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Accelerated Articles

Time-Condensed Analyses by Mass Spectrometry

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Research has focused on the development of a new set of mathematical algorithms, encoded in C^{++}, when combined with a thermal desorption sample introduction system provides quantitative analysis of a wide mixture of organic compounds in under 10 min by gas chromatography/mass spectrometry. The overall goal is to condense the time of analysis, including both the times required for sample preparation and for chromatographic separation. In this paper, results are presented where compound identification has been made for polychlorinated biphenyls, chlorinated pesticides, and polycyclic aromatic hydrocarbons present in the same solution and where gas chromatography separation times have been reduced from 40 to 5 min. For the latter, all compounds elute within 3.5 min, with structural isomers identified as the same compound. The 5-min analysis provides the foundation for rapid screening and on-line chemical measurements of multicomponent mixtures. Results are also presented where these same compounds are quantitatively analyzed in 10 min, with structural isomers identified individually, in the presence of a (25% v/v) weathered gasoline/engine oil mixture. Time-condensed complex mixture detection is now feasible making possible quantitative, high-throughput sample analyses.

Increasing demand for faster, better, and cheaper chemical analyses has led to significant improvements in automated sample delivery systems, analytical instrumentation, data interpretation algorithms, and statistical methods of analysis. These advancements have resulted in an increased understanding of materials and biological chemistry at the molecular level *and* the development of "standardized" methods that have been used to safeguard foods, drugs, the environment, and national security. For example, recent improvements in stationary-phase chemistry and in the production of higher resolution gas (GC) and liquid (LC) chromatography columns have yielded complex mixture separations in minutes rather than the tens of minutes required of earlier columns.[1−3] Integration of multidimensional GC, LC, and capillary column electrophoresis systems with statistical methods of analysis has led to combinatorial chemical libraries aimed at identifying constituents present in highly complex mixtures.[4−10]

Despite these innovations, sample preparation prior to chemical analysis continues to limit the rate at which samples can be analyzed. Variances in sample recovery, due to the number and complexity of pretreatment steps, contribute to overall method accuracy and reproducibility. For example, environmental analysis of soil samples typically requires a gel permeation cleanup step after extraction and/or subsequent fractionation followed by preconcentration. The latter can result in the loss of low-level target compounds below purported method detection limits. Although sample pretreatment can be reduced when selective

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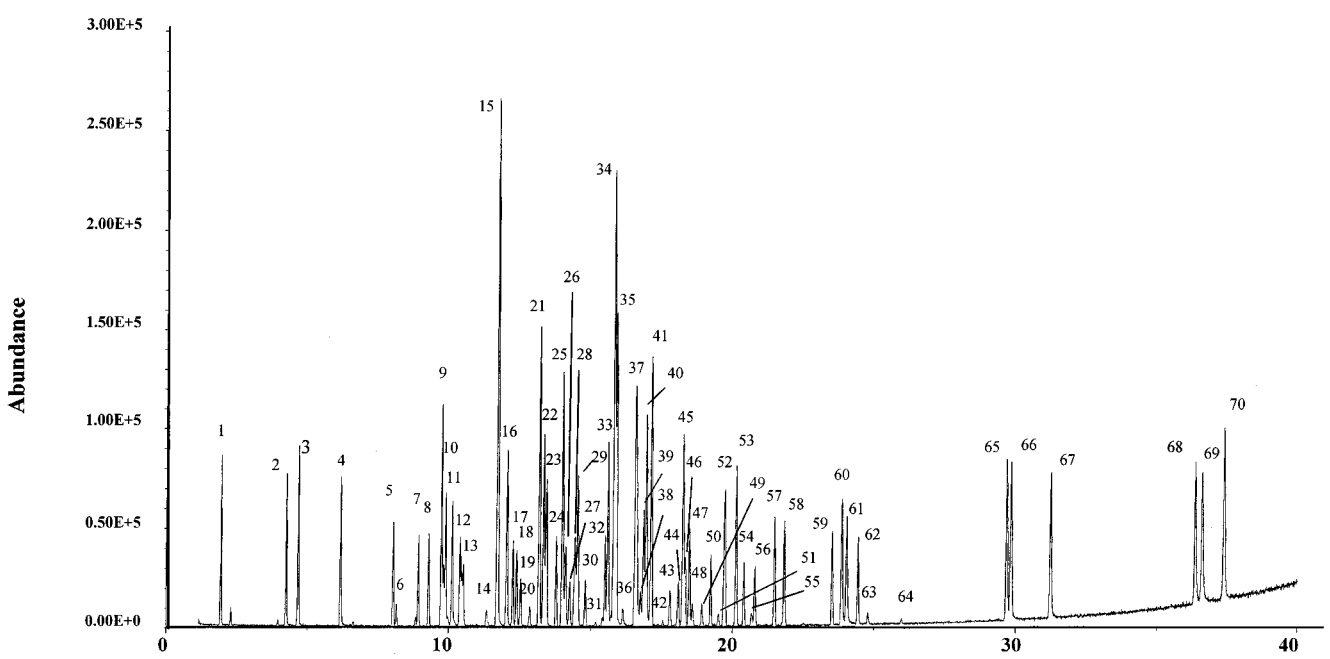

