Monitoring Chemical and Physical Changes during Thermal Flavor Generation

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On-line techniques were developed to monitor chemical and physical changes occurring during the heating of skim milk powder (SMP). Atmospheric pressure chemical ionization mass spectrometry (APCIMS) followed the generation and release of volatile compounds from SMP in a packed-bed reactor. Operating conditions were optimized to avoid condensation of high boiling compounds such as maltol, and the system was highly reproducible (CV < 7%). Differential scanning calorimetry (DSC) of SMP identified a potential glass transition at an onset temperature of 67.9 °C and a series of exothermic events that were related to different stages of the Maillard reaction. No lactose crystallization was found after heating. Using a heated stage reflectance FTIR device, spectra were obtained at different temperatures. Analysis of the data showed a correlation between the intensity ratio at wavenumbers 1017 and 1064 cm^{-1} and the glass transition measured by DSC. This FTIR system was not sensitive enough to detect Maillard intermediates. Combining data from the three techniques provides a fuller picture of the physical changes during the Maillard reaction and their effects on the chemical reactions.

KEYWORDS: APCIMS; DSC; FTIR; Maillard reaction; skim milk powder

INTRODUCTION

The flavor of many foods is the result of thermal flavor generation via reactions such as the Maillard reaction and caramelization. Many food products are solid, low-moisture systems which undergo changing time−temperature−moisture conditions during processing. To gain a better understanding of flavor generation, it is, therefore, of interest to develop methods that can mimic these conditions and monitor their effects on thermal flavor generation.

In a previous paper, we reported the use of atmospheric pressure chemical ionization mass spectrometry (APCIMS) for real-time monitoring of thermally generated volatile flavor compounds (*1*). Preliminary tests with skim milk powder (SMP) showed that volatile generation at different temperatures (in the range 70−120 °C) and starting moisture contents (0−12.7% on a dry solids basis; dsb) could be distinguished. Differences were observed in both the amounts and time profiles of different volatile compounds under different conditions.

The sensitivity of the system was adequate to follow a wide range of volatile compounds. Consistent sampling could be achieved, and there were observable differences in the time profiles of production of different volatiles. However, problems arose when the heating temperature was raised to 140 °C. High-boiling compounds were not cleared from the system, leading

to substantial tailing in the response. This delay resulted from the flow characteristics of the system, as the path of molecules between generation and detection could vary due to the relatively large headspace. The flow characteristics were also thought to be responsible for the high level of "spiking" seen on the raw data traces.

The first aim of this paper was to modify the original system to apply the continuous APCIMS technique to samples at high temperature and under changing time−temperature profiles, rather than just isothermal heating. The second aim was to develop methods capable of following further aspects of reaction. Phase changes are well-known to occur in low-moisture-content heated systems (*2, 3*). These could affect reaction (*4−6*), either through changed mobility of the reactants or through a change in free water, or both. The volatile Maillard reaction products detected by APCIMS are only a small part of the total Maillard products. It would be of interest to follow formation of nonvolatile compounds such as the Amadori compound, and semi-volatile intermediates such as 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone and 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (DDMP). Differential scanning calorimetry (DSC) and reflectance Fourier transform infrared spectroscopy (FTIR) were applied to study these phase changes and the formation of other, nonvolatile compounds. By combining results from different techniques, a fuller picture of the chemical and physical changes that take place during the Maillard reaction can be obtained.

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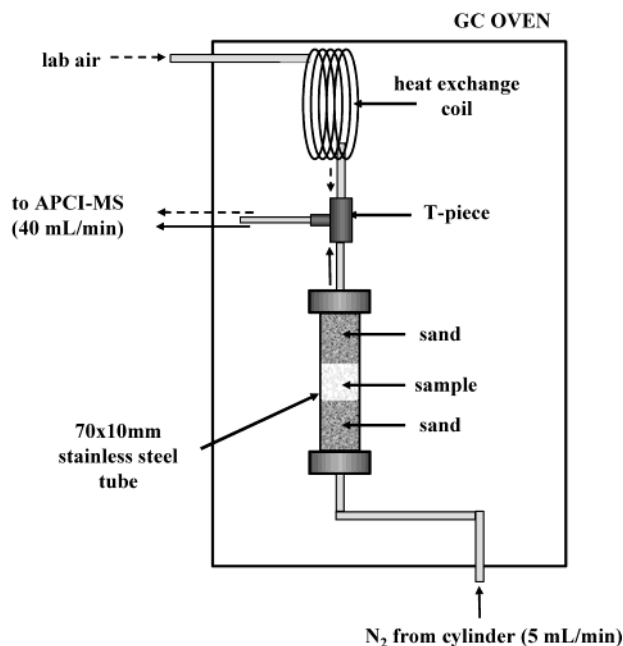
Figure 1. Packed-bed reactor system for continuous APCIMS monitoring of volatiles produced by a solid sample (skim milk powder; SMP) during heating (diagram not to scale).

