

Using EPA Method 8270 and the Pegasus GC-TOFMS to Characterize Semivolatile Analytes from Contaminated Soil Extracts

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1. Introduction

Many highly toxic residues from petrochemical wastes, coal tar pitches, pesticides, transformer PCBs and railroad tie/electric pole preservatives that find their way into the environment consist of semivolatile organic compounds. These compounds include polynuclear aromatic hydrocarbons, chlorinated esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, (including nitrophenols). The EPA has established Method 8270 to determine the concentration of such compounds in extracts prepared from solid waste matrices, soils, marine sediments, air sampling media, and water samples using GC-MS.

Before analysis can begin, Method 8270 requires rigorous quality control procedures governing surrogate and internal standard spiking, preparation of samples, internal standards and controls, as well as optimization and 5-point calibration of the mass spectrometer employed for analysis. In addition, verification of instrument parameters is required every 12 hours to evaluate GC-MS system performance. Analyte minimum response factors are compared with those determined during the initial calibration to ensure standard conditions are followed.

Using conventional instrumentation—such as a quadrupole MS—to analyze a complex mixture of semivolatile organic compounds in contaminated soil extracts takes at least an hour to run due to slow spectral acquisition rates. Therefore, only 10 samples can be run and analyzed each shift before the next system performance check is required. The LECO Pegasus® GC Time-of-Flight Mass Spectrometer (TOFMS) offers several unique advantages for reducing analysis time, taking full advantage of Fast GC techniques.

The Pegasus, with full mass range acquisition rates of up to 500 spectra per second, can easily probe narrow gas chromatographic peaks without sacrificing data quality. Complicated mixtures of coeluting compounds are rapidly analyzed using Automated Peak Find and Deconvolution algorithms. Deconvolution not only assigns the proper spectra to each coeluting component, but also assigns the correct signal intensity to each component, allowing for quick, reliable quantification of the coeluting species. The combination of fast acquisition rates and automated data analysis provided by the Pegasus can lead to an increase in environmental lab productivity of at least an order of magnitude.

2. Experimental Conditions

The power of the Pegasus to analyze semivolatile components following EPA Method 8270 was evaluated

for the rapid characterization of such compounds found in contaminated soil extracts. Using an acquisition rate of 25 to 50 spectra/second, the typical analytical run time was reduced from 1 hour to only 10 minutes. System performance checks (automatically programmed into the user-friendly Pegasus software interface—Figure 1) were performed in 1 hour instead of 5 to 6 hours. With 11 hours available until the next required performance check, as many as 55 samples can be processed over the course of a 12-hour shift.

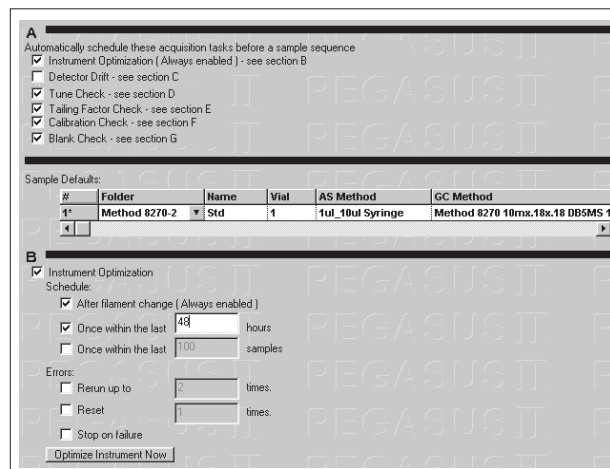


Figure 1: In compliance with EPA Method 8270 requirements, the Pegasus can be programmed to automatically perform quality assurance checks prior to sample analysis using the easy-to-follow software interface screen.

As outlined in Table 1, a general set of GC and TOFMS instrument conditions were developed. A mixture of Supelco semivolatile standards were used for calibration validation. The conditions were then applied without further optimization to the analysis of contaminated soil sample extracts.

Table 1: Pegasus GC-TOFMS conditions for an 8-minute analysis of an extract taken from contaminated soil.

