Thermal Desorption Technical Support

Note 98: Analysis of a betel-nut foodstuff by direct thermal desorption

Keywords:

Flavour/fragrance compounds, direct thermal desorption

Summary

This Application Note describes the determination of the complex VOC profile of an Indian betel-nut foodstuff, and the rapid identification of the constituent compounds by comparison against a library of flavour/fragrance compounds.

Background

The food industry is becoming increasingly aware of the need to detect low-concentration compounds in complex matrices for both product safety and quality. Typically, these compounds contribute to the flavour and aroma of the product, but increasingly there is concern over the presence of potentially harmful components. A case in point is the widespread use of foodstuffs for chewing in India, some of which contain components known to be a cause of oral cancer. The analysis of volatile components in complex matrices such as these is therefore important.

Here we use thermal desorption to analyse a sample of a complex Indian foodstuff used as a mild stimulant. This foodstuff, despite being commonly known as ‘betel nut’, is actually based on the fruit of a different plant, the areca palm (*Areca catechu*). Typically, a few slices of the nut are wrapped in a leaf of the true betel plant (*Piper betle*), along with a little tobacco and other compounds to enhance the flavour and fragrance.

In this Application Note, the inherent power of thermal desorption is demonstrated with Markes’ TD-100™ system, which is used in conjunction with TargetView™, target-compound detection software from ALMSCO International. This removes the effects of column bleed and other anomalies, and then matches the peaks to library spectra, delivering high-confidence identification even within highly complex food samples.

Finally, the capability of all Markes’ TD systems to quantitatively re-collect samples is demonstrated here. This allows samples to be kept for repeat analysis, either to validate the data, or to allow analysis of both high- and low-concentration components to be carried out (‘high/low analysis’; for more information and an example, see TDTS 94).

Experimental

A sample of the foodstuff (70.5 mg) was placed inside a TD tube, with a small amount of quartz wool at both ends. This tube was desorbed at a temperature of 50°C, using a 10:1 split ratio during secondary (trap) desorption, with the split effluent being re-collected onto a Tenax® TA tube. In order to verify the integrity of the system, this sample was then desorbed and re-collected using the same split ratio and under the same GC conditions. Instrument conditions are summarised below.

TD:

Instrument	Markes International TD-100
Flow path	180°C
Trap purge time	1 min
Primary desorption	50°C, 10 min
Focusing trap	–20°C low, 300°C high, hold time 5 min
Trap type	U-T11GPC-25 – General purpose

GC/MS:

Column	HP-5, 30 m x 0.25 mm x 0.25 µm
Pressure	11.06 psi
Initial flow	1.4 mL/min, constant flow
Temp. programme	40°C (2 min), 10°C/min (300°C, hold 5 min)
Total run time	33 min
Carrier gas	He
Mass scan range	m/z 20–350
MS source temp.	230°C
MS quad temp.	150°C

Results and discussion

Comparison against a library

An example chromatogram from the direct desorption experiment is shown in Figure 1. Of note is the large range in signal intensities, with menthol being the largest component. However, there are a large number of compounds present at much lower concentrations, so the original file was processed with TargetView software and compared against a 286-component library (mostly flavour/fragrance compounds). This analysis took just 30 seconds.

Figure 2 shows the chromatogram after processing with TargetView. Of the compounds in the library, 47 were identified in the sample (see Figure A1 for the full list). To minimise uncertainty, the software was set so that it only reported those compounds that provided a good match to the target spectra in the library (matching coefficient >0.7). Clearly, the sample contains a substantial number of flavour and fragrance compounds, such as patchouli alcohol, cedrol and terpinolene. However, diethyl phthalate (15.823 min) was also present, which in this case is likely to originate from the plastic packaging of the sample, as it does not occur naturally.

Analysing target compounds

The power of thermal desorption combined with TargetView is that it can identify minor target-library components, even when obscured by other peaks. A good example of this is phenylacetaldehyde dimethyl acetal (11.014 min), which is masked by a larger, non-target peak (Figure 3). Nevertheless, the mass spectrum of phenylacetaldehyde dimethyl acetal obtained by TargetView is a very good match to the library entry (Figure 4), as confirmed by the matching coefficient of 0.826.

