GB

NATIONAL STANDARD OF THE

PEOPLE’S REPUBLIC OF CHINA

ICS 71.100.40

G 72

GB/T 7383-2020

Replacing GB/T 7383-2007

Non-ionic Surface Active Agents - Determination of Hydroxyl Value

非离子表面活性剂 羟值的测定

(ISO 4326:1980, Non-ionic Surface Active Agents - Polyethoxylated Derivatives - Determination of Hydroxyl Value - Acetic Anhydride Method, MOD)

Issued on: December 14, 2020 **Implemented on: July 1, 2021**

Issued by: State Administration for Market Regulation;

Standardization Administration of the People’s Republic of China.

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Non-ionic Surface Active Agents - Determination of Hydroxyl Value

1 Scope

This Standard specifies the determination of hydroxyl value in non-ionic surface active agents.

This Standard is applicable to the determination of hydroxyl value (the hydroxyl value of adducts of ethylene oxide and propylene oxide of primary fatty alcohols, alkylphenols and fatty acids, and their mixtures) of aliphatic and cycloaliphatic poly alkoxy compounds, which is suitable for the determination of hydroxyl value in 10 ~ 1,000.

The phthalic anhydride method is suitable for the determination of the hydroxyl value of adducts of ethylene oxide and propylene oxide of primary and secondary fatty alcohols, alkylphenols and fatty acids, and their mixtures.

The acetic anhydride method is suitable for the determination of the hydroxyl value of adducts of ethylene oxide of primary and secondary fatty alcohols, alkylphenols and fatty acids, but not for the determination of the hydroxyl value of propoxylated products.

The near-infrared method is suitable for non-ionic surface active agents whose hydroxyl value can be determined by the phthalic anhydride method or the acetic anhydride method.

Interfering substances are as follows:

---Primary and secondary amines, amides, tertiary alcohols, thiols and epoxides generate side reactions that affect the accuracy of the method.

---Long-chain aliphatic acids and esters generate more stable anhydrides than phthalic anhydride acetic anhydride, which cannot be completely decomposed at the end of the determination.

---Other free acids cause interference due to the reaction with the sodium hydroxide standard solution, and alkalis, including certain tertiary amines, cause interference due to the reaction with the generated phthalic acid and acetic acid.

The presence of epoxides interferes with the determination. If they can be removed by the low-temperature vacuum distillation method without changing the hydroxyl value, this method is still applicable. The above-mentioned treatment can eliminate free ethylene oxide that causes interferences and with a concentration (mass fraction) higher than 0.5%.

The moisture present in the specimen will react with phthalic anhydride and acetic anhydride, but this method is still applicable if the measures described in the determination procedures are followed for prevention.

2 Normative References

The following documents are indispensable to the application of this document. In terms of references with a specified date, only versions with a specified date are applicable to this document. In terms of references without a specified date, the latest version (including all the modifications) is applicable to this document.

GB/T 601 Chemical Reagent - Preparations of Standard Volumetric Solutions

GB/T 2384 Dyes Intermediates - General Method for the Determination of Melting Range

GB/T 3143 Color Determination Method of Liquid Chemicals - Hazen Unit - Platinum - Cobalt Scale

GB/T 6365 Surface Active Agents - Determination of Free Alkalinity or Free Acidity - Titrimetric Method (GB/T 6365-2006, ISO 4314:1977, IDT)

GB/T 6372 Surface Active Agents and Detergents - Methods of Sample Division (GB/T 6372-2006, ISO 607:1977, IDT)

GB/T 8170 Rules of Rounding off for Numerical Values & Expression and Judgement of Limiting Values

GB/T 11275 Surface Active Agents - Determination of Water Content (GB/T 11275-2007, ISO 4317:1991, MOD)

GB/T 29858 Standard Guidelines for Molecular Spectroscopy Multivariate Calibration Quantitative Analysis

ISO 4327 Non-ionic Surface Active Agents - Polyalkoxylated Derivatives - Determination of Hydroxyl Value - Phthalic Anhydride Method

3 Terms and Definitions

The following terms and definitions are applicable to this document.

