ICS 71.080.60
CCS F19

Professional Standard of the People's Republic of China

T/CIQA-70-2023

Marine methanol fuel

船用甲醇燃料

(English Translation)

Note：The English translation conducted by Teamhead Marine Survey Co.,Ltd.is authorized by CIQA to publish.

Issue date:2023-09-21 Implementation date:2023-09-21

Issued by China Entry-Exit Inspection and Quarantine Association

Contents

Foreword

This document is drafted in accordance with the rules given in the GB/T 1.1—2020 *Guidelines for standardization Work — Part* 1 Rules for the: *Structure and drafting of standardizing documents.*

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. The issuing body of this document shall not be held responsible for identifying any or all such patent rights.

This document was proposed and prepared by the Inspection and Appraisal Standardization Technical Committee of the China Entry-Exit Inspection and Quarantine Association (CIQA/TC1).

Marine methanol fuel

1 Scope

This document specifies the technical content of marine methanol fuel, including requirements, test methods, inspection rules, markings, packaging, transportation, storage, and safety.

This document is applicable to methanol fuel for marine engines and boilers.

2 Normative references

The following normative documents contain provisions which, through reference in this document, constitute indispensable provisions of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

GB 190	Packaging symbol of dangerous goods
GB/T 511	Petroleum, petroleum products and additives-Method for determination of mechanical admixtures
GB/T 601	Chemical reagent - Preparation of reference titration solutions
GB/T 602	Chemical reagent - Preparation of standard solutions for impurity (ISO 6353-1:1982, NEQ)
GB/T 603	Chemical reagent - Preparation of reagent solutions for use in test methods (ISO 6353-1:1982, NEQ)
GB/T 3723	Sampling of chemical products for industrial use-Safety in sampling（ISO 3165：1976，IDT）
GB/T 4472	Determination of density and relatively density for chemical products
GB/T 6283	Chemical products-Determination of water Karl fischer method (general method) (ISO 760:1978, NEQ)
GB/T 6324.2	Test method of organic chemical products-Part 2: Determination of dry residue after evaporation on a water bath for volatile organic liquids (ISO 759:1981, MOD)
GB/T 6678	General principles for sampling chemical products
GB/T 6680	General rules for sampling liquid chemical products
GB/T 6682	Water for analytical laboratory use-Specification and test methods (ISO 3696:1987, MOD)
GB/T 8170	Rules for rounding off numerical values & expression and judgement of limit values
GB/T 9722	Chemical reagent-General rules for the gas chromatography
GB 13690	General rules for classification and hazard communication of chemicals
GB/T 16483	Safety data sheet for chemical products-Content and order of sections
GB 18350-2013	Denatured fuel ethanol
GB/T 32150	General guideline of the greenhouse gas emissions accounting and reporting for industrial enterprises
GB/T 32151	Requirements of the greenhouse gas emissions accounting and reporting
SH 0164	Petroleum packaging, storage, transportation and acceptance of delivery rules

SH/T 0604 Crude petroleum and petroleum products-Determination of density-Oscillating U-tube method

SH/T 0689 Standard test method for determinaton of total surful in light hydrocarbons, motor fuels and oils by ultraviolet fluorescence

ISO 14067 Greenhouse gases - Carbon footprint of products - Requirements and guidelines for quantification

3 Terms and definitions

The following terms and definitions apply to this document.

3.1 marine methanol fuel

fuel with methanol as its primary component

3.2 fossil methanol

methanol produced from fossil fuels such as coal, natural gas, and petroleum

3.3 green methanol

methanol that, in the entire lifecycle of raw material acquisition, production, and usage, complies with the greenhouse gas and pollutant emission standards for green product evaluations and requirements in ISO 14067, GB/T 32150, GB/T 32151, etc

See the note in Annex A

4 Requirements and Test Methods

4.1 Marine methanol fuel is categorized into two types, A and B, based on chemical composition. Technical requirements and test methods should comply with the requirements of Table 1.

4.2 Marine methanol fuel should not contain substances that might cause abnormal usage in ships.

4.3 Marine methanol fuel can have additives to improve certain performances and characteristics. However, any additives or chemical wastes that might cause the following effects should not be artificially added:

a) Endangered ship safety or adverse effects on mechanical performance;

b) Harm on human health;

c) Increased air pollution.

TABLE 1 Technical Requirements and Test Methods for Marine Methanol Fuel.

