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Comparison of extraction techniques for volatiles in a selection of tea samples

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Introduction

There are a number of techniques that can be employed for determination of volatile and semi volatile analytes, most of which can be fully automated with the GERSTEL MPS platform. Whereas static headspace provides information for those compounds present at relatively high levels in samples, other approaches that provide enrichment can be employed to determine those components at trace levels. These compounds may be present as contaminants, or be critical for understanding the characteristic flavour of a product. Simon McInulty, one of our service engineers with considerable experience in volatiles analysis, spent some time in the applications lab earlier this year. Tea samples were obtained locally and a range of techniques employed in order to evaluate the compounds observed. Techniques applied were:

- Static Headspace
- Dynamic headspace (DHS) with a single Tenax trap
- Headspace Solid Phase Microextraction (HS-SPME) using mixed (DVB/Carboxen/PDMS) fibre.

All techniques were run on a GERSTEL MPS robotic pro mounted on an Agilent GC-QQQ, with extractor ion source, using MS1 scan acquisition. Peaks were tentatively identified using NIST mass spectral library search.
The System set up is shown in Figure 1.

Instrumentation

GERSTEL MultiPurpose Sampler (Single head MPS Robotic Pro)
GERSTEL Cooled Injection System (CIS) 4 and Agilent split/splitless inlet
Agilent 7890 GC with a 7000 GC/Q-QQQ
GERSTEL Thermal desorption Unit (TDU)
GERSTEL Dynamic Headspace (DHS) and desorption tunes (Tenax™ TA sorption tubes for TDU)
GERSTEL Robotic SPME and static headspace tools and USM with Gripper for TDU.

Figure 1 MPS robotic pro (tool exchange) and DHS on Agilent GC-MS

Methods

Sample extraction:
Tea samples were analysed dry, with water and as a brew.

Static Headspace: Duplicates samples (1g) were weighed into 20ml vials and 10ml water added prior to incubation at 80°C. Different incubation times were evaluated and 40 minutes was found to give the best response. Duplicate samples of different tea types were analysed under these conditions.

DHS: Tea samples were analysed both dry and following the addition of water. Duplicates of each sample were initially incubated in an agitator at 80°C for 35 minutes, prior to DHS extraction using a Tenax TA trap (650mL at 100 mL/min), with a drying volume of 600ml.

HS-SPME: Duplicates of each sample (1g dry tea) were taken and extracted using a Mixed (DVB/Carboxen/PDMS) fibre at 60 °C.

GC/MS conditions:
DB-Wax 60m x 0.25 mm x 0.25 µm, 1.5mL/min flow. Oven ramp 40°C (2 mins) ramped at 10°C/min to 240°C (held for 8 or 23 mins).

For static headspace and SPME, the Agilent Splitless injector was used. Static headspace was run with a 10:1 split, SPME was run in splitless mode (injector at 250°C). For DHS, the TDU was run in splitless mode and the CIS was run with a 10:1 split. The system was set up to split to an MSD and FID detector at a ratio of approximately: 1:1

Results

Agilent MassHunter software was used to compare the compounds observed using each of the techniques for all of the samples.

Figures 2 shows a comparison of techniques for dry tea. Figure 3 shows some differences in the tea profiles and Figure 4 illustrates the differences obtained for samples with and without the addition of water – using the Earl Grey tea as an example.

