

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

Emerging Environmental Monitoring Applications

New targets lead to new or updated regulations

Nanoparticles

- Fate of organic and metallic nanomaterials in the environment

Persistent toxic pollutants

- Monitoring trace-level residues in abiotic and biotic materials

Trace inorganics

- Identify and quantitate metals and non-metallic elements

Indoor air testing

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

Hormones in water

- Identify and quantitate compounds and metabolites which affect marine organism physiology

Disinfection by-products

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

Perfluorinated chemicals

- Selective and specific analysis of trace-level residues

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 µg/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
  - MDLs were calculated using 0.04 µg/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
·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

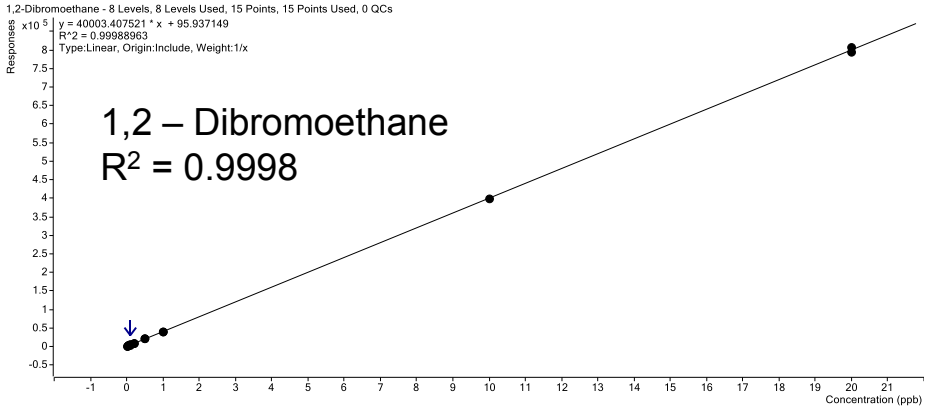
Gas Chromatograph Parameters	Agilent 7890B GC
Inlet Type	Split/Splitless Inlet (SSL)
Mode	Split
Inlet Liner	Straight, 2mm ID 250 µl (PN 5181-8818)
Heater	125°C
Column Flow	1.5 ml/min constant flow
Total Flow	25 mL/min
Septum Purge Flow	1.0 ml/min
Gas Saver	OFF
Split Ratio	15:1
Split Flow	22.5 ml/min
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	3.95 min

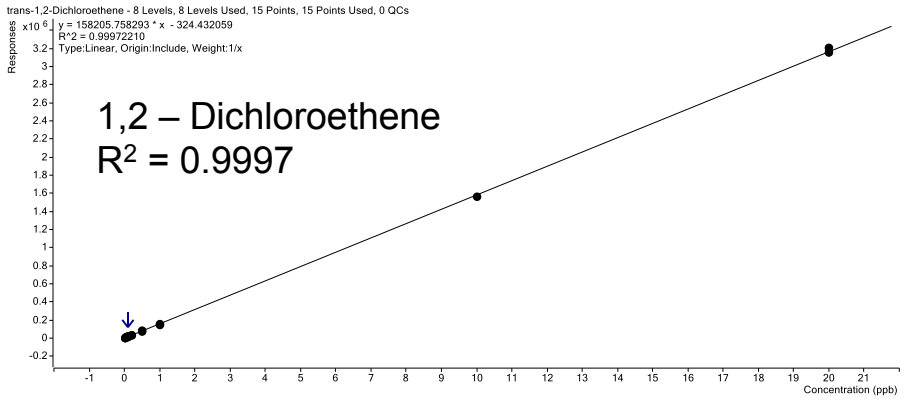
Linearity: Volatiles Analysis

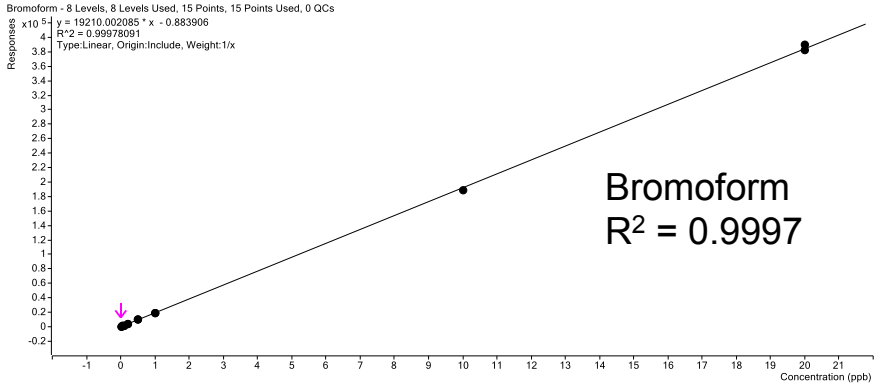
Headspace Sample Preparation: 7890B GC and 5977B MSD HES

