RESOLUTION OIV-OENO 553-2016

ANALYSIS OF VOLATILE COMPOUNDS IN WINES BY GAS CHROMATOGRAPHY

THE GENERAL ASSEMBLY,

IN VIEW of Article 2, paragraph 2 iv of the Agreement of 3 April 2001 establishing the International Organisation of Vine and Wine,

At the proposal of the "Methods of Analysis" Sub-Commission,

DECIDES to add the following type IV method to Annex A of the Compendium of International Methods of Analysis:

ANALYSIS OF VOLATILE COMPOUNDS IN WINES BY GAS CHROMATOGRAPHY

1. Object

This method is applicable to the analysis of volatile compounds in wines containing less than 20 g/L sugar.

For wines with a sugar content higher than 20 g/L and for mistelles, prior distillation (identical to that practised to obtain the ABV) is necessary; however distillation sometimes removes a significant part of the compounds.

2. Scope of application

The present method may be used for the quantification of the following compounds (non-exhaustive list):

- Ethanal,
- Ethyl acetate,
- Methanol,
- Butan-2-ol,
- Propan-1-ol,
- 2-methylpropan-1-ol,

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- Isoamyl acetate,
- Butan-1-ol,
- 2-methylbutan-1-ol,
- 3-methylbutan-1-ol,
- Pentan-1-ol,
- Acetoin,
- Ethyl lactate,
- Hexan-1-ol,
- 3-ethoxypropanol,
- Ethyl octanoate,
- Furfuraldehyde,
- (2R,3R)-butane-2,3-diol,
- (2R,3S)-butane-2,3-diol,
- Propane-1,2-diol,
- Butyrolactone,
- Diethyl succinate,
- Hexanoic acid (semi-quantitative),
- 2-phenylethanol,
- Diethyl malate,
- Octanoic acid (semi-quantitative),
- Decanoic acid (semi-quantitative).

Note: diacetyl and acetic acid cannot be quantified by this method yet they appear in the chromatograms.

3. Principle

Volatile compounds are quantified by gas chromatography after direct injection of the

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sample, added with an internal standard, into a capillary column coated with a bonded polar phase and detection using flame ionisation.

4. Reagents and products

The quantities and method of preparation are given by way of example and may be adapted as necessary to the types of wine.

4.1. Demineralised water (e.g. ISO 3696 type II or resistivity ≥ 18 MΩ.cm);

4.2. ethanol [CAS no. 64-17-5], purity ≥ 96%;

4.3. high-purity hydrogen for GC (e.g. H2O ≤ 4 ppm; O2 ≤ 2 ppm; CnHm ≤ 0.5 ppm; N2 ≤ 4 ppm);

4.4. high-purity helium for GC (H2O ≤ 3 ppm; O2 ≤ 2 ppm; CnHm ≤ 1 ppm; N2 ≤ 5 ppm);

4.5. high-purity compressed air for GC;

4.6. ethanal [CAS no. 75-07-0], purity ≥ 99%;

4.7. ethyl acetate [CAS no. 141-78-6], purity ≥ 99.5%;

4.8. methanol [CAS no. 67-56-1], purity ≥ 99.8%;

4.9. diacetyl [CAS no. 431-03-08], purity ≥ 99%;

4.10. butan-2-ol [CAS no. 15892-23-6], purity ≥ 99.5%;

4.11. propan-1-ol [CAS no. 71-23-8], purity ≥ 99.5%;

4.12. 2-methylpropan-1-ol [CAS no. 78-83-1], purity ≥ 99.5%;

4.13. isoamyl acetate [CAS no. 123-92-2], purity ≥ 97%;

4.14. butan-1-ol [CAS no. 71-36-3], purity ≥ 99.5%;

4.15. 4-methylpentan-2-ol (internal standard) [CAS no. 108-11-2], purity ≥ 99%;

4.16. 2-methylbutan-1-ol [CAS no. 137-32-6], purity ≥ 99%;

4.17. 3-methylbutan-1-ol [CAS no. 125-51-3], purity ≥ 99.5%;

4.18. pentan-1-ol [CAS no. 71-41-0], purity ≥ 99%;

4.19. acetoin [CAS no. 513-86-0], purity ≥ 96%;