Item	Category		Test Method
	A	B	
Appearance	Transparent liquid, no suspended solids or sediment		Visual Inspection[a]
Methanol content (mass fraction)/% Not less than	99.85	95.00	Annex B

Density (20℃) / (g/cm^3)	0.7910～0.7930	0.7910-0.8020	SH/T 0604[b]
Evaporation residue (mass fraction)/% Not more than	0.001		GB/T 6324.2
Moisture content (mass fraction)/% Not more than	0.15	5.00	GB/T 6283
Acidity (as acetic acid) (mass fraction)/% Not more than	0.003		Annex C
Inorganic chlorine content (as Cl-1)/ (mg/kg) Not more than	0.5		Annex D
Sulfur content/ (mg/kg) Not more than	1.0		SH/T 0689

[a] Pour the sample into a colorimetric tube with a stopper and visually inspect it under daylight or fluorescent light. If there's a discrepancy, the results determined by GB/T 511 shall prevail.

[b] If there's a discrepancy in the results, the determination method stipulated in GB/T 4472 should be followed.

[c] If the moisture content exceeds the limit, it should be discussed with the requesting party and approved by the user.

5 Inspection Rules

5.1 Grouping and Sampling

Under the conditions of unchanged raw materials and processes, the actual batch of continuous product production is considered one grouped batch. However, the time to form an inspection batch from several production batches typically does not exceed one week.

Sampling should be carried out as specified in GB/T 3723, GB/T 6678, and GB/T 6680, taking 3 L of the sample for inspection and retention. The sampling container should not contaminate the sample or pose safety risks.

5.2 Type Test

Type test covers all the items in Table 1. Under normal production conditions, type test should be carried out at least once a year. Type test should also be conducted under the following circumstances:

a) Identification testing for the trial production of new products or transfer production of old products;

b) When there is a significant change in raw materials, processes, etc., that might affect product performance after formal production;

c) When product production has been halted for more than six months and is resumed;

d) When there is a significant discrepancy between the factory inspection results and the last type test results;

e) When the market regulatory authority requests a type test.

5.3 Routine Inspection

Routine inspection items include: appearance, methanol content, density, evaporation residue, moisture, acidity, inorganic chlorine, and sulfur content.

5.4 Determination of Inspection Results

If the type test results meet the corresponding technical requirements in Clause 4, then the batch of products is deemed to have passed the routine inspection.

If the routine inspection results meet the technical requirements of Clause 4, then the batch of products is deemed to have passed the type test.

5.5 Reinspection Rules

If the factory inspection results do not meet the requirements of Clause 4, double the quantity of products should be re-sampled from the same batch as specified in GB/T 3723, GB/T 6678, and GB/T 6680, and a reinspection of the non-conforming items should be conducted. If the reinspection results still don't meet the requirements, the batch of products is deemed non-conforming.

6 Marking, Packaging, Transportation, Storage

Marking, packaging, transportation, and storage of marine methanol fuel should be in accordance with UN Dangerous Goods Number UN 1230, China Dangerous Goods Number 32058, GB 13690, GB 190, and SH 0164. Green marine methanol fuel should also come with a relevant certification report.

7 Safety

7.1 Safety Warning

Marine methanol fuel is a flammable liquid with a flash point of 8°C and an ignition temperature of 436°C. Its explosive limits in air are 6% to 36.5% (volume fraction). Exposure to heat or open flames can lead to intense combustion or explosion. Marine methanol fuel is toxic; methanol vapors can irritate the nervous system. Inhalation can lead to blindness and poisoning.

7.2 Safety Measures

If marine methanol fuel leaks, it should be immediately washed away with water. If ignited, use sand, dry powder, solvent-resistant foam extinguishers, asbestos cloth, etc., for firefighting. Avoid contact with the skin. If splashed onto the skin or into the eyes, rinse immediately with plenty of water and seek medical attention promptly.

If proper precautions are not followed, the product in this document may pose dangers during its production, transportation, loading and unloading, storage, and usage. This document does not intend to address all safety issues related to this product. Users should adopt appropriate safety and precautionary measures and ensure compliance with relevant national regulations.

Annex A

(Informative)

Green Methanol

A.1 Green Methanol

Driven by the global trend of energy system decarbonization and the country's carbon peaking and neutrality policy, green fuel has become the preferred choice for decarbonization in the shipping industry. Green methanol refers to methanol that, throughout its entire life cycle, from raw material acquisition to production and usage, meets national evaluation criteria and requirements for greenhouse gas and pollutant emissions for green products.

