Application

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Application Note 529

High-throughput, cost-effective analysis of environmental air contaminants in accordance with US EPA Method TO-15 using GC–TOF MS

Summary

This Application Note shows that the cost-effective combination of cryogen-free automation and rapid GC–TOF MS analysis delivers robust, high-throughput determination of priority hazardous air pollutants in accordance with US EPA Method TO-15. As well as allowing up to $200,000 additional revenue to be generated per year per system, the enhanced analytical performance of the new system opens up fresh application opportunities.

Introduction

US EPA Method TO-15 stipulates sampling and analytical procedures for measurement of the 97 volatile organic compounds (VOCs) within the list of hazardous air pollutants (HAPs) cited in the 1990 US Clean Air Act Amendments. Conventional GC with quadrupole MS is widely used and remains popular for TO-15, but increasing pressure on analytical laboratories has driven demand for systems offering improved sample throughput while maintaining or improving analytical performance.

One way of reducing analysis costs with the existing technological solution is to eliminate the use of liquid cryogen in the canister preconcentrator. Markes International's CIA *Advantage* system uses an efficient electrically-cooled sorbent trap to eliminate the costs, safety issues and complexities associated with cryogen-cooled focusing systems, while maintaining trapping performance for even the most volatile of the analytes specified in Method TO-15, such as propene. The CIA *Advantage* also features heated internal lines, efficient water management, uniquely effective purging of sample lines and up to 27 channels. This makes it a robust autosampler that can operate unattended for extended periods and accommodate a wide range of air concentrations and compound types.

Another option for boosting TO-15 productivity is to speed up the GC process, using shorter narrow-bore columns to reduce run times. This simple and effective step can be carried out using standard GC hardware, but it has not to date been widely applied to TO-15 because traditional quadrupole mass spectrometers struggle to handle narrow peaks at trace levels. They also suffer from spectral skew across a peak, due to the time it takes to scan across the m/z range.

In contrast, time-of-flight (TOF) mass spectrometers – of which Markes' range of BenchTOF mass spectrometers are a prime example – are inherently well-suited to handling narrow GC peaks. This is because they are dispersive (not scanning) instruments, and so effectively monitor all masses at once. These new bench-top systems can be cost-effectively coupled with any GC and provide a unique and powerful combination of performance advantages:

- **Full reference-quality spectra** (NIST/Wiley-compatible) at detection limits typical of quad-SIM means simultaneous analysis of target compounds and unknowns.
- **High speed** means greatly enhanced productivity and rapid return on investment.
- **Exceptional stability** minimises routine maintenance (*e.g.* source cleaning only required annually), and boosts productivity even further.
- **Full compliance** with EPA tuning and other standard method requirements.

This Application Note shows that, by combining the CIA *Advantage* with efficient GC and BenchTOF, users can triple their productivity while remaining fully compliant with Method TO-15 and maintaining (or enhancing) analytical performance. Proof of performance for this system is provided by running a 65-component TO-15 standard and monitoring ambient air in a clean, semi-rural environment.

Experimental

Sampling:
A 65-component TO-15 canister air standard was used to test method performance. Real air monitoring was then carried out at a sheltered, semi-rural location in the UK, 250 m west of a major road and just south of a large regional hospital. Samples were collected during the evening rush hour (17:30) when traffic flow was at a maximum.

Preconcentration:
Instrument: CIA *Advantage*-HL™ (Markes International)
Cold trap: Air toxics trap (part no. U-T15ATA-2S)
Prepurge time: 2 min at 20 mL/min
IS loop fill time: 1 min at 20 mL/min
IS loop equilibrate time: 0.0 min
IS loop inject time: 1 min at 50 mL/min
Sampling into the cold trap: Various between 10 and 50 mL/min
Cold trap low: 40 °C
Line purge: 1 min at 50 mL/min
Trap purge: 1 min at 50 mL/min
Cold trap high: 270 °C for 2 min
Trap heating rate: Maximum
Split ratio: Various
Flow path: 120 °C

