

## **OIV-OENO 601B-2021 Revision of the method OIV-MA-AS312-01A: Alcoholic strength by volume at 20°C**

THE GENERAL ASSEMBLY,

IN VIEW OF the Article 2, paragraph 2 b) iv of the Agreement of 3<sup>rd</sup> April 2001 establishing the International Organisation of Vine and Wine,

AT THE PROPOSAL of the “Methods of Analysis” Sub-Commission,

CONSIDERING that inconsistencies have been noted between the methods relative to density (OIV-MA-AS2-01A) and alcoholic strength by volume (OIV-MA-AS312-01A and OIV-MA-AS312-01B),

CONSIDERING that this mainly consists of the task of restructuring the two methods present in the *Compendium of International Methods of Wine and Must Analysis*,

DECIDES to restructure the methods OIV-MA-AS312-01A and OIV-MA-AS312-01B, giving to the method the new nomenclature OIV-MA-AS312-01: 2021, and to merge them in one method as follows:

### **Alcoholic strength by volume at 20°C**

#### **Type I and type IV methods**

**standards/revision-del-metodo-oiv-ma-as312-01a,-“grado-alcoholico-volumetrico-a-20 °c”**

#### **1. Introduction**

This resolution is made up of one part on distillate preparation, followed by 4 methods (A, B, C and D) to determine the alcoholic strength by volume of this distillate.

#### **2. Scope of application**

This resolution is applicable for determining the alcoholic strength by volume at 20 °C of vitivincultural beverages, using any of the following:

|  |                        |
|--|------------------------|
| Method A: Pycnometry   | Type I Method,         |
| Method B: Electronic densimetry using a frequency oscillator | Type I Method,         |
| Method C: Hydrostatic balance                                | Type I Method,         |
| Method D: Hydrometry and refractometry                       | Common Type IV Method. |

### 3. Definition

The alcoholic strength by volume (ABV) of a beverage is the number of litres of ethanol contained in 100 litres of hydroalcoholic solution with the same density as the beverage distillate; both volumes being determined at a temperature of 20 °C. It is expressed by the symbol '% vol.'.

### 4. Principle and methods

#### 4.1. Principle

The principle of the method consists firstly of distilling the beverage by volume to volume after alkanisation by a suspension of calcium hydroxide, which prevents the entrainment of volatile acids. This distillation enables the elimination of non-volatile substances. The homologues of ethanol, in addition to ethanol and its homologues in esters are included in the ABV since they are present in the distillate. Secondly, the density of the distillate is measured. The density of a liquid at a given temperature is equal to the quotient of its mass over its volume:

$\rho = m / V$ , and for a vitivinicultural beverage, it is expressed as g/cm<sup>3</sup>.

For hydro-alcoholic solutions such as distillates, when the temperature is known, the tables can be used to match the density up to the ABV (OIV, MA-AS312-02: R2009 Table 1). This ABV corresponds to that of the beverage (distillation by volume to volume).

#### 4.2. Methods of determination of ABV

The principle and procedure for each method are detailed in the following parts:

Part A: Determination of the alcoholic strength by volume of a beverage by measuring the density of the distillate using a pycnometer;

Part B: Determination of the alcoholic strength by volume of a beverage by measuring the density of the distillate by electronic densimetry using a frequency oscillator;

Part C: Determination of the alcoholic strength by volume of a beverage by measuring the density of the distillate by densimetry using a hydrostatic balance;

Part D: Determination of the alcoholic strength by volume of a beverage by measuring the density of the distillate by hydrometry or by refractometry.

The test temperature is set at 20 °C.

#### 4.3. Safety precautions

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

### 5. Obtaining the distillate

## 5.1. Reagents

5.1.1. Type II water for analytical usage (ISO 3696 standard), or of equivalent purity

5.1.2. Suspension of calcium hydroxide, 12% m/v

Obtain by carefully pouring 1 L of water at 60-70 °C onto 120 g of quicklime (CaO).

5.1.3. Anti-foaming agent

## 5.2. Apparatus

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

Distil a hydro-alcoholic 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.

By way of example, use one of the following two sets of apparatus.

5.2.1. Distillation apparatus, consisting of:

- a round bottomed 1-L flask with a ground-glass standard joint,
- a rectifying column of about 20 cm in height or any system designed to prevent priming,
- a source of heat (any pyrolysis of extracted matter should be prevented by a suitable arrangement),
- a condenser terminated by a tapered tube taking the distillate to the bottom of a graduated receiver flask containing several mL of water.

2. Steam distillation apparatus consisting of:

- a steam generator,
- a bubbler,
- a rectifying column,
- a condenser.

3. Preparation of the sample

Remove the bulk of any carbon dioxide from samples with bubbles (e.g. by stirring 250 to 300 mL of the wine in a 500-mL flask).

## 5.4. Procedure

5.4.1. Procedure for beverages with an ABV greater than or equal to 1.5% vol.

Take a sample of a 200-mL volume of beverage using a calibrated flask. Note the temperature of the sample.

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 approx. 5 mL of water and add this to the apparatus' flask or bubbler.

Add approx. 10 mL 2 M calcium hydroxide ((5.1.2). If necessary, several fragments of inert porous material (e.g. pumice, etc.) and/or several drops of anti-foaming agent (5.1.3) may also be added to facilitate distillation.

Collect the distillate in the 200-mL calibrated flask used to measure the beverage. Collect a volume of about three-quarters of the initial volume if distillation is used or 198-199 mL of distillate if steam distillation is used.

Make up to 200 mL with distilled water, keeping the distillate at within  $\pm 2$  °C of the initial temperature.

Carefully mix 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 sulphuric acid diluted to 10% (v/v).

#### 5.4.2. Procedure for beverages with an ABV less than 1.5% vol.

Take a sample of a 200-mL volume 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 approx. 5 mL of water and add this to the apparatus' flask or bubbler. Add approx. 10 mL 2 M calcium hydroxide (5.1.2) and, in the case of distillation, if necessary, a boiling regulating agent (e.g. pumice, etc.). In a 100-mL calibrated flask, collect a volume of distillate of about 75 mL if distillation is used or 98-99 mL of distillate if steam distillation is used.

Make up to 100 mL with distilled water, keeping the distillate at within  $\pm 2$  °C of the initial temperature. Carefully mix using a circular motion.

### **Part A: Determination of the alcoholic strength by volume of a beverage by measuring the density of the distillate using a pycnometer**

#### **(Type I Method)**

(Method A2/1978 – Resolution OIV/OENO 377/2009)

#### **A.1. Principle**

The density of the distillate is determined, which is matched to the ABV using the Tables.

The density is measured for a specific temperature using a glass pycnometer. This

comprises a flask of known capacity, onto which a hollow ground-glass stopper is fitted equipped with a capillary tube. When the flask is closed, the overflow rises in the capillary. The volumes of the flask and the capillary being known, the density is determined by weighing using precision balances before and after filling of the pycnometer.

## A.2. Reagents and products

A.2.1. Type II water for analytical usage (ISO 3696 standard), or of equivalent purity

A.2.2. Sodium chloride solution (2% m/v)

To prepare 1 litre, weigh out 20 g sodium chloride and dissolve to volume with water.

## A.3. Apparatus and material

Common laboratory apparatus, including the following:

A.3.1. Pyrex-glass pycnometer of around 100 mL capacity with a removable thermometer, with ground-glass joint and 10<sup>th</sup>-of-a-degree graduations, from 10°C to 30°C. This thermometer should be calibrated (Fig. 1).

