

Completely cryogen-free monitoring of ozone precursors, air toxics, and oxygenated volatile organic compounds in ambient air in a single run

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Keywords

Gas chromatography, GC, single quadrupole mass spectrometer, FID, flame ionization detector, ISQ 7000, cryogen-free monitoring, PAMS, photo assessment monitoring scheme, TO-15, OVOCs, oxygenated volatile organic compounds, ozone precursors, air toxics, CIA *Advantage-xr* canister autosampler, UNITY-xr thermal desorber, Kori-xr water removal device, Deans Switch, heart-cut, 2D-GC, microfluidics

Goal

To demonstrate the applicability of a cryogen-free method composed of a Markes™ CIA Advantage-xr™ canister autosampler, a Markes Kori-xr™ water removal device, and a Markes UNITY-xr™ thermal desorber coupled to a dual-column Thermo Scientific™ ISQ™ 7000 single quadrupole GC-MS, for the analysis of ozone precursors, air toxics, and oxygenated volatile organic compounds in ambient air.

Introduction

In December 2017, the Chinese Ministry of Environmental Protection issued a document relating to the Environmental Air Volatile Organic Compound Monitoring Program (EA-VOC-MP),¹ which requires the monitoring of 117 compounds comprising three main categories of hazardous airborne volatile pollutants, ozone precursors, air toxics, and oxygenated volatiles compounds:

- Ozone precursors are listed under the U.S. EPA Photochemical Assessment Monitoring Stations (PAMS),² and are monitored using either online techniques (for continuous monitoring) or remote canister sampling. Both techniques require water removal and preconcentration of the sample before injection into a GC, usually in a dual column configuration with dual flame ionization detection (FID).³

- “Air toxics” are routinely monitored and comprise polar and non-polar VOCs, as well as a number of halogenated compounds. Methodology and performance criteria are detailed in U.S. EPA Method TO-15⁴ and Chinese EPA Method HJ 759.⁵ Typically, samples are collected in canisters, with water removal and sample preconcentration water taking place prior to injection into a single-column GC-MS system.⁶
- Oxygenated volatile organic compounds (OVOCs): These are a more recent addition to target lists for air monitoring and include a range of aldehydes and ketones. They are typically monitored using derivatization and high-performance liquid chromatography, as specified in Chinese EPA Method HJ 683⁷ and U.S. EPA Method TO-11A.⁸ However, these protocols require manual processing, the use of solvents, and two analytical platforms, which add significant time and cost to the analysis.

Obtaining good peak shape and chromatographic separation for this combined compound list typically requires cryogenic cooling of the GC column, with the associated cost and inconvenience (in addition, many thermal desorption (TD) systems also require cryogen).

In this study, we demonstrate the quantitative analysis of this challenging 117-compound target list without the use of liquid nitrogen or other cryogen, and with cycle times of less than 60 minutes per sample. The analytical system comprises a canister autosampler, water removal device, thermal desorber, and dual-column GC-MS/FID configured for heart-cut 2D-GC separation. Together, these enable the monitoring of samples at 100% relative humidity, offer optimum responses for the three C₂ and two C₃ hydrocarbon isomers using FID, as well as confident compound identification and high sensitivity for the remaining compounds monitored using MS.

Experimental

Standards

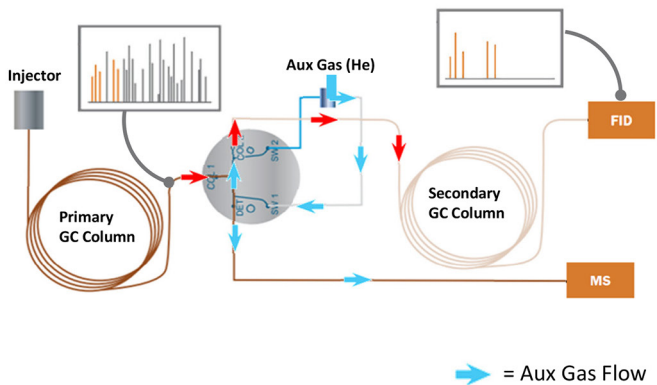
Standard gas cylinders containing 56 PAMS (ozone precursor) compounds (Restek™ 34420) and 65 TO-15 (air toxics) compounds (Restek 34436) and canisters containing five OVOCs listed in TO-11A (formaldehyde, acetaldehyde, hexanal, benzaldehyde, m-tolualdehyde) at 1 ppm in nitrogen were used to prepare standards. Unless otherwise stated, a combined standard at 10 ppb and 100% relative humidity (RH) was used. Thirteen compounds are present in both PAMS and TO-15 standards; therefore, where appropriate, testing was replicated with a single standard to generate accurate data for these compounds. The internal standard comprised bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d₅, and 1-bromo-4-fluorobenzene at 1 ppm in nitrogen (Restek 34408). For reasons of safety in our UK laboratory, (2E)-but-2-enal (crotonaldehyde), butanal, propanal, 3-methylbutanal (isovaleraldehyde), and hexanal could not be tested.

Instrument and method setup

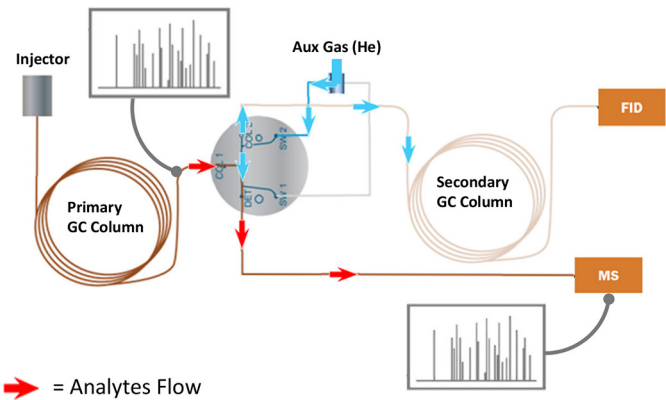
The experimental parameters are listed below, and the GC setup is shown in Figure 1, with a schematic explanation of the Deans Switch heart-cut approach. The highly efficient water removal of Markes' cryogen-free Dry-Focus3™ approach allows the GC oven to start at the relatively high temperature of 35 °C.

The analytical system configuration (Figure 2), with a schematic explanation of the Deans Switch heart-cut approach. used for this study was a CIA *Advantage*-xr canister autosampler and UNITY-xr thermal desorber with a Kori-xr water removal device (Figure 3), coupled to an ISQ 7000 single quadrupole GC-MS instrument equipped with an AEI source and coupled to a Thermo Scientific™ TRACE™ 1310 gas chromatograph (Figure 4), in a dual column/microfluidic Deans Switch configuration with dual detection FID/MS.

