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OPTIMISATION OF HEADSPACE HIGH CONCENTRATION CAPACITY METHOD FOLLOWED BY COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY MASS SPECTROMETRY APPLIED TO COFFEE BREW AROMA ANALYSIS

DAMIEN EGGERMONT

MASTER THESIS PRESENTED IN ORDER TO OBTAIN THE BIOENGINEER MASTER DIPLOMA ORIENTATION CHEMISTRY AND BIO-INDUSTRIES

ACADEMIC YEAR 2020-2021

SUPERVISOR: GIORGIA PURCARO

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Acknowledgments

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Abstract

HiSorb, as a novel HCC tool, was, here, successfully applied to the analysis of coffee brew aroma. The optimisation of extraction conditions (time, sample volume, and temperature) was achieved for HiSorb with PDMS coating. The resulting conditions were used to evaluate the analytical performances of the HiSorb and compare it with more common SPME (PDMS and DVB/CAR/PDMS coatings) methods. A Multi-Vial Multi-Cumulative Trapping (MV-MCT) approach was then explored to evaluate the performance gain over the single extraction approach and compare these two extraction tools. Finally, MV-MCT extraction was used with both HiSorb and DVB/CAR/PDMS SPME to evaluate and compare the level of information obtained through the study of the impact of coffee packaging on the VOC profile of the brewed beverage.

The use of HiSorb as an automated SBSE alternative through the innovative Centri platform (Markes International Ldt.) led to much higher extraction yield than other usual SPME tools. The MV-MCT approach has shown that several reduced time cumulative extractions gave overall better response than the equivalent time in single extraction. However, and contrary to what has been recently demonstrated for Single-Vial Multi-Cumulative Trapping (SV-MCT) extraction, this approach increases the extraction of more volatile molecules while having a minor effect on semi-VOCs (for the equivalent time in single extraction). Finally, the MV-MCT approach with both HiSorb and DVB/CAR/PDMS SPME allowed a successful discrimination of the sample packaging through the extracted VOC profile. Moreover, the two extraction tools seem to be alternating and/or complementary concerning the level of information obtained.

Résumé

Le HiSorb, en tant que nouvel outil à haute capacité de concentration (HCC), a été appliqué avec succès à l'analyse de l'arôme de café « boisson ». L'optimisation des conditions d'extraction (temps, volume d'échantillon et température) a été réalisée pour le HiSorb (revêtement PDMS). Les conditions résultantes ont été utilisées pour évaluer les performances analytiques du HiSorb et les comparer avec les méthodes SPME plus courantes (revêtement PDMS et DVB/CAR/PDMS). L'approche d'extraction par multi-piégeage cumulatif au départ de plusieurs flacons (« Multi-Vial Multi-Cumulative Trapping », MV-MCT) a ensuite été explorée pour évaluer le gain de performance par rapport à l'approche en extraction unique. Ce gain a été comparé pour les deux différents outils d'extraction. Enfin, l'extraction MV-MCT a été utilisée avec le HiSorb et la SPME DVB/CAR/PDMS pour évaluer et comparer le niveau d'information obtenu en l'appliquant à l'étude de l'impact de l'emballage du café en poudre sur le profil des molécules volatiles émises par le café « boisson ».

L'utilisation du HiSorb comme alternative automatisée à la SBSE par le biais de la plateforme innovante « Centri » (Markes International Ldt.), a conduit à un rendement d'extraction beaucoup plus important que les méthodes SPME conventionnelles. L'approche MV-MCT a montré que plusieurs extractions cumulées à temps d'extraction réduit donnaient globalement une meilleure réponse qu'une extraction unique pour un temps total d'extraction équivalent. Cependant, et contrairement à ce qui a été récemment démontré pour l'extraction par multi-piégeage cumulatif au départ d'un flacon unique (« Single-Vial Multi-Cumulative Trapping », SV-MCT), cette approche augmente l'extraction des molécules les plus volatiles tout en ayant un effet mineur sur les semi-volatiles (pour une extraction unique à temps équivalent). La dernière partie conclut que l'approche MV-MCT avec le HiSorb et la SPME DVB/CAR/PDMS permet de discriminer avec succès le conditionnement de l'échantillon grâce au profil des molécules volatiles extraites. De plus, les deux outils d'extraction semblent être interchangeables et/ou complémentaires en ce qui concerne le niveau d'information obtenu.

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1. Introduction

1.1. Instrumental aroma analysis

Volatile organic compounds (VOCs) are responsible for the perception of odours and, in a lesser extent, tastes. The analysis of VOCs is a major tool for key activities of the food industry, including sensory and hedonic properties optimisation (linked with the consumer acceptance), quality and safety (protection against spoilage and adulteration) control and monitoring of industrial processes. Techniques for VOC analysis are therefore continuously developed and improved to meet today and tomorrow's needs [1–4].

Flavour consists of the simultaneous perception of textural properties, tastes, and odours. These last components are determined by many volatile and semi-VOCs from various origins (metabolism, chemical reactions, etc.) in a very wide range of concentrations and polarities. Therefore, the challenge of VOC analysis is to isolate, identify and if necessary, quantify all VOCs present in an extremely complex blend of molecules. A deep understanding of the sample and its matrix is needed to determine the best way to analyse it while avoiding matrix interferences and artefacts formation [1,2,5].

Concerning the quality control activities, key VOCs linked with quality criteria can be identified and quantified (through targeted routine analysis for instance) to support the objective assessment of the quality of the product without the use of expensive and time-consuming panellist. For example, the monitoring of volatile has been successfully applied to detect food adulteration [6,7].

As target analytes are (semi-) volatiles, gas chromatography (GC) systems, both mono- or multidimensional, are extensively used and usually coupled with mass spectrometry (MS) detection. In the following paragraphs, the main sample preparation techniques and the GC system used for volatile analysis will be discussed in more details, with particular focus on the system used within this work [8,9].

1.1.1. Sample preparation methods

As the VOCs' content in the headspace (HS) is low, the analytical chemist often resorts to a concentration step to increase the sensitivity[1] of the method. Indeed, traditional static-SH analysis (S-HS), that transfer the HS content to the GC system by punction/injection is not extremely sensitive. More efficient tool such as dynamic-HS (D-HS) (renewing of the sample HS and trapping of the outgoing-flow) or high-capacity concentration tools (HCC-HS) have been developed over the years. HCC-HS (mainly HS-Solid-Phase Microextraction [HS-SPME]) are nowadays often preferred for VOC analysis [1–3,5,10].

[1] Sensitivity: ability to differentiate two small and close concentrations of analyte [147].

In this regard, different tools have been proposed over the years but only those used in this project will be explained in detail, along with their theoretical basis.

1.1.1. A) High-Capacity Concentration tools

High-Capacity Concentration (HCC) techniques were first introduced in the 90's and they have almost completely replaced the traditional S-HS approaches. HCC relies on sorptive extraction techniques and has been defined as a bridge technique between S-HS and D-HS, as they are simple, fast, easy to automate and reliable as the former but, at the same time, they present a high concentration factor as D-HS. Hereafter the main devices use in HCC are presented [10–12].

a) Solid Phase Micro-Extraction

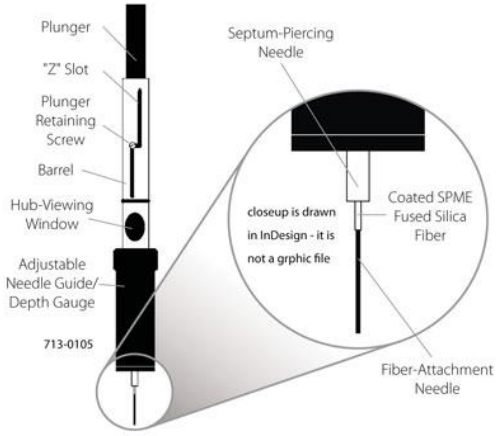


Figure 1 SPME device scheme (from Sigma-Aldrich website) [2]

Solid Phase Micro-Extraction (SPME) consists of a fused silica fibre coated with sorbent in a syringe-like fibre-holder (see Figure 1). The stationary phase (with a sorbent volume < 1 µL) can use absorption (*e.g.*: polydimethylsiloxane [PDMS] or polyacrylate [PA]) or adsorption (*e.g.*: carboxen [CAR], divinylbenzene [DVB] or triphasic [DVB/CAR/PDMS]). The existence of a plurality of sorbents allows flexible adaptation of the method towards a more specific extraction of a certain family of compounds (*e.g.*: analysis of sulphurous compounds [13,14]) or towards a large range of molecules (*e.g.*: for profiling purposes [15]). SPME is solvent-free and adaptable to several sample modes (direct immersion in liquid [DI] or gaseous samples [HS]) but is also very fragile and has a limited sorbent volume [1,16–19].

[2] https://www.sigmaaldrich.com/technical-documents/articles/reporter-us/bioanalysis-with-spme.html

b) Stir Bar Sorptive Extraction

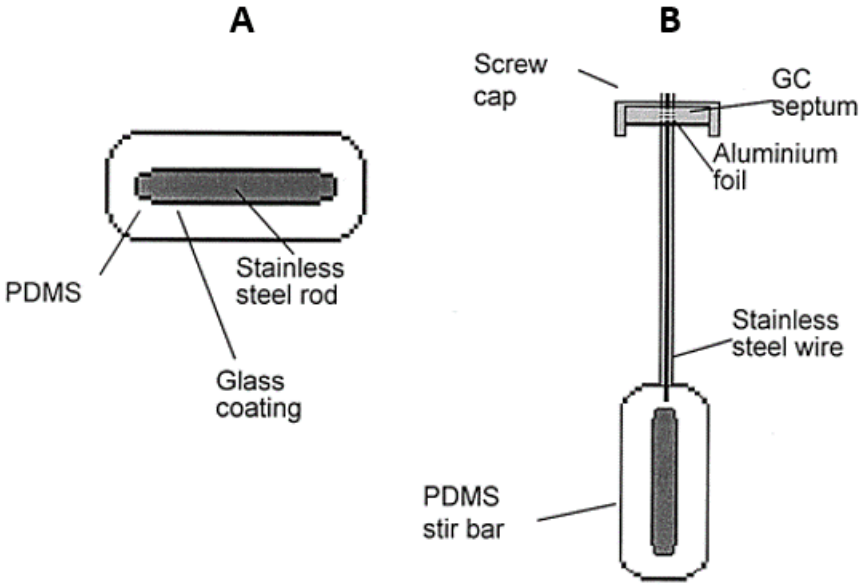


Figure 2 SBSE (A) and HSSE (B) scheme (adapted from Bicchi et al. *(2002))*

Stir Bar Sorptive Extraction (SBSE) and their HS version (Figure 2) are glass or steel rods coated with sorbent (mainly PDMS, PA, ethylene glycol modified silicone (EG-silicone) or combinations of them (multi-SBSE)). This configuration allows a higher sorbent volume (55-219 µL) for higher sensitivity. The sorptive bar (SB) is directly immersed and spun in the liquid sample. After extraction, the SB is withdrawn manually and then thermally desorbed directly into the GC inlet. Lack of repeatability has been commonly reported as an issue, associated with the manual handling of the SB [11,20–22].

c) Other forms of HCC tools

Several forms of HCC such as HiSorb or SPME arrow have been developed to attempt to increase the sensitivity and the robustness of the extraction [11,12,23].

HiSorb probes (tools mainly used in this project) consists of a stainless-steel body with 63 µL of PDMS coating of 10.5 mm long and approximately 0.8 mm thick and are manufactured only by Markes International (see Figure 3). The large volume of sorbent and the shape of the probe fill the gap between SPME (easy handling) and SBSE (good sensitivity). Two lengths of the probe are currently available. A shorter one for headspace analysis and a longer one for immersion analysis occurring in a 20 mL vial. After extraction, the probe is withdrawn and directly inserts in a dedicated liner or possibly insert in thermal desorption tube for later analysis. Since the volume of sorbent is high and therefore the amount of sorbed analytes is important, a trapping step is necessary to optimise the injection, avoiding excessive chromatographic broadening of the earlier eluted compounds. [11,12,23,24].

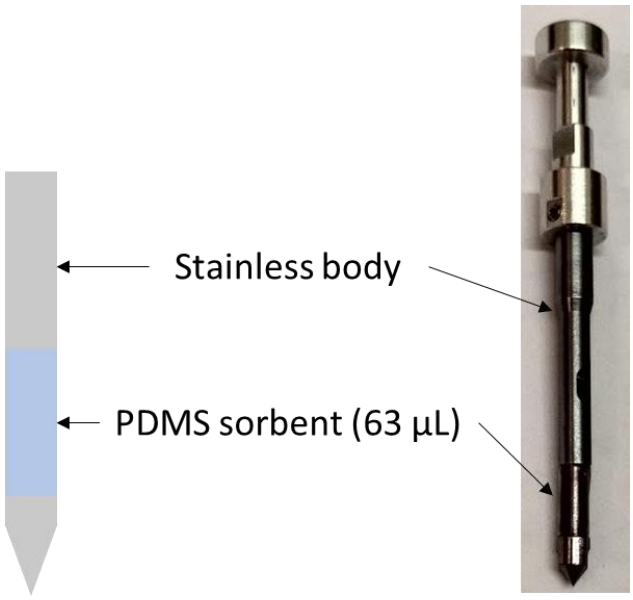


Figure 3 Representation of HiSorb probe (inspired by Markes.com)

d) Headspace analysis by HCC techniques

The headspace (HS) analysis by HCC techniques relies on the equilibrium between the three phases (sample, air and sorbent). The sample is introduced in a sealed vial and the HCC tool is inserted in the HS above the sample after reaching partition equilibrium between liquid and gas phases (see below) [11,25].

1.1.1. B) Cold Trap system

A cold trap can be placed after the injector to focus the analytes before the injection (see Figure 4). The trap consists of cooled sorbent(s) that can be rapidly heated to desorb and deliver the full amount of analyte in the GC system. This step may be necessary for HCC extraction as the high amount of extracted analyte and the slow desorption process (especially with absorption) would lead to inefficient injection. Thus, a focusing step reduces the injection time and the associated peak tail and furthermore increases the sensitivity [24,26,27].

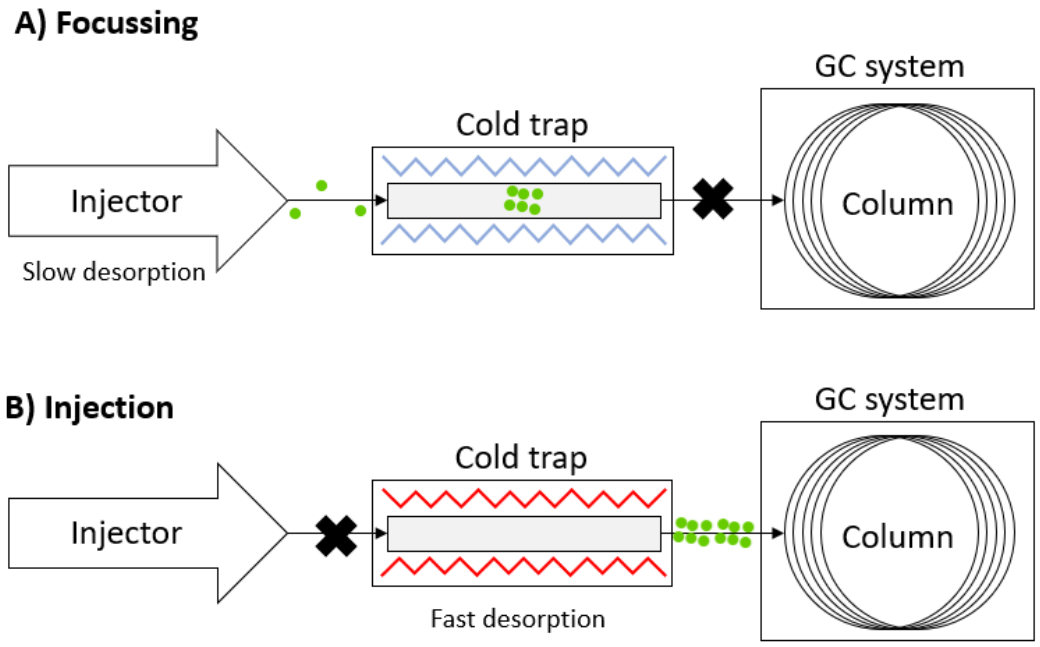


Figure 4 General scheme of a cold trap system

1.1.1. C) Theory

a) Sorption mechanisms

Sorption mechanisms refer to both absorption and adsorption. The main difference is the extent to which diffusion of the analytes occurs in the sorbent (see Figure 5) [16,28].

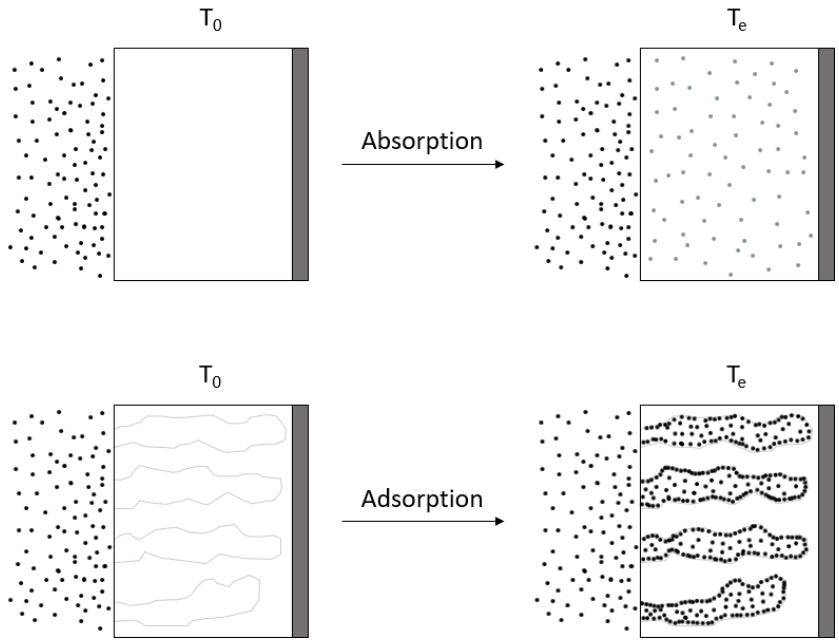


Figure 5 Absorption and adsorption phenomena representations (inspired by Gorecki et al. *(1999) and Pawliszyn (2012))*

Absorption is a slow process occurring in liquid coatings (PDMS and PA are the most known and used). Analytes are uncompetitively solvated in the liquid phase coating.