4.20. ethyl lactate [CAS no. 687-47-8], purity ≥ 98%;

4.21. hexan-1-ol [CAS no. 111-27-3], purity ≥ 99.0%;

4.22. 3-ethoxypropanol [CAS no. 111-35-3], purity ≥ 97%;

4.23. ethyl octanoate [CAS no. 106-32-1], purity ≥ 99%;

4.24. furfuraldehyde [CAS no. 98-01-1], purity ≥ 99.0%;

4.25. acetic acid [CAS no. 64-19-7], purity ≥ 99%;

4.26. (2R,3R)- and (2R,3S)-butane-2,3-diol [CAS no. 513-85-9], purity ≥ 98%;

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4.27. propane-1,2-diol [CAS no. 57-556], purity ≥ 99.5%;

4.28. butyrolactone [CAS no. 96-48-0], purity ≥ 99%;

4.29. diethyl succinate [CAS no. 123-25-1], purity ≥ 99%;

4.30. hexanoic acid [CAS no. 142-62-1], purity ≥ 99.5%;

4.31. 2-phenylethanol [CAS no. 60-12-8], purity ≥ 99%;

4.32. diethyl malate [CAS no. 7554-12-3], purity ≥ 97%;

4.33. octanoic acid [CAS no. 124-07-2], purity ≥ 99.5%;

4.34. decanoic acid [CAS no. 334-48-5], purity ≥ 99.5%.

Note: diacetyl and acetic acid cannot be quantified by this method yet they appear in the chromatograms.

Preparation of reagent solutions (the quantities are given by way of example and may be adapted as necessary to the types of matrix to be analysed)

4.35. 10% Aqueous-alcoholic mixture to be made up with ethanol (4.2) and water (4.1).

4.36. Internal standard solution

Transfer 1 mL 4-methylpentan-2-ol (4.15) into a 100-mL flask (5.2). Fill up to the calibration mark with ethanol (4.2). Divide into flasks on which the date of preparation is noted. Keep refrigerated.

4.37. Internal or external reference wine (a CRM (Certified Reference Material) wine or a wine used as a reference material from a proficiency-testing programme between laboratoriesfor example).

4.38. Stock calibration solution

The compounds are individually weighed at ± 1 mg (nominal weights given in the table below) using a precision balance (5.4). In order to avoid losses through evaporation, quickly add a small amount of ethanol (4.2). Mix and pour into a 1-L flask (5.3). Rinse with ethanol. Add 2.5 mL 4-methylpentan-2-ol (4.15). Make up to 1 L with ethanol (4.2) and mix. Divide into flasks and store in the freezer. Record the exact weights.

Compound	Nominal weight (mg)	Final concentration in the working calibration solution 4.39 (mg/L)	Compound	Nominal weight (mg)	Final concentration in the working calibration solution 4.39 (mg/L)
Ethanal (4.6)	500	50	Hexan-1-ol (4.21)	300	30

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Ethyl acetate (4.7)	1500	150	3-Ethoxypropanol (4.22)	160	16
Methanol (4.8)	650	65	Furfuraldehyde (4.24)	50	5
Diacetyl (4.9)	50	5	Ethyl octanoate (4.23)	120	12
Butan-2-ol (4.10)	160	16	Acetic acid (5.25)	5000	500
Propan-1-ol (4.11)	350	35	Butane-2,3-diol (4.26)	4000	400
2-Methylpropan-1-ol (4.12)	240	24	Propane-1,2-diol (4.27)	1000	100
Isoamyl acetate (4.13)	250	25	Butyrolactone (4.28)	50	5
Butan-1-ol (4.14)	160	16	Diethyl succinate (4.29)	500	50
2-Methylbutan-1-ol (4.16)	160	16	Hexanoic acid (4.30)	250	25
3-Methylbutan-1-ol (4.17)	1000	100	2-Phenylethanol (4.31)	500	50
Pentan-1-ol (4.18)	160	16	Diethyl malate (4.32)	1000	100
Acetoin (4.19)	250	25	Octanoic acid (4.33)	500	50
Ethyl lactate (4.20)	1500	150	Decanoic acid (4.34)	750	75

4.39. Working calibration solution

Just before use, dilute the stock calibration solution (4.38) ten times.

