



The Evolution of 8260

AGENDA

- 1 Overview of 8260**
- 2 Automated Sampling and Purge/Trap Advancements**
- 3 GC/MS Advancements**
- 4 Utilizing Advancements for Industry Needs**

QUICK OVERVIEW OF EPA METHOD 8260

Volatile Organic Compounds (VOCs) by Gas Chromatography-Mass Spectrometry

- Applicable to nearly all types of samples regardless of water content
- Able to analyze over 100 different compounds
- Various techniques for sample introduction
 - Direct Injection
 - Cryofocusing
 - Headspace
 - Purge/Trap* (EPA Method 5030 for water and 5035 for soils)

*Will focus on Purge and Trap technique for this presentation

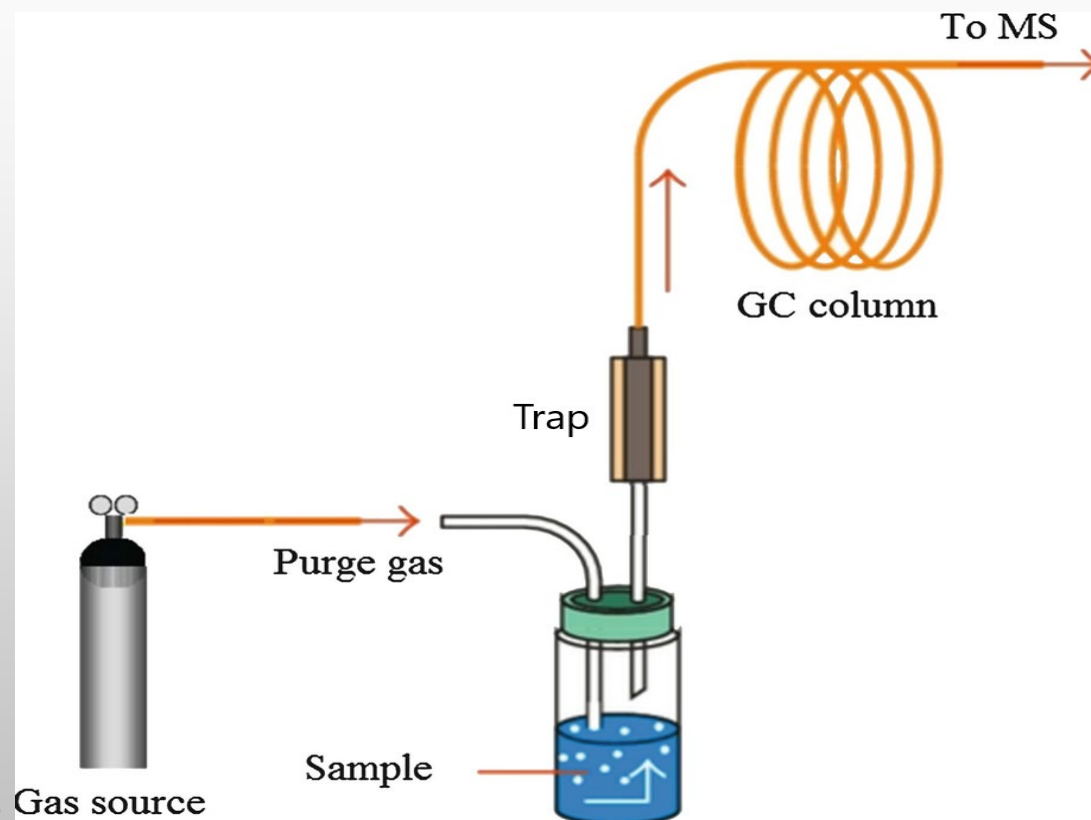
Overview of 8260 continued

Definition of Purge/Trap:

- An analytical technique designed to efficiently extract VOCs from a matrix and concentrate them for transfer onto a GC analytical column without sacrificing peak shape, recovery, or accuracy.

How is that extraction done?

- An inert gas is bubbled through a portion of the aqueous sample at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column (trap) where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.
- For soils: An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.



--Simple schematic of Purge and Trap

Overview of 8260 Continued

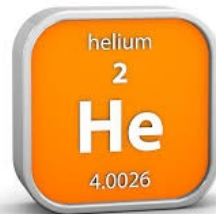
Issues with 8260 by Purge and Trap:

- Water

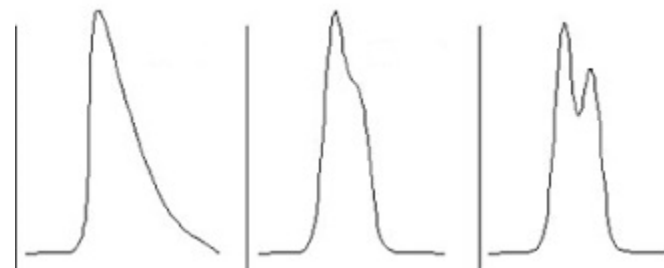


- Poor performers/Problem compounds

- Inert Gas



- Time





Should

HOW DO WE OVERCOME MANY OF THE
ISSUES THAT HAVE PLAGUED METHOD
8260?

Looking at Improvements in chemical testing equipment Technology





ENVIRONMENT. LIFE. SERVICE.

Automated Sampling and Purge/Trap Advancements

Automated Sampling has come a long way...



Tekmar ALS 2016



Varian/OI Archon



Tekmar Solatek 72



Tekmar Aquatek 70



Tekmar Aquatek 100



Tekmar Atomx



EST Centurion



Tekmar Aquatek LVA

Automated Sampling Advancements

- No longer have to hand load samples into sparge tubes
- In-line “Ink Jet” style Internal Standard and Surrogate addition
- Sample capacity has increased.
- Dual sample type automated samplers can run water or soil samples (purge in vial).
- In-line sample dilution capabilities.
- In-line sample pH recording
- Time saved on sample transfer with latest software that easily communicates between sampler and GC/MS
- More efficiently engineered automated samplers
- Can use nitrogen as a carrier gas.
- Scheduling and keeping track of sample runs has been made easier

From the Sampler to the Concentrator...



Tekmar 3000



Tekmar 3100



Tekmar Stratum



Tekmar Lumin



OI Eclipse 4550



OI Eclipse 4650



OI Eclipse 4750



EST Encon



EST Evolution



EST Evolution 2



Sample Concentrator Advancements

- **Moisture Management**

Removing water from the sampling process is one of the biggest keys to getting good chromatography.

--Concentrator moisture trapping systems have evolved over time to increase water removal during the desorbing process that sends the sample to the GC.

--Sorbent trap material has also become better at retaining problem compounds and keeping samples moisture free.

--Heated zone control has become more advanced with upgraded software capable for controlling and monitoring all areas of the concentrator that require high temps to keep moisture out of the concentrating process.

--Bake program capabilities that allow time and bake flows to be set to help reduce carryover and keep the system moisture free.

Sample Concentrator Advancements

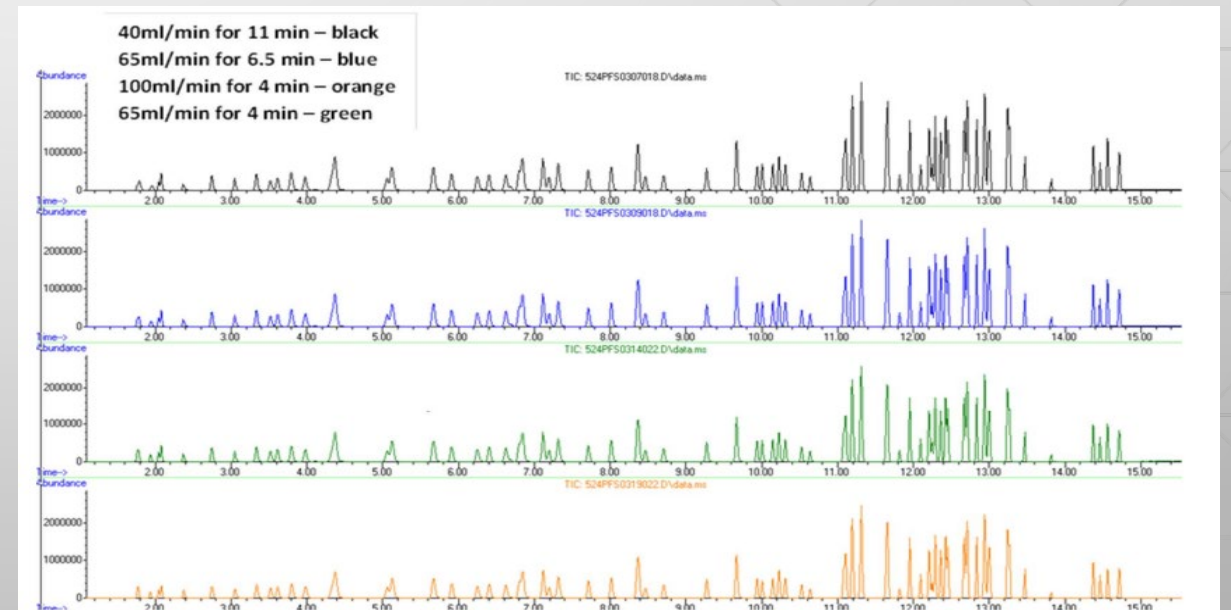
- **FLOW CONTROL AND THE USE OF NITROGEN AS A PURGE GAS**

--Flow control is no longer manual and is controlled electronically, allowing for leak checking and trouble shooting through software that monitors flow.

--Concentrators have settings to use Nitrogen as a purging/carrier gas. This allows labs to save on Helium usage.

--Flow control has allowed for quicker more efficient purge times. Higher purge flow equals lesser purge time. Decreases run time and increases sample capacity. Studies have shown that increasing flow and reducing purge time has minimal effect on compound recoveries.

Purge Flows and Times	Avg. Curve Quadratic Regression	Avg. Curve RF	Avg. Upper PIR (prediction interval of results) (0.5µg/L)	Avg. Lower PIR (prediction interval of results) (0.5µg/L)	Avg. % Recovery (20µg/L)	Avg. Precision, %RSD (20µg/L)
40ml/min for 11min	1.000	1.110	110.23	81.65	103.57	4.03
65ml/min for 6.5 min	0.999	1.220	116.53	83.31	95.11	4.66
100ml/min for 4 min	0.999	1.273	105.73	68.57	95.85	5.22
65ml/min for 4 min	0.999	1.001	112.79	76.89	105.27	2.82



Sample Concentrator Advancements

- Updated Software

The screenshot shows the 'Run Setup' interface for the EST Centurion Purge and Trap Autosampler. The software title bar includes 'EST analytical Centurion Purge and Trap Autosampler' and a 'Default' dropdown menu. The interface is divided into several sections:

- Concentrator Start Selection:** Radio buttons for 'Concentrator #1' (selected) and 'Concentrator #2'.
- Concentrator Recycle Selection:** Checkboxes for 'Concentrator #1 Cycles' and 'Concentrator #2 Cycles', both set to 1.
- Error Setup:** Checkboxes for 'Stop On No Vial', 'Automatic Correction', 'Correct Entire Sample Table', 'Disable Soil Vial Check', and 'Disable Syringe Position Check'.
- GC Selection:** A dropdown menu set to 'Dual GC'.
- Bottom Panel:** A table for sample runs and control buttons.

Start Vial	1	Insert	Delete	Priority
# of Vials	1	Select Method	Water Syringe 5ml IS1 5ul	
# of Blanks	0	Dilution	None	Extraction None
Runs Per Vial	1	Enter Description	Description	

The screenshot shows the 'System Setup' interface for the EST Centurion Purge and Trap Autosampler. The software title bar includes 'EST analytical Centurion Purge and Trap Autosampler'. The interface is divided into several sections:

- Operation Selection:** Radio buttons for 'Remote Operation' (selected) and 'Local Operation'.
- Chiller Temperature Alarm:** Checkboxes for 'Enable Alarm', 'Stop Sequence', and 'Continue Sequence'. The 'Set Point (°C)' is set to 45.
- Select Language / Locale:** A dropdown menu set to 'Locale en-US'.
- Save Button:** A prominent 'Save' button at the bottom.