MATERIALS AND METHODS

Sample Preparation. SMP (Sainsbury's, U.K.) was ground with a pestle and mortar before use. The initial moisture content was 3.7–4.6% on a dry sample basis (dsb). Sample moisture content was measured using Karl Fischer coulometric titration (Mitsubishi CA-05 moisture meter).

Packed-Bed Reactor System. The system is illustrated in **Figure 1**. Stainless steel tubes (70 mm long × 10 mm i.d.) were used as the sample cells. They were sealed at each end with liquid chromatography end-fittings fitted with perfluoroalkoxy (PFA) ferrules. This allowed the system to be dismantled for cleaning and reuse. Stainless steel frits ($^1/_2$ in. diameter, $^1/_{32}$ in. thickness, and 2.0 μm porosity) were used in both ends of the sample tube to retain large particles within the sample cell. Acid-washed sand was used to pack $^4/_5$ of the tube volume (equivalent to 7.36 g), divided equally between each end. The remaining $^1/_5$ volume in the center of the tube was filled with the sample. This was equivalent to 0.568 g for SMP.

The gas (nitrogen) flow into the cell was kept constant at 5 mL/min. It was heated before reaching the sample by passing it through a length of copper tubing in the oven. The gas stream leaving the sample cell was combined with a makeup gas (laboratory air; heated by passing through a coil of tubing in the oven) at 40 mL/min. Both were continuously drawn into the APCI ionization source through a heated (200 °C) transfer line. APCIMS (MS–NOSE, Micromass, Altrincham, U.K.) was operated in the gas phase using positive-ion full-scan mode for the mass range 40–180 amu (scan time 5 s, inter-scan delay 0.02 s). The source block and desolvation temperature were 100 °C, corona pin voltage was 3.5 kV, and the cone voltage was 18 V. MassLynx software was used to collect and process the data. Identification of the compounds contributing to different APCI ion masses was reported previously (*1*).

The product temperature was measured by inserting a thermocouple into the center of the packed-bed reactor. For isothermal treatments, the come-up time of the sample to the oven temperature was 10–15 min. For temperature gradient analysis, SMP was heated from 30 to 140 °C at a rate of 3.7 °C/min, then held at 140 °C for 10 min to allow the product to reach the final oven temperature (40 min total run time).

Differential Scanning Calorimetry (DSC). From a sample of SMP with a moisture content of 3.7% (dsb), sub-samples of between 8 and 12 mg were taken and sealed in high-pressure stainless steel DSC pans. They were analyzed using a Perkin-Elmer DSC-7, calibrated for temperature and heat flow using indium and cyclohexane with an empty
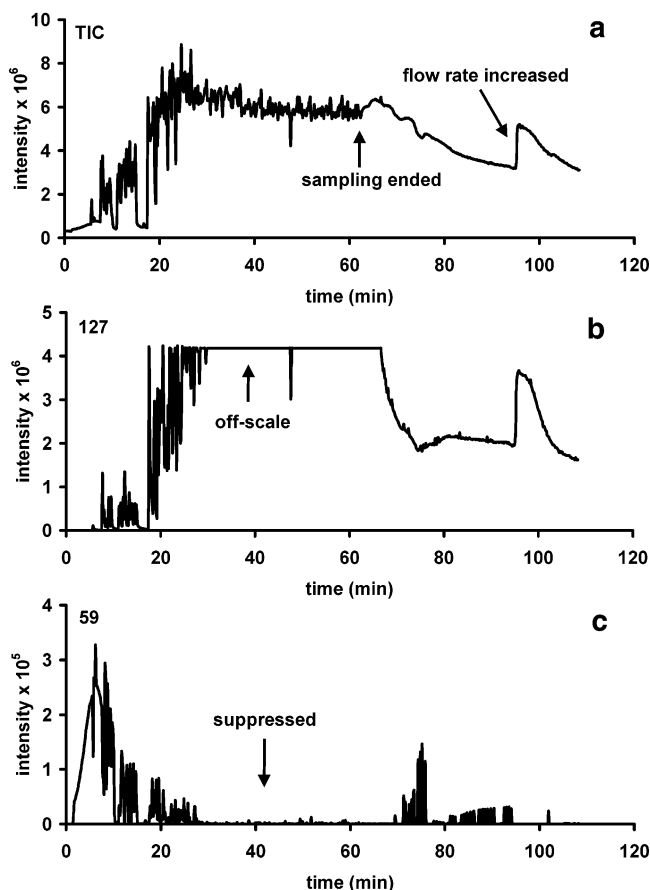
Figure 2. Results from original Schott bottle reactor: time-intensity profile of TIC, *m/z* 127, and *m/z* 59 for SMP with moisture content 10.2% dsb heated at 140 °C, showing delay in returning to baseline after sampling ended.

