TDTS 90

Automated detection of trace target compounds in complex emission profiles from products and materials

Summary

This Application Note shows how TargetView™ compound-identification software greatly speeds up the process of identifying trace-level target compounds in complex emission profiles from consumer products and construction materials. Examples chosen are plasterboard, a child's plastic toy, and mahogany.

Introduction

Manufacturers of construction products and consumer goods are increasingly responsible for identifying and measuring any dangerous chemicals which could be emitted by their products under normal use. This is to make sure that they don't pose a risk to consumers. The toxic and odorous chemicals of interest are specified in standard protocols and include a wide range of volatile and semi-volatile organic compounds (VOCs and SVOCs).

New regulations are driving industry to implement chemical emissions testing in-house, both for quality control (QC) and for research and development (R&D). Testing chemical emissions from products usually involves placing product samples in environmental chambers, or micro-chambers, with subsequent vapour sampling onto sorbent tubes and thermal desorption (TD)–GC/MS analysis. The emission profiles yielded from a product or material can be complex and contain many target compounds at trace levels. This makes them time-consuming and difficult to interpret correctly, particularly in a busy industrial QC laboratory.

In this Application Note, we show how TargetView software can be used to simplify the process of compound identification in such situations, by applying sophisticated algorithms to interpret the complex total ion chromatogram (TIC). This enables the rapid identification of target compounds (such as those from a regulatory list) far more quickly than would be possible by manual processing.

Background to TargetView[1]

TargetView is a software package allowing rapid and accurate identification of both target and 'unknown' compounds in GC/MS profiles. It is easy to learn, simple to operate, and compatible with common GC/MS file types from major vendors.

TargetView is ideal for GC/MS analysts who need to rapidly screen chromatograms against compound libraries, or those who are looking for trace-level analytes in complex matrices. It produces accurate, reliable results without requiring the high degree of expertise that is demanded by other GC/MS data-analysis packages. TargetView also offers automated identification of unknown compounds, making it suitable for all GC/MS applications.

Importing data into TargetView is quick and straightforward, and running TargetView against a typical material emissions library takes a matter of minutes. A simple report is produced that allows the analyst to see at a glance which compounds are present. In addition, an interactive chromatogram allows more detailed interpretation of results, including resolving contributions from co-eluting compounds.

Libraries of target compounds are easily prepared, either from in-house or third-party datasets. Alternatively, TargetView is available pre-programmed with target libraries for emission testing[2].

Experimental

1. Plasterboard

Sampling:
A circular piece of plasterboard (44 mm diameter) was placed into a chamber of a Micro-Chamber/Thermal Extractor™ (Markes International). Helium was applied at a flow rate of 100 mL/min, and the temperature held at 50°C for 30 min to equilibrate. Air exiting the micro-chamber was then collected for 12 min onto a 3½″ × ¼″ o.d. stainless steel TD tube (Markes International) packed with Tenax® TA. Trapped emissions were then analysed by TD–GC/MS.

TD:

Instrument:	UNITY™ 2 (Markes International)
TD split:	25:1
Primary (tube) desorb:	5 min, 300°C
Trap:	Material Emissions (U-T12ME-2S)
Trap low:	0°C
Trap high:	300°C

GC/MS:

Column:	DB-5, 30 m × 0.25 mm × 0.50 µm
MS:	Quadrupole in scan mode

2. Plastic toy

Sampling:
A plastic toy frog was bought from a major retailer. A 50 mg sample of the toy was introduced into an empty TD tube (Markes International) and analysed by direct TD–GC/MS.

TD:

Instrument:	TD-100™ (Markes International)
TD split:	20 mL/min (single split)
Flow:	40 mL/min
Primary (tube) desorb:	10 min, 60°C
Trap:	Material Emissions (U-T12ME-2S)
Trap low:	0°C
Trap high:	300°C

GC/MS:

Column:	DB-1, 60 m × 320 µm × 1.0 µm
MS:	Quadrupole in scan mode

3. Mahogany

Sampling:
A piece of mahogany was placed into a chamber of a Micro-Chamber/Thermal Extractor™ (Markes International). Helium was applied at a flow rate of 100 mL/min, and the temperature held at 60°C for 30 min to equilibrate. Air exiting the micro-chamber was then collected for 15 min onto a 3½″ × ¼″ o.d. stainless steel TD tube (Markes International) packed with Tenax® TA. Trapped emissions were then analysed by TD–GC/MS (conditions as for plasterboard).