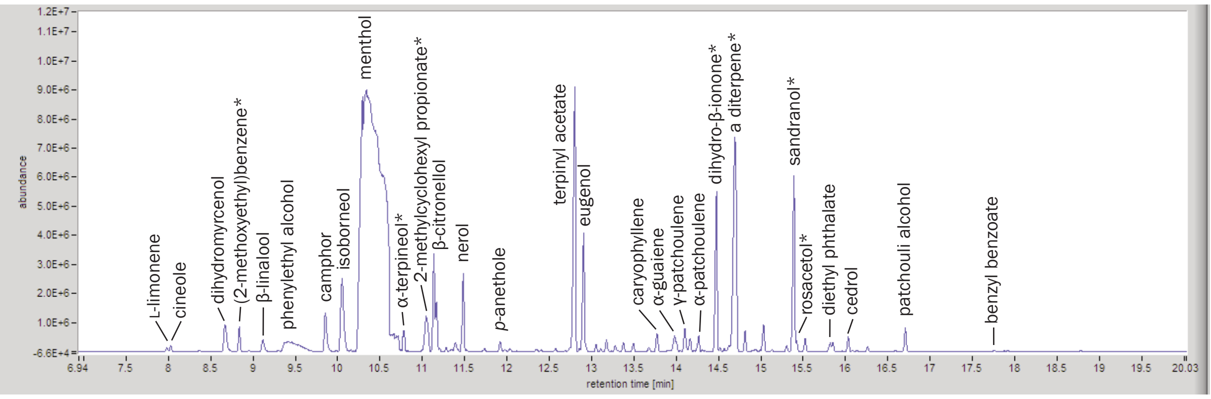


*Figure 1. The original chromatogram of the betel-nut foodstuff, with some key components labelled. [Note: Those marked * were not in the target library, and so don't appear in the TargetView report (Figure A1)]*

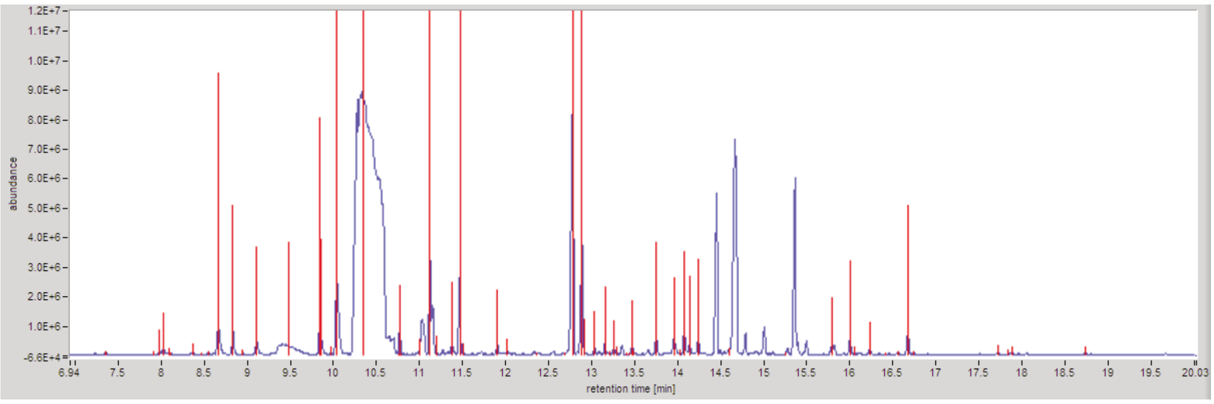


Figure 2. A screenshot of the same data as in Figure 1, reprocessed using TargetView. The hits from the target library are marked with red vertical lines (the height of each line is proportional to the abundance of the compound)

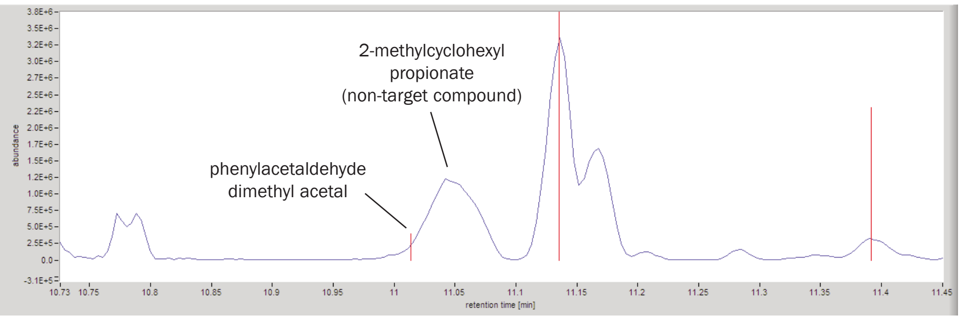


Figure 3. The confident identification of the minor component at 11.014 min (phenylacetaldehyde dimethyl acetal) is not affected by overlap with a much more abundant non-target compound (2-methylcyclohexyl propionate)