Adsorption, on the other hand, occurs more quickly in porous solid coating (DVB, CAR, etc.) in which analytes remain at the surface (in micropore) and do not (or very scarcely) diffuse. Adsorption is a competitive process in which a molecule with less affinity with the fibre can be removed by a different molecule having a higher one (this is known as the "displacement" effect). Therefore, the quantity of analytes at equilibrium varies with the sample matrix's relative composition. One advantage of adsorption over absorption is the variety of coatings that covers a larger range of molecule.

A comparison of absorption and adsorption phenomenon can be found in the Table 1.

Table 1 Comparison of absorption and adsorption phenomenon

	ABSORPTION	**ADSORPTION**
KINETICS	Slow	Moderate
COMPETITIVITY	Non-competitive	Competitive (→ displacement effect)
QUANTITY SORBED	Limited to the volume of sorbent	Limited to the area of the sorbent
RANGE OF MOLECULES COVERED	Limited (few coatings)	Extended (several coatings)

b) Direct Immersion HCC

Direct Immersion (DI-)HCC extractions are based on the partition of the analytes between the sorbent (stationary phase) and the liquid sample [16,17,29].

The partition constant ($K_{so/s}$) is defined as in Equation 1.

$$K_{so/s} = \frac{C_{so}^{\infty}}{C_{s}^{\infty}} \quad (1)$$

With:

- C_{so}^{∞} : concentration of the analyte on/in the stationary phase of the sorbent at equilibrium,
- C_{s}^{∞} : concentration of the analyte in the sample solution at equilibrium.

The molar partition ratio (k') can be defined as in Equation 2.

$$k' = \frac{n_{so}^{\infty}}{n_{s}^{\infty}} = \frac{C_{so}^{\infty}\, V_{so}}{C_{s}^{\infty}\, V_{s}} = K_{so/s}\frac{V_{so}}{V_{s}} \quad (2)$$

With:

- n_{so}^{∞} : number of moles on/in the sorbent at the equilibrium,

- n_s^∞ : number of moles in the sample solution at the equilibrium,
- V_{so} : volume of sorbent,
- V_s : volume of the sample solution.

From the previous equation, the molar quantity of analyte sorbed can be calculated as in Equation 3.

$$\Rightarrow n_{so}^\infty = K_{so/s} V_{so} C_s^\infty \quad (3)$$

Equation 3 highlights the linearity between the quantity of analyte sorbed and the concentration in the sample solution at equilibrium. Deviation from this theoretical relationship may occur at high concentration due to non-ideal phenomena.

To obtain the amount of analyte initially present in the solution, the mass balance is thus considered (Equation 4).

$$C_s^0 V_s = C_{so}^\infty V_{so} + C_s^\infty V_s \quad (4)$$

With:

- C_s^0 : initial concentration of the analyte in the sample solution.

By multiplying Equation 4 by $K_{so/s}$, then isolating C_{so}^∞ and finally multiplying by V_{so}, the quantity sorbed at equilibrium can be calculated as in Equation 5.

$$\Rightarrow n_{so}^\infty = C_{so}^\infty V_{so} = C_s^0 V_s \frac{V_{so} K_{so/s}}{K_{so/s} V_{so} + V_s} \quad (5)$$

If the sample volume (V_s) is large (compared to sorbent volume, V_{so}), Equation 5 can be simplified (Equation 6).

$$n_{so}^\infty = C_s^0 \frac{V_s V_{so} K_{so/s}}{K_{so/s} V_{so} + V_s} \approx C_s^0 \frac{V_s V_{so} K_{so/s}}{V_s} = C_s^0 V_{so} K_{so/s} \quad (6)$$

Equation 6 demonstrates the linearity between the initial analyte concentration in the sample solution and the sorbed quantity at equilibrium (*i.e.*: the quantity injected in the chromatographic system).

c) Headspace-HCC

Unlike DI-HCC, HS-HCC (or HS-sorptive extraction [HSSE]) techniques are based on partitioning between three phases: the sample, the air above it (HS) and the sorbent that is not in direct contact with the sample [16,17,25,28].

As for DI-HCC, the theory relies on mass balance (Equation 7).

$$C_s^0\ V_s = C_{so}^{\infty} V_{so} + C_s^{\infty} V_s + C_{HS}^{\infty} V_{HS} \quad (7)$$

With:

- C_{HS}^{∞} : Concentration of the analyte in the HS at equilibrium and,
- V_{HS} : Volume of HS.

From the mass balance (equation 7), the quantity sorbed at equilibrium ($n_{so}^{\infty} = C_{so}^{\infty} V_{so}$) can be expressed similarly as for Equation 5.

$$\Rightarrow n_{so}^{\infty} = C_s^0 \frac{V_{so}\ V_s\ K_{so/HS}\ K_{HS/s}}{K_{so/HS}\ K_{HS/s} V_{so} +\ K_{HS/s} V_{HS} + V_s} \quad (8)$$

With:

- $K_{so/HS} = \frac{C_{so}^{\infty}}{C_{HS}^{\infty}}$: partition constant between the sorbent and the HS,
- $K_{HS/s} = \frac{C_{HS}^{\infty}}{C_s^{\infty}}$ partition constant between the HS and the sample.

The following discussion deals with liquid polymeric coating. However, according to Pawliszyn (2012), the conclusions reached from these coatings should be applicable for other coatings [16].

The two partition constants can be linked with the Henry's constants of the analyte if the ideal gas law is assumed for the analyte in the HS as in Equations 9 and 10[3].

$$K_{so/HS} = \frac{C_{so}^{\infty}}{C_{HS}^{\infty}} = \frac{RT}{H_{so}} \quad (9)$$

$$K_{HS/s} = \frac{C_{HS}^{\infty}}{C_s^{\infty}} = \frac{H_s}{RT} \quad (10)$$

With:

- R : ideal gas constant,
- T : temperature,
- H_{so} : Henry's constants of the analyte in the liquid polymer sorbent and
- H_s : Henry's constants in the aqueous sample

Equation 8 can be simplified (Equation 12) by making the assumption in Equation 11 when the moisture effect in the HS can be neglected (detailed development can be found in [16,25]).

[3] The demonstration can be found in Zhang and Pawliszyn (1993) [25]

$$K_{so/s} = K_{so/HS}\, K_{HS/s} = \frac{H_s}{H_{so}} = K_{so/g}\, K_{g/s} \quad (11)$$

With:

- $K_{so/s}$: partition constant between the sorbent and the sample,
- $K_{so/g}$: partition constant between sorbent and gas,
- $K_{g/s}$, the partition constant between gas and sample.

$$\Rightarrow n_{so}^{\infty} = C_s^0 \frac{V_{so}\, V_s\, K_{so/s}}{K_{so/s}V_{so} + K_{HS/s}V_{HS} + V_s} \quad (12)$$

As in DI, the relation between the sorbed quantity and the initial concentration in the sample is linear. Each term (or group of terms) in the denominator expresses the analyte capacity of the related phase:

- Sorbent: $K_{so/HS}\, K_{HS/s}V_{so}$ or $K_{so/s}V_{so}$,
- HS: $K_{HS/s}V_{HS}$ (often $K_{HS/s}$ are low values. E.g.: benzene: 0.26) and
- Sample: V_s.

In the case of DI, $K_{HS/s}V_{HS}$ tends to zero and the resulting equation corresponds to Equation 5.

An interesting conclusion is that the DI and HS extraction will give approximately the same result at the equilibrium if V_{HS} is much lower than V_s.

Equation 10 can be generalised for samples and/or sorbents with multiple phase compositions. More details can be found in [16].

d) Fundamental theory for absorption

The fundamental theory for absorption also relies on the partition constant at the equilibrium of analytes between the sorbent (PDMS, for instance) and the sample. By mathematical development, it is possible to withdraw the equilibrium concentration of the solution and reveal the initial mass of the analyte in the sample (m_s^0) (Equation 13) [20].

$$K_{PDMS/s} = \frac{C_{so}^{\infty}}{C_s^{\infty}} = \frac{\frac{m_{so}^{\infty}}{V_{so}}}{\frac{m_s^{\infty}}{V_s}} = \frac{m_{so}^{\infty}}{m_s^{\infty}} \times \beta_{s/so} = \frac{m_{so}^{\infty}}{m_s^0 - m_{so}^{\infty}} \times \beta_{s/so} \quad (13)$$

With:

- m_s^{∞} : mass of the analyte in the sample at equilibrium,
- m_s^0 : initial mass of the analyte in the sample,

- m_{so}^{∞} : mass of the sorbed analyte and
- $\beta_{s/so} = \frac{V_s}{V_{so}}$: volume phase ratio.

The partition constant of the analyte between the sorbent and the sample can be approximated by its octanol/water partition constant ($K_{PDMS/W} \approx K_{O/W}$). This approximation is empirically validated for both HS and DI extraction [11,16].

With this approximation and from equation 13, the recovery of the analyte at equilibrium can be expressed by Equation 14.

$$\Rightarrow recovery = \frac{m_{so}^{\infty}}{m_s^0} = \frac{\left(\frac{K_{O/W}}{\beta_{s/so}}\right)}{1 + \left(\frac{K_{O/W}}{\beta_{s/so}}\right)} \quad (14)$$

Equation 14 shows that the higher the volume of sorbent is, compared to the sample volume (*i.e.*: the lower is the phase ratio $\beta_{s/so}$), the more efficient the extraction of less polar compounds will be. Thus, larger phase ratios $\beta_{s/so}$ allow compounds with a wider range of polarity to be extracted more efficiently. Figure 6 shows the theoretical recovery curves for several HCC PDMS tools with different phase ratios $\beta_{s/so}$ (*e.g.*: for HiSorb in 20 mL vial with 1 mL sample, $\beta_{s/so} \approx 302$) [21,30,31].

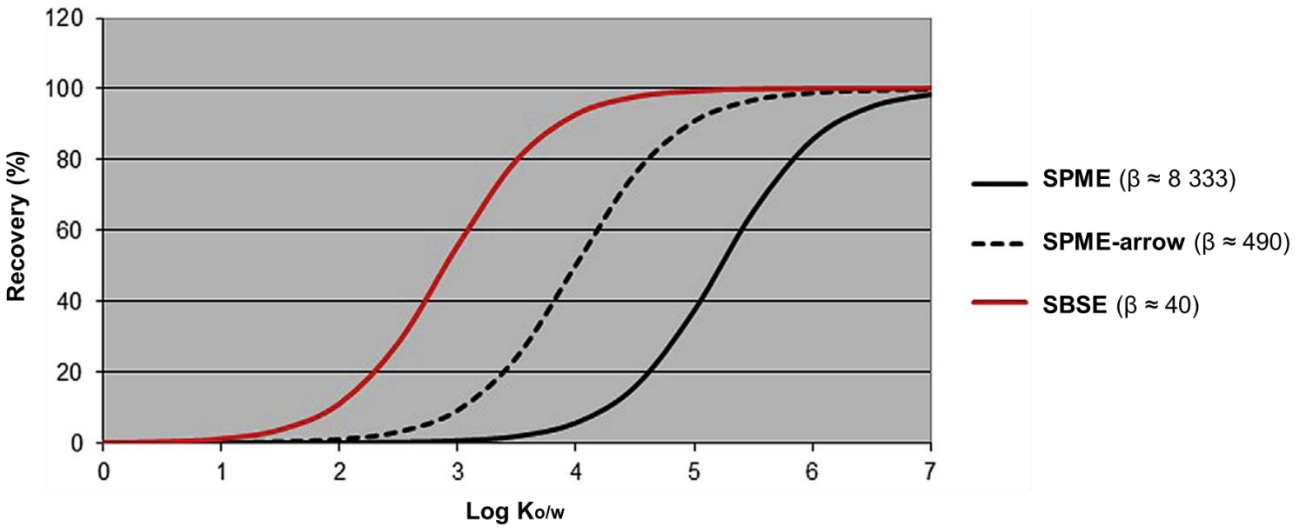


Figure 6 Theoretical recovery curve in function of log $K_{o/w}$ (adapted from David et al. *(2019))*

e) Headspace theory

The previous sections only deal with sorption phenomena, this one will focus on HS theory and the related parameters [32].

As previously defined, the partition constant between sample and HS at equilibrium is defined as in Equation 1.

To be coherent with the literature and the previous equations, the inverse of the coefficient will be used in the following section (Equation 15).

$$\Rightarrow K_{HS/s}^{-1} = \frac{C_s^{\infty}}{C_{HS}^{\infty}} = \frac{m_s^{\infty}}{m_{HS}^{\infty}} \frac{V_{HS}}{V_s} = \frac{m_s^{\infty}}{m_{HS}^{\infty}} \beta_{HS/s} \quad (15)$$

With:

- m_{HS}^{∞} : mass of the analyte in the HS at equilibrium and
- $\beta_{HS/s} = \frac{V_{HS}}{V_s}$: phase ratio between HS et sample.

From the mass balance equation ($m_s^{\infty} + m_{HS}^{\infty} = m_s^0$), Equation 16 can be drawn.

$$C_s^0 = C_{HS}^{\infty} \left[\frac{K_{HS/s}^{-1} V_s}{V_s} + \frac{V_{HS}}{V_s} \right] = C_{HS}^{\infty} \left(K_{HS/s}^{-1} + \beta_{HS/s} \right)$$

$$\Leftrightarrow C_{HS}^{\infty} = \frac{C_s^0}{\left(K_{HS/s}^{-1} + \beta_{HS/s} \right)} \quad (16)$$

Equation 16 demonstrates, firstly, a linear relationship between the initial concentration in the sample and the concentration at equilibrium in the HS. The linearity may not be respected in the case of a saturated HS. Therefore, the composition of the HS will not be representative of the solution [32].

Secondly, the denominator shows that in the case of compounds for which $K_{HS/s}^{-1}$ is significantly less than $\beta_{HS/s}$, factors impacting $K_{HS/s}^{-1}$, such as vapor pressure or activity coefficient (see below), are negligible and the phase ratio will mainly affect the sensitivity. On the contrary case ($K_{HS/s}^{-1} \gg \beta_{HS/s}$), the phase ratio will not significantly affect the sensitivity.

This partition constant ($K_{HS/s}^{-1}$), which links the theories of HCC extraction and HS analysis, is inversely proportional to the vapor pressure (p^0) and the activity coefficient (γ) of the compounds in the sample as shown in Equation 17 (see more detailed in [32]).

$$K_{HS/s}^{-1} \propto \frac{1}{p^0 \gamma} \quad (17)$$

Among the factors impacting the vapor pressure of the analyte, there is for instance the number of carbons (exponential decrease) of this analyte or the temperature (Antoine's law, exponential increase) [32].

Concerning the activity coefficient, it can be modified by adding salt (salting-out effect), water or by adjusting the pH (if molecules in solution can be ionised). However, these techniques have complex interactions with the analytes (*i.e.*: modification of the linearity range), which are difficult to predict [32,33].

1.1.2. Chromatographic separation

As aforementioned, GC represents the most common technique used for (semi-)VOC analysis. Over the years, the development of comprehensive techniques and their increased separating power overpass mono-dimensional GC. The present chapter presents the general principle of GC and then focuses on comprehensive multidimensional GC (GC×GC).

1.1.2. A) One dimensional chromatography

Mono-dimensional GC separates compounds, primarily according to their volatility, and secondarily according to their polarity. The separation can thus be optimised by applying a suitable temperature program and by choosing an appropriated stationary phase chemistry [34].

Prior to the separation in the column, samples are volatilised in the injector. The rapidity of injection directly impacts the efficiency of the separation. A slow injection will result in a broadening (tailing) of the peak and promotes coelution with a nearby peak. Other peak deformations can also occur due to interaction with impurities present in the liner. Fronting of the peak can appear if the column is overloaded [34].

After the compounds have been separated through the column, they are analysed in the detector. Different information can be obtained by the detector depending on its type. The most commonly used detector for untargeted studies is the MS [9,35].

1.1.2. B) Comprehensive bidimensional gas-chromatography (GC×GC)

GC×GC has gained popularity over the years thanks to the higher separation power compared to mono-dimensional GC, particularly useful for complex matrices and to gain a new insight into well-known matrices thanks to the gain in sensitivity (especially when cryogenic modulators are used) and the class pattern formation in the two-dimensional chromatogram [36].

GC×GC systems (see Figure 7) use two columns connected through a modulator (explained in the next section) [8].

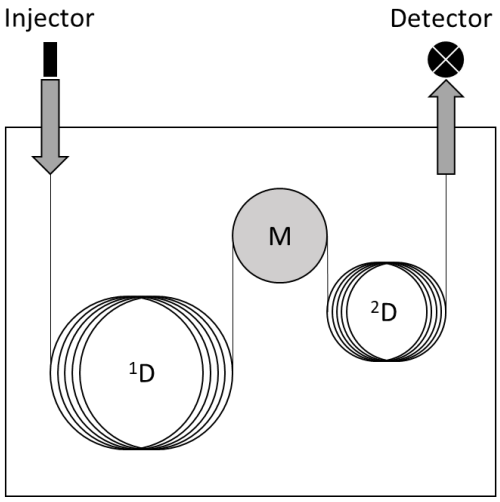


Figure 7 General representation of a GC×GC system

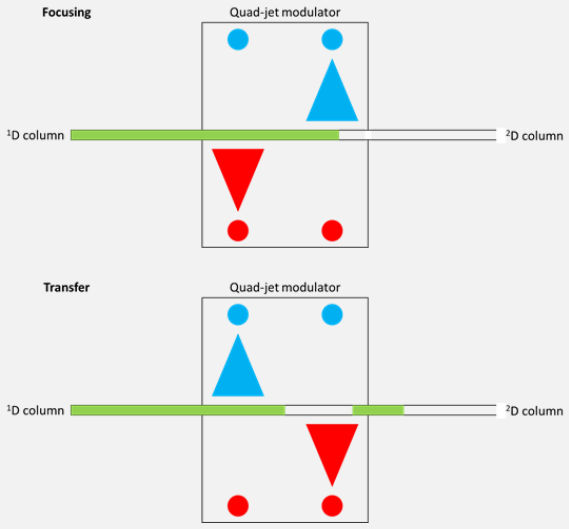
a) Modulators

The modulator has the essential role of fractionating, focusing, and injecting eluent from the first column (first dimension, ^{1}D) into the second column (second dimension, ^{2}D) as quickly and efficiently as possible [8,9].

Modulators can be separated into two main categories: thermal modulators (TMs) and flow modulators (FMs) (see example Table 2) [37–44].

