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TDTS

Thermal Desorption Technical Support

Note 96: A comparison of the VOC content of Indian tobacco and UK tobacco by headspace–thermal desorption (HS–TD)

Key Words:

Headspace-thermal desorption, VOC, tobacco

Introduction

Tobacco is a natural product, therefore the range of chemical constituents is vast. In general, the types of tobacco used in various brands of cigarettes are chemically similar, however manufacturers frequently add flavour or fragrance substances to their tobacco to make the product more palatable or distinctive. In the US, there is a list of 599 compounds that may be added to tobacco; the EU lists over 600, but this is not strictly regulated. In other parts of the world, there are no such guidelines. Therefore, it is unsurprising that cigarette brands produced in various countries have extremely complex and divergent chemical profiles. Two samples of tobacco were obtained; an Indian sample and a UK sample. It was apparent by smell alone that the fragrance of the Indian tobacco was far stronger than that of the UK tobacco, suggesting the addition of many olfactory compounds.

The chemicals responsible for the flavour and fragrance of natural substances are typically volatile organic compounds (VOCs). A well-established and efficient method for determining the VOC content of a sample is by concentrating extracted VOCs into a small volume by thermal desorption (TD) for GC/MS analysis. Various methods for extracting the VOCs from a sample exist and depend on the nature of the sample.

Headspace sampling using the HS5-TD™ followed by TD-GC/MS analysis was used here to extract and compare the VOC content of the two tobacco samples (unburnt). Fragrance compounds tend to be very volatile and as such are readily extracted by headspace sampling; however, the system was tested in this application due to the complexity and dynamic range of concentrations present in tobacco.

Conventional static headspace sampling has shown limited sensitivity in the past as a consequence of the small sample volume extracted; however, 'dynamic' sampling directly coupled with TD is possible with the HS5-TD. Vapours are repeatedly swept from a headspace vial of the HS5-TD to the focussing trap of the TD instrument (UNITY 2™) (Figure 1), which is packed with the optimum sorbents for retaining the compounds of interest. Repeated evacuation of the headspace vapour means that larger sample volumes are extracted and pre-concentrated onto the trap for analysis. This technique increases the volatility range retained and can increase the sensitivity over static headspace sampling by up to two orders of magnitude; comparable to the purge-and-trap technique but without foaming issues.

The optimum temperature for VOC extraction from the tobacco was also investigated.

Figure 1. HS5-TD accessory (left) connects directly to the UNITY 2 TD instrument (right)

Experimental

Procedure

0.5 g of Indian tobacco and 0.5 g of UK tobacco (from a ready-rolled cigarette) were weighed into separate 20 mL glass headspace vials and sealed with blue silicone PTFE septa.

An empty vial was also sealed with a blue silicone PTFE septum and used for blank run analysis.

Analytical conditions

HS-TD

Instrument configuration:	UNITY 2 + HS5-TD
Focussing trap:	General purpose (U-T2GPH-2S)
Septa:	Blue silicone PTFE
Pre-purge (flow rate):	0.5 min (20 mL/min to split)
Sample cycles:	3
Pressurise:	0.5 min
Sampling (flow rate):	1.5 min (50 mL/min to trap)
Equilibration:	0.5 min
Flush sample:	1 min
Post sampling line purge (flow rate):	1.5 min (20 mL/min)
Pre-trap fire purge (flow rate):	1 min (20 mL/min)
Trap low:	-10°C
Trap heating rate:	Maximum
Trap high:	320°C
Trap high time:	5 min
Split:	20 mL/min
Flow path:	140°C
Vial temperature:	50°C/75°C

GC

Column:	DB-1, 60 m x 0.32 mm x 1.0 µm
Pressure:	9 psi
Column flow (calculated):	1.6 mL/min
Mode:	Constant pressure
Oven program:	40°C (2 min) then15°C/min to 325°C (5 min)
Total run time:	26 min

MS

Quad temperature:	150°C
Source temperature:	230°C
Full scan range:	35–350 amu

Results

All chromatograms displayed in this report have been processed with ClearView™ software. ClearView uses sophisticated dynamic background compensation (DBC) algorithms to distinguish between chromatographic peaks and background/baseline anomalies. It reprocesses stored GC/MS and LC/MS data files, eliminating background ions from the total ion chromatogram (TIC), improving both spectral purity and peak integration.

The headspace vial containing the Indian tobacco sample was initially heated to 50°C, sampled and analysed. The results were then compared with the results of the sample when heated to 75°C. Comparing the full chromatograms of both samples shows significantly higher concentrations and more compounds extracted at the higher temperature (Figure 2). The enlarged view of the chromatograms emphasises this (Figure 3). A considerably wider range of compounds can be seen in the Indian tobacco sample when the headspace vial is heated to 75°C; a notable difference is the large nicotine peak at 18.4 min at the higher temperature, at 50°C this peak is very small even when the chromatogram is enlarged.

