OIV-MA-AS312-01 Alcoholic strength by volume

Type I and type IV methods

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 vitivinicultural 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 alkalinisation 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:

ρ = m / V, and for a vitivinicultural beverage, it is expressed as g/cm^3.

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 of 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 ± 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^{th}-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.

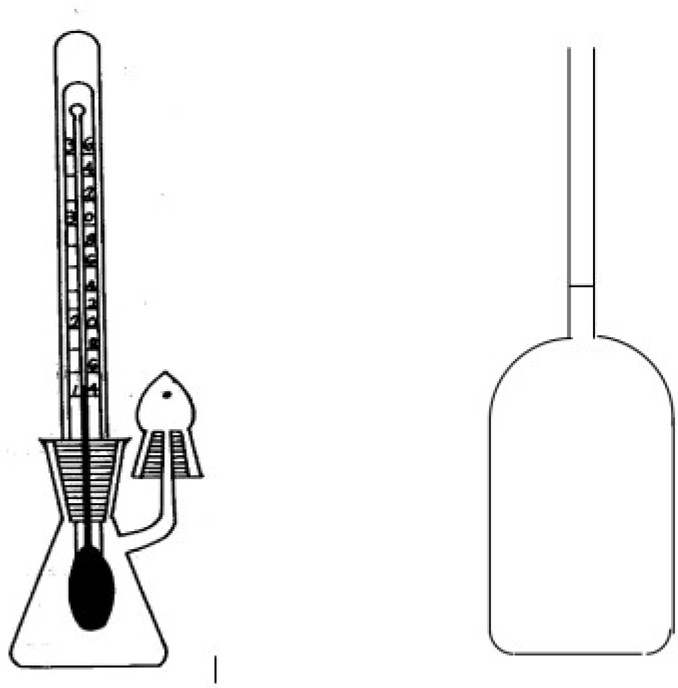

FIGURE 1: Pycnometer and its tare bottle

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 (g) = 0.0012 $(p - p')$

Volume at 20 °C in mL:

$V_{20°C}$ (mL) = $(p + m - p')$ x Ft

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

$V_{20°C}$ should be known to $\pm$ 0.001 mL

Water mass at 20 °C:

$M_{20°C} = V_{20°C}$ x 0.998203, in g

0.998203 = water density at 20 °C, in g/cm^3

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 (g) = 0.0012 (P_1 - P)

Volume at 20 °C in mL:

$$V_{20°C}(mL) = [P1 - (P - m)] \times F_t$$

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

$V_{20°C}$ should be known to $\pm$ 0.001 mL.

Water mass at 20 °C:

$$M_{20°C} = V_{20}°C \times 0.998203$$

0.998203 = water density at 20 °C, in g/cm^3

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 °C,

taking into account that the liquid mass contained in the pycnometer = $p + m - p''$,

the apparent density at t °C, in g/cm^3, is given by the following equation

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

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

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

Calculate $dT = T_1 - T_o$

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 g/cm^3, is as follows:

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

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 kg/m^3 and not g/cm^3.

The relationship is as follows: 1 g/cm^3 = 1000 kg/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 □$_t$. Use the tabular difference just below this density to calculate the density □ at this temperature, T.

On the line of the temperature, T, find the density □' immediately above □ and calculate the difference between the densities □ and □'. Divide this difference by the tabular difference just to the right of the density □'. 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 □' 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* °C + *p*”	*t* °C = 18.90 °C *corrected t* °C = 18.70 °C *p*” = 2.8074 g
p + *m* – *p*”= mass of the distillate at *t* °C Apparent density at *t* °C: $\rho_t = \frac{\mathrm{p + m - p''}}{\text{volume of the pycnometer at 20 °C}}$	105.0698 – 2.8074 = 102.2624 g
2. Calculation of the alcoholic strength: Consult the table of apparent densities of hydro-alcoholic mixtures at different temperatures, as indicated above.	$\rho_{18.7\,°C} = \frac{102.2624}{104.0299} = 0.983076$ 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 x 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.