3.1 hydroxyl value (OH)

Hydroxyl value refers to the number of milligrams of potassium hydroxide required to neutralize the acid generated by the esterification of hydroxyl groups in 1 g of specimen with phthalic anhydride or acetic anhydride.

3.2 modeling samples

Modeling samples refer to a series of representative samples selected for the establishment of the calibration model.

3.3 validation samples

Validation samples refer to a series of representative samples selected for the validation of the calibration model.

3.4 calibration

Calibration refers to the process of establishing a model by correlating the concentration or properties of a group of samples with their spectra.

3.5 calibration model

Calibration model refers to a mathematical expression that expresses the correlation between the composition and concentration or properties of a group of samples and their spectra.

3.6 estimate

Estimate refers to the process of calculating the concentration or properties of sample composition using the calibration model and the sample's spectrum.

3.7 abnormal value

Abnormal value refers to the data points corresponding to samples for which the model estimate value is significantly different from the reference value.

3.8 mahalanobis distance

Mahalanobis distance represents the covariance distance of the data, which is an effective method of calculating the similarity of two unknown sample spectra.

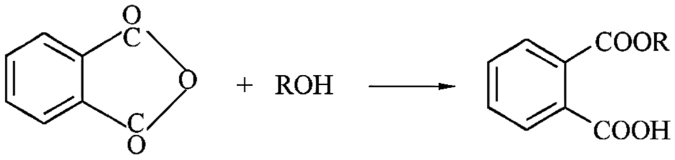
4 Method A - Phthalic Anhydride Method (arbitration method)

4.1 General Rules

The phthalic anhydride method shall comply with the method provided in ISO 4327.

4.2 Principle

In pyridine solution, use phthalic anhydride to esterify the hydroxyl value.



c (NaOH) = 0.5 mol/L, prepare in accordance with the stipulations of GB/T 601.

4.3.4 Phenolphthalein indicator

1 g of phenolphthalein is dissolved in 100 mL of pyridine.

4.4 Instruments and Equipment

4.4.1 Alkaline burette

The capacity is 50 mL.

4.4.2 Flat-bottomed flask

The capacity is 250 mL, with conical ground glass joints.

4.4.3 Air condenser

An air condenser with an effective length greater than 600 mm, with conical ground glass joints.

4.4.4 One-mark pipette

The capacity is 25 mL.

4.5 Determination

4.5.1 General rules

In accordance with the stipulations of GB/T 6372, prepare and store samples. In addition, in accordance with the stipulations of GB/T 11275, determine the water content in the sample. All operations shall be carried out in a well-ventilated fume hood. The glassware used shall be clean and dry, and the determination of two samples and two blank tests shall be simultaneously carried out. See Appendix C for the instruments and methods that need to determine the hydroxyl value outside the fume hood.

4.5.2 Weighing

In accordance with the following calculated amount, weigh the specimen into a pre-weighed dry flask (accurate to 0.001 g).

When the water content (mass fraction) is lower than 1%, the mass m_0 of the specimen is calculated in accordance with Formula (1):

$$m_0 = \frac{365}{I(\mathrm{OH})} \quad \cdots\cdots\cdots\cdots (1)$$

Where,

m_0---the mass of the specimen, expressed in (g);

blank tests and the specimens shall be between 10 mL ~ 15 mL.

If the difference between the two volumes is greater than 15 mL, it means that the specimen mass is too large (the hydroxyl value is greater than the estimated value), and the specimen size shall be reduced; if the difference between the two volumes is less than 10 mL, it means that the specimen mass is too small (the hydroxyl value is smaller than the estimated value), and the specimen size shall be increased.

4.5.6 Result expression

4.5.6.1 Calculation

The hydroxyl value *I* (OH) of the specimen shall be calculated in accordance with Formula (4):

$$I(\mathrm{OH})=\frac{(V_0-V_1)\times c\times 56.10}{m_0}+X \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (4)$$

Where,

V_0---the volume of the sodium hydroxide standard titration solution consumed by the blank specimen, expressed in (mL);

V_1---the volume of the sodium hydroxide standard titration solution consumed by the specimen, expressed in (mL);

c---the concentration of the sodium hydroxide standard titration solution, expressed in (mol/L);

m_0---the mass of the specimen, expressed in (g);

56.10---the relative molecular mass of potassium hydroxide;

X---the positive acid value or negative base value of the specimen, which is determined in accordance with the stipulations of GB/T 6365. If this value is less than or equal to 0.3, it shall be ignored. Take the arithmetic mean of the two determination results as the determination result.

