MONITORING ACRYLAMIDE IN REAL-TIME DURING FOOD PRODUCTION USING SIFT-MS

APPLICATION NOTE AS-241

Authors

Jamie Minaeian, Mark Perkins, Kathy Ridgway

Anatune Limited
Unit 4, Wellbrook Court, Girton Road, Cambridge, CB3 0NA

+44 (0)1223 279210
enquiries@anatune.co.uk

Abstract

Acrylamide, a known potential carcinogen, is produced during the baking, roasting and frying of foods. Acrylamide legislation (EU commission regulation 2017/2158) establishes best practice, mitigation and benchmark levels for the reduction of the presence of acrylamide in food. Existing methods of analysis using liquid chromatography and gas chromatography with mass spectrometric detection (LC-MS and GC-MS) do not allow for the real time monitoring of acrylamide which would enable food manufacturers to better understand and control their processes. Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) is a real-time volatile organic compounds (VOC) analyser. This study demonstrates the use of SIFT-MS to monitor, in real time, volatile compounds, such as acrylamide, that are formed during certain food production processes.

Introduction

Acrylamide, a potential carcinogen, is produced during the baking, roasting and frying of foods. Acrylamide legislation states that all food business operators are required to implement simple practical steps to manage acrylamide and have a general understanding of how acrylamide is formed in the food they produce. Regulation 2017/2158 establishes best practice, mitigation and benchmark levels for the reduction of the presence of acrylamide in food.

As the route of formation of acrylamide is through the Maillard ('browning') reaction, a method that could provide a real-time response during food processing is desirable to help food manufacturers better understand and control their processes. Real-time analysis provides data throughout the process not only on compounds that may be of toxicological concern, but also key flavour components and therefore can be used to provide real time control as opposed to finished product testing. This can be used in new product development, pilot plant trials, or full production process monitoring to ensure specifications are met.

Acrylamide is a polar, low molecular weight compound and therefore analysis presents some challenges, both chromatographically and due to a lack of significant fragmentation for detection by mass spectrometry. Several methods are available in the literature for the analysis of finished products, including GC-MS (generally after derivatisation) and LC-MS [1-5]. As these approaches are difficult to implement at-line, testing tends to be on a batch release basis, giving rise to the possibility of failed batches or product recalls.

This application note demonstrates the potential for the real-time measurement of acrylamide by SIFT-MS, which is a direct mass spectrometry technique that uses precisely controlled soft ionisation to enable real-time, quantitative analysis of volatile organic compounds (VOCs) in the gas phase. Detection limits as low as parts-per-trillion by volume (pptv) are achievable, eliminating the need for sample preparation or preconcentration. Figure 1 shows an illustration of the system.

Figure 1 : Syft Technologies Voice 2000ultra SIFT-MS

Figure 2 shows a schematic of the ionisation and quantification process for SIFT-MS which occurs in the three stages below.

Reagent ion selection – A microwave discharge through moist air forms standard SIFT-MS positive and negative ions; H_3O^+, NO^+, O_2^+, OH^-, O_2^-, O^-, NO_2^- and NO_3^- and these reagent ions are then selected using a quadrupole mass filter.

Analyte ionisation – The selected reagent ion is introduced into the flow tube and excess energy is removed through collisions with the carrier gas (either nitrogen or helium). The sample is then introduced, and an ion-molecule reaction takes place to form well-characterised product ions.

Analyte quantitation – Product ions and unreacted reagent ions pass into a second quadrupole mass analyser and the analyte concentration is calculated as a ratio of product ions to reagent ions multiplied by a rate constant, k, unique to that ion-molecule reaction. The use of eight, selectable reagent ions, coupled with a library of known reaction products and reaction rates enables SIFT-MS to quantify multiple analytes, in real-time, without the need for prior chromatographic separation.

