Method OIV-MA-BS-12 : R2009

Type II method

Determination of the acidities of spirit drinks of viti-vinicultural origin

(OIV/OENO 380/2009)

1. Scope

This method is suitable for the determination of the volatile, total, and fixed acidities of spirit drinks of viti-vinicultural origin.

2. Normative References

ISO 3696: 1987: Water for analytical use - Specifications and test methods

3. Definitions

3.1. Volatile acidity is made up of acetic and higher volatile aliphatic acids that are present in spirit drinks.

3.2. Total acidity is the sum of titratable acidities.

3.3. Fixed acidity is the acidity of the residue left after evaporating the spirit drink to dryness.

4. Principle

The total acidity is determined by direct titration of the sprit drink. The fixed acidity is determined by titration of the aqueous solution obtained after dissolving the residue from evaporation of the spirit drink. The volatile acidity is calculated by

deducting the fixed acidity from the total acidity.

5. Reagents and Materials

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

5.1. 0.05 M sodium hydroxide solution

5.2. Mixed indicator solution:

Weigh 0.1 g of indigo carmine and 0.1 g of phenol red.
Dissolve in 40 mL water and make up to 100 mL with ethanol.

6. Apparatus and Equipment

Standard laboratory apparatus, “A” grade volumetric glassware and, in particular, the following:

6.1. Equipment for applying vacuum (water pump, vacuum flask, etc.), or other system for eliminating carbon dioxide (bubbling or other).

6.2. Flat-bottomed stainless-steel cylindric capsule, of sufficient dimensions to avoid loss of liquid when evaporating.

6.3. Equipment for potentiometric titration (optional).

7. Sampling and samples

Samples are stored at room temperature prior to analysis.

8. Procedure

8.1. Total acidity

8.1.1. Preparation of sample

If necessary, the spirit is stirred for at least two minutes under vacuum to remove carbon dioxide, or the latter is eliminated by any other convenient method.

8.1.2. Titration

Pipette 25 mL of the spirit into a 500 mL conical flask.

Add about 200 mL of cooled boiled distilled water (freshly prepared) and 2-6 drops of the mixed indicator solution (5.2).

Titrate with the 0.05 M sodium hydroxide solution (5.1) until the yellow-green colour changes to violet in the case of colourless spirit drinks, or the yellow-brown colour to red-brown in the case of brown-coloured spirit drinks.

The titration may also be carried out by potentiometry, to pH 7.5.

Let n_1 mL be the volume of the 0.05 M sodium hydroxide solution added.

8.1.3. Calculation

- The total acidity (TA) expressed in milliequivalents per L of spirit drink is equal to $2 \times n_1$.
- The total acidity (TA') expressed in mg of acetic acid per L of spirit drink is equal to $120 \times n_1$.
- The total acidity (TA') expressed in g of acetic acid per hL of pure 100 % vol alcohol is equal to $120 \times n_1 \times 10/A$, where A is the alcoholic strength by volume of the spirit drink.

8.2. Fixed acidity

8.2.1. Preparation of sample

Pipette 25 mL (or a larger volume if the fixed acidity is very low) of the spirit drink into

a flat-bottomed cylindrical evaporating dish (6.2). During the first hour of evaporation the evaporating dish is placed on the lid of a boiling water bath so that the liquid will not boil, as this could lead to losses through splattering.

If necessary, complete the drying by placing the evaporating dish in a drying oven at 105 °C for two hours. Allow the evaporating dish to cool in a desiccator.

8.2.2. Titration

Take up the residue left after evaporating with cooled boiled distilled water (freshly prepared), make up to a volume of about 100 mL and add 2-6 drops of the mixed indicator solution (5.2).

Titrate with the 0.05 M sodium hydroxide solution (5.1) until the yellow-green colour changes to violet if the solution is colourless, or the yellow-brown colour to red-brown if the solution is brown-coloured.

The titration may also be carried out by potentiometry, to pH 7.5.

Let n_2 mL be the volume of the 0.05 M sodium hydroxide solution added, and V mL the volume of sample evaporated.

8.2.3. Calculation

- The fixed acidity (FA) expressed in milliequivalents per L of spirit drink is equal to 2 x n_2 x 25/V.
- The fixed acidity (FA') expressed in mg of acetic acid per L of spirit drink is equal to 120 x n_2 x 25/V.
- The fixed acidity (FA') expressed in g of acetic acid per hL of pure 100% vol alcohol is equal to 120 x n_2 x 25/V x 10/A, where A is the alcoholic strength by volume of the spirit drink.

8.3. Calculation of volatile acidity

8.3.1. Expression in milliequivalents per L :

Let:

- TA = total acidity in milliequivalents per L
- FA = fixed acidity in milliequivalents per L

- Volatile acidity,VA, in milliequivalents per L is equal to :
- TA - FA

8.3.2. Expression in mg of acetic acid per L:

Let:

- TA′ = total acidity in mg of acetic acid per L
- FA′ = fixed acidity in mg of acetic acid per L
- Volatile acidity,VA, in mg of acetic acid per L is equal to :
- TA‘ - FA’

8.3.3. Expression in g of acetic acid per hL of pure 100 % vol alcohol is equal to :

$$\frac{TA, - FA'}{A} \times 10$$

- where A is the alcoholic strength by volume of the spirit drink.

