



Application Note 169

Advances in ultra-trace air toxics analysis: Cryogen-free canister pre-concentration and GC–MS for US EPA Method TO-15A

Summary

This Application Note describes the automated, highperformance gas chromatography-mass spectrometry (GC-MS) analysis of humid 'air toxics' samples in canisters, using a cryogen-free system for preconcentration and thermal desorption (TD). Detection of 75 target compounds – ranging in volatility from propene to naphthalene – is demonstrated, with excellent analytical performance, and all well within the criteria set out in US EPA Method TO-15A.

We show how the UNITY-CIA Advantage-xr Kori-xr system (Figure 1), combining canister automation, pre-concentration, thermal desorption and selective water removal with Markes' Dry-Focus3 technology, meets the requirements of US EPA Method TO-15A.

Furthermore, we demonstrate excellent analytical performance, exceptional background levels and high sensitivity with an average instrument detection limit of 1.64 pptv for all 75 compounds, while significantly improving sample throughput from 3 to 5 samples every two hours.



Figure 1: UNITY-CIA Advantage-xr with Kori-xr. A cryogen-free automated canister thermal desorption instrument with enhanced water management capabilities

Introduction

Monitoring of chemicals in ambient air is necessary to protect human health, the environment and global climate. This requirement has driven several international regulations to be developed, primarily in response to increased concern over hazardous volatile organic compounds (VOCs) in ambient (primarily urban) air, industrial emissions and landfill gas. Efforts to reduce the release and presence of these compounds in the environment over the past 60 years has resulted in lower limits of detection being required by regulators around the world. In the USA, monitoring of a specific list of hazardous air pollutants has been carried out in line with EPA Method TO-15 since it was published for monitoring 'air toxics' in 1999. In 2020, an update to this method was released to better address the low concentrations often seen within ambient air. This is US EPA method TO-15A¹.

The aim of Method TO-15A is to reach 20 pptv method detection limits – a level which challenges every aspect of the sampling and analysis process. Whilst background interferences generated by instrumentation and sampling equipment has always been a concern for trace air toxic analysis, these levels pose even more of a challenge.

Overview of US EPA Method TO-15A

The TO-15A workflow comprises the following steps:

- **1. Sampling:** After cleaning, certifying and evacuating the canister, it is brought to the sampling site. The canister valve is opened and air is drawn in, through a filter, using a flow controller for the specified time. The canister valve is then closed and sealed with caps.
- **2. Storage:** The sample is kept at ambient temperature throughout transportation and storage and is analysed within 30 days of sampling.
- **3. Sample analysis:** Under precise flow control, a specified volume of canister air is directed through the Kori-xr water management unit and into the electrically-cooled multi-sorbent concentrator (focusing trap) of the UNITY-xr thermal desorber (Figure 2). Both the Kori-xr (water management module) and the focusing trap are cooled electrically eliminating the need for liquid cryogen².

The innovative water management technology incorporated into Kori-xr eliminates most water from the sample before it reaches the focusing trap, without changing the concentration of polar organic volatiles. Any residual traces of water are selectively purged from the focusing trap during, and immediately after, the concentration process.

The focusing trap is then heated rapidly in a reverse flow of carrier gas (helium or hydrogen) to 'backflush' the concentrated VOCs and inject/transfer them onto the GC column in a narrow band, perfect for stable, high-sensitivity GC-MS analysis, uncompromised by any water interference.

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4. Compound identification and quantitation: Most analytical systems for TO-15A combine the UNITY-CIA *Advantage*-xr (canister autosampler) with a GC and quadrupole mass spectrometry, operating in full-spectral (SCAN), and/or ion-selective scanning (SIM) mode to measure and identify the relevant target compounds as described in Method TO-15A.

Analytical equipment

Canister automation system

The analytical system used for this application was Markes' canister automation system (UNITY–CIA *Advantage-xr* with Kori-xr). The individual components of the analytical system are briefly described below.