<u>Numerical example</u>

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
	= + 0.0018
Mass of the distillate at 20.5 °C	: Lt = 167.8438 – (67.6695 + 0.0018)
	= 100.1725 g

Apparent density of the distillate : $□_{20.5\ °C}$ = 100.1725/101.8194 =

0.983825 g/cm^3

Calculation of alcoholic strength:

Refer to the table of apparent densities of hydro-alcoholic mixtures at different temperatures, as indicated above.	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. The density at 20 °C is: (98382.5 + 0.5 x 24) x 10^{-5} = 0.983945 0.98471 – 0.983945 = 0.000765 The decimal portion of the alcoholic strength is: 76.5 / 119 = 0.64 The alcoholic strength is: 10.64% vol.

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:

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

ρ = 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 ρ = 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^3 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^3 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^2/s, for which the uncertainty does not exceed 0.00005 g/cm^3 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 ± 0.02°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 g/cm^3 at 20 °C and 0.98447 g/cm^3 at 21 °C, equating to a spread of 0.00024 g/cm^3.

The test temperature is set at 20 °C. The temperature is taken at the cell level, and done with a thermometer that has a resolution accurate to 0.01 °C and is calibrated to national standards. This should enable a temperature measurement with an uncertainty of better than ± 0.07°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 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 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 g/cm^3) and the measured density is above 0.00008 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 °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.

epeatability (r) = 0.067 (% vol.)

Reproducibility (R) = 0.0454 + 0.0105 x 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 10th-of-a-degree graduations, from 10 °C to 40 °C, calibrated to ± 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 ($\square_t$).

Correct $\square_t$ using a $\square_t$ 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 $\square_{20}$, 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^{th}-of-a-degree graduations, from 0 °C to 40 °C, calibrated to ± 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, , □ expressed in kilograms per cubic metre (kg/m³) 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 □, 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 °C and +40 °C.

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

$$n = 5$$

$$m_1 = 11$$

$$m_2 = 10$$

$$m_3 = 9$$

$$m_4 = 4$$

$$m_5 = 2$$

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

Numeric coefficients for the formula

k	A_k kg/m³	B_k
1	$9{,}982\ 012\ 300 \cdot 10^{2}$	$-2{,}061\ 851\ 3 \cdot 10^{-1}$ kg/(m³ · °C)
2	$-1{,}929\ 769\ 495 \cdot 10^{2}$	$-5{,}268\ 254\ 2 \cdot 10^{-3}$ kg/(m³ · °C²)
3	$3{,}891\ 238\ 958 \cdot 10^{2}$	$3{,}613\ 001\ 3 \cdot 10^{-5}$ kg/(m³ · °C³)
4	$-1{,}668\ 103\ 923 \cdot 10^{3}$	$-3{,}895\ 770\ 2 \cdot 10^{-7}$ kg/(m³ · °C⁴)
5	$1{,}352\ 215\ 441 \cdot 10^{4}$	$7{,}169\ 354\ 0 \cdot 10^{-9}$ kg/(m³ · °C⁵)
6	$-8{,}829\ 278\ 388 \cdot 10^{4}$	$-9{,}973\ 923\ 1 \cdot 10^{-11}$ kg/(m³ · °C⁶)
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	$C_{1,k}$ kg/(m³· °C)	$C_{2,k}$ k g/(m³· °C2)
1	$1{,}693\ 443\ 461530\ 087 \cdot 10^{-1}$	$-1{,}\ 193\ 013\ 005\ 057\ 010 \cdot 10$
2	$-1{,}046\ 914\ 743\ 455\ 169 \cdot 10^{1}$	$2{,}517\ 399\ 633\ 803\ 46\ 1 \cdot 10^{-1}$
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	$3{,}924\ 090\ 430\ 035\ 045 \cdot 10^{3}$	$-5{,}029\ 988\ 758\ 547\ 014 \cdot$
6	$-1{,}210\ 164\ 659\ 068\ 747 \cdot 10^{4}$	$1{,}096\ 355\ 666\ 577\ 570 \cdot 10^{2}$
7	$2{,}248\ 646\ 550\ 400\ 788 \cdot 10^{4}$	$-1{,}422\ 753\ 946\ 421\ 155 \cdot$
8	$-2{,}605\ 562\ 982\ 188\ 164 \cdot 10^{4}$	$1{,}080\ 435\ 942\ 856\ 230 \cdot 10^{2}$
9	$1{,}852\ 373\ 922\ 069\ 467 \cdot 10^{4}$	$-4{,}414\ 153\ 236\ 817\ 392 \cdot$
10	$-7{,}420\ 201433\ 430\ 137 \cdot 10^{3}$	$7{,}442\ 971\ 530\ 188\ 783$
11	$1{,}285\ 617\ 841\ 998\ 974 \cdot 10^{3}$	

