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On-line headspace-multicapillary column-ion mobility spectrometry hyphenation as a tool for the determination of off-flavours in foods

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ABSTRACT

In this work, an ion mobility spectrometer (IMS) with a tritium ionization source on-line coupled to a headspace (HS) autosampler and a multicapillary column (MCC) was evaluated for the monitoring of lipid oxidation products in milk with different flavours (cacao, fruits, cereals and nuts) and linseed oil samples enriched with omega-3 acids. In this combination, the multicapillary column is used as an interface between the HS and the IMS, providing the efficient separation of the volatile compounds. In this way, the proposed method permits the detection of hexanal, 2-butanone, acetone and dimethyl sulfide as representative degradation products. The limits of detection were in the interval 0.3 $\mu g\,L^{-1}$ (for hexanal in milk) to 3.0 $\mu g\,L^{-1}$ (for dimethyl sulfide in linseed oil) while the limits of quantification varied between 1.1 $\mu g\,L^{-1}$ (for hexanal in milk) and 9.6 $\mu g\,L^{-1}$ (for dimethyl sulfide in linseed oil). The precision of the method was evaluated as relative standard deviation and the values were better than 8% in all cases. The evolution of the volatiles profile during 36 days under different storage conditions (temperature, oxygen and light) demonstrates the capability of the HS–MCC–IMS coupling for the estimation of the degradation of the samples. After the degradation study, it can be concluded that the stability of the milk samples during storage is more affected by the light while temperature was more critical for oil samples.

1. Introduction

Over the last 10 years, there has been an increasing industrial interest in incorporating long chain omega-3 polyunsaturated fatty acids (PUFAs), eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) in foods and dietary supplements. This is owing to the fact that there is a growing body of evidence that these omega-3 have a number of health beneficial effects [1,2]. A major challenge in relation to the use of omega-3 acids in food applications is their susceptibility to lipid oxidation, which will give rise to the formation of undesirable fishy off-flavours and odours that make the food unpalatable. The factors affecting lipid oxidation of omega-3 enriched foods are mainly oxygen, temperature, light and metal ions present as contaminants (Fe, Cu). The off-flavours formed are particularly unpleasant. Furthermore, the human sensory apparatus have a low threshold for these volatile compounds resulting from oxidation of omega-3 acids. The lipid oxidation events may take place in all the different foods such as mayonnaise, yogurts, spreads, oil (rich or enriched with omega-3 acids), milk, seafood, among others [3–12]. It is well documented that the presence of volatile ketones, alcohols and aldehydes, produced by the decomposition of peroxides are the main degradation products, mainly in fish oil [13–15].

Ion mobility spectrometry (IMS) is an analytical technique with a wide applicability [16–27]. This technique is characterized by the simplicity of its analytical information, high sensitivity, comparatively inexpensive acquisition and fast response since spectra are available in the milliseconds range. The functional principle of IMS has been described elsewhere [16,17]. Generally, the IMS can be used in different fields such as detection of explosives and chemical warfare agents [18,19], illegal drugs [20,21], control food [22], environmental contaminants [23] or volatile compounds in human exhaled air [24] and others unconventional applications [25]. However, for the analysis of individual substances in complex samples, IMS selectivity is very limited and a pre-separation of the analytes is required. Recently, a multicapillary column (MCC) has been coupled to IMS, allowing the detection of volatile organic compounds in complex matrices. This coupling combines the high selectivity of chromatographic separation with the good sensitivity of IMS. MCC have small dimensions (50–300 mm in length, 2–3 mm in external diameter, 1000 capillaries 20/100 μm in inner diameter), can work under isothermal conditions and can also eliminate the negative effect of the water vapour molecules in the IMS signal [26].

In this research, we evaluate the potential of the headspace, multicapillary column and ion mobility spectrometry hyphenation as an alternative analytical technique to obtain a volatile profile of a