GC:
Column: J&W DB-624 UI, 20 m × 0.18 mm × 1.0 µm
Oven ramp: 35 °C (1.5 min), then 20 °C/min to 110 °C (0 min), then 35 °C/min to 210 °C (0.3 min)
Total run time: 8.41 min
Flow: 1.5 mL/min (constant flow)

TOF MS:
Instrument: BenchTOF™ (Markes International)
Filament voltage: 1.8 V
Ion source temp.: 250 °C
Transfer line temp.: 210 °C
Mass range: m/z 40–300
Data rate: 6 Hz (1667 spectral accumulations per data point)
Ionisation energy: 70 eV
Solvent delay: 50 s

Results and discussion

1. Benefits of speeding up GC analysis for Method TO-15

Traditionally, the detection of TO-15 compounds has been performed by quadrupole MS in either full-scan or selected ion monitoring (SIM) mode. However, full-scan mode is limited by sensitivity, because quadrupoles are mass filters, with most ions going to waste as the instrument scans across the selected mass range. On the other hand, SIM mode is restricted to target compounds, meaning that full characterisation of the sample is not possible in a single run and retrospective searching of data is limited.

The use of a dispersive (or comprehensive) technique, such as TOF MS, overcomes this issue by providing highly sensitive detection while acquiring full-range mass spectra, to allow both target and unknown identification in a single, rapid analysis.

To illustrate the performance of the system for a wide range of environmental contaminants, Figure 1 shows the analysis of a 100 ppbv 65-component TO-15 standard.

