Thermal Desorption Technical Support

Note 47: The Analysis of Landfill Gas Compounds using Thermal Desorption GC/MS and a Retention Time Locked Database

Keywords:

VOCs, directive, compliance, identification

Introduction

As a consequence of their content and decomposition processes, landfill sites containing domestic and commercial waste produce a variety of odorous and toxic volatile organic compounds (VOCs) by a time dependent process. A recent European Directive - 1999/31/EC - on Landfill of Waste, specifies the following actions to be taken by Local Authorities involved in the disposal of waste to landfill sites. Under the directive:

- Landfill sites must be classified as either hazardous, non-hazardous (municipal) or inert

- Monitoring requirements for all sites are specified as follows:

  - the volume and composition of leachate

  - the composition of both ground water and the water of any nearby streams (if applicable)

  - monitoring of bulk gases (*e.g.* CO_2, CH_4, O_2) should be carried out monthly while the landfill site is in operation and 6-monthly during the after-care phase. Other gases must be monitored as required (see below).

  - Emissions of odours and dust must be minimised. All except 'inert' landfill sites must be monitored for the priority pollutants (see Table 1) at least annually or more frequently if required. Most of the priority pollutants are volatile organic compounds (VOCs).

  - In the UK, a standard sampling and analytical protocol for compliance with the monitoring requirements of this directive is currently being finalised by the Environment Agency. It specifies pumped sampling onto 2-bed Silcosteel sorbent tubes followed by TD-GC/MS analysis. Other European countries are also in the process of drafting compliance protocols.

Objectives

As well as the 20 target compounds listed in Table 1, landfill gas may contain several hundred VOCs and other gases. It was therefore necessary to develop a complete analysis method (thermal desorption - gas chromatography - mass spectrometry (TD GC/MS)) that would be able to sample, analyse and positively identify the presence (or absence) of each of these target compounds. Using the unique features available within the Markes ULTRA-UNITY TD system linked to the Agilent 6890 GC 5973 MS with Chemstation software the following objectives were met:

- develop a conventional tube sampling protocol for the landfill gas
- develop a TD method for analysis of the 20 target compounds
- develop a GC/MS analytical method for maximum compound separation in time by mass
- create a Retention Time Locked (RTL) method
- produce an RT Locked target compound database

1) Vinyl Chloride (Toxic)	11) 1,2-Dichloroethene (Toxic)
2) 1,3-Butadiene (Toxic)	12) 1,1-Dichloroethane (Toxic)
3) Methyl Mercaptan (Odour)	13) Propyl Mercaptan (Odour)
4) Chloroethane (Toxic)	14) Tetrachloromethane (Toxic)
5) 1-Pentene (Odour)	15) Benzene (Toxic)
6) Furan (Toxic)	16) Trichloroethene (Toxic)
7) Ethyl Mercaptan (Odour)	17) Butyl Mercaptan (Odour)
8) 1,1- Dichloroethene (Toxic)	18) Dimethyldisulphide (Odour)
9) Dimethylsulphide (Odour)	19) Ethylbutyrate (Odour)
10) Carbon Disulphide (Odour) (Toxic)	20) 2-Butoxyethanol (Toxic)

Table 1: Priority Toxic & Odorous Compounds

Method

Sampling

The nature of landfill gas poses a number of problems when sampling onto sorbent tubes for thermal desorption GC (/MS) analysis.

Firstly, the labile nature of many of the target compounds precludes the use of ordinary stainless steel sorbent tubes, as many of the compounds of interest would break down when heated in these tubes. Therefore tubes which have been specially treated with a silica based inert coating must be used. These tubes have an extremely thin (Angstroms) inert coating bonded onto the stainless steel surface of the tube. The tube, and the sorbent retaining gauzes used at the front of the tube and between the different sorbents are all coated. These inert tubes have been shown to cause little or no decomposition of labile compounds during the sampling and thermal desorption processes (further information can be found in TDTS 14).