Table 2 Overview of modulator types [38,41]

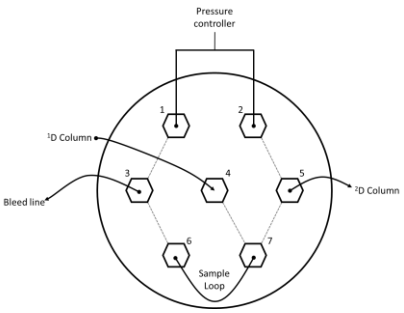
Thermal modulators



Example: Quad-Jet (LECO)

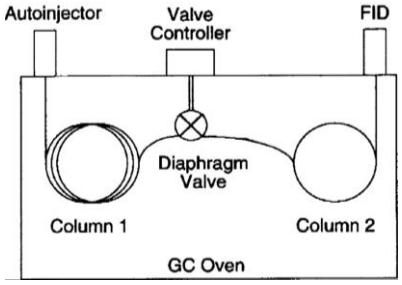
Flow modulators

Flow-based



Example: Insight (SepSolve Analytical Ltd.)

Valve-based



Example: generic valve-based GC×GC (adapted from Tranchida *et al.* (2011)) [38]

TMs focus and release fractions by applying differential temperature. They often use cryogen fluids (such as liquid CO_2 or nitrogen). Their advantages are the simplicity, the effectiveness, the high duty cycle[4] allowing a high sensitivity and the narrower injection bands in the ^{2}D. Adversely, the use of cryogens is associated with additional costs. The insufficient focusing of short-carbon chain compounds (C_4 and below) is also a common limitation of TMs, although relevant for niche and very particular applications [37,38,41,45].

Regarding FMs, a first clarification must be done concerning their classification as it varies from authors (in/out-line, differential/diversion flow, …). Therefore, the one considered in this section will follow that of Boswell *et al.* (2020). FM, deviate or collect ^{1}D effluent before the injection in the ^{2}D [41].

- Valve-based FMs use a mobile valve inside the oven that separates and connects sequentially the two columns. Several systems with different performances exist. Depending on the mechanical configuration, the duty cycle can be limited (below 50%) although great

[4] Duty cycle: ratio between ^{1}D effluent quantity reaching the modulator and quantity injected in the ^{2}D.

improvements have been made to reach the total transfer mode (duty cycle of 100%). Due to technical limitations, the valves can have a limited operating temperature range (up to 175 °C for the original version, 325 °C for more recent ones) which can limit the application range [37,38,41,45,46].

- Flow-based FMs work with permanent connexion between the two columns and do not include any moving parts inside the oven. This allows a longer lifespan and better system stability but requires a more complex pressure management system. The permanent connexion between the ^{1}D and the ^{2}D columns and the continuous incoming ^{1}D flow force the flow to be higher in the ^{2}D than the ^{1}D to overcome the pressure applied by the incoming ^{1}D flow and prevents breakthrough[5]. Figure 8 shows the overall operation of the Insight flow-based FM as an example. The high ^{2}D flow requirement makes the coupling with a MS system difficult because MS works under vacuum conditions, thus the capacity of the pump to evacuate the incoming flow limits the maximum secondary flow that can be handled by the MS system. Splitting the ^{2}D effluent is often necessary to allow coupling with MS even if this leads to a loss of sensitivity. However, splitting may offer the possibility to connect a second detector such as flame ionisation detector (FID) to provide complementary and confirmatory information (or VUV in the configuration used here). Having a too high ^{2}D flow has a negative impact on the separation performance. Indeed, the higher is the linear gas velocity, the higher will be the theoretical height plates according to Golay's equation and the lesser will be the efficiency of the separation. The use of a wider ^{2}D column (reduction of the linear velocity and consequently of the plates height) or a thinner ^{2}D stationary phase (increase the number of theoretical plates but at the expense of highly volatile compound resolution) column could address this issue. The flow ratio between ^{1}D and ^{2}D is, thus, important to optimise the separation [37,38,41,45,47,48].

Finally, both types of FMs can work in forward or reverse fill/flush mode (FFF and RFF respectively) depending on the model and the configuration. This means that the sense of the filling and the flushing of the sample loop (if applicable) can have same (FFF) or opposite (RFF) direction. At low concentration, both have similar performances but at higher concentration, RFF shows slightly better performances (less broadening, better sensitivity and peak capacity). The next section presents an example of a RFF modulator [37,49].

[5] Undesirable non-modulated ^{1}D flow that passes in the ^{2}D.

b) Insight flow modulator (SepSolve Analytical Ltd.) as example of flow-based FM

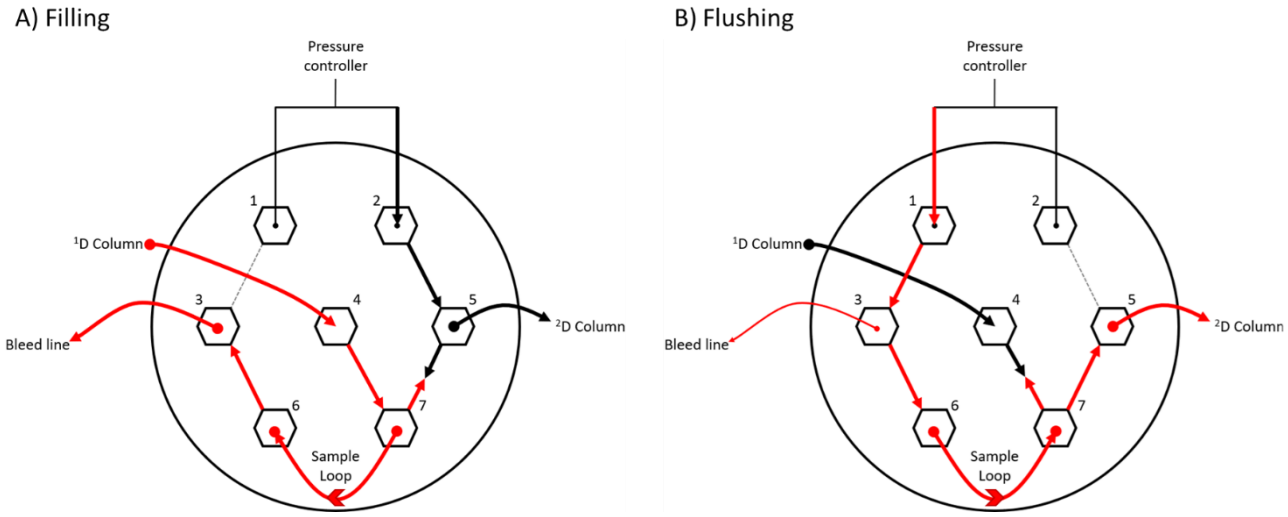


Figure 8 Schemes of Insight flow modulator (SepSolve Analytical Ltd.) during filling (A) and flushing (B) steps

This seven-port flow-based FM collects ^{1}D effluent by port 4 and fills the sample loop (between port 7 and 6) during the filling step (see Figure 8 A). At this time, the ^{2}D column is supplied with carrier gas through port 5 (connected to port 2). The pressures are set so that effluents from port 4 do not pass into port 5 through port 7 [50,51].

During the flushing step (see Figure 8 B), flows are reversed, and the sample loop is flushed into the ^{2}D column through port 5. The ^{1}D effluents are stopped by the pressure applied from the sample loop on the port 7 [50,51].

This modulator can also work in FFF mode.

1.2. Coffee sciences

1.2.1. Contextualisation

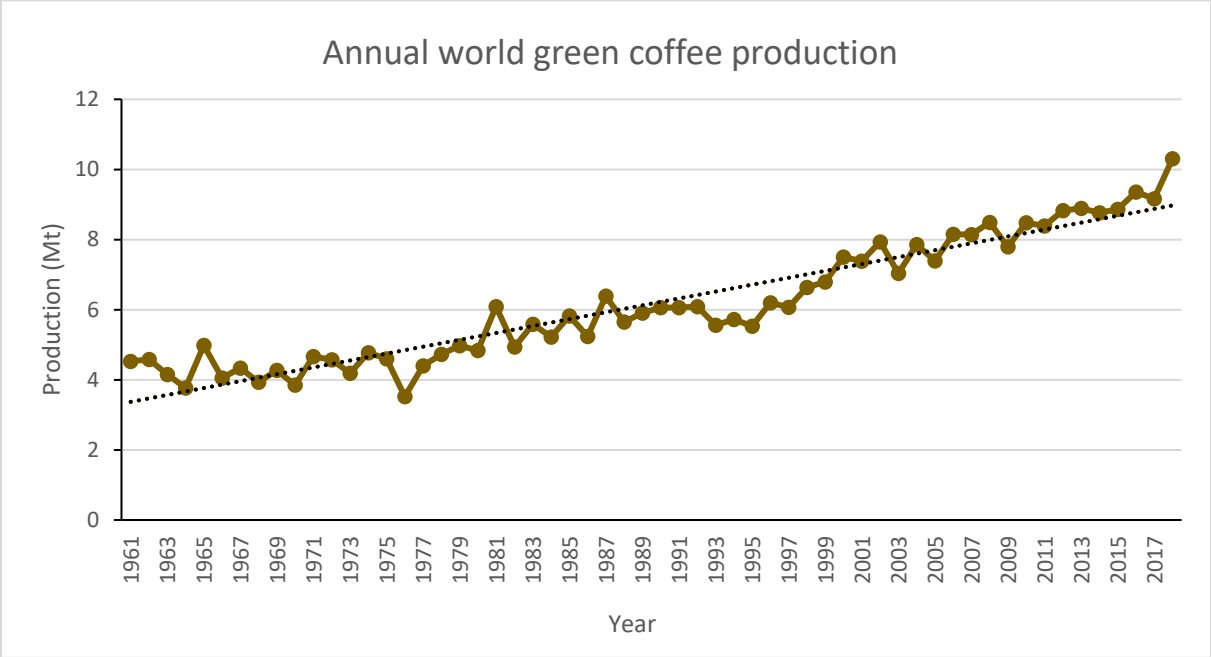


Figure 9 Evolution of the annual world green coffee production (FAO) [52]

Coffee is one of the most consumed beverages in the world and its production is constantly increasing (see Figure 9). With a primary production export of $21 billion in 2017[6], coffee is a high added value crop which is highly subject to speculation and adulteration. Frauds on coffee can consist in mixing coffee with lower quality coffee (substituting Arabica by Robusta) or other low-cost non-coffee materials such as roasted soybean, corn or coffee husks [52–55].

[6] World export value for green coffee beans (FAOSTAT).

1.2.2. Plants, culture, and post-harvesting processes

This section briefly introduces the botanical and agricultural aspects of coffee and their early post-harvesting processes. Table 3 compares the botanical characteristics of the two main coffee species.

Table 3 Comparison of the two main coffee species [56,57]

	ARABICA	**ROBUSTA**
		
SUBKINGDOM	Angiosperms	
CLASS	Eudicots	
ORDER	Asterids	
FAMILY	Rubiaceae	
TRIBE	Coffeeae (“True coffee”)	
GENUS	*Coffea* (and *Psilanthus*[7])	
MAIN COMMERCIAL SPECIES	*Coffea arabica* L.	*Coffea canephora* Pierre ex A.Froehner
PARTICULARITY	Indehiscent drupe fruit with two seeds with a “coffeanum suture” (invagination on the ventral part)	
GEOGRAPHIC REPARTITION[8]		

The coffee tree grows naturally in tropical forests and is protected by a large canopy. Evolution and consumer pressure have led to more cost-effective and easier systems to maintain such as "full sun"

[7] Previous classification system.
Coffee picture references (from left to right): H. Zell, CC BY-SA 3.0, via Wikimedia Commons, Jee & Rani Nature Photography, CC BY-SA 4.0, via Wikimedia Commons.
[8] From Herrera and Lambot (2017) [57].
Blank Mercator world map reference: $200inaire, CC BY-SA 3.0, via Wikimedia Commons.

monoculture. To preserve tropical rainforest ecosystems, coffee is increasingly grown under agroforestry systems [56].

Concerning agricultural data, the FAOSTAT has estimated in 2017 at 886.4 kg/ha the world yield of green beans with 10.6 million hectares under cultivation worldwide (about 3.5 times the size of Belgium) [52].

More information about agriculture practices can be found notably in the book of Clarke and Vitzthum (2001), the one of Folmer (2017) or Illy and Viani (2005) [58–60].

Post-harvest treatments consist mainly of cherry sorting, fermentation (optionally), drying, removal of flesh from the fruit, and roasting. Each step will have an impact on the final quality of the beverage. However, roasting is the most influential step on the aroma profile and will be discussed in the next section. It is noted that the preparation of the coffee is a traditional process that differs between the regions. Figure 10 presents an example flow-chart of the post-harvesting processing of coffee beans [61,62].

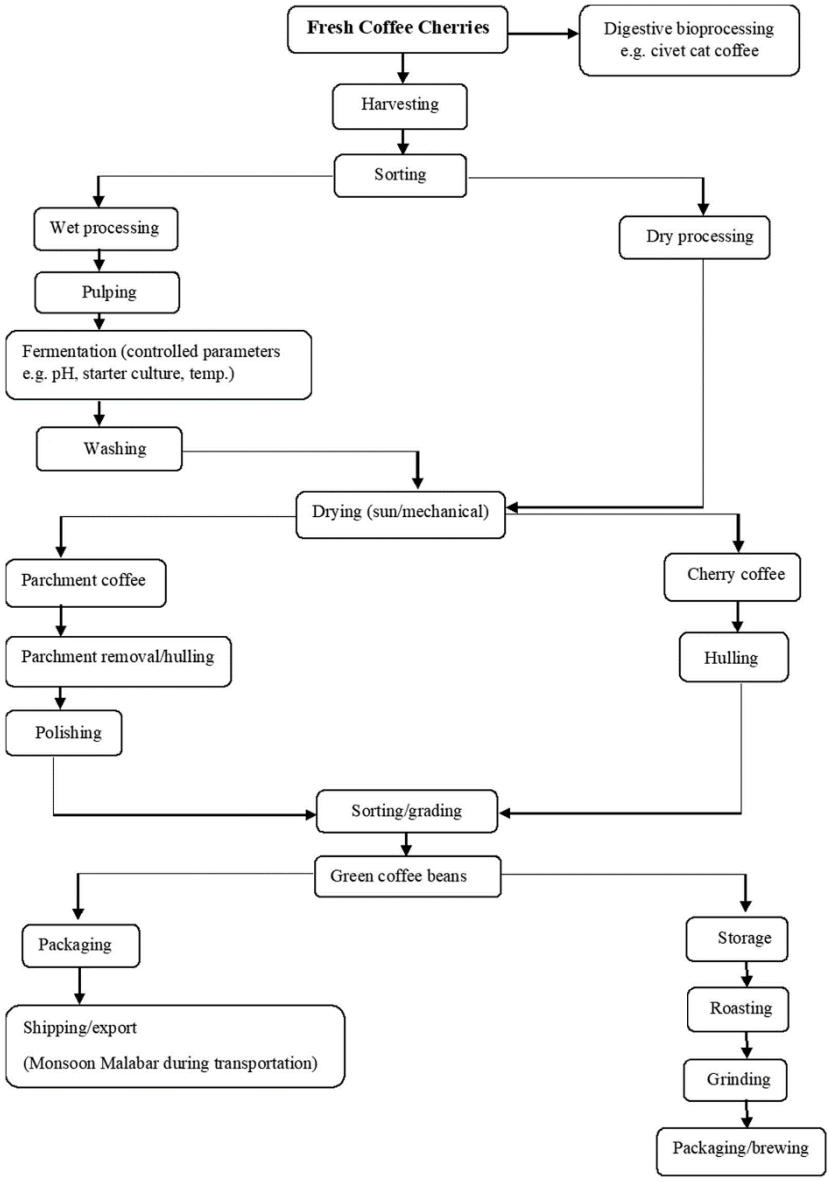


Figure 10 post-harvesting flow-chart process of coffee beans (adapted from Mahmut et al. *(2020))*

1.2.3. Roasting process

Roasting is the transformation of green coffee beans to flavourful roasted ones. The roasting process is characterised by a constant increase of temperature up to 200 – 250 °C during three to twenty minutes before cooling. The first minutes reduce the moisture content (colour: green to yellow) then the roasting phase allows chemical reactions to take place (explained below). Finally, the cooling step slows down the reactions and limits the risk of ignition during storage [63].

The bean colour (roast degree) is a monitoring indicator of the process and indicator of flavour development. Coffee beans are green at the beginning and change to yellow, orange, brown then black (with some darkness gradation at each colour stage).

Beans must be whole and not grinded to develop conventional aroma during the roasting process. During roasting, bean volume expands because gas pressure inside increases with temperature and water

evaporation in the cells; Final beans have a more porous structure with about 2.5% (g / 100 g) of water content (against 10-12% [g / 100 g] fresh) [64–66].

Chemical reactions occurring during the roasting process are numerous and will be detailed in the next section (1.2.5 Coffee aroma compounds). Moisture content and temperature influence the kinetics of the chemical reactions which impact flavour development [67,68].

The roast profile is affected by the roasting time, the temperature-to-time profile, air-to-bean ratio (quantity of hot air used to roast a batch per unit of bean mass) and degree of roasting [63,66,69].

1.2.4. Brewing methods

The preparation and consumption of coffee have become a form of routine or ritual over the years. Hence, different types of brewing can be observed around the world (see example Table 4 below) [70].

Three main types of brewing are often described [68,71]:

- decoctions, in which ground coffee is exposed to the water for a long time (*e.g.*: Turkish, boiled coffee but also cold brewed coffee),
- infusion, in which hot water passes through a bed of coffee (*e.g.*: filter coffee) and
- pressure extraction, in which the hot water passes through a packed bed of coffee under pressure (*e.g.*: espresso and moka).

Coffee brews can notably be characterised by their strengths (total dissolved solids quantity) and the extraction yield (solutes extracted per gram of grinded coffee) of their preparation method. Particle size, extraction time, coffee/water ratio, water temperature and pressure are often considered as key variables that impact the sensory quality of the coffee [68,71–73].

An extensive review of impacting parameters has been recently published by Cordoba *et al.* (2020) [71].

Because of their traditional nature, the parameters of the various preparation techniques are not necessarily constant or precise. Table 4 gives an idea of parameters found in the literature for four common methods. Different terminologies exist for the same parameter which leads to difficulty of summarising (*e.g.*: fine, very fine VS medium, fine respectively).