stainless steel pan used as reference. The samples (3 replicates) were heated from 20 to 190 °C at the same heating rate as that employed in the APCI experiment, namely 3.7 °C/min. The DSC curves were analyzed using the Perkin-Elmer Pyris software to identify the onset and endpoint of the glass transition.

Infrared Spectroscopy. SMP samples were sealed using the sapphire anvil of a heated single reflection diamond attenuated total reflectance (ATR) sampling device (Graseby Specac, UK). Mid-infrared spectra were acquired using an IFS48 spectrophotometer (Bruker Optics, U.K.) equipped with a DTGS detector. Scans (64 per spectrum, 4 cm^{-1} resolution) were acquired at 10 °C increments over the range 30–140 °C. Two minutes at each temperature was allowed prior to data acquisition to ensure thermal equilibration throughout the sample. The resulting underlying heating rate was equivalent to 3.7 °C/min. The spectra were corrected for atmospheric water vapor and subsequently vector-normalized over the range 1200 to 800 cm^{-1} in order to minimize the effects of the temperature dependency of the contact between the sample and diamond crystal.

RESULTS AND DISCUSSION

Limitations of the Original System. Problems with the original continuous APCIMS system appeared when the heating temperature was increased to 140 °C. The total ion chromatogram (TIC) did not fall after sampling had finished (**Figure 2a**), which was indicative of compounds remaining in the system due to poor flow characteristics. The cause was traced to an ion with *m/z* 127 (thought to be maltol), which was present in much greater amounts than at lower temperatures, and remained in the detector after the probe had been removed from the sample (**Figure 2b**). This also had the effect of suppressing other ions,

e.g., *m/z* 59 (**Figure 2c**). The trace did not return to the baseline, even when the flow rate through the transfer line was increased. Ion mass 145 (possibly DDMP; another high-boiling compound) was also partly responsible (data not shown).

Figure 2 also illustrates the spikiness of the data obtained using this experimental setup. As reported previously (*1*), this did not affect interpretation of results; trends could still be observed. However, it would be desirable to have smoother data so changes could more easily be monitored.

The limitations of the original setup could be summarized as follows: (1) cannot be used at temperatures above 110−120 °C; (2) tailing of high-boiling compounds in the transfer line; and (3) spikiness of trace.

These problems were addressed by considering the flow characteristics of the system. Dilution of the headspace prior to mass spectroscopic analysis should help prevent compounds sticking and tailing. This is preferable to increasing the flow rate through the sample. The extent of dilution should be sufficient to cope with the increased generation of high-boiling compounds at higher temperatures. Improving the transfer of the headspace to the APCIMS should also reduce spiking.