Figure 1. Total ion current chromatogram for a standard mixture containing polycyclic aromatic hydrocarbons, polychlorinated biphenyls (Aroclor 1248), and chlorinated pesticides.

detectors such as electron capture (ECD), chemiluminescent, or flame photometric detectors are used, they cannot provide specific compound identity. Kimbrough and co-workers[11] reported data quality results for 20 government and 153 California Environmental Laboratory Accredited Program laboratories. In their study, four soil samples were prepared (milled, sieved, and autoclaved) to contain 100, 10, 1, and 0.1 ppm of polychlorinated biphenyls (PCBs) and were analyzed by GC/ECD. The average concentrations reported for the 100 to 1 ppm samples by the reference and accredited laboratories were less than the fortified concentrations by 15% and 28%, respectively, while the reference and accredited laboratories reported results below the 0.1 ppm concentration by 10% and 68%, respectively. Approximately 60% of the commercial laboratories produced detection levels outside of the accepted error range of ±25% for the 100 and 10 ppm samples, while 30% produced data outside of the accepted range of ±50% for the 1 and 0.1 ppm samples. Despite the fact that these soils were prepared "clean" and contained only PCBs, measurement results were poor. Other studies have shown measurement error to be as high as 200% due to incomplete chromatographic separation of congeners, varying GC patterns produced by different Aroclor mixtures, attributing detector response for other organics as PCBs, and poor sample cleanup.[10,12,13] The more complex the sample, the more difficult and time-consuming it is to obtain quantitative data.

Mass filters can provide selective detection when operated in the selected ion monitoring (SIM) mode or by tandem mass spectrometry (MS/MS).[14,15] SIM (with single-ion monitoring) offers little advantage over other selective detectors unless multiple ions per compound are monitored. Current MS data systems cannot provide multiple ion SIM detection of a single compound and, at the same time, target a large enough number of compounds in a single scan to be practical. For this reason, total ion current (TIC) MS, with full fragmentation profiles, provides the best opportunity to obtain unambiguous compound identity. Nonetheless, if the extracted ion from either SIM or TIC contains ion current contribution from other organics present in the sample, quantitation of that targeted compound will be overestimated by an amount equal to the interfering signal. Tandem MS systems, with two or more mass filters, can provide selective and full-scan target analysis. The first MS transports the selected ion to the second MS, which can then produce full fragmentation identification. This process can minimize spectral interference by the matrix and represents a hardware approach toward identifying components in complex mixtures.

As separation times decrease, small changes in high-resolution column conditions can produce large changes in peak shape, retention time, and resolution. Measurement reliability is dependent, therefore, on data acquisition and interpretation systems that can provide sufficient data density to deconvolve closely eluting compounds under fast GC or LC conditions. The most

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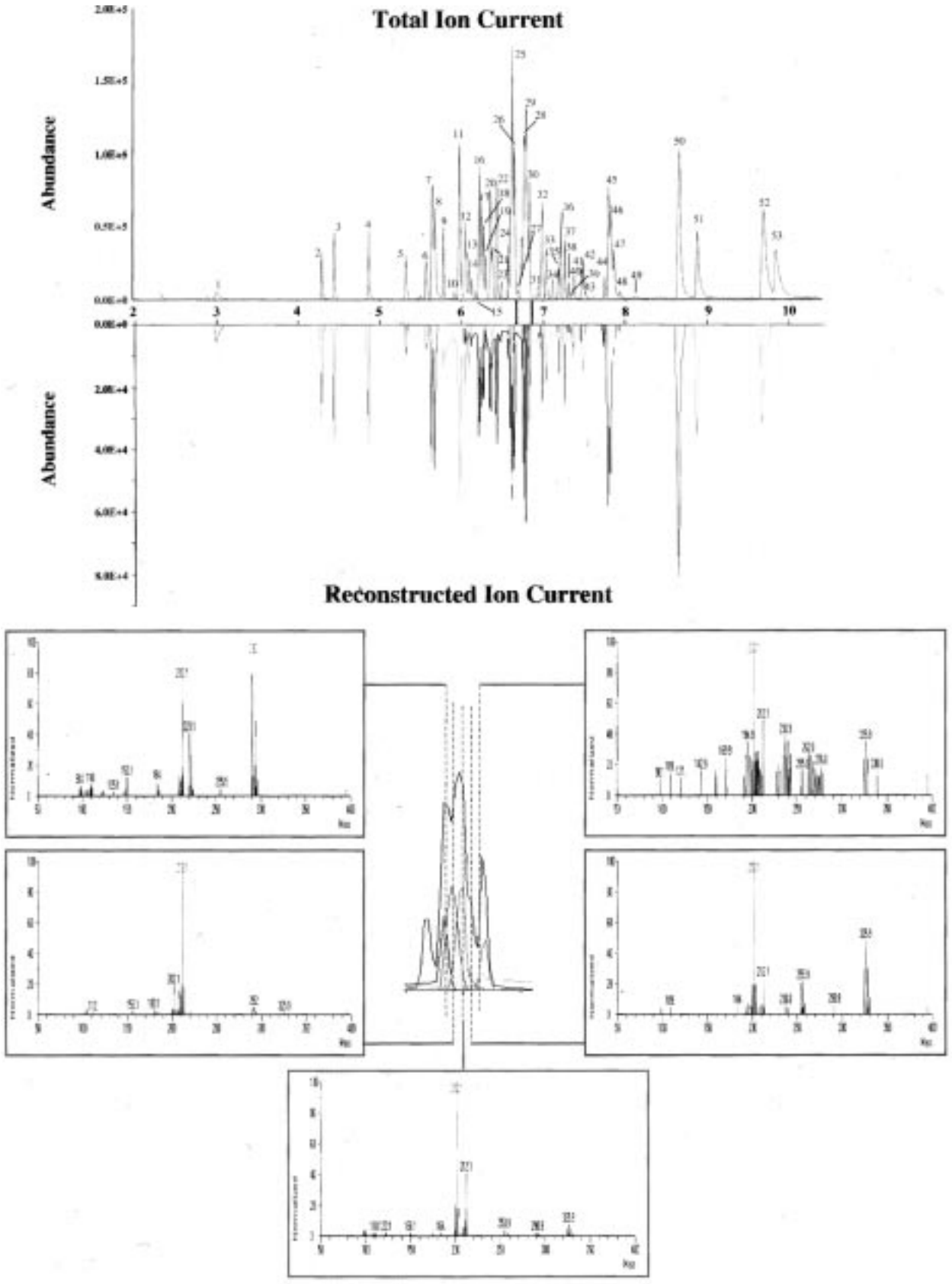