Table 4 Brew methods parameters

PARAMETER	TURKISH	FILTER	MOKA	ESPRESSO
				
TYPE	Decoction	Infusion	Pressure extraction	Pressure extraction
MODUS OPERANDIS	Coffee and water (sometimes with sugar) are brought to a boil (several times) and then cooled in a traditional pot[9]. The coffee is then decanted and served (sometimes filtered). [(a) (c)]	Hot water is added to a bed of coffee on a filter (often cellulosic). The coffee percolates and drops. [(a) (b) (c)]	Water is boiled in the lower part below the coffee bed. The pressure applied by the newly formed water vapour pushes the hot water through the coffee bed. The coffee level rises and falls in the upper vessel. [(a) (c) (e)]	Steaming water is applied at high pressure on a compact coffee bed. [(a) (c) (f)]
PARTICLE SIZE	Fine [(c)] to Very fine [(a)]	Medium [(a) (c)]	Medium [(a) (c)]	Medium [(c)]
EXTRACTION TIME	"Extended" [(b)]	"Short" [(b)] 3 – 10 min [(c)]	3 – 5 min [(c)]	30 s ± 5 [(a) (b) (f)] 25 – 30 s [(c)]
COFFEE/WATER RATIO	50 g/L [(c)]	55 ± 5.5 g/L [(b)] 50 – 76 g/L [(c)]	67 – 111 g/L [(c)]	167 – 286 g/L [(c)]
WATER TEMPERATURE	From room to boiling (several time) [(a) (c)]	93 ± 3 °C [(b)]	From room to 110 [(a)] – 120 [(e)] °C	90 ± 5 °C [(a) (b) (f)]
APPLIED PRESSURE	Atmospheric	Hydrostatic [(d)]	0.5 atm [(a)] 1-2 bar [(c) (e)]	9 atm [(a)] 9 ± 2 bar [(b) (f)]
SENSORY ASPECT	Presence of coffee ground [(a)] Bitter compounds [(b)] "Harsh character", intense, bitter, and dark chocolate flavours [(c)]	Clean, transparent [(a)] Milder, cleaner taste (than the decoction) [(b)] low in fat content, low in body/mouthfeel [(c)]	Burnt, bitter flavour [(a)] "Harsh character" [(c)]	Foam [(a) (b)] Body [(a)] "rich body, a full and fine aroma, a balanced bitter-sweet taste with an acidic note and a pleasant lingering after-taste." [(f)]

[9] *Cezve* (traditional Turkish coffee pot) for instance.
Picture references (from left to righ): Eaeeae, CC BY-SA 3.0 , via Wikimedia Commons; Image by Eray Genc; Coyau, CC BY-SA 3.0, via Wikimedia Commons; Photo by Marko Milivojevic.

References:

(a) Petracco 2001 [74]	(b) Lim 2019 [68]	(c) Mestdagh 2017 [72]
(d) Schwartz 2014 [75]	(e) Navarini 2009 [76]	(f) Illy, and Viani (2005) [60]

As example of the relation between coffee preparation method and particle size, Figure 11 shows the median particle size (MPS) and the fines (MPS < 100 µm) fraction for different brewing methods (information in this figure is to be considered with caution as no references are mentioned and that no other source entirely confirmed this repartition).

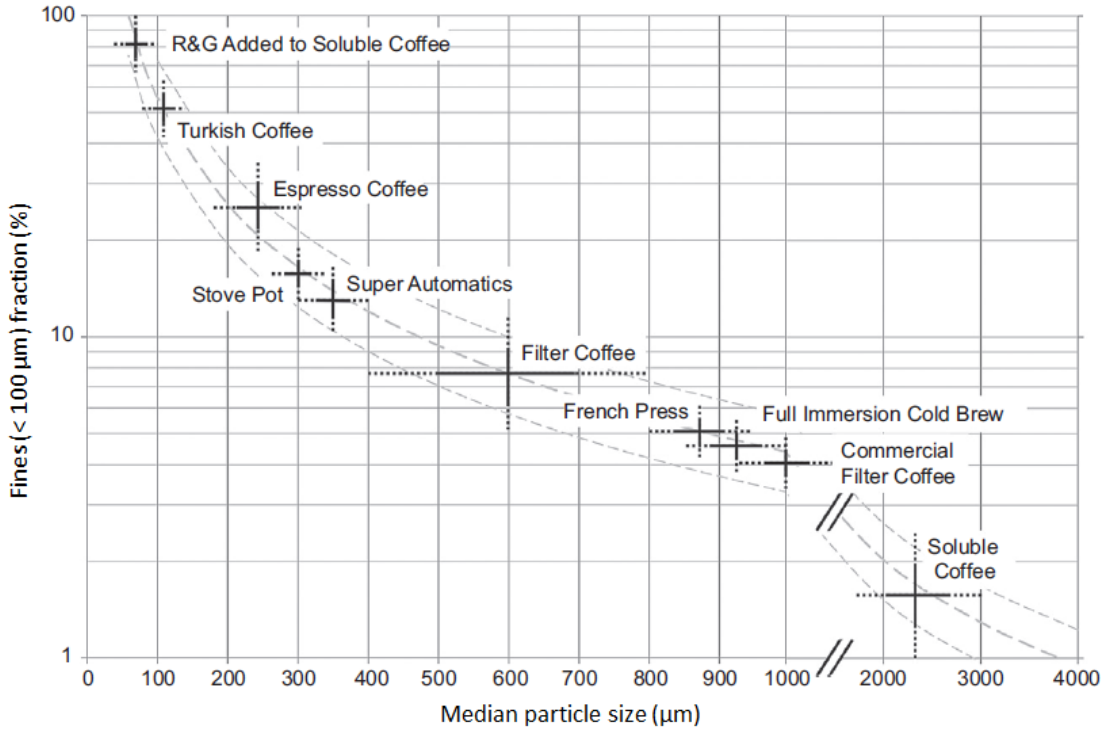


Figure 11 Median particle size and fines fraction of coffee powder for different type of preparation (adapted from von Blittersdorff and Klatt (2017))

1.2.5. Coffee aroma compounds

Coffee odorant is a complex blend of VOCs (more than a thousand) originating from several simultaneous reactions occurring during the roasting. Although all these reactions have not been completely characterized yet the most important ones for aroma development fall under the following categories: Maillard reactions[10], pyrolysis, protein denaturation, caramelisation, etc. [64–66,77].

Although all components of the green bean can lead to flavour release, carbohydrates, polypeptides, free amino acids, chlorogenic acids and trigonelline (alkaloid) are the major contributors to the aroma profile [63,69,78–80].

[10] Reducing sugars reacting with amino groups to form furans, pyrazines, pyridines, pyrroles, melanonids and other related compounds [64].

Compounds composing coffee aroma belong to several different chemical families. Among them, pyrazine and furan compounds seem to be the most abundant ones. However, not all the compounds present in the aroma bouquet effectively participate in the perception of the coffee aroma. The number of key odorant compounds (for both raw and brewed coffee) is most likely to be between fifty and one hundred. The relative abundance of these compounds is known to be strongly influenced by many factors, including the coffee origin and species, the agricultural practices, the type of extraction or roasting for instance [71,77,81].

Table 5 presents seventy-one key odorant compounds identified in Arabica coffee (green, roasted beans and brew form) in the review of Sunarharum *et al.* (2014) [81].

Table 5 Key odorant compounds identified in Arabica coffee (from Sunarharum et al. (2014) [81]*)*

Aldehydes	**Furanones**
2-methylbutanal	Dihydro-2-methyl-3(2H)-furanone
2-methylpropanal	2-ethyl-4-hydroxy-5-methyl-3(2H)-furanone
3-methylbutanal	3-Hydroxy-4,5-dimethyl-2(5H)-furanone
(E)-2-nonenal	4-Hydroxy-2,5-dimethyl-3(2H)-furanone
3-methylpropanal	5-Ethyl-3-hydroxy-4-methyl-2(5H)-furanone
Acetaldehyde	5-ethyl-4-hydroxy-2-methyl-3(2H)-furanone
Methylpropanal	**Ketones**
p-anisaldehyde	1-octen-3-one
Phenylacetaldehyde	2,3-hexadione
Propanal	2,3-butanedione
Acids	2,3-pentanedione
2-methylbutyric acid	3,4-dimethylcyclopentenol-1-one
3-methylbutyric acid	4-(4′-hydroxyphenyl)-2-butanone
Esters	1-(2-furanyl)-2-butanone
Ethyl-2-methylbutyrate	**Norisoprenoids**
Ethyl-3-methylbutyrate	(E)-β-damascenone
Furans	**Phenolic compounds**
Furfural	Guaiacol
2-((methylthio)methyl)furan	4-ethylguaiacol
2-furanemethanol acetate	4-vinylguaiacol
2-methylfuran	Vanillin
5-methyl-2-furancarboxyaldehyde	**Pyrazines**
Furfurylformiate	2,3-dimethylpyrazine
Furfurylmethyl ether	2,5-dimethylpyrazine

Furfurylformate	2,3-diethyl-5-methylpyrazine
Furfuryldisulfide	2-ethenyl-3,5-dimethylpyrazine
Sulphur-containing compounds	2-ethenyl-3-ethyl-5-methylpyrazine
Dimethyl trisulphide	2-ethyl-3,5-dimethylpyrazine
Bis(2-methyl-3-furyl)disulphide	2-ethyl-3,6-dimethyl-pyrazine
Methional	2-methoxy-3,5-dimethylpyrazine
Thiols	2-methoxy-3,2-methylpropylpyrazin
3-mercapto-3-methylbutylformate	2-methoxy-3-isopropylpyrazine
2-furfurylthiol	3-ethenyl-2-ethyl-5-methylpyrazine
2-methyl-3-furanthiol	3-isobutyl-2-methoxypyrazine
3-mercapto-3-methylbutylacetate	6,7-dihydro-5-methyl-5H-cyclopentapyrazine
3-methyl-2-butene-1-thiol	Ethylpyrazine
Methanethiol	**Pyridines**
Thiophenes	Pyridine
3-methylthiophene	**Pyrroles**
Thiazoles	1-methyl pyrrole
2,4-dimethyl-5-ethylthiazole	**Terpenes**
	Linalool
	Limonene
	Geraniol

Extensive reviews on aroma compounds were published in the past few years (*e.g.*: Toci and Boldrin (2018), Cordoba *et al.* (2020)) [71,77].

As stated earlier, the characterisation of coffee aroma composition draws important economic interests as it is essential for quality control and adulteration detection. Another motivation is the synthesis of artificial coffee aroma. For instance, the worldwide database of the European Patent Office currently lists 672 patents in the "flavour" category[11] responding to "coffee" keyword[12] [82].

[11] A23L 27/00: "Spices; Flavouring agents or condiments; Artificial sweetening agents; Table salts; Dietetic salt substitutes; Preparation or treatment thereof" [148].
[12] Title and abstract.

1.2.6. Coffee aroma analysis

As a high value-added commodity and valuable market, coffee has been extensively studied to ensure high quality of products.

Instrumental analysis of coffee flavour has evolved from old liquid techniques (such as distillation and solvent extraction) to more advanced gas chromatographic analysis (*e.g.*: HS-SPME-GC×GC-ToF-MS) [83–88].

Concerning the sample preparation, two main groups can be drawn: solvent-based (not developed here) and HS extraction. Both extraction techniques exploit the limited solubility in water and the high vapor pressure of the aroma compounds [5].

The Table 6 presents a review of the literature for the analysis of coffee brew by chromatographic means since 2010.

Table 6 Literature summary for coffee brew analysis by chromatographic determination since 2010 (SBSE: Stir Bar Sorptive Extraction, SE: Solvent Extraction, HS: Headspace, SPME: Solid-Phase Microextraction, IDA Isotope Dilution Assays, AEDA: Aroma Extract Dilution Analysis, SPE: Solid-Phase Extraction, SDE: Solvent Distillation Extraction, RAS: Retronasal Aroma Simulator, S-HS: Static Headspace, SAFE: Solvent Assisted Flavour Extraction, GC: Gas Chromatography, GC-GC: Heart cutting GC, GC×GC: Comprehensive two dimensional GC, MS: Mass Spectrometry, O: Olfactometry, FID: Flame Ionisation Detector)

YEAR	**SAMPLE PREPARATION**		**CHROMATOGRAPHIC DETERMINATION**		**TYPE OF STUDY**	**REF.**
	Technique(s)	**Sorbent(s)**	**Technique(s)**	**Detector(s)**		
2010	SBSE, SE	PDMS	GC	MS	Characterisation	[89]
2011	HS-SPME	CAR/PDMS	GC	MS	Targeted	[90]
2011	HS-SPME	DVB/CAR/PDMS	GC	MS	Characterisation	[91]
2011	HS-SPME, IDA, SE	DVB/CAR/PDMS	GC×GC	MS/O	Targeted	[14]
2012	HS-SPME	PDMS/DVB	GC	MS	Targeted	[92]
2012	HS-SPME	PDMS/DVB	GC	FID	Characterisation	[93]
2012	HS-SPME	PDMS	GC	MS	Targeted	[94]
2013	HS-SPME	DVB/CAR/PDMS	GC	MS	Characterisation	[95]
2013	AEDA, SPE, SDE	–	GC, GC-GC	MS/O, FID-MS	Odor active compounds identification	[96]
2014	HS-SPME	DVB/CAR/PDMS	GC	MS	Targeted	[97]
2014	RAS-SPME	DVB/CAR/PDMS	GC	MS/O	Targeted	[98]
2014	HS-SPME	DVB/CAR/PDMS	GC	MS	Targeted	[99]
2014	RAS-SPME	DVB/CAR/PDMS	GC	MS	Targeted	[100]
2014	S-HS	–	GC	MS	Targeted	[101]

2015	HS-SPME	PA, DVB/CAR/PDMS	GC×GC, GC-GC	MS/O	Targeted	[102]
2015	HS-SPME	DVB/CAR/PDMS	GC	MS	Characterisation	[103]
2016	HS-SPME	DVB/CAR/PDMS	GC	MS	Characterisation	[104]
2016	SE	–	GC	FID, MS	Characterisation	[105]
2018	HS-SPME	PDMS/DVB	GC	MS	Untargeted	[106]
2018	HS-SPME	DVB/CAR/PDMS	GC	MS	Characterisation	[107]
2019	HS-SPME	DVB/CAR/PDMS	GC	MS	Characterisation	[108]
2019	HS-SPME	DVB/CAR/PDMS	GC	MS	Targeted	[109]
2019	SBSE	PDMS	GC	MS, O	Odor active compounds identification	[110]
2019	HS-SPME	PA, DVB/CAR/PDMS, CAR/PDMS, PDMS/DVB	GC	MS	Targeted	[111]
2020	HS-SPME	DVB/CAR/PDMS	GC	MS	Characterisation	[112]
2020	HS-SPME	DVB/CAR/PDMS	GC	MS	Targeted	[113]
2020	HS-SPME	PDMS	GC	MS	Characterisation	[79]
2020	HS-SPME	DVB/CAR/PDMS	GC	MS	Targeted	[114]
2021	SE	–	GC	MS	Targeted	[115]
2021	HS-SPME	DVB/CAR/PDMS	GC	MS	Untargeted	[15]
2021	SAFE, SE	–	GC	MS, O	Odor active compounds identification	[116]
2021	HS-SPME	DVB/CAR/PDMS	GC	MS	Targeted	[117]

The advent of SPME facilitated the aroma analysis by making it easy to perform. This ease of operation means that it is still commonly used for coffee aroma analysis and fraud detection with the use of several combinations of coating. The triphasic (DVB/CAR/PDMS) combination is the most used one for food analysis thanks to its high recovery for a large range of polarity and structures. Concerning coffee, several fibre compositions are used (for example, triphasic, CAR/PDMS, DVB/PDMS). Although the triphasic sorbent is the most widely used (see Table 6), a recent work of Laukalēja and Krūma (2019) has reported CAR/PDMS as the most effective fibre sorbent. However, no confirmation of the latter conclusion has been made up to now. [87,111,118–121].

Currently, SPME is more used than SBSE and HSSE in coffee analysis due to easier automation. Table 6 confirms that, among the different techniques available, the HS-SPME is the most used [65,77].

As an extension of SPME, SBSE and HSSE for the analysis of odours and aroma were initially investigated by Tienpont *et al.* in 2000. Bicchi *et al.* in 2002 applied these techniques on coffee powder and brew and concluded that SBSE and HSSE have better concentration capability compared to all SPME combinations. The in-sample analysis, where SB was immersed in coffee brew, was proposed to be used in combination with HS analysis to create correlation and linkage between composition and organoleptic characteristics. Nevertheless, SBSE and HSSE have a limited use due to a lack of automation [11,120].

Concerning the separation techniques in aroma analysis, GC has become the most applied separation system for aroma analysis (see Table 6). However, multidimensional GC (mainly GC×GC) is increasingly used. GC×GC was firstly used in 2004 by Mondello *et al.* on grinded coffee extracted by HS-SPME. The enhanced separation power succeeded to separate almost all the present VOCs. A recent review of Amaral and Marriott (2019) lists the applications of GC×GC on coffee [1,61,122,123].

Regarding the detector used in the chromatographic analysis, Table 6 shows that MS system is the most used detector in these last ten years. The structural information provided by this detector offers a considerable advantage over other types of detectors. However, the olfactometry detector (use of human nose) is still used in mono-dimensional GC because it allows the detection of "key odorant compounds" or "odor active compounds" by Aroma Extract Dilution Analysis[13] or CharmAnalysis[13] [1,61,124].

Other techniques such as electronic detector (e-nose, e-tongue), Matrix Assisted Laser Desorption Ionisation, Proton Transfer Reaction-MS, Nuclear Magnetic Resonance, infrared or Raman spectrometry have emerged and have been used for coffee quality assessment (*e.g.*: adulteration detection and sensory analysis). A recent review of Wang *et al.* (2020) has been published on the analytical methods to detect adulteration in coffee [121,125–128].

[13] Ranking of aromas by importance based on the olfactory perception of experienced panellists on successive dilutions of aromatic fractions until no detection through GC-O [124].

2. Objectives

The main objectives of this thesis were:

- To investigate the extraction and analytical performances of HiSorb probes as a novel HCC tool on a food matrix. Coffee was chosen as study case;
- To compare the extraction and analytical performances of HiSorb (only available with PDMS coating) and traditional SPME techniques (PDMS and the most widely used DVB/CAR/PDMS coatings);
- To evaluate and compare the performance of both HiSorb and SPME through usual single extraction approach and through the rather novel Multi-Cumulative Trapping (MCT) approach;
- To evaluate and compare the extracted level of information by both HiSorb and DVB/CAR/PDMS SPME through Multi-Vial (MV) -MCT on an authentic industrial application (study of the impact of the coffee packaging on the aroma profile).

3. Material and method

3.1. Chemicals and reagents

Hexane (GC grade) from MilliporeSigma was used to dilute standard alkanes (C_7-C_{30}) mixture from Supelco. This standard mixture was used as a quality test of the system before batch run.

HiSorb (PDMS sorbent) short version (H1-XXABC) kindly provided by Markes International Ltd. and SPME fibres (100 µm PDMS and DVB/CAR/PDMS d_f 50/30 mm 1 cm length) kindly provided by Supelco were used as extraction tools.

