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| **Test methods for Liquid crystal monomers**  **单体液晶测试方法**  ***（English Version）*** |

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(Draft for Comment)

**Foreword**

*SAC/TC 203 is in charge of this English translation. In case of any doubt about the contents of English translation, the Chinese original shall be considered authoritative.*

This standard was drafted in accordance with the rules given in GB/T 1.1 - 2020 Directives for standardization—Part 1: Rules for the structure and drafting of standardizing documents.

This standard was proposed and prepared by SAC/TC203（National Technical Committee for Standardization of Semiconductor Equipment and Materials）.

**Test Methods for Liquid Crystal Monomers**

1 Scope

This file defines the methods for determining the purity, major impurity, volatile components, resistivity, moisture content, and concentrations of metal ions of a liquid crystal monomer material.

This file applies to liquid crystal monomer materials.

2 Normative References

The contents of the following files constitute indispensable clauses of this file through normative reference in the text. For dated references, only the edition with the corresponding date applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB/T 602 *Chemical Reagent - Preparations of Standard Solutions for Impurity*

GB/T 4946 *Terms of Gas Chromatography*

GB/T 6682 *Water for Analytical Laboratory Use - Specification and Test Methods*

GB/T 9008 *Terms of Liquid Chromatography*

GB/T 11446.1 *Electronic Grade Water*

GB/T 26792 *High Performance Liquid Chromatography*

GB/T 27417 *Conformity Assessment - Guidance on Validation and Verification of Chemical Analytical Methods*

GB/T 30431 *Gas Chromatography for Laboratory*

GB/T 34826 *Method of Performance Testing for Quadrupole Inductively Coupled Plasma Mass Spectrometer*

GB/T 39486 *Chemical Reagent - General Rules for Inductively Coupled Plasma Mass Spectrometry*

GB 50073 *Code for Design of Clean Room*

SJ/T 11203 *Terms for Liquid Crystal Materials*

3 Terms and Definitions

The terms and definitions from GB/T 4946, GB/T 9008, SJ/T 11203 apply to this file.

3.1

Dilution Factor (DF)

The ratio at which the sample is diluted. DF = the mass of sample after dilution (g) / the mass of sample before dilution (g).

3.2

Quality Control Sample (QCS)

A substance or material with one or more sufficiently stable properties that well defines or define its intended purpose for maintaining and monitoring a measuring system.

4 General Requirements

Unless otherwise indicated, the test should be carried out in the following environment conditions:

1. environmental temperature: 15⁰C - 30⁰C;
2. relative humidity: ≤ 70%;
3. atmospheric pressure: 86 kPa - 106 kPa;
4. No strong electromagnetic field, no corrosive gas, no strong vibration.

5 Test Methods

* 1. Purity

5.1.1 Method Selection

Generally, gas chromatography is the determinative method. Liquid chromatography can be adopted as the determinative method, if gas chromatography is not applicable due to sample properties, e. g. decomposition or polymerization at high temperature.

5.1.2 Gas Chromatography

5.1.2.1 Principle

The sample is gasified and introduced into a chromatographic column with a carrier gas. The analyte components are separated based on their mobilities in the column, due to their differences in physical and chemical properties, such as adsorption and desorption, between the gas phase and the solid phase. The separated components flow out of the chromatographic column into the detector in a certain order. The chromatogram and corresponding data are recorded by a data processing system.

5.1.2.1

5.1.2.2 Test Conditions

Table 1: Test Conditions for Determining the Purity of Liquid Crystal Monomer Material by Gas Chromatography

