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Inactivation of Palladium-based Oxygen Scavenger System by Volatile Sulphur Compounds Present in the Headspace of Packaged Food

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Abstract:

An oxygen scavenger based on a catalytic system with palladium (CSP) was recently developed to remove oxygen in food packagings. Although the CSP worked with various types of food, with some foods an inhibition of the CSP was observed. Since such catalytic systems are susceptible to sulphur poisoning, the aim of this study was to understand the inactivation of palladium-based catalysts in presence of foods containing volatile sulphur compounds (VSCs). To achieve this, the oxygen scavenging activity (OSA) of the CSP was evaluated in the presence of selected food products. Afterwards, VSCs mainly present in these foods, were exposed to the CSP and the influence on the OSA was evaluated. Finally, headspace analysis was performed with the diluted VSCs and with the packaged food products, using PTR-ToF-MS. It was found that the catalytic activity of the CSP was inhibited when VSCs were present in the headspace in concentrations ranging between 10.8-36.0 ppbv (dimethyl sulphide, DMS), 1.2-7.2 ppbv (dimethyl disulphide), 0.7-0.9 ppbv (dimethyl trisulphide), 2.1-5.8 ppbv (methional) and 4.6-24.5 ppbv (furfuryl thiol). It was concluded that in packaged roast beef and cheese, DMS may be the compound mainly responsible for the inactivation of the CSP. In packagings containing ham, the key compounds were hydrogen sulphide and methanethiol, in peanuts it was methanethiol and in par-baked buns an accumulation of methional, DMS, butanethiol and methionol. When potato chips were packaged, it was demonstrated that when VSCs are present in low concentrations, oxygen can still be scavenged at a reduced OSA.

Keywords: Active packaging, oxygen scavengers, palladium, volatile sulphur compounds, catalyst poisoning.

INTRODUCTION

Food packaging technologies are continuously developing in response to the increasing requirements of modern society. Consumer demands for minimally processed, more natural, fresh and convenient foods, which do not contain any preservatives but have an acceptable shelf life, have grown significantly over the last years [1-3]. To respond to this need, active packaging has been designed as an innovative technology to enhance the shelf life of food while improving its quality, safety and integrity [4-9]. The application of oxygen scavengers is one of the most important active packaging technologies. Such technologies aim to remove residual oxygen present in food packagings [3, 10-15] and thereby prevent negative effects, such as growth of aerobic microorganisms [10] or oxidation of the product [16], and hence contribute to the overall preservation of quality during storage.

Recently, an oxygen scavenger based on a catalytic system with palladium (CSP) has been developed [17-19] showing the potential to extend shelf life and improve the overall quality of oxygen-sensitive foods packaged in modified atmosphere [20]. The oxidative mode of action of this CSP is based on the catalytic oxidation of hydrogen into water [21] so that headspace oxygen can be removed when hydrogen is included in the modified atmosphere of a packaging. Although the CSP works with several types of food, for some foods, such as peanuts or cheese, an inhibition of the OSA of the CSP was observed after the food was packaged. As described in the literature, such catalytic systems are susceptible to catalyst poisoning, which is defined as the strong chemisorption of reactants, products or impurities on sites otherwise available for catalysis [22-24]. Common catalyst poisons are sulphurous compounds and the adsorption of sulphur on palladium surfaces has been well studied [25-30].

Sulphur is also present in several foods. Currently, more than 700 volatile organic sulphur compounds have been reported [31], of which over 250 different sulphur-containing volatiles occur in heated foods [32]. This suggests that an interaction of volatile sulphur compounds (VSCs) with the highly active palladium surface might be responsible for the observed inhibitory effect.

The aim of this study was to understand the inactivation of palladium-based catalysts in the presence of sulphur-containing foods. To achieve this, in a first step, the oxygen scavenging activity (OSA) of the CSP was evaluated in the presence of selected food products. Afterwards, VSCs mainly present in these foods were selected and their individual influence on the OSA was evaluated. Finally, the time-resolved presence of the VSCs in the headspace of the packaged food products was analysed using proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS). This method has already been successfully applied for the analysis of food stuffs such as coffee [33, 34], fruits [35], dried [36] or raw meat [37].

MATERIALS AND METHODS

Materials

Catalytic system based on palladium (CSP)

The palladium-coated film (PET/SiO_x/Pd) applied in this study was produced using magnetron sputtering technology [17-19, 38], according to the method described by Yildirim et al. [19]. SiO_x- and palladium (Pd) deposition thickness was 80 nm and 1.04 nm, respectively.

Chemicals

The following chemicals were used for the investigation of the individual sulphur compounds: dimethyl sulphide (DMS) ≥99%; dimethyl disulphide (DMDS) ≥98%; dimethyl trisulphide

(DMTS) $\geq 98\%$; 2-furfuryl thiol (FFT) $\geq 97\%$ and methional (MET) $\geq 97\%$. The volatile sulphur compounds (VSCs) were diluted in sodium acetate-acetic acid buffer solution (sodium acetate $\geq 99\%$ and acetic acid $\geq 99.7\%$) with pH 5. All chemicals were supplied by Sigma-Aldrich Chemie GmbH, Buchs, Switzerland.

Food products

The following food products, commercially packaged under modified atmosphere, were investigated: 425 g sliced roast beef (M Classic Englisch Braten, Migros, Switzerland), 425 g boiled cured ham (Vorderschinken, Metzgerei Bertschart, Wädenswil, Switzerland), 205 g salted potato chips (Nature, Zweifel Pomy-Chips AG, Spreitenbach, Switzerland), 120 g potato powder (Prix Garantie Kartoffelstock, Coop, Switzerland), 140 g skimmed milk powder (Sanolait, Qualité & Prix, Coop, Switzerland), 230 g cereal mix (oats, barley, spelt, brown sugar, hazelnuts, sun flower seeds, honey, dried apple; Qualité & Prix, Coop, Switzerland), 495 g roasted salted peanuts (Ültje GmbH, Schwerte, Germany), 285 g Italian hard cheese (Grana Padano, 14 months ripened, Qualité & Prix, Coop, Switzerland) and 2x 45 g par-baked buns (self made; wheat flour type 550, water, margarine, malt, salt and baker's yeast). The buns were stored in sealed bags at -16°C and defrosted in the bags at 3°C within 18 hours before analysis. Ham was sliced and cheese was coarsely grated immediately prior to the start of the measurement. Roast beef, potato chips and peanuts were removed from their packaging, weighed and tested without any subsequent processing steps being performed.

Methods

Packaging process and measurement of oxygen scavenging activity

For all experiments, packaging trays (PS-EVOH-PE with peel, 0.5 mm, 204x147x85 mm, Stäger & Co AG, Muri, Switzerland) with a volume of 1620 cm^3 were used.

In a first step, the food products were packaged and the influence on the OSA of the CSP was evaluated. Therefore, a food to headspace ratio of 1:3 was chosen in the packaging, resulting in a uniform headspace of 1215 cm^3 for all foods. To evaluate the OSA, a 25 cm^2 patch of the Pd-coated film was applied and an oxygen sensitive sensor spot (PSt6, 3 mm diameter, Presens, Regensburg, Germany) was glued to the inner side of the lidding film prior to sealing. The OSA measurements started immediately after MAP packaging with a non-destructive measurement method using fibre optic optodes Fibox 4 trace (Presens, Regensburg, Germany). After the food product was placed in the tray, a vacuum of 50 mbar was applied using a tray sealer (T200, Multivac, Hünenberg, Switzerland), the tray was flushed with a gas mixture (2 vol.% O_2 , 5 vol.% H_2 and 93 vol.% N_2) until 900 mbar was achieved and then sealed at 125°C (high barrier lidding film: PET/EVEP-LAF 60; $60\text{ }\mu\text{m}$; OTR: $1.5\text{ cm}^3/\text{m}^2\text{ d bar}$, 23°C / 35% RH; Südpack, Ochsenhausen, DE).

