Chromatography Technical Note No AS120

SPME workshop focusing on the analysis of Coffee

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Introduction

Klaus Buckendahl, Sigma Aldrich Dan Carrier, Anatune

Anatune ran four SPME workshops from 20th November to 23rd November focusing on providing participants with information on both basic and advanced aspects of SPME, new developments in SPME analysis, including new products and practical sessions dedicated to the analysis of ground coffee. Klaus Buckendahl a SPME specialist from Sigma-Aldrich, who own the Supelco brand, presented on SPME with Dan Carrier running the practical sessions. The workshops at Anatune were a success. Here is some typical feedback obtained:

"Both Klaus and Dan were great and very informative. They were both open to any questions and were happy to help with any queries that anyone had. Also, it was nice to break up the day with talks and practical sessions"

The number of compounds found in coffee increases every year. Today the number is well over 1000, and as analytical techniques become more sensitive, more will be discovered. In the practical sessions, we looked at the effect of salt addition to coffee. After the workshop, we carried out further analysis of coffee to produce this application note. Figure 1 shows the set up for SPME on the Multipurpose Sampler (MPS).

Figure 1 Photograph of SPME (gold bracket) using the Multipurpose Sampler (MPS).

The SPME fibre chosen for this work was Divinylbenzene – Carboxen - Polydimethylsiloxane (DVB/CAR/PDMS), which is considered as a good phase to enrich a broad spectrum of analytes. DVB and Carboxen particles have different size pores to retain analytes by the adsorption onto their surface. The DVB phase contains Meso and Macro pores while the Carboxen has micro pores in addition enabling the efficient retention of small analytes. DVB phase traps the larger molecules with the Carboxen phase trapping the smaller and more volatile analytes. This mechanism ensures an efficient adsorption of analytes but also in turn a good desorption. The PDMS in the fibre acts as a matrix for Carboxen and DVB and does not significantly contribute to the extraction efficiency by absorption. Figure 2 shows a cross section of the DVB/CAR/PDMS Fibre.

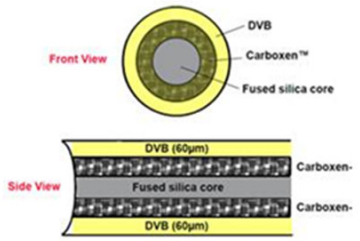

Figure 2 Cross section of the DVB/CAR/PDMS Fibre.

Instrumentation

GERSTEL Multipurpose Sampler MPS 2 XL
Maestro Version 1.4.8.14/3.5
SPME – Sigma Aldrich
Gerstel Cooled Injection System (CIS 4)
Agilent 5975 C inert XL MSD
Agilent GC 7890A

Methodology

1g of ground coffee (Brand X) was weighed out 10 times into individual 20 ml SPME vials. Table 1 shows the description of each vial.

Description	Datafile
Blank	DC231112_03
Blank (duplicate)	DC231112_04
Coffee + salt + acid*	DC231112_05
Coffee + salt + acid (duplicate)	DC231112_06
Coffee + salt + base*	DC231112_07
Coffee + salt + base (duplicate)	DC231112_08
Coffee + salt*	DC231112_09
Coffee + salt (duplicate)	DC231112_10
Coffee + water*	DC231112_11
Coffee + water (duplicate)	DC231112_12
Dry coffee*	DC231112_13
Dry coffee (duplicate)	DC231112_14

Table 1 Sample description of coffee samples analysed by SPME.

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* 5 ml of water was added to all coffee except the last two dry coffee samples. Ortho-phosphoric acid and concentrated sodium hydroxide were chosen as the acid and base. 100 µl of the acid or base was added to the vials. 2 g of sodium chloride was added for the salt samples.

SPME (Headspace) Conditions

Incubation:	5 minutes at 60 °C
Extraction:	10 minutes at 60 °C (agitated)
SPME Fibre:	DVB - Carboxen- PDMS
Desorption:	5 minutes at 270 °C

GC/MS Conditions

Injector:	270°C (Split 5:1)
Column:	DB-Wax 30m x 0.25 mm x 0.5 µm
Flow:	1 ml/min
Temperature program:	35 °C for 4 minutes then 10°C/minute to 220 °C for 7 minutes

Results

Figure 3 shows TIC chromatograms of dried coffee (in duplicate) with a blank injection. Similar reproducibility for the duplicates was obtained across all matrices of coffee. Some of the analytes in the coffee have been tentatively identified.

