

Method OIV-MA-AS312-01A

Type I methods

Alcoholic strength by volume

(Resolution Oeno 566/2016)

1. DEFINITION

The alcoholic strength by volume is the number of liters of ethanol contained in 100 liters of wine, both volumes being measured at a temperature of 20°C. It is expressed by the symbol % vol.

Note: Homologues of ethanol, together with the ethanol and esters of ethanol homologues are included in the alcoholic strength since they occur in the distillate.

2. PRINCIPLE OF METHODS

2.1. *Distillation of wine* made alkaline by a suspension of calcium hydroxide.
Measurement of the alcoholic strength of the distillate:

2.2. *Type I methods:*

- A. Measurement of the alcoholic strength of the distillate with a pycnometer
- B. Measurement of the alcoholic strength of wine by electronic densimetry using frequency oscillator.
- C. Measurement of the alcoholic strength of wine by densimetry using hydrostatic balance.

3. Method of obtaining distillate

3.1. Apparatus

3.1.1 Distillation apparatus, consisting of:

- a round-bottomed 1-liter flask with ground-glass joints.
- a rectifying column about 20 cm in height or any similar condenser.
- a source of heat; any pyrolysis of extracted matter must be prevented by a suitable arrangement.
- a condenser terminated by a drawn-out tube taking the distillate to the bottom of a graduated receiving flask containing several mL of water.

3.1.2 Steam distillation apparatus consisting of:

- a steam generator
- a steam pipe
- a rectifying column
- a condenser.

Any type of distillation or steam distillation apparatus may be used provided that it satisfies the following test:

Distil an ethanol-water mixture with an alcoholic strength of 10% vol. five times in succession. The distillate should have an alcoholic strength of at least 9.9% vol. after the fifth distillation; i.e. the loss of alcohol during each distillation should not be more than 0.02% vol.

3.2 Reagent

Suspension of calcium hydroxide, 2 M

Obtain by carefully pouring 1 liter of water at 60 to 70°C on to 120 g of quicklime, CaO.

3.3. Preparation of sample

Remove the bulk of any carbon dioxide from young and sparkling wines by stirring 250 to 300 mL of the wine in a 1000 mL flask.

3.4. Procedure

3.4.1 Procedure for beverages with an ABV greater than 1.5% vol

Measure out 200 mL of the wine using a volumetric flask. Record the temperature of the wine.

Transfer the wine to the distillation flask and introduce the steam-pipe of the steam distillation apparatus. Rinse the volumetric flask four times with successive 5 mL washings of water added to the flask or the steam-pipe. Add 10 mL of calcium hydroxide, 2 mol/L, and several pieces of inert porous material (pumice etc).

Collect the distillate in the 200 mL graduated flask used to measure the wine.

Collect a volume of about three-quarters of the initial volume if distillation is used and a volume of 198 to 199 mL of distillate if steam distillation is used. Make up to 200 mL with distilled water, keeping the distillate at a temperature within 2°C of the initial temperature.

Mix carefully, using a circular motion.

Note: In the case of wines containing particularly large concentrations of ammonium ions, the distillate may be redistilled under the conditions described above, but replacing the suspension of calcium hydroxide with 1 mL sulfuric acid diluted 10/100.

3.4.1 Procedure for beverages with an ABV lower than or equal to 1.5% vol

Take a 200 mL sample of beverage using a calibrated flask. Note the temperature of the beverage. Pour it into the flask of the distillation apparatus or into the bubbler of the steam distillation apparatus. Rinse the calibrated flask four times with 5 mL of water and add this to the apparatus' flask or bubbler.

Add a 10 mL suspension of 2 M calcium hydroxide and, in the case of distillation, if necessary, a boiling regulator (pumice stone, etc.). Collect, in a 100 mL calibrated flask, a volume of distillate equal to around 75 mL in the case of distillation or 98-99 mL in the case of steam distillation. Make up to 100 mL with distilled water while the distillate is within ± 2 °C of the initial temperature. Carefully mix using a circular motion.

Mix carefully, using a circular motion.

Precautionary safety measures

Respect the safety guidelines for the usage of distillation apparatuses, the manipulation of hydro-alcoholic and cleaning solutions.

4.A. Measurement of the alcoholic strength of the distillate using a pycnometer

(Method A2/1978 – Resolution 377/2009)

1. Apparatus

Use the standardized pycnometer as described in the chapter *Density and specific gravity* (Annex, chapter 1).

2. Procedure

Measure the apparent density of the distillate (3.4) at t °C as described in the chapter *Density and specific gravity* (Annex, chapter 1, sections 4.3.1 and 4.3.2). Let this density be ρ_t .

3. Expression of results

3.1 Method of calculation

Find the alcoholic strength at 20 °C using Table I. In the horizontal line of this table corresponding to the temperature T (expressed as a whole number) immediately below t °C, find the smallest density greater than ρ_t . Use the tabular difference just below this density to calculate the density ρ at this temperature T.

On the line of the temperature T, find the density ρ' immediately above ρ and calculate the difference between the densities ρ and ρ' . Divide this difference by the tabular difference just to the right of the density ρ' . The quotient gives the decimal part of the alcoholic strength, while the whole number part of this strength is shown at the head of the column in which the density ρ' is located.

An example of the calculation of an alcoholic strength is given in Annex I of this chapter.

Note: This temperature correction has been incorporated in a computer program and might possibly be carried out automatically.

3.2 Beverages with an ABV lower than or equal to 1.5% vol

The alcoholic strength by volume of a beverage with low alcohol content, with an ABV of less than 1.5% vol., is given by the following formula: $ABV = ABVD/2$, ABVD being the alcoholic strength by volume of the distillate.

It is expressed in "% vol.". The result is given to two decimal places.

4.3.2 *Repeatability r:*
 $r = 0.10 \text{ \% vol.}$

4.3.3 *Reproducibility R:*
 $R = 0.19 \text{ \% vol.}$

ANNEX I

Example of the calculation of the alcoholic strength of a wine

I. Measurement by pycnometer on a twin-pan balance

The constants of the pycnometer have been determined and calculated as described in chapter I. *Density and specific gravity*, section 6.1.1.

Calculations	Example
1. <i>Weighing of pycnometer filled with distillate:</i>	
Tare = pycnometer + distillate at $t\text{ }^{\circ}\text{C} + p''$	$\left\{ \begin{array}{l} t\text{ }^{\circ}\text{C} = 18.90^{\circ}\text{C} \\ t\text{ }^{\circ}\text{C corrected} = 18.70^{\circ}\text{C} \\ p'' = 2.8074\text{ g} \end{array} \right.$
$p + m - p'' = \text{mass of distillate at } t\text{ }^{\circ}\text{C}$	$\{ 105.0698 - 2.8074 = 102.2624\text{ g}$
Apparent density at $t\text{ }^{\circ}\text{C}$:	
$\rho_t = \frac{p + m - p''}{\text{volume of pycnometer at } 20^{\circ}\text{C}}$	$\left\{ \rho_{18.7^{\circ}} = \frac{102.2624}{104.0229} = 0.983076 \right.$
2. <i>Calculation of alcoholic strength:</i>	
Refer to the table of apparent densities of water-alcohol mixtures at different temperatures, as indicated above	$\left\{ \begin{array}{l} \text{On the line } 18\text{ }^{\circ}\text{C} \text{ of the table of apparent densities, \{the smallest density greater than the observed density \{of } 0.983076 \text{ is } 0.98398 \text{ in column } 11\% \text{ vol.} \\ \\ \text{The density at } 18\text{ }^{\circ}\text{C} \text{ is:} \\ 98307.6 + 0.7 \times 22 \times 10^{-5} = 0.98323 \\ 0.98398 - 0.98323 = 0.00075 \\ \\ \text{The decimal portion of the \% vol. of alcoholic strength is} \\ 75/114 = 0.65 \\ \\ \text{The alcoholic strength is:} \\ 11.65\% \text{ vol.} \end{array} \right.$

II. Measurement by pycnometer on a single pan balance

The constants of the pycnometer have been determined and calculated as described in chapter 1. *Density and specific gravity*, section 6.2.1

Calculations

1. Weighing of the pycnometer filled with distillate:

Weight of tare bottle at the time of measurement in grams:

$$T_1 = 171.9178$$

Pycnometer filled with distillate at 20.50 °C in grams:

$$P_2 = 167.8438$$

Variation in the buoyancy of air:

$$\begin{aligned} dT &= 171.9178 - 171.9160 \\ &= + 0.0018 \end{aligned}$$

Mass of the distillate at 20.50 °C:

$$\begin{aligned} L_t &= 167.8438 - (67.6695 + 0.0018) \\ &= 100.1725 \end{aligned}$$

Apparent density of the distillate:

$$\rho_{20.50^\circ} = \frac{100.1725}{101.8194} = 0.983825$$

2. Calculation of alcoholic strength:

Refer to the table of apparent densities of water-alcohol mixtures at different temperatures, as indicated above:

On the line 20°C of the table of apparent {densities, the smallest density greater than {observed density of 0.983825 is 0.98471 in {column 10% vol.