In a second step, the dissolved VSCs were exposed to the CSP. Thereby, a glass petri dish (internal diameter: 95 mm; height: 14 mm) was placed in the tray and 50 ml of DMS, DMDS, DMTS, MET and FFT solution, respectively, was filled into the petri dish immediately before packaging. The applied concentrations of the respective VSC ranged from 10^{-8} to 10^{-4} mmol/l. Packaging conditions and evaluations of the OSA were the same as for that of the food. All experiments were performed at $30^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and carried out in triplicates. Thereby, all applied food products and buffer solutions were pre-conditioned at $30^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 1 hour prior packaging.

External 3-point-calibration of PTR-TOF-MS

An external 3-point-calibration of the sulphurous buffer solutions was performed. Thereby, packaging trays with an empty glass petri dish (internal diameter: 95 mm; height: 14 mm) were packaged under modified atmosphere as described above but, without Pd-coated film and sensor spot. 50 ml of the respective VSC, in concentrations ranging from 10^{-8} to 10^{-3} mmol/l (as listed in Table 1), was prepared in a syringe (HSW NORM-JECT[®], PP/PE, Faust, Schaffhausen, Switzerland) and sealed with a parafilm (PARAFILM[™], Sigma-Aldrich

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Chemie GmbH, Buchs, Switzerland) before use. The sulphurous solution was inserted into the petri dish in the tray using a needle (BD MICROLANCE™ 3, 21 g 1½ 0.8x40 mm, Becton Dickinson AG, Allschwil, Switzerland) through a septum (15 mm diameter, Dansensor A/S, Ringsted, Denmark) and the measurements were started immediately. In addition, control measurements were obtained for empty packaging trays and/or the sodium acetate-acetic acid buffer solution without any sulphur compounds. The PTR-ToF-MS details and data processing were the same for all types of measurements.

PTR-ToF-MS measurements and data analysis

Headspace samples were taken 2 and 10 min after packaging of food or injection of VSC solutions, lasting for 120 seconds. The VSCs were monitored on-line with PTR-ToF-MS (PTR ToF 8000, Ionicon Analytik GmbH, Innsbruck, Austria). Each sample was introduced with a flow of 100 sccm via a heated transfer line (80°C, 1 mm inner diameter, PEEK tubing, BGB Analytik AG, Switzerland) into the drift tube, which was operated at 2.35 mbar, 90 °C and 600 V drift voltage. The transfer line was fixed to a needle (BD MICROLANCE™ 3, 21 g 1½ 0.8x40 mm, Becton Dickinson AG, Allschwil, Switzerland) by a pen (needle for CheckMate, Dansensor A/S, Ringsted, Denmark) and the needle was injected to 75 % of its length into the packaging headspace through a septum (15 mm diameter, Dansensor A/S, Ringsted, Denmark). For data analysis, the signal in the time window between 60-90 seconds was averaged, corresponding to an absolute sample volume of 75 cm³. All experiments were performed at 30°C ±1°C and carried out in triplicates.

PTR-ToF-MS data were recorded by ToFDAQ Viewer v.1.2.97 (Tofwerk AG, Thun, Switzerland). Mass calibration was performed on [H₃¹⁸O]⁺ and [C₃H₇O]⁺ (acetone). The average intensity of the raw data was expressed in counts per seconds (cps) and converted to normalised counts per second (ncps) [39]. Proton transfer reactions between H₃O⁺ and volatile organic compounds (VOCs) only occur if the proton affinity of the desired VOC is larger than water (166,5 kcal/mol) what is the case for VSCs [40-44]. Only signals of the most prominent isotopes with a time-intensity profile reaching an intensity of more than three times the standard deviation of the base line [39] were included (limit of detection, LOD) and only peaks of more than six times the standard deviation were quantified (limit of quantification, LOQ). The peaks were assigned to a specific VSC compound based on the sum formula of the respective VSCs, the comparison with the measurements of the differently diluted VSC standards, and the knowledge of the VSCs present in the respective food products.

For quantification of the VSCs present in the food products, the absolute headspace concentrations, expressed in parts-per-billion by volume (ppbv), were calculated from peak areas according to manufacturer information (PTR TOF 8000, Ionicon Analytik GmbH, Innsbruck, Austria). Constant values were used for the reaction rate coefficient ($k_R = 2 \times 10^{-9}$ cm³/s) [36, 43, 45, 46] and the VSC transmission factor ($T_{RH^+} = 0.9$) introducing a systematic error that is in most cases <30 % and can be accounted for if the actual rate constant is available [36, 44, 46].

RESULTS AND DISCUSSION

Evaluation of the oxygen scavenging activity of the catalytic system based on palladium in the presence of food products

To investigate the influence of food products on the oxygen scavenging activity (OSA) of the catalytic system based on palladium (CSP), milk powder, roast beef, ham, cheese, peanuts, potato chips, potato powder, a cereal mix and par-baked buns were packaged under modified atmosphere (2 vol.% O₂, 5 vol.% H₂ and 93 vol.% N₂) and the oxygen concentration in the headspace was monitored.

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2 In empty packaging trays, the oxygen concentration was reduced from 2 to 0 vol.% within
3 55 min, as illustrated in Figure 1. When milk powder was packaged, the oxygen was removed
4 within 80 min. In packagings containing cereals or potato powder, the time required to reduce
5 the initial oxygen concentration to 0 vol.% was similar with 135 and 155 min, respectively.
6 About 240 min were necessary to remove all oxygen when potato chips were present in the
7 packaging.
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10 In packagings without food, the CSP could reduce the oxygen concentration from 2 to 0.4
11 vol.% within 10 min (Figure 1). The presence of foods, however, reduced the oxygen
12 scavenging rate of the CSP. Nevertheless, all oxygen in the headspace could still be removed.
13 In contrast, for packagings containing peanuts, par-baked buns, roast beef, ham or cheese, a
14 clear inhibition in the OSA was observed within 5 to 10 min after the food was packaged
15 (Figure 2). Although, in the presence of par-baked buns, the oxygen concentration was
16 continuously reduced from 2 to 0.6 vol.%, after 155 min the OSA stagnated and no further
17 activity was observed. When cheese was packaged, oxygen concentration was reduced to 1.5
18 vol.% within the first 5 min but, 10 min after packaging, the oxygen concentration remained
19 constant at a level of 1.46 vol.%. In packagings containing roast beef, ham or peanuts, oxygen
20 could be removed only within the first 5 min, resulting in a final oxygen concentration of
21 1.66, 1.70 and 1.78 vol.%, respectively.
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24 The loss of OSA in the presence of food mentioned above cannot be explained by the lack of
25 hydrogen in the headspace. Preliminary studies (unpublished results) revealed that hydrogen
26 was still present in the applied high barrier packaging system, even after several days at 30°C.
27 The effect of the oxygen released from the food into the headspace within the time that the
28 OSA stagnated is as well negligible. An increase in oxygen concentration in the headspace
29 was first observed after several days. Furthermore, when the poisoned film was repackaged
30 with MAP with hydrogen, it did not show any OSA (unpublished results). These observations
31 suggest that some volatiles emitted from the investigated foodstuffs had an inhibitory effect
32 on the OSA of CSP. Functional principle of the CSP is based on the catalytic oxidation. As
33 described in the literature, such catalysts are susceptible to poisoning [22-24]. Common
34 catalyst poisons are sulphurous compounds and the adsorption of sulphur on palladium
35 surfaces is well studied [25-30]. Most foods contain differing amounts of volatile sulphur
36 compounds (VSCs) which may be released in the headspace after packaging. Release rates
37 and the concentration of VSCs in the headspace depend on numerous factors, such as the way
38 the food is processed, the composition of the food matrix and the temperature of the food and
39 the environment [47-52]. The inhibitory effect seen in the presence of food products (Figure
40 2) could be due to the VSCs released after packaging of these foods resulting in an inhibitory
41 concentration for the CSP in the headspace.
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45 **Evaluation of the oxygen scavenging activity of the CSP in the presence of sulphurous** 46 **buffer solutions**