A. Primary Column Flow to Secondary Column and FID



B. Primary Column Flow to MS



➡ = Aux Gas Flow ➡ = Analytes Flow

Figure 1. Dual-column GC-MS/FID instrument configuration for Deans Switch 2D-GC operation

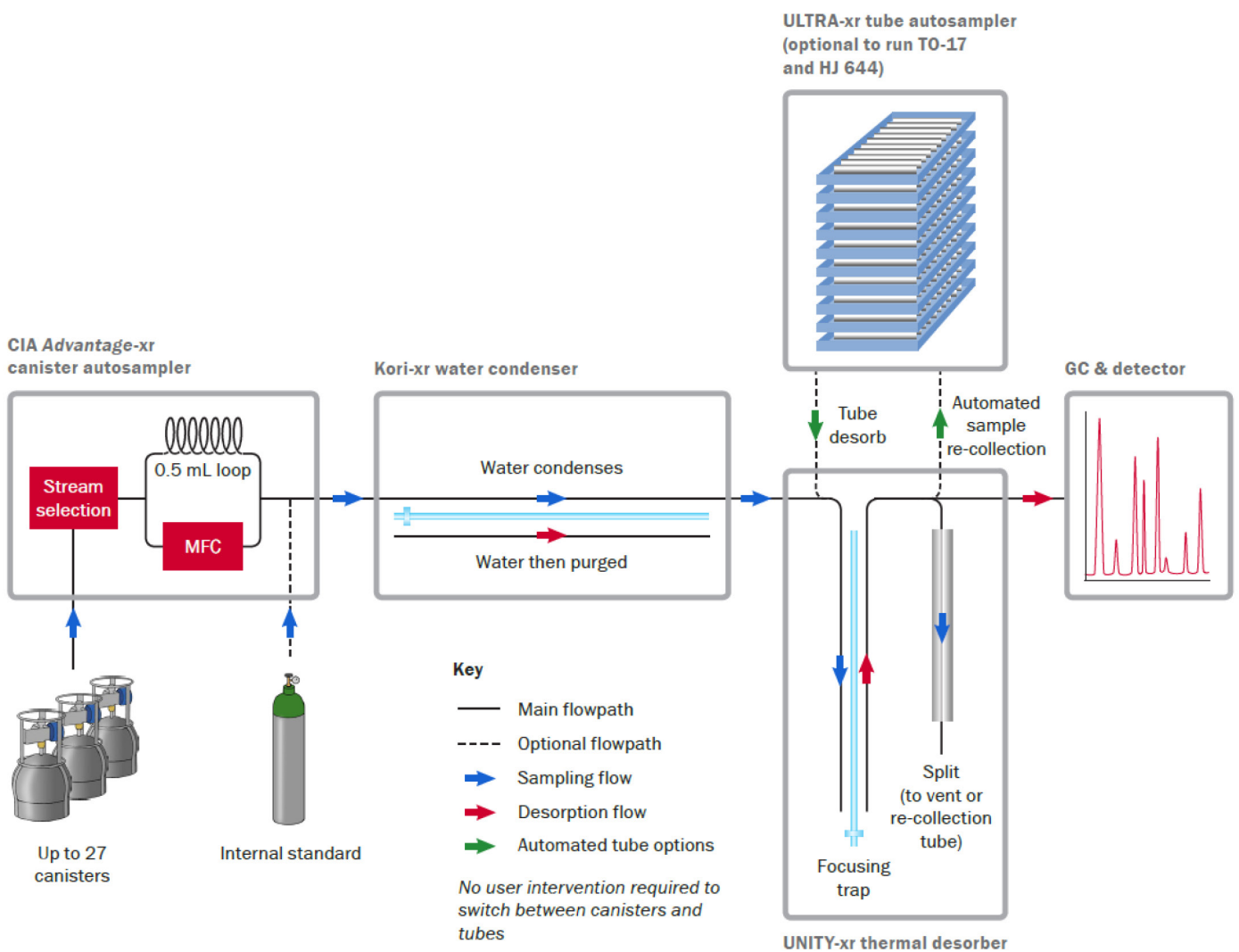


Figure 2. The analytical system configuration used for this study



Figure 3. The CIA Advantage-Kori-UNITY-xr system



Figure 4. The Thermo Scientific ISQ 7000 single quadrupole GC-MS instrument equipped with an AEI source and coupled with a Thermo Scientific TRACE 1310 gas chromatograph

The CIA Advantage-xr is an autosampler for the analysis of VOCs in canisters or bags, using either 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, and the associated increase in analytical uncertainty and the risk of contaminant introduction. It also overcomes the limitations of traditional cryogen-cooled technology for canister air analysis, such as high costs and flow path blocking caused by ice formation. The CIA Advantage-xr also offers internal standard addition via a 1 mL loop, which allows a small volume of a high-concentration internal standard gas to be used, reducing the need for dilution and saving on the consumption of expensive standard gases.

To achieve optimum results for 100% RH ambient air, the amount of residual water reaching the GC-MS system must be very low. For this reason, Markes has developed the Dry-Focus3 approach, as well as a new focusing trap that is optimized for the cryogen-free analysis of VOCs, VVOCs, and oxygenates in humid air.

Ambient air samples first pass through a Kori-xr device that, without use of liquid cryogen, efficiently removes humidity from the air stream while preserving the compounds of interest (Figure 5). With the majority of excess water removed, samples then pass into the trap of the UNITY-xr thermal desorber, held at $-30\text{ }^{\circ}\text{C}$, where the analytes are quantitatively trapped. The trap is then purged with carrier gas in the sampling direction to eliminate oxygen and further reduce water without any loss or breakthrough of the analytes retained. Finally, the flow of gas is reversed, and the trap is heated rapidly (up to $100\text{ }^{\circ}\text{C/s}$) to inject the analytes onto the GC column.

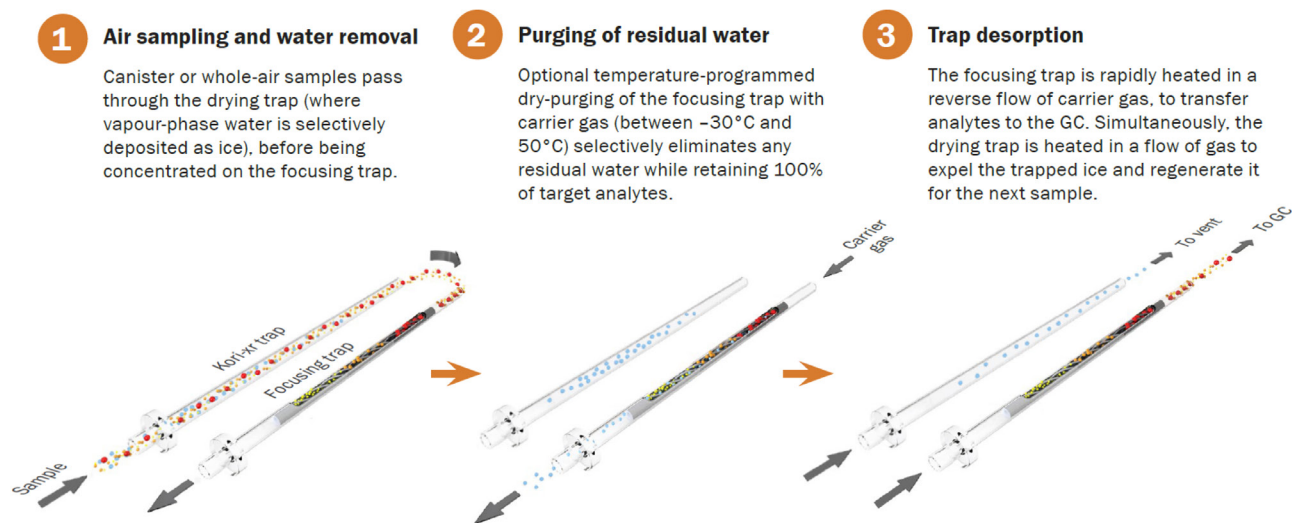


Figure 5. Operation of Dry-Focus3. For an example of the use of trap dry-purging, see Markes Application Note 133.⁶

At this point there is the ability to split the sample, either to vent or onto a clean sorbent tube for storage and re-analysis at a later time (although it should be noted that sorbent tubes are not able to retain very volatile compounds such as acetylene). The above process of sample splitting and re-collection can be fully automated by adding an ULTRA-xr tube autosampler.