Detector:	LECO Pegasus II GC-TOFMS
Transfer Line:	290°C
Source:	200°C
Acquisition Rate:	25 spectra/sec. (45 to 500 u)
GC:	Hewlett Packard® 6890*
Column:	DB-5MS 15 m x 0.180 mm ID, 0.180 µm phase film
Oven:	40°C for 1 min., then to 300°C at 35°C/min., hold for 1.57 min.
Injector:	Split/splitless at 250°C
Carrier Gas:	Helium, 1.8 ml/min. constant flow
Sample:	Extraction with methylene chloride per EPA Method 3541, 1.0 µl split (100:1) injection

*The HP6890 GC is equipped with fast oven temperature ramp capabilities and a high pressure EPC module.

3. Results and Discussion

Analysis of a Calibration Mix – Method Validation

Figure 2 presents the Analytical Ion Chromatogram (AIC) resulting from an 8-minute analysis of a Supelco® CLP semivolatile calibration mix and a Supelco 8270/ Appendix IX semivolatile calibration mix consisting of 103 analytes.

The speed of the GC temperature program caused some of the compounds in the complex calibration mixture to coelute, as illustrated in Figure 3. The positions of the coeluting compounds were located using LECO's automated Peak Find algorithm, while the mass spectra for the two analytes were accurately resolved from one another by the automatic Spectral Deconvolution algorithm. This revolutionary algorithm not only separates out ions unique to the spectra of each analyte, but also successfully assigns the appropriate amount of signal to each analyte spectrum for masses that are shared between multiple analytes in the coelution. An automated library search provided rapid, unambiguous identification of the components over a wide dynamic range, as evidenced by the identification of both abundant and trace ions coeluting within one narrow GC peak.

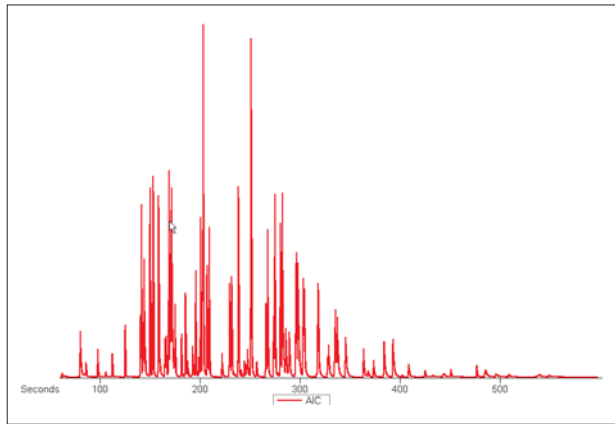


Figure 2: Analytical Ion Chromatogram for a Supelco calibration mix consisting of 103 analytes. Total analysis time was <600 seconds.