Packed-Bed Reactor System. *Setup.* The new system was based on a packed-bed design, and is shown in **Figure 1**. The main changes and improvements to the system were as follows: (1) The glass flask was replaced with a stainless steel tube. This offered better heat transfer and reduced the headspace above the sample. (2) A constant flow of 5 mL/min of nitrogen gas through the packed bed removed volatiles generated during heating for analysis by APCIMS. Flow through the sample would decrease spiking by carrying volatiles more directly to the APCIMS. There was no difference in measured volatile generation when nitrogen or air was used as the inflow gas. (3) To overcome compounds sticking to the silica tubing leading to the MS, an additional flow of air was taken through the APCI transfer line at a much higher flow rate of 40 mL/min. Use of a T-piece enabled this extra air to be taken from the laboratory atmosphere, rather than depleting the sample further. Hence, headspace volatiles were still sampled at 5 mL/min, but a constant high flow rate was achieved through the transfer line. The makeup gas acted as both a diluter and a "sweep-through" gas. Dilution of the headspace helped prevent overloading of compounds, which in turn prevents suppression of others (*7*). The high flow rate reduced tailing in the transfer line. (4) The small sample volume meant that less volatiles were generated and there was less headspace to sample, again overcoming problems of overloading and suppression. However, the amount was sufficient for detection and monitoring of compounds of interest. (5) The small sample volume was also more appropriate for comparison with other methods. The quantity used in the original system (6 g) gave longer delays in heating, phase changes, etc. than the amounts used for DSC and FTIR (few mg). Reducing the amount in APCIMS also gave the long-term potential for comparing FTIR and APCIMS data from the same sample (approximately 0.5 g) using a specially adapted FTIR cell. (6) Sand was used to pack the remaining column volume. This was preferable to using a shorter column, as it helped with headspace mixing and reducing dead volume. It gave high-boiling compounds less opportunity for condensation and sticking than would bare metal surfaces. (7) Acid-washed sand was found to give the best signal for all volatile compounds, presumably due to decreased volatile binding to the sand.

Results. **Figure 3** shows the total ion chromatogram (TIC; **Figure 3a**), *m/z* 127 (**Figure 3b**), and *m/z* 59 (**Figure 3c**) for SMP heated at 140 °C for 30 min with the packed-bed reactor.
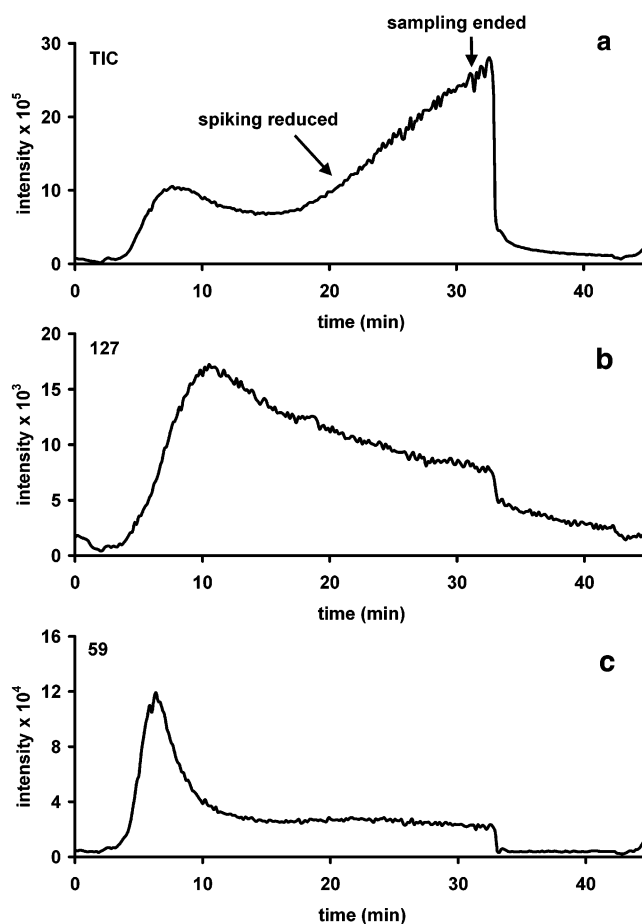

Figure 3. Results from packed-bed reactor system: time–intensity profile of TIC, *m/z* 127, and *m/z* 59 for SMP with 4.6% dsb moisture content heated at 140 °C for 30 min.

Comparison with **Figure 2** shows the improved clearance rate after sampling was ended, and the reduction in spiking. The ion with *m/z* 127 was now well on-scale and *m/z* 59 was not suppressed. The method was reproducible, with 7% CV for the total area of the TIC trace for five replicate samples heated at 140 °C for 30 min. This figure represents the system reliability and was to some extent sample-dependent. Four replicate samples of amorphous lactose under the same conditions had a CV of 14%. The higher value was thought to be due to the collapse of lactose at high temperatures (due to crystallization), which would have decreased the volume it occupied within the reactor and changed the flow characteristics of the setup.

The new method was still capable of distinguishing different ion masses in terms of amount and time profile of generation. This is illustrated in **Figure 4** for an isothermal SMP sample heated at 105 °C. Selected ion masses are shown to emphasize the differences. Note that these data were obtained using a tube completely filled with sample.