The CIA Advantage-xr is a canister autosampler system for the analysis of VOCs. Samples can be taken from up to 27 canisters (or bags), using either a 0.5 mL sample loop or a mass flow controller (MFC). Sampling via the MFC and assisted by vacuum means canisters do not need to be pressurised. This negates the requirement to dilute the sample (thus effectively increasing the compound sensitivity experienced with Markes' CIA Advantage-xr) and allows more samples to be taken from a single canister. Eliminating pressurisation of canisters also reduces error and prevents contaminant introduction. The CIA Advantage-xr additionally offers the introduction of internal standard gas into the sample stream via a 1 mL loop or MFC.

Dry-Focus3

Operation of the Kori-xr water management (dehumidification) module (shown in Figure 2) is the first step of the Dry-Focus3 process to selectively remove water from humid samples while retaining highly polar compounds. The Kori-xr dryer works on a dewpoint principle, selectively freezing out water while apolar and polar volatile organics (including oxygenates, very volatile compounds and monoterpenes) pass through to the focusing trap unretained.

Thermal desorber

With excess water now removed, sample air passes onto the focusing trap of the UNITY-xr thermal desorber. This contains a state-of-the art electrically-cooled² focusing trap, packed with separate beds of porous polymer, graphitised carbon black and carbonised molecular sieve sorbents. The specific combination of trap sorbents, has been optimised for TO-15A, allowing a wide volatility range of VOCs to be analysed in one run. Once the sample has passed through and been retained on the focusing trap, the trap is purged as step two of the Dry-Focus3 process to further remove water, while retaining all the trapped analytes. Finally, the trap is heated rapidly (up to 100°C/s) in a reverse flow of carrier gas, to release and inject the analytes onto the GC column. At the same time, the drying trap of Kori-xr is regenerated in preparation for the next sample during the GC analysis and without affecting the overall analytical cycle time.

At the point of injection to the GC–MS, the UNITY-xr is able to split the sample, either to vent or onto a clean sorbent tube for storage and repeat analysis at a later time. This quantitative re-collection facility was pioneered by Markes International and is a standard feature across Markes' range of thermal desorption instrumentation.

Experimental

Standards:

Chromatograms in Figures 3 and 4 show the analysis of 75-component 'air toxics' standards in 6 L canisters in zero air (30 psig, 50 %RH).

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.



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Canister sampling:

CIA Advantage-xr (Markes International)							
500 mL (50% RH)							
Samples from a sub ambient canister: 3 or more							
time: < 30 mins							
1							

Water removal:

Instrument: Trap temperatures:

-30°C/+300°C

Kori-xr (Markes International)

TD:

UNITY-xr (Markes International)
120°C
Loop (1 mL fixed) or MFC (5-500 mL)
50 mL/min

Post-sampling line purge: 3 min at 75 mL/min Elevated Trap purge: 3.0 min at 50 mL/min at 25°C Trap temperatures: -30°C/+280°C Trap desorption: 5 mins Cold trap: U-T015-KXR 2.5:1 Split ratio:

GC:

Column:	Rxi-624Sil MS, 60 m × 0.32 mm × 1.80 µm
Constant flow:	Helium at 2 mL/min
Oven:	35°C (3 min), 8 °C/min to 100°C
	(0 min), 30°C/min to 230°C (5 min)
GC run time:	20.5 mins

Ouadrupole MS:

A	
Source:	230°C
Transfer line:	230°C
Scan mode:	SIM/Scan
SIM:	See Table A1 for quantification ions
	used
Scan range:	35-300 m/z

Results and discussion

A listing of results is provided in Table A1 (see Appendix).

Chromatography

Figure 3 shows the analysis of 500 mL of a 50% relative humidity (RH) 5 ppbv standard prepared in zero-air.