The density at 20°C is:
 $(98382.5 + 0.5 \times 24) 10^{-5} = 0.983945$
 $(0.98471 - 0.983945 = 0.000765$

The decimal portion of the % vol.
 $76.5/119 = 0.64$

The alcoholic strength is:
10.64% vol.

ANNEX II

**Formula from which tables of alcoholic strengths
of ethanol-water mixtures are calculated**

The density " ρ " in kilograms per meter cubed (kg/m^3) of an ethanol-water mixture at temperature t in degrees Celsius is given by the formula below as a function of:

- the alcoholic strength by weight p expressed as a decimal; *
- the temperature t in °C (EIP 68);
- the numerical coefficients below.

The formula is valid for temperatures between -20 °C and $+40$ °C.

$$\rho = A_1 + \sum_{k=2}^{12} A_k p^{k-1} + \sum_{k=1}^6 B_k (t - 20^\circ\text{C})^k + \sum_{i=1}^n \sum_{k=1}^m C_{i,k} p^{k(t - 20^\circ\text{C})^i}$$

$$\begin{aligned} n &= 5 \\ m_1 &= 11 \\ m_2 &= 10 \\ m_3 &= 9 \\ m_4 &= 4 \\ m_5 &= 2 \end{aligned}$$

* For example, for an alcoholic strength of 12 % by weight. $q = 0.12$

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Numerical coefficients in the formula

<i>k</i>	<i>Ak</i> kg/m ³	<i>Bk</i>
1	9.982 012 300 · 10 ²	– 2.061 851 3 · 10 ⁻¹ kg/(m ³ · °C)
2	– 1.929 769 495 · 10 ²	– 5.268 254 2 · 10 ⁻³ kg/(m ³ · °C ²)
3	3.891 238 958 · 10 ²	3.613 001 3 · 10 ⁻⁵ kg/(m ³ · °C ³)
4	– 1.668 103 923 · 10 ³	– 3.895 770 2 · 10 ⁻⁷ kg/(m ³ · °C ⁴)
5	1.352 215 441 · 10 ⁴	7.169 354 0 · 10 ⁻⁹ kg/(m ³ · °C ⁵)
6	– 8.829 278 388 · 10 ⁴	– 9.973 923 1 · 10 ⁻¹¹ kg/(m ³ · °C ⁶)
7	3.062 874 042 · 10 ⁵	
8	– 6.138 381 234 · 10 ⁵	
9	7.470 172 998 · 10 ⁵	
1	– 5.478 461 354 · 10 ⁵	
1	2.234 460 334 · 10 ⁵	
1	– 3.903 285 426 · 10 ⁴	

<i>k</i>	<i>C1.k</i> kg/(m ³ · °C)	<i>C2.k</i> kg/(m ³ · °C ²)
1	1.693 443 461 530 087 · 10 ⁻¹	– 1. 193 013 005 057 010 ·
2	– 1.046 914 743 455 169 · 10 ¹	2.517 399 633 803 46 1 ·
3	7.196 353 469 546 523 · 10 ¹	– 2.170 575 700 536 993
4	– 7.047 478 054 272 792 · 10 ²	1.353 034 988 843 029 · 10 ¹
5	3.924 090 430 035 045 · 10 ³	– 5.029 988 758 547 014 · 10 ¹
6	– 1.210 164 659 068 747 · 10 ⁴	1.096 355 666 577 570 · 10 ²
7	2.248 646 550 400 788 · 10 ⁴	– 1.422 753 946 421 155 · 10 ²
8	– 2.605 562 982 188 164 · 10 ⁴	1.080 435 942 856 230 · 10 ²
9	1.852 373 922 069 467 · 10 ⁴	– 4.414 153 236 817 392 · 10 ¹
1	– 7.420 201 433 430 137 · 10 ³	7.442 971 530 188 783
1	1.285 617 841 998 974 · 10 ³	

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<i>k</i>	C3.k kg/(m ³ · °C3)	C4.k kg/(m ³ · °C4)	C5.k kg/(m ³ · °C5)
1	– 6.802 995 733 503 803 · 10 ⁻⁴	4.075 376 675 622 027 · 10 ⁻⁴	– 2.788 074 354 782 409 · 10 ⁻⁴
2	1.876 837 790 289 664 · 10 ⁻²	– 8.763 058 573 471 110 · 10 ⁻²	1.345 612 883493 354 · 10 ⁻²
3	– 2.002 561 813734 156 · 10 ⁻¹	6.515 031 360 099 368 · 10 ⁻¹	
4	1.022 992 966 719 220	– 1.515 784 836 987 210 · 10 ⁻¹	
5	– 2.895 696 483 903 638		
6	4.810 060 584 300 675		
7	– 4.672 147 440 794 683		
8	2.458 043 105 903 461		
9	– 5.411 227 621 436 812 · 10 ⁻¹		

**4. B. Measurement of the alcoholic strength of wine by
electronic densimetry using frequency oscillator**
(Resolution Oeno 8/2000 – 377/2009)

1. Measurement method

1.1. Strength and introduction

The alcoholic strength by volume of wine must be measured before being commercialised mainly in order to conform to labelling rules.

The alcoholic strength by volume is equal to the number of litres of ethanol contained in 100 litres of wine; these volumes are both measured at 20 °C. The symbol is “ % vol. ”.

1.2. Precautionary safety measures

Respect the safety guidelines for the usage of distillation apparatuses, the manipulation of hydro-alcoholic and cleaning solutions.

1.3. Object and field of application

The method of measurement described is electronic densimetry using a frequency oscillator.

In reference to the provision of the rules in the existing law, the trial temperature is stopped at 20 °C.

1.4. Principle and definitions

The principle of the method consists firstly of distilling the wine volume by volume. The distillation procedure is described in the Compendium. This distillation enables the elimination of non-volatile substances. The ethanol counter parts in addition to ethanol and the ethanol counter parts involved in esters are included in the alcoholic strength since they are present in the distillate

The distillate density of the distillate is measured. The density of a liquid at a given temperature is equal to the ratio of its density to its volume.

$\rho = m / V$, for a wine, it is expressed as g/ml

For hydro-alcoholic solutions such as distillates, given the known temperature, the graphs correspond to the alcoholic strength by volume (OIV, 1990). This alcoholic strength corresponds to that of wine (distillation of volume to volume).

In the present method the distillate density is measured by electronic densimetry using a frequency oscillator. The principle consists of measuring the period of oscillation of a tube containing the sample undergoing an electromagnetic stimulation. The density is thus calculated and is linked to the period of oscillation by the following formula:

$$p = T^2 \times \left(\frac{C}{4\pi^2 V} \right) - \left(\frac{M}{V} \right) \quad (1)$$

ρ = density of sample

T = period of induced vibration

M = mass of empty tube

C = spring constant

V = volume of vibrating sample

This relation is in the form of, $\rho = A T^2 - B$ (2), There is a linear relationship between density and the period squared. The A and B constants specific to each oscillator are estimated by measuring the period of fluids of the known density.

1.5. Reagents and products

1.5.1 Reference fluids

Two reference fluids are used to adjust the densimetry. The densities of reference fluids must encompass the densities of the distillates to be measured. A spread between the densities between reference fluids above 0.01000 g/ml is recommended. The density must be known with an uncertainty under +/- 0.00005 g/ml, for a temperature of 20.,00 +/- 0.05 °C.

The measuring of alcoholic strength by volume of wine by electronic densimetry of reference fluids:

- dry air (unpolluted),
- double distilled water or of an equivalent analytical purity,
- hydro alcoholic solution of density determined by pycometry (reference method),
- solutions connected to national standards of viscosity under 2 mm²/s.

1.5.2 Cleaning and drying products

- detergents, acids,
- organic solvents: ethanol 96% Vol., pure acetone.

1.6. Apparatus

1.6.1 Electronic densimetry by frequency oscillator

Electronic densimetry contains the following elements:

- a measuring cell containing a measurement tube and a temperature controlled enclosure,
- a system for setting up an oscillation tube and measurement of the period of oscillation,
- a timer,
- a digital display and possibly a calculator.

The densimetry on a perfectly stable support isolated from all vibrations.

1.6.2 Temperature control of measuring cell

The measurement tube is located in the temperature-controlled enclosure. Temperature stability must be better than ± 0.02 °C.

It is necessary to control the temperature of the measuring cell when the densimetry makes this possible, because this strongly influences the indication results. Density of this hydro alcoholic solution with an alcoholic strength by volume of 10% Vol., and is at 0.98471 g/ml at 20°C and at 0.98447 g/ml at 21°C or a spread of 0.00024 g/ml.

