

A rapid method for the analysis of air toxics based on US EPA TO-15

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Goal

The following application demonstrates an alternative chromatographic approach to US EPA Method TO-15 for the rapid determination of toxic organic compounds in ambient air using a combined TD-GC-MS solution from Markes International and Thermo Fisher Scientific.

Method linearity, RRF variation, method detection limit (MDL), and precision were assessed to evaluate method performance.

Introduction

US EPA Method TO-15 is an established method used for the measurement of hazardous air pollutants (HAPs) also known as air toxics. This subset of volatile organic compounds (VOCs) is collected and analyzed using



canister sampling methods and thermal desorption gas chromatography mass spectrometry (TD-GC-MS). Despite the popularity of canister sampling, maintaining system integrity and obtaining consistent results can be difficult for routine air analysis labs. Ingress of water to the analytical instrument can negatively impact analyte response and repeatability, as well as reduce the lifetime of the column and detector. In addition to this, traditional canister pre-concentration technologies are challenged by the wide ranges of sample compound concentrations and by the varying temperatures and humidity at sampling locations.

In this application note, we demonstrate the combined use of an innovative trap-based water removal device, alternative column choice, and a robust TD-GC-MS configuration to overcome the challenges experienced in the analysis of volatile air toxics in accordance with US EPA Method TO-15 and provide advantages in laboratory productivity.

Experimental

Sample introduction

A Markes International CIA Advantage coupled to a Unity-xr thermal desorber provided sample introduction from canisters to the GC-MS. Before entering the thermal desorber, samples were passed through a Kori-xr device to remove humidity from the air stream. The Kori-xr trap, held at -30 °C, sits in-between the sample inlet and the sorbent-packed focusing trap, causing vapor-phase water in the air sample to be deposited as ice. During this process, collection of VOCs on the focusing trap continues unaffected. When sampling is complete, the analytes are transferred from the focusing trap to the GC. Figure 1 illustrates the sample flow path to the GC-MS, and Table 1 outlines the sample introduction parameters.

GC-MS conditions

Sample evaluation was completed using the Thermo Scientific™ ISQ™ 7000 Mass Spectrometry (MS) coupled to

a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph (GC) running Thermo Scientific™ Chromeleon™ CDS for data processing and analysis. Separation of “air toxic” compounds was achieved using the Thermo Scientific™ TraceGOLD™ TG-VMS 20 m × 0.18 mm i.d. × 1 μm film (P/N 26080-4950) analytical column. Expanded method parameters for the GC-MS system are displayed in Table 2.

Table 1. Markes sample introduction conditions

CIA Advantage	
Canister sampling volume	Up to 1000 mL
Water removal	Kori-xr
IS loop fill	1 min
UNITY-xr	
Trap type	Cold trap, 'TO-15/TO-17 Air toxics', C2/3 to C30/32 {P/N U-T15ATA-2S}
Trap temperatures	-30/+300 °C
Flow path	120 °C
Loop equilibration	0.1 min
IS loop injection	1.0 min at 50 mL/min
Sample flow	50 mL/min

Table 2. GC-MS parameters

TRACE 1310 GC	
Inlet temperature	260 °C
Injection mode	Splitless, 3 min
Split flow	20 mL/min
Carrier gas flow	He, 0.8 mL/min
GC oven temp. program:	Initial 35 °C for 3 min, Ramp 14 °C/min to 100 °C, Ramp 20 °C/min to 230 °C, Hold 4 min
Total run time	18 min
ISQ 7000 mass spectrometer	
Transfer line	230 °C
Mode	Full Scan
Range	35–260 amu
Ion source	Thermo Scientific™ ExtractaBrite™
Ion source temp.	310 °C
Ionization mode	El at 70 eV
Solvent delay	1.09
Dwell/scan time	0.15 s
Emission current	25 μA