Figure 4 shows a selected ion monitoring (SIM) chromatogram from the analysis of 10 mL of a 1.0 ppbv standard (equivalent to 500 mL at 20 pptv). The excellent peak shape achieved across the volatility range is a great advocate for Markes' TD instruments, demonstrating efficient release from the focusing trap and rapid injection to the GC column (Figure 5). This produces the sensitivity necessary for this challenging application, as shown in Table 1. The highly effective water management from the Dry-Focus3 process brings about this excellent chromatography and sensitivity.

Instrument blank

Instrument blanks (IB), run at the start of each sequence, show all target compounds to be well below 20 ppt, or not detected at all (Figure 6). This high-quality instrument blank data is essential for reliable quantitation at the ppt levels required by TO-15A.

Compound	Quant ion (m/z)	RT (min)	MDL (pptv) (SIM)
Propene	41	3.645	14.41
Vinyl Chloride	62	4.391	3.21
1,3-Butadiene	54	4.447	5.41
1,1-Dichloroethene	61	6.729	3.12
Methylene Chloride	84	7.555	4.20
trans-1,2-Dichloroethene	61	8.025	1.43
cis-1,2-Dichloroethene	61	9.616	1.58
1,1,1-Trichloroethane	97	10.44	2.60
1,2-Dichloroethane	62	11.049	2.58

Table 1: Excellent level of sensitivity obtained without the use of liquid cryogen, either for analyte trapping or for refocusing components on the front of the GC column.

Method blank

In accordance with the TO-15A guidance, a method blank (MB) should be analysed at least once in each analytical sequence, and should include the internal standards. In any sequence where an initial calibration is performed (see Initial Calibration (ICAL), Linearity and Repeatability), the MB should be run prior to and after the calibration, to demonstrate the cleanliness of the analytical system. Method blank canisters were prepared using zero-air at 50% RH and analysed using the same analytical conditions as the samples.

Prior to running the MB for the first time, the zero-air source to be used for preparation of the blank canisters was analysed at the nominal sample volume, to check its cleanliness.

Note that the following factors effect the results:

- · Cleanliness of the zero-air supply
- · Impurities in the water used for blank humidification (lab air cleanliness can impact this)
- Contamination in the dilution device (lab air cleanliness can impact this)
- · Cleanliness of the canister and its fittings, for example the valve

Trace levels of ethanol, acetone, and IPA were consistently observed in the method blank (Figures 7 and 8). After an iterative process of investigation, it was possible to attribute these to the humidification water, ultra-zero air and nitrogen cylinders, and the canisters themselves.

Note that low level interference from these particular compounds is rarely a practical issue, because they are normally present at higher levels in ambient air³, and that the analytical system itself is not contributing to background levels of any TO-15A target compounds (Figure 6).

2-Butanone, tert-butanol and acrolein, were periodically observed at trace levels in MB analyses. Detection of trace levels of acrolein and other oxygenates are highlighted in TO-15A Method Sec. "6.2 Canister Sampling Media Interferences" as known interferences.

In common with all trace-level applications, TO-15A should be carried out in a stringently clean laboratory environment.

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Figure 4: SIM analysis of 10 mL of a 75 component toxic organics standard at 1.0 ppbv (50%RH in zero air), equivalent to 500 mL volume of a 20 ppt canister standard, with internal standards and surrogate.

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Figure 5: Close-up of the SIM data obtained for four challenging toxic organics at the 20 pptv level, still showing excellent peak shape.

Initial calibration, linearity and repeatability

For the initial calibration (ICAL) two standard canisters were prepared at 1.0 and 5.0 ppbv and 50% relative humidity, with ultra-zero (UZ) air. 5 to 500 mL volumes (Table 2) of these standards were sampled by MFC, producing an 11-point calibration curve, as shown in Figure 9.