The trial temperature is stopped at 20°C. The temperature is taken at the cell level and done with a resolution thermometer 0.01°C and connected to national standards. This must enable a temperature measurement with an uncertainty of under ± 0.07 °C.

1.6.3 Calibration of the apparatus

The apparatus must be calibrated before using for the first time, then every six months or if the verification is not satisfactory. The objective is to use two reference fluids to calculate the constants A and B (cf. (2)). To carry out the calibration refer to the user's manual of the apparatus. In principle, this calibration is carried out with dry air (take into account the atmospheric pressure) and very pure water (double distilled and/or very high micro filtered resistance, for example > 18 M Ω).

1.6.4 Calibration verification

In order to verify the calibration we measure the density of the reference fluids.

- Every day, a density check of the air is carried out. A difference between the theoretical density and the observed density of more than 0.00008 g/ml may indicate that the tube is clogged. In that case, it must be cleaned. After cleaning, verify the air density again. If the verification is not conclusive adjust the apparatus.
- Check the density of water, if the difference between the theoretical density and the density observed is greater than 0.00008 g/ml, adjust the apparatus.
- If the verification of cell temperature is difficult, it is possible to directly check hydro alcoholic density of the alcoholic strength by volume compared to the distillates analysed.

1.6.5 Check

When the difference between the theoretical density of the reference solution (known with an uncertainty of +/- 0.00005 g/ml) and the measurement is above 0.00008 g/ml the temperature of the cell must be taken.

1.7. Sampling and preparation of samples

(Cf. Compendium of International methods of wine and musts 1990, page 59, Obtaining distillate)

1.8. Operating procedure

After obtaining a distillate, (OIV, 1990) we measure the density or the alcoholic strength by volume by densimetry.

The operator must ensure the stability and the temperature of the measuring cell. The distillate in the densimetry cell must not contain air bubble and must be homogeneous. If there is an available lighting system, turn off quickly after checking because the heat generated by the lamp can influence the measuring temperature.

If the apparatus only provides the period, density can be calculated by the A and B constants (cf. A.4 c). If the apparatus does not provide the alcoholic strength by volume directly, we can obtain the alcoholic strength by volume using the (OIV, 1990) tables if we know the density.

1.9. Expression of results

The alcoholic strength by volume is obtained from the distillate. This is expressed as “ % vol. ”.

If the temperature conditions are not respected, a correction must be made to express the temperature at 20°C. The result is quoted to two decimal places

1.9.1 Beverages with an ABV lower than or equal to 1.5% vol

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The alcoholic strength by volume of a beverage with low alcohol content, with an ABV of less than 1.5% vol., is given by the following formula: $ABV = ABVD/2$, ABVD being the alcoholic strength by volume of the distillate.

It is expressed in "% vol.". The result is given to two decimal places.

1.10. Comments

The volume introduced into the cell must be sufficient enough to avoid possible contamination caused from the previous sample. It is thus necessary to carry out two testing. If this does not provide results included in the repeatability limits, a third testing may be necessary. In general, results from the last two testing are homogeneous and we then eliminate the first factor.

1.11 Reliability

For alcoholic strength by volume samples between 4 to 18% Vol.

Repeatability (r) = 0.067 (% vol.),

Reproducibility (R) = 0.0454 + 0.0105 x alcoholic strength by volume.

2. Interlaboratory Tests. Reliability and accuracy on additions

2.1. Samples

The samples used for this joint study are described in Table 1.

Table 1: Samples for joint study

Nu m	Nature	Approx alcoholic strength by volume (% vol.)
C0	Cider (filtered through membrane to remove CO ₂)	5
V0	Filtered wine	10
V1	Filtered wine then doped	11
V2	Filtered wine then doped	12
V3	Filtered wine then doped	13
P0	Liqueur wine	16

All samples are homogenised before filling the bottles to be sent to the participants. For wine, 40 litres of wine are homogenised before sending and carrying out the additions

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For the additions, pour absolute ethanol into a 5 litre volumetric flask and then fill up to the line with filtered wine. This operation is repeated two times. The volumes of ethanol are respectively 50, 100 and 150 ml for the V1, V2 and V3 samples.

2.2. Participating laboratories

The participating laboratories in the joint study are outlined in Table 2.

Laboratory	Zip Code	City	Contact
ALKO Group LTD	FIN-00101	Helsinki	Monsieur Lehtonen
Bénédictine	76400	Fécamp	Madame Pillon
Casanis	18881	Gemenos	Madame Cozon
CIVC	51200	Epernay	Monsieur Tusseau
Cointreau	49181	St Barthélémy d'Anjou	Madame Guerin
Courvoisier	16200	Jarnac	Monsieur Lavergne
Hennessy	16100	Cognac	Monsieur Calvo
IDAC	44120	Vertou	Madame Mars
Laboratoire Gendrot	33000	Bordeaux	Madame Gubbiotti
Martell	16100	Cognac	Monsieur Barboteau
Ricard	94320	Thiais	Monsieur Boulanger
SOEC Martin Vialatte	51319	Epernay	Madame Bertemes

In order not to introduce a methodological angle, the *Station Viticole du Bureau National Interprofessionnel du Cognac*, the joint study organiser, will not be taken into account.

2.3. Analyses

The C0 and P0 products are distilled two times, the V0, V1, V2 and V3 products three times. Three alcoholic strength by volume tests were done for each distillate. The results were carried over to the results table.

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2.4. Results

The second testing (out of the three carried out) is kept of the accuracy study (Table 3).

Table 3: Results (second testing per distillate) (% vol.)

Laboratory	C0	V0	V1	V2	V3	P0
1	6,020	9,500	10,390	11,290	12,100	17,080
	5,970	9,470	10,380	11,260	12,150	17,080
		9,450	10,340	11,260	12,150	
2	6,040	9,500	10,990	11,270	12,210	17,050
	6,040	9,500	10,390	11,280	12,210	17,050
		9,510	10,400	11,290	12,200	
3	5,960	9,460	10,350	11,280	12,170	17,190
	5,910	9,460	10,360	11,280	12,150	17,200
		9,450	10,340	11,260	12,170	
4	6,020	9,470	10,310	11,250	12,160	16,940
	6,020	9,450	10,350	11,250	12,120	17,070
		9,450	10,330	11,210	12,130	
5	5,950	9,350	10,250	11,300	12,050	17,000
	5,950	9,430	10,250	11,300	12,050	17,000
		9,430	10,250	11,300	12,050	
6	6,016	9,513	10,370	11,275	12,222	17,120
	6,031	9,513	10,336	11,266	12,222	17,194
		9,505	10,386	11,275	12,220	
7	5,730	9,350	10,230	11,440	12,080	17,010
	5,730	9,430	10,220	11,090	12,030	16,920
		9,460	10,220	11,080	11,930	
8	5,990	9,400	10,340	11,160	12,110	17,080
	6,000	9,440	10,320	11,150	12,090	17,110
		9,440	10,360	11,210	12,090	
9	6,031	9,508	10,428	11,289	12,180	17,089
	6,019	9,478	10,406	11,293	12,215	17,084
		9,509	10,411	11,297	12,215	
10	6,030	9,500	10,380	11,250	12,150	17,130
	6,020	9,510	10,380	11,250	12,150	17,100
		9,510	10,380	11,250	12,160	
11	6,020	9,480	10,400	11,260	12,150	17,040
	6,000	9,470	10,390	11,260	12,140	17,000
		9,490	10,370	11,240	12,160	

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2.5. Repeatability and reproducibility calculations

Repeatability and reproducibility calculations are carried out in compliance with the standard NF X 06-041, September 1983, ISO 5725. Table 4 presents the standard deviation per cell (laboratory x sample).

Table 4: Dispersion table (standard deviation in % vol.)

Laboratory	C0	V0	V1	V2	V3	P0
1	0,0354	0,0252	0,0265	0,0173	0,0289	0,0000
2	0,0000	0,0058	0,3436	0,0100	0,0058	0,0000
3	0,0354	0,0058	0,0100	0,0115	0,0115	0,0071
4	0,0000	0,0115	0,0200	0,0231	0,0208	0,0919
5	0,0000	0,0462	0,0000	0,0000	0,0000	0,0000
6	0,0106	0,0046	0,0255	0,0052	0,0012	0,0523
7	0,0000	0,0569	0,0058	0,2050	0,0764	0,0636
8	0,0071	0,0231	0,0200	0,0321	0,0115	0,0212
9	0,0085	0,0176	0,0115	0,0040	0,0202	0,0035
10	0,0071	0,0058	0,0000	0,0000	0,0058	0,0212
11	0,0141	0,0100	0,0153	0,0115	0,0100	0,0283

Three cells presented strong dispersions (probability with Cochran test under 1%).
These cells are represented in grey (Table 4).

