A Rapid Method for the Analysis of Air Toxics Based on US EPA TO-15

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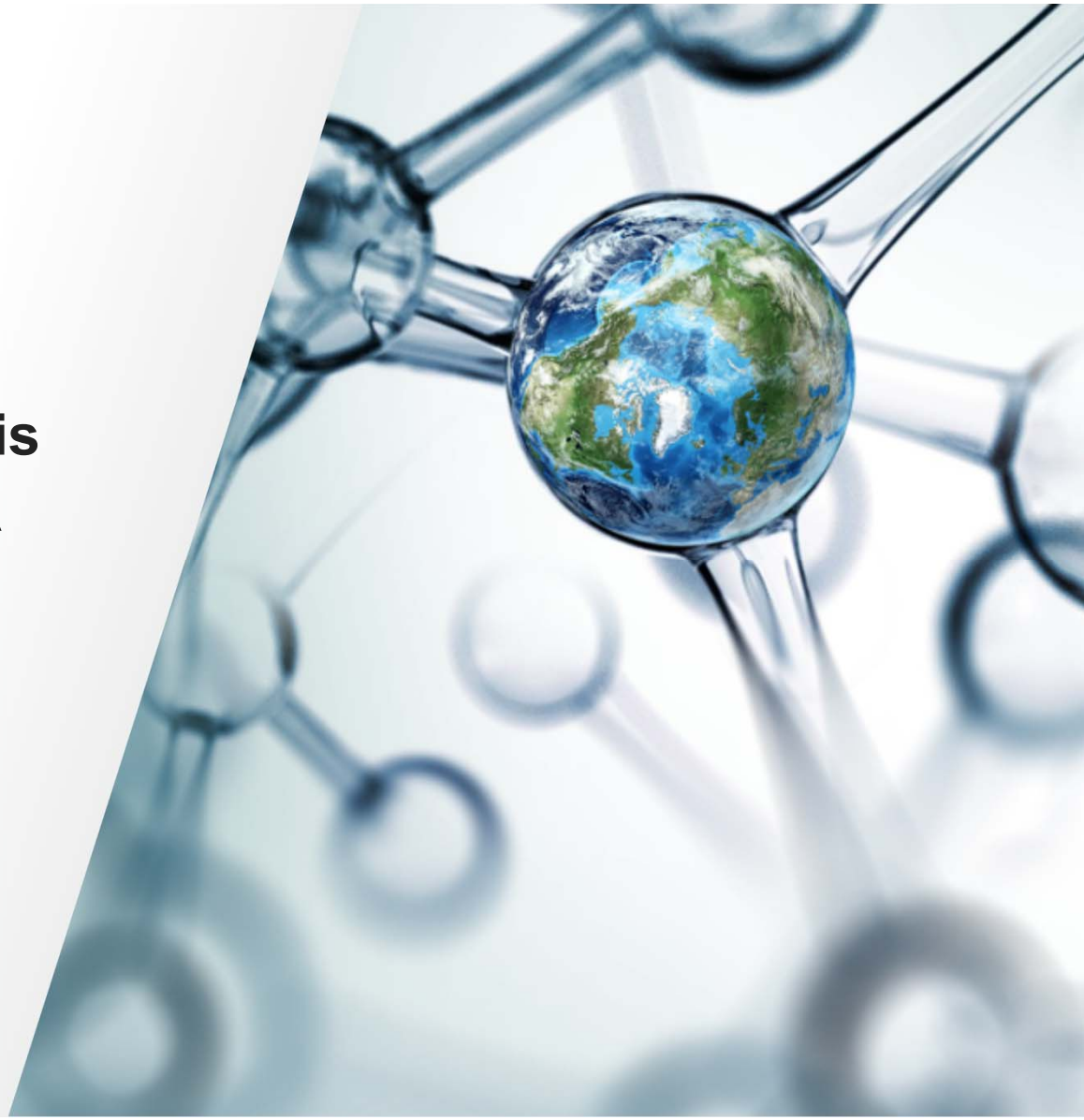
Senior Application Scientist
August 9, 2021



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What are HAPs?

- HAPs are pollutants that are known or suspected to cause serious health effects or adverse environmental effects.

- Examples include:

Benzene
Found in gasoline

Dichloromethane
Used as a solvent and paint stripper

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Background

- US EPA Method TO-15 is established method for hazardous air pollutants (HAPs).
- Utilises canister sampling method and thermal desorption gas chromatography mass spectrometry (TD-GC-MS).
- Ingress of water can negatively affect results.
- Standard run times limit sample throughput.
- Other challenges include the wide range of sample compound temperatures and varying temperature and humidity of samples.

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Objectives

- Demonstrate an alternative chromatographic approach to speed up analysis compared to US EPA TO-15.
- Demonstrate the combined use of an innovative trap-based water removal device as part of a robust TD-GC-MS system.
- Demonstrate both typical and 0.5 – 50 ppb Calibration data for US EPA TO-15

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Equipment

Sample introduction

Markes™ CIA Advantage™ canister sampler coupled to a Markes™ Kori-xr™ water removal device and a Markes™ Unity-xr™ thermal desorber

Sample analysis

Thermo Scientific™ ISQ™ 7000 mass spectrometer (MS) coupled to Thermo Scientific™ TRACE 1310 gas chromatograph (GC)

