

Fast Gas Chromatography/Mass Spectrometry Analysis in Support of Risk-Based Decisions

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Abstract: A new data analysis software system (Ion Fingerprint Detection™) has been developed to provide fast mass spectral data analysis. Methods have been developed that can provide screening to quantitative gas chromatography/mass spectrometry (GC/MS) data in 30 s to minutes. Compound selectivity is provided through a unique set of algorithms rather than GC separation. The data quality produced for volatile and semivolatile organic contaminants under fast GC/MS conditions during dynamic site investigations carried out at Hanscom Air Force Base (Bedford, MA) and Joliet Army Ammunition Plant (Joliet, IL) are discussed. More than 800 samples were analyzed in each project, with state and federal regulators accepting the data to complete remedial investigation/feasibility (RI/FS) studies. © 1999 John Wiley & Sons, Inc. *Field Analyt Chem Technol* 3:55–66, 1999

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Introduction

Over the past 10 years, we have participated in 22 hazardous waste site investigation and cleanup projects. A wide variety of decisions have been made on subjects ranging from the spatial distribution of soil contaminants to their quantitative risk to ground water. Project completion was

achieved faster, better, and cheaper when field analytics drove the on-site decision-making process. Field analyses are only cost effective, however, when sampling crews and laboratory staff do not sit idle waiting for each other to catch up.¹ This requires fast data turnaround times, and necessitates that analysis methods and instruments be capable of high sample throughput rates.

Gas chromatography/mass spectrometry (GC/MS) is the only analytical technique that, when free of background spectral interferences, can provide unambiguous identification of organic compounds in complex mixtures. In the 1970s, environmental analysis by GC/MS was expensive and cost as much as \$1500/sample. The same analysis today by EPA method 8270 can cost as little as \$400/sample. The reduction in sample costs over the years can, in part, be attributed to the mass production of more reliable instruments and GC columns and the early pioneers who integrated computers with GC/MSs to provide on-line computer control with increased data analysis automation.^{1–7} Improvements in mass spectral and peak deconvolution routines^{8–11}, statistical methods of analysis^{12–14} and automated library searches^{15–17} further decreased data reduction times.

Despite these innovations, extensive sample preparation and cleanup prior to analysis continues to limit the rate at which complex samples can be analyzed. Multistep cleanup procedures are typically employed to remove sample interferences so that high levels of nonuniform background signals do not interfere with mass spectral data analysis systems. In 1994 Stein and Scott¹⁸ followed by McLafferty, Zang, Stauffer, and Stanton¹⁹ in 1997 evaluated the most often used algorithms for the identification of unknowns against the NIST and Wiley MS databases. Relatively good correlation (50–75% accuracy) was obtained for pure spectra, with much poorer (25–50% correct) results obtained for two-component mixed spectra (85% peak purity) systems.

Deconvolution techniques have been developed and op-

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timized for specific compounds or families of compounds.^{20–25} Although these methods can provide quantitative data, they cannot be easily used to accurately quantify the wide range of environmentally targeted compounds in high levels of random background noise or when severe coelution occurs. In these cases, matrix ions will be common to the target compound quantitation ion, resulting in overestimates of concentration.

Toward this end, a more generalized data analysis method is described that is capable of providing risk-assessment quality data under fast GC/MS conditions. At least three ions per target compound are extracted from electron-ionization low-resolution mass spectra, with signal ratios computed and compared against one another²⁶. If the relative abundances meet the accepted error function then the least-interfered ion is normalized against the quantitation ion (minimum integration method). Algorithmic output and data quality are shown for a mixture of polychlorinated biphenyls (Aroclor 1248), polycyclic aromatic hydrocarbons (PAH), and chlorinated pesticides detected in the presence of gasoline and engine oil (1:3 by volume) in 5 min. Results for two dynamic site-investigation projects—carried out with the use of an adaptive sampling and analysis program—are provided to demonstrate the unique capability of the algorithms to support fast, quantitative GC/MS analyses in the field.

Experiment

Reagents and Standards

The VOC and semivolatile standards were purchased from Supelco (Milwaukee, WI) and Ultra Scientific (Hope, RI), respectively. The explosive standards were obtained from the U.S. Army Environmental Center (Aberdeen Proving Ground, MD) and Supelco. Methanol, methylene chloride, anhydrous sodium sulfate, and acetone were obtained from Fisher Scientific (Fair Lawn, NJ).

Sample Preparation and Equipment

All semivolatile analysis samples were prepared by weighing 2.0 ± 0.1 g soil and 1 g anhydrous sodium sulfate into an 8-ml Teflon-lined screw-cap vial. For PCBs, PAHs, and pesticides, a known concentration of octachloronaphthalene was added with 2.0 ml methylene chloride and hand-shaken for 3 min. For explosives, 2.0 ml acetone was added and hand-shaken for 3 min. After settling, the respective extracts were transferred to a 2-ml crimp-sealed vial for analysis. Known aliquots of extract and internal standard were co-injected into a clean glass sleeve prior to TDGC/MS analysis. VOC samples were prepared for analysis by the addition of 5 ml purified water, 5 g soil, and known concentrations of 1,4-difluorobenzene, 4-bromofluorobenzene (surrogates) and toluene-*d*₈ (internal standard) to the sparging vessel.

A Tufts (Medford, MA) -built GC with a thermal desorption sample introduction system was used in combination

with a Hewlett Packard (Palo Alto, CA) model 5972 mass spectrometer for the semivolatile analysis. The TDGC/MS was modified for field operation. For VOC analysis a Tekmar (Cincinnati, OH) model LSC 3000 purge and trap system was connected to a Hewlett Packard model 5890/5972 GC/MS and used without modification. Table 1 lists the field GC/MS operating conditions for each study.

Results and Discussion

EPA SW 846 Method 8270C was used to produce the total ion current (TIC) chromatogram shown in Figure 1 for a standard mixture of PCBs (Aroclor 1248), 16 PAHs, 19 chlorinated pesticides, and pyrene-*d*₁₀ (internal standard). The standard mixture contains 86 compounds, because Aroclor 1248 includes 50 congeners whose concentrations are at least 1% of the total PCB concentration. Compound selectivity is obtained through GC separation, where 55 semi-VOCs are baseline separated and all remaining compounds, even those that completely coelute, are easily identified by their mass spectral patterns. For example, 38 of the congeners are baseline separated, with the other 22 coeluting with PCBs from a different chlorination level. When the same standard is analyzed in under 5 min, 20 peaks are produced, with 2–7 compounds eluting per peak. Moreover, fast GC/MS analysis of the same standard in the presence of high levels of petroleum hydrocarbons gasoline/engine oil (1:3 parts by volume) results in the apparent masking of each compound's mass spectral features. The corresponding compounds and mass spectra at 2.82 min and 3.30 min are shown in Figure 2.