For laboratory 7 and the V3 product, the standard deviation of 0.0764 is maintained despite the Cochran test because it is on the same high level as that observed at the same laboratory on the V0 product.

An examination of figures for each distillate leads us to eliminate (Table 3):

- laboratory 2, product V1, value 10.990,
- laboratory 7, product V2, value 11.440.

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After eliminating these two values, the cell averages are calculated (laboratory x sample) (Table 5).

Table 5: Table of averages (averages in % vol.)

Laboratory	C0	V0	V1	V2	V3	P0
1	5,9950	9,4733	10,3700	11,2700	12,1333	17,0800
2	6,0400	9,5033	10,3950	11,2800	12,2067	17,0500
3	5,9350	9,4567	10,3500	11,2733	12,1633	17,1950
4	6,0200	9,4567	10,3300	11,2367	12,1367	17,0050
5	5,9500	9,4033	10,2500	11,3000	12,0500	17,0000
6	6,0235	9,5103	10,3640	11,2720	12,2213	17,1570
7	5,7300	9,4133	10,2233	11,0850	12,0133	16,9650
8	5,9950	9,4267	10,3400	11,1733	12,0967	17,0950
9	6,0250	9,4983	10,4150	11,2930	12,2033	17,0865
10	6,0250	9,5067	10,3800	11,2500	12,1533	17,1150
11	6,0100	9,4800	10,3867	11,2533	12,1500	17,0200

The figures given by laboratory 7 are generally low (Table 5). In the case of cider the average for this laboratory is very far from the figures of the other laboratories (associated probability to the Dixon test under 1 %). The results of this laboratory for this product are eliminated.

Table 6 presents the calculated repeatability and reproducibility.

Table 6: Calculation of repeatability and reproducibility

Sample	P	n	TAV	S2r	S2L	r	R
C0	10	20	6,002	0,000298	0,001033	0,049	0,103
V0	11	33	9,466	0,000654	0,001255	0,072	0,124
V1	11	32	10,344	0,000255	0,003485	0,045	0,173
V2	11	32	11,249	0,000219	0,003113	0,042	0,163
V3	11	33	12,139	0,000722	0,003955	0,076	0,194
P0	11	22	17,070	0,001545	0,004154	0,111	0,214

Key:

- p* : number of laboratories retained
- n* : number of values retained
- TAV* : average alcoholic strength by volume (% vol.)
- S2r* : repeatability variation (% vol.)²
- S2L* : interlaboratory variation (% vol.)²

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r : repeatability (% vol.)
 R : reproducibility (% vol.)

Reproducibility increases with the samples' alcoholic strength by volume (Figure 1). The increase in repeatability according to alcoholic strength by volume is less noticeable and global repeatability is calculated according to the average repeatability variation. As such, for the alcoholic strength by volume samples between 4 and 18% vol.,

Repeatability (r) = 0.067 (% vol.),

Reproducibility (R) = 0.0454 + 0.0105 x alcoholic strength by volume.

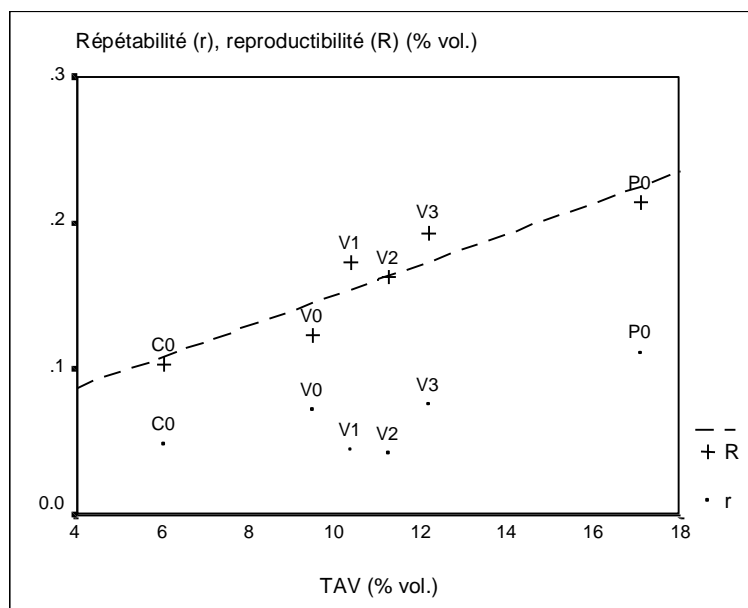


Figure 1: Repeatability and reproducibility according to alcoholic strength by volume

2.6. Accuracy on additions carried out on wine

The regression line of alcoholic strength after the addition according to the volume of ethanol supplied, for a volume of 0 ml, an estimation of the initial alcoholic strength of product (Figure 2). This regression is carried out with average values for each laboratory (Table 5).

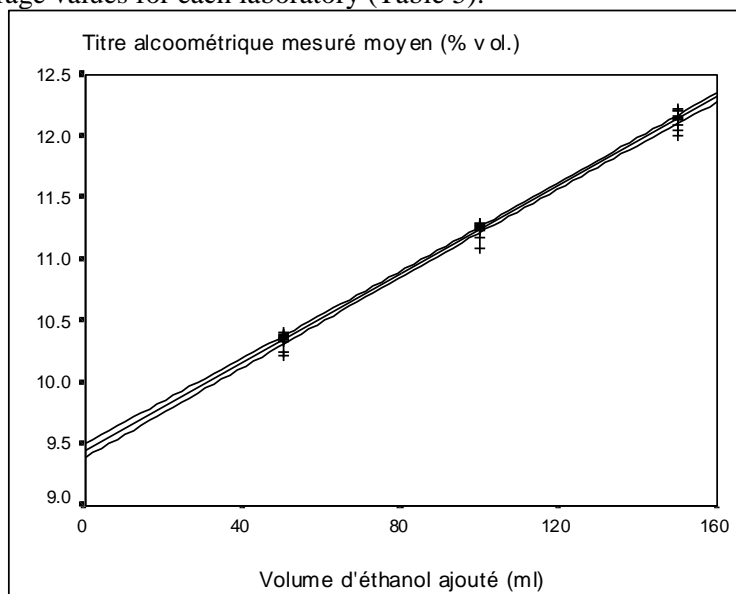


Figure 2: Regression of measures alcoholic strength by volume of added ethanol

Measurements carried out on initial products are not included in this estimation. This estimation is made up of the average of measurements taken on this product before additions; the intervals of relative confidence on these two estimations are calculated (Table 7).

Table 7: Additions on products

BI	Average measurements	BS	BI	estimation with measurements on products + additions	BS
9,440	9,466	9,492	9,392	9,450	9,508

Key: BI : lower bound of confidence interval at 95%

BS : upper bound of confidence interval at 95%

The two confidence intervals cover a large overlapping spreading centre. Thanks to the measurements on doped samples, the alcoholic strength by volume of the initial product can be found.

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2.7. Conclusion of interlaboratory trials

The repeatability and the reproducibility indications by interlaboratory trials provide the following equations, for alcoholic strength by volume products between 4 to 18% vol.:

Repeatability (r) = 0.67 (% vol.),

Reproducibility (R) = $0.454 + 0.0105 \times$ alcoholic strength by volume (% vol.).

The Horwitz indicators, Hor and HoR are weak (Table 8). These indicators provide good details of the method compared to the level of analyte measured.

Table 8: Table summary of method reliability

Samples	C0	V0	V1	V2	V3	P0
n	20	33	32	32	33	22
p	10	11	11	11	11	11
Alcoholic strength by volume	6,0019	9,4662	10,3443	11,2492	12,1389	17,0699
r	0,0489	0,0724	0,0452	0,0419	0,0760	0,1113
sr	0,0173	0,0256	0,0160	0,0148	0,0269	0,0393
RSDr	0,2878	0,2702	0,1543	0,1316	0,2214	0,2303
RSDrH	2,0159	1,8822	1,8573	1,8340	1,8131	1,7224
Hor	0,1428	0,1436	0,0831	0,0718	0,1221	0,1337
R	0,1033	0,1237	0,1731	0,1634	0,1935	0,2136
sR	0,0365	0,0437	0,0612	0,0577	0,0684	0,0755
RSDR	0,6080	0,4616	0,5912	0,5131	0,5634	0,4423
RSDRH	3,0543	2,8519	2,8141	2,7788	2,7471	2,6097
HoR	0,1991	0,1619	0,2101	0,1847	0,2051	0,1695

Key:

n : number of values retained

p : number of laboratories retained

Alcoholic strength by volume: average rate (% vol.)

r : repeatability (% vol.)

sr : Standard deviation of repeatability (% vol.)