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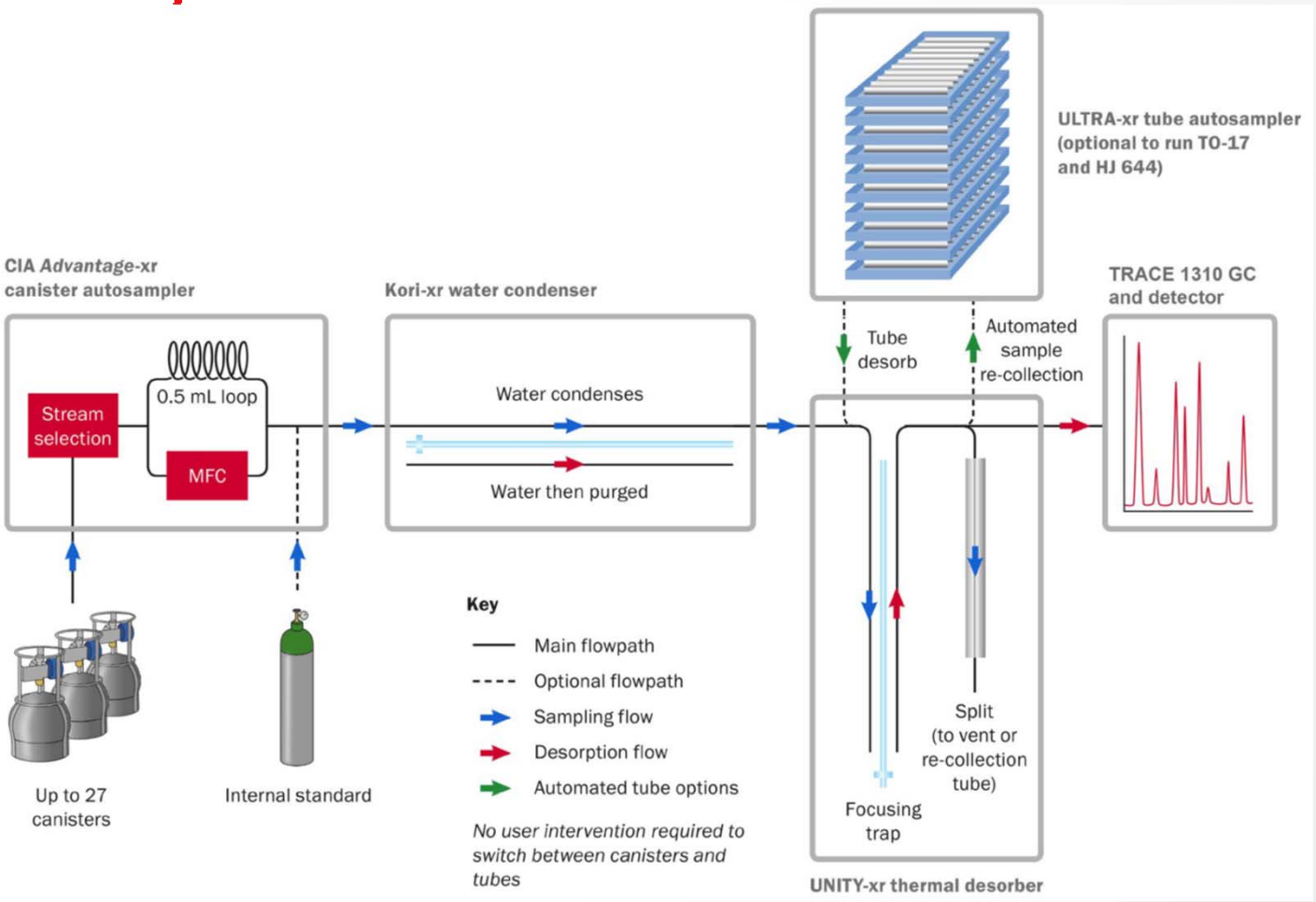
Sample flow path



Sample Preparation Method conditions

Markes™ CIA Advantage-xr™	
Canister sampling volume	Up to 1000 mL
Water removal	Kori-xr™
IS loop fill	1 min

Markes™ Unity-xr™	
Trap type	Cold trap, “TO-15/TO-17 Air toxics”
Trap temperature	-30 °C to 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

GC-MS Method conditions

Thermo Scientific™ 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 temperature program	Initial 35 °C for 3 min, Ramp 14 °C/min to 100 °C, Ramp 20 °C/min to 230 °C, hold for 4 min
Total run time	18 min
Thermo Scientific™ ISQ 7000 mass spectrometer	
Transfer line temperature	230 °C
Mode/range	Full scan, 35-260 amu
Ion source	Thermo Scientific™ ExtractaBrite™
Ion source temperature	310 °C
Ionisation mode	EI @ 70 eV
Solvent delay	1.09 min
Dwell/scan time	0.15 s
Emission current	25 µA

Column	
TG-VMS	20 m x 0.18 mm x 1.0 µm Film

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Thermo Scientific ISQ 7000 MS - Never Vent

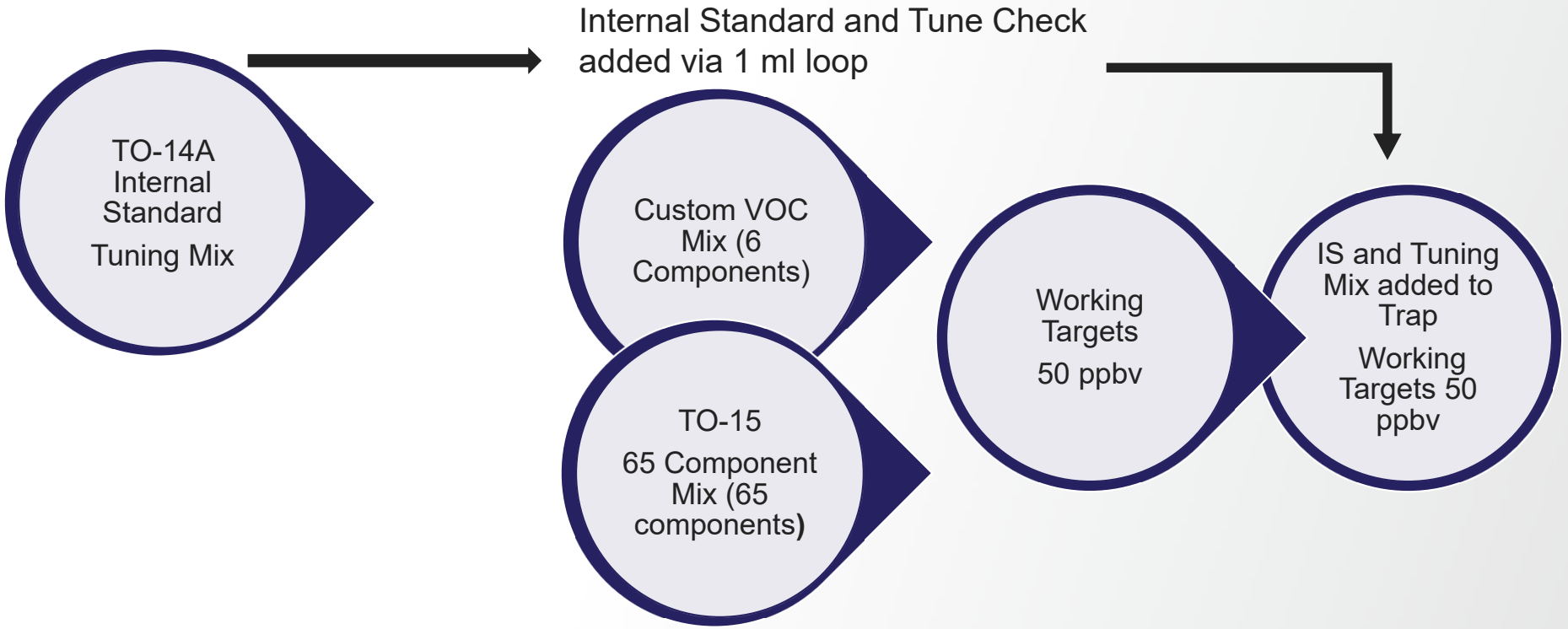
What is NeverVent technology?

