

Research Progresses on Analysis Methods for the Component in Composite Coagulant AS/PDMDAAC

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Abstract

To investigate the qualitative and quantitative analysis methods for the components in aluminum sulfate/poly dimethyl diallyl ammonium chloride (AS/PDMDAAC) composite coagulant, the existed analytical methods for analyzing independent component AS and PDMDAAC in literatures were reviewed and a three-principles to select appropriate methods from them for the components in the composite was proposed. Based on these principles, suitable matched methods were identified and then ranked according to their practicality. A preliminary feasibility analysis was performed on Fourier transform infrared spectroscopy (FTIR), which is recommended as the preferred analytical method.

Keywords: AS; PDMDAAC; Coagulant; Composite; Component; FTIR; Analysis; Methods

Abbreviations: AS: Aluminum Sulfate; PDMDAAC: Poly Dimethyl Diallyl Ammonium Chloride; FTIR: Fourier Transform Infrared Spectroscopy; AAS: Atomic Absorption Spectroscopy; IC: Ion Chromatography; ICP-MS: Inductively Coupled Plasma Mass Spectrometry; PAC: Poly Aluminum Chloride; NaTPB: Sodium Tetrphenylboron; CTMAB: Cetyltrimethylammonium Bromide; HBP-QAT: Hyperbranched Polymer with Quaternary Ammonium Terminal; PVSK: Potassium Vinyl Sulfonate; TBO: Toluidine Blue O; ATR: Attenuated Total Reflectance

Introduction

Aluminum sulfate/poly dimethyl diallyl ammonium chloride (AS/PDMDAAC) is a new type of composite coagulants. The varying proportions of its components make it suitable for broad applications in treating various surface water and wastewater [1]. Specifically, it is an efficient flocculant and decolorizing agent for printing and dyeing wastewater in textile industry [2]. As this new agent continues to be promoted and applied, there is an urgent need to establish corresponding industry and national quality standards. However, the foundation for these standards lies in the qualitative and quantitative analysis methods of the components in the composite. Until now, unfortunately, no direct method for analyzing the two components, AS and PDMDAAC, in the composite has been reported due to mutual interference between the components and difficulties in effective separation. Therefore, based on the summarization of existing analysis methods for the components and the authors' experience, a proposal was set up in this paper to research on an approach to establish qualitative and quantitative analysis methods for the components of the AS/PDMDAAC composite coagulant, along with a preliminary feasibility analysis.

Qualitative and quantitative analysis methods for AS

The detection methods for AS, in generally can be categorized into chemical analysis and instrumental analysis methods, both of which get the amount of AS by measuring the content of Al^{3+} or SO_4^{2-} . A commonly used chemical analysis method is the EDTA titration of aluminum ions (Al^{3+}), followed by metal ion back-titration to measure the Al^{3+} content, which is then converted to the AS content (expressed as aluminum oxide Al_2O_3). This is a direct quantitative analysis method. According to the Chinese national standard GB/T 31060-2014 [3], this

method is applicable for measuring aluminum oxide content in the range of $\omega(\text{Al}_2\text{O}_3) \geq 0.01\%$. Although this method provides direct measurement of the sample, the preliminary preparation takes up to $3 \text{ h} \cdot (\text{person} \cdot \text{sample})^{-1}$, and the titration analysis takes about $10 \text{ min} \cdot (\text{person} \cdot \text{sample})^{-1}$. During the analysis, other cations in the AS sample, such as Fe^{3+} , can also react with EDTA, which may affect the accuracy of the results.

The gravimetric method using BaSO_4 is an indirect quantitative analysis method. It involves adding a standard solution containing Ba^{2+} to the testing sample solution containing SO_4^{2-} . The resulting BaSO_4 precipitate is weighed to determine the SO_4^{2-} content, which is then converted to the AS content. The method has a wide testable range [$\rho(\text{SO}_4^{2-}) = (10 \sim 5000) \text{ mg/L}$] [4]. Although this method directly measures the SO_4^{2-} in a sample, the precipitate needs to be dried to a constant weight, so that the operation time- takes up to $4 \text{ h} \cdot (\text{person} \cdot \text{sample})^{-1}$. During the titration analysis, other ions that can precipitate with barium salts, such as CO_3^{2-} and SO_3^{2-} , may interfere with the results, affecting the measurement accuracy.

