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Non-Destructive Measurement of Volatile Organic Compounds in Modified Atmosphere Packaged Poultry Using SPME-SIFT-MS in Tandem with Headspace TD-GC-MS

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Abstract A methodology was developed to measure volatile organic compounds (VOCs) in a non-destructive way inside modified atmosphere packaged (MAP) poultry (chicken fillets) samples stored at 4 °C. To achieve this, a solid-phase microextraction (SPME) fiber was inserted in the headspace of the package and was later desorbed within a heated injector coupled with a selected ion flow tube mass spectrometer (SIFT-MS). As this technique is not stand-alone, it was calibrated on the same matrix using online SIFT-MS measurements and headspace thermal desorption gas chromatography (HS-TD-GC-MS) with internal standard calibration. A total of eight compounds were successfully monitored within the same samples over a storage period of 15 days. Ethanol and dimethyl sulfide presented the highest overall increase with large variations between the samples, while a clear increase was observed for 2-propanol, 2-butanone, and 3-methylbutanal by the end of shelf life. Our method provides a fast (analysis time < 5 min) non-destructive alternative for VOC measurements within modified atmosphere packaged products at refrigerated conditions. This approach can be useful to determine potential biomarkers at real storage conditions of packaged food prior to the moment of consumption.

Keywords Solid-phase microextraction · Selected ion flow tube mass spectrometry · Poultry spoilage · Volatile organic compounds · Modified atmosphere packaging · Thermal desorption gas chromatography mass spectrometry

Introduction

The use of modified atmosphere packaging (MAP) technology has been vastly utilized in food production over the last decades. Its function is to prolong the shelf life of products by slowing down the spoilage process. This is done by creating a protective atmosphere inside the package with a different composition than the atmospheric air, combining the antimicrobial effect of CO_2, the color preservation properties of O_2, and the use of N_2 as an inert filling gas. Its application for raw meat (beef, pork, lamp) and poultry (chicken, turkey) preservation is one of the most common (Arvanitoyannis and Stratakos 2012), while gas mixtures such as 70/30% (N_2/CO_2), 30/65/5% (CO_2/N_2/O_2), or 40/30/30% (CO_2/O_2/N_2) have been suggested for chicken fillet storage, respectively (Balamatsia et al. 2007; Chouliara et al. 2007; Meredith et al. 2014). Meat and poultry are very susceptible to spoilage and quality decay over time. Microbial genera like lactic acid bacteria, *Brochothrix thermosfacta*, and Enterobacteriaceae are the main specific spoilage organisms (SSOs) under MAP conditions (Nychas et al. 2008).

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These bacteria utilize nutrients from the food matrix and eventually produce volatile organic compounds (VOCs) related to off odors. The most typical VOCs associated with off odors in meat and poultry have been thoroughly reported in the study of Casaburi et al. (2015), with some of the most common ones being alcohols (ethanol, 2-propanol, and butanol), aldehydes (hexanal, heptanal, and octanal), ketones (acetoin and diacetyl), volatile fatty acids (acetic and butanoic acid), and sulfur compounds (dimethyl sulfide, dimethyl disulfide, hydrogen sulfide, and carbon disulfide). Although there has been intensive research on the spoilage process of meat and poultry and the related production of VOCs (Nychas et al. 2008; Casaburi et al. 2015), the evolution of the VOC concentration in the headspace of MAP-packaged poultry during storage has not been thoroughly investigated. Most of the research conducted on VOCs has mainly focused on raw poultry stored in air (Ahn et al. 1999; Senter et al. 2000; Lovestead and Bruno 2010; Alexandrakis et al. 2012; Mikš-Krajnik et al. 2015) or on VOC production under vacuum packaging (Mayr et al. 2003), whereas much less knowledge exists for MAP-stored poultry VOCs (Eilamo et al. 1998; Rajamäki et al. 2006; Balamatsia et al. 2007; Tománková et al. 2012) or on inoculated poultry meat (Franke and Beauchamp 2017; Klein et al. 2017).

One of the most widely used techniques to measure VOC production in meat and poultry is solid-phase microextraction (SPME) followed by gas chromatography/mass spectrometry. Generally, the samples are transferred from their original packaging and inserted in headspace vials. These are then heated or exposed to ambient temperature, to increase the rate of equilibration of the volatiles between the sample, the headspace, and the fiber (Soncin et al. 2007; Mikš-Krajnik et al. 2015). With this procedure, none of the original storage conditions (gas mixture, storage T) are preserved, which may lead to artifact formation. An alternative to this method, yet still destructive, is selected ion flow mass spectrometry (SIFT-MS), allowing real-time flow through measurements of VOCs in the headspace of the package (Noseda et al. 2010, 2012a, b; Olivares et al. 2012; Carrapiso et al. 2015). The technique has been previously correlated with SPME-GC-MS measurements showing a positive linear correlation for analytes detected in fermented sausage and beef (Olivares et al. 2011; Flores et al. 2013).

Shelf life studies focusing on VOC evolution over time, either using SIFT-MS or GC-MS, start commonly from the same batch of samples to ensure homogeneity. Then at certain time intervals, samples are analyzed from this pool to be later discarded, because it is a destructive approach. VOC concentration profiles over the shelf life of the packed product are thus not determined for an individual sample but for a group of samples. Due to the inherent within and between batch variability of biological samples however, this approach results typically in a lower repeatability or reproducibility, making interpretation of the VOC data sometimes challenging (Noseda et al. 2012b; Zhang et al. 2013; Pothakos et al. 2014). Furthermore, there is little or no knowledge on the evolution of VOCs inside each individual modified atmosphere package during storage at refrigerated temperatures. This is essential to understand how the consumer will perceive these VOCs when the package will be finally opened.

In this paper, we put forward an alternative non-destructive methodology to measure the VOCs from the headspace of MAP-packaged poultry at 4 °C, while not disturbing the headspace gas mixture—which can however evolve spontaneously over storage. This was done by exposing a SPME fiber inside the headspace of the package followed by thermal desorption of the fiber directly into the SIFT-MS. In order to achieve this, two independent analytical techniques were combined with this methodology. The study consists of three major sections: (1) method development, (2) optimization, and (3) application. During the method development, two fibers were compared in terms of their extraction efficiency towards relevant compounds and one was selected. Several spoilage VOCs were identified. Also, the MAP sampling time was investigated in order to obtain reproducible detection signals of the compounds. In the second section, a method optimization was performed in which three different techniques were used to measure the VOC concentration in the package: (1) standard HS-TD-GC-MS analysis which is our reference benchmark technique (golden standard), (2) direct analysis by on-line SIFT-MS necessary for the optimization of the obtained signals, and finally (3) SPME-SIFT-MS which is the newly developed approach. This resulted in calibration factors which are used in the third section of the manuscript to follow the concentration of VOCs in individual poultry packages under MAP. In this case, the headspace of the MA poultry package is only measured with SPME-SIFT-MS.

To our knowledge, this is the first SPME-SIFT-MS-based study monitoring VOCs inside the headspace of modified atmosphere packages under refrigerated conditions without disturbing the MAP atmosphere.

