

Application Note 145

Extending whole-air monitoring: Simultaneous cryogen-free analysis of PAMS ozone precursors and TO-15 air toxics from canisters in accordance with new Chinese air-monitoring regulations

Summary

This application note describes cryogen-free sampling and analysis of the 108 analytes of a combined list of PAMS ozone precursors and TO-15 air toxics in high-humidity environments, in compliance with the detection limit and data-quality requirements of Chinese EPA Method HJ 759 and the Chinese Environmental Air Volatile Organic Compound Monitoring Program. The use of Markes' ground-breaking Dry-Focus3 pre-concentration and water management technology results in excellent chromatographic peak shape at 100% humidity, whilst maintaining sample-to-sample cycle times below 60 minutes. The use of robust, field-proven dual-column/ Deans switch technology in the GC oven allows FID analysis of highly volatile C_2 hydrocarbons, with the remaining analytes detected using a single-quadrupole mass spectrometer operating in full-scan mode.



Introduction

Growing concerns over the harmful effects to human health of exposure to low levels of hazardous air pollutants have led to increasingly demanding VOC monitoring programs. Volatile hydrocarbons in urban atmospheres participate in photochemical reactions and are believed to contribute significantly to the formation of ozone and fine particulate (PM 2.5) pollution.

These 'ozone precursors' (often referred to as 'PAMs' in reference to their long-standing inclusion within the US EPA's Photochemical Assessment Monitoring Scheme) comprise alkanes, alkenes, alkynes and aromatic hydrocarbons in the C_2-C_{12} volatility range. Ozone precursor monitoring is typically achieved using on-line techniques for continuous monitoring or remote canister sampling, but both techniques require water removal and pre-concentration of the sample before injection into a gas chromatograph (GC), usually in a dualcolumn/Deans switch configuration with dual flame ionisation detection (FID) (see <u>Application Note 129</u>).

Another suite of routinely monitored hazardous airborne volatile pollutants are known as 'air toxics'. US EPA TO- 15^1 and Chinese EPA Method HJ 759^2 detail the methodology and performance criteria for these compounds. Air toxics comprise polar and non-polar VOCs, and include a number of halogenated compounds. Typically, samples are collected in canisters, with water removed and the sample pre-concentrated before injection into a single-column GC-MS system (see Application Note 133). It is important to note that the air toxics compound list does not include the very volatile C₂ hydrocarbons that are present in the ozone precursor list, with the result that analysis can benefit from the higher sensitivity and specificity of mass spectrometry (MS) detection (C₂ hydrocarbons produce low responses and therefore low sensitivity when analysed by MS).

In December 2017, the Chinese Ministry of Environmental Protection issued a document relating to the Environmental Air Volatile Organic Compound Monitoring Program.³ This document, hereinafter abbreviated 'EA-VOC-MP' for convenience, requires the monitoring of both PAMS and TO-15 analytes in a single run. Obtaining good peak shape and chromatographic separation of 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 use of an analytical system (comprising a canister autosampler, water removal device, thermal desorber, and dual-column-GC-MS/FID), which operates entirely without cryogen, and which meets all the performance criteria of both HJ 759 and EA-VOC-MP. In addition, the system is able to monitor samples at 100% relative humidity, and offers optimum responses for the three C_2 hydrocarbons monitored using FID, as well as confident compound identification and high sensitivity for the remaining 105 compounds monitored using MS.



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Analytical system

The analytical system used for this study was a CIA *Advantage-xr* canister autosampler and UNITY-xr thermal desorber with a Kori-xr water removal device, coupled to a GC–MS system (Figures 1 and 2). This system harnesses Dry Focus3 technology – a unique, three-stage focusing and water-management mechanism that operates entirely without liquid cryogen.



Figure 1: The CIA Advantage–Kori–UNITY-xr system used in the current study.

The **CIA** *Advantage-xr*[™] is an autosampler for the analysis of VOCs in up to 27 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 optimised for the cryogen-free analysis of VOCs, VVOCs and oxygenates in humid air using canisters.