Increase GC-MS Uptime with the vacuum probe interlock **(VPI)**

Through the VPI, no need to vent mass spec system for extracting the wireless ExtractaBrite ion source

Extends the capability of the Vacuum Probe Interlock **(VPI)** design with the newly introduced source plug, **V-Lock**

Standard Preparation



- Bromochloromethane, 1,4-Difluorobenzene, Chlorobenzene-d5 used as Internal Standards
- 4-bromofluorbenzene – Tune Mix

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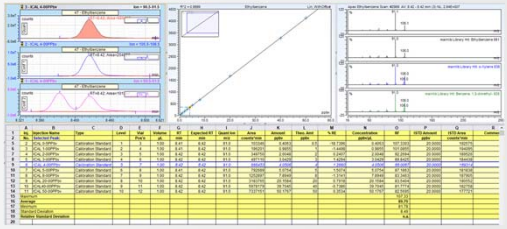
Result – Sample to Sample Cycle Time

Sample Preparation

Sample Separation & Detection

Sample Results



25 minutes – Sample to Sample

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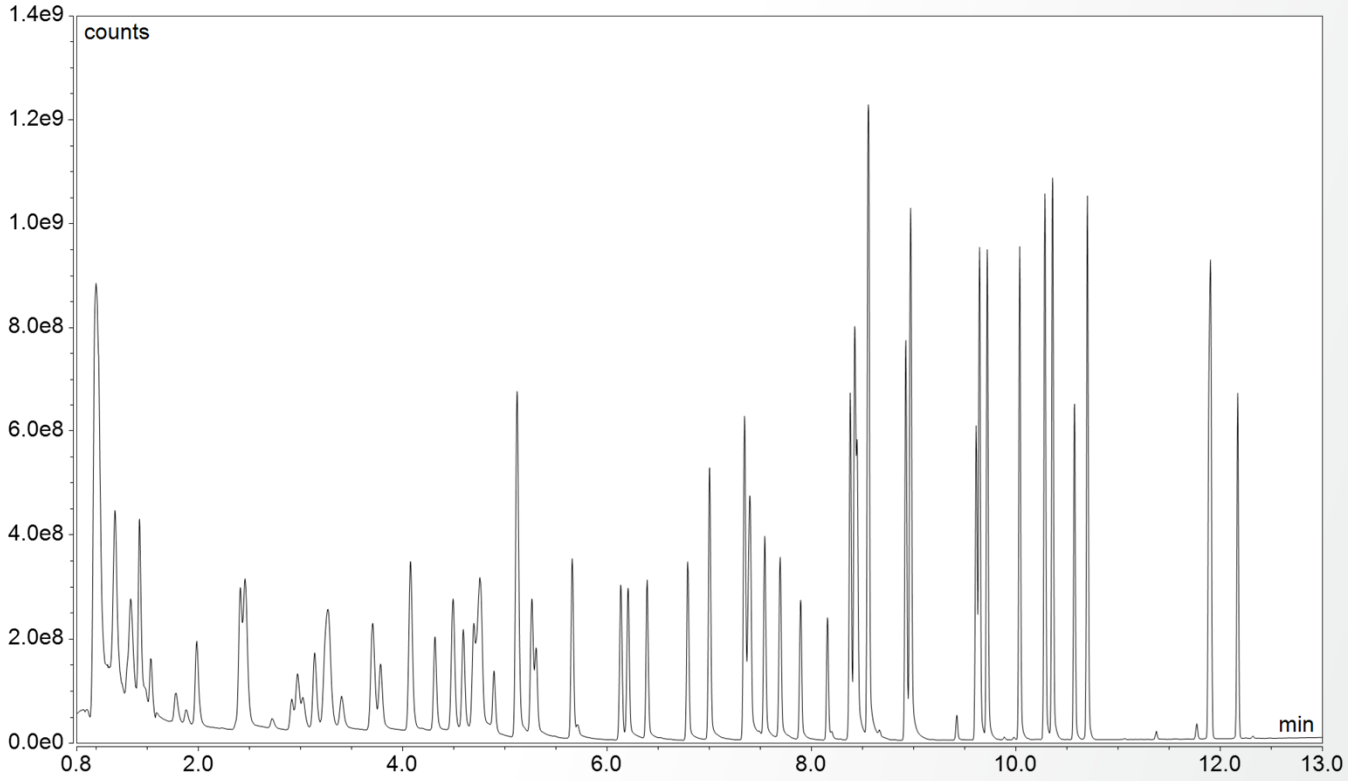
Result - Chromatography



Separation of 50 ppb standard achieved in under 13 minutes

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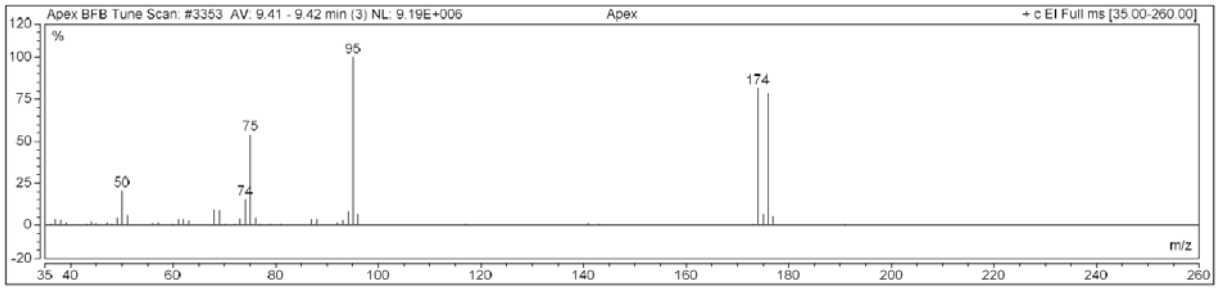
Result – BFB Tune Check

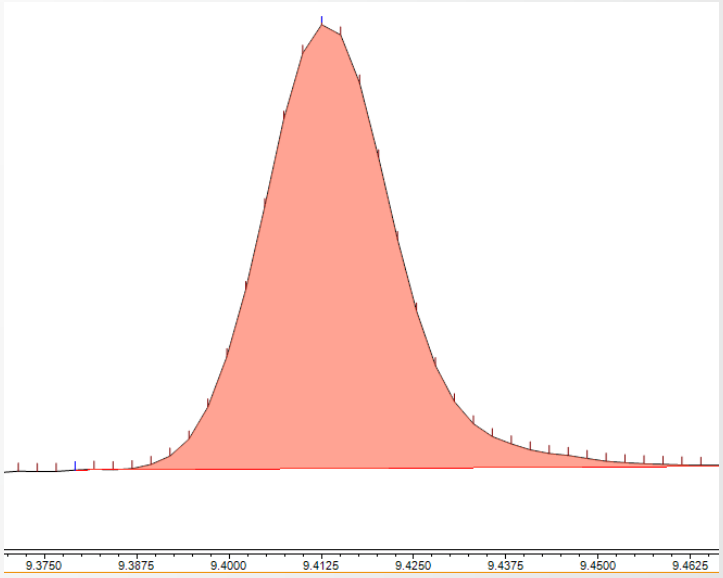
TABLE 4. 4-BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but< 101% of mass 174
177	5 to 9% of mass 176