Results and discussion

1. Plasterboard emissions

Plasterboard or 'drywall' is used extensively to create smooth walls and ceilings indoors. Although it invariably ends up being covered by paint or wallpaper, the complex mixture of chemicals emitted by some plasterboard products can migrate through most coverings and into the indoor environment. Covering the emitting product may delay the onset of high emission levels, but rarely eliminates emissions completely.

Markes International's Micro-Chamber/Thermal Extractor™ facilitates rapid qualitative and quantitative screening of chemical emissions from construction products like plasterboard, and satisfies QC requirements. The inert, uniformly heated flow path of Markes' TD equipment also ensures compatibility with a wide analyte range, including VOCs, SVOCs and reactive sulfur compounds[3].

The efficiency of the plasterboard sampling process results in a complex GC/MS chromatogram, as shown in Figure 1A. The first step in the TargetView process is therefore to remove any unwanted background signals, resulting in a much cleaner baseline (Figure 1B).

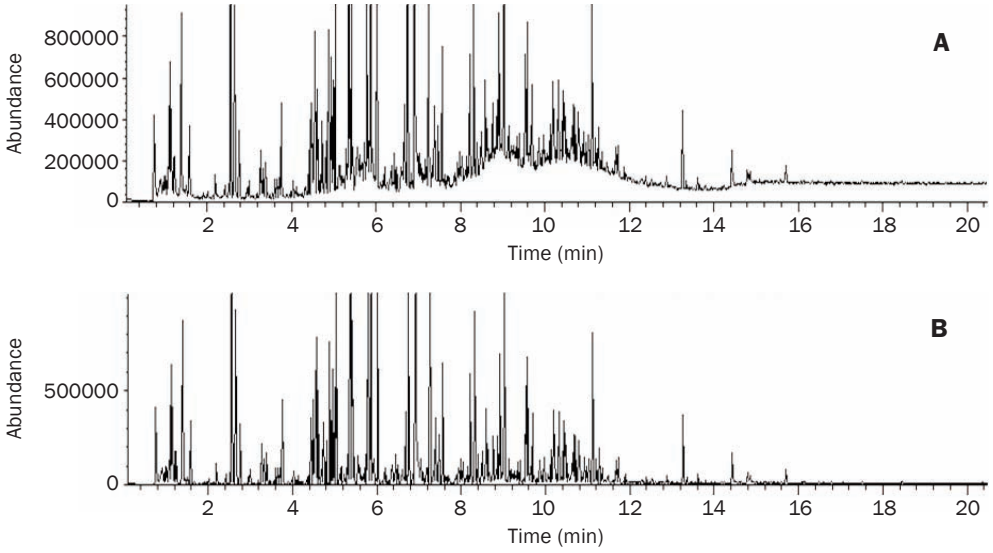

Figure 1: GC/MS analysis of plasterboard emissions, (A) before and (B) after dynamic background compensation using TargetView.