The experimental parameters are detailed in Tables 1–4.

Compound separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-VVOC B, 60 m × 0.32 mm I.D. × 5 µm film (P/N 26058-5180) as primary capillary column and a Thermo Scientific™ TracePLOT™ TG-Bond Q+, 30 m × 0.32 mm × 10 µm film (P/N 26005-6030) as secondary capillary column.

Table 1. GC and injector conditions

ISQ 7000 single quadrupole GC-MS instrument parameters

Inlet temperature (°C):	230
Carrier gas (mL/min):	He, ramped pressure
Column flow (mL/min):	
Primary column:	2
Secondary column:	3
Inlet module and mode:	SSL, splitless mode
Purge flow (mL/min):	5
Primary column:	TraceGOLD TG-VVOC B, 60 m × 0.32 mm I.D. × 5 µm film capillary column (P/N 26058-5180)
Secondary column:	TracePLOT TG-Bond Q+, 30 m × 0.32 mm × 10 µm film capillary column (P/N 26005-6030)
Restrictor (to MS):	Fused silica (4.8 m × 0.18 µm)

Oven temperature program:	<i>RT (min)</i>	<i>Rate (°C/min)</i>	<i>Target temperature (°C)</i>	<i>Hold time (min)</i>
Temperature 1	0	-	35	10.00
Temperature 2	10	6	240	0.00
Temperature 3	44	20	270	6
Run Time	52	-	-	-

Microfluidic Deans Switch device time settings:	<i>Time (min)</i>	<i>Detector</i>	<i>Column</i>
	0–7.70	FID	Secondary
	7.70–8.60	MS	Primary
	8.60–9.44	FID	Secondary
	9.44–52	MS	Primary

FID conditions		MS conditions	
Temperature (°C):	270	Transfer line (°C):	280
H ₂ flow (mL/min):	35	Ionization type:	AEI (EI)
Air flow (mL/min):	350	Ion source (°C):	300
N ₂ flow (mL/min):	40	Electron energy (eV):	45
Acquisition rate (Hz):	10 or 25	Acquisition modes:	Full-scan/SIM
Ignition threshold (pA):	1	Mass range (Da):	29–300
Peak width:	Standard	SIM windows:	0–9 min: <i>m/z</i> 29; 9–15 min: <i>m/z</i> 44

Table 2. Canister sampling conditions**Markes International CIA Advantage-xr instrument parameters**

Sample purge (mL/min):	50
Purge time (min):	4
Sample flow:	50 mL/min
Sample volume:	50–600 mL
Post-sample purge:	5 min at 50 mL/min

Table 3. Water removal conditions**Markes International Kori-xr instrument parameter**

Trap temperatures (°C):	–30 °C/300 °C
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Table 4. Thermal desorption conditions**Markes International UNITY-xr (Markes International) instrument parameters**

Focusing trap:	Containing a porous polymer, a graphitized carbon black, and a molecular sieve sorbent (Markes P/N U-T22117-2S)
Flow path (°C):	120 °C
Trap purge flow (mL/min):	50
Trap purge time (min):	2
Trap low temperature (°C):	–30 °C
Trap high temperature (°C):	250 °C
Trap high time (min):	2
Outlet split (mL/min):	3

BFB tune

According to the quality requirements of both HJ 759⁵ and EA-VOC-MP¹, the GC-MS instrument must be tuned so that 4-bromofluorobenzene (BFB) meets specific criteria for ion abundance (and compliance should be checked before starting a sequence of samples). Table 5 demonstrates that the system used in this study passes the stated criteria for all ions.

U.S. EPA Method TO-15 stipulates that BFB should be injected every 24 hours and the tune criteria assessed. If the system does not pass the acceptance criteria for the BFB tune, corrective action followed by full re-calibration must be performed. Table 5 shows the performance of this system against the BFB tune criteria, demonstrating full compliance of system performance with Method TO-15, with no user intervention.

Data processing

Data were acquired and processed using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software.

Results and discussion**Microfluidic Deans Switch device method optimization**

Using a dedicated 5-port microfluidic connector for Deans Switch 2D-GC separations (P/N 19005580), optimum sensitivity together with excellent peak shape, retention time stability, and reproducibility were obtained for this complex target list in a single 52-minute chromatographic run. The C₂ hydrocarbons ethene, acetylene, and ethane (which typically require separation on highly retentive columns) respond best to FID detectors, whereas formaldehyde facilitate best to MS detection. It is therefore

Table 5. Results obtained against the BFB tune criteria immediately after tuning

Ion (<i>m/z</i>)	Criterion	t = 0 hours (%)	Pass / Fail
50	8–40% of <i>m/z</i> 95	16.7	Pass
75	30–60% of <i>m/z</i> 95	40.6	Pass
95	Base peak, 100%	100	Pass
96	5–9% of <i>m/z</i> 95	8.5	Pass
173	<2% of <i>m/z</i> 174	0.7	Pass
174	50–120% of <i>m/z</i> 95	86.2	Pass
175	4–9% of <i>m/z</i> 174	7.4	Pass
176	93–101% of <i>m/z</i> 174	94.1	Pass
177	5–9% of <i>m/z</i> 176	6.7	Pass

important to achieve sufficient separation between the C₂ hydrocarbons and formaldehyde to facilitate the first cut to the secondary column. This separation (shown in Figure 6A) was achieved by virtue of a unique combination of optimized TD focusing trap sorbents and a GC oven start temperature of 35 °C. This relatively high initial GC oven temperature is also key to operating this method without the need for liquid cryogen cooling of the GC oven. The C₃ hydrocarbons, like the C₂ hydrocarbons, are also typically detected using FID. This means that after elution of formaldehyde, the primary column flow must be directed back to the FID for propene and propane, with sufficient separation between these and dichlorodifluoromethane to allow the flow to be directed back to the MS again (Figure 6A). Compounds from this point on respond well to the MS detector, enabling them to benefit from the enhanced selectivity. The excellent peak shape and resolution of the C₂ and C₃ hydrocarbons resulting from this double-cut method are shown in Figure 6C, with formaldehyde and dichlorodifluoromethane shown on the MS trace in Figure 6B.

Chromatography and peak shape

Figure 7 shows that good peak shape is obtained across the analyte range, including the least volatile compounds in the list. In addition, the expansion of the 30.5 -31.2 min range demonstrates identification of seven closely-eluting compounds using their extracted ions. It is important to note that the sampling and analysis are achieved within a sample-to-sample cycle time of <60 minutes, maximizing sample throughput without the use of liquid cryogen in the TD or the GC oven. This run time results from a relatively high GC oven starting temperature of 35 °C, available due to the highly efficient water removal of the Markes cryogen-free Dry-Focus3 and the thermal desorber's overlap mode, in which the next sample is loaded to the focusing trap while the current GC analysis is still running.