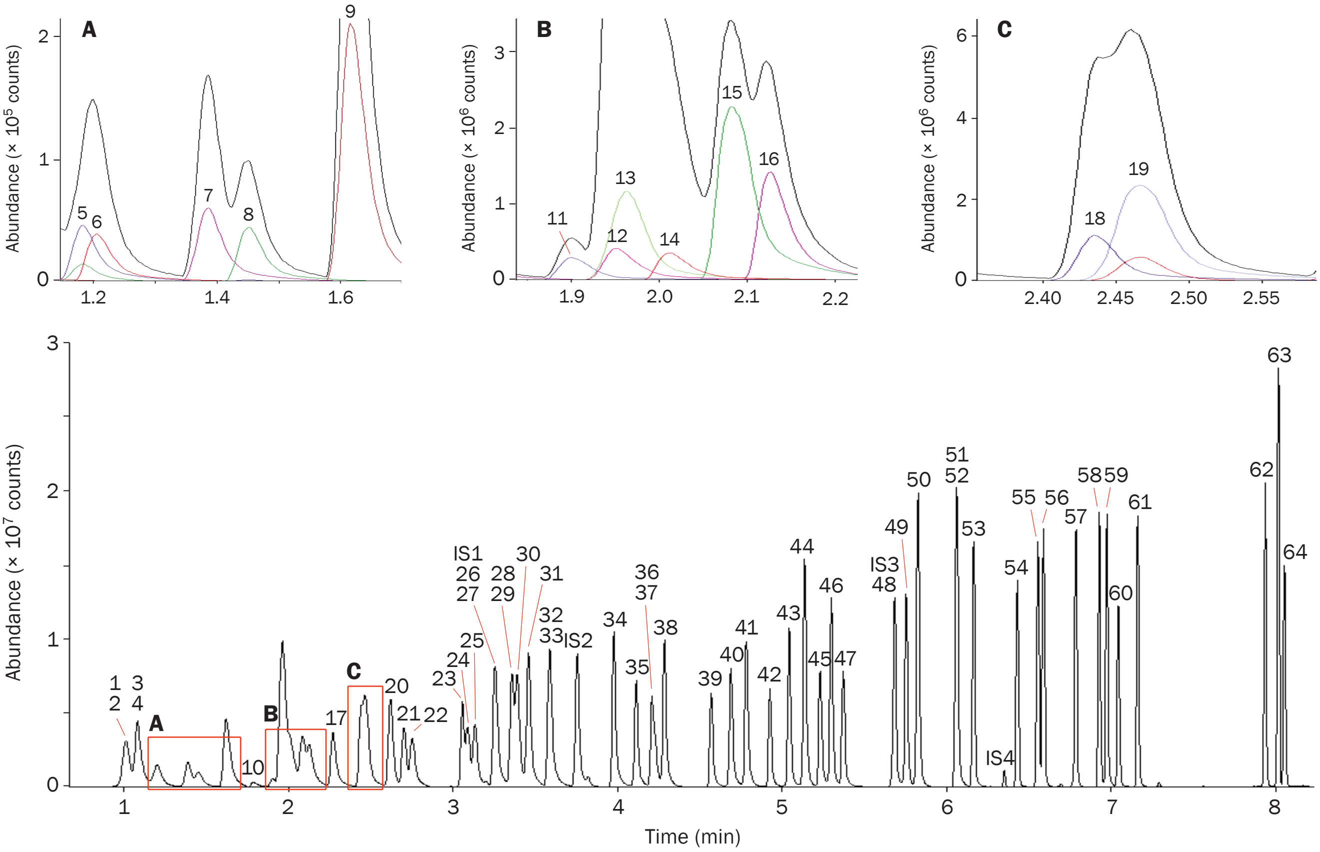

Figure 1: Analysis of 250 mL of a 100 ppbv 65-component TO-15 standard – analyte numbers are listed in Table 1. Even with a rapid GC run time of just 8.4 minutes, key target compounds can be easily distinguished based on their quantitation ions, as shown by the overlaid EICs (coloured traces) in expansions **A–C**.

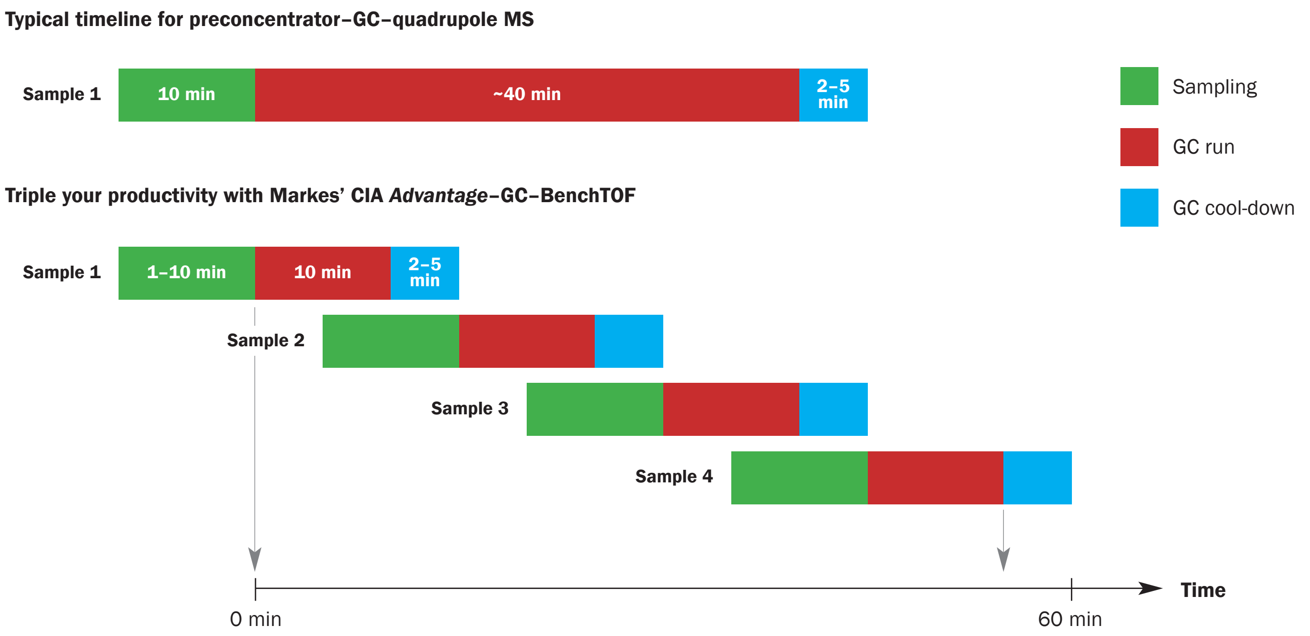

Figure 2: Illustration of how productivity is enhanced by a factor of three using the suggested analytical system. Four canister analyses can be completed in just over 1 hour by combining fast GC with the ability of the system to sample a new canister while a previous sample is being analysed (overlap mode).