|  |  |
| --- | --- |
| Parameters | Conditions |
| Injection port temperature | The temperature should be within the capability of the gas chromatographic system, and ensures that the sample and its components can be completely gasified. Recommended temperature: 300⁰C. |
| Detector temperature | The detector temperature should not be lower than the injection port temperature while taking the highest allowable temperature of the column into consideration. Recommended temperature: 300⁰C. |
| Split ratio | Generally recommended range: 10:1 - 100:1 |
| Type of Chromatographic Column | Chromatographic columns for separating nonpolar organic compounds or those with weak or moderate polarity. Optionally HP-5 (5% phenyl + 95% methyl polysiloxane) or DB-17 (50% phenyl + 50% methyl polysiloxane) fused silica capillary column;  Recommended parameters for chromatographic columns (length × inside diameter × thickness of liquid film): 30 m × 0.25 mm × 0.25 μm. |
| Control Mode | Constant pressure: 10 psi - 35 psi, 15 psi is recommended,  or constant flow rate: 0.5 mL/min - 2 mL/min, 1.0 mL/min is recommended. |
| Column Compartment Temperature | Initial temperature: Usually 5⁰C - 20⁰C higher than the environmental temperature, typically not lower than 50⁰C.  Temperature-maintaining time: For a duration at a certain temperature, but optional.  Heating rate: Generally 5⁰C/min - 20⁰C/min. Constant temperature is also optional.  Highest temperature: In principle not lower than the injection port temperature, but not higher than the detector temperature and the highest allowable temperature of the column. |
| Sample size | 0.3 μL - 2.0μL, 1.0μL is recommended. |
| Runtime | Usually not longer than 120 min. |
| Air flow | 200 mL/min - 600 mL/min, 300 mL/min is recommended. |
| Hydrogen flow | 24 mL/min - 60 mL/min, 30 mL/min is recommended. |
| Column flow plus purging gas | 10 mL/min - 60 mL/min, 25 mL/min is recommended. |
| Septum purging flow | 1. - 40 mL/min, 10 mL/min is recommended. |

5.1.2.3 Reagents

An organic solvent that can completely solve the sample of liquid crystal monomer, guaranteed reagent. Dichloromethane, cyclohexane, and toluene are recommended.

* + - 1. Apparatus

5.1.2.5 Gas chromatograph, in accordance with GB/T 30431, equipped with a corresponding gas chromatographic column and a hydrogen flame ionization detector (FID).

5.1.2.6 Electronic balance with precision of not lower than 0.01 g.

5.1.2.7 Gases

Carrier gas (highly pure nitrogen or highly pure helium with a purity of not lower than 99.999%) and burning gas (highly pure hydrogen with a purity of not lower than 99.999%; or mixed air with a volume ratio nitrogen : oxygen of 79:21, where the purities of nitrogen and oxygen should be both greater than 99.999%).

5.1.2.8 Preparation of Samples

Weigh a liquid crystal monomer sample and add an organic solvent to the sample, in order to prepare a solution at a mass concentration of 5% - 20%. Allow the solution to stand still until it is clear, in order to obtain the sample.

5.1.2.9 Procedure

The test is carried out according to the following steps.

a) Install the chromatographic column properly, and check the pressures of the carrier gas and the burning gas, which should fulfill the requirements of the instrument. Check the type of chromatographic column, which should fulfill the requirements of the sample test.

b) Turn on and connect the instrument and computer. Initiate the instrument control software for configuring the test method.

c) Configure the type of chromatographic column, set the injection port temperature, the detector temperature, the split ratio, the column compartment temperature, the runtime and other parameters according to the physical properties of different monomer materials. See table 2 for details.

Name and save the method.

d) Register the information of the sample. Select the method named in step c) and transfer the method to the instrument.

Inject 0.3 μL - 2.0 μL of the sample, when the temperature reaches the set value and becomes stable. Run the test according to the preset test procedure until the runtime is elapsed.

5.1.2.10 Test Data Processing

Initiate the data analysis software, retrieve the spectrum, and process the data using the area percentage method. The purity of the liquid crystal monomer material, expressed as *ω* in %, is calculated by dividing the peak area corresponding to the liquid crystal monomer by the sum of peak areas corresponding to all the components (except the solvent, which generally includes the peaks before 3 min) according to equation (1).

……………………………………… (1)

where:

—— peak area of the liquid crystal monomer;

—— peak area of component .

Read the test result as the purity of the liquid crystal monomer material determined by gas chromatography.

5.1.2 Liquid Chromatography

5.1.2.1 Principle

The sample is introduced into the chromatographic column with a liquid as mobile phase. The analyte components are separated based on their mobilities in the column, due to their differences in physical and chemical properties, such as adsorption and desorption, between the gas phase and the solid phase. The separated components flow out of the chromatographic column into the detector in a certain order. The chromatogram and corresponding data are recorded by a data processing system.