3.2. Coffee preparation

The coffee brew was prepared following the Turkish method according to the proposed protocol of Bicchi *et al.* (2002) [120]. Briefly, grinded coffee (Arabica 100%) purchased from a local store was added to agitated distillate boiling water in a ratio of 12 g for 60 mL in a 250 mL beaker. The coffee mixture was allowed to boil for 20 s under stirring before being left to rest for 9 min. The coffee was filtered under vacuum on a cellulose filter (MN 640 [Macherey-Nagel], average retention capacity of 4-12 µm).

Aliquots (1 or 4 mL) were directly transferred in HS vial (20 mL) after filtration. If not analysed the same day, samples were stored at 4 °C up to a maximum of five days.

3.2.1. Espresso coffee preparation

Espresso coffees were prepared using a Nespresso Inissia coffee machine (De'Longhi S.p.a.). For "pack" samples, a stainless-steel reusable capsule (CAP20-NES, Monday Morning) was filled with 5.48 ± 0.19 (n=3) g of coffee (similarly to commercial caps).

3.3. Coffee samples

For the coffee packaging study, the samples were kindly offered by a local industrial roaster. The samples consisted of 250 g or 500 g pack of ground coffee (for filter coffee) and espresso capsules for different brands, geographic origins, and types of coffee (Arabica and Robusta). Excepted for "dis_dk" brand, all coffees are non-decaffeinated. Capsules are expected to be filled with 5.52 ± 0.07 g (n=3) of grounded coffee. Biodegradable capsules are branded "IML Compost" from Capsul'in Pro SA (Luxembourg), are compostable, biobased and comply with the EN13432 standard.

The list of the industrial coffee samples can be found in the Table 7.

Table 7 List of industrial coffee samples

BRAND	PACK	ALUMINIUM CAPSULE	BIODEGRADABLE CAPSULE
PUIS	V	V	
KIV	V		V
SUM			V
MAN_PUI	V		V
MAN_SUB	V		V
SUBL_M	V	V	
DIS_DK	V	V	
EQUI	V	V	
MAN	V		V
SUBT	V	V	
MAG	V	V	
CHIA	V		V
TOTAL:	11	6	6

The granulometry (particle diameter distribution and diameters at 10% (d0.1), 50% (d0.5) and 90 % (d0.9) of the cumulated frequencies) of the coffee powder were measured on a Mastersizer 2000 (Malvern Panalytical Ltd.) laser granulometer equipped with a Scirocco 2000 dry dispersion unit (Malvern Panalytical Ltd.). Analyses were done at least in triplicate.

3.4. Sample preparation

The sample preparation (HS-HCC extraction, trapping and injection) was executed on the Centri platform provided by Markes International Ltd.

3.4.1. HiSorb

HiSorb probes were conditioned as recommended by the manufacturer (10 min at 50 °C then 90 min at 270 °C as initial conditioning; if needed, a supplementary conditioning of 15 min at 270 °C was applied).

Before extraction, samples were equilibrated for 20 min under agitation at the extraction temperature to allow phases pre-equilibration. Agitation consisted of cycle of cycles of 10 s of agitation at 350 rpm separated by 2 s resting.

The extraction step was performed at 30, 40, 50, 60 or 75 °C during 10, 30, 40 or 60 min under the same agitation conditions as the equilibration step.

After extraction, the HiSorb probes were dried under nitrogen flow (two steps with 10 s maintained under constant flux before being withdrawn at 2 mm/s under the same flux) before injection to evacuate the potential condensation.

HiSorb probes were fully desorbed at 270 °C during 10 min (with 2 min purge at 30 mL/min) then focused on a cold trap (U-T12ME-2S, Markes International Ltd., focusing temperature: 0°C). The trap was then desorbed for 3 min at 300°C (with 1 min purge at 50 mL/min), and the volatiles were transferred, with a split-ratio of 1:13.5, to the head of the ^{1}D column (injection).

3.4.1. A) HiSorb reproducibility

Three HiSorb probes coming from different manufacturing batches were used in the same conditions (1 mL sample, 30 min extraction at 60 °C) to investigate their reproducibility.

3.4.2. SPME

SPME fibres were conditioned as recommended by the manufacturer (30 min at 250 °C for PDMS and 30 min at 270 °C for DVB/CAR/PDMS). As the needle protecting the fibre is not sealed, fibres are preconditioned before each extraction (5 min at 270 °C under 50 mL/min flow).

The sample preparation and extraction were executed in the same way as for HiSorb.

As the nitrogen flow in the drying station is not adjustable and the SPME fibres are quite fragile, they were not dried prior desorption.

SPME fibres were desorbed and focused on a cold trap (see above) for 4 min without purge step. The desorption of the trap and the injection were carried similarly as for HiSorb.

3.4.3. Multi-vial multi-cumulative trapping (MV-MCT)

Several vials of the same sample were extracted in the conditions described above. Analytes from each extraction were desorbed and accumulated on the cold trap to the analytes from the previous extractions. Once the desired number of extractions was reached, all accumulated analytes were then desorbed at once in the same conditions as described above

Two different MV-MCT modalities were tested, three times ten minutes (3 x 10') and two times thirty minutes (2 x 30') of extraction. They were compared to the single-vial extraction for an equivalent duration (*i.e.*: 30 minutes and 60 minutes respectively.

3.4.4. Packaging study

The (3 x 10') MV-MCT extraction conditions were used to characterise coffee samples with the different packagings.

3.5. Chromatographic separation

Comprehensive two-dimensional GC separation was achieved on Shimadzu GCMS-TQ8050 NX system with INSIGHT flow modulator (SepSolve Analytical Ltd) using helium as carrier gas. The first column used was a BPX-5 (Trajan Scientific, 20 m × 0.18 mm i.d. × 0.18 µm) equivalent to a 5%phenylpolysilphenylene-95%siloxane. The second column was a BPX-50 (Trajan Scientific, 5 m × 0.25 mm × 0.25 µm) equivalent to a 50%phenylpolysilphenylene-50%siloxane. Data were acquired using Shimadzu GCMSolution version 4.45 from Shimadzu and VUVision 3.1.0 from VUV Analytics, Inc.

Temperature and flow programs are specified in the Table 8.

Table 8 GC×GC separation parameters

GC×GC SEPARATION PARAMETERS

COLUMNS' FLOWS		
^{1}D flow	0.6 mL/min	
^{2}D flow	16 mL/min	
Bleed line flow	0.6 mL/min	
FLOW MODULATOR PARAMETERS		
Modulation time	3.5 s	
Flush time	100 ms	
OVEN PROGRAM		
	From: 40 °C	During: 5 min
Ramp: 6 °C/min	To: 180 °C	
INJECTOR (^{1}D COLUMN) PRESSURE PROGRAM		
	From: 34.6 psi	During: 5 min
Ramp: 0.7 psi/min	To: 59.0 psi	
APC 1 (^{2}D COLUMN) PRESSURE PROGRAM		
	From: 26.5 psi	During: 5 min
Ramp: 0.56 psi/min	To: 46.3 psi	
APC 2 (BLEED LINE) PRESSURE PROGRAM		
	From: 21.7 psi	During: 5 min
Ramp: 0.48 psi/min	To: 38.5 psi	

Detection was achieved by both MS (Shimadzu) and VUV detectors (VGA-101, VUV Analytics). In the configuration used, the end of the ^{2}D column was connected to a T union that was connected to the MS and the VUV respectively by a 1.1 m x 0.1 mm ID and a 0.912 m x 0.25 mm ID capillary. This configuration splits the ^{2}D eluent to send about one-third to the MS and the two-third remaining, to the VUV. Instrumental parameters for both detectors can be found in Table 9.The splitting between the two detectors was necessary to meet the flow limitations on the MS side (about 7 mL/min). For this thesis the data acquired on the VUV side could not be used for time and technical reasons.

Table 9 Instrumental parameters for detectors

MS DETECTOR	
ION SOURCE TEMPERATURE	200 °C
INTERFACE TEMPERATURE	250 °C
IONISATION VOLTAGE	70 eV
MASS-TO-CHARGE RATIO RANGE	35-350 m/z
SCAN SPEED	20 000 amu s^{-1}
VUV DETECTOR	
ACQUISITION FREQUENCY	50 Hz
PRESSURE	0.35 psi
WAVELENGTH RANGE	125-430 nm

3.6. Data treatment and statistical analysis

The software ChromSpace and ChromCompare+ from SepSolve Analytical Ltd. were used to integrate and elaborate the results. Morpheus (https://software.broadinstitute.org/morpheus/), Excel (Microsoft Office, version 2016), Minitab (Minitab LCC, version 19.2020.1) and RStudio (RStudio PBC, version 1.4.1717, R version 4.1.0) were used for other statistical and visualisation treatments.

4. Results and discussions

4.1. HiSorb reproducibility

Before continuing with the research of optimal conditions, the reproducibility of HiSorb of three different HiSorb was assessed by extracting under the same conditions the same coffee sample. The results were deemed satisfying (between 10-30% of variation [relative standard deviation] for all untargeted features, which also includes undesirable compounds) considering the wide dynamic concentration range observed and reported on the literature [1,129,130].

4.2. Optimisation of extraction conditions

The research of the optimal conditions of extraction with HiSorb took place in two experiments. The first studied the impact of both the sample volume and the extraction time on the volatile profile. The second used the optimal extraction parameters found in the previous experiment to study the extraction temperature. Unless otherwise stated, analyses were performed in triplicate. Table 10 resumes the different parameters studied.

Table 10 Experimental parameters for optimization of the extraction conditions

PARAMETERS STUDIED	SAMPLE VOLUME (ML)	EXTRACTION TIME (MIN)	EXTRACTION TEMPERATURE (°C)
VOLUME AND EXTRACTION TIME	1 and 4	10, 30, 40 and 60	50
EXTRACTION TEMPERATURE	1	30	30, 40, 50, 60 and 75

The selection of the parameter values to be tested was based on literature data where coffee brew analysis by HCC extraction used a temperature between 50 and 80 °C, an extraction time between 10 and 60 °C and a sample-HS ratio ($\beta_{s/HS} = \frac{V_s}{V_{HS}} = \frac{V_s}{V_{total} - V_s}$) between 1.4 and 10 (in this project, the ratios were 19 for 1 mL and 4 for 4 mL in 20 mL) [15,79,132,133,91,93,94,103,106,118,120,131].

Pre-equilibration time and agitation rate were not investigated in this project. Both parameters positively influence the equilibrium in the HS and the sorbent extraction and should therefore be examined. However, very few studies consider pre-equilibrium as a variable and subsequently little information is available. In this study, it is considered that the sample-HS equilibrium is reached after the preparation time (20 min at 350 rpm) although this statement should be verified (*e.g.*: by varying the pre-equilibrium time and observing the differences) [134,135].

Regarding the drying step performed between extraction and desorption of the HiSorb probe, it was decided to add this step to eliminate the condensation forming on the probe and thus avoid water

injection in the GC system. The impact of the drying step on the extraction profile was not investigated but the desorption phenomenon is a slow process and even more at ambient temperature. However, a slight loss of high volatiles (assumed to be negligible in this context) may be possible because of their high Henry's constants. This impact could be evaluated by varying the different associated parameters (time and withdrawing rate) and observing the potential signal differences on the same extraction [134].

Targeted analysis (eleven selected compounds covering the whole chromatogram) was initially chosen to compare the different conditions. This approach allows comparison for a relatively simple data processing. However, the quality of the comparison will be linked to a limited number of monitored peaks. Moreover, the data processing was extremely time-consuming (two weeks for 27 files). Luckily a novel software (ChromCompare+) was kindly made available from the company, simplifying, and automating the data processing. This software was used to perform non-targeted analysis covering the entire chromatogram.

The untargeted analysis considers all peaks without any restrictions. This algorithmic technique allows the discovery of unexpected compounds with little intervention from the user and a better automation (one night for 27 files). Hence, more advanced statistical analysis such as data mining can be executed on a more representative data set. In this study, "tile sum" algorithm was used for the untargeted integration. This algorithm cuts the chromatogram in "tiles" of known size and calculates the total abundance of every single mass channel within each tile. the abundance for a unique mass in a given tile is called "feature".

4.2.1. Influence of sample volume and time

The results of the first experiment studied the impact of the sample volume and the extraction time on the extraction. Figure 12 displays the heatmap of the hundredth most significant features (in abscise) selected by the "feature discovery"[14] tool of ChromCompare+. This selection, although not theoretically mandatory at this stage, was technically necessary because the amount of information made it difficult to use certain computer tools. Heatmaps representation allows an easy visualisation of the data. Heatmaps presented in the following figures only show the averaged value of the three replicates for each condition tested. Detailed values are provided in Annex 1.

[14] Proprietary multivariate fisher ratio analysis algorithm

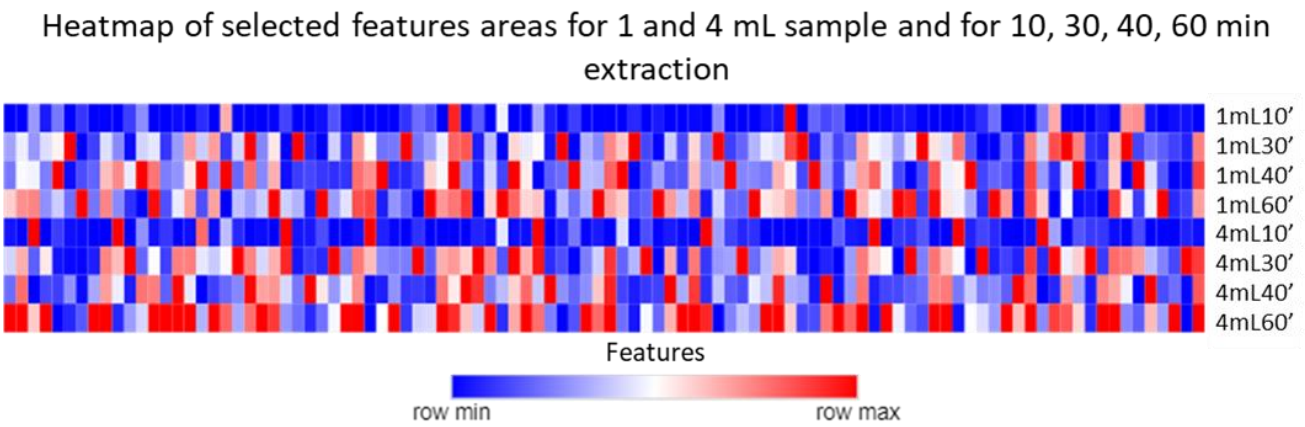


Figure 12 Heatmap of average areas of selected features for 1 and 4 mL sample and for 10, 30, 40, 60 min extraction at 50 °C after 20 min pre-equilibration time (n=3)

As can be observed from Figure 12, the sample volume does not affect the extraction substantially, except for a slightly better extraction yield at 60 minutes with 4 mL of coffee. Concerning the extraction time, a considerable difference between 10 and 30 min then a plateau is apparently reached (excepted for extraction made with 4 mL of sample and 60 min of extraction time that seems slightly higher).

To get a better idea of the performance gained applying the different conditions, areas can be expressed relatively to the respective areas obtained with the 1 mL 10 min modality. Box-and-whisker plot can be plotted to obtain a better visualisation of the calculated ratios (Figure 13).

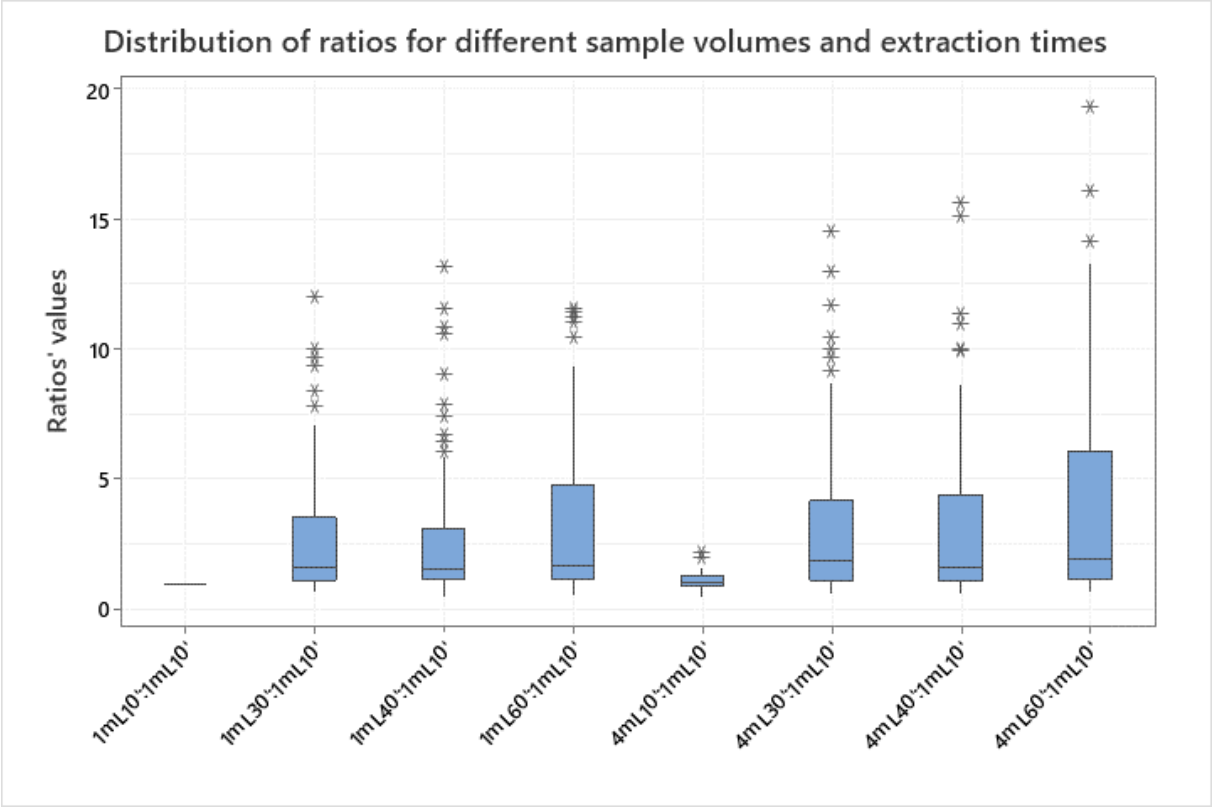


Figure 13 box-and-whisker plot of ratios relative to 1mL10 min modality for 1 and 4 mL and for 10, 30, 40 and 60 min extraction at 50°C

Figure 13, seems to confirm the trend that the extraction yield is not considerably impacted by the sample volume. Considering the absorption phenomenon of PDMS (Equation 12) at constant sorbent volume, it is better to minimise the sample volume to decrease the sample-sorbent ratio ($\beta_{s/so} = \frac{V_s}{V_{so}}$). This increases the recovery of more polar compounds with no adverse effect for less polar ones. In addition, Bicchi *et al.* in 2005 observed that higher recoveries of VOCs were generally obtained with a higher HS phase ratios ($\beta_{s/HS} = 19$ in their study) which supports the use of 1 mL of sample in a total vial volume of 20 mL [136].

