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Rapid determination of degree of substitution of sodium carboxymethylcellulose by headspace gas chromatography

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ABSTRACT

This paper reports on a practical method for rapid determination of the degree of substitution of sodium carboxymethylcellulose (CMC-Na) by a headspace gas chromatography (HS-GC). In this method, CMC-Na was treated with a strong acid cation exchange resin to completely convert it to CMC-H form in 30 min at a room temperature, which was further reacted with bicarbonate in a close vial for 15 min at 60 °C. The resulting product, *i.e.* CO_2, was then determined by HS-GC, from which the DS of CMC-Na can be calculated. The results showed that the present method has a good measurement precision (RSD $<$ 4%) and accuracy (relative differences $<$ 7% when compared with the results measured by a reference method). Since the HS-GC can perform an automated sample reaction equilibration and measurement, it could be much more efficient than the existing methods in the batch sample analysis.

1. Introduction

Sodium carboxymethylcellulose (CMC-Na) is a cellulose derivative with carboxymethyl groups ($-CH_2-COOH$) bound to some of the hydroxyl groups of glucopyranose monomers made up the cellulose backbone. CMC-Na is often used in many applications, *e.g.* as a thickener and stabilizer in food industry [1], as a drilling mud treatment agent in oil drilling industry [2], and as the medical dressing hydrocolloid and hydrogel in pharmaceutical industry [3,4]. The degree of substitution (DS) of CMC-Na (defined as the number of hydroxyl groups substituted by carboxymethyl groups on average per anhydroglucose unit) determines its solubility in water [5]. The higher DS provides the CMC-Na a better water solubility and thus makes it more effective in the application. Therefore, a method that can efficiently determine the DS of CMC-Na are of special interest in the product manufacturing and related research and development.

Traditionally, the DS of CMC-Na is determined by the acid-wash method and conductivity titration [6]. In the acid-wash method, CMC-Na is first converted to CMC-H by hydrochloric acidic treatment, followed by washing and drying. Then, the hydrogen ions in the sample react with sodium hydroxide (overdosed), from which the excess amount of sodium hydroxide is determined by the titration with a standard hydrochloric acid solution. It is observed that agglomeration takes place during the CMC-Na's acidic treatment, which leads to incomplete acidification and thus an underestimate of the DS. In addition to being a complicated and time-consuming procedure, this method is only suitable for the crude and refined CMC-Na sample with the DS below 0.85, for the CMC-Na with higher DS gives a poor accuracy in the measurement.

In the conductivity titration, CMC-Na is first dissolved in a standard sodium hydroxide solution and then titrated with a standard hydrochloric acid solution. From the curve of the conductivity vs, the volume of the hydrochloric acid solution added, two transition points can be observed. The volume of hydrochloric acid solution at the first point represents the excess amount of sodium hydroxide added. The volume of hydrochloric acid solution at the second point represents the total volume consumed by both sodium hydroxide and carboxylic acid in CMC-Na. Therefore, by subtracting the volume at the first point from that at the point, the number of carboxylic acid groups neutralized in CMC-Na can be determined and thus the DS of CMC-Na was calculated. The major problem in this method is that the transition points are not so distinct. As a result, it leads to a larger error in the determination of the number of carboxylic acid groups neutralized in the CMC-Na.

Other methods such as colorimetric [6], electrophoresis [7], and nuclear magnetic resonance (NMR) method have also reported for the analysis of DS in CMC-Na [8]. However, these methods suffer from the problems associated with not only more complicated sample pretreatment, incompleteness of the reaction (*e.g.* to convert the $-O-$⨸ $CH_2-COONa$ in CMC-Na to glycolic acids in the colorimetric method) but also the significant error in the measurement. As a result, they are

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hardly used in practical applications.

As reported previously, we have successfully applied the headspace based gas chromatography (HS-GC) to the analysis of nonvolatile compounds through chemical reactions [9–11]. For example, by HS-GC measuring the carbon dioxide from the reaction between the hydrogen ions (H^+) in carboxyl groups and the bicarbonate ions (HCO_3^-) in solution, we determined the content of carboxyl groups in pulp fibers. Based on this concept, we believe that the HS-GC technique can also be used for the determination of DS in CMC-Na. This, however, is predicated on the quantitative conversion of CMC-Na to CMC-H during sample pretreatment.

In this work, we propose a practical method for the determination DS in CMC-Na by a HS-GC technique, in which we adapt an ion exchange based CMC-Na pre-treatment method. We focus on exploring the conditions in the ion exchange (*i.e.* the selection of the resin and its dosage, time, and temperature) and the operation conditions for headspace equilibration and measurement. The present method is less time-consuming, gives greater accuracy and can be performed on a wider DS of cellulosic starting materials.

2. Experimental

2.1. Chemicals and samples

All chemicals used in the experiment were of analytical grade and from commercial sources. A cation exchange resin (001 × 7 strong acidic styrene with a total exchange capacity of 3.7 mmoL/g) was purchased from Glory Resin Limited Company (Hangzhou, China). The CMC-Na samples used in this work were obtained from Macklin Company (Shanghai, China).

