Determining fluoride ions in ammonium desulfurization slurry using an ion selective electrode method

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Abstract. Determining fluoride ions in ammonia desulphurization slurry using a fluoride ion selective electrode (ISE) is investigated. The influence of pH was studied and the appropriate total ionic strength adjustment buffer and its dosage were optimized. The impact of Fe³⁺ concentration on the detection results was analyzed under preferable conditions, and the error analysis of the ISE method’s accuracy and precision for measuring fluoride ion concentration in the range of 0.5-2000 mg/L was conducted. The quantitative recovery of F⁻ in ammonium sulfate slurry was assessed. The results showed that when pH ranged from 5.5-6 and the Fe³⁺ concentration was less than 750 mg/L, the accuracy and precision test results with quantitative recovery rates of 92.0%-104.2% were obtained.

1. Introduction
SO₂ mainly originates from the combustion of fossil energy and causes serious air pollution. Ammonia-based flue gas desulphurization has received increased attention in recent years, due to its high efficiency, low energy consumption, and recyclable ammonium sulfate used as a fertilizer [1, 2]. However, the fluoride released from coal exists in desulfurization slurry and cannot be crystallized with ammonium sulfate during desulfurization process. Highly concentrated fluoride ion accumulates in the desulfurization slurry, which causes equipment corrosion and threatens the growth of plants and human health if discharged arbitrarily to soil and water [3-5]. Many approaches have been adopted to reduce the emission of F⁻ to environment, and determining the level of fluoride ions in different media could be the key procedure in the monitoring of F⁻ [6]. Ammonium sulfate slurry contains a lot of suspended soot particles, high concentration of ammonium sulfate, Fe³⁺, and other compositions that make it difficult to accurately assess fluoride ion levels using general chemical volumetric method. To date, detecting fluoride ion in ammonia-based desulphurization slurry lacks authoritative references [7-11].

Fluoride ion selective electrode (ISE) is a primary method to determine F⁻ concentration due to the merits of good selectivity, high sensitivity, and a lower probability of being affected by the solution’s color and turbidity [12, 13]. The electrode’s sensitive membrane has a selective response to F⁻. As the electrode is immersed in a test solution containing F⁻, ion exchange and diffusion occur at the
membrane/solution interface. The original two-phase interface potential distribution changes and forms a double layer structure, producing membrane potential. However, when the method is used to detect F$^-\$ ions in ammonia-based desulfurization slurry directly, the accuracy and precision may be affected by many factors, such as Fe$^{3+}\$ easily forms complexes with F$^-$, F$^-\$ easily forms HF with H$^+$, and temperature affects electrode potential [14-17].

Herein, the determination of F$^-\$ concentration in ammonia-based desulfurization slurry is discussed. The effect of pH, Fe$^{3+}\$, and total ion strength adjustment buffer (TISAB) are investigated. To study the method’s accuracy and precision, an error analysis of experimental results is conducted. The quantitative recovery rates of F$^-\$ are assessed to determine whether the method is suitable for the detecting of F$^-\$ in ammonium sulfate slurry. The goal of this research is to establish a simple, accurate, and precise detection method for F$^-\$ in view of the unique characteristics of ammonia-based desulfurization slurry.

2. Experimental

2.1. Reagents and apparatuses
All reagents used in this experiment were of analytical purity. The TISAB-1 was comprised of 0.2 mol/L sodium citrate and 1 mol/L sodium nitrate, and the TISAB-2 was comprised of 1 mol/L hexamethylenetetramine and 0.03 mol/L Tiron. F$^-\$ stock solution containing F$^-$, ammonium sulfate solution, ferric chloride, and TISAB were used. Instruments used in the experiments including ZD-2 potentiometric titration device, PF-1-01 ion selective fluoride electrode, 217 saturated calomel electrode, and PHS-2 acidity meter.

2.2. Determination of F$^-\$
Determination of F$^-\$ was according to the standard methods [18]. Based on the experimental data, we established calibration graphs and linear regression equations. F$^-\$ ion stock solution (5000 mg/L, 500 mg/L, 50 mg/L F$^-\$ ion) was placed into a 50 mL volumetric flask, then 5 mL ammonium sulfate solution (mass fraction 40%), 0.5 mL ferric chloride solution with Fe$^{3+}\$ concentration of 4000 mg/L, and a certain amount of TISAB were added to generate a standard solution containing fluoride concentrations ranging from 1 to 1000 mg/L. A saturated calomel electrode was used as a reference electrode together with a fluoride ISE as a detecting electrode to form a primary battery. The solution was stirred at 25 °C until a stable potential value was reached. The relationship between the membrane potential and F$^-\$ ion activity in the solution accords with the Nernst equation

$$E = E^0 - \frac{2.303 RT}{F} \ln C_F^- \quad (1)$$

In this equation (1), E is the equilibrium electrode potential. $E^0$ is electrode potential under the standard conditions. R is gas constant. T is thermodynamic temperature. F is Faraday constant. $C_F^-$ is F$^-\$ ion concentration in the solution. Based on the experimental data, we established calibration curves and linear regression equations. F$^-\$ concentrations of tested samples were obtained using the detected potentials and the linear regression equations.