Typically, calibration is done with a minimum of 5 points. However, as the TO-15A method recommends running more points near the low end of the calibration, to more accurately define this part of the calibration curve, an 11-point calibration curve was adopted for this study. Overlapping calibration points were also analysed to validate linearity between the two calibration standard canisters and to eliminate any possible concentration bias due to sampling volumes which further bolstered the robustness of the ICAL.

The calibration range for all 75 compounds began at 10 pptv with R^2 values greater than 0.9940. RSDs were below 30% for all target analytes at 20 pptv levels and above, in compliance with the requirements of TO-15A.

Instrument detection limit

The instrument detection limit (IDL) is a robust and reliable method to assess mass spectrometry detection limits and precision by estimating the concentration that can be



Figure 6: Example of instrument blank (red) run prior to each analysis sequence compared to 20 pptv standard (black) using SIM showing no detectable levels of target compounds from the instrument background.



Figure 7: Overlaid TIC analysis of Method Blank canister at 50% RH in zero-air showing consistency over 7 injections for the three internal standards and surrogate used for TO-15A. 1) bromochloromethane, 2) 1,4-Difluorobenzene, 3) chlorobenzene-d5, 4) 4-bromofluorobenzene



Figure 8: SIM analysis of a typical example Method Blank (red) run from this sequence with the 20 pptv standard (black) displaying some trace compounds attributed to the humidification water, ultra-zero air and nitrogen cylinders, and the canisters.

Level	1	2	3	4	5	6	7	8	9	10	11
Canister conc. (ppbV)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	5.0	5.0	5.0	5.0
Sample volume (mL)	5	10	25	50	125	250	500	50	100	250	500
Level conc. (pptV) (500	10	20	50	100	250	500	1000	500	1000	2500	5000
equivalent)	10	20	50	100	250	500	1000	500	1000	2500	5000

Table 2: 11-Point calibration standards prepared.



Figure 9: Highlight of a range of compounds from propene to naphthalene with R² values greater than 0.9940, with an expanded view of the 10–500 pptv range from the 1.0 pptv standard canister. Full results are shown in Table A1.

detected above the instrument background. Typically, the IDL is much lower than the MDL as it does not involve the variability of multiple canisters and preparation steps. As described in the US EPA Method TO-15A: *"the IDL is determined by analysing seven or more aliquots of a standard from the same canister, calculating the standard deviation of the measurements, and multiplying the standard deviation by the appropriate Student's t-value".*

To determine instrument detection limits (IDLs) in this application note, the system was challenged using 13 aliquots of 25 mL volume of a 100 pptv canister standard, the equivalent of 500 mL of a 5pptv concentration standard. This experiment focused only on the contribution of the instrumentation to background contamination, discounting that from external sources such as humidification water, cylinders, and canisters.

Under these conditions, the Markes canister pre-concentrator demonstrated an exceptional average IDL of 1.64 pptv in 13 repeats for all 75 compounds, validating our findings that the high background observed for ethanol, acetone, isopropyl alcohol, 2-butanone, *tert*-butanol and acrolein is correctly attributed to ancillary components and not the analytical instruments.

Method detection limits

The method detection limit (MDL) is different to the IDL because it takes into account system background plus any contribution from the humidification process, repeat preparations, use of multiple canisters, the duration of the study over multiple days, and the use of large sample volumes. It is calculated from the standard deviation of the data population and takes into account method blank levels (see Section 17 of TO-15A¹). Despite the challenges of this part of the study, 69 of 75 compounds were shown to have MDL blank values of less than 20 pptv with 67 of those compounds under 10 pptv and 61 under 5 pptv. The 6 compounds above 20 pptv are attributed to contributions from canisters, humidification water, pressurisation gases and other

consumables, not the analytical system, as outlined in "Method blank" above.

To demonstrate the system's reproducibility at or near the reporting limit (reflecting real-world use) the UNITY-CIA *Advantage-xr* with Kori-xr system was challenged with nominal 10 pptv spiked canisters, prepared at 50% RH with Ultra Zero air over 3 non-consecutive days. Each preparation was sampled >7 times at 500 mL and 71 of 75 compounds were shown to have MDLs below 20 pptv. The average MDL for these 71 compounds was 5.18 pptv.