2.2. Apparatus and operation conditions

All measurements were carried out using an automated headspace sampler (Thermo HS TriPlus 300, US) and a GC system (Agilent GC 7890A, US) with a thermal conductivity detector (TCD) and a GS-Q capillary column. The headspace operating conditions were as follows: 15 min of strong shaking to allow sample equilibration at 60 °C; sample loop temperature = 70 °C; transfer line temperature = 80 °C; pressurization pressure = 2.00 bar; carrier gas pressure = 1.50 bar; vial pressurization time = 12 s; sample loop fill time = 12 s; and transfer time = 20 s; sample loop volume = 3 mL. The GC system was operated at a column temperature of 105 °C with a carrier gas (nitrogen) flow rate of 2.7 mL/min.

2.3. Procedure of sample preparation

Accurately weighed 0.03 g sample from a purified CMC-Na sample and placed in to a 50 mL breaker containing 15 mL of deionized water. The CMC-Na sample was dispersed in the deionized water by a magnetic stirrer to obtain a uniform and transparent solution. Then, 1.0 g of resin was added in the above solution and sonicated in an ultrasonic water bath for 30 min at room temperature. After that, the CMC-Na solution was obtained by filtration (separated from the resin).

Three (3) mL of the above filtrate was pipetted into a 20 mL headspace sample vial that having a tube containing 1.0 mL of 0.06 moL/L bicarbonate solution. The vial was sealed with septum and shaken up and down to fully mix the sodium bicarbonate solution in the tube with the CMC-Na solution, then the vial was ready for the automatic measurement by HS-GC.

2.4. Calculation of degree of substitution

According to the definition [6], the DS of CMC-Na can be calculated by

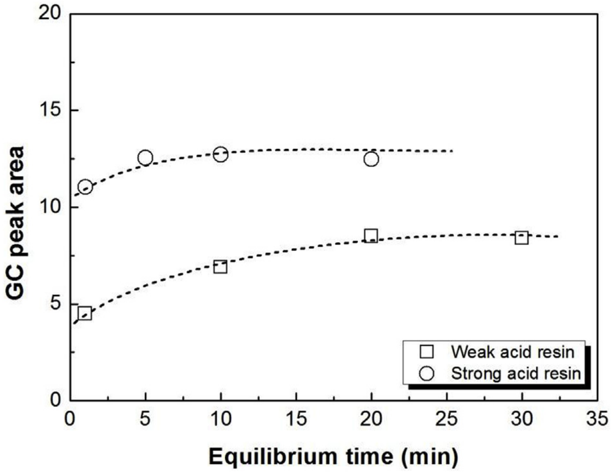

Fig. 1. The effectiveness of ion exchange by the weak and strong acidic resins.

$$DS = \frac{0.162X}{(1 - 0.058X)} \tag{1}$$

with

$$X = \frac{N}{m} \tag{2}$$

where 0.162 is the molar mass of an anhydroglucose unit, g/mmol; 0.058 is the net increase in the mass of an AGU for each carboxymethyl group substituted, g/mmol; X is the carboxyl content of per gram of sample, mmol/g; N is the total carboxyl content of the sample, mmol; and m is the absolute dry mass of the sample, g.

3. Results and discussion

3.1. Selection of the ion exchange resin for converting CMC-Na to CMC-H

In this work, two kinds of ion exchange resins, *i.e.* strong acid cation exchange resin and weak acidic cation exchange resin, were tried to convert Na^+ in CMC-Na with hydrogen ions. Fig. 1 shows the results from the pretreatment with these two kinds of acidic cation exchange resins on a given CMC-Na sample, which was evaluated by measuring the GC signal of CO_2 generated from the reaction between the ion-exchange treated CMC-H and the bicarbonate solution [12]. It is clear that the amount of H^+ exchanged by the weak acidic resin is much lower than that by the strong acidic resin. Therefore, we would use the strong acidic cation resin for the following ion exchange pretreatment of CMC-Na samples. Because only the equivalent amount of Na^+ is exchanged by H^+ from the resin, it avoids the impact of excessive acid on the acidification and thus eliminates the procedure associated with the cumbersome acid washing steps.

3.2. Optimized the conditions for the ion exchange reaction

3.2.1. Dosage of resin

To ensure a complete conversion of CMC-Na to CMC-H, an excess amount of resin is required. Fig. 2 shows that a quantitative conversion of CMC-Na to CMC-H form can be achieved by adding > 0.5 g of strong acid cation exchange resin under the given reaction conditions. Therefore, 1.0 g of strong acid cation exchange resin would be used in the following study.

3.2.2. Exchange reaction temperature and time

In general, a higher temperature is helpful to promote the ion exchange. However, the higher temperature (*e.g.* > 120 °C [13]) may damage the structure of the resin and affect its performance. Therefore, instead of elevated temperatures, we chose a room temperature but