Equations (1)–(9) are used to untangle the spectral interferences. Figure 3 depicts the reconstructed ion current (RIC) chromatograms for the semi-VOCs that have been detected in the extract. Note that matrix signals are 10^6 versus 10^4 for PAHs, 10^3 – 10^5 for pesticides and 10^2 – 10^4 for the different PCB chlorination levels. As separation efficiencies decrease, compound selectivity must be obtained through data analysis. The analyst selects between three and six (*N*) fragment ions per compound that will be used to extract the ion current signal during an expected elution time interval. The function $f_i(t)$ in Eq.(1) computes the ratio between an established library L_i and the observed relative abundance $R_i(t)$ for the *i*th ion ($1 \leq i \leq N$) at time *t*, multiplied by the observed abundance of the main ion $A_m(t)$:

$$f_i(t) = \frac{R_i(t)}{L_i} A_m(t). \quad (1)$$

The next three equations are used to determine the difference between the actual and expected abundances. The analyst selects an acceptable percent difference *K*% between the observed and library relative abundances; then Eqs. (5)–(7) compute the margin of acceptable error $\Delta(t)$ for Eqs. (2)–(4), respectively,

TABLE 1. TDGC/MS operating conditions.

	PAH/PCB (HAFB)	VOC (HAFB)	Explosives (JAAP)	45- and 5-min SVOC
Sample injection	<i>Thermal desorption:</i> evaporate solvent for 2 min at 40 °C, desorb for 1.5 min at 280 °C, use disposable glass sleeve	<i>Purge and trap:</i> Supelco trap (Tenax, charcoal, and silica gel), purge 5 min at 30 ml/min, desorb 2 min at 225 °C, bake out 6 min at 230 °C with line and valve at 180 °C	<i>Syringe injection:</i> Injector port at 250 °C	<i>Thermal desorption:</i> Evaporate solvent for 2 min at 40 °C, inject for 1.5 min at 280 °C and 2.0 ml/min.
Temperature program	<i>Total run time: 10 min</i> hold 1 min at 150 °C; heat 50 °C/min to 320 °C; hold 5.5 min	<i>Total run time: 16 min</i> hold 4 min at 50 °C heat 12 °C/min to 150 °C	<i>Total run time: 3 min</i> isothermal at 180 °C	EPA SW 846 Method 8270C <i>Total run time: 40 min</i> hold 1.5 min at 35 °C; heat 6 °C/min to 290 °C; hold 1.5 min <i>Total run time: 5 min</i> hold 1 min at 35 °C; heat 32 °C/min to 290 °C; hold 1.5 min
MS temperature	280 °C	280 °C	250 °C	250 °C
Mass range	120–500 amu	45–260 amu	SIM	120–500 amu
Scan rate	2.3 scans/s	2.3 scans/s	2 scans/s	2 scans/s
Solvent delay	1.5 min	3.0 min	1.0 min	1.5 min
Flow rate	1.0 ml/min	2.0 ml/min	1.0 ml/min	2.0 ml/min
Split flow	Splitless	40 ml/min	20 ml/min	Splitless
Split ratio	N/A	20:1	20:1	N/A
Column	DB-5 MS; 20 m, 0.25 mm ID, film thickness 0.25 μm	DB-624; 60 m, 0.25 mm ID, film thickness 0.25 μm	DB-5 MS; 30 m, 0.25 mm ID, film thickness 0.25 μm	DB-5 MS; 20 m, 0.25 mm ID, film thickness 0.25 μm

$$F_1(t) = \max_{i \leq N} [f_i(t)] - \min_{i \leq N} [f_i(t)], \quad (2)$$

$$F_2(t) = \frac{\sum_{i=1}^{N-1} \sum_{j=i+1}^N |f_i(t) - f_j(t)|}{\sum_{i=1}^{N-1} i}, \quad (3)$$

$$F_3(t) = \left| \max_{i \leq N} \frac{df_i(t)}{dt} - \min_{j \leq N} \frac{df_j(t)}{dt} \right|, \quad (4)$$

where Δ_0 is the additive error factor attributable to instrument noise or uniform background signal, and α and β are preselected coefficients. Experience has shown that acceptable default values for α and β are 0.7 and 0.5:

$$\Delta_1(t) = K\% |\max_{i \leq N} f_i(t)| + \Delta_0, \quad (5)$$

$$\Delta_2(t) = \alpha K\% |\max_{i \leq N} f_i(t)| + \Delta_0, \quad (6)$$

$$\Delta_3(t) = \beta K\% \left| \max_{i \leq N} \frac{df_i(t)}{dt} \right|. \quad (7)$$

Target compounds are considered present in the sample if $F_2(t) \leq \Delta_2(t)$ and/or $F_1(t) \leq \Delta_1(t)$ in at least four consecutive scans. If these conditions fail, $N > 3$, and $F_3(t) \leq \Delta_3$, then every possible subset is checked with the minimum $F_1(t)$ subset selected. This condition may exist when a matrix

ion coincides with a target ion and at very low signal levels where the fragmentation of low-abundance ions may be added to by noise. For the ion(s) j , not included in the subset, the library value is used to account for the additive signal from the matrix,

$$A_j^{adjusted} = \frac{\sum_{i=1, i \neq j}^N f_i(t)}{N-1} L_i, \quad (8)$$

with all ions recompared with the use of the criteria described above. If all three cases fail, the program reports the compound as not detected. The algorithmic results are shown graphically in Figure 4, where additive signals from the matrix have been spectrally separated from the target ions. Ion current produced by the matrix has been subtracted from mass fragments 200 and 203 for both fluoranthene and pyrene by the software. The bar chart under each peak depicts the number of consecutive scans, 10 in this example, that the sample spectra matched the library spectra.

For compounds that have been identified in the sample, the RIC signal is calculated as follows:

$$S = \int_{t_1}^{t_2} P_i; \quad (9)$$

if $\min_{(i \leq N)} f_i(t) > \Delta_{thresh}$ then $P_i = \min_{i \leq N} f_i(t) dt$ and if not $P_i = 0$, where Δ_{thresh} is the signal value set by the analyst and t_1 ,

