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Short Communication

DETERMINATION OF THE DEGREE OF ACETYLATION OF CHITIN AND CHITOSAN BY THERMAL ANALYSIS

*I. Garcia Alonso, C. Peniche-Covas** and *J. M. Nieto*

INSTITUTE OF CHEMISTRY AND EXPERIMENTAL BIOLOGY,
CUBAN ACADEMY OF SCIENCES, *CHEMISTRY FACULTY,
HAVANNA UNIVERSITY, HIGHER EDUCATION MINISTRY, CUBA

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Several methods for the rapid determination of the degree of acetylation of chitin and related polymers have been evaluated, including the use of the infrared and the mass spectra.

Chitin and chitosan have characteristic degradation temperatures and it is possible to determine the acetylation degree by the use of empirical correlations based on the weight losses associated with the main decomposition peaks.

This paper presents a new method for the determination of the degree of desacetylation, based on the derivative thermogravimetric analysis of chitin samples.

Experimental

Chitosan samples with different degrees of acetylation and molecular weights of the order of 10^4 were obtained in the Biopolymers Laboratory of the Institute of Chemistry and Experimental Biology, from chitin isolated from shells of lobsters (Panulirus argus) caught on the Cuban Platform.

The percentage of acetyl groups was determined by Lee's method as reported by Rutherford and Austin [1], and the degree of desacetylation was calculated assuming zero desacetylation for the lobster shell chitin (15% of acetyl groups) used as starting material.

Thermal analyses were performed in a derivatograph, using 60 mg of sample and a heating rate of 10 deg/min in an air atmosphere.

Results and discussion

The characteristics of the samples of chitin and chitosan used are summarized in Table 1.

The DTA, DTG and TG curves of chitin are depicted in Fig. 1. It is seen that this polymer does not melt, and starts to decompose at 200° (with formation of volatile and non-volatile compounds) with a maximum degradation rate at 320°, associated with a weight loss (AP) of 59%.

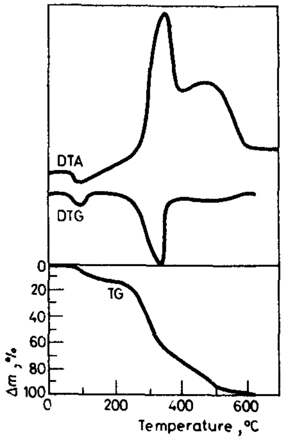

Fig. 1 DTG, TG and DTA curves of chitin isolated from lobster shell

Table 1 Percentage weight losses of chitin samples with different acetylation degrees at the characteristic decomposition temperatures (calculated for moisture- and ash-free samples)

Acetyl groups, %	DTG peak temperature, °C		
	280	320	460
17.0	1.9	59.5	39
15.0	7.3	59.0	37
10.8	24.0	38.0	38
6.0	36.8	23.7	39
5.8	36.8	20.0	43
4.6	41.3	14.9	44
3.3	44.3	14.2	40
3.3	46.2	10.7	43
3.0	46.1	12.8	41
0.8	43.0	6.7	47

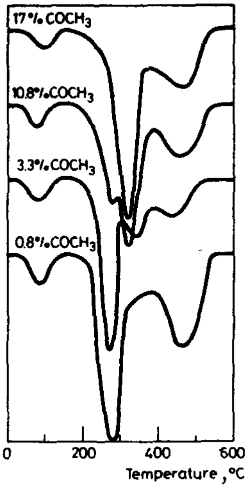

Fig. 2 DTG curves of chitin with different acetylation degree

Prior analysis of the degradation steps of this polysaccharide established that this principal thermal effect is dependent on the molecular weight and the acetylation degree of the polymer [5], as manifested by changes in the weight loss and in the peak temperatures in the DTG and DTA curves.

DTG curves obtained for samples of chitin with different desacetylation degrees are shown in Fig. 2. It can be seen from the curves that as chitin is transformed into chitosan it becomes less stable thermally, exhibiting a maximum decomposition rate at 280°, probably due to the preponderance of the non-acetylated form. When the acetylated form prevails the effect occurs at 320°, whereas as the desacetylation increases the effect at 280° becomes more intense.

The percentage weight losses associated with the fundamental thermal effects, including the exothermic effect at 460° characteristic of the residual decomposition, are shown in Table 1, together with the degree of desacetylation of the sample. It can be observed that as the degree of acetylation decreases, there is a tendency for AP to increase in the DTG curve at 280° (and for AP to decrease at 320°). With this in mind, it was decided to investigate if there was any relationship between the weight losses of the sample (referred to the ash- and moisture-free product) at 280 and 320° and the degree of desacetylation. The results are shown in Fig. 3. The regression lines obtained for the percentage weight loss as a function of the percentage of acetyl groups in the sample exhibit correlation coefficients higher than 0.98 in both cases, the one at 320° being slightly higher. Thus, for effect at 280°

$$Y = -0.33X + 17.16; \quad r = 0.9812$$

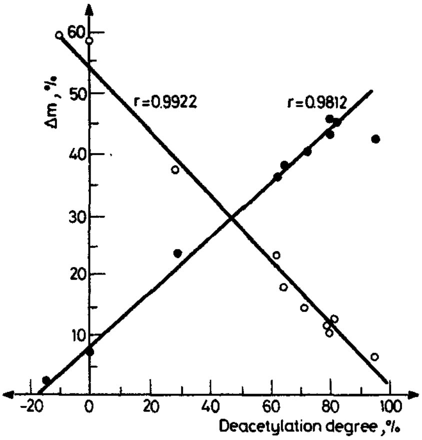

Fig. 3 Effect of desacetylation on the thermal decomposition of chitin. ○ Percentual weight loss measured at 320°C, ● Percentual weight loss measured at 280°C

and for the effect at 320°

$$Y = 0.28X - 0.23; \qquad r = 0.9922$$

where Y stands for the percentage of acetyl groups, and X for the percentage weight loss at the selected temperature.

The results also seem to indicate that the thermal effect at 280° becomes less sensitive to the variation of the percentage of acetyl groups for samples with a degree of desacetylation higher than 80%. The regression line obtained for this effect, considering only samples with a degree of desacetylation lower than 80%, is

$$Y = -0.31X + 17.6; \quad r = -0.9980$$

The high value of the correlation coefficient indicates that the method is highly satisfactory for the determination of the percentage of acetyl groups in a sample with a degree of desacetylation lower than 80%. The relative error in the estimation of the degree of acetylation turned out to be 4%, similar to the 3% obtained with the traditional quantitative method.

As shown before, the method is also applicable to samples with a degree of desacetylation higher than 80%, except that the thermal effect at 320° has to be analyzed instead.

Correlations obtained for the same samples using the IR technique were not so high and gave larger errors than the thermal method just described [6].

Conclusions

The empirical calibration technique developed for the determination of the percentage of acetyl groups in chitin samples using thermogravimetric analysis compares satisfactorily with the one that makes use of IR spectroscopy. The method allows determination of the percentage of acetyl groups in samples of chitin with different degrees of desacetylation in a more rapid and simple way than the traditional chemical methods, while being as accurate as the latter.

References

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