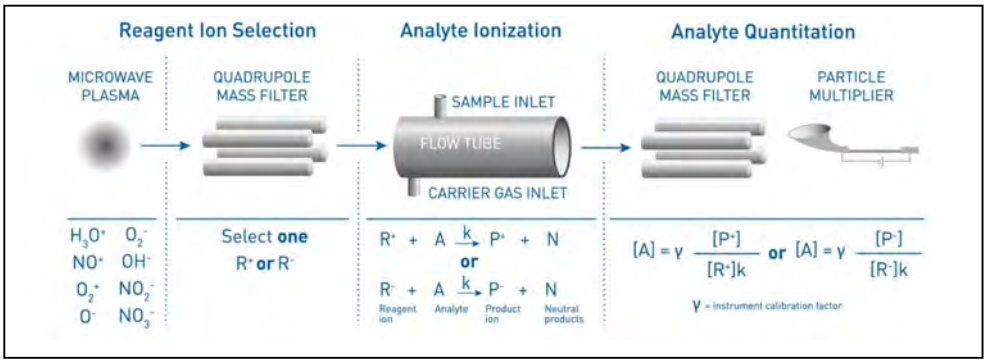

Figure 2: schematic representation of the SIFT-MS technique

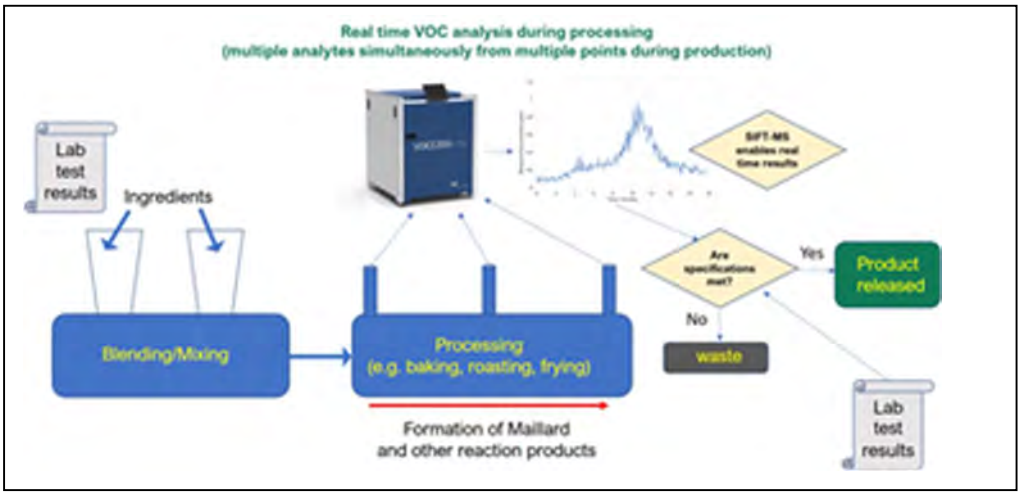

Figure 3: Food production process (SIFT-MS multiport inlet allows real time monitoring)

Experimental

The first part of this experiment was carried out using a gas standard generator (University of York), coupled to a Syft Technologies Voice200ultra SIFT-MS via the High-Performance Inlet as detailed in SnApp note SN014 and illustrated in Figure 1.

The SIFT-MS was then transported to a production site and connected to the exhaust flue of a food production process.

Due to confidentiality, the exact details of the production process monitored cannot be shared, but an example schematic of a food production process illustrating the potential of SIFT-MS real time monitoring is shown in Figure 3

METHOD

Initially, gas standards were prepared from solid acrylamide, using an in-house designed gas standards generator at the University of York. From literature values of acrylamide vapour pressure at variable gas flows, it was possible to generate known gas phase concentrations, which were directly sampled via an unheated transfer line connected to the SIFT-MS inlet. Concentrations were measured using H_3O^+, NO^+ and O_2^+ reagent ions and kinetic values from the LabSyft library. The three reagent ions react differently with acrylamide, yielding three different masses. These reactions are shown in Equations 1-3.

