Identification of potential aroma markers of coffee oxidized note

(Article begins on next page)

Identification of potential aroma markers of coffee oxidized note

Giulia Strocchi[1], Eloisa Bagnulo[1], Manuela R. Ruosi[2], Giulia Ravaioli[2], Francesca Trapani[2], Carlo Bicchi[1], Gloria Pellegrino[2], Erica Liberto[1]

1 Dipartimento di Scienza e Tecnologia del Farmaco, Università degli Studi di Torino, Via Pietro Giuria 9, Turin, Italy
2 Luigi Lavazza S.p.A., Strada Settimo 410, Turin, Italy

MS Food Day 2022 – Florence (Italy), October 5 - 7, 2022

Aim and Scope

Coffee is considered a stable product with a long shelf-life, although, **after roasting, it is still an effective 'chemical reactor'** because of the high reactivity of its components. **During storage**, roasted coffee undergoes chemical and physical changes that can affect its quality. The changes in sensory properties are generally due to the loss of volatile compounds characteristic of the aroma of roasted coffee, and the appearance of oxidation products that can cause **unpleasant flavours** [2–4]. The loss of aroma freshness during storage, known as **"staling"**, i.e. *"..**a sweet but unlovely flavour and aroma of roasted coffee which reflects the oxidization of many of the pleasant volatiles and the loss of others; a change in the flavour and the acid constituents causing a partial bland tone**.."* [5], mainly depends on temperature, humidity, presence of oxygen and barrier capacity of the packaging. Despite the number the studies in this field, they have always focused on one or two compounds in the expression of coffee loss of freshness and not on the synergism between the **components responsible to give an oxidised perception in the whole coffee volatilome**. Furthermore, due to the complexity and the dynamicity of the chemistry involved, coffee degradation studies have mainly been conducted on a single species, package or condition.

Therefore, **defining the oxidation chemical footprint of coffee** can be an **objective valuable tool** to be used in screening **as a support to the sensory panel in testing new and more sustainable packaging**.

This study investigates the **volatilome of good quality** (from now "good" for short) and **oxidised coffees** (i.e. *Coffea arabica* (Arabica) and *Coffea canephora*, (Robusta)) in different packaging (i.e. standard with metallic barrier and Eco-caps) by combining HS-SPME-GC-MS/FPD with a machine learning approach **to define a potential fingerprint describing the oxidised note of roasted coffee**.

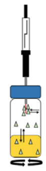
Materials and Methods

Samples included **thirty R&G** (roasted and ground) coffees **for moka** preparation from three lots **packed under vacuum in a multilayer film with a metallic barrier** (**M** samples); a set of **Eco-caps** in **modified atmosphere for espresso coffee** (5 caps) from different lots of **different blends named B and P** (100% Arabica of different origins) and **I** (50/50 Arabica and Robusta) for a total of **30 samples**.

A portion of the coffee samples was maintained **at room temperature** and the other was submitted to **accelerated ageing under stressed storage conditions** in oven at **37°C and 50% relative humidity.**

The samples were **classified as good (G) and oxidised (OX) by a trained industrial sensory panel**. The reference standard to define the oxidative note was a moka coffee that had been kept open for 4 months.
The **oxidised note** was defined as the **intensity of the smell/aroma attributable to rancid notes, walnut oil, peanut shell, old dried fruit, and "old" coffee, also often referred to as a cardboard note**, e.g. damp, or closed/stale pizza box directly/indirectly **perceived by the olfactory organ.**

HS-SPME sampling: Automated HS-SPME sampling was run on a combi-PAL AOC 5000 Autoinjector installed on a Shimadzu QP-2010 GC-MS system. **1,5 g of coffee powder** were sampled in a 20 ml vial with a **PDMS/DVB fiber** (df 65 µm, 1 cm long) **for 40 minutes at 50°C** at a stirring speed of 350 rpm. *n*-C13 was used as internal standards and previously loaded onto the fiber, by sampling 5µl of a 1000 mg/L solution in vegetable oil and sampled for 20 minutes at 50°C [6-8].



GC-MS/FPD instrument set-up
Injector temperature: 240°C; injector mode: splitless; gas carrier: Helium; flow rate: 1µl/min; fiber desorption time and reconditioning: 5 min; column: SGE SolGelwax (100% polyethylene glycol) 30 m x 0,25 mm dc x 0,25 µm df (SGE- Melbourne, Australia); temperature program: from 40°C (2 min) to 200°C at 3,5°C/min, then to 240°C (5 min) at 10°C/min.
Ionization mode: EI (70 eV); temperatures: Ion source: 200 °C; Quadrupole: 150°C; Transfer line: 260°C; Scan range: 35-350 amu. FPD detercor: 260°C.

Data elaboration Machine learning analysis was performed with Pirouette® (Infometrix) and XLSTAT® (Addinsoft). The heat map was created by gene-e (https://software.broadinstitute.org/GENE-E/).