RSDr : Repeatability coefficient of variation ($sr \times 100 / TAV$) (%)

RSDrH : Horwitz repeatability coefficient of variation ($.066 \times RSDRH$) (%)

Hor : Horrat repeatability value ($RSDr/RSDrH$)

R : Reproducibility (% vol.)

sR : Reproducibility standard deviation (% vol.)

RSDR : Reproducibility coefficient of variation ($sR \times 100 / TAV$) (%)

RSDRH : Horwitz reproducibility coefficient of variation
 $(\frac{1}{2} (1 - 0,5 \log(TAV)))$ (%)

HoR : Horrat reproducibility value ($RSDR/RSDRH$)

Interlaboratory trials' measurements carried out on wine with additions enable us to find the value obtained before the addition. We respectively find 9.45 and 9.47% vol.

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Standard ISO 5725, page 7

**4. C. Measurement of the alcoholic strength of wine by
densimetry using hydrostatic balance**
(Resolution Oeno 24/2003 – 377/2009)

1. METHOD OF MEASUREMENT

1.1 Strength and introduction

Measurement of alcoholic strength by volume should be determined before marketing notably to be in compliance with labelling rules.

Alcoholic strength by volume is equal to the number of litres of ethanol contained in 100 litres of wine measured at 20°C, referred to as “% vol.”.

1.2 Safety precaution

Respect safety measures concerning the use of distillation apparatuses, manipulation of hydro-alcoholic solutions and cleaning products.

1.3 Object and field of application

The method of measurement is densimetry using a hydrostatic balance.

In reference to regulatory provisions in force the trial temperature is set at 20°C.

1.4 Principle and definitions

The principle of this method involves firstly distilling wine volume by volume. The distilling method is described in the Compendium. Non volatile substances can be eliminated through distillation. Ethanol counterparts and ethanol found in esters are included in the alcoholic strength as they are found in the distillate.

Secondly, the volumetric weight of the distillate obtained is measured. The volumetric weight of a liquid at a given temperature is equal to the ratio of the weight over its volume: $\rho=m/V$, for wine, it is expressed in g/ml.

The alcoholic strength of wine can be measured by densimetry using a hydrostatic balance following the Archimedes principle by which any body plunged into a fluid undergoes a vertical push, from the bottom to the top, equal to the weight of the displaced fluid.

1.5 Reagents

Unless other wise indicated, only recognised analytical quality reagents should be used during the analysis with at least class 3 water corresponding to the definition of the standard ISO 3696:1987.

1.5.1 *Solution for washing float device (sodium hydroxide , 30% m/v).*

To prepare a 100 ml solution, weigh 30 g of sodium hydroxide and fill using 96% vol. ethanol.

1.6 Apparatus and material

current laboratory apparatus including:

- 1.6.1 Single-plate hydrostatic balance with 1 mg precision.
- 1.6.2 Floater with at least 20 ml volume, specifically adapted for the balance, suspended by a thread with a diameter less than or equal to 0.1 mm.
- 1.6.3 Cylindrical test tube with level indicator. The floater must entirely fill the test tube volume above the marker, only the slinging wire goes through the surface of the liquid. The cylindrical test tube should have an inside diameter at least above 6 mm of the floater.
- 1.6.4 Thermometer (or temperature measurement pipette) with degree and 10th of degree graduations, from 10°C to 40°C, calibrated to $\pm 0.05^\circ\text{C}$.
- 1.6.5 Calibrated weight by a recognized certification body.

1.7 Procedure

After each measurement, the floater and the test tube must be cleaned with distilled water, wiped with soft laboratory paper which doesn't loose its fibres and rinsed with solution whose volumetric weight is to be determined. These measurements must be carried out once the apparatus has reached a stable level in order to limit alcohol loss through evaporation.

1.7.1 Balance calibration

While balances usually have internal calibration systems, hydrostatic balances must be calibrated with controlled weights by an official certification body.

1.7.2 Floater calibration

1.7.2.1 Fill cylindrical test tube up to marker with bidistilled water (or an equivalent purity, for example microfiltered water with a conductivity of

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18.2 MΩ/cm), whose temperature between 15°C to 25°C, but preferably at 20°C.

1.7.2.2 Plunge the floater and the thermometer into the liquid, shake, note down the volumetric weight on the apparatus and, if necessary, adjust the reading in order for it to be equal to the water measurement temperature.

1.7.3 Control using a hydroalcoholic solution

1.7.3.1 Fill the cylindrical test tube up to the marker with a known titre of hydroalcoholic solution at a temperature between 15°C to 25°C, preferably at 20°C.

1.7.3.2 Plunge the floater and the thermometer into the liquid, shake, note down the volumetric weight on the apparatus (or the alcoholic strength if possible). The established alcoholic strength must be equal to the previously determined alcoholic strength.

Note 2: This alcoholic strength solution can be replaced by bidistilled water for floater calibration.

1.7.4 Measure volumetric weight of the distillate (or alcoholic strength if possible)

1.7.4.1 Pour the sample for the trial in the cylindrical test tube up to the marker level.

1.7.4.2 Plunge the floater and the thermometer into the liquid, shake, note down the volumetric weight on the apparatus (or the alcoholic strength if possible). Note the temperature if the volumetric mass is measured at t°C (\tilde{n}_t).

1.7.4.3 Correct \tilde{n}_t using a volumetric weight table \tilde{n}_t of hydroalcoholic mixtures [Table II of Annex II of the Compendium of methods of analysis of the OIV].

1.7.5 Clean the floater and cylindrical test tube.

1.7.5.1 Plunge the floater into the wash solution in the test tube.

1.7.5.2 Allow to soak 1 hour while turning the floater regularly.

1.7.5.3 Rinse with tap water, then with distilled water.

1.7.5.4 Wipe with soft laboratory paper which doesn't loose its fibres.

Carry out these operations when the floater is used for the first time and then on a regular basis when necessary.

1.7.6 Result

Using \tilde{n}_{20} , volumetric weight, calculate real alcoholic strength by using the table indicating volumetric alcoholic strength (% vol.) at 20°C according to volumetric weight at 20°C of hydroalcoholic mixtures. This is the

international table adopted by the International Organisation of Legal Metrology in its recommendation number 22.

1.7.6.1 *Beverages with an ABV lower than or equal to 1.5% vol*

The alcoholic strength by volume of a beverage with low alcohol content, with an ABV of less than 1.5% vol., is given by the following formula: $ABV = ABVD/2$, ABVD being the alcoholic strength by volume of the distillate.

It is expressed in "% vol.". The result is given to two decimal places.

2. COMPARISON OF MEASUREMENTS CARRIED OUT

using a hydrostatic balance with measurements obtained using an electronic density-meter (Annex A of the Compendium of International Methods of Analysis).

From samples whose alcoholic strength is between 4% vol. and 18% vol. the measurements of repeatability and reproducibility were performed after an inter-laboratory ring test. It is the comparison of the measurements of wine alcoholic strength of different samples using the hydrostatic balance and the electronic density-meter, including the repeatability and reproducibility values derived from pluri-annual intercomparison test trials performed on a large scale.

2.1 *Samples:* wines of different density and alcoholic strengths prepared monthly on an industrial scale, taken from a bottled stock stored under normal conditions, and supplied as anonymous products to laboratories.

2.2 *Laboratories:* laboratories participating into the monthly ring test organised by Unione Italiana Vini Verona, (Italy) according to ISO 5725 (UNI 9225) regulation and the 'International Protocol of Proficiency test for chemical analysis laboratories' established by AOAC, ISO and IUPAC (J. AOAC Intern., **1993**, 74/4) and according to guidelines ISO 43 and ILAC G13. An annual report is supplied by the cited company to all participants.

2.3 *Apparatus:*

2.3.1 Electronic hydrostatic balance (whose precision allows to give the 5th decimal of density) eventually equipped with a data treatment device.

2.3.2 Electronic density-meter eventually equipped with an autosampler.

2.4 *Analyses*

According to method validation rules (resolution OENO 6/99), each sample is analysed twice consecutively to determine the alcoholic strength.

2.5 Results

Table 1 shows the results of the measurements obtained by the laboratories using the hydrostatic balance.

Table 2 shows the results obtained by the laboratories using an electronic densimeter.

2.6 Evaluations of the results

2.6.1 The trial results were examined for evidence of individual systematic error ($p < 0.025$) using Cochran's and Grubbs' tests successively, by procedures described in the internationally agreed [*“Protocol for the Design, Conduct and Interpretation of Method-Performance Studies” Ed W Horwitz, Pure and Applied Chemistry, 1995, 67, (2), 331-343.*].

2.6.2 Repeatability (r) and reproducibility (R)

Calculations for repeatability (r) and reproducibility (R) as defined by the protocol were carried out on the results remaining after the removal of outliers. When assessing a new method there is often no validated reference or statutory method with which to compare precision criteria, hence it is useful to compare the precision data obtained from collaborative trials with “predicted” levels of precision. These “predicted” levels are calculated from the Horwitz formula. Comparison of the trial results and the predicted levels indicate as to whether the method is sufficiently precise for the level of analyte being measured.