Materials and Methods

Plan

A methodology was developed to measure VOCs inside modified atmosphere packages without altering the MAP atmosphere. This was done by inserting a SPME fiber through a septum attached on the top foil of the MAP-packaged chicken fillet, thus exposing it to the headspace (Fig. S1-A, provided as supplementary materials). The SPME fiber was desorbed within an in-house-made thermal desorption injector system which was directly coupled to the SIFT-MS inlet, as described

in the scheme (Fig. 1) and depicted in Fig. S1-B, provided as supplementary materials.

Sample Preparation and Packaging

Skinless chicken breast fillets were obtained within 24 h after slaughter from a local processing plant in Belgium and were transported to the lab under refrigerated conditions (4 °C). The fillets were thoroughly rubbed against each other prior to packaging to acquire the same level of microbial contamination. Packaging was performed with a mixture of 40/30/30% $CO_2/N_2/O_2$% with a 1:1 (*v*/*v*) gas-to-product ratio, using a tray sealer MECA900 (DecaTechnic, Herentals, Belgium). The chicken fillets (average weight 375 ± 25 g) were placed in multilayer packaging trays (tray dimensions 187/137/50 mm; polypropylene (PP)/ethylene vinyl alcohol (EVOH)/PP, with oxygen transmission rate (OTR) of 0.03 cm^3/tray day atm, at 23 °C and 50% RH, Decapac NV, Turnhout, Netherlands) covered with a multilayer film (Bemis Packaging Benelux, Monceau-sur-Sambre, Belgium) of 65-μm thickness (oriented polyamide (OPA)/EVOH/polyethylene (PE)/PP, OTR 5 cm^3/m^2 day atm at 23 °C, 50% RH). Empty trays were also filled with the same gas mixture and used as controls to verify the gas concentration during storage. After packaging, the samples were stored at 4 ± 0.5 °C throughout the experiment.

In order to permit the SPME insertion in the package without leaks, GC septa (blue septa 3/8″, Grace, Deerfield, IL, USA) were glued (without using the accompanied activator) on the top of the film of each package with instant glue (Loctite, Henkel, Belgium) used for plastics. To ensure proper attachment, the glue was left for 24 h to solidify.

To evaluate the performance of the septa prior to the experiment, six empty trays were packaged with a 50/50 CO_2/N_2 vol% gas mixture. Half of the trays were perforated (three times) through the septum with a needle, and the rest were used as controls; they were stored in ambient temperature (20 °C) for a month. Gas composition analysis was performed with a gas measurement device, Checkmate 9900 O_2/CO_2 (PBI Dansensor A/S, Ringsted, Denmark), in the headspace of the packages, for the O_2 and CO_2 levels. In this preliminary test, a minor change was observed, from an initial concentration of 49% CO_2 and > 0.1% O_2 to 48% CO_2 and ≥ 0.5% O_2 after 1 month; thus, the septa were used further.

Selection of SPME Fiber (SPME-SIFT-MS)

SPME fibers were compared on the basis of the measured peak areas, which were the result of the peak integration that appeared during a SIFT-MS measurement (Fig. S2, provided as supplementary materials) the moment that the fiber was desorbed in the heated inlet connected with the SIFT-MS. Two fiber coatings were tested to perform the extraction: carboxen/polydimethylsiloxane (CAR/PDMS) SPME fibers (75 μm, 23Ga, Supelco, Bellefonte, USA) and polydimethylosiloxane (PDMS) fibers (100 μm, Supelco, Bellefonte, USA). The fibers were conditioned before use for half an hour at 300 and 250 °C, respectively, as recommended by the manufacturer. After each analysis, the fibers were post conditioned at 250 °C for 5 min to avoid carryover. Various extraction times (30 s, 1 min, 3 min, 5 min, 10 min, 15 min, 20 min, 30 min, 60 min) were evaluated at 4 °C in a package of MAP chicken (stored for 7 days). SPME fibers were analyzed by desorption using the thermal desorption injector which was coupled with the SIFT-MS inlet. CAR/PDMS

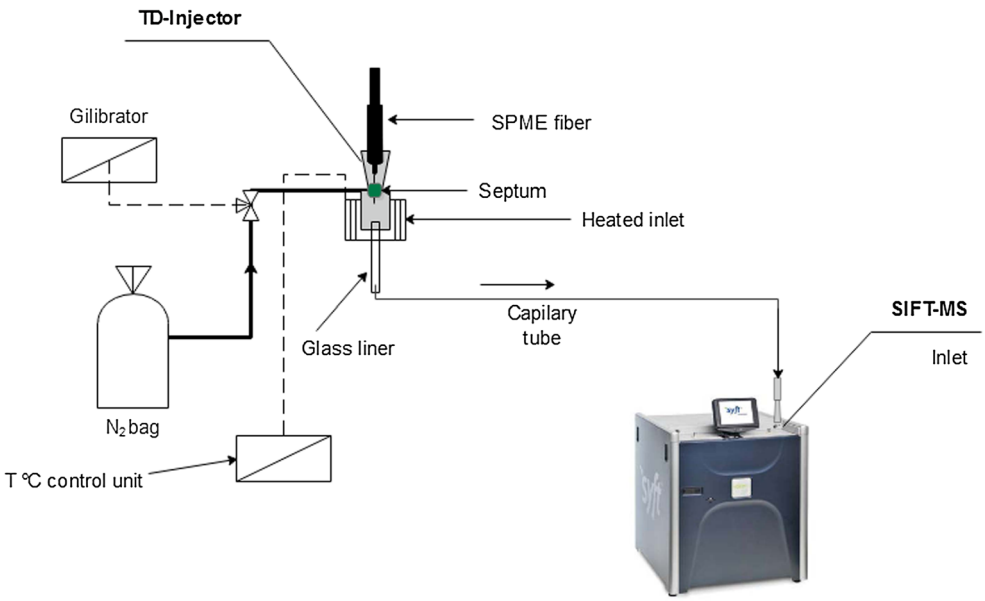

Fig. 1 Schematic of the SPME-SIFT-MS apparatus used for the VOC measurements in MAP chicken breast fillet samples

fiber presented a better response for the measured compounds and was finally selected for further research.

Selection of Compounds and Extraction Time (SPME-GC-MS)

The same batch of MAP-packaged chicken breast fillets was used throughout this experiment. All the packages were incubated at 4 °C and were stored maximum for 15 days. A different package was analyzed after 1, 7, and 14 days of storage in order to determine which VOCs are being produced in the beginning, middle, and end of the shelf life. Acetone, carbon disulfide, and 2-butanone were detected on day 1; acetic acid, 2,3-butanedione, dimethyl sulfide, acetoin, and 3-methylbutanal were detected on days 7 and 14, while ethanol was only detected on day 14 (data not shown). Based on these measurements, 13 compounds (acetic acid, acetoin, acetone, 2,3-butanedione, 2-butanone, carbon disulfide, dimethyl disulfide, dimethyl sulfide, ethanol, heptanoic acid, 2-methylbutanal, 3-methylbutanal, 2-propanol) were selected for further research.

