Heterocyclic Letters
Vol. 11| No.2|167-173| Feb-April |2021
ISSN : (print) 2231–3087 / (online) 2230-9632
CODEN: HLEEAI
http://heteroletters.org

IMPROVING THE PRACTICAL ABILITY OF UNDERGRADUATE APPLIED CHEMISTRY STUDENTS THROUGH THE MEASUREMENT OF POLYSACCHARIDE CONTENT IN OILFIELD CHEMICALS

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ABSTRACT:
In this paper, a comprehensive experiment is designed for undergraduate courses in applied chemistry to measure the polysaccharide (e.g., guar gum, starch, etc.) content in oilfield chemicals using the phenol-sulfuric acid method. In this designed experiment, the effects of factors, such as detection wavelength, treatment temperature, treatment time and dilution ratio of the stock solutions, on the measurement results are evaluated to obtain the optimized operating conditions. After this optimization, the calibration curve is created to measure the polysaccharide content in solutions with unknown polysaccharide concentrations. With this method, the content of polysaccharide in oilfield chemicals (e.g., waste water, gel broken fracturing fluids, etc.) can be quantity analyzed. The repeatability and accuracy of the measurement results under the optimized operating conditions are evaluated. It is expected that this experiment would offer an opportunity for the undergraduate students to develop their scientific thinking skills of experiment designing and improve their problem analyzing and solving abilities.

KEYWORDS: Phenol-sulfuric acid method, Polysaccharide, Calibration curve, Oilfield chemicals, Comprehensive experiment

INTRODUCTION
In recent years, environmental policy stringency has been increasing in the petroleum industry,

the application of some toxic oilfield chemicals in the oilfields in China are required to be replaced by environmentally friendly chemicals. Polysaccharide materials, such as modified starch, cellulose and plant gums, have been widely used in many areas (e.g., food, medicine, printing and dyeing industry, etc). Polysaccharide materials, which are considered to be nontoxic and biodegradable, have attracted much attention from researchers in the area of oilfield chemistry. Some studies showed that polysaccharide materials could improve the performance of the working fluids used in oilfield exploration (e.g., drilling, hydraulic fracturing, and acid stimulation, etc.) and facilitate the protection of the formations[i-iii]. Therefore, the polysaccharide materials have promising application potential in oilfield chemistry[iv-vi].

At present, there is no standard procedure for analyzing the content of polysaccharide materials in oilfield chemicals, these uncertainties limit the polysaccharide's application. For example, the content of the polysaccharides (e.g., guar gum) in broken fracturing fluid is a crucial factor to see if the broken fracturing fluid needs to be further treated before the final disposal. The methods used for the measurement of the polysaccharide materials content can be split into two categories, colorimetry and titration. The colorimetry method includes the phenol-sulfuric acid method, the anthrone-sulfuric acid method, the carbazole-sulfuric acid method, the m-hydroxybiphenyl method and the *3, 5*-dinitrosalicylic acid method, etc. While the titration method includes the Fehling's method, the indirect iodometric titration and the potassium permanganate titration, etc[vii-x]. However, each of these methods has its own strengths, weaknesses and application area.

The Applied Chemistry Section of Teaching and Research of our university has long been engaged in the research and application of green oilfield chemicals based on natural product materials. This Applied Chemistry Section has undertaken more than 20 national, provincial, municipal and enterprise funded research projects in the fields of drilling fluids, fracturing fluids and wastewater treatment. Based on these research projects, many polysaccharide-derived oilfield chemicals have been developed. Besides, the research results can also be applied in experimental teaching. Compared with other analyzing methods, the phenol-sulfuric acid method designed in this experiment has many advantages, which are easy to operate, low measurement uncertainty and high repeatability[xi]. This experiment is designed based on the theoretical knowledge of the applied chemistry and its application in oilfield exploration. The students could develop their own questions after the principles of the measurements are introduced. The scientific thinking skills of the undergraduate students can also be effectively trained through the measurement of the polysaccharide contents in the oilfield chemicals.

EXPERIMENTAL SECTION:

EXPERIMENTAL GOALS:

(1) Understand the categories and functions of the polysaccharide used in oilfield chemistry.

(2) Understand the methods that used in the content measurement of the polysaccharide in samples and the mechanisms of the measurement.

(3) Practice optimizing the operating conditions and create the calibration curve using the phenol-sulfuric acid method.

(4) Learn how to analyze the stability, repeatability and accuracy of the experimental results.

EXPERIMENTAL PRICIPLES:

In the measurement, furfural and furfural derivatives can be produced through the dehydration reaction between polysaccharide and concentrated sulfuric acid molecules as presented in Figure 1. Then the furfural and furfural derivatives react with the phenol molecules and produce a complex with light yellow color. The concentration of polysaccharide in each sample has a direct effect on the concentration of the complex and the intensity of the yellow color of the produced complex. Then the concentration of the complex in each sample can be measured using the spectrophotometer at a certain wavelength. It should be noted that the stabilities of different polysaccharide reaction products are not the same, and the products are mixtures, which may affect the accuracy of the measurement results. For example, the reaction product of hexose and acid is unstable, and the reaction of fructose and acid produces two products[xii].

