

COMPENDIUM OF INTERNATIONAL METHODS OF ANALYSIS FOR SPIRITUOUS BEVERAGES AND ALCOHOLS

DETERMINATION OF THE ACIDITIES OF SPIRIT DRINKS OF VITI-VINICULTURAL ORIGIN (Type

OIV-MA-BS-12 ^{II)} **Determination of the acidities of spirit drinks of viti-vinicultural origin**

Type II method

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 spirit 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:

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- 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 cylindrical 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

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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 $2 \times n_2 \times 25/V$.
- The fixed acidity (FA') expressed in mg of acetic acid per L of spirit drink is equal to $120 \times n_2 \times 25/V$.
- The fixed acidity (FA') expressed in g of acetic acid per hL of pure 100% vol alcohol is equal to $120 \times n_2 \times 25/V \times 10/A$, 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:

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- 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 |

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| | |
|-------|--|
| 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 |

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| | | | | | | | | | | | |
|----------|----|----|-----|----|-----|-----|----|----|-----|-----|-----|
| 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

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