The MDL spike and MDL blank results were compared and the higher of the two values was selected as the MDL for a given analyte in accordance with the method.

Results are shown in Table A1.

Autosampler bias tests

As specified in the TO-15A method, each channel of the analytical system was tested for negative and positive bias. Tests were run using method blank (positive bias) and 0.5 ppbv spiked standard canisters (negative bias).

Positive bias test

The method allows for autosampler bias (ASB) blank testing to be completed directly from a compressed air cylinder, providing the air is humidified. This option was used with a filtered UZ air cylinder plumbed into a humidification bubbler, which was then connected to the CIA *Advantage-xr via* heated sampling lines. The autosampler ports were challenged with 500 mL of filtered and humidified UZ air. Consistency was demonstrated across all 14 sampling ports with all compounds found to be below 20 pptv in the ASB blank testing, with the exception of *tert*-butanol, chloromethane, ethanol, acetone, and isopropyl alcohol, which were all identified as trace contaminants in the humidification water and UZ air during these tests.



Figure 10: TIC displaying outstanding retention time stability of 36 repeats over 3 weeks with RSD 0.65%.

Negative bias test

All 14-ports of the CIA Advantage-xr were challenged for negative bias in accordance with the method. The challenge was performed with a TO-15 reference standard at a final concentration of 500 pptv. All compounds successfully passed AS negative testing by falling well within $\pm 15\%$ accuracy.

Full results with average % accuracy \pm maximum deviation per compound are shown in Table A1.

System stability

Instrument stability over time is paramount to the success of this method in a production environment. A statistical look at the internal standards analysed during the three weeks and 36 runs of the method detection limit spike (MDL) study showed consistency in recovery with bromochloromethane (4.9% RSD), 1,4-Difluorobenzene (8.4% RSD) and chlorobenzene-d5 (8.8% RSD). Retention time stability was demonstrated by an 0.65% average standard deviation across all 75 compounds (Figure 10). The key contributors here were the precise and repeatable sample volumes delivered during

Compound	Average concentration (pptv)	% RSD
Propene	198.38	0.25
FR-12	459.43	0.32
Chloromethane	409.61	1.41
Benzene	50.33	0.75
1,2-Dichloroethane	11.17	2.11
Toluene	109.04	0.78
Tetrachloroethene	4.19	0.36
Styrene	5.85	2.43
Naphthalene	8.77	3.61

 Table 3: Repeat samples from an unpressurised canister

 demonstrate excellent %RSD values across the entire range of T0-15 compounds.

each iteration of sample analysis, the excellent reproducibility demonstrated by the focusing trap, and the Kori-xr provided exceptional water management, extending the stability of the mass spec ion source across long sequences.

Ambient air samples

Once the system had been successfully qualified for US EPA Method TO-15A, it was used for the analysis of an outdoor grab-sample from a parking lot. Canisters were opened and filled to ambient pressure.

Three 500 mL aliquots of outdoor air were analysed from a 6-liter canister (Figure 11) and demonstrated excellent reproducibility (Table 3). Nearly all RSD values were below 3% with naphthalene, a notoriously challenging TO-15A compound, the highest RSD at 3.61%, and with a measured level of 8.77 pptv, still well below the required 20 pptv detection limits.

The CIA Advantage-xr autosampler is capable of sampling multiple times from an unpressurised canister allowing for samples to be run without dilution, thereby reducing sampling preparation, while improving detection limits and reducing risk of introducing contaminants due to dilution.



Figure 11: SIM analysis showing excellent reproducibility for "an outdoor parking lot sample" from unpressurised canister sampled three times at 500 mL.

