Method OIV-MA-BS-14 : R2009

Type II method

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

(OIV/OENO 379/2009)

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. Définition

Congeners are volatile substances formed along with ethanol during fermentation, 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 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.

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-méthylpentan-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) 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 □m film thickness (stabilised polyethylene glycol) followed by a Carbowax 400 column 50 m x 0.32 mm i.d. 0.2 □m film thickness. (Columns are connected using press-fit connectors.)
	Carrier gas and pressure: Helium (135 kPa)
	Column temperature:35 °C for 17 min., 35 °C to 70 °C at 12 °C/min., hold at 70 C for 25 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 □m film thickness (stabilised polyethylene glycol). (Retention gap is connected using a press-fit connector.)
	Carrier gas and pressure: Helium (65 kPa)
	Column temperature: 35 °C for 10 min., 35 °C to 110 °C at 5 °C/min., 110 °C to 190 °C at 30 °C/min., hold at 190 °C for 2 min.
	Injector temperature: 260 □C
	Detector temperature: 300 □C
	Injection volume: 1 □l, split 55:1
3	A packed column (5% CW 20M, Carbopak B), 2 m x 2 mm i.d.
	Column temperature: 65 °C for 4 min., 65 °C to 140 °C at 10 °C/min., hold at 140 °C for 5 min., 140 °C to 150 °C at 5 °C/min., hold at 150 °C for 3 min.
	Injector temperature: 65 □C
	Detector temperature: 200 □C
	Injection volume: 1 □l

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.

8.2. 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.

8.3. 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 (IS), C. A linear plot should be obtained, with a correlation coefficient of at least 0.99.

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

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

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 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).

(1) $$\text{Response factor} = \frac{\text{Peak area of IS}}{\text{Peak area of congener}} * \frac{\text{Conc. congener (µg/g))}}{\text{conc. IS (µg/g)}}$$

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).

9.2. Sample analysis

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

(2) $$\text{Congener concentrations, (µg/g)} = \frac{\text{Peak area of congener}}{\text{Peak area of IS}} \times \frac{M_{IS}(g)}{M_{SAMPLE}(g)} \times \text{Conc. IS (µg/g)} \times \text{RF}$$

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.

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):

(3) $$\text{\% Recovery of QC sample} = \frac{\text{concentration of analyte in QC standard}}{\text{concentration of analyte in solution D}} \times 100$$

The concentration of the analyte in the QC standard is calculated using equations (1)

and (2) above.

9.4. Final presentation of results

Results are converted from µg/g to g per 100 litres absolute alcohol for samples using equation (4):

(4) Concentration in g per 100 litres absolute alcohol= Conc (µg/g) □ □ □ 10/(strength(% vol.) □ 1000)

- where □ = density in kg/m³.

Results are quoted to a maximum of 3 significant figures and a maximum of one decimal place e.g. 11.4 g per 100 l absolute alcohol.

10. Quality Assurance and Control (used for the validated method)

Using equation (2) above, calculate the concentration of each congener in the quality control standard solutions prepared by following the procedure as in 8.1.1 to 8.1.4. Using equation (3), calculate the percentage recovery of the target value. If the analysed results are within □ 10 % of their theoretical values for each congener, analysis may proceed. If not, an investigation should be made to find the cause of the inaccuracy and remedial action taken as appropriate

11. Method performance characteristics (Precision)

The following data were obtained from an international method performance study carried out on a variety of spirit drinks to internationally agreed procedures.

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5

OIV-MA-BS-14 Determination of the principal volatile substances in spirit drinks of viti-vinicultural (Type II)

Analyte	ethanal

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	28	26	27	27	28
Number of outliers (Laboratories)	2	4	3	3	2
Number of accepted results	56	52	54	54	56
Mean value $(\bar{X})\ \mu g/g$	63.4	71.67	130.4	38.4 13.8*	28.6 52.2*
Repeatability standard deviation (s_r) µg/g	3.3	1.9	6.8	4.1	3.6
Repeatability relative standard deviation (RSD_r) (%)	5.2	2.6	5.2	15.8	8.9
Repeatability limit (r) µg/g.	9.3	5.3	19.1	11.6	10.1
Reproducibility standard deviation (s_R) □g/g	12	14	22	6.8	8.9
Reproducibility relative standard deviation (RSD_R) (%)	18.9	19.4	17.1	26.2	22.2
Reproducibility limit (R) µg/g.	33.5	38.9	62.4	19.1	25.1