Different extraction times were applied (1, 3, 5, 10, 15, 20, 30, 60, 120 min) for the target compounds on each of the analyzed time points. The aim was to select a suitable extraction time in order to compromise the length of extraction and the sensitivity. Peak areas were plotted against exposure time (Fig. 2). The peak areas for each detected compound were normalized by their maximum area measurement on each individual storage day (peak $area_{t(i)}$ / (peak $area_{max}$ × 100), where $t(i)$ is each extraction time used). Within the time frame considered, no visible equilibrium was reached. However, acetone, carbon disulfide, and dimethyl disulfide approached a plateau at 120 min. If the compounds were detectable, the impact of the extraction time over the normalized peak areas was very reproducible.

Moreover, the reproducibility of the sorption was checked by performing measurements in triplicate on samples ($n = 3$) stored for 2, 9, and 15 days exposing the fiber for 3 and 30 min. The CAR/PDMS SPME fiber was inserted manually in the package through the septum. The reproducibility of the extraction procedure presented a clear increase (Table 1), with RSD% lower than 10% at 30 min of exposure for most of the compounds, with the exception of acetic acid on day 2 (RSD 11%) and acetoin and dimethyl sulfide (RSD ≤ 21%) on day 15. Since reproducible results were obtained at 30 min of extraction, 20 min of extraction was also considered in order to increase the throughput of the method. After 20 min of extraction, reproducible results were obtained from an independent sample stored for 7 and 15 days with RSD% lower than 10% (Table S1, provided as supplementary materials). Therefore, 20 min of extraction time was finally selected in order to achieve a high-throughput analysis for our samples and avoiding excessive exposure times.

SPME-GC-MS Settings

Chromatographic analysis was performed on an Agilent 7890A GC (Agilent, Palo Alto, CA) equipped with 5975C mass spectrometer. The analytes were desorbed from the fiber in a PTV inlet at 250 °C in splitless mode for 1 min, and chromatographic separation was carried out on an Agilent J&W DB-624 column (60 m × 0.25 mm ID with 1.4-μm film thickness; Agilent Technologies Belgium S.A./N.V., Diegem, Belgium). The temperature program was set as follows: 2 min at 40 °C, ramp 5 °C/min to 150 °C and kept stable for 5 min, and ramp 12 °C/min to 230 °C and kept stable for 5 min. The carrier gas was helium at a flow rate of 1 mL/min. The mass spectrometer detector (MSD) conditions were the following: capillary direct interface temperature 230 °C, ionization energy 70 eV, operating mode scan from m/z 34 to 350, and scan rate 4.7 Hz. The data were processed by the MSD ChemStation software package (D.01.02.16, Agilent Technologies, Santa Clara, CA, USA), and the identification of the observed peaks was carried out on the basis of spectrum comparison with the NIST 05 Library, and it was confirmed with the use of standard compounds.

Headspace Thermal Desorption GC-MS

Conditioning and Loading with Internal Standard

The HS-TD-GC-MS was used as a reference technique to be compared and correlated with direct SIFT-MS and SPME-SIFT-MS. The HS-TD-GC-MS method used has been described before (Demeestere et al. 2008; Do et al. 2014, 2015); one point calibration with [$^2H_8$]toluene (Tol-d_8; 99.5+ atom% D; Acros Organics, Geel, Belgium) was used for VOC quantitation.

The process used was the following. Sorbent tubes (Tenax sorbent TA 35/60, Carbotrap 20/40 Markes, Llantrisant, UK) were conditioned for 1 h at 300 °C while being flushed with helium (50 mL/min). Sorbent tubes used for sampling were initially loaded with a gaseous internal standard (Tol-d_8), separately prepared by making a two-phase (gas/liquid) system as described elsewhere (Demeestere et al. 2008). During this procedure, 500 μL from the headspace of the two-phase system, corresponding to 10.7 ng Tol-d_8, was loaded onto each sorbent tube by means of an in-house-made heated (150 °C) injection system flushed with He (100 mL/min) (Demeestere et al. 2008).

Sampling

Thereafter, a headspace volume of 10 mL was taken from a MAP-packaged chicken sample with a glass gas-tight syringe and injected onto a sorbent tube loaded with the internal standard by using the same injection system. As this analysis