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Conclusions

In summary, Markes' UNITY–CIA Advantage–Kori-xr canister pre-concentration system described delivers:

- Confident, cryogen-free, TD–GC–MS canister analysis of 'air toxics' at 50% relative humidity (RH), in accordance with US EPA Method TO-15A
- Hassle-free and low-cost operation, without liquid cryogen
- Excellent chromatographic performance for the analysis of a 75-component standard (from propene to naphthalene) at 50% RH
- Performance exceeding the requirements of Method TO-15A, even for the most volatile of components in the TO-15 mix. This is because Markes' Kori-xr module (as the first step of the Dry-Focus3 process) efficiently and selectively removes water from humid air streams, without compromising the analysis of very volatile organic compounds or polar species.
- Increased throughput using 'overlap mode' and optimised GC runtime to speed up total analysis time, enabling 5 samples to be analysed every 2 hours
- Method detection limits as low as 5 pptv (61 out of 75 components under 5 pptv MDL)
 - Markes' system was able to achieve an average IDL of 1.64 pptv for all 75 compounds
 - MDL <20 pptv achieved for 69 of 75 components in the TO-15 mix. Background contributions from canisters, humidification water, pressurisation gases and other consumables attributing to 6 of 75 components >20 pptv MDL
- All compounds successfully passed ASB negative testing by falling well within $\pm 15\%$ accuracy when challenged with the TO-15 reference standard

Two additional features of all Markes' TD systems, including the UNITY-CIA Advantage-xr system used in this study, are the ability to (a) run 3.5" x $\frac{1}{4}$ " (industry-standard) thermal desorption sample tubes, and (b) re-collect the split portions of samples onto clean sorbent tubes for easier storage (and to release the canisters for sampling).

References and notes

- US EPA MethodTO-15A https://www.epa.gov/sites/ production/files/2019-12/documents/to-15A_vocs.pdf
- Many conventional systems for canister analysis use liquid cryogen in order to trap very volatile compounds. Markes' systems instead use electrical (Peltier) cooling, allowing quantitative retention of the most volatile compounds from large sample volumes, without incurring the cost of liquid cryogen – https://markes.com/content-hub/ instant-insight/can-you-really-trap-very-volatilecompounds-without-liquid-cryogen
- 3. EPA Air Toxics 2015-2016 National Monitoring Programs Annual Report 2015-2016 National Monitoring Programs Annual Report (UATMP, NATTS, and CSATAM) (epa.gov)

Trademarks

CIA Advantage-xr[™], Kori-xr[™], ULTRA-xr[™], UNITY-xr[™] and Dry-Focus3[™] 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

