

Application Note 149

Innovative cryogen-free monitoring of volatile toxic compounds in ambient air in compliance with Chinese EPA Method HJ 759

Summary

This application note describes the sampling and analysis of toxic volatile organic compounds in ambient air. Compounds were analysed from humidified canisters using a cryogen-free thermal desorption system and GC-MS. Detection of 70 target compounds ranging in volatility from propene to naphthalene and including thermally labile compounds such as methyl mercaptan is demonstrated with excellent peak shape and superb analytical performance well within the criteria set out in Chinese EPA Method HJ 759.¹

The use of Markes' ground-breaking Dry-Focus3™ preconcentration and water management technology results in excellent chromatographic peak shape at 100% humidity, full transfer of reactive sulfur compounds and an average method detection limit of 0.104 µg/m³.



Introduction

Monitoring toxic compounds in air is practiced worldwide to safeguard human health, the environment and the global climate. Volatile organic compounds (VOCs) included in the category air toxics, also referred to as hazardous air pollutants (HAPs), are regulated because they cause serious health effects, such as cancer and birth defects, when inhaled or ingested.² Concern over their levels in air means they are monitored in a range of different environments including ambient (primarily urban) air, industrial emissions and landfill gas.

In this application note, analysis of these VOCs is carried out in accordance with the National Environmental Protection Standard of the People's Republic of China – Method HJ 759. HJ 759 specifies the method by which VOCs can be analysed in ambient air with canister sampling, preconcentration by thermal desorption (TD) and analysis using gas chromatography-mass spectrometry (GC-MS).

The range of analytes specified in environmental monitoring applications is ever-expanding and, in addition to the air toxics compounds typically monitored, this application includes three sulfur species – methyl mercaptan, dimethyl sulfide and dimethyl disulfide. Monitoring them is important because they play a role in atmospheric chemistry and are responsible for malodours that lead to complaints from residents.

Some sulfur species, particularly mercaptans, are very reactive and are sensitive to high temperatures (thermally labile), which creates a unique challenge when carrying out HJ 759. A completely inert flow path is required where temperatures must not exceed 120°C and inert-coated canisters (e.g. Restek's SilcoCan) must be used to take samples from ambient air.

In this application note, we demonstrate the quantitative analysis of the 70-compound target list without the use of liquid nitrogen using an inert analytical system comprising a canister autosampler, water removal device and thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) instruments. These instruments enable the monitoring of air toxics and sulfur compounds from air at 100% relative humidity (RH) in accordance with Chinese EPA Method HJ 759 to the required detection limits of 0.2-2 µg/m³.

Analytical equipment

The analytical preconcentration system used for this study was the CIA Advantage-xr™ canister autosampler with a Kori-xr™ water removal device and UNITY-xr™ thermal desorber. UNITY-xr provides the interface from the preconcentration system to the GC-MS (Figures 1 and 2).

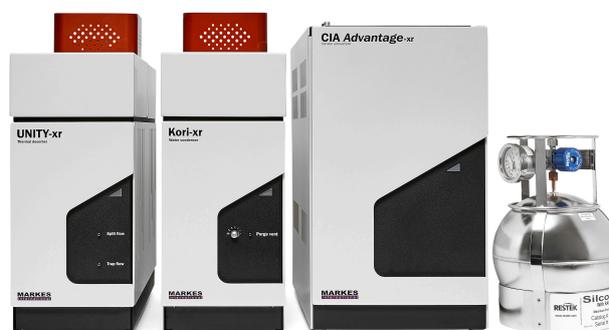


Figure 1: The CIA Advantage-Kori-UNITY-xr.