Air sampling and water removal with Dry-Focus3™

Canister or whole-air samples pass through the Kori-xr trap (where humidity is deposited as ice), before being focused on the trap of the UNITY-xr. 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.

Experimental

The experimental parameters are listed below, and the GC setup is shown in Figure 4. 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. This allows more efficient operation without compromising analyte peak shape, and reducing the cost per sample.



Figure 3: Operation of the CIA Advantage-Kori-UNITY-xr system.

Trap desorption, water purging, and outlet split

The focusing trap is rapidly heated in a

reverse flow of carrier gas, to transfer the analytes to the GC column.

Simultaneously, the Kori-xr

trap is heated in a flow of gas, expelling the

trapped water.

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Carrier bas

The operation of this system is as follows. 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 3). Note that as well as canisters and bags, Kori-xr can also be applied to on-line samples.

With the majority of excess water removed, samples then pass into the **UNITY-xr**[™] thermal desorber, containing the newly-developed 'Trace TO-15' focusing trap (part no. U-TO15-KXR). This narrow, electrically-cooled trap is filled with separate beds of porous polymer, graphitised carbon black and molecular sieve sorbents. The different strength of these sorbents ensures that compounds over a wide volatility range are quantitatively trapped.

After sample collection at a trap temperature of -30° C, the temperature is initially elevated to 25° C, and the trap is 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 through the focusing trap is reversed, and the trap is heated rapidly (up to 100° C/s), to inject the analytes onto the GC column.

Stage 2: 'Volatiles' column flow to MS



Figure 4: Dual-column GC-MS/FID instrument operation. → = Analyte flow. → = Gas flow. P = Carrier gas pressure supply. For the first ~8 minutes of the GC run, the Deans switch is set to send the primary column effluent to the secondary column and the FID detector. Once the very volatile C₂ hydrocarbons have eluted, the Deans switch switches to 'cut' the primary column effluent to the MS. This allows the majority of compounds to be identified by their spectra, and quantifier and qualifier ions to be used for confident automated quantitative analysis.

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Standards:

Standard gas cylinders containing 56 PAMS (ozone precursor) compounds (Restek 34420) and 65 TO-15 (air toxics) compounds (Restek 34436) 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 standards, so 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 (BFB) at 1 ppm in nitrogen (Restek 34408).

Canister sampling:

Instrument: CIA Advantage-xr 50-600 mL Sample volume:

Water removal:

Instrument: Kori-xr -30°C/300°C Trap temperatures:

TD: UNITY-xr Instrument: Flow path: 120°C Sample flow: 50 mL/min Trap purge: 2 min at 50 mL/min Focusing trap low: -30°C

Focusing trap high: Outlet split:

GC:

Carrier gas: Oven temperature: Run time:

FID:

Temperature: Hydrogen flow: Air flow:

30 mL/min 400 mL/min

Quadrupole MS:

250°C
280°C
200°C
m/z 29-300

Results and discussion

1. Chromatography

Figure 5 shows example chromatograms from each column for the 108-component mix at 100% RH, displaying excellent separation and chromatographic peak shape. Table 1 lists retention times and quantifier ions for each compound.

250°C for 2 min

Helium, constant flow

35°C (initial), 270°C (final)

3 mL/min

52 min

270°C



Figure 5: Analysis of 400 mL of the 10 ppb, 100% RH standard. (A) FID chromatogram of C₂ hydrocarbons ethene (#4), acetylene (#5) and ethane (#7). (B) TIC for the remaining 105 compounds. (C) EICs for: chloromethane (#6, m/z 50), chloroethene (#10, m/z 62), isopropanol (#22, m/z 45), 1,2-dichloropropane (#59, m/z 63), methyl methacrylate (#60, m/z 41), p-dioxane (#61, m/z 88), isooctane (#62, m/z 57), bromodichloromethane (#63, m/z 83), trichloroethene (#64, m/z 130), n-heptane (#65, m/z 57) and hexachlorobutadiene (#108, m/z 225). Compound identities are listed in Table 1.