The increased sensitivity of BenchTOF also means smaller samples can be taken. For example, sub-ppb detection limits that require pre-concentration of up to 1 L of sample with quadrupole instruments can now be matched with just tens of millilitres of sample using BenchTOF. This doesn't just speed up analytical cycle times, but also simplifies water management and minimises risk of breakthrough, thus extending the analyte volatility range. Further savings can also be achieved by using smaller canisters, which are cheaper to buy and easier to transport and store.

The high sensitivity of the TOF MS, combined with 15 minute GC cycle times and the ability of the CIA *Advantage* system to 'overlap' samples (*i.e.* to begin pre-concentration of a subsequent sample while analysis of the previous sample is ongoing), means that up to four samples can be analysed each hour (Figure 2).

The combined benefits of sensitivity, speed and overlap mode mean a two- or three-fold increase in sample throughput compared to regular GC–MS and swift return on investment.

A conservative estimate of one extra $80 sample per hour delivers over $200,000† additional revenue per year.

In addition, further savings can be realised, including: standardisation on smaller canisters, elimination of liquid cryogen and the general benefits of increased MS stability, such as reduced instrument down-time.

2. Spectral quality

Markes' BenchTOF time-of-flight mass spectrometers produce 'reference-quality' spectra that are directly comparable to those in commercial libraries such as NIST or Wiley. This dispenses with the need for custom weighted libraries used by other TOF systems on the market, and ensures confident identification of both targets and unknowns.

As an example of this excellent spectral quality, Figure 3 shows the spectral comparison for hexachlorobutadiene, which has forward and reverse matches of 922 and a probability of 98%.

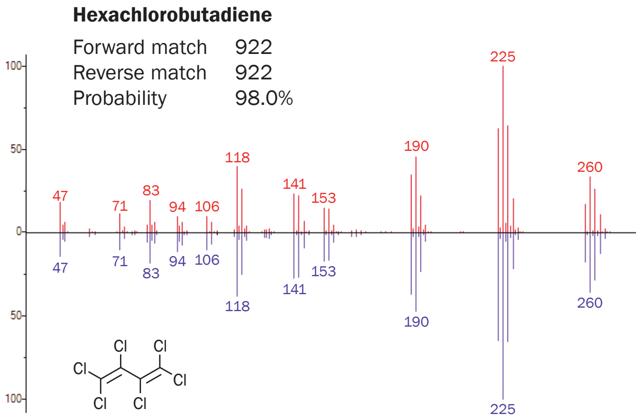

Figure 3: Comparison of the BenchTOF spectrum for hexachlorobutadiene (top, red) with the NIST14 library spectra (bottom, blue).

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† Based on 12 hours per day automated canister sample analysis, 5 days per week, 45 weeks per year.

3. Detection limits

The method detection limit (MDL), as defined by the US EPA, is the minimum concentration of a substance that can be measured and reported (with 99% confidence) to have an analyte concentration greater than zero. MDLs depend on a number of factors, including instrument and canister cleanliness, the nature of the matrix itself, detector performance, and pre-concentration sample volume limits. All must be taken into account when assessing the suitability of a system or method.

In accordance with Method TO-15, MDLs were calculated using the following equation, based on seven replicate runs of a commercial TO-15 standard.

$$\text{MDL} = t \times \text{standard deviation} \times \text{concentration}$$

where $t = 3.143$ (Student's *t*-value for 99% confidence for seven values).

Using this standard (equivalent to 0.06 ppbv in in a 500 mL sample with a 5:1 split), MDLs were found to range from 0.021 ppbv (21 pptv) for ethanol to 0.005 ppbv (5 pptv) for hexachlorobutadiene (Table 1), demonstrating the exceptional sensitivity of the CIA *Advantage*–BenchTOF for ultra-trace-level air-monitoring applications.