Any pycnometer of equivalent characteristics may be used.

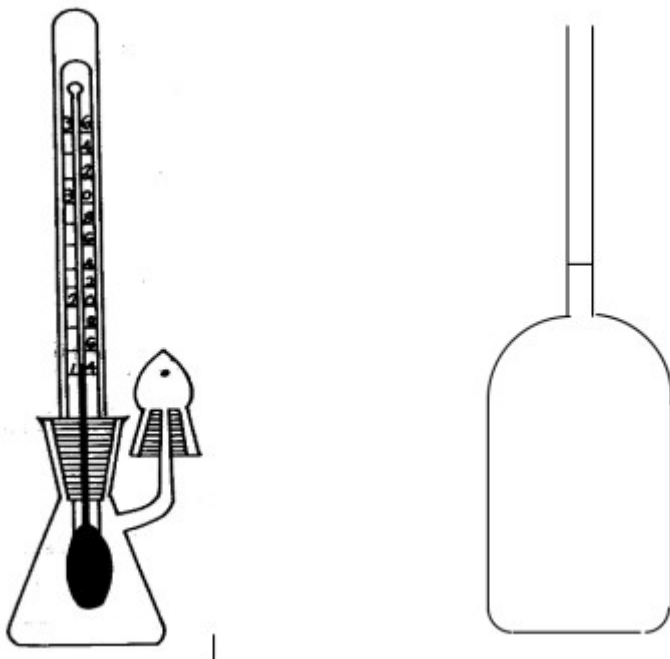


FIGURE 1: Pycnometer and its tare bottle

This pycnometer includes a side tube of 25 mm in length and an inside diameter of at most 1 mm, terminated by a ground-glass conical joint. This side tube may be capped by a 'reservoir stopper' composed of a ground-glass conical tube, terminated by a tapered joint. This stopper serves as an expansion chamber.

The two joints of the apparatus should be prepared with great care.

A.3.2. Tare bottle of the same external volume (to within 1 mL) as the pycnometer and with a mass equal to the mass of the pycnometer filled with a liquid of a density of 1.01 (2% m/v sodium chloride solution).

A.3.3. Thermally-insulated jacket that fits the body of the pycnometer exactly.

A.3.4. Twin-pan balance accurate to the nearest 0.1 mg

or

single-plate balance accurate to the nearest 0.1 mg.

A.3.5. Masses calibrated by an accredited body.

#### A.4. Procedure

##### A.4.1. Pycnometer calibration

The calibration of the pycnometer comprises the determination of the following characteristics:

- tare weight,
- volume at 20 °C,
- water mass at 20 °C.

##### 1. *Using a twin-pan balance*

Place the tare bottle on the left-hand pan and the clean, dry pycnometer with its 'reservoir stopper' on the right-hand pan. Balance them by placing weights of known mass on the pycnometer side:  $p$  grams.

Fill the pycnometer carefully with water (A.2.1) at room temperature and fit the thermometer.

Carefully wipe the pycnometer dry and place it in the thermally-insulated jacket.

Shake by inverting the container until the thermometer's temperature reading is constant. Accurately adjust the level to the upper rim of the side tube. Wipe the side tube clean and fit the reservoir stopper.

Read the temperature,  $t$  °C, carefully and if necessary correct for any inaccuracies in the temperature scale.

Weigh the water-filled pycnometer, with the weight in grams,  $p$ , making up the equilibrium.



### Calculations

Tare of the empty pycnometer:

Tare weight =  $p + m$  where  $m$  = mass of the air contained in the pycnometer, in g

- $m \text{ (g)} = 0.0012 (p - p')$

Volume at 20 °C in mL:

$$V_{20^{\circ}\text{C}} \text{ (mL)} = (p + m - p') \times F_t$$

$F_t$  = factor for temperature,  $t$  °C, taken from Table I

$V_{20^{\circ}\text{C}}$  should be known to  $\pm 0.001$  mL

Water mass at 20 °C:

$$M_{20^{\circ}\text{C}} = V_{20^{\circ}\text{C}} \times 0.998203, \text{ in g}$$

0.998203 = water density at 20 °C, in g/cm<sup>3</sup>

#### A.4.1.2. Using a single-pan balance

Determine:

- the mass of the clean, dry pycnometer: P,
- the mass of the water-filled pycnometer at  $t$  °C:  $P_1$  following the instructions outlined in A.4.1.1,
- the mass of the tare bottle, T.

### Calculations

Tare of the empty pycnometer:

Tare weight:  $P - m$  where  $m$  (g) = mass of the air contained in the pycnometer, in g

$$m \text{ (g)} = 0.0012 (P_1 - P)$$

Volume at 20 °C in mL:

$$V_{20^{\circ}\text{C}} \text{ (mL)} = [P_1 - (P - m)] \times F_t$$

$F_t$  = factor for temperature,  $t$  °C, taken from Table I

$V_{20^{\circ}\text{C}}$  should be known to  $\pm 0.001$  mL.

Water mass at 20 °C:

$$M_{20^{\circ}\text{C}} = V_{20^{\circ}\text{C}} \times 0.998203$$

0.998203 = water density at 20 °C, in g/cm<sup>3</sup>

#### A.4.2. Determination of the density of the distillate

Measure the apparent density of the distillate at  $t$  °C using a twin-pan or single-pan



balance:

A.4.2.1. *Using a twin-pan balance*

Weigh the pycnometer filled with the test sample following the instructions outlined in A.4.1.1.

Where  $p''$  represents the mass in grams that makes up the equilibrium at  $t$  °C, taking into account that the liquid mass contained in the pycnometer =  $p + m - p''$ ,

the apparent density at  $t$  °C, in  $\text{g}/\text{cm}^3$ , is given by the following equation

$$p_{t^{\circ}\text{C}} = \frac{p + m - p''}{V_{20^{\circ}\text{C}}}$$

A.4.2.2. *Using a single-pan balance*

Weigh the tare bottle, where  $T_1$  is its mass in g.

Calculate  $dT = T_1 - T_0$

Mass of the empty pycnometer at the time of measurement =  $P - m + dT$ , in g

Weigh the pycnometer filled with the test sample following the instructions outlined in A.4.1.1.

Where  $P_2$  represents its mass at  $t$  °C,

the liquid mass contained in the pycnometer at  $t$  °C =  $P_2 (P - m + dT)$ , in g

and the apparent density at  $t$  °C, in  $\text{g}/\text{cm}^3$ , is as follows:

$$p_{t^{\circ}\text{C}} = \frac{P_2 - (P - m + dT)}{V_{20^{\circ}\text{C}}}$$

A.5. Expression of results and precision parameters

A.5.1. *Method of calculation*

A.5.1.1. *Beverages with an ABV greater than or equal to 1.5% vol.*

Find the alcoholic strength at 20 °C in % vol. to 2 d.p. using Table I of Method OIV-MA-AS312-02A. Please note, this table uses the unit  $\text{kg}/\text{m}^3$  and not  $\text{g}/\text{cm}^3$ .

The relationship is as follows:  $1 \text{ g}/\text{cm}^3 = 1000 \text{ kg}/\text{m}^3$ .

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  $\rho_t$ . Use the tabular difference just below this density to calculate the density  $\rho$  at this temperature,  $T$ .