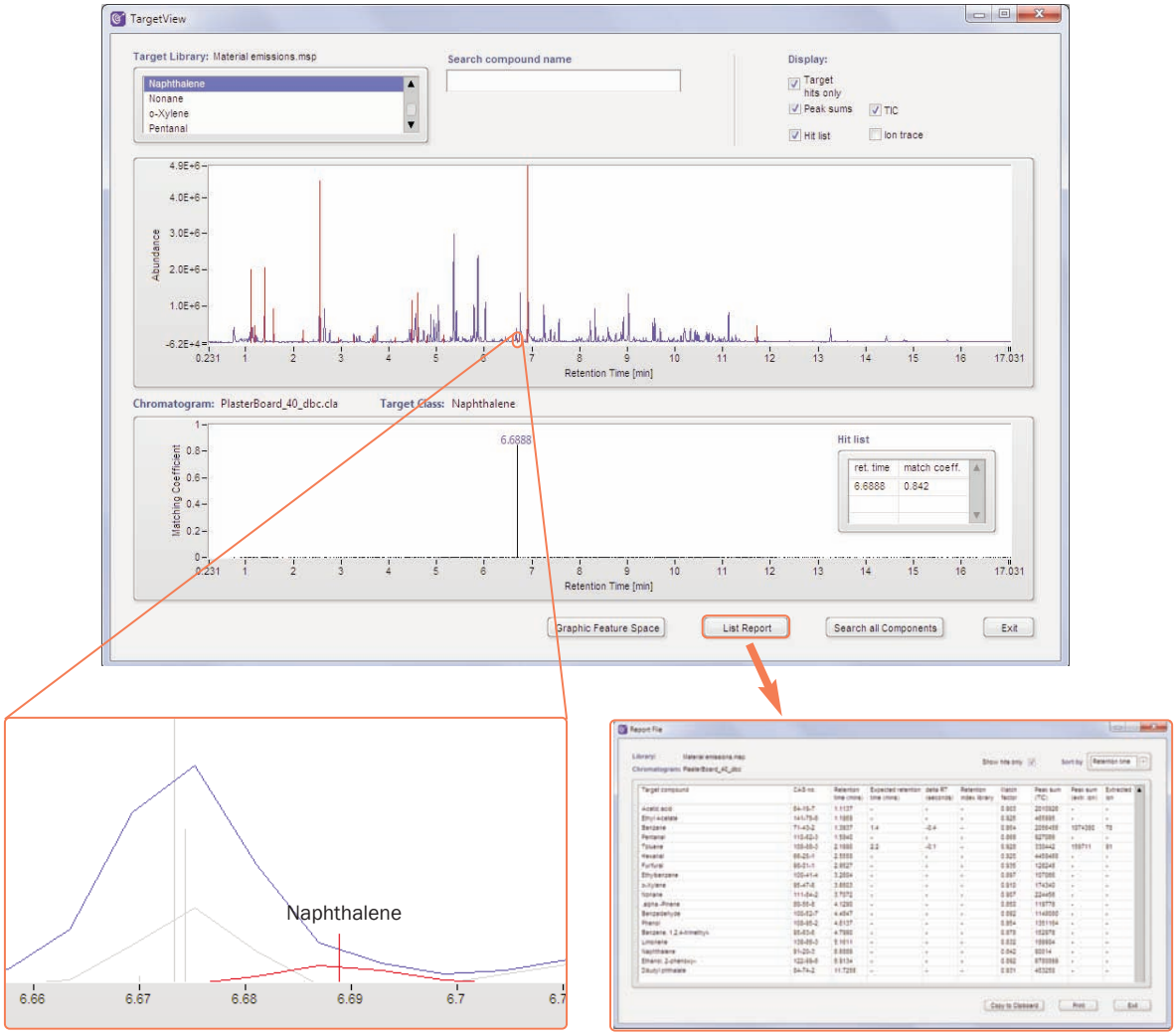

Figure 2: Top: TargetView's interactive chromatogram for the analysis of plasterboard emissions. Left inset: Zoom-in showing identification of naphthalene (red trace) with co-eluting non-targets (grey traces). Right inset: The TargetView report.

Running this chromatogram against a 20-member material emissions library produces the interactive chromatogram shown in Figure 2. This shows the background-compensated chromatogram in the top panel, overlaid with red bars indicating the target compounds found.

Zooming in on this chromatogram allows individual compounds to be studied in more detail. For example, in Figure 3, the target compound naphthalene has been selected from the drop-down box at top left. This is nearly obscured by another peak, but TargetView is able to deconvolve them, allowing visualisation of the elution profile for naphthalene and the production of a mass spectrum (Figure 3). This mass spectrum is a good match for that in the library, with a match coefficient of 0.842. It is worth noting that, without TargetView, this degree of co-elution would make such confident identification much more difficult.