A.2 Sources

Green methanol possesses both the intrinsic fuel properties of methanol and the attributes of a green product. Based on the production process, it can be divided into biomass methanol and electro-produced methanol (also known as e-methanol).

A.2.1 Biomass Methanol

Biomass methanol is synthesized from sustainable biomass raw materials through specific processes, including agricultural crop straw, forestry residues, and urban waste. Biomass raw materials are abundant and renewable, significantly reducing greenhouse gas (GHG) emissions. Hence, biomass methanol is also referred to as carbon-reducing methanol.

A.2.2 Electro-produced Methanol

Electro-produced methanol uses carbon captured from the air combined with green hydrogen produced from renewable energy electricity as raw materials. It's synthesized using renewable energy electricity. The carbon dioxide is captured and used to produce methanol, which when burned as fuel releases carbon dioxide. The released carbon dioxide is then recaptured using recycling capture technology and reused to produce methanol. This entire process is green and sustainable, achieving a "zero-carbon" emission throughout its life cycle. Thus, electro-produced methanol is also termed carbon-neutral methanol.

A.3 Carbon Emission Intensity Accounting Standards

Globally, compared to traditional fuels, methanol fuel has the advantages of wide production sources and lower pollutant and carbon emission. Its clean application can effectively address energy security and environmental protection issues. Specifically, green methanol, compared to fossil methanol, possesses more sustainable full-industry-chain development features and

controllable life-cycle carbon emission intensity, significantly supporting China's "dual carbon" long-term goals.

Green methanol produced by different processes has varying levels/degrees of "green attributes". It requires third-party institutions to calculate its entire life cycle's greenhouse gas and pollutant emissions based on specific standards or rules and issue relevant certification reports. Currently, greenhouse gas emission standards and calculation methods can refer to international standards like ISO 14067:2018, PAS 2050:2008, *GHG Protocol Greenhouse Gas Accounting System*, GB/T 32150, and GB/T 32151.

A.4 Policy Regulation

The State Council has put forward a green, low-carbon action plan for transportation, urging the quick establishment of green, low-carbon transportation modes to ensure a reduction in carbon emission intensity in transportation. For details, refer to the *Action Plan for Carbon Dioxide Peaking Before 2030*.

The Ministry of Transport has proposed development goals for green transportation, demanding further reductions in ship energy consumption and carbon emission intensity. Carbon reduction requirements and targets can be found in the *14th Five-Year Plan for Green Transportation*.

The Ministry of Transport mandates the establishment of a monitoring, reporting, and accounting system for greenhouse gas emission reductions in shipping. It also implements a monitoring and regulation pilot project for ship emission control areas. Carbon reduction requirements and targets can be consulted in the 1*4th Five-Year Plan for the Maritime System*.

Annex B

(Normative)

Determination Method for Methanol Content

B.1 Scope

This measurement method specifies the gas chromatography for determining the methanol content and impurity content in marine methanol fuel. Gas chromatography cannot guarantee the detection of all impurity components in marine methanol fuel, especially non-volatile components and components with weak or no detection signals in flame ionization detection.

B.2 Method Summary

Using gas chromatography, under selected working conditions, the sample is vaporized and passed through a capillary chromatographic column, allowing the various components to be separated. It is detected using a hydrogen flame ionization detector. Quantitative correction factors are measured, and the mass fraction of impurity components is calculated based on the internal standard method or the external standard method. Subtracting the mass fractions of impurities and water from 100 gives the mass fraction of methanol.

B.3 Reagents

B.3.1 Ethyl acetate, chromatographically pure, internal standard.

B.3.2 Other applicable internal standards.

B.3.3 Methanol: mass fraction not less than 99.98%, ethanol mass fraction not exceeding 0.001%. If the ethanol content is greater than this amount, it should be subtracted from the baseline.

B.3.4 Hydrogen gas: volume fraction not less than 99.9%, dried and purified through sili ca gel and molecular sieves.

B.3.5 Nitrogen gas: volume fraction not less than 99.9%, dried and purified through sili ca gel and molecular sieves.

B.3.6 Air: dried and purified through silica gel and molecular sieves.