Calibration linearity

- Concentration range 0.02 to 20 µg/L
- Three representative compounds

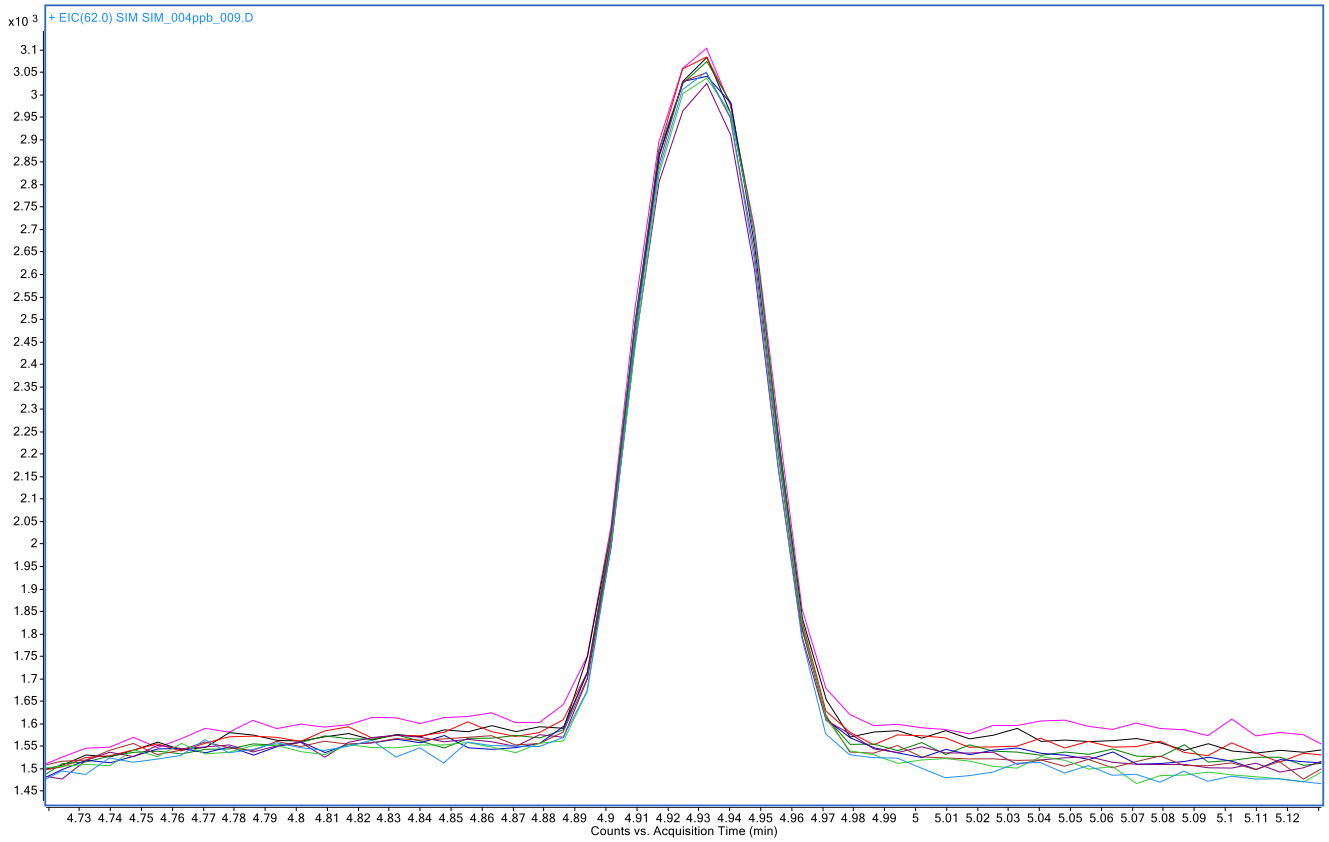






Reproducibility: Volatiles Analysis

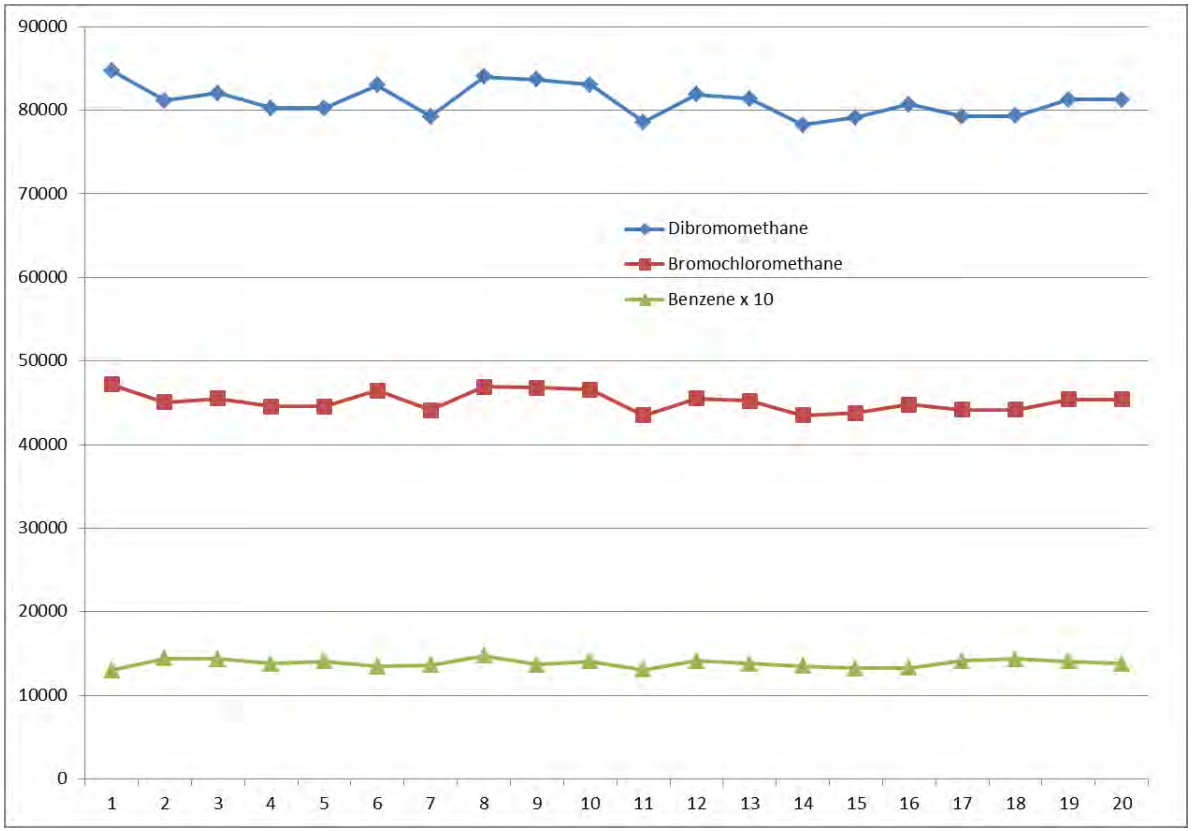
Headspace Sample Preparation: 7890B GC and 5977B MSD HES



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

MDL study

- Nine replicate injections
- Calculated using 0.04 µg/L standard.
- All MDLs are below 0.025 µg/L or 25 ppt
  - Two exceptions: which have MDLs ≤ 41 ppt.

Majority of MDLs below 0.015 µg/L

- including some compounds with relatively low response.

Tap water samples

- Injected 20 times, consecutively

Name	RT	Quant Ion	MDL
Vinyl chloride	4.934	62	0.004
Bromomethane	5.611	93.9	0.003
Chloroethane	5.806	64	0.003
1,1-Dichloroethene	7.007	95.9	0.008
trans-1,2-Dichloroethene	8.007	95.9	0.009
1,1-Dichloroethane	8.554	63	0.004
cis-1,2-Dichloroethene	9.19	95.9	0.011
2,2-Dichloropropane	9.208	77	0.013
Bromochloromethane	9.47	127.8	0.004
1,1,1-Trichloroethane	9.769	96.9	0.005
1,1-Dichloro-1-propene	9.921	75	0.012
Carbon tetrachloride	9.94	116.9	0.003
Benzene * (blank issue)	10.165	78	0.009
1,2-Dichloroethane	10.202	62	0.006
Trichloroethene	10.848	129.9	0.009
1,2-Dichloropropane	11.165	63	0.005
Dibromomethane	11.275	173.8	0.006
Bromodichloromethane	11.421	82.9	0.005
cis-1,3-Dichloropropene	11.89	75	0.014
trans-1,3-Dichloropropene	12.506	75	0.013
1,1,2-Trichloroethane	12.762	96.9	0.011
Tetrachloroethene	12.884	163.8	0.009

Name	RT	Quant Ion	MDL
1,2-Dibromoethane	13.427	106.9	0.006
Chlorobenzene	13.969	112	0.015
Ethylbenzene	14.03	91	0.014
1,1,1,2-Tetrachloroethane	14.049	130.9	0.005
o-Xylene	14.664	91	0.018
Styrene	14.683	104	0.015
Bromoform	14.975	170.8	0.006
1,1,2,2-Tetrachloroethane	15.45	82.9	0.041
1,2,3-Trichloropropane	15.567	110	0.007
Bromobenzene	15.573	155.9	0.017
n-Propylbenzene	15.63	91	0.017
2-Chlorotoluene	15.768	91	0.016
1,3,5-Trimethylbenzene	15.84	105	0.018
4-Chlorotoluene	15.914	91	0.018
tert-Butylbenzene	16.225	134	0.017
sec-Butylbenzene	16.499	105	0.016
4-Isopropyltoluene	16.67	119	0.017
1,3-Dichlorobenzene	16.719	145.9	0.02
1,4-Dichlorobenzene	16.841	145.9	0.023
n-Butylbenzene	17.194	134	0.02
1,2-Dichlorobenzene	17.316	145.9	0.021
1,2-Dibromo-3-chloropropane	18.334	154.9	0.01

* Blanks showed some low level contamination for benzene

Conclusions: Volatiles Analysis

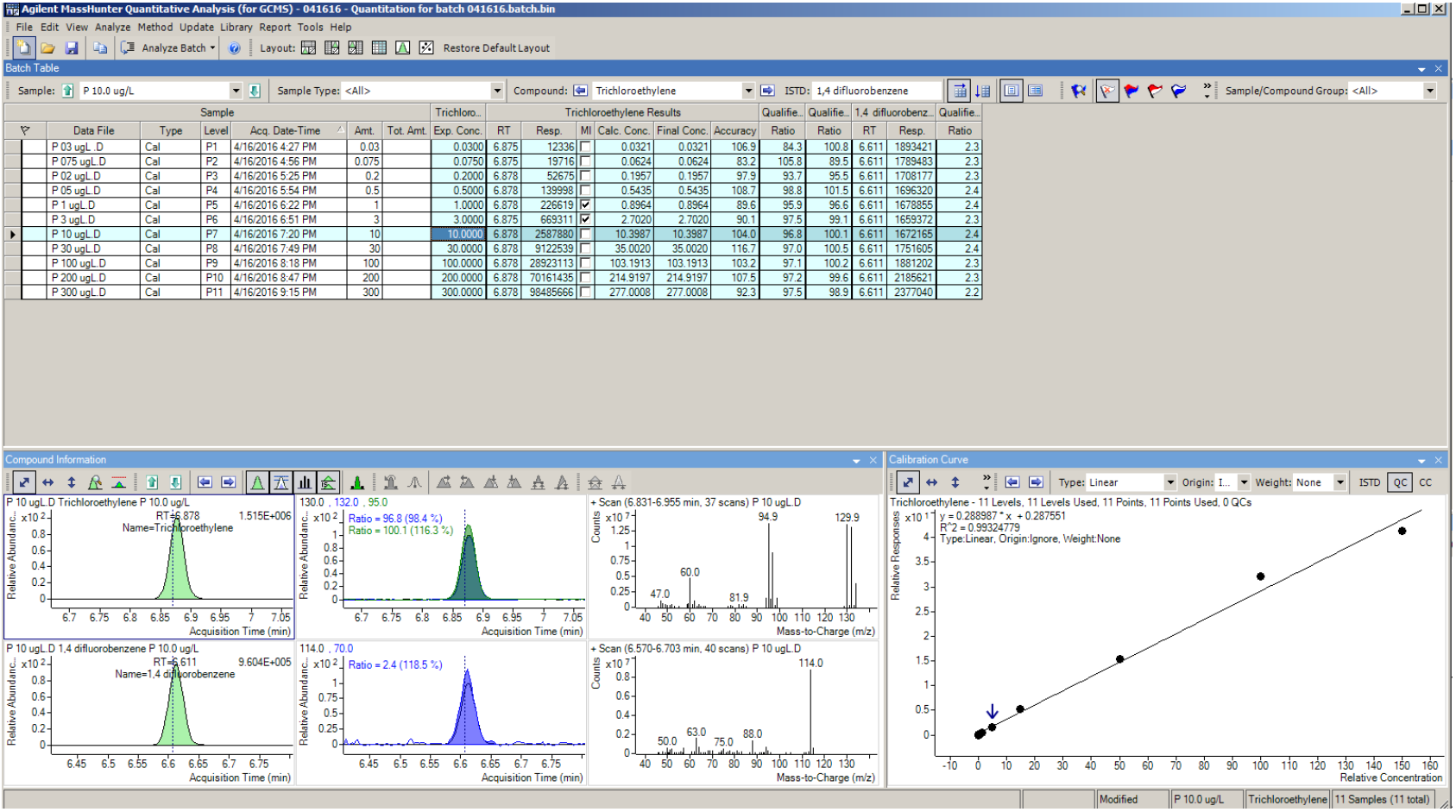
Headspace Sample Preparation: 7890B GC and 5977B MSD HES