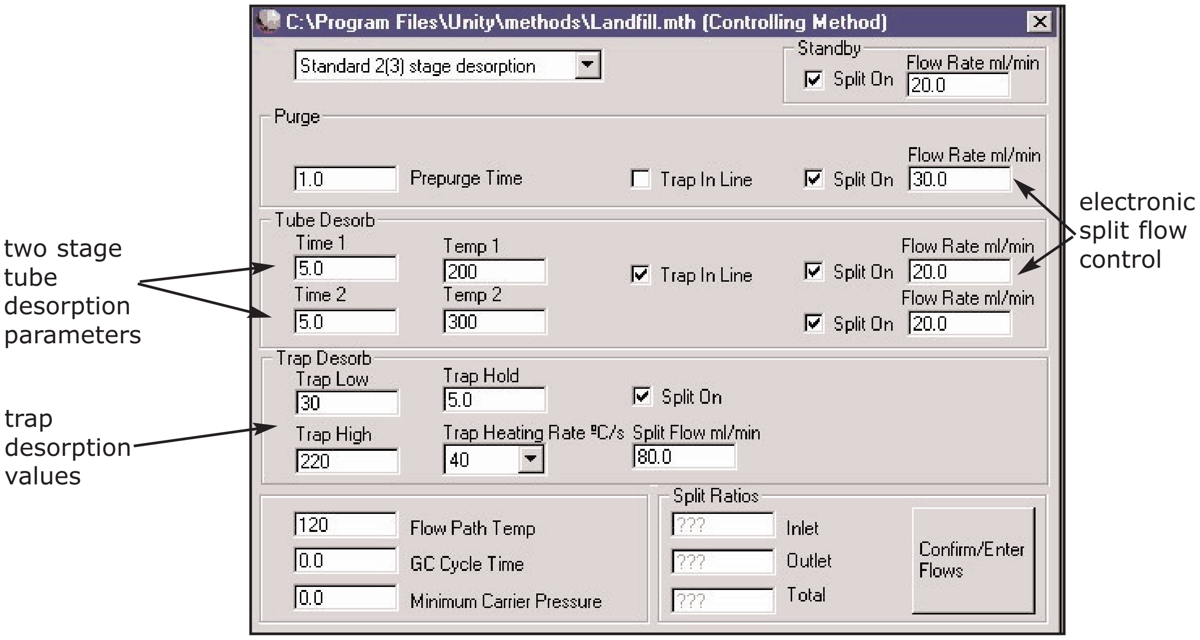
The target compound list also presents challenges with respect to the choice of sorbent material used to trap the compounds. The sorbent(s) used must be fully inert, in order not to compromise the thermally labile compounds, and must be suitable for a wide volatility range such as is found in the priority list. The sorbent mixture of choice is therefore Tenax TA™ which is suitable for trapping the less volatile compounds such as benzene, backed up by a bed of UniCarb™ (formerly known as Spherocarb™) which is a strong, carbonised molecular sieve sorbent, suitable for trapping the volatile compounds such as vinyl chloride. Both these sorbents are inert and have very low background artifact levels (<1.0 ng Tenax, <0.1 ng UniCarb).

In addition landfill gas has a very high humidity and is usually at an elevated temperature, which leads to relatively high levels of water being trapped on the tubes and therefore to the possibility of sample breakthrough and loss of some of the more volatile compounds. In order to reduce the amount of water trapped on the tube sample volumes should be restricted to 100 mL. To further remove excess water, each tube must be dry purged. Dry purging the sample tube simply involves passing a volume (in this case typically ~400 ml) of pure, dry, air or inert gas through the tube from the sampling end at a rate of ~50 ml/min, prior to analysis. Care must be taken not to exceed the breakthrough volumes for any of the retained analytes during the dry purge process.

Thermal Desorption Method

A 3-stage thermal desorption method was developed (details are shown in Figure 1).

A two-stage tube desorption method was used in order to desorb the labile sulphur compounds at the lower temperature before desorbing the remaining compounds at 300°C - a temperature which may have caused some degradation of the labile compounds.



C:\Program Files\Unity\methods\Landfill.mth (Controlling Method)

Standard 2(3) stage desorption

Standby: ☑ Split On — Flow Rate ml/min 20.0

Purge:
1.0 Prepurge Time
☐ Trap In Line
☑ Split On — Flow Rate ml/min 30.0

Tube Desorb:
Time 1 5.0 — Temp 1 200
Time 2 5.0 — Temp 2 300
☑ Trap In Line
☑ Split On — Flow Rate ml/min 20.0
☑ Split On — Flow Rate ml/min 20.0

Trap Desorb:
Trap Low 30 — Trap Hold 5.0
☑ Split On
Trap High 220 — Trap Heating Rate ºC/s 40 — Split Flow ml/min 80.0

120 Flow Path Temp
0.0 GC Cycle Time
0.0 Minimum Carrier Pressure

Split Ratios:
??? Inlet
??? Outlet
??? Total

two stage tube desorption parameters

trap desorption values

electronic split flow control

Figure 1: Thermal Desorption Method

The cold trap was also packed with Tenax TA and Unicarb. The trap low temperature was set to 30°C which allowed most of the water present in the sample to purge through the trap. A trap heating rate of 40°C/s was used (rather than the 100°C/s default rate) to give a more controlled release of compounds from the trap, again to ensure that there was no degradation of the labile compounds.

GC/MS Method

The column used was a 60 m, 0.25 mm I.D. 1.4 µm DBVRX column which was selected for optimum resolution of volatiles. GC/MS conditions were as follows:

Carrier Gas:	Helium
GC Temp 1:	40°C
Ramp Rate:	10°C/min
GC Temp 2:	225°C
MS Mode:	Scan
Mass range:	35 - 260 amu
Threshold:	50
Scans/Sec:	3.25

Injection of Standard Mix

A 50 ppm liquid standard containing the 20 target compounds was used to develop the chromatographic and MS method for optimal compound separation (Figure 2). Where complete, chromatographic resolution was not possible, compound identity was achieved from extracted ion profiles. Future quantitation would ultimately use this as well (Figure 3).

All the priority toxic and odorous compounds listed in Table 1 were identified, including the labile thiols and sulphides (Figure 4).