1) $H_3O^+ + C_3H_5NO \rightarrow H_2O + C_3H_5NO.H^+$ m/z = 72

2) $O_2^+ + C_3H_5NO \rightarrow O_2 + C_3H_5NO^+$ m/z = 71

3) $NO^+ + C_3H_5NO \rightarrow C_3H_5NO.NO^+$ m/z = 101

To enable the instrument to monitor the process, it was coupled to an exhaust from the food production process, monitoring acrylamide alongside several other volatile compounds originating from the production process. Different sample profiles were measured over 4 different production batches, with at least triplicate analyses for each batch, and the data was processed.

It should be noted that the measurement process took place in real-time and parallel to the production process. Product quality, or safety in the case of acrylamide, is measured throughout the production process. This reduces the need for post-production testing as the risk of out of specification results is reduced or eliminated. Product release times are reduced and production can be stopped more quickly when problems are identified, reducing waste, which has both financial and environmental benefits.

RESULTS AND DISCUSSION

The initial work on the analysis of standards is described in Anatune SnApp note SN014, which describes the acrylamide calibration process.

All three of the product ions (from the three different reagent ions) were observed for acrylamide, giving confidence that acrylamide could be monitored and the experiment was able to show changes in concentration.

From this study, it could be concluded that acrylamide could be monitored in real time by SIFT-MS, although there are important considerations with regards to sample introduction.

The instrument was connected to the exhaust from the food production process, measuring acrylamide, along with other volatile compounds. Several different raw materials underwent the food production process and showed different acrylamide concentration profiles.

Figure 4 shows the concentration of acrylamide measured by each reagent ion throughout the production process.

Based on previous data from calibration using standards, this data indicates that NO^+ and H_3O^+ responses are derived from acrylamide. The elevated response observed for O_2^+ indicates an additional response from other analytes for this product ion (m/z 71).This illustrates the ability of SIFT-MS to utilize a number of different reagent ions to enable selectivity without the need for chromatographic separation. In addition, the three reagent ions allow for potential unknown compounds in the matrix to be detected.

The percent relative standard deviations (%RSD) of the four processes were calculated for each reagent ion. For H_3O^+, O_2^+ and NO^+, the %RSDs for the main acrylamide peaks were 14 %, 8 % and 5 % respectively.

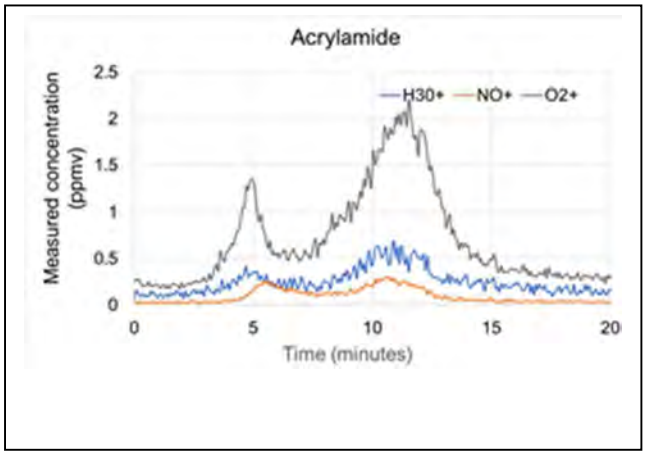

Figure 4: Acrylamide response during Food production process

Figure 5 shows the acrylamide concentration throughout four separate batch processes. All four processes show good agreement and involve two elevated levels of acrylamide production.

The first elevated concentration is potentially due to acrylamide being formed and released from the surface of the product as it begins the food production process, whilst the second, larger concentration corresponds to internal temperature increase, resulting in the Maillard reaction taking place.

It is important to note that each of these features of heating process happen in about 2- 5 minute sections in the 20 minute process, meaning that the SIFT-MS' ability to monitor in real time can distinguish them, whilst other, off-line techniques might miss the subtleties of the changing chemical profile. This enables the production team or R&D chemist, to identify the exact points where acrylamide is formed, resulting in a more targeted approach for product development or mitigation.