Compound	RT (min)	Quant ion used (m/z)	Avg. RF RSD	MDL* (pptv)	AS Positive Bias (pptv)	AS Negative Bias (% accuracy)	
Propene	3 645	41	4 487	14 41	4 89 + 2 4	101% + 10.2%	
Dichlorodifluoromethane	3.717	85	4,708	3.03	0.14 + 0.7	100% + 3.9%	
Dichlorotetrafluoroethane	3.987	85	27.640	3.27	1.45 + 0.3	100% + 3.5%	
Chloromethane	4 145	52	5 787	27.37	42 06 + 6 7	100% + 6.4%	
Butane	4 352	58	5 235	9.64	343+24	100% + 5 3%	
Vinyl Chloride	4 391	62	12 339	3 21	0.22 ± 0.6	99% + 6.5%	
1.3-Butadiene	4.447	54	20.098	5.41	0+0	99% + 8.7%	
Bromomethane	5.098	94	21.055	16.66	0 + 0	99% + 9.9%	
Chloroethane	5.296	66	9.327	3.28	0 + 0	99% + 6.1%	
Bromoethene	5.662	106	12.447	5.58	0.48 + 0.4	99% + 5.1%	
Trichlorofluoromethane	5.789	101	9.142	2.36	1.32 ± 0.2	100% + 2 2%	
Pentane	5.963	43	8.583	3.83	0.4 ± 5.2	99% + 8.3%	
Ethanol	6.035	45	25.068	419.27**	117.33 ± 49.6**	102% ± 7%	
Acrolein	6.547	56	13.186	70.94**	7.9 ± 4.8**	100% ± 12.3%	
1,1-Dichloroethene	6.729	61	14.675	3.12	1.03 ± 0.4	100% ± 7.6%	
Trichlorotrifluoroethane	6.744	151	29.171	1.94	0.14 ± 0.1	100% ± 8.4%	
Acetone	6.752	43	12.895	208.99**	210.8 ± 257.3**	101% ± 14%	
Isopropyl Alcohol	6.949	45	11.165	667.15**	380.58 ± 149.9**	99% ± 9.8%	
Carbon Disulfide	7.138	76	24.237	18.18	0.52 ± 0.2	100% ± 4.1%	
Allyl Chloride	7.343	41	19.957	2.13	0 ± 0	99% ± 9.2%	
Methylene Chloride	7.555	84	27.973	4.20	14.19 ± 2.2	100% ± 3.6%	
tert-Butanol	7.654	59	5.978	15.11	22.93 ± 3.5	100% ± 7.9%	
Methyl tert-Butyl Ether	8.002	73	12.220	2.07	0 ± 0	99% ± 6.1%	
trans-1,2-Dichloroethene	8.025	61	9.190	1.43	0.51 ± 0.2	99% ± 6.6%	
Hexane	8.472	57	9.706	3.24	0.29 ± 0.6	99% ± 10.5%	
Vinyl Acetate	8.684	43	11.642	2.28	0 ± 0	99% ± 11.7%	
1,1-Dichloroethane	8.729	63	5.611	2.53	0.42 ± 0.1	99% ± 5.5%	
2-Butanone	9.563	72	7.596	41.62**	4.68 ± 1.7**	100% ± 2.6%	
Ethyl Acetate	9.616	43	3.165	7.90	0 ± 0	100% ± 8.4%	
cis-1,2-Dichloroethene	9.616	61	6.228	1.58	0.6 ± 0.4	99% ± 7.8%	
Tetrahydrofuran	10.033	72	10.460	19.15	2.95 ± 1.8	99% ± 9.7%	
Chloroform	10.135	83	9.129	2.32	0.88 ± 1.1	100% ± 2.6%	
1,1,1-Trichloroethane	10.440	97	9.844	2.60	0.02 ± 0.2	100% ± 2.4%	
Cyclohexane	10.584	84	6.984	6.17	0.28 ± 0.1	99% ± 8.9%	
Carbon Tetrachloride	10.694	117	20.077	3.17	0 ± 0	100% ± 4.6%	
Benzene	10.990	78	6.534	6.10	6.82 ± 1.9	99% ± 7.9%	
1,2-Dichloroethane	11.049	62	5.668	2.58	0 ± 0	100% ± 2.6%	
2,2,4-Trimethylpentane	11.160	57	8.126	1.02	0 ± 0	99% ± 8.9%	
Heptane	11.397	57	7.638	3.72	0.82 ± 1.1	99% ± 8.8%	
Trichloroethene	11.930	95	8.912	2.45	0.5 ± 0.1	100% ± 5.2%	
1,2-Dichloropropane	12.261	63	8.623	6.10	0 ± 0	100% ± 2.7%	
Methyl Methacrylate	12.261	69	25.863	9.91	0.2 ± 2.6	100% ± 6.1%	
1,4-Dioxane	12.320	88	4.553	2.63	8.44 ± 1.8	100% ± 8.1%	
Bromodichloromethane	12.557	83	4.239	8.82	0.37 ± 0.4	100% ± 6.7%	
cis-1,3-Dichloropropene	13.038	75	10.192	2.30	0 ± 0	100% ± 3.7%	
4-Methyl-2-pentanone	13.159	43	7.220	6.75	1.77 ± 0.5	100% ± 5.6%	
Toluene	13.418	91	4.237	6.77	6.96 ± 3	100% ± 2.2%	
trans-1,3-Dichloropropene	13.620	75	5.219	2.73	0.03 ± 0.3	100% ± 3.1%	
1,1,2-Trichloroethane	13.822	97	7.247	6.97	0.42 ± 0.4	100% ± 5.7%	
Tetrachloroethene	13.942	166	26.740	2.67	0.18 ± 0.3	100% ± 7.7%	
2-Hexanone	13.986	58	4.255	4.74	1.71 ± 1.1	100% ± 8.3%	
Dibromochloromethane	14.207	129	4.209	7.74	0.5 ± 0.3	100% ± 9.9%	
1,2-Dibromoethane	14.334	107	5.208	4.12	0.33 ± 0.3	100% ± 5.6%	
Chlorobenzene	14.757	112	4.900	2.92	0.92 ± 0.3	100% ± 2%	