Relative response factors and linearities

System linearity was assessed by sampling 50, 100, 200, 300, 400, and 600 mL of the 100% RH, 10 ppb mixed standard. This represents the equivalent mass of each compound that would be sampled from 400 mL of samples with concentrations of 1.25, 2.5, 5, 7.5, 10, and 15 ppb, respectively.

Relative response factors (RRFs) and their relative standard deviations (RSDs) were calculated from the results in accordance with HJ 759 and EA-VOC-MP

(Tables A1 and A2, see Appendix). The mean RRF RSD over the six-point calibration was 5% with a maximum of 12%, and therefore well within the 30% limit specified in the methods.

Linearities were also calculated (Tables A1 and A2, see Appendix), and all compounds had R² values exceeding the method limit of 0.990, with 93% of the compounds having R² values >0.995. Figure 8 shows linearity plots for a selection of compounds covering the volatility and polarity range of the target list.

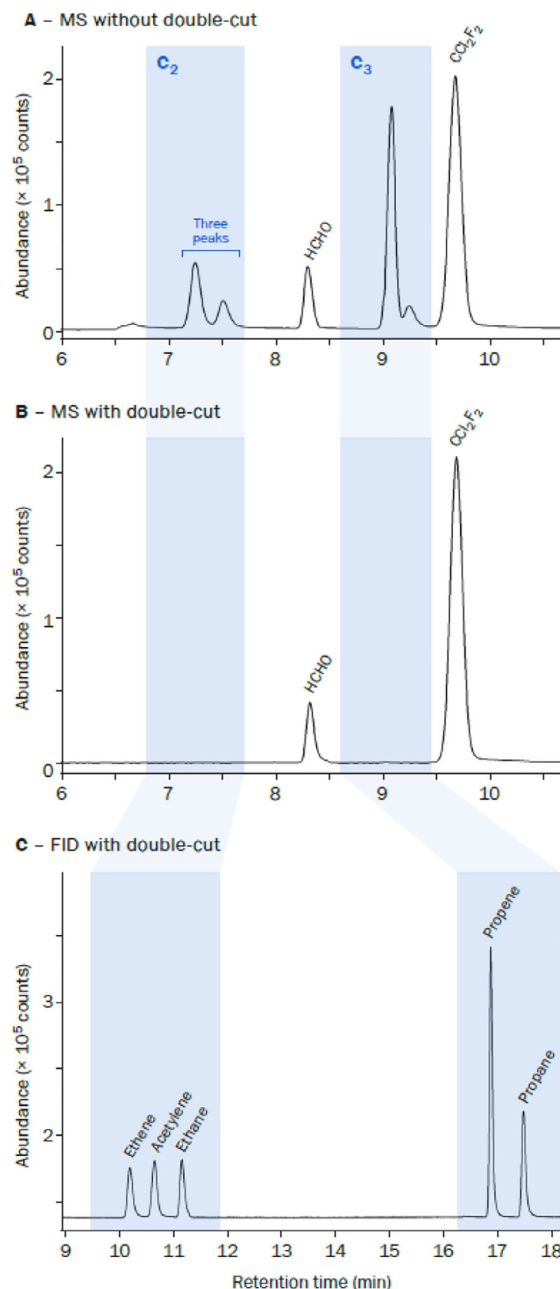


Figure 6. Analysis of 400 mL of the 10 ppb, 100% RH standard, using: (A) Composite MS (primary column) without double-cut, (B) Composite MS (primary column) with double-cut, and (C) FID (secondary column) with double-cut

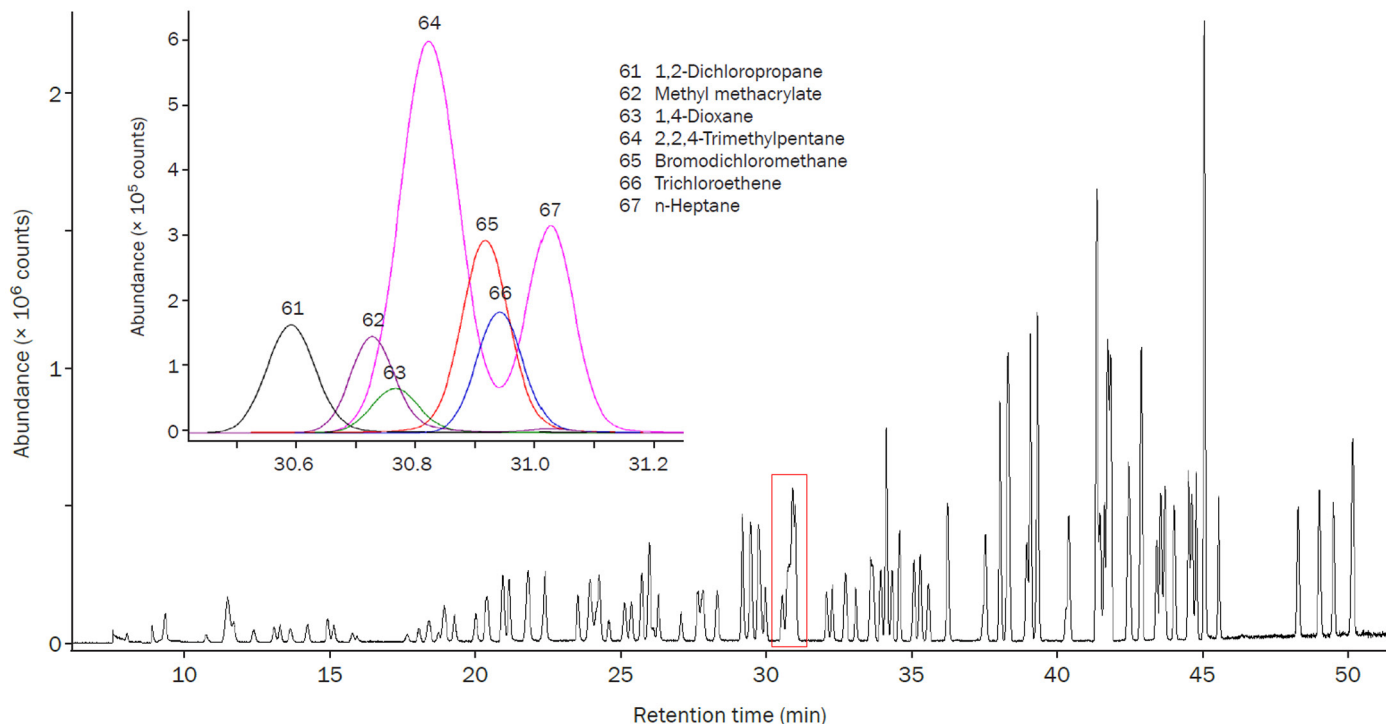


Figure 7. Total ion chromatogram (TIC) of 400 mL of the 10 ppb, 100% RH standard. The inset shows overlaid EIC responses from seven closely eluting analytes in the 30.5–31.2 min region. A full analyte listing is provided in Tables A1 and A2 (see Appendix).