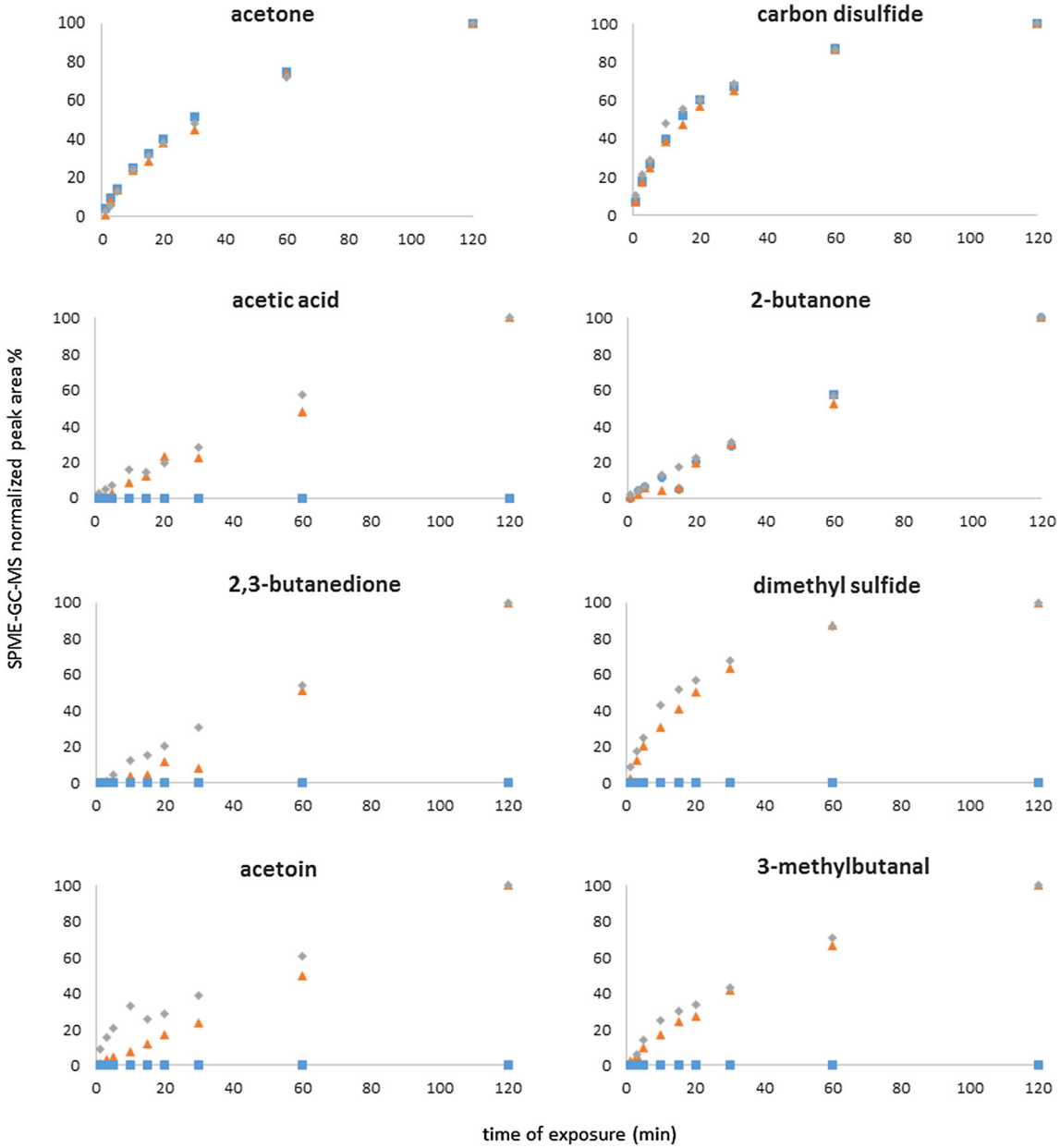

Fig. 2 Peak area results obtained during the optimization of SPME-GC-MS measured with a CAR/PDMS fiber for each targeted VOCs (normalized by its maximum value on each measurement day) plotted against the time of exposure, at the beginning, middle, and end of the shelf life. Days are represented with the following symbols: day 1 (■), day 7 (▲), and day 14 (◆)

disturbs the MAP atmosphere, it was only used to calibrate the SPME-SIFT-MS system.

HS-TD-GC-MS Settings

Desorption of the analytes preconcentrated on the sorbent tubes was performed in a Unity Series 2 Thermal Desorption System (Markes, Llantrisant, UK) set at 170 °C in splitless mode, for 1 min with a flow of 10 mL/min. The GC (Focus GC, Thermo Finnigan, Milan, Italy) was equipped with a Factor Four VF-1 ms low bleed bounded phase capillary GC column (100% polydimethylsiloxane, 30 m × 0.25 mm ID with 1-μm film thickness; Varian, Sint-Katelijne-Waver, Belgium). The GC oven temperature was set as follows: 3 min at 35 °C, ramp 8 °C/min to 150 °C, ramp 12 °C/min to 240 °C, and held constant for 10 min. The MS transfer line was heated to 240 °C; the ion source was set at 220 °C. Masses were scanned in two segments in full-scan mode (scan rate 5 Hz) from *m*/*z* 15 to 300 for the first 10 min and from *m*/*z* 29 to 300 for the rest of the method; they were recorded on a Trace DSQII Quadrupole MS (Thermo Finnigan, Austin, TX, USA), hyphenated to the GC, and operated at an electron

Table 1 Relative standard deviations (n = 3) from SPME-GC-MS measurements with the CAR/PDMS fiber on chicken breast samples from days 2, 9, and 15 at 3 and 30 min of exposure time

	Day 2		Day 9		Day 15	
	3 min	30 min	3 min	30 min	3 min	30 min
VOCs	RSD %					
Acids						
Acetic acid	84	11	13	5	19	9
Alcohols						
Ethanol	n.d.	n.d.	n.d.	n.d.	8	3
Aldehydes						
2-Methylbutanal	n.d.	n.d.	24	3	23	3
3-Methylbutanal	n.d.	n.d.	40	1	21	5
Ketones						
Acetoin	n.d.	n.d.	15	3	66	17
Acetone	11	3	2	2	6	3
2,3-Butanedione	n.d.	n.d.	1	3	51	6
2-Butanone	19	1	15	2	2	4
Sulfur compounds						
Carbon disulfide	12	6	12	4	7	2
Dimethyl disulfide	n.d.	n.d.	n.d.	n.d.	19.8	21

n.d. the compound was not detected

impact energy of 70 eV. Chromatograms and mass spectra were processed using XCalibur software (Thermo Finnigan, version 2.07), and compounds were identified on retention time and comparison of the spectra with the NIST database.

System Calibration (Golden Standard)

Sorbent tubes used for the method calibration (golden standard) were loaded using the same injection system with 1 μL of a methanol (VWR Prolabo, Belgium) solution containing Tol-d_8 (corresponding to 22.37 ng) and a range of 39–63 ng/μL of the following standards described with their respective ions used for quantitation: ethanol (45; Merck KGaA, Darmstadt, Germany), acetone (43; 58; Acros Oroganics, Geel, Belgium), 2-propanol (43; 45; Sigma-Aldrich, Overijse, Belgium), dimethyl sulfide (47; 62; Fluka), carbon disulfide (76; Sigma, Overijse, Belgium), 2,3-butanedione (43; Fluka, Geel, Belgium), 2-butanone (43, 72; Acros Oroganics), acetic acid (43; 45; 60; Sigma), 3-methylbutanal (58; 71; 86 Sigma), acetoin (43; 45; 88; Sigma), 3-methyl-1-butanol (42; 55; 70; Sigma), and dimethyl disulfide (79; 94; Sigma). Before each analytical run, HS-TD-GC-MS was calibrated, and the relative sample response factors (RSRFs), defined as the ratio of response factor of the compound (peak area per nanogram loaded on the tube) and the response factor of the internal standard, were calculated for each VOC. A compound was detectable when its signal-to-noise ratio (S/N) was higher than 3 and was quantifiable when its S/N was higher than 10. Blank correction of the samples was done only when the compound could be quantified in the blank, i.e., when the S/N ratio was higher than 10.

SIFT-MS Method Development

SIFT-MS has been used over the last years in food and environmental applications offering rapid and accurate quantitation of VOCs (Španěl et al. 2002; Noseda et al. 2010; Olivares et al. 2010). This technology relies on the chemical ionization of the VOCs by reagent ions (NO^+, O_2^+, and H_3O^+) produced through a microwave discharge on humidified air. Each specific reagent ion is selected by the quadrupole mass filter. Then, the ion stream of the selected reagent is transferred along the flow tube by a rapid flowing helium carrier gas. The sample is introduced into the flow tube through a heated capillary, while the VOCs react with the selected precursor ion, by a known reaction rate constant (k). Consequently, the product ions of the ionization reactions are guided through a second quadrupole mass spectrometer. Finally, a concentration of the target compound is being calculated, proportional to the count rate ratio of the product ion to the reagent ion. A multiple ion mode (MIM) scan was used during the method development targeting specific ions. The final form of the method used during the experiments is described in Table 2. These product ions were selected on the basis of (i) having a high branching ratio (BR) during the reaction with the precursor ions, (ii) a low relative standard deviation (RSD < 30%) of their average value during the measurements, and (iii) the absence of mass overlaps resulting in conflicts (Olivares et al. 2010). An average concentration over 5 min of measurement was used for calculations for each product ion. At each day of analysis and prior to the measurements, the instrument was routinely validated (automated procedure) to verify the proper function of all the internal parameters. Additionally, prior to each measurement, the volume uptake was monitored using a flow control measurement device (Gilian Gilibrator 2, Sensidyne, FL, USA) to ensure a constant flow rate (3.5×10^{-5} m^3/min or lower depending on the restriction used, at 110 °C) throughout the experiment.