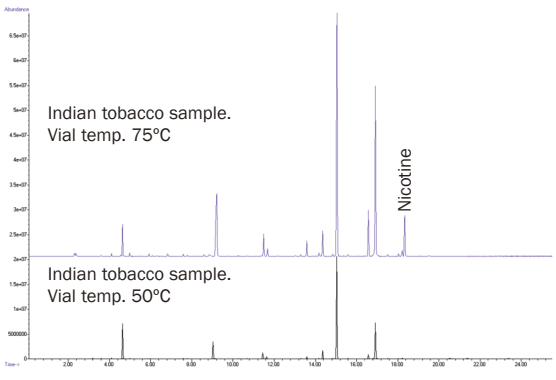

Figure 2: Chromatograms of Indian tobacco at 50°C and 75°C vial temperatures

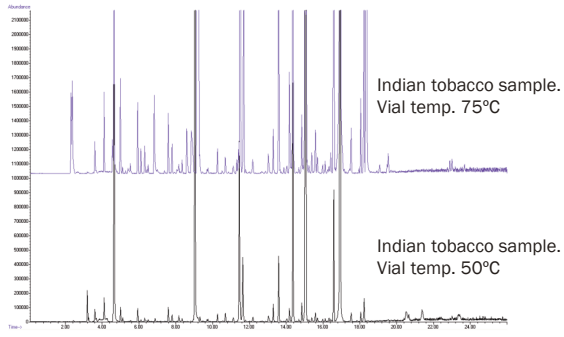

Figure 3: Enlarged view of the chromatograms in Figure 2

Due to the nature of the sample, *i.e.* the chemical complexity and wide dynamic range of concentrations, a blank was run after analysis to investigate any carryover. Minimal carryover could be seen (Figure 4) and, when enlarged to better observe any peaks (Figure 5), the largest found (3,7-dimethyl-1,6-octadien-3-ol) was at <0.5%; comfortably within acceptable levels.

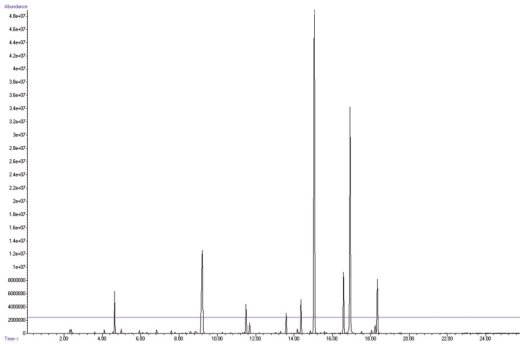

Figure 4: Indian tobacco sample at 75ºC (black) and system blank (blue)

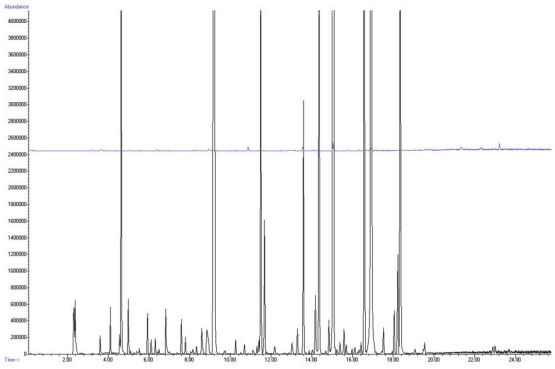

Figure 5: Enlarged view of Figure 4 showing <0.5% carryover for 3,7-dimethyl-1,6-octadien-3-ol

The subsequent stage was to compare the headspace analysis of the Indian tobacco sample to the UK tobacco sample. Since it had been found that far more compounds would be extracted at 75ºC, this temperature was also used for the UK sample. The chromatograms for each followed by a close-up of the baseline, are overlaid in Figures 6 and 7, respectively, for ease of comparison.

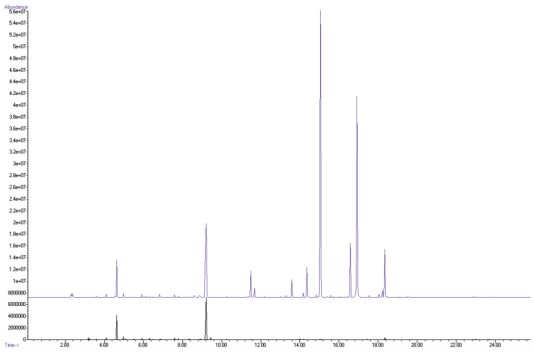

Figure 6: Comparison of UK tobacco sample (black) and Indian tobacco sample (blue)