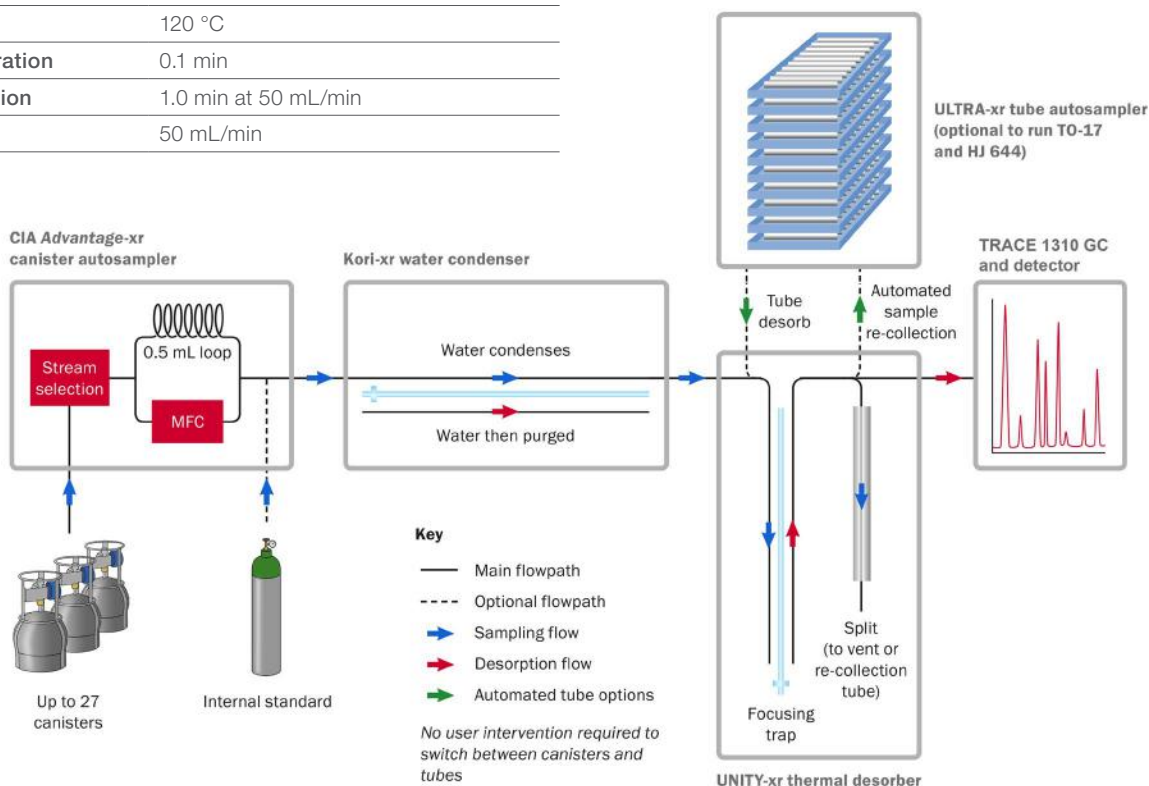


Figure 1. Flow path of the canister air samples

The ISQ 7000 mass spectrometer was operated in full scan mode, delivering ample sensitivity to meet and exceed TO-15 method requirements. During sample transfer to the analytical column, the moisture content was minimized using the Kori-xr, thereby protecting column integrity and providing consistent peak shape

and separation of the compounds. Extracted ion chromatograms are displayed in Figures 2 A and B.

Hazardous air pollutant (HAP) compound retention times and quantitation ions used for the evaluation are listed in Table 3.