Additionally SIFT-MS allows numerous volatile compounds (including other Maillard reaction products) to be monitored simultaneously, for the purposes of quality control and product development. Multiple species may be monitored to determine the progress of the production process and can be used as part of a feedback loop. Figure 6: shows profiles of four different Maillard reaction products measured over four cycles of the production process, demonstrating that the profile for the formation of acrylamide and other Mallard products is different. This highlights the benefit of real-time analysis, as this would have been missed by standard GC or LC methods.

The profiles illustrate the subtle changes in the maximum gas phase concentration of each analyte during the production process.

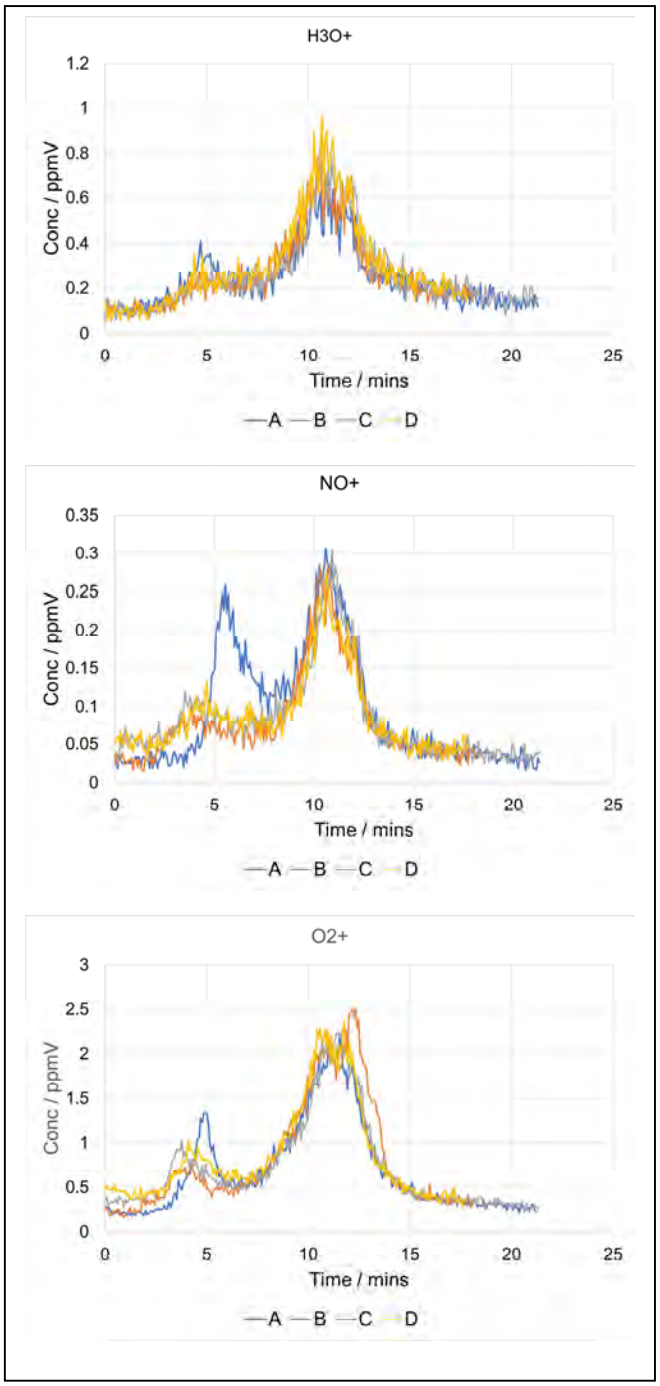

Figure 5: Four separate food production process runs overlaid and split by reagent