Comparison of the original (Schott bottle) and new (packed-bed reactor) methods revealed differences in the time profiles of generation of compounds. Compounds in the original system tended to increase gradually over the whole of the 60-min heating period. In the new system they reached a maximum more quickly, then production slowed or decreased. The difference between the systems was thought to be due to differences in headspace volume. In the Schott bottle there was about 40 mL of air to equilibrate and sample from, whereas the only headspace in the new system was the volume between particles packing the column. The air in the packed-bed reactor
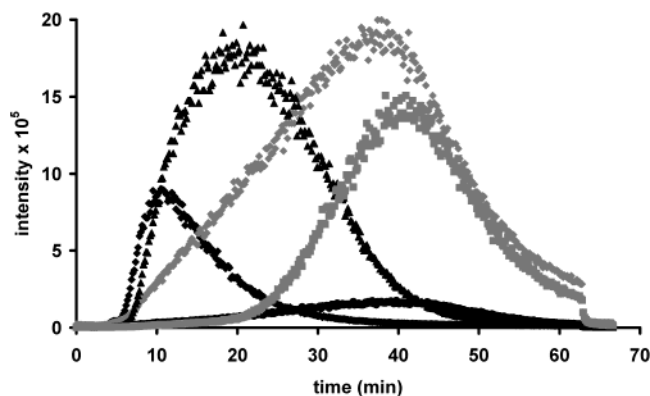
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Figure 4. Time–intensity profiles of selected ions from SMP heated at 105 °C for 60 min, using packed-bed reactor system. Ion masses: m/z 59 (black ◆); 61 (gray ◆); 89 (▲); 97 (●); 127 (gray ■).

Figure 5. DSC of SMP with moisture content 3.7% dsb.

was continuously replenished by the flow through the column, and therefore partition would have been quicker than that in the Schott bottle. These results demonstrate that although real-time measurement is possible using APCIMS, it does not give an "absolute" picture of volatile generation. The measurement system used affects the results obtained.

Other Benefits. The new setup has the potential to employ humidified air as the flow-through gas. It may then be possible to keep the moisture content of a sample constant throughout the heating period, instead of drying it out with the gas flow and elevated temperature. This would provide better control for the assessment of the effect of moisture content on reaction.

The rapid heat transfer of the stainless steel tube meant that it was possible to run a temperature program instead of isothermal heating. This had the advantage of being more comparable to a real food process, where changing temperatures are commonly encountered. It was also more suitable for investigating the effect of phase transitions, such as glass transition, lactose crystallization, etc., on the Maillard reaction. Through the use of carefully selected time−temperature profiles and by matching these for the different techniques, the type of volatile compounds released and their release kinetics can be studied at the various stages of the heating cycle in relation to the temperatures at which phase transitions occur.

State Transitions and Maillard Reaction. In a low-moisture-content system, phase changes such as glass transition or lactose crystallization can cause significant changes to Maillard reaction kinetics (*4*, *8*, *9*). For example, while the Maillard reaction was found to be diffusion-controlled in the vicinity of T_g and also in the glassy state, it was reaction-controlled above T_g; i.e., in the rubbery state (*10*). The latter authors proposed that an integrated physical and chemical approach would help in understanding the mechanisms of glassy state stabilization. This could be better achieved by combining methods that monitor phase changes, such as DSC and FTIR, with those that measure chemical changes, such as FTIR and headspace analysis using APCIMS. Experiments were designed to study the relevance of T_g to the Maillard reaction using conditions typically found in food processing.

The DSC thermograms of the SMP showed a step change in the specific heat capacity identifiable with a glass−rubber transition at an onset temperature of 67.9 ± 0.6 °C and an endpoint of 77.0 ± 0.8 °C. A typical thermogram is shown in **Figure 5**.