EST concentrator software



Sample Concentrator Advancements

Other upgrades

- ❖ Heated Purge
 - Allows sample to remain same temperature regardless of room temperature. Temperature fluctuations during purge step can affect recovery of compounds.
- ❖ Foam Detection
 - A sensor in the sparge tube will detect if a sample begins to foam and fill the sparge tube which can be detrimental to a concentrator. Once detected, it shuts the concentrator and autosampler down.
- ❖ Hot Water Rinse
 - Concentrators are now capable of rinsing the sparge tube with hot water from a reservoir that is included on the concentrator. This helps reduce carry over and keep the sparge tube clean.
- ❖ Smaller and better engineered designs
 - Newer concentrators are smaller, which takes up less bench space, and even stackable (Lumin). Sample pathways have also been reduced, making troubleshooting and maintenance much easier.



ENVIRONMENT. LIFE. SERVICE.

GC/MS ADVANCEMENTS

Desorbed to the GC....



HP/Agilent 4890



HP/Agilent 5890



HP/Agilent 6820



Agilent 6850



Agilent 6890



Agilent 7890



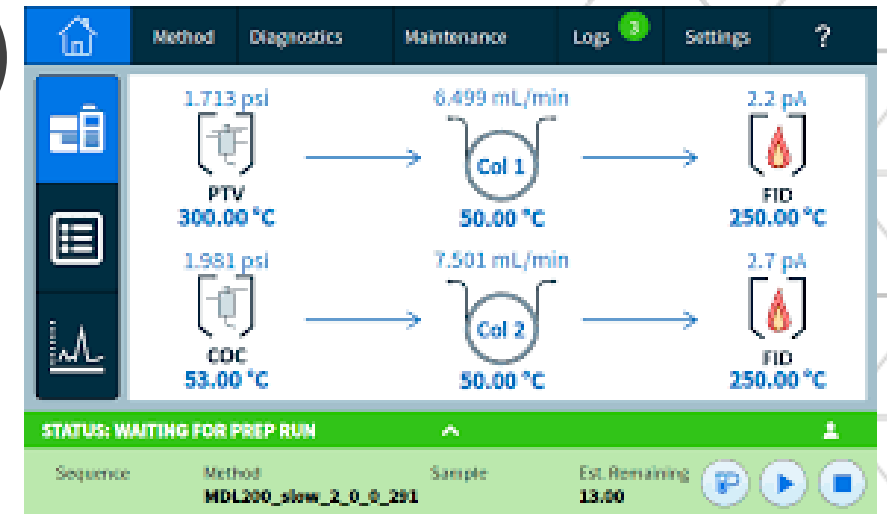
Agilent Intuvo 9000



Agilent 8890

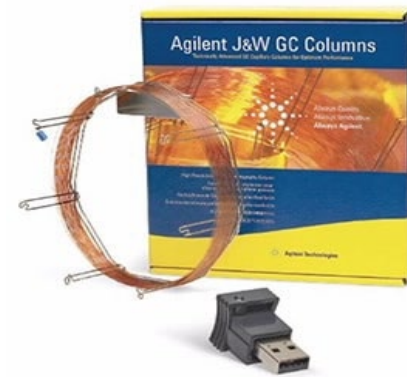
Advancements in GC Technology

- From touchpads to touchscreens
- Electronic Pressure Control (EPC)
- Compact Design



Advancements in GC technology

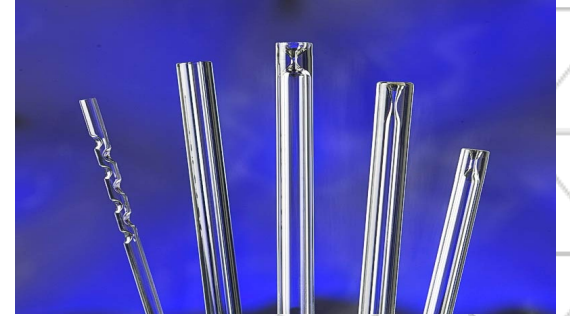
- Networking Capabilities
- Software upgrades
- Injection port design



Advancements in GC Consumables

➤ Injection Port Liners

--Liners have become more inert and proprietary coatings have helped with compound recovery and chromatography



➤ Columns

--Advancements in column production have allowed for micro capillary sizes and widths. Capillary column coatings have also been optimized specifically for method 8260.

--Shorter length columns have decreased GC run times.



Separated by the GC Analyzed by the Mass Spec



Artisan Technology Group

HP/Agilent 5970



HP/Agilent 5971



HP/Agilent 5972



Agilent 5973



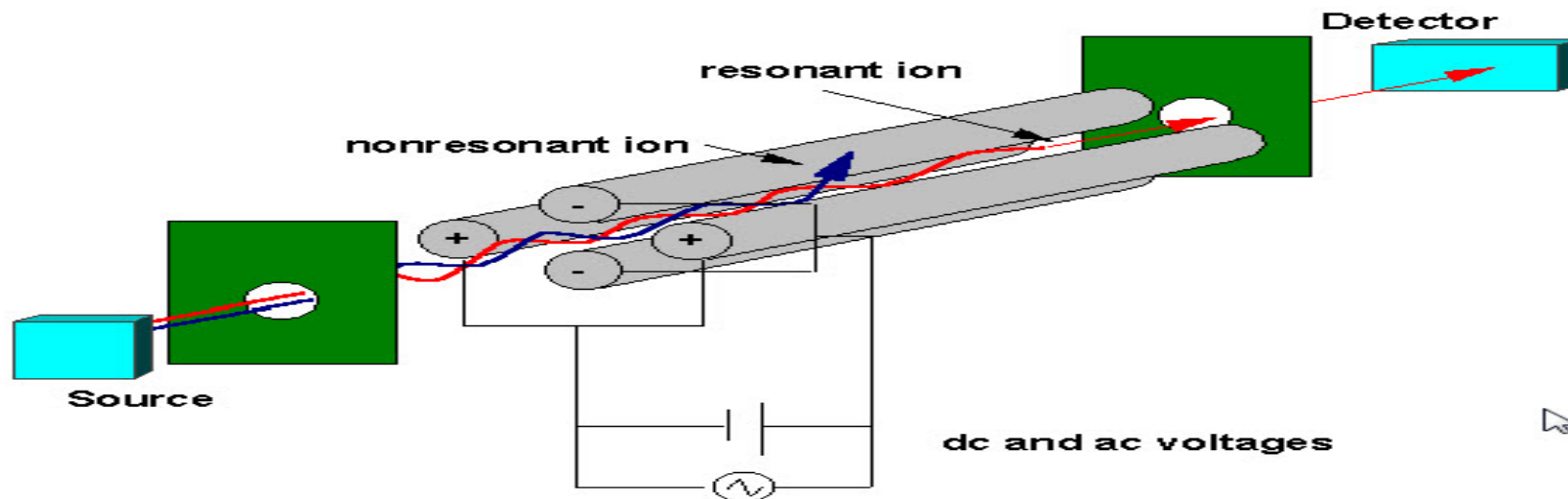
Agilent 5975



Agilent 5977

Advancements in Single Quadrupole Mass Spec Technology

In the last few decades, improvements in mass spectrometry (MS) have continued to improve drastically. Changes in quantitative accuracy, MS resolution, and data processing abilities have helped push the environmental testing industry to new heights.



Advancements in Single Quadrupole Mass Spec Technology

Source Improvements

- Stainless Steel
 - Source will work for method 8260, but advancement in source types have had great effects in testing efficiency for the method.
- Inert Ion Source
 - For high sensitivity and accurate quantitation the sample path must be highly inert including the detector surfaces. This source offers added inertness.
- Extractor EI Source
 - Has an extractor lens in place of a draw out plate made of inert material, providing enhanced response for active compounds and late eluters, and maximum, ultra-trace level sensitivity.

Advancements in Single Quadrupole Mass Spec Technology

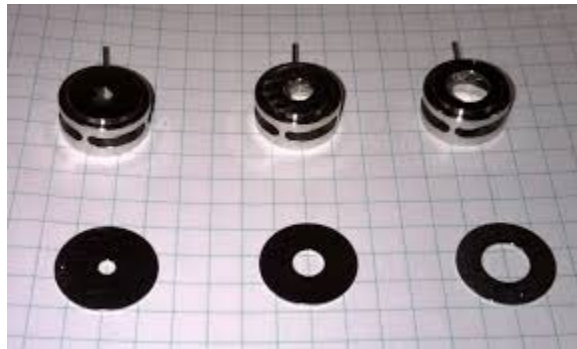
Draw Out Lens Size for the source

Draw out lenses now come in a variety of sizes

--3, 6, and 9 mm are available for use in most sources

--The 6 mm draw out lens has shown to be a more robust option for method 8260.

--The 6 mm lens showed better %RSD recoveries in calibration curves for method 8260, especially on poor responding compounds.



Advancements in Single Quadrupole Mass Spec Technology

Draw out lens size study results

Compound	USEPA Method 8260b		
	6mm Draw-out lens	3mm Draw-out lens	6mm Draw-out lens
	DB-VRX Column	DB-VRX Column	DB-624 Column
perfluorobenzene (IS)			
fluorobenzene (IS)	N/A	N/A	N/A
dichlorodifluoromethane	10.38	9.08	10.21
chloromethane	11.19	9.24	3.66
vinyl chloride	7.14	10.65	6.21
bromomethane	12.38	11.47	11.91
chloroethane	4.49	10.24	11.96
trichlorofluoromethane	7.18	7.51	4.71
diethyl ether	5.75	3.13	4.00
1,1-dichloroethene	5.83	10.43	6.41
carbon disulfide	9.76	13.01	6.19
1,1,2-trichlorofluoroethane	5.89	9.48	3.91
iodomethane	11.44	10.74	9.40
allyl chloride	9.32	7.17	10.69
methylene chloride	6.18	8.35	4.74
acetone	7.60	12.59	8.30
trans-1,2-dichloroethene	9.05	4.35	6.37
methyl acetate	9.86	10.50	12.14
MTBE	3.11	5.35	6.20
TBA	8.43	10.58	5.97
diisopropyl ether	8.49	4.24	10.44
chloroprene	8.81	9.20	7.04
1,1-dichloroethane	7.12	4.44	3.95
acrylonitrile	8.91	10.19	10.30
vinyl acetate	6.32	8.07	8.85
ETBE	6.63	3.81	3.61
cis-1,2-dichloroethene	7.26	3.52	5.03
2,2-dichloropropane	8.31	9.95	7.06
bromochloromethane	7.43	5.02	9.09
methacrylonitrile	N/A	N/A	N/A
chloroform	8.44	4.13	5.13
carbon tetrachloride	9.32	12.62	9.86
1,1,1-trichloroethane	6.99	8.66	2.10
THF	11.93	9.35	10.44
1-chlorobutane	N/A	N/A	N/A
dibromofluoromethane (surr)	10.58	4.12	4.44
methyl acrylate	7.69	11.40	11.77
1,1-dichloropropene	10.37	9.14	6.38
2-butanone (MEK)	9.38	8.82	12.56
benzene	5.04	7.25	3.14
propionitrile	4.75	5.82	9.12
tert amyl methyl ether (TAME)	4.80	6.02	4.58
1,2-dichloroethane	7.88	6.64	5.47
isobutyl alcohol	6.10	6.64	9.97
isopropyl acetate	7.83	9.80	8.32
trichloroethene	8.72	9.44	8.36
1,4-difluorobenzene (IS)			
dibromomethane	3.74	6.48	10.01
1,2-dichloropropane	9.94	8.65	4.49
bromodichloromethane	8.82	11.72	4.52