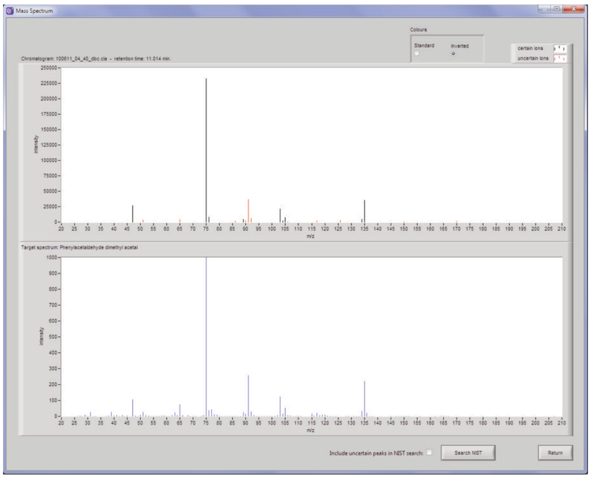


Figure 4. Comparison of (top) sample and (bottom) library mass spectra for phenylacetaldehyde dimethyl acetal. A very good match is obtained, even though the peak is low-abundance and masked by a more abundant compound

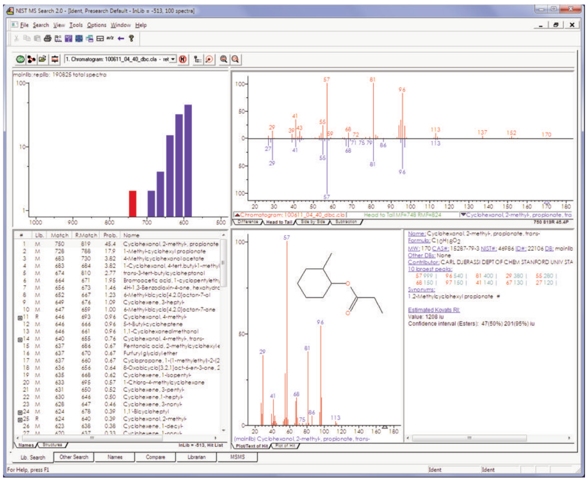


Figure 5. NIST search showing successful identification of the non-library component 2-methylcyclohexyl propionate

TargetView also allows the identification of non-target components, by comparison of the mass spectra against comprehensive spectral databases, such as that provided by NIST. Here, this allowed the identification of the non-library component 2-methylcyclohexyl propionate, as shown in Figure 5.

Re-analysing split samples

The added benefit of using Markes' systems for thermal desorption is that samples acquired with a split TD method can be re-collected and re-analysed. In this case, re-collection was automated for four consecutive runs, and the results for an example compound, patchouli alcohol (16.707 min), are shown in Figure 6. The signal intensity diminishes steadily from run to run, providing additional confirmation of the reliability of the TD-GC process.

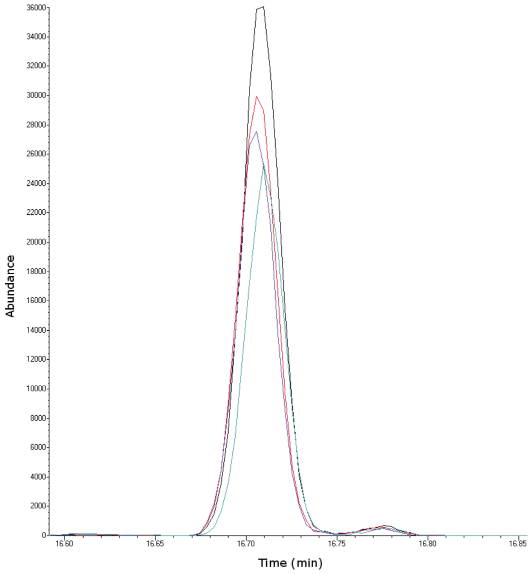


Figure 6. Zoomed-in overlaid chromatograms of the peak for patchouli alcohol, taken in consecutive runs at a 10:1 split ratio

Conclusions

This study demonstrates the efficiency of Markes' TD-100 autosampler when used to directly desorb a sample with a complex chemical matrix – in this case an Indian betel-nut foodstuff.

Processing of the GC/MS output using TargetView led to the rapid identification of a variety of target library compounds. TargetView could therefore facilitate quality control of this material and help identify components of potential concern, such as phthalates. The powerful data-mining algorithms applied to the GC/MS data allow TargetView to accurately identify target compounds within the sample, even when they are trace components obscured by other peaks.

