

# Routine Analysis of Volatile Organic Compounds in Drinking Water Using Purge & Trap Coupled to GCMS Following U.S. EPA 524.2 and EPA 524.4

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## Background

- Drinking water routinely tested for a variety of contaminants
- VOCs are one class of compounds tested
- Extremely important that labs can accurately detect and quantify these compounds in a timely manner
- Usually analyzed using headspace or purge and trap methods
- U.S. EPA methods 524.2 and 524.4 are commonly used for the analysis of the compounds



# Objective

- To demonstrate routine analytical methods that meet the requirements of U.S. EPA 524.2 and 524.4 for the analysis of VOCs in drinking water
- Method detection limits (MDLs), linearity, precision, accuracy and method reporting limits (MRLs) have been assessed to evaluate method performance



# Challenges in Routine Environmental Analysis

## Meeting regulatory requirements:

- Limits of detection
- Ongoing quality control
- Analyte compounds



## Maintaining sample throughput:

- Ensuring samples are reported on time
- Limiting sample re-analysis
- Limiting instrument downtime



## Managing laboratory costs:

- Effectively using workforce
- Limiting costs of consumables
- Simplified operation of systems





## Addressing These Challenges



Tekmar Atomx XYZ Purge & Trap (P&T) coupled with the Thermo Scientific™ ISQ™ 7000 GC-MS System and Thermo Scientific™ TRACE™ 1310 Gas Chromatograph

### A model relationship for VOC analysis:

- **The Atomx XYZ**

- Efficient trap cooling design allows more sample capacity
- Moisture control reduces peak interference and increases consumable lifetime

- **ISQ 7000 VPI**

- Eliminates downtime with vent-free column and source exchanged
- Sensitivity that exceeds the method requirements
- Inherent robustness for maximum uptime

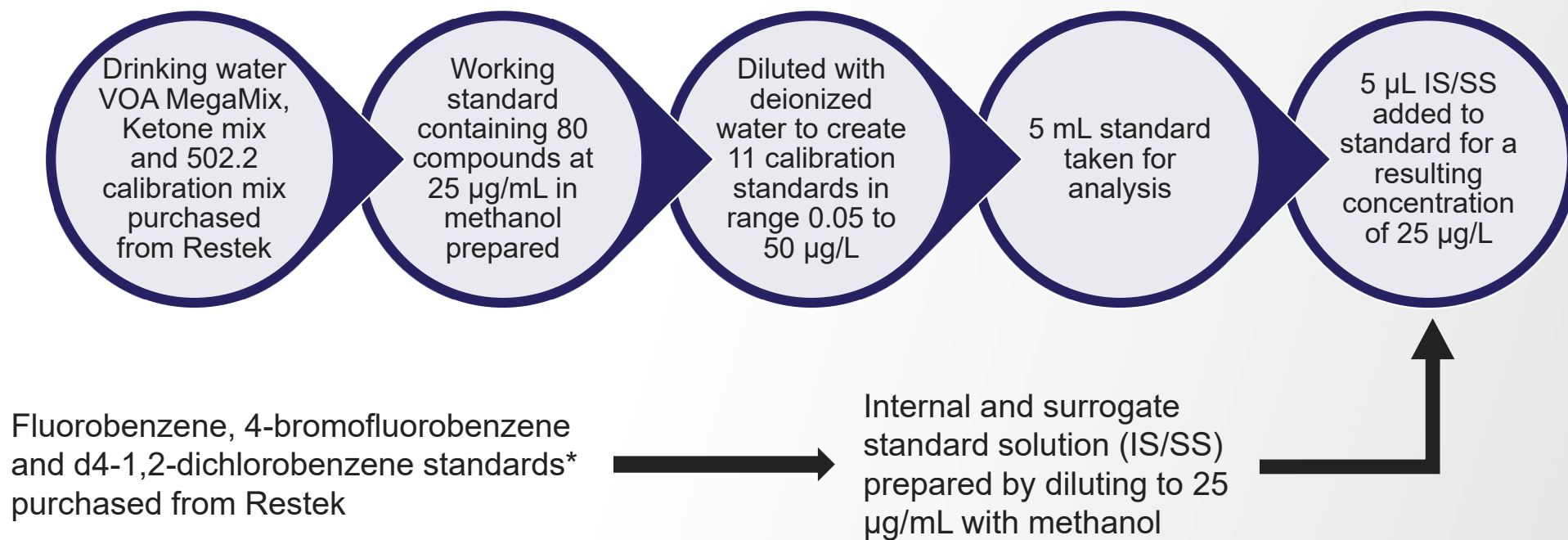
- **Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS)**

- Manage both the P&T and GCMS from one software
- Easy setup and reporting using eWorkflow™ procedures

## U.S. EPA 524.2 Outline

- Analysis of 80 VOCs
- Purge 5 mL sample for 11 minutes at 40 mL/min with a 4 min desorb time
- Response factor RSD must be <20%
- MDLs determined using 7 low level standards
- Initial demonstration of capability (IDC) shown using 7 mid-level standards
  - Accuracy 80-120%
  - RSD <20%
- Calibration check standard every 12 hours

# Standard Preparation



\*Fluorobenzene used as internal standard, 4-bromofluorobenzene and d4-1,2-dichlorobenzene used as surrogates

