Applicability of Viscosity Measuring Method to the Detection of Irradiated Spices

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The conditions for measuring viscosity of spices to detect radiation treatment and the applicability of the method to various spices were investigated. Viscosities of black and white peppers, ginger and turmeric decreased depending upon dose, when they were measured after heat gelatinization at pH 12. However, the viscosities of cinnamon and nutmeg did not show a dose dependent relation. The viscosity of irradiated onion powder was lower than that of unirradiated sample, when determined at pH 5 without any heat treatment. A normalized viscosity parameter, viscosity/starch content (mPa.s/g of starch), resulted in almost constant values for unirradiated black and white peppers, irrespective of the harvesting locality. The results in this study suggest that irradiated black and white peppers can be detected by viscosity measurement without any information about the harvesting locality.

Spices are major food items treated with ionizing radiation and are irradiated on a commercial basis in more than 15 countries¹⁾. However, the irradiation of these food commodities are not cleared in Japan; irradiated spices can not be imported or marketed in our country. It is necessary to identify irradiated foods in order that the responsible authorities properly control irradiated foods based on the regulation in the countries where food irradiation is cleared as well as those where food irradiation is banned. Internationally it is required that irradiated foods are labeled with words or sentences indicating the treatment²⁾. Reliable methods to detect irradiated foods are useful means to check the compliance with labeling regulation and to supplement labeling³⁾, and it is highly required to develop such methods.

Although no method for detecting irradiated spices has been established, several promising methods have been proposed³⁾⁻⁷⁾. One of such methods is viscosity measurement⁸⁾⁻¹¹⁾. FARKAS *et al.*⁹⁾¹⁰⁾ reported that the viscosities of black and white peppers, nutmeg and ginger

were considerably lowered by irradiation, and HEIDE *et al.*¹¹⁾ reported that the viscosity of aqueous suspension of spice was decreased by irradiation for some spices such as pepper and ginger but was increased for others such as onion powder and lemon peel. The changes in viscosity were observed in starch¹²⁾¹³⁾, pectin¹⁴⁾⁻¹⁷⁾ and cellulose¹⁴⁾. The degradation of such polysaccharides has been regarded as a major cause of the viscosity change of irradiated spices.

FARKAS *et al.*⁹⁾¹⁰⁾ and HEIDE *et al.*¹¹⁾ reported some inconsistent results on the viscosity change of spices caused by irradiation. For example, HEIDE *et al.*¹¹⁾ observed a distinct difference in the viscosity between unirradiated and irradiated onion powders, while FARKAS *et al.*⁹⁾¹⁰⁾ did not observe any difference. The difference in the condition for viscosity measurement might have influenced the inconsistent results on the viscosity changes caused by irradiation. It is necessary to establish the conditions for viscosity measurement in order that all of the scientists and inspectors at responsible authorities and private sectors can

obtain consistent results. The conditions for measuring viscosity of spices and the applicability of the method to various spices were investigated in this study.

materials and methods

Polysaccharides and spices

Starch (from corn), pectin (from citrus) and cellulose (microcrystalline) were purchased from Wako Pure Chemical Industries, LTD. White pepper, black pepper, cinnamon, ginger, nutmeg, turmeric and onion powder were donated by Japanese spice companies. The samples smaller than 700 μm were used for viscosity measurement.

Irradiation and storage of samples

The polysaccharides and spices were packed in polyethylene bags and irradiated with a Gammacell 220 (AECL, Canada, 6.0 kGy/h). Spice samples were stored at 30°C and R.H. 70 % in a dark room.

Viscosity measurement

Unless otherwise stated, the viscosity was measured immediately after irradiation, according to FARKAS *et al.*¹⁰⁾ and HEIDE *et al.*¹¹⁾, with a slight modification, as follows.