Across all the analytes in the sample, the method detection limit (MDL) was found to be at least an order of magnitude lower than the typical limit obtainable with a quadrupole instrument (~0.1 ppbv) operating in scan mode and under standard GC conditions – see Application Note 081. Note that SIM mode lowers detection limits for quadrupole instruments, but the ability to identify unknowns or perform retrospective searching for compounds of emerging concern is lost. With BenchTOF there is no compromise, because full spectral information can be collected with SIM-like sensitivity.

4. Linearity

Method TO-15 states that in the initial calibration, the calculated relative standard deviation (RSD) for the relative response factor (RRF) for each compound in the calibration table must be less than 30%, with at most two exceptions up to a limit of 40%.

A five-point calibration was performed (0.235, 0.47, 0.94, 4.7 and 23.5 ppbv) and the RSD for the relative response factors (RRFs) were calculated (Table 1). The RSDs for all RRFs passed the Method TO-15 criteria, and the average R^2 value of 0.997 indicated excellent linearity. The calibration curves for a selection of compounds in the TO-15 standard are shown in Figure 4.

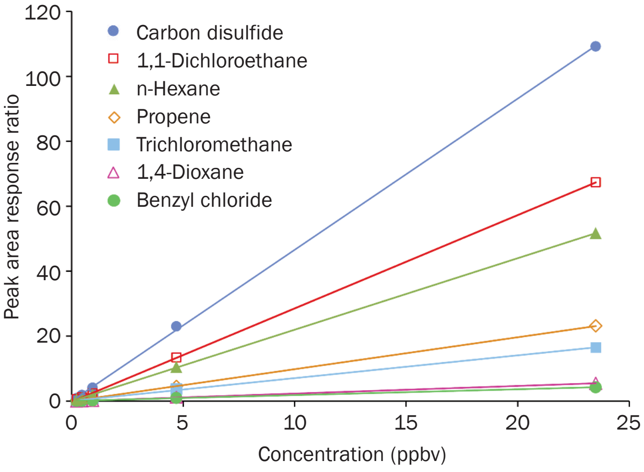

Figure 4: Five-point calibration curves for a range of TO-15 compounds.

No.	Analyte	Retention time (min)	Peak area RSD (%)	MDL (ppbv)	S:N	RRF RSD (%)
1	Propene	0.97	7.3	0.013	49	13.0
2	Dichlorodifluoromethane	1.00	4.6	0.009	645	19.5
3	1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon® 114)	1.06	4.3	0.008	713	8.2
4	Chloromethane	1.13	7.3	0.014	97	17.7
5	Chloroethene	1.17	9.2	0.017	204	24.9
6	Butadiene	1.20	9.8	0.018	101	26.3
7	Bromomethane	1.37	6.6	0.012	167	13.4
8	Chloroethane	1.44	9.9	0.018	18	20.2
9	Trichlorofluoromethane	1.60	3.1	0.006	1392	12.8
10	Ethanol	1.78	11.1	0.021	12	29.1
11	Propen-2-al (Acrolein)	1.90	8.9	0.016	40	28.5
12	1,1-Dichloroethene	1.94	3.2	0.006	286	15.0
13	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon® 113)	1.95	3.7	0.007	855	14.9
14	Acetone	2.01	9.4	0.017	80	22.0
15	Carbon disulfide	2.07	4.2	0.008	958	10.1
16	Isopropanol	2.13	9.6	0.018	125	9.9
17	Dichloromethane	2.26	3.4	0.006	174	8.6
18	*cis*-1,2-Dichloroethene	2.43	4.0	0.007	305	14.3

Table 1: Instrument and method detection limits for the each of the analytes in the 65-component TO-15 standard.