The 50 ppm standard was injected as a liquid, using the calibration solution loading rig (CSLR), onto a TD tube to be loaded into the ULTRA-UNITY system. However, real samples from the landfill site are taken as gas samples. To check that this would not affect the retention times of the target compounds an injection was made from the headspace above the methanol standard and the retention times of the target compounds was found to be the same (Figure 5).

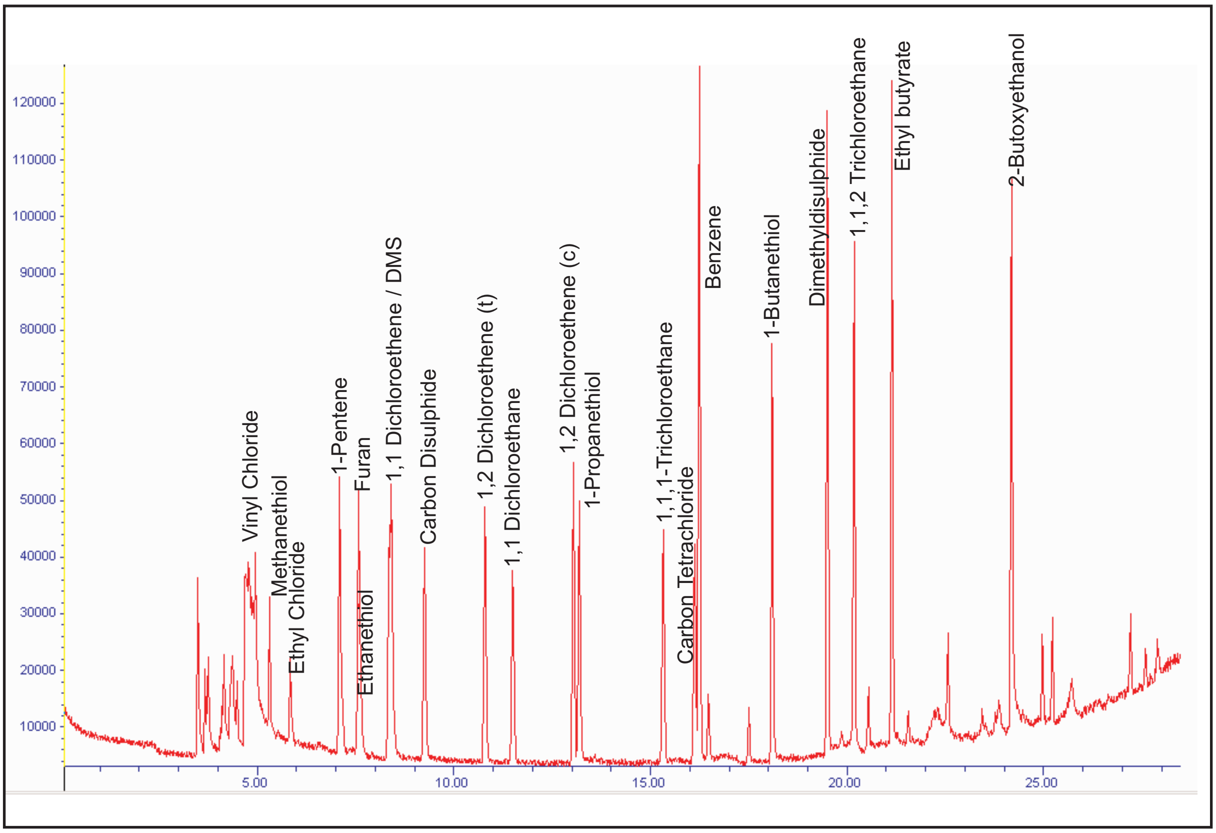
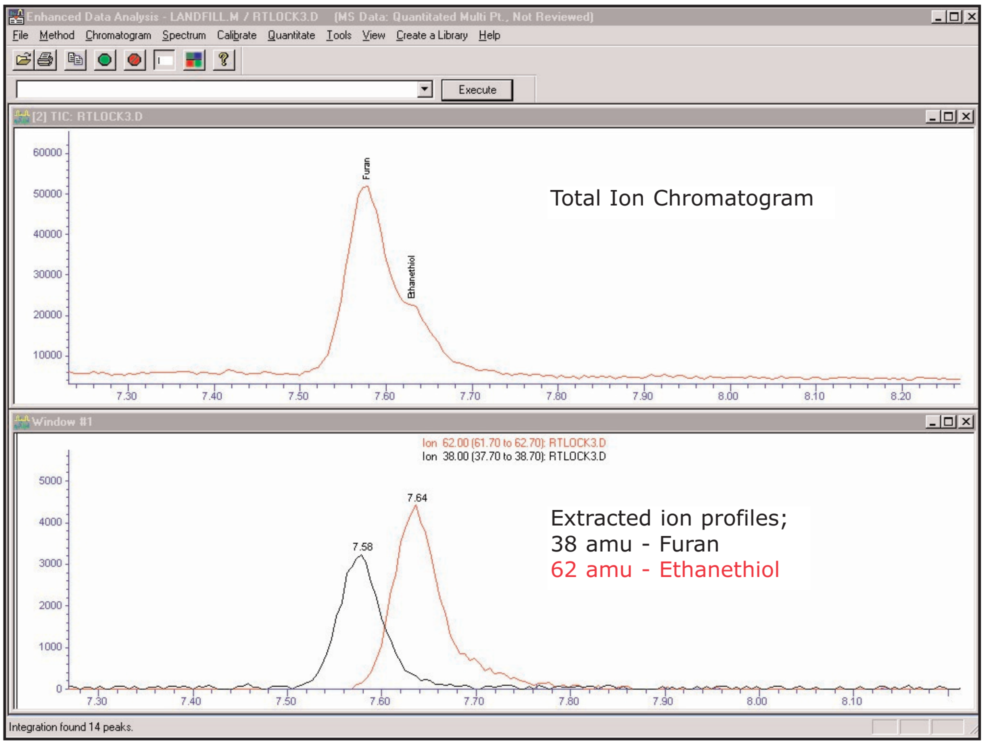


