

Estimation of functional groups and degree of substitution in carboxymethylstarch

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Estimation of carboxymethyl groups in carboxymethylstarch (Na^+ form) by titration with perchloric acid in acetic acid was examined. The method is simple, rapid, convenient and does not require a sophisticated laboratory equipment. It is suitable for large number of routine analyses and also for structural studies, which require a rapid and sufficiently precise information. The results obtained by the reference alkalimetric, our, and complexometric methods were compared. There was a good agreement between the values obtained by the first two methods. The complexometric method afforded slightly lower values.

Изучалось определение карбоксиметильных групп в карбоксиметилкрахмале (Na^+ форма) посредством титрования хлорной кислотой в уксусной кислоте. Метод отличается простотой, быстрым проведением, удобством и не требует сложной лабораторной техники. Он пригоден для проведения большого числа рутинных анализов а также и для структурных исследований, для которых необходима быстрая и достаточно точная информация. Проводится сравнение результатов, полученных сравнительным алкалиметрическим, предлагаемым и комплексометрическим методами. Два первых метода приводили к хорошо согласующимся величинам. Комплексометрический метод приводил к несколько заниженным значениям.

Carboxymethylstarch, as an important derivative, requires sufficiently precise estimation of its functional groups and degree of substitution. The nature of this type of compounds and mainly their behaviour in aqueous solutions can cause some problems in these estimations. Most of the procedures elaborated thus far are laborious and time-consuming.

Like with cellulose [1, 2], the alkalimetric estimation has been also applied for starch [3, 4]. The samples, usually stored in Na^+ form, must be recycled to H^+ form commonly with nitric or hydrochloric acids in alcoholic medium. The spectrophotometric methods used for carboxymethylcellulose [1, 5], like the conductometric estimation [1] and nephelometric method [5], were not applied for starch in greater extent. A gravimetric method has been elaborated, which lies in sample mineralization in the presence of sulfuric acid and subsequent

determination of sodium sulfate [6]. *Kessel* [7] modified the complexometric method of carboxymethylcellulose estimation [2] for lower substituted carboxymethylstarch. *Sideri* and *Osol* determined functional groups in carboxymethylcellulose titrimetrically using perchloric acid in dioxan and prior to estimation, the sample in Na^+ form was suspended in acetic acid [8].

The aim of the present work is to examine the possibility of application of the latter method for carboxymethylstarch with dioxan substitution by acetic acid. Further, we focused our attention on three estimation methods, *i.e.* our modified method, the alkalimetric method being considered as the reference, and complexometric method.

Experimental

All the chemicals applied were anal. grade. A sample of carboxymethylstarch for testing was prepared in our laboratory [4] and had degree of substitution $\text{DS} = 0.35$ determined by the alkalimetric method [4].

A digital pH-meter OP-208/1 (Radelkis, Budapest), with glass and calomel electrodes (OP-0718 P and OP-0830 P, respectively) was used. The glass electrode was stored in dry acetic acid before application. During titration, a bridge containing saturated solution of LiCl in ethanol was applied.

From the values obtained a standard deviation and variation coefficient were calculated.

Alkalimetric estimation of the carboxymethyl group

A sample of carboxymethylstarch in Na^+ form (in the amount required for H^+ form) was converted to H^+ form with nitric acid in methanol and rinsed with neutral methanol [4].

The sample (*ca.* 200 mg, dried *in vacuo* at 80°C for 5 h) was suspended in water (50 cm^3) and solution of NaOH was then added ($c = 0.1\text{ mol dm}^{-3}$; 50 % excess with respect to the consumption expected). After occasional stirring an equal volume of HCl solution ($c = 0.1\text{ mol dm}^{-3}$) was added and excess of HCl was determined with NaOH solution ($c = 0.1\text{ mol dm}^{-3}$) using the potentiometric indication.

Estimation of the carboxymethyl group with HClO_4

Preparation of titration reagent (HClO_4 solution, $c = 0.1\text{ mol dm}^{-3}$)

70 % HClO_4 (5 cm^3) and acetic acid (50 cm^3) were pipetted to a volumetric flask (100 cm^3). Acetic anhydride (25 cm^3) was then carefully added in small portions under

cooling and stirring. After cooling to $(20 \pm 3)^\circ\text{C}$, the volume was made up to 100 cm^3 with acetic acid, again in small portions. The solution prepared in this way can be, according to the needs, diluted to lower concentrations, again with acetic acid.