On the line of the temperature,  $T$ , find the density  $\rho'$  immediately above  $\rho$  and calculate the difference between the densities  $\rho$  and  $\rho'$ . Divide this difference by the tabular difference just to the right of the density  $\rho'$ . 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  $\rho'$  is located.

An example of calculation of the alcoholic strength is given in Annex 1 to this Chapter.

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

**A.5.1.2. Beverages with an ABV less than 1.5% vol.**

Identical to A.5.1.1, dividing the alcoholic strength by volume of the distillate (ABVD) by 2.

$ABV = ABVD/2$ , % vol. to 2 d.p.

**A.6. Precision**

*Repeatability (r):*

- $r = 0.10$  % vol.

*Reproducibility (R)*

- $R = 0.19$  % vol.

The validation parameters for beverages with a low alcohol content are given in Annex II.

**A.7. Example of the calculation of the alcoholic strength of a wine**

**A.7.1. Measurement by pycnometer on a twin-pan balance**

The constants of the pycnometer have been determined and calculated as described in the method OIV-MA-AS2-01, 'Density and specific gravity', paragraph A.7.

*A.4.2.1 Using a twin-pan balance*

Numerical example



1. Weighing of the distillate-filled pycnometer:  
Tare = pycnometer + distillate at  $t\text{ }^{\circ}\text{C} + p''$

$p + m - p''$  = mass of the distillate at  $t\text{ }^{\circ}\text{C}$   
Apparent density at  $t\text{ }^{\circ}\text{C}$ :

$$\rho_t = \frac{p + m - p''}{\text{volume of the pycnometer at } 20\text{ }^{\circ}\text{C}}$$

2. Calculation of the alcoholic strength:  
Consult the table of apparent densities of hydro-alcoholic mixtures at different temperatures, as indicated above.

$$\left\{ \begin{array}{l} t\text{ }^{\circ}\text{C} = 18.90\text{ }^{\circ}\text{C} \\ \text{corrected } t\text{ }^{\circ}\text{C} = 18.70\text{ }^{\circ}\text{C} \\ p'' = 2.8074\text{ g} \\ 105.0698 - 2.8074 = 102.2624\text{ g} \\ \rho_{18.7^{\circ}\text{C}} = \frac{102.2624}{104.0299} = 0.983076 \end{array} \right.$$

$\text{g/cm}^3$

On the line 18 °C of the table of apparent densities, the smallest density greater than the observed density of 0.983076 is 0.98398, in the column 11%.  
The density at 18 °C is:  
 $(98307.6 + 0.7 \times 22) 10^{-5} = 0.98323$   
 $0.98398 - 0.98323 = 0.00075$   
The decimal portion of the alcoholic strength is:  $75 / 114 = 0.65$   
The alcoholic strength is: 11.65% vol.

A.7.2. Measurement by pycnometer on a single-pan balance

The constants of the pycnometer have been determined and calculated as described in the method OIV-MA-AS2-01, 'Density and specific gravity', paragraph A.7.

Numerical example

Weighing of the pycnometer filled with distillate:



|  |  |
|--|--|
| Weight of tare bottle at the time of measurement | : T1 = 171.9178 g                                      |
| Pycnometer filled with distillate at 20.50 °C    | : P2 = 167.8438 g                                      |
| Variation in the buoyancy of air                 | : $dT = 171.9178 - 171.9160$<br>= + 0.0018             |
| Mass of the distillate at 20.5 °C                | : $Lt = 167.8438 - (67.6695 + 0.0018)$<br>= 100.1725 g |

Apparent density of the distillate :  $\rho_{20.5\text{ °C}} = 100.1725/101.8194 = 0.983825 \text{ g/cm}^3$

Calculation of alcoholic strength:

|  |  |
|--|--|
| <p>Refer to the table of apparent densities of hydro-alcoholic mixtures at different temperatures, as indicated above.</p> | <p>On the line 20 °C of the table of apparent densities, the smallest density greater than the observed density of 0.983825 is 0.98471, in the column 10% vol.</p> <p>The density at 20 °C is:<br/> <math>(98382.5 + 0.5 \times 24) \times 10^{-5} = 0.983945</math><br/> <math>0.98471 - 0.983945 = 0.000765</math></p> <p>The decimal portion of the alcoholic strength is: <math>76.5 / 119 = 0.64</math></p> <p>The alcoholic strength is: 10.64% vol.</p> |
|--|--|

## Part B Determination of the alcoholic strength by volume of a beverage by measuring the density of the distillate by electronic densimetry using a frequency oscillator

(Type I method)

(Resolution OENO 8/2000 – OIV/OENO 377/2009)

## B.1.Principle

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 electromagnetic stimulation. The density is thus calculated and is linked to the period of oscillation by the following formula:

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

$\rho$  = density of the sample

T = period of induced vibration

M = mass of empty tube

C = spring constant

V = volume of vibrating sample

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

## B.2.Reagents and products

### B.2.1Reference fluids

Two reference fluids are used to adjust the densimeter. The densities of the reference fluids should encompass the densities of the distillates to be analysed. A spread of greater than 0.01000 g/cm<sup>3</sup> between the densities of the reference fluids is recommended.

The reference fluids for the determination of the ABV of vitivinicultural beverages by electronic densimetry are as follows:

- dry air (unpolluted),
- Type II water for analytical usage (ISO 3696 standard), or of equivalent purity,
- hydro-alcoholic solutions of densities determined by another reference method, for which the uncertainty does not exceed 0.00005 g/cm<sup>3</sup> at the temperature of 20.00 ± 0.05°C,
- solutions calibrated with traceability to the International System of Units (SI), with viscosities of less than 2 mm<sup>2</sup>/s, for which the uncertainty does not exceed 0.00005 g/cm<sup>3</sup> at the temperature of 20.00 ± 0.05°C.

### B.2.2. Cleaning and drying products

Use products that ensure the perfectly clean and dried state of the measuring cell, according to the manufacturer's indications. For example:

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

## B.3. Apparatus and equipment

### B.3.1. Electronic densimeter with frequency oscillator

The electronic densimeter consists of the following elements:

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

The densimeter is placed on a perfectly stable support isolated from all vibrations.

### B.3.2. Temperature control of the measuring cell

Locate the measuring tube in the temperature-controlled enclosure. Temperature stability should be better than  $\pm 0.02^\circ\text{C}$ .

It is necessary to control the temperature of the measuring cell when the densimeter makes this possible because this strongly influences the determination results. The density of a hydro-alcoholic solution with an ABV of 10% vol. is  $0.98471 \text{ g/cm}^3$  at  $20^\circ\text{C}$  and  $0.98447 \text{ g/cm}^3$  at  $21^\circ\text{C}$ , equating to a spread of  $0.00024 \text{ g/cm}^3$ .

The test temperature is set at  $20^\circ\text{C}$ . The temperature is taken at the cell level, and done with a thermometer that has a resolution accurate to  $0.01^\circ\text{C}$  and is calibrated to national standards. This should enable a temperature measurement with an uncertainty of better than  $\pm 0.07^\circ\text{C}$ .

### B.3.3. Calibration of the apparatus

The apparatus should be calibrated before using it for the first time, then periodically or if the verification is not satisfactory. The objective is to use two reference fluids to calculate the constants A and B [see formula (2), B.1). To carry out the calibration in practice, refer to the user manual of the apparatus. In principle, this calibration is carried out with dry air (taking into account the atmospheric pressure) and very pure water (B.2.1).