It is widely believed that this glass transition reflects the behavior of the lactose component of SMP (*11*). However, there has been no experimental support for this assumption, which
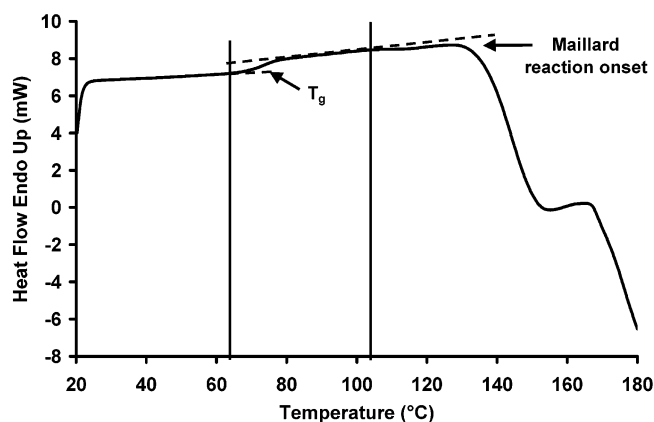
has been inferred only as a result of the similarities between the temperature of this transition and the T_g of amorphous lactose at similar water content. Such an assumption is risky because the value of T_g is highly dependent on the level of plasticizing water. Thus, it is the amount of water associated with lactose that is the determining factor, not the overall water content. Indeed, unequal partitioning of water between the components of a range of mixed systems has been demonstrated, for example in protein−sugar mixtures (*12*), and the subsequent effect of this differential hydration on the individual T_g values was quantified (*13*). The use of FTIR spectroscopy to assess the assignment of this glass transition to the lactose component of SMP is described later in this paper.

The DSC thermogram also showed a series of exothermic events, the first with an onset temperature at around 105 °C, with the main event occurring at approximately 130 °C. To assign these transitions, various DSC analyses were stopped at different temperatures: 100 °C (i.e., before the first exotherm), 125 °C (i.e., between the first and the main exotherms), and 140 °C (i.e., well within the main exotherm). The DSC pans were taken off the machine and opened as quickly as possible so that the color of the sample could be inspected visually. The sample heated to 125 °C showed no noticeable difference in color compared to that of the original SMP material, but the sample heated to 140 °C had a dark brown color indicative of extensive Maillard reaction. This shows that the SMP system, despite receiving some limited heat treatment during manufacture, is capable of further reaction under the conditions used in this study. The exotherm centered around 130 °C was first thought to be due to a limited lactose crystallization process, but no evidence of crystallinity was found in these samples when examined under polarized light microscopy. Furthermore, wide-angle X-ray diffraction (XRD) analysis on a sample subjected to the same time−temperature history as in the DSC (due to the quantity of sample required for XRD) showed no evidence of lactose crystallization (results not shown). It is therefore believed that the various exotherms were due to the Maillard reaction rather than sugar crystallization.

FTIR was used in an attempt to assign the various transitions observed by DSC to physical and chemical changes to the constituents of SMP. FTIR spectroscopy is a particularly useful technique for the study of protein−carbohydrate systems (*14*), as there are several readily identifiable regions of the mid-infrared spectrum where the chemical fingerprints of carbohydrates and proteins do not overlap significantly. The most distinctive spectral features for proteins are the strong amide I and II bands centered at approximately at 1650 and 1540 cm^{-1} respectively. For carbohydrates, a series of overlapping peaks

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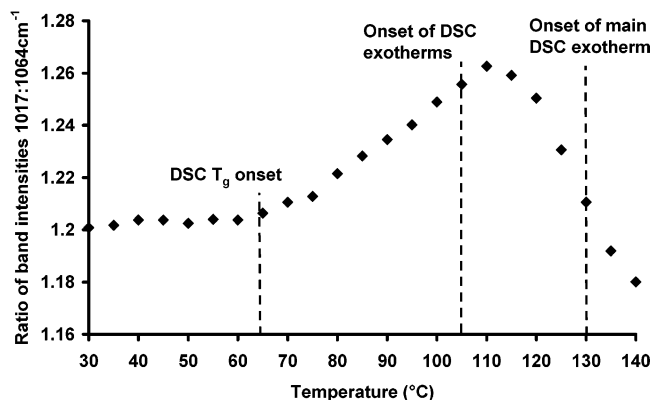
Figure 6. Ratio of normalized infrared band intensities (1017:1064 cm^{-1}) for SMP, plotted against sample temperature.

Figure 7. Time–intensity profiles of selected ions from SMP heated from 30 to 140 °C at 3.7 °C/min, using packed-bed reactor system. Ion masses: *m/z* 59 (black ◆); 61 (gray ◆); 89 (▲); 97 (●); 127 (gray ■).

located in the region of 1180−953 cm^{-1} results from vibration modes such as the stretching of C−C and C−O and the bending mode of C−H bonds. These are often referred to as the "saccharide" bands and are the most intense bands in the mid-infrared spectrum (*15*). These absorptions are weak in the spectra of most proteins. Both the glass−rubber and the amorphous−crystalline transitions in carbohydrates can be readily monitored by FTIR, and the transition temperatures correlate well with those measured by DSC under comparable conditions (*16*). Typically, the glass transition leads to a series of changes in intensity/wavenumber, whereas crystallization leads to systematic increase in spectral resolution (Ottenhof and Farhat, unpublished results).