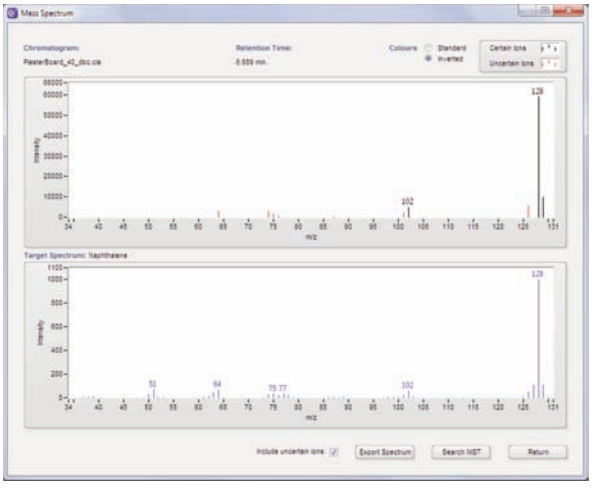

Figure 3: Obtained mass spectrum for naphthalene (top) compared against the library spectrum (bottom).

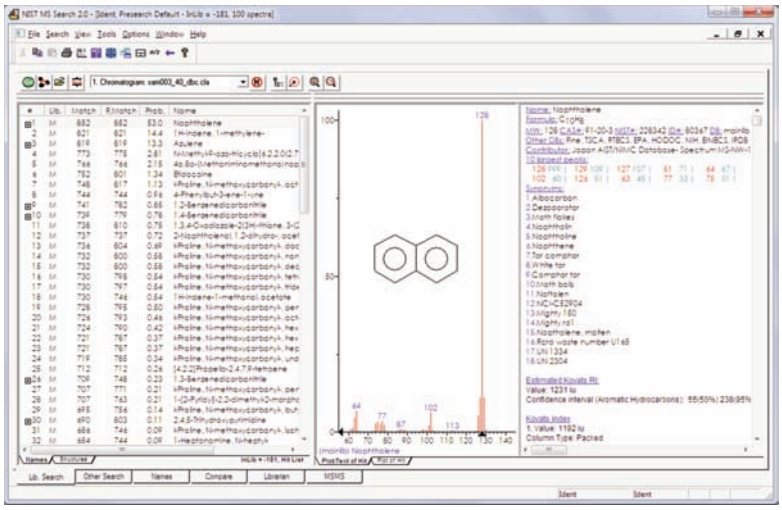

Figure 4: A NIST search of the sample spectrum confirms its identification as naphthalene.

Target compound	CAS no.	Retention time (min)	Match coefficient	Peak sum (TIC)
Acetic acid	64-19-7	1.114	0.903	2 010 926
Ethyl acetate	141-78-6	1.197	0.925	465 995
Benzene	71-43-2	1.394	0.954	2 056 456
Pentanal	110-62-3	1.584	0.868	927 066
Toluene	108-88-3	2.199	0.928	330 442
Hexanal	66-25-1	2.556	0.925	4 458 468
Furfural	98-01-1	2.953	0.935	128 248
Ethylbenzene	100-41-4	3.280	0.897	107 066
o-Xylene	95-47-6	3.660	0.910	174 340
Nonane	111-84-2	3.707	0.907	224 456
α-Pinene	80-56-8	4.129	0.850	119 778
Benzaldehyde	100-52-7	4.485	0.892	1 148 080
Phenol	108-95-2	4.614	0.954	1 351 164
1,2,4-Trimethylbenzene	95-63-6	4.799	0.878	152 978
Limonene	138-86-3	5.161	0.832	189 904
Naphthalene	91-20-3	6.689	0.842	90 014
2-Phenoxyethanol	122-99-6	6.913	0.892	6 780 899
Dibutyl phthalate	84-74-2	11.73	0.931	453 250

Table 1: List of identified target compounds identified from the plasterboard, exported from the TargetView report.