# U.S. EPA 524.2 Instrument Parameters

Standby	Variable	Desorb	Variable
Valve Oven Temp	140 °C	Methanol Needle Rinse	Off
Transfer Line Temp	140 °C	Methanol Needle Rinse Volume	0.00 mL
Sample Mount Temp	90 °C	Water Needle Rinse Volume	7.00 mL
Transfer Line Temp	140 °C	Methanol Needle Rinse Volume	0.00 mL
Sample Vial Temp	20 °C	Desorb Preheat Temp	245 °C
Soil Valve Temp	100 °C	GC Start Signal	Begin Desorb
Standby Flow	10 mL/min	Desorb Time	4.00 min
Condensate Ready Temp	45 °C	Drain Flow	300 mL/min
Purge Ready Temp	40 °C	Desorb Temp	250 °C
Purge	Variable	Bake	Variable
Sample Equilibrate Time	0.00 min	Methanol Glass Rinse	Off
Pre-sweep Time	0.25 min	Number of Methanol Glass Rinses	0
Prime Sample Fill Volume	3.00 mL	Methanol Glass Rinse Volume	0.00 mL
Sample Volume	5.00 mL	Water Bake Rinses	1
Sweep Sample Time	0.25 min	Water Bake Rinse Volume	7.00 mL
Sweep Sample Flow	100 mL/min	Bake Rinse Sweep Time	0.25 min
Spurge Vessel Heater	Off	Bake Rinse Sweep Flow	100 mL/min
Spurge Vessel Temp	20 °C	Bake Rinse Drain Time	0.40 min
Pre-purge Time	0.00 min	Bake Time	2.00 min
Pre-purge Flow	0 mL/min	Bake Flow	200 mL/min
Purge Time	11.00 min	Bake Temp	280 °C
Purge Flow	40 mL/min	Condensate Bake Temp	180 °C
Purge Temp	20 °C		
Condensate Purge Temp	20 °C		
Dry Purge Time	1.00 min	Trap	K
Dry Purge Flow	100 mL/min	Chiller Tray	Off
Dry Purge Temp	20 °C	Purge Gas	Nitrogen

## Thermo Scientific TRACE 1310 GC conditions

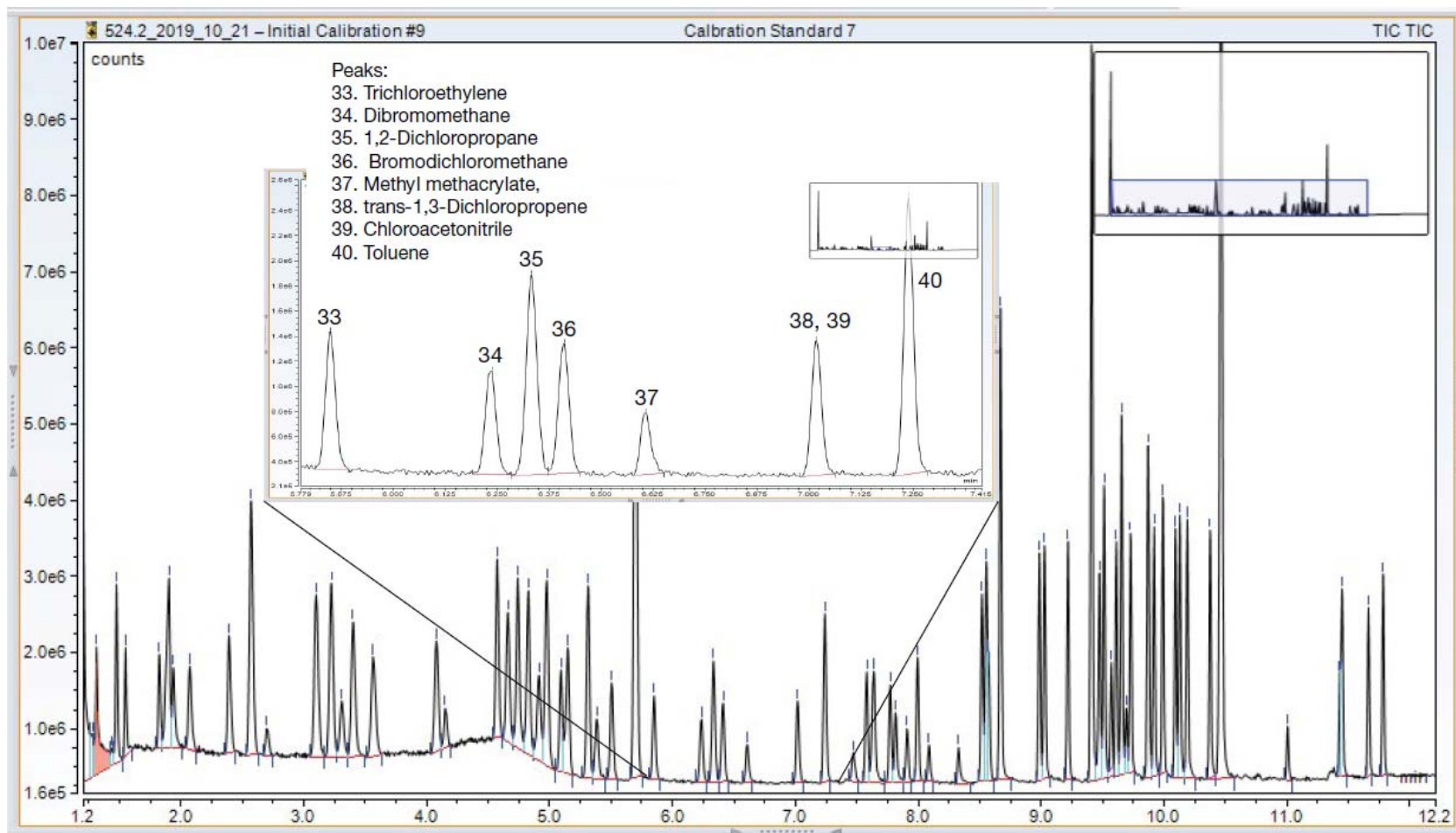
Column	Rtx® VMS, 20 m × 0.18 mm 1 µm film
Carrier gas	Helium – 0.8 mL/min constant flow
Oven temperature	35 °C, 3 min 12 °C/min to 85 °C 25 °C/min to 225 °C 2 min Hold Run time 14.767 min
Inlet temperature and injection mode	SSL, 200 °C, 50:1 split

## Thermo Scientific ISQ 7000 MS conditions

Transfer line temperature	230 °C
Ion source temperature	280 °C
Acquisition mode	Full scan 35 <i>m/z</i> to 260 <i>m/z</i> Solvent delay 0.50 min Dwell time 0.15 s
Emission current	25 µA Gain 1.00E+005



