Food Control 64 (2016) 17–21

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Using ion mobility spectrometry for screening the autoxidation of peanuts

Manon Tzschoppe [a], Helen Haase [a], Michaela Höhnisch [b], Doris Jaros [a, *], Harald Rohm [a]

[a] Chair of Food Engineering, Technische Universität Dresden, 01062 Dresden, Germany
[b] IfU GmbH Privates Institut für Analytik, 09669 Frankenberg, Germany

ARTICLE INFO

Article history:
Received 9 November 2015
Received in revised form
4 December 2015
Accepted 14 December 2015
Available online 17 December 2015

Keywords:
Ion mobility spectrometry
Rancidity
Peanuts

ABSTRACT

Autoxidation is a critical process in many fat containing foods that leads to reduced palatability because of the formation of off-flavour compounds. The aim of the study was to evaluate the applicability of ion mobility spectrometry (IMS) for detecting volatile off-flavour indicators from roasted peanuts which were subjected to storage at elevated temperature. IMS measurements were carried out using a sample inlet system that allowed to keep the reactant ion peak constant. It is evident from the ion mobility spectra that the level of autoxidation significantly affects the signal intensities in particular drift time regions. Supported by the IMS measurement of pure hexanal, and by qualitative analysis for volatile aldehydes and organic acids, the IMS peaks at relative drift times of approx. 1.7 have a large potential for being used as rancidity indicators.

1. Introduction

Lipid oxidation is an important group of reactions that, once in progress, lead to the formation of compounds which significantly affect the sensory quality of foods by causing off-flavour, and deviations in appearance and texture. Primary oxidation products that are further decomposed have also been suggested as having negative health implications, and reducing the nutritional value of fat-containing foods (Decker, Elias, & McClements, 2010; Guèraud et al., 2010).

The fatty acid composition of peanuts largely depends on the cultivar. For example, the contents of oleic and linoleic acid, being the most dominant in peanuts, varied for US-grown peanuts of the type Runner from 49 to 57% and 22–31%, respectively (Shin, Pegg, Phillips, & Eitenmiller, 2010). Similar cultivars from Argentina significantly differed with respect to these fatty acids (40–49% oleic acid, and 33–41% linoleic acid; Grosso, Lamarque, Maestri, Zygadlo, & Guzmán, 1994). In regular oleic cultivars, hexanal, octanal, nonanal, and decanal can be considered as the major reaction products of autoxidation (Nawar, 1985). Hexanal is, for example, a frequently used marker to follow the progress of lipid oxidation in meat products and butter (Brunton, Cronin, Monahan, & Durcan, 2000; Panseri, Soncin, Chiesa, & Biondi, 2011), infant formula (Guadalupe García-Llatas, 2007), potato crisps (Sanches-Silva, Rodríguez-Bernaldo de Quirós, López-Hernández, & Paseiro-Losada, 2004), nuts (Pastorelli, Valzacchi, Rodriguez, & Simoneau, 2006; Williams et al., 2006), and baked foods (Purcaro, Moret, & Conte, 2008). Different extraction methods have been applied for monitoring volatiles from lipid oxidation, for example solid phase micro-extraction (SPME) (Brunton et al., 2000; Guadalupe García-Llatas, 2007; Panseri et al., 2011; Pastorelli et al., 2006; Purcara et al., 2008), or automated dynamic headspace gas chromatography (Ha & Wang, 2013). Electronic noses were also used for analysing volatiles generated by autoxidation of nuts (Pastorelli et al., 2007; Williams et al., 2006). Although there is a wide range of research applications for e-noses, they are still far away from being applied in industrial processes because of shortcomings such as sensor poisoning, sensor drift and a lack of sensitivity (Loutfi, Coradeschi, Mani, Shankar, & Rayappan, 2015).

