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Investigations into Off Notes in Foods, Products and Materials by GC-Olfactometry

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GC-Olfactometry (GC-O) is the most powerful tool for characterization of odour compounds. This technique is widely used, especially in the sector of products and materials, and allows identifying the odour relevant compounds in the sample(s). GC-O data can also be used for quality control, development of value added products or to measure how efficient implemented modifications have been. This research describes case studies of the detection and identification of off notes in food samples such as tea, soy milk or chicken aroma production, and other products and materials such as polymers, packaging and cosmetics. The results obtained show a visual comparison of the aromatic profiles of samples, allowing clear conclusions to be drawn about products. In addition, chemical and sensory identifications of off notes are very important, as they allow acting directly on the product for example by changing the production chain or eliminating the raw material causing the undesirable odour. One of the cases shown in this study refers to the detection of off notes in food (ice cream) coming from the packaging. The use of low-quality recycled cardboard was responsible for the presence of volatile compounds such as aldehydes and sulphides. These compounds were responsible for generating fatty, aldehydic and garlic odour notes.

1. Introduction

Every day we are facing the challenge of determining the compounds responsible for undesirable odours in countless products, foods and materials. Odours are generated by the presence of odour-active chemical compounds (odourants) in the product during the interacting process with the olfactive receptors located in our nose. Depending on the concentration in air, some odourants can be perceived while others are not, because their concentration is below the olfactory detection threshold. One of the main challenges to measure concentrations in odourous compounds lies precisely in the low values of odour threshold of some compounds; often their odour threshold value (OTV) is quite below the limit of detection of most of the analytical instruments, even for the most sophisticated ones (Buettner, 2017).

Gas Chromatography - Mass Spectrometry (GC-MS) is one of the most powerful technique to analyse the chemical composition of samples. When it is coupled to a thermal desorption (TD) instrument, the detection limits in air samples can improve significantly because the system, called TDGC-MS, is able to analyse high volumes of air (and molecules) contained in an internal solid phase of a thermodesorption tube. Although GC-MS can provide chemical identification of volatile compounds, it does not provide qualitative information about sensory perception of the odour molecules. GC-Olfactometry (GCO) improves the performance of GC-MS systems in terms of odour analysis because it allows obtaining a sensory description (given by a trained assessor) of each odour molecule eluted from a chromatographic run while at the same time (or in an additional run, with the same instrumental parameters) those molecules are identified by a chemical detector, commonly MS. In this way, a GCO-MS system is probably the most powerful technique for odour analysis (van Ruth 2001; Zellner et al., 2008).

Sensitivity has a crucial role in this type of analysis. Many odours are detected by the human nose at very low concentrations (low ppt), so it is necessary to use a highly sensitive detector in this type of instrumental

configuration to avoid, to the extent possible, cases of odours detected by the human nose with no spectral signal in the GC-MS instrument. Time of Flight-Mass Spectrometer (ToFMS) is the most sensitive chemical detector able to detect molecular traces at concentration levels of 10 -100 times lower than standard MS detectors (Villatoro, et al., 2016).
The aim of these investigations was to demonstrate the feasibility of using the GC-O technique to determine the key odour molecules responsible for off-notes. Knowing the chemical and sensory composition through GCMS and GC-O can provide an important source of information to detect the quality of the product in terms of odour aspects.

2. Experimental

2.1. Sample preparation

Odour is perceived primarily through the detection of volatile compounds in the vapour phase during inhalation. To capture the odours being released by each material the following approach was adopted: a known volume of the sample was placed into a sealed microchamber, isolated from external influences. A specific temperature (30 ºC) was applied on a case-by-case basis to promote the release of volatile compounds. Clean nitrogen airflow was then introduced through the micro-chamber and the exhaust air collected onto a thermodesorption tube (Figure 1). Additionally, one thermodesorption tube without sample and under the same sampling conditions was collected as a blank in each microchamber. Once the samples were collected, the tubes were hermetically closed and introduced into a thermal desorption unit coupled to the GC-MS/ToF instrument.

