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## Anhydrous Hydrogen Fluoride for Industrial Use

工业无水氟化氢

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**Standardization Administration of the People's Republic of China.**

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# Anhydrous Hydrogen Fluoride for Industrial Use

**WARNING: in accordance with the provisions of Chapter 6 in GB 12268-2012, this product belongs to Category 8 corrosive substances, and the secondary hazard is Category 6 Item 6.1 toxic substances. Be careful during operation! If it splashes on your skin or eyes, immediately rinse with water. In severe cases, immediately seek medical advice. Personnel adopting this document shall have practical experience in formal laboratory work. This document does not identify all possible safety issues. Users are responsible for taking appropriate safety and health measures and ensuring the compliance with the conditions stipulated in relevant national regulations.**

## 1 Scope

This document specifies the requirements, test methods, inspection rules, markings, accompanying documents, packaging, transportation and storage of anhydrous hydrogen fluoride for industrial use.

This document is applicable to anhydrous hydrogen fluoride for industrial use.

**NOTE:** this product is mainly used as the raw material for preparing electronic grade hydrofluoric acid, fluorinating agents, fluorohaloalkane, reagent hydrofluoric acid and other fluorine-containing products, etc.

## 2 Normative References

The contents of the following documents constitute indispensable clauses of this document through the normative references in the text. 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 190 Packing Symbol of Dangerous Goods

GB/T 6682-2008 Water for Analytical Laboratory Use - Specification and Test Methods

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

HG/T 3696.1 Inorganic Chemicals for Industrial Use - Preparations of Standard and Reagent Solutions for Chemical Analysis - Part 1: Preparations of Standard Volumetric Solutions

HG/T 3696.2 Inorganic Chemicals for Industrial Use - Preparations of Standard and Reagent Solutions for Chemical Analysis - Part 2: Preparations of Standard Solutions for Impurity

HG/T 3696.3 Inorganic Chemicals for Industrial Use - Preparations of Standard and Reagent Solutions for Chemical Analysis - Part 3: Preparations of Reagent Solutions

1---specimen entrance;

2---plastic welding support;

$3_1$, $3_2$---plastic welding fixed platinum electrodes;

4---plastic welding specimen outlet capillary;

5---thermometer (or temperature sensor) equipped with polyethylene sleeve.

**Figure 1 -- U-shaped Structure Conductivity Cell**

**6.5.3.2** Conductivity meter: measurement range: 0 μs/cm ~ 100,000 μs/cm.

**6.5.3.3** Polyethylene bottle: with a volume of 500 mL, with gas-liquid phase pipe.

**6.5.3.4** Thermometer or temperature sensor, which shall comply with the following requirements.

a) Thermometer: with a division value of 0.1 °C, and a measurement range of 0 °C ~ 50 °C. When in use, install it in the polyethylene sleeve.

b) Temperature sensor: with a display resolution of 0.1 °C, a measurement range of 0 °C ~ 60 °C, a measurement accuracy of not lower than ± 1 °C, and with automatic temperature compensation function. When in use, install it in the polyethylene sleeve.

**6.5.3.5** Injection needle: No.4 or No.5 medical needle.

**6.5.4 Determination of conductivity cell constant**

Use a dry hot air flow to blow the conductivity cell to make it completely dry, inject the potassium chloride standard solution of the required concentration (rinse 2 ~ 3 times first), then, connect the conductivity cell electrode to the conductivity meter, insert a thermometer (or temperature sensor) into the upper port of the conductivity cell, and meanwhile, measure the conductivity value and temperature of the solution in the conductivity cell. Repeat the measurement for over 5 times and take the average value of the measurement as the conductivity value and temperature of the potassium chloride standard solution. In addition, from Table 2, obtain the conductivity of the potassium chloride standard solution at the above temperature.

6, 7---determination wires;

8---waste acid collection bottle for pipeline system flushing;

9---conductivity meter;

10---thermometer with polyethylene sleeve.

**Figure 2 -- Schematic Diagram of Moisture Determination Device by Conductivity Method**

Take the arithmetic mean of the parallel determination results as the determination result. The absolute difference between the two parallel determination results shall not be greater than 0.0006% for superior products, not greater than 0.001% for first-class products, and not greater than 0.0015% for qualified products.

## 6.6 Determination of Fluorosilicic Acid Content

### 6.6.1 Principle

Use sodium chloride to react with fluorosilicic acid in the specimen to generate non-volatile salt and evaporate to remove the hydrogen fluoride. In a weakly acidic medium, add an appropriate amount of boric acid to suppress the interference of fluorine, add ammonium molybdate to react with silicate to generate silicon-molybdenum heteropoly acid (yellow), then, add sulfuric acid solution and oxalic acid solution to eliminate the interference of phosphate. Selectively reduce silicon-molybdenum heteropoly acid to silicon-molybdenum blue, at a wavelength of 815 nm, measure the absorbance of the blue complex.