47 The major chemical class of VSCs present in food is represented by sulphides, particularly the
48 disulphide group, followed by thiazoles, thiophenes, and thiols [31]. Among the VSCs,
49 dimethyl sulphide, dimethyl disulphide, dimethyl trisulphide, methional and furfuryl thiol
50 have been reported to be mainly present in food products [31, 53-59] and also in those tested
51 in this study (Figure 2). Therefore, the influence of these VSCs on the OSA of the catalytic
52 system based on palladium (CSP) was evaluated. For that purpose buffer solutions containing
53 VSCs were prepared in decreasing dilution steps of one order of magnitude within the range
54 of 10^{-4} to 10^{-8} mmol/l, individually exposed to the CSP and the OSA was evaluated.
55

56 When buffer solution without VSCs was placed in the packaging tray, the oxygen
57 concentration was reduced from 2 vol.% to 0 vol.% within 75 min, as illustrated in Figure 3.
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2 The presence of 10^{-7} mmol/l DMS or 10^{-6} mmol/l FFT, prolonged the time necessary to
3 remove all the oxygen to 145 min. Packagings containing 10^{-7} mmol/l DMTS and 10^{-5} mmol/l
4 MET resulted in a further reduction in OSA and all the oxygen in the packagings was
5 scavenged within 165 and 265 min, respectively.
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9 The results shown in Figure 3 indicate that although the presence of VSCs in the headspace
10 reduced the OSA, it was possible to remove all the oxygen in the packaging. However, when
11 the amount of the respective VSC was increased, each by one order of magnitude, an
12 inhibition on the OSA of the CSP was observed (Figure 4). In the first 5 min, the OSA of the
13 CSP in the presence of the buffer solutions containing the VSCs was similar to that without
14 VSCs. Afterwards, the buffer solutions containing VSCs continuously reduced the OSA.
15 After 160 min, the oxygen concentration remained constant at a level of 0.53 ± 0.06 vol.% for
16 DMTS (10^{-6} mmol/l), 0.54 ± 0.06 vol.% for MET (10^{-4} mmol/l) and 0.66 ± 0.06 vol.% for DMS
17 (10^{-6} mmol/l) and no further OSA was observed. For DMDS (10^{-7} mmol/l) after 120 min, the
18 OSA stagnated at an oxygen concentration of 0.96 ± 0.07 vol.% and when FFT was exposed to
19 the CSP at a concentration of 10^{-5} mmol/l, no further OSA was observed after 80 min at a
20 level of 1.15 ± 0.14 vol.% oxygen. On the other hand, all the oxygen in the packaging
21 containing buffer solution without any VSC could be removed within 75 min.
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24 The results showed that the VSCs tested inhibit the OSA of the CSP. Therefore, these might
25 be the main sulphur compounds in the food responsible for the inactivation of the OSA of the
26 CSP (Figure 2). Moreover, the results shown in Figure 3 and 4, clearly indicate that when
27 sulphurous buffer solutions are exposed to the CSP at the applied conditions, the minimum
28 inhibitory concentration of the VSC lies in the range between 10^{-7} to 10^{-6} mmol/l for DMS,
29 10^{-8} to 10^{-7} mmol/l for DMDS, 10^{-7} to 10^{-6} mmol/l for DMTS, 10^{-5} to 10^{-4} mmol/l for MET
30 and 10^{-6} to 10^{-5} mmol/l for FFT.
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33 **Minimum inhibitory concentration of VSCs**

34 We found that the interaction of VSCs with the palladium surface can lead to the inactivation
35 of the catalytic system (CSP) and we defined the minimum inhibitory concentration of
36 exposed VSC-solutions responsible for this inhibition. The results showed that the inhibitory
37 effect occurred within the first 10 min (Figure 4). Thus, to obtain a comprehensive and in
38 particular a time resolved understanding of the inhibition of the CSP by sulphur in buffer
39 solutions or food, VSCs in the headspace had to be analysed within the first 10 minutes after
40 packaging, requiring a time resolved analysis.
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43 In a first step of PTR-ToF-MS, an external 3-point-calibration of the sulphurous buffer
44 solutions was performed to assure that the VSC signals, measured in the applied sulphurous
45 buffer solutions as well as those presumed in the food products, were well within the linear,
46 dynamic range of the PTR-ToF-MS. Thereby, solutions of DMS, DMDS, DMTS, MET and
47 FFT in concentrations ranging from 10^{-8} to 10^{-3} mmol/l were packaged under modified
48 atmosphere and headspace analysis was performed taking samples, each 2 and 10 min after
49 packaging.
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52 The three calibration points were chosen based on the following factors: The *second*
53 calibration point for the respective VSC was chosen according to the concentration, shown in
54 Figure 4, where a CSP inhibition was observed. The *first* and *third* calibration points were
55 defined based on literature values of the investigated food stuffs, listed in Table 2 and 3.
56 Considering that the H_3O^+ -ions signal intensity was essentially constant throughout the
57 experiments, it could be assumed that the response of PTR-ToF-MS was linear over the range
58 investigated in this study [39]. A small deviation from linearity was noticed for the sulphides,
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2 but this is believed to be due to a concentration dependent fragmentation pattern, rather than a
3 saturation of the proton-transfer reaction. Moreover, the control measurements applied to
4 empty packaging trays and/or the sodium acetate-acetic acid buffer solution without any
5 sulphur compounds revealed that no measurement-disturbing compounds were detected.