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

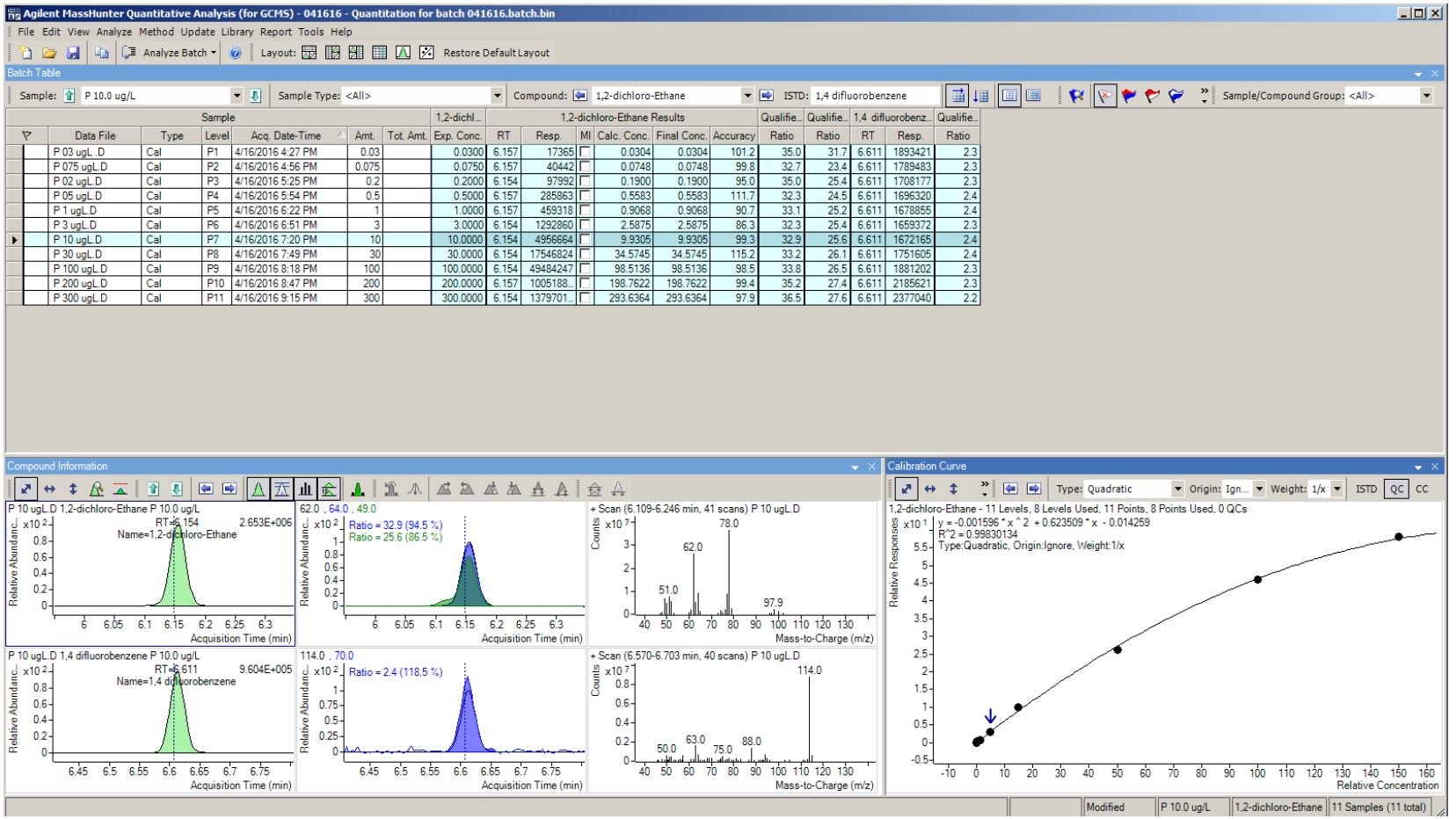
Volatiles Analysis: Trichloroethylene

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



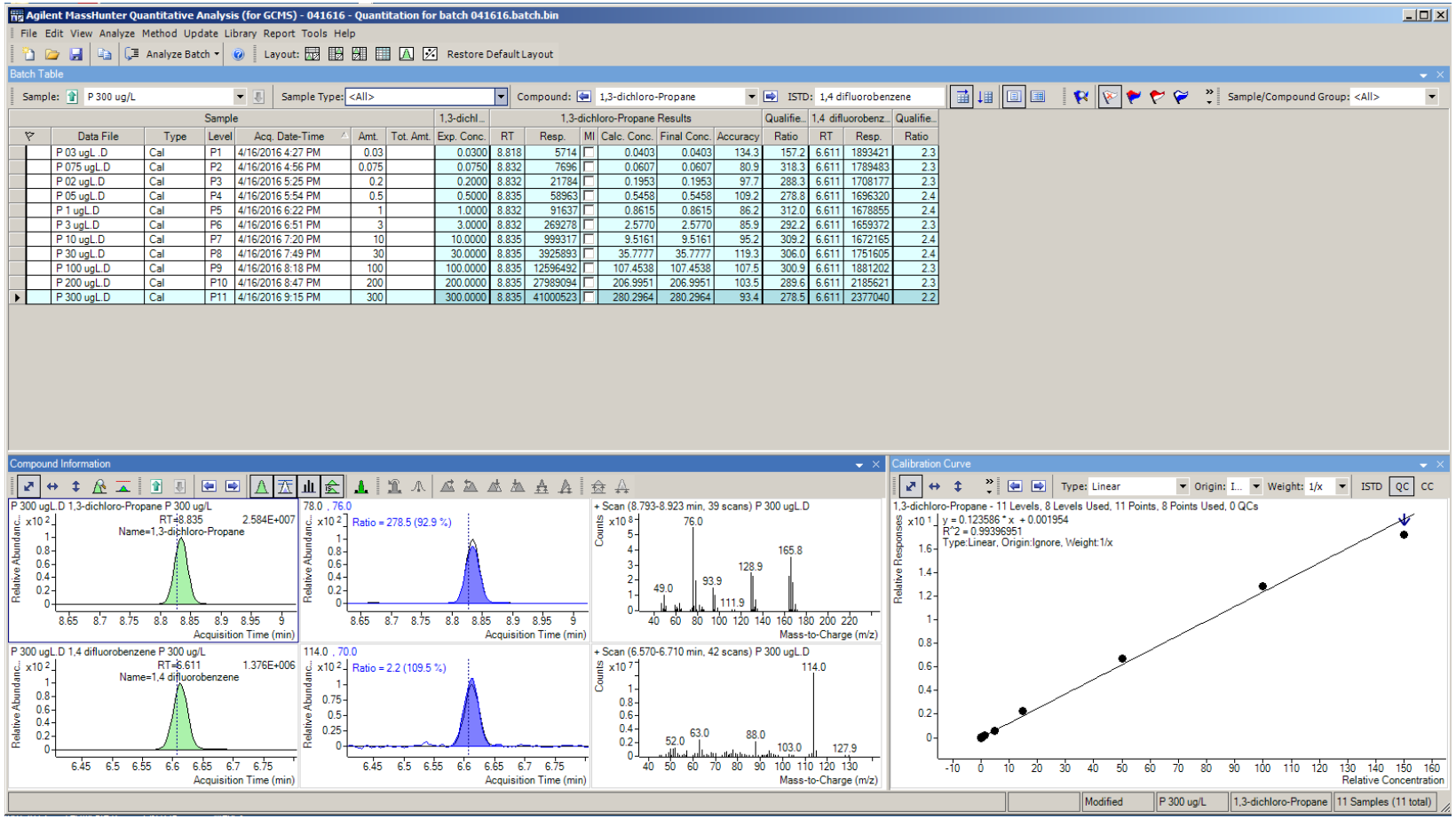
Volatiles Analysis: 1,2 dichloro-Ethane

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



Volatiles Analysis: 1,3-dichloro-Propane

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



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

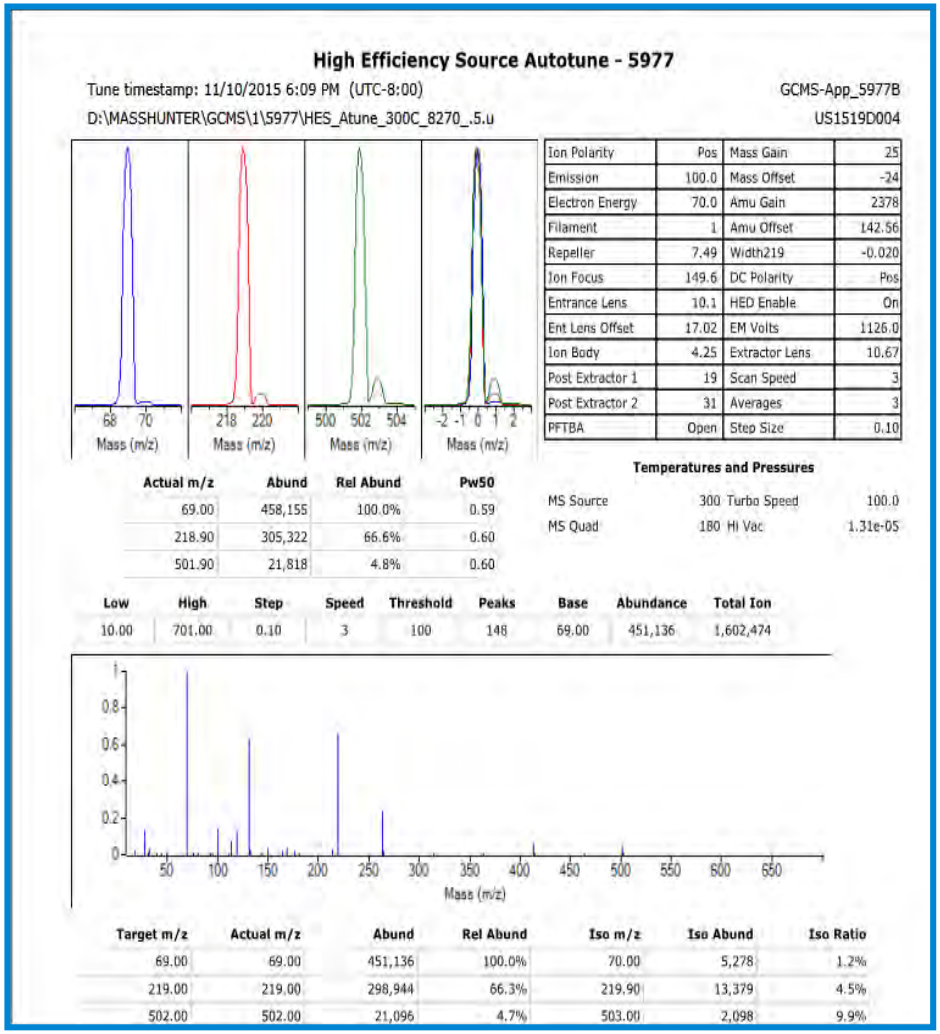
Run time	25 min.		
Oven Temperature			
(Initial)	40°C	Hold time	0.5 min.
Post run	40°C	#1 Rate	10°C/min.
#1 Value	100°C	#1 Hold Time	0 min.
#2 Rate	25°C/min.	#2 Value	260°C
#2 Hold Time	0 min.	#3 Rate	10°C/min.
#3 Value	280°C	#3 Hold Time	0 min.
#4 Rate	25°C/min.	#4 Value	320°C
#4 Hold Time	8.5 min.		

Agilent 5190-2293: 900 µL (sp'less, 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