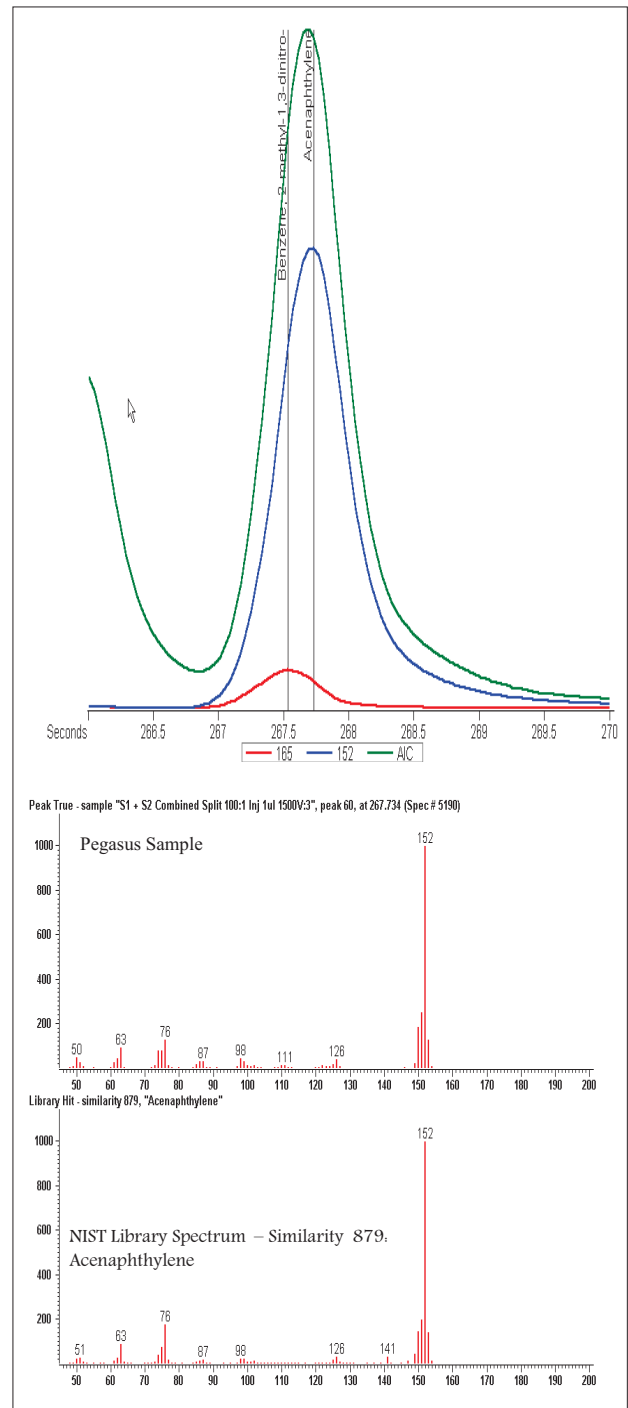


Figure 3: Extracted ion profile chromatogram showing the coelution of 2-methyl-1,3-dinitrobenzene (blue trace) and acenaphthylene (red trace). The AIC is shown in green. Markers indicate the location of peaks determined by the Pegasus Peak Find algorithm. Data from the automated library search is presented for the trace component, acenaphthylene.

Analysis of Contaminated Soil Sample Extracts

The validated method was applied to the analysis of extracts from a contaminated soil sample. Internal standards (40 ng/ μ L) were spiked into the extracts. Table 2 provides a list of compounds identified and quantitated during analysis of a typical soil extract from which 277 analytes were identified in 10 minutes.

Table 2: Peak table for selected peaks from extract sample #819-1.

