

Flavor and Browning Enhancement by Electrolytes during Microwave Irradiation of the Maillard Model System

Helen C. H. Yeo and Takayuki Shibamoto*

Department of Environmental Toxicology, University of California, Davis, California 95616

The volatile compounds obtained from an L-cysteine/D-glucose system with various electrolytes during microwave irradiation were analyzed by gas chromatography and mass spectrometry. The effects of electrolytes on browning intensity were measured by a UV spectrophotometer. The electrolytes studied included sodium chloride, calcium chloride, ferrous chloride, and sodium sulfate over a concentration range of 0-0.5 M. All electrolytes used exhibited an enhancement in both flavor production and browning intensity. Sodium chloride promoted the greatest amount of volatiles (7 times more than the control) and ferrous chloride the least (3 times more than the control) in this model system. Adding sodium chloride also gave the highest browning intensity, with maximum absorbance units (AU) of 1.93; ferrous chloride gave the lowest, with 0.81 AU.

Foods prepared in microwave ovens have not been well accepted in most households due to the lack of browning and desirable flavors. Some attempts have been made to increase browning and crisping in microwaved foods. The recent development of cooking gadgets such as susceptor packings has partially overcome this problem. However, in addition to browning and crispness, odors, off-flavors, and occasional fire hazards developed (McCowan and Brown, 1988). Other attempts include the use of food coating compositions containing starches and salts (Hsia and Ogasawara, 1985). Maillard mixtures consisting of either lactose and L-serine (Nagai, 1973a) or lactose and DL-threonine (Nagai, 1973b) were also applied. Despite these developments, more research is still needed to improve the production of both browning and desirable flavors in microwavable foods.

The theory of microwave heating has been much discussed in the literature (Goldblith, 1967; Copson, 1975; Mudgett, 1989). There are two mechanisms by which microwaves heat: dipole rotation and ionic polarization (Decareau and Peterson, 1986). Dipole rotation occurs when polar molecules (e.g., water, in the case of most food systems) attempt to align in an electromagnetic field. The friction resulting from rotation causes the materials to heat up and disrupts weak hydrogen bonds. Ionic polarization, in contrast, occurs in samples containing ions such as electrolytes. In the presence of an electromagnetic field, the positive ions (e.g., Na⁺) undergo electrophoretic migration toward the negative pole and the negative ions similarly move to the positive poles. In doing so they collide with other ions and molecules, thus generating heat. Hasted et al. (1948) demonstrated that dissolved salts or electrolytes in the presence of a microwave field affect the dielectric behavior of water in food by binding to water molecules and depressing the dielectric constant to levels below those of pure water.

In the present study, common electrolytes such as sodium chloride, calcium chloride, sodium sulfate, and ferrous chloride were used to investigate their effects on microwave browning and the production of flavor chemicals during microwave irradiation. There are a few papers concerning the effect of electrolytes on Maillard browning in model systems (Kaanane and Labuza, 1989; Chen et al., 1988). The Maillard system, consisting of D-glucose and L-cysteine, was used because it is widely known to be one

of the major processes causing browning in thermally treated foods (Hodge, 1953; Shibamoto, 1989).

EXPERIMENTAL PROCEDURES

Materials. L-Cysteine and D-glucose were purchased from the Aldrich Chemical Co. (Milwaukee, WI); dichloromethane was obtained from the J. T. Baker Chemical Co. (Phillipsburg, NJ). The stock solution of internal standard for GC analysis was prepared by adding 1 mg of undecane to 10 mL of dichloromethane and stored at 5 °C. All authentic chemicals were purchased from reliable commercial sources.