Sample types

A Brandy; blind duplicates

B Kirsch; blind duplicates

C Grappa; blind duplicates

D Whisky; split levels*

E Rum; split levels*

OIV-MA-BS-14 Determination of the principal volatile substances in spirit drinks of viti-vinicultural (Type II)

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5
Analyte	ethyl acetate

Samples	**A**	**B**	**C**	**D**	**E**
Number of laboratories retained after eliminating outliers	24	24	25	24	24
Number of outliers (Laboratories)	2	2	1	2	2
Number of accepted results	48	48	50	48	48
Mean value $(\overline{X})\ \mu g/g$	96.8	1046	120.3	112.5 91.8*	99.1 117.0*
Repeatability standard deviation (s_r) µg/g	2.2	15	2.6	2.1	2.6
Repeatability relative standard deviation (RSD_r) (%)	2.3	1.4	2.1	2.0	2.4
Repeatability limit (r) µg/g.	6.2	40.7	7.2	5.8	7.3
Reproducibility standard deviation (s_R) µg/g	6.4	79	8.2	6.2	7.1
Reproducibility relative standard deviation (RSD_R) (%)	6.6	7.6	6.8	6.2	6.6
Reproducibility limit (R) µg/g.	17.9	221.9	22.9	17.5	20.0

Sample types

A Brandy; blind duplicates

B Kirsch; blind duplicates

C Grappa; blind duplicates

D Whisky; split levels*

E Rum; split levels*

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5
Analyte	acetal

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	20	21	22	17	21
Number of outliers (Laboratories)	4	3	2	4	3
Number of accepted results	40	42	44	34	42
Mean value ($\overline{X}$) $\mu g/g$	35.04	36.46	68.5	20.36 6.60*	15.1 28.3*
Repeatability standard deviation (s_r) µg/g	0.58	0.84	1.6	0.82	1.9
Repeatability relative standard deviation (RSD_r) (%)	1.7	2.3	2.3	6.1	8.7
Repeatability limit (r) µg/g.	1.6	2.4	4.4	2.3	5.3
Reproducibility standard deviation (s_R) ¤g/g	4.2	4.4	8.9	1.4	3.1
Reproducibility relative standard deviation (RSD_R) (%)	12.1	12.0	13.0	10.7	14.2

Reproducibility limit (R) µg/g.	11.8	12.2	25.0	4.0	8.7

Sample types
A Brandy; blind duplicates
B Kirsch; blind duplicates
C Grappa; blind duplicates
D Whisky; split levels*
E Rum; split levels*

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5
Analyte	total ethanal

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	23	19	22	21	22
Number of outliers (Laboratories)	1	5	2	3	2
Number of accepted results	46	38	44	42	44
Mean value ($\overline{X}$) $\mu g/g$	76.5	85.3	156.5	45.4 15.8*	32.7 61.8*
Repeatability standard deviation (s_r) µg/g	3.5	1.3	6.5	4.4	3.6
Repeatability relative standard deviation (RSD_r) (%)	4.6	1.5	4.2	14.2	7.6
Repeatability limit (r) µg/g.	9.8	3.5	18.3	12.2	10.0

Reproducibility standard deviation (s_R) µg/g	13	15	24.1	7.3	9.0
Reproducibility relative standard devRSD_Rn ()(%)	16.4	17.5	15.4	23.7	19.1
Reproducibility limit (R) µg/g.	35.2	41.8	67.4	20.3	25.2

Sample types

A Brandy; blind duplicates

B Kirsch; blind duplicates

C Grappa; blind duplicates

D Whisky; split levels*

E Rum; split levels*

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5
Analyte	Methanol

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	26	27	27	28	25
Number of outliers (Laboratories)	4	3	3	1	4
Number of accepted results	52	54	54	56	50
Mean value ($\overline{X}$) $\mu g/g$	319.8	2245	1326	83.0. 61.5*	18.6. 28.9*
Repeatability standard deviation (s_r) µg/g	4.4	27	22	1.5	1.3