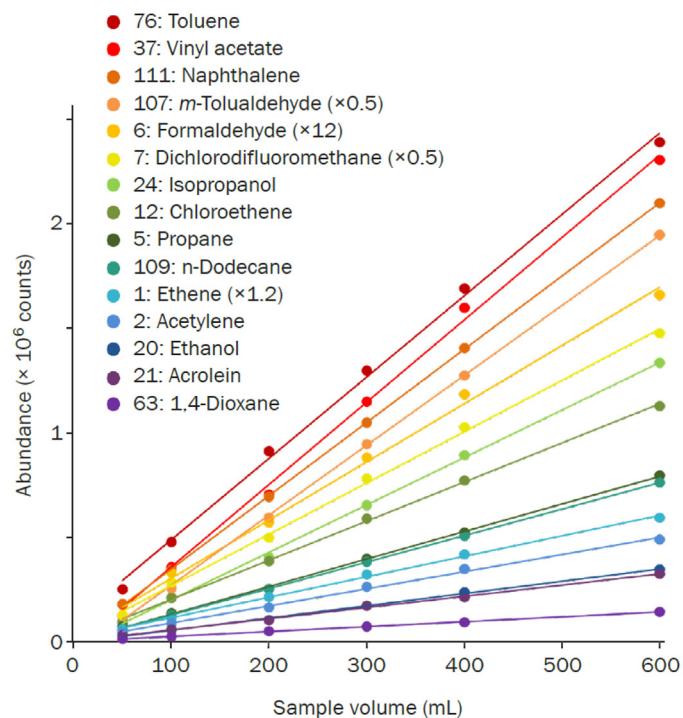


Figure 8. Linearity plots for selected compounds from the 10 ppb, 100% RH standard, over the range 50–600 mL. The scalings indicated have been applied for clarity.

Reproducibility

The nature of the two-column setup means that retention times can be affected by the pressure balance in the system. However, electronic carrier gas control between the GC and the CIA *Advantage*–UNITY-xr, and the efficient removal of water using Dry-Focus3 technology, means that stable retention times are achieved on both columns. Retention-time reproducibility can be expressed as the RSD across a series of analyses, and these values are provided in Tables A1 and A2 (see Appendix).

Excellent retention-time stabilities were achieved over sixteen replicates, with a mean RSD of 0.035% and a maximum of 0.17%—well within the limit of 6% specified in EA-VOC-MP. Such excellent stability of retention times makes it possible to automate the data processing of long sequences of multitarget analyses (for example, like those required by EA-VOCMP), without requiring manual peak integrations or retention time adjustments.

The reproducibility of analyte response was investigated by analyzing ten replicate 400 mL samples at 100% RH. All compounds showed good reproducibility, with <7.5% RSD for all compound areas without the need for internal standard correction. The excellent reproducibility of absolute peak area response and retention time of selected compounds spanning the full range of analytes is shown in Figure 9, and the full list of values can be found in Tables A1 and A2.

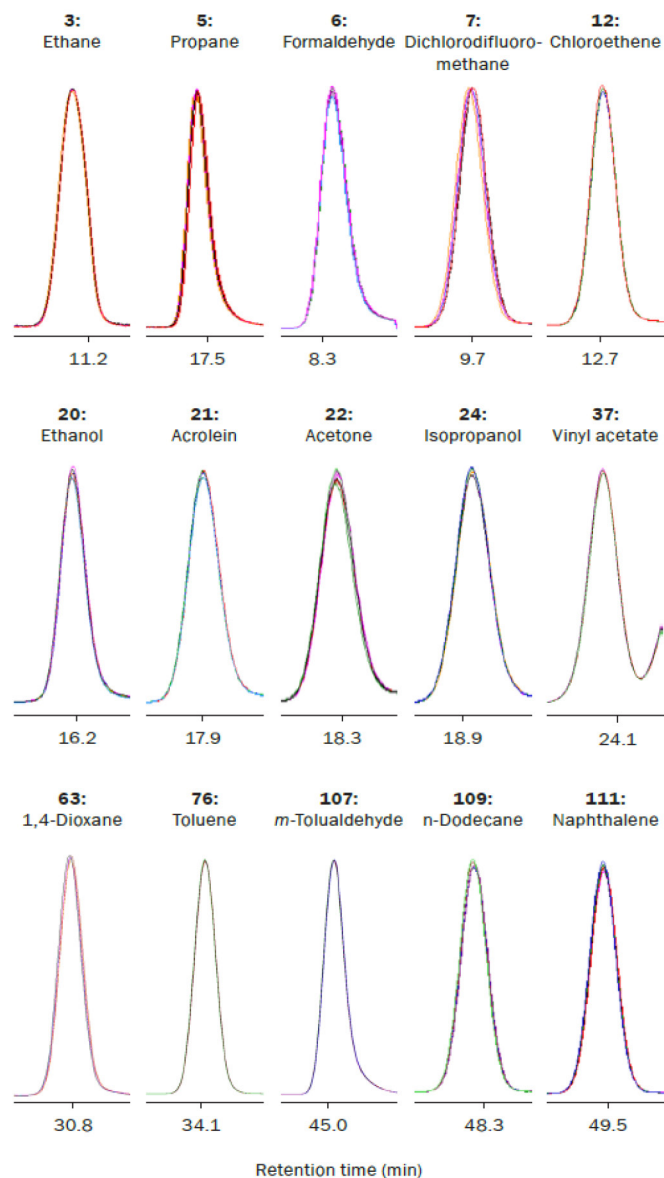


Figure 9. Example overlaid responses (FID for ethane and propane, MS SIM for formaldehyde, MS EIC otherwise) for ten repeat analyses of 400 mL of the 10 ppb, 100% RH standard, demonstrating excellent retention time and response stability

Furthermore, as specified in HJ 759, a gas-phase internal standard (1 mL, 1 ppm) was automatically added to the focusing trap with every sample. Excellent precision was achieved, with all four internal standard compounds yielding absolute response reproducibility <2.1% RSD. This inherent system stability allows confident correction of analyte response across long sequences, which in turn enables the use of the same calibration over an extended period of time, with the obvious benefit of maximizing instrument uptime to run real samples.

In fact, it is important to note that running a complete set of standards in triplicate, at the six concentration levels used in this study, would take approximately 18 hours, so confidence in internal standard response is vital to maintaining high sample throughput.

Confidence in the stability of the internal standard compound responses also allows these compounds to form part of the quality control checks for system performance. As the four-component internal standard is automatically added to every sample, continuous monitoring of the retention time and response of these compounds can provide early warning of changes in the analytical system and reduce the number of external standard quality control samples required throughout the analytical sequence—again increasing the overall laboratory throughput.

Carryover and blank levels

It is important that the instrumentation used for analyzing trace-level samples has minimal memory effects (“carryover”), from previous samples—even if they are at a higher concentration than those typically analyzed. High levels of carryover affect recovery results and require additional blanks to be built into the sequences to prevent any compounds interfering with subsequent samples.

To assess carryover, 400 mL of the 20 ppb, 100% RH standard was analyzed, followed immediately by a 400 mL sample of clean nitrogen. The sample loading in this case represents double the concentration of the highest calibration standard (at the sample volume specified in EA-VOC-MP), and therefore challenges the analytical system with significantly higher concentrations than would be likely in a sampling campaign.

The level of carryover for each compound was quantified both as a percentage of the 20 ppb response (which according to EA-VOC-MP must have a carryover <2.0%), and in terms of the concentration (which must be <0.4 ppb). The majority of compounds were not detected in the carryover test at all, with those that were having a

mean value of just 0.028 ppb (0.14%). Figure 10 shows the TIC for the 20 ppb standard, overlaid with the carryover test analysed immediately afterwards. The insets show minimal carryover for both the most and least volatile compounds in the list (formaldehyde and hexachlorobutadiene).