Ion Polarity	Pos	Mass Gain	25
Emission	100.0	Mass Offset	-24
Electron Energy	70.0	Amu Gain	2378
Filament	1	Amu Offset	142.56
Repeller	7.49	Width219	-0.020
Ion Focus	149.6	DC Polarity	Pos
Entrance Lens	10.1	HED Enable	On
Ent Lens Offset	17.02	EM Volts	1126.0
Ion Body	4.25	Extractor Lens	10.67
Post Extractor 1	19	Scan Speed	3
Post Extractor 2	31	Averages	3
PFTBA	Open	Step Size	0.10

Actual m/z	Abund	Rel Abund	Pw50
69.00	458,155	100.0%	0.59
218.90	305,322	66.6%	0.60
501.90	21,818	4.8%	0.60

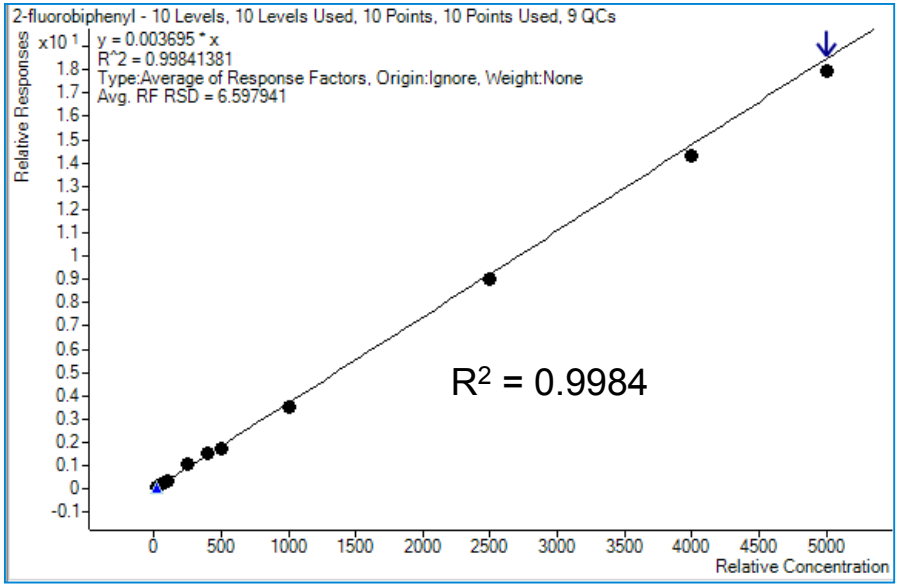
Low	High	Step	Speed	Threshold	Peaks	Base	Abundance	Total Ion
10.00	701.00	0.10	3	100	148	69.00	451,136	1,602,474

Target m/z	Actual m/z	Abund	Rel Abund	Iso m/z	Iso Abund	Iso Ratio
69.00	69.00	451,136	100.0%	70.00	5,278	1.2%
219.00	219.00	298,944	66.3%	219.90	13,379	4.5%
502.00	502.00	21,096	4.7%	503.00	2,098	9.9%