# U.S. EPA 524.2 Results



# U.S. EPA 524.2 Results

## Calibration and sensitivity results

- Response factor %RSDs at or below 10% for 33 of the 80 target compounds. All were <20%
- MDLs below 0.25 ppb for ALL compounds and below 0.15 ppb for 60 of 80 compounds
- IDC achieved with all compounds having recovery of 100±20% except for iodomethane and <20% RSD of recovery

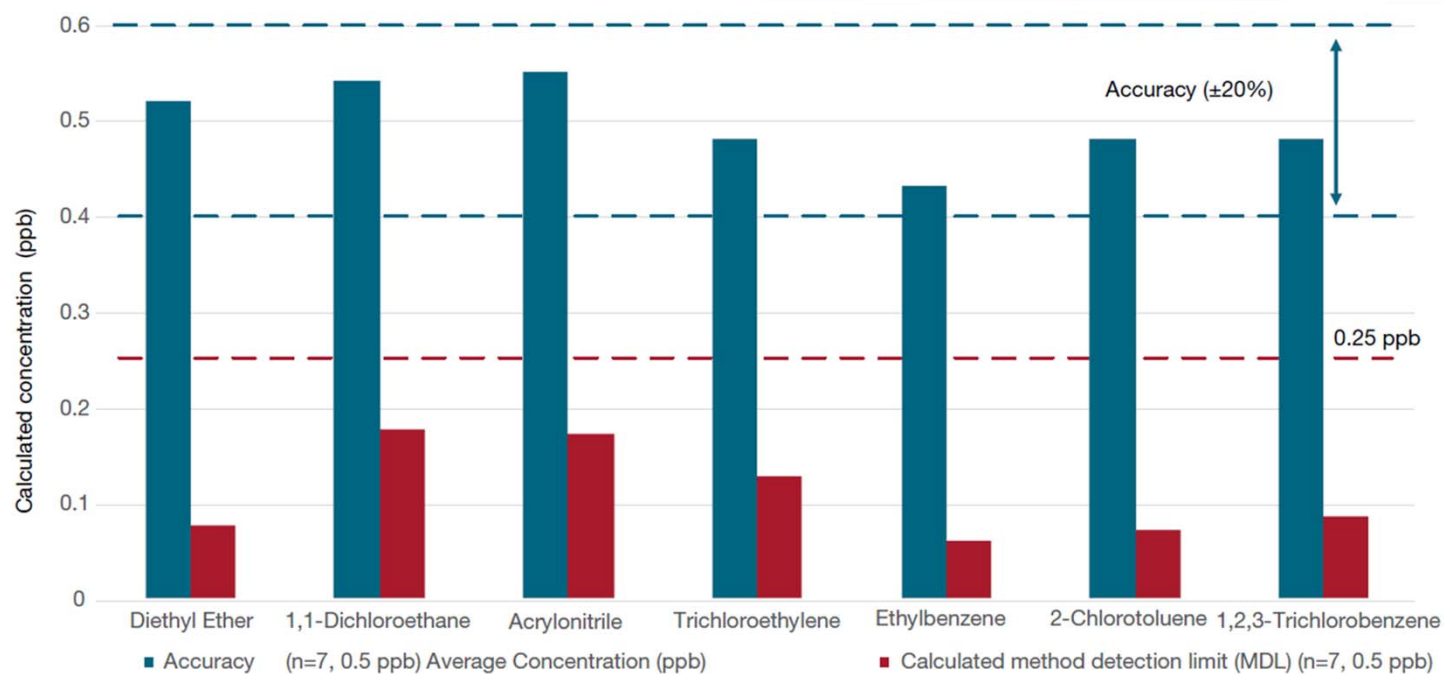
Compound	Calibration		MDL	
	%RSD	Avg RF	(ppb)	%RSD
Dichlorodifluoromethane	14.7	0.46	0.15	8.9
Chloromethane	19.1	1.28	0.17	9.5
Vinyl Chloride	15.2	0.64	0.21	13.0
Bromomethane	19.2	0.52	0.21	9.7
Chloroethane	10.0	0.56	0.13	7.8
Trichlorofluoromethane	18.6	0.57	0.19	11.2

Compound	Calibration		MDL	
	%RSD	Avg RF	(ppb)	%RSD
Methyl-tert-butyl-Ether	14.3	0.91	0.08	4.9
1,3-Dichlorobenzene	12.1	0.61	0.09	6.2
1,4-Dichlorobenzene	11.4	0.58	0.10	6.7
1,2-Dichlorobenzene	8.9	0.65	0.11	6.9
Bromobenzene	8.1	0.70	0.15	8.2
2-chlorotoluene	6.0	0.93	0.07	4.9
4-chlorotoluene	11.7	0.99	0.10	8.0
1,2,4-Trimethylbenzene	19.3	0.92	0.13	10.5
sec-Butylbenzene	19.6	1.13	0.10	8.6
Nitrobenzene	13.7	0.03	0.16	11.0
1,2,4-Trichlorobenzene	11.4	0.28	0.17	9.4
Naphthalene	6.2	0.79	0.09	5.8
1,2,3 Trichlorobenzene	9.2	0.33	0.09	5.7