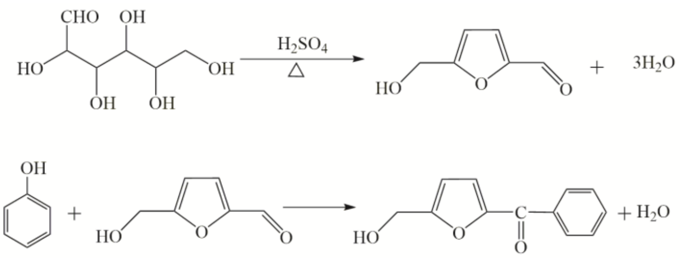

Figure 1 The reactions in the measurement with the phenol-sulfuric acid method

EXPERIMENTAL PROCEDURE:

MATERIALS:

Guar gum was purchased from Renqiu Qiankun Chemical Engineering Technology Co., Ltd. Corn starch was obtained from Suzhou Wangan Fine Chemical Co., Ltd. Phenol (analytical grade) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Concentrated sulfuric acid (analytical grade) was provided by Xi'an Chemical Reagent Factory.

PREPARATION OF THE STOCK SOLUTIONS:

Before the experiment, stock solutions need to be prepared. 1.0g guar gum is placed into a 1000 mL volumetric flask, distilled water is then added into the flask to around 3/4 full. The flask is then slowly mixed to dissolve the guar gum in the water completely. After the dissolving of the guar gum, distilled water is then carefully added into the flask to the volume mark. After homogenized by handshaking, the volumetric flask is then kept under static conditions for 4h to make sure the guar gum is completely dissolved. Then the solution is centrifuged for 15 min at 3000 r/min, the clear phase in the up layer is considered to be the 1.0 g/L guar sum solution and used in the next steps. Using the same procedure described above to prepare the 1.0 g/L corn starch solution. The 5% phenol solution is prepared by the following procedure: 5.0 g phenol is added into the 100 mL volumetric flask and distilled water is added to the flask to around 3/4 full. The flask is then slowly shaken to dissolve the phenol completely. After the dissolving of the phenol, distilled water is then carefully added into the flask to the volume mark.

HAZARDS:

Students should wear safety glasses, lab gloves and lab coats during the operation. Waste should be properly treated based on the local environmental regulations.

OPTIMIZATION OF THE OPERATION CONDITIONS

(1) Detection wavelength optimization

In this section, 5 mL guar gum solution (1.0 g/L) is added into a 100 mL volumetric flask and then distilled water is introduced into the flask to the volume mark to yield a guar gum solution with a concentration of 50 mg/L. Then 5.0 mL concentrated sulfuric acid and 1.0 mL phenol solution (5%) are carefully added in 1 mL guar gum solution (50 mg/L) and completely homogenized. After the homogenization, the mixed solution is kept undisturbed for 30 min. Then the solution is scanned with a UV-vis spectrophotometer (UV-2550) in the wavelength range of 400-600 nm to find the wavelength (λ_{max}) of maximum absorbance.

(2) Treatment temperature optimization

In this section, 6 guar gum solutions with the same concentration of guar gum (50 mg/L) are prepared. The volume of each guar gum solution is 1 mL. Then 5.0 mL concentrated sulfuric acid and 1.0 mL phenol solution (5%) are carefully added in 1 mL guar gum solution (50 mg/L) and completely homogenized. Then each of these 6 mixed solutions is kept undisturbed for 30 min at a certain temperature ranging from 30 °C to 80 °C (30 °C, 40 °C, 50 °C, 60 °C, 70 °C and 80 °C). Finally, each of these solutions is measured with the spectrophotometer at the same wavelength (λ_{max}) to check the absorbance. If no significant difference among the absorbance values is observed, then it means that temperature can not obviously affect the quantitative spectrophotometric measurement.

(3) Treatment time optimization

In this section, a guar gum solution with a concentration of 50 mg/L and a volume of 1 mL is prepared. Then 5.0 mL concentrated sulfuric acid and 1.0 mL phenol solution (5%) are carefully added to the 1 mL guar gum solution (50 mg/L) and completely homogenized. Then the mixed solution is kept undisturbed at ambient conditions and measured every 10 min to check the effect of treatment time on the absorbance.

(4) Determination of the concentration range of guar gum solution

In this section, the stock solution (1 g/L guar gum solution) is diluted with distilled water to yield solutions of varying dilutions from 10 mg/L to 650 mg/L. Then each of these solutions is measured with a spectrophotometer at the optimized wavelength (λ_{max}) to obtain the absorbance value. Then plot absorbance against the guar gum concentration. Usually, it is easy to find that in a concentration range that a linear relationship between absorbance and concentration can be observed. The concentration range corresponding to the linear curve will be used to create the calibration curve.