k	$C_{3,k}$ kg/(m³· °C3)	$C_{4,k}$ kg/(m³ · °C4)	$C_{5,k}$ kg/(m³· °C5)
1	$-6{,}802\ 995\ 733\ 503\ 803 \cdot 10^{-4}$	$-4{,}075\ 376\ 675\ 622\ 027 \cdot 10$	$-2{,}788\ 074\ 354\ 782\ 409 \cdot 10^{-8}$
2	$-1{,}876\ 837\ 790\ 289\ 664 \cdot 10^{-2}$	$-8{,}763\ 058\ 573\ 471\ 110 \cdot 10$	$1{,}345\ 612\ 883493\ 354 \cdot 10$
3	$-2{,}002\ 561\ 813734\ 156 \cdot 10^{-1}$	$6{,}515\ 031\ 360\ 099\ 368 \cdot 10^{-8}$	
4	$-1{,}022\ 992\ 966\ 719\ 220$	$-1{,}515\ 784\ 836\ 987\ 210 \cdot 10$	
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 Montpelllier	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

LAB	POSITION :											
	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 RSDr	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 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 RSDr	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 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_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

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 d'Anjou

Courvoisier	16200	Jarnac
Hennessy	16100	Cognac
IDAC	44120	Vertou
Laboratoire Gendrot	33000	Bordeaux
Martell	16100	Cognac
Ricard	94320	Thiais
SOEC Martin 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
	6.020	9.500	10.390	11.290	12.100	17.080
1	5.970	9.470	10.380	11.260	12.150	17.080
		9.450	10.340	11.260	12.150	
	6.040	9.500	10.990	11.270	12.210	17.050
2	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	

	6.020	9.470	10.310	11.250	12.160	16.940
4	6.020	9.450	10.350	11.250	12.120	17.070
		9.450	10.330	11.210	12.130	
	5.950	9.350	10.250	11.300	12.050	17.000
5	5.950	9.430	10.250	11.300	12.050	17.000
		9.430	10.250	11.300	12.050	
	6.016	9.513	10.370	11.275	12.222	17.120
6	6.031	9.513	10.336	11.266	12.222	17.194
		9.505	10.386	11.275	12.220	
	5.730	9.350	10.230	11.440	12.080	17.010
7	5.730	9.430	10.220	11.090	12.030	16.920
		9.460	10.220	11.080	11.930	
	5.990	9.400	10.340	11.160	12.110	17.080
8	6.000	9.440	10.320	11.150	12.090	17.110
		9.440	10.360	11.210	12.090	
	6.031	9.508	10.428	11.289	12.180	17.089
9	6.019	9.478	10.406	11.293	12.215	17.084
		9.509	10.411	11.297	12.215	
	6.030	9.500	10.380	11.250	12.150	17.130
10	6.020	9.510	10.380	11.250	12.150	17.100
		9.510	10.380	11.250	12.160	
	6.020	9.480	10.400	11.260	12.150	17.040
11	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^2r	S^2L	r	R
[1]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^2r*:* repeatability variance (% vol.)^2

S^2L*:* interlaboratory variance (% vol.)^2

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.