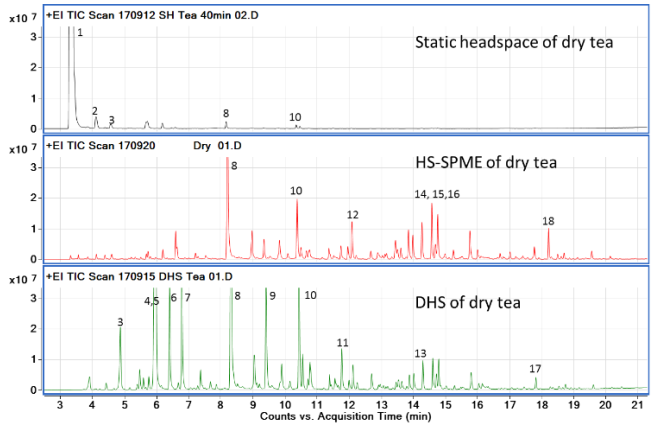

Figure 2: Comparison of Techniques for dry Tea
1) Oxalic acid, 2) Dimethyl sulphide, 3) Isobutanal, 4) 2-methylbutanol, 5) 3-methyl butanal, 6)Furan, 2-ethyl, 7) Pentanal, 8)Hexanal, 9) 1-Penten-3-ol, 10)2-hexenal, 11) 2-penten-1-ol, 12) 5-Hepten-2-one, 6-methyl, 13)2,4-heptadienal, 14) 3,5-octadien-2-one, 15)Benzaldehyde, 16) Linalool, 17) Methyl salicylate, 18) Hexanoic acid

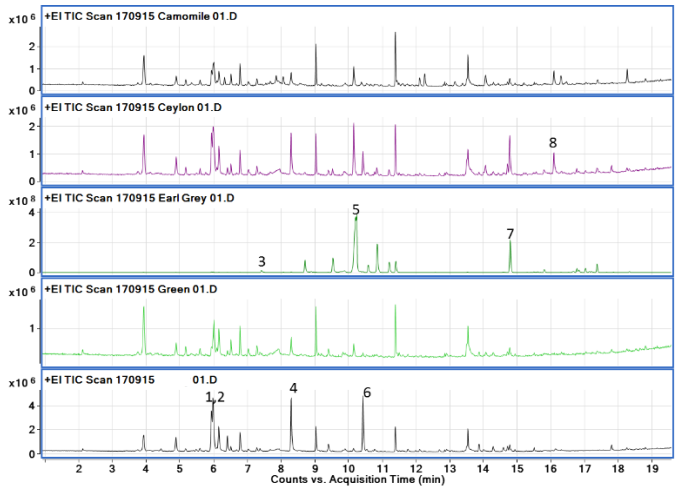

Figure 3: Comparison of Tea profiles (dry) by DHS
Peak IDs from NIST: 1) 2-methylbutanol, 2) 3-methyl butanal, 3) α-Pinene, 4) Hexanal, 5) Limonene, 6) Hexenal, 7) Linalool 8) Levomenthol

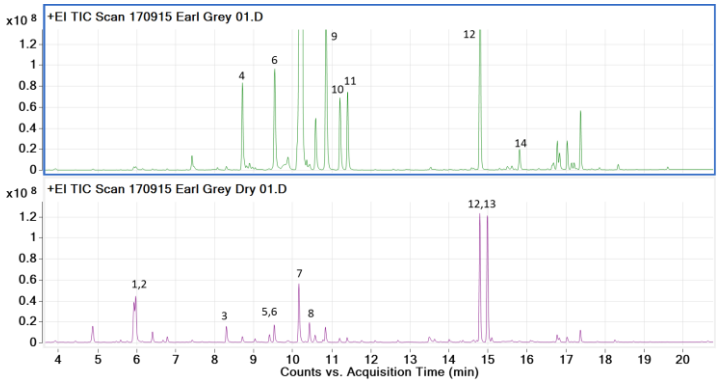

Figure 4: Comparison of Earl Grey Tea profiles (dry and with water) by DHS
1), 2-methylbutanol, 2) 3-methyl butanal, 3) Hexanal, 4) β-pinene, 5)1-penten-3-ol, 6) Myrcene, 7) Limonene, 8) Hexenal, 9) γ-Terpinene, 10) o-Cymene, 11) Terpinolene 12) Linalool, 13) Bergamol (linalyl acetate), 14) Caryophyllene

Discussion

The results show that the most suitable technique will depend on the analytes of interest. Static headspace will only show those compounds at relatively high concentrations in the samples. HS-SPME and DHS, in general give the broadest range of analytes, but each may be suited for a different range of analytes. Some components were only observed by DHS, such as 2 and 3 methyl butanal, whereas Limonene and linalool, although observed by both DHS and SPME, gave a larger response with the later technique.

The results shown in Figure 4 illustrate the influence of the sample matrix on the headspace profile obtained. The addition of water can help to release compounds, but can also lead to lower partitioning into the headspace, particularly for the more lipophilic compounds, that prefer to remain in the aqueous matrix.