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				Quant ion	t _R RSD	Response		RSD RRF	MDL
No.	Compound	Detector	t _R (min)	(m/z)	(%)	RSD (%)	R ²	(%)	(ppb)
1	Propene (Propylene)	MS	8.82	41	0.078	0.94	1.000	11.9	0.06
2	Propane	MS	8.95	29	0.104	5.08	0.996	27.8	0.17
3	Dichlorodifluoromethane	MS	9.41	85	0.100	3.27	0.998	13.0	0.05
4	Ethene (Ethylene)	FID	9.82	N/A	0.061	1.48	0.999	7.2	0.11
5	Acetylene	FID	10.05	N/A	0.060	2.05	0.999	7.6	0.09
6	Chloromethane	MS	10.78	50	0.093	4.19	0.994	6.2	0.13
7	Ethane	FID	10.86	N/A	0.051	1.05	1.000	5.7	0.05
8	Dichlorotetrafluoroethane	MS	11.55	85	0.099	0.76	0.998	5.2	0.12
9	Isobutane	MS	11.79	43	0.073	2.91	0.996	4.8	0.06
10	Chloroethene (Vinyl chloride)	MS	12.42	62	0.084	1.06	0.996	7.5	0.16
11	trans-2-butene	MS	13.13	41	0.075	1.70	0.999	6.7	0.04
12	Butadiene	MS	13.33	39	0.078	3.22	0.999	4.5	0.22
13	n-Butane	MS	13.34	43	0.070	2.73	0.998	6.8	0.07
14	cis-But-2-ene	MS	14.27	41	0.075	1.71	0.998	7.2	0.07
15	Bromomethane	MS	14.99	94	0.065	1.63	0.999	6.0	0.05
16	But-1-ene	MS	15.20	41	0.068	1.32	0.999	5.1	0.03
10	Chloroethane	IVIS	15.84	64 21	0.047	1.55	0.997	5.7	0.04
18	Ethanol	IVIS	16.00	31	0.030	4.08	0.997	13.1	0.16
19	Acrolem	IVIS	10.15	12	0.037	3.84	0.991	7.9	0.10
20	Acetone	IVIS	10.15	43	0.028	1.20	0.999	2.4	0.08
21		IVIS	10.47	43	0.039	2.47	0.999	12.4	0.12
22	Trichlorofluoromothono	IVIS	10.00	40	0.035	3.20	0.991	13.0	0.08
23		MS	19.02	55	0.041	1.17	0.999	4.0	0.00
24	Pent-1-ene	MS	19.30	12	0.042	0.80	0.998	3.0	0.04
26	n-Pentane	MS	20.09	/13	0.036	1 39	0.000	6.8	0.07
20	Isonrene	MS	20.03	67	0.035	0.95	0.997	5.7	0.03
28	trans-Pent-2-ene	MS	20.52	55	0.033	0.67	0.998	4 7	0.03
29	1.1-Dichloroethene	MS	21.03	61	0.032	2.02	0.997	5.4	0.05
30	cis-Pent-2-ene	MS	21.03	55	0.029	0.98	0.997	5.5	0.03
31	Dichloromethane	MS	21.24	49	0.030	2.02	0.997	6.1	0.07
32	1.1.2-Trichloro-1.2.2-trifluoroethane	MS	21.90	101	0.028	1.40	1.000	8.9	0.06
33	2,2-Dimethylbutane	MS	22.45	43	0.031	1.25	0.997	2.0	0.16
34	Carbon disulfide	MS	22.49	76	0.025	1.04	0.992	11.8	0.21
35	trans-1,2-Dichloroethene	MS	23.62	61	0.021	3.30	0.998	28.6	0.17
36	tert-Butyl methyl ether	MS	24.00	73	0.022	1.15	0.999	4.8	0.04
37	Vinyl acetate	MS	24.02	43	0.024	1.38	0.998	9.3	0.06
38	1,1-Dichloroethane	MS	24.11	63	0.019	1.06	0.996	4.6	0.05
39	2,3-Dimethylbutane	MS	24.23	43	0.030	5.59	0.999	8.9	0.09
40	2-Methylpentane	MS	24.36	42	0.015	2.60	0.997	6.3	0.11
41	Butan-2-one (Methyl ethyl ketone, MEK)	MS	24.67	72	0.021	1.41	0.997	6.1	0.05
42	3-Methylpentane	MS	25.22	57	0.022	2.06	0.996	6.0	0.08
43	1,2-Dichloroethene	MS	25.80	61	0.020	1.20	0.997	5.2	0.06
44	Ethyl acetate	MS	25.80	43	0.020	1.59	0.996	5.3	0.04
45	n-Hexane	MS	26.07	57	0.021	0.75	0.996	3.6	0.04
IS1	Bromochloromethane	MS	26.21	49	0.022	2.10	-	-	_
46	Chloroform	MS	26.39	83	0.029	0.74	0.998	4.4	0.07
47	Tetrahydrofuran	MS	27.17	42	0.015	2.38	0.998	4.6	0.09
48	2,4-Dimethylpentane	MS	27.76	43	0.017	1.13	0.998	4.8	0.03
49	1,2-Dichloroethane	MS	27.86	62	0.016	1.74	0.998	4.5	0.06
50	Hex-1-ene	MS	27.94	56	0.013	7.23	0.995	5.5	0.08
51	Methylcyclopentane	MS	27.95	56	0.015	1.74	0.999	4.7	0.17
52	1,1,1-Trichloroethane	MS	28.40	97	0.021	0.95	0.999	8.6	0.05
53	Benzene	MS	29.28	78	0.013	0.59	1.000	6.1	0.04
IS2	1,4-Difluorobenzene	MS	29.52	114	0.014	1.17	_		_
54	Tetrachloromethane	MS	29.56	117	0.019	1.06	0.999	5.6	0.07

