



Advances in GC/MS Technology: Improving Analytical Efficiency and Reducing Cost of Operation for Volatile and Semi-Volatile Organic Compound Analysis

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Presentation Overview

Topics

- Introduction and general market overview
- Introduction to the Model 5977B with High Efficiency Source (HES)
- Volatiles Organic Compounds (VOC) analysis by HSP/GC/MS HES
- Semi-Volatile Compounds (SVOCs) analysis by GC/MS HES
- Nitrosamines in Drinking Water by GC/MS/MS with HES





Environmental issues in the headlines What's important?

Each year worldwide

- Millions of acute/chronic respiratory illnesses
- Millions live without water sanitation
- Billions of dollars lost due to unsafe drinking water
- Thousands of plant/animal species threatened

Why?

- Population growth: 7 billion people and counting
- New chemical pollutants identified
- Clean air/water a lower priority than food/jobs/energy
- Natural/man-made catastrophes



Opportunity

The demand for new applications is growing quickly – especially in the areas of potable water and water reuse



Core Environmental Monitoring Applications Demand for lower MRLs drives method update



Pharmaceutical and personal care products (PPCP)

• LC/MS/MS: low nanogram per liter or parts per trillion (ppt) levels



Pesticides/endocrine disrupters

- Quantification of known pesticides
- Identification/quantification of new pesticides and metabolites



Volatile and semi-volatile hydrocarbons

• Conformity with global regulators for continuous monitoring



Industrial contaminants (perchlorates)

• Sensitive detection for drinking and surface water testing

The challenge

Increase speed and sensitivity while decreasing cost

> Environmental Market Overview July 7, 2016



Emerging Environmental Monitoring Applications New targets lead to new or updated regulations



Nanoparticles

• Fate of organic and metallic nanomaterials in the environment



Hormones in water

 Identify and quantitate compounds and metabolites which affect marine organism physiology



Persistent toxic pollutants

Monitoring trace-level residues in abiotic and biotic materials



Disinfection by-products

 Balancing the benefits of disinfection (microbial control) with potential risks



Trace inorganics

Identify and quantitate metals and non-metallic elements



Perfluorinated chemicals

 Selective and specific analysis of trace-level residues

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Indoor air testing

 Fast screening for solvents, paints, and other volatile organics in buildings and vehicle cabins



Non-targeted screening

 Identification of trace level "unknowns" in environmental matrices



Volatiles Analysis





Environmental Monitoring Requirements Volatiles Analysis

Overview

- Volatile organic analysis (VOA) monitors compounds with a wide range of boiling points
- Requires particularly challenging sample extraction
- Response factors for the many potential analytes vary widely.

Project Scope

- Survey select compounds of environmental interest as an indication of what may be achieved with the new 5977B GC/MSD in this approach.
- Determine if High Efficiency Source increases ion current created that may lead to improvement in sensitivity and significant improvements in detection limits for VOC targets.
- Determine overall stability of the analysis through replicate injection of local tap water to monitor some naturally occurring compounds.



Experimental Design: Volatiles Analysis Headspace Sample Preparation: 7890B GC and 5977B MSD HES

Overview of Analytical Conditions

- Standards
 - 10 mL water spiked with 48 compounds at 0.02 20 $\mu\text{g/L}$
- Injection
 - Split mode using a 15:1 split
- GC Column
- Dimensions: 60 m x 0.25 mm id x 1.4 μm with a 6% cyanopropylphenyl phase
- Oven Ramp
 - 32°C to 220°C
- Source and Quadrupole
 - Temperatures: 300°C and 150°C, respectively
 - Detector gain was 3
 - Tune: Autotune
- MDL Calculations and Sample Analysis
 - Nine replicate injections
 - \bullet MDLs were calculated using 0.04 $\mu\text{g/L}$ standard.
 - Tap water samples were injected 20 times, consecutively



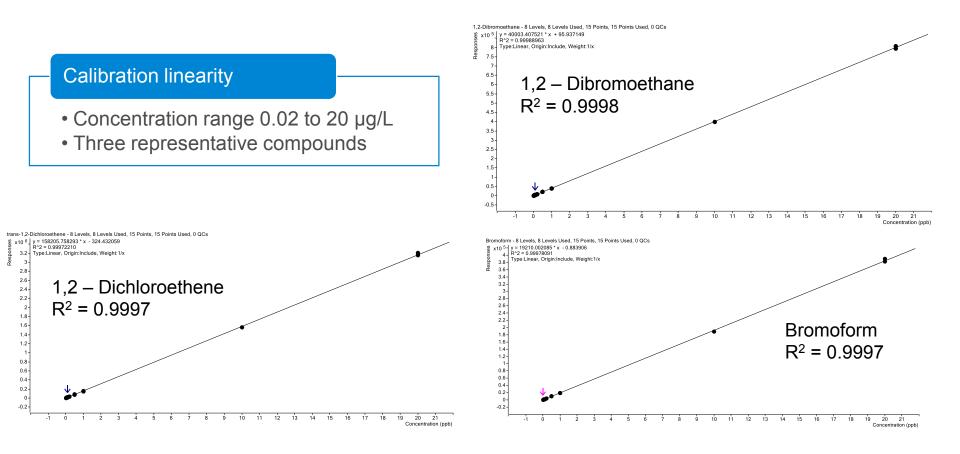
Operating Parameters: Volatiles Analysis Headspace Sample Preparation: 7890B GC and 5977B MSD HES

	Headspace Parameters	Agilent 7697A Headspace Sampler
^r ument Settings	Loop Size	1 mL
	Transfer Line Type	Fused Silica, deactivated,
		(PN 160-2535-5)
	Transfer Line Diameter	0.53 mm
	HSS-GC coupling	Transfer Line Interface (G3520A)
	Carrier Control	GC Instrument
	Pressurization gas	Helium
	Vial standby flow	20ml/min
perature Settings	Oven Temperature	75 °C
	Loop Temperature	75 °C
	Transfer Line Temperature	110 °C
	Transfer Line Interface	115 °C
ng Settings	Vial Equilibration Time	12 min
	Injection Duration	0.3 min
	GC Cycle Time	30 min
and Loop Settings	Vial Size	20 mL
	Vial Shaking	Level 7
	Fill Pressure	10 psi
	Fill Time	0.2 min
	Loop Ramp Rate	20 psi/min
	Loop Final Pressure	7 psi
	Loop Equilibration Time	0.01 min
	Post Injection Purge	100 ml/min for 2 min
	Leak Check	Default 0.2 ml/min

Gas Chromatograph Parameters	Agilent 7890B GC
Inlet Type	Split/Splitless Inlet (SSL)
Mode	Split
Inlet Liner	Straight, 2mm ID 250 μl (PN 5181-8818)
Heater	125°C
Column Flow	1.5 ml/min constant flow
Total Flow	25 mL/min
Septum Purge Flow	1.0 ml/min
Gas Saver	OFF
Split Ratio	15:1
Split Flow	22.5 ml/min
Column	Agilent VF-624 MS
Column Dimensions	60 m x 0.25 mm x 1.4 μm
Equilibration Time	0.25 min
Temperature Program	32°C (2 min), 12°C/min to 220°C (5 min)
Mass Selectice Detector Parameters	Agilent 5977B
Source Type	High Efficiency Source (HES EI)
Source Temperature	300°C
Quad Temperature	150°C
Transfer Line Temperature	280°C
Tune File	HES Auto Tune (HES_Atune.u)
Acquisition Type	SIM
Solvent Delay	2 Q5 min

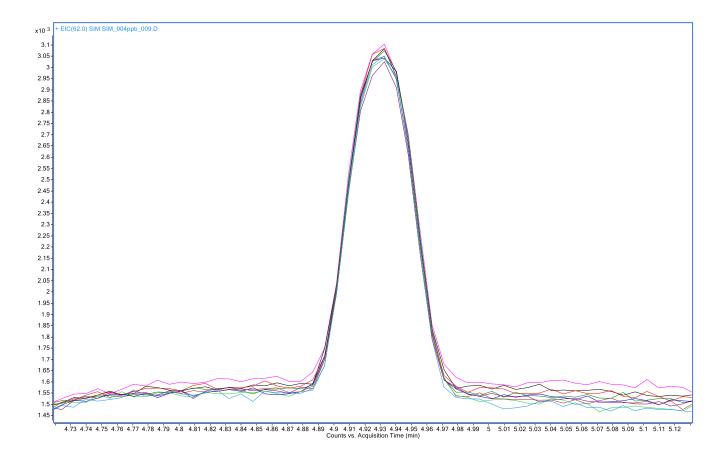


Linearity: Volatiles Analysis Headspace Sample Preparation: 7890B GC and 5977B MSD HES





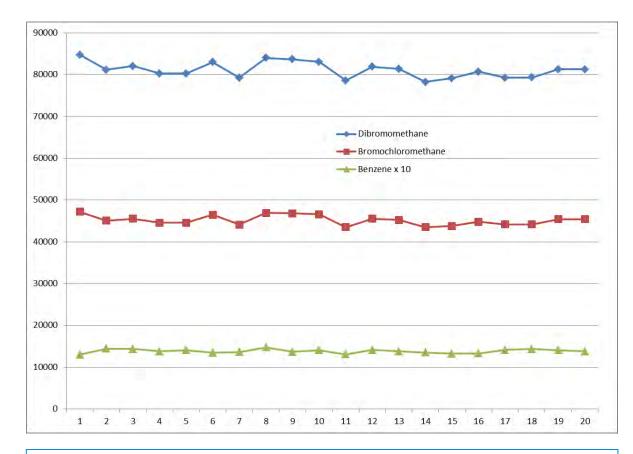
Reproducibility: Volatiles Analysis Headspace Sample Preparation: 7890B GC and 5977B MSD HES



Overlay of nine extracted ion chromatograms (EIC), which shows stability obtained in the case of vinyl chloride, a particularly challenging analyte.



