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YS

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**Chemical analysis methods and physical properties of cryolite -
Part 3: Determination of fluoride content by distillation-thorium
nitrate titration**

冰晶石化学分析方法和物理性能测定方法 第3部分：氟含量的测定

(English Translation)

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1 Scope

This Part specifies the method for determination of chlorine content in cryolite.

This Part is applicable to the determination of chlorine content in cryolite. The determination range is: 40.00% ~ 60.00%.

The "Distillation - Thorium nitrate titration method" is the arbitration method.

2.1 Summary of methods

Dissolve the sample with sodium carbonate. Separate the chlorine, through sulfuric acid (or perchloric acid)-steam distillation. Use sodium alizarin sulfonate-methylene blue as the indicator. Use thorium nitrate solution for titration, to calculate the fluorine content in the sample.

2.2 Reagents

Unless otherwise stated, only reagents and deionized water determined to be of analytical grade are used in the analysis.

2.2.1

Anhydrous sodium carbonate, superior grade pure.

2.2.2

Perchloric acid ($\rho \sim 1.60$ g/mL).

2.2.3

Hydrochloric acid (1 + 199).

2.2.4

Sodium hydroxide solution (20 g/L).

2.2.5

Sulfuric acid (2 + 1).

2.2.6 Buffer solution (pH value 2.7): Weigh 9.45 g of monochloroacetic acid. Dissolve

in 50 mL of sodium hydroxide (1 mol/L). Use water to dilute it to 100 mL. Mix well.

2.2.7 Thorium nitrate standard titration solution:

- Preparation: Weigh 4.5 g of thorium nitrate tetrahydrate $[\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}]$. Use water to dissolve it. Dilute it to 1 L. Mix well.
- Calibration: Weigh 0.2800 g of anhydrous sodium chloride (preliminarily burned at 600 °C and cooled to room temperature in a desiccator). Use 20 mL ~ 30 mL of water, to transfer it into a distillation flask. Follow analysis steps 2.5.4.3 ~ 2.5.4.4 to calibrate the thorium nitrate standard titration solution. At the same time, conduct blank test.
- The titer f of thorium nitrate standard titration solution to fluorine is calculated, according to formula (1):

Where:

m_1 - Weighing amount of sodium chloride, in milligrams (mg);

0.4525 - Coefficient for converting sodium chloride into fluorine;

V_1 - The volume of thorium nitrate standard titration solution, which is consumed during calibration, in milliliters (mL);

V_2 - The volume of the thorium nitrate standard titration solution, which is consumed during the blank test, in milliliters (mL).

2.2.8 Alizarin sodium sulfonate solution (0.5 g/L).

2.2.9 Methylene blue solution (0.5 g/L).

2.3 Instruments and equipment

2.3.1

Platinum crucible

Upper diameter 30 mm, lower diameter 15 mm, height 30 mm, with lid.

2.3.2

High temperature furnace

The temperature can be controlled at $800\text{ }^{\circ}\text{C} \pm 20\text{ }^{\circ}\text{C}$.

2.3.3

Water steam generator

A flask, which has a volume of 3 L; three glass tubes with an inner diameter of 6 mm are inserted into the stopper, as follows:

- Hyperbolic conduit: Used to introduce vapor into the distillation flask;
- Vapor adjustment tube: The exposed end is covered with a rubber tube with a spring clip;
- Safety tube: The length is 1 m.

2.3.4 Distiller: Blown with boric acid glass, ground joints, composed of the following

2.3.6 pH meter: It is equipped with glass electrode.

2.3.7 Silica glass conical beaker: The capacity is 250 mL.

2.4 Specimen

The sample is ground and mixed, to make it through a $75\text{ }\mu\text{m}$ standard sieve. Bake it in an oven, at $110\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$ for 2 hours. Cool it to room temperature, in a desiccator.

2.5.1 Sample

Weigh 0.25 g of specimen (2.4), accurate to 0.0001 g.

2.5.2 Parallel test

Do two tests in parallel. Take the average value.

2.5.3 Blank test

Conduct a blank test, along with the sample.

2.5.4.1 Weigh 2.5 g of anhydrous sodium carbonate (2.2.1). Place it in a platinum

crucible (2.3.1). Add the sample (2.5.1). Mix evenly. Cover with platinum lid.

2.5.4.2 Place the platinum crucible (2.5.4.1) into the high-temperature furnace (2.3.2), which was preheated to $200\text{ }^{\circ}\text{C}$. Raise the temperature to $800\text{ }^{\circ}\text{C} \pm 20\text{ }^{\circ}\text{C}$. Melt it for 20 minutes. Take it out. Place the bottom of the platinum crucible into cold water to quickly cool it. Move the melt directly into a distillation flask, which contains several glass balls (diameter

2 mm ~ 3 mm).

2.5.4.3 Place a 500 mL volumetric flask under the serpentine condenser, to collect the distilled solution. Connect the distillation flask and the serpentine condenser. Pass the cooling water through. Cover the distillation flask. Add 50 mL of sulfuric acid (2.2.5) or 30 mL of perchloric acid (2.2.2), through the dropping funnel. At the same time, heat the steam generator, which contains two thirds of water and a few small pieces of pumice. Open the steam adjustment tube, before the water boils. Use an electric heater, to heat the distillation flask to 150 °C. Use the spring clamp on the steam adjustment tube, to adjust the steam flow to 250 g/h ~ 300 g/h. Keep the solution temperature in the distillation flask at 150 °C ± 1 °C. Collect 400 mL distillate in about 90 minutes.

Then stop distilling. Use water to rinse the condenser. Dilute the collected solution to the mark. Mix well.

2.5.4.4 Pipette 50.00 mL of the distilled solution into the beaker (2.3.7). Add 0.5 mL of alizarin sodium sulfonate solution (2.2.8). Dropwise add the sodium hydroxide solution

3.2 Reagents

Unless otherwise stated, only reagents determined to be of analytical grade and water of distilled or equivalent purity are used in the analysis.

3.2.1

Anhydrous sodium potassium carbonate.

3.2.2

Quartz sand.

3.2.3

Nitric acid ($\rho = 1.42 \text{ g/mL}$).

3.2.4

Nitric acid (1 + 3).

3.2.5

Nitric acid (2 mol/L).

3.2.6

Glacial acetic acid ($\rho = 1.05 \text{ g/mL}$).

3.2.7

Sodium nitrosoferrocyanide solution (100 g/L).