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## Fragrance/Flavor substances - Determination of carbonyl value and carbonyl compounds content

香料 羰值和羰基化合物含量的测定

(ISO 1271:1983, Essential oils - Determination of carbonyl value - Free hydroxylamine method; ISO 1279:1996, Essential oils - Determination of carbonyl value - Potentiometric methods using hydroxylammonium chloride, MOD)

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# Fragrance/Flavor substances - Determination of carbonyl value and carbonyl compounds content

## 1 Scope

Method I of this Part of GB/T 14454 specifies the method for determination of the carbonyl value of essential oils and the carbonyl compounds content in isolated and synthetic fragrance/flavor substances using hydroxylammonium chloride.

A cold oximation reaction with hydroxylammonium chloride of this method applies to fragrance/flavor substances whose main constituents are easily oximable aldehydes and ketones, with the exception of citronellal which needs a low temperature to avoid cyclization phenomena and acetalization. A hot oximation reaction with hydroxylammonium chloride applies to fragrance/flavor substances whose main constituents are ketones which are in general oximable only with difficulty.

Note 1: For the determination of essential oil containing citronellal, use free hydroxylamine method. See Method II.

Note 2: Examples of essential oils concerned containing oximable aldehydes or ketones are lemongrass, hesperydus and rue oils.

Note 3: Examples of essential oils concerned are vetiver, Dalmation sage and white artemisia oils which contain methylketones oximable only with difficulty.

Method II of this Part of GB/T 14454 specifies the method for determination of the carbonyl value of essential oils and the carbonyl compounds content in isolated and synthetic fragrance/flavor substances using free hydroxylamine method.

This method applies to fragrance/flavor substances which contain carbonyl compounds (especially ketones, excluding methylketones) which are difficult to convert to oximes by the method specified in Method I. The method is not applicable to fragrance/flavor substances which contain substantial amounts of esters or other alkali-sensitive constituents.

Method III of this Part of GB/T 14454 specifies the method for determination of the carbonyl compounds content in fragrance/flavor substances using the neutral sodium sulfite method. It is applicable to the determination of the content of carbonyl compounds in aldehyde and certain ketone fragrance/flavor

Conversion of the carbonyl compounds to oximes by reaction with hydroxylammonium chloride.

USE sodium hydroxide standard solution to titrate the hydrochloric acid released by this reaction. [Translator note: “potassium hydroxide standard solution”?]

**4.2 Reagents**

The reagents used are all analytically pure reagents. The water is distilled water or water of equivalent purity. Unless otherwise specified, the preparation method shall be carried out in accordance with GB/T 14454.14.

**4.2.1** Sodium hydroxide standard solution, c(KOH)=0.5 mol/L.

**4.2.2** Bromophenol blue indicator solution.

**4.2.3** Hydroxylammonium chloride solution.

**4.3 Apparatus**

Usual laboratory equipment and, in particular, the following.

**4.3.1** Beaker, of capacity 100 mL, tall form.

**4.3.2** Conical flask, of capacity 250 mL.

**4.3.3** pH meter.

**4.3.4** Glass electrode.

**4.3.5** Burette, with a capacity of 50 mL and a scale of 0.1 mL.

**4.4 Operating procedure**

**4.4.1 Preparation of test sample**

According to the requirements of GB/T 14454.1.

**4.4.2 Test portion**

WEIGH 1 g~1.5 g of fragrance/flavor substance in a tall-form beaker (4.3.1) or conical flask (4.3.2), accurate to 0.0002 g.

Note: If the test sample should be larger, this will be stated in the appropriate product standard for the fragrance/flavor substance concerned.

**4.4.3 Determination**

The meanings of V, c, and m are the same as formula (1).

The tolerance of the parallel test results:

1.0 for the carbonyl value; 0.5% for the carbonyl compounds content.

# 5 Method of hot oximation with hydroxylammonium chloride

### 5.1 Principle

Conversion of the carbonyl compounds to oximes by reaction with hydroxylammonium chloride.

USE sodium hydroxide solution to titrate the hydrochloric acid released by this reaction. [Translator note: “potassium hydroxide standard solution”?]

### 5.2 Reagents

Same as 4.2.

### 5.3 Apparatus

Usual laboratory equipment and, in particular, the following.