Compound	USEPA Method 8260		
	6mm Draw-out lens	3mm Draw-out lens	6mm Draw-out lens
	DB-VRX Column	DB-VRX Column	DB-624 Column
methyl methacrylate	6.16	8.49	11.94
chloroacetonitrile	N/A	N/A	N/A
n-propyl acetate	9.57	9.84	11.43
2-cleve	5.94	8.71	6.73
cis-1,3-dichloropropene	5.65	11.21	6.76
toluene-d8 (surr)	4.29	10.01	4.84
toluene	5.60	4.06	3.14
2-nitropropane	9.22	12.13	10.45
tetrachloroethene	11.70	7.30	8.56
1,1-dichloro-2-propanone	N/A	N/A	N/A
4-methyl 2-pentanone	9.99	11.52	9.91
1,1,2-trichloroethane	7.24	8.28	5.69
trans-1,3-dichloropropene	N/A	N/A	N/A
ethyl methacrylate	7.95	8.96	7.19
dibromochloromethane	9.74	11.21	8.76
1,3-dichloropropane	5.47	6.04	4.60
1,2-dibromoethane	7.94	11.41	6.94
n-butyl acetate	9.14	11.21	10.35
2-hexanone	3.32	7.47	11.41
chlorobenzene-d5 (IS)			
chlorobenzene	6.07	6.79	3.51
ethylbenzene	6.18	8.37	4.33
1,1,1,2-tetrachloroethane	9.76	10.21	3.98
m&p xylene	10.21	9.04	6.09
ortho xylene	9.00	5.27	2.47
styrene	10.36	4.55	6.28
bromoform	6.38	14.71	11.22
isopropylbenzene	8.62	6.50	6.91
n-amyl acetate	11.68	9.87	6.57
BFB (surr)	10.25	14.49	12.26
n-propylbenzene	8.44	8.65	10.93
1,2,3-trichloropropane	N/A	N/A	N/A
trans-1,4-dichloro-2-butene	9.66	9.78	0.999
nitrobenzene	11.94	0.995	0.997
bromobenzene	9.18	8.31	3.79
1,1,2,2-tetrachloroethane	9.13	9.59	6.26
1,3,5-trimethylbenzene	8.58	6.44	6.32
pentachloroethane	N/A	N/A	N/A
2-chlorotoluene	9.02	5.15	2.63
cis-1,4-dichloro-2-butene	9.11	13.98	7.82
4-chlorotoluene	7.67	10.03	6.76
tertbutylbenzene	10.04	4.35	6.55
1,2,4-trimethylbenzene	6.89	9.44	5.18
sec-butylbenzene	5.54	7.03	11.46
p-isopropyltoluene	9.39	7.44	10.24
1,3-dichlorobenzene	10.93	6.68	8.31

Compound	USEPA Method 8260		
	6mm Draw-out lens	3mm Draw-out lens	6mm Draw-out lens
	DB-VRX Column	DB-VRX Column	DB-624 Column
1,4-dichlorobenzene-d4 (IS)			
1,4-dichlorobenzene	9.01	8.63	8.98
1,2-dichlorobenzene-d4 (surr)	N/A	N/A	N/A
n-butylbenzene	5.38	5.75	12.44
1,2-dichlorobenzene	11.49	7.10	6.63
hexachloroethane	N/A	N/A	N/A
1,2-dibromo-3-chloropropane	7.62	14.53	12.46
hexachlorobutadiene	7.60	9.34	13.51
1,2,4-trichlorobenzene	8.49	3.12	12.03
naphthalene	3.76	6.56	9.83
1,2,3-trichlorobenzene	6.26	9.28	11.54

Method Optimization App Note.docx; 24-Mar-09
Teledyne Tekmar

Advancements in Single Quadrupole Mass Spec Technology

Electron Multiplier Advancements

- Triple Axis Detector Electron Multiplier
 - At a given operating gain, the new detector provides higher signal intensity by collecting more ions emerging from the quadrupole.
 - Although signal is enhanced, neutral noise is substantially reduced through the off-axis design.
 - Detector lifetime is also increased under proper operation.
- Provides many benefits during analysis
 - Enhanced detection limits
 - Increases in compound relative response ratios
 - Calibration curves with greater slopes
 - Lower tuning voltages, increasing lifetime of multiplier

Advancements in Single Quadrupole Mass Spec Technology

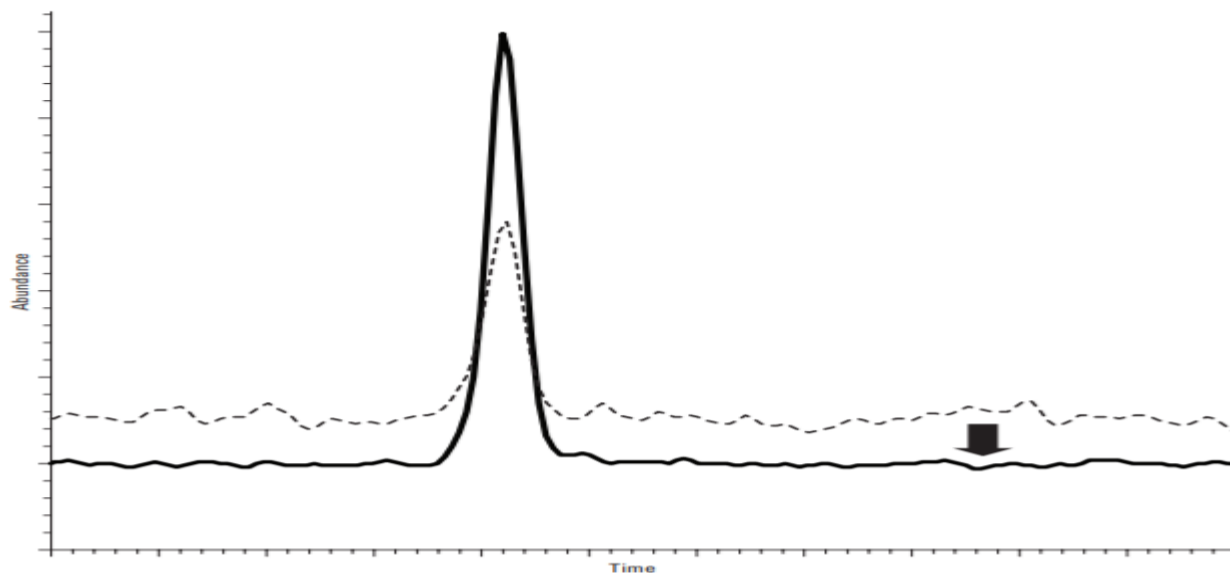
Electron Multiplier Advancements



Electron Multiplier



Triple Axis Detector Electron Multiplier



Signal to noise difference with Triple Axis Detector (dark black line)

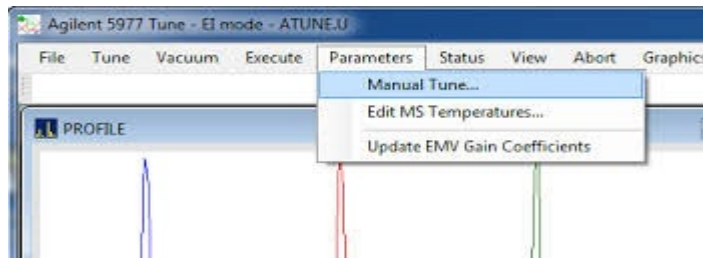
Advancements in Single Quadrupole Mass Spec Technology

Other Upgrades

- Diffusion Pumps to Turbo Pumps



- Software upgrades



- Newer mass spec analyzers can handle higher temperatures, which is helpful in resolution and removal of contaminants.

Advancements in Single Quadrupole Mass Spec Technology

Other upgrades

- GC/MS transfer line



- Source cleaning procedures and materials
- Magnetic Rough Pumps
- Mass production



WHAT DO ALL THESE
TECHNOLOGICAL
ADVANCEMENTS
MEAN FOR METHOD
8260?



Utilizing Advancements for Industry Needs

- Improvements in automated sampling, sample concentrators, and GC/MS throughout the years has led regulators to lower reporting limits on a number compounds.
 - Most labs now calibrate at sub part per billion (ppb) levels for all compounds.

Compound (all.sb)	0.200000	0.400000	1.0000	4.0000	10.0000	20.0000	Curve	b	Coefficients		%RSD or R^2
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6			m1	m2	
	50.0000 Level 7	100.0000 Level 8	250.0000 Level 9								
3 Vinyl chloride	0.27093	0.42045	0.46761	0.44523	0.46255	0.47028					
	0.45890	0.48366	0.46541				AVRG		0.43834		14.88665
25 Methyl-tert-butyl ether	0.67816	0.97567	0.82536	0.89181	0.96004	0.95010					
	0.92749	1.04313	0.94385				AVRG		0.91062		11.57215
47 Benzene	1.29894	1.38111	1.05260	1.24400	1.34885	1.35273					
	1.35098	1.48946	1.34995				AVRG		1.31874		9.04889
86 Ethylbenzene	1.16018	1.28432	0.95761	1.08160	1.17312	1.13742					
	1.13738	1.25082	1.13759				AVRG		1.14667		8.21038
88 m&p-Xylene	0.38288	0.47202	0.35320	0.40377	0.44689	0.44448					
	0.43748	0.48652	0.43959				AVRG		0.42965		9.87762
89 o-Xylene	0.35676	0.45069	0.34814	0.39564	0.44395	0.42470					
	0.41776	0.46616	0.43224				AVRG		0.41512		9.84614



Utilizing Advancements for Industry Needs

Optimizing run times by using all advancements in technology

- Taking advantage of software to make sure sampler and concentrator are operating in sync, decreasing time between sampling
- Shortening purge times by optimizing purge flow
- Decreasing desorb time to minimize the amount of moisture going into the GC
- Using advancements in consumables to optimize recovery and continually keep system free of contaminants
- Exploiting column advancements to decrease run times and optimize compound separation

Utilizing Advancements for Industry Needs

Optimizing run times by using all advancements in technology

- Average run time throughout network between 14-20 minutes per sample for 8260 analysis. Ideally 80-100 samples per instrument per day.

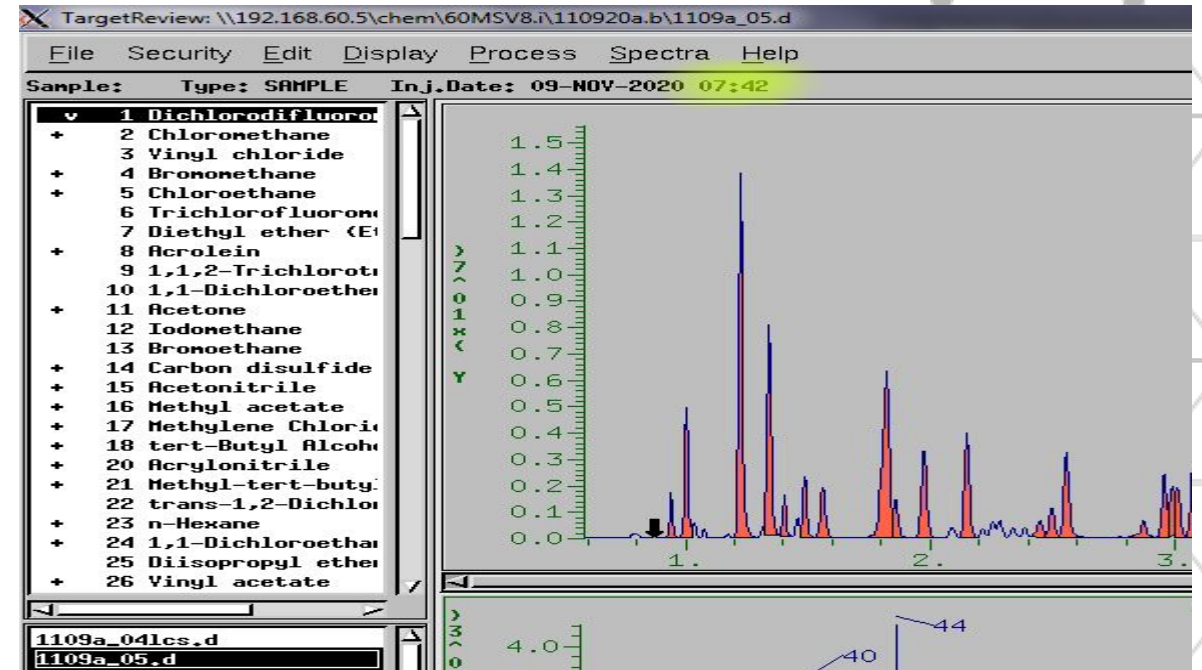
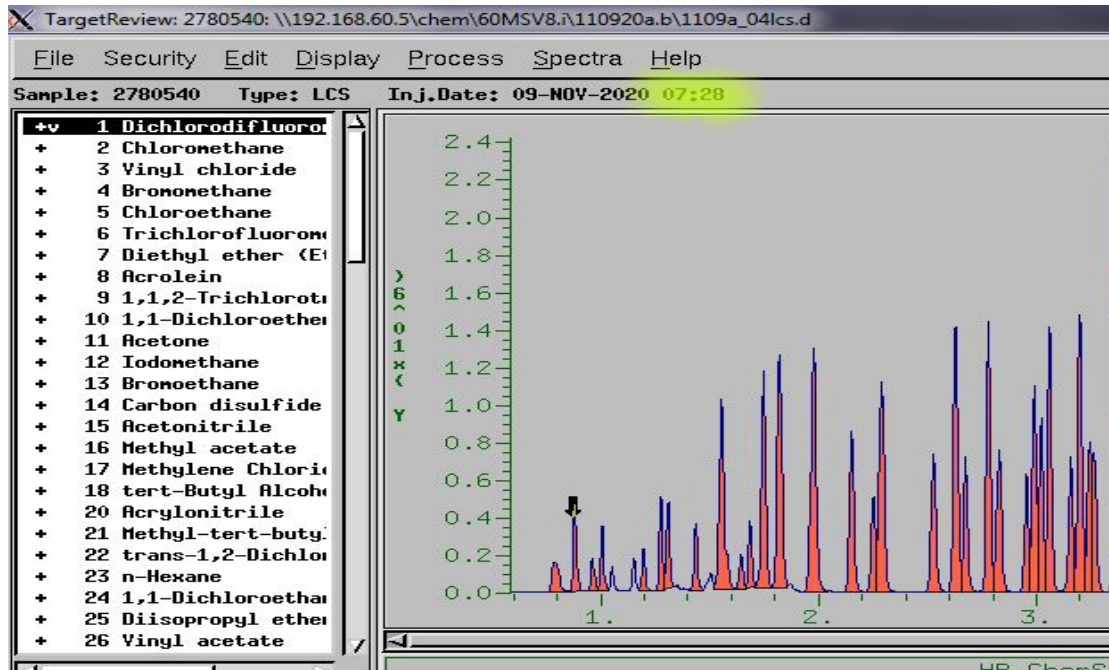


Image of concurrent sequence runs showing a 14-minute sample to sample time.