No.	Analyte	Retention time (min)	Peak area RSD (%)	MDL (ppbv)	S:N	RRF RSD (%)
19	*tert*-Butyl methyl ether	2.47	4.0	0.007	674	5.4
20	n-Hexane	2.61	3.9	0.007	422	6.2
21	1,1-Dichloroethane	2.69	6.3	0.012	446	8.8
22	Vinyl acetate	2.75	3.9	0.007	152	9.0
23	*trans*-1,2-Dichloroethene	3.05	4.8	0.009	518	14.0
24	Butan-2-one (Methyl ethyl ketone)	3.09	3.9	0.007	222	18.5
25	Ethyl acetate	3.13	6.6	0.012	288	6.3
IS1	Bromochloromethane	3.20	–	–	–	11.3
26	Chloroform	3.24	4.5	0.008	519	16.7
27	Tetrahydrofuran	3.26	4.0	0.007	141	11.8
28	1,1,1-Trichloroethane	3.35	4.2	0.008	578	14.2
29	Cyclohexane	3.39	3.7	0.007	375	12.4
30	Carbon tetrachloride	3.45	3.6	0.007	1211	14.4
31	Benzene	3.58	4.9	0.009	726	14.6
32	1,2-Dichloroethane	3.59	9.9	0.018	18	15.1
33	n-Heptane	3.75	4.2	0.008	361	10.4
IS2	*p*-Difluorobenzene	3.84	–	–	–	2.1
34	Trichloroethene	3.97	8.2	0.015	1353	15.2
35	1,2-Dichloropropane	4.11	3.5	0.006	390	17.2
36	Methyl methacrylate	4.21	8.2	0.015	129	18.5
37	1,4-Dioxane	4.23	4.7	0.009	385	17.5
38	Bromodichloromethane	4.28	8.9	0.016	314	17.5
39	*cis*-1,3-Dichloropropene	4.57	8.0	0.015	909	16.8
40	Methyl isobutyl ketone	4.69	6.8	0.013	544	20.3
41	Toluene	4.78	3.5	0.006	630	18.4
42	*trans*-1,3-Dichloropropene	4.92	6.8	0.013	657	13.9
43	1,1,2-Trichloroethane	5.04	3.4	0.006	809	11.9
44	Tetrachloroethene	5.13	5.2	0.010	2115	13.1
45	Methyl n-butyl ketone	5.23	4.6	0.009	375	17.0
46	Dibromochloromethane	5.30	3.5	0.006	2288	14.8
47	1,2-Dibromoethane	5.37	3.5	0.006	1631	13.9
IS3	d_5-Chlorobenzene	5.67	–	–	–	1.3
48	Chlorobenzene	5.68	4.4	0.008	5504	15.8
49	Ethylbenzene	5.75	4.7	0.009	1734	17.1
50	*m*- and *p*-Xylene	5.82	4.4	0.008	2962	27.4
51	*o*-Xylene	6.06	4.3	0.008	538	22.1
52	Styrene	6.06	4.7	0.009	565	19.2
53	Bromoform	6.16	5.5	0.010	4563	14.7
IS4	4-Bromofluorobenzene	6.35	–	–	–	2.3
54	1,1,2,2-Tetrachloroethane	6.43	3.0	0.005	2367	21.7
55	1-Ethyl-4-methylbenzene	6.55	3.9	0.007	1104	22.1
56	1,2,4-Trimethylbenzene	6.59	4.1	0.008	3127	19.4
57	1,3,5-Trimethylbenzene	6.78	4.2	0.008	2600	21.0
58	1,3-Dichlorobenzene	6.93	4.6	0.009	2550	19.0
59	1,4-Dichlorobenzene	6.97	4.7	0.009	1857	19.8
60	Benzyl chloride	7.04	3.2	0.006	891	14.8
61	1,2-Dichlorobenzene	7.16	4.4	0.008	2519	20.1
62	1,2,4-Trichlorobenzene	7.94	5.1	0.009	1812	15.4
63	Hexachlorobutadiene	8.02	2.9	0.005	537	20.3
64	Naphthalene	8.05	3.2	0.006	3026	7.2

Table 1 (continued): Instrument and method detection limits for the each of the analytes in the 65-component TO-15 standard.