The mid-infrared spectra acquired on the SMP at different temperatures showed subtle but systematic changes in the 1200−800 cm^{-1} region, resulting mainly from lactose. No evidence of lactose crystallization was obtained, confirming the polarized light microscopy and XRD results. To quantify the effect of temperature on this part of the spectrum, the ratio of the intensity of the band at 1017 cm^{-1} to that at 1064 cm^{-1} was plotted against temperature (**Figure 6**). The ratio remained constant between 30 °C and 65 °C, before showing a clear inflection followed by a linear increase up to 110 °C. The first transition temperature correlated with the T_g onset measured by DSC (**Figure 5**). The second inflection occurred at a temperature just above (by 5 °C) that of the onset of the first post-T_g exotherm in DSC, believed to be associated with the Maillard reaction. These results provided clear experimental evidence confirming the following: (i) the DSC-measured glass transition in SMP did relate to the lactose component and (ii) the exotherms often observed during the heating of SMP were not the result of lactose crystallization but were due to the Maillard reaction.

It might be expected that the chemical changes accompanying the Maillard reaction in SMP would lead to several changes in the mid-infrared spectrum as a result of the consumption of some functional groups and the appearance of others. Functional groups that might be lost include NH$_2$, typically from lysine, while those associated with Maillard products such as the Amadori compound (C=O), Schiff base (C=N), and pyrazines (C−N) may increase. However, it is important to take into consideration the actual concentrations of the reactants and products involved. When lactose is present in high concentration, it is only depleted by a few percent via the Maillard reaction, due to the low concentration of reactive amino groups. Lysine, for example, the predominant reacting amino function in proteins because of the reactivity and availability of its ϵ-amino group, comprises less than 3% by mass of SMP. Subsequently, the concentration of the reaction products will be relatively low.
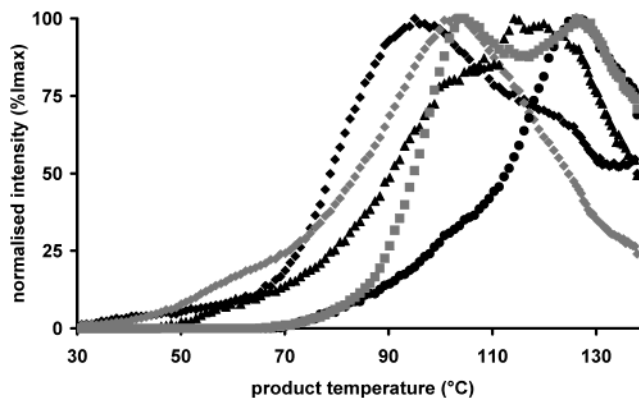
In addition, reactants and products will share many functional groups, so any changes may be hard to detect. The present FTIR methodology would not be sufficiently sensitive to reliably monitor such small spectral changes. The interpretation is further complicated by the effect of temperature on the FTIR spectrum. Direct difference techniques can be employed to alleviate the issue of the reliable detection of small spectral changes. The background spectrum is acquired on the SMP at room temperature, allowing only the change of the spectrum with temperature to be monitored. This approach has been described elsewhere (*14*).

Flavor Generation and Release. Continuous APCIMS was performed using the same temperature ramp as that used for DSC and FTIR so that the data were comparable. This is particularly important for the T_g, which is a second-order transition and under kinetic control, meaning the temperature at which it occurs depends on the heating rate. **Figure 7** shows the results for SMP, each ion being normalized to its maximum intensity to facilitate comparison of time profiles. Different volatile compounds appeared at different times, in a way similar to that of isothermal heating, but in this case corresponding to different product temperatures. Some ion masses (*m/z* 97 and 127) increased only above 70 °C. Further investigation would be required to determine whether it was simply coincidence that this corresponded to the T_g measured by DSC. Other compounds were formed at temperatures lower than T_g.

It is interesting to note that formation of volatile compounds appeared to be nearing completion by the time the product temperature reached 130 °C. This was the "onset" temperature of browning found in DSC and could therefore represent the transition between the intermediate and final stages of the Maillard reaction.