Utilizing Advancements for Industry Needs

Helium Gas Usage Reduction

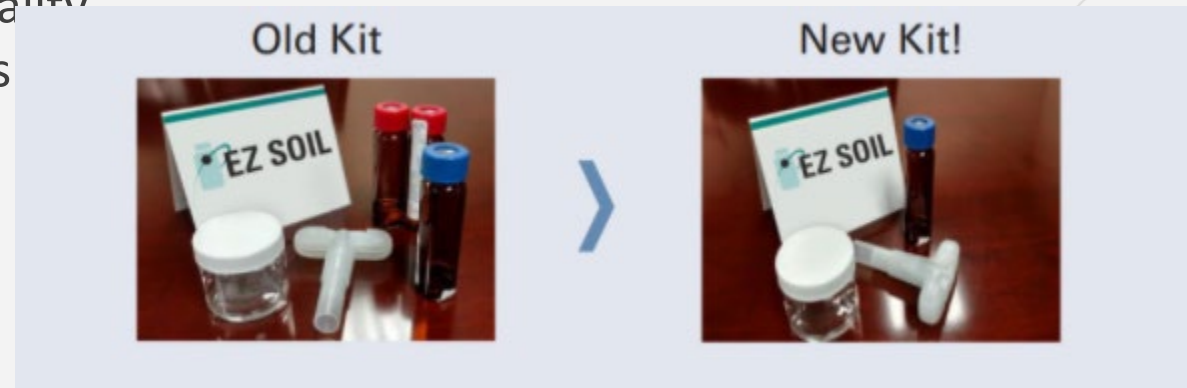
- ❖ Applying automated sampler and concentrator Nitrogen gas options for carrier and purge gas use
- ❖ Optimizing methods to reduce flow of Helium during sample runs
- ❖ Employing the Gas Saver option on sample runs to reduce Helium usage
- ❖ Updated EPC's reduce Helium loss, optimize flows and help keep instrumentation clean from contamination.

Utilizing Advancements for Industry Needs

Pace Analytical offers “EZ Soil”



- By leveraging the technical advancements now available for chemical testing equipment specific to method 8260 Pace Analytical has created a method to eliminate running low level soils that directly purge in vial.
- Why is this significant?
 - Increases productivity, both in the lab and in the field
 - Reduces turn around time (hold time from 2 days to 14 days)
 - Improve data quality
 - Reduces





Evolution of 8260

Conclusion

Using the advances made in testing equipment, instrumentation and consumables we have been able to enhance method 8260 to be more efficient, provide better data, and reduce our footprint. As the industry pushes towards more production and lower compound report limits, we have been able to leverage the progress made on testing equipment to increase sample loads and look lower than we ever have before. The evolution of 8260 has been a direct response of increasingly changing technology and the environmental testing world's needs.

Questions? Comments?

US EPA Method 524.2: Measurement of Purgeable Organic Compounds in Drinking Water by Agilent 8860/5977B GC/MSD

Bruce D. Quimby, Ph.D.
Senior GC/MS Applications Scientist
Agilent Technologies
Wilmington, Delaware

Purge and Trap vs. Headspace Analysis for VOCs

EPA 524.2 requires the use of purge and trap

METHOD 524.2

MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This is a general purpose method for the identification and simultaneous measurement of purgeable volatile organic compounds in surface water, ground water, and drinking water in any stage of treatment (1,2). The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection by-products, that have sufficiently high volatility and low water solubility to be removed from water samples **with purge and trap procedures**. The following compounds can be determined by this method.

6.2 **PURGE AND TRAP SYSTEM** - The purge and trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are commercially available from several sources that meet all of the following specifications.

US EPA Method 524.2 VOCs in Water

EPA method 524.2 provides procedures and requirements for the quantitation of VOCs in surface water, ground water, and drinking water by GC/MS

Four specific groups of VOCs

- Trihalomethanes (THMs)
- Gases
- Aromatics
- Products of dehydrohalogenation

Dichlorodifluoromethane	Methyl acrylate	Toluene	1,4-Dichlorobut-2-ene
Chloromethane	Bromochloromethane	trans-1,3-Dichloropropene	Propylbenzene
Chloroethene	Methylacrylonitrile	Ethyl methacrylate	2-Chlorotoluene
Bromomethane	Tetrahydrofuran	1,1,2-Trichloroethane	Mesitylene (1,3,5-Trimethylbenzene)
Ethyl chloride	Trichloromethane	Tetrachloroethylene	tert-Butylbenzene
Trichloromonofluoromethane	1,1,1-Trichloroethane	1,3-Dichloropropane	1,2,4-Trimethylbenzene
Ethyl ether	1-Chlorobutane	2-Hexanone	1-Methylpropyl benzene
1,1-Dichloroethene	Carbon Tetrachloride	Dibromochloromethane	1,3-Dichlorobenzene
Acetone	1,1-Dichloropropene	1,2-Dibromoethane	p-Cymene (4-Isopropyltoluene)
Iodomethane	Benzene	Chlorobenzene	1,4-Dichlorobenzene
Carbon disulfide	1,2-Dichloroethane	1,1,1,2-Tetrachloroethane	1,2-Dichlorobenzene-d4 (SURR)
Allyl chloride	Fluorobenzene (ISTD)	Ethylbenzene	1,2-Dichlorobenzene
Methylene chloride	Trichloroethylene	m+p-Xylene	n-Butylbenzene
Acrylonitrile	1,2-Dichloropropane	o-Xylene	Hexachloroethane
trans-1,2-Dichloroethylene	Dibromomethane	Styrene	1,2-Dibromo-3-chloropropane
Methyl tert-butyl ether	Methyl methacrylate	Tribromomethane	Nitrobenzene
1,1-Dichloroethane	Bromodichloromethane	Isopropylbenzene	1,2,4-Trichlorobenzene
2,2-Dichloropropane	2-Nitropropane	p-Bromofluorobenzene (SURR)	1,1,2,3,4,4-Hexachlorobuta-1,3-diene
cis-1,2-Dichloroethylene	cis-1,3-Dichloropropene	Bromobenzene	Naphthalene
2-Butanone	2,2-Dimethoxybutane	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
Propanenitrile	Methyl Isobutyl Ketone (MIBK)	1,2,3-Trichloropropane	

80 target compounds

Summary of the Parameters for GC, MSD, and P&T Necessary for Success

Application note 5991-0029EN

- Provided a detailed summary on advances and key parameters for successfully performing EPA 524.2 and EPA 8260 with a 7890/5975C and P&T
- Introduced BFB Autotune that enabled meeting the EPA criteria for spectral correspondence and improved sensitivity and stability



Volatile Organic Compound Analysis Using Purge and Trap

Success with VOC analysis using the Agilent 5975C Mass Selective Detector

Application Note

Environmental

Authors

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Abstract


Despite the status and widespread application of Purge and Trap (P&T) with GC/MS for volatile organics, various issues appear in consistent operation over the desired concentration ranges and at the required detection limits. This application note introduces an approach implemented and tested at several beta sites that consistently produces outstanding data. Detailed in this note are the hardware requirements, the P&T and GC/MS parameters, volatile organic compound (VOC) standard preparation, and a new automated tuning approach to meet USEPA tuning requirements that provides enhanced sensitivity and robustness. Initial calibration studies over the specified (USEPA 524.2) concentration range of 0.25 µg/L to 50 µg/L routinely produce VOC average relative response factors less than the 20% relative standard deviation (RSD) specified for average relative response factor quantitation. Data is also presented for the method detection limits determined at 0.10 µg/L as well as average relative response factors over the concentration range of 0.10 µg/L to 100 µg/L. Adhering to the details of this approach will help insure similar results are obtained for VOC analysis with P&T and GC/MS.

EPA Method 524.2 with Agilent 8860/5977B

Application note 5994-0833EN

- Demonstrated applicability of an Agilent 8860/5977B GC/MSD system (a cost-effective mid-range solution) coupled with a Teledyne Tekmar Lumin purge and trap (P&T) concentrator, and an AQUATEk LVA (liquid vial autosampler) ICAL range 0.25–50 µg/L
- MDLs in ppt levels
- Deconvoluted spectra for compound identification
- Several VOCs were identified and quantified in real-world drinking water samples

Application Note
Environmental



Agilent
Trusted Answers

US EPA Method 524.2: Successful Measurement of Purgeable Organic Compounds in Drinking Water by Agilent 8860/5977B GC/MSD

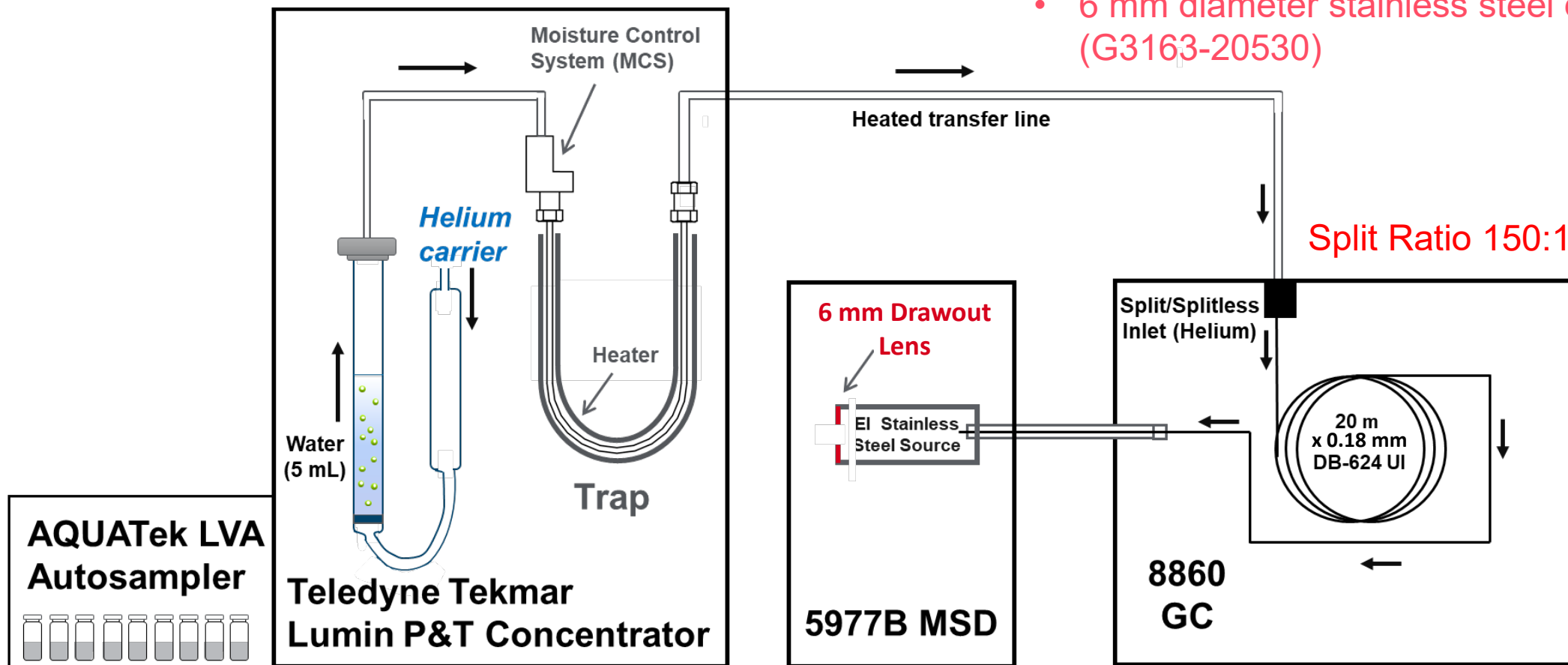
Authors
Bruce D. Quimby and
Anastasia A. Andrianova
Agilent Technologies, Inc.