Table 1: Performance data for the combined list of PAMS and TO-15 compounds. (Continued on next page)

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				Ouant ion	t _n RSD	Response		RSD RRF	MDL
No.	Compound	Detector	t _R (min)	(m/z)	(%)	RSD (%)	R ²	(%)	(ppb)
55	2-Methylhexane	MS	29.59	43	0.016	1.22	0.999	4.2	0.06
56	Cyclohexane	MS	29.84	56	0.010	1.09	0.993	6.2	0.04
57	2,3-Dimethylpentane	MS	29.91	43	0.018	4.53	0.998	6.8	0.06
58	3-Methylhexane	MS	30.06	43	0.017	1.89	0.997	5.2	0.12
59	1,2-Dichloropropane	MS	30.63	63	0.013	0.70	0.993	8.0	0.09
60	Methyl methacrylate	MS	30.80	41	0.013	3.50	0.996	14.0	0.18
61	<i>p</i> -Dioxane	MS	30.84	88	0.023	6.00	0.999	5.8	0.11
62	Isooctane (2,2,4-Trimethylpentane)	MS	30.89	57	0.014	1.02	0.998	5.8	0.05
63	Bromodichloromethane	MS	30.98	83	0.013	0.60	0.997	5.6	0.06
64	Trichloroethene	MS	31.00	130	0.017	0.73	0.998	5.5	0.09
65	n-Heptane	MS	31.09	57	0.016	4.14	1.000	2.8	0.36
66	4-Methylpentan-2-one (Methyl isobutyl ketone, MIBK)	MS	31.12	43	0.015	1.37	0.998	5.7	0.08
67	cis-1,3-Dichloropropene	MS	32.36	75	0.015	0.89	0.997	5.7	0.07
68	Methylcyclohexane	MS	32.83	83	0.007	0.75	0.998	5.0	0.07
69	trans-1,3-Dichloropropene	MS	33.18	75	0.014	1.09	0.997	6.1	0.08
70	1,1,2-Trichloroethane	MS	33.69	97	0.021	0.67	0.998	5.4	0.08
71	2,3,4-Trimethylpentane	MS	33.78	43	0.010	1.03	0.998	3.5	0.04
72	2-Methylheptane	MS	34.04	43	0.016	1.68	0.998	3.7	0.09
73	Hexan-2-one (Methyl n-butyl ketone)	MS	34.21	43	0.011	4.76	0.996	9.9	0.12
74	3-Methylheptane	MS	34.40	43	0.011	2.07	0.997	4.2	0.08
75	Toluene	MS	34.43	91	0.015	0.59	1.000	4.7	0.04
76	Chlorodibromomethane	MS	35.18	129	0.011	0.93	0.996	6.3	0.05
77	n-Octane	MS	35.40	43	0.014	0.87	0.998	3.9	0.03
78	1,2-Dibromoethane	MS	35.69	107	0.013	0.55	0.997	5.9	0.05
