OIV-MA-BS-03 Reference method for the determination of real alcoholic strength by volume of spirit drinks of viti-vinicultural origin: measurement by pycnometry

Type II method

1. Principle

The alcoholic strength by volume is obtained from the density of the distillate measured by pycnometry.

2. Reagents and Materials

During the analysis, unless otherwise is stated, use only reagents of recognised analytical grade and water of at least grade 3 as defined in ISO 3696:1987.

2.1. Sodium chloride solution (2 % w/v)

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

3. Apparatus and Equipment

Usual laboratory apparatus and in particular the following.

3.1. Analytical balance capable of reading 0.1 mg.

3.2. Thermometer, with ground glass joint, calibrated in tenths of a degree from 10 to 30 °C. This thermometer must be certified or checked against a certified thermometer.

3.3. Pyrex glass pycnometer of approximately 100 ml capacity fitted with a removable ground-glass thermometer (A.3.2). The pycnometer has a side tube 25 mm in length and 1 mm (maximum) in internal diameter ending in a conical ground joint. Other pycnometers as described in ISO 3507 e.g. 50 ml may be used if appropriate.

3.4. A 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 density 1.01 (sodium chloride solution A.2.1).

3.5. Thermally insulated jacket that fits the body of the pycnometer exactly.

Note 1: The method for determining the densities in vacuo of spirits calls for the use of a twin-pan balance, a pycnometer and a tare bottle of the same outside external volume to cancel out the effect of air buoyancy at any given moment. This simple technique may be applied using a single-pan balance provided that the tare bottle is weighed again to monitor changes in air buoyancy over time.

4. Procedure

Preliminary remarks:

- The following procedure is described for the use of 100-ml pycnometer for determination of the alcoholic strength; this gives the best accuracy. However, it is also possible to use a smaller pycnometer, for example 50 ml.

4.1. Calibration of pycnometer

The pycnometer is calibrated by determining the following parameters:

- tare of the empty pycnometer,
- volume of the pycnometer at 20 °C,
- mass of the water-filled pycnometer at 20 °C.

1. Calibration using a single-pan balance

Determine:

- the mass of the clean, dry pycnometer (P),
- the mass of the water-filled pycnometer at t °C (P1)
- the mass of the tare bottle (T0).

1. Weigh the clean, dry pycnometer (P).
2. Fill the pycnometer carefully with distilled water at ambient temperature and fit the thermometer.

Carefully wipe the pycnometer dry and place it in the thermally-insulated jacket. Agitate by inverting the container until the thermometer's temperature reading is constant

Set the pycnometer flush with the upper rim of the side tube. Read the temperature t °C carefully and if necessary correct for any inaccuracies in the temperature scale.

Weigh the water-filled pycnometer (P1).

4.1.1.3. Weigh the tare bottle (T0).

4.1.1.4. Calculation

- Tare of the empty pycnometer = P - m
- where m is the mass of air in the pycnometer.
- m = 0.0012 x (P1 - P)

Note 2: 0.0012 is the density of dry air at 20 °C at a pressure of 760 mm Hg

- Volume of the pycnometer at 20 °C:

$V_{20°C}$ = [P1 - (P - m)] x F_t

where F_t is the factor for temperature t °C taken from Table I below.

$V_{20°C}$ must be known to the nearest 0.001 ml.

- Mass of water in the pycnometer at 20 °C :

$M_{20°C}$ = $V_{20°C}$ x 0.998203

where 0.998203 is the density of water at 20 °C.

Note 3: If necessary, the value 0.99715 of the density in air can be used and the alcoholic strength calculated with reference to the corresponding density in HM Customs and Excise tables in air.

4.1.2. Calibration method using a twin-pan balance:

4.1.2.1. Place the tare bottle on the left-hand pan and the clean, dry pycnometer with its collecting stopper on the right-hand pan. Balance them by placing weights on the pycnometer side: p grams. (p)

4.1.2.2. Fill the pycnometer carefully with distilled water at ambient temperature and fit the thermometer; carefully wipe the pycnometer dry and place it in the thermally insulated jacket; agitate by inverting the container until the thermometer's temperature reading is constant.

Accurately adjust the level to the upper rim of the side tube. Clean the side tube, fit the collecting stopper; read the temperature t °C carefully and if necessary correct for any inaccuracies in the temperature scale.

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

4.1.2.3. Calculation

- Tare of the empty pycnometer = p + m

where m is the mass of air in the pycnometer.

m = 0.0012 x (p - p')

- Volume of the pycnometer at 20 °C:

$V_{20°C}$ = (p + m - p') x F_t

where F_t is the factor for temperature t °C taken from Table I below.