Linearity: Volatiles Analysis in Tap Water Headspace Sample Preparation: 7890B GC and 5977B MSD HES



Response over 20 injections of incurred dibromomethane (blue), bromochloromethane (red) and benzene, multiplied by 10 (green), in local tap water.



MDL: Volatiles Analysis Headspace Sample Preparation: 7890B GC and 5977B MSD HES

	Name	RT	Quant Ion	MDL	Name	RT	Quant Ion	MDL
	Vinyl chloride	4.934	62	0.004	1,2-Dibromoethane	13.427	106.9	0.006
	Bromomethane	5.611	93.9	0.003	Chlorobenzene	13.969	112	0.015
	Chloroethane	5.806	64	0.003	Ethylbenzene	14.03	91	0.014
MDL study	1,1-Dichloroethene	7.007	95.9	0.008	1,1,1,2-Tetrachloroethane	14.049	130.9	0.005
	trans-1,2-Dichloroethene	8.007	95.9	0.009	o-Xylene	14.664	91	0.018
Nine replicate injections	1,1-Dichloroethane	8.554	63	0.004	Styrene	14.683	104	0.015
•Calculated using 0.04 µg/L standard.	cis-1,2-Dichloroethene	9.19	95.9	0.011	Bromoform	14.975	170.8	0.006
 All MDLs are below 0.025 µg/L or 25 ppt Two exceptions: which have MDLs ≤ 41 	2,2-Dichloropropane	9.208	77	0.013	1,1,2,2-Tetrachloroethane	15.45	82.9	0.041
ppt.	Bromochloromethane	9.47	127.8	0.004	1,2,3-Trichloropropane	15.567	110	0.007
	1,1,1-Trichloroethane	9.769	96.9	0.005	Bromobenzene	15.573	155.9	0.017
Majority of MDLs below 0.015 µg/L	1,1-Dichloro-1-propene	9.921	75	0.012	n-Propylbenzene	15.63	91	0.017
	Carbon tetrachloride	9.94	116.9	0.003	2-Chlorotoluene	15.768	91	0.016
 including some compounds with 	Benzene * (blank issue)	10.165	78	0.009	1,3,5-Trimethylbenzene	15.84	105	0.018
relatively low response.	1,2-Dichloroethane	10.202	62	0.006	4-Chlorotoluene	15.914	91	0.018
	Trichloroethene	10.848	129.9	0.009	tert-Butylbenzene	16.225	134	0.017
Tap water samples	1,2-Dichloropropane	11.165	63	0.005	sec-Butylbenzene	16.499	105	0.016
	Dibromomethane	11.275	173.8	0.006	4-Isopropyltoluene	16.67	119	0.017
 Injected 20 times, consecutively 	Bromodichloromethane	11.421	82.9	0.005	1,3-Dichlorobenzene	16.719	145.9	0.02
	cis-1,3-Dichloropropene	11.89	75	0.014	1,4-Dichlorobenzene	16.841	145.9	0.023
	trans-1,3-Dichloropropene	12.506	75	0.013	n-Butylbenzene	17.194	134	0.02
	1,1,2-Trichloroethane	12.762	96.9	0.011	1,2-Dichlorobenzene	17.316	145.9	0.021
	Tetrachloroethene	12.884	163.8	0.009	1,2-Dibromo-3-chloropropane	18.334	154.9	0.01



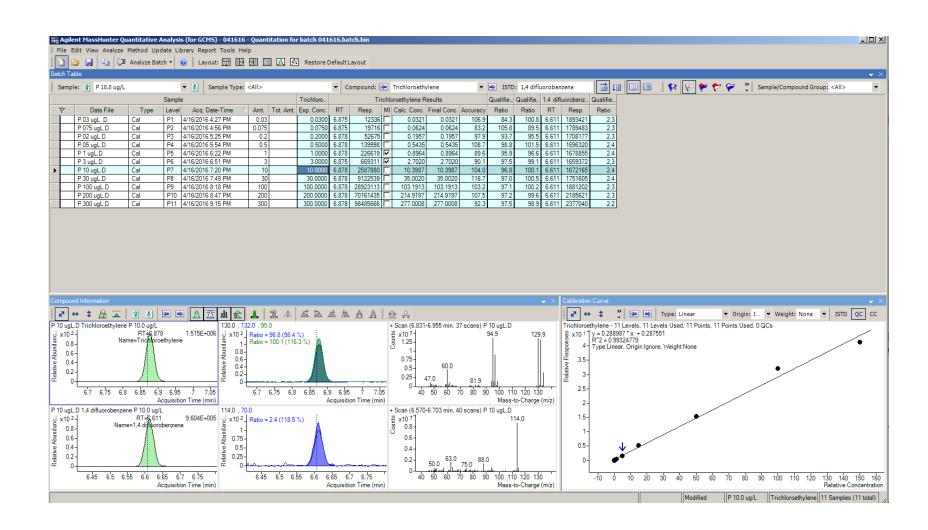
Conclusions: Volatiles Analysis Headspace Sample Preparation: 7890B GC and 5977B MSD HES

5977B HES Performance

- Preliminary results suggest a significant improvement in detection limits is possible in VOA applications
- Signal improvement provided is not complicated by interferences, and results in clear enhancements in detection.
- Performance with Headspace addresses VOC applications not requiring Purge-and-Trap sample preconcentration



Volatiles Analysis: Trichloroethylene Purge-and-Trap Sample Preparation: 7890B GC and 7010 HES





Volatiles Analysis: 1,2 dichloro-Ethane Purge-and-Trap Sample Preparation: 7890B GC and 7010 HES

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	03 ugL .D	Type Level Acq. Date-Tim	ne 🛆 Amt. Tot. A	Amt. Exp. Conc. RT	Resp. MI	Calc. Conc. Final Conc	c. Accuracy Ratio	Ratio RT	Resp. R	atio				
		Cal P1 4/16/2016 4:27 PN		0.0300 6.15		0.0304 0.0304		31.7 6.611		2.3				
	075 ugL.D	Cal P2 4/16/2016 4:56 PN Cal P3 4/16/2016 5:25 PN		0.0750 6.15		0.0748 0.0748 0.0748 0.1900 0.1900		23.4 6.611 25.4 6.611	1789483 1708177	2.3				
	02 ugL.D 05 ugL.D	Cal P3 4/16/2016 5:25 PM Cal P4 4/16/2016 5:54 PM		0.5000 6.15		0.1900 0.1900			1696320	2.3				
	1 ugL.D	Cal P5 4/16/2016 6:22 PM		1.0000 6.15		0.9068 0.906			1678855	2.4				
		Cal P6 4/16/2016 6:51 PN		3.0000 6.15		2.5875 2.5875		25.4 6.611		2.3				
	10 ugL.D 30 ugL.D	Cal P7 4/16/2016 7:20 PN Cal P8 4/16/2016 7:49 PN		10.0000 6.15 30.0000 6.15		9.9305 9.930 34.5745 34.5745		25.6 6.611 26.1 6.611	1672165 1751605	2.4				
		Cal P9 4/16/2016 7:49 PM		100.0000 6.15		34.5/45 34.5/45 98.5136 98.5136			1/51605	2.4				
	200 ugL.D	Cal P10 4/16/2016 8:47 PM		200.0000 6.15		198.7622 198.7622			2185621	2.3				
		Cal P11 4/16/2016 9:15 PN	4 300	300.0000 6.15	54 1379701 🗖	293.6364 293.6364	4 97.9 36.5	27.6 6.611	2377040	2.2				
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gL.D 1 0 2 - 0.8 - 0.6 - 0.4 -		P 10 0 ug/l 62	0 64 0 49 0			+ Scan (6.109-6.246 min, 을 x10 ^{7 -} 3 - 62.0	78.0			* 🔹 🖬 🖬	and the state of the	tate 0 Detate (< ISTO QC
gL.D 1 0 2 - 0.8 - 0.6 - 0.4 -		P 10 0 ug/l 62				+ Scan (6.109-6.246 min, ************************************	78.0		1,2-dichloro-Et S x10 1 y = R ² 2 S 5.5- Typ C 5- -4tpag 4.5- -4tpag 4-	*	and the state of the	tate 0 Detate (< ISTD QC
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Volatiles Analysis: 1,3-dichloro-Propane Purge-and-Trap Sample Preparation: 7890B GC and 7010 HES