Ion mobility spectrometry (IMS) is an analytical technique for characterising chemical substances on the basis of the velocity of gaseous ions in an electrical field at ambient pressure (Eiceman, Karpas, & Hill, 2013). The analytical use stems from the correlation between the chemical composition of a sample and the

Abbreviations: HS-GC-IMS, headspace gas chromatography–ion mobility spectrometry; IMS, ion mobility spectrometry; PDMS, polydimethylsiloxane; PP, polypropylene; PTFE, polytetrafluorethylene; RIP, reactant ion peak; SPME, solid phase micro-extraction.

* Corresponding author. Institute of Food Technology and Bioprocess Engineering, Technische Universität Dresden, Bergstrasse 120, 01062 Dresden, Germany.
E-mail address: doris.jaros@tu-dresden.de (D. Jaros).

http://dx.doi.org/10.1016/j.foodcont.2015.12.017
0956-7135/

gaseous ions that are released from it (Eiceman, 2002). IMS was initially used for real-time detection of warfare agents and drugs in small amounts, but further investigations discovered it as promising technique for domains such as food characterisation (Karpas, 2013). One of the earliest studies on the use of stand-alone IMS in the context with foods is from Karpas, Tilman, Gdalevsky & Lorber (2002) who successfully determined volatile biogenic amines in muscle foods. The same analyte was chosen by Karpas, Chaim, Gdalevsky, Tilman & Lorber (2002) for evaluating the diagnostic potential of microbial infections. In combination with a simple sample inlet system IMS was used to detect volatile compounds in fish or, in combination with a thermo reactor, it was applied to investigate the feeding regime of pigs by analysing the volatiles in their fat (Alonso et al., 2008; Menéndez, Garrido-Delgado, Arce, & Valcárcel, 2008). Márquez-Sillero, Cárdenas, and Valcárcel (2011) determined 2,4,6-trichloroanisole in wine with a single-drop ionic liquid extraction coupled to a multicapillary column separation and subsequent IMS detection and, in a follow-up study, they used a headspace multicapillary column ion mobility spectrometer for that purpose Márquez-Sillero, Cárdenas, and Valcárcel (2012). IMS coupled to a multicapillary column has also been tested for controlling and predicting the quality and shelf life of olive oil (Garrido-Delgado et al., 2015). Shuai et al. (2014) investigated a rapid screening method to detect the adulteration of flaxseed oil by using a pulsed glow discharge ionization source in negative mode, followed by multivariate analysis. The quantitation of hexanal in linseed oil and milk was possible using a coupled headspace – multicapillary column – IMS system (Márquez-Sillero, Cárdenas, Sielemann, & Valcárcel, 2014). This system allowed the separation of volatile compounds, but shows the disadvantage of the loss of the possibility for in-line measurements. Banach, Tiebe, and Hübert (2012) investigated IMS applicability for detecting spice adulteration, and concluded that conventional chemical analysis and olfactometric investigations are not obsolete, but e-nose and IMS may be useful tools for cost efficient quality monitoring by pre-identifying suspect samples for further analysis.

The aim of this study was to investigate the potential of using an IMS without any additional upstream equipment for tracing the autoxidation progress of blanched, roasted peanuts as affected by storage time. Advantages of this experimental set-up are a fast response, low purchase and maintenance costs, and a robust, transportable hardware for screening a high number of samples.

2. Materials and methods

2.1. Peanut samples and chemicals

Blanched peanuts from Argentina (lot A, Runner, size class 40/50), from Brazil (lot B, Runner, size class 38/42), and a retained sample rated as rancid by a sensory panel were kindly provided by Lorenz Nuss GmbH (Kreba-Neudorf, Germany). Blanched peanuts (2000 ± 10 g) were dry roasted at 180 °C for 20 min in a MIWE Condo C-2-68 rack oven (MIWE Michael Wenz GmbH, Arndorf, Germany). After cooling to room temperature, the peanuts were grinded at 5000 rpm for 5 s using a Grindomix GM100 mill (Retsch GmbH, Haan, Germany). To speed up the autoxidation process, 250 ± 1 g aliquots were then stored at 65 °C in 500 mL Erlenmeyer flasks either open (O) or sealed (S) for 14 or 21 d, and further stored at 4 °C until analysis. All analytical grade chemicals were from Sigma–Aldrich GmbH (Steinheim, Germany).