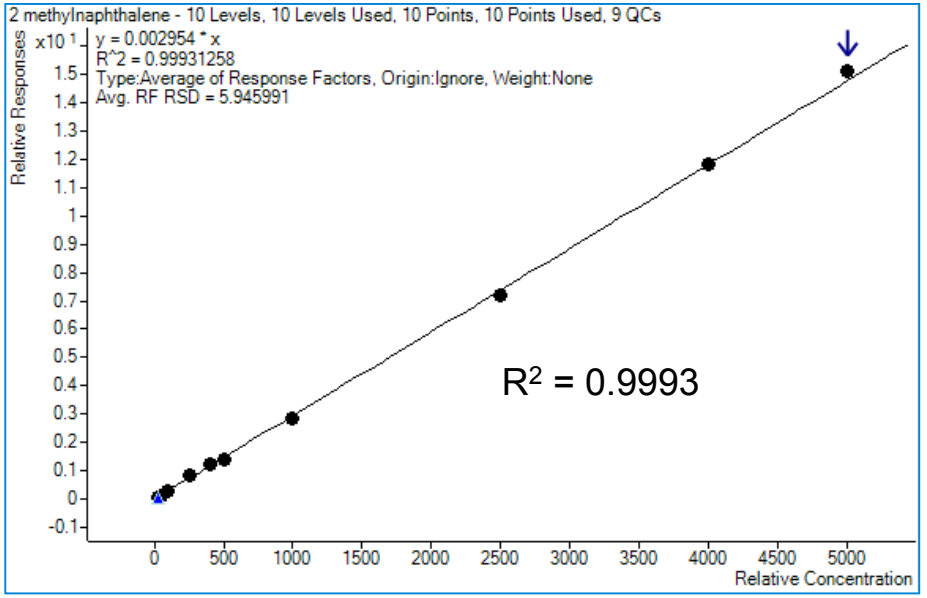
HES Autotune

Linearity: Semi-Volatiles Analysis

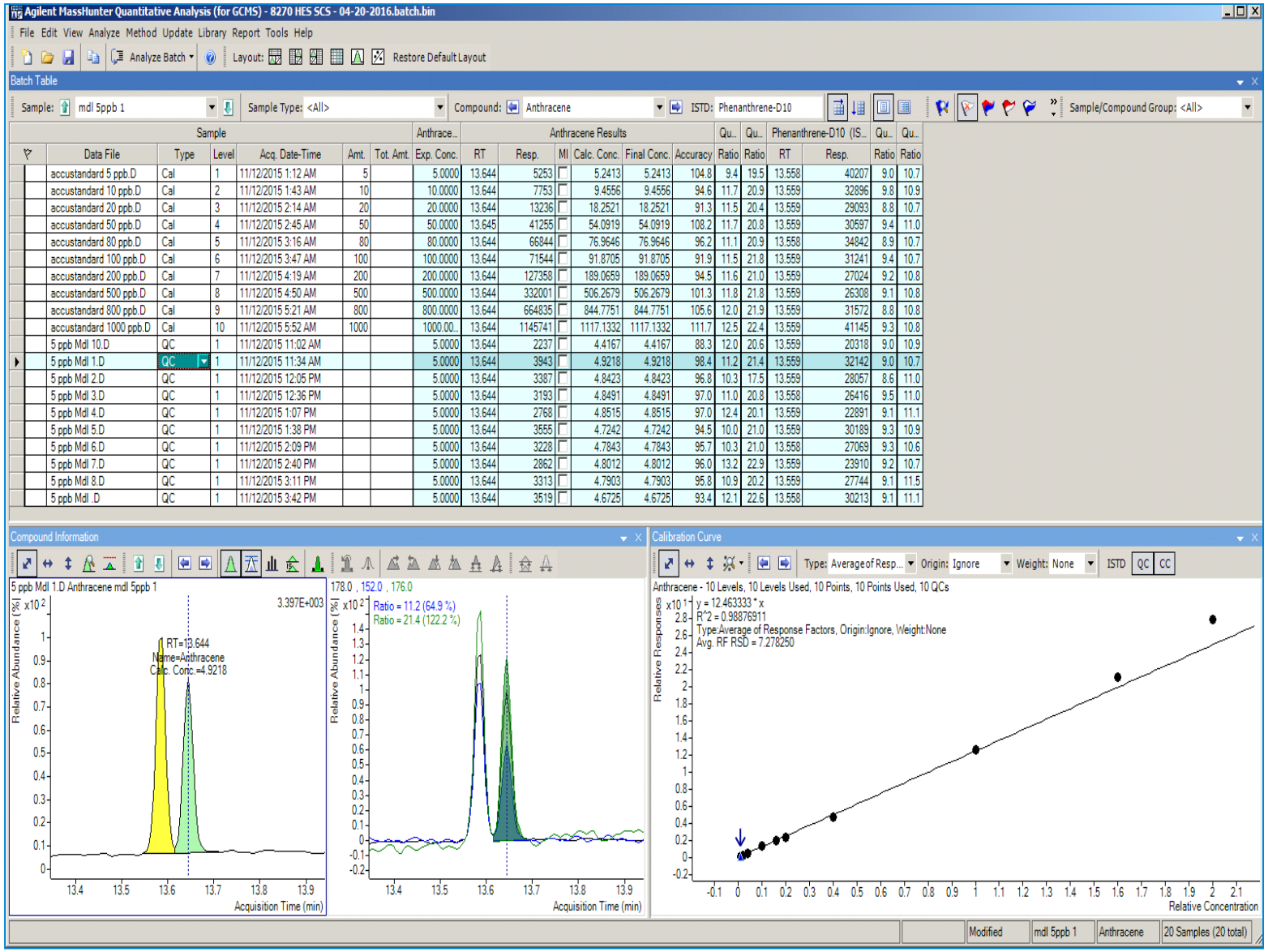
2-fluorobiphenyl



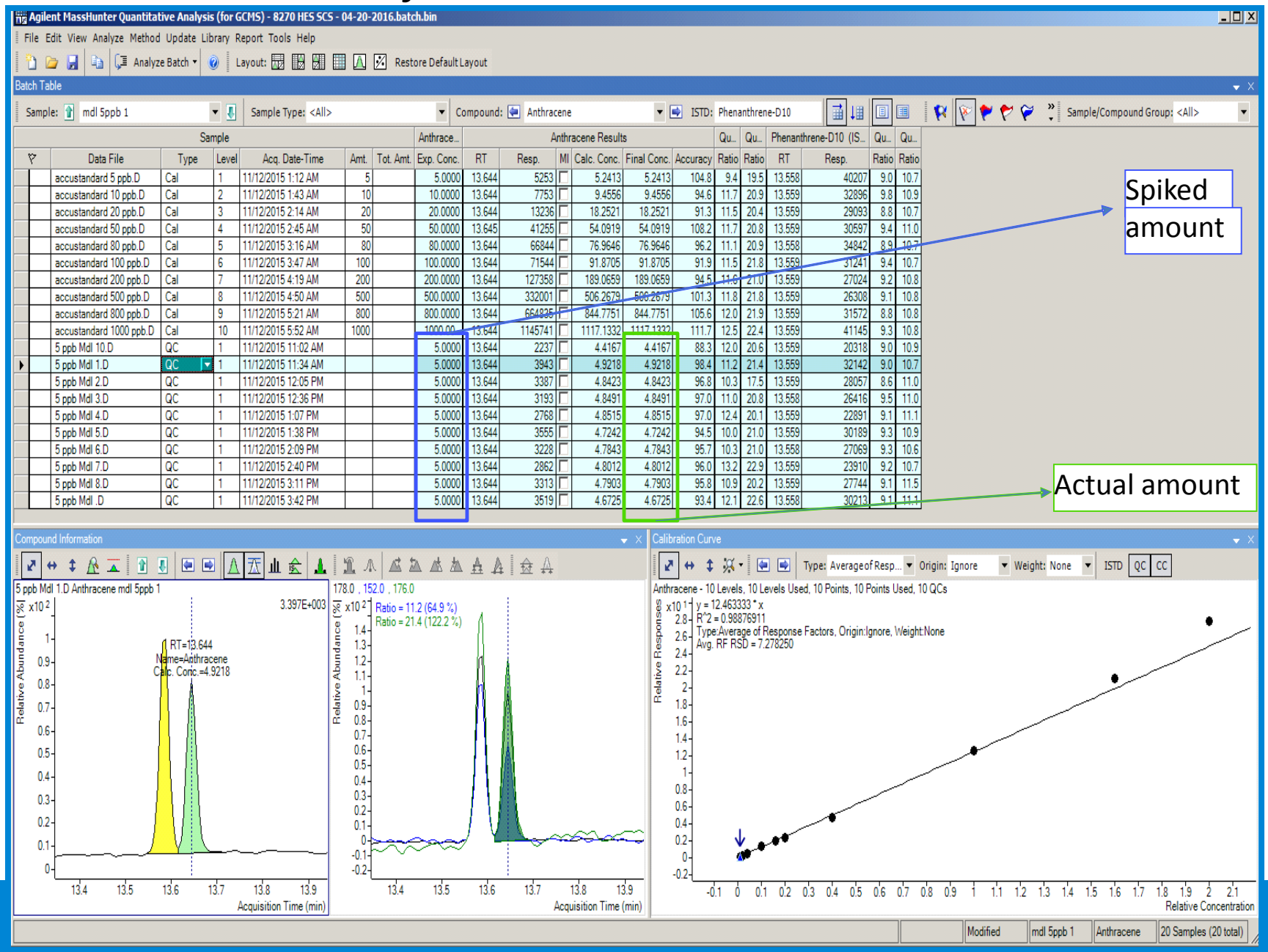
2-methylnaphthalene



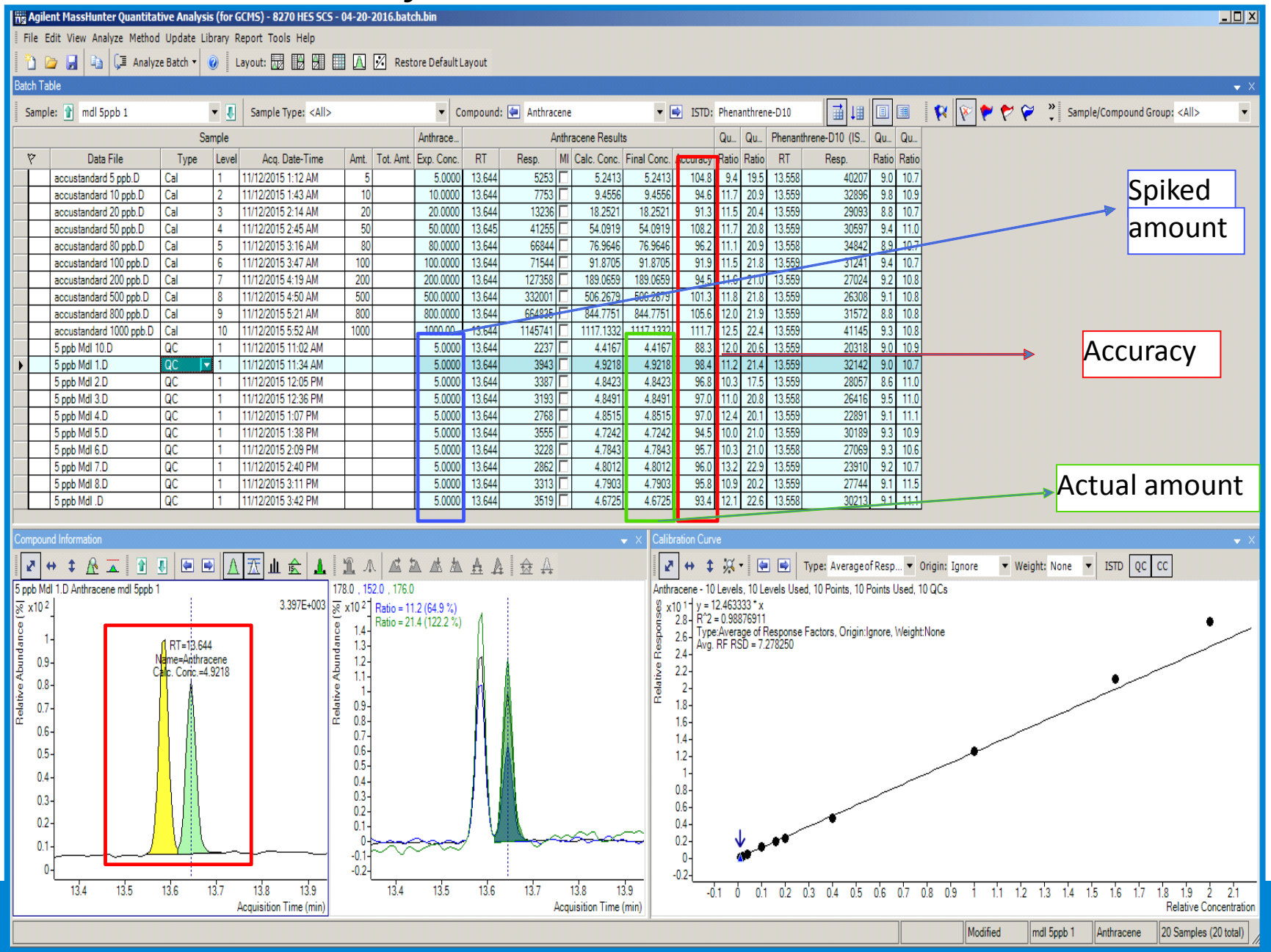
Semi-Volatiles Analysis: Anthracene



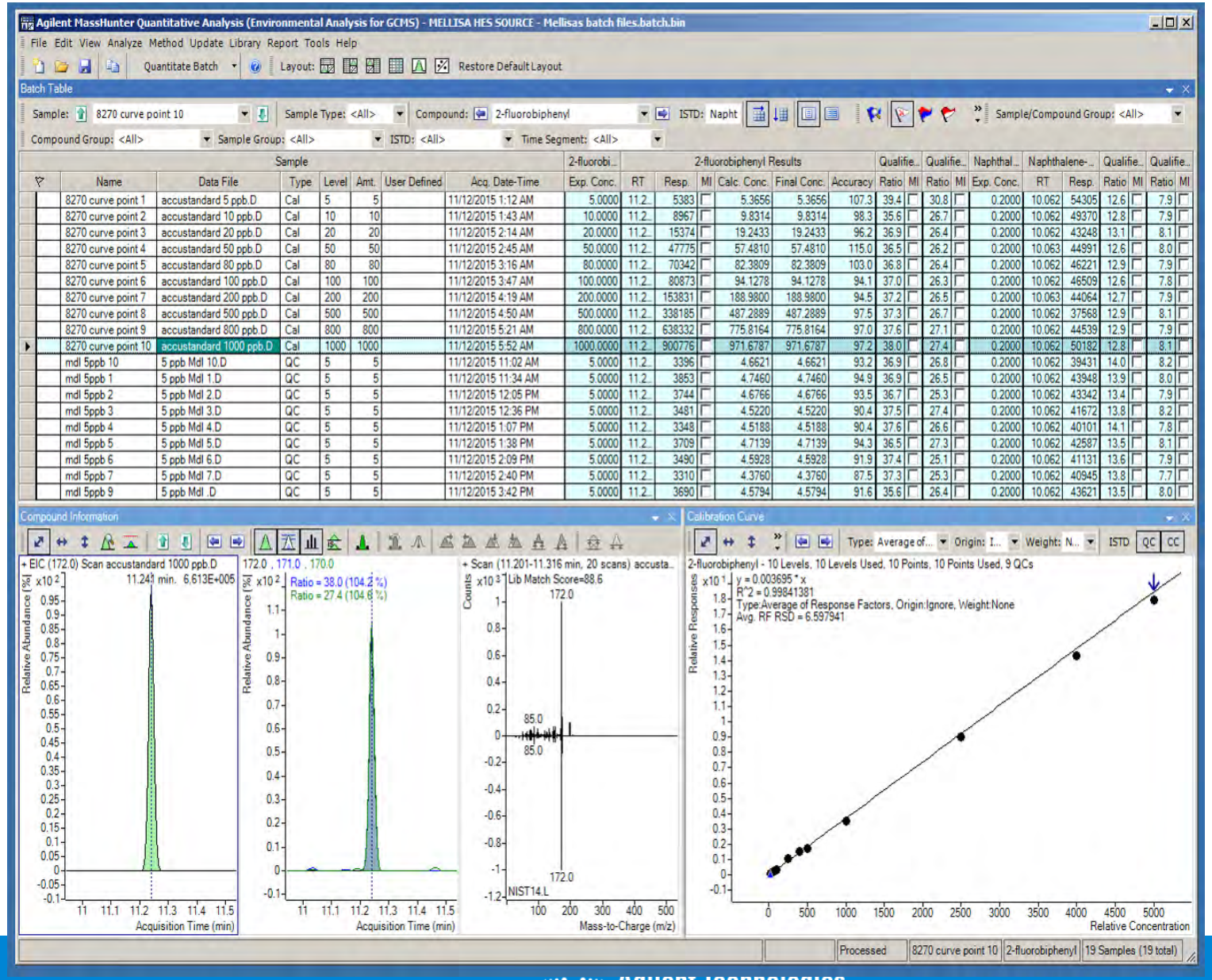
Semi-Volatiles Analysis: Anthracene



Semi-Volatiles Analysis: Anthracene



Semi-Volatiles Analysis: 2-Fluorobiphenyl



MDLS: Semi-Volatiles Analysis

Name	RT	Transition	Avg Conc.	Std. Dev.	Avg Conc./Std. Dev.	Conc. RSD	MDL	LOQ	LOD	Avg Height	Avg. Resp	Resp. RSD
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