Online SIFT-MS Measurements

To measure the headspace concentration inside the packages, a destructive technique was employed. Therefore, a capillary Teflon tube of OD 1/16″ (ID 0.007″) was connected from the SIFT-MS inlet to a needle, which was later introduced in the headspace of the MAP package. A second needle was inserted in the package to prevent under pressure formation during the measurements, thereby disturbing the gas-phase composition inside the MAP package which however evolves and changes during storage because of microbial proliferation (Meredith

Table 2 SIFT-MS multiple ion mode method used for monitoring VOCs in poultry samples with the coinciding precursor ions, mass-to-charge ratio (*m*/*z*), branching ratio, and reaction rate coefficient (*k*)

Volatile compound	Precursor ion	*k*	Branching ratio %	*m*/*z*	Product ion
Acids					
Acetic acid	NO^+	9.00E−10	100	90	$NO^+{\cdot}CH_3COOH$
				108	$NO^+{\cdot}CH_3COOH.H_2O$
Alcohols					
2-Propanol	NO^+	2.40E−09	100	59	$C_3H_7O^+$
3-Methyl-1-butanol	O_2^+	2.10E−09	85	59	$C_3H_7O^+$
Ethanol	NO^+	1.20E−09	100	45	$C_2H_5O^+$
				63	$C_2H_5O^+{\cdot}H_2O$
				81	$C_2H_5O^+{\cdot}2H_2O$
Aldehydes					
3-Methylbutanal	NO^+	3.00E−09	100	85	$C_5H_9O^+$
Ketones					
Acetoin	NO^+	2.50E−09	100	118	$C_4H_8O_2{\cdot}NO^+$
Acetone	NO^+	1.20E−09	100	88	$NO^+{\cdot}C_3H_6O$
2,3-Butanedione	NO^+	1.30E−09	35	43	$C_2H_3O^+$
	NO^+	1.30E−09	65	86	$C_4H_6O_2^+$
2-Butanone	NO^+	2.80E−09	100	102	$NO^+{\cdot}C_4H_8O$
Nitrogen compounds					
Ammonia	H_3O^+	2.60E−09	100	18	NH_4^+
				36	$NH_4^+{\cdot}H_2O$
Sulfur compounds					
Carbon disulfide	O_2^+	7.00E−10	100	76	CS_2^+
Dimethyl disulfide	NO^+	2.40E−09	100	94	$(CH_3)_2S_2^+$
Dimethyl sulfide	NO^+	2.20E−09	100	62	$(CH_3)_2S^+$
Hydrogen sulfide	O_2^+	1.40E−09	100	34	H_2S^+
	H_3O^+	1.60E−09	100	35	H_3S^+
				53	$H_3S^+{\cdot}H_2O$

et al. 2014). For this reason, the package could be used only once since the initial packaging gas mixture could not be used again. Thus, the second needle was connected with a bag filled with pure N_2 gas, to avoid introduction of contaminated background inside the package.

SPME-SIFT-MS Measurements

This section contains the description of the developed setup enabling measurements of the VOC concentrations inside the package. For each measurement, the SPME fiber was exposed in the headspace of an MAP package, and after the extraction, it was inserted in the in-house-made heated injector (containing parts from a Variant 3700 GC; Fig. S3, provided as supplementary materials) and analyzed using the SIFT-MS as detector. The desorption temperature of the injector was set at 150 °C. Nitrogen was used as a carrier gas. Therefore, an inert bag filled with N_2 was connected to the injector. The N_2 was pushed through the injector by the suction of the SIFT-MS. The SIFT-MS flow was checked using a flow control measuring device (Gilibrator), and all measured concentrations were corrected for this flow. The VOCs were transferred from the SPME fiber through a glass liner of the injector through an OD 1/16″ Teflon tubing (ID 0.007″) to the SIFT-MS (Fig. 1).

Calibration (HS-TD-GC-MS, SIFT-MS, SPME-SIFT-MS)

Twelve packages of MAP-packed chicken filets were prepared as described in the "Materials and Methods" section and were stored at refrigerated conditions (4 °C). Nine out of 12 packages were used for calibration purposes. At each 2nd, 7th, and 14th day of storage, three packages were taken and three different analyses were performed on each package. First, the packages were analyzed by exposing (20 min) a CAR/PDMS fiber in the headspace of the package after which an analysis was performed by SIFT-MS (SPME-SIFT-MS). Second, a volume of headspace was taken and injected onto a sorbent tube and analyzed by HS-TD-GC-MS. Finally, the headspace was directly measured by online SIFT-MS thereby piercing the foil of the package resulting in a disturbance of the gas composition inside the package. After these analyses, the packages were discarded.

These analyses enabled us to perform a quality assurance during our measurements (for the complete analysis scheme, see Fig. S4, provided as supplementary materials). Online SIFT-MS data were only used if the relative standard deviation (RSD%) on the average measured concentration over 5 min was lower than 25%. The SPME-SIFT-MS analysis resulted into peak area units (SIFT-$MS_{peak\ areas}$) for each measured product ion. These SIFT-$MS_{peak\ areas}$ were only used for further data processing if the signal was significantly different from the blank signal. The HS-TD-GC-MS analysis was performed as a reference (golden standard) to which the other techniques were calibrated.

Data Analysis

Data analysis was conducted using MS Excel; JMP 12 statistical software (SAS Institute Inc. 2013) was used for the regression models. IBM SPSS Statistics 24.0 was used for the curve fitting, Pearson's correlations, and the analysis of variance with post hoc analysis (Welch's ANOVA was used in the cases where the homogeneity of variance assumption was not met). A non-parametric ANOVA (Kruskal-Wallis) was used if the normality assumption was not met.

Results and Discussion

Impact of SPME-SIFT-MS Measurements on Package Integrity

At the end of the SPME-SIFT-MS experiment, the gas composition of the packaged poultry samples perforated from the septum due to the insertion of the SPME fiber was evaluated and compared with unperforated poultry packages used as controls, stored at the same conditions 15 days at 4 °C. The initial gas mixture was 40/30/30% $CO_2/O_2/N_2$%; the gas concentration in the packages was measured after 14 days of storage. The average measured CO_2 level on day 15 was 53 ± 1% (SE, n = 3) for the control packages and 44 ± 0.4% (SE, n = 3) for the perforated ones. In both cases, the CO_2 concentration was higher than the initial 40%, while O_2 levels were below the limit of detection. During the shelf life of the product, the O_2 used in the initial gas mixture is being converted to CO_2 due to microbial metabolism; thus, the absolute CO_2 concentration will increase. However, a small drop was observed in the CO_2 concentration in the packages where the VOCs were measured with the SPME-SIFT-MS approach. A minor gas exchange would have been expected due to the permeability of the packaging material which is affected by the low temperature and the relative humidity. This decrease in concentration will not have a practical effect on the spoilage process of the poultry for two main reasons. First, from a microbiological and preservation perspective, the minimum CO_2 concentration required in the package equals 40%, especially to retain bacteriostatic activity against *Campylobacter* sp. (Meredith et al. 2014), which was lower than the measured average. Thus, in both sets of samples, the spoilage process was unaffected by the CO_2 concentration. Secondly, it should be stated that the limited loss of CO_2 could only be observed over a very long time span (14 days) explaining as well that potential permeation of oxygen inside the package was not observable. Consequently, the impact on the VOCs present in the headspace of the samples was considered to be very limited as well, taking also into account the fact that the headspace is in constant equilibrium with the solid matrix in the package where the VOCs are constantly produced.