5. Apparatus

5.1. 20-mL volumetric flasks (class A);

5.2. 100-mL volumetric flasks (class A);

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5.3. 1-L volumetric flasks (class A);
5.4. precision balance with an accuracy of ± 1 mg;
5.5. gas chromatograph equipped with:

- "split-splitless" injector,
- autosampler (optional),
- detector: flame ionisation (FID);

5.6. fused-silica capillary column:

- Carbowax 20 M type with a bonded polar phase,
- 50 m in length,
- internal diameter of 0.32 mm,
- film thickness of 0.45 µm.

Note: other systems may be used on condition that they are capable of satisfactorily separating the different compounds.

6. Preparation of the samples

Conduct a preliminary degassing of sparkling wine samples (for example, by first taking a sample using an automatic pipette and collecting it in a tube).
Distil the wines containing more than 20 g/L of sugar and the mistelles prior to preparation.
Introduce the sample into a 20-mL flask (5.1). Add 0.5 mL internal standard solution (4.36) and fill up to the calibration mark with wine.

7. Procedure

Analyse using the gas chromatograph (5.5) equipped with a capillary column (5.6).
Analytical conditions (given by way of example):
Carrier gas (4.4): P_{helium}= 90 kPa
Note: another carrier gas such as hydrogen may be used, but nitrogen is best avoided.
Septum flow rate: 2.5 mL/min

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Split flow rate: 40 mL/min
Split mode of injection
Volume injected: 1 µL
Temperature of the injector: 200 °C
Detector: FID (flame ionisation)

- Detector temperature at 250 °C
- Flame: $P_{hydrogen}$ (4.3) = 50 kPa and Pair (4.5) = 130 kPa

Temperature programming:

- . temp. 1 = 32 °C at 2.5 °C/min, up to 80 °C - t_1 = 0 min
- . temp. 2 = 80 °C at 4 °C/min, up to 170 °C - t_2 = 20 min
- . temp. 3 = 170 °C at 10 °C/min, up to 220°C - t_3 = 20 min

Calibration
Inject the working calibration solution (4.39) before each analysis series.
Calculation of response factors:

$$RF_i = (area_i \times Cc_{is})/(Cc_i \times area_{IS})$$

- Cc_i= concentration of the constituent of the calibration solution
- $area_i$= area of the constituent of the calibration solution
- Cc_{is}= concentration of the internal standard in the calibration solution
- $area_{IS}$= area of the internal standard in the calibration solution

It is also possible to use a calibration curve.
By way of example, chromatograms of a standard solution and a wine sample are given in the Annexes.

8. Calculations

In the case of use of a response factor, calculation of the concentrations is as follows:

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$$Cc_i = (area_i \times Cc_{IS})/(RF_i \times area_{IS})$$

9. Precision

See Annex C.

10. Quality assurance and control

Traceable to the international references through mass, volume and temperature.

Synthetic mixtures or samples coming, for instance, from proficiency ring test are used as internal quality control. A control chart may be used.

11. Results

Express concentrations in mg/L to the number of decimal places indicated below.

Analytical parameters	No. of decimal places	Analytical parameters	No. of decimal places
Ethanal	0	Ethyl lactate	0
Ethyl acetate	0	Hexan-1-ol	1
Methanol	0	3-Ethoxypropanol	0
Butan-2-ol	1	Ethyl octanoate	0
Propan-1-ol	0	Furfuraldehyde	1
2-Methylpropan-1-ol	0	(2R,3R)-Butane-2,3-diol	0
Isoamyl acetate	1	(Meso)-butane-2,3-diol	0
Butan-1-ol	1	Propane-1,2-diol	0
2-Methylbutan-1-ol	0	Butyrolactone	0

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3-Methylbutan-1-ol	0	Diethyl succinate	0
Pentan-1-ol	1	2-Phenylethanol	0
Acetoin	0	Diethyl malate	0