TargetView allows compounds to be cross-searched against an established database (such as NIST) to confirm compound identification. In this case, a NIST search of the mass spectrum shown in Figure 4 confirms it as naphthalene, with a match factor of 852.

Finally, clicking 'List Report' at the bottom of the interactive chromatogram produces a short report (see Figure 2). This can be exported to a spreadsheet program such as Excel® – the results for the plasterboard sample are shown in Table 1.

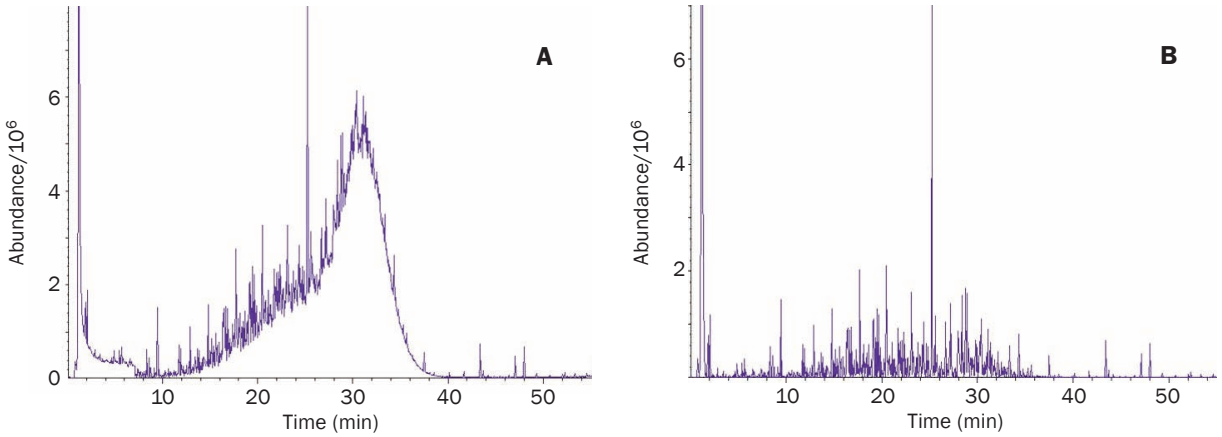

Figure 5: GC/MS analysis of emissions from a plastic toy, (A) before and (B) after dynamic background compensation using TargetView.