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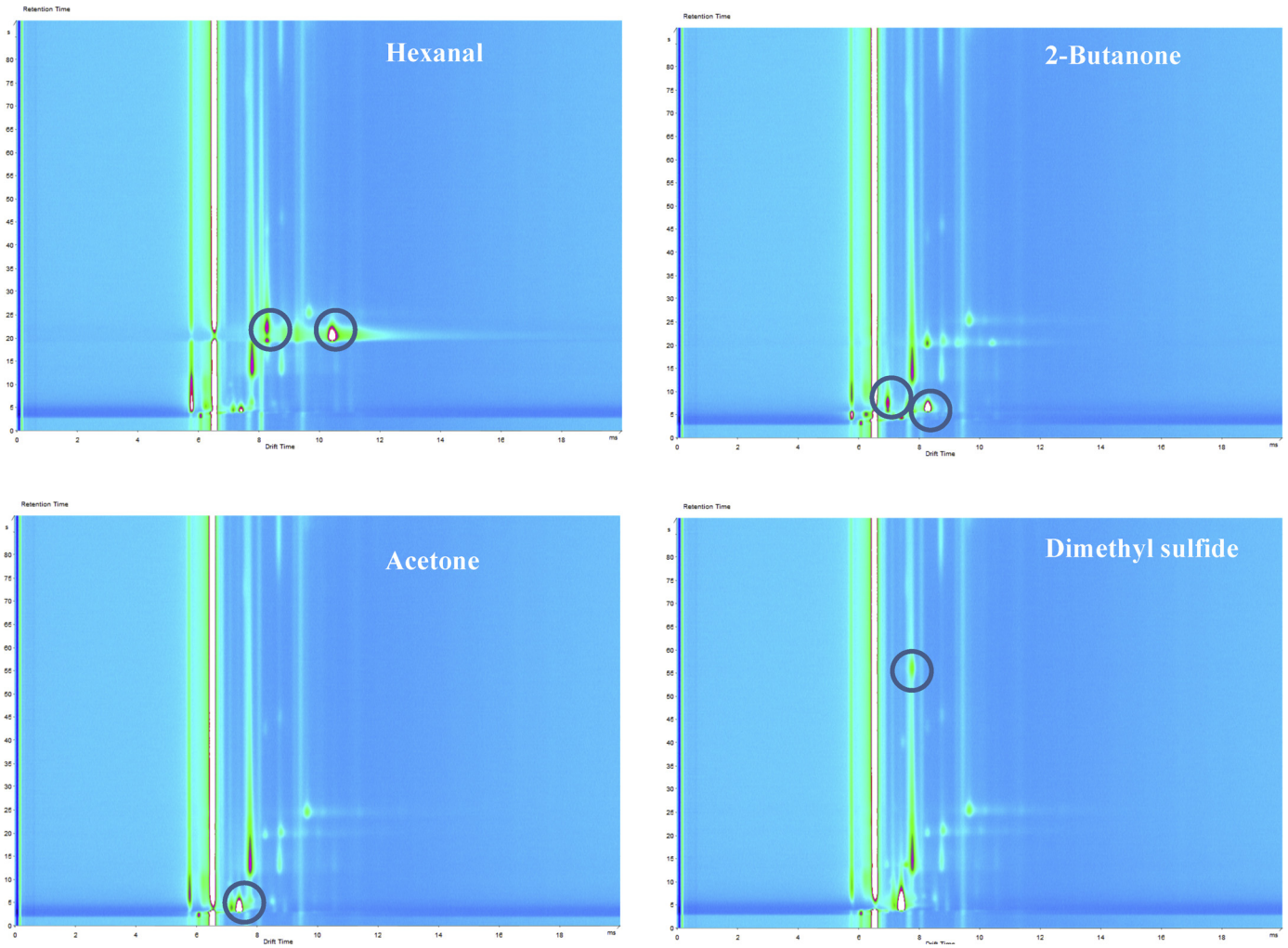

Fig. 1. Topographic plot of the identification of the IMS signal with the volatile compounds studied.

sample in order to monitor the lipid degradation produced in food samples and the potential influence of long chain omega-3 polyunsaturated acids in this process. The chemical profile of volatiles permits to characterize and classify the samples. Also, the identification and quantification of the main secondary products generated by the lipid oxidation in milk and linseed oil samples is achieved. The main secondary products are hexanal, 2-butanone, acetone and dimethylsulfide. This research will contribute to expand the applicability of IMS in the food analysis, mainly focused on the quality control.

2. Materials and methods

2.1. Reagents and samples

All reagents were of analytical grade or better. The analytes, 2-butanone, acetone and dimethyl sulfide, were obtained from Sigma–Aldrich (Munich, Germany) and hexanal was purchased from Fluka (Munich, Germany). Methanol from Sigma–Aldrich and Milli-Q ultrapure water (Millipore, Darmstadt, Germany) were also employed in the development of the analytical method.

Stock standard solutions of each analyte were prepared in methanol, at a concentration of 10 mg L^{-1} and stored in dark at 4 °C until analysis.

Working standard solutions used for calibration were obtained by dilution of the stocks in Milli-Q water. In addition, working standard solutions prepared in linseed oil and milk samples were used in the recovery study.

2.2. Apparatus

Analyses were performed on a FlavourSpec® IMS fabricated by Gesellschaft für Analytische Sensorsysteme (G.A.S. mbH, Dortmund, Germany). The instrument was equipped with a heated splitless injector, which enabled direct sampling of the headspace and was coupled to an automatic sampler unit (CTC-PAL, CTC Analystics AG, Zwingen, Switzerland). The sample headspace was injected with a 2.5 mL gastight HS-syringe. The analytes were separated on a multicapillary column OV-1701MCC, 14% - cyanopropylphenyl, 86% - dimethylpolysiloxane (Multichrom, Ltd.,

Table 1
Storage conditions used during 36 days for every type of sample.

Storage conditions	Temperature (°C)	Oxygen	Light
Control sample	4		
1	4	√	
2	23	√	
3	23	√	√
4	40	√	