79	Tetrachloroethene	MS	36.34	166	0.015	0.67	0.998	7.0	0.06
IS3	Chlorobenzene-d ₅	MS	37.56	117	0.015	0.70	_	_	_
80	Chlorobenzene	MS	37.63	112	0.011	0.48	0.998	5.7	0.05
81	Ethylbenzene	MS	38.14	91	0.010	0.39	1.000	3.4	0.04
82+83	<i>m</i> - + <i>p</i> -Xylene	MS	38.41	91	0.014	0.35	1.000	3.0	0.06
84	Bromoform	MS	39.05	173	0.012	2.97	0.995	8.0	0.04
85	n-Nonane	MS	39.18	43	0.012	0.91	0.998	3.8	0.08
86	Styrene	MS	39.19	104	0.009	0.29	1.000	2.2	0.02
87	1,1,2,2-Tetrachloroethane	MS	39.41	83	0.013	0.46	0.999	4.4	0.05
88	o-Xylene	MS	39.44	91	0.010	0.51	1.000	3.5	0.04
IS4	1-Bromo-4-fluorobenzene (BFB)	MS	40.39	95	0.014	1.28	_	_	_
89	Isopropylbenzene	MS	40.50	105	0.010	0.80	0.998	5.8	0.04
90	n-Propylbenzene	MS	41.59	91	0.009	0.62	0.999	3.9	0.08
91	1-Methyl-3-ethylbenzene	MS	41.71	105	0.007	2.26	0.998	5.7	0.05
92	1,2,3-Trimethylbenzene	MS	41.73	119	0.008	1.85	0.999	4.7	0.07
93	1-Methyl-2-ethylbenzene	MS	41.86	105	0.010	2.05	0.998	5.0	0.14
94	1,2,4-Trimethylbenzene	MS	41.93	119	0.008	5.95	1.000	4.6	0.11
95	1,3,5-Trimethylbenzene	MS	41.94	105	0.010	2.39	0.998	6.4	0.06
96	n-Decane	MS	42.60	57	0.008	0.55	0.998	4.4	0.04
97	Benzyl chloride	MS	43.51	91	0.010	0.47	0.997	5.4	0.03
98	1-Metnyl-4-etnylbenzene	MS	43.53	105	0.010	0.47	1.000	2.0	0.09
99	1,3-Dichlorobenzene	MS	43.67	146	0.008	0.79	0.998	1.1	0.24
100	1,3-Diethylbenzene	MS	44.62	119	0.006	0.82	0.998	5.5	0.03
101	1,4-Dichlorobenzene	IVIS NAC	44.73	146	0.010	0.57	0.998	7.2	0.06
102	1,2-Dichlorobenzene	MS	44.74	146	0.010	0.56	0.998	7.2	0.06
103		IVIS MC	44.90	119	0.007	0.72	0.998	5.3	0.03
105		IVIS	45.66	5/	0.011	0.72	0.998	3.8	0.04
105		IVIS MC	48.40	5/	0.008	0.84	0.998	4.3	0.06
107		IVIS MC	49.12	100	0.008	0.60	0.998	0.0	0.06
100		IVIS	49.61	128	0.009	1.02	0.998	0.0	0.07
TUQ	пеласниоторицаціене	IVIS	50.29	220	0.008	1.23	0.990	1.4	0.05