5.1.2.2 Test Conditions

Table 2: Test Conditions for Determining the Purity of Liquid Crystal Monomer Material by Liquid Chromatography

|  |  |
| --- | --- |
| Parameters | Conditions |
| Pump flow rate | The pump flow rate should be within the capability of the liquid chromatographic system. The backpressure of the liquid chromatographic column should not exceed the capability of the instruments. For HPLC, 1.0 mL/min is recommended; and for UPLC, 0.3 mL/min - 0.5 mL/min is recommended. |
| Mobile phase | The type of reagents should be suitable for the liquid chromatographic system. Methanol, acetonitrile and water are recommended.  The elution mode of the mobile phase is configurable, e. g. in isocratic or gradient mode.  The above-mentioned parameters should be adjusted according to the specific situation of separation. |
| Detector wavelength | Wavelength: For an absorptive spectrum, the liquid crystal monomer is subjected to full wavelength scanning in UV range (200 nm - 400 nm). A liquid crystal monomer may have multiple wavelengths which correspond to peaks on the spectrum. The wavelength corresponding to the largest or second largest peak is usually selected. |
| Type of Chromatographic Column | Chromatographic columns for separating organic compounds with weak or moderate polarity. C18 reversed-phase chromatographic column is recommended. |
| Chromatographic Column Temperature | The chromatographic column temperature should be selected within the temperature range suitable for the chromatographic column itself and for the sample. 25⁰C - 40⁰C is recommended. |
| Sample size | Generally 1.0 μL - 50.0μL; 10.0μL is recommended. |
| Runtime | Usually not longer than 120 min |

5.1.2.3 Reagents

Water, first grade according to GB/T 6683, or an organic solvent that can completely solve the sample of liquid crystal monomer, guaranteed reagent at a purity ≥ 99.9% with only impurities which do not interference with the test. Methanol and acetonitrile are recommended.

For the formulation of a proper mobile phase, the ratio of the organic solvent to water is adjusted according to the separation of the liquid crystal monomer.

5.1.2.4 Apparatus

Liquid chromatograph, in accordance with GB/T 26792, equipped with a corresponding chromatographic column and a UV-Vis absorbance detector (UV-VIS).

Electronic balance with precision of not lower than 1 mg.

5.1.2.5 Sample

Weigh a liquid crystal monomer sample and add a mobile phase to the sample, in order to prepare a solution at a mass concentration of 0.05% - 0.50%. Obtain the sample when the solution is clear to the naked eye.

5.1.2.6 Procedure

The test is carried out according to the following steps.

a) Supply sufficient mobile phase. Turn on and connect the instrument and computer. Initiate the instrument control software for configuring the test method.

b) Configure the flow rate, the wavelength, the ratio of mobile phase, and the column compartment temperature according to the physical properties of different liquid crystal materials. See table 3 for details. Name and save the method.

c) Register the information of the sample. Select the method named in step b) and transfer the method to the instrument.

Inject the sample, when the parameters reach the set value and become stable. Run the test according to the preset test procedure until the runtime is elapsed.

5.1.2.7 Test Data Processing

Process the data using the area percentage method.

The purity of the liquid crystal monomer material is calculated by dividing the peak area corresponding to the main component by the sum of peak areas corresponding to all the components (except the solvent peak). See 5.1.1.7 for the specific calculation. Solvent peak: The sum of peaks in the spectrum obtained by solely injecting the solvent under the same test conditions.

Read the test result as the purity of the liquid crystal monomer material determined by liquid chromatography.

5.2 Major Impurity (Gas or Liquid Chromatography)

Major impurity is the component with the largest proportion other than the main components. The data is read directly from the spectrum data acquired by the method for purity determination in 5.1.

5.3 Volatile Components (Gas Chromatography)

5.3.1 Principle

The sample is gasified and introduced into a chromatographic column with a carrier gas. The analyte components are separated based on their mobilities in the column, due to their differences in physical and chemical properties, such as adsorption and desorption, between the gas phase and the solid phase. The separated components flow out of the chromatographic column into the detector in a certain order. The chromatogram and corresponding data are recorded by a data processing system.