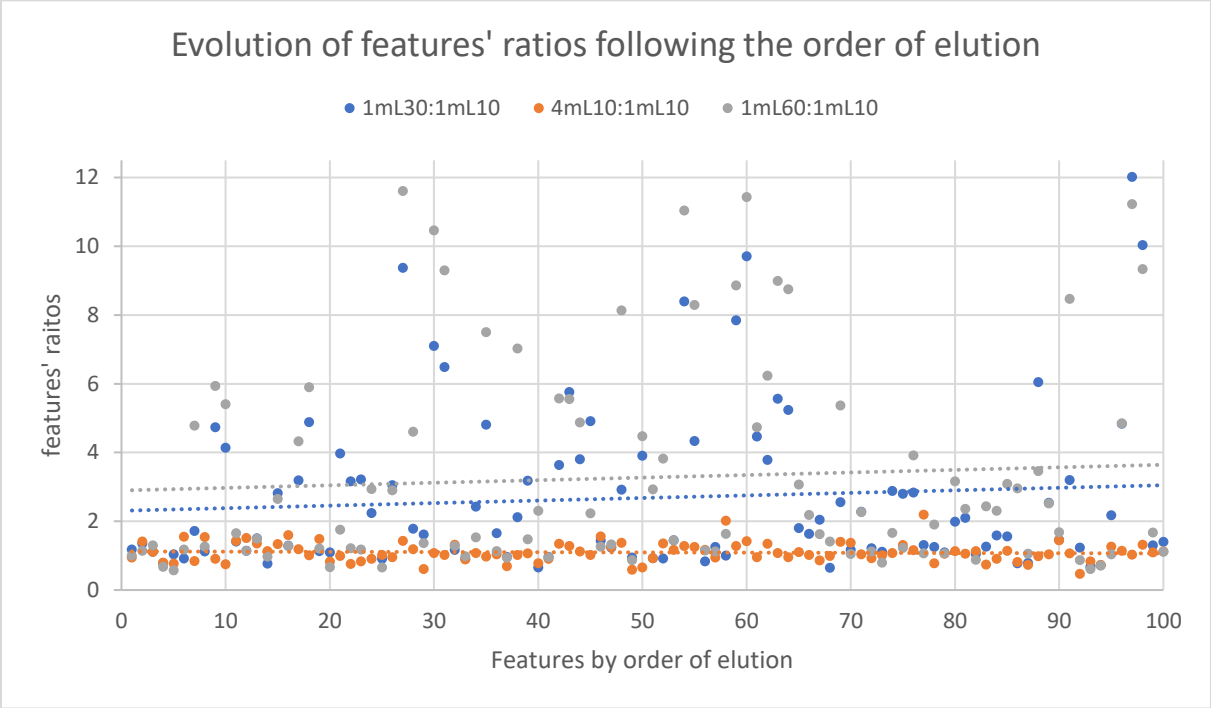


Figure 14 Plot of features' ratios for volume variation (1, 4 mL with 10 min extraction orange) and extraction time variation (1 mL with 30 min (blue) and 60 min (grey) of extraction) by order of elution

Figure 14 displays the ratios of different features obtained with different extraction conditions by increasing order of elution. As expected, the volume seems to have no influence on the volatility range of the extracted molecules. Indeed, the ratios remain stable on the whole range (orange dots and line). According to Equation 14, an increase in sample volume leads to a decrease of $\beta_{HS/s}$ and a theoretical rise in HS concentration. However, the same equation states that less volatile compounds (*i.e.*: low p^0) have a higher $K_{HS/s}^{-1}$ ratio. Therefore, it could be expected that the decrease of $\beta_{HS/s}$ will have less impact on more volatile compounds (as $\left|K_{HS/s}^{-1}\right| \gg \beta_{HS/s}$) than less volatile compounds. In this case, no great differences are visible. It is suggested that the volatility range of observed compounds is too small to observe a difference.

As expected, it is observed that the longer is the extraction time, the higher is the amount of extracted compounds. This trend is supported by the literature [136,137]. Although 60 minutes of extraction gives a better response for most of compounds, the gain between 30, 40 and 60 minutes is considered not worth the additional required time.

For less volatile molecules, on the contrary, the extraction time seems to slightly increase their extraction, as it can be deducted from the barely positive lines. This trend seems similar (similar slopes) for both 30 (blue dots and line) and 60 min (grey dots and line). This was expected since less volatile compounds (small Henry's constants in aqueous solution) have a lower ability to be volatilised into the HS and are extracted more slowly than more volatile compounds. This has already by observed in the literature [16,138,139].

A sample volume of 1 mL and an extraction time of 30 min after 20 min of pre-equilibration was selected for further analysis.

4.2.2. Influence of extraction temperature

The second experiment studied the impact of the extraction temperature on the extraction. Figure 15 shows the heatmap of the average areas of each feature of the hundredth most important features (in abscise) selected by the "feature discovery" tool of ChromCompare+ for 1 mL sample extracted 30 min after 20 min pre-equilibration at 30, 40, 50, 60 and 75 °C. It looks visually that extraction at 30 and 40 °C yields similar results, while extraction at higher temperatures leads to higher yields, as expected. Detailed values can be found in Annex 2.

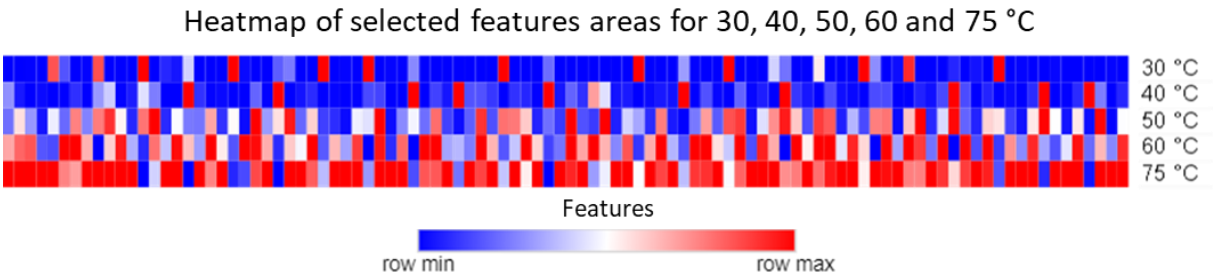


Figure 15 Heatmap of average areas of selected features for 1 mL sample extracted 30 min after 20 min pre-equilibration time for different extraction temperatures (n=3)

The analysis of the distribution of ratios relatives to 30 °C (Figure 16) clearly pinpoints an increase in the amount of extracted analytes with the temperature. This trend can be explained by the Antoine's law which describes an exponential relationship between the vapor pressure and the temperature; and by the partition constants $K_{so/HS}$ and $K_{HS/s}$ that are influenced directly (Equation 9 and 10) and indirectly by increasing Henry's constants ($\ln H_i = A - \frac{B}{T} + C \ln T$) [32,140]. This can therefore have a negative effect on the extraction by decreasing the constant $K_{so/HS}$ which favors the desorption of analytes from the fibre. Bicchi *et al.* (2005) observed this phenomenon for VOCs with low affinity for the fibre (low $K_{O/W}$) [136]. In this case, the analysis is untargeted and a detailed characterisation at this stage is out of the scope of this work. Nevertheless, from a careful visual analysis of the heatmap it can be noticed that the extraction efficiency at 75°C versus 60°C decreases slightly for certain features.

Figure 17, presenting the evolution of features' ratios with elution order for the different temperatures, indicates that the higher is the temperature, the better the extraction of highly volatile compounds (the slope of the trend line decrease at 60°C (yellow dots and line) and 75 °C (blue dots and line)). Interestingly at 50 °C (grey dots and line), the trend is inversed and presents a slightly positive slope.

Concerning the extractions at 30 and 40 °C, a difference (ratio 40:30, orange dots and line) is present but not substantial (Q1 = 0.93; median = 1.32; Q3 = 1.52).

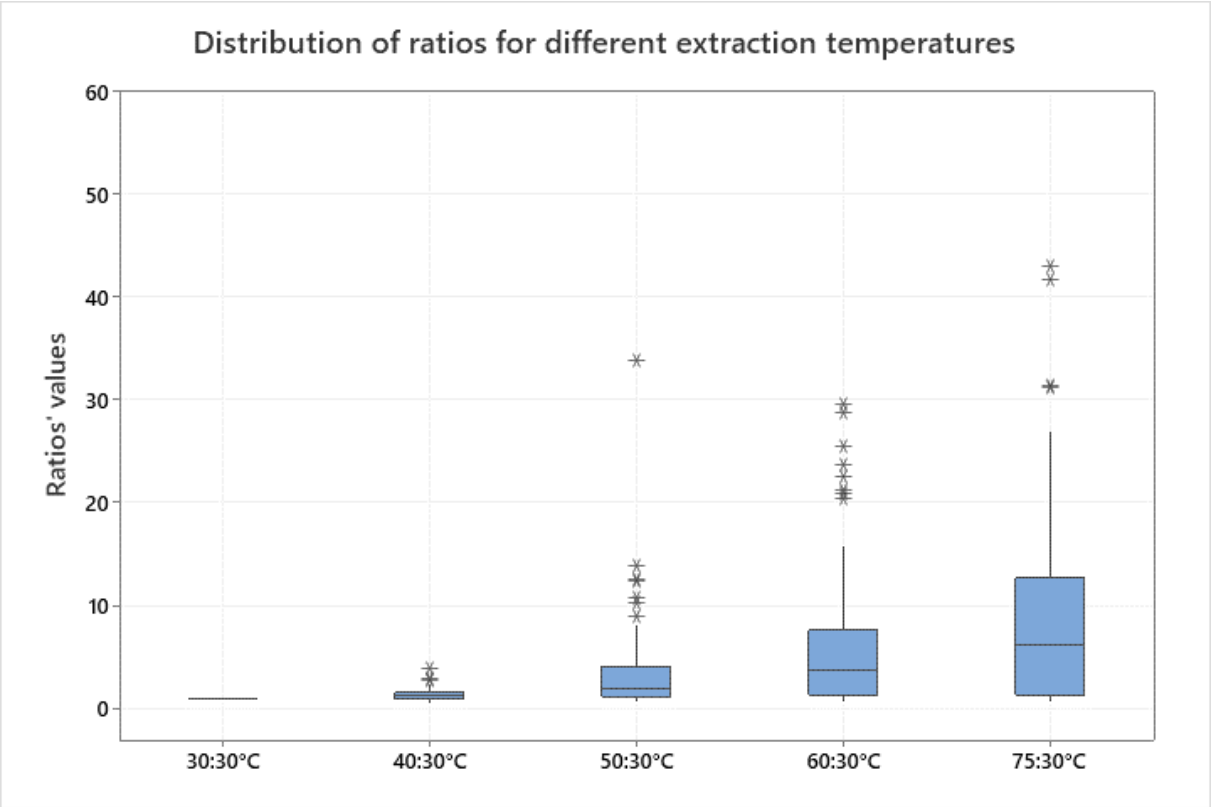


Figure 16 box-and-whisker plot of ratios relative to 30 °C modality (1mL, 30 min extraction) for 40, 50, 60 and 75 °C [15]

[15] Feature 58 not displayed for 50:30°C, 60:30°C, 75:30°C series

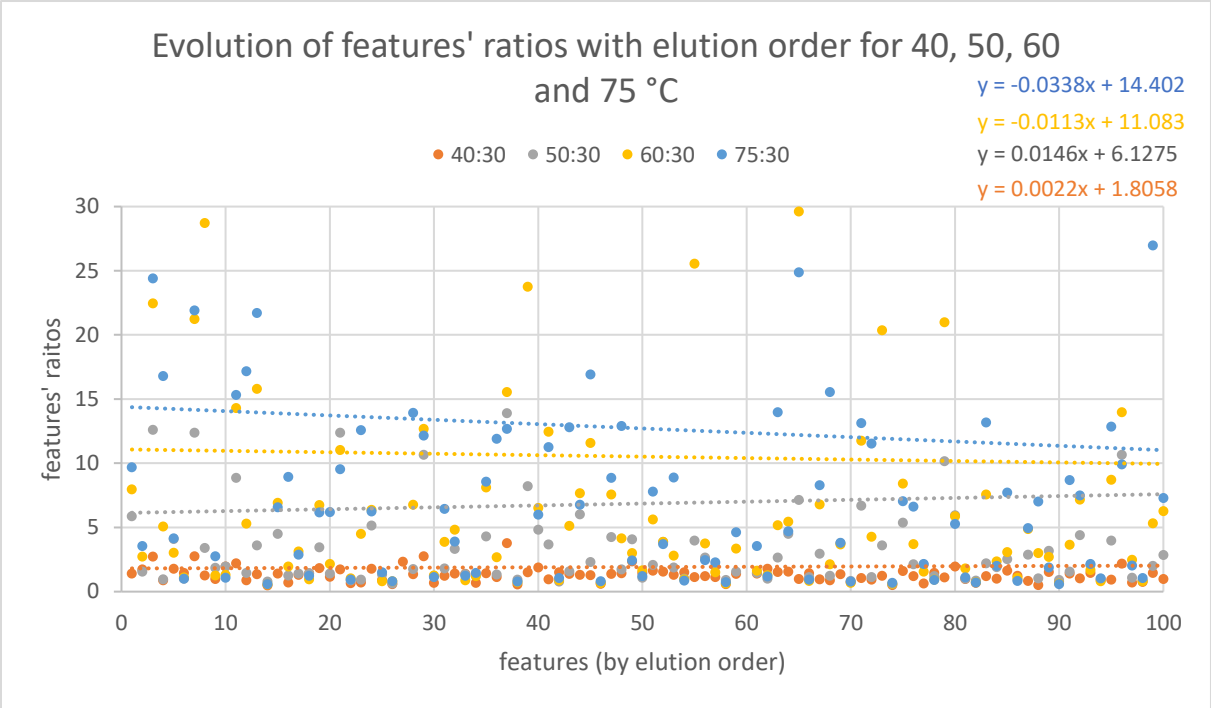


Figure 17 Evolution of features' ratios with elution order for 40, 50, 60 and 75 °C [16]

Although the extraction yield is the highest at 75°C (and maybe greater at higher temperatures), the preferred consumption temperature range of hot beverages is 55-71 °C ("130 to 160 °F") [141]. An extraction temperature of 60°C was thus selected as it is more representative of the consumption conditions. The loss of sensitivity obtained by these conditions can be estimated by calculating the ratios between 60 and 75 °C for each feature. The median of these ratios is 0.87 (Q1 = 0.60; Q3 = 1.09), which means that extracting at 60 °C leads to a loss of 13% of sensitivity compared to an extraction at 75 °C (other parameters being unchanged).

An extraction of 30 min at 60 °C with a sample volume of 1 mL after 20 min of pre-equilibration was selected for further analysis.

[16] Adapted vertical axis for the sake of clarity

4.3. Tool comparison and multi-cumulative trapping experiments

Once the optimal extraction conditions (for HiSorb) were determined, HiSorb performances were compared with SPME fibres (PDMS and DVB/CAR/PDMS) (n=3). The first comparison between PDMS fibre and HiSorb allows the observation of the impact of the sorbent ratio and volume on the analytical performance while the comparison with the DVB/CAR/PDMS fibre evaluates the difference with the most used tool in aroma analysis and the new HiSorb.

Additionally, the use of HS multi-cumulative trapping (MCT) as the extraction method was evaluated. MCT extraction was proposed for the first time in 2000 by Lipinsky for SPME analysis of pesticides in water. This approach has the advantage of increasing the amount of analytes transferred to the separation system in one injection and thus it increases the sensitivity of the analysis. A more systematic investigation, recently carried out by Mascrez and Purcaro (2020) showed that, for adsorption-type sorptive extraction, using single-vial (SV)-MCT for shorter extraction time increases the sensitivity with particular benefits for the semi-VOCs. Moreover, the extracted information for cross-sample investigations compared to the equivalent single time extraction was significantly more relevant [26,27,142].

In contrast to these studies, in which SV-MCT was used, in this thesis the extractions were done in different vials (multi-vial (MV-) MCT) due to the impossibility of performing SV-MCT using HiSorb (after the first extraction the septum remains definitively open).

MV-MCT extractions (3 × 10 min and 2 × 30 min) were performed with HiSorb and SPME fibres (n=3).

Table 11 resumes the modalities of the different parameters studied and Figure 18 show a 2D contour plot chromatogram as an example of the separation obtained.

Table 11 Modalities of the different parameters for the tool comparison and multi-cumulative trapping experiments

EXPERIMENT	TOOL	SAMPLE VOLUME (ML)	EXTRACTION TIME (MIN)	EXTRACTION TEMPERATURE (°C)
SINGLE EXTRACTION	HiSorb and SPME (PDMS, DVB/CAR/PDMS	1	30	60
MV-MCT	HiSorb and SPME (PDMS, DVB/CAR/PDMS	1	3 × 10 min and 2 × 30 min[17]	60

[17] Analysis performed in 2 replicates for DVB/CAR/PDMS 2 × 30'.