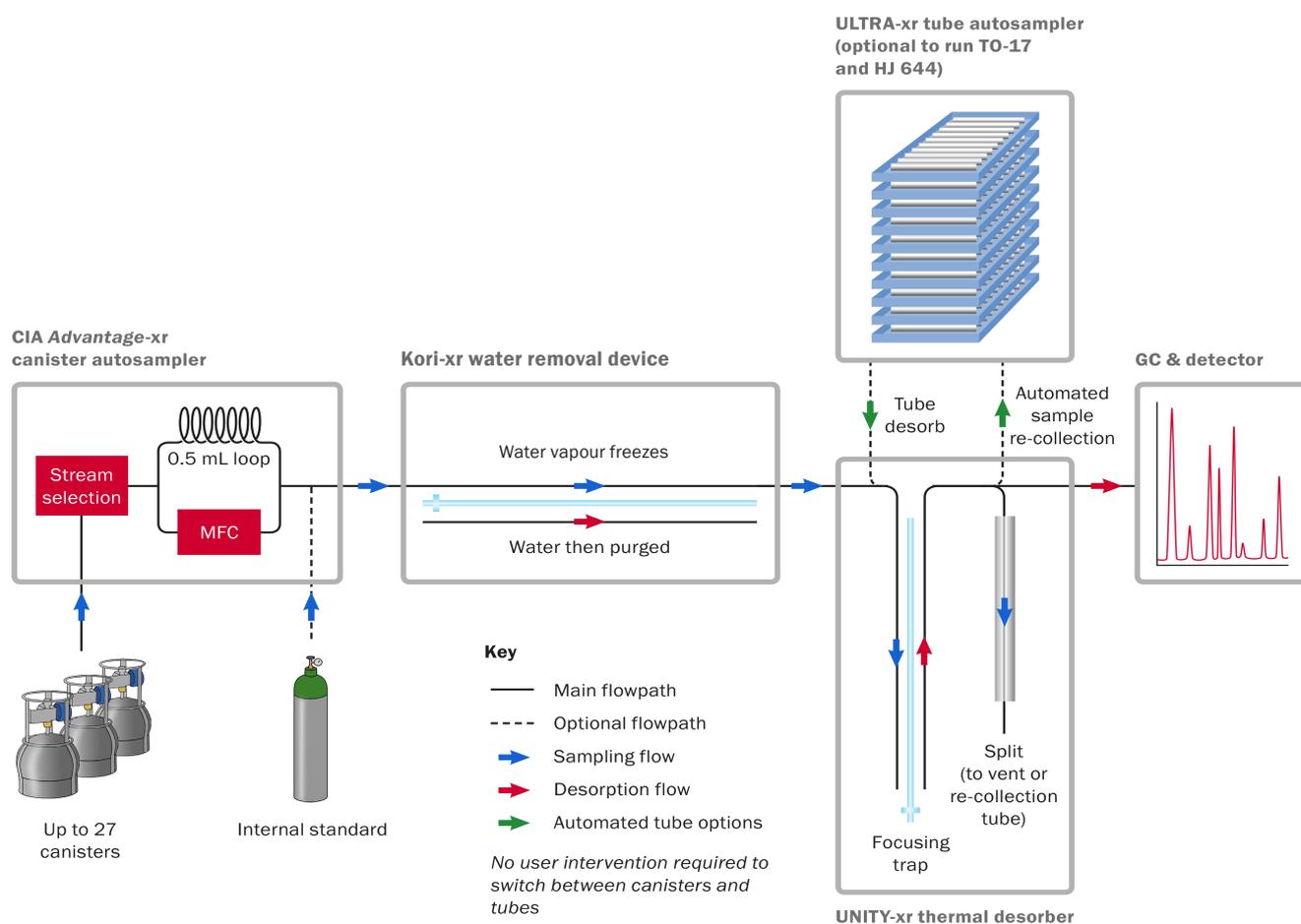


Figure 2: Schematic representation of the TD-GC-MS instrumentation used in this study.

CIA Advantage-xr is an autosampler for the analysis of VOCs in canisters or bags. Samples can be taken using either a 0.5 mL sample loop or a mass flow controller (MFC). These sampling options allow the analysis of both high- and low-concentration samples in a single automated sequence, avoiding the need to dilute the samples and the associated risk of contamination and increased analytical uncertainty. The sample stream then passes through Kori-xr, where humidity is selectively removed, before reaching the focusing trap in the UNITY-xr for analyte preconcentration. This configuration overcomes the limitations of traditional cryogen-cooled technology for canister air analysis, such as high cost and flow path blocking caused by ice formation.

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 – a unique three-stage focusing and water management mechanism – and a focusing trap optimised for the cryogen-free analysis of VOCs, VVOCs and sulfur-containing compounds in humid air (Figure 3).

During injection to the GC column, the analyst has the option to split the sample or inject everything in a splitless analysis. A split sample can be sent to vent or sent to a clean sorbent

tube to store and re-analyse at a later date. Re-collecting and storing samples in tubes avoids the need to store the samples in bulky canisters, which saves space in the laboratory and prevents any ongoing reactions within the sample. Sample splitting and re-collection can be fully automated by adding an ULTRA-xr™ tube autosampler. Addition of an ULTRA-xr also allows methods such as HJ 644³ to be carried out on the same system. The ULTRA-xr and CIA Advantage-xr can be sequenced together to run tube and canister samples with no need for user intervention. This flexible system set-up maximises the GC instrument capacity and accelerates return on investment.

Experimental

Standards

Two standard gas cylinders containing 65 TO-15 compounds (Restek 34436) and 4 sulfur compounds (Restek 34561) both at 1 ppm in nitrogen, and a separate canister made to 13 ppm with dimethyl disulfide were used to prepare the analytical standards. Unless stated, a combined standard at 10 ppb in nitrogen and 100% relative humidity (RH) was used.

1 Air sampling and water removal

Canister or whole-air samples pass through the drying trap (where vapour-phase water is selectively deposited as ice), before being concentrated on the focusing trap.

2 Purging of residual water

Optional temperature-programmed dry-purging of the focusing trap with carrier gas (between -30°C and 50°C) selectively eliminates any residual water while retaining 100% of target analytes.

3 Trap desorption

The focusing trap is rapidly heated in a reverse flow of carrier gas, to transfer analytes to the GC. Simultaneously, the drying trap is heated in a flow of gas to expel the trapped ice and regenerate it for the next sample.



Figure 3: Operation of Dry-Focus3.⁴

Note that recovery of reactive sulfur compounds from canisters can be impaired at very low concentrations (sub ppb). In this study, detection limits were verified for such compounds using Tedlar® bags for sub-ppb standards.⁵

The internal standard gas comprised bromochloromethane, 1,4-difluorobenzene, chlorobenzene- d_5 and 1-bromo-4-fluorobenzene in nitrogen (Restek 34408) and was added directly to the focusing trap during each sample analysis.