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7 In Table 1, the normalised average ion intensities and the resulting calibration formulae are
8 listed at each calibration point of the respective VSC. Based on these results, the absolute
9 headspace concentration was calculated, as described in the paragraph "*PTR-ToF-MS*
10 *measurements and data analysis*". This was performed for a) the concentration of the
11 respective VSC where a CSP inhibition was observed (shown in Figure 4 and second
12 calibration point in Table 1), and b) the concentration of the respective VSC where no CSP
13 inhibition was observed, as shown in Figure 3. Out of a) and b), the minimum inhibitory
14 concentration of the respective VSC was defined to be in the range between 10.8-36.0 ppbv
15 for DMS, 1.2-7.2 ppbv for DMDS, 2.1-5.8 ppbv for MET, 4.6-24.5 ppbv for FFT and 0.7-
16 0.9 ppbv for DMTS; these values are listed in Table 2. Thus, inhibitory concentrations of
17 VSCs in the headspace lie between those concentrations and if the concentration of the
18 individual VSC is above this range, the CSP will be inactivated at the applied conditions.
19 According to the literature values listed in Table 2, these compounds are also highly abundant
20 in the selected food systems. Thus, it is assumed that the presence of those VSCs might be
21 responsible for the CSP inactivation by the foods shown in Figure 2.
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24 **Headspace analysis of the packaged food products**

25 To understand the inhibition of the catalytic system based on palladium (CSP) by food
26 (Figure 2), we analysed the presence and the concentration of the VSCs in the headspace of
27 the packaged food.
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29 In general, food volatiles are expected to be continually released from the food immediately
30 after their formation. After packaging of the food, volatiles are still emitted into the headspace
31 of the packaging, until a thermodynamic equilibrium is achieved. Thereby, not only the
32 concentration of the volatile compounds in the food but rather the affinity of the compounds
33 for the different phases and their availability for release into the gaseous phase is essential for
34 their partition [48, 60]. As food matrices are generally multiphasic, containing liquid, solid,
35 and gaseous phases, volatile compound retention is a complex process, as has been described
36 in several studies [47-52, 61]. The prediction of the headspace concentration of VSCs for
37 different food products is hence not straightforward and has to be determined experimentally.
38 Therefore, headspace analysis was performed with modified atmosphere packaged beef, ham,
39 cheese, peanuts, par-baked buns and potato chips using PTR-ToF-MS.
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41 The obtained VSC concentrations in the headspace were compared with the minimum
42 inhibitory concentration ranges that had been defined above for DMS, DMDS, DMTS, MET
43 and FFT and are listed in Table 2. VSC concentrations in foods which exceeded this ranges,
44 were marked with ">", VSCs within the inhibition range were marked as "~" and those VSCs
45 below this range were marked with "<" and are listed in Table 2. In addition, a range of
46 additional VSCs, reported to be present in the respective food products in numerous studies,
47 were tentatively identified and their concentrations in the headspace are listed in Table 3.
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50 *Roast Beef*

51 Thermally-processed meat is reported as being one of the foods with the highest number of
52 VSCs. This is mainly due to the high protein content of meat and hence, the high availability
53 of sources of sulphur in the form of the sulphur amino acids cysteine and methionine [32].
54 During roasting, baking or boiling of meat, VSCs are mainly generated out of those amino
55 acids in the Maillard reaction [32, 62-64]. Thus, the CSP inhibition in the presence of roast
56 beef and ham, shown in Figure 2, is strongly assumed to be caused by a wide range of VSCs
57 present in meat. Headspace analysis of roast beef revealed that dimethyl sulphide was by far
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the most abundant sulphurous volatile with concentrations of 100.0 and 168.3 ppbv, 2 and 10 min after packaging, respectively. This finding is in accordance with the findings of several studies on meat [31, 58, 62]. With respect to the previously defined CSP inactivation levels in this work, for roast beef, 2 min after packaging the concentration of DMS was far beyond the upper range (36.0 ppbv) of CSP inactivation, as shown in Table 2. The concentration of DMDS was within the defined inactivation range (1.2-7.2 ppbv) with 6.9 ppbv after 2 min and had exceeded the upper level after 10 min with 11.0 ppbv. For MET, FFT and DMTS, the concentration was below the CSP inactivation level. Additional VSCs identified in the headspace of roast beef reaching concentrations within the ppbv-range were methylethyl disulphide, butanethiol and methionol and a range of further VSCs in the pptv-range, as listed in Table 3. For roast beef it is therefore strongly assumed that DMS is the compound mainly responsible for the inactivation of the CSP as its concentration in the headspace was up to two orders of magnitude higher than that for the other detected VSCs.

Ham

In packagings containing ham, only the concentration of DMS reached a level lying within the CSP inactivation range (10.8-36.0 ppbv) with 13.3 ppbv after 10 min (Table 2). Although this concentration might even be sufficient to inhibit the CSP, it is assumed that other tentatively detected VSCs in the headspace of packaged ham might be responsible for the observed inactivation of the CSP, in particular the highly volatile hydrogen sulphide (14.8 ppbv) and methanethiol (49.2 ppbv). All other VSCs detected in the headspace showed concentrations in the parts-per-trillion by volume (pptv) range except methylethyl disulphide (3.5 ppbv) or butanethiol (7.7 ppbv) (Table 2 and 3).

Cheese

VSCs of Italian hard cheeses are well studied [65-69]. Sulphur compounds primarily arise from biodegradation of methionine and cysteine by the cheese microflora where the common precursors methional and hydrogen sulphide, respectively, were formed and further decomposed to VSCs such as DMS, DMDS, DMTS or methanethiol during cheese ripening [59, 68-71]. Headspace analysis of cheese packagings revealed highest amounts for DMS, exceeding the upper level of CSP inactivation (36.0 ppbv) with 49.7 ppbv immediately after 2 min (Table 2). Additionally, FFT was within the inactivation range (4.6-24.5 ppbv) with a concentration of 21.0 ppbv after 2 min but did not exceed the upper level after 10 min. The concentrations of DMDS with 0.9 ppbv and MET 1.8 ppbv were slightly below the corresponding inactivation ranges. DMTS with a concentration in the pptv-range was much lower than its inactivation range (0.7-0.9 ppbv). Other main VSCs tentatively identified in the headspace were methanethiol, methyl ethyl disulphide, butanethiol and methionol with a concentration of 13.8, 1.2, 5.7 and 6.0 ppbv, respectively (Table 3). Among the detected VSCs in cheese, DMS is assumed to be the compound that is mainly responsible for the CSP inactivation, since its concentration was by far the highest of all VSCs identified in the headspace exceeding the upper inactivation level after the cheese was packaged.

Peanuts

VSCs in peanuts are mainly generated through degradation of the amino acids cysteine and methionine during the roasting procedure [32, 62, 63, 72]. However, apart from the five selected compounds previously described and listed in Table 2, only few VSCs were reported in roasted peanuts. Some of these are methanethiol, 2-acetylthiophene, 2-acetylthiazole or propyl disulphide [54, 72-74], as listed in Table 3. Headspace analysis of peanuts revealed that the amount of DMDS was above the upper inactivation level (7.2 ppbv) with 8.1 ppbv immediately after 2 min and the headspace concentration increased to 10.1 ppbv after 10 min. Concentration of DMS was just below the CSP inactivation level with 8.6 ppbv after 10 min.