Repeatability relative standard deviation (RSD_r) (%)	1.4	1.2	1.7	2.1	5.6
Repeatability limit (r) µg/g.	12.3	74.4	62.5	4.3	3.8
Reproducibility standard deviation (s_R) µg/g	13	99	60	4.5	2.8
Reproducibility relative standard deviation (RSD_R) (%)	3.9	4.4	4.6	6.2	11.8
Reproducibility limit (R) µg/g.	35.2	278.3	169.1	12.5	7.9

Sample types

A Brandy; blind duplicates

B Kirsch; blind duplicates

C Grappa; blind duplicates

D Whisky; split levels*

E Rum; split levels*

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	4
Analyte	butan-2-ol

Samples	A	B	C	E
Number of laboratories retained after eliminating outliers	21	27	29	22
Number of outliers (Laboratories)	4	3	1	3
Number of accepted results	42	54	58	44

Mean value ($\bar{X}$) $\mu g/g$	5.88	250.2	27.57	5.83 14.12*
Repeatability standard deviation (s_r) µg/g	0.40	2.2	0.87	0.64
Repeatability relative standard deviation (RSD_r) (%)	6.8	0.9	3.2	6.4
Repeatability limit (r) µg/g.	1.1	6.1	2.5	1.8
Reproducibility standard deviation (s_R) µg/g	0.89	13	3.2	0.87
Reproducibility relative standard deviation (RSD_R) (%)	15.2	5.1	11.5	8.7
Reproducibility limit (R) µg/g.	2.5	35.5	8.9	2.4

Sample types
A Brandy; blind duplicates
B Kirsch; blind duplicates
C Grappa; blind duplicates
E Rum; split levels*

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5
Analyte	propan-1-ol

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	29	27	27	29	29
Number of outliers (Laboratories)	2	4	3	2	2

Number of accepted results	58	54	54	58	58
Mean value ($\overline{X}$) $\mu g/g$	86.4	3541	159.1	272.1 229.3*	177.1 222.1*
Repeatability standard deviation (s_r) µg/g	3.0	24	3.6	2.3	3.3
Repeatability relative standard deviation (RSD_r) (%)	3.4	0.7	2.3	0.9	1.6
Repeatability limit (r) µg/g.	8.3	68.5	10.0	6.4	9.1
Reproducibility standard deviation (s_R) µg/g	5.3	150	6.5	9.0	8.1
Reproducibility relative standard deviation (RSD_R) (%)	6.1	4.1	4.1	3.6	4.1
Reproducibility limit (R) µg/g.	14.8	407.2	18.2	25.2	22.7

Sample types
A Brandy; blind duplicates
B Kirsch; blind duplicates
C Grappa; blind duplicates
D Whisky; split levels*
E Rum; split levels*

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	3
Analyte	butan-1-ol

Samples	A	B	C
Number of laboratories retained after eliminating outliers	20	22	22
Number of outliers (Laboratories)	4	4	6
Number of accepted results	40	44	44
Mean value ($\overline{X}$) $\mu g/g$	3.79	5.57	7.54
Repeatability standard deviation (s_r) µg/g	0.43	0.20	0.43
Repeatability relative standard deviation (RSD_r) (%)	11.2	3.6	5.6
Repeatability limit (r) µg/g.	1.1	0.6	1.2
Reproducibility standard deviation (s_R) µg/g	0.59	0.55	0.82
Reproducibility relative standard deviation (RSD_R) (%)	15.7	9.8	10.8
Reproducibility limit (R) µg/g.	1.7	1.5	2.3

Sample types
A Brandy; blind duplicates
B Kirsch; blind duplicates
C Grappa; blind duplicates*

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5
Analyte	2-methylpropan-1-ol

OIV-MA-BS-14 Determination of the principal volatile substances in spirit drinks of viti-vinicultural (Type II)