Peak #	Name	R.T.	Quant Masses	Concentration	Area
9	Phenol, 2-fluoro-	106.21	112	108.75 ng/ μ L	591400
17	Phenol-d6-	142.53	99	126.79 ng/ μ L	902690
18	Phenol	142.97	94	18.41 ng/ μ L	166180
21	1,4-Dichlorobenzene-d4	150.15	152	40.00 ng/ μ L	471550
25	Benzene, 1,3-dichloro--:2	158.01	146	Out of calibration range: 0.04 ng/ μ L	5528
29	Phenol, 2-methyl-	164.81	107	116.83 ng/ μ L	658010
33	Phenol, 4-methyl-	171.01	107	234.81 ng/ μ L	1905900
37	Benzene-d5-, nitro-	173.37	82	77.29 ng/ μ L	1441500
49	Isoforon	184.33	82	Out of calibration range: 0.00 ng/ μ L	5027
55	Phenol, 2,4-dimethyl-	191.17	122	Out of calibration range: 575.82 ng/ μ L	2074600
60	Benzoic Acid	198.93	122	133.45 ng/ μ L	245020
61	Naphthalene-d8	200.13	136	40.00 ng/ μ L	1411500
62	Naphthalene	201.43	128	saturated(Out of calibration range: 2288.01 ng/ μ L)	saturated(94924000)
97	Benzocycloheptatriene	228.63	141	Out of calibration range: 910.65 ng/ μ L	14321000
113	4,4'-Difluorobiphenyl	241.91	190	92.45 ng/ μ L	26854
118	1,1'-Biphenyl, 2-fluoro-	245.15	172	84.73 ng/ μ L	1738500
144	Biphenylene	264.47	152	Out of calibration range: 9.92 ng/ μ L	226560
148	Acenaphthene-d10	270.91	164	40.00 ng/ μ L	499160
151	Acenaphthene	272.37	154	Out of calibration range: 868.76 ng/ μ L	13413000
160	Dibenzofuran	278.85	168	Out of calibration range: 621.83 ng/ μ L	14071000
167	2,4-Dinitrotoluene	282.71	165	Out of calibration range: 4.88 ng/ μ L	10235
172	Fluorene	292.75	166	Out of calibration range: 676.09 ng/ μ L	9609200
181	Nitrosodiphenylamine	299.49	169	Out of calibration range: 6.82 ng/ μ L	31511
182	Azobenzene	299.97	77	Out of calibration range: 8.91 ng/ μ L	117440
184	Phenol, 2,4,6-tribromo-	303.61	330	98.50 ng/ μ L	102410
205	Phenol, pentachloro-	326.83	266	49.51 ng/ μ L	37420
207	Phenanthrene-d10	330.21	188	40.00 ng/ μ L	477160
208	Phenanthrene	331.47	178	Out of calibration range: 1831.07 ng/ μ L	24387000
209	Anthracene	332.63	178	Out of calibration range: 510.13 ng/ μ L	8257600
212	Carbazole	341.25	167	179.39 ng/ μ L	2323800
237	Fluoranthene	379.73	202	Out of calibration range: 849.81 ng/ μ L	10159000
239	Pyrene	388.37	202	Out of calibration range: 726.94 ng/ μ L	8564500
245	p-Terphenyl-d14	397.39	244	82.36 ng/ μ L	413460
262	Benzo[a]anthracene	437.71	228	152.46 ng/ μ L	637820
263	Chrysene-d12	438.31	240	40.00 ng/ μ L	192360
265	Chrysene	439.35	228	100.22 ng/ μ L	709800
267	3,3'-Dichlorobenzidine	441.71	252	Out of calibration range: 0.06 ng/ μ L	7035
270	Benzo[b]fluoranthene	479.46	252	48.37 ng/ μ L	189890
271	Benzo[k]fluoranthene	479.99	252	45.78 ng/ μ L	318560
273	Benzo[a]pyrene	490.53	252	48.00 ng/ μ L	238850
274	Perylene-d12	492.71	264	40.00 ng/ μ L	165420
275	Indeno[1,2,3-cd]pyrene	530.43	276	20.44 ng/ μ L	77512
276	Dibenz[a,h]anthracene	531.77	278	Out of calibration range: 8.45 ng/ μ L	28139
277	Indeno[1,2,3-cd]pyrene:2	541.05	276	14.29 ng/ μ L	58687
	Total			11971.01 ng/ μ L	216210000

RT - Retention time, in seconds.

The AIC for this experiment is shown in Figure 4, where automated peak find, deconvolution, and library searches allowed the identification of 100% of the peaks meeting EPA Method 8270 threshold requirements for analysis.

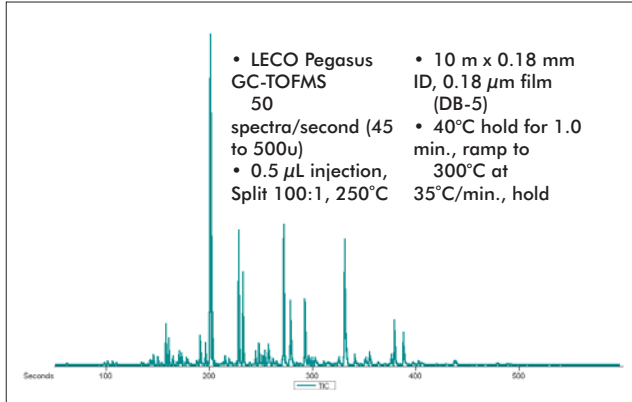


Figure 4: AIC for a mixture of 277 semivolatiles extracted from soil sample #819-1.

4. Conclusions

In this work, the LECO Pegasus GC-TOFMS was used to analyze contaminated soil sample extracts following the rigorous EPA Method 8270 criteria. The fast acquisition rate of Pegasus, coupled with powerful data manipulation and interpretation algorithms, provided full mass range analysis of complex mixtures of semivolatiles in less than 600 seconds. By using the Pegasus, environmental lab productivity can be increased by over an order of magnitude as compared with conventional MS instrumentation.