5.3.2 Test Conditions

An initial temperature of 50⁰C is recommended. The other parameters are set according to the same principle explained in 5.1.1.2.

5.3.3 Reagents

An organic solvent that can completely solve the sample of liquid crystal monomer, guaranteed reagent at a purity not lower than 99.9% with only impurities which do not interference with the test. Anisole, N,N-dimethyl formamide, and dimethyl sulfoxide are recommended.

5.3.4 Apparatus

See 5.1.1.4.

5.3.5 Preparation of Samples

Weigh a liquid crystal monomer sample and add a suitable organic solvent to the sample, in order to prepare a solution at a mass concentration of 5% - 20%. Obtain the sample when the solution is clear to the naked eye.

* + 1. Procedure

5.3.6.1 First test the organic solvent for 10 - 15 min, following the steps described in 5.1.1.6.

5.3.6.2 Then test the sample at the same sample size as the organic solvent, following the steps described in 5.1.1.6.

5.3.7 Test Data Processing

Process the data using the area percentage method.

Delete all the peaks, which have the same retention time as that in the spectrum of the organic solvent, from the spectrum of the sample. The volatile component content of the liquid crystal monomer material is calculated by dividing the sum of the peak areas of the remaining components, which have retention time shorter than that of the solvent peak, by the peak areas of the main components of the liquid crystal monomer.

5.4 Resistivity (*ρ*)

5.4.1 Principle

Place the sample of liquid crystal monomer into an electrode. Apply a constant DC-voltage over the sample with a high resistance meter. Measure the response current *I* and calculate the resistivity ρ of the liquid crystal monomer according to equation (2).

……………………………… (2)

The electrode factor is defined by equation (3):

……………………………………… (3)

where:

ρ—— resistivity of the liquid crystal monomer in ohm·centimeter (Ω·cm);

*R*—— resistance of the liquid crystal monomer in ohm (Ω);

*S*—— bottom area of the liquid crystal layer in the electrode in square centimeter (cm2);

*L*—— height of the liquid crystal layer in the electrode in centimeter (cm);

*U*—— voltage in Voltage (V);

*I*—— current in Ampere (A);

*K*—— electrode factor in centimeter (cm).

5.4.2 Test Environment

Class N5 Cleanroom or better, in accordance with GB 50073. Relative humidity not greater than 30%.

5.4.3 Test Conditions

Table 3: Test Conditions for Determining the Resistivity of Liquid Crystal Monomer Material

|  |  |
| --- | --- |
| Parameters | Conditions |
| Type of Voltage | DC |
| Voltage | 10 V is recommended |
| Delay time | 30 is recommended |

5.4.4 Reagents

A solvent with a fixed ratio of monomers and capable of completely solving the sample of liquid crystal monomer. A liquid crystal monomer in liquid state or a purified mixture of liquid crystal monomers at a certain ratio is recommended.

The resistivity of the solvent should not be lower than 5.0×1011Ω·cm.

5.4.5 Apparatus

High resistance meter; electronic balance with precision of 1 mg; magnetic stirrer.

5.4.6 Preparation of Samples

Weigh a liquid crystal monomer sample and add a solvent selected according to 5.4.4, in order to prepare a solution at a mass concentration of 1% - 10%. (Depending on the solubility, a higher concentration in the range should be selected and fixed.) Put in a clean magnetic stir bar. Heat and stir until the monomer is dissolved. Stir homogeneously, in order to obtain the sample to be tested.

5.4.7 Procedure

The test is carried out according to the following steps.

1. Turn on the instrument, and initiate the test program.
2. Fill the test electrode with the sample.
3. Place the test electrode in a shielding box, and connect electrode wires.
4. Configure the test conditions. See table 4 for details.
5. Input the electrode factor. Start the test. Read the test results when it is finished.

5.4.8 Test Data Processing

Read the test result as the resistivity of the liquid crystal monomer material.