In instrumental analysis methods, Fourier transform infrared spectroscopy (FTIR) is based on the characteristic absorption peaks and their strength of bonds vibrations and rotations in a molecule at specific infrared wavelengths. It is used for both qualitative and quantitative analysis. Wei et al. [5] used the FTIR method to qualitatively analyze the Na_2SO_4 solution, confirming the presence of $\nu_{\text{as}}(\text{SO}_4^{2-})$ and its concentration by the characteristic peak at 1133 cm^{-1} and its peak area. This method has a wide range for determining SO_4^{2-} [$\omega(\text{AS}) \geq 0.1\%$] [6]. The preliminary preparations, such as creating the standard curve, take about $2 \text{ h} \cdot (\text{person} \cdot \text{batch})^{-1}$, while the measurement itself takes about $2 \sim 5 \text{ min} \cdot (\text{person} \cdot \text{sample})^{-1}$. Other substances that produce the peaks at the same peak position can interfere with the qualitative and quantitative analysis results.

Atomic absorption spectroscopy (AAS) is based on the absorption of characteristic spectral lines produced by ground-state metallic elements in the vapor of the testing sample, which excites them and allows for their direct qualitative and quantitative analysis in the sample. According to the Chinese National Standard GB/T 23837-2009 [7], the sample is acidified with nitric acid and digested to extract aluminum atoms in the water sample. This extracted solution is then aspirated into the AAS flame, and its absorbance at a wavelength of 309.3 nm is measured to determine the aluminum content. The method has a testable range of $\rho(\text{Al}) = (5 \sim 100) \text{ mg/L}$. The preliminary preparations, such as creating the standard curve, take about $2 \text{ h} \cdot (\text{person} \cdot \text{batch})^{-1}$, while the analysis operation itself takes about $1 \sim 10 \text{ min} \cdot (\text{person} \cdot \text{sample})^{-1}$. The aluminum content analysis results can be converted to AS content, but it is important to note that the total salt content in the sample solution should not exceed 15 g/L , as higher salt concentrations can interfere with the results.

Spectrophotometry is a method based on the selective absorption of light by the analyte in a testing solution, combined with the Lambert-Beer law, and it uses a standard curve for

quantitative analysis. The Chinese National Standard GB/T 23944-2009 [8] employs this method to determine the Al^{3+} content in samples, with a testable range of $\rho(\text{Al}^{3+}) = (0.02 \sim 0.2) \mu\text{g/mL}$. When analyzing AS, its content can be calculated based on the Al^{3+} content. The sample preparation and analysis procedures for this method take about $1.5 \text{ h} \cdot (\text{person} \cdot \text{batch})^{-1}$. Additionally, the chromogenic reagent Chrome Azurol S can form complexes with other metal ions such as Fe^{3+} , which can interfere with the determination of Al^{3+} content at the same absorption wavelength.

Ion chromatography (IC) is a method that separates ions in the mobile phase by exchanging them with ions on a stationary phase ion-exchange resin. It uses chromatographic retention time and peak area-content standard curves for qualitative and quantitative analysis. This method can determine the SO_4^{2-} content, which can then be converted to the AS content. The Chinese National Standard GB/T 14642-2009 [9] uses this method to determine the SO_4^{2-} content in water samples, with a preparation time of about $2 \text{ h} \cdot (\text{person} \cdot \text{batch})^{-1}$ and an analysis time consumed of $3 \sim 10 \text{ min} \cdot (\text{person} \cdot \text{sample})^{-1}$. The method has a testable range of $\rho(\text{SO}_4^{2-}) = (0.20 \sim 500.0) \text{ mg/L}$. High concentrations of other anions in the solution can cause interference, requiring pretreatment to remove them or dilution of the sample.

Potentiometric titration involves inserting a reference electrode and an indicator electrode into the sample solution to quantitatively analyze the ions by measuring the relationship between the electromotive force of the cell and the related ion activity in the sample. The Chinese National Standard GB/T 6911-2017 [10] uses this method with a Ba^{2+} ion-selective electrode and a reference electrode, titrating SO_4^{2-} in water samples with a BaCl_2 standard solution. The analysis results can be converted to the AS content. Similarly, this method does not require a standard curve and has a measurable range of $\rho(\text{SO}_4^{2-}) = (5 \sim 1000) \text{ mg/L}$. The preparation time is only $1 \text{ h} \cdot (\text{person} \cdot \text{sample})^{-1}$, and the analysis time is $5 \text{ min} \cdot (\text{person} \cdot \text{sample})^{-1}$. However, if phosphates or polyphosphates are present in the solution, they will cause significant interference and need to be removed by dilution or co-precipitation.

