A Simple Preprocessing Method using Ion Exchange Resins for the Analysis of Fluoride Content in Gypsum

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A simple preprocessing method to allow the analysis of the fluoride content of gypsum is proposed for use in gypsum board recycling. The perchloric acid distillation method is well established as a method to quantify the fluoride content of gypsum. However, this method is a long, complex operation using hazardous chemicals. As an alternative, we propose a simple preprocessing method, using cationic and anionic ion exchange resins to allow the analysis of the fluoride content of gypsum using a commercially available kit based on the Lanthanum-Alizarin complexone (La-ALC) method. This preprocessing technique results in greatly increased solubility of calcium sulfate coupled with the separation of fluoride contaminants for quantitative analysis. This makes the determination of fluoride in gypsum by the La-ALC method possible because the preprocessing process does not remove the fluoride ionic species. This method is proposed as a suitable technique for on-site fluoride analysis.

Key Words: ion exchange resin, fluoride, gypsum, waste gypsum board

1. Introduction

Gypsum board is commonly used as a house building material and so presents in large quantities when buildings are demolished. In Japan, about three million tons of gypsum board is manufactured every year for building construction. As well, every year about 1.7 million tons of waste gypsum board is generated from demolition work. Most waste gypsum board is sent to landfill sites; hence, the need to recycle is driven by a lack of landfill capacity. Recently, attempts have been made to use waste gypsum board for ground improvement as a roadbed material, a sludge stabilizer or as fertilizer.

However, there are difficulties in gypsum recycling related to entrained impurities such as fluorides because these impurities cause soil contamination by leaching into groundwater. On-site monitoring of fluoride content is essential for the recycling process of gypsum because the amount of inosolubilizing agent for gypsum that prevents leaching of fluoride into groundwater can be estimated from the monitoring data.

A method to measure the content of fluoride has been established; however, the method requires complicated processes such as dissolution of fluoride into the analytical solution, degradation with perchloric acid and purification by the steam distillation before colorimetric analysis by Lanthanum-Alizarin complexone method. In order to dissolve and to degrade fluoride in gypsum into the analytical solution, heating process is inevitable due to low solubility of gypsum. Degradation and distillation require hazardous perchloric acid and large-scale apparatus, which is not suitable for on-site analysis.

The use of chelating agents has been proposed as a suitable pretreatment to increase solubility of gypsum samples for analysis. This method increases the solubility of gypsum in water without hazardous reagents. However, the interference from sulfate ions, which is one of the major components of gypsum, made the practical application of the colorimetric analysis by Lanthanum-Alizarin complexone difficult.

Recently, a simple and rapid preprocessing technique has been devised that greatly increases the solubility of normally slightly-soluble inorganic salts such those present in gypsum and removes interfering species simultaneously. As noted, gypsum is mainly calcium sulfate, and in the proposed method, the dissolution of calcium sulfate is...
promoted with cationic and anionic ion exchange reaction as the resins remove calcium and sulfate ions from the solution. (Fig.1). Note that with this method, the concentration of the interfering ionic species of sulfate is maintained low by the ion exchange reaction. On the contrary, most of fluoride remains in solution because of the low affinity of fluorides for the ion exchange resins.\(^6\,\,7\)

A simplified preprocessing method to dissolve fluoride in gypsum into solution using ion exchange resin is therefore proposed.

![Fig.1 Promotion of dissolution of gypsum by the proposed method. R: Cationic resin, R’: Anionic ion exchange resin](image)

2.2 The effect of the amount of ion exchange resins on solubility of gypsum.

Various amount of ion exchange resins (cation-anion=2:1) and 0.06g of reagent gypsum were put in 20ml of distilled water to elucidate the effect of the ion exchange reaction on solubility of gypsum. After the mixture was shaken for 5 minutes with 2200rpm/min., the amount of exchanged calcium was calculated from the difference between the calcium added as gypsum and that remained in the solution.

2.3 Selectivity of the ion exchange resins

The ion exchange resins to increase solubility of gypsum for determination of fluoride should have the properties that they are exchangeable for calcium and sulfate ions but unexchangeable for fluoride ion. In order to confirm the properties, 0.5g of gypsum was added to distilled water containing 1mg/l of fluoride, and the solution was immersed with 0.16g of cation exchange resin and 0.37g of anion exchange resin. The concentrations of fluoride, calcium and sulfate were measured every 5 minutes. The concentration of calcium ions was measured by chelatometric titration and the concentration of sulfate ions was measured by barium sulfate precipitation nephelometry (JIS K8001).