9. Method performance characteristics (Precision)

The following data were obtained in 2000 from an international method-performance study on a variety of spirit drinks, carried out following internationally-agreed procedures.
Key to the tables below:

nLT	Number of laboratories (2 results per laboratory)
nL	Number of laboratories to calculate precision values
r	repeatability limit

Sr	repeatability standard deviation
RSDr	repeatability standard deviation expressed in % of the level
R	reproducibility limit
SR	reproducibility standard deviation
RSDR	reproducibility standard deviation expressed in % of the level
PRSDR	RSDR predicted with the Horwitz formula (%)
HoR	HorRat value = RSDR / PRSDR
SH240	Aqueous-alcoholic solution: acetic acid (240 mg/L), tartaric acid (200 mg/L), sucrose (10 g/L)

All the acidities are expressed as mg of acetic acid per L of spirit drink.

9.1. Total acidity

	nLT	nL	Mean (mg/L)	r (mg/L)	Sr (mg/L)	RSDr (%)	R (mg/L)	SR (mg/L)	RSDR (%)	PRSDR (%)	HoR
Rum 1	18	18	53	8	2,7	5,1	34	12	23	8,8	2,6
Slibowitz	18	17	55	10	3,7	6,7	19	6,6	12	8,8	1,4
Brandy	20	18	193	16	5,7	2,9	43	15	7,9	7,2	1,1
Brandy	18	18	194	16	5,8	3,0	38	13	6,9	7,2	1,0
Calvados	18	17	282	21	7,5	2,7	34	12	4,3	6,8	0,6
SH240	20	17	400	14	4,9	1,2	18	6,2	1,6	6,5	0,2
Marc	18	18	547	16	5,8	1,1	42	15	2,7	6,2	0,4
Armagnac	20	19	580	27	9,4	1,6	53	19	3,2	6,1	0,5
Rum 2	18	18	641	41	14,3	2,2	66	23	3,7	6,0	0,6

9.2. Fixed acidity

	nLT	nL	Mean (mg/L)	r (mg/L)	Sr (mg/L)	RSDr (%)	R (mg/L)	SR (mg/L)	RSDR (%)	PRSDR (%)	HoR
Slibowitz	18	16	9,5	5,1	1,8	19	14	4,9	52	11	4,6
Rum 1	18	18	22	6,1	2,2	9,7	28	10	45	10	4,5
Calvados	18	16	25	7,7	2,7	10,8	24	8,4	34	9,9	3,4
Rum 2	18	18	25	5,7	2,0	7,9	28	9,9	39	9,8	4,0
Marc	18	17	51	25	8,8	17	60	21	42	8,8	4,7
Brandy	18	18	87	17	6,0	6,9	47	17	19	8,2	2,3
Brandy	20	19	89	12	4,2	4,7	33	12	13	8,1	1,6
Armagnac	20	19	159	13	4,7	2,9	80	28	18	7,5	2,4
SH240	20	17	162	12	4,1	2,5	32	11	7,1	7,4	1,0

9.3. Volatile acidity

	nLT	nL	Mean (mg/L)	r (mg/L)	Sr (mg/L)	RSDr (%)	R (mg/L)	SR (mg/L)	RSDR (%)	PRSDR (%)	HoR
Rum 1	18	18	30	10	3,5	12	24	8,4	28	9,6	2,9
Slibowitz	18	14	46	10	3,7	8,1	13	4,6	10	9,0	1,1
Brandy	20	18	107	23	8,0	7,5	44	16	15	7,9	1,8
Brandy	18	18	107	19	6,6	6,2	38	13	13	7,9	1,6
SH240	20	17	242	21	7,2	3,0	48	17	6,9	7,0	1,0
Calvados	18	16	257	23	8,0	3,1	24	8,5	3,3	6,9	0,5
Armagnac	20	17	418	22	7,8	1,9	62	22	5,2	6,5	0,8

Marc	18	18	492	24	8,5	1,7	69	24	5,0	6,3	0,8
Rum 2	18	18	616	42	15	2,4	71	25	4,1	6,1	0,7

10. Bibliography

1. R. Wittkowski, A. Bertrand, P. Brereton, C. Guillou, 2000. PROJECT SMT4-CT96-2119, Validation of analytical methods of analysis for spirit drinks. REPORT NO. 02/08- WORKSTREAM 8
2. P. Brereton, S. Hasnip, A. Bertrand, R. Wittkowski, C. Guillou, Analytical methods for the determination of spirit drinks, Trends in Analytical Chemistry, Vol. 22, No. 1, 19-25, 2003
3. FV 1322 (2009), Measurement of acidities in spirits - estimation of precision