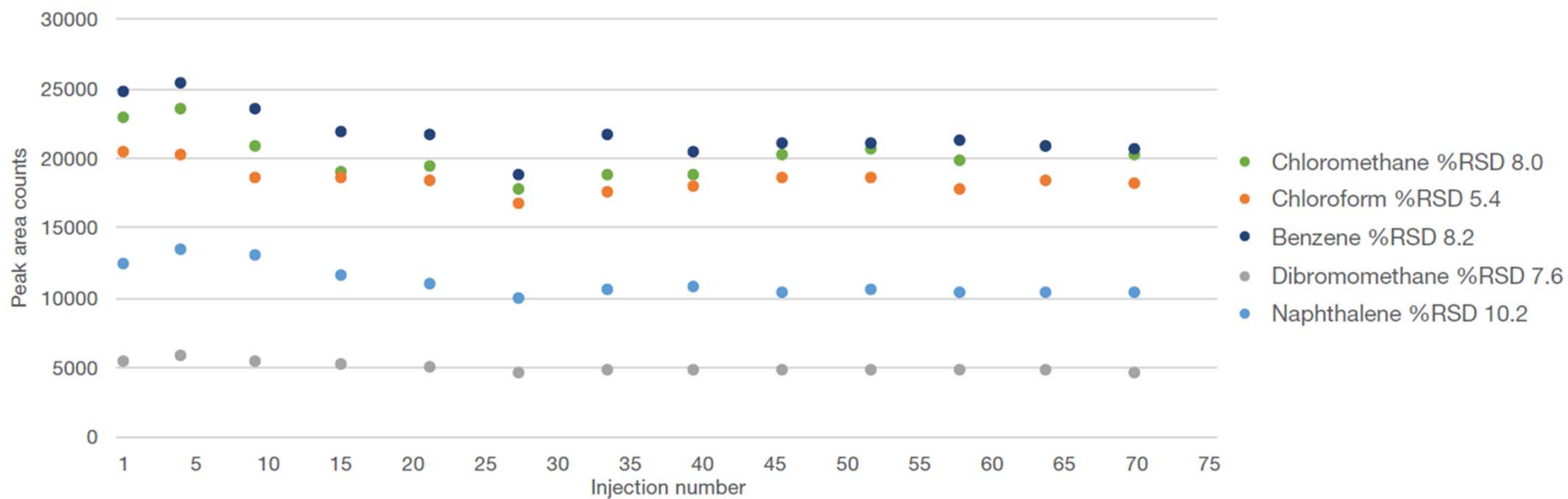
# U.S. EPA 524.2 Results

## Precision and accuracy results

- IDC achieved with all compounds having recovery of  $100 \pm 20\%$  except for iodomethane and  $<20\%$  RSD of recovery



# U.S. EPA 524.2 Results



## Transitioning from U.S. EPA 524.2



**U.S. EPA 524.2**

**U.S. EPA 524.4**



## U.S. EPA 524.4 Differences

- Analysis of 75 VOCs
- More flexibility with method parameters but stricter QC requirements
- Response factor RSD must be <20%
- MDLs determined using 7 low level standards
- Initial demonstration of capability (IDC) shown using 7 mid-level standards
  - Accuracy 80-120%
  - RSD <20%
- Calibration check standard every 12 hours

## U.S. EPA 524.4 Differences

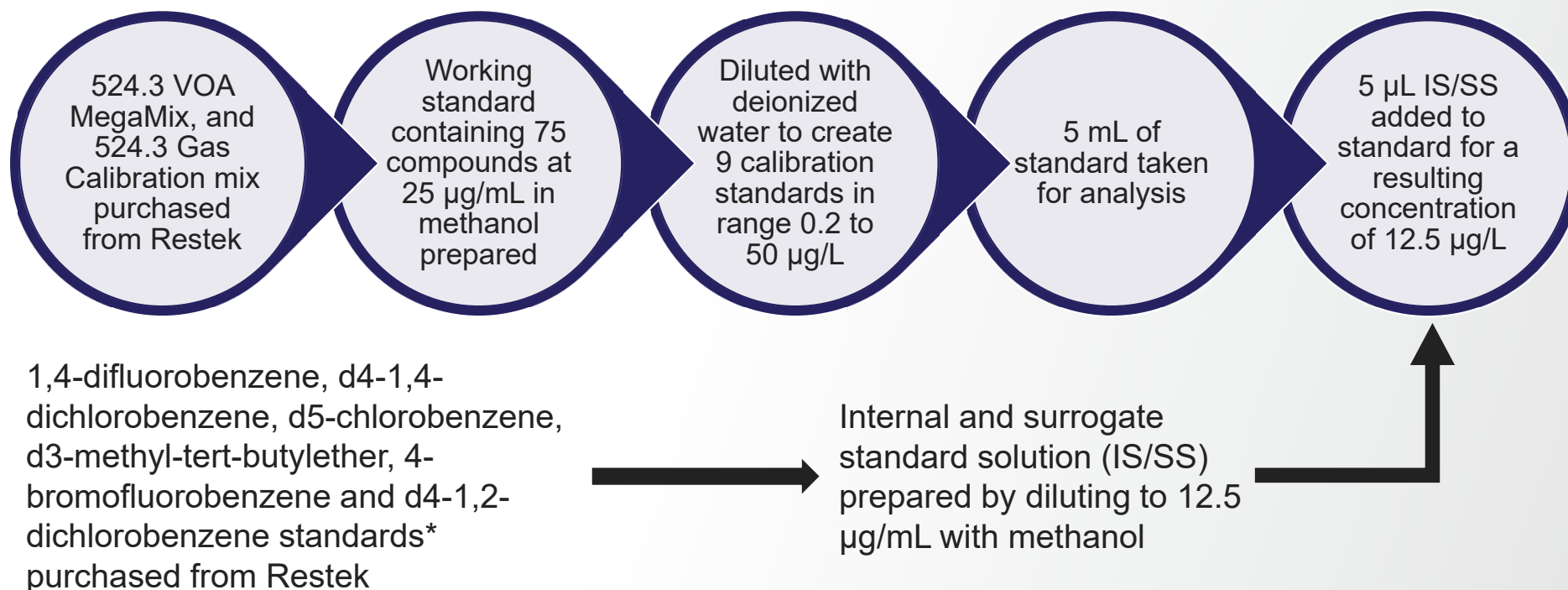
- BFB (Bromofluorobenzene) criteria changes – 50 and 75 m/z removed
- MS Tune Check (BFB) prior to Initial Calibration and after MS Maintenance
  - Daily BFB analysis is not required

**TABLE 1. 4-BROMOFLUOROBENZENE (BFB) MASS INTENSITY CRITERIA**

<i>m/z</i>	Required Intensity (relative abundance)
95	Base peak, 100% relative abundance
96	5 to 9% of <i>m/z</i> 95
173	Less than 2% of <i>m/z</i> 174
174	Greater than 50% of <i>m/z</i> 95
175	5 to 9% of <i>m/z</i> 174
176	Greater than 95% but less than 105% of <i>m/z</i> 174
177	5 to 10% of <i>m/z</i> 176