2.3 Determination of fluoride content in gypsum

The outline of the measurement for fluoride concentration is shown in Fig.2. Aliquots (0.12g) of the reagent gypsum or actual gypsum samples obtained from two different gypsum manufacturers and 0.5g of the cationic and anionic ion exchange resins were put in 20mL of distilled water after adding certain amounts of fluoride. The gypsum content of the actual samples was measured by the standard method (JISR9101) separately. The mixture was shaken for 5 min at 2200 rev/min. The concentration of fluoride in the solution was measured by absorptiometry with La-ALC, the La-ALC method, at a wavelength of 620 nm. The Digital pack test-multi was also used to determine the fluoride concentration to shorten the time for analysis.
3. Results and Discussion

3.1 The effect of the amount of ion exchange resins on dissolution of solubility of gypsum.

Fig. 3 is the photograph showing the effect of ion exchange resins on the dissolution of gypsum. The solution with ion exchange resins (A) was transparent within 5 min. while the solution without resins (B) was remained turbid. Fig. 4 shows the change in dissolution of the reagent gypsum according to the amount of the ion exchange resins. The solubility of the reagent gypsum increased proportionally to the amount of ion exchange resins.

![Fig. 3: Dissolution of reagent gypsum](image)
A : distilled water 20mL + gypsum 0.5 g (with ion exchange resin)
B : distilled water 20mL + gypsum 0.5 g

![Fig. 4: Reagent gypsum solubility vs. amount of ion exchange resin](image)

3.2 Selectivity of the ion exchange resins

Fig. 5 shows the time course of concentrations of calcium, sulfate, and fluoride ions. The concentrations of calcium and sulfate ions decreased with time, while the concentration of fluoride ion remained constant. It was confirmed that the resin does not adversely affect the measurement of fluoride concentration.

![Fig. 5: Time course of the concentrations of calcium, sulfate and fluoride after the ions were contacted with ion exchange resins](image)

3.3 Determination of fluoride content in gypsum

The determination of the amount of fluoride in the reagent gypsum (200–1000 mg kg⁻¹) was examined using the proposed method. The results are shown in Fig. 6 and Table 1.

![Fig. 6: Calibration curve for cationic and anionic ion exchange resins (0.5g distilled water 20mL, sample 0.12g, 5min agitation, 2200rev/min)](image)
Table 1: Relative Standard Deviation

<table>
<thead>
<tr>
<th>Concentration (mg kg⁻¹)</th>
<th>R.S.D. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>3.09</td>
</tr>
<tr>
<td>100</td>
<td>4.58</td>
</tr>
</tbody>
</table>

The calibration curve obtained has a relative standard deviation (R.S.D.) (based on 8 samples) at 1000 mg kg⁻¹ and 100 mg kg⁻¹ of fluorine was 3.09%, and 4.58%.

A recovery rate of ≥90% was achieved when measuring actual gypsum samples as shown in Table 2. Although initially sodium fluoride was added as a model fluoride source, similar results were obtained when other fluoride compounds (calcium fluoride and sodium hexafluorosilicate) were added.

Table 2: Analytical results for chemical gypsum

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content Fluoride mg kg⁻¹</th>
<th>Added Fluoride mg kg⁻¹</th>
<th>Detection</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.1</td>
<td>193</td>
<td>208</td>
<td>381</td>
<td>95</td>
</tr>
<tr>
<td>No.2</td>
<td>2094</td>
<td>995</td>
<td>2802</td>
<td>91</td>
</tr>
</tbody>
</table>

*Recovery = Detection / (content + added)*

Results from the digital pack test-multi are shown in Fig.7. The linear line indicates the theoretical fluoride concentration against fluoride content in the gypsum when 100% of fluoride is transferred from 0.12g of gypsum to the 20mL of solution. All of the data plotted around the theoretical line indicate that the method using ion exchange resins combined with the digital pack test-multi for determination of the fluoride concentration had a sufficient accuracy for this purpose. It should also be noted that the total processing time was significantly decreased, from 65 to 15min.

4. Conclusion

The solubility of gypsum can be greatly increased in a short time by using the ion exchange resins. An additional benefit is that the sulfate ions (from the principal component of gypsum), which interfere with the analysis, can be simultaneously removed from solution. This allows the La-ALC method to be used for the determination of the fluorine content of gypsum.

The proposed method is expected to be highly practical as a pre-analysis technique allowing for the on-site analysis of fluoride in gypsum. The determination of the fluoride content with a simple commercially available analysis method also showed a high accuracy, indicating that this method could be a promising method to determine the content of fluoride in gypsum on-site.

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References