The predicted Horwitz value is calculated from the Horwitz formula.

$$RSD_R = 2^{(1-0.5 \log C)}$$

where C = measured concentration of analyte expressed in decimals.
(e.g. 1 g/100g = 0.01) [*Horwitz, W., Analytical Chemistry, 1982, 54, 67A-76A.*].

The Horrat value gives a comparison of the actual precision measured with the precision predicted by the Horwitz formula for the method and at that particular level of concentration of the analyte. It is calculated as follows:
 $Ho_R = RSD_R(\text{measured})/RSD_R(\text{Horwitz})$

2.6.3 Interlaboratory precision

A Horrat value of 1 usually indicates satisfactory inter-laboratory

precision, whereas a value of more than 2 usually normally indicates unsatisfactory precision, i.e. one that is too variable for most analytical purposes or where the variation obtained is greater than that expected for the type of method employed. H_o_r is also calculated, and used to assess intra-laboratory precision, using the following approximation:

$RSD_r(\text{Horwitz}) = 0.66 RSD_R(\text{Horwitz})$ (this assumes the approximation $r = 0.66 R$).

Table 3 shows the differences between the measurements obtained by laboratories using an electronic densimeter and those using a hydrostatic balance. Excluding the sample of 2000/3 with very low alcohol strength and for which both techniques show poor reproducibility, a very good concordance is generally observed for the other samples.

2.6.4 Fidelity parameters

Table 4 shows the averaged overall fidelity parameters computed from all monthly trials carried out from January 1999 until May 2001.

In particular:

Repeatability (r)= 0.074 (% vol.) for the hydrostatic balance and 0.061 (% vol.) for electronic densitometry;

Reproducibility (R)= 0.229 (% vol.) for the hydrostatic balance and 0.174 (% vol.) for electronic densitometry, this latter value is concordant to the value estimated for the electronic densitometry from the OIV Compendium of International Methods of Analysis;

2.7 Conclusion

The results concerning the determination of the alcoholic strength of a large range of wines show that the measurements carried out with the hydrostatic balance are concordant with those carried out by electronic densitometry using a flexion resonator and that the validation parameter values are similar for both methods.

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Legend:

mean the mean of all the data used in the statistical analysis

n total number of sets of data submitted

nc number of results excluded from statistical analysis due to non-compliance

outliers number of results excluded from statistical analysis due to determination as outliers by either Cochran's or Grubbs' tests

n₁ number of results used in statistical analysis

r repeatability limit

S_r the standard deviation of the repeatability

RSD_r the relative standard deviation of the repeatability ($S_r \times 100/\text{MEAN}$).

Ho_r the HORRAT value for repeatability is the observed *RSD_r* divided by the *RSD_r* value estimated from the Horwitz formula using the approximation $r = 0.66R$

R reproducibility limit

S_R the standard deviation of the reproducibility

Ho_R the HORRAT value for reproducibility is the observed *RSD_R* value divided by the *RSD_R* value calculated from

$\text{Ho}_R = \text{RSD}_R(\text{measured})/\text{RSD}_R$

Table 1: Hydrostatic Balance (HB)

	MEAN	n	outliers	n1	r	sr	RSDr	Hor	R	sR	RSDR	HoR	no. of replicates	critical difference CrD95
1999/1	11.043	17	1	16	0.0571	0.0204	0.1846	0.1004	0.1579	0.0564	0.5107	0.18	2	0.1080
1999/2	11.247	14	1	13	0.0584	0.0208	0.1854	0.1011	0.1803	0.0644	0.5727	0.21	2	0.1241
1999/3	11.946	16	0	16	0.0405	0.0145	0.1211	0.0666	0.1593	0.0569	0.4764	0.17	2	0.1108
1999/4	7.653	17	1	16	0.0502	0.0179	0.2344	0.1206	0.1537	0.0549	0.7172	0.24	2	0.1057
1999/5	11.188	17	0	17	0.0871	0.0311	0.2780	0.1515	0.2701	0.0965	0.8622	0.31	2	0.1860
1999/6	11.276	19	0	19	0.0846	0.0302	0.2680	0.1462	0.2957	0.1056	0.9365	0.34	2	0.2047
1999/7	8.018	17	0	17	0.0890	0.0318	0.3964	0.2054	0.2573	0.0919	1.1462	0.39	2	0.1764
1999/9	11.226	17	0	17	0.0580	0.0207	0.1846	0.1423	0.2796	0.0999	0.8896	0.45	2	0.1956
1999/10	11.026	17	0	17	0.0606	0.0216	0.1961	0.1066	0.2651	0.0947	0.8588	0.31	2	0.1850
1999/11	7.701	16	1	15	0.0643	0.0229	0.2980	0.1535	0.2330	0.0832	1.0805	0.37	2	0.1616
1999/12	10.987	17	2	15	0.0655	0.0234	0.2128	0.1156	0.1258	0.0449	0.4089	0.15	2	0.0827
2000/1	11.313	16	0	16	0.0986	0.0352	0.3113	0.1699	0.2577	0.0920	0.8135	0.29	2	0.1754
2000/2	11.232	17	0	17	0.0859	0.0307	0.2731	0.1489	0.2535	0.0905	0.8060	0.29	2	0.1740
2000/3	0.679	10	0	10	0.0680	0.0243	3.5773	1.2783	0.6529	0.2332	34.3395	8.10	2	0.4604
2000/4	11.223	18	0	18	0.0709	0.0253	0.2257	0.1230	0.2184	0.0780	0.6951	0.25	2	0.1503
2000/5	7.439	19	1	18	0.0630	0.0225	0.3023	0.1549	0.1522	0.0544	0.7307	0.25	2	0.1029
2000/6	11.181	19	0	19	0.0536	0.0191	0.1710	0.0932	0.2783	0.0994	0.8890	0.32	2	0.1950
2000/7	10.858	16	0	16	0.0526	0.0188	0.1731	0.0939	0.1827	0.0653	0.6011	0.22	2	0.1265
2000/9	12.031	17	1	16	0.0602	0.0215	0.1787	0.0985	0.2447	0.0874	0.7263	0.26	2	0.1704
2000/10	11.374	18	0	18	0.0814	0.0291	0.2555	0.1395	0.2701	0.0965	0.8482	0.31	2	0.1866
2000/11	7.644	18	0	18	0.0827	0.0295	0.3863	0.1988	0.2289	0.0817	1.0694	0.36	2	0.1565
2000/12	11.314	19	1	18	0.0775	0.0277	0.2447	0.1336	0.2421	0.0864	0.7641	0.28	2	0.1667
2001/1	11.415	19	0	19	0.0950	0.0339	0.2971	0.1623	0.2410	0.0861	0.7539	0.27	2	0.1636
2001/2	11.347	19	0	19	0.0792	0.0283	0.2493	0.1361	0.1944	0.0694	0.6119	0.22	2	0.1316
2001/3	11.818	16	0	16	0.0659	0.0235	0.1990	0.1093	0.2636	0.0941	0.7965	0.29	2	0.1834
2001/4	11.331	17	0	17	0.1067	0.0381	0.3364	0.1836	0.1895	0.0677	0.5971	0.22	2	0.1229
2001/5	8.063	19	1	18	0.0782	0.0279	0.3465	0.1797	0.1906	0.0681	0.8442	0.29	2	0.1290

Table 2: Electronic Densimetry (ED)