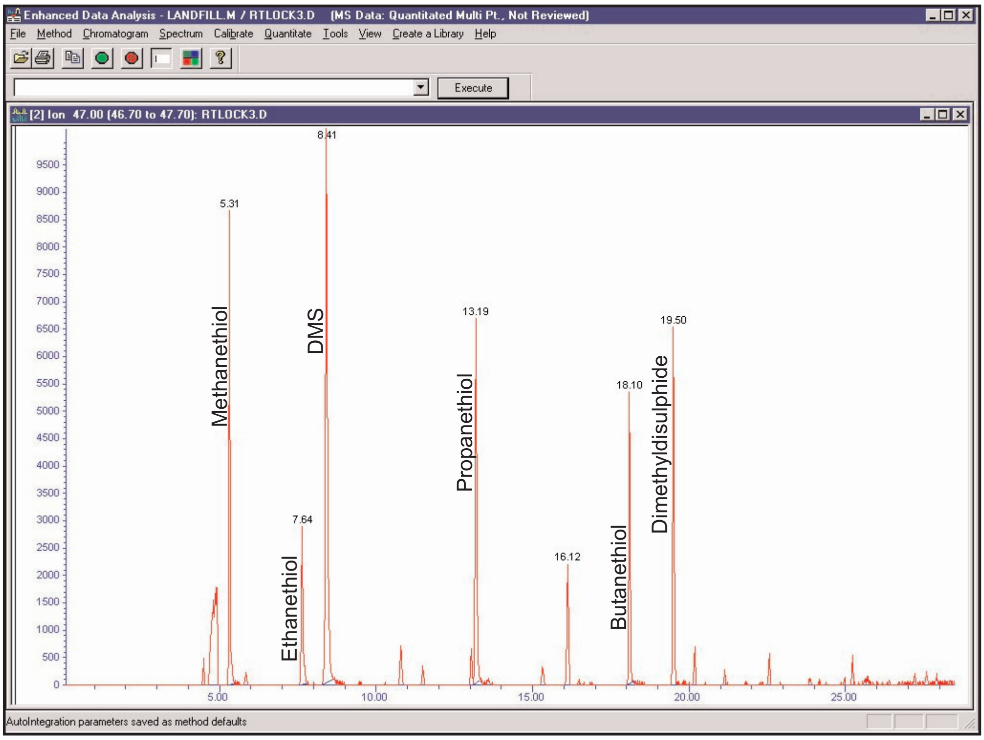
Figure 2: A 1 µl injection of a 50 ppm standard mix



Ion 62.00 (61.70 to 62.70): RTLOCK3.D
Ion 38.00 (37.70 to 38.70): RTLOCK3.D

Integration found 14 peaks.

Figure 3: Total Ion Chromatogram and Extracted ion profiles of furan and ethanethiol



Enhanced Data Analysis - LANDFILL.M / RTLOCK3.D (MS Data: Quantitated Multi Pt., Not Reviewed)