Figure 2. Ten-minute total (a, top) and reconstructed (b, middle) ion current chromatograms *and* selected mass spectra found between 6.7 and 6.9 min (c, bottom) for the standard mixture.

often used mass filter is the linear quadrupole, operated in either the SIM or full-scan mode. Although data acquisition rates are limited by the applied scan voltages, the work presented in this paper will demonstrate that sufficient data density is achievable

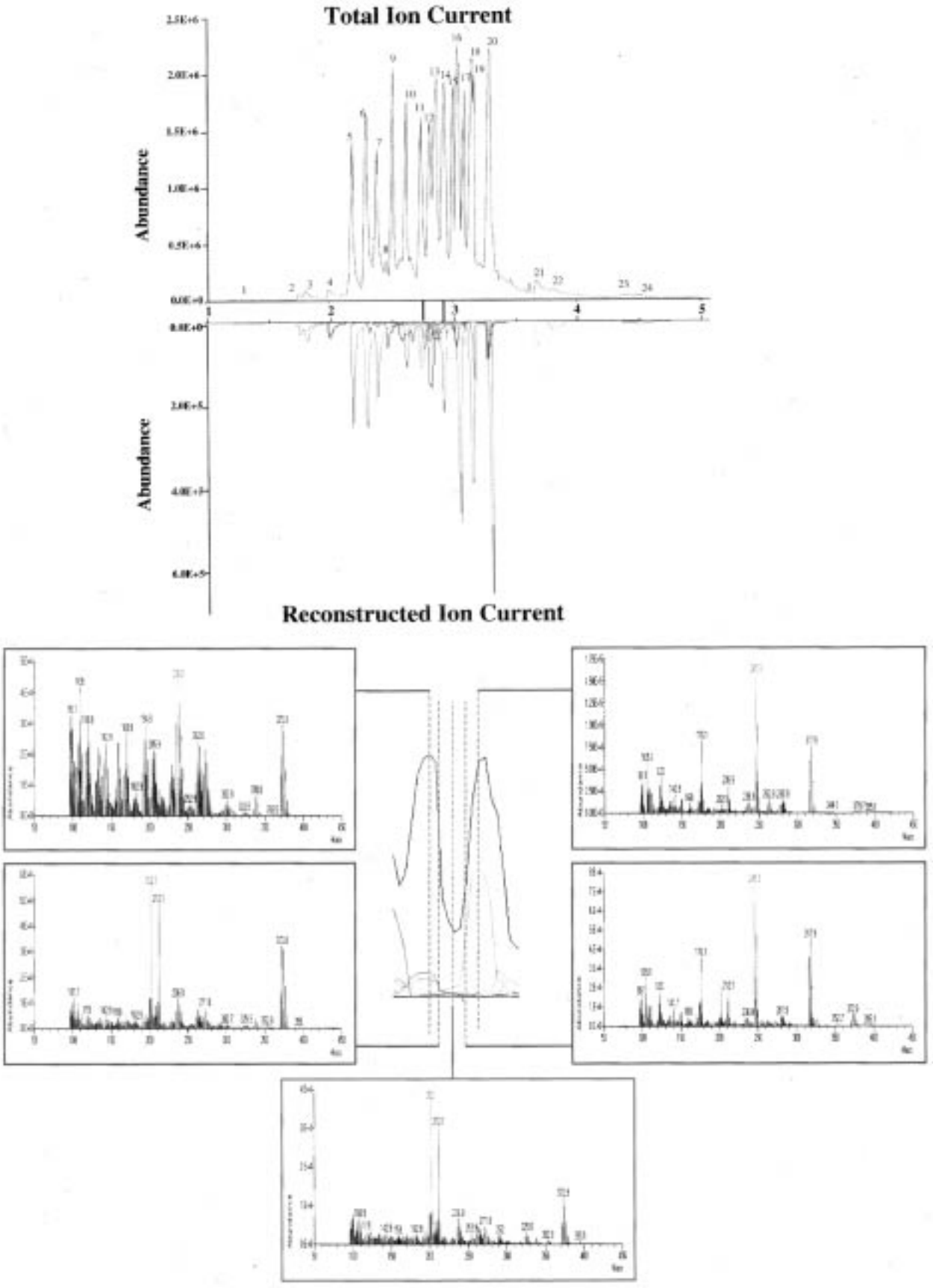

Figure 3. Five-minute total (a, top) and reconstructed (b, middle) ion current chromatograms *and* selected mass spectra found between 2.8 and 2.9 min (c, bottom) for the standard mixture.

Table 1. Compound Identification and Retention Times (RT)

peak no.	40-min separation	RT, min	10-min separation	RT, min	5-min separation	RT, min
1	naphthalene	1.94	naphthalene	3.02	naphthalene	1.30
2	acenaphthylene	4.27	acenaphthylene	4.30	acenaphthylene	1.78
3	acenaphthene	4.69	acenaphthene	4.45	acenaphthene	1.83
4	fluorene	6.19	fluorene	4.87	fluorene	2.02
5	α-BHC	8.05	α-BHC; Cl-2	5.33	α-BHC; Cl-2	2.18
6	Cl-2	8.18	*γ*-BHC; *β*-BHC	5.57	*γ*-BHC; *β*-BHC; Cl-3; Cl-4	2.29
7	*γ*-BHC	8.94	phenanthrene; Cl-3	5.65	*δ*-BHC; phenanthrene; anthracene; Cl-3; Cl-4	2.38
8	*β*-BHC	9.30	anthracene	5.68	Cl-3	2.46
9	Cl-3	9.71	*δ*-BHC; Cl-3	5.78	heptachlor; Cl-3; Cl-4	2.51
10	phenanthrene	9.90	Cl-3	5.91	aldrin; Cl-3; Cl-4	2.62
11	anthracene	10.14	Cl-3	5.98	heptachlor epoxide; Cl-5	2.74
12	*δ*-BHC	10.41	heptachlor; Cl-3; Cl-4	6.05	fluoranthene; chlordane; Cl-4; Cl-5	2.82
13	Cl-3	10.53	Cl-3; Cl-4	6.10	endosulfan I; pyrene-d_{10}; pyrene; Cl-4; Cl-5	2.86
14	Cl-3	11.34	Cl-4	6.13	DDE; dieldrin; Cl-5	2.93
15	Cl-3	11.72	Cl-4	6.18	endrin; endosulfan II; Cl-5; Cl-6	3.00
16	Cl-3; Cl-4	12.06	Cl-4	6.22	DDD	3.04
17	heptachlor	12.26	Cl-4	6.25	endrin aldehyde; Cl-5; Cl-6	3.08
18	Cl-3	12.39	Cl-4	6.27	endosulfan sulfate; DDT; Cl-5; Cl-6	3.15
19	Cl-4	12.55	aldrin; Cl-4	6.30	endrin ketone	3.18