No.	Name	Eval. Result	Operator	Ref. Value 1	Ref. Value 2	Result
1	m/z 50 - 15 to 40% of m/z 95	20.4	between	15	40	Passed
2	m/z 75 - 30 to 60% of m/z 95	53.8	between	30	60	Passed
3	Base Peak (m/z 95)	95.1	=	95		Passed
4	m/z 96 - 5 to 9% of m/z 95	6.4	between	5	9	Passed
5	m/z 173 - Less than 2% of m/z 174	0.6	<	2		Passed
6	m/z 174 - Greater than 50% of m/z 95	81.4	>	50		Passed
7	m/z 175 - 5 to 9% of m/z 174	7.5	between	5	9	Passed
8	m/z 176 - 95 to 101% of m/z 174	96.3	between	95	101	Passed
9	m/z 177 - 5 to 10% of m/z 176	6.8	between	5	10	Passed
					Overall Result:	Passed

> 20 Scans across Peak



Tune Check – Top 3 scans across apex of peak

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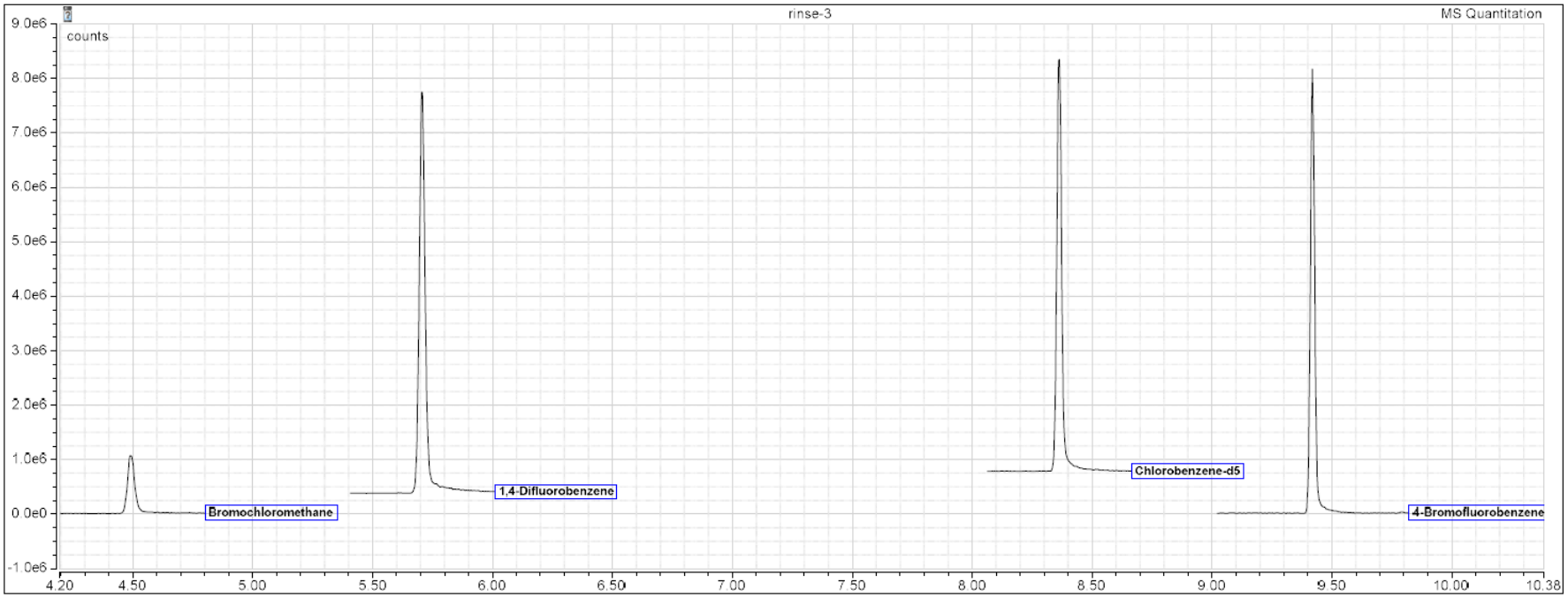
Result – Internal Standard Chromatography



Internal Standards and Tuning Component

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Result – Internal Standard Stability

Injection Name	Area Counts MS Quantitation Bromochloromethane		Area Counts MS Quantitation 1,4-Difluorobenzene		Area Counts MS Quantitation Chlorobenzene-d5	
Blank-1	48866		236955		215257	
ICAL 0-5PPbv	37589		200913		192575	
ICAL 1-00PPbv	40130		199230		194095	
ICAL 2-00PPbv	44729		201277		189526	
ICAL 3-00PPbv	46003		206774		184438	
ICAL 4-00PPbv	47968		210992		189314	
ICAL 5-00PPbv	47224		205001		181838	
ICAL 8-00PPbv	49643		218012		187905	
ICAL 20-00PPbv	48914		218198		190552	
ICAL40-00PPbv	48219		212215		182758	
ICAL 50-00PPbv	47111		216549		177721	
rinse 1	45987		207411		177078	
rinse-2	46395		207897		178401	
rinse-3	45286		207740		178508	
MDL -1	34067		182574		173666	
MDL -2	33658		177160		174686	
MDL -3	33827		176371		174661	
MDL -4	34406		176554		177583	
MDL -5	35442		184933		181716	
MDL -6	35523		182928		182437	
MDL -7	35703		185743		182678	
MDL -8	35878		190579		187870	
Validation-1	47590		218333		194671	
Validation-2	48807		215986		198117	
Validation-3	49122		224642		199111	
Validation-4	51248		231040		209124	
Validation-5	50179		226201		207141	
Validation-6	49717		224492		204090	
Validation-7	52020		231826		213275	
Average	**43836**		**206156**		**188993**	
Standard Deviation	**6368**		**17851**		**11978**	
% RSD	**15%**		**9%**		**6%**	

% RSD

- **Bromochloromethane = 15 %**
- **1,4-Difluorobenzene = 9 %**
- **Chlorobenzene-d5 = 6 %**