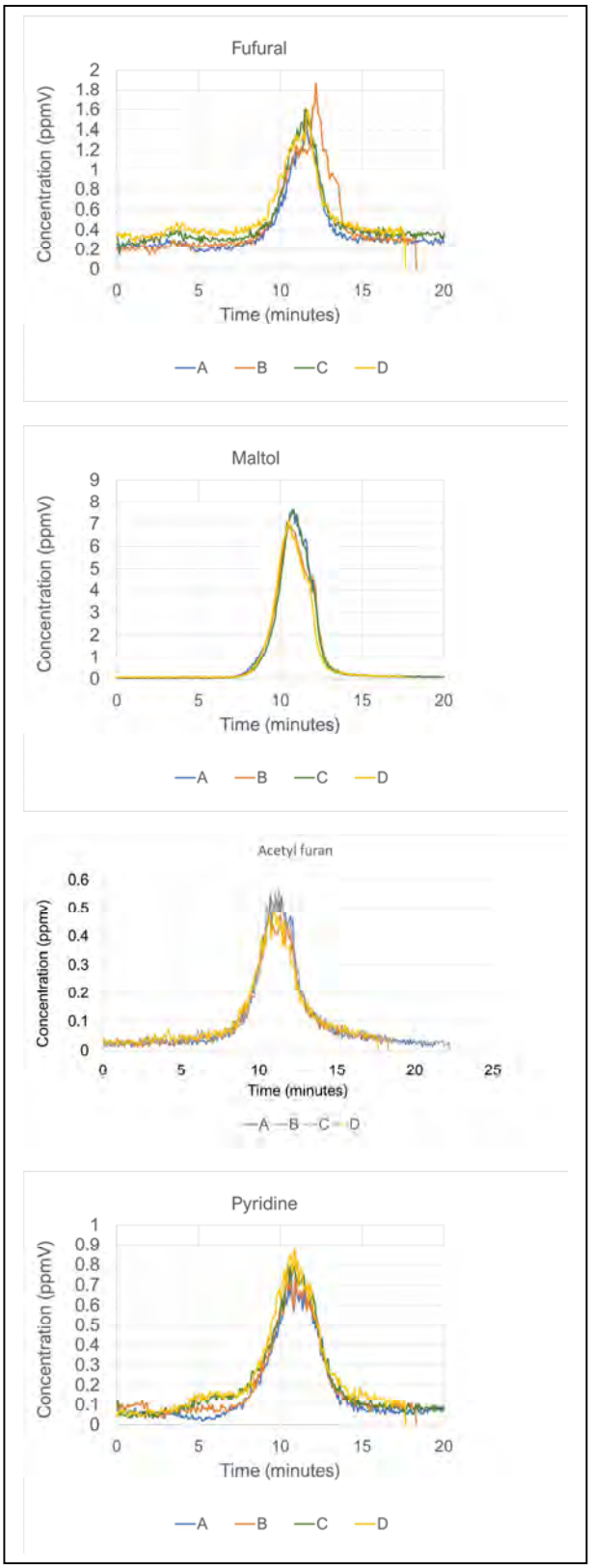

Figure 6: Profiles of four different Maillard reaction products measured over 4 cycles of the production process.

CONCLUSIONS

This application note demonstrates the ability of SIFT-MS to measure acrylamide in an industrial food production process, along with other volatile compounds. The inherent speed of analysis of SIFT-MS provides more definitive profiles for acrylamide and other volatile compounds which are monitored in real time.

Using this approach to measure 'in- production' real time concentrations could lead to a reduction in waste product having both a financial and environmental benefit. By understanding the production process more closely, the mitigation steps taken to eliminate potentially harmful contaminants can be designed during product development prior to scale up to factory production.

Note that due to the confidentiality of this work, it is not possible to give further detail of the production process used.

ACKNOWLEDGEMENTS

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To discuss implementing this application for your process monitoring, contact us and we will be delighted to work with you from conception to method transfer into your laboratory or production facility.