Sample Preparation. L-Cysteine (0.05 mol) and D-glucose (0.05 mol) were dissolved in 200 mL of deionized water to make a model mixture. Solutions for irradiation were prepared by mixing 50 mL of the model mixture with various amounts of sodium chloride (0, 2.5, 5.0, and 10.0 mmol). The solution containing no sodium chloride served as the control sample. The group of solutions was then irradiated at the high setting of a 700-W microwave oven for 16.5 min. This irradiation time was chosen because browning did not occur until this time. At 4-min intervals, the irradiation was interrupted and the samples were rotated 90° to ensure uniform irradiation. The uniformity of the sample was confirmed by placing identical samples in different starting positions and irradiating the sample for the same time period. No significant variations in the total yield of volatiles were observed. The samples were prepared in open systems to mimic actual cooking conditions.

After irradiation, each brown mass formed was dissolved in 100 mL of deionized water. Five milliliters of each of the samples was used for absorbance measurements. After 1:10 dilution, the degree of browning in the sample was determined by measuring the visible absorbance of the aqueous sample at 420 nm.

The remaining 95 mL was adjusted to pH 8 with 6 N NaOH to enhance the extraction efficiency of nitrogen-containing heterocyclic compounds. The microwave products were extracted with 50 mL of dichloromethane with a liquid-liquid continuous extractor for 6 h, and the extract was dried over anhydrous sodium sulfate for 12 h. The sodium sulfate was then removed by filtration, and the filtrate was concentrated to slightly in excess of 1 mL by fractional distillation with a Vigreux column. The solution was then transferred into a concentration tube and its volume reduced to exactly 1 mL under a purified nitrogen stream. Undecane (0.5 mL of stock solution) was then added as a gas chromatographic internal standard, and the solution was further reduced to 0.5 mL under a nitrogen stream.

The effects of calcium chloride, ferrous chloride, and sodium sulfate were also studied by using the same methodology as above. Each experiment was performed in duplicate.

Identification of Products Formed in the L-Cysteine/D-Glucose Model System. The samples were analyzed by gas

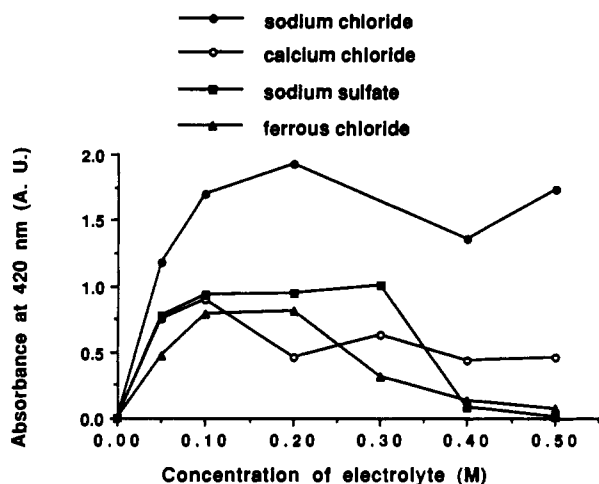


Figure 1. Effects of electrolytes on the degree of browning in the L-cysteine/D-glucose model system upon microwave irradiation.

chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Identification of the chromatographic peaks of the samples was made by comparing their mass spectra and gas chromatographic retention indices to those of authentic compounds.

Instruments. A Quasar Model MQ 7796 AW, 700-W, Easy-Matic Cooking microwave oven was used for the irradiation of the samples.

A Hewlett-Packard (HP) Model 8452A diode array spectrophotometer with HP 89510 UV-vis software was used to measure the degree of browning at 420 nm.

A HP Model 5890 gas chromatograph equipped with a flame ionization detector (FID) and a 60 m × 0.25 mm i.d. DB-WAX bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA) was used for routine analysis. Peak areas were integrated by using a Spectra Physics Chromjet integrator. The GC oven was held at 60 °C for 4 min and then programmed at 4 °C/min to a final temperature of 180 °C, which was held for 30 min. The temperatures of the injector and the detector were 240 and 250 °C, respectively. The helium carrier gas flow rate was 27.8 cm/s. The injector split ratio was 1:45.

