Thermal Desorption Technical Support

Note 66: Improving the identification and measurement of trace odorous and toxic components during materials emissions testing

Keywords

material emissions, (S)VOCs, certification protocols, retention time locking (RTL), target compound database, mass spectral deconvolution

Introduction

Concern is growing over emissions of VOCs and semi-VOCs from materials due to their potential impact on human health/comfort. Manufacturers of construction products, furnishings, furniture, car trim components and consumer products need to monitor emissions of individual and total VOCs to assess the environmental impact of their products indoors and in vehicle cabins. In some cases emissions data are also used for product certification and/or to demonstrate compliance with VOC emission limits - Examples of certification protocols include (1) the US Greenguard protocol, (2) the German AgBB scheme for flooring materials and (3) the Californian 'High Performance' school initiative. Manufacturers may also use the data to compare and categorize different indoor materials/products of similar function and to develop new types of materials/products with lower emissions and lower potential environmental impact.

(S)VOCs are measured using conventional emission chambers/cells to simulate real-world conditions (ISO/EN 16000 -9/-10, ENV 13419) or by direct thermal desorption/extraction (See TDTS 65, and also VDA Method 278). In either case, thermal desorption (TD) with GC/MS is required for analysis. TD-GC/MS often produces very complex chromatograms making it difficult and time-consuming to confidently identify key odorous and toxic compounds which may only be present at trace levels. It is usually impossible to chromatographically resolve all of the components within a reasonable time and many target/interfering analytes have similar mass spectra. However, accurate identification and measurement of trace toxic compounds is becoming increasingly important - both for consumer acceptance and for compliance with certification protocols. For example, the German AgBB scheme, Californian CHPS program and prEN 15052 (4) all require emissions data to be evaluated for low level carcinogens and other toxic compounds.

This paper describes a new technique using stabilised retention times combined with mass spectral deconvolution and library searching (with deconvoluted spectra) to improve, simplify and automate the analysis of trace target compounds in complex chromatograms, while minimising false positives and negatives.

Retention time locking

As described in the Markes leaflet - Mi BEPC 'Electronic Pneumatic Control of Carrier Gas', back pressure regulated electronic pneumatic control (as used on the split/splitless injector of an Agilent 6890 GC) has now been integrated into the Markes (ULTRA-)UNITY thermal desorber such that carrier gas pressure can be precisely maintained at the head of the capillary column, independent of the status and configuration of the thermal desorber *i.e.* independent of the type of sorbents in use, system temperatures, split flows, *etc*. (Figure 1). Effectively the retention times through the entire TD-GC/MS system become 'locked'.

On its own, retention time locking (RTL) offers several advantages. For example; it allows analyte retention times to be fixed for multiple TD-GC/MS systems in multiple laboratories, thus shortening the learning curve for new