5.5 Moisture

5.5.1 Principle

The test is carried out using an anode electrolyte containing iodine ions with a Karl-Fischer titrator. Iodine is yielded from the anode electrolyte when current is fed through. During the test, water reacts with iodine, sulfur dioxide, organic base and methanol according to equation (4):

 (4)

Iodine is yielded in the anode electrolyte containing iodine ions, as described in equation (5):

……………………………… (5)

If water exists in the sample, the resultant iodine reacts with water. In accordance with Faraday's law, the amount of the resultant iodine is proportional to the amount of consumed electricity. Therefore, the measurement of the total consumption of electricity can be used to determine the total moisture content in the sample.

5.5.2 Test Environment

Relative humidity not greater than 30%.

5.5.3 Test Conditions

Table 4: Test Conditions for Determining the Moisture Content of Liquid Crystal Monomer Material

|  |  |
| --- | --- |
| Parameters | Conditions |
| Polarizing current | 0.5 μA - 2.0 μA |
| Initial voltage for titration | 400 mV - 500 mV |
| Endpoint voltage for titration |  |

5.5.4 Reagents

An organic solvent that can completely solve the sample of liquid crystal monomer material. Toluene and n-heptane are recommended.

The moisture content of the solvent should not be greater than 50 mg/Kg.

5.5.5 Apparatus

Karl-Fischer titrator.

Electronic balance with precision of 1 mg.

5.5.6 Preparation of Samples

Liquid sample: 2 mL - 3 mL of liquid crystal monomer material

Solid sample: Weigh 1.0 g ± 0.1 g of liquid crystal monomer material, and solve it in 5.0 g ± 0.1 g of pure toluene, which should have a moisture content of no greater than 50 mg/Kg.

5.5.7 Procedure

5.5.7.1 Procedure for liquid sample

The test is carried out according to the following steps.

1. Turn on the instrument, and initiate the test program. Finish the pre-titration, where the drift should be lower than 20 μL/min.
2. Pipet 1.0 mL - 2.0 mL of the liquid sample with a micro sampling syringe and weigh on the electronic balance for the total mass.
3. Add the liquid sample into a cell of the titrator after pre-titration and configuring the test method according to table 5. Weigh the micro sampling syringe on the electronic balance. Calculate the mass of the sample from the difference between the total mass and the mass of the micro sampling syringe. Input the mass of the sample into the titrator, so that the titrator automatically calculates the moisture content in the liquid crystal monomer material.

5.5.7.2 Procedure for solid sample

The test is carried out according to the following steps.

a) Pipet 1.0 mL - 2.0 mL of toluene with a micro sampling syringe and weigh on the electronic balance for the total mass.

b) Add the toluene into a cell of the titrator after pre-titration and configuring the test method. Weigh the micro sampling syringe on the electronic balance. Calculate the mass of toluene m1 from the difference between the total mass and the mass of the micro sampling syringe. Input the mass of toluene into the titrator, so that the titrator automatically calculates the moisture content in the toluene *X1*.

c) Pipet 1.0 mL - 2.0 mL of the solid sample with a micro sampling syringe and weigh on the electronic balance for the total mass.

d) Add the solid sample into an anode cell of the titrator after pre-titration and configuring the test method. Weigh the micro sampling syringe on the electronic balance. Calculate the mass of the solid sample m2 from the difference between the total mass and the mass of the micro sampling syringe. Input the mass of the solid sample into the titrator, so that the titrator automatically calculates the moisture content in the solid sample X2.

e) The moisture content of liquid crystal monomer material is calculated according to equation (6):

……………………… (6)

where:

*X*—— moisture content of the liquid crystal monomer material in milligram per kilogram (mg/Kg);

*m2*—— mass of the solid sample in gram (g);

*X2*—— moisture content of the solid sample in milligram per kilogram (mg/Kg);

*m1*—— mass of toluene for solving the sample in gram (g);

*X1*—— moisture content of toluene in milligram per kilogram (mg/Kg);

*m0*—— mass of the liquid crystal monomer material in gram (g).

5.5.8 Test Data Processing

The final calculated value represents the moisture content of the liquid crystal monomer material.

5.6 Concentrations of Metal Ions

5.6.1 Principle

The sample is sent to an ICP source by a sampling system, and is evaporated, decomposed, atomized, and ionized in a high-temperature torch tube. Most of the metal ions become monovalent ions, which then enter a vacuum system of a mass spectrometer through a sampler cone and a skimmer cone in a high speed. During their passage through an electrical field of an ion lens, the ions are focused into beams and sent to a quadrupole ion separation system for sequential separation according to mass-charge ratio. They are finally detected by an ion detector. The thus generated signals are amplified and then received by a signal measurement system.