Selection of SPME Fiber (SPME-SIFT-MS)

SPME fibers were compared on the basis of the measured peak areas, which were the result of the peak integration that appeared during a SIFT-MS measurement the moment that the fiber was desorbed in the heated inlet connected with the SIFT-MS. Two fiber coatings were compared, PDMS and CAR/PDMS, in order to select the optimal fiber to monitor the VOCs in chicken breast fillets. Both fiber types have been previously used in poultry VOC determination (Senter et al. 2000; Soncin et al. 2007; Alexandrakis et al. 2012; Mikš-Krajnik et al. 2015) and in meat (Leroy et al. 2009; Olivares et al. 2011; Lorenzo 2014; Met and Şahin Yeşilçubuk 2017). Ethanol, acetone, dimethyl sulfide, 3-methyl-1-butanol, 2,3-butanedione, and acetoin were detected with the CAR/PDMS fiber from the headspace of a chicken sample stored at 4 °C, 7 days after packaging. A higher response was observed for the CAR/PDMS against the plain PDMS fiber and is presented in Table 3. Based on our findings, CAR/PDMS was selected for further research since it provided a better response with most of the measured compounds.

Table 3 CAR/PDMS to PDMS area ratio for different extraction times on chicken breast fillet samples

Time (s)	Acetone	3-Methyl-1-butanol	2,3-Butanedione
30	4	1	< LOD
60	5	1	2
180	7	1	2
300	8	1	1
600	13	2	1
900	18	2	2
1200	22	2	4
1800	32	3	3
3600	47	9	15

HS-TD-GC-MS and SIFT-MS Measurements

The HS-TD-GC-$MS_{conc.}$ was correlated with the SIFT-$MS_{conc.}$ using a regression model. The data were plotted, and Pearson's correlation coefficients were determined to define the degree of linearity. The Pearson's coefficient r, for $p \leq 0.01$, for each measured compound is presented in Table 4. The strongest significant correlation, $r \geq 0.9$ with $p \leq 0.002$, was observed for dimethyl sulfide, ethanol, carbon disulfide, 3-methylbutanal, 2-propanol, and acetoin, respectively. 2-Butanone and acetone presented as well a good significant correlation with $r = 0.836$ with $p \leq 0.01$ and $r = 0.795$ with $p = 0.002$, respectively. Non-linear correlations were observed for 2,3-butanedione, 3-methyl butanol, and acetic acid. Strong significant correlations have been also reported for SIFT-MS and SPME-GC-MS in fermented sausage for ethanol, 1-2-propanol, 2-butanone, and sulfur compounds depending on the fat content (Olivares et al. 2011). A linear regression fit was applied only for compounds having a $R^2 > 0.7$; the other compound was not used for further calculations. The regression plots of all the selected compounds between SIFT-MS and HS-TD-GC-MS are presented in Fig. 3.

When the SIFT-$MS_{peak\ areas}$ were plotted against the online SIFT-MS concentration measurements, no linear relationship was observed; this behavior is visualized by plotting the average value of the SIFT-$MS_{peak\ areas}$ to online SIFT-MS ratio (peak area/conc) against the age of the package (Fig. S5, provided as supplementary materials). This plot shows a decreasing trend which can be explained by the competitive sorption effect occurring at the SPME fiber as the chicken fillets get older, resulting into a higher concentration of spoilage VOC. Due to the nature of the adsorption-type fibers, a competition will result in the displacement of the VOCs at increasing concentrations (Risticevic et al. 2010). The sum of the total measured peak areas was between 1.9 and 3.0×10^5 area units on days 2, 7, and 14, respectively, while the sum of the concentrations measured by online SIFT-MS was 7.6×10^2, 1.7×10^3, and 1.0×10^4 mg/m^3 on days 2, 7, and 14, respectively, presenting two orders of magnitude increase. This can be also illustrated in the case of ethanol where the measured peak areas present only a small increase between days 7 and 14 (Table S2, provided as supplementary materials). As a result of that, a fit (polynomial or linear) was used for this time-dependent behavior (Fig. S5 provided as supplementary materials). This relationship was used to interpolate the ratio obtained previously on days 1, 3, 6, 9, 12, and 15, only if the measured compound was above the limit of detection, hence enabling us to calculate the concentrations of the three remaining MAP chicken fillet packages during these days using only SPME-SIFT-MS. The latter method enables us to follow up the concentrations of the target VOCs in each individual package during its shelf life without disturbing the gas composition inside.

Table 4 Pearson's correlation coefficients of VOCs obtained by SIFT-MS and HS-TD-GC-MS during the calibration measurements on chicken breast fillet samples from days 2, 7, and 14 of storage

VOCs	r	p
Acids		
Acetic acid	− 0.419	> 0.01
Alcohols		
Ethanol	0.975	< 0.001
3-Methyl butanol	− 0.266	> 0.01
2-Propanol	0.918	0.001
Aldehydes		
3-Methylbutanal	0.938	0.002
Ketones		
Acetoin	0.901	0.002
Acetone	0.795	0.003
2,3-Butanedione	0.444	> 0.01
Butanone	0.836	0.01
Sulfur compounds		
Carbon disulfide	0.952	< 0.001
Dimethyl sulfide	0.988	< 0.001

SPME-SIFT-MS Application

The evolution of the selected VOCs for each of the packages is presented in Fig. 4. For the alcohol group, ethanol became detectable from the sixth day of storage, while its concentration was the highest from all the measured VOCs, presenting an overall significant increase (Welch's ANOVA, $F(5, 5.046) = 468.127$, $p < 0.0001$) on day 12 while reaching 18 ± 4 mg/m^3 at the end of the storage (day 15), although a high variation was present between the samples. An increasing trend was observed for 2-propanol at the end of storage, which was significant (Kruskal-Wallis, $\chi^2(5) = 13$, $p = 0.023$) reaching 0.4 ± 0.1 mg/m^3 after day 12. Generally, alcohol production can be linked to anaerobic metabolism and several other metabolic pathways (Casaburi et al. 2015). Ethanol is the most common metabolite produced as an end product by the anaerobic metabolism of microorganisms, associated with lactic acid bacteria, *Br. thermosfacta* and Enterobacteriaceae (Casaburi et al. 2015). It has been detected multiple times in aerobically stored chicken meat studies (Senter et al. 2000; Alexandrakis et al. 2012; Mikš-Krajnik et al. 2015) and in chicken fillets stored under vacuum (Mayr et al. 2003), whereas an increasing trend for ethanol production was observed in chicken legs stored under MAP (Eilamo et al. 1998); however, no significant increase was observed after 9 days of storage on broiler chicken cuts (Rajamäki et al. 2006). 2-Propanol has been identified in aerobic poultry spoilage (Senter et al. 2000), while it has been associated with late spoilage and lipid oxidation in cooked ham (Leroy et al. 2009). Both ethanol and 2-propanol could serve as potential biomarkers for spoiled MAP-packaged chicken since they presented a significant increase towards the end of shelf life (day 12).