Results and discussion

1. Chemical profiling of good and oxidised samples

The analysed coffee samples were described by the 147 volatiles. In figure 1 is reported an **illustrative pattern of the chemical signatures of the good and oxidised moka samples** (M) visualized with a heat map of the normalized volatile responses *versus* the IS (*n*-C13). Samples are clustered using ascendant hierarchical clustering based on Euclidean distances using the average linkage agglomerative method. The samples in the heat map are clustered into two groups, good (MG) and oxidised samples (MOX). **A comparison of the two groups enables us to distinguish the pool of components** in lower abundance (in orange), i.e. those that are **lost or degraded** with the oxidation of coffee, **from the components** that are more abundant in the MOX samples (in brown), indicating their **possible formation or increase with oxidation.**

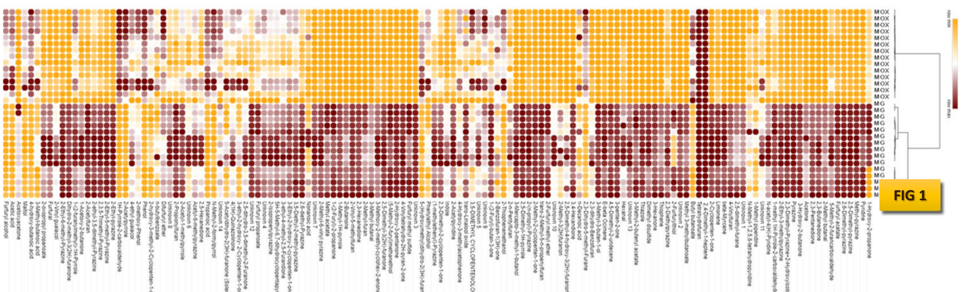


FIG 1

2. Extraction of the informative volatiles of the oxidised note

Supervised **PLS-DA machine learning** was applied to the whole sample set **to extract informative volatiles** that describe the **oxidised coffee note**.

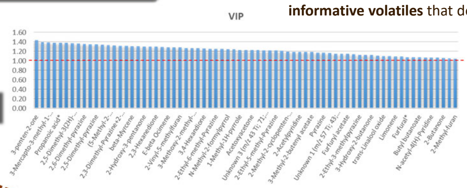


FIG 2

71/147 volatiles were found with a VIP (variable importance in projection) > 1 in **describing the oxidised samples** (Figure 2).
VIP scores estimate the importance of variables in the projection used in the PLS-DA model and are often used to select variables; when a variable presents a VIP that is close to or greater than 1, it can be considered important in the given model.

3. Potential markers of the oxidised coffee note

Twenty-five highly significant volatiles describing the oxidised coffees **with a similar trend in all of the investigated blends and packaging,** and with a CV% of at least 20, **were identified as potential markers of oxidised coffees.**

Most of them are present in **lower amounts in oxidised** samples, **few are already known** to decrease over time and **others behave differently from previous studies**. These components are all heterocycles and are highly reactive, in particular in the presence of moisture and oxygen, which may explain their decrease in oxidised coffees.
The coffee volatilome includes both **odourant and non-odourant** compounds, the latter of **which contribute to synergism in the aroma perception**. In figure 3 is reported the **"sensory footprint"** of volatiles describing oxidized note.

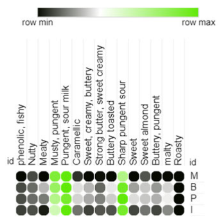


FIG 3

These data show that several volatiles are more abundant in oxidised samples and, some of them, are common to all packaging. Although the coffee aroma is the result of synergism between several volatiles, some of those that are better correlated to oxidation have been described as having an unpleasant odour.

Conclusions and future perspectives

Twenty-five target components of the coffee volatilome have been identified as **markers of coffee oxidation** because they present the same behaviour and statistical meaning in all of the investigated samples, **independently on packaging and blend**. **All together**, they **have a synergistic role in the recognition of oxidised coffee** and can be considered the fingerprint of the oxidised note.
The literature survey suggests several compounds although not standardized as markers of decrease of aroma quality of R&G coffee during storage. However, most of the suggested markers and indices seem to be more closely related to the freshness of the coffee aroma. These data provide information on the oxidised note and demonstrate **that artificial intelligence can successfully be used to define instrumentally define the evolution of the quality of coffee aroma over time**, and can be an **objective valuable tool** to be **used in screening as a support to the sensory panel [6-8]** in testing new and more sustainable packaging, driving the research toward the developing of Artificial Smelling Machine tools.

References

[1] Czerny, M., Schieberle, P. (2001). *19 th International Scientific Colloquium on Coffee*, Trieste, Italy. [2] Lytou, A. E., Panagou, E. Z., & Nychas, G. J. E. (2019). Current Opinion in Food Science. [3] Folmer, B. The craft and science of coffee. (2017). London, UK: Academic Press. [4] Glöss, A. N., Schönbächler, B., Rast, M., Deuber, L., & Yeretzian, C.. *Chimia*, (2014), 68(3),179–182. [5] Manzocco, L., Calligaris, S., Anese, M., & Nicoli, M. C. In P. Subramaniam & P. Wareing (Eds.), The stability and shelf life of foods (2016) (pp. 375–396). Elsevier. [6] Bressanello, D.; Liberto, E.; Cordero, C.; Rubiolo, P.; Pellegrino, G.; Ruosi, M. R.; Bicchi, C. *Food Chem.* (2017), pp 218–226. [7] Bressanello, D.; Liberto, E.; Cordero, C.; Sgorbini, B.; Rubiolo, P.; Pellegrino, G.; Ruosi, M. R.; Bicchi, C. J. Agric. Food Chem. (2018), pp 7096–7109. [8] Bressanello, D.; Marengo, A.; Cordero, C.; Strocchi, G.; Rubiolo, P.; Pellegrino, G.; Ruosi, M. R.; Bicchi, C.; Liberto, E. J. Agric. Food Chem. (2021), 69 (15), 4550–4560.