# Effects of sodium chloride, potassium chloride and calcium chloride on flavour formation during heating of a wheat flour-glucose model system

# TOLGAHAN KOCADAĞLI<sup>1</sup>, Dimitris P. Balagiannis<sup>1</sup>, Vural Gökmen<sup>2</sup> and Jane K. Parker<sup>1</sup>

<sup>1</sup> Department of Food and Nutritional Sciences, University of Reading, Whiteknights, Reading RG6 6AP, United Kingdom

<sup>2</sup> Food Quality and Safety (FoQuS) Research Group, Department of Food Engineering, Hacettepe University, 06800 Beytepe Campus, Ankara, Turkey

### Abstract

The presence of metal salts in a food system can change the quantitative distribution of the reaction products formed during Maillard and caramelisation reactions. In this respect, dough formulae containing NaCl, KCl and CaCl<sub>2</sub> were prepared and a set of heating experiments was performed at 180 °C. To determine the volatile compounds formed during the Maillard reaction, headspace analyses were carreid out using solid-phase microextraction (SPME) coupled with gas chromatography mass spectrometry (GC-MS). It was found that the quantitative distribution of aroma compounds, such as Strecker aldehydes, pyrazines, pyrroles and furan derivatives, changed in the presence of salts.

# Introduction

Metal cations can interact with sugars and amino acids in a food system, especially during thermal processing when they can alter the kinetics of rate-limiting pathways that control the Maillard and caramelisation reactions. Degradation of sugars is accelerated in the presence of metal cations, and 5-hydroxymethyl-2-furfural and 2-furfural are formed in higher concentrations as a result [1,2]. On the contrary, the reactions of amino acids may be inhibited in the presence of metal cations, as evidenced by the mitigation of acrylamide formation from asparagine in the presence of calcium salts during the Maillard reaction [1,3].

Metal cations directly interact with the nucleophilic oxygens of sugars, which are key in dehydration, and isomerisation reactions [4]. It has also been suggested that metal cations coordinate with the ring oxygen, facilitating ring-opening reactions [5]. Alkali metal cations change the quantitative distribution of the products in two different ways: (*i*) by increasing the rate of isomerisation and (*ii*) changing the rates of different dehydration and fragmentation reactions [6]. It has been shown that under pyrolytic conditions, the sodium ion changes the reaction rate constants of glucose degradation by catalysing most of the reactions but also inhibiting others [7]. The effect of sodium cations is related to how the particular stereochemistry of the transition state interacts with the ions, therefore changing the reaction rate constants [7]. In contrast to the metal cations, chloride anions interact with the partially positively charged hydrogen atoms by locating farther from reaction centres [4].

Although the effect of sodium, potassium and calcium on the formation of acrylamide and furfurals is well established, their effect on the formation of flavor compounds during the Maillard reaction is not entirely known. The aim of this study was to investigate changes in the flavour profile generated in Maillard reaction model systems composed of wheat flour and glucose in the presence of NaCl, KCl, CaCl<sub>2</sub>.

#### Experimental

Wheat flour (100 g) was mixed with 50 mmol glucose, 5 mmol of either NaCl, KCl or CaCl<sub>2</sub>, and 50 mL water to form a dough. The dough was freeze-dried and ground prior to dry heating at elevated temperatures. The ground dried mixtures (0.5 g) were transferred to tubes with PTFE sealed screw caps and heated in duplicate at 180 °C for 1, 3, and 5 min in an oil bath.

Heated mixtures were analysed by headspace SPME-GC/MS after adding 1 mL saturated NaCl solution containing the internal standards of 2-methylpentanal (0.5 mg/L), isopropylpyrazine (0.05 mg/L) and 3-furfural (0.05 mg/L). Saturated NaCl solution was used for adjusting the ionic strength in all the formulae, to standardise the flavour release. A Supelco 50/30  $\mu$ m DVB/CAR/PDMS SPME fibre was used. Volatile analyses were carried out on an Agilent 7890A GC system coupled to an Agilent 5975C mass spectrometer. A ZB-WAX column (30 m × 0.25 mm i.d., 1  $\mu$ m film thickness; Phenomenex, UK) was used for chromatographic separation. The data were approximately quantified as ng of volatile compounds in 0.5 g of heated mixture by comparing the area of the analytes to the response of the internal standards.

## **Results and discussion**

A model system, simulating the drying conditions on the surface of bakery products during thermal treatment, was created to monitor the effect of salts on the Maillard reaction. Although sucrose is the major sugar source in bakery products, glucose was chosen as a reducing sugar. It is known that sucrose hydrolysis and degradation increase in the presence of metal salts, producing glucose and fructose [8]. Therefore, the aim was to observe the effects with a single reducing sugar by keeping the model system simpler at first.

The concentration of volatile compounds was found to increase during 5 min heating at 180 °C. NaCl and KCl, at concentrations of 0.3 and 0.4 g/100 g flour respectively, had minor effects on aroma formation compared to the control (Figure 1). Slight increases were observed in the Strecker aldehydes, 2-methylbutanal and 3-methylbutanal, in the presence of KCl. CaCl<sub>2</sub>, at a concentration of 0.6 g/100 g flour, had no effect on Strecker aldehyde formation during heating.

Remarkable changes were observed for pyrazines and furan derivatives in the presence of CaCl<sub>2</sub>. Pyrazines were found to decrease in the presence of CaCl<sub>2</sub> whereas furan derivatives increased dramatically. Pyrrole and pyridine derivatives showed an increment in case of prolonged heating.

In conclusion, the quantitative distribution of flavour compounds changed in the presence of salts to varying degrees. The effect of salts on the Maillard reaction and caramelisation needs detailed investigation to be able to control flavour development during processing when considering sodium reduction and use of calcium salts to reduce acrylamide formation.



**Figure 1:** Formation of certain volatile compound during heating wheat flour-glucose mixture in the absence of salts (control,  $\blacksquare$ ) and presence of NaCl ( $\blacksquare$ ), KCl ( $\blacksquare$ ) and CaCl<sub>2</sub> ( $\blacksquare$ ).

### References

- 1. Gökmen, V., and Şenyuva, H. Z. (2007) Eur. Food Res. Technol. 225(5-6): 815-820.
- 2. Açar, Ö. Ç., Pollio, M., Di Monaco, R., Fogliano, V., and Gokmen, V. (2012) Food Bioprocess. Technol. 5(2): 519-526.
- 3. Gökmen, V., and Şenyuva, H. Z. (2007) Food Chem. 103(1): 196-203.
- 4. Mayes, H. B., Tian, J. H., Nolte, M. W., Shanks, B. H., Beckham, G. T., Gnanakaran, S., and Broadbelt, L. J. (2014) J. Phys. Chem. B, 118(8): 1990-2000.
- Zhao, H., Holladay, J. E., Brown, H., and Zhang, Z. C. (2007). Science, 316(5831): 1597-1600.
- 6. Kocadağlı, T., and Gökmen, V. (2016) J. Agric. Food Chem. 64(32): 6333-6342.
- 7. Mayes, H. B., Nolte, M. W., Beckham, G. T., Shanks, B. H., and Broadbelt, L. J. (2015) ACS Catal. 5(1): 192-202.
- Fiore, A., Troise, A. D., Mogol, B. A., Roullier, V., Gourdon, A., Jian, S. E., Hamzalioglu, B. A., Gokmen, V., and Fogliano, V. (2012) J. Agric. Food Chem. 60: 10808–10814.