A HP Model 5890 GC interfaced to a VG Trio II mass spectrometer with a VG 11-250 computer data system was used for MS identification of the GC components. The ionization voltage was 70 eV, and the ion source temperature was 150 °C. The column and oven conditions for GC/MS were as described for the HP 5890 GC/FID analysis.

RESULTS AND DISCUSSION

Figure 1 shows the absorbance of the aqueous Maillard sample over concentrations of 0–0.5 M sodium chloride, sodium sulfate, ferrous chloride, and calcium chloride. During the irradiation time studied, there was no significant browning in each control sample. The average absorbance at 420 nm was 0.002 absorbance units (AU). All samples containing an electrolyte showed an enhancement in the browning intensity. The enhancement may partly be a consequence of the increased absorption of microwave irradiation resulting from ionic polarization.

This observation may also be attributed to the different dielectric properties of the sample in the various electrolytes. It is widely known that electrolytes/salts change the dielectric properties of a solution (Hasted et al., 1948). Dissociated salts such as sodium chloride and calcium chloride, for example, exhibit a relatively higher dielectric property than associated salts (Mudgett et al., 1971). However, the response difference between sodium chloride and calcium chloride may be due to the ionic size and charge on the cations. Increasing charge or decreasing

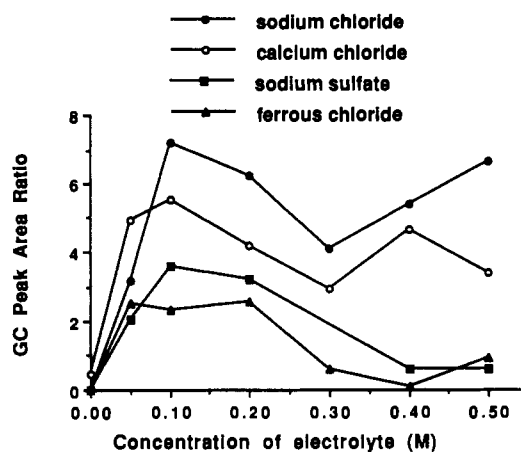


Figure 2. Effects of electrolytes on the total yield of volatiles in the L-cysteine/D-glucose model system upon microwave irradiation.

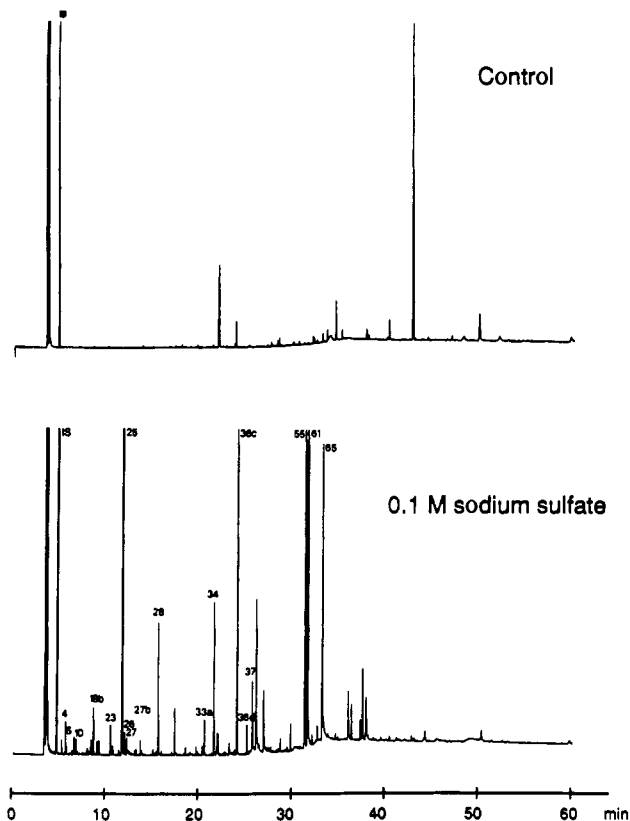


Figure 3. Typical chromatogram of dichloromethane extract of L-cysteine/D-glucose model reaction in the control sample (above) and in the presence of sodium sulfate (below).

radius causes a greater immobilization of water around the cation (Burgess, 1978).