Abstract
An Agilent 8860/5977B GC/MSD system coupled with a Teledyne Tekmar Lumin purge and trap (P&T) concentrator and an AQUATEk liquid vial autosampler (LVA) was successfully used for the analysis of volatile organic compounds (VOCs) to the requirements of United States Environmental Protection Agency (US EPA) method 524.2. The analysis of VOCs in water following this or similar methods are widely used around the world as part of insuring the safety of potable water supplies.

US EPA Method 524.2 Instrument Configuration

Consumables:

- 1.0 mm inlet liner (5190-4047)
- DB-624UI, 20m x 0.18 mm x 1 μ m column (121-1324UI)
- 6 mm diameter stainless steel drawout lens (G3163-20530)

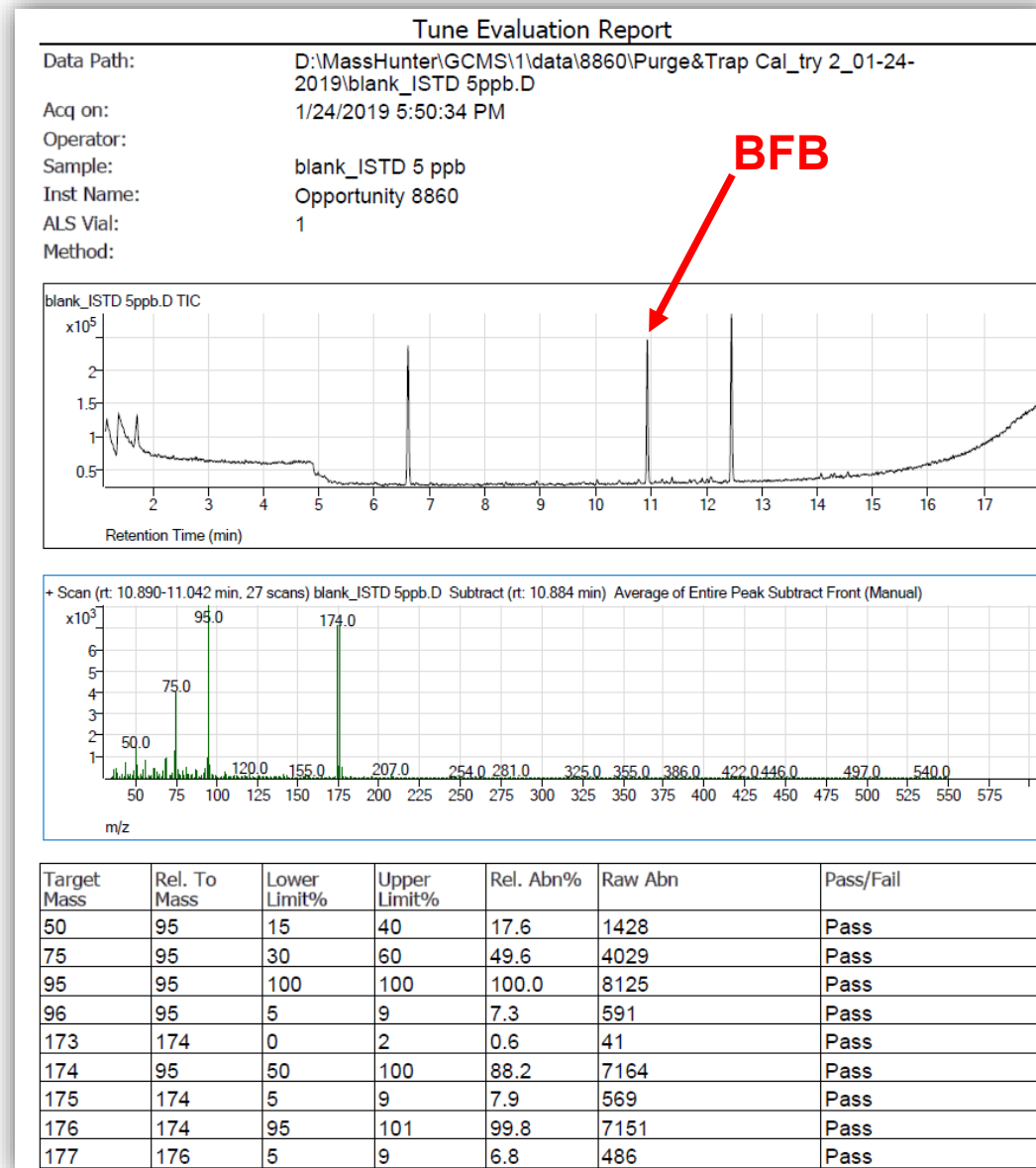


Tune Evaluation: Meeting BFB Tune Check Criteria

EPA 524.2 requires that the spectrometer must produce a mass spectrum that meets all criteria in Table 3 when 25 ng or less of 4-bromofluorobenzene (BFB) is introduced into the GC.

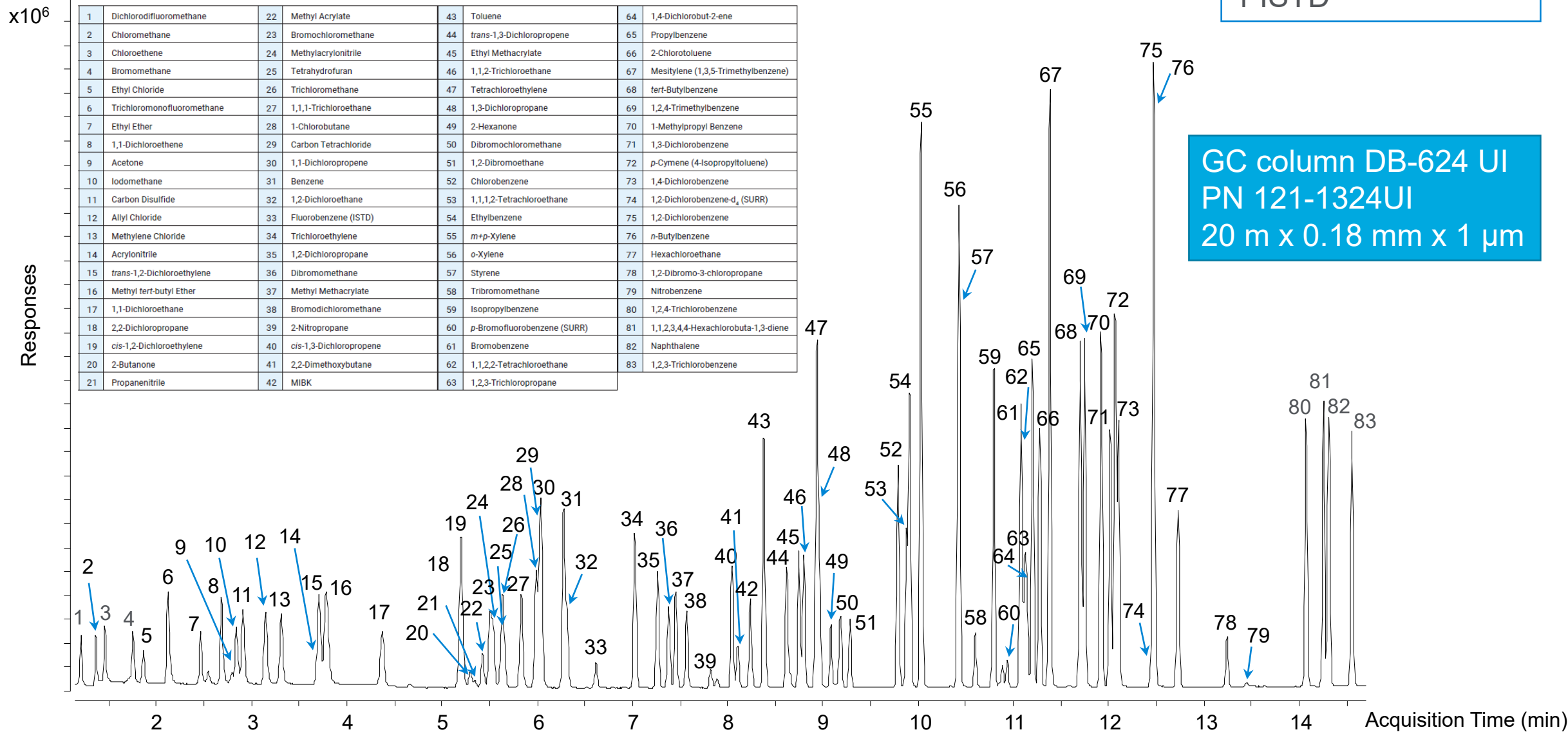
TABLE 3. ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROENZENE (BFB)

Mass (M/z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% 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


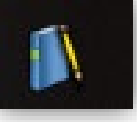



Total Ion Chromatogram of Method 524.2 50 µg/L Standard, ISTD and Surrogates (5 µg/L)

80 target compounds
2 surrogates
1 ISTD



Setting up EPA 524.2 Analysis with MassHunter

1. Analyze a standard to create a spectral library with retention times using MassHunter Unknowns Analysis 
2. Export deconvoluted spectra to MassHunter Library Editor 
3. Create quantitative analysis method in MassHunter Quantitative Analysis using acquired scan data with library search 

Add targeted deconvolution to quantitative analysis if desired

Create calibration levels from the analyzed calibration standards

Analyze real-world samples

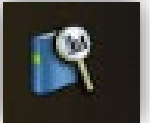
Step 1: Analyzing a Standard

Analyze a calibration standard with Unknowns Analysis against the NIST library

The screenshot displays the Agilent MassHunter Unknowns Analysis interface. On the left, a 'Samples' table lists '50 ppb_ISTD 5' with 603 components. Below it, a 'Components' table lists various compounds with their retention times and match factors. The top component is Dichlorodifluoromethane at 1.2065 min with a 96.2% match factor. A yellow box labeled 'Sample' is overlaid on the top of the components table.

The central 'Method' window is open to the 'Library Search' tab. It shows the library path 'O:\MassHunter\Library\NIST17.L' and search criteria set to 'Normal'. The 'Forward-Reverse Search' section has a 'Pure Weight Factor' of 0.7. The 'Match factor' section is set to 'Use RT Match' with a 'Multiplicative' RT mismatch penalty and a 'Max RT penalty' of 20. A yellow box labeled 'Library search against NIST' is overlaid on the match factor settings.

On the right, a mass spectrum plot shows 'Acquisition Time (min)' on the x-axis (11,000 to 17,000) and 'Mass-to-Charge (m/z)' on the y-axis (150 to 600). The spectrum features several sharp peaks, with the most prominent ones labeled with their retention times: 10.5996, 10.7914, 10.8330, 11.0227, 11.3202, 11.4008, 11.9190, 12.7271, 13.2406, 14.0716, 14.2558, and 14.5510.



Step 2: Creating a Spectral Library

Analyze a calibration standard with Unknowns Analysis against the NIST library

The screenshot displays the Agilent MassHunter Unknowns Analysis interface. A table of search results is visible, with a context menu open over it. The menu includes options like 'Copy', 'Set Best Hits', and 'Export...'. An 'Export Component Table' dialog box is overlaid, showing options to export all components/hits to a library, with 'Automatically name compounds for non-hit components' checked. The 'Prefix' is set to 'Unknown'. Three spectra are shown: a Total Ion Chromatogram (TIC) at the top right, a deconvoluted spectrum in the middle right, a NIST library spectrum in the bottom right, and an apex spectrum at the bottom left.

