High-Throughput GC-TOFMS Analysis Using EPA Method 8270D

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1. Introduction

EPA method 8270D describes the methodology for the determination of semi-volatile organic compounds in extracts from air, soil, solid waste, and water using GCMS. Target compounds include alcohols, amines, aromatics, phenols, and solvents. The wide variety of analytes presents a chromatographic challenge, particularly for a high-speed analysis. The use of a high-speed GC method requires a detector with a fast data acquisition rate. Time-of-flight MS has the advantage over scanning instruments because of its high-speed acquisition over a full mass range at all times during the experiment.

EPA 8270D is a commonly used method in environmental laboratories in which many analyses are done over a short period of time. Typical experiments target a subset of 70 to 100 compounds with an overall run time of up to 40 minutes. Fast experimental setup and optimization, EPA tune compliance, limited maintenance downtime, and high sample throughput are therefore of high importance.

In this application note we present a fast analysis of a mid-level standard from an 8270D extract containing 90 analytes of interest. The complete experiment was finished in 11.2 minutes. Prior to sample analysis, a system optimization and decafluorotriphenylphosphine (DFTPP) tune was done that successfully meets all of the recommended manufacturer specifications for abundance criteria in compliance with section 11.3.1.2 of EPA Method 8270D. These DFTPP tune criteria are accepted by the EPA through an alternative test procedure (ATP*) for LECO GC-TOFMS instruments.

2. Instruments and Methods

GC: Agilent 6890 GC
Column: Restek Rxi-5MS, 20 m x 0.18 mm x 0.18 mm df
Oven: 35°C (0.2 min) to 320°C at 30°C/min (2.5 min)
Inlet Temperature: 250°C
Carrier Gas: He at a constant flow of 1.0 mL/min
Injection: 1 μL with a 10:1 split
MS Transfer Line: 280°C

MS: LECO TruTOF™ HT
Ionization: EI at -70 eV
Stored Mass range (u): 30 to 500
Spectral Acquisition Rate: 20 spectra/second
Ion Source Temperature: 250°C

Instrument Control and Data Review: ChromaTOF® software optimized for TruTOF HT

3. Results

Shown in Figure 1 is the DFTPP tune check report that is automatically generated by the new EPA reporting feature in ChromaTOF. The report shows compliance with all of the abundance criteria along with the chromatogram and mass spectrum for a DFTPP injection.
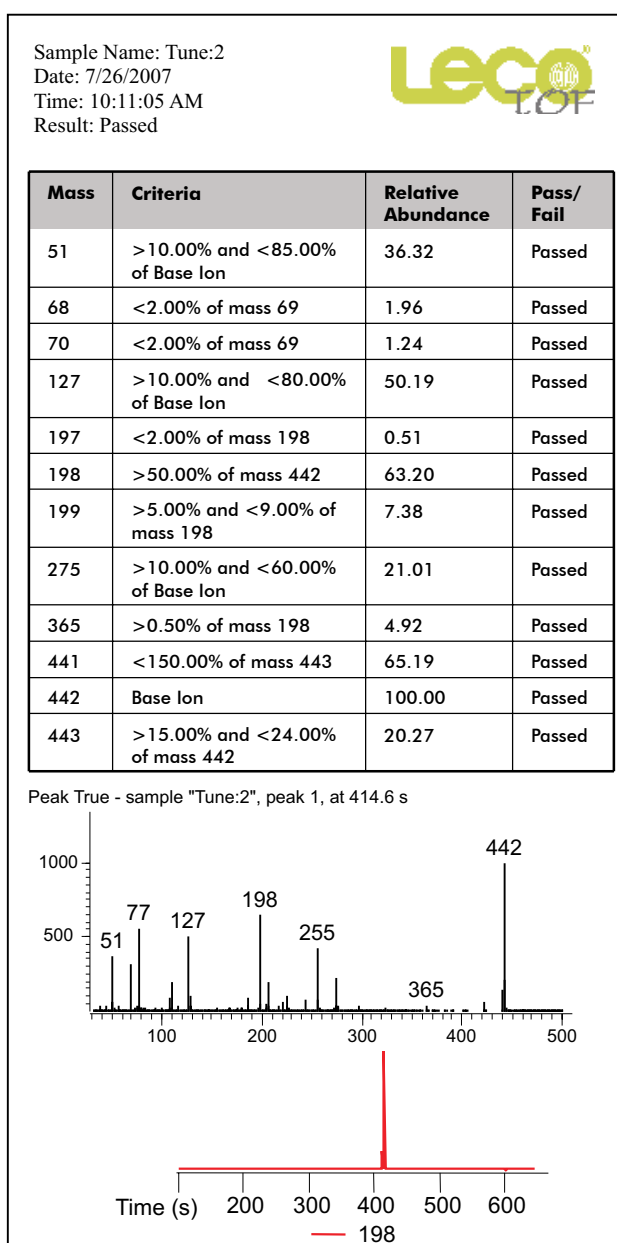
Sample Name: Tune:2
Date: 7/26/2007
Time: 10:11:05 AM
Result: Passed