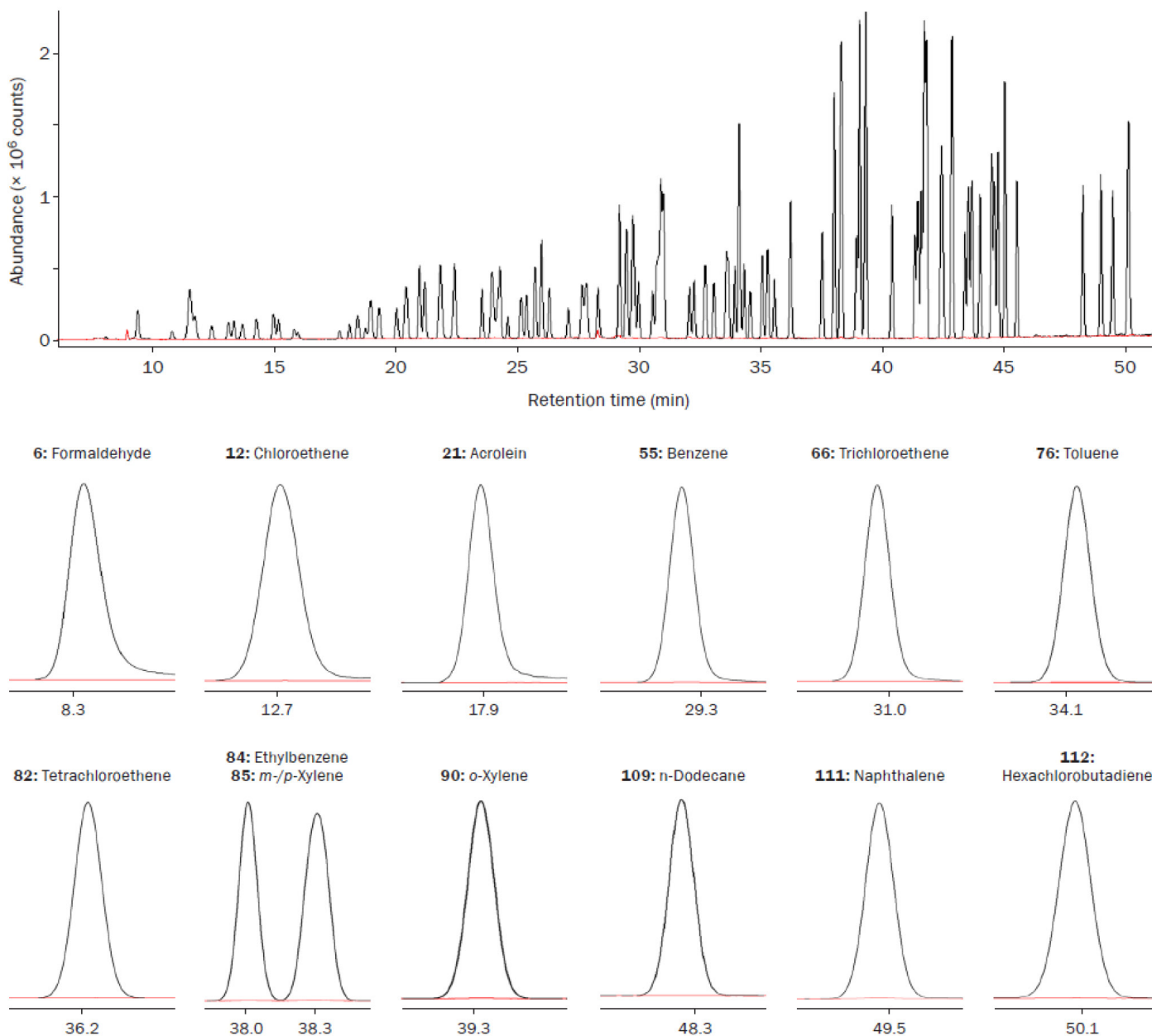


Figure 10. (Top) Analysis of 400 mL of the 20 ppb, 100% RH mixed standard (black) overlaid with a 400 mL nitrogen blank (red), analyzed immediately afterwards to test for carryover. (Bottom) Expansions (MS SIM for formaldehyde, MS EIC otherwise) showing minimal carryover for a range of analytes.

Conclusions

- The CIA *Advantage*–UNITY-xr preconcentration system with Dry-Focus3 technology allows simultaneous, cryogen-free analysis of PAMS ozone precursors, TO-15 air toxics and OVOCs listed in the Chinese Environmental Air Volatile Organic Compound Monitoring Program (EA-VOC-MP).
- The microfluidic Deans Switch two-dimensional GC-MS/FID strategy employed in this work provides confident identification and quantitation, with maximum sensitivity achieved in this challenging application by using the optimum separation and detection system for the various compound types.
- Markes' cryogen-free Dry-Focus3 water management technology has been demonstrated to produce data that satisfies the performance criteria for HJ 759 and EA-VOC-MP for very volatile C₂ hydrocarbons, formaldehyde and acetaldehyde, oxygenated polar VOCs such as acrolein and ethanol, and the less volatile air toxics such as naphthalene, even at 100% relative humidity.
- The analytical system used in the experiments described in this application note provides fully automated analysis for up to 27 sample channels and offers excellent method detection limits, retention time stability, reproducibility and linearity. When combined with the optimised chromatographic method and the overlap mode available (in which the next sample is loaded to the focusing trap while the current GC analysis is still running), sample-to-sample cycle times of less than 60 minutes can be achieved, maximizing laboratory productivity.
- In addition to analyzing the full suite of compounds from canisters, the ability of the CIA *Advantage*-xr to sample

from unpressurized sources means that the same instruments can be deployed for remote, unattended, continuous online monitoring of the same compounds with no modifications.

- Additional features of the CIA *Advantage*–UNITY-xr system, are the ability to (a) run sorbent-tube TD analysis in accordance with U.S. EPA Method TO-17 and Chinese EPA Method HJ 644, and (b) re-collect the split portions of samples onto clean sorbent tubes for easier storage and to release the canisters for cleaning and sampling. Moreover, canister and sorbent-tube analyses can be sequenced and run automatically on the same analytical system, without user intervention.

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Appendix

Table A1. Performance data for the compounds from the combined list detected by FID

No.	Compound	t _R (min)	t _R RSD (%) (n=16)	Response RSD (%) (n=10)	R ²	RSD RRF (%)	MDL (ppb)
1	Ethene	10.20	0.120	1.493	0.998	3.6	0.092
2	Acetylene	10.68	0.149	1.860	0.997	3.4	0.099
3	Ethane	11.17	0.101	3.471	0.995	6.6	0.189
4	Propene	16.90	0.095	0.861	1.000	4.4	0.017
5	Propane	17.47	0.092	2.133	0.999	3.3	0.022

Table A2. Performance data for the compounds from the combined list detected by MS