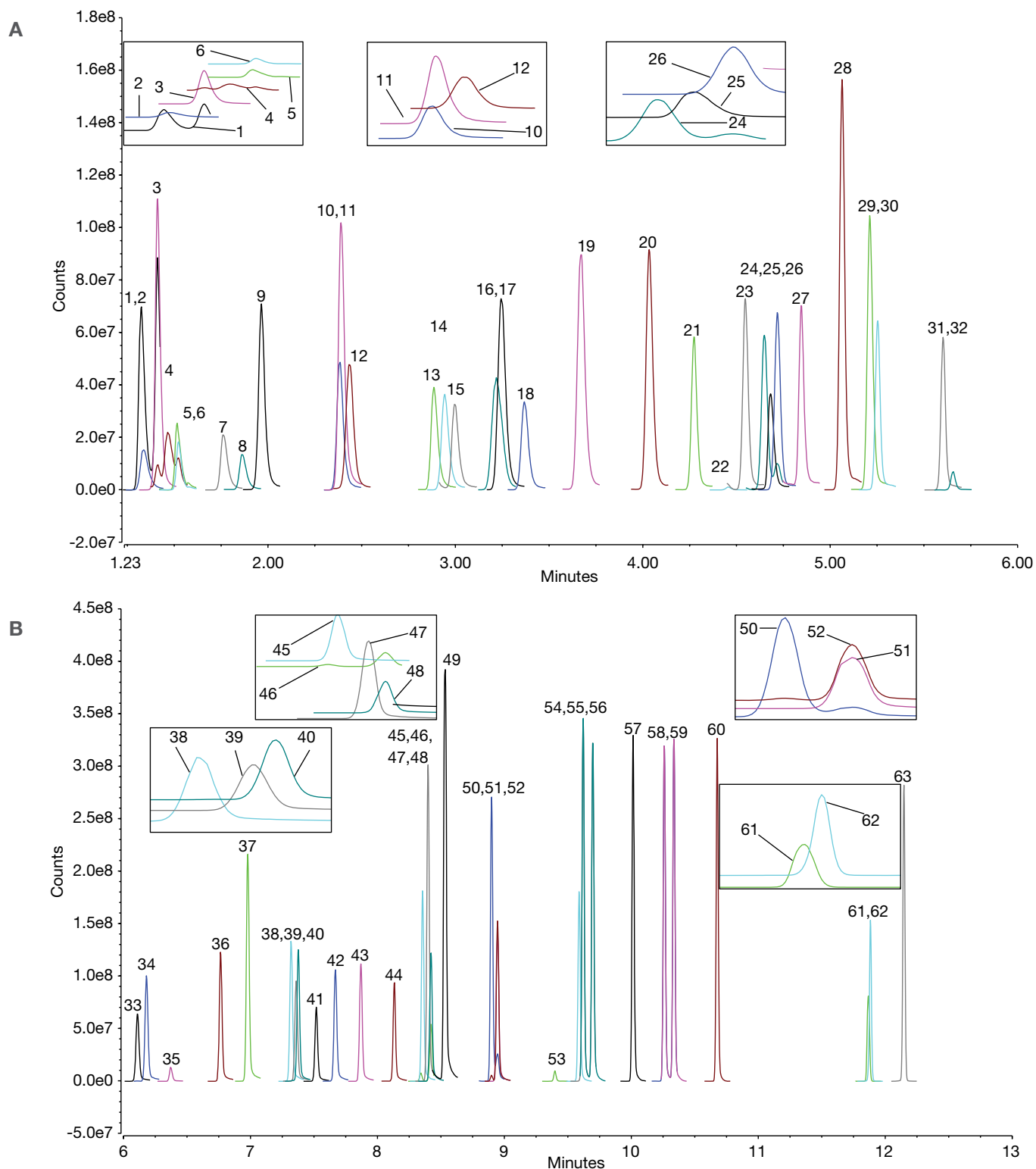


Figure 2. A) Extracted ion chromatograms for quantitation ion for each compound from 1.23–6 minutes, and B) extracted ion chromatograms for quantitation ion for each compound from 6–13 minutes