Inductively coupled plasma mass spectrometry (ICP-MS) analysis is based on ionizing the sample at high temperatures, followed by separating and detecting the ion signals and their masses with a mass spectrometer for qualitative and quantitative analysis. Nong et al. [11] used ICP-MS to analyze Al^{3+} in the water treatment agent poly aluminum chloride (PAC), converting it to PAC content based on Al^{3+} levels. The method has a measurable range of $\rho(\text{Al}^{3+}) = (1.0 \sim 2.0 \times 10^6) \mu\text{g/L}$. However, if this method is used to analyze AS, the AS content can be calculated from the Al^{3+} analysis results. The method requires approximately $3 \text{ h} \cdot (\text{person} \cdot \text{batch})^{-1}$ for sample pretreatment by nitric acid decomposition and preparation of standard solutions for instrument calibration, while the analysis time is only $2 \sim 5 \text{ min} \cdot (\text{person} \cdot \text{sample})^{-1}$. The minor plasma interferences produced by ICP-MS (e.g., the interference of $^{27}\text{Al}^+$ with $^{54}\text{Fe}^{2+}$) can be removed by increasing the mass spectrometer resolution [12] or using collision/reaction cell technology [13].

Qualitative and quantitative analysis methods for PDMDAAC

PDMDAAC belongs to a type of quaternary ammonium salts. Its qualitative and quantitative detection methods can also be divided into chemical analysis and instrumental analysis methods, and can be conducted by analyzing its molecules, quaternary ammonium cations, or Cl⁻. In the chemical analysis method, the sodium tetraphenylborate (NaTPB) titration-cetyltrimethylammonium bromide (CTMAB) back titration method is a direct quantitative analysis method for determining the content of quaternary ammonium cations, i.e., the number of quaternary ammonium units. Li et al. [14] accurately determined the content of several quaternary ammonium salts using this method, with a detection limit of $\omega(\text{quaternary ammonium salt}) \geq 0.10\%$. The method requires approximately 1 h·(person · sample)⁻¹ for preliminary preparation and 15 min·(person · sample)⁻¹ for analysis. Additionally, this method is suitable for analyzing the cationic unit fraction-the cationicity-in poly quaternary ammonium salts. For example, Feng et al. [15] used this method to measure the cationicity of hyperbranched polymer with quaternary ammonium terminal (HBP-QAT) as 44.2%. However, this method determines the total amount of all types of quaternary ammonium units in the solution, rather than the content of a single quaternary ammonium salt.

The potassium polyvinyl sulfate (PVSK) colloidal titration method is a quantitative analysis method for determining the cationicity in poly quaternary ammonium salts. This method uses toluidine blue O (TBO) as an indicator and performs precipitation titration with a standard solution of low-molecular-weight anionic polymer PVSK. By calculating the anion content of the PVSK required for titration, the cationicity of the poly quaternary ammonium salt can be determined. Mocchiutti et al. [16] accurately determined the content of PDMDAAC using this method. The preliminary preparation for this method takes approximately 5 h·(person · batch)⁻¹, and the titration process takes 0.5 h·(person · sample)⁻¹. However, when the polymer concentration in the solution is high, the resulting colloidal precipitate may adsorb the indicator, making it difficult to determine the endpoint [17]. Therefore, selecting the titration concentration based on the sample's molecular weight is particularly important.

The Mohr method uses K₂CrO₄ as an indicator and AgNO₃ standard solution to perform precipitation titration of Cl⁻ in water samples. The results of Cl⁻ analysis can be indirectly used to calculate the cationic unit content of PDMDAAC. According to the Chinese National Standard GB/T 15453-2018 [18], the Mohr method is used to determine Cl⁻ concentrations in water samples within the testable range of $\rho(\text{Cl}^-) = (3 \sim 150) \text{mg/L}$. The preliminary preparation for this method takes approximately 4 h·(person · batch)⁻¹, and the titration analysis takes about 20 min·(person · sample)⁻¹. This method is susceptible to interference from other ions that form precipitates with AgNO₃, such as SO₄²⁻.