Internal Standard Area Count Stability

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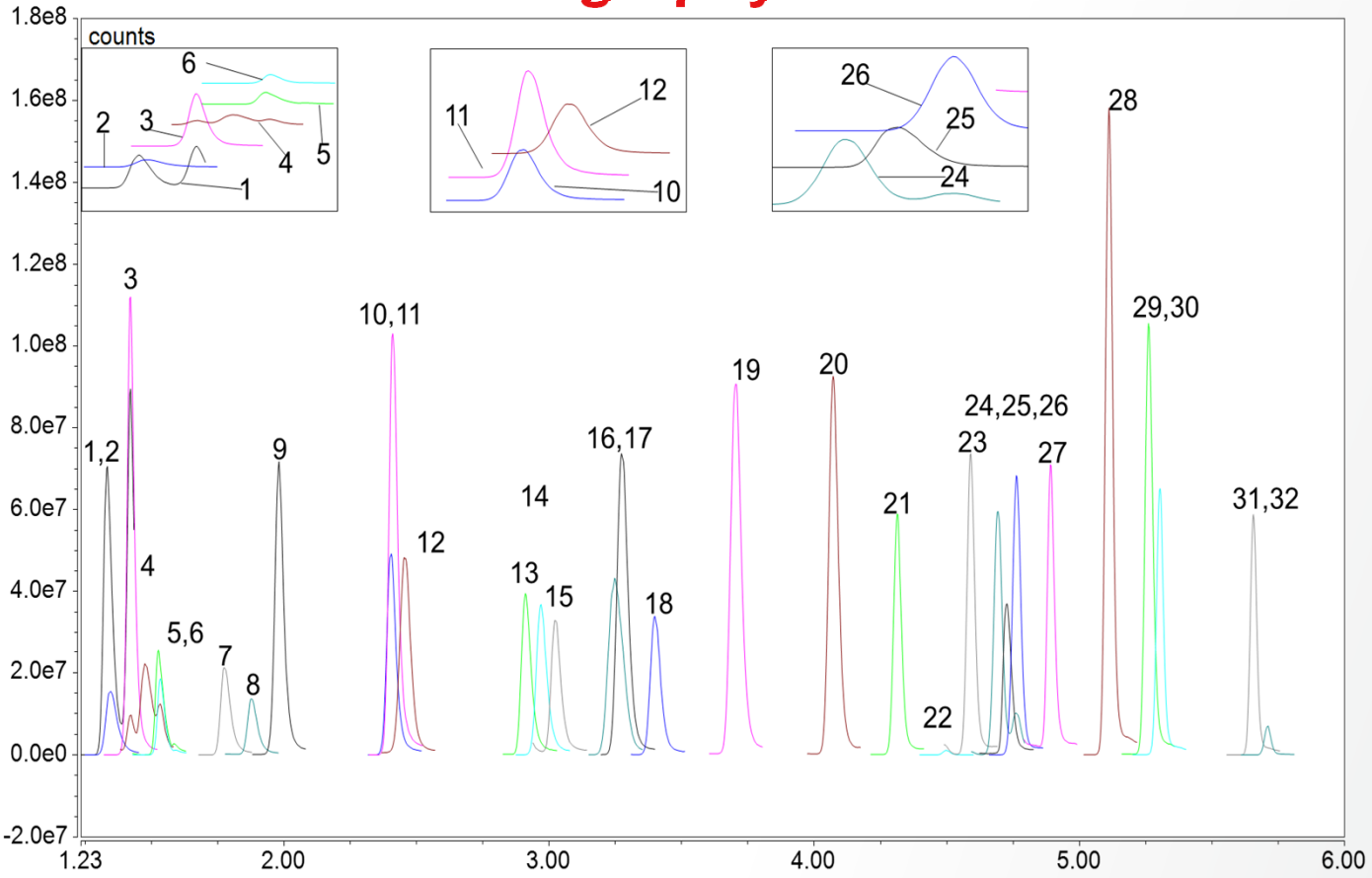
Results - Chromatography



Peak number	HAP	Retention time (min)	Quantitation ion (*m/z*)
1	Dichlorodifluoromethane	1.33	85
2	1,1-Difluoroethane	1.35	65
3	1,2-Dichlorofluoromethane	1.42	135
4	Chloromethane	1.48	50
5	Vinyl chloride	1.53	62
6	1,3-Butadiene	1.53	54
7	Bromomethane	1.78	94
8	Chloroethane	1.88	64
9	Trichlorofluoromethane	1.98	101
10	1,1-Dichloroethene	2.42	61
11	Carbon disulfide	2.42	76
12	Freon 113	2.47	101
13	Isopropyl Alcohol	2.93	45
14	Methylene chloride	2.98	49
15	Acetone	3.04	43
16	Hexane	3.25	57
17	MTBE	3.30	73
18	tert-butanol	3.41	59
19	Diisopropyl ether	3.70	45
20	ETBE	4.07	59
21	cis-1,2-Dichloroethene	4.31	61
22	Bromochloromethane	4.50	128
23	Chloroform	4.59	83
24	Carbon Tetrachloride	4.69	119
25	Tetrahydrofuran	4.73	42
26	1,1,1-Trichloroethane	4.76	97
27	2-Butanone	4.89	43
28	Benzene	5.12	78
29	TAME	5.26	73
30	1,2-dichloro-ethane	5.30	62
31	Trichloroethylene	5.66	130
32	1,4-Difluorobenzene	5.71	114

EIC for a 50-ppb standard from 1.23 min to 6 min

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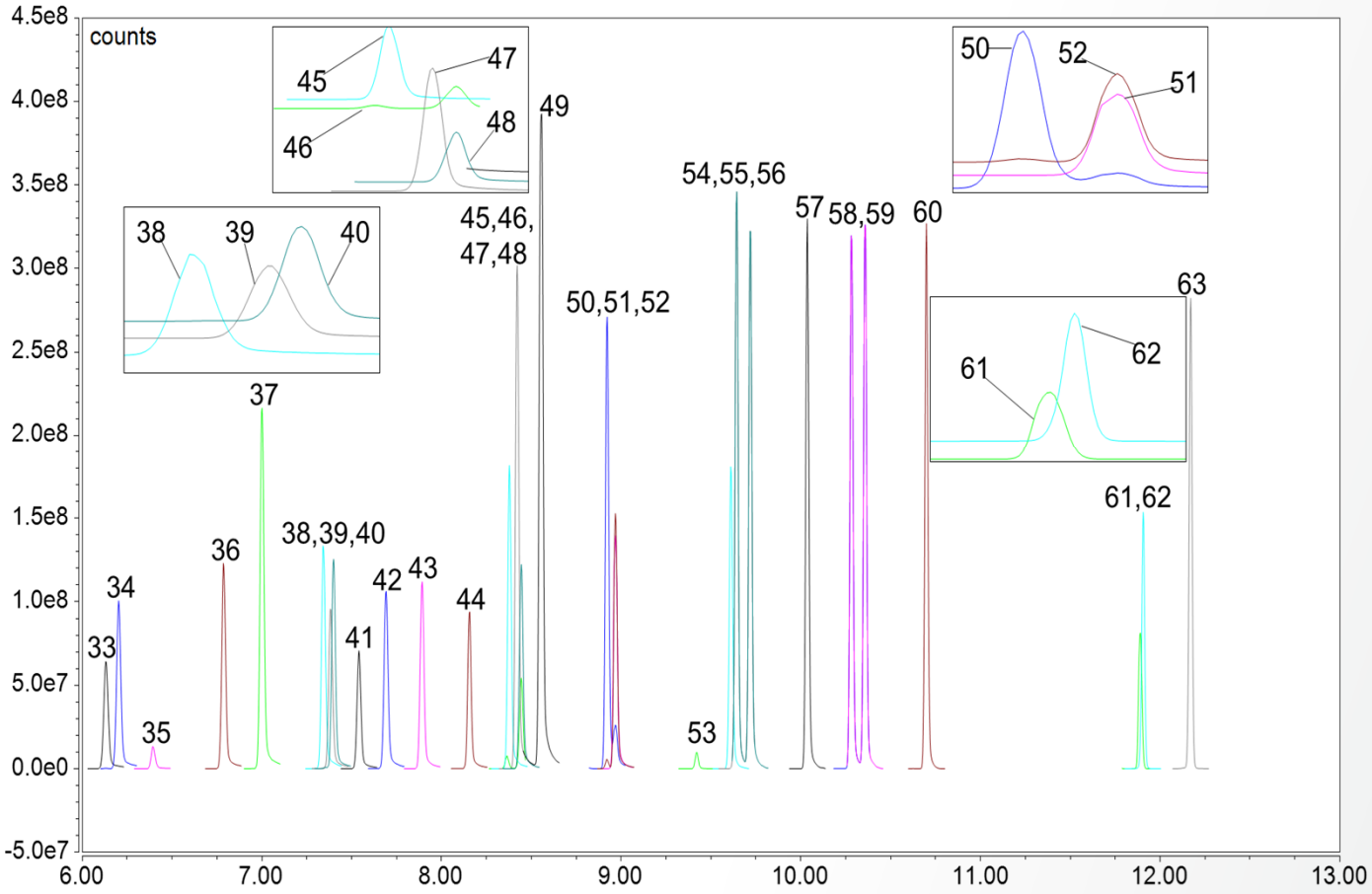
Results - Chromatography



