

Méthode OIV-MA-AS315-27

Méthode Type IV

Analysis of volatile compounds in wines by gas chromatography

(Resolution OIV-OENO 553/2016)

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,
- 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 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 $\geq 18 \text{ M}\Omega\cdot\text{cm}$);
- 4.2 - ethanol [CAS no. 64-17-5], purity $\geq 96\%$;
- 4.3 - high-purity hydrogen for GC (e.g. $\text{H}_2\text{O} \leq 4 \text{ ppm}$; $\text{O}_2 \leq 2 \text{ ppm}$; $\text{C}_n\text{H}_m \leq 0.5 \text{ ppm}$; $\text{N}_2 \leq 4 \text{ ppm}$);
- 4.4 - high-purity helium for GC ($\text{H}_2\text{O} \leq 3 \text{ ppm}$; $\text{O}_2 \leq 2 \text{ ppm}$; $\text{C}_n\text{H}_m \leq 1 \text{ ppm}$; $\text{N}_2 \leq 5 \text{ ppm}$);
- 4.5 - high-purity compressed air for GC;
- 4.6 - ethanal [CAS no. 75-07-0], purity $\geq 99\%$;
- 4.7 - ethyl acetate [CAS no. 141-78-6], purity $\geq 99.5\%$;
- 4.8 - methanol [CAS no. 67-56-1], purity $\geq 99.8\%$;
- 4.9 - diacetyl [CAS no. 431-03-08], purity $\geq 99\%$;
- 4.10 - butan-2-ol [CAS no. 15892-23-6], purity $\geq 99.5\%$;
- 4.11 - propan-1-ol [CAS no. 71-23-8], purity $\geq 99.5\%$;
- 4.12 - 2-methylpropan-1-ol [CAS no. 78-83-1], purity $\geq 99.5\%$;
- 4.13 - isoamyl acetate [CAS no. 123-92-2], purity $\geq 97\%$;
- 4.14 - butan-1-ol [CAS no. 71-36-3], purity $\geq 99.5\%$;
- 4.15 - 4-methylpentan-2-ol (internal standard) [CAS no. 108-11-2], purity $\geq 99\%$;
- 4.16 - 2-methylbutan-1-ol [CAS no. 137-32-6], purity $\geq 99\%$;
- 4.17 - 3-methylbutan-1-ol [CAS no. 125-51-3], purity $\geq 99.5\%$;

- 4.18 - pentan-1-ol [CAS no. 71-41-0], purity $\geq 99\%$;
- 4.19 - acetoin [CAS no. 513-86-0], purity $\geq 96\%$;
- 4.20 - ethyl lactate [CAS no. 687-47-8], purity $\geq 98\%$;
- 4.21 - hexan-1-ol [CAS no. 111-27-3], purity $\geq 99.0\%$;
- 4.22 - 3-ethoxypropanol [CAS no. 111-35-3], purity $\geq 97\%$;
- 4.23 - ethyl octanoate [CAS no. 106-32-1], purity $\geq 99\%$;
- 4.24 - furfuraldehyde [CAS no. 98-01-1], purity $\geq 99.0\%$;
- 4.25 - acetic acid [CAS no. 64-19-7], purity $\geq 99\%$;
- 4.26 - (2R,3R)- and (2R,3S)-butane-2,3-diol [CAS no. 513-85-9], purity $\geq 98\%$;
- 4.27 - propane-1,2-diol [CAS no. 57-556], purity $\geq 99.5\%$;
- 4.28 - butyrolactone [CAS no. 96-48-0], purity $\geq 99\%$;
- 4.29 - diethyl succinate [CAS no. 123-25-1], purity $\geq 99\%$;
- 4.30 - hexanoic acid [CAS no. 142-62-1], purity $\geq 99.5\%$;
- 4.31 - 2-phenylethanol [CAS no. 60-12-8], purity $\geq 99\%$;
- 4.32 - diethyl malate [CAS no. 7554-12-3], purity $\geq 97\%$;
- 4.33 - octanoic acid [CAS no. 124-07-2], purity $\geq 99.5\%$;
- 4.34 - decanoic acid [CAS no. 334-48-5], purity $\geq 99.5\%$.

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 laboratories for 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.

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| 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 |
| 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);

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): $P_{\text{helium}} = 90$ kPa

Note: another carrier gas such as hydrogen may be used, but nitrogen is best avoided.

Septum flow rate: 2.5 mL/min

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: $P_{\text{hydrogen (4.3)}} = 50 \text{ kPa}$ and $P_{\text{air (4.5)}} = 130 \text{ kPa}$

Temperature programming:

. temp. 1 = 32 °C at 2.5 °C/min, up to 80 °C - $t_1 = 0 \text{ min}$

. temp. 2 = 80 °C at 4 °C/min, up to 170 °C - $t_2 = 20 \text{ min}$

. temp. 3 = 170 °C at 10 °C/min, up to 220°C - $t_3 = 20 \text{ min}$

Calibration

Inject the working calibration solution (4.39) before each analysis series.

Calculation of response factors:

$$RF_i = (\text{area}_i \times C_{\text{IS}}) / (C_i \times \text{area}_{\text{IS}})$$

C_i = concentration of the constituent of the calibration solution

Area_i = area of the constituent of the calibration solution

C_{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:

$$C_i = (\text{area}_i \times C_{\text{IS}}) / (RF_i \times \text{area}_{\text{IS}}).$$

9 – Precision

See Annex C.