In instrumental analysis method, the FTIR method can be also used as a basis for both qualitative and quantitative analysis

of the PDMDAAC quaternary ammonium salt functional group by identifying the characteristic absorption peak of $\delta_{\text{as}}(\text{N-CH}_3)$ around 1470cm⁻¹ and its strength in the sample. The testing range for this method is $\omega(\text{PDM}) \geq 0.1\%$. Levakov et al. [19] used FTIR for the qualitative analysis of PDMDAAC. By employing the attenuated total reflectance (ATR) technique, they avoided the drawback of accurately adding amount of the sample, which is a necessity of the traditional KBr pellet method, originally. The preliminary preparation for this method takes approximately 1 h·(person · batch)⁻¹, and the analysis operation time can be shortened to 2 min·(person · sample)⁻¹. Similarly, the presence of other substances with functional groups that exhibit peaks at the same wavenumber can interfere with the qualitative and quantitative analysis results.

Spectrophotometry can also be used for the direct quantitative analysis of quaternary ammonium salts. Liu et al. [20] used a spectrophotometer at 500nm to measure the formation of a pink ion-association complex between titan yellow and CTMAB under alkaline conditions. The measurable range of this method is approximately $\rho(\text{quaternary ammonium salt}) = (0 \sim 12) \text{mg/L}$. Other cations in the solution, such as Al³⁺ and Fe³⁺, can directly participate in the association, thereby interfering with the analysis.

Due to the difficulty of analyzing polymeric substances with IC, necessary pre-treatment steps such as precipitation and alkaline fusion are required to separate or degrade and remove them. Therefore, when analyzing PDMDAAC, NaTPB can be added to precipitate and separate the quaternary ammonium cations. Subsequently, the residue Cl⁻ are qualitatively and quantitatively analyzed based on the chromatographic retention time and peak area. The results are then converted to the PDMDAAC content through the cationic unit contents. According to the Chinese national standard GB/T 14642-2009 [9], this method determines Cl⁻ concentration in the testable range of $\rho(\text{Cl}^-) = (0.10 \sim 500) \text{mg/L}$. The preliminary preparation of this method takes approximately 5 h·(person · batch)⁻¹, and the chromatographic analysis time is about 5 min·(person · sample)⁻¹. Other high-concentration anions, such as SO₄²⁻, can interfere with the results, and thus need to be removed or diluted in advance.

Potentiometric titration is also a simple method for quantitatively determining Cl⁻ content, and based on the results, it can be used for the indirect quantitative analysis of PDMDAAC. According to the Chinese national standard GB/T 15453-2018 [18], an Ag/AgCl electrode is used as the reference electrode and an Ag electrode as the indicator electrode, with the AgNO₃ standard solution being automatically titrated to the endpoint determined by potential. The testable range of this method is $\rho(\text{Cl}^-) = (5 \sim 1000) \text{mg/L}$. The presence of SO₄²⁻ during titration significantly interferes with the results.

Additionally, ICP-MS can also be used to analyze Cl⁻. Nie et al. [21] precisely determined the chlorine content in dust-free samples using this method after acidifying and digesting the samples with ultrapure nitric acid. Similarly, the PDMDAAC content can be quantitatively analyzed based on the results of Cl⁻ analysis. The detection limit of this method can reach $\rho(\text{Cl}^-) \geq 0.06 \mu\text{g/L}$.

Suggestions for qualitative and quantitative analysis methods of AS/PDMAAC

A three-principles for screening research methods and their efficiency ranking: From the literature summarized in Sections 1 and 2, it is known that the two components, AS and PDMDAAC in the composite coagulant, each has its own independent and mature qualitative and quantitative analysis methods. These methods can serve as the basis for analyzing the components in the composite. However, the uniform dispersion of the two components due to their mutual solubility and the wide relative content distribution poses challenges. The former makes the approach of simple separation followed by analysis unfeasible, while the latter restricts the detection limit to the presence of extremely low content of either component in the composite. Therefore, to develop a method suitable for further research that directly uses the composite coagulant as the sample and features rapid, accurate, and low-cost analysis, this paper proposed the screening of AS/PDMAAC component analysis methods based on a three-principles derived from single component analysis methods. The methods to be studied should meet the following criteria:

- When detecting any component in the composite, it should not be interfered with other component, or such interference should be measurable.
- The detection limits (testable range) for each component in the composite must be closer or similar.

- The method should be able to measure both components in the composite, parallel or simultaneously. Additionally, the selected methods should be ranked based on their rapidity in speed (time consumption) and ease of industrial application (low cost).