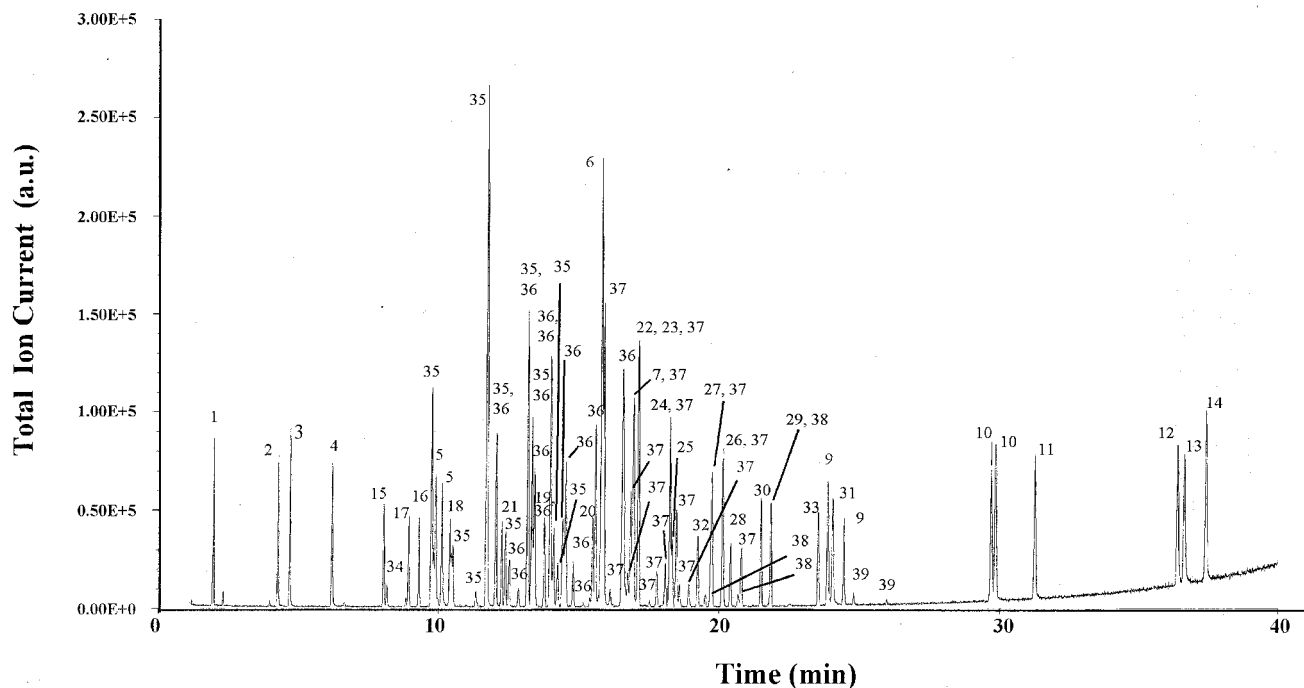


FIG. 1. Total ion current chromatogram of a standard mixture of PCBs, PAHs, and chlorinated pesticides.

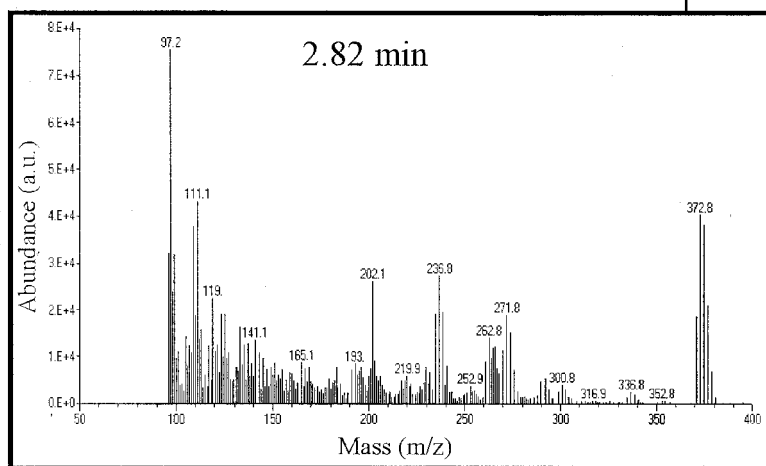
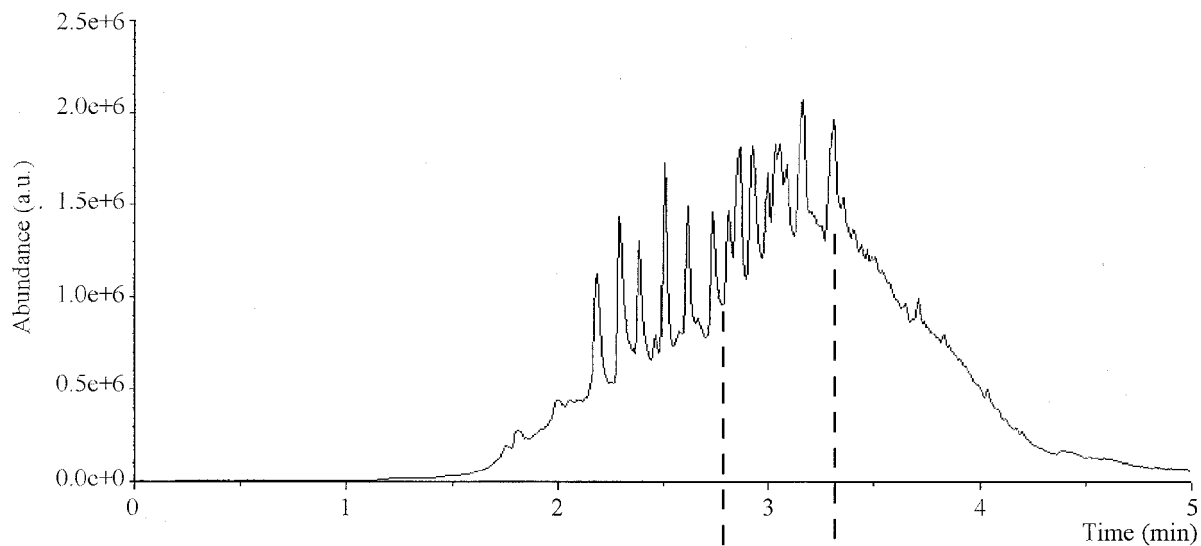
t_2 are the beginning and the end of the retention time interval. The RIC chromatograms in Figure 3(a) at 2.8 and 2.9 min are the black peak lines in Figure 4, which depict the minimum envelope calculation for each compound whose area is determined by Eq. (9).

Measurement accuracy for the 5- and 40-min GC/MS analyses can be found in Table 2. The fast TDGC/MS results produce data of comparable quality to the EPA standardized method. The algorithms positively identified each compound in a highly complex matrix and with no sample cleanup. In method 8270C semi-VOCs are analyzed by GC/MS after gel permeation cleanup, with the PCB/pesticide fraction analyzed by GC/electron capture detection (SW 846 Method 8081/8082). Adaptive sampling and analysis programs (i.e., dynamic investigations) cannot be supported by field analysis if semivolatile methods require a 1-h sample cleanup followed by two 20-min analyses.

If the purpose of the site investigation is to produce risk-assessment data, then those organics that drive the risk analysis must be detected uniquely. For example, the EPA soil screening level to determine risk to groundwater at the 20 dilution attenuation factor for benz(a)anthracene is 2 ppm and chrysene 1600 ppm. Although the semi-VOC method can detect PCBs/PAHs in 5 min by TDGC/MS with the IFD data analysis software, these two compounds coelute and have the same mass spectral pattern. Therefore, longer GC run times (10 min) were used during the Hanscom Air Force Base (HAFB, Bedford, MA) site investigation to separate these two compounds. A total of 10% of the soil samples collected was sent to an off-site laboratory for PAH (SW 846 Method 8270B) and PCB (SW 846 Method 8080) anal-

ysis. No semi-VOCs were found by either the field or commercial laboratory.