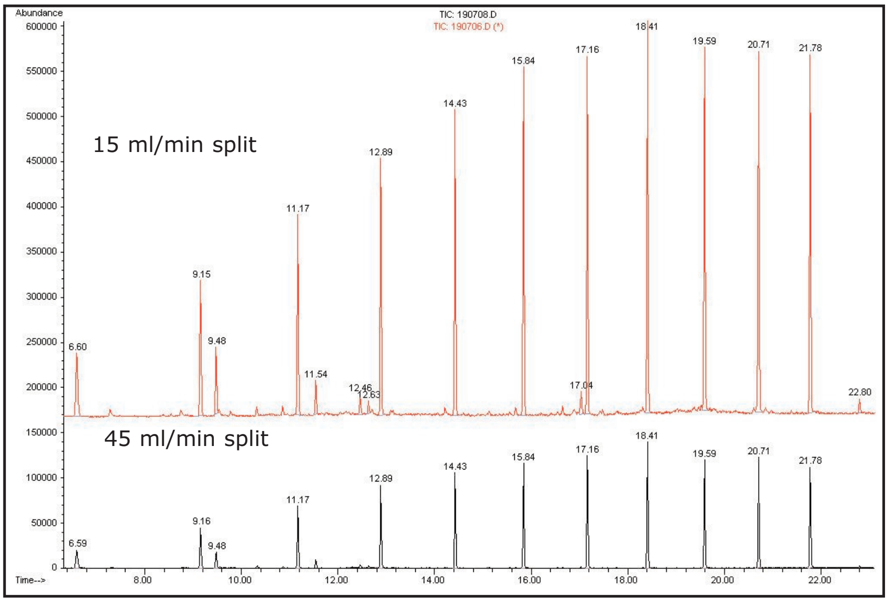


Figure 1: Using back-pressure regulated EPC (Agilent 6890 GC) through a Markes (ULTRA-) UNITY TD to 'Lock' retention times independent of split flow, system temperatures, sorbents, etc.

operators and simplifying troubleshooting/lab. accreditation procedures. However, perhaps the main benefit is that retention times become sufficiently stable to enable the creation of databases of target compounds using retention time (RT) as a key search criteria *i.e.* precise retention times can then be used to qualify the results from mass spectral searching. Further, this enables application of deconvolution reporting software (DRS) whereby target compounds can be separated from co-eluting interferences.

Spectral deconvolution

Spectral deconvolution was pioneered by NIST in their **AMDIS** product (**A**utomatic **M**ass-spectral **D**econvolution and **I**dentification **S**oftware). AMDIS allows target compounds to be separated from co-eluting interferences by deconvoluting all the individual mass spectra in a composite GC peak (Figure 2).

AMDIS is a powerful and flexible tool in its own right but is still usually carried out as a manual and relatively lengthy data reprocessing operation. However, it has recently been integrated into the conventional Agilent ChemStation GC/MS data processing package together with retention time locking. The new combined software package is called '**DRS**' - **D**econvolution **R**eporting **S**oftware - and combines a) conventional quantitative and qualitative analysis using target and qualifier ions (MS) and 'locked' retention times; b) searching of the AMDIS deconvoluted spectra against an RT-Locked database of target compounds; and c) further confirmation of peak identity with reverse spectral searching of the deconvoluted MS data against the full NIST-02 library.

Development of the analytical method and target compound database

A target database of toxic and odorous organic chemicals relevant to materials emissions has been developed. Compound sources are listed in Table 1 and the list itself comprises several hundred compounds. After intensive method development/optimisation, the following GC analytical parameters were established:

Capillary column:	60 m x 0.25 mm ID x 0.25 µm film thickness DB-1 MS (translatable to 30 m equivalent)
GC oven programme:	45°C (5 mins), then 6°C/min to 170°C, then 15°C/min to 300°C for 5 mins