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	28	31	30	26	25
Number of outliers (Laboratories)	3	0	1	5	6
Number of accepted results	56	62	60	52	50
Mean value ($\overline{X}$) $\mu g/g$	174.2	111.7	185.0	291.0 246.8*	115.99 133.87*
Repeatability standard deviation (s_r) µg/g	2.3	1.6	2.5	1.8	0.74
Repeatability relative standard deviation (RSD_r) (%)	1.3	1.4	1.3	0.7	0.6
Repeatability limit (r) µg/g.	6.4	4.5	6.9	5.0	2.1
Reproducibility standard deviation (s_R) µg/g	8.9	8.9	9.7	6.0	6.2
Reproducibility relative standard deviation (RSD_R) (%)	5.1	8.0	5.2	2.2	5.0
Reproducibility limit (R) µg/g.	24.9	24.9	27.2	16.9	17.4

Sample types

A Brandy; blind duplicates

B Kirsch; blind duplicates

C Grappa; blind duplicates

D Whisky; split levels*

E Rum; split levels*

Year of interlaboratory test	1997
Number of laboratories	32

OIV-MA-BS-14 Determination of the principal volatile substances in spirit drinks of viti-vinicultural (Type II)

Number of samples	5
Analyte	2-methyl-butan-1-ol

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	25	26	25	27	25
Number of outliers (Laboratories)	3	2	3	1	2
Number of accepted results	50	52	50	54	50
Mean value ($\overline{X}$) $\mu g/g$	113.0	48.3	91.6	72.1 45.2*	39.5 61.5*
Repeatability standard deviation (s_r) µg/g	2.1	1.5	1.7	2.3	2.3
Repeatability relative standard deviation (RSD_r) (%)	1.9	3.1	1.8	3.9	4.5
Repeatability limit (r) µg/g.	6.0	4.2	4.7	6.4	6.3
Reproducibility standard deviation (s_R) µg/g	7.4	3.8	6.6	4.7	4.5
Reproducibility relative standard deviation (RSD_R) (%)	6.6	7.9	7.2	8.1	8.8
Reproducibility limit (R) µg/g.	20.8	10.7	18.4	13.3	12.5

Sample types

A Brandy; blind duplicates

B Kirsch; blind duplicates

C Grappa; blind duplicates

D Whisky; split levels*

E Rum; split levels*

OIV-MA-BS-14 Determination of the principal volatile substances in spirit drinks of viti-vinicultural (Type II)

Year of interlaboratory test	1997
Number of laboratories	32
Number of samples	5
Analyte	3-methyl-butan-1-ol

Samples	A	B	C	D	E
Number of laboratories retained after eliminating outliers	23	23	24	27	21
Number of outliers (Laboratories)	5	5	4	1	6
Number of accepted results	46	46	48	54	42
Mean value ($\overline{X}$) $\mu g/g$	459.4	242.7	288.4	142.2 120.4*	212.3 245.6*
Repeatability standard deviation (s_r) µg/g	5.0	2.4	3.4	2.4	3.2
Repeatability relative standard deviation (RSD_r) (%)	1.1	1.0	1.2	1.8	1.4
Repeatability limit (r) µg/g.	13.9	6.6	9.6	6.6	9.1
Reproducibility standard deviation (s_R) µg/g	29.8	13	21	8.5	6.7
Reproducibility relative standard deviation (RSD_R) (%)	6.5	5.2	7.3	6.5	2.9
Reproducibility limit (R) µg/g.	83.4	35.4	58.8	23.8	18.7

Sample types

A Brandy; blind duplicates

B Kirsch; blind duplicates

C Grappa; blind duplicates

D Whisky; split levels*

E Rum; split levels*

12. Bibliography

1. Commission Regulation (EC) N° 2870/2000 of 19 December 2000 laying down Community reference methods for the analysis of spirits drinks, *OJEC of 29 December 2000, L333/20*
2. P. Brereton, S. Hasnip, A. Bertrand, R. Wittkowski, C. Guillou, Analytical methods for the determination of spirit drinks, Trends in Analytical Chemistry, Vol. 22, No. 1, 19-25, 2003