Canister sampling

Instrument: CIA Advantage-xr (Markes International)
 Sample purge: 4 min at 50 mL/min
 Sample flow: 50 mL/min
 Sample volume: 20–600 mL
 Post-sample purge: 4 min at 50 mL/min

Water removal

Instrument: Kori-xr (Markes International)
 Trap temperatures: $-30^{\circ}\text{C}/300^{\circ}\text{C}$

TD

Instrument: UNITY-xr (Markes International)
 Flow path: 120°C
 Sample flow: 50 mL/min
 Trap purge: 1.0 min at 50 mL/min
 Focusing trap: 'HJ 759' (U-HJ759-KXR)
 Focusing trap low: -20°C
 Focusing trap high: 300°C (2 min)
 Outlet split: 5 mL/min
 Trap heat rate: MAX

GC

Column: J&W DB-624™, 60 m × 0.25 mm × 1.40 μm
 Carrier gas: Helium, constant flow
 Column flow: 2 mL/min

Oven: 35°C (5 min), $6^{\circ}\text{C}/\text{min}$ to 80°C , $10^{\circ}\text{C}/\text{min}$ to 160°C , $25^{\circ}\text{C}/\text{min}$ to 230°C (5 min)

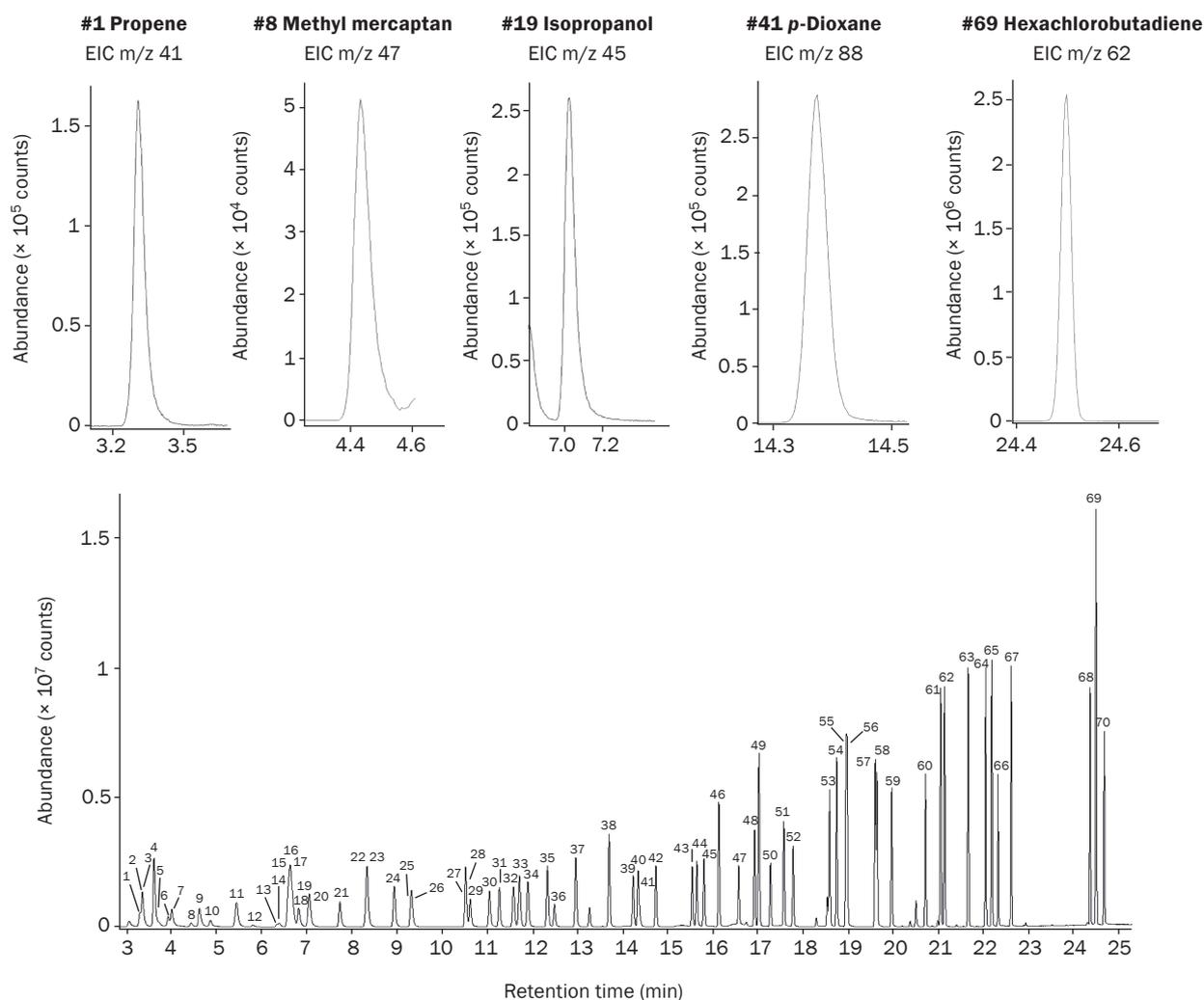
MS

Source: 250°C
 Transfer line: 200°C
 Quadrupole: 200°C
 Scan range: m/z 35–350
 SIM windows: 4.2–4.6 min: m/z 47,
 5.6–6.1 min: m/z 45,
 6.1–6.5 min: m/z 62.