Furthermore, it is easy to automate sample re-collection, either using the same conditions (to validate recovery and check reproducibility), or using different column conditions, which allows quantitative analysis of components of widely differing concentration.

Trademarks

TD-100™ is a trademark of Markes International Ltd, UK.

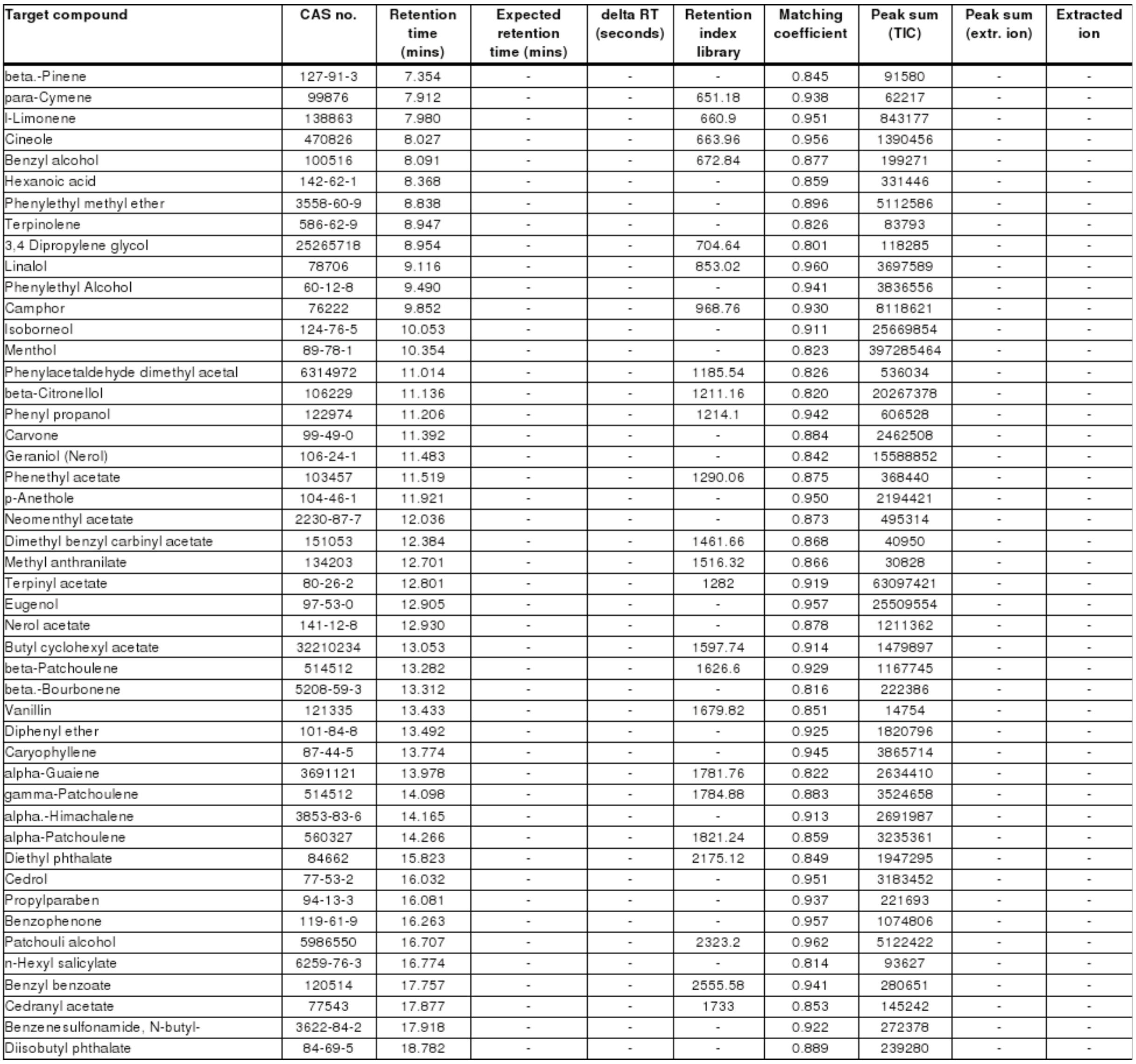
TargetView™ is a trademark of ALMSCO International, UK.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.