20	Cl-4	12.85	Cl-4	6.36	benz[*a*]anthracene; chrysene; methoxychlor	3.32
21	Cl-3; Cl-4	13.19	Cl-4; Cl-3	6.38	Cl-7	3.47
22	Cl-3; Cl-4	13.35	Cl-4	6.44	benzo[*b* and *k*]fluoranthene; Cl-7	3.63
23	Cl-4	13.44	Cl-4	6.49	benzo[*a*]pyrene	3.68
24	aldrin; Cl-4	13.79	heptachlor epoxide	6.58	indeno[1,2,3-*cd*]pyrene; dibenz[*a*,*h*]anthracene	4.40
25	Cl-3; Cl-4	14.00	fluoranthene; Cl-4	6.63	benzo[*ghi*]perylene	4.53
26	Cl-3	14.12	Cl-4; Cl-5	6.65		
27	Cl-3	14.26	Cl-5	6.69		
28	Cl-4	14.44	pyrene-d_{10}; Cl-5	6.77		
29	Cl-4	14.52	pyrene; endosulfan I; Cl-5	6.80		
30	Cl-4	14.79	chlordane; Cl-5	6.84		
31	Cl-4	15.16	Cl-5	6.94		
32	heptachlor epoxide	15.49	DDE; dieldrin	6.99		
33	Cl-4	15.60	Cl-5	7.04		
34	fluoranthene	15.81	Cl-5	7.11		
35	Cl-5	15.88	Cl-5	7.19		
36	Cl-5	16.13	endrin; endosulfan II; Cl-5	7.21		
37	Cl-4	16.58	DDD; Cl-5	7.26		
38	Cl-5	16.74	endrin aldehyde	7.31		
39	pyrene-d_{10}; Cl-5	16.86	Cl-6	7.34		
40	pyrene; Cl-5	16.95	Cl-5	7.37		
41	endosulfan I; chlordane; Cl-5	17.12	endosulfan sulfate	7.47		
42	Cl-5	17.53	DDT; Cl-6	7.49		
43	Cl-5	17.77	Cl-6	7.51		
44	Cl-5	18.08	endrin ketone	7.75		
45	DDE; Cl-5	18.24	benz[*a*]anthracene	7.80		
46	dieldrin	18.32	methoxychlor	7.87		
47	Cl-5	18.46	chrysene	7.83		
48	Cl-5	18.57	Cl-7	7.94		
49	Cl-5	18.91	Cl-7	8.11		
50	endrin	19.22	benzo[*b* and *k*]fluoranthene	8.66		
51	Cl-6	19.49	benzo[*a*]pyrene	8.88		
52	endosulfan II; Cl-5	19.73	indeno[1,2,3-*cd*]pyrene; dibenzo[*a*,*h*]anthr.	9.68		
53	DDD; Cl-5	20.13	benzo[*ghi*]perylene	9.83		
54	endrin aldehyde	20.41				
55	Cl-6	20.66				
56	Cl-5	20.79				
57	endosulfan sulfate	21.48				
58	DDT; Cl-6	21.81				
59	endrin ketone	23.52				
60	benz[*a*]anthracene	23.86				
61	methoxychlor	24.44				
62	chrysene	24.03				
63	Cl-7	24.78				
64	Cl-7	25.96				
65	benzo[*b*]fluoranthene	29.65				
66	benzo[*k*]fluoranthene	29.80				
67	benzo[*a*]pyrene	31.24				
68	indeno[1,2,3-*cd*]pyrene	36.33				
69	dibenz[*a*,*h*]anthracene	36.60				
70	benzo[*ghi*]perylene	37.35				