Results and discussion**1. Chromatography**

Figure 4 shows a typical total ion chromatogram (TIC) for the 10 ppbv HJ 759 standard at 100% RH. Inset images show the excellent peak shape of the early-eluting compound propene, thermally labile and reactive compound methyl mercaptan, as well as highly polar compounds such as isopropanol and *p*-dioxane, and the late-eluting higher boiling compound hexachlorobutadiene.

These sharp, well-focused peaks demonstrate how the power of Dry Focus3 water removal and the desorption efficiency of the UNITY-xr combine and result in the generation of high-quality data across a wide range of polarity and functionality. Another noteworthy aspect is the highly recognisable TO-15 profile in which the response for the latest eluting, or higher boiling, compounds is significantly higher at a given ppb value than the earlier eluting compounds. This is a key visual indicator that the system is working well for the full analyte range and confirms recovery of the heaviest compounds through the full analytical system.



1 Propene	19 Isopropanol	37 Heptane	55 <i>p</i> -Xylene
2 Carbonyl sulfide	20 Carbon disulfide	38 Trichloroethene	56 <i>m</i> -Xylene
3 Dichlorodifluoromethane	21 Dichloromethane	39 1,2-Dichloropropane	57 <i>o</i> -Xylene
4 Dichlorofluoromethane	22 <i>tert</i> -Butyl methyl ether	40 Methyl methacrylate	58 Styrene
5 Chloromethane	23 1,2-Dichloroethene	41 <i>p</i> -Dioxane	59 Tribromomethane
6 Vinyl chloride	24 Hexane	42 Bromodichloromethane	60 1,1,2,2-Tetrachloroethane
7 Butadiene	25 1,1-Dichloroethane	43 <i>cis</i> -1,3-Dichloropropene	61 4-Ethyltoluene
8 Methyl mercaptan	26 Vinyl acetate	44 Dimethyl disulfide	62 1,3,5-Trimethylbenzene
9 Bromomethane	27 Methyl ethyl ketone	45 4-Methylpentan-2-one	63 1,2,4-Trimethylbenzene
10 Chloroethane	28 <i>trans</i> -1,2-Dichloroethene	46 Toluene	64 1,3-Dichlorobenzene
11 Trichlorofluoromethane	29 Ethyl acetate	47 <i>trans</i> -1,3-Dichloropropene	65 1,4-Dichlorobenzene
12 Ethanol	30 Tetrahydrofuran	48 1,1,2-Trichloroethane	66 Benzyl chloride
13 Ethyl mercaptan	31 Chloroform	49 Tetrachloroethene	67 1,2-Dichlorobenzene
14 Acrolein	32 1,1,1-Trichloroethane	50 Methyl <i>n</i> -butyl ketone	68 1,2,4-Trichlorobenzene
15 1,1-Dichloroethane	33 Cyclohexane	51 Chlorodibromomethane	69 Hexachlorobutadiene
16 1,1,2-Trichlorofluoroethane	34 Tetrachloromethane	52 1,2-Dibromoethane	70 Naphthalene
17 Acetone	35 Benzene	53 Chlorobenzene	
18 Dimethyl sulfide	36 1,2-Dichloroethane	54 Ethylbenzene	

Figure 4: Total ion chromatogram (TIC) of 400 mL of a 10 ppb 100% RH HJ 759 standard. The insets show excellent peak shape for the extracted ion chromatograms (EICs) of five compounds spanning the wide range of volatility, functionality and polarity required by Chinese EPA method HJ 759.

2. Linearity

System linearity was assessed by sampling the 10 ppbv 100% RH standard at volumes of 20, 50, 100, 200, 300, 400 and 600 mL, equivalent to 400 mL of a sample containing 0.5, 1.25, 2.5, 5, 7.5, 10 and 15 ppb, respectively.

Excellent linearity was achieved with all compounds with R^2 values >0.99 with an average of 0.9987 across all compounds (Table A1).

The relative response factors (RRFs) and their relative standard deviations (RSDs) were calculated in accordance with HJ 759. The mean RSD over the seven-point calibration was 6.8% and all compounds are within the 30% tolerance specified in the method. This demonstrates quantitative retention and desorption of the full compound list, including the highly reactive sulfur compounds.

Figure 5 shows linearity plots for a selection of compounds covering the volatility, polarity and reactivity range of the target list. The linear response up to 600 mL sample volumes for even the most volatile compounds ensures quantitative retention without analyte breakthrough for sample volumes larger than required by HJ 759.