### B.3.4. Calibration verification

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

Every day of use, a density check of the air is carried out. A difference between the theoretical density and observed density of more than  $0.00008 \text{ g/cm}^3$  may indicate that the tube is clogged. In that case, it should be cleaned. After cleaning, verify the air density again. If the verification is not conclusive, adjust the apparatus.

Check the density of the water; if the difference between the theoretical density and the density observed is greater than  $0.00008 \text{ g/cm}^3$ , adjust the apparatus.

If verification of the cell temperature is difficult, it is possible to directly check the density of a hydro-alcoholic solution of comparable ABV to those of the distillates analysed.

#### B.3.5. Checks

When the difference between the theoretical density of the reference solution (known with an uncertainty of  $\pm 0.00005 \text{ g/cm}^3$ ) and the measured density is above  $0.00008 \text{ g/cm}^3$ , the calibration of the apparatus should be checked.

#### B.4. Procedure

After obtaining a distillate, measure the density by densimetry and match to the ABV using the Tables.

Ensure the stability of the temperature of the measuring cell. The distillate in the densimeter cell should not contain air bubbles and should be homogeneous. If there is a lighting system available that makes it possible to verify the absence of bubbles, turn it off quickly after checking because the heat generated by the lamp can influence the measuring temperature.

For apparatus with a permanent lighting system, this statement is not applicable.

If the apparatus only provides the period, the density can be calculated from the A and B constants (see Annex I). If the apparatus does not provide the ABV directly, by knowing the density, obtain the ABV using the tables (Table I, OIV-MA-312-02).

#### B.5. Expression of results

##### B.5.1. Expression of results

##### B.5.1.1. Beverages with an ABV greater than or equal to 1.5% vol.

The alcoholic strength by volume of the beverage is obtained from the distillate. This is expressed as '% vol'.

If the temperature conditions are not respected, a correction should be made to express the temperature at  $20 \text{ }^\circ\text{C}$ . The result is given to two decimal places.

##### B.5.1.2. Beverages with an ABV less than 1.5% vol.

Identical to B.5.1.1, dividing the alcoholic strength of the distillate (ABVD) by 2.

$ABV = ABVD/2$ , % vol. to 2 d.p.

The validation parameters for beverages with a low alcohol content are given in Annex II

#### B.5.2. Comments

The volume introduced into the cell should be sufficient enough to avoid possible contamination caused from the previous sample. It is thus necessary to carry out at least two tests. If these do not provide results included in the repeatability limits, a third test is necessary. In general, the results from the last two tests are homogeneous and the first value can then be eliminated.

#### B.6. Precision

For samples with an ABV of greater than 4% vol., the validation data and precision results are given in Annex III.

repeatability ( $r$ ) = 0.067 (% vol.)

Reproducibility ( $R$ ) =  $0.0454 + 0.0105 \times ABV$  (% vol.)

For samples with an ABV of less than 4% vol. the validation data and precision results are given in Annex II

### Part C: Determination of the alcoholic strength by volume of a beverage by measuring the density of the distillate by densimetry using a hydrostatic balance (Type I Method)

(Resolution Oeno 24/2003 – OIV/OENO 377/2009)

#### C.1. Principle

The alcoholic strength by volume can be determined by densimetry using a hydrostatic balance following the Archimedes principle, by which any body immersed in a fluid experiences an upward force equal to the weight of the displaced fluid.

#### C.2. Reagents and products

C.2.1. Type II water for analytical usage (ISO 3696 standard), or of equivalent purity,

C.2.2. Floater-washing solution (sodium hydroxide, 30% m/v).

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

#### C.3. Common laboratory apparatus, including the following:

C.3.1. Single-pan hydrostatic balance with 1 mg precision.

C.3.2. Floater with at least 20 mL volume, specifically adapted for the balance, suspended by a thread with a diameter of less than or equal to 0.1 mm.

C.3.3. Cylindrical test tube with level indicator.

The floater should be able to fit entirely within the test tube volume below the level indicator; only the hanging thread should break the surface of the liquid. The cylindrical test tube should have an inside diameter at least 6 mm greater than that of the floater.

C.3.4. Thermometer (or temperature-measurement probe) with degree and 10<sup>th</sup>-of-a-degree graduations, from 10 °C to 40 °C, calibrated to  $\pm 0.05$  °C.

C.3.5. Masses calibrated by an accredited body.

#### C.4. **Procedure**

After each measurement, the floater and the test tube should be cleaned with distilled water, wiped with soft laboratory paper that does not lose its fibres and rinsed with solution whose density is to be determined. These measurements should be carried out once the apparatus has reached a stable level in order to limit alcohol loss through evaporation.

##### C.4.1. Apparatus calibration

###### C.4.1.1. Balance calibration

While balances usually have internal calibration systems, hydrostatic balances should be calibrated with weights with traceability to the International System of Units (SI).

###### C.4.1.2 Floater calibration

Fill the cylindrical test tube up to the level indicator with water (C.2.1) whose temperature is between 15 °C and 25 °C, but preferably at 20 °C.

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

###### C.4.1.3. Control using a hydro-alcoholic solution

Fill the cylindrical test tube up to the level indicator with a known titre of hydro-alcoholic solution at a temperature of between 15°C and 25 °C, preferably at 20°C.

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

*Note:* This solution of known alcoholic strength can also replace water for floater calibration.

##### C.4.2. Measurement of the density of the distillate (or alcoholic strength if possible)

Pour the test sample into the cylindrical test tube up to the level indicator.

Plunge the floater and the thermometer into the liquid, shake and note down the density on the apparatus (or the alcoholic strength if possible).



Note the temperature if the density is measured at  $t$  °C ( $\rho_t$ ).

Correct  $\rho_t$  using a  $\rho_t$  density table of hydro-alcoholic mixtures (Table II in Annex I of the method OIV-MA-AS312-02 in the OIV *Compendium of International Methods of Analysis*).

C.4.3. Cleaning of the floater and cylindrical test tube

Plunge the floater into the washing solution in the test tube.

Allow to soak for one hour while turning the floater regularly.

Rinse with tap water, then with distilled water.

Wipe with soft laboratory paper that does not lose its fibres.

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

### C.5. Expression of results

C.5.1. Beverages with an ABV greater than or equal to 1.5% vol.

Using the density  $\rho_{20}$ , calculate the real alcoholic strength using the table indicating the alcoholic strength by volume (% vol.) at 20°C according to the density at 20°C of the hydro-alcoholic mixtures. This is the international table adopted by the International Organization of Legal Metrology in its Recommendation No. 22 (1973).

The values are expressed in % vol. to 2 d.p.

C.5.2. Beverages with an ABV less than or equal to 1.5% vol.

Identical to C.5.1, dividing the alcoholic strength of the distillate (ABVD) by 2.

$ABV = ABVD/2$ , % vol. to 2 d.p.

The validation parameters for beverages with a low alcohol content are given in Annex II.

### C.6. Precision

Repeatability (r)= 0.074 (% vol.)

Reproducibility (R)= 0.229 (% vol.)

## Part D: Determination of the alcoholic strength by volume of a wine by measuring the density of the distillate by hydrometry or refractometry (Type IV Method)

### D.1. Principle

The alcoholic strength may be determined by densimetry using an alcoholometer following the Archimedes principle. A weighted cylinder equipped with a graduated stem is more or less immersed into the distillate whose density is to be determined.

