculate the percentage recovery of the target value for each congener in the Quality Control standards (5.14.7):

Сделано



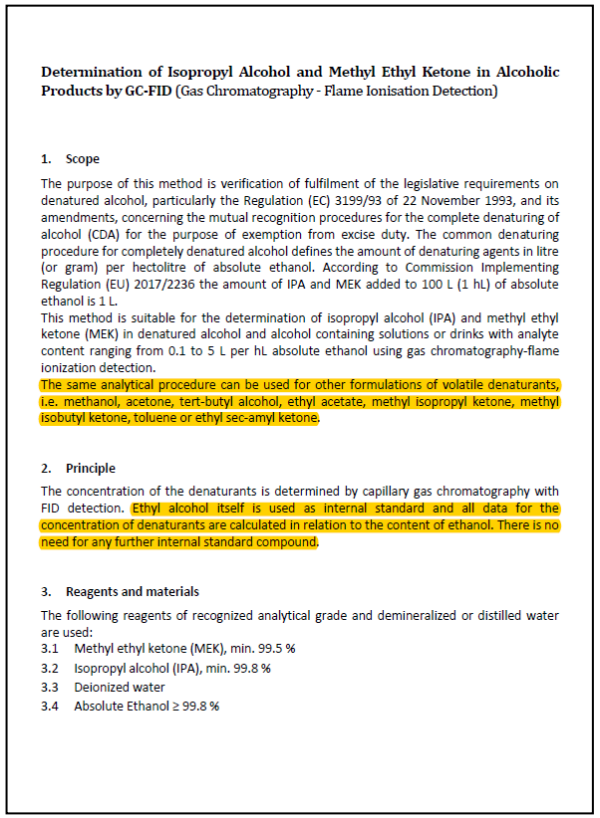
Customs Laboratories
European Network

ILIADe 453:2021 | CLEN Method

Determination of Isopropyl Alcohol and Methyl Ethyl Ketone in Alcoholic Products by GC-FID

Version 2 February 2021

This table shows the most important changes that have been made compared with the latest former version	
Date of the latest former version: 14 October 2019	
Section	**Changes**
8. Precision	Precision data units corrected. Expression of the precision data as repeatability and reproducibility (limit of r and limit of R) instead of their standard deviations and relative standard deviations.



Determination of Isopropyl Alcohol and Methyl Ethyl Ketone in Alcoholic Products by GC-FID (Gas Chromatography - Flame Ionisation Detection)

1. Scope

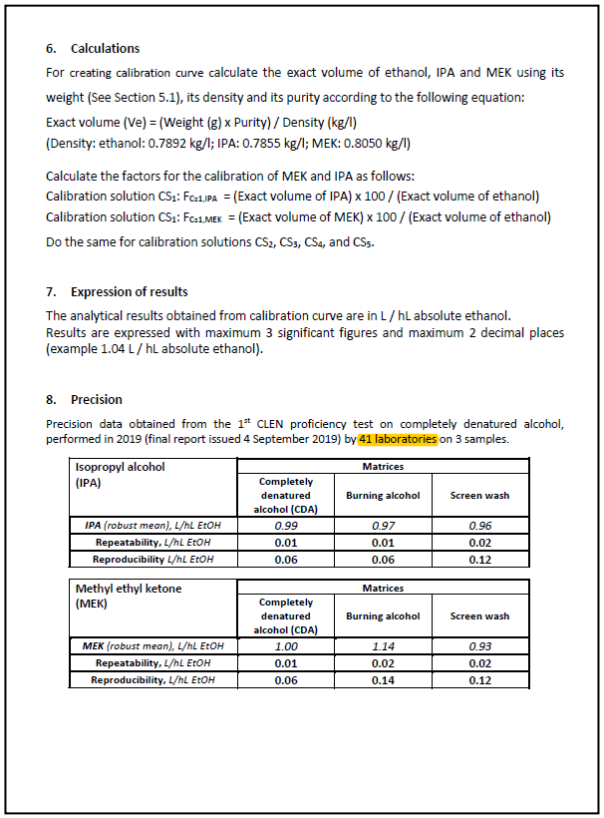
The purpose of this method is verification of fulfilment of the legislative requirements on denatured alcohol, particularly the Regulation (EC) 3199/93 of 22 November 1993, and its amendments, concerning the mutual recognition procedures for the complete denaturing of alcohol (CDA) for the purpose of exemption from excise duty. The common denaturing procedure for completely denatured alcohol defines the amount of denaturing agents in litre (or gram) per hectolitre of absolute ethanol. According to Commission Implementing Regulation (EU) 2017/2236 the amount of IPA and MEK added to 100 L (1 hL) of absolute ethanol is 1 L.
This method is suitable for the determination of isopropyl alcohol (IPA) and methyl ethyl ketone (MEK) in denatured alcohol and alcohol containing solutions or drinks with analyte content ranging from 0.1 to 5 L per hL absolute ethanol using gas chromatography-flame ionization detection.
The same analytical procedure can be used for other formulations of volatile denaturants, i.e. methanol, acetone, tert-butyl alcohol, ethyl acetate, methyl isopropyl ketone, methyl isobutyl ketone, toluene or ethyl sec-amyl ketone.