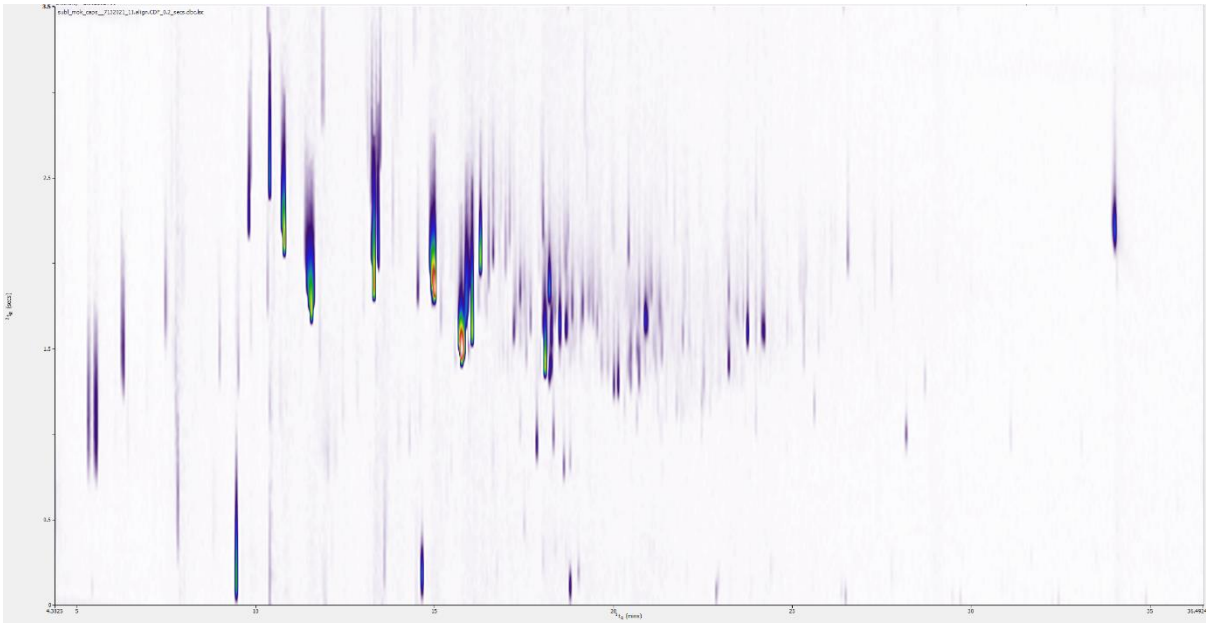


Figure 18 Chromatogram of aluminium caps "subl_mok" coffee extracted 3 x 10' at 60 °C by HiSorb

4.3.1. Extraction tools comparison

The comparison between HiSorb and PDMS fibres can be visualised by the heatmap of the average areas of each feature of the hundredth most important features (in abscise) selected by the "feature discovery" tool of ChromCompare+. (Figure 19). Detailed values can be found in Annex 3.

It directly appears that HiSorb gave a higher extraction than the SPME fibres. This is confirmed by the ratios' distribution through a box-and-whisker plot (Figure 20). Indeed, the SPME fibres gave ratios in general less than one meaning that the extraction is less efficient than with HiSorb. The sorbent volume (64 and <1 µL for HiSorb and SPME, respectively) could mainly explain this difference.

For the PDMS (sorbent operating in absorption mode), an increase in volume reduces the phase ratio which, in accordance with theory, increases the recovery of compounds with a lower $K_{O/W}$ (see Figure 6). In addition, an increase in the volume of sorbent increases the amount of extracted analytes according to Equation 12.

In contrast, DVB/CAR/PDMS fibre works in adsorption mode, which is a surface phenomenon. Previous studies demonstrated better extraction performance for VOCs extraction of DVB/CAR/PDMS over PDMS in SPME [138,143]. However, the comparison between DVB/CAR/PDMS SPME and HiSorb (PDMS sorbent) is difficult since the coating and the volume are different. Nevertheless, since at the moment of this study, HiSorb probes were only available with PDMS sorbent, the goal was to evaluate whether the increased extraction yield linked to the higher sorbent volume may compensate for the different selectivity linked to the chemical nature of the sorbent. In fact, it can be observed in Figure 19, that while SPME PDMS gave much lower extracted features compared to SPME DVB/CAR/PDMS,

HiSorb provided a much higher intensity for almost all the considered features compared to SPME DVB/CAR/PDMS.

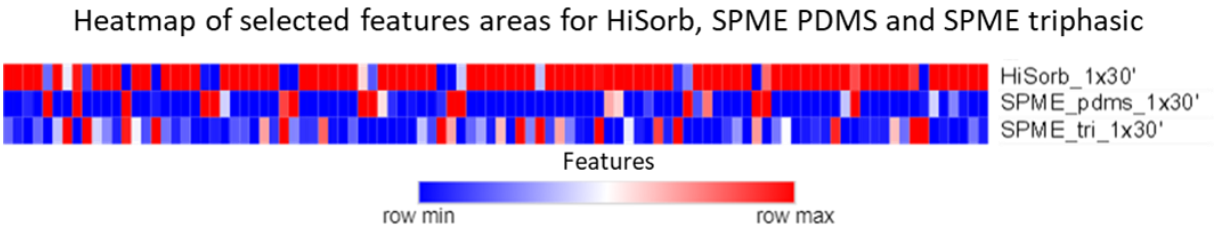


Figure 19 Heatmap of average areas of selected features for 1 mL sample with 30 min extraction after 20 min pre-equilibration time at 60 °C for HiSorb, SPME PDMS and DVB/CAR/PDMS (n=3)

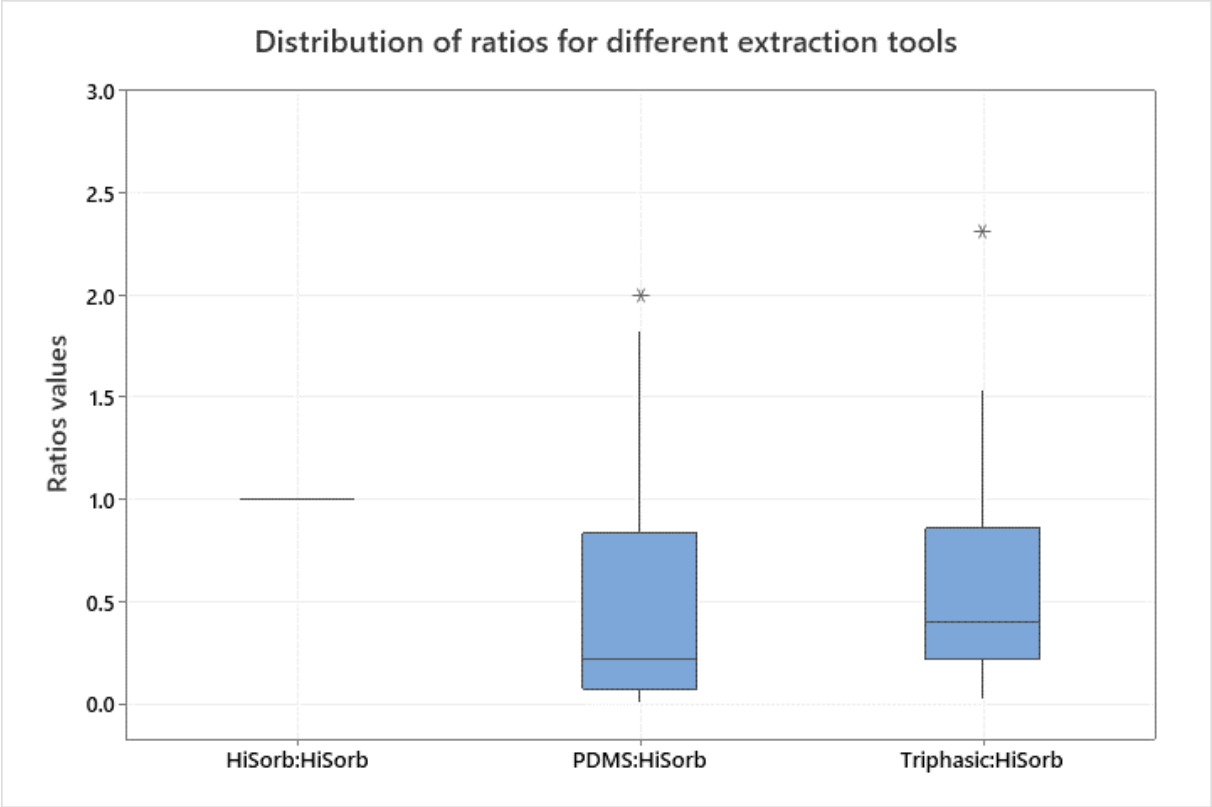


Figure 20 box-and-whisker plot of ratios relative to HiSorb extraction (1 mL, 30 min extraction at 60 °C) for HiSorb, PDMS and SPME DVB/CAR/PDMS ("triphasic") [16]

4.3.2. Multi-vial multi-cumulative trapping

MV-MCT experiments consist of a repetition of identical extraction on different aliquots of the same sample. The analyte content of each extraction is focussed on a cold trap before a unique injection into the GC system. It is therefore expected that the quantity of extracted analytes increases arithmetically with the number of extractions (*e.g.*: $n_{3\times10\,min} = 3 \times n_{1\times10\,min}$). The goal is to evaluate whether the use of MV-MCT with shorter extraction time will improve the overall yield compared to the equivalent extraction time in a unique extraction.

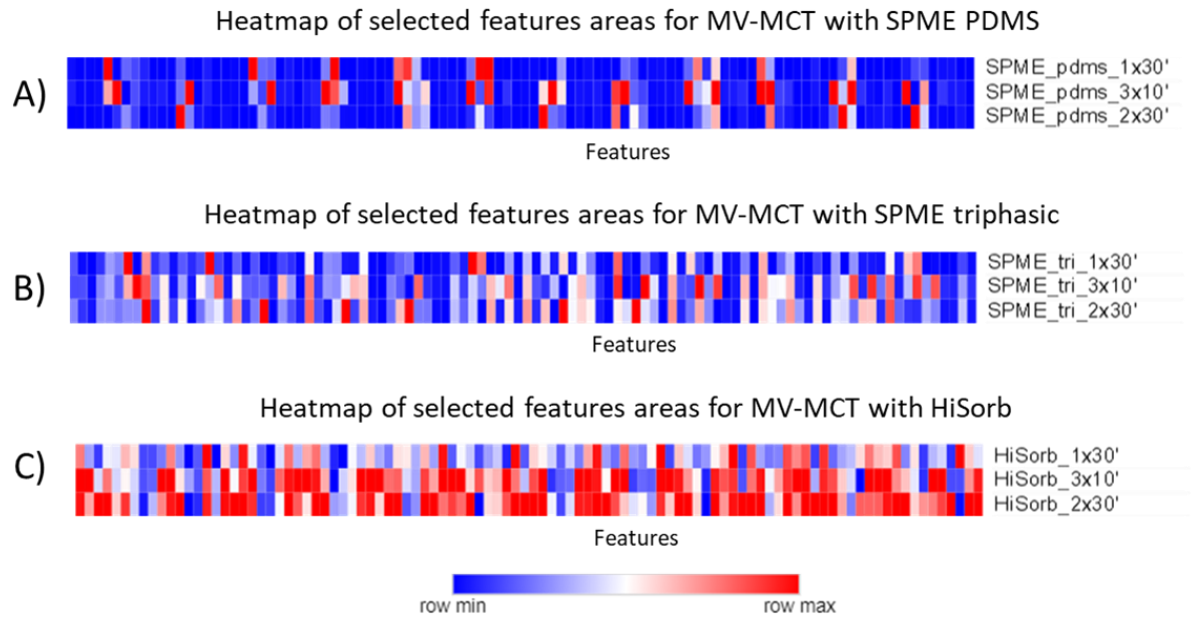


Figure 21 Heatmap of average areas of selected features for 1 mL sample with 1 × 30 min, 3 × 10 min and 2 × 30 min extraction at 60 °C after 20 min pre-equilibration time for SPME PDMS (A), SPME DVB/CAR/PDMS ("triphasic") (B) and HiSorb (C) (n=3) [18]

[18] Excepted for 3 × 10 and 2 × 30 min with SPME DVB/CAR/PDMS which was done in duplicate

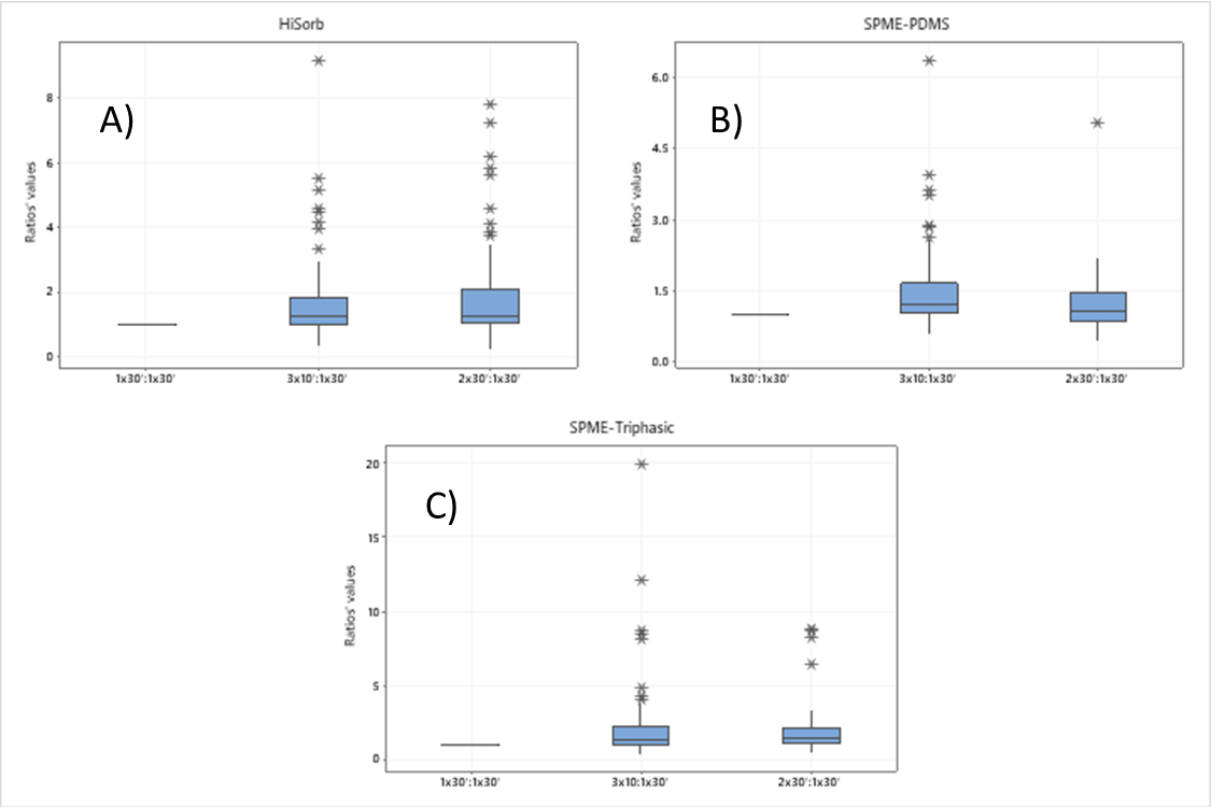


Figure 22 box-and-whisker plot of ratios relative to 1 x 30 min for HiSorb (A), SPME PDMS (B) and SPME DVB/CAR/PDMS ("Triphasic") (C)

Figure 21 shows the heatmap of the average areas of each feature of the hundredth most important features (in abscise) selected by the "feature discovery" tool of ChromCompare+ for 1 mL sample with 1 × 30 min, 3 × 10 min, and 2 × 30 min extraction at 60 °C for both SPME PDMS and DVB/CAR/PDMS, and HiSorb. Figure 22 displays box-and-whisker plots of ratios relative to 1 × 10 min modality. The 3 × 10 min modality seems slightly better than 2 × 30 min and much higher than 1 × 30 min. This trend was already observed for DVB/CAR/PDMS [26,28]. Detailed values can be found in Annex 3.

Moreover, the increase observed with multiple shorter times may be explained by the primary extraction of volatiles equilibrated in the HS during the first minutes (most probably up to 10 min). Afterwards, the HS is impoverished, and the extraction rate slows down. Since mass transfer from aqueous sample to the HS and then to the sorbent is a slow phenomenon, the amount of sorbed analyte in the second part of the extraction time would be lower than in the first ten minutes. Thus, extracting three times the first ten minutes would give a higher signal than extracting two times thirty minutes.

Concerning the volatility range of extracted compounds and as discussed above (4.2.1 Influence of sample volume and time), higher extraction time leads to better extraction of less volatile compounds. This is confirmed by Figure 23 showing the evolution of average features' ratios relative to 1 × 30 min extraction by order of elution (*i.e.*: roughly approximated to decrease of volatility) for HiSorb extraction. Indeed, the less volatile compounds (represented by the features with a higher order of elution) seem

less extracted (roughly estimated up to ~-43%[19]) with 3 × 10 min than with 2 × 30 min. On the other hand, more volatile ones are better extracted (up to ~18%[20]) for half the time.

An alternative to avoid weak extraction of less volatile compounds would be to use the 2 × 30 min extraction. However, the gain is not worth the additional analysis time. Another possibility would be to extract 3 × 10 min at 75 °C to conserve analysis time and to compensate for the lack of low volatile analytes (see Influence of extraction temperature). Nevertheless, the analysis of heavier compounds can be done more efficiently by other ways (*e.g.*: DI-HCC, etc.).

A last alternative would be to extract from the same vial to significantly increase the sensibility of low VOCs as Mascrez and Purcaro (2020) observed. However, the HiSorb probes do not allow this possibility. The comparison between MV- and SV-MCT sorptive extraction could only be done by SPME [26,27].

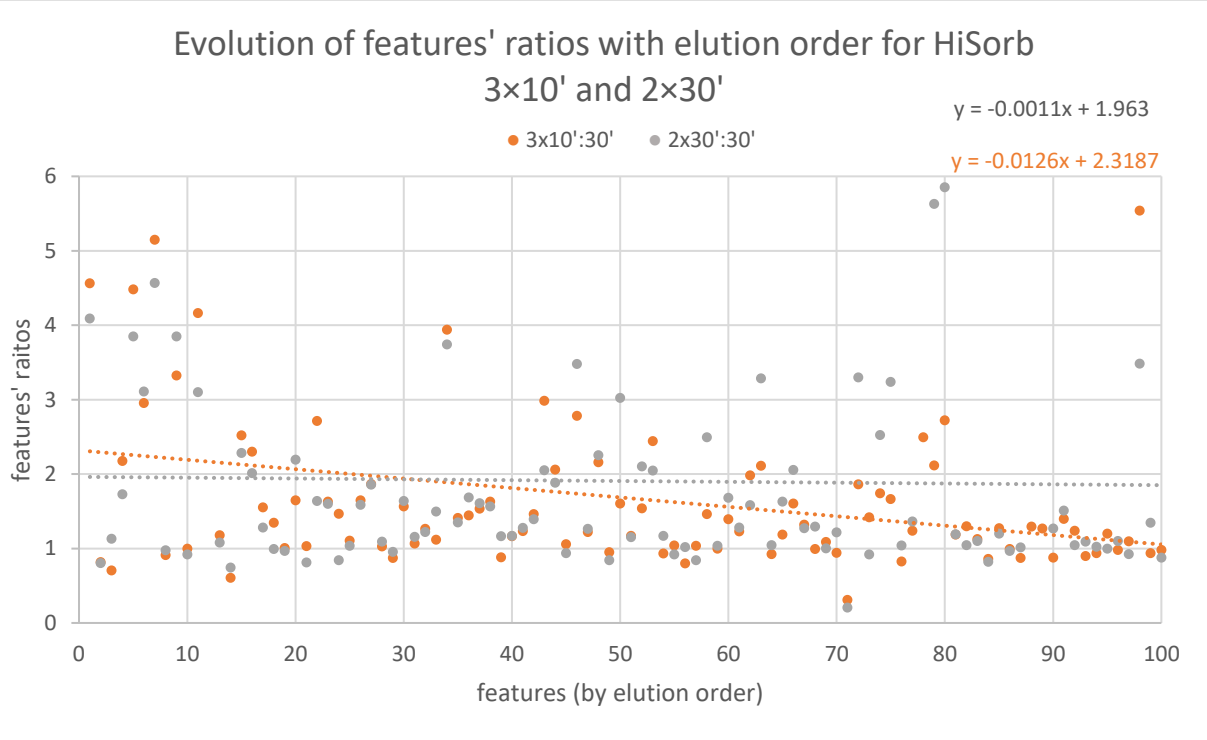


Figure 23 Evolution of features' ratios relative to HiSorb 1 × 30' with elution order for HiSorb 3 × 10 min and 2 × 30 min [16]

[19] Calculated through regression equation by using (g(x)-f(x))/f(x) with f(x), 2 × 30':30'; g(x), 1 × 10':30' and for x = 100

[20] Calculated through regression equation by using (g(x)-f(x))/f(x) with f(x), 2 × 30':30'; g(x), 1 × 10':30' and for x = 0

4.4. Coffee packaging study

In the precedent parts, extraction conditions (time, sample volume, and extraction temperature) were determined (1 mL extracted at 60 °C during 30 min for HiSorb). Then, the efficiencies of MV-MCT extractions and of different coatings and tools were investigated. Extracting three times ten minutes was selected for both HiSorb and DVB/CAR/PDMS SPME fibres. HiSorb giving better extraction profile than other tools.