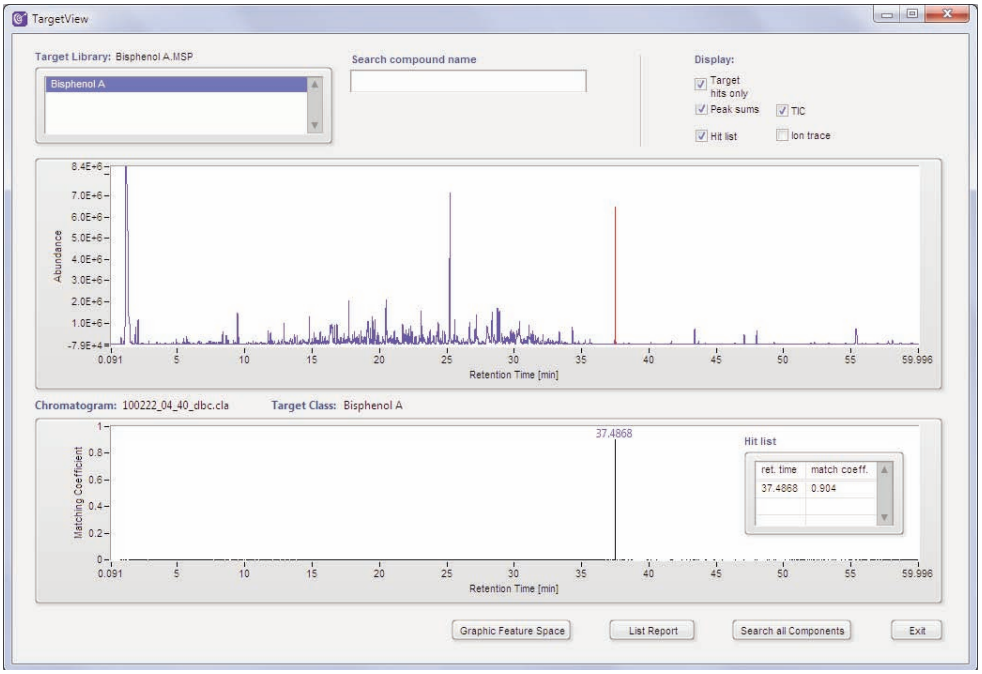

Figure 6: Top: TargetView's interactive chromatogram for the analysis of emissions from a child's toy. The red bar marks the position of bisphenol A.

2. Chemicals in childrens' toys

Bisphenol A (BPA) is a common additive to the type of rigid polycarbonate plastics often used to make drink bottles or toys. It is also used as an additive to the inner coating of food cans and water supply pipes. However, BPA is a known endocrine disrupter, and its presence in consumer products, especially those intended for babies and children, is the focus of ongoing concern.

Sampling by direct desorption led to a highly complex chromatogram (Figure 5A), but the large background signal was easily removed by TargetView (Figure 5B). Note that the original file is always retained for future use – for example, for total VOC (TVOC) calculations.

Processing this background-compensated chromatogram against a target 'library' containing just BPA clearly identifies this compound (Figure 6), with the mass spectral match (Figure 7) reflecting the high match coefficient of 0.904.

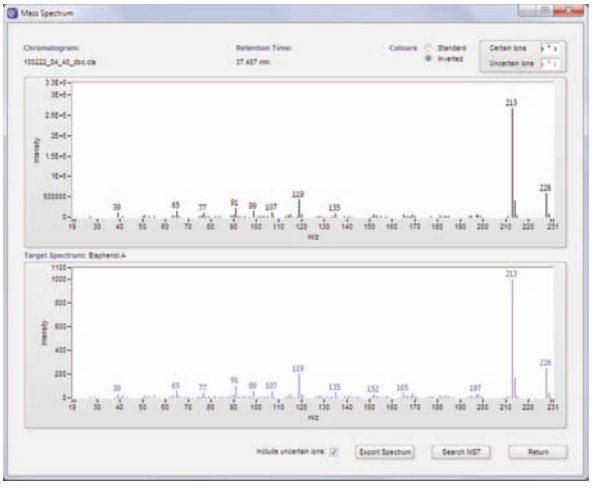

Figure 7: Obtained mass spectrum for bisphenol A (top) compared against the library spectrum (bottom).

3. Mahogany emissions

Timber and wood-based products are used extensively for building construction, interior design and furniture manufacture. The wood and wood-product industries have always been at the forefront of emissions testing and control, particularly with respect to formaldehyde. Timber and wood-based products can also emit significant levels of VOCs. In this study, the Micro-Chamber/Thermal Extractor was used to rapidly screen VOC emissions from mahogany.[4]

The mahogany sample was found to emit a wide range of volatile and semi-volatile organic compounds. The TargetView screenshot in Figure 8 shows the background-compensated chromatogram with an expansion showing two key target compounds.

By linking to NIST, TargetView also allows non-target ('unknown') peaks to be identified. Figure 9 shows an example of this for the peak eluting at 5.866 min. Unselecting "Target hits only" at the top of the main screen shows all the components present, and the mass spectrum for the component of interest is then displayed by a simple click. Searching this against NIST allows identification of the compound as nonanal.