Peak number	HAP	Retention time (min)	Quantitation ion (*m/z*)
33	1,2-Dichloropropane	6.13	63
34	Bromodichloromethane	6.20	83
35	1,4-Dioxane	6.39	88
36	Cis-1,3-Dichloropropene	6.79	75
37	Toluene	7.00	91
38	Tetrachloroethylene	7.34	166
39	4-Methyl2-pentanone (MIBK)	7.38	43
40	Trans-1,3Dichloropropene	7.39	75
41	1,1,2-trichloroethane	7.54	97
42	Dibromochloromethane	7.69	129
43	1,1-Dibromoethane	7.89	107
44	2-Hexanone	8.15	43
45	Chlorobenzene-d5	8.37	117
46	Chlorobenzene	8.38	112
47	Ethylbenzene	8.42	91
48	1,1,12-Tetrachloroethane	8.44	133
49	M,p-Xylene	8.56	91
50	O-Xylene	8.92	91
51	Bromoform	8.97	173
52	Styrene	8.97	104
53	4-Bromofluorobenzene	9.42	95
54	1,1,2,2-Tetrachloroethane	9.61	83
55	4-Ethyltoluene	9.64	105
56	1,3,5-Trimethylbenzene	9.72	105
57	1,2,4-Trimethylbenzene	10.04	105
58	1,3-Dichlorobenzene	10.28	146
59	1,4-Dichlorobenzene	10.36	146
60	1,2-Dichlorobenzene	10.70	146
61	Hexchlorobutadiene	11.89	225
62	1,2,3-Trichlorobenzene	11.90	180
63	Naphthalene	12.17	128

EIC for a 50-ppb standard from 6 min to 13 min

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Result – Method Validation

- Multi point Calibration
  - 10 calibration points
  - 0.5 – 50 ppbv
- Minimum Detection Limit Study
  - 0.5 ppbv standard
- Initial Demonstration of Capability (IDC)
  - 8.0 ppbv standard

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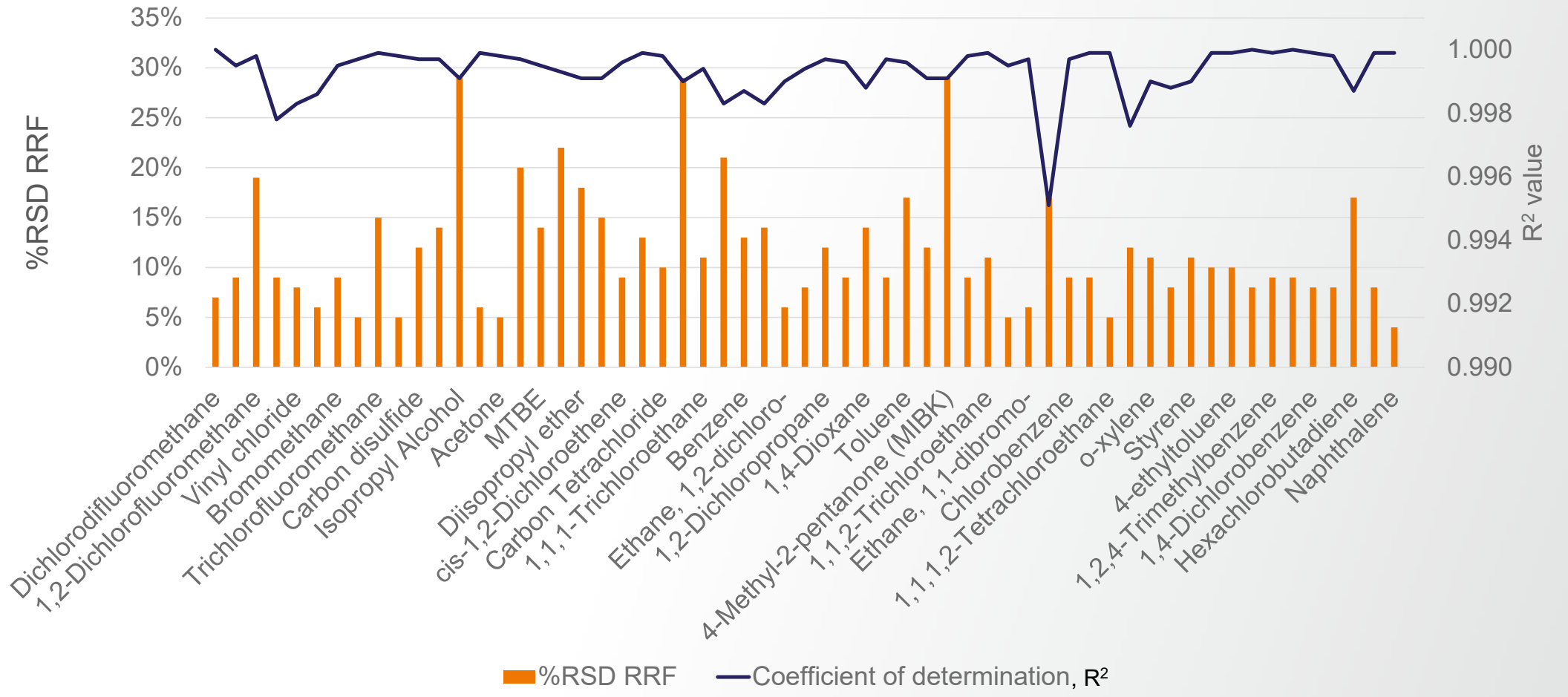
Results - Calibration