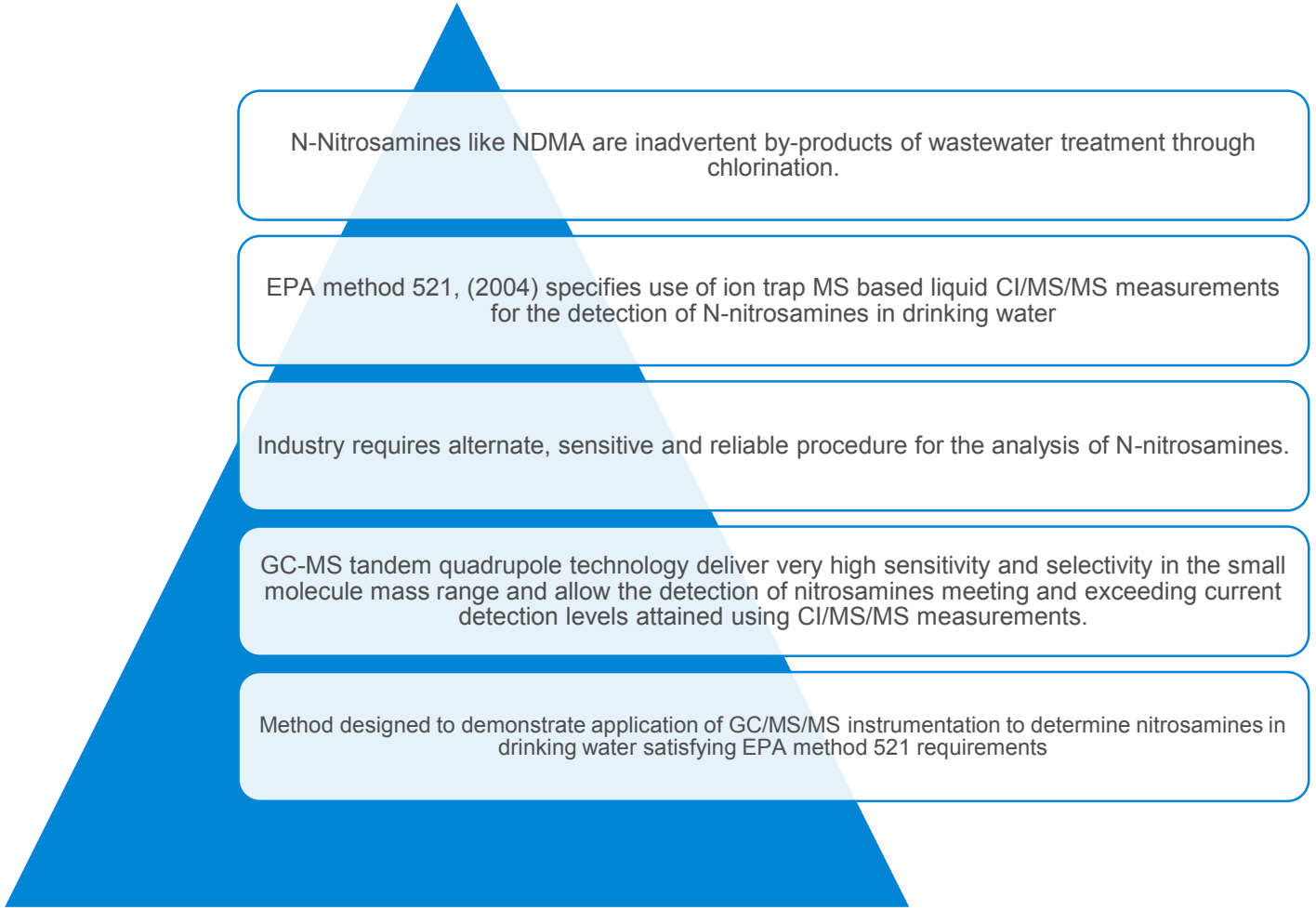
HES Performance:

- Preliminary results suggest a significant improvement in linearity and system stability at the lowest concentration level
- 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



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 0.5 microliter extract 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^2
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 R^2

MRM Transitions: N-Nitrosamines in Drinking Water

GC-MS/MS with HES

Compound	Transition	CE		Compound	Transition	CE
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

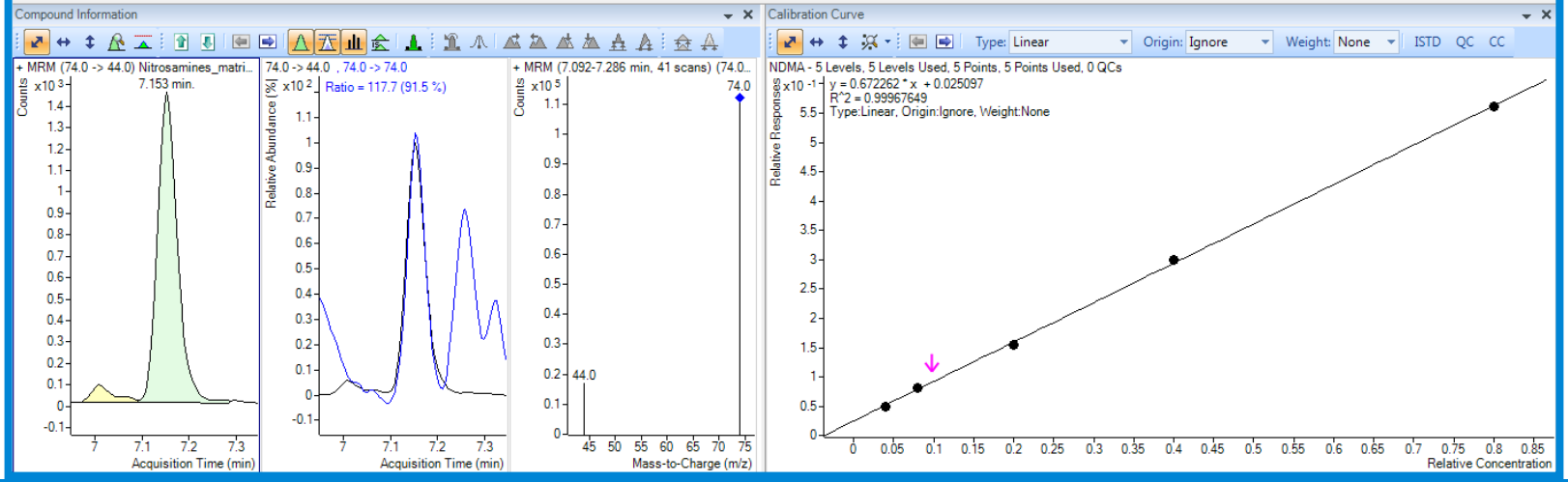
Compound	Conc	Ave. Calc. Conc.	Ave. Recovery	Limits
NDMA	2	2.36	118.20	70-130
NMEA	2	2.23	111.65	70-130
NDEA	2	2.06	102.92	70-130
NDPA	2	1.99	99.70	70-130
NMOR	2	1.94	97.12	70-130
Npyr	2	2.24	111.92	70-130
Npip	2	2.16	107.83	70-130
NDBA	2	2.03	101.55	70-130