[2] Ion 47.00 (46.70 to 47.70): RTLOCK3.D

AutoIntegration parameters saved as method defaults

Figure 4: Extracted ion profile at 47 amu - thiols and sulphides

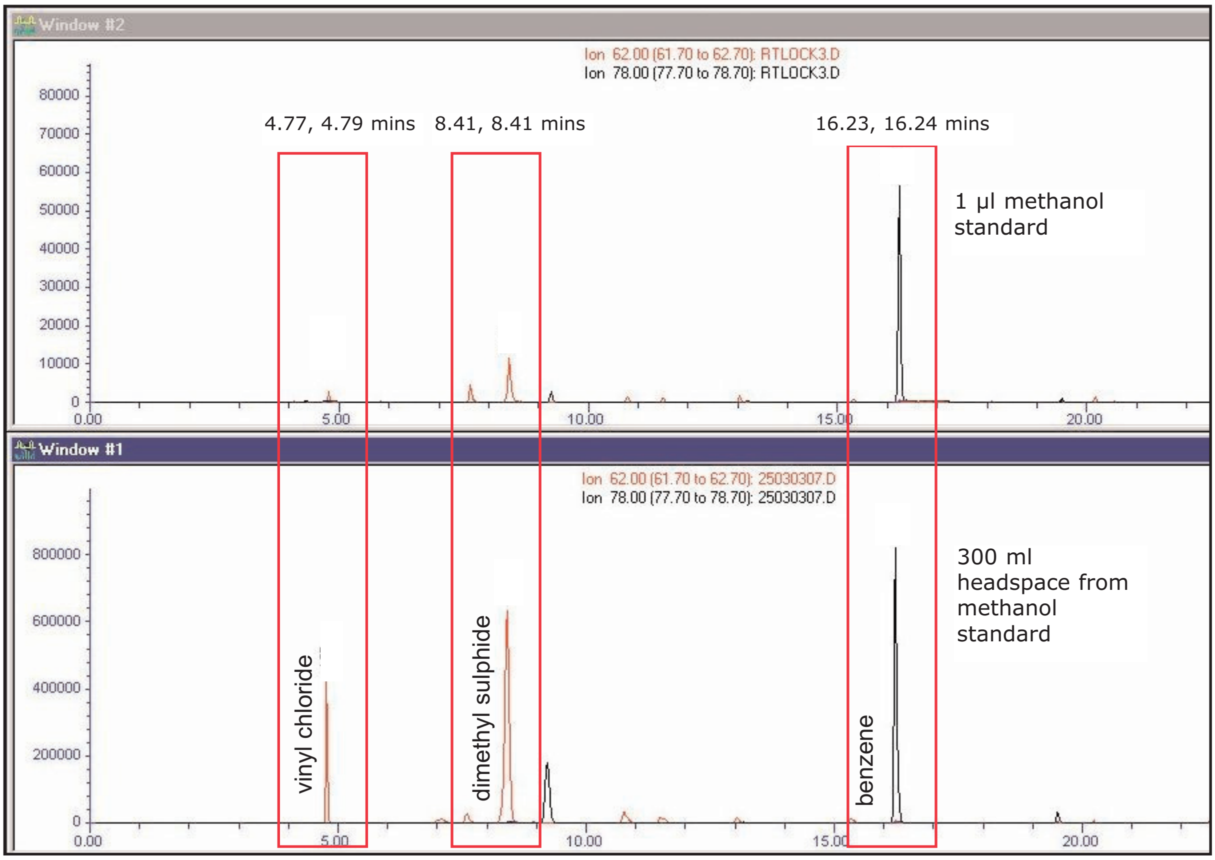


Figure 5: Comparison of standard by liquid injection and standard by headspace injection

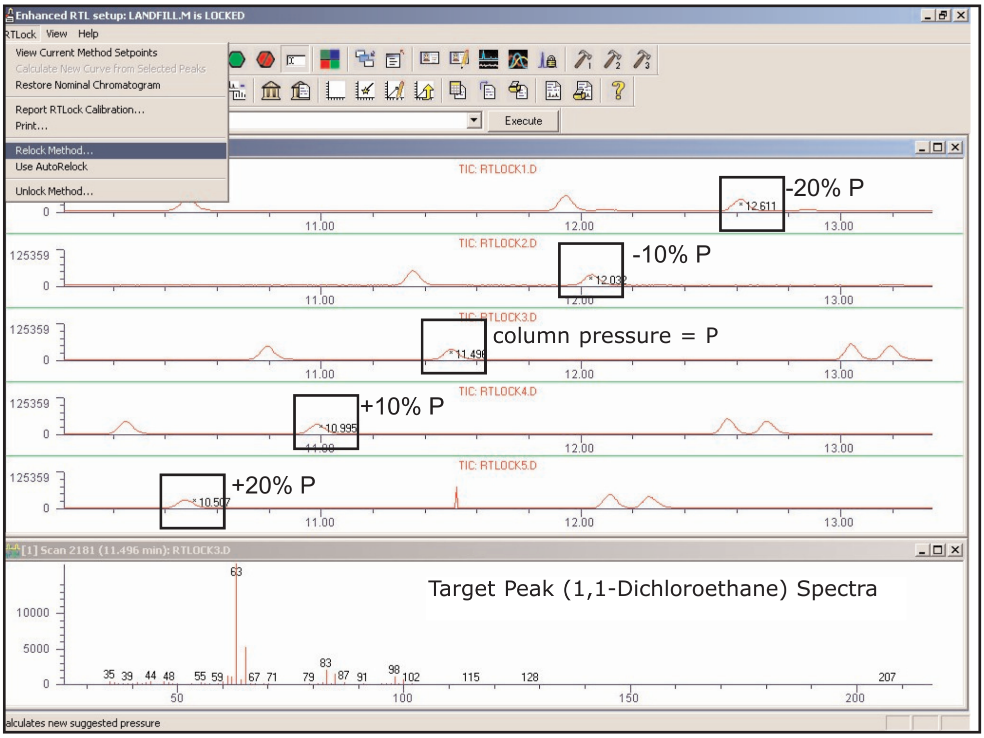


Figure 6: 5 data files acquired at different pressures

Compound Identification

A conventional MS (PBM) database was created for each target compound from the standard solution.

