海藻煮熟工程におけるポリ燐酸塩の寒天抽出効果 II

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Effects of Polyphosphates on Extractability of Agar in the Cooking Process of Seaweeds—II. Effects of Concentration of Polyphosphates and Cooking Period on Extractability of Agar and Gel Properties

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Agar extraction from alkali-treated *Gracilaria* was effectively promoted by an increasing concentration of sodium hexametaphosphate or sodium tripolyphosphate. Melting point and gel strength of the extract became maximum at around $1\times$ to 2×10^{-3} M level, and were reduced at the higher concentrations.

As for cooking period on agar extraction, the highest yield of agar was obtained in 2 to 3 hr. by 2×10^{-3} M sodium hexametaphosphate without acid.

It was shown that sulfuric acid could be replaced by the proper polyphosphates in the agar extraction process.

The useful action of polyphosphates on extraction of agar in the cooking process of seaweeds was pointed out, and the relationship between the comparative effectiveness and the condensation degree of polyphosphates was discussed in the previous report by the author.[1] For the alkali-treated *Gracilaria*, polyphosphates could extract agar much better than sulfuric acid.

In the agar manufacturing industry, sulfuric acid or acetic acid has been solely used as a very necessary agent for extraction of agar from seaweeds in certain cooking conditions.[2] Whereas, it has become a well known fact that any kind of acid works destructive to agar.[2–4]

Therefore, in the extraction process of agar, it is a difficult but an important thing to find out the most appropriate concentration of acid in cooking water with respect to cooking time and temperature. In industry, agar manufacturers have had informations by experience for the required amount of acid which will be variable depending on the kinds of seaweeds and several other factors.[2,5] In the previous study,[1] unnegligible reductions of melting point of extract gels and lowering pH of the extract sols were observed in some of the cases when polyphosphates were used.

The purpose of the study reported here is to determine whether the use of increasing concentration of polyphosphates in cooking water will be effective in promoting extractability of agar and to quantify the influence of increasing concentration of polyphosphates on physical properties of the extracts such as gel strength and melting point of gel. The

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effect of cooking time both on extractability and gel properties of agar was also investigated in this study. Selection of the testing seaweeds and polyphosphates was based on the results of the previous report.[1)]

Experimental

Polyphosphates Sodium hexametaphosphate and sodium tripolyphosphate listed in Table 1 in the first report[1)] were used. Monobasic sodium orthophosphate in the same table was also used as a comparative agent.

Agar seaweeds The same alkali-treated *Gracilaria* (refined dry product) as described in the first report,[1)] was used. The original raw material seaweeds were harvested at Akkeshi Bay, Hokkaido in 1966.

Cooking of seaweeds The seaweeds were cooked in almost the same condition described in the first report,[1)] but cooking extraction was performed only once. Ten g of alkali-treated *Gracilaria* was taken in one liter flask and soaked in 400 ml of 0.025% H_2SO_4 aqueous solution for one hr. Then, the seaweeds were cooked with one of the above mentioned phosphates in several different concentration levels, at the boiling temperature for 2.5 hr under reflux condensers. For the additional one series with hexametaphosphate, no sulfuric acid was used in cooking water. In the case when the effects of cooking period were investigated, no acid was used except 1×10^{-3} M or 2×10^{-3} M hexametaphosphate, and cooking was continued at the boiling temperature for 1 to 4 hr.

Measurements of gel properties and determination of yield of agar Measurements of pH, melting point and gel strength, and determinations of agar concentration of extract gels and yield of agar were all performed by the previously described methods.[1)] Gel strength in this report are shown by the nomographical values at 1.2% absolute concentration level, which are based on the apparent gel strengths of raw gels.

Results and Discussion

Effects of concentration of polyphosphates on agar extraction As can be seen in Fig. 1, extraction of agar was promoted by the increasing concentration of the phosphates. There were trends that yield of agar as well as agar concentration of extract equilibrated by 2 to 3×10^{-3} M sodium hexametaphosphate which was followed up by 3×10^{-3} M sodium tripolyphosphate, and that sodium hexametaphosphate combined with sulfuric acid accelerated extraction of agar. The highest values in yield of agar on the graph were close to the content of agar of the seaweeds. The weights of dried residue corroborated the yield or concentration of agar. The extractability of sodium monobasic orthophosphate at 6×10^{-3} M concentration level was nearly equivalent to that of 1 to