The soil samples sent for off-site analysis during the Joliet Army Ammunition Plant (JAAP, Joliet, IL) site investigation did contain TNT and DNT. The laboratory hired to analyze the split samples by SW 846 Method 8330/USAED 30 failed to meet the project's data-quality objectives for two different batches of samples. Based on this performance, no additional soil samples were sent to this laboratory for analysis. At the conclusion of the field investigation, split samples were sent to a second laboratory. Comparing the field and off-site laboratory (SW 846 Method 8330/USAED 30) results for TNT and DNT concentrations showed that 27/37 and 22/37 samples were within the JAAP DQOs, see Table 3(a). Differences in concentration may be attributable to the fact that these compounds exist in soil as nuggets of contamination. Sample inhomogeneity can adversely affect measurement precision, which subsequently can affect accuracy. Although measurement precision was within the DQOs for nearly all samples, it was evident that for some locations differences of 9 to 18 in. resulted in the presence or absence of TNT or DNT. To test this observation, seven samples were collected within a 3-in. radius from eight different locations. The average concentration %RSD for this set of replicates was 38%. Measurement precision within this small sampling area was excellent. Nonetheless, at one location samples collected within the first 6 in. of the surface contained 350 ppm TNT and at 1.5 ft. 3800 ppm. At another location, samples collected within 6 in. of the surface contained 24,000 ppm TNT, and at 1.5 ft. 160 ppm. The most extreme case was when DNT was measured at 100,000 ppm



2.82 min	
Compound Present	Signal
Chlordane	3.54e+04
Fluoranthene	2.01e+04
Heptaclor	1.21e+04
Cl-4	8.83e+03
Endosulfan 1	6.19e+03
Cl-5	7.40e+02
Heptaclor epoxide	4.18e+02

3.30 min	
Compound Present	Signal
Methoxychlor	1.28e+05
Benzo[a]anthracene/ Chrysene	2.78e+04
Endrin ketone	1.86e+04
Endrin	1.78e+04
DDT	2.68e+03
Cl-4	8.63e+02

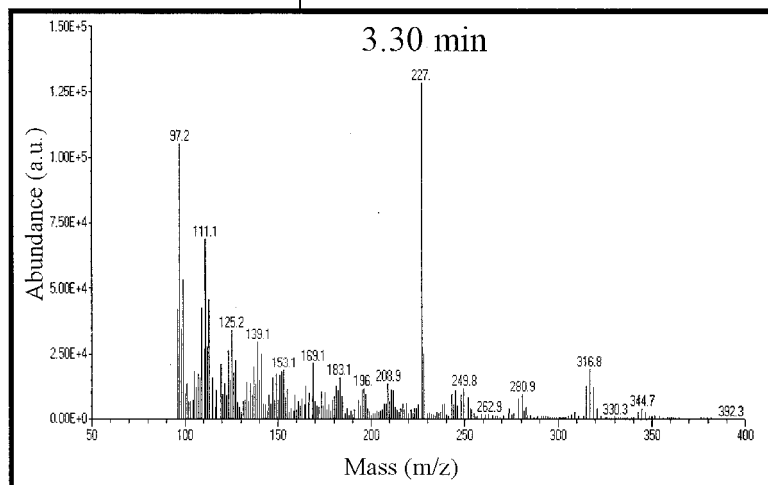


FIG. 2. Total ion current chromatogram of a gasoline/engine oil (1:3 by volume) extract fortified with the standard mixture analyzed in 5 min.

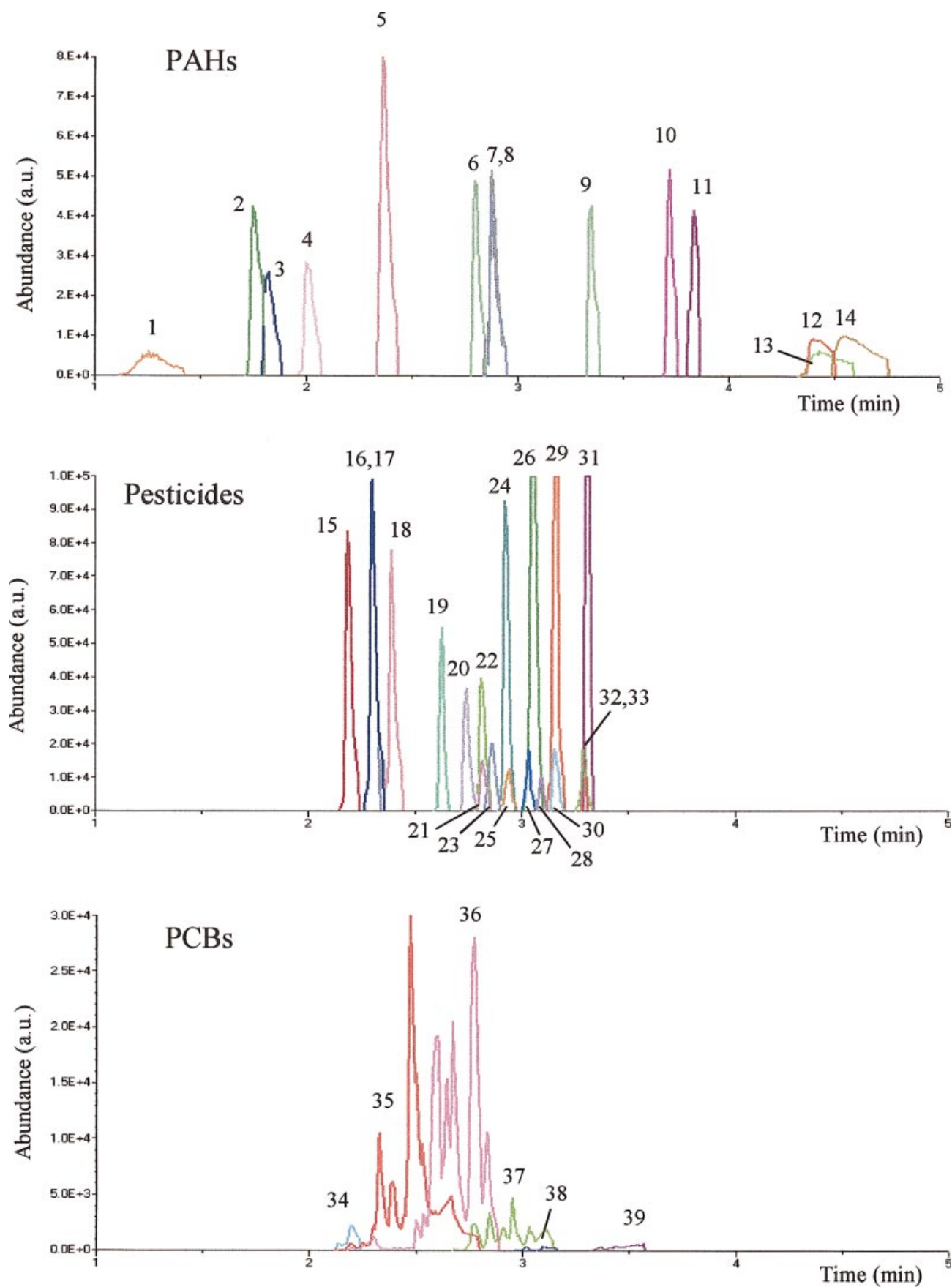


FIG. 3. Reconstructed ion current chromatograms of (a) PAH, (b) chlorinated pesticides, and (c) PCBs extracted from the data shown in Figure 2.