The density of the liquid is read directly on the graduation of the stem at the level of the meniscus.

## D.2. Hydrometry

### D.2.1. Apparatus and materials

#### D.2.1.1. *Alcoholometer*

The alcoholometer should meet the specifications for Class I or Class II alcoholometers as defined in OIML (International Organization of Legal Metrology) International Recommendation 44 “Alcoholometers and alcohol hydrometers for use in alcoholometry”.

This apparatus should be calibrated with traceability to the International System of Units (SI).

D.2.1.2. Thermometer calibrated with traceability to the International System of Units (SI) with degree and 10<sup>th</sup>-of-a-degree graduations, from 0 °C to 40 °C, calibrated to  $\pm 0.05$  °C.

D.2.1.3. Measuring cylinder with dimensions that allow for the immersion of the thermometer and the alcoholometer without contact with the sides, held vertically.

#### D.2.2. Procedure

Pour the distillate into the measuring cylinder, ensure that the cylinder is kept vertical, and insert the thermometer and alcoholometer. Stir and wait 1 minute to allow temperature equilibration of the measuring cylinder, the thermometer, the alcoholometer and the distillate before reading the thermometer. Remove the thermometer and, after 1 minute of rest, read the apparent alcoholic strength.

Take at least three readings from the bottom of the meniscus using a magnifying glass. Correct the apparent strength measured at  $t$  °C to account for the effect of the temperature using the Tables. The temperature of the liquid must differ very little from the room temperature (at most, by 5 °C).

## D.3. Refractometry

### D.3.1. Apparatus

Refractometer enabling the refractive indices in the range 1.330 to 1.346 to be measured.

Depending on the type of apparatus, measurements are taken:

either at 20°C, with a suitable instrument,

or at room temperature,  $t$ °C, with a thermometer enabling the temperature to be determined to within at least 0.05°C (a temperature correction table will be provided with the apparatus).

### D.3.2. Procedure

The refractive index of the wine distillate (5) is measured by following the procedure prescribed for the type of instrument used.

### D.3.3. Expression of results

Table IV in Chapter OIV-MA-AS312-02 is used to find the alcoholic strength corresponding to the refractive index at 20°C.

*Note:* Table IV gives the alcoholic strengths corresponding to the refractive indices for both pure hydro-alcoholic mixtures and for wine distillates. In the case of wine distillates, it takes into account the presence of impurities in the distillate (mainly higher alcohols). The presence of methanol lowers the refractive index and thus the alcoholic strength.

*Note:* To obtain the alcoholic strength from the density of the distillate, use Tables I, II and III in Chapter OIV-MA-AS312-02. These have been calculated from the international alcoholometric tables published in 1972 by the International Organization of Legal Metrology in its Recommendation No. 22 and adopted by the OIV.

## 7. Annexes

### Annex I

Formula for the calculation of alcoholic strength tables for mixtures of ethanol and water.

The density,  $\rho$ , expressed in kilograms per cubic metre ( $\text{kg}/\text{m}^3$ ) of a mixture of ethanol and water at the temperature  $t$ , expressed in degrees Celsius, is given by the following formula, according to the following:

the mass concentration  $\varpi$ , expressed by a decimal number (\*),

the temperature  $t$ , expressed in degrees Celsius (IPTS 68),

the numerical coefficients in the tables below.

The formula is valid for temperatures of between  $-20\text{ }^\circ\text{C}$  and  $+40\text{ }^\circ\text{C}$ .

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

$$n = 5$$

$$m_1 = 11$$



$$m_2 = 10$$

$$m_3 = 9$$

$$m_4 = 4$$

$$m_5 = 2$$

(\*) E.g. For a mass concentration of 12%,  $p = 0.12$ .

**Numeric coefficients for the formula**

| $k$ | $A_k$<br>kg/m <sup>3</sup>    | $B_k$   |
|-----|-------------------------------|---|
| 1   | $9,982\ 012\ 300 \cdot 10^2$  | $-2,061\ 851\ 3 \cdot 10^{-1} \text{ kg/(m}^3 \cdot ^\circ\text{C)}$    |
| 2   | $-1,929\ 769\ 495 \cdot 10^2$ | $-5,268\ 254\ 2 \cdot 10^{-3} \text{ kg/(m}^3 \cdot ^\circ\text{C}^2)$  |
| 3   | $3,891\ 238\ 958 \cdot 10^2$  | $3,613\ 001\ 3 \cdot 10^{-3} \text{ kg/(m}^3 \cdot ^\circ\text{C}^2)$   |
| 4   | $-1,668\ 103\ 923 \cdot 10^3$ | $-3,895\ 770\ 2 \cdot 10^{-7} \text{ kg/(m}^3 \cdot ^\circ\text{C}^4)$  |
| 5   | $1,352\ 215\ 441 \cdot 10^4$  | $7,169\ 354\ 0 \cdot 10^{-9} \text{ kg/(m}^3 \cdot ^\circ\text{C}^5)$   |
| 6   | $-8,829\ 278\ 388 \cdot 10^4$ | $-9,973\ 923\ 1 \cdot 10^{-11} \text{ kg/(m}^3 \cdot ^\circ\text{C}^6)$ |
| 7   | $3,062\ 874\ 042 \cdot 10^5$  |   |
| 8   | $-6,138\ 381\ 234 \cdot 10^5$ |   |
| 9   | $7,470\ 172\ 998 \cdot 10^5$  |   |
| 10  | $-5,478\ 461\ 354 \cdot 10^5$ |   |
| 11  | $2,234\ 460\ 334 \cdot 10^5$  |   |
| 12  | $-3,903\ 285\ 426 \cdot 10^4$ |   |

| $k$ | $C_{1,k}$<br>kg/(m <sup>3</sup> · °C)     | $C_{2,k}$<br>kg/(m <sup>3</sup> · °C <sup>2</sup> ) |
|-----|---|---|
| 1   | $1,693\ 443\ 461\ 530\ 087 \cdot 10^{-1}$ | $-1,193\ 013\ 005\ 057\ 010 \cdot 10^{-1}$          |
| 2   | $-1,046\ 914\ 743\ 455\ 169 \cdot 10^1$   | $2,517\ 399\ 633\ 803\ 461 \cdot 10^{-1}$           |
| 3   | $7,196\ 353\ 469\ 546\ 523 \cdot 10^1$    | $-2,170\ 575\ 700\ 536\ 993$                        |
| 4   | $-7,047\ 478\ 054\ 272\ 792 \cdot 10^2$   | $1,353\ 034\ 988\ 843\ 029 \cdot 10^1$              |
| 5   | $3,924\ 090\ 430\ 035\ 045 \cdot 10^3$    | $-5,029\ 988\ 758\ 547\ 014$                        |
| 6   | $-1,210\ 164\ 659\ 068\ 747 \cdot 10^4$   | $1,096\ 355\ 666\ 577\ 570 \cdot 10^2$              |
| 7   | $2,248\ 646\ 550\ 400\ 788 \cdot 10^4$    | $-1,422\ 753\ 946\ 421\ 155$                        |
| 8   | $-2,605\ 562\ 982\ 188\ 164 \cdot 10^4$   | $1,080\ 435\ 942\ 856\ 230 \cdot 10^2$              |
| 9   | $1,852\ 373\ 922\ 069\ 467 \cdot 10^4$    | $-4,414\ 153\ 236\ 817\ 392$                        |
| 10  | $-7,420\ 201\ 433\ 430\ 137 \cdot 10^3$   | $7,442\ 971\ 530\ 188\ 783$                         |
| 11  | $1,285\ 617\ 841\ 998\ 974 \cdot 10^3$    |   |