under fast GC or LC conditions. Ion trap mass spectrometers offer the unique advantage of providing SIM and full-scan MS in the same analysis. However, only a small number of compounds can be simultaneously targeted in this mode of operation. Neither

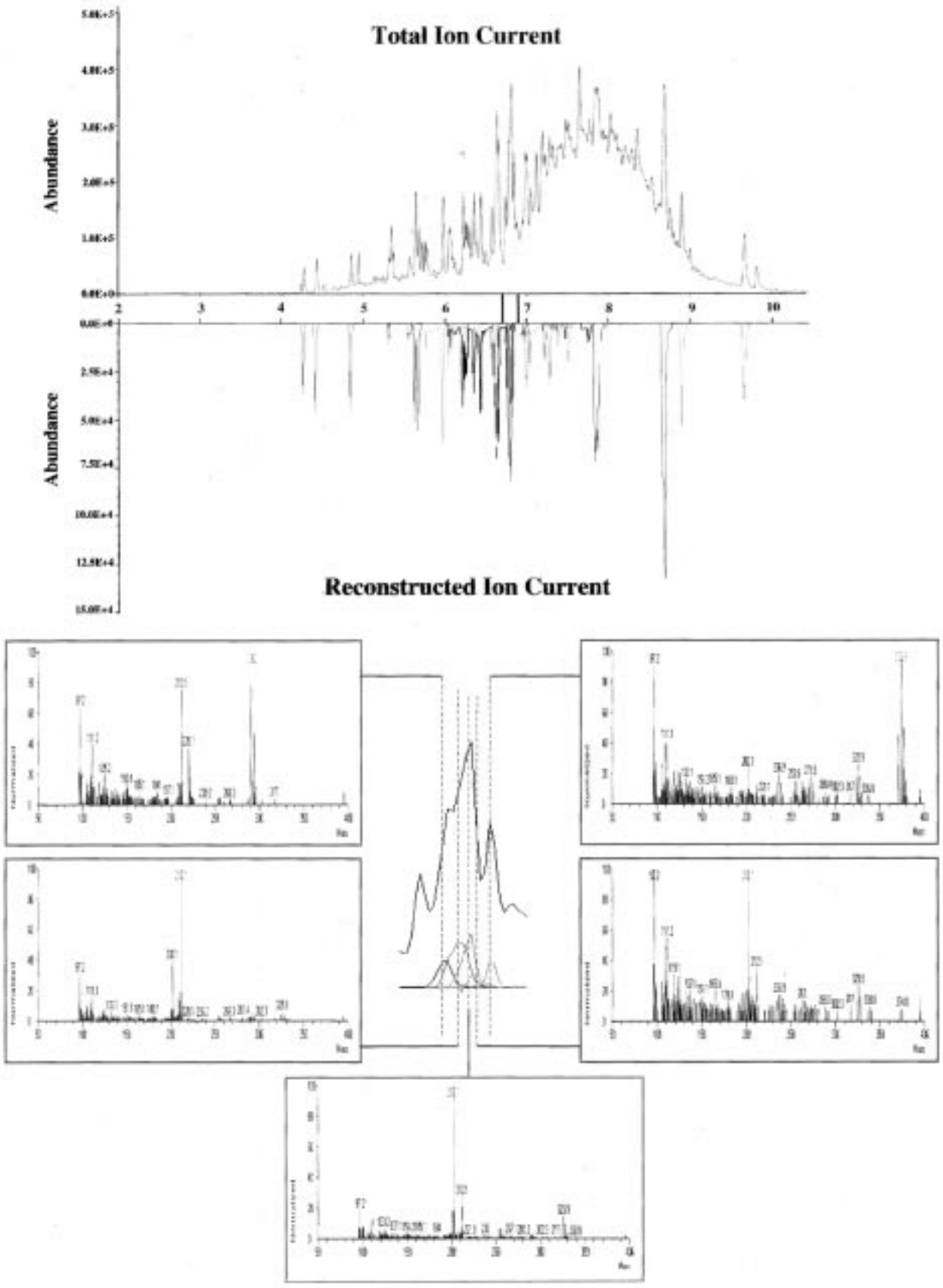

Figure 4. Ten-minute total (a, top) and reconstructed (b, middle) ion current chromatograms *and* selected mass spectra found between 6.7 and 6.9 min (c, bottom) for the standard mixture fortified with a weathered gasoline/engine oil mixture (25% v/v).

Table 2. Target Compound List

compound	ions (abundance, %)
	PAHs
naphthalene	128 (100), 129 (11), 127 (10)
acenaphthylene	152 (100), 151 (22), 153 (14)
acenaphthene	154 (100), 153 (87), 152 (48), 151 (14)
fluorene	166 (100), 165 (87), 167 (15), 163 (12)
phenanthrene	178 (100), 176 (15), 179 (15), 177 (8)
anthracene	178 (100), 176 (15), 179 (15), 177 (8)
fluoranthene	202 (100), 203 (20), 200 (16), 201 (11)
pyrene	202 (100), 203 (20), 200 (16), 201 (11)
benz[*a*]anthracene	228 (100), 226 (22), 229 (20), 227 (7)
chrysene	228 (100), 226 (22), 229 (20), 227 (7)
benzo[*b*]fluoranthene	252 (100), 250 (34), 253 (25), 251 (13)
benzo[*k*]fluoranthene	252 (100), 250 (34), 253 (25), 251 (13)
benzo[*a*]pyrene	252 (100), 250 (34), 253 (25), 251 (13)
indeno[1,2,3-*cd*]pyrene	276 (100), 277 (24), 275 (12), 274 (14)
dibenz[*a*,*h*]anthracene	278 (100), 279 (23)
benzo[*ghi*]perylene	276 (100), 277 (24), 274 (18)
	Pesticides
α-BHC	181 (100), 219 (75), 221 (39)
γ-BHC	181 (100), 219 (75), 221 (39)
β-BHC	181 (100), 219 (75), 221 (39)
δ-BHC	181 (100), 219 (75), 221 (39)
heptachlor	100 (100), 274 (52), 272 (65)