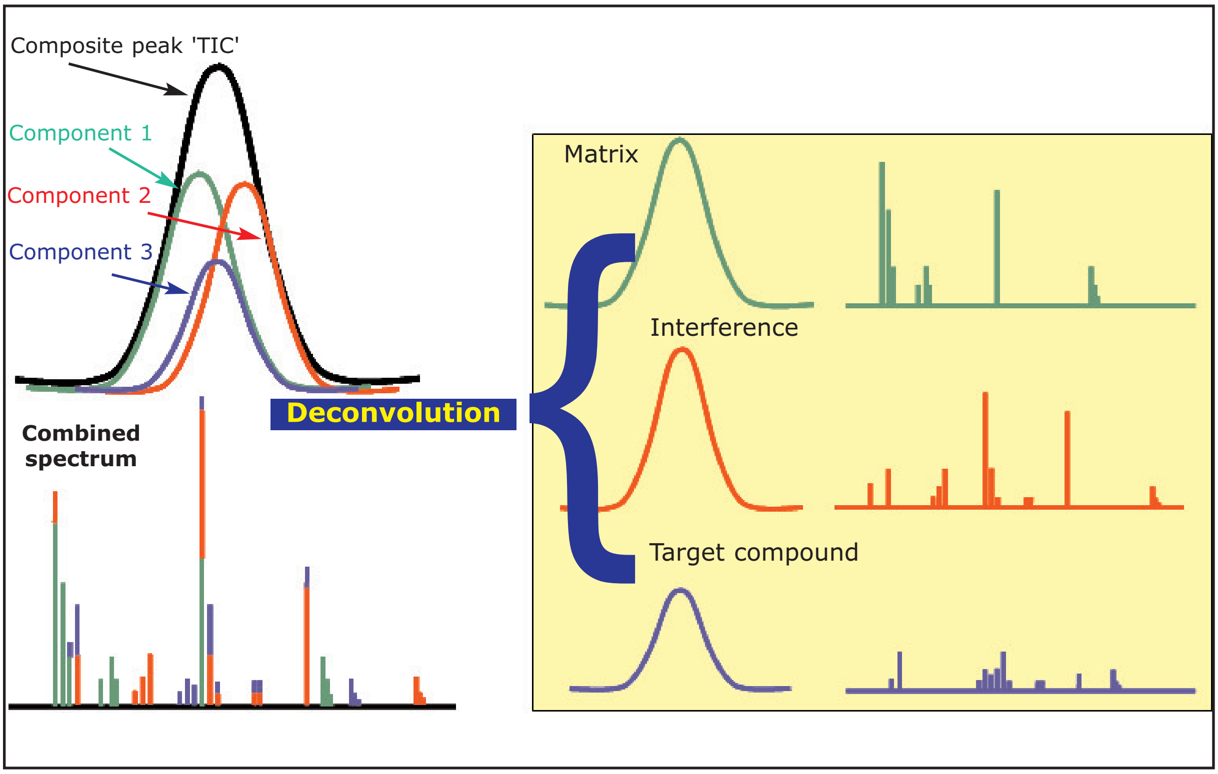


Figure 2: An illustration of mass spectral deconvolution as carried out by AMDIS

Source	Compound description
Cal 01350 CHPS	Common compounds of interest (Alevantis 2003 (5))
Cal 01350 CHPS	Chemicals with Chronic Reference Exposure Levels (CRELS) : 08/03
Cal 01350 CHPS	Carcinogens, mutagens, *etc*. from Cal. EPA 'Prop 65' list : 12/04
Cal 01350 CHPS	Cal. EPA ARB Toxic Air Contaminants (TACS) : 12/04
AgBB	NIKs (LCIs) from AgBB : 07/04
AgBB	Class 1 or 2 carcinogens (www.dguv.de/bgia/de/fac/kmr/index.jsp) : 06/04
prEN 15052	GC compatible carcinogens as required by prEN 15052 : 10/04
rEN 15052	NIKs (LCIs) as listed in prEN 15052 : 10/04

Table 1: Target compounds used for development of materials emissions database

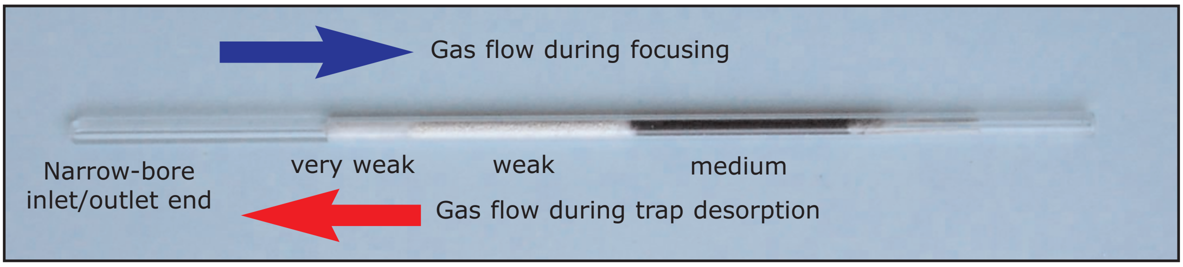


Figure 3: Multi-sorbent focusing trap for materials emissions testing, desorbed in backflush direction for simultaneous analysis of VOCs and SVOCs