**5.3.1** Burette, with a capacity of 50 mL and a scale of 0.1 mL.

**5.3.2** Beaker, of capacity 100 mL, tall form.

**5.3.3** Saponification bottle, made of alkali-resistant glass, with frosted bottle mouth. The capacity is 100 mL~250 mL. It is fitted with a frosted-mouth glass air condenser with a length of at least 1 m and an inner diameter of 1 cm~1.5 cm.

**5.3.4** pH meter.

**5.3.5** Glass electrode.

**5.3.6** Heater with magnetic stirrer.

### 5.4 Operating procedure

#### 5.4.1 Preparation of test sample

According to the requirements of GB/T 14454.1.

### 5.4.2 Test portion

WEIGH 2 g~2.5 g of fragrance/flavor substance into the saponification bottle (5.3.3), accurate to 0.0002 g. See the note to 4.4.2.

### 5.4.3 Determination

ADD 50 mL of hydroxylammonium chloride solution (4.2.3) to the test portion (5.4.2). ADD 3 drops of bromophenol blue indicator solution (4.2.2) and mix thoroughly. USE sodium hydroxide standard solution (4.2.1) to titrate to the same yellow-green color as hydroxylammonium chloride solution (4.2.3). Connect the saponification bottle to the reflux tube. PUT the saponification bottle on the heater (5.3.6) and heat with stirring, to make the temperature appropriate enough to maintain a constant reflux. After 10 min, cool, add 3 drops of bromophenol blue indicator solution (4.2.2); USE sodium hydroxide standard solution (4.2.1) to titrate slowly to the same yellow-green color as hydroxylammonium chloride solution (4.2.3). PUT the saponification bottle on the heater. REPEAT this operation every 10 min, until the sodium hydroxide standard solution added can ensure that the end of the titration has been reached.

Note 1: When the color of the sample is dark, or its own color may interfere with the judgment of the end point, the potentiometric titration method shall be used. ADD 50 mL of hydroxylammonium chloride solution (4.2.3) to the test portion (5.4.2) and mix thoroughly. INSERT a glass electrode (5.3.5) into the solution. USE sodium hydroxide standard solution (4.2.1) to titrate, until the pH value of the solution is less than 4.20. Connect the saponification bottle to the reflux tube. PUT the saponification bottle on the heater (5.3.6) and heat with stirring, to make the temperature appropriate enough to maintain a constant reflux. After 10 min, cool, add 3 drops of bromophenol blue indicator solution (4.2.2); USE sodium hydroxide standard solution (4.2.1) to titrate slowly, until the pH value of the solution is less than 4.20. During the determination, make sure that the pH value does not exceed 4.20. When the color of the solution starts to change, stop the titration. PUT the saponification bottle on the heater. REPEAT this operation every 10 min, until the sodium hydroxide standard solution added can ensure that the end of the titration has been reached.

Note 2: The determination time is usually 2 h. But for some fragrance/flavor substances, this time is not enough. In this case, continue to determine, until the equivalence point appears. USE the volume of the potassium hydroxide standard solution (4.2.1) used in the titration process as a function; DRAW a pH graph: pH=f(V). RECORD the equivalence point.

### 5.4.4 Expression of results

**8.3** Hydroxylamine solution.

# 9 Apparatus

Usual laboratory equipment and, in particular, the following.

**9.1 For the two operating techniques (colorimetric titration and potentiometric titration)**

**9.1.1** Saponification bottle, made of alkali-resistant glass, with frosted bottle mouth. The capacity is 100 mL~250 mL. It is fitted with a frosted-mouth glass air condenser with a length of at least 1 m and an inner diameter of 1 cm~1.5 cm.

**9.1.2** Burettes, with capacities of 50 mL and 100 mL and a scale of 0.1 mL.

**9.1.3** Analytical balance.

**9.2 For the potentiometric titration**

**9.2.1** Potentiometer (preferably recording potentiometer), with combined glass electrodes.

**9.2.2** Magnetic stirrer.

# 10 Operating procedure

**10.1 Preparation of test sample**

According to the requirements of GB/T 14454.1.

**10.2 Test portion**

WEIGH the sample in a saponification bottle (9.1.1), accurate to 0.0002 g. The amount of sample to be weighed will be specified in the product standard for the fragrance/flavor substance concerned.

**10.3 Blank test**

Simultaneously with the determination, carry out a blank test using the same reagents and following the same procedure, but omitting the test portion.

If the technique by potentiometric titration is used (see 10.4.2), it is important that the blank test is performed immediately, in order to operate at the same temperature.

