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Routine monitoring of airborne VOCs using TD–GC×GC–TOF MS/FID

This study demonstrates the suitability of a TD–GC×GC system with dual TOF MS/FID detection for the routine, automated analysis of volatile organic compounds (VOCs) in complex air samples. Analysis of a TO-15 standard demonstrates excellent peak shape and repeatability, with integrated control and simple data processing on a single platform.

Introduction

The identification and quantitation of volatile organic pollutants in air can be challenging, largely because of the complexity of the samples. Analysts may attempt to address this using longer columns and/or slower oven temperature ramps, but this inevitably leads to longer analysis times. However, in recent years, the complexity of such samples has been revealed using comprehensive two-dimensional GC (GC×GC).^[1]

In this study, we demonstrate how the increased separation capacity of GC×GC techniques provides increased confidence in the identification of compounds in complex air samples, even when using simple detectors, such as flame ionisation detection (FID).

Here, we couple flow-modulated GC×GC–TOF MS/FID with thermal desorption on the UNITY–CIA Advantage-Kori-xr[™] system from Markes International. This TD system allows automated trace-level analysis of very volatile VOC and VOCs from canisters, bags and on-line samples, with Kori-xr water management allowing sampling from environments with up to 100% relative humidity.

The cryogen-free operation of the UNITY-CIA *Advantage*-Kori-xr is complemented by consumable-free flow modulation, which works by filling and flushing a sample loop. This simple operation stands in contrast to thermal modulators, which use a cold zone (usually a jet of nitrogen gas cooled by a chiller unit or liquid nitrogen) to trap and focus analytes, and a hot zone to release the analytes onto the secondary column. This results in additional expense (as well as laboratory space), and in addition the nature of the thermal modulation process makes it incompatible with the most volatile species.





The INSIGHT[®] flow modulator from SepSolve Analytical uses reverse fill/flush dynamics, meaning that the sample loop is filled in the forward direction from the primary column and then rapidly flushed in the reverse direction onto the secondary column. This ensures breakthrough is eliminated, for sharp and symmetrical peaks for all analytes, including volatiles.

An added advantage of flow modulation is that it enables simple configuration of parallel detection. In this study, both TOF MS and FID data are acquired in a single analysis for confident identification (using reference-quality spectra) and robust quantitation. These detectors are integrated with the other instruments into a single analytical platform with one software interface, and we show how this allows robust, repeatable and affordable GC×GC analysis of hazardous air pollutants.

Experimental

Samples: 200 mL of a 1 ppm gas standard in a 6 L canister, pressurised to 35 psi to give approximately 10 ppb.

TD: UNITY–CIA Advantage-Kori-xr[™] (Markes International).^[2]

GC×GC: INSIGHT[®] flow modulator (SepSolve Analytical).

FID: H₂ flow: 40 mL/min; Air flow: 400 mL/min; Temperature: 300°C.

TOF MS: BenchTOF-Select[™].

Software: ChromSpace[®] GC×GC software for full control of the entire analytical system and data processing.

Please contact SepSolve for full analytical parameters.

Results and discussion

1. Chromatography

To demonstrate system performance, a 65-component canister gas standard was analysed. Figure 1A shows the results obtained using FID detection, which is ideal for achieving robust quantitation. All components of the standard were separated with a run time of less than 25 minutes, and the high peak capacity of GC×GC is immediately obvious. Figure 1B shows two compounds that would have co-eluted in a conventional 1D separation.







Figure 1

(A) TD-GC×GC-FID surface chart showing the enhanced separation of analytes in the 65-component, 10 ppb TO-15 standard. (B) Expanded region showing two compounds that would have co-eluted in a convenentional 1D separation – bromodichloromethane (1) and 1,4-dioxane (2).

2. Peak shape

The excellent peak shape evident in Figure 1 is a result both of the efficient focusing onto the trap of the thermal desorber (which passes the analytes to the GC in a narrow band), and of the reverse fill/flush dynamics of the INSIGHT[®] modulator (which ensures that breakthrough onto the second column is eliminated).