With very complex chromatograms, such as those obtained from real landfill gas samples, target peaks can be obscured by other co-eluting, or partially co-eluting compounds. Positive identification in such complex samples can be further complicated by tiny shifts in the retention times of target compounds due to small changes in carrier gas pressure each time the GC system is set up.

Therefore it is necessary to look for further levels of compound identification in order to confirm the presence or absence of a particular target analyte. To this end, a retention time locked database can be created

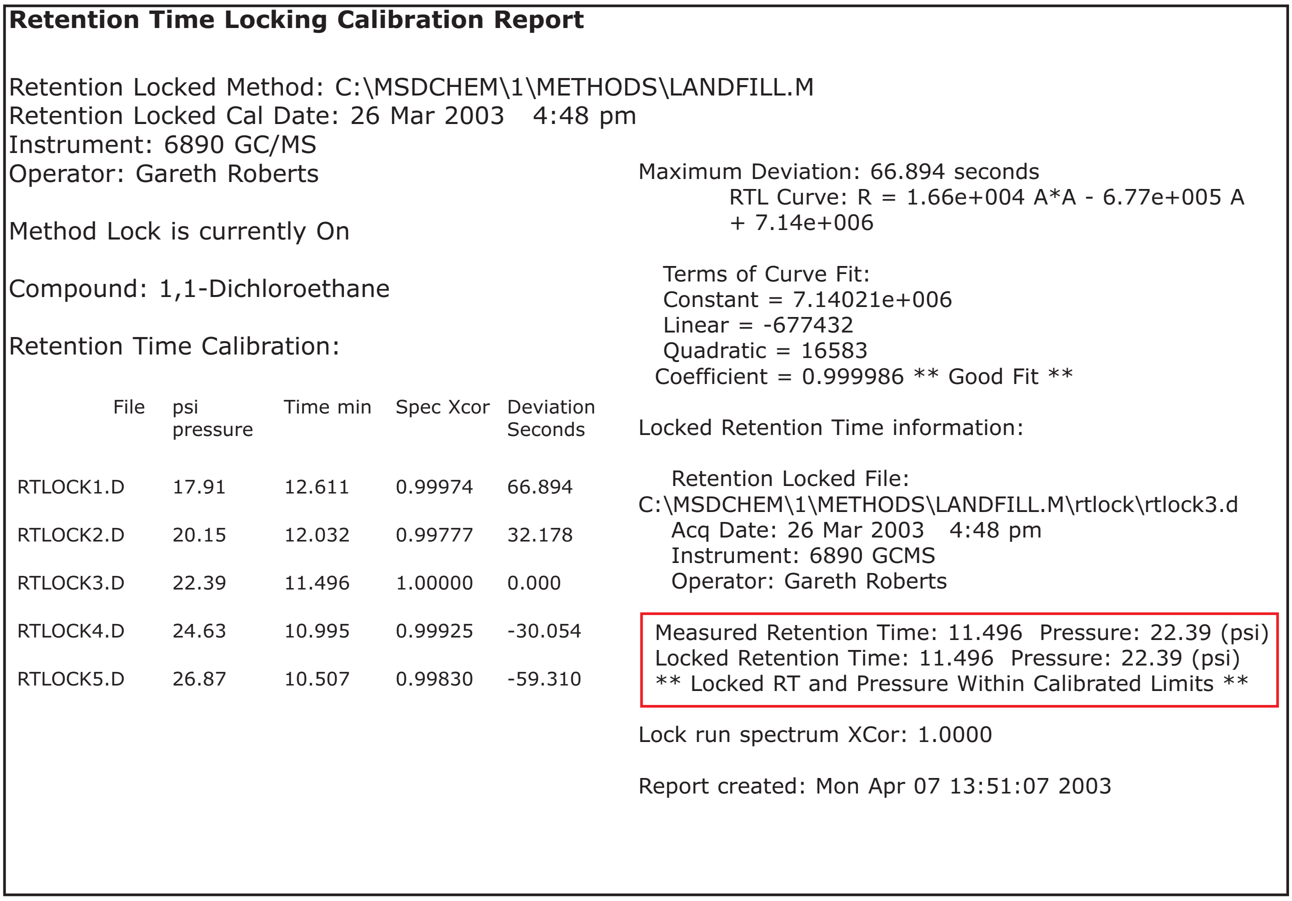
Using the 50 ppm standard as previously, five data files were acquired at different carrier gas pressures (±20%, ±10% and method value) (Figure 6) and retention time was calibrated against pressure. A target peak was specified - in this case 1,1 dichloroethane, and the retention time defined as given in the Retention Time Locking Calibration Report (Figure 7). The method is then locked to the target peak retention time.

The landfill MS library created from the standard solution is then converted to an RTL Target Database (Table 2) where against each target compound is listed a target ion, an expected retention time and 3 qualifying ions - these ions can be edited by the user if required. The RTL Database is then assigned to a method.