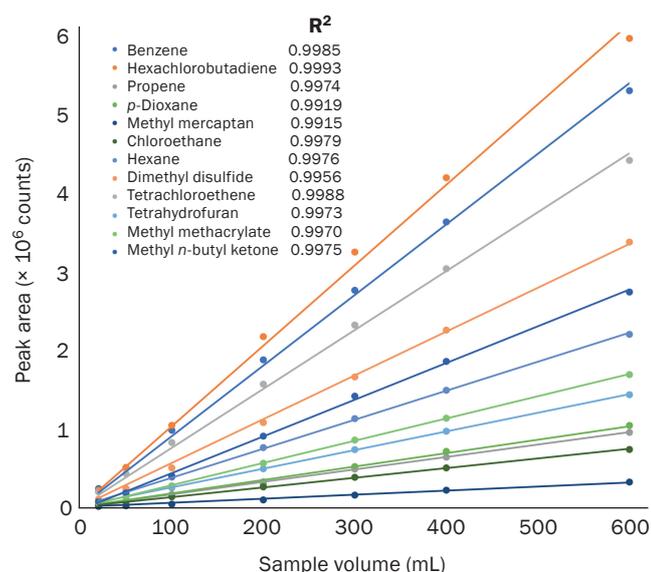


Figure 5: Linearity plots for selected compounds from the 10 ppb 100% RH standard over the range 20–600 mL, equivalent to 0.5–15 ppb at 400 mL sample volumes.

3. Carryover

In HJ 759, a laboratory blank and field blank are required and any resulting peaks for target compounds must be lower than the detection limits specified. It is important that instrumentation used in the analysis of trace-level samples exhibits negligible memory effects, or carryover, from previous samples – even if they are at a higher concentration than a typical sample. To assess carryover, 400 mL of a high concentration standard (15 ppb) was analysed followed immediately by a 400 mL nitrogen blank. Less than 1% carryover for all compounds, including high boiling compounds such as hexachlorobutadiene and naphthalene, is shown with

an average of 0.2%. These low levels of carryover confirm quantitative recovery of all target compounds through the system and mean that the analyst does not need to build additional blanks into their sequences – maximising laboratory productivity.

Figure 6 illustrates the TIC comparison of the standard and subsequent blank. The inset images compare the extracted ion chromatograms (EICs) of *p*-dioxane, 1,2,4-trichlorobenzene, hexachlorobutadiene and naphthalene. *p*-Dioxane has previously been seen as an issue for canister methods⁶ and the three least volatile target compounds will be the most likely to carryover.

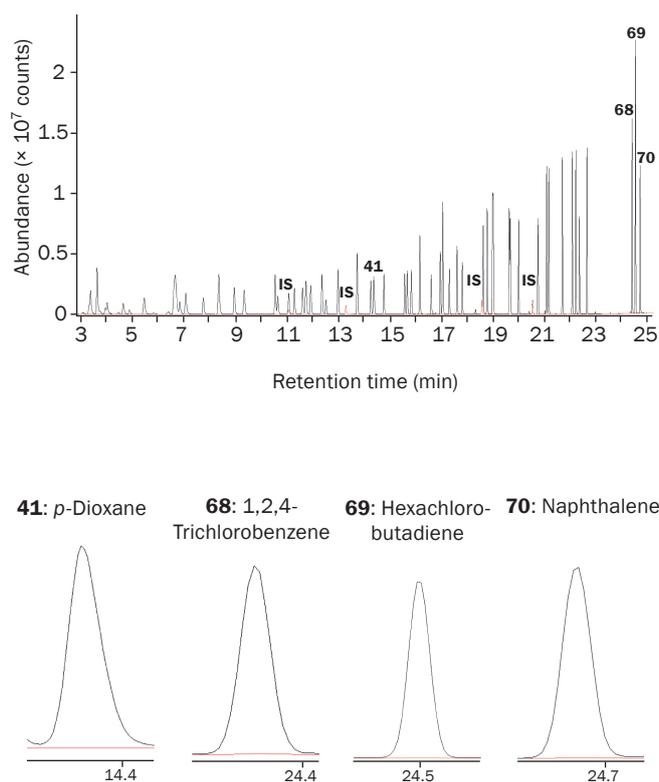


Figure 6: Analysis of 600 mL of a 10 ppbv 100% RH standard (black) overlaid with a 400 mL nitrogen blank (red) analysed immediately afterwards to assess carryover. The four red peaks are internal standard compounds (IS). Below are images of EICs that show the minimal carryover (red) observed for specific target analytes (black).

4. Reproducibility

Reproducibility of the analytical system was assessed, in terms of stability of response and retention time, by analysing seven replicates of a 10 ppb standard at 100% RH.

The results are listed in Table A1 and show an average relative standard deviation of just 0.15% across all 70 compounds without requiring internal standard correction. This high level of reproducibility highlights the reliability of the full analytical system for routine analysis of very volatile and reactive compounds in highly humid samples, a critical consideration for high-throughput HJ 759 analysis.

The average retention time RSD was calculated to be 0.017% with a maximum value of 0.09%. Retention time stability is key for minimising data review across large data sets and the values shown here enable robust automated quantitation.

5. Method detection limits

The method detection limit (MDL)⁷ is defined as 'the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte'. In this study, the MDLs were calculated by performing seven replicate analyses with a low concentration standard at/near the detection limit. A 400 mL volume of the 0.5 ppbv 100% RH standard was used and the results were multiplied by 3.14 (the Student's t-value for 99% confidence for seven values) to determine the MDL values.

The average MDL was calculated to be 0.104 µg/m³ or 0.028 ppt with a maximum of 0.235 µg/m³ for *p*-dioxane. The average is much lower than the detection limits of 0.2–2 µg/m³ specified in HJ 759 and the MDL for *p*-dioxane of 0.5 µg/m³. The low method detection limits shown here highlight the versatility of the CIA *Advantage*-Kori-UNITY-xr, which allows analysts to go beyond the requirements of standard methods and identify trace-level emerging contaminants and develop the standard methods for the future.