## Standard Preparation

\* 1,4-difluorobenzene, d4-1,4-dichlorobenzene, d5-chlorobenzene used as internal standard, d3-methyl-tert-butylether, 4-bromofluorobenzene and d4-1,2-dichlorobenzene used as surrogates



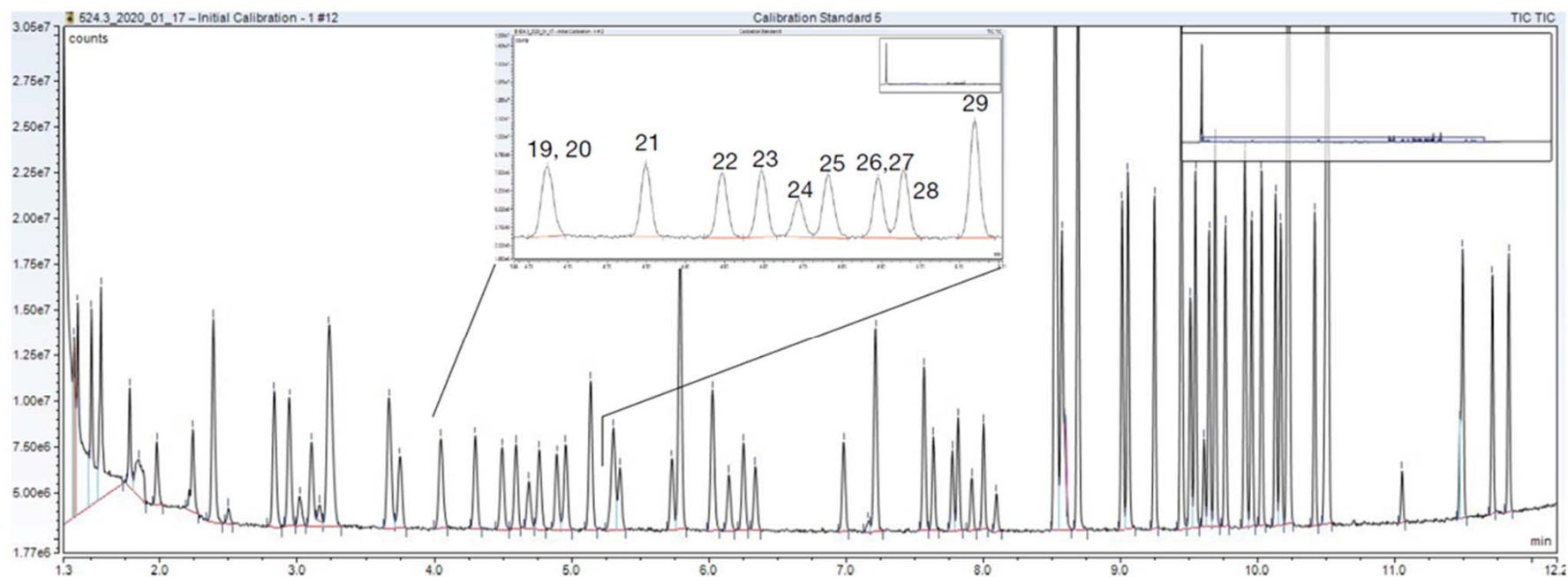
# U.S. EPA 524.4 Method

Standby	Variable	Desorb	Variable
Valve oven temperature	140 °C	Methanol needle rinse	Off
Transfer line temperature	140 °C	Methanol needle rinse volume	0.00 mL
Sample mount temperature	90 °C	Water needle rinse volume	7.00 mL
Water heater temperature	90 °C	Sweep needle time	0.25 min
Sample vial temperature	20 °C	Desorb preheat temperature	245 °C
Soil valve temperature	100 °C	GC start signal	Begin Desorb
Standby flow	10 mL/min	Desorb time	1.00 min
Purge ready temperature	40 °C	Drain flow	300 mL/min
		Desorb temperature	250 °C
Purge	Variable	Bake	Variable
Sample equilibrate time	0.00 min	Methanol glass rinse	Off
Pre-sweep time	0.25 min	Number of methanol glass rinses	0
Prime Sample fill volume	3.00 mL	Methanol glass rinse volume	0.00 mL
Sample volume	5.00 mL	Water bake rinses	1
Sweep sample time	0.25 min	Water bake rinse volume	7.00 mL
Sweep sample flow	100 mL/min	Bake rinse sweep time	0.25 min
Spurge vessel heater	Off	Bake rinse sweep flow	100 mL/min
Spurge vessel temperature	N/A	Bake rinse drain time	0.40 min
Pre-purge time	0.00 min	Bake time	6.00 min
Pre-purge flow	0 mL/min	Bake flow	200 mL/min
Purge time	5.50 min	Bake temperature	280 °C
Purge flow	80 mL/min	Condensate bake temperature	180 °C
Purge temperature	20 °C		
Condensate purge temperature	20 °C		
Dry purge time	0.00 min	Trap	K
Dry purge flow	0 mL/min	Chiller tray	On
Dry purge temperature	20 °C	Purge gas	Nitrogen

Parameter	Value
<b>TRACE 1310 GC</b>	
Column	TraceGOLD TG-VMS, 20 m x 0.18 mm, 1 µm film Carrier gas: helium @ 1 mL/min
Oven temperature program	35 °C, 3 min, 12 °C/min to 85 °C, 25 °C/min to 225 °C, 2 min hold Run time 14.8 min
Inlet	200 °C, 50:1 split Purge flow 0.5 mL/min
<b>ISQ 7000 MS</b>	
	Transfer line 230 °C; Ion source 280 °C
Scan mode	Range: 35 amu to 260 amu; Solvent delay: 0.50 min Dwell/scan time: 0.15 s
Filament current	Emission current: 25 µA Detector gain: 3.00E+005