Suspensions of spices (10%, w/v) were homogenized with a Polytron PCD-2 (KINETICA GmbH, Switzerland) for 1 min at the maximum speed and the pH was adjusted to 12 with 33% NaOH. The suspensions were heated in boiling water under agitation for 30 min, followed by incubation for 3 h at 30°C. The viscosity of the gelatinized suspension was measured at 30°C with a HAAKE Rotovisco RV 12 and a

coaxial cylinder type Rotor NV (HAAKE Mess-Technik GmbH, Germany). The suspension (9 ml) was put in the rotorcup and the shear rate was raised at 128 rpm/min to 256 rpm, and then the apparent viscosity (mPa.s) was measured at 256 rpm.

Determination of starch content of spices

Ten mg of spice was incubated with 1N HCl for 2.5 h at 100°C, and then liberated glucose was determined with the aid of enzyme reactions of glucose oxidase and peroxidase according to HAYASHI *et al.*¹⁸⁾

Results and Discussion

Viscosity change of carbohydrates by irradiation

The pH of the suspensions of starch, pectin and cellulose were adjusted to 5 or 12 with 3 N HCl and 33% NaOH, and then the viscosity was measured at 30°C. The same suspensions were heated in boiling water for 30 min followed by incubation for 3 h at 30°C, and then the viscosity was measured at the temperature.

The difference in the viscosity between unirradiated starch and irradiated one was the largest, when it was measured at pH 12 after the heat treatment (Table 1). The heat treatment under an alkaline condition facilitated the swelling and gelatinization of starch which resulted in a distinct difference in viscosity between unirradiated and irradiated samples. The viscosity of pectin was decreased by irradiation when measured at pH 5 without heat treatment, and a significant alteration of viscosity of cellulose could not be observed by

Table 1 Effect of pH and heating on the viscosity of polysaccharides (mPa · s)

		Non-heating		Heating	
		pH=5	pH=12	pH=5	pH=12
Starch	0 kGy	1.8±0.1	1.6±0.1	71.7±3.6	92.7±3.0
(5.5%)	10 kGy	1.6±0.1	1.7±0.1	17.1±1.5	11.8±1.5
Pectin	0 kGy	107.0±7.9	12.3±1.1	59.3±9.9	8.2±1.7
(2.5%)	10 kGy	60.7±4.7	11.5±1.2	34.2±7.2	10.5±2.6
Cellulose	0 kGy	2.1±0.2	1.9±0.5	2.0±0.5	1.7±0.2
(2.5%)	10 kGy	1.6±0.6	1.9±0.4	2.1±0.2	1.8±0.1

Mean value ± standard deviation for 3 measurements.

the method employed in this study.

HEIDE *et al.*¹¹⁾ reported that the optimum condition for viscosity measurement for detecting irradiated spice is different with item of spice. Based on the results shown in Table 1 and those reported by HEIDE *et al.*¹¹⁾ it is suggested that the condition for measuring viscosity of spice is different depending upon the major carbohydrate in the spice: the viscosities of spices with high starch contents should be measured under an alkaline condition after heat treatment, and those of spices with high pectin contents should be measured under an acidic condition without heat treatment. The viscosity measurement after heat treatment under an alkaline condition would get rid of most of the influences of pectin and cellulose, because the influence of radiation on the viscosities of the two carbohydrates were small under the condition.

Viscosities of spices under different conditions

The viscosities of black and white peppers, ginger and turmeric were significantly different between unirradiated and irradiated samples, when the viscosities were measured after heat

treatment at pH 12; the irradiated spices gave lower viscosity values than the unirradiated ones (Table 2). However, no significant difference was observed between unirradiated and irradiated samples for cinnamon and nutmeg. Most of these results agreed with those reported by FARKAS *et al.*¹⁰⁾ and HEIDE *et al.*¹¹⁾. However, FARKAS *et al.*¹⁰⁾ reported a difference in viscosity between unirradiated nutmeg and irradiated one, and HEIDE *et al.*¹¹⁾ reported a difference between unirradiated cinnamon and irradiated one, which were inconsistent with the results in this study. The viscosity measuring systems such as apparatus and suspension concentration were different among the 3 research groups, which might have resulted in inconsistent results.