This is particularly well-demonstrated for the volatile compounds in the standard, as demonstrated by the peak shape shown in Figure 2. It is worth noting that the early-eluting compounds dichlorodifluoromethane and prop-2-enal would be difficult or impossible to modulate using a thermal device (liquid cryogen is compatible with C₄ and above, while a chiller unit is only compatible with C₈ and above). This limitation restricts the use of thermal modulation for the analysis of VOCs in air.

A: Prop-2-enal (m/z 56)



C: *cis*-1,3-Dichloropropene (m/z 75)



B: 1,1,2,3,4,4-Hexachlorobutadiene (m/z 225)



Figure 2

Colour plots (left) and surface plots (right) for four components of the 65-component, 10 ppb TO-15 standard.

D: Dichlorodifluoromethane (m/z 85)





3. Analyte identification

A key benefit of INSIGHT flow modulation is the ease by which parallel detection can be configured, and in this study TOF MS and FID data were acquired simultaneously. Mass spectra are widely used to aid confident identification, and this is particularly the case because, unlike other time-of-flight mass spectrometers, the BenchTOF[™] instrument used here acquires 'reference-quality' spectra, enabling easy comparison to existing in-house or commercial libraries acquired on quadrupole instruments.

Forward match factors (widely used as a measure of identification) were all greater than 900 against the NIST 17 library for all analytes in the standard. Figure 3 shows spectral matches for the four compounds shown in Figure 2.



Figure 3

BenchTOF spectra (top, red) and NIST 17 spectra (bottom, blue) for four compounds from the 65-component, 10 ppb TO-15 standard.

4. Repeatability

Repeatability was evaluated by running ten replicate TD–GC×GC–FID analyses of the TO-15 standard in an automated sequence using the templating facility (see Section 5). Table A1 (see Appendix) demonstrates the excellent results, with mean RSDs of 0.12%, 0.17% and 1.83%, for ${}^{1}t_{R}$, ${}^{2}t_{R}$ and peak areas, respectively. Furthermore, all retention-time RSDs were <1%, and all peak-area RSDs were <3.5%.

This high degree of repeatability is a consequence of the precisely-defined microfluidic design of the INSIGHT modulator, which allows identical configurations to be installed across multiple instruments. This stands in contrast to thermal devices, where small variations in column position can have a large impact on results. With thermal modulators, there are also well-known issues of blocked jets and thermal stress on the column to contend with – meaning that this approach is often only considered for R&D laboratories where optimum productivity isn't the main focus.

5. Software

The ChromSpace[®] GC×GC software used in this study controls the entire analytical system using a single global method, including the TD preconcentrator, GC×GC system, and detector(s). This saves time and reduces training/ familiarisation requirements. It also offers flexible view settings, which allow interrogation of data as a reconstructed 1D chromatogram (Figure 4), to assist those users unfamiliar with GC×GC.



Figure 4

A section of the TD-GC×GC-FID chromatogram shown in Figure 1 viewed as (**A**) a traditional GC×GC colour plot and (**B**) a reconstructed 1D chromatogram. Both plots highlight *trans*-1,2dichloroethene.



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ChromSpace also offers simplified presentation of data acquired from parallel detection, with the ability to open both datafiles in the same window (Figure 5). This allows individual peaks to be identified quickly and reliably on the basis of the TOF data, and then added to a 'stencil' that can be applied to the FID data, for streamlined peak assignment of subsequent runs. In this study, this facility proved valuable when carrying out the ten replicate TD–GC×GC–FID runs for the repeatability work.



Figure 5

Screenshot of processing in ChromSpace, showing FID data (top left), TOF MS data (bottom left) and the mass spectrum (right) open in a single window.

Conclusions

This study has demonstrated that:

- The TD–GC×GC–TOF MS system described offers excellent chromatography, repeatability and ease-of-use for routine monitoring of the full range of TO-15 air pollutants, without requiring liquid cryogen.
- A high degree of analyte separation is possible using GC×GC, and this is assisted by the excellent peak shape resulting from the use of thermal desorption preconcentration and the reverse fill/flush dynamics of the INSIGHT[®] flow modulator.
- In contrast to thermally-modulated systems, INSIGHT does not suffer from any volatility constraints, enabling efficient modulation of volatiles from C₁ upwards.



- Parallel detectors are easily configured, enabling acquisition of complementary datasets in a single run – in this case TOF MS for identification and FID for quantitation.
- Streamlined workflows are possible using ChromSpace[®] software for full instrument control and data processing.