Table 3. HAP compounds under study with retention times and quantitation ions

	HAP name	Retention time (min)	Quantitation ion (m/z)		HAP name	Retention time (min)	Quantitation ion (m/z)
1	Dichlorodifluoromethane	1.33	85	33	1,2-Dichloropropane	6.13	63
2	1,1-Difluoroethane	1.35	65	34	Bromodichloromethane	6.20	83
3	1,2-Dichlorofluoromethane	1.42	135	35	1,4-Dioxane	6.39	88
4	Chloromethane	1.48	50	36	<i>cis</i> -1,3-Dichloropropene	6.79	75
5	Vinyl chloride	1.53	62	37	Toluene	7.00	91
6	1,3-Butadiene	1.53	54	38	Tetrachloroethylene	7.34	166
7	Bromomethane	1.78	94	39	4-Methyl-2-pentanone (MIBK)	7.38	43
8	Chloroethane	1.88	64	40	<i>trans</i> -1,3-Dichloropropene	7.39	75
9	Trichlorofluoromethane	1.98	101	41	1,1,2-Trichloroethane	7.54	97
10	1,1-Dichloroethene	2.42	61	42	Dibromochloromethane	7.69	129
11	Carbon disulfide	2.42	76	43	1,1-Dibromo-ethane	7.89	107
12	Freon 113	2.47	101	44	2-Hexanone	8.15	43
13	Isopropyl Alcohol	2.93	45	45	Chlorobenzene-d5	8.37	117
14	Methylene chloride	2.98	49	46	Chlorobenzene	8.38	112
15	Acetone	3.04	43	47	Ethylbenzene	8.42	91
16	Hexane	3.25	57	48	1,1,1,2-Tetrachloroethane	8.44	133
17	MTBE	3.30	73	49	<i>m,p</i> -Xylene	8.56	91
18	tert-Butanol	3.41	59	50	<i>o</i> -Xylene	8.92	91
19	Diisopropyl ether	3.70	45	51	Bromoform	8.97	173
20	ETBE	4.07	59	52	Styrene	8.97	104
21	<i>cis</i> -1,2-Dichloroethene	4.31	61	53	4-Bromofluorobenzene	9.42	95
22	Bromochloromethane	4.50	128	54	1,1,2,2-Tetrachloroethane	9.61	83
23	Chloroform	4.59	83	55	4-Ethyltoluene	9.64	105
24	Carbon tetrachloride	4.69	119	56	1,3,5-Trimethylbenzene	9.72	105
25	Tetrahydrofuran	4.73	42	57	1,2,4-Trimethylbenzene	10.04	105
26	1,1,1-Trichloroethane	4.76	97	58	1,3-Dichlorobenzene	10.28	146
27	2-Butanone	4.89	43	59	1,4-Dichlorobenzene	10.36	146
28	Benzene	5.12	78	60	1,2-Dichlorobenzene	10.70	146
29	TAME	5.26	73	61	Hexachlorobutadiene	11.89	225
30	1,2-Dichloro-ethane	5.30	62	62	1,2,3-Trichloro-benzene	11.90	180
31	Trichloroethylene	5.66	130	63	Naphthalene	12.17	128
32	1,4-Difluorobenzene	5.71	114				

Chromleon CDS software, version 7.2. was used to collect, process, and evaluate all data. Customizable ePanels, eWorkflows™ and reports within Chromleon software automate routine method workflows like TO-15.

Results and discussion

Separation of components was achieved in under 15 min using the alternative column dimensions of the TraceGOLD TG-VMS column (20 m × 0.18 mm i.d. × 1 μm film) (Figure 3). Use of a shorter column with a reduced diameter and thicker phase maintains the required capacity and efficiency for adequate separation of analytes at varying concentrations. However, it alters compound interaction dynamics with the column phase leading to shortened retention times, faster run times, and lower overall cycle times.

Bromochlorobenzene, 1,4-difluorobenzene, and chlorobenzene-d₅ were used as internal standards, and bromofluorobenzene is present as a surrogate standard. Calibration standards for 60 hazardous air pollutant (HAP) VOCs were evaluated from 0.5 to 50 μg/L with correlation coefficients determined for all compounds. %RSD of relative response factors (RRF) met requirements of <30%. Method detection limits (MDL) were evaluated according to procedures outlined in the TO-15 method using n=7 replicates of a 0.5 ppb standard. Method precision was assessed by analyzing n=7 replicates of an 8 ppb standard. Table 4 contains a review of results against method requirements.