No.	Compound	Mode	t _R (min)	Quant ion (m/z)	Qual ion 1 (m/z)	Qual ion 2 (m/z)	t _R RSD (%) (n = 16)	Response RSD (%) (n = 10)	R ² (1.25– 15 ppb)	RSD RRF (%)	MDL (ppb)
6	Formaldehyde	SIM	8.33	29	—	—	0.073	3.301	0.996	9.8	0.105
7	Dichlorodifluoromethane	EIC	9.70	85	50	—	0.092	6.315	0.998	5.2	0.022
8	Chloromethane	EIC	11.11	50	52	—	0.088	4.577	0.999	6.0	0.095
9	Dichlorotetrafluoroethane	EIC	11.80	85	87	—	0.066	5.489	0.999	5.2	0.034
10	Isobutane	EIC	11.88	43	57	58	0.058	3.427	0.999	4.3	0.022
11	Acetaldehyde	SIM	11.88	44	—	—	0.054	3.171	0.998	10.0	0.019
12	Chloroethene	EIC	12.71	62	35	64	0.054	4.734	0.999	3.8	0.047
13	<i>trans</i> -But-2-ene	EIC	13.40	41	39	55	0.040	4.280	0.999	5.0	0.050
14	Butadiene	EIC	13.60	39	53	54	0.045	5.174	0.999	8.6	0.085
15	<i>n</i> -Butane	EIC	13.95	43	39	41	0.048	4.342	0.999	4.4	0.060
16	<i>cis</i> -But-2-ene	EIC	14.52	41	39	56	0.047	4.256	0.999	6.3	0.059
17	Bromomethane	EIC	15.22	94	96	—	0.035	6.372	0.996	6.1	0.035
18	But-1-ene	EIC	15.41	41	56	39	0.034	4.248	0.999	6.5	0.041
19	Chloroethane	EIC	16.05	64	49	66	0.059	5.041	0.997	6.1	0.050
20	Ethanol	EIC	16.18	31	45	46	0.044	2.154	0.998	9.1	0.043
21	Acrolein	EIC	17.90	56	55	27	0.033	5.495	0.998	4.1	0.032
22	Acetone	EIC	18.28	43	57	42	0.026	5.384	0.999	5.0	0.017
23	2-Methylbutane	EIC	18.62	72	71	—	0.036	4.348	0.999	4.7	0.073
24	Isopropanol	EIC	18.93	45	43	—	0.028	3.131	0.999	8.8	0.114
25	Trichlorofluoromethane	EIC	19.15	101	103	66	0.026	6.046	0.999	4.6	0.037
26	Pent-1-ene	EIC	19.49	42	55	70	0.028	3.954	0.999	8.2	0.083
27	<i>n</i> -Pentane	EIC	20.21	43	41	42	0.032	3.949	0.999	6.6	0.062
28	Isoprene	EIC	20.55	67	68	53	0.023	5.141	1.000	3.5	0.057
29	<i>trans</i> -Pent-2-ene	EIC	20.61	55	70	42	0.016	4.646	0.999	5.1	0.037
30	1,1-Dichloroethene	EIC	21.12	61	98	96	0.026	4.938	0.999	3.6	0.034
31	<i>cis</i> -Pent-2-ene	EIC	21.14	55	42	70	0.023	4.655	0.999	6.1	0.049
32	Dichloromethane	EIC	21.34	49	84	86	0.018	3.032	0.997	3.7	0.099
33	1,1,2-Trichlorotrifluoroethane	EIC	21.97	101	103	151	0.026	6.336	0.998	4.5	0.054
34	2,2-Dimethylbutane	EIC	22.53	43	77	57	0.025	3.838	0.999	4.6	0.066
35	Carbon disulfide	EIC	22.57	76	44	78	0.014	5.653	0.999	4.4	0.045
36	<i>trans</i> -1,2-Dichloroethene	EIC	23.67	61	96	98	0.017	4.787	0.999	8.0	0.036
37	Vinyl acetate	EIC	24.04	43	42	86	0.027	5.064	0.999	3.5	0.072
38	<i>tert</i> -Butyl methyl ether	EIC	24.06	73	41	57	0.015	5.239	0.998	5.8	0.143
39	1,1-Dichloroethane	EIC	24.15	63	65	83	0.016	4.678	0.997	4.3	0.060
40	2,3-Dimethylbutane	EIC	24.31	43	42	57	0.029	5.237	0.997	10.0	0.080
41	2-Methylpentane	EIC	24.41	42	43	57	0.020	3.407	0.999	3.7	0.062
42	Cyclopentane	EIC	24.40	70	40	55	0.025	5.370	0.999	3.4	0.038
43	Butan-2-one	EIC	24.71	72	57	—	0.021	4.678	1.000	4.2	0.057
44	3-Methylpentane	EIC	25.25	57	41	56	0.022	5.269	0.998	6.7	0.051
45	Hex-1-ene	EIC	25.48	56	41	42	0.024	5.446	0.996	12.1	0.102
46	Ethyl acetate	EIC	25.80	43	45	61	0.022	2.812	0.999	7.1	0.033
47	1,2-Dichloroethene	EIC	25.84	61	96	98	0.021	4.806	0.999	4.2	0.044
48	<i>n</i> -Hexane	EIC	26.08	57	41	43	0.013	4.422	0.999	5.8	0.078
IS1	Bromochloromethane	EIC	26.23	130	49	—	0.021	2.904	—	—	—

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Table A2. Performance data for the compounds from the combined list detected by MS (continued from previous page)