Flow-modulated GC×GC, as used in this study, also has significantly lower capital and running costs, and INSIGHT can also be retrofitted to existing GCs, enabling easy upgrade to GC×GC.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

References

- [1] M.S. Alam, C.E. West, A.G. Scarlett, S.J. Rowland and R.M. Harrison, Application of 2D-GCMS reveals many industrial chemicals in airborne particulate matter, *Atmospheric Environment*, 2013, 65: 101–111, http://doi.org/10.1016/j.atmosenv.2012.10.014.
- [2] The canister sample can be introduced to the analytical system either by using a 0.5 mL sample loop or a mass flow controller (MFC). These sampling options allow the automated analysis of both high- and low-concentration samples in a single automated sequence, avoiding the need to resort to dilution of high-concentration samples (with their associated analytical uncertainty and risk of contamination).

Appendix

	Mean			RSD (%)		
Compound	¹ t _R (min)	² t _R (s)	Area	¹ t _R (min)	² t _R (s)	Area
Dichlorodifluoromethane (Freon 12)	1.661	0.393	9.51 × 10 ⁵	0.08	0.12	1.28
1,2-Dichloro- tetrafluoroethane (Freon 114)	1.828	0.395	3.23 × 10 ⁵	0.07	0.15	2.47
Chloromethane	1.886	0.412	2.90×10^{5}	0.16	0.11	3.25
Vinyl chloride	1.984	0.413	3.73×10^{5}	0.05	0.13	3.04
Butadiene	2.020	0.403	1.30×10^6	0.03	0.16	2.57
Propylene	2.110	0.451	3.05×10^5	0.06	0.12	2.69
Bromomethane	2.341	0.440	2.86×10^{5}	0.05	0.13	1.71
Chloroethane	2.420	0.426	5.92 × 10 ⁵	0.14	0.09	1.76

Table A1

Average retention times $({}^{1}t_{R})$ and ${}^{2}t_{R}$) and peak areas for 10 replicate analyses of the TO-15 standard.

	Mean			RSD (%)			
Compound	¹ t _R (min)	² t _R (s)	Area	¹ t _R (min)	² t _R (s)	Area	
Trichlorofluoromethane (Freon 11)	2.718	0.412	1.01 × 10 ⁵	0.25	0.32	2.91	
Ethanol	2.904	0.722	3.96×10^5	0.05	0.15	1.82	
2-Propenal	3.155	0.548	5.36×10^5	0.09	0.12	1.47	
1,1-Dichloroethene	3.237	0.439	6.71×10^5	0.10	0.22	2.04	
Acetone	3.263	0.510	7.72 × 10 ⁵	0.09	0.13	1.68	
1,2,2-Trifluoro- trichloroethane (Freon 113)	3.269	0.423	9.46 × 10 ⁴	0.18	0.57	3.24	
Isopropanol	3.360	0.667	5.39×10^5	0.05	0.15	1.19	
Carbon disulfide	3.410	0.514	5.58×10^4	0.14	0.41	3.30	
Dichloromethane	3.744	0.647	2.69×10^{5}	0.05	0.13	2.76	
Methyl tert-butyl ether	4.012	0.420	1.14×10^6	0.09	0.13	1.61	
cis-1,2-Dichloroethene	4.075	0.522	5.36×10^5	0.05	0.12	1.75	
Hexane	4.429	0.394	1.67×10^6	0.08	0.11	1.15	
1,1-Dichloroethane	4.500	0.539	5.31×10^5	0.08	0.12	3.32	
Vinyl Acetate	4.566	0.547	6.61×10^5	0.11	0.11	2.25	
Butan-2-one	5.214	0.534	8.53×10^5	0.12	0.12	2.89	
trans-1,2-Dichloroethene	5.244	0.668	5.91×10^5	0.12	0.11	2.19	
Ethyl acetate	5.282	0.516	7.12 × 10 ⁵	0.11	0.12	3.35	
Chloroform	5.549	0.711	2.08×10^{5}	0.14	0.12	2.25	
Tetrahydrofuran	5.685	0.484	7.87 × 10 ⁵	0.14	0.12	1.54	
1,1,1-Trichloroethane	5.936	0.489	6.01×10^5	0.15	0.11	0.87	
Cyclohexane	6.123	0.405	1.66×10^6	0.13	0.13	0.70	
Carbon tetrachloride	6.284	0.477	2.14×10^5	0.17	0.17	2.90	
Benzene	6.533	0.530	1.74×10^6	0.16	0.11	0.99	
1,2-Dichloroethane	6.590	0.735	5.88×10^{5}	0.16	0.14	1.09	
Heptane	6.934	0.391	1.94×10^{6}	0.16	0.11	0.91	
Trichloroethene	7.452	0.549	6.18×10^5	0.16	0.12	1.67	
1,2-Dichloropropane	7.786	0.608	8.72×10^5	0.17	0.14	1.61	
Methyl methacrylate	7.919	0.544	9.64×10^5	0.18	0.14	1.13	
Bromodichloromethane	8.184	0.821	2.59×10^5	0.17	0.18	3.12	
1,4-Dioxane	8.201	0.619	4.62×10^5	0.18	0.17	2.25	
Methyl isobutyl ketone	8.988	0.512	1.09×10^6	0.17	0.13	3.12	
cis-1,3-Dichloropropene	9.037	0.687	8.11×10^{5}	0.17	0.17	0.63	
Toluene	9.607	0.527	1.93×10^{6}	0.17	0.13	0.89	
trans-1,3-Dichloropropene	10.018	0.768	7.42 × 10 ⁵	0.16	0.20	0.98	
1,1,2-Trichloroethane	10.400	0.872	5.55×10^5	0.16	0.23	2.35	