2.3. Quantitative recovery of ammonium sulfate slurry
Standard addition method was adopted to verify the quantitative recovery rate of F$^-\$ in slurry [19]. Three samples of slurry collected at different times were filtered through filter paper and a homemade polyethylene glycol octylphenol ether/polypropylene adsorption filtration to remove ash, organic matters, dyes, and other macromolecules. The clarified filtrates were numbered I, II, and III, respectively. The F$^-\$ concentration of samples were measured with and without addition of F$^-\$. Quantitative recovery rates were calculated using the following formula.

$$\text{Recovery}\% = \frac{\text{total } F^- \text{ value (mg)} - \text{initial } F^- \text{ value (mg)}}{\text{added } F^- \text{ (mg)}} \quad (2)$$
3. Results and discussion

3.1. Effect of pH
To select a suitable pH range, the potential values were measured at 50 mg/L and 500 mg/L F\(^-\) solution at different pH levels. Figure 1 shows the influence of pH on the potential. The potential increases when pH level ranges from 2.5 to 5.5, but decreased when the pH at about 6.0~7.0. When the pH of the solution is between 5.5 and 6.0, potentials do not change significantly. A low pH leads to the F\(^-\) ion partially forming HF and HF\(_2^--\), influencing F\(^-\) ion detection [15]. When pH ranges from 1.0-2.5, F\(^-\) ions can form the complex FeF\(_n\)(3-n)+ with Fe\(^{3+}\) [16]. A high pH is associated with higher F\(^-\) detection rates when OH\(^-\) in the solution are substituted for F\(^-\) ions in the LaF\(_3\) membrane. Researchers suggested that LaF\(_x\)(OH)\(_{3x}\) formed on the membrane influences electrode response to F\(^-\) ions [17].

![Figure 1. Influence of pH on the potential (25 °C, insert is enlarged part).](image)

3.2. Selection of TISAB
A complexing agent and pH buffers are needed to avoid the disturbing metal ions and to control the solution pH. Based on the results above, the TISAB pH values were adjusted to 5.8, which is in the range of 5.5-6. Potential values of 1, 5, 10, 50, 100, 500, and 1000 mg/L F\(^-\) solution were detected when treated with 10 mL TISAB-1, 10 mL TISAB-2, and 15 mL TISAB-2, respectively. Figure 2 shows the calibration graphs of the detected potential values against the relevant lg C\(_F^-\). Table 1 shows the associated linear regression equations. The table shows that TISAB-2 leads to a better linearity on the calibration curve. TISAB-2 with volume of 15 mL is more effective as a buffer than TISAB-1 with the linear correlation coefficient of -0.999 and the standard deviation (SD) of 0.99.

TISAB-2 is composed of hexamethylenetramine, Tiron, and potassium nitrate. Hexamethylenetetramine-HCl is an effective buffer solution to control solution pH. Tiron functions as a metal-hidden agent, effectively masking Al\(^{3+}\), Ca\(^{2+}\), and Fe\(^{3+}\). Potassium nitrate is an inert electrolyte, and it does not participate in the reaction but inhibits ion movement in the electrode reaction. Therefore, TISAB-2 can keep the solution pH stable, keep total ionic strength constant, and conceal interfering ions.
Figure 2. Calibration curves with different TISAB additions (25 °C, 4 wt% (NH₄)₂SO₄, 40 mg/L Fe³⁺).

Table 1. The result of fitted calibration curves.

| TISAB       | Linear regression equations         | $R^2$ | SD (%) |
|-------------|-------------------------------------|-------|--------|
| TISAB-1 (10 mL) | $E=242.49(±2.37)-58.07(±1.26)\log C_F$ | -0.998 | 3.38   |
| TISAB-2 (10 mL) | $E=235.48(±0.96)-57.26(±0.51)\log C_F$ | -0.999 | 1.36   |
| TISAB-2 (15 mL) | $E=233.71(±0.70)-58.30(±0.37)\log C_F$ | -0.999 | 0.99   |

3.3. Influence of Fe³⁺
The influence of Fe³⁺ on the F⁻ ion detection was also investigated. A set volume of 4000 mg/L FeCl₃ solution was added to derive test solutions containing different Fe³⁺ concentrations. Table 2 shows the F⁻ ion concentrations determined through these tests. These data show that when Fe³⁺ concentrations are higher than approximately 750 mg/L, the method’s relative errors (RE) are high. When the TISAB-2 in the solution cannot mask all the Fe³⁺, the unmasked Fe³⁺ ion affects F⁻ ion detection, which leads to an error rate greater than 5%. The Fe³⁺ concentration in ammonium sulfate slurry is usually less than 400 mg/L, so the Fe³⁺ in ammonium sulfate slurry can be completely masked without affecting F⁻ ion determination.

