Determination of Degree of Substitution of Sodium Carboxymethylcellulose

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THE increasing industrial importance of sodium carboxymethylcellulose has created interest in methods for its analysis. The degree of substitution—i.e., the average number of sodium carboxymethyl groups substituted per anhydroglucose unit—markedly affects the properties of this compound and convenient methods for its determination have therefore become necessary.

Hollabaugh, Burt, and Walsh (5) have published a complete review and bibliography on the uses and applications of this product. Brown and Houghton (4) in another review described a method for determining degree of substitution of the acid form of carboxymethylcellulose based upon electrometric titration. Another method reported by the same authors (1) involves precipitation of the copper or aluminum salts and determination of the metal content of the precipitate.

Schmidt, Meinel, Jandebeur, and Simson (7) describe a conductometric method for determining carboxyl in cellulose which is of interest in connection with one of the methods discussed in the present paper. Sakurada (6) reports three methods for determining substitution, one involving potentiometric or conductometric titration with sodium hydroxide, another requiring ashing the sodium salt, and the third consisting in titration of the free acid with sodium hydroxide. Since none of these procedures fulfilled the need for methods suitable for control purposes and applicable to both purified and unpurified samples of the sodium salt of varying degrees of substitution, the methods presented here were developed.

This paper describes three methods—acid-wash, conductometric and colorimetric—for determination of the degree of substitution of sodium carboxymethylcellulose. With appropriate modifications, however, the methods would be applicable also to the free acid form. Quantitative determination of the amount of carboxymethylcellulose present in admixture with other materials would be possible but would require previous knowledge of the degree of substitution. Each of these methods is best adapted to a certain type of sample, although the applications may sometimes overlap.

ACID-WASH METHOD

This method involves conversion of the sodium salt of carboxymethylcellulose to the acid form by treating with methanol acidified with hydrochloric or nitric acid, removal of the excess acid by
Three methods are described for determining the degree of substitution of sodium carboxymethylcellulose. This material may be converted to its free acid form by treatment with acidified alcohol, freed from excess acid, and the carboxyl content determined by an acidimetric procedure using phenolphthalein indicator. Alternatively, the sodium salt may be dissolved in water containing excess sodium hydroxide, and the solution titrated conductometrically with standard hydrochloric acid solution. In the analysis of purified, dry samples, the use of this latter method results in a considerable saving in time over that required in the former. A third method involving treatment of the carboxymethylcellulose with sulfuric acid to produce glyeolic acid, which is then determined colorimetrically using 2,7-dihydroxynaphthalene, is recommended for use with difficulty soluble samples. Possible use of this method in quantitative determination of carboxymethylcellulose in mixtures is suggested. The three methods give comparable results when applied to samples having a degree of substitution ranging from 0.2 to 1.3. The most advantageous application of each method is suggested.

Table I. Degree of Substitution of Typical Carboxymethylcellulose Samples by Various Methods

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductometric</th>
<th>Acid-Wash</th>
<th>Acid-Wash</th>
<th>Colorimetric</th>
</tr>
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<td>Found</td>
<td>Av.</td>
<td>Found</td>
<td>Found</td>
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</table>

where the constants are derived from the molecular weight of the anhydroglucose unit of cellulose (102) and from the net increase in the weight of the anhydroglucose unit for each carboxymethyl group substituted (58).

When the hydrochloric acid reagent was used, the sample of carboxymethylcellulose was given three 1-hour steeps, using 100 ml. of fresh reagent for each steep instead of the 3 to 4 hours' shaking period used with a single portion of nitric acid reagent as described above. Either may be used, although the nitric acid procedure is more convenient.

CONDUCTOMETRIC PROEDURE

Early attempts to titrate the sodium carboxymethylcellulose with hydrochloric acid either electrometrically or with use of an indicator were abandoned because an indistinct inflection occurs in the titration curve at the completion of formation of the carboxymethylcellulose free acid. It was found, however, that this same end point could be satisfactorily determined conductometrically. In this procedure, the sodium carboxymethylcellulose is dissolved in distilled water containing a small known amount of standard sodium hydroxide solution. This alkali serves to speed solution and convert any carboxymethylcellulose free acid to the sodium salt. The solution is then titrated con-
ductometrically with standard hydrochloric acid solution. As is shown by Figure 1, three linear segments are obtained which are extrapolated to two intersections. The volume of acid corresponding to the difference between points $V_1$ and $V_2$ is a measure of the carboxyl groups in the sample. The titration vessel and the electrode system used are illustrated in Figure 2. Results obtained on five samples covering a range of substitutions are given in Table I.