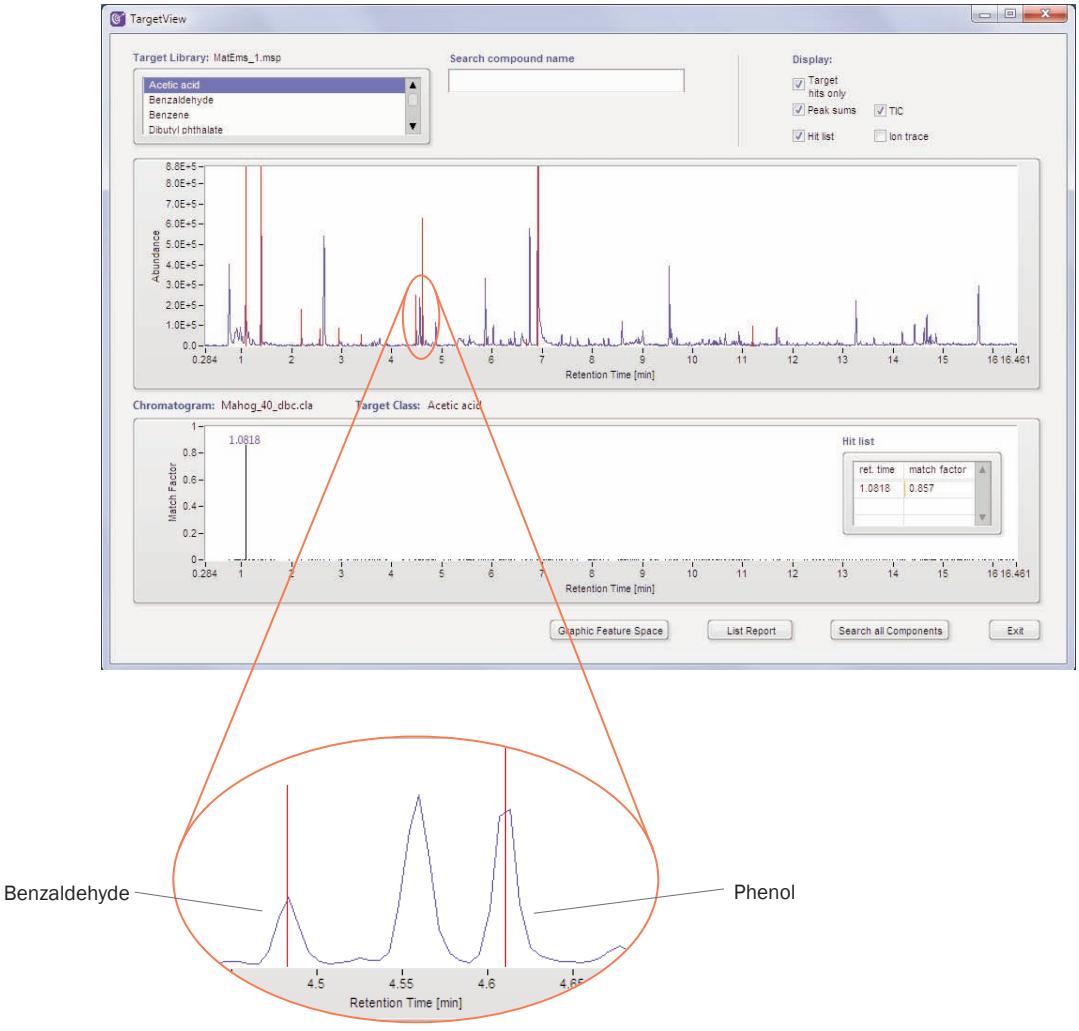

Figure 8: TargetView's interactive chromatogram for the analysis of emissions from mahogany. The inset shows an expansion indicating the position of two key target compounds.