| $k$ | $C_{3,k}$<br>kg/(m <sup>3</sup> · °C <sup>3</sup> ) | $C_{4,k}$<br>kg/(m <sup>3</sup> · °C <sup>4</sup> ) | $C_{5,k}$<br>kg/(m <sup>3</sup> · °C <sup>5</sup> ) |
|-----|---|---|---|
| 1   | $-6,802\ 995\ 733\ 503\ 803 \cdot 10^{-4}$          | $-4,075\ 376\ 675\ 622\ 027 \cdot 10^{-1}$          | $-2,788\ 074\ 354\ 782\ 409 \cdot 10^{-4}$          |
| 2   | $-1,876\ 837\ 790\ 289\ 664 \cdot 10^{-2}$          | $-8,763\ 058\ 573\ 471\ 110 \cdot 10^{-1}$          | $1,345\ 612\ 883\ 493\ 354 \cdot 10^{-4}$           |
| 3   | $-2,002\ 561\ 813\ 734\ 156 \cdot 10^{-1}$          | $6,515\ 031\ 360\ 099\ 368 \cdot 10^{-8}$           |   |
| 4   | $-1,022\ 992\ 966\ 719\ 220$                        | $-1,515\ 784\ 836\ 987\ 210 \cdot 10^{-4}$          |   |
| 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   | $-5,411\ 227\ 621\ 436\ 812 \cdot 10^{-1}$          |   |   |

## Annex II Validation parameters relating to the measurement of the ABV of beverages with a low alcohol content

This document presents the results of the validation study for the method for beverages with a low alcohol content (update).

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

### 1. Sample

| 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 ABV in %vol. | < 0.5       | 0.5   | 1.5   | 2.5                             | 4.5   | 6.5                 |

Table 1: Samples analysed for the validation

### 2. Analyses

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

OIV reference method with use of 200 mL and recovery of 200 mL of distillate,

Alternative method with use of 200 mL and recovery of 100 mL of distillate.

### 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 Lisboa | 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    | Porto 4050-253               | 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      |

Table 2: Laboratories that took part in the validation

#### 4. Results

|     | Sample No. 1 |      | Sample No. 2 |      | Sample No. 3 |      | Sample No. 4 |      | Sample No. 5 |      | Sample No. 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 |

Table 3: Results obtained for a 200 mL distillation with recovery volume of 200 mL  
 Results not presented were rejected in accordance with the Cochran (variance outliers) test with a 2.5% significance level (one-tailed test) and the Grubbs (outliers from the mean) test with significance levels of 2.5% (two-tailed test).

*Note:* The absent values have not been provided by the laboratory in question.

|     | Sample No. 1 | Sample No. 2 | Sample No. 3 | Sample No. 4 | Sample No. 5 | Sample No. 6 |      |      |      |      |      |      |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|------|------|------|------|------|------|
|     | POSITION :   |              |              |              |              |              |      |      |      |      |      |      |
| LAB | 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 |

Table 4: Results obtained for a 200 mL distillation with recovery volume of 100 mL

Results not presented were rejected in accordance with the Cochran (variance outliers) test with a 2.5% significance level (one-tailed test) and the Grubbs (outliers from the mean) test with significance levels of 2.5% (two-tailed test).

*Note:* The absent values have not been provided by the laboratory in question.

|                              | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|------------------------------|----------|----------|----------|----------|----------|----------|
| No. of laboratories selected | 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 <sub>r</sub>            | 3.36    | 2.90    | 2.52    | 2.29    | 2.09    | 1.99    |
| Horrat <sub>r</sub>                 | 3.3     | 1.1     | 0.7     | 0.2     | 0.2     | 0.2     |
| Horwitz RSD <sub>R</sub>            | 5.10    | 4.39    | 3.82    | 3.46    | 3.17    | 3.01    |
| Horrat <sub>R</sub>                 | 4.4     | 2.5     | 0.8     | 0.5     | 0.3     | 0.2     |

Table 5: Data obtained for a 200 mL distillate from a 200 mL sample

|  | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|--|----------|----------|----------|----------|----------|----------|
|--|----------|----------|----------|----------|----------|----------|

|                                     |         |         |         |         |         |         |
|-------------------------------------|---------|---------|---------|---------|---------|---------|
| No. of laboratories selected        | 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 <sub>r</sub>            | 3.27    | 2.88    | 2.52    | 2.29    | 2.10    | 2.00    |
| Horrat <sub>r</sub>                 | 1.0     | 0.4     | 0.4     | 0.4     | 0.2     | 0.3     |
| Horwitz RSD <sub>R</sub>            | 4.96    | 4.36    | 3.82    | 3.47    | 3.18    | 3.03    |

|                     |     |     |     |     |     |     |
|---------------------|-----|-----|-----|-----|-----|-----|
| Horrat <sub>R</sub> | 2.8 | 1.0 | 0.8 | 0.8 | 0.9 | 0.9 |
|---------------------|-----|-----|-----|-----|-----|-----|

Table 6: Data obtained for a 100 mL distillate from a 200 mL sample

### Annex III Validation parameters relating to the measurement of the ABV by electronic densimetry (Part B)

#### 1. Inter-laboratory tests: precision and accuracy on additions

##### 1.1. Samples

The samples used for this joint study are described in Table 7.

| No. | Nature   | Approximate ABV (% vol.) |
|-----|--|--------------------------|
| C0  | Cider (filtered through a membrane to remove CO <sub>2</sub> ) | ~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                      |

Table 7: Samples for the joint study

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

For the additions, absolute ethanol was poured into a 5-L volumetric flask, then filled up to the line with filtered wine. This was repeated two times. The volumes of ethanol were 50, 100 and 150 mL respectively for the V1, V2 and V3 samples.

##### 1.2. Participating laboratories

The participating laboratories in the joint study are outlined in Table 8.

| Laboratory     | Postcode  | City     |
|----------------|-----------|----------|
| ALKO Group LTD | FIN-00101 | Helsinki |
| Bénédictine    | 76400     | Fécamp   |
| Casanis        | 18881     | Gemenos  |
| CIVC           | 51200     | Epernay  |

|                         |       |                          |
|-------------------------|-------|--------------------------|
| Cointreau               | 49181 | St Barthélémy<br>d'Anjou |
| Courvoisier             | 16200 | Jarnac                   |
| Hennessy                | 16100 | Cognac                   |
| IDAC                    | 44120 | Vertou                   |
| Laboratoire<br>Gendrot  | 33000 | Bordeaux                 |
| Martell                 | 16100 | Cognac                   |
| Ricard                  | 94320 | Thiais                   |
| SOEC Martin<br>Vialatte | 51319 | Epernay                  |

Table 8: List of laboratories participating in the joint study

In order to not introduce a methodological bias, the results of the Station Viticole du Bureau National Interprofessionnel du Cognac (the joint-study organiser) are not taken into account.

#### 1.2.1. Analyses

The C0 and P0 products were distilled independently two times, and the V0, V1, V2 and V3 products three times. Three ABV tests were done for each distillate. The results are displayed in the results table.