5. Semi-rural air analysis

To evaluate system performance for trace level samples of real air, a 50 mL sample of semi-rural ambient air was drawn into the system at 50 mL/min and analysed using a 10:1 split. The total ion current (TIC) chromatogram (Figure 5) was searched against the NIST 14 database. A number of TO-15 compounds were confidently identified (as annotated). Moreover, BenchTOF's ability to collect full spectral information with high sensitivity enabled other compounds of potential concern to be identified, such as the allergen limonene. This would not have been possible using a quadrupole in SIM mode.

Even with only 50 mL of sample and the 10 minute GC analysis time used here, we have demonstrated that TO-15 compounds and unknowns can be detected at <0.1 ppbv in semi-rural air. Figure 6 shows a sequence of three runs for tetrachloroethene – a real air sample, 0.1 ppb standard and blank – demonstrating negligible carryover (<0.002 ppb) and indicating that even at trace levels, samples can be safely sequenced with standards. This efficiency streamlines the whole automation process while maintaining high-quality data. Moreover, using BenchTOF means that targets *and* unknowns can be confidently identified at trace levels in a single analysis, extending the reporting capabilities of laboratories.

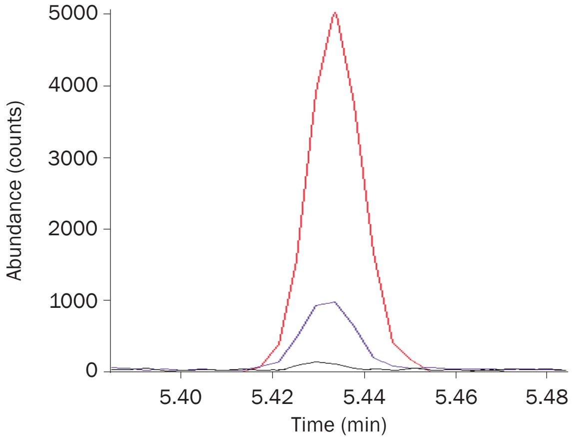

Figure 6: EIC chromatogram for tetrachloroethene (m/z 166, blue) overlaid with a 50 mL 0.1 ppb standard (red) and a system blank (black).