Table 2. Influence of concentration of Fe³⁺ on the method.

| Fe³⁺ (mg/L) | Detected F⁻ (mg/L) | RE (%) |
|------------|--------------------|--------|
| 10.00      | 100.13             | 0.13   |
| 20.00      | 100.16             | 0.16   |
| 50.00      | 100.22             | 0.22   |
| 80.00      | 100.19             | 0.19   |
| 120.00     | 100.38             | 0.38   |
| 300.00     | 100.43             | 0.43   |
| 500.00     | 96.54              | 3.96   |
| 750.00     | 96.54              | 3.96   |
| 1000.00    | 117.62             | 17.62  |

* 25 °C. 15 mL TISAB-2, 4 wt% (NH₄)₂SO₄, 100 mg/L F⁻ ions.
3.4. Error Analysis

It is believed that fluoride ISE enables the determination of fluoride ions in the range of 0.02-1900 mg/L [20]. To assess $F^-$ ion test solutions at different concentrations, different amounts of $F^-$ stock solutions were added to 50 mL volumetric flask. 5 mL $(NH_4)_2SO_4$ solution, 0.5 mL 400 mg/L $FeCl_3$ solution, and 15 mL TISAB-2 were also added. Table 3 shows the detected potentials of these test solutions. When $F^-$ ion concentration ranges from 0.5 to 1800 mg/L, the RE and relative standard deviation (RSD) are less than 3%. We can conclude that the detected $F^-$ ion with concentration of 0.5-1800 mg/L showed good accuracy and precision of the method.

Table 3. Influence of $F^-$ concentration on the accuracy*.

| $F^-$ (mg/L) | Determined $F^-$ concentration ($X_i$) | $\bar{X}$ | RE (%) | RSD (%) |
|--------------|-------------------------------------|--------|--------|--------|
| 0.50         | 0.48 0.48 0.50 0.47 0.48            | 0.48   | 4.17   | 2.33   |
| 5.00         | 4.99 4.99 4.80 4.80 4.80            | 4.88   | 2.46   | 2.13   |
| 30.00        | 30.71 29.52 30.71 29.52 29.52       | 30.00  | 0      | 0.02   |
| 100.00       | 104.48 104.48 104.48 100.44 100.44 | 102.86 | 2.86   | 2.13   |
| 500.00       | 507.16 507.16 507.16 507.16 527.59 | 511.25 | 2.24   | 1.79   |
| 1000.00      | 992.52 992.52 1032.5 1032.5 1032.5 | 992.52 | 1008.52| 0.08   |
| 1500.00      | 1532.5 1532.5 1473.2 1532.5 1532.5 | 1473.22| 1508.83| 0.06   |
| 1800.00      | 1794.8 1867.1 1867.1 1794.8 1794.8 | 1794.86| 1823.78| 1.30   |
| 2000.00      | 1942.3 1942.3 1867.1 1867.1 1942.3 | 1942.39| 1912.30| 4.58   |

* 25 °C. 15 mL TISAB-2, 4 wt% $(NH_4)_2SO_4$, 40 mg/L $Fe^{3+}$, 50 mL test solutions.

3.5. Analyses of $F^-$ ions in ammonium sulfate slurry and its quantitative recovery

Following experimental methods presented in 2.3, the determination of $F^-$ ions in ammonium sulfate slurry were conducted with and without addition of $F^-$ stock solution. Quantitative recoveries of the method of determining $F^-$ ions in ammonium sulfate slurry using F-ISE are from 92.0% to 104.2% (table 4).

Table 4. Quantitative recoveries of $F^-$ in ammonium sulfate slurry*.

| Slurry | Volume (mL) | Initial $F^-$ (mg) | Added $F^-$ (mg) | Total $F^-$ (mg) | Recovery rate (%) |
|--------|-------------|--------------------|-----------------|-----------------|------------------|
| I      | 5.00        | 10.60              | 10.00           | 20.01           | 94.10            |
| II     | 5.00        | 12.45              | 10.00           | 21.65           | 92.00            |
| III    | 5.00        | 8.07               | 10.00           | 18.49           | 104.20           |

* 25 °C. 5 mL slurry, 15 mL TISAB-2, 50 mL test solutions.
4. Conclusions
The solution pH of 5.5 to 6.0 has a minimal effect on the determination results. The addition of TISAB-2 solution (15 mL TISAB-2 of 50 mL solution, pH of 5.5 to 6, $F^-$ of 1 to 1000 mg/L) completely conceals the Fe$^{3+}$ in ammonium sulfate slurry and yields a better standard linear curve. When $F^-$ ion concentration ranges from 0.5-1800 mg/L, the RE and RSD are all less than 3%. Quantitative recoveries of $F^-$ in ammonium desulfurization slurry is in the range of 92.00~104.20%. We can conclude that the using of fluoride ISE is easy and accurate in determining $F^-$ ion levels in ammonia desulfurization slurry.

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