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P 1 ugL.D	Cal P5 4/16/2016 6:22 PM	1	1.0000 8.832		0.8615 0.8615	86.2 312.0 6.611 16788						
P 3 ugL.D	Cal P6 4/16/2016 6:51 PM	3	3.0000 8.832	269278 🗖 2	2.5770 2.5770	85.9 292.2 6.611 16593	72 2.3					
P 10 ugL.D	Cal P7 4/16/2016 7:20 PM	10	10.0000 8.835		9.5161 9.5161	95.2 309.2 6.611 16721						
P 30 ugL.D	Cal P8 4/16/2016 7:49 PM Cal P9 4/16/2016 8:18 PM	30	30.0000 8.835		5.7777 35.7777	119.3 306.0 6.611 17516 107.5 300.9 6.611 18812						
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P 300 ugL.D	Cal P11 4/16/2016 9:15 PM	300	300.0000 8.835		0.2964 280.2964	93.4 278.5 6.611 23770						
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• + ‡ <u>A</u>			a a a a	▲ A ☆ A			₽	‡ 🕴 💽 🖬	Type: Linear		Origin: L 💌 Weight: 1/x	▼ ISTD Q
↔ ‡ <u>&</u>	o-Propane P 300 ug/L 78.0	, 76.0		+ Scan	(8.793-8.923 min, 39 s		I,3-dichlore	🗘 🐥 🔚 🖬	, 8 Levels Used, 11 I			▼ ISTD Q
↔ ‡ <u>&</u>	o-Propane P 300 ug/L RT=8.835 2.584E+007			+ Scan	(8.793-8.923 min, 39 s		الالا الالالا الالالالالالالالالالالالال	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			• ISTD Q
↔ ‡ <u>&</u>	o-Propane P 300 ug/L RT=8.835 2.584E+007	1, 76.0 (10 ²] Ratio = 278.5 (92 1- 0.8-		+ Scan 왈 x10	(8.793-8.923 min, 39 s		الالا الالالا الالالالالالالالالالالالال	* * * Propane - 11 Levels = 0.123586 * x + 0.	, 8 Levels Used, 11 1 01954			• ISTD Q
↔ ‡ <u>&</u>	o-Propane P 300 ug/L RT=8.835 2.584E+007	. 76.0 10 ² Ratio = 278.5 (92 1- 0.8- 0.6-		+ Scan 욑 x10 이	(8.793-8.923 min, 39 s 8-76.0 5- 4- 3-	scans) P 300 ugL D 165.8 128.9	الالا الالالا الالالالالالالالالالالالال	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			• ISTD Q
↔ ‡ <u>&</u>	o-Propane P 300 ug/L RT=8.835 2.584E+007	, 760 10 ² Ratio = 278.5 (92 1- 0.8- 0.6- 0.4-		+ Scan 욑 x10 이	(8.793-8.923 min, 39 s 8 76.0 5 76.0 4 76.0 3 76.0 4 76.0 5 76.0	scans) P 300 ugL D 165.8 128.9	الالا الالالا الالالالالالالالالالالالال	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			• চচ ০
↔ ‡ <u>&</u>	o-Propane P 300 ug/L 78.0 RT=8.835 2.584E+007	. 76.0 10 ² Ratio = 278.5 (92 1- 0.8- 0.6-		+ Scan 욑 x10 이	(8.793-8.923 min, 39 e 8- 76.0 5- 4- 3- 2- 1- 49.0 93.9 L	scans) P 300 ugL D 165.8 128.9	1,3-dichlore 8 x10 1_ 5 x10 1_ 1.6-	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			• ISTO Q
↔ ‡ ▲ ugL.D 1.3-dichlo 0.2 1.3-dichlo 0.2 0.6- 0.4- 0.4- 0.2- 0	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-dichloro-Propane	, 760 10 ² Ratio = 278.5 (92 1- 0.8- 0.6- 0.4-	(% 6	+ Scan 욑 x10 이	(8.793-8.923 min, 39 e 8-76.0 5- 4- 3- 2- 49.0 0- 49.0 1- 49.0 1- 10- 10- 10- 10- 10- 10- 10-	scans) P 300 ugL D 165.8 128.9	الالا الالالا الالالالالالالالالالالالال	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			▼ ISTD Q
	c-Propane P 300 ugL Name=1,3-diphloro-Propane 8,75 8/8 8,85 8/9 8,95 9 Acquisition Time (min)	. 76.0 10 ² Ratio = 278.5 (92 1- 0.6- 0.4- 0.2- 0.4- 0.2- 0.4- 0.2- 0.5- 0.4- 0.5- 0.4- 0.5- 0.4- 0.5-	8.8 8.85 8.9	+ Scan	(8.793-8.923 min, 39 e 8 76.0 5 4 4 - 2 49.0 1 49.0 40 60 80 100	scans) P 300 ugL.D 165.8 128.9 11.9 120 140 160 180 200 220 Mass-to-Charge (m/z)	1.3-dichlor sex101 uodsat 1.6- ax101 1.6- ax101 1.6- ax101 1.2- 1.2- 1-	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			• ISTD Q
	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-diblioro-Propane 8.75 8/8 8.85 8/9 8.95 9 Acquisition Time (min)	, 760 10 ² 10 ² 10 ³ 10 ⁴ 10	9%) 8/8 8/85 8/9 Acquisitio	8.95 9 an Time (min) + Scan	(8.793-8.923 min, 39 e - 76.0 - 49.0 - 49.0	scans) P 300 ugL D 165.8 11.9 11.9 126.9 13.9 140 160 180 200 220 Mass-to-Charge (m/z) scans) P 300 ugL D	1,3-dichlor 8 ×10 1 0 0 0 1.4-	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			• ISTD Q
	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-diblioro-Propane 8.75 8/8 8.85 8/9 8.95 9 Acquisition Time (min)	, 760 10 ² 10 ² 10 ³ 10 ⁴ 10	9%) 8/8 8/85 8/9 Acquisitio	8.95 9 an Time (min) + Scan	(8.793-8.923 min, 39 e - 76.0 - 49.0 - 49.0	scans) P 300 ugL.D 165.8 128.9 11.9 120 140 160 180 200 220 Mass-to-Charge (m/z)	1.3-dichlor sex101 uodsat 1.6- ax101 1.6- ax101 1.6- ax101 1.2- 1.2- 1-	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 1 01954			• ISTD Q
0 ugL D 1,3-dichlo 10 2 1- 0.8 0.6 0.4 0.2 0 8.65 8.7 0 ugl D 14 difluer	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-diblioro-Propane 8.75 8/8 8.85 8/9 8.95 9 Acquisition Time (min)	, 760 10 ² 10 ² 10 ³ 10 ⁴ 10	9%) 8/8 8/85 8/9 Acquisitio	8.95 9 an Time (min) \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	(8.793-8.923 min, 39 e a 76.0 5 4 4 - 2 49.0 1 49.0 1 40 60 80 100 (6.570-6.710 min, 42 e 7 1	scans) P 300 ugL D 165.8 11.9 11.9 126.9 13.9 140 160 180 200 220 Mass-to-Charge (m/z) scans) P 300 ugL D	1,3-dichlor 8 ×10 1 0 0 0 1.4-	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 I 01954			
	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-diblioro-Propane 8.75 8/8 8.85 8/9 8.95 9 Acquisition Time (min)	, 760 10 ² 10 ² 10 ³ 10 ⁴ 10	9%) 8.8 8.85 8.9 Acquisitie	8.95 9 an Time (min) 9 200	(8.793-8.923 min, 39 e 8 - 76.0 5 - 93.9 1 - 10 - 40.60 80 100 (6.570-6.710 min, 42 e 7 - 1 1 - 8 - 1 - 8 - 1 - 8 - 1 - 8 - 8 - 8 - 8 - 8 - 8 - 8 - 8	scans) P 300 ugL D 165.8 11.9 11.9 126.9 13.9 140 160 180 200 220 Mass-to-Charge (m/z) scans) P 300 ugL D	1.3-dichlord sex 10 ¹ 1.6- sex 10 ¹ 1.6- 1.4- 1.2- 1.2- 1.2- 0.8- 0.6- 0.4-	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 I 01954			• ISTD Q
1 ↔ ‡ A 0 ugLD 1.3-dichlo 10 ² 1- 0.8- 0.4- 0.2- 0.4- 0.2- 0.4- 0.2- 0.4- 0.2- 0.4- 0.2- 0.	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-diblioro-Propane 8.75 8/8 8.85 8/9 8.95 9 Acquisition Time (min)	, 760 10 ² 10 ² 10 ³ 10 ⁴ 10	9%) 8.8 8.85 8.9 Acquisitie	8.95 9 an Time (min) \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	(8,793-8,923 min, 39 ¢	scans) P 300 ugL D 165.8 11.9 128.9 129.9 120.140.160.180.200.220 Mass-to-Charge (m/z) Scans) P 300 ugL D 114.0	Image: Constraint of the second se	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 I 01954			
	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-diblioro-Propane 8.75 8/8 8.85 8/9 8.95 9 Acquisition Time (min)	, 760 10 ² 10 ² 10 ³ 10 ⁴ 10	9%) 8.8 8.85 8.9 Acquisitie	8.95 9 an Time (min) 9 0.0 0 0 0 0 0 0 0 0	(8,793-8,923 min, 39 4 8 1 76.0 4 3 4 49.0 4 49.0	scans) P 300 ugL D 165.8 128.9 11.9 120 140 160 180 200 220 Mass-to-Charge (m/z) scans) P 300 ugL D 114.0 88.0	1.3-dichlord sex 10 ¹ 1.6- sex 10 ¹ 1.6- 1.4- 1.2- 1.2- 1.2- 0.8- 0.6- 0.4-	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	, 8 Levels Used, 11 I 01954			
	o-Propane P 300 ug/L RT48.835 2.584E+007 Name=1.3-diblioro-Propane 8.75 8/8 8.85 8/9 8.95 9 Acquisition Time (min)	. 76.0 10 ² Ratio = 278.5 (92 1- 0.6- 0.4- 0.2- 0.4- 0.2- 0.4- 0.2- 0.5- 0.4- 0.5- 0.4- 0.5- 0.4- 0.5-	8.8 8.85 8.9 Acquisiti	8.95 9 an Time (min) + Scan g x10 + Scan g x10 0.0 0.0 0.0 0.0	(8,793-8,923 min, 39 # * 76.0 * 76.0 * 93.9 * 49.0 * 93.9 * 1 * 49.0 * 1 * 1 * 1 * 1 * 1 * 1 * 1 * 1	scans) P 300 ugL D 165.8 11.9 128.9 129.9 120.140.160.180.200.220 Mass-to-Charge (m/z) Scans) P 300 ugL D 114.0	1.3-dichlor g x10 ⁻¹ . si x1	Propane - 11 Levels = 0.123586 * x + 0. (*2 = 0.99396951	8 Levels Used, 11 01954 nore, Weight 1/x	Points, 8 Points		