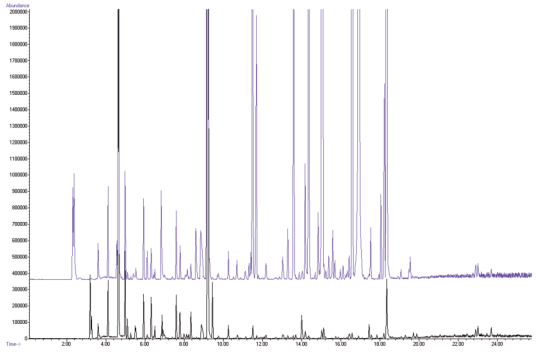

Figure 7: Enlarged view of UK tobacco sample (black) and Indian tobacco sample (blue)

Figure 6 already gives a clear picture of the difference in VOC content between the two samples; *i.e.* far more, high abundance peaks are seen in the chromatogram for the Indian tobacco sample. The enlarged view gives a better representation of the vast difference in VOC content. As expected from the strong fragrance of the tobacco, there are far more, and significantly larger, peaks in the Indian tobacco sample, indicating the presence of fragrance additives; analysis of the compounds present can determine which additives in particular.

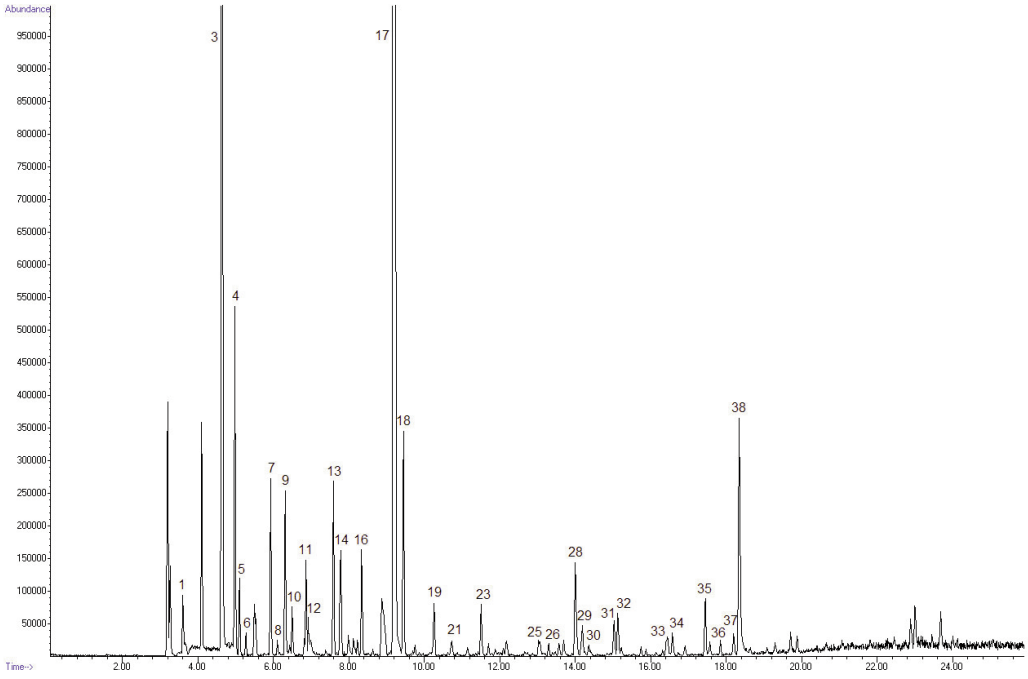

Figure 8: Chromatogram for UK tobacco sample

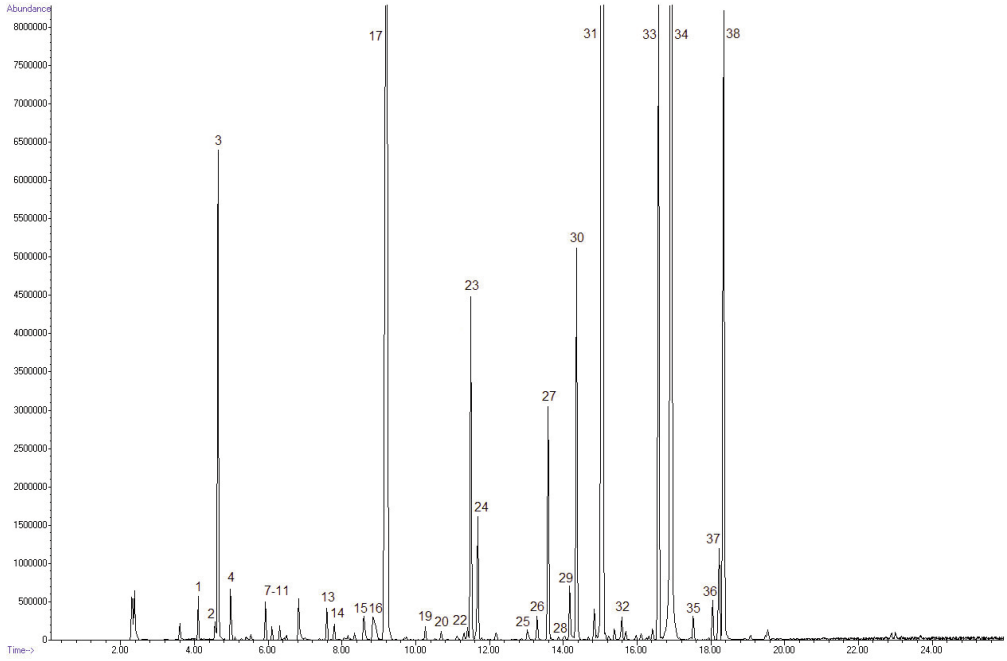

Figure 9: Chromatogram for Indian tobacco sample

Number	Compound	Number	Compound
1	Acetaldehyde	20	Methyl pyrazine
2	Trimethyl amine	21	3-furanmethanol
3	Ethanol	22	1-(1-3-dioxolan-2-yl)-2-propanone
4	Acetone	23	2-acetate-1,2-propanediol
5	IPA	24	2,6-dimethyl pyridine
6	DMS	25	Benzaldehyde
7	2-methyl propanal	26	6-methyl-5-hepten-2-one
8	Methacrolein	27	Beta myrcene
9	2,3-butanedione	28	3,7-dimethyl-(Z)-1,3,6-octatriene
10	2-butanone	29	Limonene
11	2-methyl furan	30	Cis-linalool oxide
12	Ethyl acetate	31	3,7-dimethyl-1,6-octadien-3-ol
13	3-methyl butanal	32	Pyrrolidine
14	1-butanol	33	3,7-dimethyl-(r)-6-octen-1-ol
15	2-methyl butanal	34	3,7-dimethyl-1,6-octadien-3-ol acetate
16	Pentanal	35	1-acetoxymethyl-3-isopropenyl-2-methyl-cyclopentane
17	Propylene glycol	36	3,7-dimethyl-acetate-(Z)-2,6,octadien-1-ol
18	1-ethoxy-2-propanol	37	2-(3,3-dimethylcyclohexylidene)-(Z)-ethanol
19	Hexanal	38	Nicotine

Table 1: Compounds found in the Indian and UK tobacco samples

Figures 8 and 9 show the chromatograms for each sample; table 1 lists some compounds identified in each.

Odorous additive compounds are seen in very large quantities in the Indian tobacco sample (relative to the UK sample), for example:

- Beta myrcene: Fruity, herbaceous, sweet, woody