# U.S. EPA 524.4 Results

- |                              |                           |
|------------------------------|---------------------------|
| Peaks:                       | 24. Carbon tetrachloride  |
| 19. tert-butyl alcohol       | 25. Tetrahydrofuran       |
| 20. tert-butyl ethyl ether   | 26. 1,1,1-trichloroethane |
| 21. trans-1,2-dichloroethene | 27. 1,1-dichloropropene   |
| 22. Bromochloromethane       | 28. 1-chlorobutane        |
| 23. Chloroform               | 29. Benzene               |





# U.S. EPA 524.4 Results

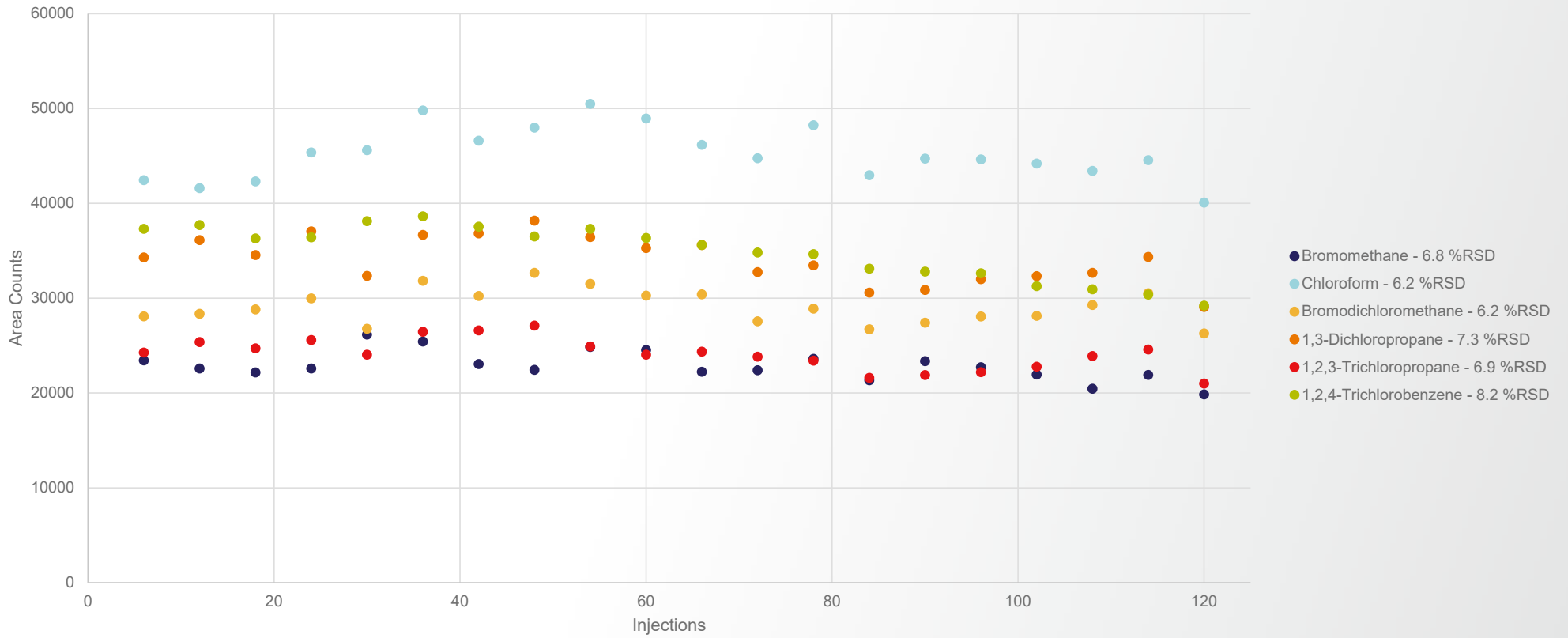
## Calibration results

- $r^2 \geq 0.999$  for 40 of the 75 target compounds
- Only 4 target compounds had a quadratic calibration
- MDLs below 0.25 ppb for all compounds, except for Iodomethane and at or below 0.10 ppb for 45 of 75 compounds
- MRL confirmation for all compounds
- IDC criteria met with precision <9% RSD and recovery between 96-120%

Compound	Calibration		MDL		MRL Confirmation	
	$r^2$	Avg. RF	(ppb)	%RSD	LPIR ( $\geq 50\%$ )	UPIR ( $\leq 150\%$ )
Dichlorodifluoromethane	0.999	0.339	0.11	7.9	61	117
Chlorodifluoromethane	0.998	0.851	0.10	5.1	96	144
Chloromethane	0.999	1.27	0.14	9.9	53	121
Vinyl Chloride	0.998	0.470	0.11	6.0	91	148
1,3-Butadiene	0.999	0.415	0.13	7.0	84	149
Bromomethane	0.997	0.416	0.13	9.8	52	117
Trichlorofluoromethane	0.999	0.481	0.11	6.3	88	146