Screening results and ranking of analysis methods:

The analysis methods from Sections 1 and 2 that meet all three principles, along with their operational characteristics, time and cost consumption, on one side, and uncertainty factors on the other side, are summarized in Table 1. In this paper, the adjustable range of the mass ratio of the two components in the AS/PDMAAC composite coagulant [$\omega(\text{PDMDAAC}):\omega(\text{AS})$] is preliminarily supposed to be 1:50 to 50:1. From Table 1, it can be seen that: firstly, FTIR, IC, and ICP-MS methods all meet the requirements of all three principles. Secondly, each of the three methods has its own uncertainties for further analysis, namely:

- In FTIR, whether the composite's spectrum contains a distinct absorption peak for one of two, at least or not;
- In IC, whether the components can be effectively separated or if their chromatographic peaks will be not overlapped;
- In ICP-MS, whether the pre-treatment process can completely digest the polymer or not. Finally, considering procedure speed, accuracy, and cost, the priority order of the three methods from high to low is: (1) FTIR, (2) IC, (3) ICP-MS.

Table 1: Analysis methods and specific criteria which fully satisfy the three principles.

Table Abbreviations: Fourier transform infrared spectroscopy (FTIR); Ion chromatography (IC); Inductively coupled plasma mass spectrometry (ICP-MS); Poly dimethyl diallyl ammonium chloride (PDMDAAC); Aluminum sulfate (AS); Sodium tetraphenylborate (NaTPB).

Method Name	FTIR	IC	ICP-MS
Interference between components	Interference between PDMDAAC and AS is measurable	Interference between Cl^- and SO_4^{2-} is measurable	No interference between Cl^- and Al^{3+}
Methodic testable range (Detection limit)	$\omega(\text{PDMDAAC}) \geq 0.1\%$ $\omega(\text{AS}) \geq 0.1\%$	$\rho(\text{Cl}^-) = (0.10 \sim 500) \text{mg/L}$ $\rho(\text{SO}_4^{2-}) = (0.20 \sim 500) \text{mg/L}$	$\rho(\text{Cl}^-) \geq 0.06 \mu\text{g/L}$ $\rho(\text{Al}^{3+}) = (1.0 \sim 2 \times 10^6) \mu\text{g/L}$
Simultaneous determination of both components	Simultaneous determination of PDMDAAC and AS	Simultaneous determination of Cl^- and SO_4^{2-}	Simultaneous determination of Cl^- and Al^{3+}
Preparation time/ $h \cdot (\text{person} \cdot \text{batch})^{-1}$	1~2	2~5	3
Testing time/ $\text{min} \cdot (\text{person} \cdot \text{sample})^{-1}$	2~5	3~10	2~5
Instrument price per system (USD)/ $\times 10^4$	1~3	2~5	10~20
Accuracy level of results	Accurate	Accurate	Highly accurate
Pretreatment or preparation	Drying only required	NaTPB precipitation and separation of poly-quaternary required	Nitric acid acidification and digestion of organic matter required
Uncertainty in methods	Whether one independent peak existed for one of component, at least	Whether the components effectively separated or without peaks overlapped	Whether the polymer can be completely digested or removed
Method priority ranking	1	2	3

FTIR spectrum analysis results: Based on the work done in Section 3.2, the method with the highest priority is the FTIR method. Here, ATR-FTIR method was used to measure solid samples of AS, PDMDAAC, and AS/PDMAAC [$\omega(\text{PDMDAAC}):\omega(\text{AS})=1:1$], in order to observe whether the composite component spectrum

contains distinct characteristic absorption peaks, one of which is independently, at least or not, so that the preliminary feasibility of using the FTIR method to test the components, qualitatively and quantitatively in AS/PDMAAC, could be confirmed. The obtained spectra are shown in Figure 1. From the spectrum of composite in

Figure 1 and in comparison of all three spectra with each other, it can be seen that in the FTIR spectrum of AS/PDMAAC, the peak at 3047cm^{-1} is mainly formed by the overlapping of the $\nu(\text{-OH})$ of water [22] and the $\nu(\text{Al-OH})$ of AS [23], which covers the original PDMDAAC absorption peaks at 3003cm^{-1} [$\nu_{\text{as}}(\text{-CH}_3)$] [24], 2931cm^{-1} [$\nu_{\text{as}}(\text{-CH}_2)$], and 2867cm^{-1} [$\nu_{\text{s}}(\text{-CH}_2)$] [25] in this range. The peak at 1646cm^{-1} is attributed to the $\delta(\text{-OH})$ of water [22]. The peak at

