Quality Control of Polyacrylamide Products with Infrared Spectroscopy

Yunyan Peng1, Yan Rong1, Shichun Feng1, Dong Jin1*

1 China Special Equipment Inspection and Research Institute, Beijing, 100029, China
* Corresponding author: bjjd1969@163.com

Abstract. The anionic, cationic and nonionic polyacrylamide samples, as well as four kinds of inorganic salt samples, including sodium sulfate, sodium chloride, sodium carbonate and ammonium sulfate, were respectively analyzed with Fourier transform infrared spectroscopy (FT-IR) to establish their standard reference infrared spectra, meanwhile the characteristic peaks are distinguished. At the same time, the polyacrylamide samples containing different concentration and different kinds of inorganic salts were respectively analyzed with FT-IR to establish their IR spectra. Then a method used for quality control of polyacrylamide products was established, which can be used to evaluate the purity of the products, determine the impurities and relevant contents preliminarily.

1. Introduction

Polyacrylamide, as a kind of water-soluble polymer, has important application background in petrochemical industry, water treatment and many other industrial fields[1-4]. In petrochemical industry, most oilfields in China have basically entered the stage of tertiary oil recovery with the rapid development of petroleum industry. Polyacrylamide is one of the main raw materials in tertiary oil recovery, and its application in polymer flooding oil recovery technology continues to expand. At present, the application of polyacrylamide in oil recovery in our country accounts for nearly 70%, and 90% of the polyacrylamide worldwide used in oil recovery is used in China. However, in order to reduce the cost, some poor manufacturers and distributors add some cheap inorganic salts into it. The salinity in some oil wells is very high, which makes it difficult to exploit. If the injected polyacrylamide brings in a large amount of inorganic salts, the reservoir conditions will become more severe, and further increase the difficulty of mining. In addition, polyacrylamide is used as a flocculant of sewage treatment and a dewatering agent of sludge in water treatment, which is an essential chemical material for large-scale sewage treatment plant. The usage not only meets the needs of wastewater treatment, but also makes wastewater reuse possible. However, the product quality of polyacrylamide has not been effectively controlled at present. In order to reduce the cost, some poor manufacturers and distributors add some cheap inorganic salts, which will have a great impact on the product quality and subsequent process. If a large amount of inorganic salts are added into polyacrylamide, the difficulty of wastewater treatment will be further increased.

Chen et al. [5] measured the transmission spectrum of polyacrylamide powder by pressing polyacrylamide powder, and analyzed its infrared spectrum characteristics. Sun et al. [6] applied IR spectrum to characterize the structure of cationic polyacrylamide prepared by UV initiated polymerization. However, no specific quality control method has been reported. In this paper, infrared analysis is carried out on the standard samples of anionic, cationic and nonionic polyacrylamide, and infrared analysis is carried out on the common inorganic salts, so as to establish a quality control
method to identify whether polyacrylamide contains impurities and the types of impurities by infrared analysis.

2. Experimental

2.1. Materials and reagents
Anionic polyacrylamide (APAM) of 30% ionic degree with 10,000,000 molecular weight.
Cationic polyacrylamide (CPAM): The cationic monomer is (2-(acyloyloxy) ethyl) trimethylammonium chloride (DAC).
Nonionic polyacrylamide (NPAM) with 10,000,000 molecular weight.
Potassium bromide (KBr): spectroscopic pure.
Sodium chloride (NaCl): analytically pure.
Sodium sulfate (Na2SO4): analytically pure.
Sodium carbonate (Na2CO3): analytically pure.
Ammonium sulfate ( (NH4)2SO4): analytically pure.

2.2. Instrumentation
BRUKER Tensor 27 Fourier transform infrared spectrometer.

2.2.1. Spectral Characterization
Weigh 0.05g (accurate to 0.00001g) sample, add 0.95g (accurate to 0.00001g) KBr powder, and determine the infrared spectrum with 4cm-1 resolution in the wave number range of 400 to 4000cm-1 by KBr compression method.