B.4 Instruments

B.4.1 Gas chromatograph: equipped with a flame ionization detector. The overall sensitiv ity and stability of the instrument should comply with the relevant provisions of GB/T 97 22.

B.4.2 Recorder: chromatographic data processor or chromatographic workstation.

B.4.3 Injector: micro-injector, 0.5 μL or 1 μL.

B.4.4 Chromatographic column and typical chromatographic operating conditions.

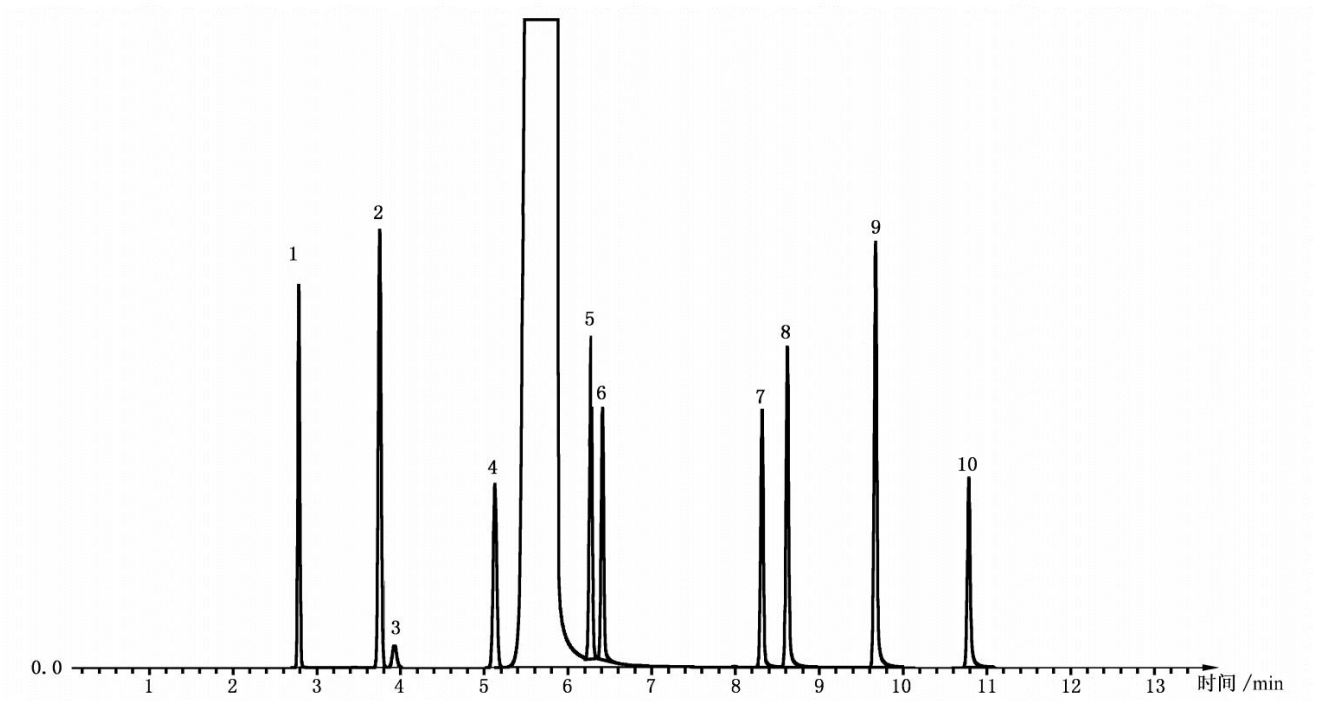
The recommended capillary chromatographic column and typical chromatographic operating conditions, see Table B.1. Typical capillary column chromatograms and methanol sample chromatograms for fuel, see Figure B.1. Other chromatographic columns and operating conditions that achieve equivalent separation can also be used.

Table B.1 Recommended capillary chromatographic column and typical chromatographic operating conditions.

Chromatographic column	**Melted quartz capillary column with PEG-20M as the stationary phase.**
Column length/Column inner diameter/Film thickness	30 m×0.32 mm×0.5 μm
Column temperature	40 ℃ (4 min), 10 ℃/min, 100 ℃ (6 min)
Vaporization chamber temperature/° C	150
Detector temperature/° C	200
Carrier gas (N2) flow rate/(mL/min)	0.7
Air flow rate/(mL/min)	300
Hydrogen flow rate/(mL/min)	30
Split ratio	20:1
Injection volume/μL	0.8

B.5 Analytical Steps

Start the gas chromatograph and adjust the instrument according to the chromatographic operating conditions listed in Table B.1. Once stabilized, prepare for sample analysis. Use the sampler for analysis and process the results with a chromatographic data processor or integrator.