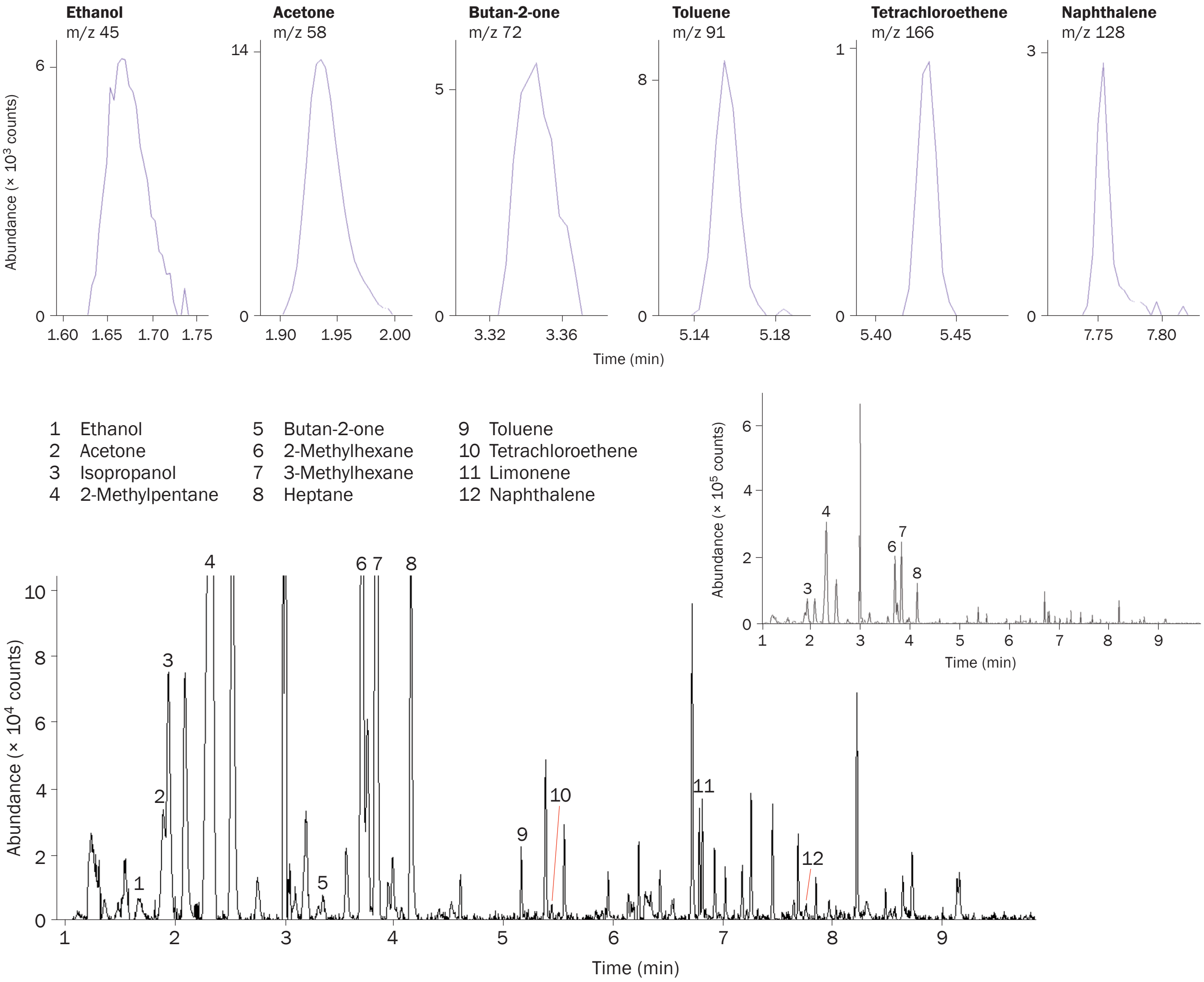

Figure 5: Bottom: Original and expanded TIC chromatograms for a 50 mL semi-rural air sample analysed using CIA *Advantage*–GC–TOF MS (split 10:1). Top: EIC chromatograms for six trace-level TO-15 compounds.

6. Tuning requirements

According to Method TO-15, the GC–MS system must be tuned in such a way that 4-bromofluorobenzene (BFB) meets specific criteria for ion abundance. This helps to ensure meaningful comparison between data acquired on instruments of different design.

The criteria for BFB are listed in Table 2, and the results obtained in the current analysis are provided. The system used passes the criteria on all counts.

Ion (m/z)	BFB criterion	Result (%)	Pass/Fail
50	8–40% of m/z 95	19.1	Pass
75	30–66% of m/z 95	44.6	Pass
95	Base peak, 100%	100.0	Pass
96	5–9% of m/z 95	6.7	Pass
173	<2% of m/z 174	0.4	Pass
174	50–120% of m/z 95	99.2	Pass
175	4–9% of m/z 174	5.8	Pass
176	93–101% of m/z 174	98.0	Pass
177	5–9% of m/z 176	5.1	Pass

Table 2: Results obtained against the BFB tuning criteria.

Conclusions

This Application Note has shown that the CIA *Advantage*–GC–TOF MS system provides considerable productivity improvements over existing platforms for the analysis of environmental contaminants in accordance with US EPA Method TO-15.

The use of BenchTOF as an alternative to quadrupole MS enables fast acquisition, high sensitivity and confident identification of all sample components in a single analysis. In particular, the reduction in sampling and analysis times means that it is possible to run the same number of samples in a fraction of the time it would take on conventional systems, without the need to change working practices or compromise on data quality. Additional revenue generation potential, from this aspect alone, has been conservatively estimated at $200,000 per year per system.

Other system advantages have been shown to include reduced sample sizes, the elimination of liquid cryogen and the exceptional sensitivity of BenchTOF for confident identification of targets and unknowns in a single run. In turn, this opens up new application opportunities to environmental labs for detailed screening of uncharacterised atmospheres at ultra-trace levels.

Trademarks

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