Table 1: Performance data for the combined list of PAMS and TO-15 compounds. (Continued from previous page)

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Figure 5C shows the excellent peak shape for the early-eluting compounds chloromethane (#6) and chloroethene (#10), as well as the polar species isopropanol (#22). The fact that this is possible without requiring cryogenic cololing demonstrates the efficient trap desorption and water management of the UNITY-CIA *Advantage*-Kori-xr system. The sharp peak for hexachlorobutadiene (#108) highlights the efficient transfer of the less volatile compounds through the analytical system.

Figure 5C also shows an expansion of the 30.5–31.3 min range, demonstrating identification of the closely-eluting compounds present (#59 to #65) by displaying the responses from the corresponding extracted ions, allowing confident, automated identification and quantitation.

The efficiency of this method for the 108-compound target list is further enhanced by the 52-minute GC run time, which results from a relatively high GC oven starting temperature of 35°C 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. In this way, sample-to-sample cycle times below 60 minutes are achieved without the need for liquid cryogenic cooling, maximising sample throughput.

2. Relative response factors and linearities

System linearity was assessed by sampling 50, 100, 200, 300, 400 and 600 mL of the 10 ppb, 100% RH 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 (Table 1). The mean RSD over the six-point calibration for the 108 compounds was 6.4%, with only two compounds (propane (#2) and *trans*-1,2-dichloroethene (#35)) exceeding 20%, and all being below the 30% RRF RSD limit specified in the method.

Linearities were also calculated (Table 1), and all compounds had R^2 values >0.990, which satisfies the method criteria. Figure 6 shows linearity plots for a selection of compounds covering the volatility and polarity range of the target list.



Figure 6: Linearities for selected compounds from the 10 ppb, 100% RH standard, over the range 50–600 mL.

3. Reproducibility

The nature of the two-column set-up means that retention times can be affected by the pressure balance in the system. However, electronic carrier gas control between the GC and the UNITY-CIA *Advantage*-xr and the efficient removal of water using Kori-xr means that stable retention times are achieved on both columns. The retention-time reproducibility can be expressed as RSDs across a series of analyses, and these values are provided in Table 1. Excellent retention-time stabilities were achieved across ten replicate 400 mL samples of the 10 ppb, 100% RH standard, with an average RSD of 0.03% and a maximum of 0.1%. Such excellent stability of retention times makes it possible to automate the data processing of long sequences of multi-target analyses (for example, like those required by EA-VOC-MP), without requiring manual peak integrations or retention time adjustments.

The reproducibility of analyte response was investigated by analysing ten replicate 400 mL samples at 100% RH. The RSDs of the absolute peak area responses were then calculated, and are listed in Table 1. All compounds showed good reproducibility, with <7.5% RSD for all compounds across ten runs without the need for internal standard correction, and with 95% of the compounds giving values below 5% RSD.

The excellent reproducibility of absolute response and retention time on both columns is demonstrated in Figure 7.



Retention time (min)

Figure 7: Example overlaid responses (FID for ethane, MS otherwise) for ten repeat analyses of 400 mL of the 10 ppb, 100% RH standard, demonstrating excellent retention time and response stability.

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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 reproducibilities <2.5% RSD. This 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 maximising instrument uptime to run real samples.

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 sample throughput.

4. Carryover and blank levels

It is important that the instrumentation used for analysing trace-level samples has minimal memory effects ('carryover'), from previous samples – even if they are at a higher concentration than those typically analysed. High levels of carryover affect recovery results and also 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 analysed 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 the ppb-level response (which must be <0.4 ppb). The majority of compounds were not detected in the carryover test at all, and the 13 compounds that were detected had a mean carryover of 0.06 ppb (0.3%), with the maximum being for naphthalene (1.0%). Figure 8 shows the TIC for the 20 ppb standard overlaid with the carryover test analysed immediately afterwards.