No.	Compound	Mode	t _R (min)	Quant ion (m/z)	Qual ion 1 (m/z)	Qual ion 2 (m/z)	t _R RSD (%) (n = 16)	Response RSD (%) (n = 10)	R ² (1.25–15 ppb)	RSD RRF (%)	MDL (ppb)
49	Chloroform	EIC	26.40	83	47	85	0.021	5.984	0.999	3.1	0.034
50	Tetrahydrofuran	EIC	27.17	42	41	72	0.018	3.469	0.999	5.5	0.084
51	2,4-Dimethylpentane	EIC	27.73	56	41	57	0.025	4.898	0.999	5.8	0.040
52	1,2-Dichloroethane	EIC	27.85	62	49	64	0.020	4.623	0.999	4.7	0.049
53	Methylcyclopentane	EIC	27.93	56	41	69	0.017	4.620	0.995	5.2	0.083
54	1,1,1-Trichloroethane	EIC	28.39	97	61	99	0.021	6.401	0.998	4.9	0.118
55	Benzene	EIC	29.26	78	51	77	0.015	5.579	0.998	3.8	0.014
IS2	1,4-Difluorobenzene	EIC	29.50	114	—	—	0.016	6.012	—	—	—
56	Tetrachloromethane	EIC	29.54	117	119	121	0.015	7.312	0.997	8.5	0.026
57	2-Methylhexane	EIC	29.55	43	42	85	0.013	3.359	0.996	8.4	0.026
58	Cyclohexane	EIC	29.79	84	41	—	0.013	5.609	0.996	7.3	0.008
59	2,3-Dimethylpentane	EIC	29.81	56	43	57	0.018	3.937	0.996	9.3	0.028
60	3-Methylhexane	EIC	30.03	43	57	85	0.016	4.676	0.999	8.2	0.158
61	1,2-Dichloropropane	EIC	30.62	63	41	62	0.012	4.919	0.999	8.3	0.057
62	Methyl methacrylate	EIC	30.75	69	51	89	0.014	4.642	1.000	1.1	0.032
63	1,4-Dioxane	EIC	30.79	88	31	58	0.013	2.563	0.999	5.2	0.120
64	2,2,4-Trimethylpentane	EIC	30.85	57	41	56	0.014	4.102	0.995	6.2	0.033
65	Bromodichloromethane	EIC	30.94	83	47	85	0.017	5.625	0.999	3.2	0.037
66	Trichloroethene	EIC	30.97	130	95	132	0.013	6.668	0.999	6.5	0.029
67	<i>n</i> -Heptane	EIC	31.05	57	41	71	0.016	4.722	0.999	8.1	0.068
68	4-Methylpentan-2-one	EIC	32.11	43	41	58	0.012	1.961	1.000	2.4	0.084
69	<i>cis</i> -1,3-Dichloropropene	EIC	32.31	75	39	77	0.016	5.182	0.999	3.7	0.018
70	Methylcyclohexane	EIC	32.76	83	41	55	0.015	5.279	0.998	7.8	0.050
71	<i>trans</i> -1,3-Dichloropropene	EIC	33.11	75	39	77	0.011	5.001	0.999	2.7	0.046
72	1,1,2-Trichloroethane	EIC	33.62	97	61	83	0.014	5.816	0.998	6.3	0.092
73	2,3,4-Trimethylpentane	EIC	33.70	43	70	71	0.013	3.083	0.997	5.5	0.042
74	2-Methylheptane	EIC	33.96	43	42	—	0.014	3.733	0.997	6.8	0.038
75	Hexan-2-one	EIC	34.12	58	57	—	0.014	1.369	0.998	7.9	0.035
76	Toluene	EIC	34.16	91	65	92	0.012	5.521	0.998	8.0	0.008
77	3-Methylheptane	EIC	34.34	43	41	57	0.010	3.876	0.993	5.7	0.065
78	Hexanal	EIC	34.60	44	56	—	0.012	2.020	0.999	5.9	0.058
79	Chlorodibromomethane	EIC	35.09	129	127	131	0.011	6.661	1.000	1.6	0.051
80	<i>n</i> -Octane	EIC	35.30	43	41	57	0.012	3.472	0.997	5.4	0.017
81	1,2-Dibromoethane	EIC	35.59	107	81	109	0.011	5.990	0.999	3.3	0.025
82	Tetrachloroethene	EIC	36.25	166	129	164	0.011	7.337	0.998	7.7	0.032
IS3	Chlorobenzene-d5	EIC	37.45	117	—	—	0.012	5.780	—	—	—
83	Chlorobenzene	EIC	37.54	112	—	—	0.012	6.415	0.998	6.5	0.053
84	Ethylbenzene	EIC	38.03	91	51	106	0.009	5.767	0.998	5.6	0.008
85	<i>m</i> -/ <i>p</i> -Xylene	EIC	38.31	91	105	106	0.011	5.698	0.998	5.4	0.012
86	Bromoform	EIC	38.95	173	171	175	0.010	7.264	1.000	6.3	0.044
87	Styrene	EIC	39.06	104	78	103	0.008	3.198	0.999	4.0	0.041
88	<i>n</i> -Nonane	EIC	39.07	43	41	57	0.013	5.835	0.997	4.1	0.005
89	1,1,2,2-Tetrachloroethane	EIC	39.30	83	85	95	0.009	5.037	0.998	4.2	0.071
90	<i>o</i> -Xylene	EIC	39.32	91	105	106	0.009	5.753	0.997	6.0	0.007

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Table A2. Performance data for the compounds from the combined list detected by MS (continued from previous page)

No.	Compound	Mode	t _R (min)	Quant ion (m/z)	Qual ion 1 (m/z)	Qual ion 2 (m/z)	t _R RSD (%) (n = 16)	Response RSD (%) (n = 10)	R ² (1.25–15 ppb)	RSD RRF (%)	MDL (ppb)
IS4	1-Bromo-4-fluorobenzene	EIC	40.28	95	—	—	0.010	5.361	—	—	—
91	Isopropylbenzene	EIC	40.38	105	77	120	0.009	6.163	0.998	4.8	0.025
92	Benzaldehyde	EIC	41.34	106	—	—	0.009	2.928	0.998	11.1	0.078
93	<i>n</i> -Propylbenzene	EIC	41.45	91	92	120	0.007	5.424	0.997	3.7	0.037
94	1-Methyl-3-ethylbenzene	EIC	41.72	105	91	120	0.011	4.801	0.997	5.0	0.054
95	1,2,3-Trimethylbenzene	EIC	41.81	119	79	120	0.008	4.285	0.997	3.9	0.037
96	1-Methyl-2-ethylbenzene	EIC	42.40	105	91	120	0.006	6.005	0.997	5.1	0.038
97	<i>n</i> -Decane	EIC	42.46	57	41	43	0.007	3.722	0.997	3.2	0.018
98	1,3,5-Trimethylbenzene	EIC	42.85	105	119	—	0.008	6.044	0.998	4.0	0.023
99	1-Methyl-4-ethylbenzene	EIC	42.86	120	77	91	0.034	5.996	0.998	3.5	0.011
100	Benzyl chloride	EIC	43.38	91	126	65	0.009	5.735	0.998	3.3	0.082
101	1,3-Dichlorobenzene	EIC	43.53	146	111	148	0.012	6.636	1.000	2.6	0.078
102	1,4-Dichlorobenzene	EIC	43.66	148	111	75	0.007	6.566	0.999	2.7	0.028
103	1,2,4-Trimethylbenzene	EIC	43.99	105	77	120	0.009	7.136	0.999	2.6	0.031
104	1,3-Diethylbenzene	EIC	44.48	119	134	105	0.010	6.123	0.999	1.8	0.013
105	1,2-Dichlorobenzene	EIC	44.59	146	111	—	0.007	6.760	0.999	2.7	0.025
106	1,4-Diethylbenzene	EIC	44.74	119	105	134	0.009	6.258	0.999	1.5	0.015
107	<i>m</i> -Tolualdehyde	EIC	45.03	91	120	—	0.009	1.933	1.000	12.1	0.070
108	<i>n</i> -Undecane	EIC	45.50	57	43	71	0.008	2.817	0.999	1.3	0.072
109	<i>n</i> -Dodecane	EIC	48.27	57	43	71	0.010	5.050	1.000	1.2	0.073
110	1,2,4-Trichlorobenzene	EIC	48.95	180	145	182	0.012	6.452	1.000	1.6	0.080
111	Naphthalene	EIC	49.43	128	127	129	0.007	5.496	1.000	1.3	0.026
112	Hexachlorobutadiene	EIC	50.08	225	223	227	0.011	7.401	1.000	2.0	0.054
104	1,3-Diethylbenzene	EIC	44.48	119	134	105	0.010	6.123	0.999	1.8	0.013
105	1,2-Dichlorobenzene	EIC	44.59	146	111	—	0.007	6.760	0.999	2.7	0.025
106	1,4-Diethylbenzene	EIC	44.74	119	105	134	0.009	6.258	0.999	1.5	0.015
107	<i>m</i> -Tolualdehyde	EIC	45.03	91	120	—	0.009	1.933	1.000	12.1	0.070
108	<i>n</i> -Undecane	EIC	45.50	57	43	71	0.008	2.817	0.999	1.3	0.072
109	<i>n</i> -Dodecane	EIC	48.27	57	43	71	0.010	5.050	1.000	1.2	0.073
110	1,2,4-Trichlorobenzene	EIC	48.95	180	145	182	0.012	6.452	1.000	1.6	0.080
111	Naphthalene	EIC	49.43	128	127	129	0.007	5.496	1.000	1.3	0.026
112	Hexachlorobutadiene	EIC	50.08	225	223	227	0.011	7.401	1.000	2.0	0.054

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