RESOLUTION OIV/OENO 380/2009

UPDATE OF THE OIV COMPENDIUM OF METHODS OF ANALYSIS OF SPIRIT DRINKS OF VITIVINICULTURAL ORIGIN – PART 2

THE GENERAL ASSEMBLY

CONSIDERING article 2 paragraph 2 iv of the Agreement of 3 April 2001 establishing the International Organisation of Vine and Wine,

IN VIEW OF the actions of the 2009-2012 OIV Strategic plan, particularly those focused on reorganising publications related to the vitivinicultural methods of analysis

CONSIDERING the works of the Methods of Analysis sub-commission

IN VIEW OF the 1994 publication of the Compendium of International Methods of Analysis of spirituous beverages, alcohol and the aromatic fraction of beverages

DECIDES given the evolution of methods and availability of inter-laboratory validation parameters to retain the following methods as Type II methods of analysis;

DECIDES to introduce these methods into the new edition of the "Compendium of international methods of analysis of spirituous beverages of vitivinicultural origin"

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

Type II method

Year : 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. Definition

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

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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

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8.1.0. 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 x n_1.

The total acidity (TA') expressed in mg of acetic acid per L of spirit drink is equal to 120 x n_1.

The total acidity (TA') expressed in g of acetic acid per hL of pure 100 % vol alcohol is equal to 120 x n_1 x $10/A$, 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.

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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

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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

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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

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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

DETERMINATION OF SUGARS IN SPIRIT DRINKS OF VITI-VINICULTURAL ORIGIN

Type II method

Year : 2009

Introduction

Spirit drinks of viti-vinicultural origin may be sweetened by various compounds, and in certain legislations the concentrations of sweetener are subject to minimum or maximum levels.

1. Scope

This method is suitable for the determination of the glucose, fructose, and sucrose contents of spirit drinks of viti-vinicultural origin. It is not suitable for spirit drinks containing dairy products or eggs.

2. Normative References

ISO 3696:1897 Waters for analytical use - Specifications and test methods.

3. Principle

High performance liquid chromatography (HPLC) to determine the glucose, fructose, and sucrose concentrations.

This method is described as an example. It uses an alkylamine stationary phase and differential refractometry detection. Other columns/detectors may be used, for example anion exchange resins as the stationary phase.

4. Reagents and Materials

4.1. Glucose (CAS 50-99-7), at least 99 % pure.

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4.2. Fructose (CAS 57-48-7), at least 99 % pure.

4.3. Sucrose (CAS 57-50-1), at least 99 % pure.

4.4. Pure acetonitrile (CAS 75-05-8) for HPLC analysis.

Acetonitrile is a highly flammable liquid. It is toxic by inhalation, in contact with skin and if swallowed. It is irritating to eyes.

4.5. Distilled or demineralised water, preferably micro-filtered.

4.6. Solvents (example)

The elution solvent is prepared beforehand by mixing:

- 75 parts by volume of acetonitrile (4.4),
- 25 parts by volume of distilled or demineralised water (4.5).

Pass helium through at a slow rate for 5 - 10 minutes prior to use to degas.

If the water being used has not been micro-filtered, it is advisable to pass the solvent through a filter for organic solvents with a pore size less than or equal to 0.45 µm.

4.7. Ethanol, absolute (CAS 64-17-5).

4.8. Ethanol solution (5 %, v/v).

4.9. Preparation of stock standard solution (20 g/L)

Weigh 2 g each of the sugars to be analysed (4.1 to 4.3), transfer them without loss to a 100 mL volumetric flask. Adjust to 100 mL with a 5 % vol. alcohol solution (4.8), shake and store at around +4 °C. Prepare a new stock solution once a week if necessary.

4.10. Preparation of working standard solutions (2.5, 5.0, 7.5, 10.0 and 20.0 g/L)

Dilute the stock solution, 20 g/L, (4.9) appropriately with a 5% vol. alcohol solution (4.8) to give five working standards of 2.5, 5.0, 7.5, 10.0 and 20.0 g/L. Filter with a filter of a pore size less than or equal to 0.45 µm (5.3.).

5. Apparatus and Equipment (as an example - other systems that provide equivalent performance can be used)

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

5.1. HPLC system capable of achieving baseline resolution of all of the sugars.

5.1.1. High-performance liquid chromatograph with a six-way injection valve fitted with a 10 µL loop or any other device, whether automatic or manual, for the reliable injection of micro-volumes.

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5.1.2. Pumping system enabling one to achieve and maintain a constant or programmed rate of flow with great precision.