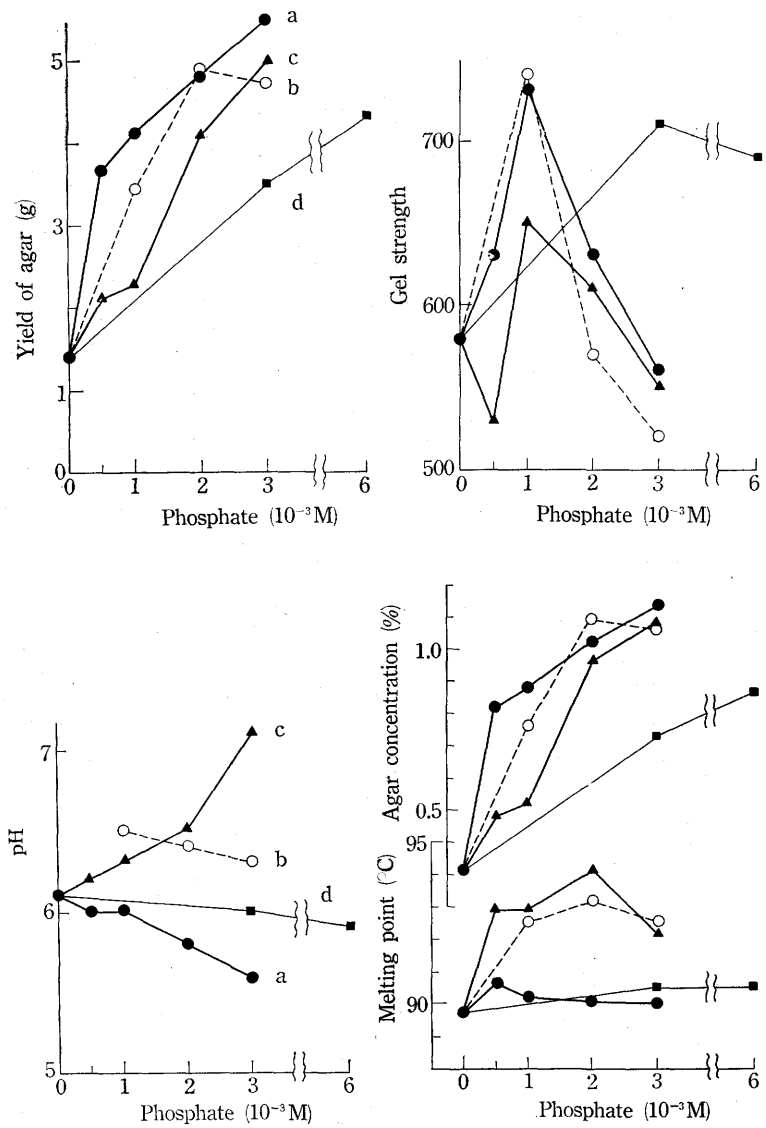

Fig. 1. Effects of phosphate concentration on agar extraction and properties of raw gels (or hot aqueous extracts).

(1) Except one case of mark 'b', phosphates were used in cooperation with 0.025% sulfuric acid. Cooking period of seaweeds was 2.5 hr, respectively.
- a —●— ; Sodium hexametaphosphate and sulfuric acid.
- b ·····○····· ; Sodium hexametaphosphate, without sulfuric acid.
- c —▲— ; Sodium tripolyphosphate and sulfuric acid.
- d —■— ; Monobasic sodium phosphate and sulfuric acid.

(2) Yield of agar is expressed by weight of absolutely dried agar processed from 10 g of seaweeds, alkali-treated *Gracilaria* in air dry condition.

(3) Gel strengths are nomographical values at 1.2% absolute concentration level, which are based on the apparent strengths of raw gels.

2×10^{-3} M hexametaphosphate or tripolyphosphate. The rank order of the comparative extractability for these polyphosphates and monobasic orthophosphate agrees with the result in the previous report.[1]

Effects of concentration of polyphosphates on gel properties of agar Gel strength (nomographical value at 1.2% concentration level) became maximum at 1×10^{-3} M for both of the polyphosphates. There was almost no difference between gel strength graphs of agar extracted by use of hexametaphosphate and hexametaphosphate combined with sulfuric acid. Melting point (at the individual concentration level) became highest at 2×10^{-3} M concentration levels of tripolyphosphate with acid and hexametaphosphate without acid, but was reduced by hexametaphosphate combined with acid at all the concentration levels between $0.5\times$ and 3×10^{-3} M. Taking account of the agar concentrations of gels at which the individual melting points were measured, enhancement of melting point reduction was also observed for monobasic orthophosphate. The general relationship between melting point of agar gel and agar concentration was previously reported by MATSUHASHI.[6] Though a close relationship between melting point and gel strength of the industrially processed agar was also pointed out by the same author,[6] melting point of gel is considered to be a more sensitive indicator than gel strength to such destructive actions by acid or monobasic orthophosphate.