1471cm^{-1} is an independent absorption peak of PDMDAAC's $\delta_{\text{as}}(\text{N-CH}_3)$ [24]. The peak at 1041cm^{-1} is a composite peak formed by AS's $\nu_{\text{as}}(\text{SO}_4^{2-})$ [26] and other peaks of PDMDAAC within a certain wavenumber range, such as 1305cm^{-1} , 1244cm^{-1} , and 1138cm^{-1} [$\nu(\text{C-N})$] [27], as well as 947cm^{-1} [$\gamma(\text{-CH})$] [22]. The peak at 593cm^{-1} is formed by the overlapping of AS's $\delta_{\text{as}}(\text{SO}_4^{2-})$ [28] and $\delta(\text{Al-OH})$ [29].

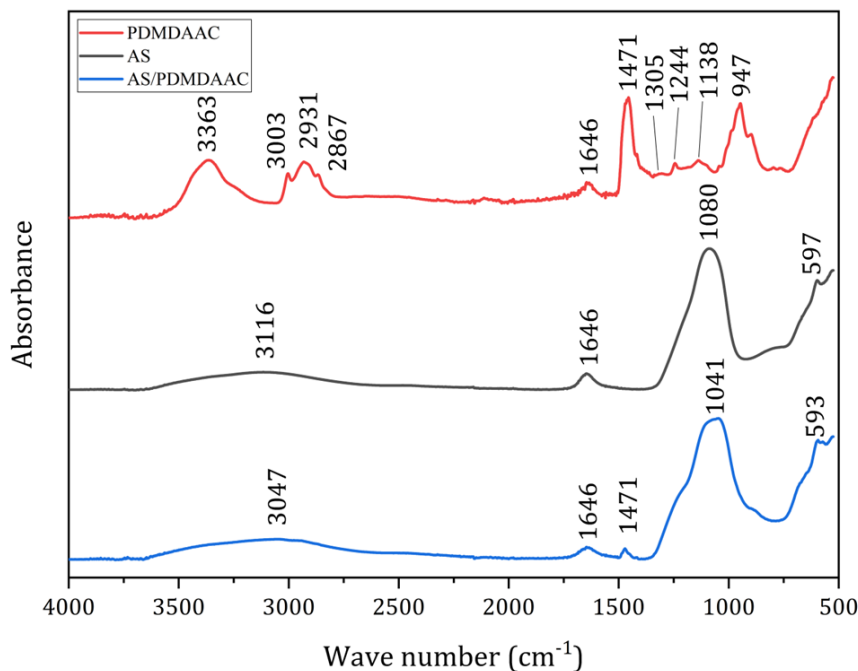


Figure 1: FTIR spectrum of samples of AS, PDMDAAC, and AS/PDMAAC [$\omega(\text{PDMDAAC})$: $\omega(\text{AS})=1:1$].

In the FTIR spectrum of the AS/PDMAAC composite, since the solid sample still contains a small amount of water, the absorption peaks associated with water are not considered in this use. Although the peak at 593cm^{-1} is an independent absorption peak of AS, its peak shape is poorly symmetrical, making it probably difficult to use as a quantitatively testable peak. The other independent (or minimally interfered) absorption peaks are located at 1471cm^{-1} and 1041cm^{-1} . The former can be used as a quantitatively testable peak for characterizing PDMDAAC, but the position and shape of the latter peak may vary with the relative content of AS and PDMDAAC, leading to multiple overlapping phenomena in the spectra of the two components in the composite. This might provide fortunately the possibility for subsequent research on calculating their mutual change of the two component contents in the composite. Thus, the preliminary feasibility of research on the FTIR method for the qualitative and quantitative analysis of two components in composite AS/PDMAAC was verified.

Conclusion

For the new type of composite coagulant AS/PDMAAC with its two components, in order to establish a qualitative and quantitative analysis method of the rapidity, accuracy, and easy to apply, the analytic principles, detection limits, and anti-interference characteristics of existing analysis methods for AS and PDMDAAC

were reviewed in this paper. Then three principles of screening the methods for the component analysis in the composite coagulant were proposed, the FTIR, IC, and ICP-MS methods were selected accordingly and ranked by their priority in applicability. Finally, a preliminary feasibility on the FTIR method recommended for further research was verified.

Conflict of Interest

No conflict of interest.

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