Review search results

Export Component Table

Export from:
 All components/hits
 Selected components/hits

Export to:
Library

Automatically name compounds for non-hit components

Prefix:
Unknown

Add index
 Add retention time

Deconvoluted spectrum

NIST spectrum

Apex spectrum



Step 2: Creating a Spectral Library

Export deconvoluted spectra to the Library Editor and review



Library Editor - ref_VOCs libr.reflibrary.xml

File Edit Tools Help

Compound Table

Compound ID	Compound Name	CAS#	Formula	Molecular Weight	Retention Time	Retention Index
3	Methane, bromo-	74-83-9	CH3Br	93.942	1.7522	
4	Ethyl Chloride	75-00-3	C2H5Cl	64.008	1.8575	445.0000
5	Trichloromonofluoromethane	75-69-4	CCl3F	135.905	2.1205	
6	Ethyl ether	60-29-7	C4H10O	74.073	2.4663	495.0000
7	Ethene, 1,1-dichloro-	75-35-4	C2H2Cl2	95.953	2.6828	540.0000
8	Acetone	67-64-1	C3H6O	58.042	2.7934	455.0000
9	Methane, iodo-	74-88-4	CH3I	141.928	2.8410	
10	Carbon disulfide	75-15-0	CS2	75.944	2.9071	
11	Allyl chloride	107-05-1	C3H5Cl	76.008	3.1450	535.0000
12	Methylene chloride	75-09-2	CH2Cl2	83.953	3.3099	
13	Acrylonitrile	107-13-1	C3H3N	53.027	3.6961	555.0000
14	Ethylene, 1,2-dichloro-, trans-	156-60-5	C2H2Cl2	95.953	3.7091	580.0000
15	Methyl tert-butyl ether	1634-04-4	C5H12O	88.089	3.7866	510.0000
16	Ethane, 1,1-dichloro-	75-34-3	C2H4Cl2	97.969	4.3699	566.0000
17	Propane, 2,2-dichloro-	594-20-7	C3H6Cl2	111.985	5.1918	550.0000
18	Ethylene, 1,2-dichloro-, cis-	156-59-2	C2H2Cl2	95.953	5.2017	580.0000
19	2-Butanone	78-93-3	C4H8O	72.058	5.2960	555.0000
20	Propanenitrile	107-12-0	C3H5N	55.042	5.3463	565.0000
21	2-Propenoic acid, methyl ester	96-33-3	C4H6O2	86.037	5.4245	576.0000
22	Methane, bromochloro-	74-97-5	CH2BrCl	127.903	5.5029	

Spectrum View

Max. # of panes: 2

SingleQuadrupole + Scan Trichloromonofluoromethane (75-69-4)

Displayed Compounds: 83 | Total Compounds: 83 | Spectra: 83

Step 3: Creating Quantitative Analysis Method

New method from acquired scan data with library search

The screenshot shows the Agilent MassHunter Quantitative Analysis software interface. The 'Method' menu is open, and the option 'New Method from Acquired Scan Data with Library Search...' is highlighted. An orange arrow points to this option. The background displays a data table with the following columns: Area, Accuracy, Ratio, MI, and various qualifiers (e.g., Qualifier (96.0) Re..., Qualifier (98.0) Re..., Qualifier (63.0) Re..., Benzene, fluoro- (ISTD) Re..., Qualifier (77.0) Re...). The table contains several rows of data, including peak areas, accuracies, ratios, and molecular ion (MI) values.

Area	Accuracy	Ratio	MI	Qualifier (96.0) Re...	Qualifier (98.0) Re...	Qualifier (63.0) Re...	Benzene, fluoro- (ISTD) Re...	Qualifier (77.0) Re...
982		40.3	<input type="checkbox"/>			32.6	6.613	206229 1.6
5760	107.7	57.2	<input type="checkbox"/>	37.4		27.5	6.613	205629 1.6
2296	81.7	82.3	<input type="checkbox"/>	71.9		52.3	6.613	205977 1.6
11233	107.0	70.7	<input type="checkbox"/>	40.2		28.8	6.614	204995 2.0
54171	103.6	61.7	<input type="checkbox"/>	39.2		33.4	6.613	206678 1.7
103157	100.0	62.0	<input type="checkbox"/>	41.8		33.8	6.613	204278 1.6
262043	101.0	61.8	<input type="checkbox"/>	40.4		31.6	6.619	205609 1.8
518953	99.0	66.3	<input type="checkbox"/>	41.3		32.6	6.613	207830 1.8

Step 3: Creating Quantitative Analysis Method

Define ISTD and surrogates

The screenshot displays the Agilent MassHunter Quantitative Analysis interface. The 'Method Table' is open, showing a list of compounds. The 'Type' column for 'Benzene, fluoro-' is set to 'ISTD', which is highlighted by a yellow arrow. The table includes columns for Name, RT, Scan, Type, MZ, CAS#, and Match Factor.

Quantifier	Name	RT	Scan	Type	MZ	CAS#	Match Factor
	1-Propene, 1,1-dichloro-	6.038	Scan	Target	75.0	563-58-6	100.0
	Benzene	6.274	Scan	Target	78.0	71-43-2	99.9
	Ethane, 1,2-dichloro-	6.308	Scan	Target	62.0	107-06-2	99.5
	Benzene, fluoro-	6.614	Scan	Target	96.0	462-06-6	100.0
	Trichloroethylene	7.023	Scan	Target	130.0	79-01-6	100.0
	Propane, 1,2-dichloro-	7.261	Scan	ISTD	63.0	78-87-5	100.0
	Methane, dibromo-	7.379	Scan	Surrogate	174.0	74-95-3	100.0
	Methyl methacrylate	7.453	Scan	Matrix Spike	100.0	80-62-6	100.0
	Methane, bromodichloro-	7.568	Scan	Target	83.0	75-27-4	99.2
	Propane, 2-nitro-	7.820	Scan	Target	43.0	79-46-9	99.5
	1-Propene, 1,3-dichloro-, cis-	8.044	Scan	Target	75.0	10061-01-5	100.0
	2,2-Dimethoxybutane	8.105	Scan	Target	89.0	3453-99-4	99.9
	Methyl Isobutyl Ketone	8.237	Scan	Target	58.0	108-10-1	99.7
	Toluene	8.380	Scan	Target	91.0	108-88-3	100.0
	1-Propene, 1,3-dichloro-, trans-	8.619	Scan	Target	75.0	10061-02-6	100.0
	Methacrylic acid, ethyl ester	8.748	Scan	Target	69.0	97-63-2	100.0
	Ethane, 1,1,2-trichloro-	8.797	Scan	Target	97.0	79-00-5	99.8
	Tetrachloroethylene	8.933	Scan	Target	164.0	127-18-4	99.9
	Propane, 1,3-dichloro-	8.961	Scan	Target	76.0	142-28-9	99.8
	2-Hexanone	9.082	Scan	Target	58.0	591-78-6	99.6
	Methane, dibromochloro-	9.181	Scan	Target	129.0	124-48-1	99.6
	Ethane, 1,2-dibromo-	9.284	Scan	Target	109.0	106-93-4	99.7
	Benzene, chloro-	9.787	Scan	Target	112.0	108-90-7	100.0
	Ethane, 1,1,1,2-tetrachloro-	9.875	Scan	Target	133.0	630-20-6	99.1
	Ethylbenzene	9.909	Scan	Target	91.0	100-41-4	100.0
	m-p-Xylene	10.028	Scan	Target	91.0	108-38-3	100.0
	o-Xylene	10.418	Scan	Target	91.0	95-47-6	100.0
	Styrene	10.431	Scan	Target	104.0	100-42-5	100.0
	Methane, tribromo-	10.600	Scan	Target	173.0	75-25-2	100.0
	Benzene, (1-methylethyl)-	10.791	Scan	Target	105.0	98-82-8	100.0
	p-Bromofluorobenzene	10.933	Scan	Target	174.0	460-00-4	100.0
	Benzene, bromo-	11.074	Scan	Target	158.0	108-86-1	100.0
	Ethane, 1,1,2,2-tetrachloro-	11.083	Scan	Target	83.0	79-34-5	100.0

Step 3: Creating Quantitative Analysis Method

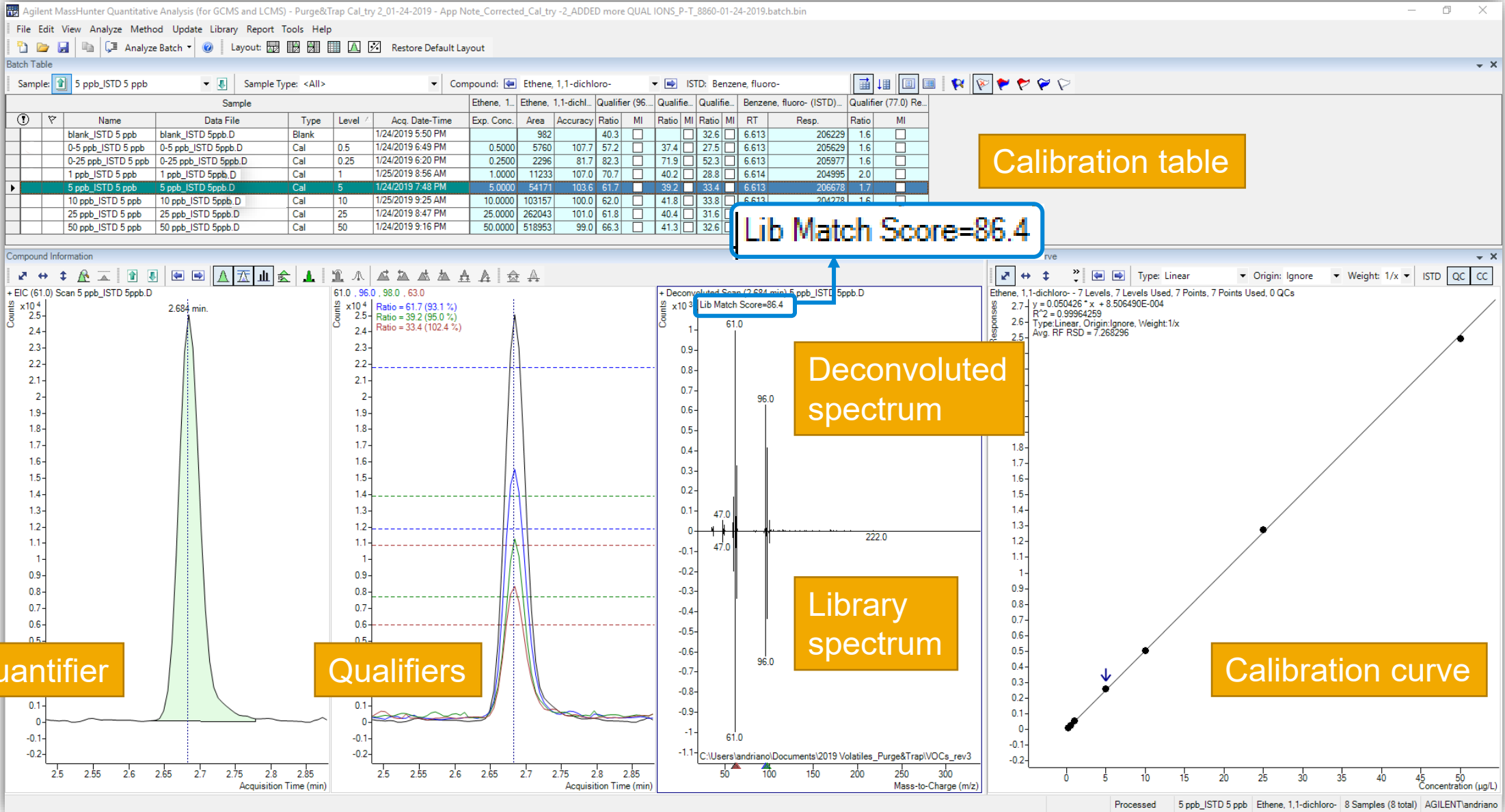
Add target deconvolution (optionally)

The screenshot displays the Agilent MassHunter software interface. On the left, the 'Method Tasks' pane is visible, with 'Target Deconvolution Setup' highlighted in a yellow box and an arrow pointing to it. The main window shows the 'Target Deconvolution Setup' dialog box. The dialog box has the following sections:

- Reference Library:** A text field with a 'Setup Reference Library...' button.
- Library Method:** A text field containing the path 'C:\Users\andriano\Documents\2019 Volatiles_Purge&Trap\P&T UA lib method.uamethod.xml', with 'Edit...', 'New...', and 'Choose...' buttons.
- Spectrum Setup:** Four checked checkboxes: 'Deconvoluted scan as Spectrum Extraction Override', 'Show reference spectrum', 'Show override spectrum', and 'Show match scores'.
- Outlier Setup:** 'Library Match Score Minimum' (input field: 60), 'Min. Percent Purity' (input field: 60), and 'Alternative Peak Criteria' (dropdown menu: Deconvoluted Library Match Score).