5.1.3. Differential refractometer.

5.1.4. Computational integrator or recorder, the performance of which is compatible with the rest of the set-up.

5.1.5. Pre-column:

It is recommended that a suitable pre-column is attached to the analytical column.

5.1.6. Column (example):

Material: stainless steel or glass

Internal diameter: 2-5 mm

Length: 100-250 mm (depending on the packing particle size), for example 250 mm if the particles are 5 µm in diameter

Stationary phase: cross-linked silica with radicals containing the alkylamine functional group, maximum particle size 5 µm.

5.1.7. Chromatography conditions (example):

Elution solvent (4.6), flow rate: 1 mL/minute

Detection: Differential refractometry

To make certain that the detector is perfectly stable, it may be advisable to switch it on a few hours before use. The reference cell must be filled with the elution solvent.

5.2. Analytical balance accurate to 0.1 mg.

5.3. Filtration equipment for small volumes using a 0.45 µm membrane.

6. Sample storage

On receipt, samples are to be stored at room temperature prior to analysis.

7. Procedure

7.1. PART A: Sample Preparation

7.1.1. Shake the sample.

7.1.2. Filter the sample through a filter with a pore size less than or equal to 0.45 µm (5.3).

7.2. PART B: HPLC

7.2.1. Determination

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Inject 10 µL of the standard solutions (4.10) and samples (7.1.2.). Perform the analysis under suitable chromatography conditions, for example those described above.

7.2.2. Should any peak of a sample have a greater area (or height) than the corresponding peak in the most concentrated standard, then the sample should be diluted with distilled or demineralised water and re-analysed.

8. Calculation

Compare the two chromatograms obtained for the standard solution and spirit. Identify the peaks by their retention times. Measure their areas (or heights) to calculate the concentrations by the external standard method. Take into account any dilutions made to the sample.

The final result by convention is the sum of sucrose, glucose, and fructose, in g/L.

9. Method performance characteristics (Precision)

The following data were obtained in 2000 from an international method-performance study carried out on a variety of spirit drinks, 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 (%)

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HoR	HorRat value = RSDR / PRSDR

9.1. Glucose

	nLT	nL	Mean (mg/L)	r (mg/L)	Sr (mg/L)	RSDr (%)	R (mg/L)	SR (mg/L)	RSDR (%)	HoR
Liqueur 1	26	24	92.4	5.4	1.9	2.1	13	4.8	5.2	1.8
Liqueur 2	24	23	93.2	9.7	3.5	3.7	28	10	11	3.8

9.2. Fructose

	nLT	nL	Mean (mg/L)	r (mg/L)	Sr (mg/L)	RSDr (%)	R (mg/L)	SR (mg/L)	RSDR (%)	HoR
Liqueur 1	26	22	87	3.2	1.2	1.3	8.5	3.0	3.5	1.2
Liqueur 2	24	21	93	6.6	2.3	2.5	22	7.7	8.3	2.9

9.3. Saccharose

	nLT	nL	Mean (mg/L)	r (mg/L)	Sr (mg/L)	RSDr (%)	R (mg/L)	SR (mg/L)	RSDR (%)	HoR
Liqueur 1	26	24	174	12	4.2	2.4	24	8.7	5.0	1.9
Liqueur 2	24	18	320	12	4.3	1.3	45	16	5.0	2.1

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Liqueur 3	24	18	349	22	8.0	2.3	30	11	3.1	1.3
Pastis	24	19	11	0.2	0.1	0.8	2.2	0.8	7.3	1.9
Ouzo	24	19	24	2.1	0.8	3.1	2.6	0.9	3.8	1.1
Kirsch	24	20	103	6.1	2.2	2.1	12	4.2	4.0	1.4

9.4. Sucres totaux

	nLT	nL	Mean (mg/L)	r (mg/L)	Sr (mg/L)	RSDr (%)	R (mg/L)	SR (mg/L)	RSDR (%)	HoR
Liqueur 1	26	21	353	8.7	3.1	0.9	41	15	4.2	1.8
Liqueur 2	24	18	510	16	5.6	1.1			2.9	1.3
Liqueur 3	24	18	349	22	8.0	2.3	30	11	3.1	1.3
Pastis	24	20	11	0.4	0.1	1.2	2.2	0.8	7.3	1.8
Ouzo	24	19	24	2.1	0.8	3.1	2.6	0.9	3.8	1.1
Kirsch	24	20	103	6.1	2.2	2.1	12	4.2	4.0	1.4

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. 02/09 - WORKSTREAM 10.
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,

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