#### 1.2.2. Results

The second test (out of the three carried out) was kept for the precision study (Table 9).

| 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 |        |
|            | 5.960 | 9.460 | 10.350 | 11.280 | 12.170 | 17.190 |

|    |       |       |        |        |        |        |
|----|-------|-------|--------|--------|--------|--------|
| 3  | 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 |        |

Table 9: Results (second test per distillate) (% vol.)

### 1.2.3. Repeatability and reproducibility calculations

The repeatability and reproducibility calculations were carried out in compliance with the standard NF X 06-041, September 1983, ISO 5725. Table 10 presents the standard deviation per cell (laboratory x sample).

| 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 |

Table 10: Dispersion table (standard deviation in % vol.)

Three cells presented strong dispersions (probability with Cochran test under 1%). These cells are represented in grey (Table 10). For laboratory 7 and the V3 product, the standard deviation of 0.0764 was maintained despite the Cochran test because it is on the same high level as that observed at the same laboratory for the V0 product.

An examination of the figures for each distillate (Table 9) led to the elimination of the following:

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

After eliminating these two values, the cell averages were calculated (laboratory x sample). The results are presented in Table 11.

| 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 |

Table 11: Table of averages (means in % vol.)

The figures given by laboratory 7 are generally low (Table 11). In the case of cider, the average for this laboratory is very far from the figures of the other laboratories (probability with the Dixon test under 1%). This laboratory's results for this product were eliminated.

Table 12 presents the calculated repeatability and reproducibility.

| Sample          | P  | n  | ABV    | S <sup>2</sup> r | S <sup>2</sup> L | r     | R     |
|-----------------|----|----|--------|------------------|------------------|-------|-------|
| <sup>1</sup> 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 |

Table 12: Repeatability and reproducibility calculations

Key:

p: number of laboratories retained

n: number of values retained

ABV: mean ABV (% vol.)



$S^2_r$ : repeatability variance (% vol.)<sup>2</sup>

$S^2_L$ : interlaboratory variance (% vol.)<sup>2</sup>

*r*: repeatability (% vol.)

*R*: reproducibility (% vol.)

Reproducibility increases with the sample's ABV (Figure 2). The increase in repeatability according to ABV is less noticeable and the overall repeatability was calculated according to the mean repeatability variance. As such, for the samples with an ABV of between 4 and 18% vol.,

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

Reproducibility (*R*) = 0.0454 + 0.0105 x ABV.

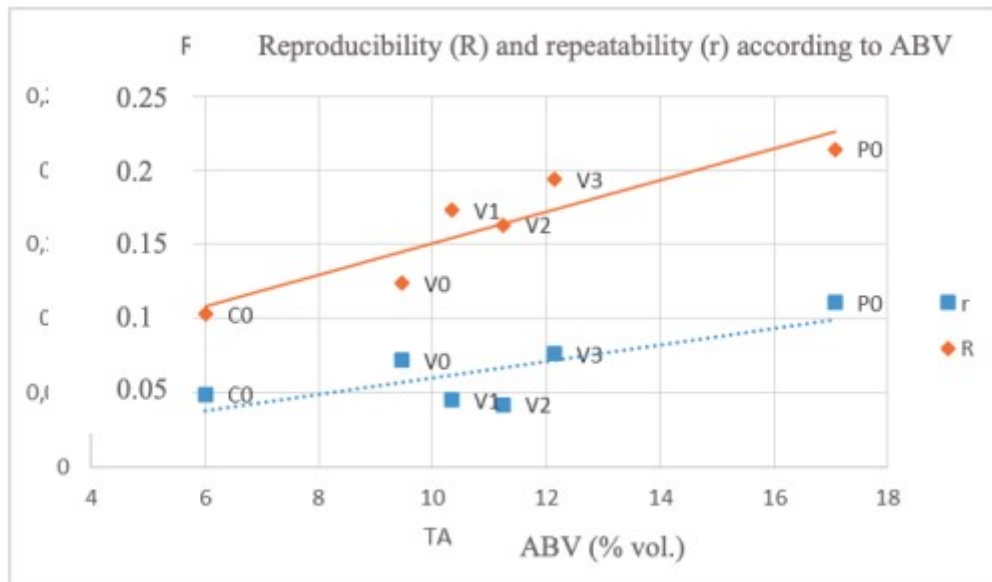


Figure 2: Repeatability and reproducibility according to ABV

1.2.4. Accuracy with regard to additions carried out on wine

The regression line of alcoholic strength after addition according to the volume of ethanol added provides, for a volume of 0 mL, an estimation of the initial alcoholic strength of the product (Figure 3). This regression is carried out with mean values for each laboratory (Table 11).

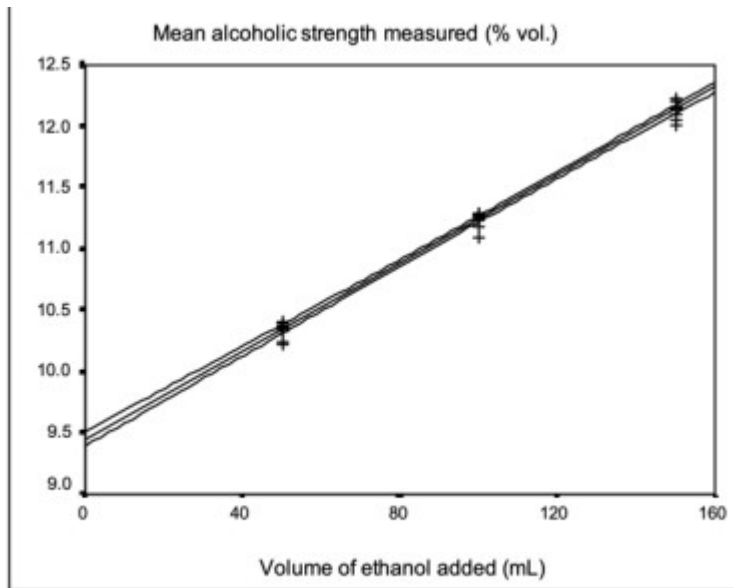


Figure 3: Regression of ABV measured by volume of ethanol added

Measurements carried out on initial products are not included in this estimation. This estimation was compared with the mean of the measurements taken on this product before additions; the intervals of relative confidence on these two estimations were calculated (Table 13).

| LB    | mean of measurements | UB    | LB    | estimation with measurements of products + additions | UB    |
|-------|----------------------|-------|-------|--|-------|
| 9.440 | 9.466                | 9.492 | 9.392 | 9.450  | 9.508 |

Table 13: Additions to products

Key:

LB: lower bound of confidence interval at 95%

UB: upper bound of confidence level at 95%

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

### 1.2.5. Conclusion of inter-laboratory tests

The repeatability and reproducibility indications by inter-laboratory tests provide the following equations, for products with ABVs of between 4% and 18% vol.:

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

Reproducibility (R) =  $0.0454 + 0.0105 \times \text{ABV (\% vol.)}$ .

The Horwitz indicators, Hor and HoR, are low (Table 14). This therefore indicates good precision of the method in relation to the analyte measured.

| Sample | C0     | V0     | V1      | V2      | V3      | P0      |
|--------|--------|--------|---------|---------|---------|---------|
| n      | 20     | 33     | 32      | 32      | 33      | 22      |
| p      | 10     | 11     | 11      | 11      | 11      | 11      |
| ABV    | 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  |

Table 14: Summary table of method precision

Key:

*n*: number of values retained

*p*: number of laboratories retained

*ABV*: mean ABV (% vol.)

*r*: repeatability (% vol.)