$V_{20 °C}$ must be known to the nearest 0.001 ml.

- Mass of water in the pycnometer at 20 °C:

$M_{20°C} = V_{20°C}$ x 0.998203

where 0.998203 is the density of water at 20 °C.

4.2. Determination of alcoholic strength of test sample

4.2.1. Using a single-pan balance.

4.2.1.1. Weigh the tare bottle, weight T1

4.2.1.2. Weigh the pycnometer with the prepared distillate (see Annex I), P2 is its weight at t °C.

4.2.1.3. Calculation

- dT = T1 - T0
- Mass of empty pycnometer at moment of measuring

= P – m + dT

- Mass of the liquid in the pycnometer at t °C

= P2 – (P – m + dT)

- Density at t °C in g/ml
- $\rho_{t\,°C} = [P_2 - (P - m + dT)]/V_{20\,°C}$

Express the density at t °C in kilograms per m^3 by multiplying $\rho_{t\,°C}$ by 1000, the value being known as ρ_t.

- Correct ρ_t to 20 using the table of densities ρT for water-alcohol mixtures in the Manual of Analysis Methods for Wines of the OIV.

In the table find the horizontal line corresponding to temperature T in whole degrees immediately below t °C, the smallest density above ρ_t. Use the table difference found below that density to calculate the density ρ_t of the spirit at that temperature T in whole degrees.

- Using the whole temperature line, calculate the difference between density ρ' in the table immediately above ρ_t and the calculated density ρ_t. Divide that difference by the table difference found to the right of density ρ'. The quotient provides the decimal portion of the alcoholic strength while the integer of the alcoholic strength is found at the top of the column in which density ρ' is found (Dt, the alcoholic strength).

Note 4: Alternatively keep the pycnometer in a water bath maintained at 20 °C (± 0.2 °C) when making up to the mark.

4.2.1.4. Result

Using the density ρ_{20} calculate the real alcoholic strength using the alcoholic strength tables identified below:

The table giving the value of the alcoholic strength by volume (% vol.) at 20 °C as a function of the density at 20 °C of water-alcohol mixtures is the international table adopted by the International Legal Metrology Organisation in its Recommendation no. 22.

4.2.2. Method using a single-pan balance

4.2.2.1. Weigh the pycnometer with the distillate prepared (see part I), p" is mass at t °C.

4.2.2.2. Calculation

- Mass of the liquid in the pycnometer at t °C

$= p + m - p''$

- Density at t °C in g/ml

$\rho_{t\,°C} = (p + m - p'')/V_{20\,°C}$

- Express the density at t °C in kilograms per m^3 and carry out the temperature correction in order to calculate the alcoholic strength at 20 °C, as indicated above for use of the single-pan balance.

5. Method performance characteristics (Precision)

5.1. Statistical results of the interlaboratory test

The following data were obtained from an international method performance study carried out on a variety of spirit drinks to internationally agreed procedures.

Year of interlaboratory test	1997
Number of laboratories	20
Number of samples	6

Samples	A	B	C

Number of laboratories retained after eliminating outliers	19	20	17
Number of outliers (Laboratories)	1	-	2
Number of accepted results	38	40	34
Mean value ($\bar{X}$) % vol.	23.77	40.04	40.29
	26.51*		
Repeatability standard deviation (s_r) % vol.	0.106	0.176	0.072
Repeatability relative standard deviation (RSD_r) (%)	0.42	0.44	0.18
Repeatability limit (r) % vol.	0.30	0.49	0.20
Reproducibility standard deviation (s_R) % vol.	0.131	0.236	0.154
Reproducibility relative standard deviation (RSD_R) (%)	0.52	0.59	0.38
Reproducibility limit (R) % vol.	0.37	0.66	0.43

Sample types

A Fruit liqueur; split level*

B Brandy; blind duplicates

C Whisky; blind duplicates

Samples	D	E	F
Number of laboratories retained after eliminating outliers	19	19	17
Number of outliers (Laboratories)	1	1	3
Number of accepted results	38	38	34
Mean value ($\bar{X}$) % vol.	39.20	42.24	57.03
	42.93*	45.73*	63.03*

Repeatability standard deviation (s_r) % vol.	0.103	0.171	0.190
Repeatability relative standard deviation (RSD_r) (%)	0.25	0.39	0.32
Repeatability limit (r) % vol.	0.29	0.48	0.53
Reproducibility standard deviation (s_R) % vol.	0.233	0.238	0.322
Reproducibility relative standard deviation (RSD_R) (%)	0.57	0.54	0.53
Reproducibility limit (R) % vol.	0.65	0.67	0.90

