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Comparative Analysis of Two National Standard Methods for Chloride Ions in Flue Gas Desulfurization Gypsum

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Abstract

This study addresses the significant discrepancy in results when determining chloride ion content in flue gas desulfurization (FGD) gypsum using two different national standard methods: GB/T 5484-2024 "Chemical Analysis Methods for Gypsum" and GB/T 176-2017 "Chemical Analysis Methods for Cement." A comparative analysis of the two standard methods was conducted. Results show that compared to silver nitrate titration, the ion chromatography method demonstrated relative standard deviations of 0-5.56% across three samples, produced results closer to the true values when testing standard samples, and exhibited higher accuracy, making it more suitable for determining chloride content in low-concentration gypsum samples. Method validation revealed a detection limit of 0.0002% for chloride ions, precision of 9.1%, and spike recovery rates between 84.5% and 98.5%. This method's low detection limit and high accuracy provide valuable reference for frontline testing applications.

Keywords

Coal-fired Power Plants; FGD Gypsum; Chloride Ion; Silver Nitrate Titration; Ion Chromatography.

1. Introduction

Following the implementation of the "Emission Standard of Air Pollutants for Thermal Power Plants" (GB 13223-2011), China's thermal power industry has gradually completed ultra-low emission retrofits[1]. Among the various technologies employed, limestone-gypsum flue gas desulfurization (FGD) has been widely adopted by domestic coal-fired power plants due to its high desulfurization efficiency, broad coal adaptability, and economic advantages[2-3]. This technology uses limestone as an absorbent to chemically react with SO_2 in coal combustion flue gas, removing SO_2 while simultaneously producing large quantities of FGD gypsum as a byproduct. In China, FGD gypsum is primarily utilized in building materials and cement industries. The chloride ion content in gypsum significantly affects its dehydration performance, strength, water resistance, and adhesive properties, making it a crucial parameter for evaluating FGD gypsum quality. The quality of FGD gypsum directly relates to its utilization rate, and the national standard GB/T 37785-2019 specifically stipulates that chloride ion content in tertiary gypsum should be controlled within 600 mg/kg to ensure the safety of gypsum products used as building materials[4]. Therefore, accurate measurement of chloride ion content in FGD gypsum can effectively guide production, improve gypsum yield and comprehensive utilization rate, and prevent resource waste and ecological environmental impacts caused by large-scale stockpiling.

Currently, the main methods for measuring chloride ion content in FGD slurry and gypsum include silver nitrate titration, automatic potentiometric titration, ion chromatography, and mercuric thiocyanate colorimetry[5]. Silver nitrate titration, the recommended method in GB/T 5484-2024 "Chemical Analysis Methods for Gypsum," is widely applied due to its simple manual titration operation. However, in routine testing work, accurately determining the titration endpoint color ("the first appearance of brick-red precipitate") is challenging, often leading to over or under titration and consequent experimental errors[6-8]. Mercuric thiocyanate colorimetry and automatic potentiometric titration have limited detection ranges suitable for trace chloride ion measurement, involve complex operational procedures, and require longer detection times. Ion chromatography, recommended in GB/T 176-2017 "Chemical Analysis Methods for Cement" for chloride ion content determination, has been widely adopted by professionals in related fields[9].

Accurate measurement of chloride ion content in FGD slurry and gypsum is of significant importance for the stable and safe operation of desulfurization systems. Based on this research background, this paper employs two widely used methods—silver nitrate titration and ion chromatography-to measure chloride ions in FGD gypsum, thoroughly comparing their principles and differences to standardize methodology, reduce experimental errors, and ultimately improve the accuracy of chloride ion content detection in FGD gypsum.

2. Experimental Section

2.1 Method Overview

2.1.1 Silver Nitrate Titration Method

The measurement principle of silver nitrate titration involves grinding and sieving gypsum samples after determining attached water content, dissolving them in water, and filtering. A specific volume of filtrate is taken, and chromate indicator is added to the neutral or weakly alkaline test solution, which is then titrated with standard silver nitrate solution. Silver chloride, a white precipitate with relatively low solubility, precipitates first. After complete precipitation of chloride ions in the solution, silver nitrate reacts with the chromate indicator to form brick-red silver chromate precipitate, changing the test solution from yellow to slightly brick-red, indicating the endpoint. The chloride ion content in gypsum can be calculated using the volume and concentration of standard silver nitrate solution consumed[10]. The calculation formula is as follows:

$$w(\mathrm{Cl^-}) = \frac{(V_1 - V_0) \times 4}{m_1 \times 1000} \times c(\mathrm{AgNO_3}) \times 35.45 \times 100\%$$

Where, w(Cl-) is the water-soluble chloride ion content (mass fraction), %.c(AgNO3) is the concentration of standard silver nitrate titration solution, mol/L.V1 is the volume of standard silver nitrate titration solution consumed during titration, mL.V0 is the volume of standard silver nitrate titration solution consumed during blank titration, mL.m1 is Sample mass, g.4 is the volume ratio of total sample solution to aliquot taken.35.45 is Molar mass of Cl, g/mol.