Conclusions: Volatiles Analysis Purge-and-Trap Sample Preparation: 7890B GC and 7010 HES

5977B HES Performance

- Significant improvement in detection limits
- Signal improvement provided is not complicated by interferences, and results in clear enhancements in detection.
- Extends dynamic range of P/T application





Semi-Volatiles Analysis



Environmental Monitoring Requirements Analysis of Semi-Volatile Compounds (SVOCs)

Overview

- •SVOCs are a broad class of environmentally significant contaminants of global interest.
- Included in a target analyte lists for GC/MS methods such as EPA methods 8270, 625 and 525 methods

GC/MS Analysis

- •Listed as targets and appropriate to selected ion monitoring (SIM) in GC/MS analysis
- •Surveying samples by scanning GC/MS provides advantages:
- •Full scan spectra for compound confirmation
- •Tentatively identifying unexpected unknowns in samples that would escape SIM,
- · In the past scan sensitivity was borderline or insufficient
- •When compared to SIM
- •To meet the required detection limits.

Project Scope

- •Survey select compounds of environmental interest as an indication of what may be achieved with the new 5977B GC/MSD in this approach.
- •Determine if High Efficiency Source (HES) increases ion current created that may lead to improvement in sensitivity and significant improvements in detection limits for VOC targets.
- •Evaluate new HES capability to produce scan detection limits for SVOCs that were formerly only approached by SIM.
- •Determine instrument detection limits (IDLs) for a few SVOCs across the classes of compounds typical to this analysis.



Environmental Monitoring Requirements Analysis of Semi-Volatile Compounds

GC Summary

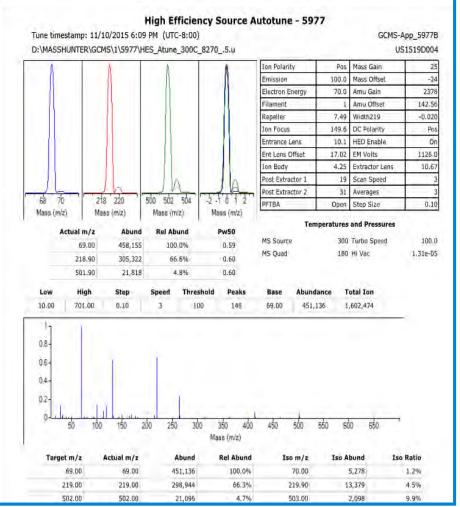
Run time	25 min.		
Oven Temperature			
(Initial)	40°C	Hold time	0.5 min.
Post run	40°C	#1 Rate	10°C/min.
#1 Value	100°C	#1 Hold Time	0 min.
#2 Rate	25°C/min.	#2 Value	260°C
#2 Hold Time	0 min.	#3 Rate	10°C/min.
#3 Value	280°C	#3 Hold Time	0 min.
#4 Rate	25°C/min.	#4 Value	320°C
#4 Hold Time	8.5 min.		

Agilent 5190-2293: 900 µL (splitless, single taper, ultra inert)

MS Parameters

Acquisition Mode	Scan	Normal or Fast Scanning Normal Scanning
Solvent Delay	3.0 min.	EM Setting Mode Gain 0.1
Trace Ion Detection	On	
[Scan Parameters]		
Start Time	3.0 min.	
Low Mass	50	High Mass 550
Threshold	75	A/D Samples 4
MS Source	350°C	Maximum 350°C
MS Qual	180°C	Maximum 200°C

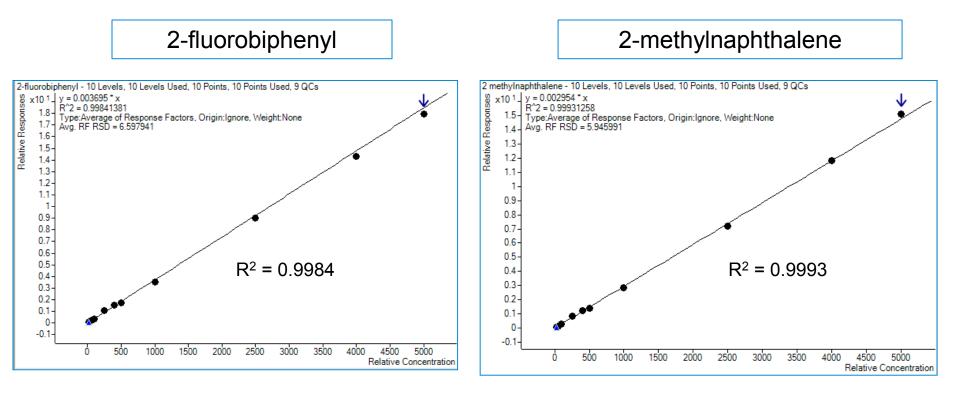
Parameters for SVOC analysis



HES Autotune



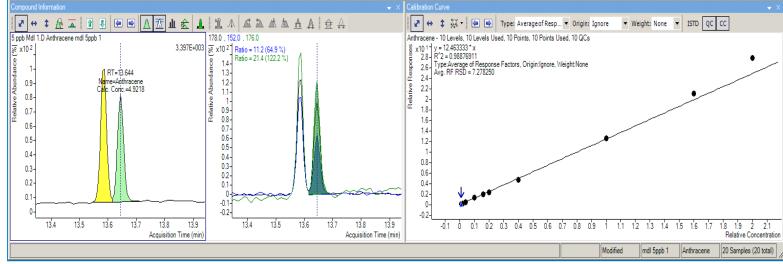
Linearity: Semi-Volatiles Analysis





Semi-Volatiles Analysis: Anthracene

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ch Ta	ble																				
Sampl	e: 👔 mdl 5ppb 1		-	Sample Type: <all></all>			- C	ompound	I: 🔄 Anthrac	cene	•	ISTD:	Phenanti	hrene-D10	∎ †≣			1 🙀 🔯 🚩 1	7	Sample/Compound Group: <all></all>	
		Sa	ample				Anthrace		A	Anthracene Res	ults		Qu Q	u Phenant	hrene-D10 (IS						
7	Data File	Туре	Level	Acq. Date-Time	Amt	Tot. Amt.	Exp. Conc.	RT	Resp.	MI Calc. Con	c. Final Conc.	-			Resp.	Ratio					
Ė	accustandard 5 ppb.D	Cal	1	11/12/2015 1:12 AM	5		5.0000	13.644					9.4 1		40207		10.7				
	accustandard 10 ppb.D	Cal	2	11/12/2015 1:43 AM	10		10.0000	13.644					11.7 2		32896	9.8	10.9				
	accustandard 20 ppb.D	Cal	3	11/12/2015 2:14 AM	20		20.0000	13.644					11.5 2		29093		10.7				
	accustandard 50 ppb.D	Cal	4	11/12/2015 2:45 AM	50		50.0000	13.645	41255	54.09	9 54.0919	108.2	11.7 2	0.8 13.559	30597	9.4	11.0				
	accustandard 80 ppb.D	Cal	5	11/12/2015 3:16 AM	80		80.0000	13.644	66844	76.964	6 76.9646	96.2	11.1 2	0.9 13.558	34842	8.9	10.7				
	accustandard 100 ppb.D	Cal	6	11/12/2015 3:47 AM	100		100.0000	13.644	71544	91.870	15 91.8705	91.9	11.5 2	1.8 13.559	31241		10.7				
	accustandard 200 ppb.D	Cal	7	11/12/2015 4:19 AM	200		200.0000	13.644	127358	189.06	9 189.0659	94.5	11.6 2	1.0 13.559	27024		10.8				
	accustandard 500 ppb.D	Cal	8	11/12/2015 4:50 AM	500		500.0000	13.644	332001	506.26	9 506.2679	101.3	11.8 2	1.8 13.559	26308		10.8				
	accustandard 800 ppb.D	Cal	9	11/12/2015 5:21 AM	800		800.0000	13.644	664835	844.77	844.7751		12.0 2		31572		10.8				
		Cal	10	11/12/2015 5:52 AM	1000		1000.00	13.644					12.5 2		41145		10.8				
	5 ppb MdI 10.D	QC	1	11/12/2015 11:02 AM			5.0000	13.644					12.0 2		20318		10.9				
	5 ppb MdI 1.D	QC 🔽	1	11/12/2015 11:34 AM			5.0000	13.644					11.2 2		32142		10.7				
	5 ppb MdI 2.D	QC	1	11/12/2015 12:05 PM			5.0000	13.644					10.3 1		28057		11.0				
	5 ppb MdI 3.D	QC	1	11/12/2015 12:36 PM			5.0000	13.644					11.0 2		26416		11.0				
	5 ppb MdI 4.D	QC	1	11/12/2015 1:07 PM			5.0000	13.644					12.4 2		22891		11.1				
	5 ppb MdI 5.D	QC	1	11/12/2015 1:38 PM			5.0000	13.644					10.0 2		30189		10.9				
	5 ppb MdI 6.D	QC	1	11/12/2015 2:09 PM			5.0000	13.644				95.7		1.0 13.558	27069						
	5 ppb MdI 7.D	QC	1	11/12/2015 2:40 PM			5.0000	13.644					13.2 2		23910		10.7				
	5 ppb Mdl 8.D 5 ppb Mdl .D	QC QC	1	11/12/2015 3:11 PM 11/12/2015 3:42 PM			5.0000 5.0000	13.644 13.644					10.9 2	0.2 13.559	27744 30213		11.5				