### 6.6.2 Reagents or materials

**6.6.2.1** Sodium chloride solution: 10 g/L.

**6.6.2.2** Sulfuric acid solution: 1 + 3.

**6.6.2.3** Hydrochloric acid solution: 1 + 5.

**6.6.2.4** Boric acid solution: 40 g/L.

**6.6.2.5** Oxalic acid solution: 100 g/L.

**6.6.2.6** Ammonium molybdate solution: 100 g/L (when the solution precipitates, re-preparation is required).

**6.6.2.7** Ascorbic acid solution: 10 g/L. The usage period is 10 days.

**6.6.2.8** Fluorosilicic acid standard solution: 1 mL of solution contains 1.000 mg of fluorosilicic acid ($H_2SiF_6$). Weigh-take 0.417 g of silica that has been burned at 1,000 °C to a constant mass, place it in a platinum crucible, add 5 g of anhydrous sodium carbonate, and thoroughly mix it. Place it in a high-temperature furnace of 1,000 °C to slowly melt it, then, leave it to cool. Add

hot water to dissolve it, after cooling, transfer it all into a 1,000 mL volumetric flask; use water to dilute to the scale and shake it well. Immediately transfer it to a polyethylene bottle. The usage period does not exceed 30 days.

**6.6.2.9** Fluorosilicic acid standard working solution: 1 mL of solution contains 0.020 mg of fluorosilicic acid ($H_2SiF_6$). Transfer-take 2 mL of fluorosilicic acid standard solution (see 6.6.2.8), place it in a 100 mL volumetric flask; use water to dilute to the scale and shake it well. Prepare this solution right before use.

**6.6.3 Instruments and equipment**

**6.6.3.1** Spectrophotometer: equipped with a 2 cm or 3 cm cuvette.

**6.6.3.2** Platinum dish: with a volume of approximately 100 mL.

**6.6.4 Test steps**

**6.6.4.1 Drawing of working curve**

In a series of 100 mL volumetric flasks, respectively add 0.00 mL, 1.00 mL, 2.00 mL, 4.00 mL, 6.00 mL and 8.00 mL of fluorosilicic acid standard working solution (6.6.2.9), add water to approximately 10 mL, add 4 mL of sodium chloride solution. While stirring, add 5 mL of hydrochloric acid solution and 35 mL of boric acid solution, and leave it for 5 minutes. Add 10 mL of ammonium molybdate solution, shake it well, and leave it for 15 minutes. While stirring, respectively add 5 mL of oxalic acid solution and 20 mL of sulfuric acid solution, shake it well, then, add 2 mL of ascorbic acid solution; use water to dilute to the scale, shake it well, and leave it for 20 minutes.

Adjust the wavelength of the spectrophotometer to 815 nm, use a 2 cm (or 3 cm) cuvette, and use water as a reference to determine the absorbance of each standard solution.

Subtract the absorbance of the reagent blank solution from the absorbance of each standard solution, with the mass (mg) of fluorosilicic acid as the *x*-coordinate and the corresponding absorbance as the *y*-coordinate to draw the working curve.

**6.6.4.2 Test**

Add 5 mL of sodium chloride solution to the platinum dish, weigh it, accurate to 0.01 g. Add 1 g ~ 10 g (including about 0.5 g ~ 2 g of specimen) of laboratory sample (see 6.2), re-weigh it, accurate to 0.01 g, and calculate the mass of the laboratory sample taken. Place it on a water bath and evaporate it to dryness, add 10 mL of water and 35 mL of boric acid solution, and leave it for 5 minutes. Add 4 mL of hydrochloric acid solution and 10 mL of ammonium molybdate solution, mix it well; transfer all the solution into a 100 mL volumetric flask, shake it well and leave it for 15 minutes. While stirring, respectively add 5 mL of oxalic acid solution and 20 mL of sulfuric acid solution, shake it well, then, add 2 mL of ascorbic acid solution; use water to dilute to the scale, shake it well and leave it for 20 minutes. This solution is the test solution.

**6.7.2.3** Sodium thiosulfate standard titration solution: $c(Na_2S_2O_3) \approx 0.01$ mol/L. Use a pipette to transfer-take 100 mL of $c(Na_2S_2O_3) \approx 0.1$ mol/L standard titration solution prepared in accordance with HG/T 3696.1, dilute it to 1,000 mL and shake it well. Prepare this solution right before use.

**6.7.2.4** Starch indicator solution: 10 g/L (when the solution appears turbid, re-preparation is required).

**6.7.3 Instruments and equipment**

**6.7.3.1** Micro-burette: with a division value of 0.02 mL.

**6.7.3.2** Polyethylene beaker with a lid.

**6.7.4 Test steps**

Take 70 mL ~ 100 mL of water and place it in the polyethylene beaker with a lid, accurately add 5.00 mL of iodine standard titration solution (if the solution is colorless after addition, you may add more), add 1 mL of potassium iodide solution, and weigh it, accurate to 0.1 g. Add about 10 g ~ 30 g of laboratory sample (see 6.2), re-weigh it, accurate to 0.1 g, and calculate the mass of the laboratory sample taken, and leave it for 5 minutes. Place the sodium thiosulfate standard titration solution into a micro-burette, use sodium thiosulfate standard titration solution to titrate it, until the solution turns light yellow, add 1 mL of starch indicator solution, and continue titrating, until the blue color disappears.