2.2. Headspace solid phase micro-extraction GC–MS analysis

4 ± 0.1 g peanuts were transferred into 20 mL glass vials, and closed with PP caps with PTFE/silicon septa (Phenomenex GmbH, Aschaffenburg, Germany). The samples were then kept at 50 °C for 15 min in a water bath. Adsorption of volatiles was performed at 50 °C using an SPME unit equipped with a conditioned (1 h at 250 °C) 50/30 μm divinylbenzene/carboxen/PDMS fibre (Supelco Analytical, Bellefonte, PA, USA) by inserting the fibre for 40 min into the headspace above the sample.

The qualitative detection of autoxidation products was carried out using an Agilent 7890A GC equipped with a HP-5ms column (30 m × 0.25 mm, 0.25 μm film thickness) coupled to a MSD 5975C mass spectrometer (Agilent Technologies Deutschland GmbH, Waldbronn, Germany). Measurements were carried out in splitless mode using a He flow of 1 mL/min; oven temperature was increased from 40 °C (hold time 4 min) to 160 °C at 3 °C/min, and from 160 to 230 °C at 6 °C/min; final hold time was 5 min. Measurements started after the fibre had been thermally desorbed in the GC injector for 6 min at 250 °C. Compound identification was carried out by comparing GC retention times with those of standard compounds, or by comparing mass spectra using the NIST MS Search 2.0.

2.3. Ion mobility spectrometry

Analyses were carried out with an ambient pressure SMELLMASTER® ion mobility spectrometer (IfU GmbH Privates Institut für Analytik, Frankenberg, Germany) that uses β^- – radiation for ionisation (50 mBq). Instrumental parameters are outlined in Table 1.

For IMS measurement, 4 ± 0.1 g peanuts were weighed into 20 mL glass vials that were closed with PP caps with PTFE/silicon septa, and immediately connected with the sample inlet system (Fig. 1) by simultaneously piercing two stainless steel syringe needles (neoLab Migge Laborbedarfs-Vertriebs GmbH, Heidelberg, Germany) through the septa. A constant flow of 1 L/min compressed air, generated by an SM11 compressor equipped with an activated carbon adsorber (Kaeser Kompressoren, Coburg, Germany) and controlled by a GFM17 flow meter (Aalborg Instruments and Controls Inc., New York, NY), streamed through the inlet system. Before connecting the sample vial valve 1 was closed, and the entire air flow passed only through bypass valve 2 (see Fig. 1). After starting data collection, control valve 1 was manually opened to an extent that ensured a reactant ion peak (RIP) intensity of 30–40% of its initial value without sample. This procedure also ensured a constant product ion concentration in the ionisation region.

The SMELLMASTER® IMS was controlled by the IMS Monitor software 2.0.5.0. During operation, an averaged spectrum consisting of 10 individual spectra was sent to the software per second. Subsequently, the spectra that were obtained within 10 s were averaged again before filing. Drift time was normalized to the drift time of the RIP at standard operation temperature of 80 °C and atmospheric pressure (101.23 hPa), and each single drift time spectrum was corrected with respect to actual temperature and pressure which were continuously recorded. Relative drift t_D time is therefore dimensionless. For each sample measurement, spectra

Table 1
Operating parameters of the SMELLMASTER® ion mobility spectrometer.

Parameter	Value and unit
Drift tube temperature	80 °C
Drift length	56 mm
Drift tube diameter	10 mm
Drift gas flow	400 mL/min
Sample inlet flow	30 mL/min
Shutter grid opening time	60 μs
Voltage	2 kV
Electric field	400 V/cm