6. Instrument performance inspection

BFB tune

The quality requirements for HJ 759 require the GC-MS instrument to be tuned so that 4-bromofluorobenzene (BFB) meets specific criteria for ion abundance. Compliance must be checked before starting a sequence of samples. If the system does not pass the BFB acceptance criteria, corrective action and a full system re-calibration must be performed, costing significant instrument time.

Ion (m/z)	Criteria	Result				Pass?
		Day 1	Day 2	Day 4	Day 7	
50	8–40% of 95	8.85	9.19	9.43	9.65	✓
75	30–66% of 95	31.97	32.16	32.59	33.77	✓
95	Base peak 100%	100	100	100	100	✓
96	5–9% of 95	7.27	6.73	7.54	7.86	✓
173	<2% of 174	0.807	0.84	1.10	1.19	✓
174	50–120% of 95	103.26	100.88	102.13	93.90	✓
175	4–9% of 174	7.363	7.57	6.61	7.13	✓
176	93–101% of 174	98.20	96.00	93.28	96.92	✓
177	5–9% of 176	6.44	6.29	6.08	7.41	✓

Table 1: Results obtained against the BFB tune criteria, specified by HJ 759, over a seven-day period of continuous running.

Table 1 shows the performance of this system against the BFB criteria across seven days of continuous operation, demonstrating full compliance with no user intervention, which means the instrument can be utilised at maximum capacity for samples.

Internal standards

Use of a gas-phase internal standard (IS) is also required by HJ 759, which recommends between one and three internal standard compounds combined with BFB. The internal standard should be automatically added to the focusing trap with each analysis to verify the system performance for each sample, standard and blank.

The method recommends that 50 mL of a dilute internal standard is added to the focusing trap during each analytical cycle. The excellent reproducibility achieved by the CIA *Advantage*-Kori-UNITY-xr using 50 mL of 100 ppb internal standard is shown in Table 2.

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 (1–10 ppm) to be used. The high-concentration standard is connected directly to the instrument, removing the need for dilution and the associated risks of contamination and errors.

	Bromochloromethane RSD (%)	1,4-Difluorobenzene RSD (%)	Chlorobenzene-d ₅ RSD (%)
IS stability	2.39	2.12	2.57

Table 2: Stability of MFC (n = 50) addition of the three internal standard compounds from a sequence lasting over 24 hours.

7. Real air sample

Real air samples (400 mL) from a light industrial location were analysed over a 24-hour period to demonstrate its performance in real-world situations (Figure 7).

The average conditions on the date of sampling were 80% RH, 6.75°C and a wind speed of 29 km/h. Six compounds were seen at quantifiable levels: propene, carbonyl sulfide, chloromethane, ethanol, acetone and hexane.

The level of chloromethane in the air remained consistent throughout the day. In ambient air, chloromethane is generated almost entirely from natural sources so this stability is to be expected.⁸ Peaks of ethanol⁹ and hexane occurred during the same periods of the day; both species are primary vehicle exhaust emissions and the peaks suggest high levels of traffic. The location of the measurement site – within a valley, next to a hospital and a major road – may explain the high emission levels during the night.

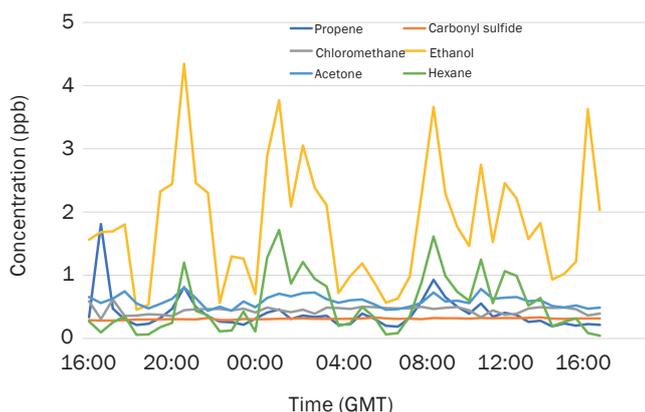


Figure 7: Time plot showing the concentrations of six compounds detected in air from a light industrial location over 24 hours of continuous on-line sampling.

Conclusions

In summary, the CIA *Advantage*-Kori-UNITY-xr preconcentration system utilising Dry-Focus3 water management technology has demonstrated compliance with Chinese EPA Method HJ 759 for the analysis of air toxics and sulfur compounds.

The addition of reactive sulfur compounds beyond the target list of US EPA TO-15 has highlighted the inertness of the flow path of the full TD instrument. This, in combination with quantitative recovery of even the heaviest TO-15 compounds at the low flow path temperatures required for labile sulfur species, demonstrates the versatility of the CIA *Advantage*-Kori-UNITY-xr to meet the requirements of the most challenging global air monitoring methods.