aldrin	101 (100), 263 (100), 261 (65), 293 (43)
heptaclor epoxide	353 (100), 355 (81), 351 (52), 357 (39)
endosulfan I	195 (100), 241 (87), 207 (75)
chlordane	373 (100), 375 (91), 377 (51), 371 (43)
DDE	246 (100), 318 (81), 316 (60)
dieldrin	108 (100), 263 (20), 277 (15)
endrin	317 (100), 315 (70), 345 (45), 319 (34)
endosulfan II	195 (100), 241 (87), 207 (75)
DDD	235 (100), 237 (65), 165 (45), 178 (11)
endrin aldehyde	345 (100), 347 (56), 343 (64), 349 (22)
endosulfan sulfate	272 (100), 274 (93), 277 (45)
DDT	235 (100), 237 (70), 246 (20)
endrin ketone	317 (100), 319 (65), 315 (69), 311 (21)
methoxychlor	227 (100), 228 (18)
	PCBs (Aroclor1248)
Cl-2	222 (100), 224 (70), 226 (11)
Cl-3	256 (100), 258 (100), 260 (34)
Cl-4	292 (100), 290 (81), 294 (60)
Cl-5	326 (100), 328 (70), 324 (65)
Cl-6	360 (100), 362 (92), 358 (52)
Cl-7	394 (100), 396 (100), 392 (45)
	Internal Standard
pyrene-d_{10}	212 (100), 211 (56), 210 (31)

chemometric methods aimed at improving mass spectral peak deconvolution[16−19] or probabilistic library matching routines[20−24] nor advances in MS detector hardware[25−29] have minimized the need for extensive sample preparation prior to analysis.

EXPERIMENTAL SECTION

Reagents and Standards. Aroclor 1248 and a standard mixture containing one congener per chlorination level were obtained from Ultra Scientific (Hope, RI). Standard solutions of polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides (Cl-pesticide), and pyrene-d_{10}, used as an internal standard, were obtained from Supelco, Inc. (Bellefonte, PA). To evaluate matrix interferant identification, these standards were combined and fortified with a 25% gasoline/75% engine oil mixture.