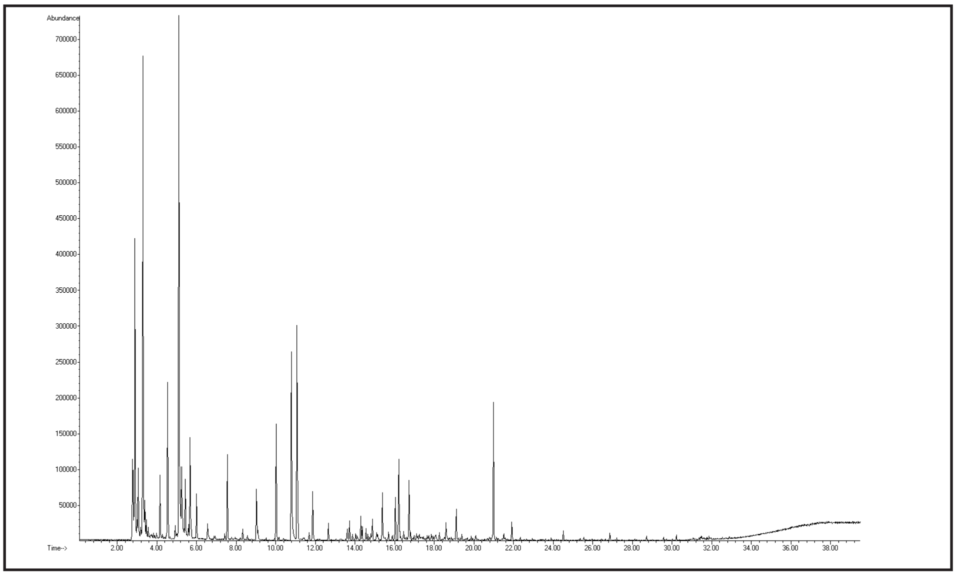
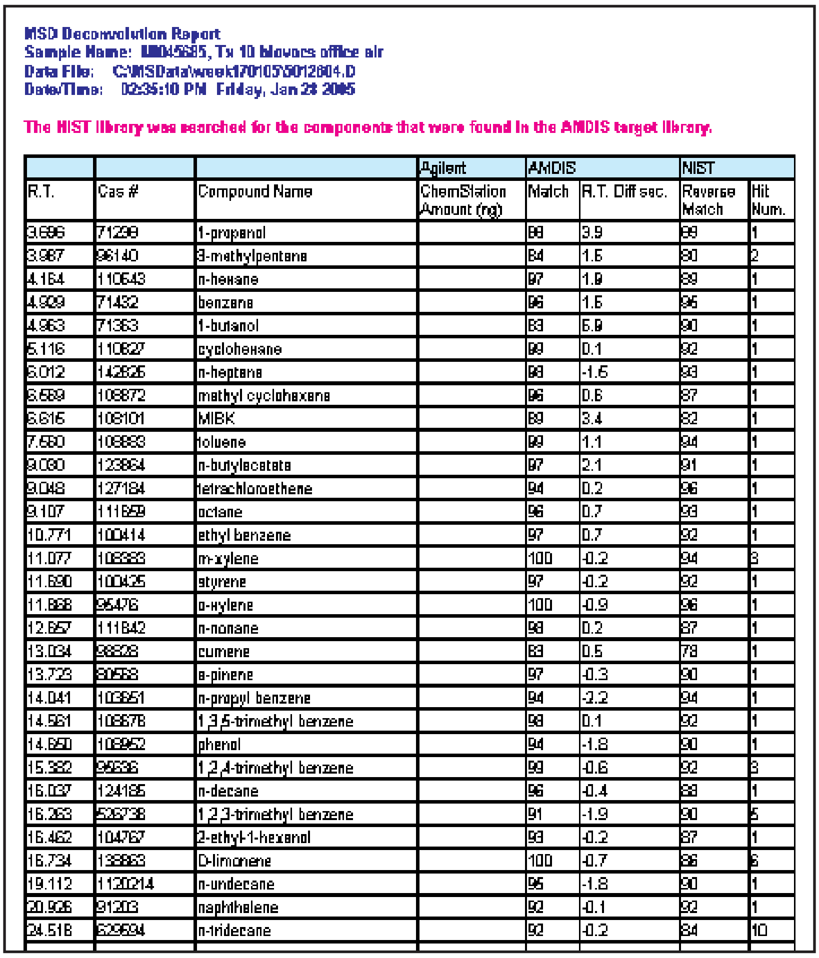