Estimation of the titration reagent concentration

Sodium carbonate (0.53002 g, dried *in vacuo* at 80°C for 5 h) was dissolved in dry acetic acid and the solution was made up to 100 cm^3 with the same solvent at $(20 \pm 3)^\circ\text{C}$.

The solution of sodium acetate (5 cm^3) was titrated with HClO_4 solution under the same conditions as applied for the estimation of carboxymethylstarch sample.

Estimation of the carboxymethyl groups in carboxymethylstarch sample

A sample of carboxymethylstarch in Na^+ form (*ca.* 200 mg) was heated with occasional stirring in dry acetic acid (30 cm^3) at 80°C . After cooling to $(20 \pm 3)^\circ\text{C}$, the sample was titrated with HClO_4 solution ($c = 0.1\text{ mol dm}^{-3}$) using potentiometric indication and the bridge containing saturated solution of LiCl in ethanol.

Calculation of the degree of substitution $\text{DS}(-\text{CH}_2\text{COONa})$

$$\text{DS}(-\text{CH}_2\text{COONa}) = \frac{\frac{1610 \cdot a}{b}}{100 - \frac{810.3 \cdot a}{b}} \quad (1)$$

where a is consumption of titration reagent (cm^3) and b mass of sample (mg).

Results and discussion

The elaborated method of carboxymethyl group estimation in carboxymethylstarch (Na^+ form) does not require recycling to H^+ form. Non-aqueous medium excludes swelling of the sample connected with a worse penetration of reagent. It is made use of the phenomenon that perchloric acid forms an acetonium ion in acetic acid which is even stronger proton donor than the hydroxonium ion formed in aqueous medium. Preparation of the dry reagent does not require special measures in analytical laboratory. The results obtained by the individual methods are summarized in Tables 1 and 2.

Both the standard deviation and variation coefficient were calculated from 10 measurements in the estimation of functional groups in the sample of car-

Table 1

Estimation of the carboxymethyl groups in carboxymethylstarch (in Na⁺ form) titrimetrically with perchloric acid in acetic acid

Measurement	Sample mass mg	HClO ₄ (<i>c</i> = 0.1 mol dm ⁻³) consumption cm ³	$x_i(-\text{CH}_2\text{COONa})$ %	$\{(x_i - \bar{x})^2\}$
1	202.0	3.82	15.3234	0.0532
2	201.0	3.92	15.8028	0.0618
3	202.2	4.03	16.1498	0.3547
4	205.0	3.79	14.9806	0.3290
5	200.0	3.86	15.6387	0.0071
6	202.5	3.90	15.6057	0.0026
7	205.5	3.92	15.4568	0.0094
8	208.0	4.01	15.6216	0.0045
9	203.0	3.95	15.7669	0.0452
10	200.2	3.75	15.1779	0.1416

$$\{\bar{x}\} = 15.5524; \quad \sum \{(x_i - \bar{x})^2\} = 1.0091$$

$$\text{Standard deviation } s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{(n - 1)}} = \sqrt{\frac{1.0091}{9}} \% = 0.334 \%$$

$$\text{Variation coefficient } v = \frac{s}{\bar{x}} \cdot 100 \% = \frac{33.4}{15.5524} \% = 2.14 \%$$

Table 2

Comparison of the functional group ($-\text{CH}_2\text{COONa}$) estimations and degrees of substitution DS($-\text{CH}_2\text{COONa}$) in the sample of carboxymethylstarch by various methods

Methods of estimation	$(-\text{CH}_2\text{COONa})$	
	$\bar{x}/\%$	DS
Titrimetric estimation with HClO_4 in CH_3COOH	15.5524	0.366
Reference method — alkalimetric estimation after recycling the sample to H^+ form	15.2182	0.357
Complexometric estimation [7]	14.1780	0.328

Note: \bar{x} Values are the average values from 10 estimations. DS values were calculated from \bar{x} values.

boxymethylstarch. From the values obtained, a good reproducibility of the method has been confirmed.

A comparison of the values obtained by the individual methods confirmed a good agreement of the method elaborated with the reference alkalimetric method. The complexometric method [7] gave slightly lower values.

With respect to the dilatation coefficient of acetic acid, some authors require in the preparation of its solutions and for estimations in this solvent a constant temperature. In our work, we achieved a sufficient preciseness and reproducibility in the temperature range of $(20 \pm 3)^\circ\text{C}$, which should not cause any serious problems in analytical laboratory.

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