Mass	Criteria	Relative Abundance	Pass/ Fail
51	>10.00% and <85.00% of Base Ion	36.32	Passed
68	<2.00% of mass 69	1.96	Passed
70	<2.00% of mass 69	1.24	Passed
127	>10.00% and <80.00% of Base Ion	50.19	Passed
197	<2.00% of mass 198	0.51	Passed
198	>50.00% of mass 442	63.20	Passed
199	>5.00% and <9.00% of mass 198	7.38	Passed
275	>10.00% and <60.00% of Base Ion	21.01	Passed
365	>0.50% of mass 198	4.92	Passed
441	<150.00% of mass 443	65.19	Passed
442	Base Ion	100.00	Passed
443	>15.00% and <24.00% of mass 442	20.27	Passed

Peak True - sample "Tune:2", peak 1, at 414.6 s

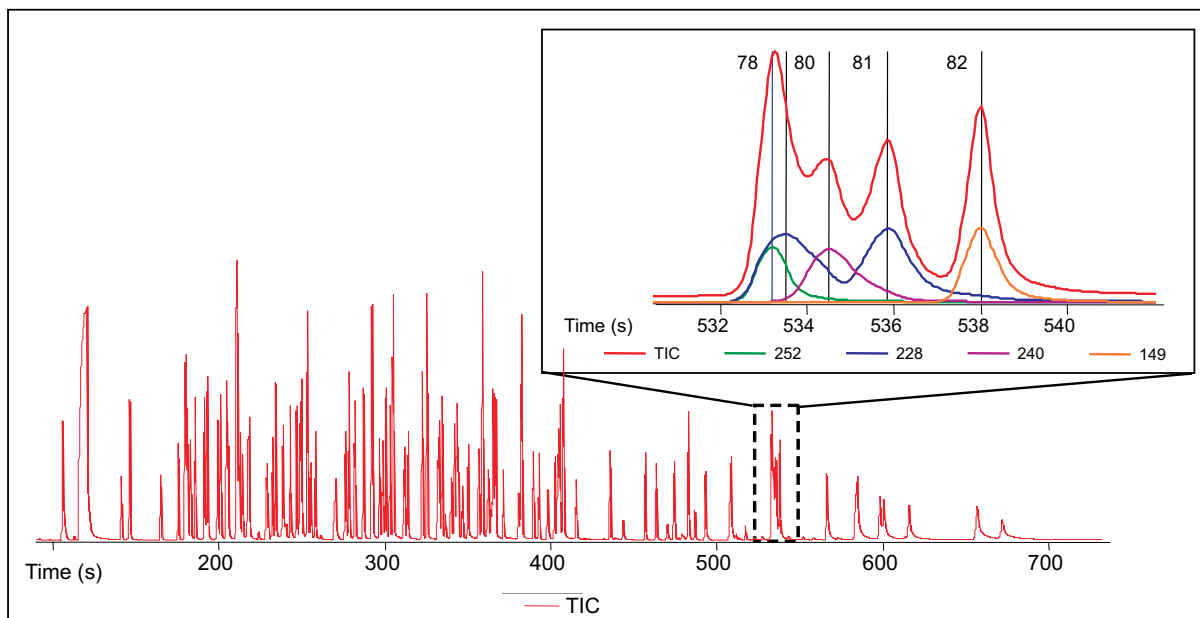*Figure 1. DFTPP Tune report generated by ChromaTOF.*

Figure 2. TIC chromatogram of a mid-level EPA 8270 standard containing 90 analytes of interest. A close-up view of a group of closely-eluting compounds is shown in the inset.

Table 1. Analytes of interest for the chromatogram shown in Figure 2.