**Figure 1. Conductometric Titration of Sodium Carboxymethylcellulose**

**Reagents.** Hydrochloric acid, 0.33 N, accurately standardized. Sodium hydroxide, 0.5 N, accurately standardized. Methanol, 70% by weight.

**Apparatus.** Conductivity cell, made from a 500-ml Florence flask, indented, 8-mm. side arm for introduction of gas; side neck for electrodes fitted with standard-taper joint (see Figure 2). Electrodes. Platinum foil electrodes 7 X 7 mm. reinforced at the edges with No. 18 platinum wires and spaced approximately 7 to 10 mm. apart. The two electrodes are separated by sealing in separate glass tubes which are in turn sealed into a standard-taper joint, to fit the side neck of the cell. Contact is made between the electrodes and the lead wires through a few drops of mercury placed in the glass tube. For satisfactory performance the electrodes should be platinized.

Variable-speed motor stirrer.

Buret, 10-ml. capacity, 0.02-ml. subdivisions, with side filling tube. Offset tips are sealed on in place of the straight tips regularly supplied.

Constant-temperature bath maintained at 25° = 0.2° C.

Iodine flasks, 250 ml.

Conductivity bridge. Leeds & Northrup, Philadelphia, Pa., portable electrolytic resistance indicator, Catalog No. 4960; or Model RC-1, Industrial Instruments, Inc., Bayonne, N. J.; or equivalent.

**Procedure.** Grind the sample in a laboratory micro Wiley mill or equivalent, using a 20-mesh screen. Weigh roughly about 0.3- to 0.4-gram sample of medium- or high-substituted material or up to 1.8-gram sample of low-substituted material (less than 0.3 degree of substitution) into a glass-stoppered weighing dish. Dry the sample 1 hour in an oven at 100° to 105° C. Remove, stopper, cool in a desiccator, and weigh to the nearest 0.001 gram. Transfer the contents of the weighing dish to a dry 250-ml. iodine flask and weigh the empty bottle to get the sample weight by difference. Add 15 ml of 70% methanol solution and allow the sample to soak for 10 minutes. Add 200 ml of carbon dioxide-free distilled water and 3 ml of 0.5 N sodium hydroxide solution from a buret or pipet. Flush the air from the flask with a stream of nitrogen, stopper immediately, and shake until the sample is dissolved. Add 200 ml of bromine—free distilled water and 3 ml of 0.5 N sodium hydroxide solution from a buret or pipet. Stir vigorously but avoid introducing bubbles into the body of the liquid by too rapid stirring.

Determine the resistance of the solution with the conductivity bridge and then titrate with the 0.33 N hydrochloric acid, adding the acid in 0.5- to 0.4-ml. portions. Take a resistance reading after each addition of acid, allowing sufficient time for adequate mixing. After 10 ml of acid have been added, continue additions in 0.5-ml. portions to a total volume of 16 ml. A total volume of 16 ml of 0.33 N acid is usually sufficient for a sample having a substitution of 1.2 or less.

Calculate values of the reciprocal of the resistance and plot these against milliliters of hydrochloric acid solution as shown in the sample curve, Figure 1. Ignore the points obtained up to about 25% beyond the second end point and then draw the best straight line from the points between 25 and 75% excess hydrochloric acid. Extrapolate the three linear portions of the curve to obtain the two end-point intersections and determine the volumes of hydrochloric acid solution $V_1$ and $V_2$ corresponding to these intersection points.

**Calculation.** Total Carboxyl. The milliequivalents of total carboxyl per gram of sample are measured by the difference between $V_1$ and $V_2$.

$$ \frac{(V_2 - V_1) \times N}{\text{grams of sample}} = \text{milliequivalents of total carboxyl per gram. Value A}$$

$V_1$ and $V_2$ are defined above and $N$ is the normality of the hydrochloric acid used.

Free Carboxyl.

$$ \frac{(\text{ml. of NaOH} \times N) - (V_1 \times N)}{\text{grams of sample}} = \text{milliequivalents of free carboxyl per gram. Value B}$$

$V_1$ is defined above.