4.5.6.2 Precision

4.5.6.2.1 Repeatability

The relative deviation of this method shall be less than 1.5%. The determination results shall comply with the stipulations of GB/T 8170.

4.5.6.2.2 Reproducibility

The values in Table 1 were obtained in 21 laboratories, and at least two results were provided by an analyst in each laboratory.

glass bottle with a ground stopper. Use the platinum-cobalt color number, in accordance with the stipulations of GB/T 3143, conduct the determination. If the solution chromaticity exceeds 100 Hazen units, then, it cannot be used.

5.2.4 Sodium hydroxide standard titration solution

c (NaOH) = 0.5 mol/L, prepare in accordance with the stipulations of GB/T 601.

5.2.5 Phenolphthalein indicator

1 g of phenolphthalein is dissolved in 100 mL of pyridine.

5.3 Instruments and Equipment

5.3.1 Alkaline burette

The capacity is 50 mL.

5.3.2 Flat-bottomed flask

The capacity is 250 mL, with conical ground glass joints.

5.3.3 Air condenser

The effective length is 400 mm; the inner tube consists of connected spheres; with conical ground glass joints.

5.3.4 One-mark pipette

The capacity is 15 mL.

5.4 Determination

5.4.1 General rules

In accordance with the stipulations of GB/T 6372, prepare and store samples. In addition, in accordance with the stipulations of GB/T 11275, determine the water content in the sample. All operations shall be carried out in a well-ventilated fume hood. The glassware used shall be clean and dry, and the determination of two samples and two blank tests shall be simultaneously carried out. See Appendix C for the instruments and methods that need to determine the hydroxyl value outside the fume hood.

5.4.2 Weighing

In accordance with Table 2, weigh the specimen (accurate to 0.001 g), and place it in a dry and weighed flask.

frequency absorption with bending vibration just fall into the near-infrared spectral region, the most frequently observed spectral band in the near-infrared region is the hydrogen-containing group (X-H), and the concentration of the hydrogen-containing group (X-H) and its absorbance are in a linear relation. Taking the hydroxyl value as an example, use the stoichiometric method to correlate the hydroxyl value of the known surface active agent sample with its absorbance, determine the quantitative relations (calibration model) between the two, then, determine the absorbance of the unknown sample spectrum, and the hydroxyl value of the unknown sample can be predicted through the calibration model.

This detection method is based on the detection data of Method A or Method B, and its accuracy depends on the accuracy of Method A or Method B. After excluding the influence of sample type, chemical composition and physical properties, etc., the detection results are only valid for the chemical composition and hydroxyl value range of the samples participating in the calibration.

6.2 Instruments and Equipment

6.2.1 Near-infrared spectrometer

It shall comply with the requirements of GB/T 29858 for the instrument, be equipped with transmission acquisition accessories. The accompanying software shall have the functions of near-infrared spectrum acquisition, pre-processing, calculation and modeling.

6.2.2 Constant-temperature heater

6.2.3 Near-infrared sample tube

Special-purpose quartz glass tube.

6.3 Operating Steps

6.3.1 Instrument preparation

Before the determination, in accordance with the requirements of the instruction of the near-infrared analyzer, pre-heat the instrument and conduct a self-test.

6.3.2 Selection of modeling samples

The modeling samples need to be representative and include the chemical composition existing in the sample to be tested. The hydroxyl value content among the modeling samples needs to be evenly distributed, covering the characteristics of the sample to be analyzed, and there needs to be a large quantity, so as to be able to statistically determine the mathematical relations between the spectral variables and the hydroxyl value. After removing the abnormal value, each modeling sample set needs to include at least 30 samples.