1 - Dimethoxymethane;

2 - Acetone;

3 - Unknown substance;

4 - Ethyl acetate (internal standard);

5 - Isopropanol;

6 - Ethanol;

7 - 2-Butanol;

8 - 1-Propanol;

9 - Isobutanol;

10 - 1-Butanol.

Figure B.1: Typical chromatogram of the prepared sample.

B.6 Quantitative Method

Internal standard method or external standard method.

B.7 Calculation of Results

B.7.1 For the internal standard method:

The mass fraction w_i of impurity components in marine methanol fuel, expressed in %, is calculated according to formula (B.1):

$$w_i = \frac{A_i \times f_i \times m_s}{A_s \times m} \times 100 \cdots\cdots (B.1)$$

Where:

A_i —— Peak area of the measured impurity component;

f_i —— Relative correction factor of the measured impurity component;

m_s—— Mass of the internal standard, in grams (g);

A_s —— Peak area of the internal standard;

m —— Mass of the sample, in grams (g).

B.7.2 For the external standard method:

The mass fraction w_i of impurity components in marine methanol fuel, expressed in %, is calculated according to formula (B.2):

$$w_i = \frac{w_{is} \times A_i}{A_s} \quad \text{(B.2)}$$

Where:

w_{is} —— Mass fraction of component i in the standard sample, expressed in %;

A_i —— Peak area of component i in the sample;

A_s —— Peak area of component i in the standard sample.

B.7.3 Calculation of the mass fraction of marine methanol fuel:

The mass fraction w of marine methanol fuel, expressed in %, is calculated according to formula (B.3):

$$w = 100 - \sum w_i - w_{water} \quad \text{(B.3)}$$

Where:

$\sum w_i$——Sum of the mass fractions of impurity components in the marine methanol fuel;

w_{water} ——The mass fraction of water in marine methanol fuel measured according to the requirements in Table 1.

B.7.4 Allowable Difference

The arithmetic average of two parallel measurements is taken as the reported result. The absolute difference between the two parallel measurements is no more than 20% of the average for impurities and no more than 0.2% for the main component.

Annex C
(Normative)
Determination Method of Acid

C.1 Method Summary

Based on the principle of acid-base neutralization, using phenolphthalein as an indicator, titrate the sample with sodium hydroxide standard titration solution until it turns slightly red and remains so without fading for 30 seconds, which indicates the endpoint.

C.2 Instrument

C.2.1 Conical flask with stopper: 250 mL

C.2.2 Pipette: 50 mL

C.2.3 Alkalimetric burette: 10 mL, with a graduation of 0.05 mL

C.3 Reagents and Solutions

C.3.1 All reagents used in this determination method are analytically pure unless otherwise specified. Water used meets the GB/T 6682 third-level requirements unless otherwise mentioned.

C.3.2 Phenolphthalein test solution: 10 g/L.

C.3.3 Sodium hydroxide standard stock solution: $c(NaOH)$ = 0.1 mol/L。

C.3.4 Sodium hydroxide standard titration solution: $c(NaOH)$ = 0.05 mol/L. When using, accurately dilute the 0.1 mol/L sodium hydroxide standard stock solutionwith water by a factor of 2.

C.4 Procedure

Take 50 mL of water, add it to a 250 mL conical flask, add 0.5 mL of phenolphthalein test indicator, and titrate with 0.05 mol/L sodium hydroxide standard titration solution until the solution turns slightly red and remains so without fading for 30 seconds.

Using a pipette, accurately draw 50.0 mL of the sample and transfer it to a 250 mL conical flask. Titrate with 0.05 mol/L sodium hydroxide standard titration solution

until the solution turns slightly red and remains so without fading for 30 seconds. Record the volume of sodium hydroxide standard titration solution consumed.

C.5 Calculation

The acid content (as acetic acid) w, expressed in %, is calculated according to equation (C.1):

$$w = \frac{V \times c \times 0.12}{\rho} \quad \text{(C.1)}$$

Where:

V —— Volume of sodium hydroxide standard titration solution consumed during titration, in mL;

c —— Concentration of sodium hydroxide titration standard solution, in mol/L;

ρ —— Density of the sample, in g/mL.