The viscosity of onion powder was lowered by irradiation, when the viscosity was measured at pH 5 without heat treatment. The viscometric condition in the present study was same as that of HEIDE *et al.*¹¹⁾, but irradiated onion powder gave a higher value than unirradiated one in the study of HEIDE *et al.*¹¹⁾ FARKAS *et al.*¹⁰⁾ did not observe any viscosity change of onion powder by irradiation. The

Table 2 Effect of pH and heating on the viscosity of spices (mPa · s)

		Non-heating		Heating	
		pH=5	pH=12	pH=5	pH=12
White pepper	0 kGy	35.4± 5.6	34.5± 2.7	134.9±10.2	128.8± 6.4
	10 kGy	30.5± 5.8	27.8± 7.6	79.0± 8.8	59.4± 2.9
Black pepper	0 kGy	72.3±10.1	64.8± 3.7	83.4± 5.4	85.4± 2.6
	10 kGy	74.4± 1.4	71.0±11.0	45.7± 4.2	41.3± 0.6
Cinnamon	0 kGy	— — — a	— — — a	45.0± 3.4	36.2±19.8
	10 kGy	— — — a	— — — a	28.6±25.6	29.1±14.7
Ginger	0 kGy	66.6± 7.8	33.7± 5.5	92.6±11.0	94.3± 4.0
	10 kGy	49.5± 5.3	31.5±10.8	59.8± 2.8	48.5± 0.5
Nutmeg	0 kGy	— — — a	— — — a	23.7± 1.1	20.0± 0.4
	10 kGy	— — — a	— — — a	28.1± 5.6	17.8± 1.6
Turmeric	0 kGy	— — — a	— — — a	97.0±18.7	96.3± 9.0
	10 kGy	— — — a	— — — a	70.6±19.3	60.8± 3.5
Onion powder	0 kGy	55.0± 7.1	23.5± 0.8	49.4± 4.7	26.8± 6.3
	10 kGy	37.4± 6.1	20.5± 1.1	35.3± 7.8	35.2± 5.2

Mean value±standard deviation for 3 measurements.

a: Viscosity could not be measured.

difference in the viscosity of onion powder was insignificant, when the viscosity was measured at pH 12 (Table 2). FARKAS *et al.*¹⁰⁾ measured the viscosity of onion powder at pH 12 after heat treatment, which would have led to the same viscosity value of unirradiated and irradiated samples.

Dose dependence of viscosities of spices

The viscosities of black and white peppers, ginger and turmeric decreased depending upon dose, when they were measured after heat treatment at pH 12 (Table 3). However, the viscosities of cinnamon and nutmeg did not show a dose dependent relation. These results agreed with those shown in Table 2. Although the viscosities of black and white peppers showed a decrease depending upon dose, they varied with harvesting locality.

It was expected that a parameter consisting of viscosity and starch content would be better than a viscosity value itself for detecting irradiated spices, because starch greatly contributed to the viscosity change caused by irradiation as shown in Table 1.

The starch contents of peppers were not influenced by irradiation; $42.1 \pm 1.9\%$ for black pepper from Sarawak, $40.3 \pm 0.5\%$ for black pepper from India, $58.7 \pm 2.0\%$ for white pepper from Sarawak, $51.9 \pm 0.8\%$ for white pepper from Indonesia, $14.3 \pm 1.2\%$ for cinnamon, $43.5 \pm 1.5\%$ for ginger, $26.8 \pm 1.5\%$ for nutmeg, and $44.2 \pm 3.1\%$ for turmeric. The results on viscosity (Tables 2 and 3) and starch contents indicated that spices with high starch contents could be detected by viscosity measurement after heat treatment under an alkaline condition; black and white peppers, ginger and turmeric all of which contained starch at levels higher than 40% showed a decrease in viscosity depending upon dose.

