Customs Laboratories
European Network

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

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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 %

4. Apparatus

4.1 Analytical balance with precision of 0.1 mg

4.2 Flask with a tight closing cap (for weighing calibration solutions), 110 mL at least, maximum weight 110 g (in the case of weighing capacities of analytical balance up to 200 g)

4.3 A gas chromatograph with split / split less injector, flame ionisation detector (FID), auto sampler or the necessary equipment for manual injection, PC for control of the GC and data processing or integrator

4.4 GC capillary column: Gas chromatographic column capable of separating the analytes with minimum resolution at least 1.5, e.g. Restek RTX Volatiles ID 0.32 mm, length 60 m, 1.5 µm

4.5 Chromatographic parameters

Chromatographic parameters for Restek RTX column (60 m x 0.32 mm x 1.5 µm) are as follows:

- Carrier gas: Helium
- Flow rate: 1.7 ml / min
- Injection temperature: 230 °C
- Detector temperature: 260 °C
- Temperature program: 40 °C - 7 min; 10 °C / min to 140 °C; 40 °C / min to 230 °C
- Injection volume: 1 µl
- Auto sampler cleaning mode: pre injection solvent flushes: two times, pre injection sample flushes: two times, post injection solvent flushes (e.g. methanol and cyclohexane): two times
- Split ratio: 1:100

Alternative GC capillary columns and experimental conditions are shown in Annex.

5. Procedure

5.1 Preparation of the calibration solutions

In order to simplify the calculation the original procedure of denaturing is followed during the preparation of the calibration solutions. The respective denaturants are added to 100 mL of absolute ethanol. The unit used is mL denaturant added to 100 mL absolute ethanol or L denaturant added to 1 hL absolute ethanol (for example 1 L MEK added to 1 hL absolute ethanol).

Data for calibration curve construction are obtained by the measurement of 5 calibration solutions covering a concentration range from 0.1 to 5.0 mL per 100 mL of absolute ethanol. As an internal standard ethanol itself is used so the calibration solutions contain only ethanol, MEK and IPA.
The chemicals are weighted into flasks by means of an analytical balance.

Solutions for calibration points from CS_1 to CS_5 are prepared as follows:

- CS1: add 100 ml of ethanol in the weighted flask, weight it, then add 0.1 ml of MEK, weight it, then add 0.1 ml of IPA, weight it.

  Repeat weighing as follows:

- CS2: 100 ml ethanol, 0.5 ml MEK, 0.5 ml IPA;
- CS3: 100 ml ethanol, 1.0 ml MEK, 1.0 ml IPA;
- CS4: 100 ml ethanol, 3.0 ml MEK, 3.0 ml IPA;
- CS5: 100 ml ethanol, 5.0 ml MEK, 5.0 ml IPA.

Shake well each solution, transfer the solutions into the GC vials used for the auto-sampler of the gas chromatograph for analysis. No further dilution is necessary.

Calibration solutions should be stored in a refrigerator.

5.2 Creating calibration curve

Before creating a calibration curve the retention times of ethanol, MEK and IPA at the specific GC conditions must be determined.

Calibration factors should be entered into the integrator of the GC system:

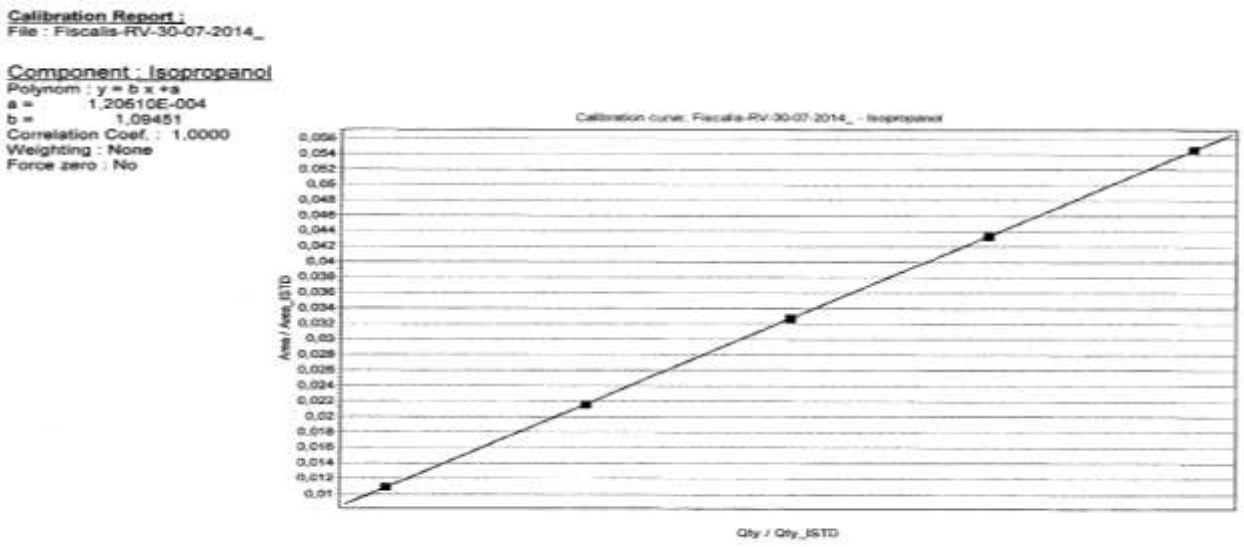
- for internal standard ethanol, factor 100,
- for every calibration solution, the respective factor for MEK and IPA calculated according to Section 6.