Table A1

Average retention times $({}^{1}t_{R})$ and ${}^{2}t_{R}$) and peak areas for 10 replicate analyses of the TO-15 standard (continued from previous page).



	Mean			RSD (%)			
Compound	¹ t _R (min)	² t _R (s)	Area	¹ t _R (min)	² t _R (s)	Area	
Hexan-2-one	10.580	0.530	8.61×10^5	0.17	0.14	1.73	
Tetrachloroethene	10.725	0.475	6.12×10^5	0.17	0.12	1.79	
Dibromochloromethane	11.168	0.895	2.56×10^5	0.16	0.23	2.80	
1,2-Dibromoethane	11.488	0.771	5.20×10^5	0.08	0.22	1.72	
Chlorobenzene	12.336	0.627	1.47×10^{6}	0.15	0.18	0.84	
Ethylbenzene	12.533	0.513	1.96×10^6	0.15	0.16	0.81	
m-+p-Xylene	12.758	0.516	3.81×10^6	0.15	0.17	0.79	
o-Xylene	13.613	0.534	1.88×10^6	0.11	0.16	0.87	
Styrene	13.709	0.609	1.69×10^6	0.14	0.19	0.82	
Bromoform	14.250	0.948	2.43×10^5	0.14	0.26	3.14	
1,1,2,2-Tetrachloroethane	15.139	0.985	4.78×10^{5}	0.03	0.15	1.84	
4-Ethyltoluene	15.569	0.502	1.89×10^6	0.12	0.16	0.70	
1,3,5-Trimethylbenzene	15.718	0.515	1.79×10^6	0.12	0.18	0.83	
1,2,4-Trimethylbenzene	16.549	0.523	1.73 × 10 ⁶	0.12	0.16	1.09	
1,3-Dichlorobenzene	17.221	0.641	1.10×10^{6}	0.11	0.19	1.16	
1,4-Dichlorobenzene	17.464	0.664	1.13×10^{6}	0.11	0.20	1.00	
Benzyl chloride	17.910	0.743	1.14×10^6	0.11	0.22	0.86	
1,2-Dichlorobenzene	18.287	0.685	1.09×10^6	0.10	0.20	0.94	
1,2,4-Trichlorobenzene	22.130	0.658	6.86×10^{5}	0.09	0.16	1.49	
Hexachlorobutadiene	22.597	0.499	5.86×10^{5}	0.08	0.15	2.15	
Naphthalene	22.825	0.759	8.93×10^5	0.08	0.18	3.32	

Table A1

Average retention times $({}^{1}t_{R}$ and ${}^{2}t_{R})$ and peak areas for 10 replicate analyses of the TO-15 standard (continued from previous page).

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