The average of two parallel measurements is reported as the result, accurate to 0.0001%. The absolute difference between the two parallel measurements should not exceed 0.0005%.

Annex D

(Normative)

Determination Method of Inorganic Chlorine Content

D.1 Precipitation Titration

D.1.1 Method Summary

In a neutral to slightly alkaline range (pH 6.5 to 10.5), using potassium chromate as an indicator, titrate chloride with silver nitrate. Due to the solubility of silver chloride being smaller than that of silver chromate, chloride ions are precipitated first. The chromate ions react with an excess of silver nitrate and precipitate in the form of silver chromate, producing a brick-red color indicating the titration endpoint. The precipitation titration reactions are:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4\downarrow \ (\text{Brick Red})$$

D.1.2 Reagents

D.1.2.1 All reagents used in this determination method are analytically pure unless otherwise specified. Water used meets the GB/T 6682 third-level requirements unless otherwise mentioned.

D.1.2.2 Sulfuric acid solution: 1+99.

D.1.2.3 Sodium hydroxide solution: 2 g/L.

D.1.2.4 Potassium chromate (K_2CrO_4) solution: 50 g/L. Weigh 5 g of potassium chromate (K_2CrO_4), dissolve in a small amount of water, add silver nitrate solution until a red precipitate is formed. Shake well, let stand for 12 h, filter, and dilute with water to 100 mL.

D.1.2.5 Silver nitrate standard titration solution: c ($AgNO_3$) = 0.01 mol/L。

D.1.2.6 Phenolphthalein indicator solution: Weigh 0.5 g of phenolphthalein, dissolve in 50 mL of ethanol (95%), add 50 mL of water, then add sodium hydroxide solution until it turns slightly pink.

D.1.3 Procedure

D.1.3.1 Sample preparation:

Take 300 mL of the sample in a porcelain evaporating dish, adjust the pH to 8-9 with sodium hydroxide solution, evaporate on a water bath, place in a muffle furnace, and incinerate at 600℃ for 1 h. Cool, soak in 70 mL of water for about 20 minutes, then wash the evaporating dish 3 times with 30 mL of water and transfer quantitatively to a 250 mL conical flask.

D.1.3.2 Measurement

Add a drop of phenolphthalein indicator to the sample solution, and adjust the sample solution to a pink color that just fades using a sulfuric acid solution or sodium hydroxide solution. Add 2 mL of potassium dichromate solution, and titrate with a silver nitrate standard titration solution until a brick-red color just appears, indicating the endpoint.

D.1.3.3 Blank Experiment

During the measurement, follow the same steps as the measurement, but replace the sample with 100 mL of water, and use the same amount of reagent solution for the blank test.

D.1.3.4 Result Calculation

The chloride content w, expressed in mg/kg, is calculated according to formula (D.1):

$$w = \frac{(V_2 - V_1) \times c \times M \times 1\,000}{V \times \rho} \quad \text{(D.1)}$$

Where:

V_1 —— volume of silver nitrate standard titration solution consumed by the blank, in milliliters (mL);

V_2 —— volume of silver nitrate standard titration solution consumed by the sample, in milliliters (mL);

c —— accurate concentration of the silver nitrate standard titration solution, in moles per liter (mol/L);

V —— volume of the sample, in milliliters (mL);

ρ —— density of the sample, in grams per milliliter (g/mL);

M —— molar mass of chlorine, in grams per mole (g/mol) (M=35.45).

The arithmetic mean of two parallel measurement results is taken as the measurement result, and the absolute difference between the two parallel measurement results should not exceed 0.13 mg/kg.

D.2 Potentiometric Titration Method (Arbitration Method)

D.2.1 Method Summary

Using a glass electrode as the reference electrode and a silver electrode as the indicator electrode, titrate the chloride ions in the sample with a silver nitrate standard titration solution. Determine the titration endpoint based on the potential jump point (second derivative method). Calculate the chloride ion content in the sample based on the amount of silver nitrate standard titration solution consumed.

D.2.2 Analysis Steps

Instruments and equipment, reagents and solutions, operating steps, and result calculations follow the first method in Appendix C of GB 18350-2013.

The arithmetic mean of two parallel measurement results is taken as the measurement result, and the difference between the two parallel measurement results should not exceed 0.13 mg/kg.

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