3. Results and discussion

3.1. Infrared spectra of pure PAM
The samples APAM, CPAM and NPAM were determined by infrared spectroscopy according to the method described in 2.3, and the spectra were obtained as shown in Figure 3.

The IR spectrum of APAM was similar to that of NPAM, and the characteristic peaks were as follows: the characteristic absorption peak of free -NH2 in polyacrylamide was 3415cm⁻¹, that of methylene antisymmetric stretching vibration was 2922cm⁻¹, that of methylene symmetric stretching vibration is 2852cm⁻¹, that of carboxyl group (C=O stretching vibration) was 1667cm⁻¹, the N-H
bending vibration absorption peak was 1617\textsuperscript{cm}{-1}, and the methylene deformation absorption peak was 1454\textsuperscript{cm}{-1}.

In addition to the characteristic peaks of acrylamide, the characteristic peaks of DAC were added to the IR spectrum of CPAM, the C-H stretching vibration absorption peak of N-CH\textsubscript{3} was 2820\textsuperscript{cm}{-1}, the stretching vibration absorption peak of ester carbonyl C=O was 1730\textsuperscript{cm}{-1}, and the asymmetric stretching vibration absorption peak of C-O-C was 1188\textsuperscript{cm}{-1}, the C-N stretching vibration absorption peak of N+(CH\textsubscript{3})\textsubscript{3} was 954\textsuperscript{cm}{-1}.

Fig. 3. IR Spectra of APAM, CPAM and NPAM (From top to bottom: APAM, CPAM and NPAM)

Fig. 4. IR Spectra of Na\textsubscript{2}SO\textsubscript{4}

Fig. 5. IR Spectra of Na\textsubscript{2}CO\textsubscript{3}
3.2. Infrared spectra of pure Inorganic Salts

The reagents, sodium chloride, sodium sulfate, sodium carbonate and ammonium sulfate, which were often added into polyacrylamide for cost reduction, were analyzed by infrared spectroscopy. Sodium chloride had no infrared absorption. The infrared spectra of Na₂SO₄, Na₂CO₃ and (NH₄)₂SO₄ were shown in Figure 4, 5 and 6. The characteristic peaks of Na₂SO₄ were 1140 cm⁻¹ and 640 cm⁻¹, those of Na₂CO₃ were 1460 cm⁻¹, 880 cm⁻¹ and 700 cm⁻¹, and those of (NH₄)₂SO₄ were 1400 cm⁻¹, 1100 cm⁻¹ and 615 cm⁻¹.

3.3. Infrared spectra of PAM containing different concentrations of sodium sulfate

3.3.1. Infrared spectra of APAM containing different concentrations of sodium sulfate

A series of APAM samples with different concentrations of Na₂SO₄ were prepared in the laboratory. The concentrations were 5%, 10%, 20%, 30% and 40% respectively. IR analysis were carried out on them respectively, and the spectra were shown in Figure 7. It can be seen from Figure 7 that the characteristic peaks of Na₂SO₄ at 1140 cm⁻¹ and 640 cm⁻¹ increased obviously with the increase of Na₂SO₄ content in APAM, which can be used to judge whether there was some sodium sulfate in the APAM samples.

3.3.2. Infrared spectra of CPAM containing different concentrations of sodium sulfate

Because not too much salt can be added in the CPAM synthesis process, a series of CPAM samples with different concentrations of Na₂SO₄ were prepared in the laboratory. The concentrations were 5%, 10% and 20% respectively. IR analysis were carried out on them respectively, and the spectra were
shown in Figure 8. It can be seen from Figure 8 that the characteristic peaks of \( \text{Na}_2\text{SO}_4 \) at 1140 cm\(^{-1}\) and 640 cm\(^{-1}\) increased obviously with the increase of \( \text{Na}_2\text{SO}_4 \) content in CPAM, which can be used to judge whether there was some sodium sulfate in the CPAM samples.