2.1.2 Ion Chromatography

The measurement principle of ion chromatography involves dissolving the sample with nitric acid, then introducing the solution into an ion chromatography column with ion exchange resin as the stationary phase. Using an appropriate eluent, chloride ions are separated based on their different affinities with the resin. When flowing through a self-regenerating electrolytic suppressor, the background conductivity of the eluent is eliminated, enhancing the conductivity response of the target ions. Finally, the chloride ion concentration is determined by measuring changes in conductivity using a conductivity detector[11]. The calculation formula is as follows:

$$w(\mathrm{Cl^-}) = \frac{c_2 \times 100}{m_2 \times 1000} \times 100\%$$

Where, w(Cl-) represent the water-soluble chloride ion content (mass fraction), %.c_2: chloride ion concentration in the test solution after blank correction, mg/mL.m_2 is the Sample mass, g.100 is the sample volume, mL.

2.2 Instruments and Reagents.

Experimental instruments included analytical balance, drying oven, grinder, standard sieve, magnetic stirrer, beakers, conical flasks, measuring cylinders, funnels, funnel stands, stirring rods, filter paper, pipettes, brown acid burettes, wash bottles, ion chromatograph, ultrasonic cleaner (Model 2500TH, reaction temperature 25°C, ultrasonic power 100W), etc.

Reagents included FGD gypsum samples, standard samples (batch number: 201850), deionized water, standard silver nitrate solution (0.01001 mol/L), standard chloride ion solution (0.02 mol/L), potassium chromate indicator (50 g/L), phenolphthalein indicator (10 g/L), nitric acid (0.1 mol/L), and sodium hydroxide (0.1 mol/L).

2.3 Experimental Methods

Sample preparation: FGD gypsum samples collected from the field were dried in an oven at 45°C for 4 hours, crushed, and sieved. Approximately 10 g of sample (accurate to 0.0001 g) was placed in a 250 mL dry ground-glass stoppered conical flask, and 200 mL of CO2-free distilled water was added.

(1) Silver nitrate titration method (Method 1): The sample was placed on a magnetic stirrer with a stirring rod, stirred for 30 minutes, and allowed to settle for 5 minutes. The mixture was filtered using dry rapid filter paper. 50.00 mL of filtrate was transferred to a 250 mL conical flask, 1-2 drops of phenolphthalein indicator solution were added, and 0.1 mol/L sodium hydroxide was used to adjust the solution until it turned red. Nitric acid was then added to just decolorize the red color. After adding 10 drops of potassium chromate indicator, the solution was titrated with standard silver nitrate solution, and the consumed volume was recorded. A blank experiment was conducted simultaneously[10].

(2) Ion chromatography method (Method 2): The sample was placed in an ultrasonic cleaner for 10 minutes, transferred to a 250 mL volumetric flask, filled to the mark, and mixed well. The mixture was filtered using dry rapid filter paper. 5.00 mL of filtrate was placed in a 50 mL volumetric flask, 5.00 mL of 0.1 mol/L potassium hydroxide solution was added, filled to the mark, and mixed well. This solution was filtered through a Ba column and a 0.22 μm membrane filter, and the filtrate was directly analyzed using an ion chromatograph. The blank solution was prepared following the same procedure without adding the sample[11].

(3) When measuring standard samples, the main steps were consistent with Methods 1 and 2, with the primary difference being that the standard sample mass was 1 g (accurate to 0.0001 g).

3. Results and Analysis

3.1 Comparison of FGD Gypsum Sample Test Results

Seven replicate tests were conducted on FGD gypsum samples using both methods. The chloride ion content in gypsum was calculated on a dry basis, and the standard deviation and relative standard deviation of the test values were calculated. Results were rounded to three decimal places, as shown in Table 1.

Table 1 shows that the relative standard deviations of chloride ion content measured by both ion chromatography and silver nitrate titration methods for the three gypsum samples were all within 10%. Compared to silver nitrate titration, ion chromatography demonstrated relative standard deviations of 5.56%, 0%, and 0% for the three samples. The lower the chloride ion content in the gypsum sample, the lower the relative standard deviation of ion chromatography detection, and the closer the results were to the true values, which is consistent with the research findings of Guo Yali et al[5]. The silver nitrate titration method showed relative standard deviations of 4.76%, 7.69%, and 5.26% for the three samples, with errors occurring during the detection process.

Table 1. Mass fraction of desulfurization gypsum samples by the two test methods

Test Method	Test Sample	Test Values							Mean	Standard Deviation	Relative Standard Deviation
		1	2	3	4	5	6	7			
Method 1	FGD Gypsum 1	0.021	0.020	0.022	0.021	0.020	0.021	0.021	0.021	0.001	4.76
	FGD Gypsum 2	0.013	0.014	0.014	0.013	0.013	0.013	0.013	0.013	0.001	7.69
	FGD Gypsum 3	0.018	0.019	0.019	0.018	0.019	0.019	0.019	0.019	0.001	5.26
Method 2	FGD Gypsum 1	0.019	0.018	0.019	0.019	0.019	0.019	0.019	0.018	0.001	5.56
	FGD Gypsum 2	0.013	0.013	0.013	0.013	0.013	0.013	0.013	0.013	0	0
	FGD Gypsum 3	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0.018	0	0

3.2 Comparison of Standard Sample Test Results

Seven replicate tests were conducted on standard samples using both methods. The chloride ion content in the standard samples was calculated on a dry basis, and the standard deviation and relative standard deviation of the test values were calculated. Results were rounded to three decimal places, as shown in Table 2.