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2 The amounts of MET, FFT and DMTS were much lower than their inactivation level (Table
3 2). Additional VSCs, such as hydrogen sulphide, alkyl thiols or thiophenes, were also
4 tentatively identified (Table 3). However, by far the highest concentration and thus, assumed
5 to be the main VSC responsible for CSP inactivation, was methanethiol with 39.7 ppbv after 2
6 min. Its concentration in the headspace increased to 92.9 ppbv after 10 min being one order of
7 magnitude higher than DMS and DMDS and more than two orders of magnitude higher than
8 all the other detected VSCs in the headspace. Peanuts inhibited the OSA much stronger than
9 other tested foods (Figure 2). This might be due to the presence of DMDS as well as the high
10 concentration of methanethiol in the headspace.
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12 *Par-baked Buns*

13 The composition of volatile compounds in bread depends on the ingredients, the conditions of
14 dough fermentation and the baking process [75]. VSC in wheat bread crumb are mainly
15 formed by the fermentative activity of yeast from amino acids in the flour [75-77]. During
16 fermentation, methional is emerged from methionine and can be further transformed to
17 methionol, methanethiol [77, 78] or sulphides [53, 79-81].
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19 In packagings containing par-baked buns, the headspace concentrations of DMS, DMDS and
20 FFT were below the respective inactivation level with amounts of 5.1, 0.5 and 1.2 ppbv,
21 respectively, after 10 min. The concentration of DMTS was below the detection limit of PTR-
22 ToF-MS. Exceptionally for MET, after 10 min, a concentration of 2.1 ppbv was observed,
23 lying just within the range of CSP inactivation (Table 2). Additional VSCs, tentatively
24 identified and exceeding the pptv-range, were butanethiol, methionol and methanethiol with
25 4.4, 4.2 and 1.8 ppbv, respectively, after 10 min (Table 3). Par-baked buns had the least
26 poisoning effect on the CSP compared to the other foods tested (Figure 2). Since MET was
27 the only VSC with a concentration just within the CSP inactivation range, a cumulative and/or
28 synergistic effect of VSCs is presumed to have finally blocked the entire active surface of the
29 CSP.
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32 *Potato Chips*

33 When potato chips were packaged with the CSP, although all the oxygen could be removed in
34 the headspace, a reduction in the oxygen scavenging rate was observed (Figure 1). Therefore,
35 additional to the foods that inactivated the CSP (Figure 2), potato chips were selected and the
36 VSCs in the headspace were analysed with PTR-ToF-MS. Similar to other thermally
37 processed foods, VSCs in potato chips were formed from sugar-amino acid interactions
38 during the frying process, mainly from methional which is the Strecker aldehyde of
39 methionine [32, 62, 72, 82]. Headspace analysis of potato chips revealed that the evaluated
40 compounds were far below the respective inactivation levels, with resulting concentrations in
41 the pptv-range (Table 2). This was also true for further tentatively identified VSCs, such as
42 alkyl thiols or methionol, listed in Table 3. The only exception was methylbenzenethiol,
43 having the highest concentration in the headspace of potato chips with 2.1 ppbv after 2 and
44 10 min. Thus, the results obtained indicate that although a certain interaction of VSCs with
45 the CSP might have occurred, however, the VSC concentration in the headspace of potato
46 chips packagings was not high enough to inactivate the catalytic activity of the CSP under
47 measurement conditions.
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52 It has been reported in several studies [22-24, 26, 28] that a number of sulphur compounds,
53 particularly sulphides and thiols [26], form strong covalent bonds with metal atoms as its
54 unshared electron pairs can lead to very strong chemisorption on the metal surface thereby
55 leading to remarkable reduction in catalytical activity, the so-called "catalyst poisoning".
56 Beside the concentration of the VSCs, the toxicity increases with increasing electronegativity,
57 molecular weight and with the complexity of the chain length or the ring of the sulphurous
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molecule [24, 26]. The two last points were clearly confirmed when comparing the determined CSP inactivation levels of DMS (10.8-36.0 ppbv, 62.13 g/mol), DMDS (1.2-7.2 ppbv, 94.20 g/mol) and DMTS (0.7-0.9 ppbv, 126.26 g/mol), reflecting that the higher the molecular weight, as well as the longer the chain, the lower the inhibitory concentration, in other words, the higher the observed toxicity. Moreover, it is reported by Maxted [24] that sulphides, which contain two hydrocarbon chains, are more toxic than the corresponding thiols, which contain only one chain. This might be an explanation therefore, why a higher concentration of FFT (4.6-24.5 ppbv, 114.17 g/mol) was required to inactivate the CSP than it was the case for DMDS. Since the adsorption on the surface is typically dissociative, leaving a reduced sulphur atom strongly bonded to the surface, poisoning of the Pd-coated film by VSCs can be considered as irreversible [22, 26]. Consequently, once the VSCs have diffused from the packaged food to the Pd-surface, the active sites otherwise available for the catalysis of oxygen and hydrogen into water are occupied by VSCs and hence no further oxygen can be scavenged.

Overall it can be stated that the catalytic activity of the applied palladium-based oxygen scavenger system was inhibited when volatile sulphur compounds in concentration ranges between 10.8 and 36.0 ppbv for DMS, 1.2 and 7.2 ppbv for DMDS, 0.7 and 0.9 ppbv for DMTS, 2.1 and 5.8 ppbv for MET and 4.6 and 24.5 ppbv for FFT were present in the packaging headspace. Moreover, entire inactivation of the Pd-based catalyst was demonstrated when headspace concentrations exceeded the upper inhibition ranges of the respective compounds. The results revealed that the key compounds responsible for the inactivation of the CSP in food are most likely: DMS in roast beef and cheese, hydrogen sulphide and methanethiol in ham, methanethiol in peanuts, and in par-baked buns, an accumulation of methional, DMS, butanethiol and methionol. Moreover, by the application of potato chips, it was demonstrated that when VSCs are present in low concentrations, oxygen can still be scavenged but, at a reduced OSA.

CONCLUSION

In this study we identified that the interaction of volatile sulphur compounds with the highly active palladium surface is responsible for the inhibitory effect of the palladium-based oxygen scavenger system. In addition, it was demonstrated that the catalytic activity of the scavenger system was inhibited when volatile sulphur compounds were present in the food products. Finally, the main VSCs in selected foods that might be responsible for the inactivation of the catalytic system based on palladium were determined.

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Table 1: Calibration points and formulae of the external 3-point-calibration of dimethyl sulphide (DMS), dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), 2-furfuryl thiol (FFT), and methional (MET). Mean values ($n = 3$). Systematic standard uncertainty ($< 30\%$).

VSC*	1. Cal. Point			2. Cal. Point (CSP Inhibition)			3. Cal. Point			VSC Calibration after 2 min		VSC Calibration after 10 min	
	mmol/l	ncps 2 min	ncps 10 min	mmol/l	ncps 2 min	ncps 10 min	mmol/l	ncps 2 min	ncps 10 min	Formula	Correlation coefficient (R^2)	Formula	Correlation coefficient (R^2)
DMS	1.E-05	7.7E+05	9.0E+05	1.E-06	2.3E+05	2.7E+05	1.E-08	3.5E+04	3.7E+04	$y = 1E + 08x^{0.4421}$	0.9950	$y = 2E + 08x^{0.4561}$	0.9971
DMDS	1.E-05	1.1E+06	1.3E+06	1.E-07	4.8E+04	5.3E+04	1.E-08	7.8E+03	8.8E+03	$y = 6E + 09x^{0.7277}$	0.9950	$y = 7E + 09x^{0.7313}$	0.9921
MET	1.E-03	1.9E+05	2.1E+05	1.E-04	4.5E+04	4.3E+04	1.E-06	9.8E+02	9.6E+02	$y = 2E + 08x + 13229$	0.9829	$y = 2E + 08x + 11113$	0.9905
FFT	1.E-04	9.8E+05	1.0E+06	1.E-05	1.4E+05	1.8E+05	1.E-07	3.4E+03	4.1E+03	$y = 1E + 10x + 24239$	0.9981	$y = 1E + 10x + 40890$	0.9946
DMTS	1.E-05	1.5E+04	1.2E+04	1.E-06	6.8E+03	6.6E+03	1.E-08	3.1E+03	3.0E+03	$y = 172792x^{0.221}$	0.9593	$y = 119050x^{0.2023}$	0.9859

*mmol/l: concentration of the VSC in buffer solution exposed the catalytic system based on palladium (CSP).
ncps 2 min /10 min: normalised average ion intensities of the respective VSCs in the headspace 2 and 10 min after packaging.