Peak #	Name	R.T. (s)	S/N		Peak #	Name	R.T. (s)	S/N
1	N-Nitrosodimethylamine	105.85	4086.8		46	Dimethyl phthalate	322.65	25360
2	Pyridine	106.05	6763.9		47	Acenaphthylene	325.7	29593
3	Phenol, 2-fluoro-	146.45	8326.3		48	m-Nitroaniline	332.25	6549.2
4	Benzaldehyde	175.8	8169.9		49	Acenaphthene-d10	333.15	22179
5	Phenol-d6-	179.8	9900.6		50	Acenaphthene	334.75	20545
6	Phenol	180.3	7241		52	Phenol, 2,4-dinitro-	336.75	15530
7	Aniline	181.3	15009		53	Phenol, 4-nitro-	340.4	10194
8	Bis(2-chloroethyl) ether	183.25	5558.3		54	Dibenzofuran	342.3	21180
9	Phenol, 2-chloro-	185.95	9496.7		55	2,4-Dinitrotoluene	344.5	6496.2
10	Benzene, 1,3-dichloro-	191.45	14213		56	Diethyl Phthalate	356.9	19809
11	1,4-Dichlorobenzene-D4	192.8	13782		57	Fluorene	358.6	11911
12	Benzene, 1,4-dichloro-	193.5	11034		58	4-Chlorophenyl phenyl ether	359.2	5528.5
13	Benzyl Alcohol	199.6	9096.3		59	p-Nitroaniline	362.7	15318
14	Benzene, 1,2-dichloro-	201.35	14325		60	Phenol, 2-methyl-4,6-dinitro-	364.35	24092
15	Phenol, 2-methyl-	204.75	14118		61	Benzenamine, N-phenyl-	365.6	14426
16	Bis(2-chloroisopropyl) ether	205.7	10708		62	Azobenzene	366.95	23068
17	Acetophenone	210.65	13232		63	Phenol, 2,4,6-tribromo-	371.6	43916
19	Phenol, 3&4-methyl-	211.5	1092.6		64	4-Bromophenyl phenyl ether	382.55	23882
20	N-Nitrosodi-N-propylamine	213.1	2177.1		65	Benzene, hexachloro-	389.7	23441
21	Ethane, hexachloro-	214.5	22367		66	Atrazine	393.2	39586
22	Nitrobenzene-D5	217.8	7094.1		67	Phenol, pentachloro-	398.35	34949
23	Benzene, nitro-	218.65	10939		68	Phenanthrene-D10	404.4	37355
24	Isophorone	229.15	10223		69	Phenanthrene	405.4	6780.8
25	Phenol, 2-nitro-	232.55	12690		70	Anthracene	405.6	22002
26	Phenol, 2,4-dimethyl-	234.4	8087.9		71	Carbazole	415.55	18823
27	Methane, bis(2-chloroethoxy)-	238.8	12869		72	Dibutyl phthalate	435.85	24217
28	Benzoic acid	240.75	5234.3		73	Fluoranthene	463.7	10287
29	Phenol, 2,4-dichloro-	243.25	11828		74	Benzidine	470.3	6211.2
30	Benzene, 1,2,4-trichloro-	247.1	16809		75	Pyrene	474.55	8607.7
31	Naphthalene-D8	249.05	18516		76	p-Terphenyl-d14	482.95	119099
32	Naphthalene	250.05	11722		77	Benzyl butyl phthalate	508.75	42957
33	p-Chloroaniline	253.55	22213		78	Dichlorobenzidine	533.2	21281
34	Hexachlorobutadiene	258.35	42941		79	Chrysene	533.5	56713
35	Caprolactam	270.7	11323		80	Chrysene-D12	534.5	45664
36	Phenol, 4-chloro-3-methyl-	276.45	10508		81	Benz[a]anthracene	535.85	50096
37	Naphthalene, 2-methyl-	282	5850.3		82	Bis(2-ethylhexyl) phthalate	538	42506
38	Benzene, 1,2,4,5-tetrachloro-	292.05	1277.2		83	Di-n-octyl phthalate	566.45	51407
39	Hexachlorocyclopentadiene	293.15	26088		84	Benzo[b]fluoranthene	583.85	278.55
40	Phenol, 2,4,6-trichloro-	297.05	26236		85	Benzo[k]fluoranthene	584.85	1745.6
41	Phenol, 2,4,5-trichloro-	299	28543		86	Benzo[a]pyrene	598.3	31830
42	1,1'-Biphenyl, 2-fluoro-	300.6	6552		87	Perylene-D12	600.8	53724
43	Biphenyl	304.9	147.25		88	Indeno[1,2,3-cd]pyrene	616	27590
44	Naphthalene, 2-chloro-	305.6	4966.5		89	Dibenz[a,h]anthracene	656.95	36289
45	o-Nitroaniline	312.25	8112.8		90	Benzo[ghi]perylene	672.1	37069

Figure 2 shows the Total Ion Chromatogram (TIC) for a mid level (50 ppm) standard. The chromatogram shows a full chromatographic separation that is completed in just over 11 minutes with resolution and identification of all 90 analytes of interest. This fast analysis was achieved through the use of a relatively fast temperature programming rate along with a high spectral acquisition rate.