In summary, the improved APCIMS continuous monitoring technique was successful in both isothermal and temperature-programmed applications. Running a temperature program to match that used in DSC and FTIR enabled comparison between the techniques. These were used to investigate the various physical and chemical transformations occurring during the heating of SMP. DSC allowed the reliable determination of T_g and the onset of the Maillard reaction. FTIR enabled the assignment of these transitions, clearly showing the T_g of the lactose controls the reaction kinetics and that no lactose crystallization occurs during the heating of SMP. Further work is underway to investigate the more subtle changes that occur in the FTIR spectra due to chemical changes during the Maillard reaction.

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LITERATURE CITED

(1) Turner, J. A.; Linforth, R. S. T.; Taylor, A. J. Real-time monitoring of thermal flavor generation in skim milk powder using atmospheric pressure chemical ionization mass spectrometry. *J. Agric. Food Chem.* **2002**, *50*.

(2) Roos, Y. Characterization of food polymers using state diagrams. *J. Food Eng.* **1995**, *24*, 339−360.

(3) Roos, Y.; Karel, M. Differential scanning calorimetry study of phase transitions affecting the quality of dehydrated materials. *Biotechnol. Prog.* **1990**, *6*, 159−163.

(4) Lievonen, S. M.; Laaksonen, T. J.; Roos, Y. H. Glass transition and reaction rates: Nonenzymatic browning in glassy and liquid systems. *J. Agric. Food Chem.* **1998**, *46*, 2778−2784.

(5) Karmas, R.; Karel, M. Modeling Maillard browning in dehydrated food systems as a function of temperature, moisture-content, and glass-transition temperature. In *Flavor Technology: Physical Chemistry, Modification, and Process*; Ho, C.-T., Tan, C. T., Tong, C. H., Eds.; American Chemical Society: Washington DC, 1995; pp 64−73.

(6) Bell, L. N.; Touma, D. E.; White, K. L.; Chen, Y. H. Glycine loss and Maillard browning as related to the glass transition in a model food system. *J. Food Sci.* **1998**, *63*, 625−628.

(7) Brauss, M. S.; Balders, B.; Linforth, R. S. T.; Avison, S.; Taylor, A. J. Fat content, baking time, hydration and temperature affect flavor release from biscuits in model and real systems. *Flavour Fragrance J.* **2000**, *14*, 351−357.

(8) Byrn, S. R.; Xu, W.; Newman, A. W. Chemical reactivity in solid-state pharmaceuticals: formulation implications. *Adv. Drug Deliv. Rev.* **2001**, *48*, 115−136.

(9) Kim, M. N.; Saltmarch, M.; Labuza, T. P. Nonenzymatic browning of hygroscopic whey powders in open versus sealed pouches. *J. Food Process. Preserv.* **1981**, *5*, 49−57.

(10) Craig, I. D.; Parker, R.; Rigby, N. M.; Cairns, P.; Ring, S. G. Maillard reaction kinetics in model preservation systems in the vicinity of the glass transition: experiment and theory. *J. Agric. Food Chem.* **2001**, *49*, 4706−4712.

(11) Jouppila, K.; Roos, Y. H. Glass transitions and crystallization in milk powders. *J. Dairy Sci.* **1994**, *77*, 2907−2915.

(12) Farhat, I. A.; Blanshard, J. M. V. On the extrapolation of the melting temperature of dry starch from starch-water data using the Flory−Huggins equation. *Carbohydr. Polym.* **1997**, *34*, 263−265.

(13) Mousia, Z.; Farhat, I. A.; Blachot, J. F.; Mitchell, J. R. Effect of water partitioning on the glass-transition behaviour of phase separated amylopectin-gelatin mixtures. *Polymer* **2000**, *41*, 1841−1848.

(14) Farhat, I. A.; Orset, S.; Moreau, P.; Blanshard, J. M. V. FTIR study of hydration phenomena in protein-sugar systems. *J. Colloid Interface Sci.* **1998**, *207*, 200−208.

(15) Cael, J. J.; Koenig, J. L. Infrared and Raman spectroscopy. *Carbohydr. Res.* **1974**, *32*, 79−91.

(16) Buitink, J.; van den Dries, I. J.; Hoekstra, F. A.; Alberda, M.; Hemminga, M. A. High critical temperature above T-g may contribute to the stability of biological systems. *Biophys. J.* **2000**, *79*, 1119−1128.

JF0203803