At the bottom of the dialog box are 'OK' and 'Cancel' buttons. The background shows the 'Method Table' and 'Compound Information' panes.

ICAL Review in MassHunter Quantitative Analysis 10.1



Calibration table

Lib Match Score=86.4

Quantifier

Qualifiers

Deconvoluted spectrum

Library spectrum

Calibration curve

Initial Calibration (ICAL)

0.25–50 µg/L for 68 compounds (85%)

0.50–50 µg/L for 74 compounds (93%)

79 compounds out of 80 met the EPA criteria of less than 20% RSD with linear calibration

A quadratic fit with R^2 of 0.9963 was used for iodomethane

The %RSDs for the internal standard and surrogate compounds introduced by the AQUATek LVA were <5% RSD

Table 4. ICAL for Method 524.2 From 0.25 to 50 µg/L.

Compound	RT (min)	0.25 µg/L	0.5 µg/L	1 µg/L	5 µg/L	10 µg/L	25 µg/L	50 µg/L	Avg RRF	%RSD
		RRF	RRF	RRF	RRF	RRF	RRF	RRF		
Fluorobenzene (ISTD)	6.613	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	ISTD	1.000	0.6
Dichlorodifluoromethane	1.207	0.087	0.150	0.178	0.136	0.157	0.153	0.153	0.145	19.6
Chloromethane	1.362	0.148	0.178	0.143	0.159	0.170	0.162	0.161	0.160	7.5
Chloroethene	1.462	0.244	0.182	0.212	0.180	0.191	0.183	0.184	0.196	12.0
Bromomethane	1.752				0.149	0.145	0.119	0.117	0.132	12.8
Ethyl Chloride	1.858	0.066	0.118	0.104	0.099	0.115	0.113	0.112	0.104	17.2
Trichloromonofluoromethane	2.120	0.299	0.353	0.342	0.337	0.334	0.337	0.336	0.334	5.0
Ethyl Ether	2.466	0.062	0.096	0.115	0.099	0.105	0.105	0.106	0.098	17.4
1,1-Dichloroethene	2.683	0.223	0.280	0.274	0.262	0.252	0.255	0.250	0.257	7.3
Acetone	2.793				0.021	0.022	0.020	0.020	0.021	5.1
Iodomethane	2.841	0.186	0.160	0.177	0.171	0.209	0.275	0.297	0.211	0.9963*
Carbon Disulfide	2.907	0.603	0.515	0.516	0.477	0.489	0.483	0.489	0.510	8.5
Allyl Chloride	3.145	0.074	0.089	0.071	0.091	0.099	0.089	0.089	0.086	11.8
Methylene Chloride	3.310	0.225	0.182	0.178	0.179	0.174	0.171	0.171	0.183	10.5

Method Detection Limits (MDLs)

<0.10 µg/L for 58 compounds (73%)

<0.15 µg/L for 66 compounds (83%)

8 trials at 0.25 µg/L for 66 compounds

For the compounds with higher reporting limits – 8 trials at 0.5 and 1 µg/L

$$MDL = s \times t_{(n-1, 1-\alpha=99)} = s \times 2.998$$

1.2 Method detection limits (MDLs) (3) are compound, instrument and especially matrix dependent and vary from approximately 0.02 to 1.6 µg/L.

MDLs in pg level

Table 5. Calculated MDLs for VOCs.

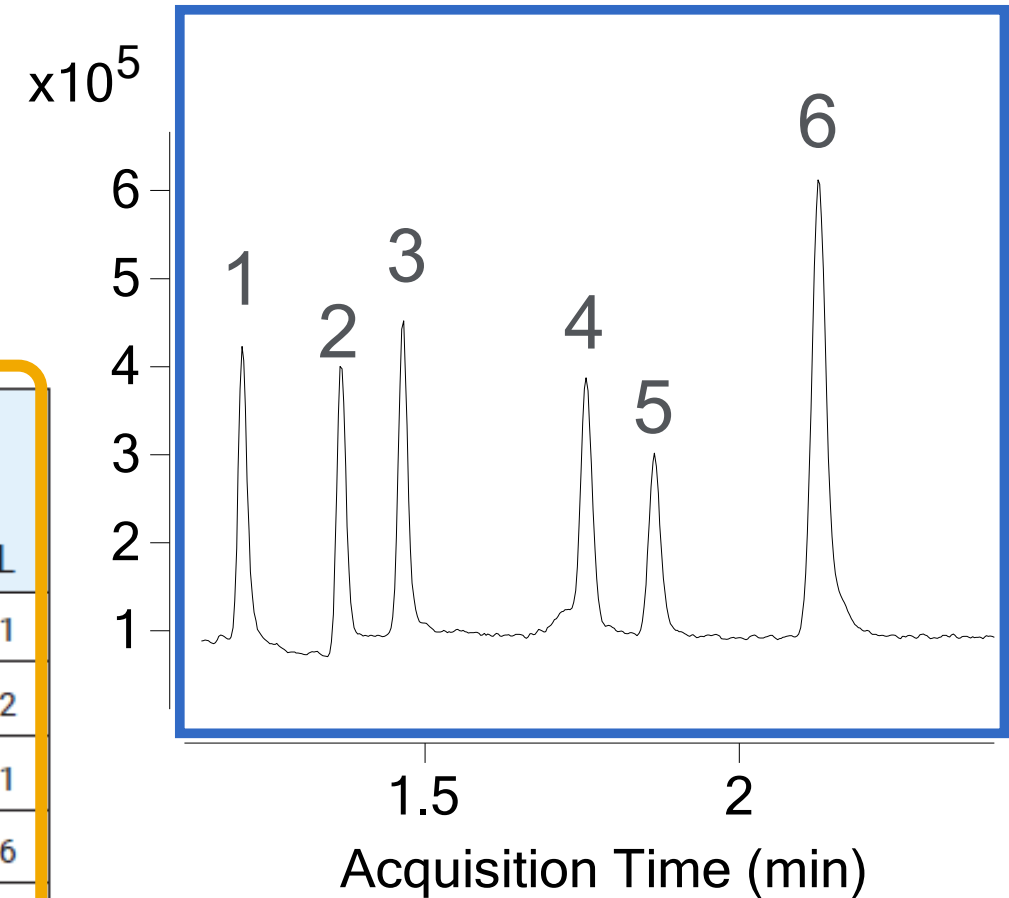
Compound	RT (min)	Calculated Concentration in the Sample (µg/L)									Average concentration (µg/L)	SD	MDL	
		Spike (µg/L)	Samp. 1	Samp. 2	Samp. 3	Samp. 4	Samp. 5	Samp. 6	Samp. 7	Samp. 8				
Fluorobenzene (ISTD)	6.613	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	N/A	N/A
Dichlorodifluoromethane	1.207	0.25	0.23	0.24	0.24	0.24	0.26	0.22	0.24	0.23	0.24	0.24	0.010	0.031
Chloromethane	1.362	0.25	0.26	0.26	0.25	0.24	0.23	0.29	0.25	0.26	0.26	0.26	0.017	0.052
Chloroethene	1.462	0.25	0.17	0.17	0.14	0.14	0.18	0.15	0.16	0.19	0.16	0.16	0.017	0.051
Bromomethane	1.752	1.00	0.88	1.03	0.90	0.91	0.78	0.74	0.75	0.97	0.87	0.106	0.316	
Ethyl Chloride	1.858	0.25	0.36	0.34	0.29	0.35	0.29	0.38	0.37	0.37	0.34	0.035	0.103	
Trichloromonofluoromethane	2.120	0.25	0.25	0.24	0.18	0.23	0.18	0.26	0.20	0.21	0.22	0.030	0.091	
Ethyl Ether	2.466	0.25	0.28	0.21	0.29	0.27	0.33	0.23	0.27	0.30	0.27	0.038	0.114	
1,1-Dichloroethene	2.683	0.25	0.24	0.24	0.27	0.23	0.24	0.21	0.24	0.25	0.24	0.019	0.057	
Acetone	2.793	1.00	1.04	1.21	1.51	1.33	1.37	1.25	1.03	1.08	1.23	0.173	0.518	

MDLs for Gases

$$MDL = s \times t_{(n-1, 1-\alpha=99)} = s \times 2.998$$

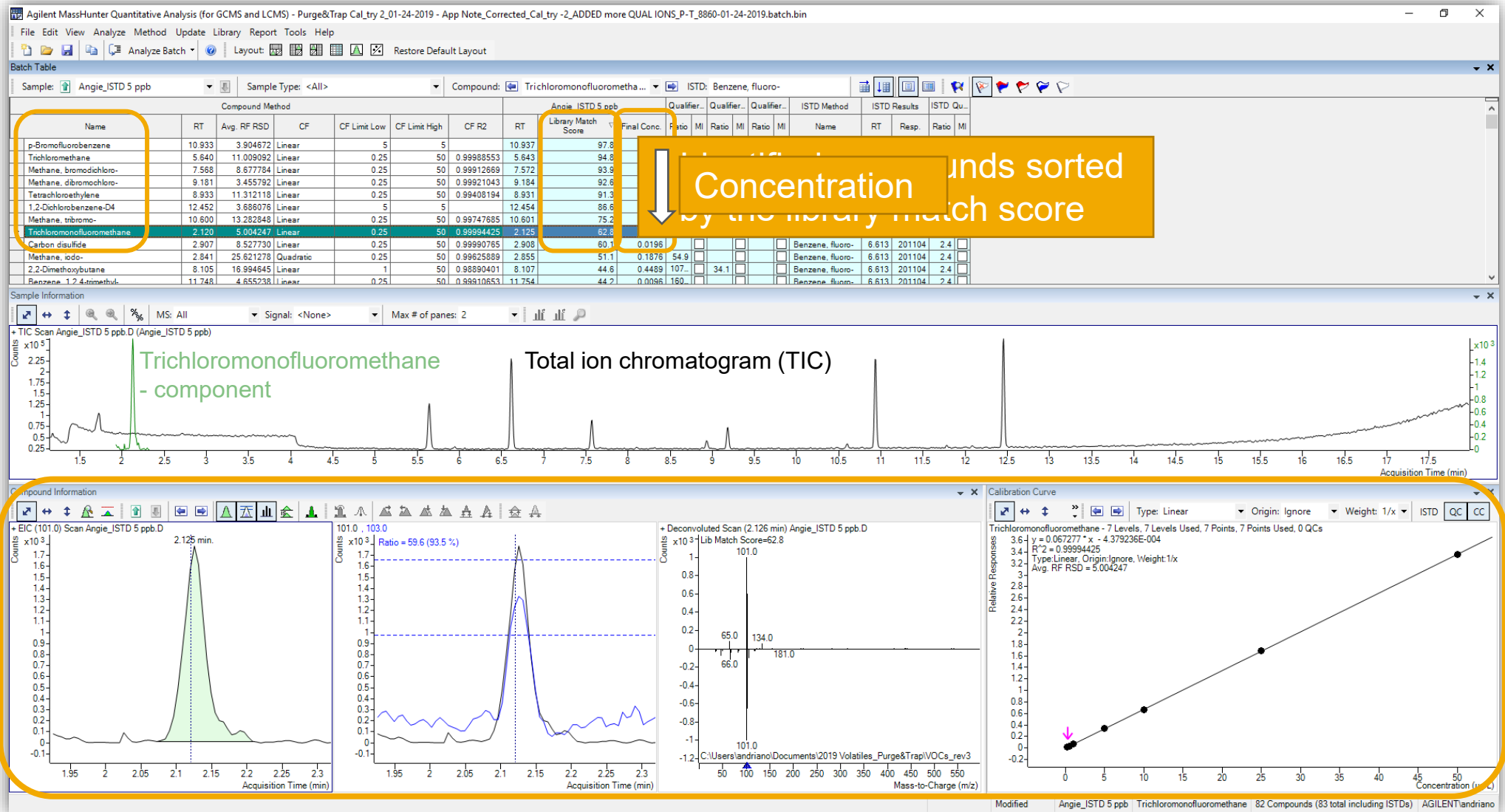
Table 5. Calculated MDLs for VOCs.