Among the electrolytes with chloride anions, sodium chloride promotes the highest degree of browning, followed by calcium chloride and ferrous chloride (Figure 1). This may be explained by the difference in size and charge of the cation mentioned above. Between the electrolytes with sodium cations, sodium sulfate showed a lower enhancement in the browning intensity than sodium chloride. This is because sodium sulfate contains twice the amount of Na⁺ ion compared to sodium chloride at the same concentration. Thus, the higher amount of Na⁺ may lead to greater immobilization of water molecules and lower microwave absorption.

Sodium sulfate caused a sudden decrease in browning intensity at concentrations higher than 0.3 M (Figure 1).

Table I. Volatiles Produced in an L-Cysteine/D-Glucose Model System upon Microwave Irradiation in the Presence of 0.1 M Electrolytes

compd	peak no. ^b	GC peak area ratio ^a							
		NaCl		CaCl ₂		FeCl ₂		Na ₂ SO ₄	
		I	II	I	II	I	II	I	II
trimethyloxazole	2	0.9	0.6	c	c	c	c	c	c
2-methylpyridine	4	4.8	2.4	d	d	0.6	0.6	0.7	1.1
thiazole	5	2.2	1.4	0.1	0.1	d	d	0.3	0.3
1,2-ethanedithiol	10	2.9	2.9	1.0	1.1	d	d	0.8	0.7
acetic acid	18b	5.0	3.5	d	d	c	c	1.3	1.4
furfural	23	0.9	0.9	d	d	1.0	1.2	0.8	1.6
2-acetylfuran	25	302.1	261.1	62.5	71.1	23.3	20.6	129.8	132.2
2-thiophenethiol	26	6.8	5.5	2.2	2.6	d	d	0.9	0.8
3-thiophenethiol	27	1.1	1.1	c	c	c	c	c	c
5-methyl-2-furfural	27b	2.4	2.3	c	c	0.6	0.5	0.8	0.9
α -furfuryl alcohol	28	9.7	7.6	d	d	c	c	3.8	4.2
unknown	33a	5.2	3.0	c	c	1.2	1.0	1.0	1.5
C ₇ H ₁₂ O ₂	34	26.1	23.6	c	c	9.1	6.3	5.8	6.7
2-acetylpyrrole	36c	62.8	66.1	20.1	26.9	20.8	18.2	26.5	23.4
C ₆ H ₆ O ₃	36d	1.9	1.8	3.2	4.6	40.9	45.4	1.4	1.8
4-hydroxy-6-methyl-2H-pyran-2-one	37	7.3	6.3	6.0	10.8	c	c	7.3	3.7
3,5-dihydroxy-2-methyl-4H-pyran-4-one	55	73.6	114.5	215.5	320.1	57.8	63.4	51.5	50.0
C ₆ H ₇ NO	61	51.1	80.3	40.3	63.3	27.3	26.5	49.6	48.2
C ₆ H ₄ OS ₂	65	6.0	10.1	c	c	9.1	11.0	9.8	21.0

^a GC peak area of product/GC peak area of internal standard. Duplicate samples I and II are presented. ^b Values correspond to the peak number on the gas chromatogram in Figure 3. ^c Not detected. ^d Trace level. GC peak area ratio less than 0.05.

The more drastic decrease in the browning intensity compared with the other electrolytes suggests that it is probably due to the higher amounts of Na⁺ present, leading to a greater immobilization of water molecules. Over the concentration of electrolytes studied, the presence of sodium chloride and ferrous chloride in the model system induced a maximum in the browning intensity at around 0.1–0.2 M; the presence of calcium chloride was around 1.0 M, and that of sodium chloride was around 0.1–0.3 M. At this point it can only be speculated that the browning maximum observed in these solutions may be due to two competing factors: ionic polarization and immobilization of water. At concentrations below the maximum point, ionic polarization is the dominating factor in promoting browning. However, as the concentration of electrolytes increases above the maximum point, the immobilization of water by the cations in solutions may be the dominating factor leading to a decrease in browning.