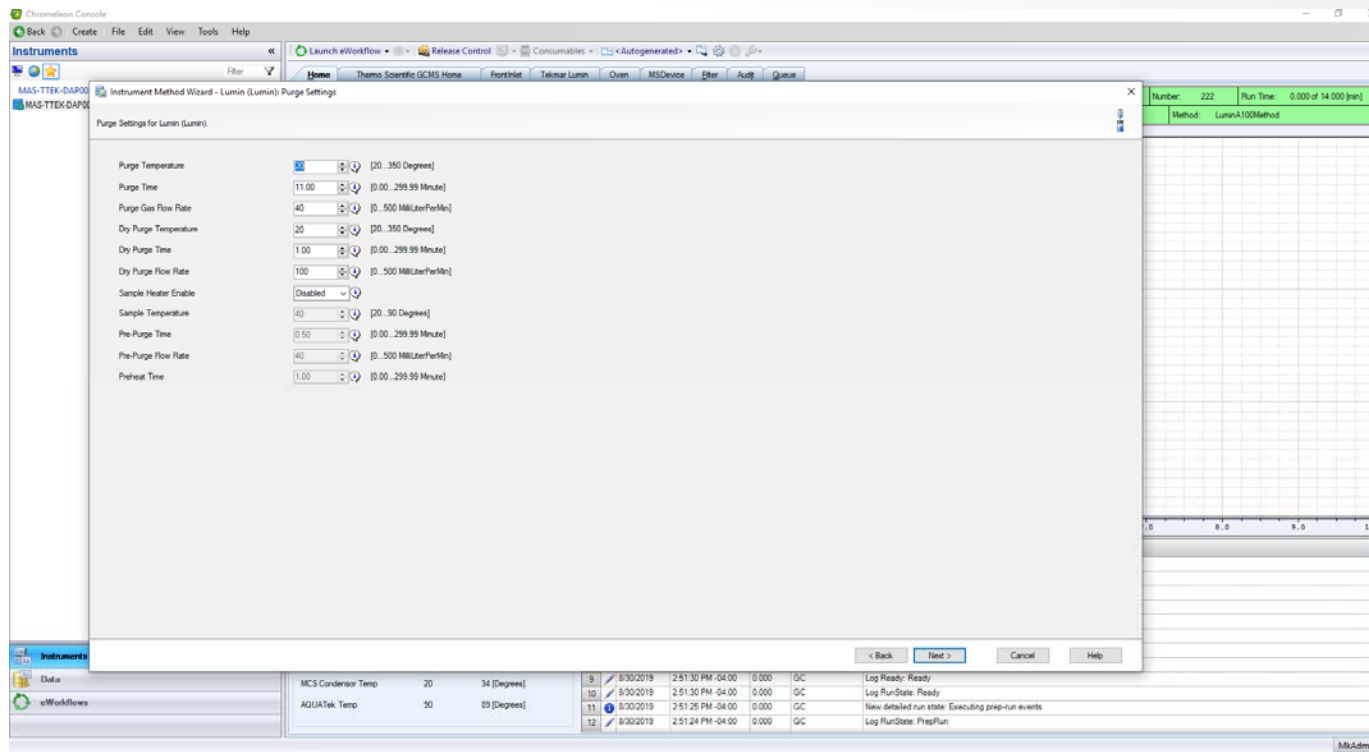
Compound	Calibration		MDL		MRL Confirmation	
	$r^2$	Avg. RF	(ppb)	%RSD	LPIR ( $\geq 50\%$ )	UPIR ( $\leq 150\%$ )
Methyl-tert-butyl-Ether	0.995	0.878	0.10	5.6	85	133
1,3-Dichlorobenzene	0.999	1.44	0.13	6.8	86	149
1,4-Dichlorobenzene	0.999	1.47	0.14	7.9	78	150
1,2-Dichlorobenzene	0.999	1.41	0.14	7.7	77	146
Bromobenzene	0.998	0.847	0.06	3.2	104	135
2-chlorotoluene	0.999	1.88	0.12	7.2	78	139
4-chlorotoluene	0.999	1.96	0.12	6.7	84	144
1,2,4-Trimethylbenzene	0.999	1.96	0.13	7.4	79	145
sec-Butylbenzene	0.999	2.50	0.13	8.0	72	139
1,2,4-Trichlorobenzene	0.995	0.922	0.19	10.2	86	147
Naphthalene	0.996	1.85	0.12	6.6	82	143
1,2,3 Trichlorobenzene	0.995	0.887	0.15	8.5	74	149