	Compound	RT (min)	Average concentration (µg/L)	SD	MDL
1	Dichlorodifluoromethane	1.207	0.24	0.010	0.031
2	Chloromethane	1.362	0.26	0.017	0.052
3	Chloroethene	1.462	0.16	0.017	0.051
4	Bromomethane	1.752	0.87	0.106	0.316
5	Ethyl Chloride	1.858	0.34	0.035	0.103
6	Trichloromonofluoromethane	2.120	0.22	0.030	0.091

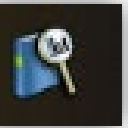


US EPA Method 524.2: Real World Samples

Tested tap water sample from Eastern Pennsylvania: MassHunter Quantitative Analysis



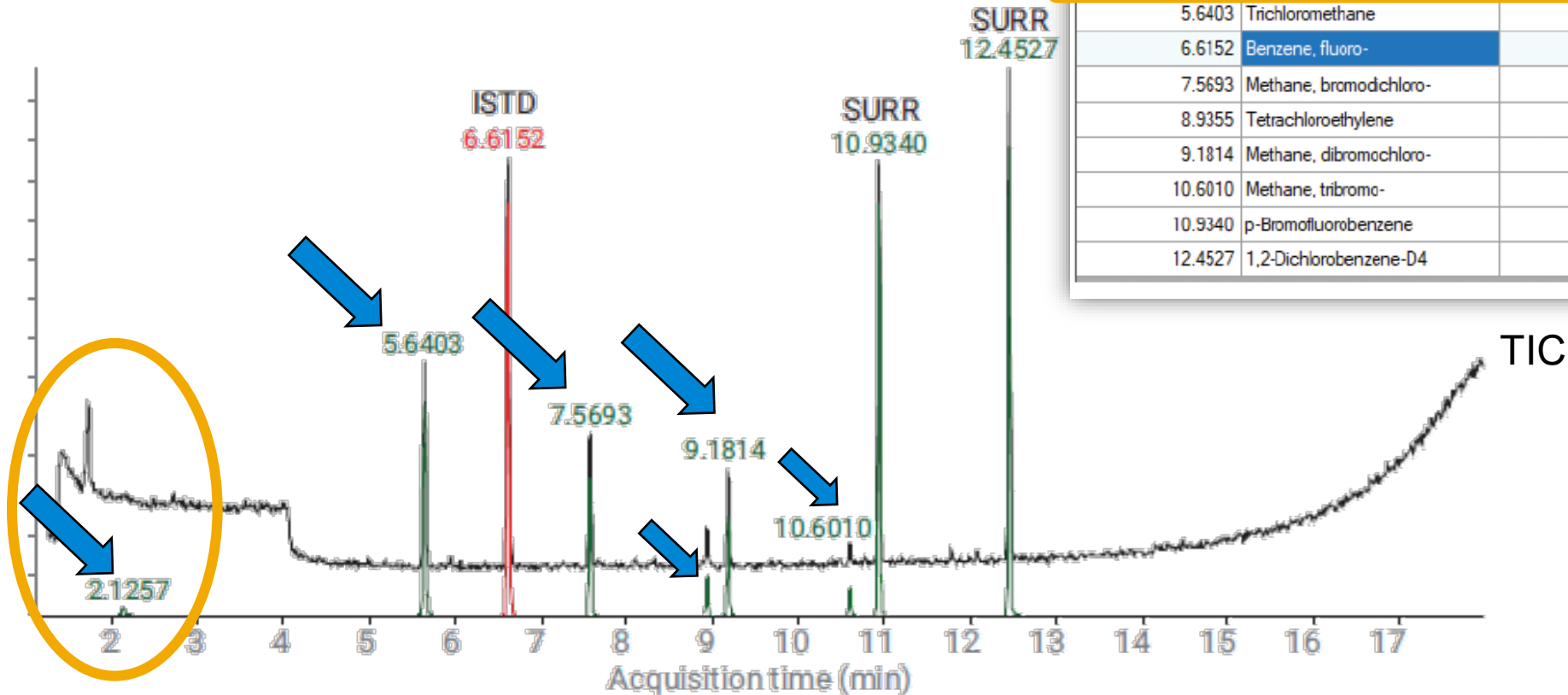
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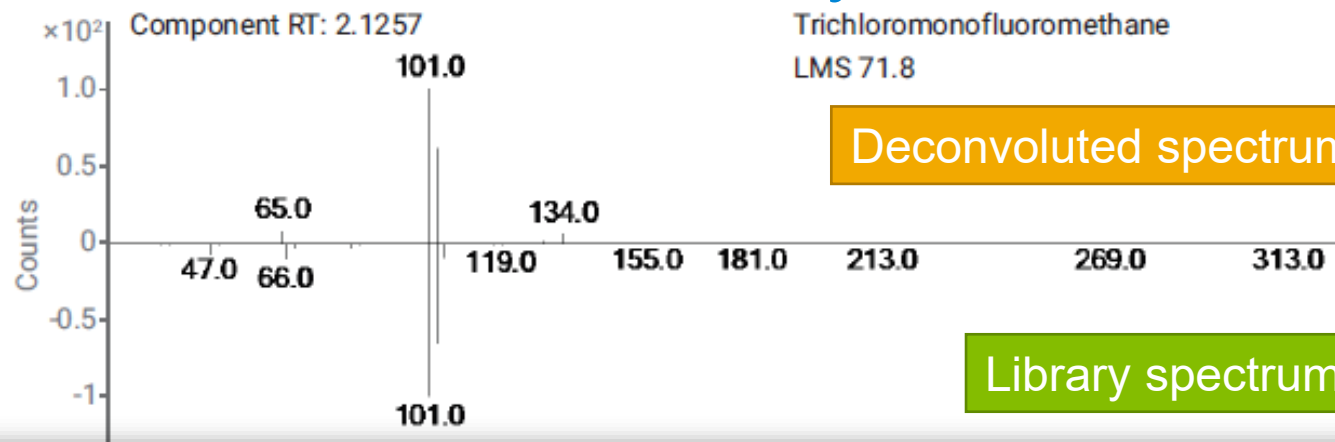
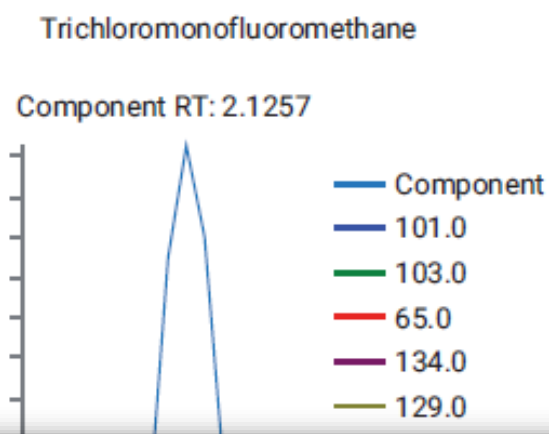
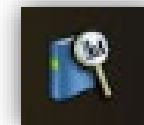
Tested tap water sample from Eastern Pennsylvania: MassHunter Unknowns Analysis

VOCs found:

Component RT	Compound Name	Match Factor	Best Hit	Formula	Library RT	Delta RT
2.1257	Trichloromonofluoromethane	71.8	<input checked="" type="checkbox"/>	CCl3F	2.1205	-0.0052
5.6403	Trichloromethane	95.2	<input checked="" type="checkbox"/>	CHCl3	5.6396	-0.0007
6.6152	Benzene, fluoro-	97.5	<input checked="" type="checkbox"/>	C6H5F	6.6141	-0.0011
7.5693	Methane, bromodichloro-	95.3	<input checked="" type="checkbox"/>	CHBrCl2	7.5681	-0.0012
8.9355	Tetrachloroethylene	91.9	<input checked="" type="checkbox"/>	C2Cl4	8.9325	-0.0029
9.1814	Methane, dibromochloro-	94.3	<input checked="" type="checkbox"/>	CHBr2Cl	9.1810	-0.0004
10.6010	Methane, tribromo-	75.5	<input checked="" type="checkbox"/>	CHBr3	10.5996	-0.0014
10.9340	p-Bromofluorobenzene	98.3	<input checked="" type="checkbox"/>	C6H4BrF	10.9330	-0.0010
12.4527	1,2-Dichlorobenzene-D4	87.0	<input checked="" type="checkbox"/>	C6D4Cl2	12.4523	-0.0004



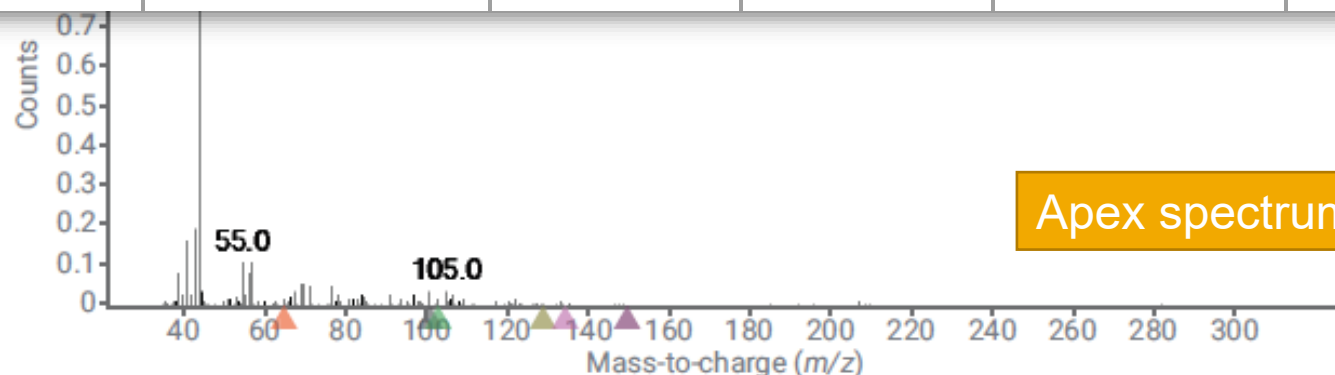
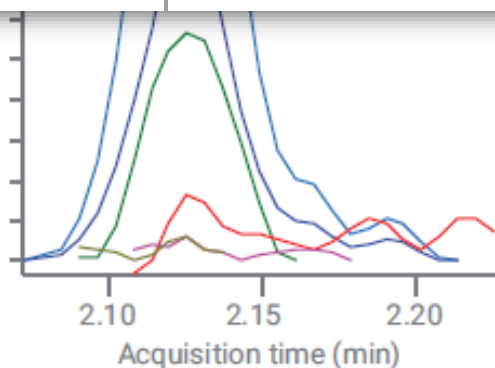
Trichloromonofluoromethane Found in a Tap Water Sample from Eastern Pennsylvania: Review in Unknowns Analysis



Library spectrum

Components

Component RT	Compound Name	Match Factor	Best Hit	Formula	Library RT	Delta RT
2.1257	Trichloromonofluoromethane	71.8	<input checked="" type="checkbox"/>	CCl3F	2.1205	-0.0052



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VOCs found in a tap water sample from four sources in Pennsylvania

Compound	RT (min)	Concentration (µg/L)			
		Southern Pennsylvania	Eastern Pennsylvania	Southeastern Pennsylvania	City of Philadelphia
Trichloromonofluoromethane	2.120		0.30		
Trichloromethane (Chloroform)	5.640	1.05	7.15	12.56	14.06
Bromodichloromethane	7.568		5.15	4.81	5.77
Toluene	8.380	0.29			
Tetrachloroethylene	8.933		0.36		
Dibromochloromethane	9.181		4.49	1.03	1.44
Tribromomethane	10.600		1.26		

Summary

The 8860/5977B GC/MSD system equipped with a 6 mm diameter drawout lens, coupled with a Teledyne Tekmar Lumin P&T concentrator, and an AQUATEk LVA is suitable for analyzing VOCs with an ICAL range of 0.25 to 50 µg/L

BFB Autotune provides high sensitivity and stability, while maintaining the required ion abundance ratios in the BFB spectrum

Several VOCs were identified and quantified in real world tap water samples at concentrations varying over the range of 0.3 to 14.1 µg/ L, in many cases much lower than current EPA 524.2 MCLs