2. Principle

The concentration of the denaturants is determined by capillary gas chromatography with FID detection. Ethyl alcohol itself is used as internal standard and all data for the concentration of denaturants are calculated in relation to the content of ethanol. There is no need for any further internal standard compound.

3. Reagents and materials

The following reagents of recognized analytical grade and demineralized or distilled water are used:
3.1 Methyl ethyl ketone (MEK), min. 99.5 %
3.2 Isopropyl alcohol (IPA), min. 99.8 %
3.3 Deionized water
3.4 Absolute Ethanol ≥ 99.8 %



6. Calculations

For creating calibration curve calculate the exact volume of ethanol, IPA and MEK using its weight (See Section 5.1), its density and its purity according to the following equation:

Exact volume (Ve) = (Weight (g) x Purity) / Density (kg/l)
(Density: ethanol: 0.7892 kg/l; IPA: 0.7855 kg/l; MEK: 0.8050 kg/l)

Calculate the factors for the calibration of MEK and IPA as follows:
Calibration solution CS_1: $F_{c\text{s}1,IPA}$ = (Exact volume of IPA) x 100 / (Exact volume of ethanol)
Calibration solution CS_1: $F_{c\text{s}1,MEK}$ = (Exact volume of MEK) x 100 / (Exact volume of ethanol)
Do the same for calibration solutions CS_2, CS_3, CS_4, and CS_5.

7. Expression of results

The analytical results obtained from calibration curve are in L / hL absolute ethanol.
Results are expressed with maximum 3 significant figures and maximum 2 decimal places (example 1.04 L / hL absolute ethanol).

8. Precision

Precision data obtained from the 1st CLEN proficiency test on completely denatured alcohol, performed in 2019 (final report issued 4 September 2019) by 41 laboratories on 3 samples.

Isopropyl alcohol (IPA)	Matrices		
	Completely denatured alcohol (CDA)	Burning alcohol	Screen wash
IPA (robust mean), L/hL EtOH	*0.99*	*0.97*	*0.96*
Repeatability, *L/hL EtOH*	0.01	0.01	0.02
Reproducibility *L/hL EtOH*	0.06	0.06	0.12

Methyl ethyl ketone (MEK)	Matrices		
	Completely denatured alcohol (CDA)	Burning alcohol	Screen wash
MEK (robust mean), L/hL EtOH	*1.00*	*1.14*	*0.93*
Repeatability, *L/hL EtOH*	0.01	0.02	0.02
Reproducibility, *L/hL EtOH*	0.06	0.14	0.12

Метод принят в качестве официального в таможенных лабораториях на основе межлабораторных испытаний в 41 аккредитованной лаборатории Евросоюза

1 400 млн

1 400 млн

450 млн

333 млн

Республика Беларусь не должна отказаться от того, чтобы контроль качества и безопасности миллионов литров алкогольной продукции, ежедневно производимой по всему миру, выполнялся по белорусскому методу.

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