Semi-Volatiles Analysis: Anthracene

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	nt MassHunter Quantita				- 04-20-	2016.Datch	1.DIN												
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Batch Ta	ble																		▼ X
Sampl	le: 👔 mdl 5ppb 1		-	Sample Type: <all></all>			- C	ompound:	Anthracene		-	ISTD: Ph	enanthre	ene-D10	■ ↓		🛛 🛠 🕅 🏲 🏞 💝	Sample/Compound Group: <a< p=""></a<>	All>
-		Sar	nple			,	Anthrace		Anthr	acene Results		Q	u Qu.	Phenanth		Qu Qu			
7	Data File	Туре	Level	Acq. Date-Time	Amt.	Tot. Amt. E	Exp. Conc.	RT	Resp. MI	Calc. Conc.	Final Conc.	Accuracy Ra	atio Rati	o RT	Resp.	Ratio Ratio			
	accustandard 5 ppb.D	Cal	1	11/12/2015 1:12 AM	5		5.0000	13.644	5253	5.2413	5.2413	104.8 9	9.4 19.	5 13.558	40207	9.0 10.7		c · ·	
	accustandard 10 ppb.D	Cal	2	11/12/2015 1:43 AM	10		10.0000	13.644	7753 🗖	9.4556	9.4556	94.6 11	1.7 20.9	9 13.559	32896	9.8 10.9		Spike	a 🛛
	accustandard 20 ppb.D	Cal	3	11/12/2015 2:14 AM	20		20.0000	13.644	13236 🗌	18.2521	18.2521		1.5 20.4		29093	8.8 10.7			
	accustandard 50 ppb.D	Cal	4	11/12/2015 2:45 AM	50		50.0000	13.645	41255 🗌	54.0919	54.0919	108.2 11			30597	9.4 11.0		amo	unt
	accustandard 80 ppb.D	Cal	5	11/12/2015 3:16 AM	80		80.0000	13.644	66844	76.9646	76.9646		1.1 20.		34842	8.9 10.7			
	accustandard 100 ppb.D	Cal	6	11/12/2015 3:47 AM	100		100.0000	13.644	71544	91.8705	91.8705		1.5 21.0		31241	9.4 10.7			
_	accustandard 200 ppb.D accustandard 500 ppb.D	Cal Cal	8	11/12/2015 4:19 AM 11/12/2015 4:50 AM	200		200.0000 500.0000	13.644 13.644	127358	189.0659 506.2679	189.0659 506.2679	94.5 11 101.3 11	_		27024 26308	9.2 10.8 9.1 10.8			
	accustandard 500 ppb.D accustandard 800 ppb.D	Cal	0 9	11/12/2015 4:50 AM	800		800.0000	13.644	664835	844.7751	844,7751		2.0 21.		31572	8.8 10.8			
	accustandard 1000 ppb.D	Cal	10	11/12/2015 5:52 AM	1000		1000.0000	13.644	1145741	1117.1332	1117 1222		2.5 22.4		41145	9.3 10.8			
	5 ppb Mdl 10.D	QC	1	11/12/2015 11:02 AM	1000	- 6	5.0000	13.644	2237	4.4167	4.4167		2.0 20.0		20318	9.0 10.9			
	5 ppb Mdl 1.D	QC 🔽	1	11/12/2015 11:34 AM			5.0000	13.644	3943	4.9218	4.9218		1.2 21.4		32142	9.0 10.7			
	5 ppb Mdl 2.D	QC	1	11/12/2015 12:05 PM			5.0000	13.644	3387 🗖	4.8423	4.8423		0.3 17.		28057	8.6 11.0			
	5 ppb Mdl 3.D	QC	1	11/12/2015 12:36 PM			5.0000	13.644	3193 🗖	4.8491	4.8491	97.0 11	1.0 20.	8 13.558	26416	9.5 11.0			
	5 ppb MdI 4.D	QC	1	11/12/2015 1:07 PM			5.0000	13.644	2768 🗖	4.8515	4.8515		2.4 20.1	1 13.559	22891	9.1 11.1]		
	5 ppb MdI 5.D	QC	1	11/12/2015 1:38 PM			5.0000	13.644	3555 🗖	4.7242	4.7242		0.0 21.0		30189	9.3 10.9			
	5 ppb MdI 6.D	QC	1	11/12/2015 2:09 PM			5.0000	13.644	3228 🗖	4.7843	4.7843		0.3 21.0		27069	9.3 10.6			
	5 ppb Mdl 7.D	QC	1	11/12/2015 2:40 PM			5.0000	13.644	2862	4.8012	4.8012		3.2 22.		23910	9.2 10.7			
	5 ppb Mdl 8.D	QC	1	11/12/2015 3:11 PM	_		5.0000	13.644	3313	4.7903	4.7903		0.9 20.1		27744	9.1 11.5		Actual amore	Sunt
	5 ppb MdI .D	QC	1	11/12/2015 3:42 PM			5.0000	13.644	3519	4.6725	4.6725	93.4 12	2.1 22.	6 13.558	30213	311 11.1			
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	II 1.D Anthracene mdl 5ppb 1	1				2.0 , 176.0									, 10 Points, 10 P	oints Used, i	10 QCs		
<u>ङ</u> x10 ²				14				A			% x1	0 1 - y = 12.4 2.8 - R^2 = 0.							
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ja 0.9	4 6	Vame=Anthrac anc. Conc.=4.9	ene 9218	1	1.2- 1.1-			11				2.2-						. /	
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·도 콩 0.7	4			14	0.9-			. 11 . 1			<u> </u>	1.8-							
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	13.4 13.5	13.6 1	3.7	13.8 13.9 Acquisition Time (min)		13.4	13.5	13.6		13.8 13 uisition Time (-0.1	ό o	.1 0.2 0	3 0.4 0.5	0.6 0.7	0.8 0.9 1 1.1 1.2	1.3 1.4 1.5 1.6 1.7 1.8 1. Relat	9 2 2.1 ive Concentration
											1						Modified n	dl 5ppb 1 Anthracene 20 San	nples (20 total)