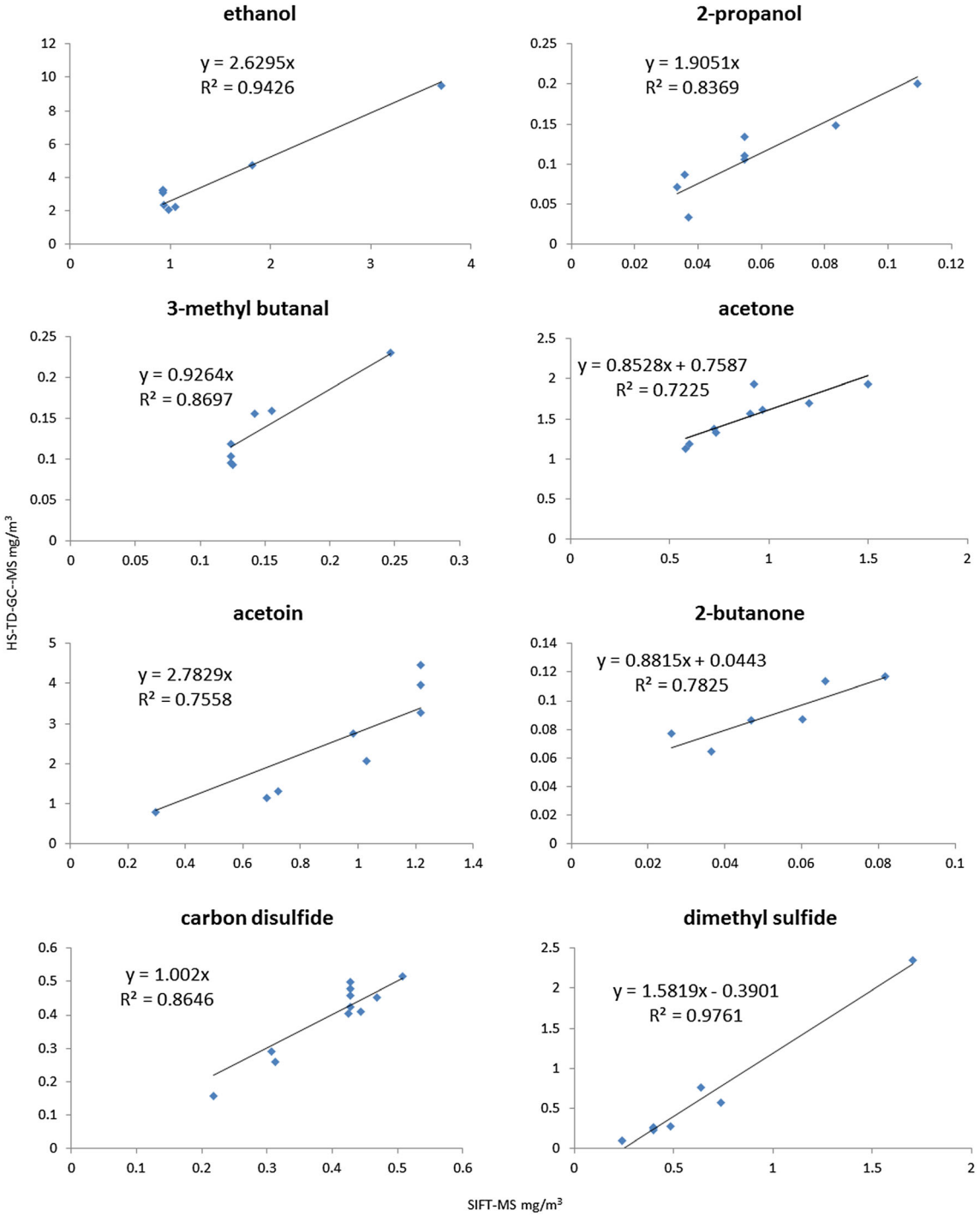

Fig. 3 Regression plots of the VOCs measured by the HS-TD-GC-MS against online SIFT-MS concentrations measured during the calibration step, with the respective equations and R^2

From the aldehydes, 3-methylbutanal showed a significant overall increase (Welch's ANOVA, $F(5, 5.444) = 971.018$, $p < 0.0001$) reaching 0.24 ± 0.003 mg/m^3 on day 15. Aldehydes can be produced from lipid oxidation, and amino acid transamination associated with *Pseudomonas* spp. and *S. liquefaciens* activity (Casaburi et al. 2015). In our study, 3-methylbutanal showed a significant increase from the sixth day of storage making it suitable to be considered as an early spoilage detection biomarker for MAP chicken; an increasing trend was also observed in *Escherichia coli*-inoculated chicken fillets stored under MAP (Klein et al. 2017).

From the ketones, both acetoin and butanone presented a significant increase over the storage period ($F(3, 8) = 9.853$,