# U.S. EPA 524.4 Results



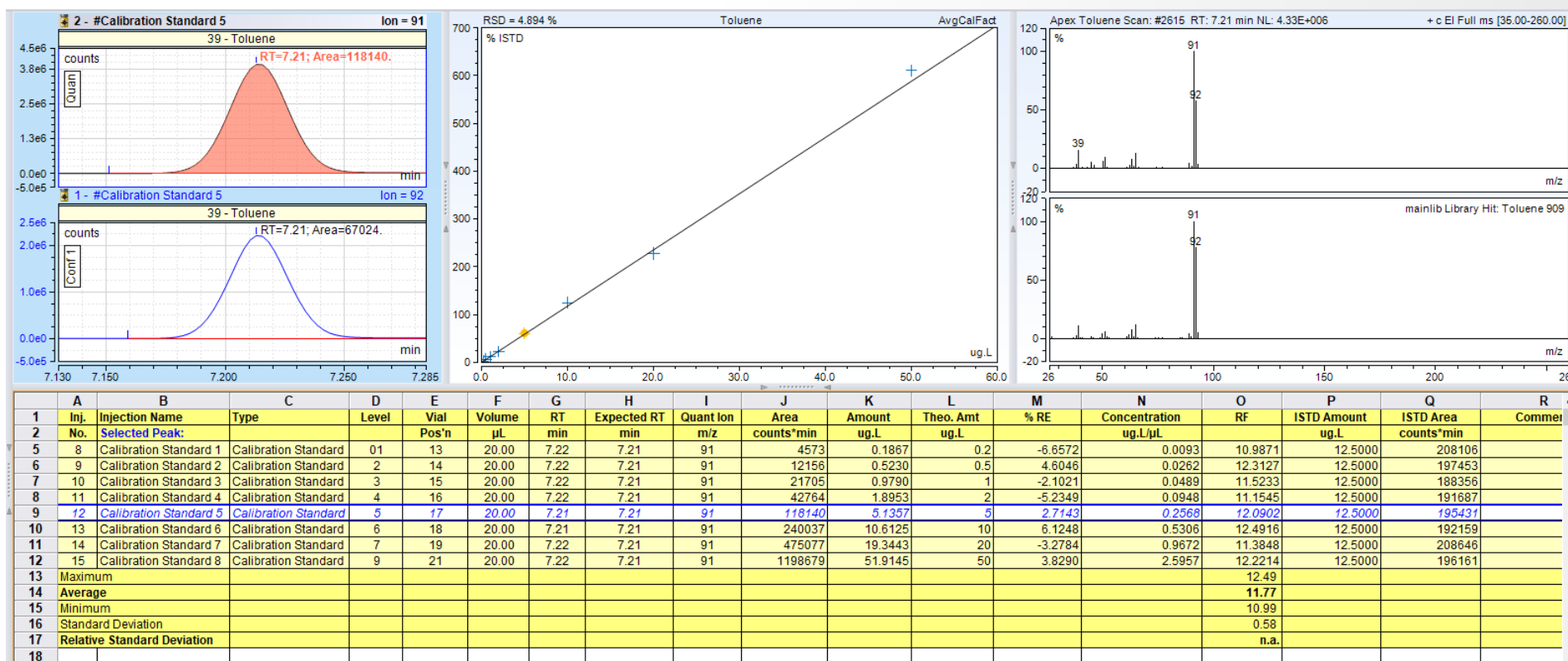
# Chromeleon CDS Benefits

- One Software Control for GCMS and Tekmar Purge and Trap



# Chromeleon CDS Benefits

- Data Review – at a glance



## Conclusions

- The combined analytical solution with the TRACE 1310 GC coupled to the ISQ 7000 MS system and the Atomx XYZ P&T system provides clear advantages for U.S. EPA Method 524.2 and EPA 524.4
- Combination of the Atomx XYZ P&T system, the TRACE 1310 GC and the ISQ7000 MS, addresses the challenges of VOC analysis, providing a robust, sensitive solution ensuring maximized instrument output and routine regulatory method compliance
- The system exceeds all the requirements outlined in U.S. EPA Methods 524.2 and 524.4 for analysis of purgeable VOCs in water
- Excellent calibrations were achieved meeting the  $r^2$  and response factor RSD requirements
- Excellent MDL, precision, accuracy and MRL confirmation was obtained showing no interference from excessive water and produced very reproducible results for both methods
- Instrument stability has been demonstrated over longer runs, ensuring consistent results can be obtained



# Application Notes AN65632 and AN73415

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APPLICATION NOTE 65632

## Routine analysis of volatile organic compounds in drinking water with ISQ 7000 GC-MS

Authors: Adam Ladak<sup>1</sup>, David Lee<sup>2</sup>, and Amy Nutter<sup>3</sup>

<sup>1</sup>Thermo Fisher Scientific, Groton, MA, USA

<sup>2</sup>Thermo Fisher Scientific, Runcorn, UK

<sup>3</sup>Teledyne Tekmar, Mason, OH, USA

Keywords: EPA 524.2, VOCs, drinking water, trace analysis, gas chromatography, single quadrupole mass spectrometry, purge and trap, sensitivity, THM, environmental laboratory, environmental sample analysis, contract laboratories

### Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA Method 524.2 for the quantitation of volatile organic compounds (VOCs) in drinking water, using a purge and trap (P&T) system coupled to a single quadrupole GC-MS. Method detection limit (MDL), linearity, precision, and accuracy were assessed to evaluate method performance.

### Introduction

U.S. EPA Method 524.2 is widely used in routine environmental analysis laboratories to test water samples for VOCs.<sup>1</sup> The method tests for a wide range of VOCs, including the four trihalomethane disinfection by-products that have sufficiently high volatility and low water solubility, to be removed from water samples with P&T procedures. Routine drinking water monitoring regulatory standards require contract testing labs to analyze for the presence of VOCs due to the potentially negative health effects associated with public water source contamination. It is



extremely important that routine laboratories ensure both accurate and rapid detection and quantitation of VOCs to ensure public safety.

There are several challenges that routine analysis laboratories face when performing U.S. EPA Method 524.2. Initially, laboratories must demonstrate achievement of method acceptance criteria including detection limit requirements for an assortment of compounds over a wide range of concentrations. The analytical method must be robust and reproducible to ensure consistent results are reported. Another significant challenge is the management of the moisture when analyzing water samples. Analysis of water samples can introduce moisture into the GC analytical column and cause damage if not properly managed. The resulting unplanned downtime of an analytical instrument can disrupt or delay sample reporting, which could in turn jeopardize the safety of a public water system.

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APPLICATION NOTE 73415

## Routine analysis of purgeable organic compounds in drinking water with ISQ 7000 GC-MS

Authors: Adam Ladak<sup>1</sup>, Terry Jeffers<sup>1</sup>, David Lee<sup>2</sup>, and Amy Nutter<sup>3</sup>

<sup>1</sup>Thermo Fisher Scientific, USA

<sup>2</sup>Thermo Fisher Scientific, Runcorn, UK

<sup>3</sup>Teledyne Tekmar, Mason, OH, USA

Keywords: EPA, VOCs, phthalates, trace analysis, gas chromatography, single quadrupole mass spectrometry, selected ion monitoring, sensitivity, GRO, THM, volatiles, environmental lab, environmental sample analysis, contract labs

### Goal

Demonstration of a routine analytical method that meets the requirements outlined in U.S. EPA Method 524.4 for the quantitation of purgeable organic compounds (POCs) in drinking water, using the Teledyne Tekmar Atorx XYZ purge and trap (P&T) system along with a Thermo Scientific<sup>®</sup> ISQ<sup>™</sup> 7000 Mass Spectrometry (MS) system coupled with a Thermo Scientific<sup>™</sup> TRACE<sup>™</sup> 1310 Gas Chromatograph (GC) along with a single software control for the entire system, the Thermo Scientific<sup>™</sup> Chromeleon<sup>™</sup> Chromatography Data System (CDS). Method linearity, method detection limit (MDL), precision, accuracy, and minimum reporting level (MRL) confirmation were assessed to evaluate method performance.



### Introduction

It is essential that routine environmental laboratories monitor drinking water for the presence of purgeable organic compounds. POCs have the potential to cause negative health effects when consumed. EPA Method 524.4 is used in environmental analysis labs to test water samples for volatile organic compounds (VOCs).<sup>1</sup> It is extremely important that routine laboratories accurately detect and quantitate VOCs to ensure water is safe for the public. This method is a revised version of EPA Method 524.2 on which more details can be found here. Due to technological advances in analytical instrumentation and techniques, this method allows the analyst to modify P&T parameters and GC/MS conditions. This can result in reduced sample run time and increased laboratory throughput in a 12-hour period.

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# Thank you