*sr*: repeatability standard deviation (% vol.)

*RSDr*: repeatability coefficient of variation ( $sr \times 100 / ABV$ ) (%)

*RSDrH*: Horwitz repeatability coefficient of variation ( $0.66 \times RSDrH$ ) (%)

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

*R*: reproducibility (% vol.)

*sR*: reproducibility standard deviation (% vol.)

*RSDR*: reproducibility coefficient of variation ( $sR \times 100 / ABV$ ) (%)

*RSDRH*: Horwitz reproducibility coefficient of variation ( $2^{(1-0.5\log(ABV))}$ ) (%)

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

The measurements carried out during inter-laboratory tests on wine with additions made it possible to find the value obtained before the addition. The values 9.45% and 9.47% vol. were found respectively.

#### Annex IV

Comparison of measurements carried out using a hydrostatic balance (Method C) with those obtained by electronic densimetry (Méthode B)

Using samples with alcoholic strengths between 4% vol. and 18% vol., the repeatability and reproducibility were measured using an inter-laboratory test. The alcoholic strength of the different samples as measured using a hydrostatic balance and using electronic densimetry were compared, including the repeatability and reproducibility values derived from the multi-year inter-comparison tests performed on a large scale.

1. *Samples*: Wines with different densities and alcoholic strengths prepared monthly on an industrial scale, taken from a stock of bottles stored under normal conditions, and supplied anonymously to the laboratories.
2. *Laboratories*: Laboratories participating in the monthly tests organised by *Unione Italiana Vini* (Verona, Italy) according to ISO 5725 (UNI 9225) regulations and the International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories produced by the AOAC, ISO and IUPAC (J. AOAC Intern., 1993, 74/4), and ISO 43 and ILAC G13 guidelines. An annual report is provided by the above-mentioned organisation to all participants.

### 3. Apparatus:

- An electronic hydrostatic balance (with precision to 5 decimal places), equipped if possible with a data-processing device.
- An electronic densimeter, equipped if possible with an autosampler.

### 4. Analyses

The measurement of the distillate was repeated twice.

### 5. Results

Table 15 shows the results of the measurements obtained by the laboratories using a hydrostatic balance.

Table 16 shows the results obtained by the laboratories using an electronic densimeter.

### 6. Evaluation of results

Interlaboratory reproducibility

A Horrat value of 1 usually indicates satisfactory interlaboratory reproducibility, whereas a value of more than 2 normally indicates unsatisfactory reproducibility, i.e. one that is too variable for analytical purposes or where the variation obtained is greater than that expected for the type of method employed. Hor is also calculated and used to assess interlaboratory reproducibility, using the following approximation:

$RSDr \text{ (Horwitz)} = 0.66 RSDR \text{ (Horwitz)}$  (this assumes the approximation that  $r = 0.66 R$ ).

Table 17 shows the differences between the measurements obtained by laboratories using an electronic densimeter and those using a hydrostatic balance. Excluding the sample 2000/3, which has a very low alcohol strength and for which both techniques show poor reproducibility, good concordance is generally observed for the other samples.

### 7. Precision parameters

Table 18 shows the overall averages of the precision parameters calculated from all monthly tests carried out between January 1999 and May 2001.

In particular:

Repeatability ( $r$ ) = 0.074 (% vol.) for the hydrostatic balance and

0.061 (% vol.) for electronic densimetry,

Reproducibility ( $R$ ) = 0.229 (% vol.) for the hydrostatic balance and

0.174 (% vol.) for electronic densimetry.

Table 15: Hydrostatic balance (HB)

|         | mean   | n  | outliers | n1 | r      | sr     | RSDr   | Hor    | R      | sR     | RSDR    | HoR  | no. of replicates | difference |
|---------|--------|----|----------|----|--------|--------|--------|--------|--------|--------|---------|------|-------------------|------------|
| 1999/1  | 11.043 | 17 | 1        | 16 | 0.0571 | 0.0204 | 0.1846 | 0.1004 | 0.1579 | 0.0564 | 0.5107  | 0.18 | 2                 | 0.108      |
| 1999/2  | 11.247 | 14 | 1        | 13 | 0.0984 | 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 | 0.278  | 0.1515 | 0.2701 | 0.0965 | 0.8622  | 0.31 | 2                 | 0.186      |
| 1999/6  | 11.276 | 19 | 0        | 19 | 0.0846 | 0.0302 | 0.268  | 0.1462 | 0.2057 | 0.1056 | 0.9365  | 0.34 | 2                 | 0.2047     |
| 1999/7  | 8.018  | 17 | 0        | 17 | 0.089  | 0.0318 | 0.3964 | 0.2054 | 0.2573 | 0.0919 | 1.1462  | 0.39 | 2                 | 0.1764     |
| 1999/9  | 11.226 | 17 | 0        | 17 | 0.058  | 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                 | 0.185      |
| 1999/11 | 7.701  | 16 | 1        | 15 | 0.0643 | 0.0229 | 0.298  | 0.1535 | 0.233  | 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 | 0.092  | 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 | 0.806   | 0.29 | 2                 | 0.174      |
| 2000/3  | 0.679  | 10 | 0        | 10 | 0.068  | 0.0243 | 3.5773 | 1.2783 | 0.6529 | 0.2332 | 34.3395 | 8.1  | 2                 | 0.4604     |
| 2000/4  | 11.223 | 18 | 0        | 18 | 0.0709 | 0.0253 | 0.2257 | 0.123  | 0.2184 | 0.078  | 0.6951  | 0.25 | 2                 | 0.1503     |
| 2000/5  | 7.439  | 19 | 1        | 18 | 0.063  | 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 | 0.171  | 0.0932 | 0.2783 | 0.0994 | 0.889   | 0.32 | 2                 | 0.195      |
| 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 | 0.095  | 0.0339 | 0.2971 | 0.1623 | 0.241  | 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 | 0.199  | 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                 | 0.129      |

Table 16: Electronic densimetry (ED)

|          | MEAN no.1 | n  | outliers | n1 | r      | Sr     | RSDr   | Hor    | R      | sR     | RSDR    | HoR   | no. of replicates | difference |
|----------|-----------|----|----------|----|--------|--------|--------|--------|--------|--------|---------|-------|-------------------|------------|
| 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 | 0.1286 | 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 | 0.4786  | 0.17  | 2                 | 0.0999     |
| D2000/9  | 11.983    | 22 | 1        | 21 | 0.0841 | 0.0300 | 0.2907 | 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 | 0.0796 | 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 | 0.0679 | 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 17: Comparison of results from a hydrostatic balance (HB) and from electronic densimetry (ED)

|         | Mean (HB) | n  | Values | n1 |  | Mean (ED) | n  | Values | n1 | %ABV (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 | 7.761     | 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  | 0.839     | 10 | 0      | 10 | D2000/3                                | 0.826     | 12 | 1      | 11 | * 0.153      |
| 2000/4  | 11.223    | 18 | 0      | 18 | D2000/4                                | 11.225    | 19 | 1      | 18 | -0.002       |
| 2000/5  | 7.419     | 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        |
|         |           |    |        |    | Overall difference / %ABV (HB-ED)      |           |    |        |    | 0.014        |
|         |           |    |        |    | Standard deviation/difference          |           |    |        |    | 0.036        |
|         |           |    |        | *  | Test 2000/3 was not taken into account |           |    |        |    |              |

Table 18: Precision parameters

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

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