Semi-Volatiles Analysis: Anthracene

Liiii Aaila	nt MassHunter Quantitat	tivo Analysis	lfor C		04 20	J	h hin													_ 🗆 X
	dit View Analyze Method				04-20-	2010.040	11.0111													
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Sampl	e: 👔 mdl 5ppb 1	•	•	Sample Type: <all></all>			▼ C	ompound:	Anthracen	e	•	ISTD:	Phenanthr	ene-D10	■ 1		🛛 🗱 🖗 🏲 🏷	' 衬 义 Sa	mple/Compound Group: <	All>
		Sam	nple				Anthrace		Anth	racene Results	1		Qu Qu	Phenanth	rene-D10 (IS	Qu Qu				
Ÿ	Data File	Туре	Level	Acq. Date-Time	Amt.	Tot. Amt.	Exp. Conc.	RT	Resp. M	Calc. Conc.	Final Conc.	ccuracy	Ratio Rat	io RT	Resp.	Ratio Ratio	0			
	accustandard 5 ppb.D	Cal	1	11/12/2015 1:12 AM	5		5.0000	13.644	5253	5.2413	5.2413	104.8	9.4 19.	5 13.558	40207	9.0 10.7	7		Cusila	
	accustandard 10 ppb.D	Cal	2	11/12/2015 1:43 AM	10		10.0000	13.644	7753 🗖	9.4556	9.4556	94.6	11.7 20.		32896	9.8 10.9			Spik	ea
	accustandard 20 ppb.D	Cal	3	11/12/2015 2:14 AM	20		20.0000	13.644	13236 🗌	18.2521	18.2521	91.3	11.5 20		29093	8.8 10.7				
	accustandard 50 ppb.D	Gui	4	11/12/2015 2:45 AM	50		50.0000	13.645	41255	54.0919	54.0919	108.2	11.7 20.		30597	9.4 11.0			amo	unt
	accustandard 80 ppb.D		5	11/12/2015 3:16 AM 11/12/2015 3:47 AM	80		80.0000	13.644 13.644	66844 C	76.9646 91.8705	76.9646 91.8705	96.2 91.9	11.1 20. 11.5 21.		34842 31241	8.9 10. 9.4 10.7				
	accustandard 100 ppb.D accustandard 200 ppb.D	Cal	7	11/12/2015 3:47 AM 11/12/2015 4:19 AM	200		200.0000	13.644	127358	189.0659	189.0659	91.9	11.5 21.		27024	9.4 10.7	_			
	accustandard 500 ppb.D	Cal	8	11/12/2015 4:15 AM	500		500.0000	13.644	332001	506.2679	506.2679	101.3	11.8 21.		2/024	9.1 10.8				
	accustandard 800 ppb.D		9	11/12/2015 5:21 AM	800		800.0000	13.644	664835	844.7751	844.7751	101.5	12.0 21.		31572	8.8 10.8				
	accustandard 1000 ppb.D	Cal	10	11/12/2015 5:52 AM	1000		1000.00	13.644	1145741	1117,1332	1117 1332	111.7	12.5 22		41145	9.3 10.8			-	
	5 ppb MdI 10.D	QC	1	11/12/2015 11:02 AM			5.0000	13.644	2237	4.4167	4.4167	88.3	12.0 20.		20318	9.0 10.9			Accurac	v
•	5 ppb Mdl 1.D	QC 🔽	1	11/12/2015 11:34 AM			5.0000	13.644	3943	4.9218	4.9218	98.4	11.2 21.	4 13.559	32142	9.0 10.7	7		Accurac	У
	5 ppb MdI 2.D	QC	1	11/12/2015 12:05 PM			5.0000	13.644	3387 🗖	4.8423	4.8423	96.8	10.3 17.		28057	8.6 11.0	ס			
	5 ppb MdI 3.D	QC	1	11/12/2015 12:36 PM			5.0000	13.644	3193 🗖	4.8491	4.8491	97.0	11.0 20.	_	26416	9.5 11.0				
	5 ppb MdI 4.D	QC	1	11/12/2015 1:07 PM			5.0000	13.644	2768 🗖	4.8515	4.8515	97.0	12.4 20.		22891	9.1 11.1	-			
	5 ppb MdI 5.D	QC	1	11/12/2015 1:38 PM			5.0000	13.644	3555	4.7242	4.7242	94.5	10.0 21.		30189	9.3 10.9				
	5 ppb Mdl 6.D	QC	1	11/12/2015 2:09 PM			5.0000	13.644	3228	4.7843	4.7843	95.7	10.3 21.		27069	9.3 10.6				
	5 ppb Mdl 7.D	QC	1	11/12/2015 2:40 PM			5.0000	13.644	2862	4.8012	4.8012	96.0	13.2 22.		23910 27744	9.2 10.7	-	Δ	atual ama	~
	5 ppb Mdl 8.D 5 ppb Mdl .D	QC QC	1	11/12/2015 3:11 PM 11/12/2015 3:42 PM			5.0000 5.0000	13.644 13.644	3313	4.7903	4.7903 4.6725	95.8 93.4	10.9 20. 12.1 22.	_	30213	9.1 11.8	_	A	ctual am	ount
	o ppo mar.o	u(C	· 1	11/12/2010 0.4211			5.0000	10.044	3010 []	4.0723	4.0723	33.4	12.1 22.	0 10.000	50215					
Compour	d Information										× Calibr	ation Curv	e							▼ X
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=	+ ‡ 🕅 🛣 🚹	↓ ●				0000 0000000000000000000000000000000000		± 4	₿		2		× •					Weight: None	▼ ISTD QC CC	
	I 1.D Anthracene mdl 5ppb 1					2.0 , 176.0									, 10 Points, 10 F	oints Used,	10 QCs			
<u>ङ</u> x10 ²	-					Ratio = 11	.2 (64.9 %)	4				n n l ¤^n -	2.463333 * = 0.988769	11						•
0 2 1				20	1.4-	rtatio = 21	.4 (122.2 %)	1				2.6 Type	:Average o	f Response F	actors, Origin:	gnore, Weigl	ht:None			• /
epu '		RT=13.644 ame=Anthrace		pa pa	1.3-			- J.			le Be	2.4 - Avg.	RF RSD =	7.278250						
1 Belative Abundance 8.0 Abundance 8.0 Selative Abundance	i di	alp. Conc.=4.9	218	Relative Abundance	1.2- 1.1-			- 11	t i		,e	2.2-							•	r
ē 0.8	-			e,	1-			Ы			Relative	2-							•	
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	13.4 13.5	13.6 13	3.7 А	13.8 13.9 cquisition Time (min)		13.4	13.5	13.6	13.7 Acc	13.8 13 juisition Time (-0.	1 0 ().1 0.2 0	.3 0.4 0.5	0.6 0.7	0.8 0.9 1 1.1	1.2 1.3 1.4		1.9 2 2.1 ative Concentration
				,							× 11						Modified	mdl 5ppb 1		amples (20 total)

Semi-Volatiles Analysis: 2-Fluorobiphenyl

201111	able ple: 🍸 8270 curve p	oint 10 👻 🎝	Sampl	e Type:	<all></all>	Compound: 🐖 2-fluorobiph	enyl		📑 ISTD	Napht			*		» Sampl	le/Compoun	d Group: <	JI>	
	pound Group: <all></all>	▼ Sample Grou	1		-		egment: <all></all>		-						*= · · ·				
	Cound Croups, Shire	TELEVISION AND AND AND AND AND AND AND AND AND AN	Sample	_	C	The source of the second secon	2-fluorobi		-	Alexabishand D			Outifie	Qualifie.	Machibal	Naphthale	Oust	- 0	
	1	1		1	La la	a stall the second	10.0000000	-		-fluorobiphenyl R		torn or hard						ie Q	
7	Name	Data File	Туре		1.		Exp. Conc.	RT		MI Calc. Conc.			Ratio M				esp. Ratio	Contraction of the second	
11	8270 curve point 1	accustandard 5 ppb.D	Cal	5	5	11/12/2015 1:12 AM	5.0000	11.2_	5383	5.3656	5.3656	107.3	39.4		0.2000		4305 12.6		7
-	8270 curve point 2	accustandard 10 ppb.D	Cal	10	10	11/12/2015 1:43 AM	10.0000	11.2_	8967		9.8314	98.3	35.6	26.7	0.2000		9370 12.8		7
1	8270 curve point 3	accustandard 20 ppb.D	Cal	20	20	11/12/2015 2:14 AM	20.0000	11.2_	15374	10.00100	19.2433	96.2	36.9	26.4	0.2000		3248 13.1		8
1	8270 curve point 4	accustandard 50 ppb.D	Cal	50	50	11/12/2015 2:45 AM	50.0000	11.2_	47775	57.4810	57.4810	115.0	36.5	26.2	0.2000		4991 12,6		8
-	8270 curve point 5	accustandard 80 ppb.D	Cal	80	80	11/12/2015 3:16 AM	80.0000	11.2_	70342	82.3809	82.3809	103.0	36.8	26.4	0.2000		6221 12,9		7
-	8270 curve point 6	accustandard 100 ppb.D	Cal	100	100	11/12/2015 3:47 AM	100.0000	11.2_	80873	94.1278	94.1278	94.1	37.0	26.3	0.2000		6509 12.6		7
-	8270 curve point 7	accustandard 200 ppb.D	Cal	200	200	11/12/2015 4:19 AM	200.0000	11.2_	153831	188.9800	188.9800	94.5	37.2	26.5	0.2000		4064 12.7		7
_	8270 curve point 8	accustandard 500 ppb.D	Cal	500	500	11/12/2015 4:50 AM	500.0000	11.2_	338185	487.2889	487.2889	97.5	37.3	26.7	0.2000		7568 12.9		8
	8270 curve point 9	accustandard 800 ppb.D	Cal	800	800	11/12/2015 5:21 AM	800.000	11.2	638332	775.8164	775.8164	97.0	37.6	27.1	0.2000		4539 12.9		7
	8270 curve point 10		Cal	1000	1000	11/12/2015 5:52 AM	1000.0000	11.2	900776	971.6787	971.6787	97.2	38.0	27.4	0.2000		0182 12.8		8
	mdl 5ppb 10	5 ppb MdI 10.D	QC	5	5	11/12/2015 11:02 AM	5.0000	11.2_	3396	4.6621	4.6621	93.2	36.9	26.8	0.2000		9431 14.0		8
	mdl 5ppb 1	5 ppb Mdl 1.D	QC	5	5	11/12/2015 11:34 AM	5.0000	11.2	3853	4.7460	4.7460	94.9	36.9	26.5	0.2000		3948 13.9		8
	mdl 5ppb 2	5 ppb Mdl 2.D	QC	5	5	11/12/2015 12:05 PM	5.0000	11.2	3744		4.6766	93,5	36.7	25.3	0.2000		3342 13.4		7
_	mdl 5ppb 3	5 ppb Mdl 3.D	QC	5	5	11/12/2015 12:36 PM	5.0000	11.2_	3481		4.5220	90.4	37.5	27.4	0.2000		1672 13.8		8
	mdl 5ppb 4	5 ppb Mdl 4.D	QC .	5	5	11/12/2015 1.07 PM	5.0000	11.2_	3348		4.5188	90.4	37.6	26.6	0.2000		0101 14.1		7
_	mdl 5ppb 5	5 ppb Mdl 5.D	QC	5	5	11/12/2015 1:38 PM	5.0000	11.2_	3709	4.7139	4.7139	94.3	36.5	27.3	0.2000		2587 13.5		8
	mdl 5ppb 6	5 ppb MdI 6.D	QC	5	5	11/12/2015 2:09 PM	5.0000	11.2_	3490	4.5928	4.5928	91.9	37.4	25.1	0.2000		1131 13.6		7
	mdl 5ppb 7	5 ppb Mdl 7.D	QC	5	5	11/12/2015 2:40 PM	5.0000	11.2	3310		4.3760	87.5	37.3	25.3	0.2000		0945 13.8		7
	mdl 5ppb 9	5 ppb MdI .D	QC	5	5	11/12/2015 3:42 PM	5.0000	11.2	3690	4.5794	4.5794	91.6	35.6	26.4	0.2000	10.062 4	3621 13.5		8
10 0.9	5- 9- 5-	Belative Abundance (.1- 1- .9-	= 27.4 (104,6 %)	دع ۱- 0.8- 0.6- 0.4-	172.0		Relative Respons	x101_y = 0.003 1.8 R ² = 0.9 Type:Avi 1.7 Avg. RF 1.6- 1.5- 1.4- 1.3- 1.2- 1.1-	99841381 Frage of Resp RSD = 6.5979	oonse Fac 941	tors, Origi	in:Ignore, V	/eight:None	/	/		
0. 0.8 0.7 0.7 0.6 0.5 0. 0.5 0. 0.4 0.3 0.2	5- 7- 5- 6- 5- 5- 5- 5- 3-	であり、 の、 の、 の、 の、 の、 の、 の、 の、 の、 の、 の、 の、 の、	.7- .6- .5- .4-			0.2- 85.0 	¢Į.		-	1- 0.9- 0.8- 0.7- 0.6- 0.5-			/	/					