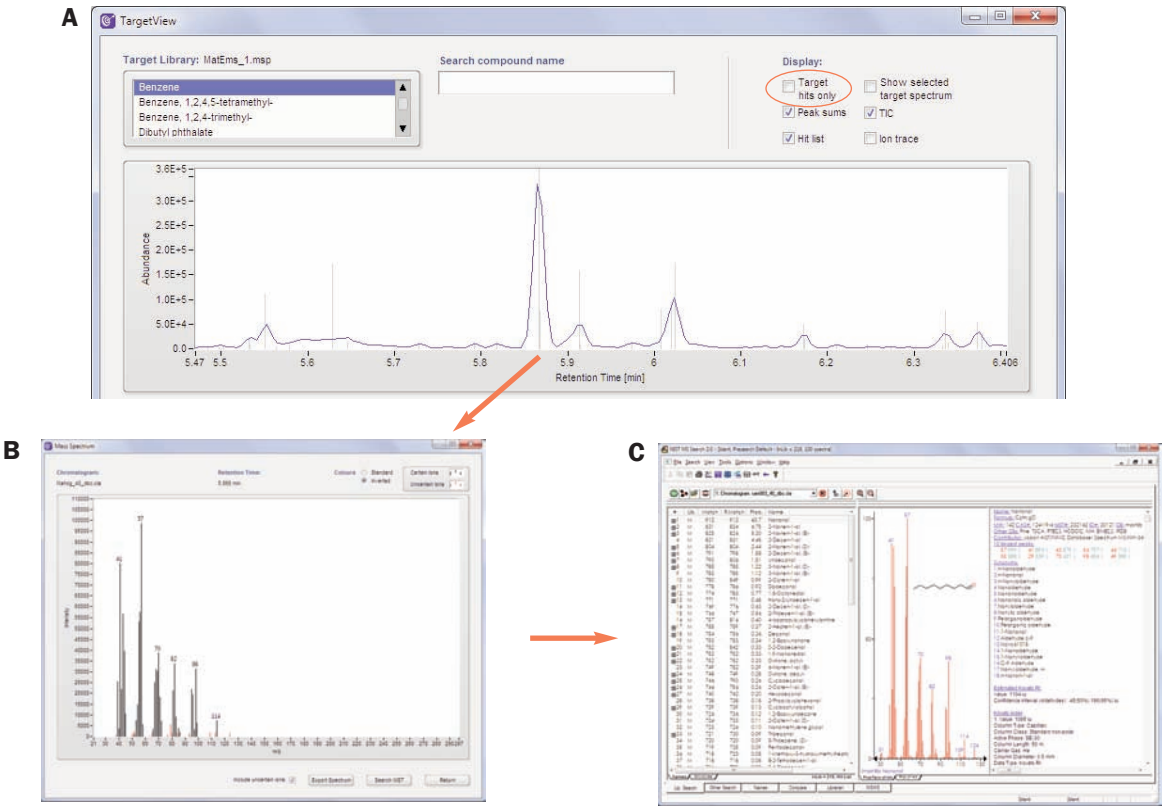

Figure 9: (A) The upper panel of TargetView's interactive chromatogram for the analysis of emissions from mahogany, following zooming-in on a peak of interest and unchecking "Target hits only" (circled) so that all components are displayed. (B) The mass spectrum for the unknown component. (C) The results of a NIST search, with identification confirmed as nonanal.

Conclusion

These examples have shown that TargetView is a powerful software package for automating identification of trace-level target compounds in complex material emission profiles. The straightforward, Excel-compatible report dispenses with the need for time-consuming manual interpretation and greatly speeds up data interpretation for busy industrial laboratories.

At the same time, the ability of TargetView to interface with comprehensive libraries such as NIST allows results to be cross-checked, and non-target compounds to be identified. It therefore also has broad application in service laboratories and in advanced research applications.

Trademarks

References

1. For more information about TargetView, please visit http://www.almsco.com/Products/Targetview/default.aspx.
2. Examples include:
   - AgBB 'LCI' compounds (lowest concentrations of interest). See http://www.umweltbundesamt.de/produkte-e/bauprodukte/agbb.htm.
   - AFSSET 'LCI' compounds (lowest concentrations of interest). See http://www.afsset.fr/upload/bibliotheque/834140219913200241733014951209/COV_rapport_2009VF.pdf.
   - California 01350 'CREL' compounds (chronic reference exposure level). See http://standards.nsf.org/apps/group_public/download.php/19152/CDPH%2001350%20V1-1.pdf.
3. For more information about the Micro-Chamber/Thermal Extractor, please visit http://www.markes.com/Instrumentation/Micro-ChamberThermal-Extractor-CTE.aspx.
4. The Micro-Chamber/Thermal Extractor is also compatible with monitoring formaldehyde emissions using DNPH cartridges and HPLC.

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

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