A normalized viscosity parameter, viscosity/starch content (mPa.s/g of starch), resulted in almost constant values for unirradiated peppers, irrespective of the harvesting locality (Table 4). The normalized parameters for unirradiated black peppers were almost the same as those for unirradiated white peppers. The parameters determined after the storage

Table 3 Dose dependence of viscosity of various spices (mPa · s)

	0 kGy	5 kGy	10 kGy	15 kGy
Black pepper (Sarawak)	89.0 ± 1.6	61.0 ± 2.1	39.0 ± 1.7	30.6 ± 1.9
Black pepper (India)	83.5 ± 2.1	58.7 ± 2.1	34.1 ± 1.8	27.2 ± 0.5
White pepper (Sarawak)	131.9 ± 3.2	89.2 ± 2.9	40.8 ± 1.7	32.6 ± 1.8
White pepper (Indonesia)	109.2 ± 1.2	71.2 ± 1.5	36.6 ± 1.5	22.2 ± 0.5
Cinnamon	36.0 ± 18.9	38.6 ± 18.9	29.7 ± 15.7	28.8 ± 12.6
Ginger	110.3 ± 7.1	67.6 ± 2.0	52.9 ± 1.2	37.3 ± 1.7
Nutmeg	19.9 ± 0.6	15.9 ± 1.8	17.1 ± 2.4	14.3 ± 1.9
Turmeric	96.8 ± 8.5	72.2 ± 5.0	64.1 ± 1.5	53.1 ± 1.2

Mean value $\pm$ standard deviation for 3 measurements.

Table 4 Dose dependence of viscosity/starch of black and white peppers immediately after irradiation (mPa · s/g of starch)

	0 kGy	5 kGy	10 kGy	15 kGy
Black pepper (Sarawak)	211.4 ± 3.9	144.8 ± 5.1	92.7 ± 4.1	72.7 ± 4.6
Black pepper (India)	207.2 ± 5.2	145.7 ± 5.2	84.6 ± 4.5	67.5 ± 1.2
White pepper (Sarawak)	224.7 ± 5.5	152.0 ± 4.9	69.5 ± 2.9	55.5 ± 3.1
White pepper (Indonesia)	210.4 ± 2.3	137.2 ± 2.9	70.5 ± 2.9	42.8 ± 1.0

Mean value $\pm$ standard deviation for 3 measurements.

Table 5 Dose dependence of viscosity/starch of black and white peppers 6 months after irradiation (mPa · s/g of starch)

	0 kGy	5 kGy	10 kGy	15 kGy
Black pepper (Sarawak)	223.1±4.1	159.4±5.8	101.2±6.1	71.8±3.2
Black pepper (India)	206.8±2.1	145.2±3.4	88.1±5.6	69.2±2.8
White pepper (Sarawak)	224.0±4.1	155.5±5.1	75.5±3.5	55.1±1.5
White pepper (Indonesia)	227.9±9.5	137.0±2.7	69.3±0.3	41.0±1.2

Mean value±standard deviation for 3 measurements.

for 6 months at 30°C were not significantly different from those determined immediately after irradiation (Tables 4 and 5), which indicated that the parameters did not notably change during the storage at 30°C.

The results in the present study were consistent with those reported by FARKAS *et al.*¹⁰⁾ and HEIDE *et al.*¹¹⁾, in that spices with high starch contents could be detected by measuring the viscosity after heat gelatinization under an alkaline condition. The viscosity measuring method can be applied to at least black and white peppers for detecting radiation treatment. A normalized parameter (viscosity/starch content) could avoid the effect of harvesting locality of peppers and was concluded to be a better parameter than a viscosity value.

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粘度測定による照射香辛料の検知の可能性

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照射処理の検知のための香辛料の粘度測定条件と粘度測定による照射香辛料の検知の可能性について検討した。pH 12 で加熱処理してから粘度測定を行うと、黒コショウ、白コショウ、ジンジャー、ターメリックの粘度は線量に依存して低下した。シナモンとナツメグの粘度は放射線の影響をあまり受けなかった。加熱処理を行わずに pH 5 で粘度を測定すると、照射によるオニオンパウダーの粘度の低下が観察された。非照射の黒コショウおよび白コショウの「粘度/澱粉含量」の値は、収穫地の影響を受けずほとんど一定であった。