Results: N-Nitrosamines in Drinking Water

GC-MS/MS with HES

Calibration from 1.0 to 20 ng/L

Sample						NDMA M...	NDMA Results							Qualifier...		NDMA-d6 (IS...		Qualifie...		Qualifie...	
	Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	RT	Resp.	MI	Calc. Conc.	Final Conc.	Accuracy	Ratio	MI	RT	Resp.	Ratio	MI	Ratio	MI
	Nitrosamines_Cal_2_03	Nitrosamines_Cal_2_03.D	Cal	2	2/9/2015 9:24 PM	2.0000	7.158	2994		2.1200	2.1200	106.0	128.1		7.130	36469	17.6		42.7	
	Nitrosamines_Cal_2_04	Nitrosamines_Cal_2_04.D	Cal	2	2/9/2015 9:46 PM	2.0000	7.149	3226		2.1746	2.1746	108.7	114.4		7.126	38595	17.0		41.9	
	Nitrosamines_Cal_5_01	Nitrosamines_Cal_5_01.D	Cal	3	2/9/2015 11:55 PM	5.0000	7.158	6347		4.8576	4.8576	97.2	137.6		7.130	40760	17.1		41.6	
	Nitrosamines_Cal_5_02	Nitrosamines_Cal_5_02.D	Cal	3	2/10/2015 12:16 AM	5.0000	7.158	6363		4.8110	4.8110	96.2	130.9		7.130	41190	17.0		41.1	
	Nitrosamines_Cal_5_03	Nitrosamines_Cal_5_03.D	Cal	3	2/10/2015 12:38 AM	5.0000	7.158	6717		4.9091	4.9091	98.2	123.0		7.130	42757	17.2		42.1	
	Nitrosamines_Cal_10_01	Nitrosamines_Cal_10_01.D	Cal	4	2/10/2015 1:42 AM	10.0000	7.153	12449		10.2407	10.2407	102.4	134.6		7.130	41432	17.1		42.2	
	Nitrosamines_Cal_10_02	Nitrosamines_Cal_10_02.D	Cal	4	2/10/2015 2:04 AM	10.0000	7.149	12527		10.1310	10.1310	101.3	134.8		7.121	42104	16.9		41.8	
	Nitrosamines_Cal_10_03	Nitrosamines_Cal_10_03.D	Cal	4	2/10/2015 2:25 AM	10.0000	7.158	11986		10.2157	10.2157	102.2	128.4		7.130	39981	17.1		42.1	
	Nitrosamines_Cal_20_01	Nitrosamines_Cal_20_01.D	Cal	5	2/10/2015 4:56 AM	20.0000	7.158	22693		19.8555	19.8555	99.3	135.2		7.130	40595	17.0		42.0	
	Nitrosamines_Cal_20_02	Nitrosamines_Cal_20_02.D	Cal	5	2/10/2015 5:17 AM	20.0000	7.158	22925		19.8203	19.8203	99.1	134.5		7.130	41078	17.2		42.5	
	Nitrosamines_Cal_20_03	Nitrosamines_Cal_20_03.D	Cal	5	2/10/2015 5:39 AM	20.0000	7.153	23777		20.1153	20.1153	100.6	134.6		7.130	42008	17.0		42.4	
	Nitrosamines_matrix_5_2_01	Nitrosamines_matrix_5_2_01.D	Sample		2/10/2015 7:48 AM		7.153	4300		2.4413	2.4413		117.7		7.126	47389	17.1		41.6	
	Nitrosamines_matrix_5_2_02	Nitrosamines_matrix_5_2_02.D	Sample		2/10/2015 8:10 AM		7.153	4149		2.3264	2.3264		116.1		7.125	47328	17.2		42.7	
	Nitrosamines_matrix_5_2_03	Nitrosamines_matrix_5_2_03.D	Sample		2/10/2015 8:31 AM		7.153	4222		2.3292	2.3292		114.4		7.126	48120	17.3		42.4	
	Nitrosamines_matrix_7_2_01	Nitrosamines_matrix_7_2_01.D	Sample		2/10/2015 10:40 AM		7.149	12478		9.5176	9.5176		126.7		7.126	44400	17.1		42.3	
	Nitrosamines_matrix_7_2_02	Nitrosamines_matrix_7_2_02.D	Sample		2/10/2015 11:02 AM		7.153	12463		9.4633	9.4633		97.4		7.125	44579	17.4		42.0	
	Nitrosamines_matrix_7_2_03	Nitrosamines_matrix_7_2_03.D	Sample		2/10/2015 11:23 AM		7.149	12633		9.4350	9.4350		136.2		7.126	45312	17.0		42.7	
	Nitrosamines_matrix_9_2_01	Nitrosamines_matrix_9_2_01.D	Sample		2/10/2015 1:32 PM		7.149	25437		17.8681	17.8681		130.1		7.126	50313	16.7		41.8	
	Nitrosamines_matrix_9_2_02	Nitrosamines_matrix_9_2_02.D	Sample		2/10/2015 1:54 PM		7.153	24786		18.0645	18.0645		135.1		7.125	48517	17.4		42.7	
	Nitrosamines_matrix_9_2_03	Nitrosamines_matrix_9_2_03.D	Sample		2/10/2015 2:16 PM		7.149	25295		17.8358	17.8358		115.2		7.126	50119	16.9		41.4	
	Nitrosamines_matrix_sample_01	Nitrosamines_matrix_sample_01.D	MatrixBlank		2/13/2015 8:48 AM															
	Nitrosamines_matrix_sample_02	Nitrosamines_matrix_sample_02.D	MatrixBlank		2/13/2015 9:09 AM															
	Nitrosamines_matrix_sample_03	Nitrosamines_matrix_sample_03.D	MatrixBlank		2/13/2015 9:31 AM															



Results: N-Nitrosamines in Drinking Water

GC-MS/MS with HES (all concentrations in ng/L)

Name	TS	RT	Avg. Conc.	Std. Dev.	MDL	LOQ	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

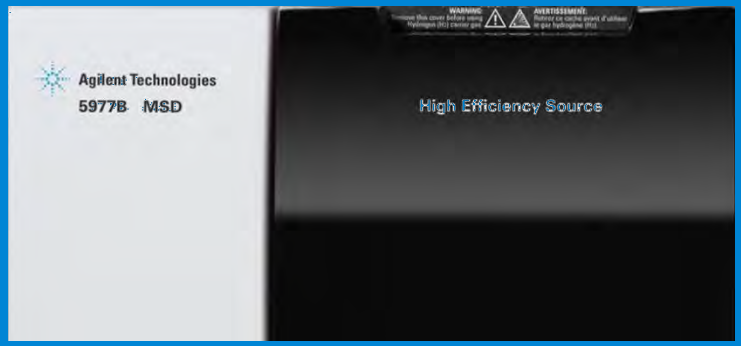
Conclusions: N-Nitrosamines in Drinking Water

GC-MS/MS with HES

HES Performance:

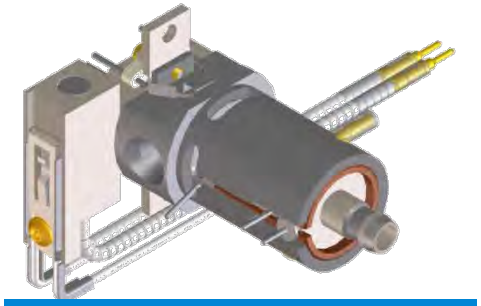
- The enhanced EI sensitivity of the HES ion source meets and exceeds the detection requirements of EPA Method 521,
  - Excellent alternative to the method specified PCI MS/MS Ion Trap systems.
- Rapid EI/MS/MS method demonstrated good stability
- Calibration in the 1-20 ng/L range
- Excellent detection 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

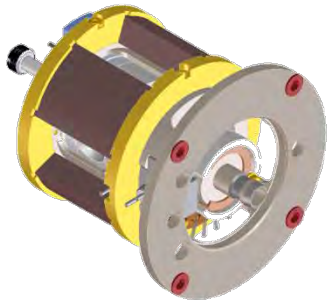


The Source of New Possibilities

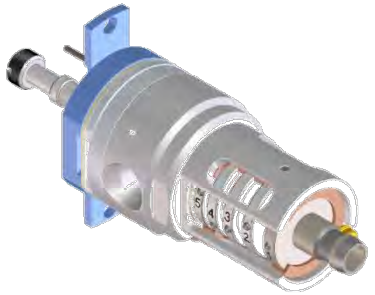
The Most Powerful EI GC/MS Source



5977A Extractor Source



NEW! 5977B High Efficiency Source



5977B High Efficiency Source with Magnet Removed

More intense electron beam…

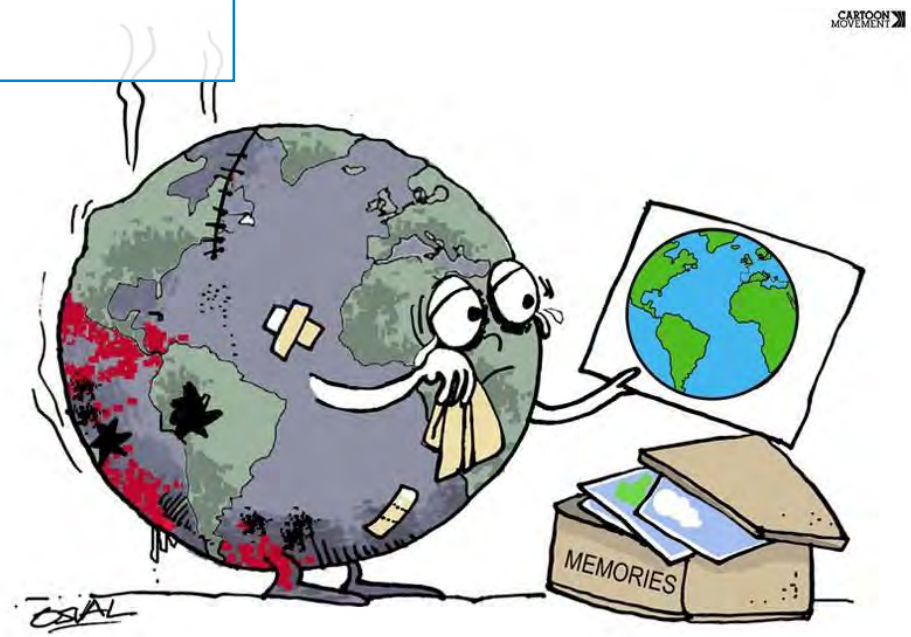
Times a longer path length for electron beam/effluent interaction

Yields up to 20x More Ions Produced

Driving Technology Innovation
Inspiring discoveries for a better world

Your research helps protect:

- the air we breath
- the water we drink
- the soil we depend on for food



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