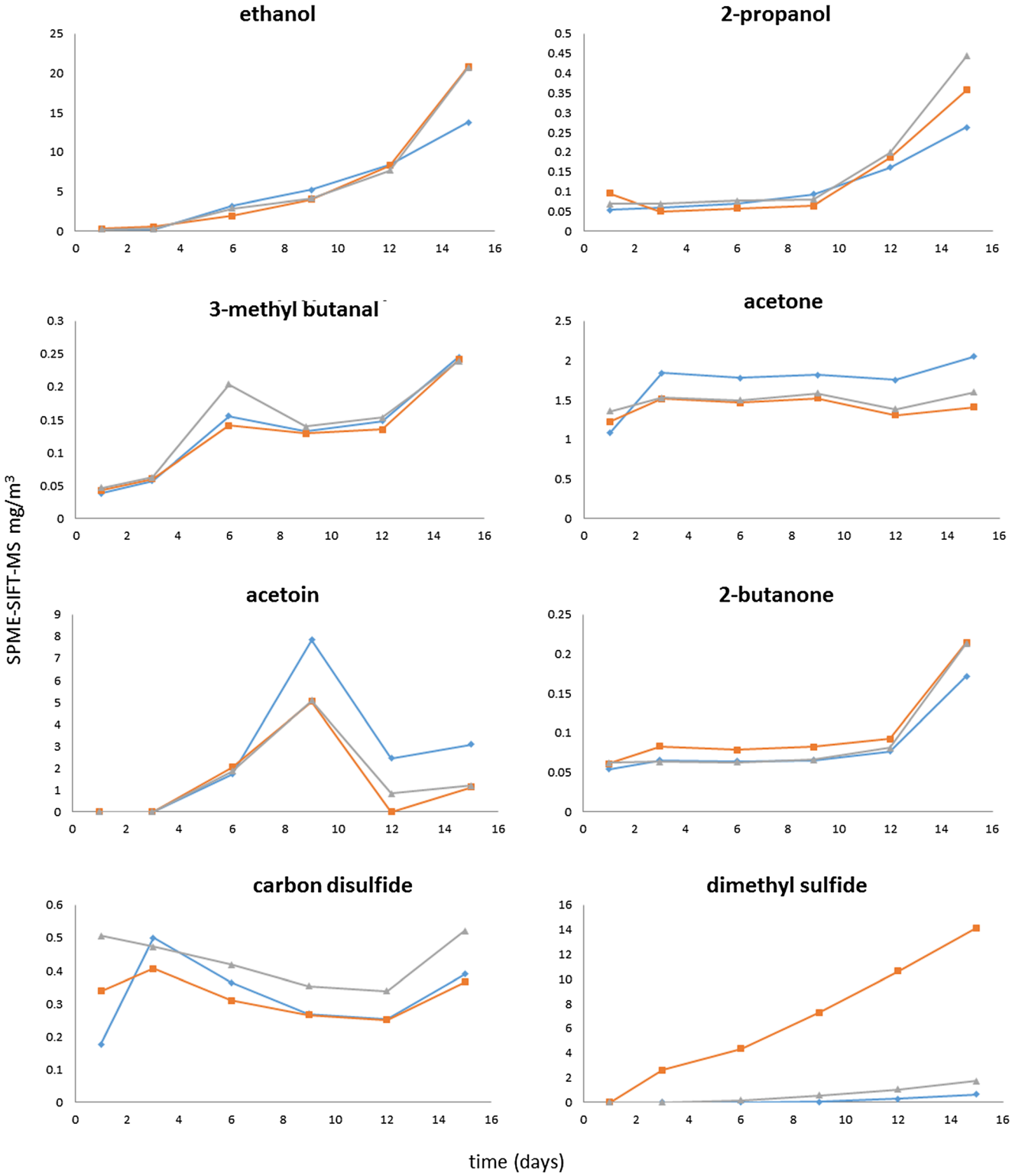

Fig. 4 Evolution of the VOC concentrations in the three MAP-packaged poultry samples stored at 4 °C measured only with SPME-SIFT-MS. The different colors represent the three different samples

$p = 0.005$ and $\chi^2(5) = 13.444$, $p = 0.020$, respectively) with acetoin becoming detectable from the sixth day of storage while reaching the highest concentration of 6 ± 2 mg/m^3 on day 9; additionally, butanone reached 0.20 ± 0.02 mg/m^3 on day 15; acetone levels remained stable during the storage period with an average concentration of 1.5 ± 0.2 mg/m^3.

Ketones can originate from lipolytic activity, alkane degradation, and glucose catabolism, while acetoin production is

highly linked with *Br. thermosphacta*, *Carnobacterium* spp., and *Lactobacillus* spp. (Casaburi et al. 2015). Acetoin is mostly abundant in spoiled meat, with a typical buttery-like odor, associated with a non-fresh odor in MAP meat (Casaburi et al. 2015; Pothakos et al. 2015). The highest concentrations of acetoin were measured on day 9 (5–8 mg/m^3). Nevertheless, a reduction in acetoin concentrations was observed after day 9, possibly linked with its degradation and formation of 2,3-butanedione and 2,3 butanediol (Von Wright and Axelsson 2011). 2-Butanone has been also reported in spoiled meat (Casaburi et al. 2015), while it is also linked with fatty acid oxidation (Leroy et al. 2009). Lastly, acetone was found in most poultry studies (Eilamo et al. 1998; Senter et al. 2000; Rajamäki et al. 2006), and it is probably associated with the natural aroma of fresh chicken, as it did not present a significant increase during storage. This was comparable with the study of Senter et al. (2000) who reported 0.95 mg/m^3 of acetone at day 0 in chicken breast fillets stored under air.

Sulfur compounds derived from proteolytic activity on proteins containing sulfur-containing amino acids. No significant increase was observed for the carbon disulfide with its average value stable at 0.4 ± 0.1 mg/m^3; however, a large variation was observed for dimethyl sulfide with concentrations ranging from 0.1 to 14 mg/m^3 during storage, while only one package presented a significant clear increase reaching 14 mg/m^3; it is also worthy of mentioning that the human odor threshold for dimethyl sulfide in water is 0.3 mg/m^3 (Casaburi et al. 2015). Carbon disulfide has been detected under aerobic conditions in poultry fillets (Alexandrakis et al. 2012). A decreasing trend in the concentrations was observed in chicken parts stored aerobically for 5 days at 4 °C starting from 0.88 mg/m^3 on day 0 in chicken breast fillets (Senter et al. 2000). Dimethyl sulfide has been reported in aerobically stored chicken (Alexandrakis et al. 2012), while an increasing concentration in chicken breast fillets was observed (Senter et al. 2000) with concentrations reaching approximately 1.5 mg/m^3 after 4 days of storage at 4 °C under air. An initial concentration of approximately 1 mg/m^3 was reported in MAP broiler cuts stored at 80/20% CO_2/N_2% at 3 °C, reaching approximately 4 mg/m^3 after 12 days of storage (Rajamäki et al. 2006). These findings are in general agreement with the concentrations observed in our study, although a large difference was prominent among the analyzed samples. Dimethyl sulfide concentrations are dependent on the duration of the storage time, the temperature (Eilamo et al. 1998), and the microbial composition (Rajamäki et al. 2006). This variation has been also observed in independent experiments on poultry conducted in our lab (unpublished results).

Conclusions

Significant and positive correlations were observed between SIFT-MS and HS-TD-GC-MS measurements for the measured VOCs: ethanol, 2-propanol, 3-methylbutanal, acetoin, acetone, 2-butanone, carbon disulfide, and dimethyl sulfide in MAP poultry stored at 4 °C. These VOCs were successfully quantified with the SPME-SIFT-MS methodology at 4 °C in the same samples, without disturbing the original packaging gas mixture. This study demonstrates that the SPME-SIFT-MS method is a fast, valuable non-destructive alternative to monitor selected VOCs in the headspace of packages that could serve as potential biomarkers. The technique provides a rapid analysis time (< 5 min) since no chromatographic separation is required. However, this approach can only work in combination with other analytical techniques, since a calibration step is necessary to obtain reliable results. Moreover, the combination of SPME-SIFT-MS with online SIFT-MS is required for the quality control of the measured signals.

In the case of MAP-packaged poultry, there is a clear indication that even in homogenized samples deriving from the same pool, large variations can be expected in terms of VOC production—especially in ethanol and dimethyl sulfide production. Thus, a fast non-destructive method measuring each individual package can offer a useful insight for monitoring VOCs in complex food matrices. Further research is needed to correlate the reported concentrations with microbial spoilage and sensory analysis, in order to fully conclude upon which VOCs could be used for overall quality control.

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Compliance with Ethical Standards

Conflict of Interest Angelos-Gerasimos Ioannidis declares that he has no conflict of interest. Christophe Walgraeve declares that he has no conflict of interest. Mike Vanderroost declares that he has no conflict of interest. Herman Van Langenhove declares that he has no conflict of interest. Frank Devlieghere declares that he has no conflict of interest. Bruno De Meulenaer declares that he has no conflict of interest.

Ethical Approval This article does not contain any studies with human or animal subjects performed by any of the authors.

Informed Consent Informed consent was not applicable for this study.

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