This part of the study was conducted in partnership with a local roaster who wanted to study the impact of packaging on the aromatic profile of coffee brew. Three types of packaging (aluminium packs and capsules, and biodegradable capsules) were studied. All samples were prepared and stored in the fridge before analysis. All analysis were performed within four days.

Concerning the data treatment, a summary diagram of the techniques used can be found in Figure 24. The integration of data led to more than 450 thousand features. Features selection was performed by the integrated ChromCompare+ tool that uses Random Forest (RF) algorithms. The dataset was firstly separated by the extraction tool used, then data were normalised using Probabilistic Quotient Normalisation (PQN) based on the median followed by a logarithmic transformation to approach the distribution's normality and stabilise the variance. RF was applied after a pre-selection of 50% of the initial features by the discovery tool of ChromCompare+. The features selection aimed to reduce the number of features to find the most discriminant ones. In this case, the final number of wanted features corresponds to the number of samples (23) [27,144,145].

Detailed values can be found in Annex 4 for HiSorb and Annex 5 for SPME.

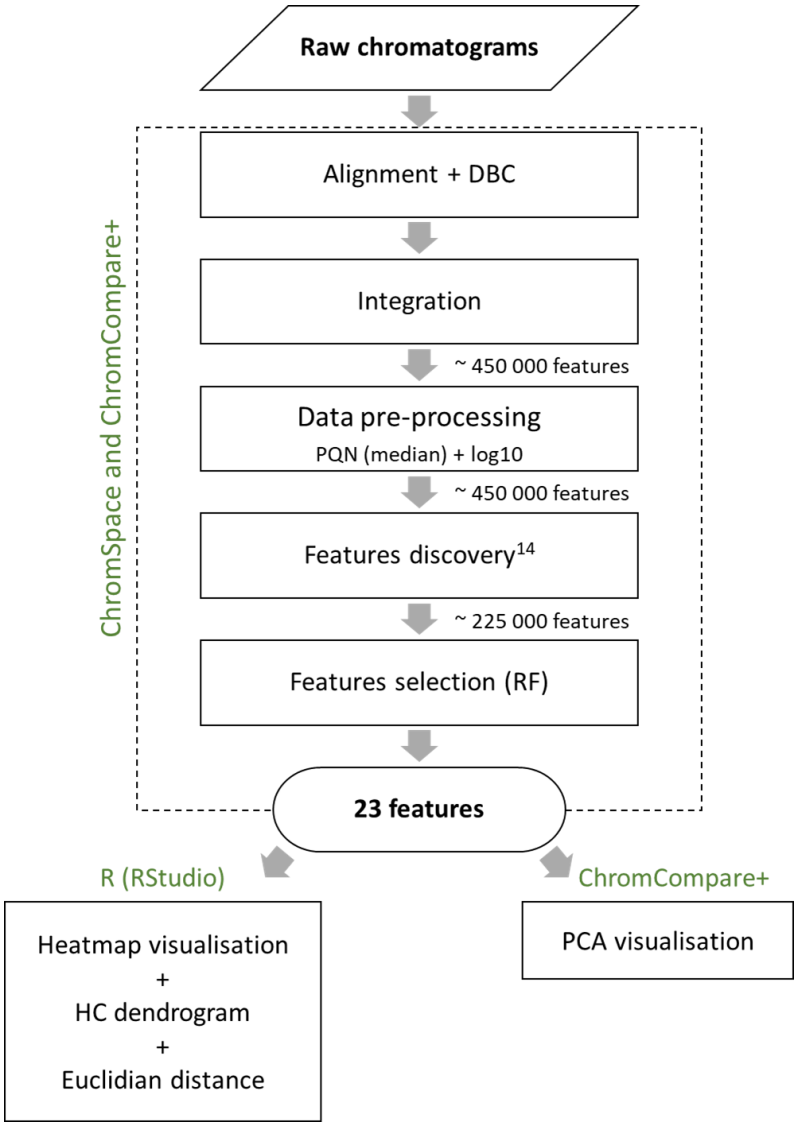


Figure 24 Flow chart of the data treatment (DBC: Dynamic Background Compensation, PQN: Probabilistic Quotient Normalisation, RF: Random Forest, HC: Hierarchical Clustering, PCA: Principal Component Analysis), the used software is displayed in green

Once the features have been selected, the identification of potential associated compounds can be carried out. However, due to lack of time, this was not done.

The PCA plots of the two subsets (Figure 25) shows a clear separation of the sample based on the packaging through the analysis of VOCs with these methods. For both HiSorb and SPME, the first component divides the samples in two groups (biodegradable caps and pack/aluminium caps) while the second component allows the separation between pack and aluminium caps (biodegradable caps being unaffected). This last separation is less pronounced for SPME than for HiSorb.

Heatmap and Hierarchical Clustering (HC) based on Euclidian distance (Figure 26,

Table 12) was also performed to support the above statements. The Euclidian distances confirm the separation between the three groups with a higher efficiency for HiSorb. However, for HiSorb extraction, the three first groups shown by the dendrogram do not directly and correctly separate the three different packaging modalities unlike the SPME extractions. Several explanations such as the impact of decaffeination on aroma ("dis_dk" brand being the unique decaffeinated brand in this experiment) or simply an outlier, can be advanced.

It is also known that the coffee granulometry can affect the aroma profile (see 1.2.4 Brewing methods). To investigate this factor, the coffee particles distributions (especially the d0.1, d0.5 and d0.9 parameters) were measured, although on a limited number of samples since all samples were not available at the moment of the granulometry measurement. The results can be found in Annexe 6. However, the dispersion of particle size does not appear to reflect packaging-related clustering.

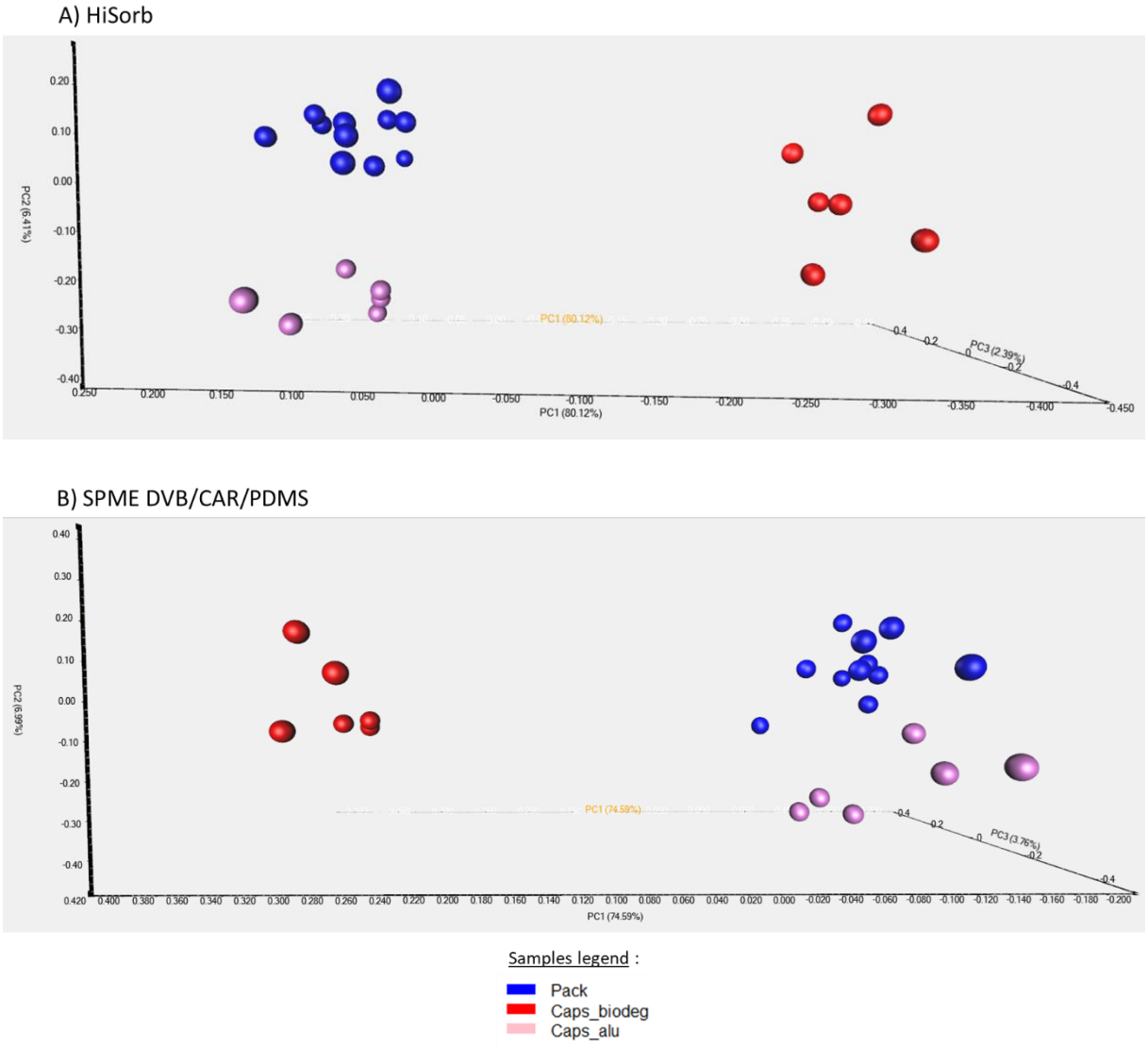


Figure 25 PCA plots of the 1st and the 2nd component of selected feature for A) HiSorb and B) SPME DVB/CAR/PDMS through ChromCompare+

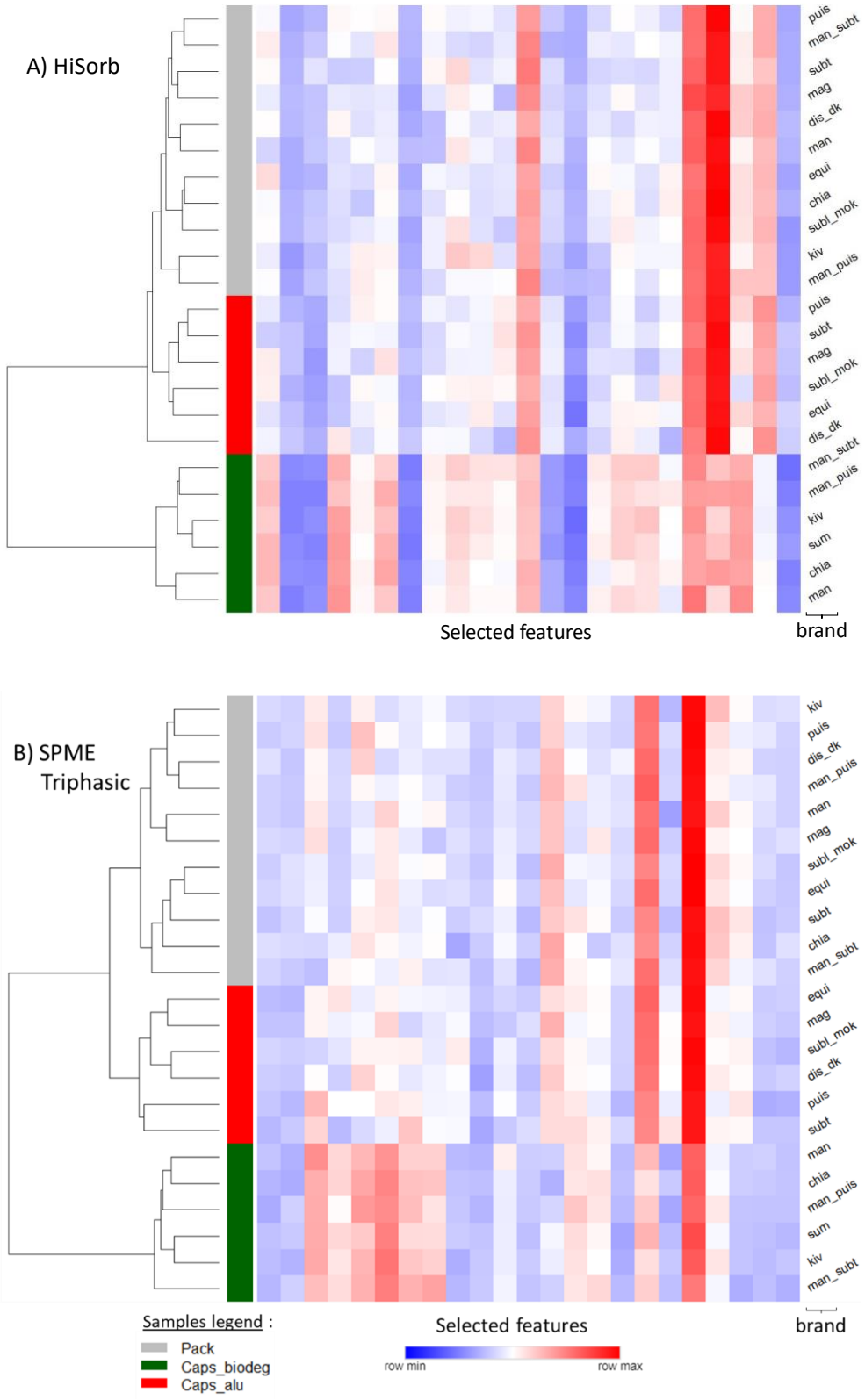


Figure 26 Heatmap and HC dendrogram associated of selected features for A) HiSorb and B) SPME DVB/CAR.PDMS ("triphasic")

Table 12 Table of Euclidian distances

	ALU VS BIO CAPS	ALU CAPS VS PACK	PACK VS BIO CAPS
HISORB	2.9	0.9	3.0
SPME DVB/CAR/PDMS	1.8	0.8	1.7

The last step would have been to identify the associated compounds which has not been done for time constraints. Nevertheless, the evaluation of the overlap of the feature selection was performed based on the ^{1}D and ^{2}D retention time. Strict cross-matching of selected features of both extraction tools leads to only four common extracted compounds. Although, this could have been expected considering the different chemistry of the sorbent. It is interesting to notice that both extraction tools provide a satisfactory separation of the different packaging used. Therefore, it could be concluded that HiSorb and SPME extraction could be complementary for the discriminant extracted VOCs. Hence, combining them together, could increase the level of information obtained. Further investigations must be done to confirm this statement.

5. Conclusions and perspectives

HiSorb, as a novel HS-HCC tool, was successfully applied to the analysis of coffee brew aroma. The optimisation of extraction conditions (time, sample volume, and temperature) was achieved for HiSorb with PDMS coating. The resulting conditions were used to evaluate the analytical performance of the HiSorb and compare it with more common SPME (PDME and DVB/CAR/PDMS) methods. A MV-MCT approach was then explored to evaluate the performance gain over the single extraction approach and compare these the two extraction tools. Finally, MV-MCT extraction was used with both HiSorb and DVB/CAR/PDMS SPME to evaluate and compare the level of information obtained through the study of the impact of coffee packaging on the VOC profile of the brewed beverage.

The use of HiSorb as an automated SBSE alternative through the innovative Centri platform led to much higher extraction yield than other usual SPME tools. The MV-MCT approach has shown that several reduced time cumulative extractions gave overall better response than the equivalent time in single extraction. However, and contrary to what has been recently demonstrated for SV-MCT, this approach increases the extraction of more volatile molecules while having a minor effect on semi-VOCs (for the equivalent time in single extraction). Finally, the MV-MCT approach with both HiSorb and DVB/CAR/PDMS SPME allowed a successful discrimination of the sample packaging through the extracted VOCs profile. Moreover, the two extraction tools seem to be alternative and/or complementary concerning the level of information obtained. However, more investigation is needed to identify the selected compounds and understand their significance in the context of the industrial question asked and if the consumer can perceive such a difference at sensory level.

This thesis raises broader questions that need to be explored further.

Complementarity of HiSorb and SPME appears to be very interesting, and it would be interesting to merge the data matrices for a more comprehensive chemometrics elaboration.

A next step would be the evaluation of the HiSorb performance in DI mode which should provide a better extraction of the semi-VOCs. The potentiality of the trapping system in the Centri platform can also be exploited to merge the HS and DI extractions focussing the VOCs and semi-VOCs extracted in the two different procedures on the cold trap before a single injection into the GC×GC system for a more comprehensive fingerprinting of the brewed coffee aroma.

At the end of this thesis work, new HiSorb probes with different sorbent coatings were made available. Therefore, it would be of high interest to compare them with the present results.

The comparison of SV- and MV-MCT for SPME also merits further research as it has never been explored up to now, although, no real advantages of MV-MCT are foreseen for untargeted analysis but mainly for target trace analysis.

A final perspective, which has been left out due to lack of time and software availability, is to explore the possibilities of the VUV system as a potential tool to aid in identification and quantification.

The first part of this work was presented as poster at the XXIII International Symposium on Advances in Extraction Technologies (Extech 2021). The poster can be found in Annex 7 [146].

6. References

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