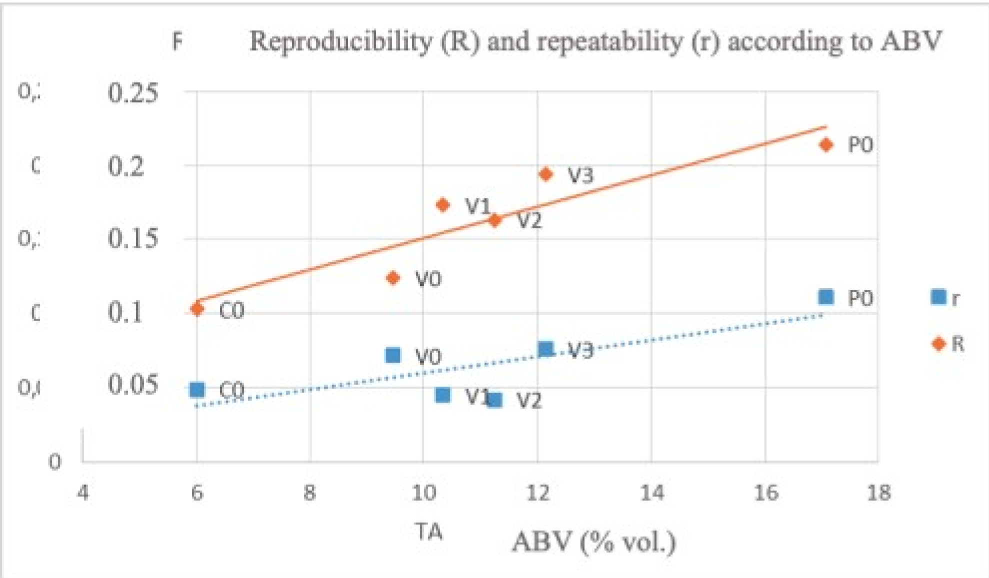

Figure 2: Repeatability and reproducibility according to ABV

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).

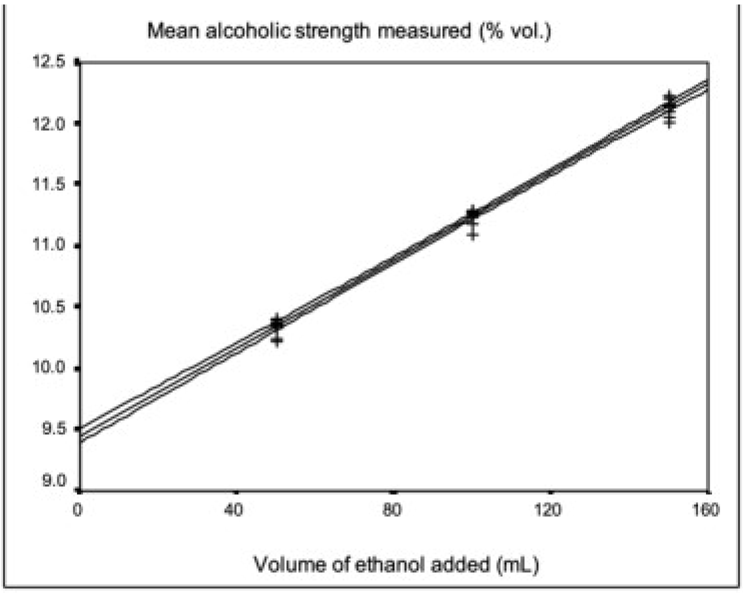

Figure 3: Regression of ABV measured by volume of ethanol added

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 x 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 x 100 / ABV) (%)

RSDrH: *Horwitz repeatability coefficient of variation (0.66 x RSDRH) (%)*

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

R: *reproducibility (% vol.)*

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

RSDR: *reproducibility coefficient of variation (sR x 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 (Horwitz) = 0.66 RSDR (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	0.0584	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	0.278	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	0.2957	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	0.1206	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 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	7.701	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
					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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