Enter the unit of the results (L / hL of absolute ethanol) in the GC calibration method.
Measure the peak areas of ethanol, MEK and IPA, using an integrator or another data system.
Plot the following relationships:

- x-axis: quantity / quantity ISTD
- y-axis: area / area of ISTD

Do not force it through zero. (See Fig. 1)

Fig. 1. Example of a calibration curve for isopropanol



5.3 Quality assurance and control

Inject every calibration solution at minimum three times and calculate the arithmetic mean and the standard deviation (SD). The maximum allowed deviation of the single values is 2 SD. The calibration curve must have a correlation coefficient higher than 0.999. If not, the calibration must be repeated.
The maximum acceptable intercept of the calibration curve (line) is |0.01| (absolute value). In case of a higher intercept, it is necessary to find the source of this problem and to repeat the calibration.

For system check blank samples (pure ethanol) are treated the same way as the samples themselves. It should produce a gas chromatogram exhibiting a clean baseline only.

Daily, before the first measurement one of the calibration solutions, or a separately prepared reference solution or a reference material, is injected for performing QC verification. If the results are within ± 5 % of their theoretical values for each denaturant, analysis may proceed. If not, an investigation should be made to find the cause of the inaccuracy and remedial action taken as appropriate (i.e. new calibration curve).

5.4 Analysis of samples

No specific sample preparation is required. The samples are injected directly into the GC system using the parameters described in Section 4.

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: $F_{Cs1,IPA}$ = (Exact volume of IPA) x 100 / (Exact volume of ethanol)
Calibration solution CS_1: $F_{Cs1,MEK}$ = (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**

Annex

(annex to section 4.5)

Alternative GC capillary columns and experimental conditions:

Column	Conditions
DB-624 (60 m x 0.250 mm x 1.4 µm)	Split 1:50 T program: 45°C – 5 min, 10°C/min to 50°C – 8 min, 30°C/ min to 220°C – 1 min; or: Split 1:100 T program: 40°C – 7 min, 10°C/min to 140°C; 40°C/ min to 230°C – 2 min.
DB-624 (30 m x 0.32 mm x 1.8 µm)	Split: 1:18 T program: 45°C – 2 min, 7°C/min to 90°C; 20°C/ min to 220°C – 8 min.
RXI-624 SiLMS (60 m x 0.32 mm x 1.8 µm)	Split 1:60 T program: 45°C, 15°C/min to 200°C – 4 min.
RTX-624 (60 m x 0.32 mm x 1.8 µm)	Split 1:150 T program: 45°C - 4 min, 10°C/min to 90°C; 20°C/min to 200°C - 2 min.
TRB 624 (60 m x 0.25 mm x 1.4 µm)	Split 1:100 T program: 40°C – 7 min, 10°C/min to 140°C, 40°C/ min to 230°C.
RTX-Volatiles (60 m x 0.32 mm x 1.5 µm)	Split flow 170 (1:98) T program: 40°C – 7 min, 10°C/min to 140°C, 40°C/ min to 230°C – 1 min.
SPB 624 (60 m x 0,25 mm x1,4 µm)	Split 1:100 T program: 40°C – 7 min, 10°C/min to 140°C, 40°C/ min to 230°C.
HP-5 (30 m x 0.32 mm x 0.25 µm)	Split 1:20 T program: 30°C – 4.5 min, 40°C/min to 210°C - 3 min.
HP-5 (30 m x 0.25 mm x 0.25 µm)	Split 1:150 T program: 40°C – 4 min, 15°C/min to 150°C – 4 min.
DB-1 (40 m x 0.18 mm x 0.4 µm)	Split 1:200 T program: 45°C – 4 min, 10°C/min to 90°C, 20°C/ min to 200°C – 2 min.
ZB-Bioethanol (30 m x 0.25 mm x 1 µm)	Split 1:100 T program: 50°C – 5 min, 80°C/min to 300°C – 2 min.