Meanwhile, carry out a blank test in the same manner. Except that no laboratory sample is added, other operations, and the type and amount of reagent added (except the standard titration solution) are the same as the determination test.

**6.7.5 Test data processing**

The content of sulfur dioxide shall be calculated as the mass fraction $w_4$ of sulfur dioxide ($SO_2$) and in accordance with Formula (5):

$$w_4 = \frac{[(V_0 - V_1)/1\ 000]cM}{w_1 m} \times 100\% \qquad \cdots\cdots(5)$$

Where,

$V_0$---the volume of sodium thiosulfate standard titration solution consumed by titrating the blank solution, expressed in (mL);

$V_1$---the volume of sodium thiosulfate standard titration solution consumed by titrating the test solution, expressed in (mL);

$c$---the accurate value of the concentration of the sodium thiosulfate standard titration solution, expressed in (mol/L);

$M$---the value of the molar mass of sulfur dioxide ($1/2SO_2$), expressed in (g/mol) ($M$ = 32.03);

$w_1$---the mass fraction of hydrogen fluoride in the laboratory sample, expressed in (%);

$m$---the mass of the laboratory sample, expressed in (g).

Take the arithmetic mean of the parallel determination results as the determination result. The absolute difference between the two parallel determination results shall not be greater than 0.0006% for superior products, and not greater than 0.001% for first-class products and qualified products.

## 6.8 Determination of Non-volatile Acid Content

### 6.8.1 Principle

After removing the volatile acid through evaporation, take phenolphthalein as an indicator, and use sodium hydroxide standard titration solution to titrate the non-volatile acid.

### 6.8.2 Reagents or materials

**6.8.2.1** Sodium hydroxide standard titration solution: $c$(NaOH) ≈ 0.01 mol/L. Take 100 mL of $c$(NaOH) ≈ 0.1 mol/L standard titration solution prepared in accordance with HG/T 3696.1, use carbon dioxide-free water to dilute it to 1,000 mL and shake it well. Prepare this solution right before use.

**6.8.2.2** Phenolphthalein indicator solution: 10 g/L. Weigh-take about 1 g of phenolphthalein, add 100 mL of 95% ethanol, stir until it dissolves. Dropwise add the sodium hydroxide standard titration solution, until the solution appears light pink.

**6.8.2.3** Carbon dioxide-free water.

### 6.8.3 Instruments and equipment

**6.8.3.1** Platinum dish: with a volume of approximately 150 mL.

**6.8.3.2** Micro-burette: with a division value of 0.02 mL.

### 6.8.4 Test procedures

Weigh-take 20 g ~ 50 g of laboratory sample (see 6.2), accurate to 0.1 g, place it in a platinum dish, and evaporate it to nearly dryness on a boiling water bath in a fume hood. Add 5 mL of water and evaporate to dryness (repeat twice). Add about 10 mL of carbon dioxide-free water to the platinum dish and add 3 drops of phenolphthalein indicator solution. Place the sodium hydroxide standard titration solution in a micro-burette and use the sodium hydroxide standard titration solution to titrate it, until it turns light pink.

### 6.8.5 Test data processing

The content of non-volatile acid shall be calculated as the mass fraction $w_5$ of sulfuric acid

# 8 Markings and Accompanying Documents

**8.1** The packaging containers for anhydrous hydrogen fluoride for industrial use shall have firm and clear markings, which shall include the product name, the "toxic substances" and "corrosive substances" markings and safety labels in GB 190; the content should include the manufacturer's name and address, serial No. of this document and emergency phone number.

**8.2** Each batch of products exiting the factory shall be accompanied by a quality certificate, which shall include the manufacturer's name, product name, factory address, grade, net content, batch No. (or production date), a proof that the product quality complies with this document, and serial No. of this document.

# 9 Packaging, Transportation and Storage

**9.1** Anhydrous hydrogen fluoride for industrial use shall be packed in clean and dry special-purpose tankers or steel cylinders. The packaging container shall have gas-liquid phase inlet and outlet, and the filling factor shall be not greater than 0.83 kg/L. The steel cylinder shall be painted gray, printed with black characters and equipped with a safety helmet and anti-shock rubber ring.

**9.2** During the transportation of anhydrous hydrogen fluoride for industrial use, it shall be ensured that the container does not leak, collapse, fall or be damaged. It shall not be mixed and transported together with alkali, active metal powder and glass products, etc. During transportation, the transport vehicle shall be equipped with emergency treatment equipment in case of leakage. During transportation, high temperature shall be protected. During highway transportation, follow the prescribed route and shall not stop in residential areas or densely populated areas.

**9.3** The steel cylinders of anhydrous hydrogen fluoride for industrial use shall be stored in sheds or warehouses, and they shall not be mixed with flammable and explosive items.

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