The fast spectral acquisition rate offered by the TruTOF allows for the spectral deconvolution of overlapping chromatographic peaks that frequently occur during high-speed separations. The benefit of the high spectral acquisition rate is shown in detail in the inset of Figure 2, which shows a close-up view of peaks 78-82. The inset shows the chromatogram plotted for each of the unique masses for the analytes of interest along with the TIC. The black vertical lines designate the individual peaks and the peak markers are as listed in Table 1. The automated peak find and deconvolution algorithms were able to correctly identify all of the analytes shown in this chromatogram.

Shown in Figure 3 is a more detailed example of peak deconvolution for peaks 1 and 2 which are chromatographically separated by only 200 ms. A close-up view of the TIC is shown along with the unique masses for N-nitrosodimethylamine (m/z 74) and pyridine (m/z 79). Shown along with the chromatogram are the caliper, peak true (deconvoluted), and library hit spectra. Note the ions circled in red in the caliper spectra which come from the other component in the coeluting peak pair. The Peak Deconvolution algorithm recognizes these ions as being from another component and automatically removes them.

4. Conclusions

This study describes a relatively fast separation for 8270D analysis. High-speed temperature programming significantly reduced the overall analysis time as compared to traditional methods. Detection by TOFMS gives all of the sensitivity needed in order to identify trace level components while simultaneously providing the data density needed to define narrow GC peaks and deconvolute overlapping peaks.

Alternative Test Procedure (ATP letter 2-9-05, case numbers D04-002 and N04-002). [See EPA APPROVAL LETTER at www.leco.com]
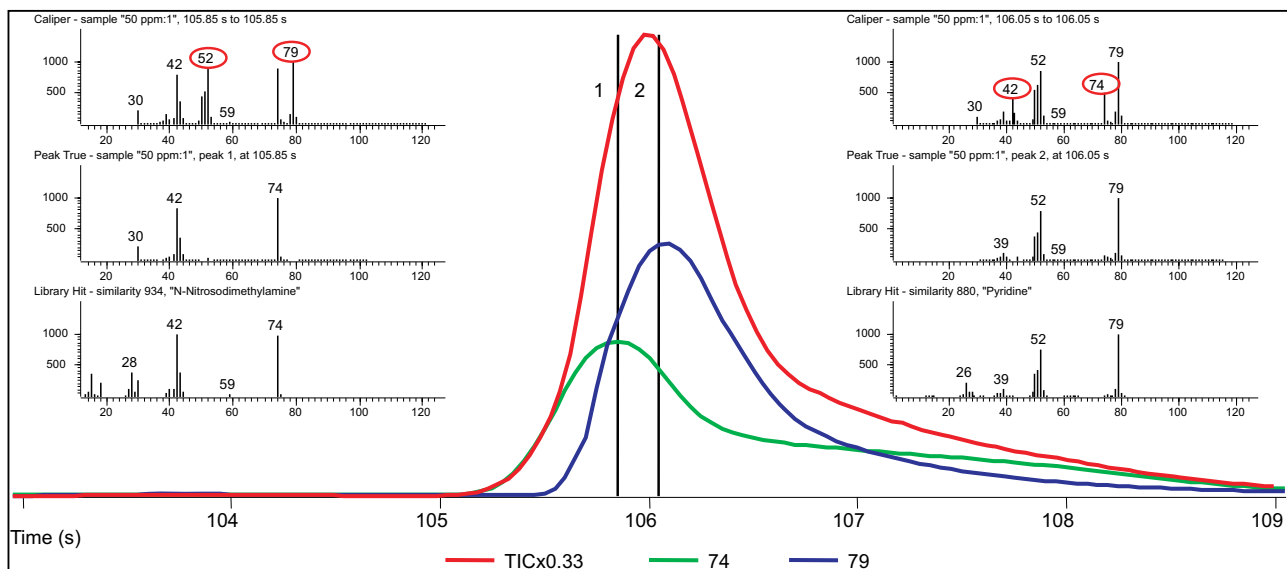

Figure 3. Close-up view of peaks 1 and 2 along with their corresponding mass spectra.

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