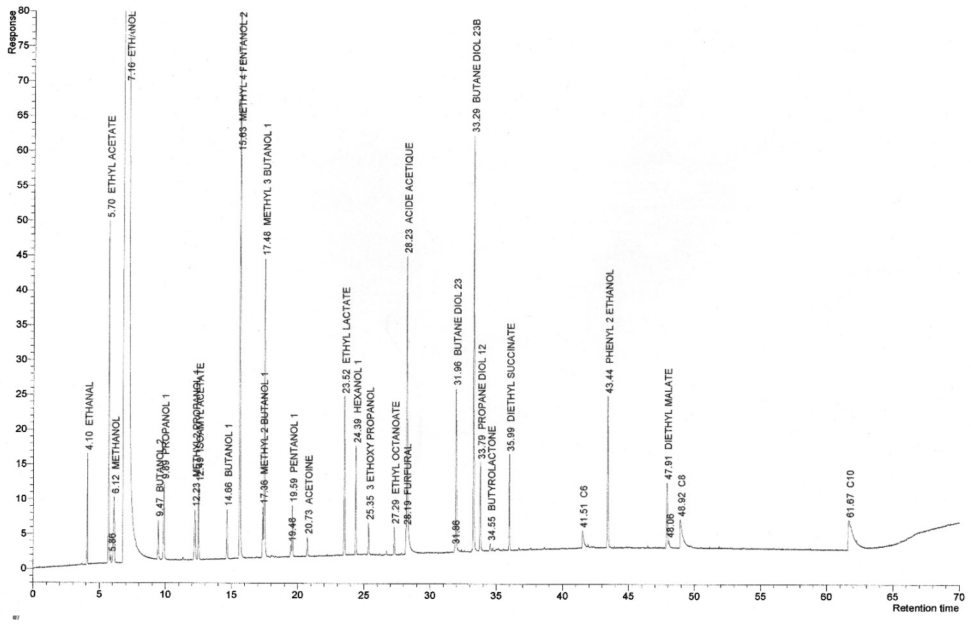
Annex A

Bibliography

1. BERTRAND A., GUEDES DE PINHO P. and ANOCIBAR BELOQUI A. (1994). Les constituants majoritaires du vin, FV 971, OIV, 15 pages.

ANNEX B

Example chromatograms



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Figure 1: Chromatogram of a standard solution of volatile compounds

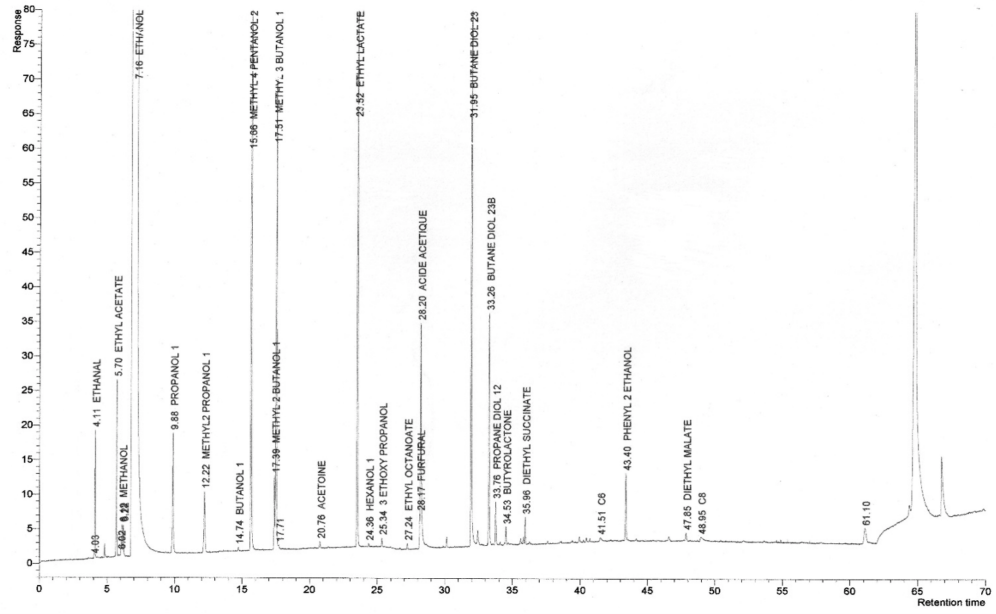


Figure 2: chromatogram of volatile compounds in a white wine (sugar < 15 g/L)

Annex C

Statistical results of the interlaboratory analysis

To be communicated in April 2017

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