10 – Quality assurance and control

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

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

Annex A
Bibliography



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

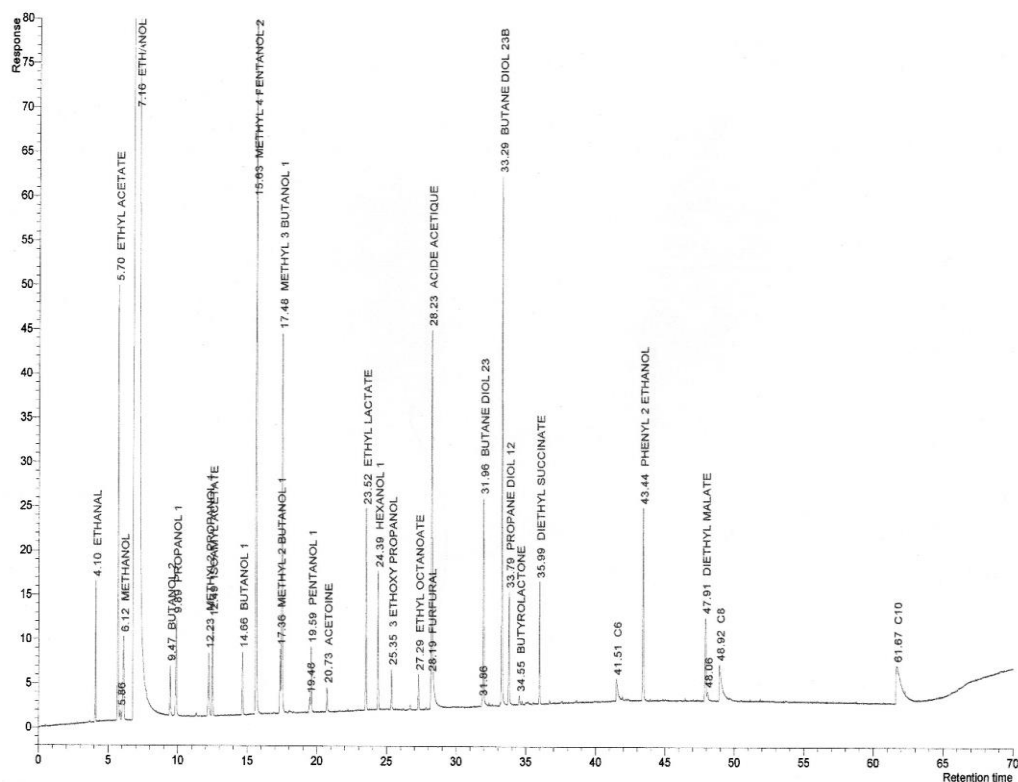


Figure 1: chromatogram of a standard solution of volatile compounds

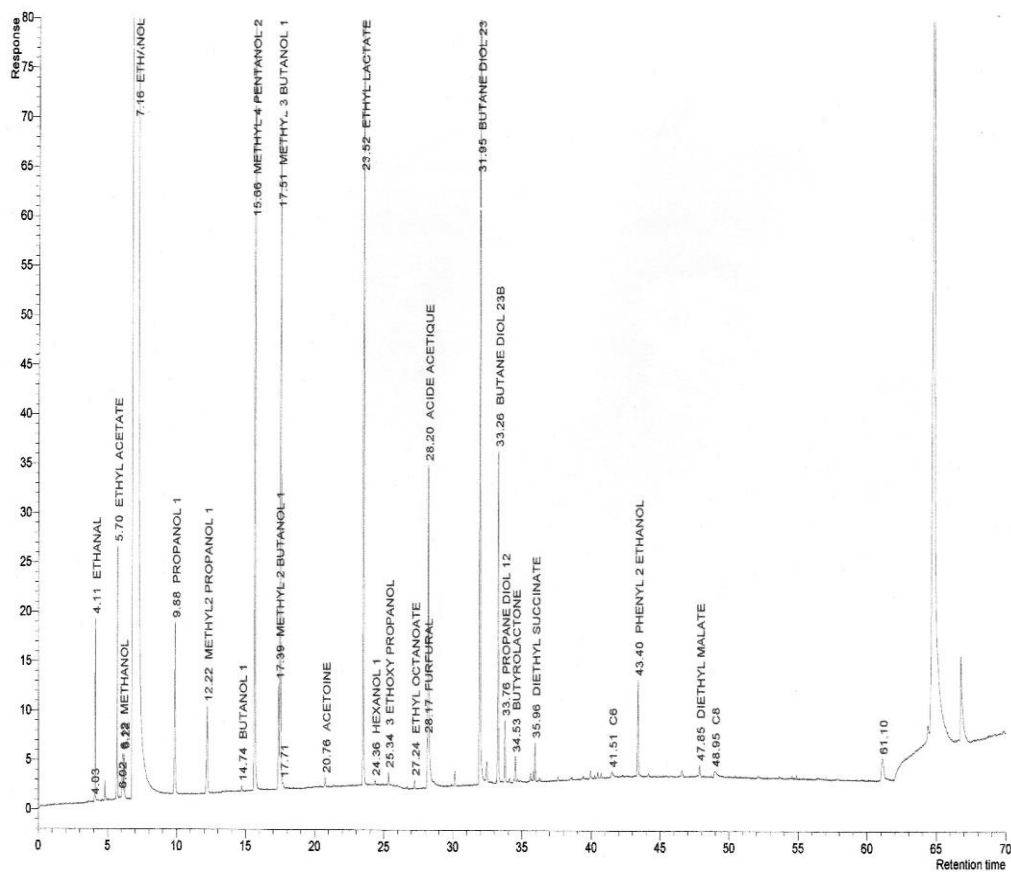


Figure 2 : chromatogram of volatile compounds in a white wine (sugar < 15 g/L)