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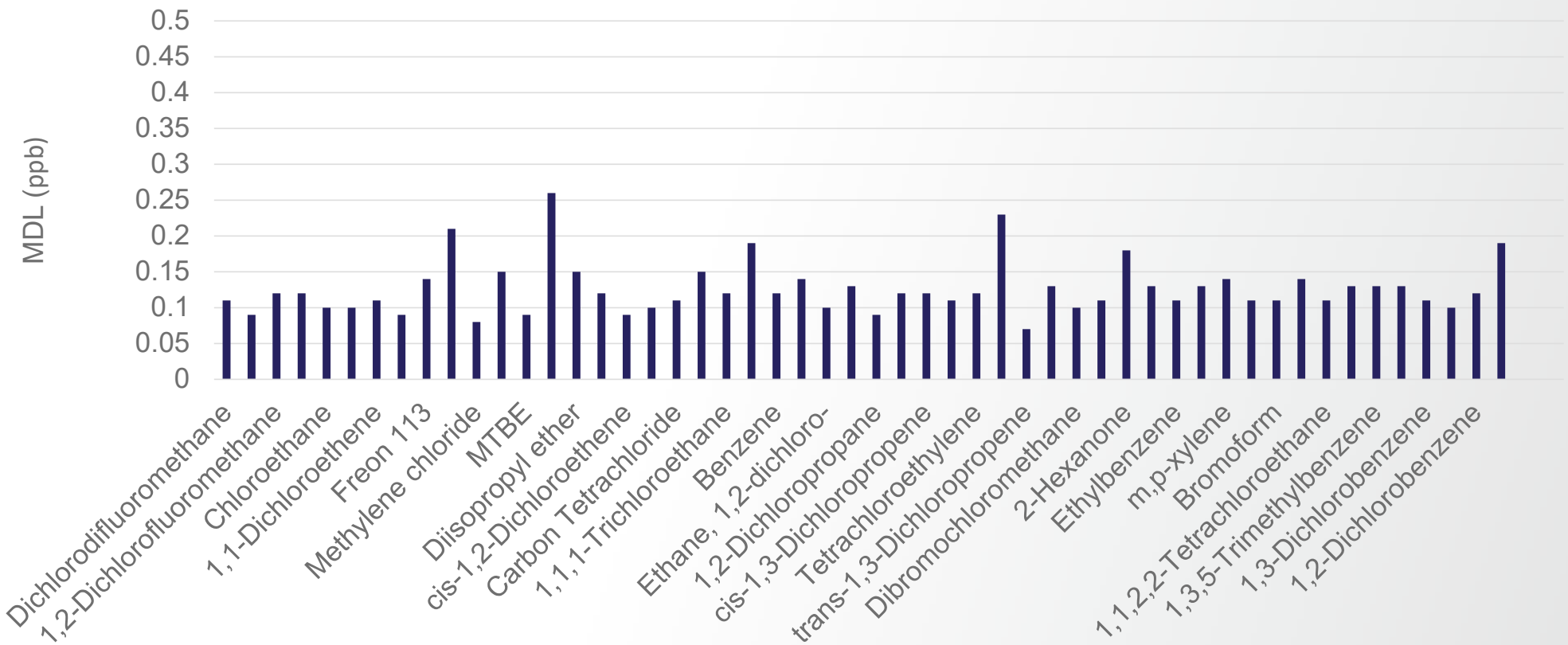
Results – Sensitivity



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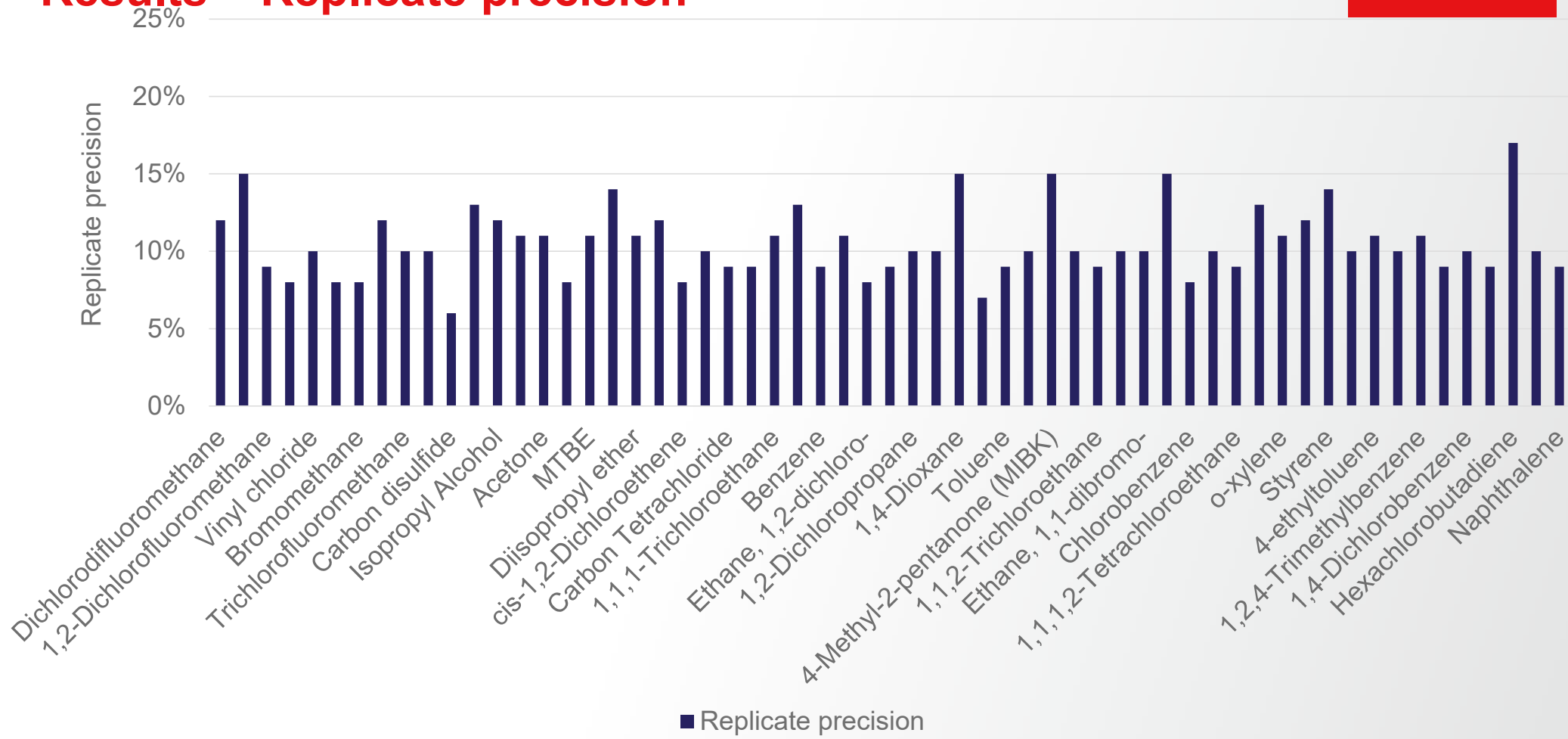
Results – Replicate precision