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

First released: July 2011

Appendix



Target compound	CAS no.	Retention time (mins)	Expected retention time (mins)	delta RT (seconds)	Retention index library	Matching coefficient	Peak sum (TIC)	Peak sum (extr. ion)	Extracted ion
beta.-Pinene	127-91-3	7.354	-	-	-	0.845	91580	-	-
para-Cymene	99876	7.912	-	-	651.18	0.938	62217	-	-
l-Limonene	138863	7.980	-	-	660.9	0.951	843177	-	-
Cineole	470826	8.027	-	-	663.96	0.956	1390456	-	-
Benzyl alcohol	100516	8.091	-	-	672.84	0.877	199271	-	-
Hexanoic acid	142-62-1	8.368	-	-	-	0.859	331446	-	-
Phenylethyl methyl ether	3558-60-9	8.838	-	-	-	0.896	5112586	-	-
Terpinolene	586-62-9	8.947	-	-	-	0.826	83793	-	-
3,4 Dipropylene glycol	25265718	8.954	-	-	704.64	0.801	118285	-	-
Linalol	78706	9.116	-	-	853.02	0.960	3697589	-	-
Phenylethyl Alcohol	60-12-8	9.490	-	-	-	0.941	3836556	-	-
Camphor	76222	9.852	-	-	968.76	0.930	8118621	-	-
Isoborneol	124-76-5	10.053	-	-	-	0.911	25669854	-	-
Menthol	89-78-1	10.354	-	-	-	0.823	397285464	-	-
Phenylacetaldehyde dimethyl acetal	6314972	11.014	-	-	1185.54	0.826	536034	-	-
beta-Citronellol	106229	11.136	-	-	1211.16	0.820	20267378	-	-
Phenyl propanol	122974	11.206	-	-	1214.1	0.942	606528	-	-
Carvone	99-49-0	11.392	-	-	-	0.884	2462508	-	-
Geraniol (Nerol)	106-24-1	11.483	-	-	-	0.842	15588852	-	-
Phenethyl acetate	103457	11.519	-	-	1290.06	0.875	368440	-	-
p-Anethole	104-46-1	11.921	-	-	-	0.950	2194421	-	-
Neomenthyl acetate	2230-87-7	12.036	-	-	-	0.873	495314	-	-
Dimethyl benzyl carbinyl acetate	151053	12.384	-	-	1461.66	0.868	40950	-	-
Methyl anthranilate	134203	12.701	-	-	1516.32	0.866	30828	-	-
Terpinyl acetate	80-26-2	12.801	-	-	1282	0.919	63097421	-	-
Eugenol	97-53-0	12.905	-	-	-	0.957	25509554	-	-
Nerol acetate	141-12-8	12.930	-	-	-	0.878	1211362	-	-
Butyl cyclohexyl acetate	32210234	13.053	-	-	1597.74	0.914	1479897	-	-
beta-Patchoulene	514512	13.282	-	-	1626.6	0.929	1167745	-	-
beta.-Bourbonene	5208-59-3	13.312	-	-	-	0.816	222386	-	-
Vanillin	121335	13.433	-	-	1679.82	0.851	14754	-	-
Diphenyl ether	101-84-8	13.492	-	-	-	0.925	1820796	-	-
Caryophyllene	87-44-5	13.774	-	-	-	0.945	3865714	-	-
alpha-Guaiene	3691121	13.978	-	-	1781.76	0.822	2634410	-	-
gamma-Patchoulene	514512	14.098	-	-	1784.88	0.883	3524658	-	-
alpha.-Himachalene	3853-83-6	14.165	-	-	-	0.913	2691987	-	-
alpha-Patchoulene	560327	14.266	-	-	1821.24	0.859	3235361	-	-
Diethyl phthalate	84662	15.823	-	-	2175.12	0.849	1947295	-	-
Cedrol	77-53-2	16.032	-	-	-	0.951	3183452	-	-
Propylparaben	94-13-3	16.081	-	-	-	0.937	221693	-	-
Benzophenone	119-61-9	16.263	-	-	-	0.957	1074806	-	-
Patchouli alcohol	5986550	16.707	-	-	2323.2	0.962	5122422	-	-
n-Hexyl salicylate	6259-76-3	16.774	-	-	-	0.814	93627	-	-
Benzyl benzoate	120514	17.757	-	-	2555.58	0.941	280651	-	-
Cedranyl acetate	77543	17.877	-	-	1733	0.853	145242	-	-
Benzenesulfonamide, N-butyl-	3622-84-2	17.918	-	-	-	0.922	272378	-	-
Diisobutyl phthalate	84-69-5	18.782	-	-	-	0.889	239280	-	-

Figure A1. The report automatically generated by TargetView for the matching of the betel-nut foodstuff against the library of flavour/fragrance compounds. The retention time is automatically included, and the level of confidence in the assignment is indicated by the matching coefficient (fourth column from the right)