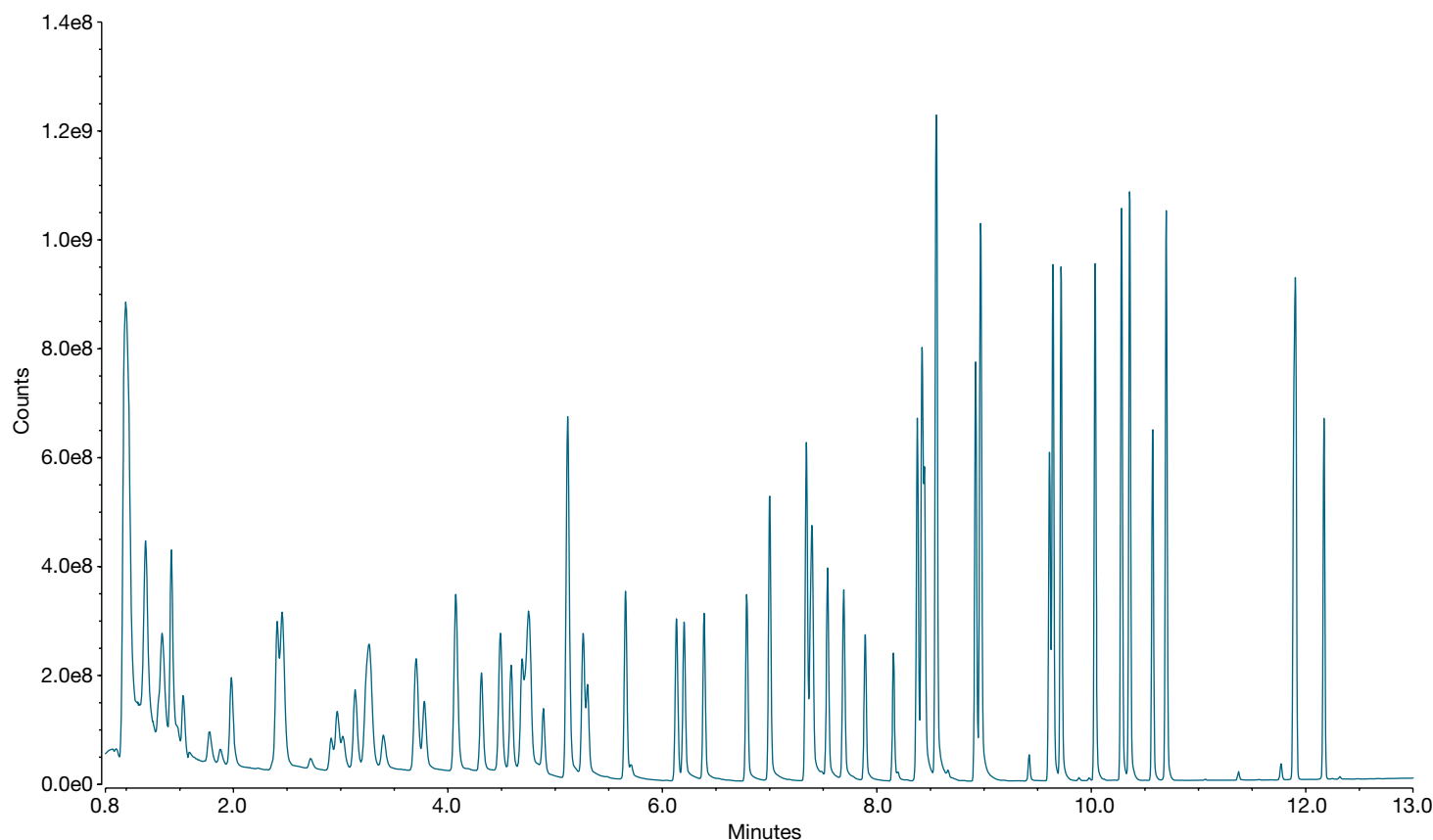


Figure 3. Total ion chromatograph (TIC) of all compounds eluted in under 13 minutes

Table 4. Calibration - R², RRF, minimum detection limit, and precision results. Note: Problematic compounds hexachlorobutadiene, and 1,2,3-trichlorobenzene produced quadratic curves and are omitted from the table.