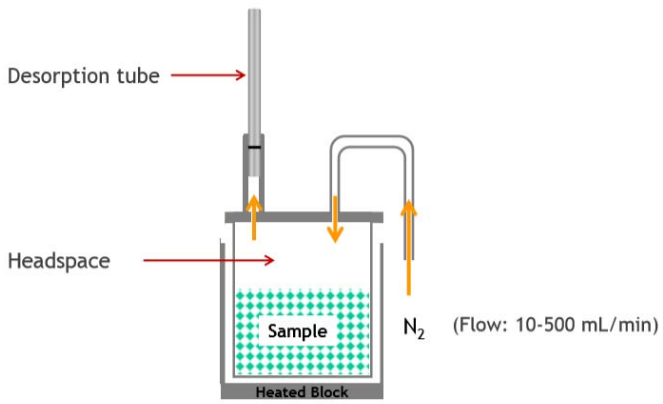

Figure 1. Schematic representation of sampling by microchamber

Desorption of the volatile compounds retained on the sorbent tubes was carried out in a Unity Thermal Desorption system. In the primary desorption, tubes were heated up to 300 ºC with a helium flow rate of 50 mL min^{-1} for 8 minutes. This was done to desorb the volatile compounds which were refocused on a hydrophobic general purpose cold trap, filled with inert Sulphur trap (U-T6SUL-2S), cooled at 10 ºC. After flash-heating of the cold trap at 320 ºC during 5 minutes, volatiles compounds were injected into the chromatographic column.
Separation and detection were performed in a 7890N Gas Chromatograph and Time-of-Flight Mass spectrometer, using a mid-polar DB-624 capillary column (60 m, 250 µm, 1.4 µm) and helium gas (6.0) as the carrier at a flow rate of 1.5 mL min^{-1}. The oven temperature of the GC was initially held at 40 ºC for 5 min, then raised to 230 ºC at a rate of 4 ºC min^{-1} and held at that temperature for 5 min. The GC-MS interface was set at 230 ºC. The mass spectrometer acquired data in scan mode with an m/z interval from 28 to 330, operating at an electron impact energy of 70 eV.

2.2. Gas Chromatography-Olfactometry (GC-O) analysis

An important portion of the eluted airstream was directed to the olfactory detector port (OP275 GL Sciences Inc., Japan) where odorous compounds can be detected and characterized by two trained olfactory assessors. This allows descriptors to be ascribed to the chemically detected compounds, therefore helping to identify the chemicals present with the most significant contribution to the overall sensory perception. When the assessor detected an odour, character and intensity values (from 1 to 5) were assigned.

During the analysis, each assessor takes on the GC-O task for 15 minutes before handing over to the other assessor, to cover the 45 minutes (approx.) of the whole chromatographic process (Figure 2). The assessment is divided into 3 periods in order to avoid sensory fatigue. In total, the process is repeated four times and the order of assessors is switched, so that each assessor covers the entire chromatogram twice. The second run for each assessor is used to confirm observations and/or to try to find additional odours not detected in the previous assessment. Therefore, four sample injections were necessary to analyse each sample. The blank and the real sample were analysed in duplicate.

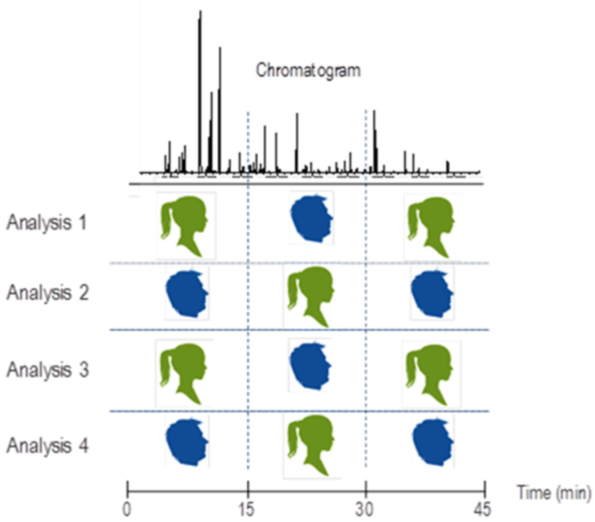

Figure 2. Systematic process of GC-O

2.3. Data processing

All compounds detected by MS were chemically identified using TargetView software referencing to the NIST11 spectral library. Compounds above 80 % of similarity were identified. Before assigning a chemical compound name (chemical structure) to each of the odours perceived, four checks were performed: (1) Direct check through MS identification. (2) Search for candidates based on Kovats Index (KI) and odour descriptor. An additional tube containing C6-C18 hydrocarbons was analysed to find their retention times on the GC method used. These retention times were used as reference to calculate the KI of the rest of compounds, from a defined KI value assigned to hydrocarbons. Candidate compounds were compared with public databases, Flavournet (www.flavournet.org), VCF (www.vcfonline.nl), based on experimental odour descriptor and KI. Also, an internal Odournet database was used based on previous analysis. (3) Automatic scan by using a library prepared exclusively for this project containing all relevant candidate compounds and their retention times. (4) Exhaustive manual searching based on the presence of target ions of candidate compounds in key retention times. After completing all checks listed above, a compound was confirmed.