Analysis of real landfill samples

100 mL of Landfill gas sample was drawn through a sorbent tube packed with Tenax TA and UniCarb, and the tube analysed using the thermal desorption method developed above. The chromatogram is shown in Figure 8. The Chemstation retention time locked method then produced a Retention Time Locked Screen Report detailing which target compounds had been found shown in Table 3.

The report for this analysis is shown below. It consists of an identification status, X for a definite hit. ? for a partial hit; the expected retention time and deviation DRT; the target ion mass and response; qualifiers out of range which results in a partial (?) indentification; and finally the XCR value which is a number



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Retention Time Locking Calibration Report

Retention Locked Method: C:\MSDCHEM\1\METHODS\LANDFILL.M
Retention Locked Cal Date: 26 Mar 2003   4:48 pm
Instrument: 6890 GC/MS
Operator: Gareth Roberts

Method Lock is currently On

Compound: 1,1-Dichloroethane

Retention Time Calibration:

      File     psi        Time min   Spec Xcor   Deviation
               pressure                          Seconds

 RTLOCK1.D     17.91      12.611     0.99974     66.894

 RTLOCK2.D     20.15      12.032     0.99777     32.178

 RTLOCK3.D     22.39      11.496     1.00000     0.000

 RTLOCK4.D     24.63      10.995     0.99925     -30.054

 RTLOCK5.D     26.87      10.507     0.99830     -59.310

Maximum Deviation: 66.894 seconds
        RTL Curve: R = 1.66e+004 A*A - 6.77e+005 A
        + 7.14e+006

  Terms of Curve Fit:
  Constant = 7.14021e+006
  Linear = -677432
  Quadratic = 16583
 Coefficient = 0.999986 ** Good Fit **

Locked Retention Time information:

   Retention Locked File:
C:\MSDCHEM\1\METHODS\LANDFILL.M\rtlock\rtlock3.d
   Acq Date: 26 Mar 2003   4:48 pm
   Instrument: 6890 GCMS
   Operator: Gareth Roberts

 Measured Retention Time: 11.496  Pressure: 22.39 (psi)
 Locked Retention Time: 11.496  Pressure: 22.39 (psi)
 ** Locked RT and Pressure Within Calibrated Limits **

Lock run spectrum XCor: 1.0000

Report created: Mon Apr 07 13:51:07 2003
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Figure 7: Retention Time Locking Calibration Report

comparing the spectrum of the compound to the library. A low XCR value should not be taken as non-identification, it could be the correct compound but occluded by a co-eluting non-target compound, producing a poor spectral match.

From this report it is evident that 8 compounds were definitely found and 5 were absent. With the remaining 10 compounds it was not possible to state with complete certainty whether they were present or absent from the sample. This is almost certainly due to the complexity of the ‘real’ sample compared with the standard.

Further confirmatory compound identification using spectral deconvolution (AMDIS) and NIST searching software can be used to obtain additional positive identification (see TDTS 62).

Conclusions

A complete thermal desorption GC/MS method has been successfully developed for the highly complex mixture of toxic and priority odourous VOCs found in landfill gas.

Markes International inert coated 2-bed sorbent tubes were used to take small (100 ml) samples of landfill gas and the tubes were dry purged prior to analysis to remove excess water.

Using the power of the Agilent GC/MS Chemstation, the presence (or absence) of target compounds was confirmed using a Retention Time Locked screenable database. This multiple level of identification confirmation is necessary when analysing such complex mixtures as those found in landfill gas sites.

Additional confirmatory techniques can be used for identification which utilises different library search algorithms, such as AMDIS, NIST *etc*.

Cpd#	**Compound Name**	**TIon**	**Exp_RT**	**Q1**	**Q2**	**Q3**
1	Ethene, chloro-	62	4.79	27	64	26
2	1,3-Butadiene	39	5.07	54	53	27
3	Methanethiol	47	5.32	48	45	46
4	Ethyl Chloride	64	5.85	66	49	26
5	1-Pentene	42	7.10	55	41	70
6	Furan	98	7.58	39	38	40
7	Ethanethiol	82	7.64	29	47	34
8	Ethene, 1,1-dichloro	91	8.36	96	98	63
9	Dimethyl sulfide	92	8.42	47	45	46
10	Carbon disulfide	76	9.26	44	78	77
11	Ethene, 1,2-dichloro-, (E)-	61	10.80	96	98	26
12	Ethane, 1,1-dichloro-	63	11.51	65	27	83
13	Ethene, 1,2-dichloro-, (Z)-	61	13.05	96	98	63
14	1-Propanethiol	76	13.20	43	47	42
15	Ethane, 1,1,1-trichloro-	97	15.33	99	61	117
16	Carbon Tetrachloride	117	16.13	119	121	82
17	Benzene	78	16.24	77	51	50
18	Trichloroethylene	95	17.63	130	132	97
19	1-Butanethiol	41	18.10	56	27	90
20	Diusulfide, dimethyl	94	19.51	79	45	46
21	Ethane, 1,1,2-trichloro-	97	20.18	83	99	85
2285	Butanoic acid, ethyl ester	71	21.14	43	88	27
2327	Ethanol, 2-butoxy-	57	24.18	45	87	56