5. Method detection limits

Method detection limits (MDLs) are typically defined as 'the minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results'.¹

MDLs are calculated based on data from seven replicate samples with a concentration at or near the detection limit. In this study, MDLs were determined from seven replicate measurements of 400 mL of the 0.5 ppb, 100% RH standard, with the resulting concentrations for each measurement being multiplied by 3.14 (the Student's *t*-value for 99% confidence for seven values) to determine MDL values in ppb. Data for the 13 duplicate compounds was generated using a single PAMS standard. Results are listed in Table 1.

6. BFB tune

According to the quality requirements of both HJ 759 and EA-VOC-MP, the GC-MS instrument must be tuned in such a way that 1-bromo-4-fluorobenzene (BFB) meets specific criteria for ion abundance, and this compliance should be checked before starting a sequence of samples. Table 2 lists these criteria and demonstrates that the system used in this study passes the stated criteria for all ions.





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		<i>t</i> = 0 hours		t = 24	hours	<i>t</i> = 40 hours		
lon (m/z)	Criteria	Result (%)	Pass/Fail	Result (%)	Pass/Fail	Result (%)	Pass/Fail	
50	8-40% of m/z 95	18.2	Pass	16.1	Pass	19.6	Pass	
75	30-60% of m/z 95	45.0	Pass	46.2	Pass	42.5	Pass	
95	Base peak, 100%	100	Pass	100	Pass	100	Pass	
96	5-9% of m/z 95	7.1	Pass	8.3	Pass	8.4	Pass	
173	<2% of m/z 174	1.1	Pass	1.4	Pass	0.4	Pass	
174	50-120% of m/z 95	81.5	Pass	81.1	Pass	78.5	Pass	
175	4-9% of m/z 174	7.6	Pass	7.2	Pass	8.1	Pass	
176	93-101% of m/z 174	97.7	Pass	97.3	Pass	99.6	Pass	
177	5-9% of m/z 176	6.7	Pass	7.1	Pass	8.6	Pass	

Table 2: Results obtained against the BFB tube criteria immediately after tuning, after 24 hours, and after 40 hours.

On the other hand, US EPA 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 2 shows the performance of this system against the BFB tune criteria at 0, 24 and 40 hours of continuous analysis, demonstrating full compliance in system performance for TO-15 with no user intervention.

Conclusions

In summary, we have shown that the UNITY-CIA Advantage-xr pre-concentration system with water removal by Kori-xr allows simultaneous, cryogen-free analysis of the 108 ozone precursor and air toxics compounds listed in the Chinese Environmental Air Volatile Organic Compound Monitoring Program (EA-VOC-MP). The dual-column/Deans switch GC-MS/FID strategy employed here provides confident identification and quantitation, with maximum sensitivity achieved in this challenging application by using the optimum detector for the various compound types.

Markes' ground-breaking cryogen-free Dry Focus3 watermanagement technology has been demonstrated to produce data that satisfies the performance criteria for HJ 759 and EA-VOC-MP, for very volatile C₂ hydrocarbons, 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 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 on Markes' instruments (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, maximising laboratory productivity.

Two additional features of all Markes' TD systems, including the UNITY–Kori–CIA *Advantage-xr* system used in this study, are the ability to (a) run sorbent-tube TD analysis in accordance with US 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.

Finally, whilst all the performance criteria for the methods in question are met in this study, to further extend the system sensitivity the mass spectrometer could be operated in selected ion monitoring (SIM) mode to improve sensitivity and reduce MDL values by up to an order of magnitude.

References and notes

- Compendium Method TO-15: Determination of volatile organic compounds (VOCs) in air collected in speciallyprepared canisters and analyzed by gas chromatography/ mass spectrometry (GC/MS), Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air (second edition), US EPA, 1999, www.epa.gov/ homeland-security-research/epa-air-method-toxicorganics-15-15-determination-volatile-organic.
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