3. Results and discussion

3.1. Case Study 1: Tea

The main objective of this study was to determine the relevant compounds causing changes in aroma complex in tea-based liquid products which were undergoing heat treatment and to detect those volatile molecules responsible for the perceived starchy and potato note in the liquid tea concentrates. During GC-O analysis, the assessors perceived odours like starchy and potato in five different times. Four of them were chemically identified (Table 1). 3-methylbutanal, perceived in the analyses like cocoa, pungent and starchy is described in bibliography like almond, cocoa, fresh green, malt, and pungent. 2-methylbutanal had a similar description in the GC-O analyses and bibliography (almond, cocoa, fermented, hazelnut, malt) than 3-methylbutanal. 3-methylbutanal and 2-methylbutanal were identified in previous studies in black tea (Guth and Grosch, 1993). Pentanal, perceived like starchy, caramel and butter was described in bibliography like almond, bitter, malt, oil, pungent. 1-pentanol, described in bibliography like balsamic, fruit, green, pungent, yeast was associated to potato odour in real samples. This compound was identified in other studies in tea samples (Zhu et al., 2008). In another study of tea samples, some compounds with putrid odor off notes were identified. The chemicals responsible were the methanethiol and dimethyl sulfide. There were also fatty and oily off notes being responsible the aldehyde 2,4-Heptadienal, (E,E)-.

3.2. Case Study 2: Chicken aroma production

This study was based on the identification of key compounds perceived in the chicken aroma samples produced in the production line. Large multinationals are developing advanced chicken flavour programme to understand and control aroma release for identifying and creating the most natural, rich and authentic chicken flavours. Through the GC-O technique, we can identify those compounds that impart meaty aromas and those that give species character, as well as those which generate off-notes. In the sample, the following compounds were identified such as thiols, pyrazines, lactones, furans and pyridines were identified, giving characteristic odour notes to roasted, nutty, caramel, spicy and sulphurous (Table 1). These compounds are predominantly derived from the Maillard reaction a complex process involving the reaction between reducing sugars and an amino nitrogen, and they are usually heterocyclic, belonging to chemical classes such as furans, oxazoles, pyrroles, pyrazines, thiophenes, thiazoles, thiazolines, and sulphides (Baruth et al., 2013; Jayasena et al., 2013; Buettner, 2017)

3.3. Case Study 3: Soy milk

The key compounds contributing to the soymilk aromas have not yet been fully clarified. The off-odor components in soy milk are thought to be decomposition products from soybean lipid by autoxidation, photo-oxidation, and an enzymatic reaction, especially by lipoxygenase and hydroperoxide-lyase.
The objective of the present investigation was to determine the compounds responsible for the off-flavour in soymilk through its odour producing characteristic. The results of the GC-O versus the control sample showed that the test sample stood out for its more intense aldehydic, pungent and fatty notes. The responsible compounds were the aldehydes (pentanal, hexanal, heptanal and octanal), acetic acid and 2-octen-1-ol, (E) alcohol (Table 1). Previous investigations have shown the presence of these compounds from three different soybean cultivars (Kaneko et al., 2011)

3.4. Case Study 4: Packaging

The volatile composition of paper and cardboard is very complex. However, only some publications are available focussing on the elucidation of odor-active compounds in paper and cardboard by GC/O approaches or considering volatile concentration in relation to odor threshold. The main aim of this work was to detect off notes in food coming from the packaging. Three sulphur compounds were identified from the packaging, generating a garlic odour in the ice cream. The compounds identified were dimethyl disulphide, diallyl sulphide and diallyl disulphide (Table 1). Therefore, care must be taken in the selection and quality of the packaging to ensure that the packaging itself is not a source of substances that can adversely affect the organoleptic properties. To solve the problem and return the packaging to its normal quality standard, it is essential to identify the chemical nature and source of the off-notes. Since the off-notes are usually present at very low levels, the analytical investigation requires sensitive analytical instrumentation and an analyst with the necessary experience and expertise (Tice and Offen, 1994).

3.5. Case Study 5: Cosmetics

The cosmetics industry has experienced rapid growth in recent years, and the world cosmetics industry's revenue is projected to be about $344 billion a year by 2020. The main objective of our research was to show some results of GC-O applied in raw material for cosmetics and a capillary product. Some capillary products are characterised by unpleasant odours during their application, and are not accepted on the global market. So, the main goal for the cosmetics producers is to improve the global perception of capillary products. Through the GC-O, we evaluate three raw formulas (without perfume). We could detect several sulphur compounds responsible for off-notes odours: hydrogen sulphide, carbon disulphide, diethyl sulphide, diethyl disulphide, ethyl 2-thiolpropanoate, 2-mercaptopropanoic acid and diethyl trisulfide. This group of compounds generates putrid, sewage and rotten eggs odours. The biggest challenge for cosmetic producers is to achieve masking of these odour-generating compounds in order to improve the overall perception of the product.