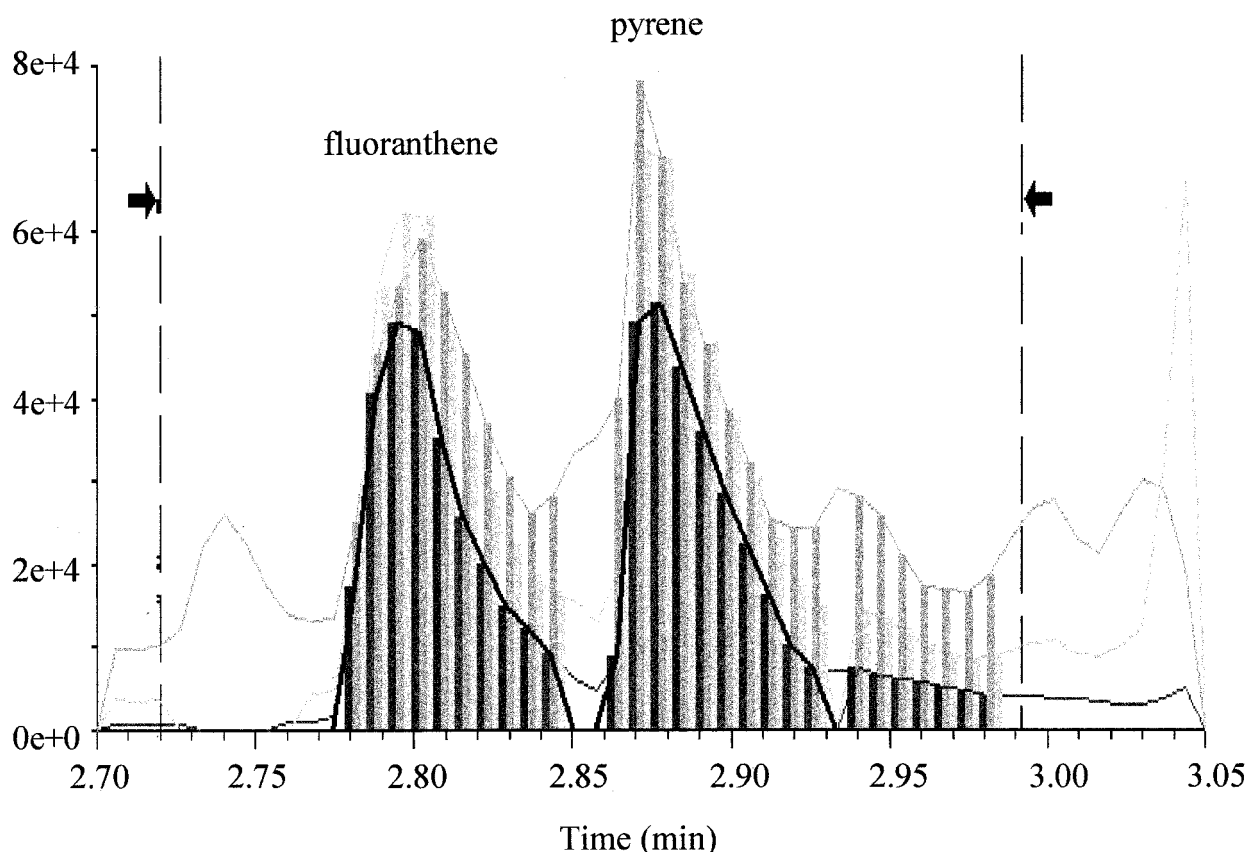


FIG. 4. Target ion extraction and minimum envelope output used to produce the reconstructed ion current chromatograms for fluoranthene and pyrene.

at a depth of 1.5 ft, but at the surface no contamination was detected.

Data quality can further be assessed through the calibration plots, internal standard and surrogate recoveries; see Table 3(b). For both projects, the initial and continuing calibration verification data were well within the SW 846 modified 8270B field methods, as agreed upon by the respective state regulators for Massachusetts and Illinois and EPA Regions I and V. At HAFB surrogate analyses were performed for every sample, whereas for JAAP a laboratory control check standard was analyzed at the beginning and conclusion of each day. Compound recoveries were within the acceptable range established for each project. As the number of target compounds and/or QC samples increase, the number of site samples that can be analyzed per day decreases. Based on the initial HAFB conceptual model, it was thought that 42 samples would require analysis, all from the same site. As the project proceeded field results suggested that samples from two other sites also required analysis. A total of 70 samples was analyzed for PCB and PAHs. The fact that both classes of compounds could be analyzed by the same method in 10 min allowed time to add and analyze surrogates. On the other hand, JAAP began with the expectation of analyzing 90 samples per day. This number quickly reached 125 samples/day, principally due to the expansive nature of the site and the fact that it was difficult to

determine the spatial distribution of TNT and DNT within the contaminated areas without additional sampling. Soil samples were collected from 702 locations to determine the amount of contaminated soil at four of the manufacturing sites. A total of 1074 site and QC samples was analyzed without increasing personnel or equipment during the 2-week project.

During the HAFB site investigation 601 soil samples were screened for VOCs over an 8-day period. These measurements were obtained in 30 s by placing the TD sampling probe head directly over an incision made in 4-ft Geoprobe™ tubes at 1-ft intervals. Each tube was cut into a 2-ft section where the greatest VOC concentration was found. The 2-ft sleeves were then cut lengthwise, with soil collected over the length of the tube without homogenization. Purge-and-trap GC/MS analyses were performed daily to confirm the screening results *and* to determine the boundaries of VOC contamination and their risk to groundwater. Quantitative measurements were made on 158 2-ft composite soil samples. Whenever the screening results indicated the presence or absence of VOCs at the site-specific quantitation limits, quantitative GC/MS confirmed this finding 90% (142/158 samples) of the time. This result is remarkable in that the direct measuring GC/MS analyses were made over a hole the size of a nickel as compared to the 2-ft composite sample for quantitative analysis. Six samples were found to contain

TABLE 2. Percent recoveries for the 40-min and 5-min analyses of standard/oil mixture based on the results of the 40-min standard mixture.