In addition to analysing the full suite of compounds from canisters, the ability of the CIA *Advantage*-xr to sample from unpressurised sources means that the same instruments can be deployed for remote, unattended, continuous on-line monitoring of the same compounds with no modifications. Two additional features of all Markes' TD systems, including the CIA *Advantage*-UNITY-xr system used in this study, are the ability to (a) run sorbent-tube TD analysis in accordance with Chinese EPA Method HJ 644⁵ and (b) to 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.

The results of the study demonstrate the system's capability to not only meet the criteria for the method, but go beyond what is currently required, enabling analysts to be confident that they will be prepared for lower MDLs and tighter instrument performance criteria in the future.

References

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9. R. Dunmore, L. Whalley, T. Sherwen *et al*, *Faraday Discuss.*, 2016, 189, 105.

Trademarks

CIA *Advantage*-xr™, Dry-Focus3™ Kori-xr™, ULTRA-xr™ and UNITY-xr™ are trademarks of Markes International.

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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.

Appendix

No.	Compound	Mode	Quantifier m/z	t _R (min)	t _R RSD (% n = 10)	Response RSD (%) (n = 7)	R ² (0.5–15 ppb)	RSD RRF (%)	MDL (ppt)	MDL (µg/m ³)
1	Propene (propylene)	EIC	41	3.303	0.05%	0.83%	0.9999	2.2%	34.08	0.059
2	Carbonyl sulfide	EIC	60	3.359	0.06%	0.56%	0.9972	7.6%	53.55	0.132
3	Dichlorodifluoromethane	EIC	85	3.363	0.00%	0.75%	0.9996	2.2%	7.70	0.038
4	Dichlorofluoromethane	EIC	85	3.617	0.04%	0.57%	0.9989	2.5%	22.86	0.096
5	Chloromethane	EIC	50	3.73	0.09%	1.67%	0.9966	6.5%	60.23	0.124
6	Vinyl chloride (chloroethylene)	EIC	62	3.934	0.06%	0.73%	0.9999	4.8%	51.13	0.131
7	Butadiene	EIC	54	4.01	0.05%	0.79%	0.9999	5.7%	15.70	0.035
8	Methyl mercaptan (methanethiol)	SIM	47	4.441	0.00%	1.09%	0.9973	26.3%	24.21	0.048
9	Bromomethane	EIC	94	4.626	0.04%	0.95%	0.9996	5.2%	11.55	0.045
10	Chloroethane	EIC	64	4.864	0.07%	1.92%	0.9998	6.8%	89.02	0.235
11	Trichlorofluoromethane	EIC	101	5.447	0.05%	0.56%	0.9996	6.7%	19.11	0.107
12	Ethanol	SIM	45	5.811	0.01%	4.29%	0.9964	14.9%	79.24	0.149
13	Ethyl mercaptan	SIM	62	6.343	0.00%	1.81%	0.9949	28.0%	26.35	0.067
14	Acrolein	EIC	56	6.394	0.05%	3.21%	0.9998	5.4%	40.43	0.093
15	1,1-Dichloroethene	EIC	61	6.588	0.02%	1.05%	0.9996	6.7%	57.08	0.226
16	1,1,2-Trichlorofluoroethane	EIC	101	6.637	0.04%	0.78%	0.9994	8.3%	15.79	0.121
17	Acetone	EIC	43	6.701	0.04%	1.04%	0.9991	5.5%	40.75	0.097
18	Dimethyl sulfide	EIC	62	6.826	0.03%	0.59%	0.9998	7.0%	69.61	0.177
19	Isopropanol	EIC	45	7.034	0.03%	4.76%	0.9954	16.5%	127.79	0.314
20	Carbon disulfide	EIC	76	7.064	0.03%	0.92%	0.9997	9.3%	15.32	0.048
21	Dichloromethane	EIC	49	7.741	0.02%	0.87%	0.9997	11.1%	16.42	0.057
22	tert-Butyl methyl ether	EIC	73	8.33	0.02%	0.93%	0.9998	3.1%	23.11	0.083
23	1,2-Dichloroethene	EIC	96	8.346	0.02%	0.85%	0.9998	8.9%	48.15	0.191
24	Hexane	EIC	57	8.939	0.02%	0.45%	0.9999	5.3%	19.58	0.069
25	1,1-Dichloroethane	EIC	63	9.313	0.00%	0.90%	0.9995	9.8%	21.36	0.086
26	Vinyl acetate	EIC	43	9.34	0.01%	0.68%	0.9999	1.6%	25.43	0.090
27	Methyl ethyl ketone	EIC	43	10.523	0.00%	0.87%	0.9997	1.7%	49.90	0.147
28	trans-1,2-Dichloroethene	EIC	96	10.527	0.01%	0.79%	0.9998	8.2%	43.34	0.172
29	Ethyl acetate	EIC	43	10.629	0.00%	0.80%	0.9990	3.0%	43.87	0.158
30	Tetrahydrofuran	EIC	42	11.056	0.02%	1.09%	0.9999	6.5%	65.02	0.192
31	Chloroform	EIC	83	11.272	0.01%	0.54%	0.9996	10.3%	17.14	0.084
32	1,1,1-Trichloroethane	EIC	97	11.589	0.01%	0.65%	0.9997	7.6%	8.99	0.049
33	Cyclohexane	EIC	56	11.718	0.02%	0.79%	0.9998	6.1%	21.95	0.076
34	Tetrachloromethane	EIC	117	11.907	0.02%	0.83%	0.9995	6.6%	17.65	0.111
35	Benzene	EIC	78	12.342	0.01%	0.66%	0.9996	8.8%	13.64	0.044
36	1,2-Dichloroethane	EIC	62	12.497	0.02%	0.97%	0.9994	11.3%	57.07	0.231
37	Heptane	EIC	43	12.969	0.02%	0.63%	0.9994	5.4%	19.81	0.081
38	Trichloroethene	EIC	130	13.706	0.01%	0.75%	0.9995	8.4%	10.52	0.057
39	1,2-Dichloropropane	EIC	63	14.239	0.01%	0.68%	0.9995	7.7%	26.00	0.120
40	Methyl methacrylate	EIC	69	14.349	0.01%	1.42%	0.9999	3.7%	21.26	0.087
41	p-Dioxane	EIC	88	14.372	0.00%	4.56%	0.9965	13.6%	65.27	0.235
42	Bromodichloromethane	EIC	83	14.746	0.01%	0.56%	0.9997	6.6%	31.51	0.211
43	cis-1,3-Dichloropropene	EIC	75	15.547	0.01%	0.47%	1.0000	1.7%	17.94	0.081
44	Dimethyl disulfide	EIC	94	15.652	0.01%	0.83%	0.9997	7.3%	18.00	0.069
45	4-Methylpentan-2-one	EIC	43	15.808	0.00%	0.80%	0.9981	2.7%	24.16	0.099
46	Toluene	EIC	91	16.137	0.00%	0.65%	0.9989	5.9%	19.86	0.075
47	trans-1,3-Dichloropropene	EIC	75	16.579	0.00%	0.85%	0.9999	1.7%	18.05	0.082
48	1,1,2-Trichloroethane	EIC	97	16.927	0.01%	0.94%	0.9991	4.1%	13.02	0.071
49	Tetrachloroethene	EIC	166	17.026	0.00%	0.89%	0.9994	8.1%	13.89	0.094
50	Methyl n-butyl ketone	EIC	43	17.279	0.01%	2.15%	0.9991	12.1%	11.91	0.049
51	Chlorodibromomethane	EIC	129	17.578	0.00%	0.95%	0.9990	3.8%	27.22	0.232