5.6.2 Test Environment

Class N7 Cleanroom or better, in accordance with GB 50073.

5.6.3 Test Conditions

Table 5: Test Conditions for ICP-MS

|  |  |
| --- | --- |
| Parameters | Conditions |
| Carrier gas and auxiliary gas | Argon at pressure of 0.70 MPa - 0.75 MPa |
| Optional gas | Argon/Oxygen at pressure of 0.50 MPa - 0.55 MPa |
| Speed of peristaltic pump | 0.1 rps |
| Instrument ventilation rate | 8 m/s - 10 m/s |
| Spray room temperature | -5℃ |

5.6.4 Reagents

An organic solvent that can completely solve the sample and has a content of any single metal element ≤ 0.5 μg/Kg. NMP and dimethyl benzene are recommended.

Standard solution prepared according to GB/T 602 or certified reference material.

Water used in this test should meet the requirements of GB/T 11446.1.

5.6.5 Apparatus

Quadrupole inductively coupled plasma-mass spectrometer (ICP-MS) in accordance with GB/T 39486, carrier gas and auxiliary gas (argon or helium with a purity ≥ 99.999%), optional gas of an argon mixture (the volume ratio of argon to oxygen of 80 : 20, each with a purity ≥ 99.999%).

Electronic balance with precision of 1 mg.

5.6.6 Preparation of Samples

Prepare samples necessary for the points on the standard curve in the relevant interval and quality control sample, according to GB/T 602.

Weigh a sample having a weight of 0.2 g - 0.6 g and dissolve the sample completely in an organic solvent, in order to formulate a sample solution with a certain dilution factor (DF = 15±0.5 is recommended). Obtain the sample when the solution is clear to the naked eye.

5.6.7 Procedure

The test is carried out according to the following steps.

1. Adjust the parameters such as the carrier gas and auxiliary gas, the speed of peristaltic pump, the instrument ventilation rate, the spray room temperature, etc. See table 6 for details. Check the testing system for the instrument. Purge the instrument for 30 min.
2. Ignite the plasma when the instrument is stable. Initiate analysis mode of the instrument. Pre-heat for 30 min. Adjust the sensitivity and signal to noise ratio of the instrument by means of a tuning solution according to GB/T 34826, in order to fulfill the test requirements.
3. Start running under the set conditions and record the spectrum of standard curve. Inject the quality control sample to check the bias of the standard curve, and test the sample when qualified.

5.6.8 Test Data Processing

The ion contents of the individual elements in the sample are calculated in mass proportion. The ion content ω of a certain element in the liquid crystal monomer is calculated according to equation (7).

………………………… (7)

where:

ω—— mass concentration of the analyte element in the sample in μg/g;

ρ1—— mass concentration of the analyte element in the sample solution in μg/g;

ρ0—— mass concentration of the analyte element in a blank sample in μg/g;

—— dilution factor.

6 Result Processing and Allowable Error

Purity is determined and recorded once, where the result should be rounded to 3 decimal places.

Major impurity is determined and recorded once, where the result should be rounded to 3 decimal places.

Volatile components are determined and recorded once, where the results should be rounded to 4 decimal places.

Moisture content is determined and recorded once, where the result should be rounded to 1 decimal place.

Contents of metal ions are determined and recorded once, where the results should be rounded to 1 decimal place.

Resistivity is determined and recorded once, where the result should be rounded to 1 decimal place.

Purity, major impurity, volatile components, moisture content and concentrations of metal ions: 5 independent test results under repeatability condition should meet the requirement for coefficient of variation in laboratory (see GB/T 27417 *Conformity Assessment - Guidance on Validation and Verification of Chemical Analytical Methods*, Annex B).

Resistivity: The absolute differences between 5 independent test results under repeatability condition should not exceed 30% of their arithmetic average.

7 Test Report

A test report should contain the following contents:

-- Sample name;

-- Test conditions;

-- Test date;

-- Test results;

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-- Tester;