Peak Compound	% Recovery of Standard/ Oil Mixture	
	40 min	5 min
3 Acenaphthene	112	106
2 Acenaphthylene	109	96
19 Aldrine	120	89
15 α -BHC	92	103
11 Benzo(a)pyrene	120	118
14 Benzo(g,h,i)perylene	91	91
9 Benzo[a]anthracene/Chrysene	96	96
10 Benzo[b]/(k)fluoranthene	116	113
16 β -BHC	95	95
34 C1-2	120	102
35 C1-3	96	96
36 C1-4	111	106
37 C1-5	96	92
38 C1-6	128	87
39 C1-7	96	93
22 Chlordane	111	109
26 DDD	103	103
24 DDE	97	100
29 DDT	99	100
18 δ -BHC	83	93
13 Dibenz(a,h)anthracene	83	87
25 Dieldrine	124	119
28 Endrin aldehyde	86	86
23 Endosulfan 1	126	123
27 Endosulfan 2	123	123
30 Endosulfan sulfate	131	122
32 Endrin	124	101
33 Endrin keton	89	84
6 Fluoranthene	110	110
4 Fluorene	95	95
17 γ -BHC	88	85
21 Heptachlor	118	118
20 Heptachlor Epoxide	112	117
12 Indeno(1,2,3-c,d)pyrene	88	90
31 Methoxychlor	122	122
1 Naphthalene	148	128
5 Phenanthrene/Anthracene	92	96
7 Pyrene	116	116
Average (%RSD)	107 (15%)	103 (12%)

Note: The peaks and their corresponding number are also shown in Figure 3.

VOCs by screening while quantitative analysis found no measurable contaminants (4% false positive); in contrast, quantitative GC/MS detected VOCs in 10 samples where direct measuring GC/MS did not (6% false negative). Comparing measurement accuracy other than by false positives or negatives for discrete and composite VOC soil analysis is nonsensical. Fast GC/MS analysis provided an excellent tool to determine the location and boundary of VOC contamination.

Two-thirds of the 158 samples selected for quantitative analysis contained target compounds and high levels of matrix interferences, primarily petroleum. Of the 205 compounds identified by the algorithms and Hewlett Packard's data anal-

ysis software, 85% had RPDs \leq 50%, and 65% had RPDs \leq 20%. In no instance was the RPD greater than 80%, even at the lowest measurable concentrations. This is remarkable, given that both data analysis systems identify peaks and integrate signals very differently. Where differences did occur the algorithms were better able to quantify target compound concentrations where matrix constituents added signal to target compounds (overestimation) and where the instrument's data analysis system cut peaks in half depending upon where the peak maxima was determined by the software (underestimation). IFD data analysis required manual integration of four (2%) sample data files, whereas 16% of the data files (25 samples) had to be manually integrated when the instrument's software was used, because of failure to associate sample spectra with target compounds or miss integration of peaks. The internal standard signal fell within the accepted DQO of 50–150% for 140/158 samples when the algorithms were used for a 92% success rate; see Table 4(a). The signal ratio of sample internal standard to the average 5-point calibration internal standard was biased negatively (<50% but >40%) for all 18 samples. This small but systematic error may be attributable to miss-injection of the internal standard, because the failure occurred within sequential sample analysis runs. Conversely, the instrument's data analysis software had a 78% success rate. In addition to the same 18 samples below the accepted DQO range, another 17 samples had internal standard ratios greater than 150%. The algorithms eliminate additive current from the matrix where traditional data analysis software cannot. Similar DQO statistics were also found for the surrogate analysis; see Table 4.

The field laboratory found VOCs in five samples versus two for the off-site laboratory.⁹ Because matrix concentrations were high, the laboratory diluted these samples by as much as 50 : 1. Low-level contaminants were diluted below method detection limits and/or loss during sample storage, making statistical comparisons between the field and laboratory data not possible.^{27,28} Another advantage of the software's ability to see through interfering ion signals is the fact that samples can be analyzed without dilution or the need for multiple reanalysis to detect a wide range of target compound concentrations. In both projects, the highest concentration calibration point was at least 50 times the action level for VOCs and 1000 times for semiVOCs. Sample concentrations exceeding the calibration curve were not diluted, which resulted in no reanalysis of samples. This benefit maximized the number of site samples analyzed per day, increasing the cost-effectiveness of the HAFB and JAAP site investigation projects.⁶

Review of the VOC measurement precision data indicates that the relative percent difference (RPD) and percent relative standard deviation (%RSD) for all replicate analyses fall within the acceptable criteria. The initial and continuing VOC calibration data were also within the project-specific DQO's. Measurement sensitivity experiments were performed in the field before the start of sample collection. The method detection limits listed in Tables 3(a) and 4(a) are based on the site-specific action levels according to EPA's

TABLE 3. TDGC/MS (a) method and (b) instrument DQOs and field results for quantitative SVOC analysis.

QC Parameters	Laboratory Method Requirements SW-846 Method 8270C	Field Method Requirements SW-846 Modified Method 8270B	Field Method Results for PCB/PAH	Field Method Results for TNT and DNT
(a) Selectivity	Can do up to 350 SVOC with 2–5 ions per compound; adjust chromatography to separate SVOC of interest	Up to 350 SVOC with 2–6 ions per compound; minimal GC separation, selectivity by data analysis algorithms	Analyzed 17 PAH and 10 PCB chlorination levels, three ions per compound identification; 10-min GC separation	Analyzed TNT and DNT, three ions per compound identification; 3-min GC separation
Sensitivity	660 ppb to 3300 ppb	QL ^a PAH (compound specific) 1 ppm to 21,500 ppm QL total PCB 0.5 ppm QL TNT 100 ppm QL DNT 4 ppm	MDL ^b PAH 0.087–0.374 ppm MDL total PCB 0.153 ppm	MDL TNT 1.5 ppm MDL DNT 1.5 ppm
Precision	Replicate analysis QC acceptance criteria	conc. > 5 × QL, RPD < 60% conc. < 5 × QL, PRD < 100%	10 samples analyzed replicate analysis contained no measurable concentrations	Within DQO ^a TNT 76/78 samples DNT 78/78 samples
Accuracy	Internal standard recovery within 50%–200% of the daily calibration internal standard For each sample or QC run, laboratory established surrogate recovery limits (e.g., 20–140%)	Internal standard recovery within 50%–150% of the daily calibration internal standard Surrogate recovery 20–140%	Within DQO 67/70 samples Surrogate recovery within DQO, 70 samples analyzed, average recovery 94%	Within DQO 702/702 samples None performed
		Field versus lab; conc. > 5 × QL, RPD < 60% conc. < 5 × QL, RPD < 100%	Seven samples analyzed measured concentrations below site-specific QL	Within DQO ^c TNT 27/37 samples DNT 22/37 samples
(b) Instrument performance tests for MS tuning	Perform check as per instrumental method, minimum once to initiate 12-hr shift	Perform check as per instrumental method, minimum once to initiate shift	Performed check as required at the beginning of each day	Performed check as required at the beginning of each day
Initial 5-point calibration	Calibration check compounds (CCC) %RSDs must be < 30%, if all RF %RSD ≤ 15% then use Ave. RF, else use linear regression	DQO dependent; can match SW 846 or all RF %RSDs ≤ 40% and no more than 1/3 > 30%	Average %RSD within DQO 17 PAH/PCB < 30% 5 PAH/PCB ≤ 40%	Average %RSD within DQO TNT 23% DNT 19%
Continuing calibration verification	One per 12-h shift; CCCs < 20%. All analytes within ± 25% of expected value	DQO dependent; can match SW 846 or begin and end of day, % difference for all compounds ≤ 40% and no more than 1/3 > 30%	Average % difference within DQO 18 PAH/PCB < 30% 4 PAH/PCB ≤ 40%	Average % difference within DQO TNT 18% DNT 14%
Laboratory control check sample	After each initial calibration and once per 12-h shift; percent accuracy within 80% to 120%	DQO sample throughput dependent; begin and end of day, percent accuracy within 60% to 140%	Non performed	TNT 19/20 within DQO DNT 20/20 within DQO
Method blank	One per extraction batch; all target compound concentrations < PQL	Once per extraction batch; all target compound concentrations < PQL	No target compounds detected	No target compounds detected
Other	Carryover monitored by analysis of blanks, watch baseline on chromatograms	Carryover monitored by analysis of blanks, watch baseline on chromatograms	Carryover monitored by analysis of blanks, watched baseline of chromatograms	Carryover monitored by analysis of blanks, watched baseline of chromatograms