Figure 4: 1.3 L sample of office air collected using multi-sorbent tubes and analysed using thermal desorption with the GC/MS parameters as detailed above



MSD Deconvolution Report
Sample Name: UU045685, Tx 10 blovocs office air
Data File: C:\MSData\week170105\5012604.D
Date/Time: 02:35:10 PM Friday, Jan 28 2005

The NIST library was searched for the components that were found in the AMDIS target library.

			Agilent	AMDIS		NIST	
R.T.	Cas #	Compound Name	ChemStation Amount (ng)	Match	R.T. Diff sec.	Reverse Match	Hit Num.
3.696	71238	1-propanol		88	3.9	89	1
3.987	96140	3-methylpentane		84	1.5	80	2
4.164	110543	n-hexane		97	1.9	89	1
4.929	71432	benzene		96	1.5	95	1
4.963	71363	1-butanol		83	5.9	90	1
5.116	110827	cyclohexane		99	0.1	92	1
6.012	142825	n-heptane		98	-1.5	93	1
6.569	108872	methyl cyclohexane		96	0.6	87	1
6.615	108101	MIBK		89	3.4	82	1
7.580	108883	toluene		99	1.1	94	1
9.030	123864	n-butylacetate		97	2.1	91	1
9.048	127184	tetrachloroethene		94	0.2	96	1
9.107	111659	octane		96	0.7	93	1
10.771	100414	ethyl benzene		97	0.7	92	1
11.077	108383	m-xylene		100	-0.2	94	3
11.690	100425	styrene		97	-0.2	92	1
11.868	95476	o-xylene		100	-0.9	96	1
12.657	111842	n-nonane		98	0.2	87	1
13.034	98828	cumene		83	0.5	78	1
13.723	80568	a-pinene		97	-0.3	90	1
14.041	103651	n-propyl benzene		94	-2.2	94	1
14.561	108678	1,3,5-trimethyl benzene		98	0.1	92	1
14.650	108952	phenol		94	-1.8	90	1
15.382	95636	1,2,4-trimethyl benzene		99	-0.6	92	3
16.037	124185	n-decane		96	-0.4	88	1
16.263	526738	1,2,3-trimethyl benzene		91	-1.9	90	5
16.462	104767	2-ethyl-1-hexanol		93	-0.2	87	1
16.734	138863	D-limonene		100	-0.7	86	6
19.112	1120214	n-undecane		95	-1.8	90	1
20.926	91203	naphthalene		92	-0.1	92	1
24.518	629594	n-tridecane		92	-0.2	84	10

Figure 5: DRS report from the office air sample, showing 31 compounds positively identified

MS scan:	33 to 300 amu; with 2.76 scans per second
Source:	230°C; Quad 150°C; Aux 260°C

A special multi-sorbent cold trap was also developed (Figure 3). This was desorbed in 'backflush' mode to facilitate simultaneous analysis of VOCs and semi-VOCs. In short, semi-volatiles were retained and quantitatively released from the weak sorbents in the front of the cold trap, whereas more volatile compounds were quantitatively retained and released from the stronger sorbents at the rear of the trap. Examples of analytical thermal desorption parameters for materials emissions testing are given in relevant standard methods and other publications (TDTS 56 and 65).