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MDLS: Semi-Volatiles Analysis

					Avg							
Name	RT	Transition	Avg Conc.	Std. Dev.	Conc./Std.	Conc. RSD	MDL	100	LOD	Avg Height	Avg. Resp	Resp. RSD
indire.		Transition	ing conci	otor been	Dev.	concriso			200		118 nesp	nesprinse
1,4-dichlorobenzene	8.477	146	2.5604	0.0507	50.54	2	0.133	0.5066	0.152	1447	2634	5.9
1,2-dichlorobenzene	8.68	146	2.5889	0.0744	34.82	2.9	0.1951	0.7435	0.2231	1390	2503	5.8
Anthracene	13.662	178	2.3763	0.0471	50.49	2	0.1235	0.4707	0.1412	1960	3029	15.9
Benz[a]anthracene	17	228	2.894	0.094	30.79	3.2	0.2467	0.94	0.282	919	1600	23.3
2-fluorophenol	6.354	112	1.8707	0.1018	18.38	5.4	0.2671	1.0177	0.3053	371	1036	10.3
Phenol-d5-	7.853	99	2.0789	0.1061	19.59	5.1	0.2785	1.061	0.3183	585	1353	9.2
Phenol	7.872	94	2.0978	0.0753	27.85	3.6	0.1977	0.7533	0.226	605	1406	4.7
Aniline	7.968	93	2.0027	0.1123	17.83	5.6	0.2948	1.1232	0.337	974	1854	8.1
Bis(2-chloroethyl) ether	8.044	93	2.4595	0.1975	12.45	8	0.5183	1.9747	0.5924	836	1856	7.5
2-chlorophenol	8.149	128	1.8842	0.1333	14.13	7.1	0.3499	1.3333	0.4	412	942	9.7
1,3-dichlorobenzene	8.378	146	2.5532	0.0566	45.14	2.2	0.1485	0.5657	0.1697	1399	2575	5.9
Dibenz[a,h]anthracene	22.325	278	5.8961	0.4339	13.59	7.4	1.1388	4.3391	1.3017	224	970	23.9
Benzyl alcohol	8.604	108	2.6224	0.6737	3.89	25.7	1.768	6.7365	2.021	337	857	26.3
Dibenzofuran	12.202	168	2.6192	0.0787	33.28	3	0.2066	0.7871	0.2361	2574	3904	10.5
o-Cresol	8.732	108	2.9833	0.9942	3	33.3	2.6092	9.9416	2.9825	535	1434	34.2
Bis(2-chloro-1-methylethyl) ether	8.79	121	3.72	0.1907	19.51	5.1	0.5005	1.9072	0.5722	241	684	8.9
p-Cresol	8.924	108	2.4153	0.653	3.7	27	1.7138	6.5301	1.959	489	1153	27.4
N Nitroso-di-n-propylamine	8.953	70	2.8614	0.4659	6.14	16.3	1.2227	4.6589	1.3977	524	1448	20.4
Hexachloroethane	9.14	117	2.4922	0.1367	18.24	5.5	0.3586	1.3665	0.41	503	798	5.8
Nitrobenzene-D5	9.166	82	2.2607	0.0589	38.4	2.6	0.1545	0.5887	0.1766	861	1688	6.2
Nitrobenzene	9.192	77	2.1995	0.1304	16.87	5.9	0.3422	1.3038	0.3911	816	1458	9.3
Isophorone	9.484	82	2.0293	0.0875	23.2	4.3	0.2295	0.8746	0.2624	1078	1899	8.5
2,4-dimethylphenol	9.602	107	1.808	0.0766	23.61	4.2	0.2009	0.7657	0.2297	531	897	8.5
bis(2-chloroethoxy)-methane	9.721	93	2.2003	0.0797	27.62	3.6	0.2091	0.7968	0.239	1142	1805	4.6
2,4-dichloro-phenol	9.87	162	1.3744	0.1568	8.76	11.4	0.4116	1.5684	0.4705	253	457	16.6
1,2,4-trichlorobenzene	9.984	180	2.5619	0.0646	39.65	2.5	0.1696	0.6462	0.1939	1337	2057	6.7
Naphthalene	10.086	128	2.5072	0.033	76.08	1.3	0.0865	0.3295	0.0989	3723	5908	6.4
4-Chloroaniline	10.117	127	2.141	0.256	8.36	12	0.6718	2.5596	0.7679	795	1720	14.4
Hexachlorobutadiene	10.219	227	2.002	0.4507	4.44	22.5	1.1828	4.5068	1.352	553	621	25.5
4-chloro-3-methyl-phenol	10.629	142	2.6386	0.3667	7.2	13.9	0.9625	3.6673	1.1002	256	540	18.5
2 methylnaphthalene	10.863	141	2.4774	0.2275	10.89	9.2	0.597	2.2747	0.6824	1857	2953	7.5
2-fluorobiphenyl	11.24	172	2.2854	0.0579	39.49	2.5	0.1519	0.5787	0.1736	2365	3421	7.8
2 chloronaphthalene	11.396	162	2.3329	0.057	40.96	2.4	0.1495	0.5695	0.1709	1889	2857	8.4
2-Nitroaniline	11.472	65	2.0706	0.3219	6.43	15.5	0.8448	3.2188	0.9657	179	294	17.7
Dimethyl phthalate	11.635	163	2.2032	0.0793	27.8	3.6	0.208	0.7925	0.2378	1601	2510	6.9
2,6 Dinitrotoluene	11.71	89	2.3394	0.3694	6.33	15.8	0.9696	3.6943	1.1083	143	200	18.3
Acenapthylene	11.845	152	2.5816	0.2025	12.75	7.8	0.5315	2.0252	0.6076	2327	3699	7.6
3-Nitroaniline	11.896	92	0.465	0.3278	1.42	70.5	0.8603	3.2781	0.9834	119	215	25.8
Acenaphthene	12.024	152	2.9098	0.4256	6.84	14.6	1.117	4.2561	1.2768	1163	1805	11.4
2,4-dinitro-toluene	12.135	165	10.127	0.2458	41.2	2.4	0.6451	2.4578	0.7373	142	208	18.4
Diethyl Phthalate	12.358	149	5.1659	0.9011	5.73	17.4	2.3648	9.0105	2.7032	3467	4979	21.6



Conclusions: Semi-Volatiles Analysis 7890B GC and 5977B MSD HES

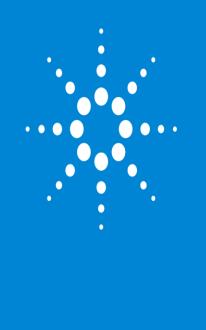
HES Performance:

- Preliminary results suggest <u>a significant improvement in linearity and system</u> <u>stability at the lowest concentration level</u>
- Wide Dynamic Range
 - Possibly eliminates need to dilute and reanalyze samples which would have been over range on previous systems.
 - Reduces re-runs
- Signal improvement provided a more stable platform to perform day-to-day analysis





Nitrosamines Analysis





N-Nitrosamines in Drinking Water GC/MS/MS with HES

N-Nitrosamines like NDMA are inadvertent by-products of wastewater treatment through chlorination.