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Table 2: Concentrations of DMS, DMDS, MET, FFT and DMTS tentatively identified in the headspace of different food products, each within 2 and 10 min after packaging under modified atmosphere. Concentrations marked with “>” (bold) were found as being above, “~” (bold) within and “<” below the range of the inactivation of the oxygen scavenger based on a catalytic system with palladium. (LOD = Limit of detection, LOQ = Limit of quantification, q = qualitative). Mean values (n=3). Systematic standard uncertainty (< 30 %).

VSC [ppbv]	Sum Formula	Range of minimum inhibitory concentration [ppbv]	Roast beef		Ham		Cheese		Peanuts		Par-baked buns		Potato Chips							
			2-10 min	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature					
DMS	C ₂ H ₆ S	10.8 - 36.0	100.0 168.3	> >	105 ppb [31, 58], q. [55]	9.0 13.3	< ~	-	49.7 52.2	> >	19-120 ppb [59, 67, 69] q. [68, 70, 71]	4.2 8.6	< <	q. [72]	2.8 5.1	< <	q. [53]	0.9 1.2	< <	q [83]
DMDS	C ₂ H ₆ S ₂	1.2 - 7.2	6.9 11.0	~ >	q. [31]	0.2 0.3	< <	q. [31]	0.6 0.9	< <	8.3-180 ppb [59, 67, 69] q. [68, 70, 71]	8.1 10.1	> >	q. [73]	0.3 0.5	< <	q. [53, 79, 80]	0.6 0.6	< <	10 ppb [82] q. [84]
Methional	C ₄ H ₈ O ₈	2.1 - 5.8	1.0 1.3	< <	13-36 ppb [55, 58, 85, 86]	0.2 0.2	< <	11-23 ppb [55, 58]	1.9 1.8	< <	1-150 ppb [59, 65, 67, 69] q. [68, 70, 71]	0.2 0.4	< <	40 ppb [54] q.[73, 87].	1.6 2.1	< ~	29 ppb [58] q. [75, 78-80, 88, 89]	0.2 0.2	< <	0.78-15 ppb [55, 82, 90] q. [91-93]
FFT	C ₃ H ₆ OS	4.6 - 24.5	1.0 1.3	< <	0.5-29 ppb [55, 58] 8 ppb [85]	0.7 0.8	< <	0.1-9.5 ppb [55, 58, 94]	21.0 21.8	~ ~	-	0.8 1.0	< <	8.8-100 ppb [54] q. [87]	0.7 1.2	< <		0.3 0.3	< <	-
DMTS	C ₂ H ₆ S ₃	0.7 - 0.9	0.09 0.04	< <	13-35 ppb [85, 86]	0.05 0.05	< <	q. [95]	0.06 0.06	< <	1.4-11 ppb [59, 67, 69] q. [68, 70, 71]	<LOQ <LOQ	< <	1.4 ppb [54]	<LOD <LOD	< <	5.1 ppb [58] q. [53, 79-81]	<LOD <LOD	< <	0.033-8 ppb [82, 90]

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Table 3: Concentrations of VSCs tentatively identified in the headspace of different food products, each within 2 and 10 min after packaging under modified atmosphere. (LOD = Limit of detection, LOQ = Limit of quantification, q = qualitative). Mean values (n=3). Systematic standard uncertainty (< 30 %).

VSC [ppbv]	Sum Formula	Roast beef		Ham		Cheese		Peanuts		Par-baked buns		Potato Chips	
		2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature
Hydrogensulphide	H ₂ S	0.4 1.4	q. [31, 96]	9.5 14.8	q. [96]	0.5 0.8	0.001-0.019 ppb [67] q. [96]	0.3 0.7	-	0.04 0.1	-	<LOQ <LOQ	-
Methanethiol	CH ₄ S	1.1 1.6	0.3-0.31 ppb [55, 58] q. [31, 96]	32.9 49.2	0.28-0.5 ppb [38, 41]	11.2 13.8	0.0019-0.028 ppb [67] q. [55, 59, 68, 71]	39.7 92.9	113 ppb [54] q. [72]	0.8 1.8	q. [77]	0.3 0.5	1.24 ppb [90]
Methylethyl sulphide	C ₃ H ₈ S	3.9 5.4	-	2.0 3.5	-	0.8 1.2	-	0.2 0.4	-	0.2 0.3	-	<LOQ <LOQ	-
Thiophene	C ₄ H ₄ S	0.1 0.1	-	0.06 0.07	-	0.1 0.1	-	0.7 0.9	-	0.3 0.4	-	0.05 0.05	-
Thiazole	C ₃ H ₃ NS	0.05 0.05	0.0036- 0.0072 ppb [31, 86]	<LOD <LOD	-	<LOD <LOD	-	0.1 0.2	-	<LOQ <LOQ	q. [77]	<LOD <LOD	-
2-Methylthio-acetaldehyde	C ₃ H ₆ OS	0.7 0.3	-	<LOD <LOD	-	<LOD <LOD	q. [59]	0.1 0.1	-	<LOD <LOD	-	<LOD <LOD	q. [92]
Butanethiol	C ₄ H ₁₀ S	1.4 3.5	-	4.9 7.7	-	5.9 5.7	q. [96]	0.3 0.3	-	2.0 4.4	-	0.1 0.1	-
2-Methylthiophene	C ₅ H ₆ S	0.5 0.2	0.0072- 0.0076 ppb [86]	0.2 0.2	q. [31]	0.3 0.3	-	0.9 1.2	-	0.5 0.6	-	0.08 0.08	-
4-Methylthiazole	C ₄ H ₅ NS	0.1 0.1	0.0006- 0.0084 ppb [85, 86]	<LOD <LOD	trace- 0.00001 ppb [94]	<LOD <LOD	-	<LOD <LOD	-	0.07 0.08	-	<LOD <LOD	-
Methionol	C ₄ H ₁₀ OS	5.0 7.8	-	0.3 0.3	-	5.7 6.0	0.019-0.22 ppb [67] q. [68]	<LOD <LOD	-	3.1 4.2	q. [77, 79]	0.4 0.4	-
3-Mercapto-2-pentanon	C ₅ H ₁₀ OS	0.5 0.8	0.069 ppb [58]	<LOD <LOD	0.066 ppb [58]	<LOD <LOD	-	<LOD <LOD	-	<LOD <LOD	-	<LOD <LOD	-
Methylpropylsulfide	C ₄ H ₁₀ S ₂	0.1 0.1	-	0.1 0.1	-	0.3 0.4	-	<LOD <LOD	-	0.2 0.2	-	<LOD <LOD	2 ppb [82]