^a Quantitation limit (QL) was established at one-half the site-specific action level for both HAFB and JAAP, which was determined based on the USEPA Generic Soil Screening Levels (PB 9355, 4-23, April 1996) for each compound. No U.S. EPA levels for PCBs were available; for the HAFB site investigation the QL was set at 0.5 ppm.

^b Method detection limit (MDL) studies were performed at the beginning of each project to ensure that the field laboratory achieved the site-specific QLs. The MDL study was not performed at the lowest possible level for TNT and DNT, because the action levels are much higher than what is achievable.

^c Inhomogeneity of the soil samples resulted in large deviations between field and laboratory concentrations.

TABLE 4. Purge-and-trap GC/MS (a) method and (b) instrument DQOs and field results for quantitative VOC analysis.

QC Parameters	Laboratory Analysis Requirements SW-846 Method 8260A	Field Method Requirements SW-846 Modified Method 8260A	HAFB Field Method Results for VOC
(a) Selectivity	Can do up to 97 VOCs with 1–6 ions per compound; adjust chromatography to separate VOCs of interest, typically 35 min/sample analysis	Can do up to 97 VOCs with 2–6 ions per compound; minimal separation employed, selectivity by data analysis algorithms	Analyzed 18 VOCs; identification based on three ions per compound, with 15-min GC separation
Sensitivity	5–2500 ppb levels, matrix dependent	QL ^a compound-specific 5–2500 ppb, matrix dependent	MDL VOC 3–33 ppb
Precision	Replicate analysis QC acceptance criteria	Concentration > 5 × QL, RPD/RSD < 60% Concentration < 5 × QL, RPD/RSD < 100%	RPDs and RSDs within the DQO Eight duplicate samples avg. RPD 40% Nine triplicate samples avg. RSD 39%
Accuracy	Internal standard recovery within 50%–200% of the daily calibration internal standard For each sample, or QC run, laboratory established surrogate recovery limits (e.g., 20–140%)	Internal standard recovery within 50%–150% of the daily calibration internal standard Surrogate-dependent recovery of 20–140% Field versus lab conc. > 5 × QL, RPD < 60% conc. < 5 × QL, RPD < 100%	Internal standard recovery within DQO for 140/158 samples, 18 samples biased low Surrogate recovery within DQO 158 samples analyzed, average recovery 87 ± 40% VOCs detected in 5/14 samples by the field and 2/14 samples by the off-site lab; field results ≫ off-site laboratory
(b) Instrument performance tests for MS tuning	Perform check per instrumental method, minimum once to initiate 12-h shift	Perform check per instrumental method, minimum once to initiate shift	Performed check as required at the beginning of each day
Initial 5-point calibration	Calibration check compounds (CCC) %RSDs must be < 30%, if all RF %RSD ≤ 15% then use avg. RF, else use linear regression	DQO dependent; can match SW 846 or all RF %RSDs ≤ 40% and no more than 1/3 > 30% or all RF %RSDs ≤ 30%	Average %RSD within DQO 18 VOCs < 30%
Continuing calibration verification	Once per 12-h shift; CCCs < 20%. All analytes within ± 25% of expected value	DQO dependent; can match SW 846 or begin and end of day, percent difference for all compounds ≤ 40% and no more than 1/3 > 30%	Average % difference within DQO 15 VOCs < 30% 3 VOCs ≤ 40%
Laboratory control check sample	After each initial calibration and once per 12-h shift; percent accuracy within 80% to 120%	Sample throughput dependent, can match SW 846	None performed
Method blank	One per analytical batch; all target compound concentrations < PQL	Once per day and after highly contaminated sample; all target compound concentrations < PQL	No target compound detected
Other	Carryover monitored by analysis of blanks, watch baseline on chromatograms	Carryover monitored by analysis of blanks, watch baseline on chromatograms	Carryover monitored by analysis of blanks, watch baseline on chromatograms

^a Quantitation Limit (QL) was established at one-half the site-specific action level for HAFB, which was determined based on the USEPA Generic Soil Screening Levels (PB 9355,4-23, April 1996) for each compound.

^b Method Detection Limit (MDL) studies were performed at the beginning of the project to ensure that the field laboratory achieved the site specific QLs.

Generic Soil Screening Level guideline and were agreed upon by the regulators for each project. The data quality objective was met by fortifying soil samples collected from the site.

Conclusion

The U. S. EPA and ASTM have promoted the use of dynamic site investigations and field analytics to expedite

hazardous waste site cleanups.^{29,30} To support this goal, nearly 1100 analyses were made at JAAP to determine the volume of contaminated soil for four TNT manufacturing lines.³¹ From these estimates, projections were made for eight additional lines located at the site. Another 760 samples were screened and quantitatively analyzed for VOCs at HAFB. The goal was to better understand what, if any, risk existed for further contamination of the groundwater from soil and to determine why the current means of collecting

and treating the groundwater was ineffective.^{32,33} A second objective was to determine whether PCBs and PAHs were in soil collected from fire training areas located within the airfield. A total of 70 samples were analyzed, with PCBs and PAHs below the risk-based soil levels of concern. In these projects the field data supported adaptive sampling and analysis programs and are now part of the Record of Decision. These successes prove that data of known quality can be produced in the field quickly enough to support dynamic site investigations and cleanups. We also showed that the algorithms can dramatically reduce the number of manually integrated sample files or samples requiring reanalysis because internal standard or surrogate quantitation ions become suppressed or masked by the matrix, thus failing to meet data-quality requirements.