Table 2: Landfill MS Library converted to RTL Target Database

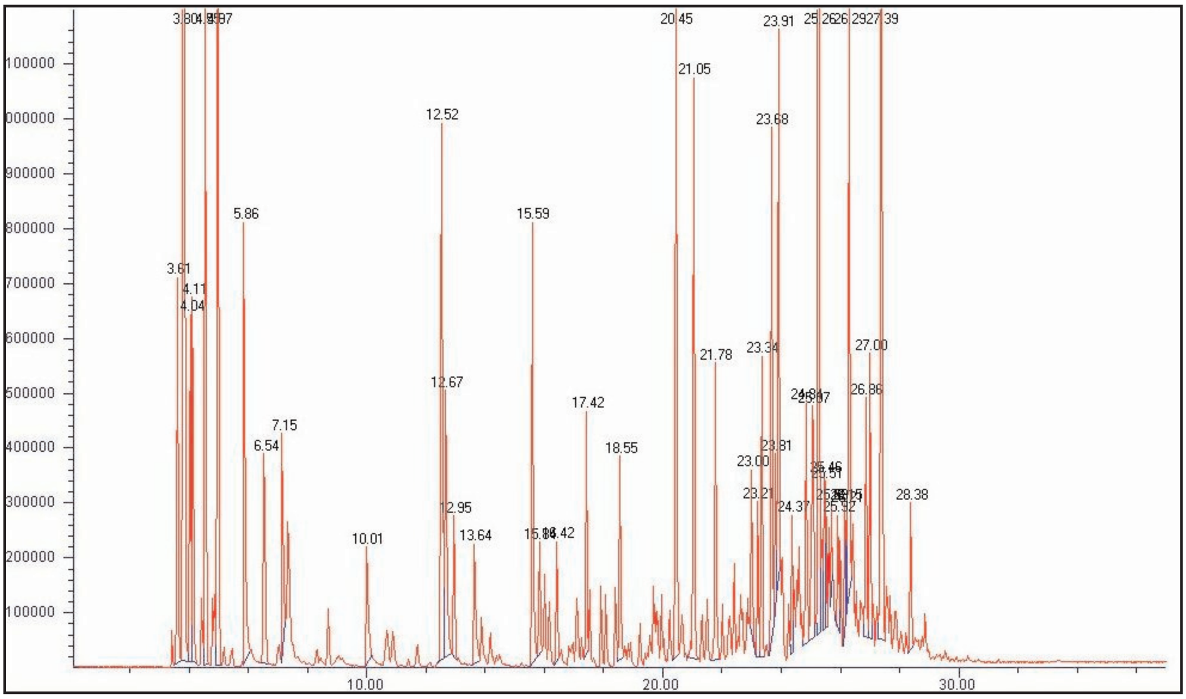

Figure 8: 100 mL landfill gas sample

	Compound	Status	ExpRT	DeltaRT	Tgt	Tgt Response	Q ions out of Range	XCR
1	Ethene, chloro-	?	4.79	0.008	62	1790570	27, 26	0.6
2	1,3-Butadiene	?	5.07	-0.099	39	2684920 7	54, 53, 27	0.06
3	Methanethiol		5.32		47	-Not Found-		
4	Ethyl Chloride	?	5.85	-0.041	64	118661 6	26	0.64
5	1-Pentene	?	7.10	0.046	42	301883 0	55, 41, 70	0.06
6	Furan	x	7.58	-0.066	98	289780		0.97
7	Ethanethiol		7.64		82	-Not Found-		
8	Ethene, 1,1-dichloro-	?	7.86	-0.050	91	147586	96, 98	0.39
9	Dimethyl sulfide	x	8.42	-0.094	92	209966		0.82
10	Carbon disulfide	x	9.26	-0.078	76	266235		0.98
11	Ethene, 1,2-dichloro-, (E)	?	10.8	-0.099	61	160590	26	0.49
12	Ethane, 1,1-dichloro-	?	11.51	-0.102	63	299526	27	0.97
13	Ethene, 1,2-dichloro- (Z)	x	13.05	-0.099	61	3006044		0.99
14	1-Propanethiol		13.20		76	-Not Found-		
15	Ethane, 1,1,1-trichloro	x	15.33	-0.092	97	79064		0.99
16	Carbon Tetrachloride		16.13		117	-Not Found-		
17	Benzene	x	16.24	-0.087	78	1570194		0.99
18	Trichloroethylene	x	17.63	-0.099	95	769325		0.99
19	1-Butanethiol	?	18.10	-0.021	41	210295	56, 27, 90	0.15
20	Disulfide, dimethyl	x	19.51	-0.099	94	215921		0.98
21	Ethane, 1,1,2-trichloro-		20.18		97	-Not Found-		
22	Butanoic acid, ethyl ester	?	21.14	-0.093	71	6419284	27	0.88
23	Ethanol, 2-butoxy-	?	24.18	-0.131	57	548700	45, 46	0.79

Table 3: Retention Time Locked Screen Report

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