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VSC [ppbv]	Sum Formula	Roast beef		Ham		Cheese		Peanuts		Par-baked buns		Potato Chips	
		2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature	2 min 10 min	Literature
Methylbenzenethio l	C ₇ H ₈ S	0.3 0.1	-	0.07 0.08	-	<LOQ <LOQ	0.004 ppb [55]	<LOQ <LOQ	-	<LOQ <LOQ	-	2.1 2.1	-
2-Acetylthiophene	C ₆ H ₆ OS	1.1 0.4	-	0.08 0.09	-	0.08 0.07	-	<LOQ <LOQ	q. [73, 74]	0.2 0.2	q. [79]	<LOQ <LOQ	-
2-Acetylthiazole	C ₅ H ₅ NOS	0.1 <LOQ	0.007 ppb [85]	<LOQ <LOQ	0.00043- 0.00054 ppb [94]	<LOQ <LOQ	-	<LOQ <LOQ	q. [72]	<LOQ <LOQ	q. [79]	<LOQ <LOQ	-
2,4,5- Trimethylthiazole	C ₆ H ₉ NS	0.1 0.1	0.13 ppb [31]	<LOQ <LOQ	0.00008 ppb [94]	<LOQ <LOQ	-	<LOQ <LOQ	-	<LOQ <LOQ	-	<LOQ <LOQ	-
Methylfurfurylthiol	C ₆ H ₈ OS	0.2 0.1	-	0.07 0.07	-	<LOQ <LOQ	-	<LOQ <LOQ	-	0.1 0.1	-	<LOQ <LOQ	-
Tetramethylthioure a	C ₅ H ₁₂ N ₂ S	0.2 0.3	-	<LOQ <LOQ	-	0.4 0.4	q. [69]	<LOQ <LOQ	-	0.2 0.6	-	0.1 0.1	-
Benzothiazole	C ₇ H ₅ NS	0.1 0.1	0.0005-0.005 ppb [85, 86]	0.2 0.1	0.00002 ppb [94]	<LOQ <LOQ	q. [66, 69, 71]	<LOQ <LOQ	-	0.1 0.1	-	<LOQ <LOQ	-
Ethyl 3- (methylthio) propanoate	C ₆ H ₁₂ O ₂ S	0.5 0.4	-	<LOQ <LOQ	-	0.2 0.2	<0.01 ppb [66]	<LOQ <LOQ	-	<LOQ <LOQ	-	<LOQ <LOQ	-
2- Methylbenzothiazole	C ₈ H ₇ NS	0.1 0.1	-	<LOQ <LOQ	-	<LOQ <LOQ	q. [66]	<LOQ <LOQ	-	<LOQ <LOQ	-	<LOQ <LOQ	-
Propyldisulphide	C ₆ H ₁₄ S ₂	0.3 0.3	-	0.1 0.1	-	<LOQ <LOQ	-	0.1 <LOQ	q. [73]	0.1 0.1	-	<LOQ <LOQ	-
Bis-(2-methyl-3- furyl) disulphide	C ₁₀ H ₁₀ O ₂ S ₂	<LOQ <LOQ	q. [57]	<LOQ <LOQ	-	<LOQ <LOQ	-	<LOQ <LOQ	-	<LOQ <LOQ	-	<LOQ <LOQ	-

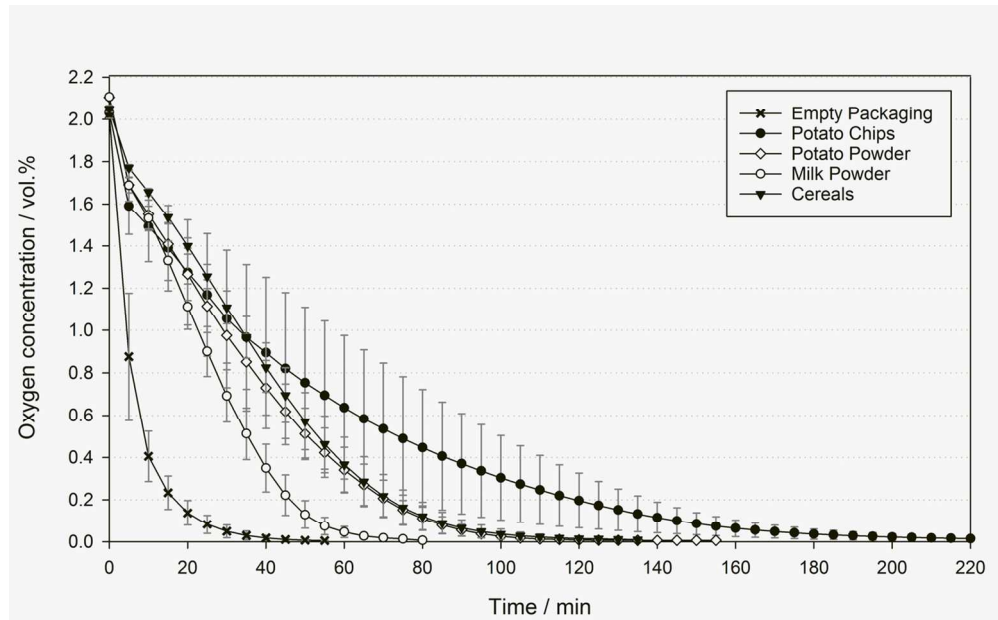


Figure 1: Reduction in oxygen concentration in the packaging tray with milk powder, cereals, potato powder and potato chips. Headspace volume (HSV) of empty packaging = 1620 cm³, HSV of food packagings = 1215 cm³. Mean values \pm standard deviation (n = 3). 119x73mm (300 x 300 DPI)

Review

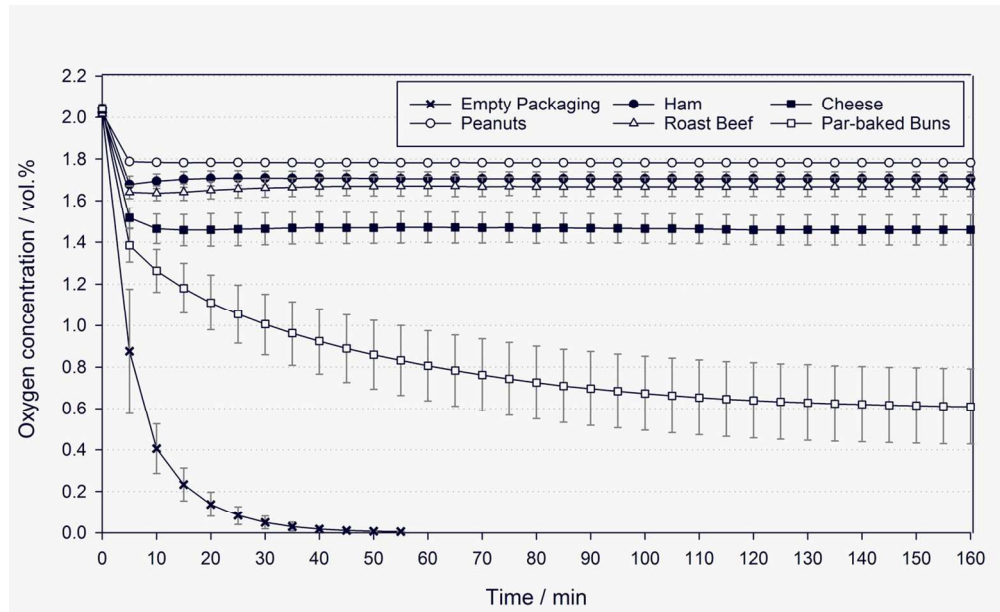


Figure 2: Reduction in oxygen concentration in the packaging tray containing peanuts, par-baked buns, roast beef, ham and cheese. Headspace volume (HSV) of empty packaging = 1620 cm³, HSV of food packagings = 1215 cm³. Mean values \pm standard deviation (n = 3).
119x72mm (300 x 300 DPI)