Sample types

D grappa; split level*

E aquavit; split level*

F rum; split level*

TABLE I

F factors by which the mass of water contained in the Pyrex pycnometer at t °C has to be multiplied in order to calculate the pycnometer volume at 20 °C

t °C	F	t °C	F	t °C	F	t °C	F	t °C	F	t °C	F	t °C	F
10,0	1,000398	13,0	1,000691	16,0	1,001097	19,0	1,001608	22,0	1,002215	25,0	1,002916	28,0	1,003704
,1	1,000406	,1	1,000703	,1	1,001113	,1	1,001627	,1	1,002238	,1	1,002941	,1	1,003731
,2	1,000414	,2	1,000714	,2	1,001128	,2	1,001646	,2	1,002260	,2	1,002966	,2	1,003759
,3	1,000422	,3	1,000726	,3	1,001144	,3	1,001665	,3	1,002282	,3	1,002990	,3	1,003787
,4	1,000430	,4	1,000738	,4	1,001159	,4	1,001684	,4	1,002304	,4	1,003015	,4	1,003815
10,5	1,000439	13,5	1,000752	16,5	1,001175	19,5	1,001703	22,5	1,002326	25,5	1,003041	28,5	1,003843
,6	1,000447	,6	1,000764	,6	1,001191	,6	1,001722	,6	1,002349	,6	1,003066	,6	1,003871
,7	1,000456	,7	1,000777	,7	1,001207	,7	1,001741	,7	1,002372	,7	1,003092	,7	1,003899
,8	1,000465	,8	1,000789	,8	1,001223	,8	1,001761	,8	1,002394	,8	1,003117	,8	1,003928
,9	1,000474	,9	1,000803	,9	1,001239	,9	1,001780	,9	1,002417	,9	1,003143	,9	1,003956
11,0	1,000483	14,0	1,000816	17,0	1,001257	20,0	1,001800	23,0	1,002439	26,0	1,003168	29,0	1,003984
,1	1,000492	,1	1,000829	,1	1,001273	,1	1,001819	,1	1,002462	,1	1,003194	,1	1,004013
,2	1,000501	,2	1,000842	,2	1,001290	,2	1,001839	,2	1,002485	,2	1,003222	,2	1,004042
,3	1,000511	,3	1,000855	,3	1,001306	,3	1,001859	,3	1,002508	,3	1,003247	,3	1,004071
,4	1,000520	,4	1,000868	,4	1,001323	,4	1,001880	,4	1,002531	,4	1,003273	,4	1,004099
11,5	1,000530	14,5	1,000882	17,5	1,001340	20,5	1,001900	23,5	1,002555	26,5	1,003299	29,5	1,004128
,6	1,000540	,6	1,000895	,6	1,001357	,6	1,001920	,6	1,002578	,6	1,003326	,6	1,004158
,7	1,000550	,7	1,000909	,7	1,001374	,7	1,001941	,7	1,002602	,7	1,003352	,7	1,004187
,8	1,000560	,8	1,000923	,8	1,001391	,8	1,001961	,8	1,002625	,8	1,003379	,8	1,004216
,9	1,000570	,9	1,000937	,9	1,001409	,9	1,001982	,9	1,002649	,9	1,003405	,9	1,004245
12,0	1,000580	15,0	1,000951	18,0	1,001427	21,0	1,002002	24,0	1,002672	27,0	1,003432	30,0	1,004275
,1	1,000591	,1	1,000965	,1	1,001445	,1	1,002023	,1	1,002696	,1	1,003458		
,2	1,000601	,2	1,000979	,2	1,001462	,2	1,002044	,2	1,002720	,2	1,003485		
,3	1,000612	,3	1,000993	,3	1,001480	,3	1,002065	,3	1,002745	,3	1,003513		
,4	1,000623	,4	1,001008	,4	1,001498	,4	1,002086	,4	1,002769	,4	1,003540		
12,5	1,000634	15,5	1,001022	18,5	1,001516	21,5	1,002107	24,5	1,002793	27,5	1,003567		
,6	1,000645	,6	1,001037	,6	1,001534	,6	1,002129	,6	1,002817	,6	1,003594		
,7	1,000656	,7	1,001052	,7	1,001552	,7	1,002151	,7	1,002842	,7	1,003621		
,8	1,000668	,8	1,001067	,8	1,001570	,8	1,002172	,8	1,002866	,8	1,003649		
,9	1,000679	,9	1,001082	,9	1,001589	,9	1,002194	,9	1,002891	,9	1,003676		