Equipment. A fused-silica 15-m × 0.32-mm-i.d. capillary column, with 0.25-μm stationary-phase film thickness of 5% diphenyl, 94% dimethyl, and 1% vinylpolysiloxane (Supelco SPB-5) was used to provide GC separation. A Hewlett-Packard (Palo Alto, CA) model 5890 GC oven and controller unit was modified and interfaced to a model 5972 mass spectrometer for this study. This instrument employed a ballistically heated thermal desorption (TD) sample introduction system designed and built at Tufts University (Medford, MA). Known aliquots of each standard or the standards and gasoline/oil mixture were injected into a clean glass sleeve and placed into the thermal desorption unit. The TD was heated from ambient to 300 °C in 30 s. Organics were swept from the TD onto the capillary column by helium at 2 mL/min. Three different GC temperature programs were employed: (1) 35 (isothermal for 1.5 min) to 290 °C (isothermal for 1.5 min) at 6 °C/min; (2) 35 (isothermal for 1 min) to 290 °C (isothermal for 1.5 min) at 32 °C/min; (3) 70 (isothermal for 0.3 min) to 290 °C (isothermal for 1.5 min) at 57 °C/min.

RESULTS AND DISCUSSION

Figures 1, 2a, and 3a show the total ion current chromatograms for a standard mixture containing 16 PAHs, 19 Cl-pesticides, and Aroclor 1248, which consists of ∼50 PCBs each with a concentration greater than 1%. A total of 1000 ng of PCBs, 20 ng of Cl-pesticide, 40 ng of PAHs, and 50 ng of pyrene-d_{10} (internal standard) were injected into the glass sleeve of the thermal desorber. The sample was ballistically heated and transferred to the GC column by carrier gas. As the separation time decreased, the 70 well-defined peaks shown in Figure 1 become 24 peaks under fast GC separation conditions; see Figure 3a. Table 1 shows the peak number for each GC/MS run, the corresponding retention time, and the target compounds identified. A total of 55, 17, and 3 peaks were produced with one compound eluting per peak for the 40-min, 10-min, and 5-min run times, respectively. Where coelution occurred, typically two compounds per peak were found in the 40-min and 10-min chromatograms, while 12 of the 24 peaks in the 5-min chromatogram contained between three and five compounds per peak.

Compound identification was provided by a set of mathematical algorithms that were coded in C^{++}. The analyst selects N fragment ions (see Table 2), typically between three and six per

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compound, that will be used to extract ion current signal during an expected elution time interval. The function $f_i(t)$ computes the ratio between an established library, L_i, and the observed relative abundance, $R_i(t)$, for the ith ion ($1 \le i \le N$) at time, t, multiplied by the observed abundance of the main ion, $A_m(t)$: $f_i(t) = (R_i(t)/L_i)A_m(t)$. Three functions are used to determine the difference between the actual and expected abundances, functions 1−3.

$$F_1(t) = \max_{i \le N}[f_i(t)] - \min_{j \le N}[f_j(t)] \quad (1)$$

$$F_2(t) = \frac{\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}|f_i(t) - f_j(t)|}{\sum_{i=1}^{N-1} i} \quad (2)$$

$$F_3(t) = \max_{i \le N}\frac{df_i(t)}{dt} - \min_{j \le N}\frac{df_j(t)}{dt} \quad (3)$$

The anayst selects an acceptable percent difference, $K^{\%}$, between the observed and library relative abundances. Functions 4−6

$$\Delta_1(t) = K^{\%}|\max_{i \le N} f_i(t)| + \Delta_o \quad (4)$$

$$\Delta_2(t) = \alpha K^{\%}|\max_{i \le N} f_i(t)| + \Delta_o \quad (5)$$

$$\Delta_3(t) = \beta K^{\%}|\max_{i \le N}\frac{df_i(t)}{dt}| \quad (6)$$

compute the margin of acceptable error $\Delta(t)$ for functions 1−3, respectively, 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. Target compounds are considered present in the sample if $F_1(t) \le \Delta_1(t)$ and/or $F_2(t) \le \Delta_2(t)$ in at least four consecutive MS scans. If these conditions fail, $N > 3$ and $F_3(t) \le \Delta_3$, then every possible subset of at least three ions 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 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, $A_j^{\text{adjusted}} = (\sum_{i=1,i\neq j}^{N} f_i(t)/N - 1)L_i$, with all ions re-compared using the criteria described above. If all three cases fail, the program reports the compound as not detected.

For detected compounds, the ion current signal S is calculated as follows:

$$S = \int_{t_1}^{t_2} P_i \quad (7)$$

If $\min_{i \le N} f_t(t) > \Delta_{\text{thresh}}$, then $P_i = \min_{i \le N} f_t(t)\, dt$ and if not $P_i = 0$, where Δ_{thresh} is the signal value set by the analyst and t_1, t_2 are the beginning and the end of the retention time interval. Note that expression 7 uses the least affected ion for each scan.