Degree of Substitution.

$$ A \times 0.162 \left(1 + \frac{0.022 B - 0.080 A}{A} \right) = \text{degree of substitution}$$

where 0.080 is the net increase (divided by 1000) in the weight of the amyllose unit of cellulose for each sodium carboxymethyl group substituted; and 0.022 is obtained by combining terms containing the constants 0.080 and 0.055 previously defined.

**Figure 2. Conductivity Cell and Electrode System**

The term 0.022 $B$ may be neglected if the sample is known to be entirely in the sodium salt rather than partly in the free acid form.

**COLORIMETRIC METHOD**

Chowdhury (3) reports that treatment of carboxymethylcellulose with phosphorus trioxide and water yields glycolic acid. Calkins (2) describes the use of 2,7-dihydroxynaphthalene as a spot test reagent for glycolic acid; and Calkins (2) describes a quantitative procedure for the determination of glycolic and oxalic acids.
using this same reagent. In order to avoid possible interference from the iodide ion in the determination of the glycolic acid produced from the carboxymethylcellulose, sulfuric acid was successfully tried as the ether-cleaving reagent to replace phosphorus triiodide and water. Briefly the method involves solution of the sample in sodium hydroxide solution, acidification with sulfuric acid, and heating under reflux to produce glycolic acid. The procedure of Calkins is then used with slight modifications to determine the glycolic acid in an aliquot of the resulting solution. Some aldehydes (especially formaldehyde, glycolic acid), and sodium glycolate will interfere in the colorimetric step in this procedure. Results obtained on four samples of varying degrees of substitution are given in Table I.

Reagents and Apparatus. Sodium hydroxide solution, 6%. Dissolve 90 grams of reagent grade sodium hydroxide in 470 ml. of water. Dihydroxynaphthalene solution. Dissolve 0.100 gram of 2,7-dihydroxynaphthalene (Eastman Kodak Co. Catalog No. 4408) in 1 liter of 6% sulfuric acid. Allow this solution to stand until the initial yellow color disappears before using. (Usually 5 to 6 hours are required.) Store this solution in a dark cabinet.

Sulfuric acid solution. Store this solution in a 250-ml. volumetric flask. Prepare a fresh solution each time a calibration is carried out.

Procedure. Using a 1-ml. graduated pipet, measure accurately 0.2-, 0.5-, and 1.0-ml. portions of the standard glycolic acid solution into separate 8 × 1.75 inch Pyrex test tubes and add 20 ml. of the dihydroxynaphthalene solution to each with a gradu- ate. Place the test tubes in a beaker of boiling water for 20 minutes. Place the test tubes in a container of cold tap water and allow to cool. Prepare the contents of the test tubes to 50-ml. volumetric flasks, rinse the test tubes with three 5-ml. portions of distilled water, and add the washings to the flasks with the aid of a small funnel. The water should be added carefully with adequate swirling to mix, taking care to prevent the mixing from taking place in the neck of the flask. Caution: Watch for possible spattering of the acid solution. Raising the funnel slightly with the forefinger to provide an air vent during additions to the flask is recommended.

Cool the flasks and contents to room temperature in a water bath, and make up to volume with water, cooling again if necessary. Pipet 1 ml. of the standards with a Beckman spectrophotometer or other convenient photometer against a blank of 20 ml. of color reagent treated in the same fashion as the standards. Plot a curve of optical density against concentration of material under typical conditions which would interfere in other procedures; previous knowledge of the degree of substitution, however, is necessary in calculating the results. The method gives high and unreliable results for weak acids and their salts other than carboxymethylcellulose present.

The analysis time for the colorimetric method is comparable to that for the conductometric method. The method may be used to the best advantage in the analysis of low-substituted samples, since the 6% sodium hydroxide facilitates complete solution of sufficiently soluble material. The specificity of the action of sulfuric acid to produce glycolic acid from the carboxymethylcellulose lends itself to the quantitative analysis of samples containing material which would interfere in other procedures; previous knowledge of the degree of substitution, however, is necessary in calculating the results. The method gives high results when applied to samples containing such interfering substances as formonaldehyde, glycolic acid, and sodium glycolate.

Summary

Three methods are described for the determination of the degree of substitution of sodium carboxymethylcellulose. These methods were developed for research and control purposes and for application to purified and unpurified samples with various degrees of substitution. The most advantageous application of each method is suggested.

Literature Cited

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