Experiments and results

Application of the prototype database was evaluated for a 1.3 L sample of office air collected using a multi-sorbent tube (Figure 4). This was initially processed using conventional GC/MS software (ChemStation) using retention time locking plus target and qualifier ions to identify target compounds from a screenable database. Using this standard procedure 45 compounds were 'detected' - 21 of which were confirmed with a good match, with a further 24 compounds having one or more qualifier ions out of range *i.e.* only tentatively identified. Under normal circumstances, these tentatively identified compounds would then require time-consuming manual investigation by a skilled analyst to qualify whether or not the compound was actually present.

The same chromatographic data were then reprocessed using DRS and the new materials emissions database *i.e.* The data were reprocessed using a combination of standard retention-time-locked GC/MS software with additional automatic spectral deconvolution of overlapping components and comparison of the deconvoluted spectra with those included into the materials emissions database. The result from this was then further confirmed by cross checking the deconvoluted spectra from the sample with a reverse search of the NIST02 database. After this, 31 compounds were positively identified with RT +/- 5 seconds and >80% spectral match (Figure 5). No additional manual investigation was required.

The entire DRS process *i.e.* conventional data processing with retention time locking, spectral deconvolution, comparison with spectra in the materials emissions database and cross-checking against the full NIST library - is fully automated and takes 2-3 minutes, depending on the power of the PC used. The integration of automated spectral deconvolution greatly enhances the detection and identification of trace target compounds *i.e.* it reduces false negatives, but without increasing the risk of false positives.

This aspect was further explored using a similar, but much smaller database, developed by Markes International for improving the detection of chemical warfare agents in civilian environments as a guard against terrorist attack or other chemical incident. In the area of civil defence, false negatives and positives must both be avoided, because unnecessary evacuation of a major public building or transport system (*e.g.* underground railway station) can seriously endanger human life. In this experiment, a 2.5 ppm level standard of 21 chemical warfare agents was prepared in diesel.

Even with the benefit of Retention Time Locking, only 3 of the 21 compounds were correctly detected in initial analysis of the chromatographic data using conventional Chemstation GC/MS data processing as described (Figure 6).

Subsequent re-analysis of this data using the Markes CW database and Agilent's DRS software successfully identified 14 of the chemical agents (Figure 7). This dramatic improvement would make a significant difference to agent detection/civil defence in the real world.

Summary and relevance to materials emissions testing

Although civil defence is a very different field, materials emissions protocols such as the German AgBB protocol for flooring, the Californian CHPS program for school buildings and the provisional new CEN standard prEN 15052, all require identification and measurement of trace toxic compounds against potentially very complex backgrounds. Data shown here indicate that DRS software in combination with the new extensive database of toxic compounds of interest to materials emissions (>200 compounds) will make a significant difference to materials emissions testing as required by such protocols *i.e.* It should allow automated, cost-effective and accurate analysis of materials emissions data for trace target components with reasonable confidence that there will be minimal false positives or negatives.

References

1. GREENGUARD^{TM} Certification - www.greenguard.org

2. AgBB protocol: Health-related evaluation procedure for VOC and SVOC emissions from building products - July 2004. Available from DIBT (German Institute of Building Technology, Berlin) (Also see prEN 15052 available from European National Standards Institutes.)

3. The Collaborative for High Performance Schools (CHPS) - Section 01350 - Special Environmental Requirements (www.chps.net)

4. prEN 15052 - Resilient, textile and laminate floor coverings - Evaluation and requirements of VOC emissions

5. Alevantis L. 2003. 'Building material emissions study'. California Integrated Waste Management Board Publication No. 433-03-015. Also accessible at: www.ciwmb.ca.gov/GreenBuilding/Specs/Section01350/METStudy.htm