### 10.4 Determination

#### 10.4.1 Colorimetric titration

USE a burette (9.1.2) to accurately add 75 mL of hydroxylamine solution (8.3) to a saponification bottle (9.1.1) containing the test portion (10.2); MIX well. Allow the saponification bottle containing the mixture to stand at room temperature, or boil under reflux. The time for standing or reflux is specified in the product standard for the fragrance/flavor substance concerned. If boiling reflux is carried out, before removing the reflux condenser, it shall cool rapidly.

ADD 3 drops of bromophenol blue indicator solution (8.2); USE hydrochloric acid standard solution (8.1) to titrate, until the solution is greenish-yellow. Titration shall be performed in a place with sufficient natural light.

Note: This method is applicable to lightly colored fragrance/flavor substances. For strongly colored fragrance/flavor substances, the potentiometric method specified in 10.4.2 or, if a potentiometer is not available, the modified procedure described in Annex A should be used.

#### 10.4.2 Potentiometric titration

USE a burette (9.1.2) to accurately add 75 mL of hydroxylamine solution (8.3) to a saponification bottle (9.1.1) containing the test portion (10.2); MIX well. Allow the saponification bottle containing the mixture to stand at room temperature, or boil under reflux. The time for standing or reflux is specified in the product standard for the fragrance/flavor substance concerned. If boiling reflux is carried out, before removing the reflux condenser, it shall cool rapidly.

Titrate potentiometrically with the hydrochloric acid standard solution (8.1), while stirring with the magnetic stirrer (9.2.2). The use of a recording potentiometer will greatly simplify this operation.

Calculate the volume of hydrochloric acid solution used at the equivalence point from the titration curve or from readings of the change in pH. It must be emphasized that, the pH value at the end point is related to the fragrance/flavor substance being tested and is not always the same.

For the molecular weight and reaction time of some carbonyl compounds, see Annex B.

## 11 Expression of results

The carbonyl value C, expressed in milligrams of potassium hydroxide per gram of essential oil, is given by the formula (3):

of the sample.

## Method III -- Neutral sodium sulfite method

## 13 Principle

Neutral sodium sulfite solution and aldehyde or ketone are reacted in a boiling water bath, to release sodium hydroxide. Gradually use an acid to neutralize to make the reaction complete.

## 14 Reagents

The reagents used are all analytically pure reagents. The water is distilled water or water of equivalent purity. Unless otherwise specified, the preparation method shall be carried out in accordance with GB/T 14454.14.

**14.1** Neutral sodium sulfite saturated solution: USE phenolphthalein as the indicator solution; ADD sodium bisulfite solution (30%) to the clear sodium sulfite saturated solution to make it neutral. The reagent shall be freshly prepared and filtered when used.

**14.2** Acetic acid aqueous solution (1 : 1).

**14.3** Phenolphthalein indicator solution.

## 15 Apparatus

Usual laboratory equipment and, in particular, the following.

**15.1** Aldehyde bottle, 150 mL. Neck length is about 150 mm, with 10 mL scale and 0.1 mL scale graduation. The zero line of the scale shall be slightly higher than the bottom of the cylindrical neck. The angle formed by the conical wall and the vertical neck is about 30°.

**15.2** Pipette, 10 mL.

**15.3** Boiling water bath.

## 16 Operating procedure

### 16.1 Preparation of test sample

# Annex A

**(Normative)**

**Operating procedure for determination of strongly colored fragrance/flavor substances**

When the potentiometric titration method cannot be used for the determination of strongly colored fragrance/flavor substances, the following operating procedure can be used.

USE a burette (9.1.2) to pipette 75 mL of hydroxylamine solution (8.3) into the saponification bottle (9.1.1) A and mix well.

POUR this mixture into another saponification bottle (9.1.1) B containing the sample. Do not wash saponification bottle A. Allow the saponification bottle B containing the mixture to stand, or boil under reflux. The time for standing or reflux is specified in each product standard for the fragrance/flavor substance concerned. If boiling reflux is carried out, before removing the reflux condenser, it shall cool rapidly.

USE hydrochloric acid standard solution (8.1) to titrate, until the solution is greenish-yellow.

POUR about half of the solution in saponification bottle B into the reserved saponification bottle A; neutralize until the solution is lemon-yellow; then, pour this solution into saponification bottle B and mix well; then pour half of the mixture into the saponification bottle A.

REPEAT this operation until the addition of two drops of the hydrochloric acid standard solution (8.1) to the solution contained in one of the two bottles causes no further change of color when compared with the solution contained in the other bottle.

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