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THERMAL DECOMPOSITION OF ALGINS
AS DETERMINED BY THERMO-BALANCE METHOD*

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Faculty of Fisheries (Hakodate), Hokkaido University.

In general, previous to making a chemical investigation the humidity in the sample must be determined. As water in solid algin combines firmly with algin molecule, it is hardly possible to exactly determine the water content by ordinary method drying at 100°C, and moreover, at higher temperature, thermal decomposition may take place.

Studies on dehydration process of algin are very important not only for chemical investigation on algin, but for industrial manufacture of that substance. However few studies on the dehydration of algin have been made. T. Seiyama(1) pointed out that dehydration of algin was so difficult that constant weight might be obtained by drying for 30 hours at 100°C; moreover, Na-alginate was fairly stable for heat in comparison with other polymolecular substances, and its thermal decomposition proceeded gradually at temperatures from 100 to 170°C, but, over 170°C, the algin has suddenly decomposed.

The present author has observed the process of thermal decomposition of various algins with the thermo-balance and ascertained the decomposition temperatures from the weight reduction curves.

Experimental

As raw material for algins in this experiment, Mitsuishi Kombu, Laminaria angustata Kjellm., was used.

First, alginic acid was made by Suzuki's method(2): The plant was preliminarily treated with boiling water, CaCl₂ solution and with NaCl solution. The treated material was dissolved by adding Na₂CO₃, and the insoluble residue was filtered out. The filtrate was acidified with HCl, where alginic acid was coagulated out. The crude alginic acid was purified repeatedly by the ordinary method. Na-alginate was prepared by adding NaOH to the alginic acid, and insoluble algins (M-Alginate) were derived by double decomposition with their corresponding salts (M-chloride).

The thus prepared algins, such as alginic acid, Na-alginate, Ca-alginate, Fe-alginate, and Al-alginate, were washed with ethanol and next with ether, and dried at 95°C for 2 hours.

But, of Na-alginate, two samples were prepared with different coagulating agents, viz., ethanol and methanol.

* This paper was presented at the annual meeting of the Japanese Society of Scientific Fisheries, Tokyo, April, 1952.
The thermal decomposition was observed with HONDA’s thermo-balance (3) (Fig. 1) at the physico-chemical laboratory of the Science Faculty, Tohoku University.

In the experiment, 0.5 g of the sample was put in Pt-crucible (C), and heated gradually with electric heater (H), and the reduction in weight by drying was observed with reflector (R). The temperature in the electric heater was measured with thermo-couple set in the heater. The oil damper (D) was effective for preventing fluctuation in balancing.

As the velocity of reaction in a solid is very slow, the heating ought to be done as slowly as possible. It took 4-5 hours for elevation from room temperature to 250°C.

Fig. 2 shows the decomposition curves on various algins; their decomposition temperatures are summarized in Table 1.

According to the results the algins seem to be fairly stable against heat.

The weight of algin decreased remarkably till 100°C, where the greater part of free water would be removed, but over 100°C, the curve became almost flat, where a little decomposition of algin or gradual liberation of bound water would take place. However the algin began to decompose suddenly at a certain temperature in the range of 186°C-231.5°C, and gave off a distinct burning smell.

It seems that the decomposability of algin depends upon the combined metal ion of the salt, or on the preparatory treatment: Alginic acid appears to be less stable than the salts, and especially Na-alginate is most stable against heat.

The above results seem to indicate that the metal ion in the salt defends the algin molecule from thermal decomposition, and the defending effect is most remarkable in the case of Na-ion, whose hydration energy is greater than the others.

Even treating in lower temperatures than that of decomposition, the colloidal properties of aqueous solution of the treated algin would be different from the untreated. Colloid-chemi-

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**Results**

The thermal decomposition was observed with HONDA’s thermo-balance (3) (Fig. 1) at the physico-chemical laboratory of the Science Faculty, Tohoku University.

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As the velocity of reaction in a solid is very slow, the heating ought to be done as slowly as possible. It took 4-5 hours for elevation from room temperature to 250°C.

**Table 1. Thermal decomposition temperatures of algins**

<table>
<thead>
<tr>
<th>Algin</th>
<th>Decomposition temperature (°C)</th>
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<tbody>
<tr>
<td>Alginic acid</td>
<td>186</td>
</tr>
<tr>
<td>Na-alginate(1)</td>
<td>221.5</td>
</tr>
<tr>
<td>Na-alginate(2)</td>
<td>231.5</td>
</tr>
<tr>
<td>Ca-alginate</td>
<td>204.5</td>
</tr>
<tr>
<td>Al-alginate</td>
<td>196</td>
</tr>
<tr>
<td>Fe-alginate</td>
<td>218.5</td>
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(1) Na-alginate coagulated with ethanol.
(2) Na-alginate coagulated with methanol.
Fig. 2 Thermal Decomposition of Algins.
A : alginic acid
B : Al-alginate
C : Ca-alginate
D : Fe-alginate
E : Na-alginate (coagulated with ethanol)
F : Na-alginate (coagulated with methanol)

Fig. 2 Thermal Decomposition of Algins.

Summary

Thermal decomposition of various algins, such as alginic acid and its Na-, Ca-, Fe- and Al-salts, was observed respectively with a thermo-balance. Their decomposition temperatures were ascertained from the obtained thermal decomposition curves.

Every investigated algins was fairly stable against heat, especially Na-alginate.

Acknowledgement

The author wishes to thank Prof. N. SUZUKI for his constant encouragement during this work, and Prof. H. TOMINAGA for the use of thermo-balance.

Literature