Table 2. Mass fraction of standard samples by the two test methods

Test Method	Test Sample	Test Values							True Value	Standard Deviation	Relative Standard Deviation
		1	2	3	4	5	6	7			
Method 1	Standard Sample 1	0.150	0.148	0.152	0.151	0.150	0.149	0.151	0.16±0.02	0.150	0.002
	Standard Sample 2	0.030	0.030	0.033	0.032	0.030	0.031	0.030	0.01±0.002	0.031	0.003
Method 2	Standard Sample 1	0.150	0.150	0.151	0.150	0.150	0.149	0.150	0.16±0.02	0.150	0.001
	Standard Sample 2	0.010	0.011	0.011	0.010	0.011	0.011	0.010	0.01±0.002	0.011	0.001

Table 2 shows that both ion chromatography and silver nitrate titration methods produced results within the true value range when measuring high-concentration samples (Standard Sample 1), meeting the requirements of the standard certificate. However, when measuring low-concentration samples (Standard Sample 2), the silver nitrate titration method yielded an average value of 0.031, significantly higher than the true value of the standard sample. In contrast, the ion chromatography method produced results very close to the true value of the standard sample, demonstrating excellent accuracy.

3.3 Method Validation

Based on the test results of chloride ion content in FGD gypsum samples and standard samples using the two methods in Sections 2.1 and 2.2, ion chromatography showed superior accuracy to silver nitrate titration when determining low-concentration gypsum samples. Therefore, this paper further investigated the accuracy of ion chromatography measurements through comparative experiments with standard samples.

3.3.1 Linearity and Method Detection Limit

A series of chloride ion standard solutions with different mass concentrations were prepared and their concentrations were measured using ion chromatography. Analysis showed that the correlation coefficient of the chloride ion standard solution calibration curve could reach above 0.999. Blank solutions were prepared following the same procedure as the samples but without adding any sample. The chloride ion concentration was measured 10 times using ion chromatography, and the detection limit was calculated to be 0.0002%.

3.3.2 Accuracy Test Results

The chloride ion content in the filtrate of Standard Sample 2 after pretreatment was 0.011%. After adding 10.00 mL of chloride ion standard solution (0.02 mol/L) and analyzing with ion chromatography, the seven spike recovery rates were all between 84.5% and 98.5%, as shown in Table 3.

Table 3. Spike recovery rates of chloride ion content in standard samples by ion chromatography

Test Sample	true value	Spike Value (g)	Test Value (%)	Recovery Rate (%)
Standard Sample 2	0.01±0.002	0	0.011	
Standard Sample 2 with spike	0.01±0.002	0.0071	0.018	98.5
Standard Sample 2 with spike	0.01±0.002	0.0071	0.017	84.5
Standard Sample 2 with spike	0.01±0.002	0.0071	0.017	84.5
Standard Sample 2 with spike	0.01±0.002	0.0071	0.017	84.5
Standard Sample 2 with spike	0.01±0.002	0.0071	0.018	98.5
Standard Sample 2 with spike	0.01±0.002	0.0071	0.017	84.5
Standard Sample 2 with spike	0.01±0.002	0.0071	0.018	98.5

3.3.3 Precision Test Results

The filtrate of Standard Sample 2 after pretreatment was measured seven times using ion chromatography. The relative standard deviation of the chloride ion mass fraction in the seven replicate experiments was 9.1%.

4. Conclusion

(1) This paper compared and analyzed two national standard methods-silver nitrate titration and ion chromatography-for determining chloride ion content in FGD gypsum. Results showed that the relative standard deviations of chloride ion content measured by both methods for the three gypsum samples were all within 10%. Compared to silver nitrate titration, ion chromatography demonstrated relative standard deviations of 0-5.56% for the three samples, produced results closer to the true values when testing standard samples, exhibited higher accuracy, and was more suitable for determining chloride content in low-concentration gypsum samples.

(2) When measuring with ion chromatography, the correlation coefficient of the chloride ion standard curve reached above 0.999. Analysis of sample blanks yielded a method detection limit of 0.0002% for chloride ions. Spike recovery analysis of Standard Sample 2 showed recovery rates between 84.5% and 98.5% across seven replicates. The relative standard deviation of chloride ion mass fraction in repeated experiments was 9.1%. The method validation results comply with the requirements of GB/T 27417-2017 "Conformity assessment-Guidelines for confirmation and validation of chemical analysis methods." This method offers advantages of high sensitivity, low detection limit, and rapid and efficient operation for detecting chloride ion content in FGD gypsum products, making it applicable for frontline testing in gypsum product research and analysis.

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