EPA method 521, (2004) specifies use of ion trap MS based liquid CI/MS/MS measurements for the detection of N-nitrosamines in drinking water

Industry requires alternate, sensitive and reliable procedure for the analysis of N-nitrosamines.

GC-MS tandem quadrupole technology deliver very high sensitivity and selectivity in the small molecule mass range and allow the detection of nitrosamines meeting and exceeding current detection levels attained using CI/MS/MS measurements.

Method designed to demonstrate application of GC/MS/MS instrumentation to determine nitrosamines in drinking water satisfying EPA method 521 requirements



Method: N-Nitrosamines in Drinking Water GC-MS/MS with HES

Leveraging Technological Advance

•Method was developed using Agilent 7890B GC coupled to the 7010 Mass Spectrometer (MS) in positive electron ionization mode (EI), using HES (high efficiency source).

GC configuration

- •Multi-mode inlet (MMI)
- •30 meter DB-1701 column
- •7693 Autosampler (A/S).

Sample Prep

• In this study solid phase extraction for sample preparation following the protocol outlined in EPA Method 521

Analysis

- •Run time was less than 14.0 minutes.
- •Triplicate calibration curves were set up using 5 levels
- •1.0 ng/L to 20 ng/L extracted
- •1.25 ng/L to 20 ng/L solvent standards
- •Data analysis was carried out using MassHunter Software



Approach: Method: N-Nitrosamines in Drinking Water GC-MS/MS with HES

Analytical Approach

- Only <u>0.5 microliter extract</u> was injected into a GC/MS/MS system employing electron ionization.
 - EPA method 521 utilizes large volume injections (20µL) to reach the required minimum reporting limits (MRLs)
 - 1.2 ng/L for NDPA)
 - 2.1 ng/L for NDEA
- Using surrogate (NDMA-d6) and internal standards (NDPA-d14, NDEA-d10) ensures accurate quantitation
 - Accounts for analytical variability that may occur during sample processing, extraction, and instrumental analysis.





Target Analytes: N-Nitrosamines in Drinking Water GC-MS/MS with HES

Name	ABR	R∕ T	Quant Mass	R
N-nitrosodimethylamine	NDMA-d6	7.10	80>50	IS/ Surr
N-nitrosodimethylamine	NDMA	7.15	74>44	0.99968
N-nitrosomethyethylamine	NMEA	8.28	88>71	0.99981
N-nitrosodiethylamine	NDEA-d10	9.10	112>94	IS
N-nitrosodiethylamine	NDEA	9.13	102>85	0.99996
N-nitrosodipropylamine	NDPA-14	11.00	144>126	IS
N-nitrosodipropylamine	NDPA	11.08	113>71	0.99922
N-nitrosomorpholine	NMOR	11.47	86>56	0.99993
N-nitrosopyrrolidine	NPYR	11.64	100>70	0.99131
N-nitrosopiperdine	NPIP	11.85	114>84	0.99837
N-nitrosodi-n-butylamine	NDBA	12.56	116>99	0.99937

Retention Times, Quantitation Mass, and Linearity R²



MRM Transitions: N-Nitrosamines in Drinking Water GC-MS/MS with HES

Compound	Transition	Œ	Compound	Transition	Œ
NDMA-d6	80>50.1	6	NDPA	130>43	20
NDMA-d6	80>48.1	14	NDPA	130>113	8
NDMA	74>42.1	14	NMOR	116>56.1	20
NDMA	74>44.1	6	NMOR	116>86	4
NMEA	88>71	6	NPYR-d8	108>78.1	10
NMEA	88>43	10	NPYR-d8	108>62.1	14
NDEA-d10	112>94.1	10	NPYR	100>70	10
NDEA-d10	112>62	20	NPYR	100>55	10
NDEA	102>56.1	20	NPIP	114>97	10
NDEA	102>85	10	NPIP	114>84	10
NDPA-d14	144>126.1	4	NDBA	158>99	20
NDPA-d14	144>50.1	20	NDBA	158>141.1	12



Analysis: Method: N-Nitrosamines in Drinking Water GC-MS/MS with HES

Analytical Approach

- Matrix blanks were interspersed during the calibration and MDL injection sequence to verify there was no carryover.
- All calibration levels were performed using three replicates.
- Matrix blanks were spiked at three levels (2, 8, and 15 ppt) to verify recovery. Results at the 2ppt level are listed in the next slide.





Recovery Results: N-Nitrosamines in Drinking Water GC-MS/MS with HES

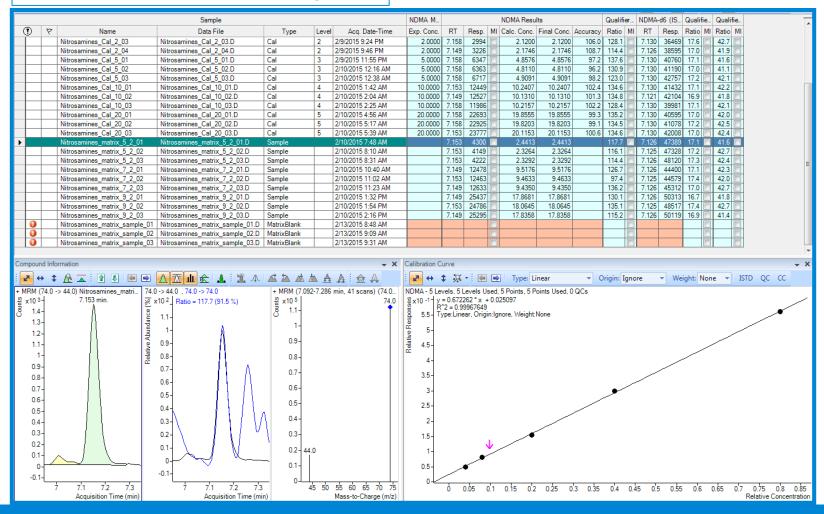
Average of 3 replicates of 2 ppt Matrix spike

Compound	Conc	Ave. Calc. Conc.	Ave. Recovery	Limits
NDMA	2	2.36	118.20	70-130
NMEA	2	2.23	111.65	70-130
NDEA	2	2.06	102.92	70-130
NDPA	2	1.99	99.70	70-130
NMOR	2	1.94	97.12	70-130
Npyr	2	2.24	111.92	70-130
Npip	2	2.16	107.83	70-130
NDBA	2	2.03	101.55	70-130



Results: N-Nitrosamines in Drinking Water GC-MS/MS with HES

Calibration from 1.0 to 20 ng/L





Results: N-Nitrosamines in Drinking Water GC-MS/MS with HES (all concentrations in ng/L)

Name	TS	RT	Avg. Conc.	Std. Dev.	MDL	LQQ	LOD	EPA MRLs	Noise	S⁄ N	Avg. Resp	Resp. RSD(%)
NDMA	1	7.15	1.62	0.0471	0.141	0.471	0.141	1.6	5	228	3275	3.9
NMEA	2	8.28	1.48	0.0287	0.086	0.287	0.086	1.5	3	258	2073	4.1
NDEA	3	9.13	1.43	0.0579	0.174	0.579	0.174	2.1	3	Inf.	1347	5.3
NDPA	4	11.08	1.29	0.1423	0.427	1.423	0.427	1.2	10	214	238	8.9
NMOR	5	11.47	1.19	0.0411	0.123	0.412	0.123		3	1912	2478	3.9
NPyr	5	11.64	1.32	0.124	0.372	1.240	0.372	1.4	1	1525	375	7.5
NPip	6	11.85	1.41	0.045	0.135	0.450	0.135	1.4	3	216	1206	3.5
NDBA	7	12.56	1.47	0.0595	0.178	0.595	0.178	1.4	8	Inf.	928	3.8

MDL/LOQ/LOD at 95% confidence level: Calculated from 8 replicates at 1.25 ng/L using 0.5 μL injections

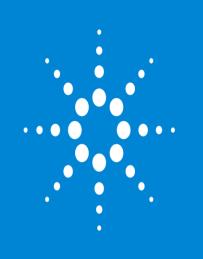


Conclusions: N-Nitrosamines in Drinking Water $_{\mbox{GC-MS/MS with HES}}$

HES Performance:

- The enhanced EI sensitivity of the HES ion source meets and exceeds the detection requirements of EPA Method 521,
 - Excellent alternative to the method specified PCI MS/MS Ion Trap systems.
- Rapid EI/MS/MS method demonstrated good stability
- Calibration in the 1-20 ng/L range
- Excellent detection levels ranging from 0.08 0.4 ng/L
 - Well below the required levels with only a 0.5 µL sample injection.
- Recoveries at multiple levels all demonstrated highly sensitive, accurate and reliable performance.
- Smaller injection volume led to less sample on column, less matrix and longer time between system maintenance





Agilent Model 5977B GC/MSD



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