3.6. Case Study 6: Polymeric and foam material

The odours in the interior air in cars are one of the main complaints by car users across the world. For this reason, plastic components inside the cabin of an automobile need very strict rules to be accomplished in terms of odour. Petrolium-like, chemical and rubber odours were described by the human detector (assessors) in each sample of polymeric material and were the most important in terms of presence and intensity in the samples. These odours were identified by the chemical detector (ToFMS) as styrene, cyclohexanone, benzenemethanol, a,a-dimethyl-, benzyl methyl ketone and butanoic acid (Table 1) (Chien Y.C, 2007).

Another material of interest, because it could generate off notes, is polyurethane foam, a raw material for the manufacture of consumer goods. Our research in this area, showed the identification of key compounds that generate fishy off notes. Among them we found dimethyamine and trimethylamine as main responsible. These results are in line with those obtained by Light, 2017.

Table 1: Sensory and chemical information of compounds associated to off-notes in different matrix

KI(*)	MS identification	CAS nº	Odour descriptor	Matrix
718	Butanal, 3 methyl	590-86-3	cocoa, pungent, starch (potato)	Tea
727	Butanal, 2-methyl-	96-17-3	cocoa, fermented, starch (potato)	Tea
745	Pentanal	110-62-3	starch (potato), caramel, butter	Tea
851	1-pentanol	71-41-0	pungent, green, starch (potato)	Tea
440	methanethiol	74-93-1	putrid, sulphur	Tea
540	Dimethyl sulfide	75-18-3	putrid, sulphur	Tea
1083	2,4-Heptadienal, (E,E)-	4313-03-5	fatty, oily	Tea
949	Pyrazine, 2,5-dimethyl	123-32-0	roasted, meaty	Chicken
1038	2-Furancarboxaldehyde, 5-methyl-	620-02-0	spicy, caramel	Chicken
1085	2-Acetylthiazole	24295-03-2	nutty, roasted	Chicken
1097	Ethanone, 1-(2-pyridinyl)-	1122-69-9	popcorn, fatty	Chicken
1389	2(3H)-Furanone, 5-butyldihydro-	104-50-7	coconut, creamy	Chicken
1474	2(3H)-Furanone, dihydro-5-pentyl-	104-61-0	coconut, sweet	Chicken
781	Disulfide, dimethyl	624-92-0	garlic, sulphurous	Packaging
891	Diallyl sulphide	592-88-1	garlic, mushrooms	Packaging
1133	Diallyl disulphide	2179-57-9	sulphurous, pungent	Packaging
300	Hydrogen sulfide	7664-93-9	putrid, rotten eggs	Cosmetics
551	Carbon disulfide	75-15-0	putrid, sewer	Cosmetics
730	Diethyl sulphide	352-93-2	sulphurous, meaty	Cosmetics
970	Diethyl disulphide	110-81-6	sulphurous, cabbage	Cosmetics
976	Ethyl 2-thiolpropanoate	19788-49-9	sulphurous, green	Cosmetics
1088	2-Mercaptopropanoic acid	79-42-5	sulphurous, organic	Cosmetics
1213	Diethyl trisulfide	3600-24-6	sulphurous, onion	Cosmetics
745	Pentanal	110-62-3	aldehydic, fatty	Soy milk
766	Acetic acid	64-19-7	sour, pungent	Soy milk
847	Hexanal	66-25-1	green, aldehydic	Soy milk
951	Heptanal	111-71-7	aldehydic, plastic	Soy milk
1035	2-Octen-1-ol, (E)	18409-17-1	fatty, metal	Soy milk
1056	Octanal	124-13-0	aldehydic, waxy	Soy milk
865	Butanoic acid	107-92-6	cheesy	Polymer
927	Styrene	100-42-5	petroleum-like, rubber	Polymer
957	Cyclohexanone	108-94-1	petroleum-like, sweet	Polymer
1163	Benzenemethanol, a,a-dimethyl-	617-94-7	green, sweet	Polymer
1213	Benzyl methyl ketone	103-79-7	sweet, chemical	Polymer
424	Dimethylamine	124-40-3	fishy, pungent	Foam
424	Trimethylamine	75-50-3	fishy, pungent	Foam

(*) kovats index: each compound is located between two consecutive alkanes obtained by commercial standard (C8-C20). MS means mass spectrometry.

4. Conclusions

These case studies have shown that the GC-O technique is a powerful tool to identify the chemical name of aroma active compounds, since most volatile organic compounds (VOC) are not aroma relevant. No other technique can replace GC-O, since none of them have the capabilities of a human nose. There are many applications that require GC-O, the most important is quality control (characterization of raw materials or final products, aroma specifications, ensure stable products or same product quality made in different locations) and identification of off-notes. Other applications of GC-O are new product development, optimization of existing processes, and assessment and optimization of new technologies.

The chemical and sensory identifications of off notes are very important, as they allow acting directly on the product, for example by changing the production chain or eliminating the raw material causing the undesirable odour. Improved processes or materials with lower VOC emission potential should be used to minimize VOC sources in foods and products and materials.

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