(5) Create the calibration curve

In this section, the stock solution (1 g/L guar gum solution) is diluted with distilled water to yield solutions of varying dilutions from 10 mg/L to 650 mg/L. The volume of each solution is 1 mL. Then 5.0 mL concentrated sulfuric acid and 1.0 mL phenol solution (5%) are carefully added in 1 mL guar gum solution (50 mg/L) and completely homogenized. After the homogenization, the mixed solutions are kept undisturbed at room temperature for 30 min. Then each of these solutions is measured with a spectrophotometer at the optimized wavelength

(λ_{max}) to obtain the absorbance. Then plot absorbance against the guar gum concentration. Usually, it is easy to find that in a concentration range that the absorbance value increases linearly with the guar gum concentration. The linear curve serves as the calibration curve.
The experimental procedure of measuring the corn starch content is the same as the procedure of measuring the guar gum content.

ANALYTICAL DISCUSSION:
(1) Stability of the measurement results
In this section, the stock solution (1 g/L guar gum solution) is diluted with distilled water to yield a solution with a concentration of 70 mg/L. Then the diluted solution is kept undisturbed at room temperature and measured the absorbance every 10 min (within 1 hour) to check the stability of the absorbance values.
(2) Accuracy of the measurement results
In this section, the stock solution (1 g/L guar gum solution) is diluted with distilled water to yield a solution with a concentration of 70 mg/L. Label 5 clean tubes with the concentration 70 mg/L and volume of 1 mL that they will contain. Then 5.0 mL concentrated sulfuric acid and 1.0 mL phenol solution (5%) are carefully added to each of the tubes with 1 mL guar gum solution (70 mg/L) and completely homogenized. Then each of the mixed solutions is measured with the spectrophotometer to obtain its absorbance. Calculate the relative standard deviation (RSD) of these five absorbance values. The repeatability of the measurement results can also be analyzed using this method.
(3) Standard specimen recovery
In this section, the stock solution (1 g/L guar gum solution) is diluted with distilled water to yield 5 solutions with concentrations of 10mg/L, 20 mg/L, 40 mg/L, 60 mg/L and 80 mg/L. Then each of these diluted solutions (1 mL) is loaded in a clean tube. After the loading, a standard polysaccharide solution with a concentration of 200 mg/L and a volume of 1 mL is added in each of these tubes. Then 5.0 mL concentrated sulfuric acid and 1.0 mL phenol solution (5%) are carefully added to each of the tube and completely homogenized. Then each of the mixed solutions is measured with the spectrophotometer to obtain its absorbance. The standard specimen recovery (s) of these five absorbance values is calculated from

$$s = 100 \times \frac{c}{c_0 + c_i} \qquad (1)$$

where s is the standard specimen recovery, %, c_0 is the original concentration of the solution directly diluted from the stock solution, mg/L, c_i is the concentration contributed by the standard solution, mg/L, c is the concentration value measured with the spectrophotometer, mg/L.

QUESTIONS:
(1) Compared with other polysaccharide content measuring method, what are the advantages and the disadvantages of the phenol-sulfuric acid method?
(2) As both the guar gum and starch belong to polysaccharide materials, can the calibration curve used for measuring the guar gum content be also used for the starch content measurement?

(3) The calibration curve created with the phenol-sulfuric acid method can only be used in a limited range of the polysaccharide concentration. For a polysaccharide solution with an unknown concentration, what is the proper procedure of the content measurement?

CONCLUSIONS:

This paper presents a comprehensive experiment for undergraduate course in applied chemistry. The conduction of this experiment allows the students to inspire their own questions after understanding the basic principles of spectrophotometer. At present, there are few reports on the measurement of polysaccharide content in oilfield chemicals. In this designed experiment, the methods of determining polysaccharide content in solutions have been applied in many other research fields, such as the food and pharmaceutical industries. Considering the application of polysaccharide materials in oilfield chemistry, guar gum and starch are used in this experiment. The phenol-sulfuric acid method is employed to measure the polysaccharide content in chemicals. The design of this experiment is expected to be feasible for undergraduate applied chemistry students.

In this experiment, the students need to learn and master the operations of the polysaccharide content measurement with the phenol-sulfuric acid method. Besides, the students should have an understanding of the compositions of polysaccharide materials used in oilfield chemicals. Students should be good at thinking and analyzing problems during the experiment. The experiment not only requires students to master the operation method of the polysaccharide determination but also to analyze the possibility of using calibrate curve method for other substances. In the process of optimizing the measurement conditions, the students should thoroughly understand the principles that can also be tools for their scientific research in the future. The process of this experiment is relatively clear, however, collaboration from group members is also required.

ACKNOWLEDGEMENT:

This work was financially supported by the grants from Shaanxi Provincial Key Research and Development Program (2019ZDLGY06-03), the Education Innovation Project of Xi'an Shiyou University (2019-23) and The Youth Innovation Team of Shaanxi Universities. The support from the Modern Analysis and Testing Center of Xi`an Shiyou University is also appreciated.

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Received on February 14, 2021.