- Cis-linalool oxide: Sweet, earthy, floral, spice, lavender
- 3,7-dimethyl-1,6-octadien-3-ol: Floral, herbal, woody, rosewood
- 3,7-dimethyl-(r)-6-octen-1-ol: Floral
- 3,7-dimethyl-1,6-octadien-3-ol acetate: Sweet, floral, fruity

Far fewer additives are seen in the UK tobacco sample, hence the large difference in overall aroma. However, the UK sample contains solvents such as IPA and 1-ethoxy-2-propanol, which are not present in the Indian sample.

The Indian tobacco sample contained significantly more nicotine than the UK sample, as well as acetaldehyde which has been suggested to contribute to nicotine addiction[1].

For a more detailed compound analysis of the samples, investigating basic, acidic, neutral, neutral-CO and fragrance compounds in both samples, please see ALMSCO International application note ANTV13 (*Aroma profiling of tobacco using an integrated headspace-thermal desorption (HS-TD) GC/MS system and TargetView software*).

Conclusion

The ability of the HS5 to extract, and the TD-GC/MS system to analyse, a wide range of volatile compounds with very good sensitivity is shown. Comprehensive flavour/fragrance profiles of both samples of tobacco have been obtained by this dynamic headspace sampling method. The temperature of extraction and the sorbent choice may be optimised for the application to ensure the retention of all compounds of interest, whilst interferants are purged to vent. The efficiency of desorption using UNITY 2 further enhances the sensitivity and therefore reliability of the GC/MS data.

Obtaining such comprehensive VOC profiles enables a vast amount of useful information regarding the fragrance composition of tobacco samples to be determined and compared.

References

1. Talhout R., Opperhuizen A., van Amsterdam J.G. (2007) Role of acetaldehyde in tobacco smoke addiction. Eur Neuropsychopharmacol 17 (10): 627-636

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Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

Markes International Ltd T: +44 (0) 1443 230935 F: +44 (0) 1443 231531 E: enquiries@markes.com