Judging from the melting points, sulfuric acid used together with hexametaphosphate had much stronger influence to reduce gelling properties than hexametaphosphate without acid. Nevertheless, tripolyphosphate with acid was far less destructive to melting point of gel than hexametaphosphate with acid. The relatively high pH values of sols, or the buffer action by tripolyphosphate might be the cause for that. However, comparing with two data resulted by 2×10^{-3} M and 3×10^{-3} M tripolyphosphate with acid, the reduction of melting point or gel strength was not interrupted by the increased concentration of tripolyphosphate. These things may suggest that the actions of sodium hexametaphosphate and sodium tripolyphosphate on gelling properties of agar are fundamentally caused by their chemical structures as the condensed phosphates.

The pH values showed trends to decrease with the increasing concentration of both hexametaphosphate with acid and hexametaphosphate without acid. In contrast, the pH curve by tripolyphosphate with acid directed upward with the increasing concentration of tripolyphosphate, which did not agree with the pH curves of the commercial polyphosphates reported by MATSUHASHI in the other paper.[7] It is considered that the buffer action of such polyphosphates is more complicated in agar solution or seaweeds extract than in water.

Effects of period of cooking with hexametaphosphate on extraction and gel properties of agar Fig. 2 shows the effects of cooking period. By use of 2×10^{-3} M sodium hexametaphosphate, agar extraction was equilibrated in 2 to 3 hr. cooking, and the yields

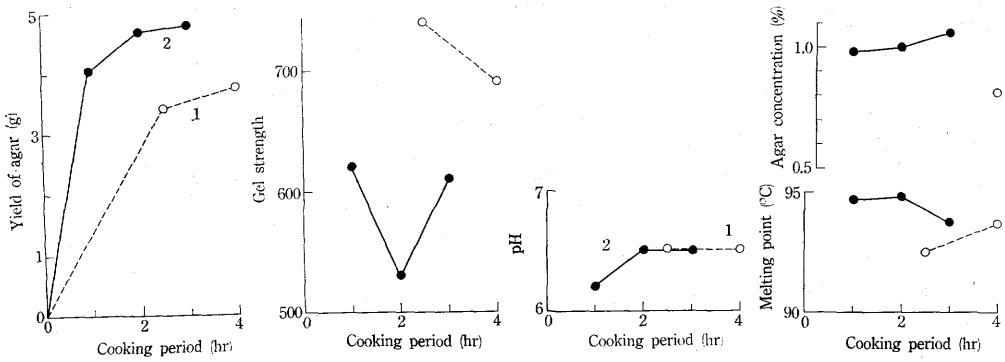

Fig. 2. Relationship between cooking period of seaweeds and agar extraction, in the case when sodium hexametaphosphate was used.

(1) Sodium hexametaphosphate was used at the following concentration levels.
1 ·····○····· ; 1×10^{-3} M.
2 ——●—— ; 2×10^{-3} M.

(2) The values of yeild of agar, gel strength and melting point, are similarly expressed as in the case of Fig. 1 ,respectively.

were close to the content of agar of the seaweeds. By use of 1×10^{-3} M hexametaphosphate, however, agar extraction was incomplete in 4 hr. cooking.

Melting point and gel strength were little affected by cooking period. Elimination of sulfuric acid was probably the principal reason. In Fig. 2, the sudden drop of gel strength at 2 hr. cooking with 2×10^{-3} M hexametaphosphate would be caused by an unknown factor other than the effect of the extracting agent.

Effective use of polyphosphate The influence of sulfuric acid as well as polyphosphates in higher concentration and longer cooking period on melting point and gel strength of the extract were quite similar to these influences on gels of the commercial powder agar, as reported by the same author.[8] Therefore, when an effective polyphosphate such as sodium hexametaphosphate is used in the extraction process of agar, sulfuric acid can be avoided.

For instance, 2 or 3 hr. cooking with 2×10^{-3} M sodium hexametaphosphate may be the most appropriate extracting condition of agar from the alkali-treated *Gracilaria*, the species used in this experiment. The combined use of sodium hexametaphosphate and sodium tripolyphosphate is postulated to be a more practical extracting agent with respect to both yield of agar and gel properties.

In the industrial view point, the use of sulfuric acid is decisively more economical than the use of polyphosphates, provided that an expected amount of agar with reasonable gel properties is produced. However, in the case when sulfuric acid does not work as an extracting agent, as in the case of the alkali-treated *Gracilaria* of this experiment, the use of polyphosphates for extraction of agar is quite significant. As a chemical, any kind of polyphosphate is more expensive than sulfuric acid, but much more inexpensive than

agar. Therefore, the cost of polyphosphates can be well covered by the increased amount of products. Elimination of sulfuric acid which is very destructive to gel properties[3] will be another advantage for agar processing. Furthermore, by the use of polyphosphates in the cooking process of seaweeds, whitening effect on dry agar which is due to the chelating action of polyphosphates[7,9,10] will be naturally expected in some extent. All of the sodium polyphosphates which are listed in Table 1 of the first report[1] are the approved food additives by the Japanese Food Sanitation Law as well as by the Federal Food, Drug, and Cosmetic Act of the United States of America.

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