![Fig. 8. IR Spectra of CPAM with Na\(_2\)SO\(_4\) (Red: CPAM; Blue: 5%; Rose red: 10%; Green: 20%)](image)

3.4. Infrared spectra of PAM containing different concentrations of sodium carbonate

3.4.1. Infrared spectra of APAM containing different concentrations of sodium carbonate.

A series of APAM samples with different concentrations of \( \text{Na}_2\text{CO}_3 \) were prepared in the laboratory. The concentrations were 5%, 10%, 20%, 30% and 40% respectively. IR analysis were carried out on them respectively, and the spectra were shown in Figure 9. It can be seen from Figure 9 that the characteristic peaks of \( \text{Na}_2\text{CO}_3 \) at 1460 cm\(^{-1}\), 880 cm\(^{-1}\) and 700 cm\(^{-1}\) increased obviously with the increase of \( \text{Na}_2\text{CO}_3 \) content in APAM, which can be used to judge whether there was some sodium carbonate in the APAM samples.

![Fig. 9. IR Spectra of APAM with Na\(_2\)CO\(_3\) (Red: 5%; Rose red: 10%; Blue: 20%; Green: 30%; Dark blue: 40%)](image)

3.4.2. Infrared spectra of CPAM containing different concentrations of sodium carbonate

Because not too much salt can be added in the CPAM synthesis process, a series of CPAM samples with different concentrations of \( \text{Na}_2\text{CO}_3 \) were prepared in the laboratory. The concentrations were 5%, 10% and 20% respectively. IR analysis were carried out on them respectively, and the spectra were shown in Figure 10. It can be seen from Figure 10 that the characteristic peaks of \( \text{Na}_2\text{CO}_3 \) at 1460 cm\(^{-1}\),
880cm\(^{-1}\) and 700cm\(^{-1}\) increased obviously with the increase of Na\(_2\)CO\(_3\) content in CPAM, which can be used to judge whether there was some sodium carbonate in the CPAM samples.

3.5. Infrared spectra of PAM containing different concentrations of ammonium sulphate

3.5.1. Infrared spectra of APAM containing different concentrations of ammonium sulphate

The addition amount of ammonium sulfate in the synthesis of PAM was not more than 8%, so APAM samples with 4% and 8% of (NH\(_4\))\(_2\)SO\(_4\) were prepared in the laboratory. IR analysis were carried out on them respectively, and the spectra were shown in Figure 11. It can be seen from Figure 11 that the characteristic peaks of (NH\(_4\))\(_2\)SO\(_4\) at 1400cm\(^{-1}\), 1100cm\(^{-1}\) and 615cm\(^{-1}\) increased obviously with the increase of (NH\(_4\))\(_2\)SO\(_4\) content in APAM, which can be used to judge whether there was some sodium carbonate in the APAM samples.

3.5.2. Infrared spectra of CPAM containing different concentrations of ammonium sulphate

CPAM samples with 4% and 8% of (NH\(_4\))\(_2\)SO\(_4\) were also prepared in the laboratory. IR analysis were carried out on them respectively, and the spectra were shown in Figure 12. As shown in Figure 12, the characteristic peaks of (NH\(_4\))\(_2\)SO\(_4\) at 1400cm\(^{-1}\), 1100cm\(^{-1}\) and 615cm\(^{-1}\) increased obviously with the increase of (NH\(_4\))\(_2\)SO\(_4\) content in CPAM, which can be used to judge whether there was some sodium carbonate in the CPAM samples.
4. Conclusions
In this paper, a quality control method of polyacrylamide was established by infrared spectroscopy. This method can determine whether the polyacrylamide sample contained impurities directly, quickly and accurately, and can determine the type and approximate content of impurities. An accurate and reliable method was established for the quality control of polyacrylamide.

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