Detection of Picogram or Sub-Picogram Semi-Volatile Compounds by Full Scan GCMS Using a High Efficiency Source – a Game Changer?

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Introduction

Semi-volatile organic compounds (SVOCs) are a broad class of environmentally significant contaminants of global interest. These compounds are found on a variety of target analyte lists in GCMS methods such as the USEPA 8270 and 525 methods and comparable methods elsewhere. Although listed as targets that are appropriate for selected ion monitoring (SIM) mode in GCMS analysis, scan mode would provide the advantage of full scan spectra for compound confirmation. In the past, however, method detection limits (MDL) could not be reached using scan mode. We report that the High Efficiency Source (HES) represents a revolution in ion source design with greatly enhanced sensitivity that can be exploited to produce scan detection limits for SVOCs that were formerly only approached by SIM.

Method

A 7890GC coupled to a 5977B GCMS with the High Efficiency Source was operated in scan mode from 50 to 550 u (sampling = 4). Detector gain was set to 0.1. A 5% phenyl phase GC column (DB-8270D column, 30 m x 0.25 mm i.d. x 0.25 µm) was used as is common in this analysis. Ongoing experiments utilize smaller i.d. and thinner film approaches. Standards were made in dichloromethane and 0.5 µL was injected, via 5 µL syringe, in pressure-pulsed splitless mode into a double-taper liner.

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

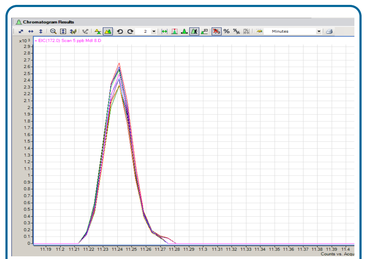
Acquisition Mode	**Scan**	**Normal or Fast Scanning**	**Normal**
Solvent Delay	**3.0 min.**	**EM Setting Mode Gain**	**0.1**
Trace Ion Detection	**On**		
[Scan Parameters]			
Start Time	**3.0 min.**		
Low Mass	**50**	**High Mass**	**550**
Threshold	**75**	**A/D Samples**	**4**
MS Source	**350°C**	**Maximum**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

MDL (IDL) Determination

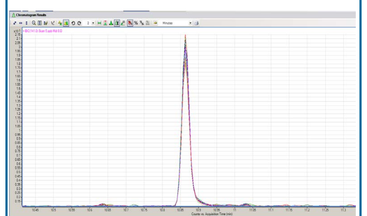
The system acquired a ten point calibration curve using the following concentrations; 5, 10, 20, 40, 50, 80, 100, 200, 500, 800, 1000 µg/L. Following the analytical curve the system acquired eight replicate injections at the low point of the curve to produce a MDL typical for an analytical laboratory. Replicate injections of a 5 ng/mL standard were used to determine an instrument detection limit (IDL) for each compound, where IDL = $t_{99\%}$ × (RSD/100 %) × amount measured. In this case, IDL represents MDL due to the use of non-extracted standards. Calibration was from 2.5 µg/L – 1000 µg/L.

Results

System stability demonstrated by injected standards



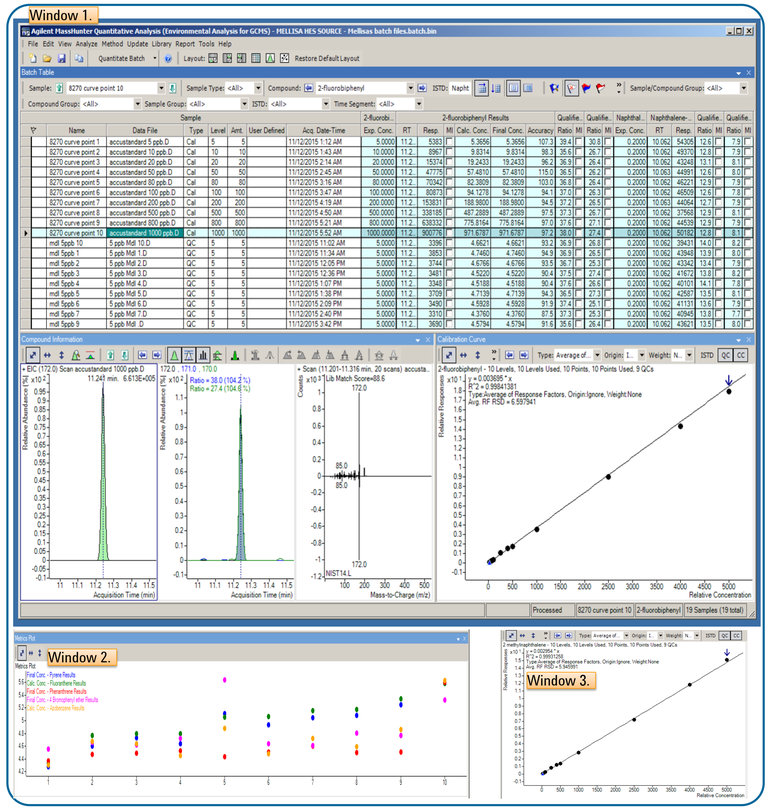
10 injections of 5 ppb 2-Fluorobiphenyl (2.5 pg)



10 injections of 5 ppb 2-Methylnaphthalene (2.5 pg)

Full Scan Mode Analysis of Semi-Volatiles

Batch view showing results for 2-flurobiphenyl (Window 1.) The NIST library match score is 88.6. Window 2. shows a metric plot for 10 injections of pyrene, fluoranthene, phenanthrene, 4-bromophenyl ether, and azobenzene in a 5 ppb standard (2.5 pg injected). Window 3. shows calibration results for 2-methylnaphthalene.



Reach MDLs in Scan That Were Formerly Approached Only in SIM

As can be seen in the table below, sub-picogram scan detection is common with a few compounds showing picogram levels due primarily to lowered compound target ion response. Compound chromatography also played a role in some cases (e.g., benzo[b]&[k]fluoranthene).

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

Inject Less or Collect Less Sample Due to Sub-pg MDLs

Clearly, compound detection in scan mode is now able to discern amounts previously attained only in SIM mode. This advantage allows several analytical strategies to be explored and applied. The "inject less and get more" approach means one can do split injections with accelerated run times if high concentration levels wish to be maintained. Injecting less sample would also put less matrix in the liner, column, etc. and allow the analyst to "get more" runs before servicing is required. The "prep less and save more" approach means processing less sample. This would save time and costs not only in prep but in solvent use and disposal. These dramatically lowered scan MDLs/IDLs also suggest that SIM IDLs will be enhanced and so a combination of both strategies is possible to result in the most time and cost effective analysis possible.