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References

- Robbat A, Jr. Field analytics, dynamic workplans. In: Meyers RA, editor. *The Encyclopedia of Environmental Analysis and Remediation*. New York: Wiley; 1998. vol 3, p 1674–1687.
- Hites R, Biemann K. Computer evaluation of continuously scanned mass spectra in gas chromatographic effluents *Anal Chem* 1970;42:855–860.
- Sweeley CC, Ray BD, Wood WI, Holland JF, Krichevsky MI. On-line digital computer system for high-speed single focusing mass spectrometry. *Anal Chem* 1970;42:1505–1516.
- Venkataraghavan R, McLafferty FW: Power of a GC[*gas chromatograph*]-mass spec/computer system *Chem Technol* 1972;2:364–367.
- Holland JF, Enke CG, Allison J, Stults JT, Pinkston JD, Newcome B, Watson JT. Mass spectrometry on the chromatographic time scale: Realistic expectations. *Anal Chem* 1983;55:997A.
- Chapman JR, Ryan PA. Developments in computer aided mass spectrometry: A networked workstation environment for data analysis. *Trends Anal Chem* 1988;7:244–250.
- Holland JF, Newcome B, Tecklenburg RE, Davenport M, Allison J, Watson JT, Enke CG. Design, construction and evaluation of an integrating transient recorder for data acquisition in capillary gas chromatography/time-of-flight mass spectrometry. *Rev Sci Instrum* 1991;62:69–76.
- Ferrige AG, Seddon MJ., Jarvis S. Maximum entropy deconvolution in electrospray mass spectrometry. *Rapid Commun Mass Spectrom* RCM 1991;5:374–377.
- Colby BN Spectral deconvolution for overlapping GC/MS components. *J Am Soc Mass Spectrom* 1992;3:558–562.
- Hindmarch P, Demir C, Breerton G Deconvolution and spectral clean-up of two-component mixtures by factor analysis of gas chromatographic–mass spectrometric data *Analyst* 1996;121:993–1001.
- Zhang Z, Guan S, Marshall AG. Enhancement of the effective resolution of mass spectra of high-mass biomolecules by maximum entropy-based deconvolution to eliminate the isotopic natural abundance distribution. *J Am Soc Mass Spectrom* 1997;8:659–670.
- van Dongen WD, Ruijters HPM, Luinge HJ, Heerma W, Haverkamp. Statistical analysis of mass spectral data obtained from singly protonated peptides under high-energy collision-induced dissociation conditions. *J Mass Spectrom*. 1996;31;1156–1162.
- Karjalainen EJ. Isolation of pure spectra in GC/MS by mathematical chromatography: Entropy considerations. In: Meuzelaar HLC, editor. *Computer enhanced analytical spectroscopy*. New York: Plenum; 1990.
- Lavine BK. Chemometrics. *Anal. Chem* 1998;70:209R–228R.
- Hertz HS, Hites RA, Biemann K. Identification of mass spectra by computer-searching a file of known spectra. *Anal Chem* 1971;43:681–690.
- Venkataraghavan R, Dayringer HE, Pesyna GM, Atwater BL, Mun IK, Cone MM, McLafferty FW. Computer-assisted structure identification of unknown mass spectra. *ACS Symp Ser* 1977;54:1–17.
- Varmuza K, Werther W, Henneberg D, Weimann B. Computer-aided interpretation of mass spectra by a combination of library search with principal component analysis. *Rapid Commun Mass Spectrom* 1990;4:159–162.
- Stein SE, Scott DR. Optimization and testing of mass spectral library search algorithms for compound identification. *J Am Soc Mass Spectrom* 1994;5:859–866.
- McLafferty FW, Zang MY, Stauffer DB, Stanton Y. Comparison of algorithms and database for matching unknown mass spectra. *J Am Soc Mass Spectrom*, 1998;9:92–95.
- Dowdall E, Tardif M, Chiu C. Automated PCB analysis, quantitation and reporting. *Int J Environ. Anal Chem* 1995;60:175–184.
- Hindmarch P, Demir C, Breerton RG. Deconvolution and spectral clean-up of two mixtures by factor analysis of gas chromatographic–mass spectrometric data. *Analyst* 1996;121:993–1001.
- Qian K, Peru DA, Petti TF, Zhao X, Yaluris G, Harding RH, Cheng WC, Rajagopalan K. Characterization and classification of gas oils by mass spectrometry/chemometrics for application in fluid catalytic cracking. Preprint Am Chem Soc Div Pet Chem 1998;43:169–171.
- Robbat A, Jr, Liu C, Liu TY. Field detection of organochlorine pesticides by thermal desorption gas chromatography/mass spectrometry. *J Chromatogr* 1992;625:277–288.
- Abraham B, Liu TY, Robbat A, Jr. Data comparison study between field and laboratory detection of polychlorinated Biphenyls and polycyclic aromatic hydrocarbons at superfund sites. *Hazardous Waste Hazardous Materials* 1993;10:461–473.
- Jiao K, Robbat A, Jr. Performance-based field methods for the analysis of substituted Phenols by thermal desorption gas chromatography/mass spectrometry. *J AOAC Int* 1996;79:131–142.
- Gankin Y, Gorshteyn A, Smarason S, Robbat A, Jr. Time-condensed analyses by mass spectrometry. *Anal Chem* 1998;70:1655–1663.
- Hewitt AD, Jenkins TF, Grant CL. Collection, handling, Storage: Keys to improved data quality. *Am Environ Lab*, 1995;2:25–28.
- Hewitt AD, Lukash NJE. Sampling for in-vial analysis of volatile organic compounds in soil. *Am Environ Lab* 1996;8:15–19.
- May 1, 1996, Federal Register 61FR 19431–19463.
- Provisional guideline for expedited site characterization for hazardous waste contaminated Sites. In: American Society for Testing and Materials 1996 PS-85-96. Philadelphia: ASTM.

31. Johnson R, Quinn J, Durham L, Williams G, Robbat A, Jr. Adaptive sampling and analysis programs for contaminated soils. *Remediation* 1997;7:81–96.
32. Robbat A, Jr. A Dynamic Site Investigation/Adaptive Sampling and Analysis Program for Operable Unit 1 at Hanscom Air Force Base, Bedford, MA. Tufts University (or Smaldone J. U.S. EPA Region I, Boston, MA).
33. Robbat A, Jr., Smarason S, Gankin Y. Dynamic workplans & field analytics, the keys to cost-effective hazardous waste site investigations. *Field Anal Chem Technol FACT*, 1998; 2(5):253–265.