6.3.3 Determination of chemical method data

In accordance with the operation method specified in Method A or Method B, determine the hydroxyl value of the samples in the modeling sample set and obtain the standard hydroxyl value data for the establishment of the model.

6.3.4 Sample spectrogram acquisition

6.3.4.1 Spectral condition setting

In accordance with the nature of the product, select appropriate spectral conditions, such as: spectral scanning range, spectral resolution, constant temperature, number of scans and constant-temperature time, etc., check the instrument signal and set the information of the sample being determined.

6.3.4.2 Determination of spectral measurement mode

Non-ionic surface active agents are uniform and transparent liquids with good fluidity at a certain temperature. Select the spectral measurement mode of transmission, and the spectral acquisition temperature during the modeling needs to be consistent with the subsequent detection temperature.

6.3.4.3 Sample collection

Put the samples of the modeling sample set whose hydroxyl value is already known into a clean and dry sample tube and accurately number them. Maintain the temperature in the constant-temperature heater for not less than 2 min. In accordance with the selected spectral conditions, collect the blank and collect the sample spectrum. For each sample, collect three to four spectra, accurately record the sample information and save it.

6.3.5 Establishment of calibration model

Utilize the principle of chemometrics to establish the calibration model. Adopt the data preprocessing mode provided in the modeling software to preprocess the spectrum, optimize the wavelength or frequency with a high correlation with the change of the hydroxyl value of the component. Through the cross-validation of the calibration spectrum, obtain R^2 and RMSECV of the model, so as to evaluate the detection accuracy of the model, and finally form the calibration model (see Appendix E).

6.3.6 Validation of calibration model

6.3.6.1 Selection of validation samples

The validation of the model is the process of judging the accuracy and repeatability of the estimated near-infrared hydroxyl value of the validation samples in the validation sample set and the standard hydroxyl value of the chemical method. In accordance with the same conditions as the selection of the calibration sample set, select the validation sample set, and the following conditions need to be followed:

---The validation sample set needs to have a sufficient number to reflect the feasibility of the model, and its hydroxyl value range must cover at least 95% of the hydroxyl value range of the calibration sample set, and the distribution shall be uniform;

- ---The chemical composition of the validation sample set must be within the calibration sample set.

6.3.6.2 Validation and optimization of model

Through the validation of the validation samples, the precision requirements of the model and the arbitration method in 4.5.6.2 and 5.4.7 can be evaluated. If necessary, multiple optimized models under different conditions can be compared, and the model with the highest accuracy, optimum repeatability and most robustness is selected to finally form a calibration model that can be used for detection.

6.3.7 Model update and maintenance

During application, in order to ensure the accuracy of the calibration model and enhance the applicability of the model, it is necessary to continuously test the accuracy and repeatability of the model, and add calibration samples to the existing model to increase the scope of use of the model.

6.4 Determination of Hydroxyl Value

In accordance with the determined spectral conditions, pour the sample to be tested into the sample tube and put it into a constant-temperature heater to heat to the set temperature. Utilize the software to scan the blank first (before each analysis, a blank test is required to deduct the blank value), then, measure the sample. The instrument will automatically provide the detection result of the hydroxyl value of the non-ionic surface active agent to be tested. Other free acids have interference due to the reaction with sodium hydroxide standard solution. Alkalis, including certain tertiary amines, cause interference due to the reaction with the generated phthalic acid and acetic acid. Under this circumstance, the acidity or alkalinity needs to be corrected (in accordance with the rules provided in GB/T 6365).

6.5 Result Processing and Expression

The processing and expression of results shall comply with the following three requirements:

- ---In order to obtain valid results, the determination results shall be within the hydroxyl value content range covered by the calibration model used by the instrument, and the Mahalanobis distance of the results shall be within the limit of the calibration model used by the instrument;
- ---Carry out a parallel test on the same sample (reloading is required), and report the result as the arithmetic mean, accurate to 0.1;
- ---For the abnormal data of the instrument alarm, or the abnormal data with obvious difference from the arbitration method, it is not regarded as a valid determination result.

Translated by: Field Test Asia Pte. Ltd. (Incorporated & taxed in Singapore. Tax ID: 201302277C)
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