	MEAN n1	n	outliers	n1	r	sr	RSDr	Hor	R	sR	RSDR	HoR	no. of replicates	critical difference CrD95
D1999/1	11.019	18	1	17	0.0677	0.0242	0.2196	0.1193	0.1996	0.0713	0.6470	0.23	2	0.1370
D1999/2	11.245	19	2	17	0.0448	0.0160	0.1423	0.0776	0.1311	0.0468	0.4165	0.15	2	0.0900
D1999/3	11.967	21	0	21	0.0701	0.0250	0.2091	0.1151	0.1552	0.0554	0.4631	0.17	2	0.1040
D1999/4	7.643	19	1	18	0.0610	0.0218	0.2852	0.1467	0.1340	0.0479	0.6262	0.21	2	0.0897
D1999/5	11.188	21	3	18	0.0260	0.0093	0.0829	0.0452	0.2047	0.0731	0.6536	0.24	2	0.1442
D1999/6	11.303	21	0	21	0.0652	0.0233	0.2061	0.1125	0.1466	0.0523	0.4631	0.17	2	0.0984
D1999/7	8.026	21	0	21	0.0884	0.0316	0.3935	0.2039	0.1708	0.0610	0.7600	0.26	2	0.1124
D1999/9	11.225	17	0	17	0.0372	0.0133	0.1183	0.0645	0.1686	0.0602	0.5366	0.19	2	0.1178
D1999/10	11.011	19	0	19	0.0915	0.0327	0.2969	0.1613	0.1723	0.0615	0.5588	0.20	2	0.1129
D1999/11	7.648	21	1	20	0.0615	0.0220	0.2872	0.1478	0.1538	0.0549	0.7183	0.24	2	0.1043
D1999/12	10.999	16	1	15	0.0428	0.0153	0.1389	0.0755	0.2015	0.0720	0.6541	0.23	2	0.1408
D2000/1	11.248	22	1	21	0.0697	0.0249	0.2212	0.1206	0.1422	0.0508	0.4516	0.16	2	0.0944
D2000/2	11.240	19	3	16	0.0448	0.0160	0.1424	0.0776	0.1619	0.0578	0.5145	0.19	2	0.1123
D2000/3	0.526	12	1	11	0.0327	0.0117	2.2185	0.7630	0.9344	0.3337	63.4009	14.39	2	0.6605
D2000/4	11.225	19	1	18	0.0476	0.0170	0.1514	0.0825	0.1350	0.0482	0.4295	0.15	2	0.0924
D2000/5	7.423	21	0	21	0.0628	0.0224	0.3019	0.1547	0.2635	0.0941	1.2677	0.43	2	0.1836
D2000/6	11.175	23	2	21	0.0606	0.0217	0.1938	0.1056	0.1697	0.0606	0.5424	0.20	2	0.1161
D2000/7	10.845	21	5	16	0.0440	0.0157	0.1449	0.0786	0.1447	0.0517	0.4766	0.17	2	0.0999
D2000/9	11.983	22	1	21	0.0841	0.0300	0.2507	0.1380	0.2410	0.0861	0.7183	0.26	2	0.1651
D2000/10	11.356	22	1	21	0.0635	0.0227	0.1997	0.1090	0.1865	0.0666	0.5866	0.21	2	0.1280
D2000/11	7.601	27	0	27	0.0521	0.0186	0.2448	0.1258	0.1685	0.0602	0.7916	0.27	2	0.1162
D2000/12	11.322	25	1	24	0.0476	0.0170	0.1503	0.0820	0.1594	0.0569	0.5028	0.18	2	0.1102
D2001/1	11.427	29	0	29	0.0706	0.0252	0.2207	0.1206	0.1526	0.0545	0.4771	0.17	2	0.1020
D2001/2	11.320	29	1	28	0.0675	0.0241	0.2128	0.1161	0.1570	0.0561	0.4952	0.18	2	0.1057
D2001/3	11.826	34	1	33	0.0489	0.0175	0.1476	0.0811	0.1762	0.0629	0.5322	0.19	2	0.1222
D2001/4	11.339	31	2	29	0.0639	0.0228	0.2012	0.1099	0.1520	0.0543	0.4788	0.17	2	0.1026
D2001/5	8.058	28	0	28	0.0473	0.0169	0.2098	0.1088	0.2025	0.0723	0.8976	0.31	2	0.1412

Table 3: Comparison of results between hydrostatic balance and electronic densimetry

	MEAN (HB)	n	outliers	n1		MEAN (ED)	n	outliers	n1	Δ TAV(HB-ED)
1999/1	11.043	17	1	16	D1999/1	11.019	18	1	17	0.024
1999/2	11.247	14	1	13	D1999/2	11.245	19	2	17	0.002
1999/3	11.946	16	0	16	D1999/3	11.967	21	0	21	-0.021
1999/4	7.653	17	1	16	D1999/4	7.643	19	1	18	0.010
1999/5	11.188	17	0	17	D1999/5	11.188	21	3	18	0.000
1999/6	11.276	19	0	19	D1999/6	11.303	21	0	21	-0.028
1999/7	8.018	17	0	17	D1999/7	8.026	21	0	21	-0.008
1999/9	11.226	17	0	17	D1999/9	11.225	17	0	17	0.002
1999/10	11.026	17	0	17	D1999/10	11.011	19	0	19	0.015
1999/11	7.701	16	1	15	D1999/11	7.648	21	1	20	0.052
1999/12	10.987	17	2	15	D1999/12	10.999	16	1	15	-0.013
2000/1	11.313	16	0	16	D2000/1	11.248	22	1	21	0.065
2000/2	11.232	17	0	17	D2000/2	11.240	19	3	16	-0.008
2000/3	0.679	10	0	10	D2000/3	0.526	12	1	11 *	0.153
2000/4	11.223	18	0	18	D2000/4	11.225	19	1	18	-0.002
2000/5	7.439	19	1	18	D2000/5	7.423	21	0	21	0.016
2000/6	11.181	19	0	19	D2000/6	11.175	23	2	21	0.006
2000/7	10.858	16	0	16	D2000/7	10.845	21	5	16	0.013
2000/9	12.031	17	1	16	D2000/9	11.983	22	1	21	0.049
2000/10	11.374	18	0	18	D2000/10	11.356	22	1	21	0.018
2000/11	7.644	18	0	18	D2000/11	7.601	27	0	27	0.043
2000/12	11.314	19	1	18	D2000/12	11.322	25	1	24	-0.008
2001/1	11.415	19	0	19	D2001/1	11.427	29	0	29	-0.012
2001/2	11.347	19	0	19	D2001/2	11.320	29	1	28	0.027
2001/3	11.818	16	0	16	D2001/3	11.826	34	1	33	-0.008
2001/4	11.331	17	0	17	D2001/4	11.339	31	2	29	-0.008
2001/5	8.063	19	1	18	D2001/5	8.058	28	0	28	0.004
Average difference/ Δ TAV (HB-ED)										0.014
standard deviation on difference										0.036
* round 2000/3 is not taken into account (very low grade)										

Table 4: Fidelity parameters

MEAN	Hydrostatic balance	Electronic densimeter
n1	441	557
Weighted repeatability variance	0.309	0.267
r	0.074	0.061
sr	0.026	0.022
Weighted reproducibility variance	2.948	2.150
R	0.229	0.174
sR	0.082	0.062

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ANNEXE

**validation parameters relating to the measurement of the
ABV of beverages with low alcohol content**

This document presents the results of the validation study corresponding to the method for beverages with low alcohol content (updated).

The study was carried out in accordance with the OIV documents MA-F-AS1-08-FIDMET and MA-F-AS1-09-PROPER.

1/ Samples

Sample no.	1	2	3	4	5	6
Nature	Grape juice	Beverage obtained by dealcoholisation of wine	Beverage obtained by partial dealcoholisation of wine	Partially fermented grape juice	Cider	Wine-based beverage
Approximate value of ABV (% vol.)	< 0.5	0.5	1.5	2.5	4.5	6.5

The samples were sent to the participating laboratories, applying the double-blind principle.

2/ Analyses

Each of the 12 samples received by the laboratories was analysed by simple distillation or steam distillation, according to the two following procedures:

- OIV reference method involving the use of 200 mL and recovery of 200 mL of distillate,
- alternative method involving the use of 200 mL and recovery of 100 mL of distillate.

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Alcoholic strength by volume – Type I methods

3/ Participating laboratories

19 laboratories from different countries took part:

Laboratório CVRVV	4050-501 Porto	Portugal
Laboratório de Análises da CVRA	7006-806 Évora	Portugal
Testing Laboratory CAFIA	603 00 Brno	Czech Republic
Laboratório ASAE - LBPV	1649-038 Lisbon	Portugal
Agroscope - Site de Changins	1260 Nyon 1	Switzerland
Labo SCL de Bordeaux	33608 Pessac	France
Labo SCL de Montpellier	34196 Montpellier	France
Laboratorio Arbitral Agroalimentario	28023 Madrid	Spain
Estación Enológica de Haro	26200 Haro La Rioja	Spain
Instituto dos Vinho do Douro do Porto	4050-253 Porto	Portugal
IVICAM	13700 Tomelloso, Ciudad Real	Spain
INCAVI	08720 Vilafranca del Penedès	Spain
ICQRF Laboratorio di Conegliano/Susegana	31058 Susegana (TV)	Italy
ICQRF Laboratorio di Catania	95122 Catania	Italy
ICQRF Laboratorio di Modena	41100 Modena	Italy
ICQRF laboratorio di Perugia	06128 Perugia	Italy
ICQRF laboratorio di Salerno	84098 Salerno	Italy
ICQRF Laboratorio centrale di Roma	00149 Rome	Italy
Laboratoires DUBERNET	11100 Narbonne	France

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Alcoholic strength by volume – Type I methods**