Review

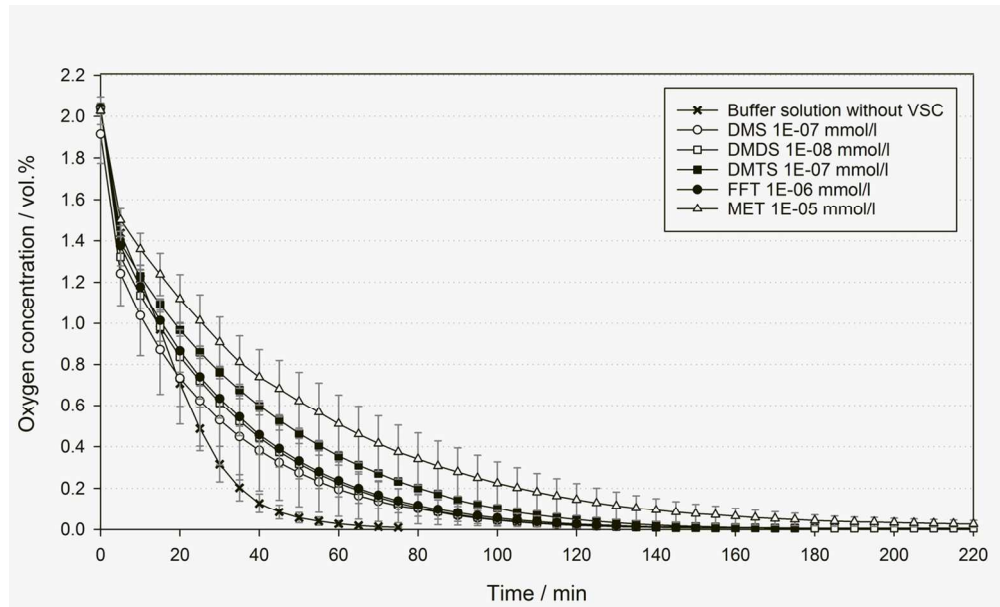


Figure 3: Reduction in oxygen concentration in the packaging tray containing buffer solutions with dimethyl sulphide (DMS), dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), methional (MET) and furfuryl thiol (FFT) in concentrations between 10^{-5} to 10^{-8} mmol/l and buffer solution without VSCs. Headspace volume = 1550 cm^3 . Mean values \pm standard deviation ($n = 3$).
119x72mm (300 x 300 DPI)

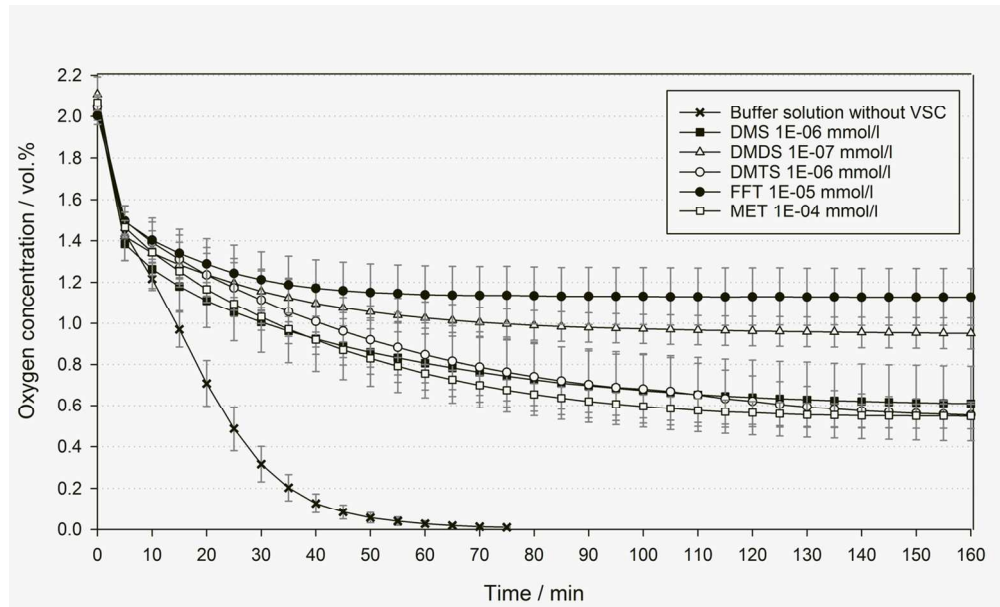


Figure 4: Reduction in oxygen concentration in the packaging tray containing buffer solutions with dimethyl sulphide (DMS), dimethyl disulphide (DMDS), dimethyl trisulphide (DMTS), methional (MET) and furfuryl thiol (FFT) in concentrations between 10^{-4} to 10^{-7} mmol/l and buffer solution without VSCs. Headspace volume = 1550 cm^3 . Mean values \pm standard deviation ($n = 3$).
119x72mm (300 x 300 DPI)

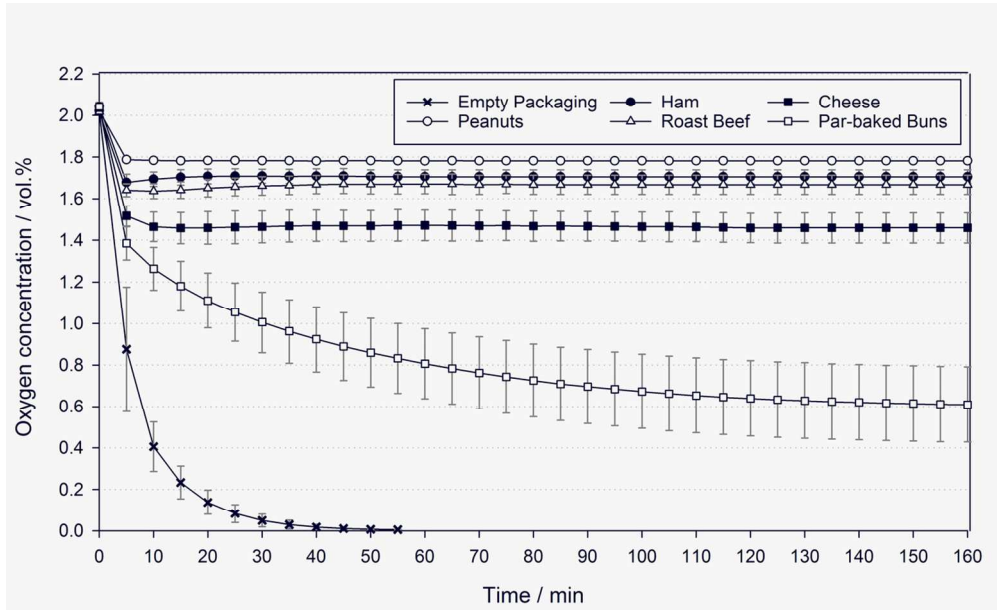
Inactivation of Palladium-based Oxygen Scavenger System by Volatile Sulphur Compounds Present in the Headspace of Packaged Food

Bettina Röcker, Nadine Rüegg, Alexia N. Glöss, Chahan Yeretzian, Selçuk Yildirim*

An inhibition in the oxygen scavenging activity of our recently developed oxygen scavenger based on a catalytic system with palladium (CSP) was observed in the presence of some foods. In this study we identified that the interaction of volatile sulphur compounds (VSCs) with the palladium surface is responsible for this inhibitory effect and it was demonstrated that the catalytic activity of the CSP was inhibited when VSCs were present in food. Moreover, the main VSCs in selected foods that might be responsible for the inactivation of the CSP were identified.

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