Table 3. Data Comparison between Standard and Standard/Petroleum Mixtures

compound	main ion	std sol	std/ petroleum mix	RPD[a] (%)
acenaphthene	153	0.850	0.949	−11
acenaphthylene	152	1.453	1.581	−8
aldrin	101	0.056	0.067	−18
α-BHC	181	0.291	0.267	9
benzo[*a*]pyrene	252	3.512	4.207	−18
benzo[*ghi*]perylene	276	1.780	1.614	10
benzo[*a*]anthracene/chrysene	228	2.801	2.698	4
benzo[*b* and *k*]fluoranthene	252	3.679	4.276	−15
β-BHC	181	0.291	0.277	5
Cl-2	222	0.128	0.154	−18
Cl-3	256	1.670	1.602	4
Cl-4	292	1.557	1.731	−11
Cl-5	326	0.568	0.543	4
Cl-6	360	0.075	0.096	−24
Cl-7	396	0.089	0.085	4
chlordane	373	0.704	0.784	−11
DDD	235	0.874	0.903	−3
DDE	246	0.630	0.612	3
DDT	235	0.888	0.876	1
δ-BHC	181	0.189	0.156	19
dibenz[*a*,*h*]anthracene	278	2.238	1.850	19
dieldrin	108	0.057	0.071	−22
endrin aldehyde	345	0.127	0.109	15
endosulfan I	195	0.107	0.135	−23
endosulfan II	195	0.099	0.121	−20
endosulfan sulfate	272	0.107	0.140	−27
endrin	317	0.047	0.059	−22
endrin ketone	317	0.287	0.255	12
fluoranthene	202	3.010	3.308	−9
fluorene	166	0.367	0.349	5
γ-BHC	181	0.291	0.256	13
heptachlor	100	0.179	0.212	−17
heptaclor epoxide	353	0.428	0.481	−12
indeno[1,2,3-*cd*]pyrene	276	1.870	1.654	12
methoxychlor	227	1.033	1.259	−20
naphthalene	128	0.204	0.302	−39
phenanthrene/anthracene	178	2.543	2.335	9
pyrene	202	2.851	3.308	−15

[a] RPD $= 2(R - R_p)/(R + R_p) \times 100$ where R is the relative response, (compound signal)/(internal standard signal), of each compound in a clean sample; R_p is the relative response of each compound in the same sample spiked with petroleum.

Figures 2b and 3b depict the reconstructed ion (RI) chromatograms obtained from the 10- and 5-min GC separations. Figure 2c illustrates an expanded view of the 10-min chromatogram between 6.7 and 6.9 min. As the rate of column heating increases, pyrene-d_{10} and pyrene are no longer baseline separated, with pyrene-d_{10} eluting between peaks 28 and 29. Complex mixture identification is further illustrated by Figure 3c, peaks 12−14, where fluoranthene, pyrene, pyrene-d_{10}, Cl-4, Cl-5, Cl-6, chlordane, DDD, DDE, DDT, dieldrin, heptachlor, and endosulfan I all elute within 0.11 min. In this experiment, all compounds elute within 3.5 min with structural isomers identified as the same compound. Mass fragments appear at nearly every mass between 95 and 400 amu. Sufficient data density is obtained, resulting in unambiguous identification of each target compound.

This type of analysis can support rapid screening measurements of environmental contaminants where individual isomer identification is not important, for example, in the location of contaminant boundaries as opposed to risk analysis during the characterization and cleanup of hazardous waste sites. To further condense detection times, time-of-flight mass filters should be used

where data acquisition rates of 150 scans/s can provide increased mass spectral data density, synergistically matching the strengths of the algorithms.

Quantitative analysis is demonstrated through measurement of the same standard mixture fortified by a weathered gasoline/engine oil mixture (25% v/v). Parts a and b of Figure 4 illustrate the total ion and reconstructed ion current chromatograms obtained under the same experimental conditions that produced Figure 2. Although the absolute signal for the standard solution fortified by petroleum in Figure 4 appears twice as large as the standard solution in Figure 2b, the data are within experimental MS run-to-run variations (see Figure 1). Table 3 compares the RI signal divided by the internal standard signal for each compound for both the standard solution and standard solution/petroleum mixture. Differences are within the 30% benchmark required by the U.S. Environmental Protection Agency standardized methods with the exception of naphthalene. Poorer results were obtained for naphthalene because of volatile loss during the oxygen purge step of the thermal desorber prior to transport to the GC column. For unknowns, work is in progress to use standard reference libraries to obtain the ions for tentatively identified compounds and then use the algorithms for positive identification and quantification.

CONCLUSIONS

To date, analysts have relied on extensive sample preparation procedures and/or tandem mass spectrometry to minimize sample component interferents. For example, in small-molecule combinatorial chemistry where thousands of compounds require screening, fast LC separations are employed with compound identification dependent on single-ion monitoring only or SIM followed by full-scan MS. In this paper, an alternative data analysis method has been described that reduces the time and analyte loss attributable to complex sample preparation procedures as well as the reliance on multi-MS techniques.

Although all MS data analysis systems can perform selected ion extraction, they cannot handle the large number (92) of unique fragment ions used in this study and at the same time compare their probabilistic match against standard libraries. Moreover, when the contribution from complex matrixes is considered, standard library matching techniques fail to provide unambiguous identification. This approach has general applicability to supporthigh-throughput sample analysis typically required of environmental, bioanalytical (metabolite), drug discovery (combinatorial chemistry), and illicit drug applications.

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