HAP name	R ²	%RSD RRF	MDL (ppb)	Precision (≤25%)
Dichlorodifluoromethane	1.000	7%	0.11	12%
1,1-Difluoroethane	0.9995	9%	0.09	15%
1,2-Dichlorofluoromethane	0.9998	19%	0.12	9%
Chloromethane	0.9978	9%	N/A	8%
Vinyl chloride	0.9983	8%	N/A	10%
1,3-Butadiene	0.9986	6%	N/A	8%
Bromomethane	0.9995	9%	0.12	8%
Chloroethane	0.9997	5%	0.1	12%
Trichlorofluoromethane	0.9999	15%	0.1	10%
1,1-Dichloroethene	0.9998	5%	0.11	10%
Carbon disulfide	0.9997	12%	0.09	6%
Freon 113	0.9997	14%	0.14	13%
Isopropyl Alcohol	0.9991	29%	0.21	12%
Methylene chloride	0.9999	6%	0.08	11%
Acetone	0.9998	5%	N/A	11%
Hexane	0.9997	20%	0.15	8%
MTBE	0.9995	14%	0.09	11%
tert-Butanol	0.9993	22%	0.26	14%
Diisopropyl ether	0.9991	18%	0.15	11%
ETBE	0.9991	15%	0.12	12%
cis-1,2-Dichloroethene	0.9996	9%	0.09	8%
Chloroform	0.9999	13%	0.10	10%
Carbon Tetrachloride	0.9998	10%	0.11	9%
Tetrahydrofuran	0.999	29%	0.15	9%
1,1,1-Trichloroethane	0.9472	11%	0.12	11%
2-Butanone	0.9983	21%	0.19	13%
Benzene	0.9987	13%	0.12	9%
TAME	0.9983	14%	0.14	11%
1,2-Dichloro-ethane	0.999	6%	0.10	8%
Trichloroethylene	0.9994	8%	0.13	9%

HAP name	R ²	%RSD RRF	MDL (ppb)	Precision (≤25%)
1,2-Dichloropropane	0.9997	12%	0.09	10%
Bromodichloromethane	0.9996	9%	0.12	10%
1,4-Dioxane	0.9988	14%	N/A	15%
cis-1,3-Dichloropropene	0.9997	9%	0.12	7%
Toluene	0.9996	17%	0.11	9%
Tetrachloroethylene	0.9991	12%	0.12	10%
4-Methyl-2-pentanone (MIBK)	0.9991	29%	0.23	15%
trans-1,3-Dichloropropene	0.9998	9%	0.07	10%
1,1,2-Trichloroethane	0.9999	11%	0.13	9%
Dibromochloromethane	0.9995	5%	0.1	10%
1,1-Dibromo-ethane	0.9997	6%	0.11	10%
2-Hexanone	0.9951	17%	0.18	15%
Chlorobenzene	0.9997	9%	0.13	8%
Ethylbenzene	0.9999	9%	0.11	10%
1,1,1,2-Tetrachloroethane	0.9999	5%	0.13	9%
m,p-Xylene	0.9976	12%	0.14	13%
o-Xylene	0.9990	11%	0.11	11%
Bromoform	0.9988	8%	0.11	12%
Styrene	0.9990	11%	0.14	14%
1,1,2,2-Tetrachloroethane	0.9999	10%	0.11	10%
4-Ethyltoluene	0.9999	10%	0.13	11%
1,3,5-Trimethylbenzene	1.0000	8%	0.13	10%
1,2,4-Trimethylbenzene	0.9999	9%	0.13	11%
1,3-Dichlorobenzene	1.0000	9%	0.11	9%
1,4-Dichlorobenzene	0.9999	8%	0.10	10%
1,2-Dichlorobenzene	0.9998	8%	0.12	9%
Hexachlorobutadiene	0.9987	17%	0.13	17%
1,2,3-Trichloro-benzene	0.9999	8%	0.11	10%
Naphthalene	0.9999	4%	0.19	9%

N/A = Not determined

Conclusion

The combined Markes international / Thermo Scientific TD-GC-MS solution provides clear advantages for execution of US EPA TO-15. The consistent performance needed in air analysis labs and demonstrated in this application is most notably attributed to the combination of the KORI-xr moisture management system, the robust performance of the ExtractaBrite ion source, and the rapid separation TraceGOLD TG-VMS column, among other system features. The advantage of reduced run times from the alternative column dimensions used in this method reduces overall cycle times for canister analysis, providing labs with an improved method for TO-15 that saves time and in turn improves resource earning potential. Advantages of this configuration for TO-15 analysis are attributed to the following:

- Effective separation and quantitation of 60 HAPs from 0.5 to 50 ppb in under 13 minutes.

- Excellent linearity, RRF RSDs, and precision results comfortably achieved all method acceptance criteria. RSDs were well below the replicate precision requirement of <25%.
- MDL confirmation for n=7 0.5 ppb standards showed absence of interference from excessive moisture with lower method detection limits than required by the published method.

References

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