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Compound	RT (min)	Quant ion used (m/z)	Avg. RF RSD	MDL* (pptv)	AS Positive Bias (pptv)	AS Negative Bias (% accuracy)	
Ethylbenzene	14.811	91	9.685	2.96	0.96 ± 0.5	100% ± 2.5%	
Nonane	14.902	43	7.425	5.17	0 ± 0	100% ± 2.5%	
<i>m,p</i> -Xylene	14.920	91	8.978	1.34	1.19 ± 0.7	100% ± 2.1%	
o-Xylene	15.236	91	6.847	1.27	0.63 ± 0.3	100% ± 2.8%	
Styrene	15.254	104	5.369	1.99	2.91 ± 0.4	99% ± 4.6%	
Bromoform	15.426	173	7.034	5.14	0.56 ± 0.3	100% ± 6.3%	
Isopropylbenzene	15.517	105	2.791	0.54	0.35 ± 0.2	99% ± 3.3%	
1,1,2,2-Tetrachloroethane	15.734	83	7.318	10.36	1.47 ± 0.6	100% ± 3.6%	
Propyl Benzene	15.833	120	8.977	4.33	1.15 ± 0.2	99% ± 3.5%	
4-Ethyltoluene	15.914	105	6.141	7.33	1.09 ± 0.4	99% ± 4%	
o-Chlorotoluene	15.923	126	8.241	1.28	0.03 ± 0.4	100% ± 2.1%	
1,3,5-Trimethylbenzene	15.950	120	9.986	4.56	0.87 ± 0.3	100% ± 5.9%	
1,2,4-Trimethylbenzene	16.240	120	11.293	17.44	2.62 ± 0.4	99% ± 4.5%	
1,3-Dichlorobenzene	16.493	146	6.894	3.14	0.58 ± 0.6	100% ± 3.8%	
1,4-Dichlorobenzene	16.574	146	7.269	3.43	0.38 ± 0.6	100% ± 3.6%	
Benzyl Chloride	16.637	126	7.151	3.02	0.06 ± 0.7	99% ± 3.2%	
1,2-Dichlorobenzene	16.854	146	16.200	3.83	0.32 ± 0.6	100% ± 3.4%	
1,2,4-Trichlorobenzene	18.201	180	10.298	9.03	0.59 ± 1.2	99% ± 5.2%	
Hexachlorobutadiene	18.292	225	22.581	13.57	0.42 ± 0.4	99% ± 6.4%	
Naphthalene	18.491	128	11.144	8.36	2.31 ± 1.1	98% ± 9.2%	

Table A1: Data obtained for TO-15A method testing (continued from previous page)

*MDL value is derived from the highest value between the MDL blank and the MDL spike

** As stated in the 'Method blank' section above, the MDLs for ethanol, acetone, IPA, 2-butanone, *tert*-butanol and acrolein are affected by their presence in either: the humidification water, ultra-zero air and nitrogen cylinders, or the canisters themselves.