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AS180

Wellbrook Court I Girton Road I Cambridge I CB3 0NA I
I tel: +44 (0) 1223 279210 I fax: +44 (0) 1223 279253
I email: enquiries@anatune.co.uk I anatune.co.uk

COMPARISON OF EXTRACTION TECHNIQUES FOR VOLATILES IN A SELECTION OF SPIRITS AND LIQUEURS

Dr Kathy Ridgway, Anatune Ltd., Girton, Cambridgeshire (UK).

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. Spirit and liqueur samples were obtained locally and a range of techniques employed in order to evaluate the compounds observed. Techniques applied were:

- Dynamic Headspace (DHS) with a single Tenax trap
- Stir Bar Sorptive Extraction (SBSE) with PDMS Twister™
- Multi-Volatile Method (MVM), using sequential DHS extraction (Shincarbon and Tenax traps)

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 tubes (Tenax™ TA and Carbopack™ B/Carbopack™ X/Shincarbon X sorption tubes for TDU 2)

Figure 1: MPS Robotic Pro (tool exchange) and DHS on Agilent GC-MS

METHOD

Sample Preparation

DHS: Duplicates of each sample (20 µl) were taken and following incubation at 80 °C for 5 minutes, extracted using a Tenax TA trap (2 Litres at 100 ml/min)

Twister: Duplicates of each sample (1 ml) were diluted with 4 ml water and extracted with PDMS Twister for 3 hours, stirring at 1000 rpm. (Vodka not analysed by this approach)

MVM: Duplicates of each sample (50 µl) were taken and extracted with 3 traps as per MVM protocol. (Gin and Vodka not analysed by this approach)

GC/MS Conditions:

DB-wax 60 m x 0.25 mm x 0.25 µm, 1 ml/min flow. Oven ramp 35 °C (0.5 mins) ramped at 5 °C/min to 250 °C (held for 1.5 mins)

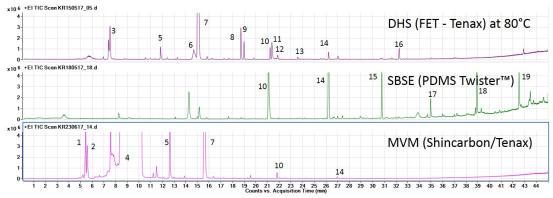
For DHS, Twister and MVM, the TDU was run in splitless mode and the CIS was run with a 20:1 split. The system was set up to split to an MSD and FID detector at a ratio of approximately: 1:1

Table 1: Number of components observed (average n=2)

	DHS (FET)	Twister	MVM
Brandy	39	58	40
Dark Rum	43	56	63
Jack Daniels	47	66	73
Cognac	51	77	72
Tia Maria	29	38	43
Drambuie	69	96	62
Becherovka	25	95	36
Gin	23	72	-
Vodka	13	-	-

RESULTS

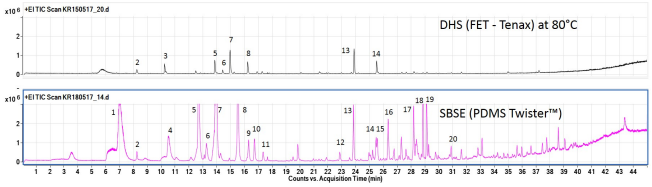
MassHunter unknowns analysis was used to determine the number of compounds observed using each of the techniques for all of the samples (Table 1). Figures 2 and 3 show differences for some of the samples by each approach.



Peak IDs (based on NIST)

1) Ethoxyethene, 2) Acetaldehyde, 3)Acetal, 4)Ethanol, 5) isobutanol, 6)Amyl alcohol, 7)isoamylalcohol , 8)ethyl lactate, 9)hexanol, 10) Ethyl octanoate, 11) Acetic acid, 12) Furfural, 13) Benzaldehyde, 14) Ethyl decanoate, 15) Ethyl dodecanoate, 16) Phenylethyl alcohol 17) octanoic acid, 18) Decanoic acid, 19) Dodecanoic acid

Figure 2: Comparison of Brandy profiles



Peak IDs (based on NIST)

1) α pinene, 2) Ethanol, 3) Thujene, 4) β-Pinene, 5)Myrcene, 6) Carene, 7) Limonene, 8) γ-Terpinene, 9) Cymene, 10) Terpinolene, 11) Sabinene hydrate? , 12) Copaene, 13) Linalool, 14) Terpinen-4-ol, 15) Caryophyllene 16) β-Elemene, 17)Germacrene, 18) Geranyl actetate, 19) Cadinene, 20) γ-Elemene, 21) Cinnamaldehyde, 22) Isoeugenol

Figure 3: Comparison of Gin profiles

DISCUSSION

The results show that the most suitable technique will depend on the analytes of interest. DHS (FET) and MVM, in general give the broadest range of analytes, although MVM did give a large response for Ethanol. Only a small response for Ethanol was observed using DHS (Tenax trap only) and SBSE (PDMS). The SBSE direct immersion approach appears to be more suitable for the less volatile analytes (as illustrated for the Gin), although did not extract the more polar analytes (such as phenyl ethyl alcohol) in the Brandy. The Shincarbon trap used in the MVM method was able to extract highly volatile analytes, such as acetaldehyde.