4/ Results

	Sample N° 1	Sample N° 2	Sample N° 3	Sample N° 4	Sample N° 5	Sample N° 6						
	POSITION :											
LAB	2	7	4	11	6	12	5	8	9	10	1	3
A	0,21	0,21	0,55	0,55	1,34	1,34	2,58	2,58	4,59	4,60	6,54	6,50
B	0,11	0,14	0,49	0,50	1,32	1,38	2,60	2,57	4,68	4,72	6,52	6,55
C	0,33	0,28	0,68	0,61	1,43	1,35	2,63	2,60	4,63	4,66	6,58	6,51
D			0,62	0,62	1,38	1,36	2,68	2,67	4,69	4,73	6,62	6,64
E	0,20	0,21	0,55	0,56	1,36	1,40	2,61	2,62	4,67	4,68	6,56	6,55
F	0,18	0,12	0,52	0,51	1,31	1,30	2,56	2,56	4,70	4,66	6,51	6,54
G	0,22	0,22	0,55	0,56	1,37	1,37	2,62	2,62	4,68	4,68	6,58	6,57
H			0,41	0,42	1,25	1,27	2,46	2,49	4,57	4,56	6,39	6,40
I	0,20	0,13	0,54	0,48	1,32	1,28	2,60	2,58	4,62	4,62	6,57	6,55
J	0,24	0,24	0,58	0,60	1,41	1,37	2,63	2,63	4,69	4,67	6,55	6,55
K	0,22	0,22	0,56	0,55	1,35	1,35	2,63	2,63	4,67	4,68	6,59	6,58
L	0,22	0,23	0,56	0,57	1,38	1,36	2,63	2,61	4,66	4,67	6,56	6,57
M	0,18	0,18	0,53	0,53	1,33	1,29			4,66	4,65	6,53	6,52
N	0,22	0,23	0,56	0,57	1,38	1,41	2,26	2,61	4,67	4,67	6,51	6,57
O	0,12	0,19	0,53	0,52	1,33	1,33	2,64	2,62	4,67	4,67	6,51	6,55
P	0,25	0,25	0,57	0,58	1,39	1,41	2,66	2,65	4,70	4,68	6,62	6,62
Q	0,22	0,20	0,55	0,59	1,34	1,33	2,61	2,63	4,65	4,63	6,52	6,54
R	0,21	0,21	0,55	0,52	1,29	1,28	2,52	2,55	4,62	4,56	6,50	6,53
S	0,18	0,17	0,41	0,42	1,38	1,37	2,61	2,58	4,63	4,58	6,51	6,48

Results table obtained for a distillation of 200 mL with a recovery volume of 200 mL. The values in bold correspond to the values rejected by the Cochran test (variance outliers) with a significance level of 2.5% (1-tail test) and by the Grubbs test (means outliers) with a significance level of 2.5% (2-tail test).

Note: The values absent were not provided by the laboratory in question.

COMPENDIUM OF INTERNATIONAL ANALYSIS OF METHODS-OIV
Alcoholic strength by volume – Type I methods

	Sample N° 1	Sample N° 2	Sample N° 3	Sample N° 4	Sample N° 5	Sample N° 6						
LAB	POSITION :											
	2	7	4	11	6	12	5	8	9	10	1	3
A												
B	0,17	0,18	0,52	0,53	1,34	1,36	2,62	2,62	4,62	4,60	6,48	6,52
C	0,25	0,25	0,56	0,62	1,35	1,36	2,50	2,46	4,48	4,44	6,12	6,19
D	0,29	0,29	0,63	0,63	1,43	1,42	2,66	2,65	4,68	4,69	6,58	6,59
E	0,24	0,24	0,58	0,58	1,39	1,39	2,64	2,64	4,66	4,67	6,55	6,57
F	0,21	0,18	0,53	0,53	1,31	1,27	2,41	2,48	4,30	4,31	6,22	5,89
G	0,24	0,24	0,56	0,57	1,35	1,36	2,58	2,57	4,57	4,56	6,46	6,43
H	0,19	0,18	0,48	0,55	1,33	1,32	2,51	2,55	4,59	4,54	6,38	6,42
I	0,25	0,18	0,56	0,53	1,34	1,33	2,62	2,61	4,64	4,64	6,25	6,28
J	0,24	0,24	0,55	0,56	1,31	1,32	2,49	2,53	4,37	4,34	6,14	6,12
K	0,25	0,25	0,57	0,57	1,37	1,38	2,60	2,61	4,60	4,61	6,48	6,38
L	0,24	0,24	0,55	0,55	1,35	1,31	2,52	2,47	4,38	4,31	6,09	6,06
M	0,19	0,20	0,55	0,55	1,34	1,31			4,68	4,67	6,52	6,54
N	0,28	0,26	0,58	0,59	1,28	1,28	2,52	2,47	4,44	4,32	6,01	6,15
O	0,19	0,25	0,57	0,57	1,39	1,39	2,63	2,64	4,66	4,66	6,57	6,57
P	0,25	0,26	0,57	0,57	1,36	1,36	2,58	2,56	4,54	4,53	6,34	6,38
Q	0,24	0,24	0,57	0,57	1,38	1,38	2,63	2,62	4,66	4,67	6,56	6,56
R	0,23	0,23	0,54	0,55	1,32	1,30	2,54	2,56	4,56	4,52	6,40	6,35
S	0,27	0,26	0,55	0,57	1,34	1,34	2,46	2,43	4,53	4,51	6,36	6,36

Results table obtained for a distillation of 200 mL with a recovery volume of 100 mL. The values in bold correspond to the values rejected by the Cochran test (variance outliers) with a significance level of 2.5% (1-tail test) and by the Grubbs test (means outliers) with a significance level of 2.5% (2-tail test).

Note: The values absent were not provided by the laboratory in question.

COMPENDIUM OF INTERNATIONAL ANALYSIS OF METHODS-OIV
Alcoholic strength by volume – Type I methods

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
No. of laboratories considered	17	19	19	17	19	18
No. of repetitions	2	2	2	2	2	2
Minimum	0.11	0.41	1.25	2.46	4.56	6.48
Maximum	0.33	0.68	1.43	2.68	4.73	6.64
Overall average	0.20	0.54	1.35	2.60	4.65	6.55
Repeatability variance	0.00052	0.00033	0.00050	0.00019	0.00036	0.00047
Reproducibility variance	0.00211	0.00345	0.00190	0.00229	0.00181	0.00147
Inter-laboratory standard deviation	0.043	0.057	0.041	0.047	0.040	0.035
Repeatability standard deviation	0.02	0.02	0.02	0.01	0.02	0.02
r limit	0.06	0.05	0.06	0.04	0.05	0.061
Repeatability CV	11.1	3.3	1.7	0.5	0.4	0.3
Reproducibility standard deviation	0.046	0.059	0.044	0.048	0.043	0.038
R limit	0.130	0.166	0.123	0.135	0.120	0.109
Reproducibility CV	22.5	10.9	3.2	1.8	0.9	0.6
Horwitz RSD _r	3.36	2.90	2.52	2.29	2.09	1.99
Horrat _r	3.3	1.1	0.7	0.2	0.2	0.2
Horwitz RSD _R	5.10	4.39	3.82	3.46	3.17	3.01
Horrat _R	4.4	2.5	0.8	0.5	0.3	0.2

Table: Data obtained for a 200 mL distillate from a 200 mL sample.

COMPENDIUM OF INTERNATIONAL ANALYSIS OF METHODS-OIV
Alcoholic strength by volume – Type I methods

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
No. of laboratories considered	16	15	18	17	17	17
No. of repetitions	2	2	2	2	2	2
Minimum	0.17	0.52	1.27	2.41	4.30	6.01
Maximum	0.29	0.63	1.43	2.66	4.69	6.59
Overall average	0.24	0.56	1.35	2.56	4.55	6.38
Repeatability variance	0.00006	0.00003	0.00016	0.00050	0.00039	0.00135
Inter-laboratory standard deviation	0.03209	0.02496	0.03752	0.07013	0.12167	0.17621
Reproducibility variance	0.001	0.001	0.001	0.005	0.015	0.031
Repeatability standard deviation	0.01	0.01	0.01	0.02	0.02	0.04
r limit	0.02	0.02	0.04	0.06	0.06	0.104
Repeatability CV	3.2	1.0	0.9	0.9	0.4	0.6
Reproducibility standard deviation	0.033	0.025	0.039	0.072	0.122	0.178
R limit	0.092	0.071	0.109	0.203	0.347	0.504
Reproducibility CV	13.8	4.5	2.9	2.8	2.7	2.8
Horwitz RSD _r	3.27	2.88	2.52	2.29	2.10	2.00
Horrat _r	1.0	0.4	0.4	0.4	0.2	0.3
Horwitz RSD _R	4.96	4.36	3.82	3.47	3.18	3.03
Horrat _R	2.8	1.0	0.8	0.8	0.9	0.9

Table: Data obtained for a 100 mL distillate from a 200 mL sample.