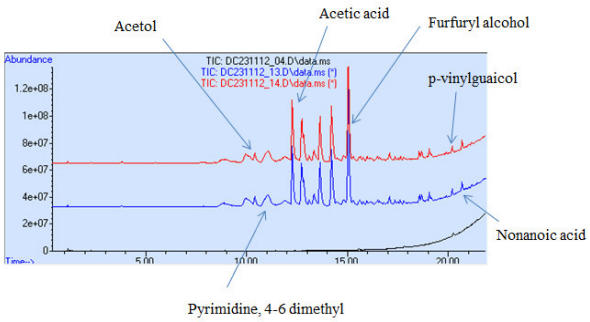

Figure 3 TIC chromatograms of dried coffee (in duplicate) with blank injection.

Figure 4 shows some differences in the analytes detected in wet and dry coffee.

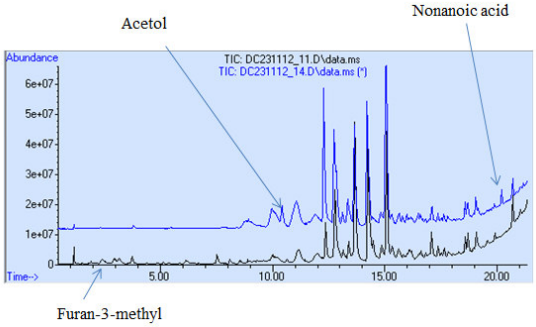

Figure 4 TIC chromatograms of wet (black trace) and dry (blue trace) coffee.

It is thought that water liberates certain analytes from the coffee e.g. Furan-3-methyl. Secondly, the addition of water ensures a more homogeneous sample. However, as you would expect, polar analytes such as Acetol and Nonanoic acid decrease in sensitivity as these analytes remain in the water phase.

Figure 5 shows some subtle differences in analytes detected in wet coffee and wet coffee plus the addition of salt.

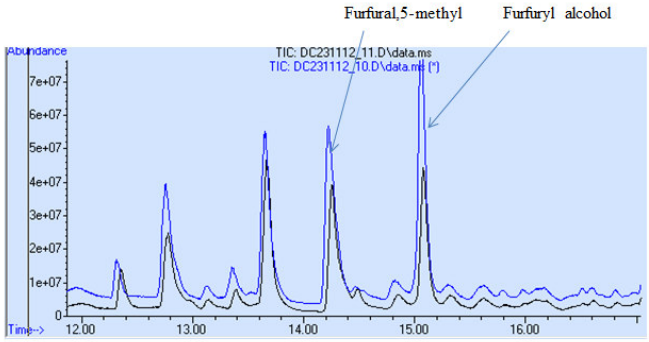

Figure 5 TIC chromatograms of wet coffee (black trace) and wet coffee plus the addition of salt.

Salt is commonly used to decrease the solubility of certain analytes in water and force them into the headspace. Additionally, the saturation with salt sets a defined ionic strength which could give better reproducibility for natural samples with varying salt content.

Figure 6 shows some differences in the analytes detected by varying the pH of the sample.

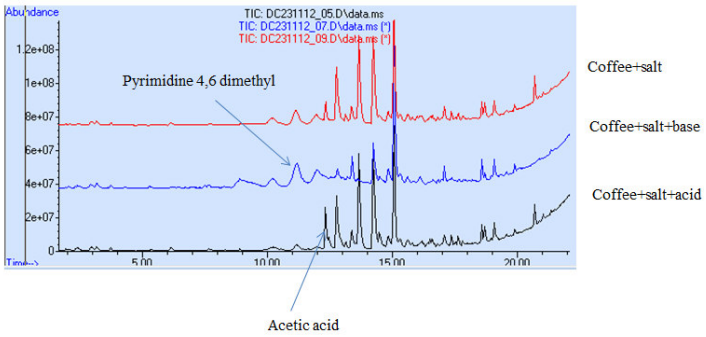

Figure 6 TIC chromatograms of coffee in neutral, acidic and basic conditions.

Acetic acid will be in a neutral state in acidic conditions and therefore will move to a higher degree into the headspace. Therefore, a higher MS response is observed for acetic acid in acidic conditions. Conversely, 4,6 dimethyl pyrimidine will be neutral in basic conditions. Therefore, a higher MS response is observed for 4,6 dimethyl pyrimidine in basic conditions.

Discussion

We originally intended to run the SPME workshop for three days. However, we had to extend to four due to popular demand.

For increased sensitivity of analytes, a longer extraction time (30 minutes) is recommended. Due to time constraints of the workshop, the extraction time was set to 10 minutes. It is known that longer extraction times will allow full equilibration of the headspace with the SPME fibre.

Please contact Anatune, if you are interested in seeing how SPME can help your analysis.

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