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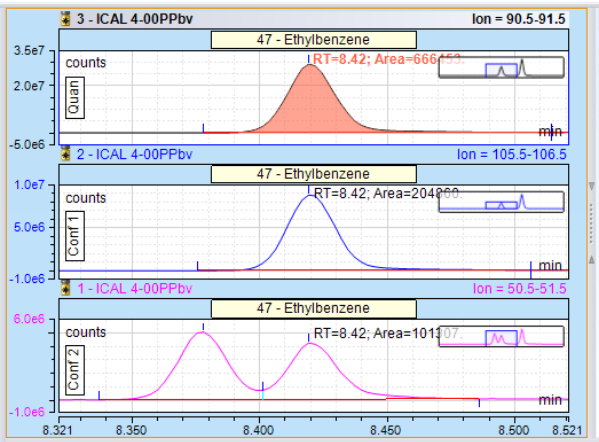
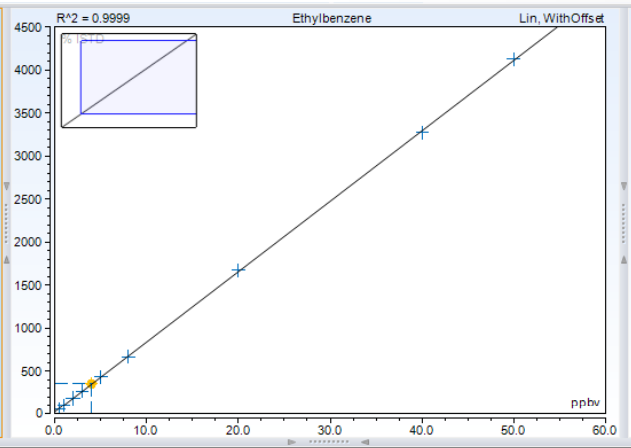
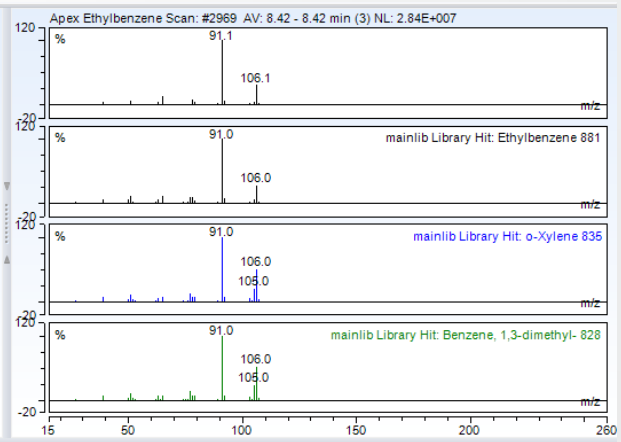
Chromeleon CDS Benefits

- Data Review – at a glance







	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1	Inj.	Injection Name	Type	Level	Vial	Volume	RT	Expected RT	Quant Ion	Area	Amount	Theo. Amt	% RE	Concentration	RF	ISTD Amount	ISTD Area	Commer
2	No.	Selected Peak:			Pos'n	µL	min	min	m/z	counts*min	ppbv	ppbv		ppbv/µL		ppbv	counts*min	
5	2	ICAL 0-5PPbv	Calibration Standard	1	3	1.00	8.41	8.42	91.0	103346	0.4063	0.5	-18.7396	0.4063	107.3303	20.0000	192575	
6	3	ICAL 1-00PPbv	Calibration Standard	2	4	1.00	8.41	8.42	91.0	196201	0.9855	1	-1.4498	0.9855	101.0855	20.0000	194095	
7	4	ICAL 2-00PPbv	Calibration Standard	3	5	1.00	8.42	8.42	91.0	349750	2.0048	2	0.2407	2.0048	92.2694	20.0000	189526	
8	5	ICAL 3-00PPbv	Calibration Standard	4	6	1.00	8.42	8.42	91.0	497110	3.0429	3	1.4294	3.0429	89.8425	20.0000	184438	
9	*6*	*ICAL 4-00PPbv*	*Calibration Standard*	*5*	*7*	*1.00*	*8.42*	*8.42*	*91.0*	*666453*	*4.0506*	*4*	*1.2660*	*4.0506*	*88.0087*	*20.0000*	*189314*	
10	7	ICAL 5-00PPbv	Calibration Standard	6	8	1.00	8.41	8.42	91.0	792689	5.0754	5	1.5074	5.0754	87.1863	20.0000	181838	
11	8	ICAL 8-00PPbv	Calibration Standard	7	9	1.00	8.42	8.42	91.0	1252897	7.8949	8	-1.3141	7.8949	83.3463	20.0000	187905	
12	9	ICAL 20-00PPbv	Calibration Standard	8	10	1.00	8.42	8.42	91.0	3183765	20.1584	20	0.7918	20.1584	83.5404	20.0000	190552	
13	10	ICAL40-00PPbv	Calibration Standard	9	11	1.00	8.42	8.42	91.0	5978179	39.7045	40	-0.7386	39.7045	81.7774	20.0000	182758	
14	11	ICAL 50-00PPbv	Calibration Standard	10	12	1.00	8.42	8.42	91.0	7337151	50.1767	50	0.3534	50.1767	82.5695	20.0000	177721	
15	Maximum														107.33			
16	**Average**														**89.70**			
17	Minimum														81.78			
18	Standard Deviation														8.49			
19	**Relative Standard Deviation**														**n.a.**			
20																		

Application Notes 10729

thermoscientific

APPLICATION NOTE 10729

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

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Keywords: US EPA, VOCs, TO-15 volatiles, air toxics, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, thermal desorption gas chromatography mass spectrometry, TD-GC-MS, canister, environmental lab, air analysis, ambient air monitoring

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.

ThermoFisher SCIENTIFIC

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Conclusions

- Alternative column dimensions reduces analysis times, increasing sample throughput.
- Effective chromatographic separation and accurate quantitation of 60 HAPs in under 13 minutes is achieved.
- Sample to Sample run time is 25 minutes
- Excellent linearity was obtained over a concentration range of 0.5 to 50 ppb, comfortably meeting the requirements of <30% RRF RSDs.
- Replicate precision for all target compounds was below the requirement of <25% from n=7 replicates
- Sensitivity assessment demonstrated that lower method detection limits were achieved than required by the published method

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Thank you

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