Table A1: Data obtained from the HJ 759 standard at 100% RH. (Continued on next page.)

No.	Compound	Mode	Quantifier m/z	t _R (min)	t _R RSD (%) (n = 10)	Response RSD (%) (n = 7)	R ² (0.5–15 ppb)	RSD RRF (%)	MDL (ppt)	MDL (µg/m ³)
52	1,2-Dibromoethane	EIC	107	17.784	0.01%	0.70%	0.9992	4.0%	19.22	0.148
53	Chlorobenzene	EIC	112	18.595	0.01%	0.56%	0.9987	5.4%	13.36	0.062
54	Ethylbenzene	EIC	91	18.75	0.00%	0.66%	0.9983	3.1%	15.54	0.067
55	<i>p</i> -Xylene	EIC	91	18.976	0.04%	0.54%	0.9967	4.5%	14.88	0.065
56	<i>m</i> -Xylene	EIC	91	18.976	0.04%	0.54%	0.9967	4.5%	14.88	0.065
57	<i>o</i> -Xylene	EIC	91	19.604	0.00%	0.63%	0.9985	2.6%	21.08	0.092
58	Styrene	EIC	104	19.645	0.01%	0.64%	0.9976	3.4%	10.18	0.043
59	Tribromomethane	EIC	173	19.967	0.00%	1.27%	0.9998	1.3%	18.70	0.193
60	1,1,2,2-Tetrachloroethane	EIC	174	20.719	0.01%	0.58%	0.9983	5.0%	8.84	0.061
61	4-Ethyltoluene	EIC	105	21.056	0.01%	0.68%	0.9963	3.5%	11.11	0.055
62	1,3,5-Trimethylbenzene	EIC	105	21.139	0.00%	0.60%	0.9952	5.2%	7.68	0.038
63	1,2,4-Trimethylbenzene	EIC	105	21.664	0.00%	0.81%	0.9958	3.8%	6.55	0.032
64	1,3-Dichlorobenzene	EIC	146	22.05	0.00%	0.72%	0.9974	5.7%	11.63	0.070
65	1,4-Dichlorobenzene	EIC	146	22.186	0.00%	0.66%	0.9974	5.6%	8.81	0.053
66	Benzyl chloride	EIC	91	22.326	0.00%	0.84%	0.9994	5.9%	15.65	0.081
67	1,2-Dichlorobenzene	EIC	146	22.617	0.00%	0.56%	0.9972	6.2%	16.11	0.097
68	1,2,4-Trichlorobenzene	EIC	180	24.367	0.00%	1.51%	0.9991	11.7%	6.33	0.047
69	Hexachlorobutadiene	EIC	225	24.5	0.01%	0.54%	0.9974	3.1%	16.77	0.179
70	Naphthalene	EIC	128	24.681	0.01%	1.64%	0.9980	12.7%	4.39	0.023
	Mean values				0.02%	1.05%	0.9987	6.82%	27.63	0.104

Table A1: Data obtained from the HJ 759 standard at 100% RH. (Continued from previous page.)