Figure 2 shows the total volatiles obtained from the model system in the presence of different electrolytes. The total volatiles were expressed as total GC peak area ratio. There was a promotion of the amount of volatiles obtained when electrolytes were added. The samples with sodium chloride gave the highest amount of volatiles, followed by calcium chloride, sodium sulfate, and ferrous chloride.

Figure 3 shows a typical gas chromatogram of the control sample and the sample with 0.1 M sodium sulfate. There is a dramatic enhancement in the production of volatile compounds in the presence of an electrolyte. However, this may not necessarily correspond to the formation of desirable flavors. The peak at approximately 43 min in the control sample is a contaminant.

Maximum quantities of major volatile compounds were generated at electrolyte concentrations of 0.1 M. Table I shows data for duplicate samples at 0.1 M concentration of each electrolyte. A total of 19 compounds were detected in samples with sodium chloride, 13 compounds with calcium chloride, 14 compounds with ferrous chloride, and 17 compounds with sodium sulfate. The major compounds obtained were furan and pyrone derivatives including furfural, 2-acetylfuran, 5-methyl-2-furfural, α -furfuryl alcohol, 4-hydroxy-6-methyl-2H-pyran-2-one, and 3,5-dihy-

droxy-2-methyl-4H-pyran-4-one. With the exception of α -furfuryl alcohol, which has been shown to contribute to bitter flavor (Hodge, 1967), furan derivatives are known to give caramel-like, sweet, and pungent characteristics (Hodge, 1967). The pyrones detected in these samples also contribute roasted or caramel flavor to foods (Hurrell, 1982). The detection of these compounds is also indicative of the low degree of sugar fragmentation during microwave irradiation (Shibamoto and Bernhard, 1977).

Other heterocyclic compounds obtained include trimethyloxazole, thiazole, 2-methylpyridine, 2-thiophenethiol, and 3-thiophenethiol. These compounds are present in relatively small amounts. In food systems, 2-methylpyridine generates a green note (Pittet and Hruza, 1974). Thiazoles generally possess nutty and meaty flavors (Baltes, 1979).

When the concentration of electrolyte was greater than 0.3 M, the formation of volatile compounds was reduced, in the case of sodium sulfate and ferrous chloride. This observation is probably due to the lower degree of browning at these electrolyte concentrations or the possible loss of compounds to volatilization. The apparent increasing trend observed for sodium chloride may be due to the corresponding increase in the degree of browning. The volatiles obtained for calcium chloride tend to level off after 0.2 M as did the browning intensity.

The chemical inhibition or promotion mechanism of these electrolytes on the Maillard browning reaction is not well understood. In the case of microwave irradiation, the dielectric properties of the electrolyte solutions, such as size and charge of the ions, and the degree of dissociation of the electrolytes may cause an overall increase in the degree of browning and generation of volatiles.

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Registry No. L-Cysteine, 52-90-4; D-glucose, 50-99-7; sodium chloride, 7647-14-5; calcium chloride, 10043-52-4; ferrous chloride, 7758-94-3; sodium sulfate, 7757-82-6; trimethoxazole, 20662-84-4; 2-methylpyridine, 109-06-8; thiazole, 288-47-1; 1,2-ethanedithiol, 540-63-6; acetic acid, 64-19-7; furfural, 98-01-1; 2-acetylfuran, 1192-62-7; 2-thiophenethiol, 7774-74-5; 3-thiophenethiol, 7774-73-4; 5-methyl-2-furfural, 620-02-0; α -furfuryl alcohol, 98-00-0; 2-acetylpyrrole, 1072-83-9; 4-hydroxy-6-methyl-2H-pyran-2-one, 675-10-5; 3,5-dihydroxy-2-methyl-4H-pyran-4-one, 1073-96-7.