Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants

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Summary

Operational characteristics have been determined for fused silica capillary column (FSCC) GC/MS as applied to "extractable" priority pollutants. Chromatographic data show excellent relative retention time (RRT) intralaboratory precision and interlaboratory accuracy when multiple internal standards are employed. Potential chromatographic problems, such as column overload and "double peaking", are addressed. Response factor relative standard deviations (RSD) at 50 ng for most of the extractable priority pollutants over the long term indicated precise determination (i.e. RSD generally <10%). Linearity was demonstrated over two orders of magnitude for FSCC GC/MS analysis of compounds with relatively low and high RF (response factor) values. Potential quantitative problems, such as saturation, are discussed. For certain aromatic priority pollutants interlaboratory RF agreement was observed. This was noted as perhaps the most important property of FSCC GC/MS analysis when the multiple internal standard approach is utilized. Determinations of extractable priority pollutants are directly compared for packed column GC/MS and FSCC GC/MS analysis of separate and composited extracts. For six extracts analyzed in triplicate, the latter configuration was shown to produce more consistent results. In view of the superior analysis logistics of composite extract FSCC GC/MS analysis, this approach was established as the preferred method for the analysis of priority pollutants classified as extractable.

1 Introduction

The U.S. Environmental Protection Agency (EPA) has proposed analytical protocols for the analysis of extractable priority pollutants [1]. These protocols have been employed by the EPA for the determination of priority pollutants in hazardous waste [2]. Sample preparation procedures utilized to isolate priority pollutants from aqueous and nonaqueous samples generally involve liquid extraction procedures which generate at least two extracts containing base/neutral and acid extractable priority pollutants. Current analysis protocols require the separate GC/MS analysis of each extract using different packed GC columns.

We originally reported that fused silica capillary columns (FSCC) coupled directly to the ion source of the mass spectrometer could be employed for the simultaneous GC/MS analysis of acid, base/neutral, and pesticide priority pollutants [3, 4]. This analysis configuration affords a potential reduction of GC/MS acquisition time of approximately 60% as compared to existing packed column GC/MS methods and, therefore, should significantly lower the cost of priority pollutant analysis. As importantly, initial results indicated that the data were generally of better quality. The analysis time reduction is realized because extracts can be combined and analyzed in one injection rather than two. Compositing of extracts is possible because capillary columns provide higher resolution (more effective theoretical plates) per unit time. Moreover, direct coupling of FSCC to the ion source and the apparent inertness of fused silica provides for consistent chromatographic elution for reactive (e.g. hexachlorocyclopentadiene) and very polar analytes (e.g. isophorone); therefore, the extractable priority pollutants can be analyzed simultaneously. Analysis methods which reduce costs, and produce data of equivalent or better accuracy and precision, are of obvious benefit to the U.S. Environmental Protection Agency and to others testing for priority pollutants.

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The objective of this paper is to present operational characteristics of FSCC GC/MS as applied to extractable priority pollutant analysis. Qualitative and quantitative properties of FSCC GC/MS analysis are presented for the analysis of standards and spiked hazardous waste extracts. Data generated at three laboratories are presented. The limitations of this methodology, and practical considerations of FSCC GC/MS analysis configuration were examined at each laboratory. Standard solutions of organic compounds were analyzed at the participating laboratories to determine the "best" analysis configuration. Chromatographic resolution, composite standard compatibility, analysis precision, dynamic range, quality control, and other considerations of the analysis configuration were examined. Finally, GC/MS data acquired via a packed column analysis configuration and the proposed FSCC configuration are compared for spiked extracts of hazardous waste. This paper reports the advantages and limitations of FSCC GC/MS analysis for extractable priority pollutants.

2 Experimental

Three laboratories participated in this work: the Environmental Monitoring Systems Laboratory at Las Vegas, Nevada (I); TRW Inc., Redondo Beach, California (II); and Systems, Science and Software, San Diego, California (III). Experimental GC/MS parameters are presented below:

2.1 FSCC GC/MS

Laboratories I and II acquired all FSCC GC/MS results with Finnigan 4023 quadrupole mass spectrometers equipped with Finnigan 9610 gas chromatographs and a Grob type split/splitless injector. The system at Laboratory I differed from that at Laboratory II, in that the source and multiplier were modified for Pulsed Positive Ion Negative Ion Chemical Ionization (PPINICI). Additionally, Laboratory I had a Finnigan model LC/MS interface in place during the experiments reported here.

All capillary column GC/MS data from Laboratory III were acquired on a Finnigan Model 1020 mass spectrometer equipped with a Perkin-Elmer Sigma II gas chromatograph and a modified [5] SGE capillary injector. Each laboratory utilized Finnigan software for data acquisition and processing.

All spectra were acquired in the electron impact ionization mode at 70 eV energy. Source temperatures were maintained at 240 °C at Laboratories I and II. The 1020 instrument at Laboratory III did not have an electrically heated source. A 0.95 s linear upward scan with 0.05 s settling time was utilized from 45 to 450 amu. Perfluorotri-*n*-butylamine (PFTBA) was used for mass calibration, and decafluorotriphenylphosphine (DFTPP) was utilized for ion abundance verification [7].

Fused silica capillary columns were purchased from J & W Scientific, Rancho Cordova, California. Both 0.25 mm and 0.32 mm i.d. × 30 m SE-54 columns were used for the data reported herein. The injection technique was splitless with septum sweep (10 ml/min) and split (30 ml/min) flows initiated automatically (Laboratories I and II) at 30 s after injection. At Laboratory III, sweep and split flows were activated manually.

Helium was employed as the carrier gas with linear velocities of approximately 20 cm/s (0.25 mm i.d. column) and approximately 50-70 cm/s for the 0.32 mm i.d. column. Temperature programs were initiated with a 2 or 4 minute hold at the initial temperature (30 or 35 °C) and ramped to 265 °C at 10 °C/min and held for 3 (0.32 mm i.d.) or 12 (0.25 mm i.d.) minutes.

For FSCC GC/MS experiments relative retention time and relative response factors were calculated using multiple internal standards (IS). In initial experiments naphthalene-d_8, anthracene-d_{10}, and chrysene-d_{12} were employed. Later, two additional internal standards, phenol-d_5 and benzo[a]pyrene-d_{12}, were added to the internal standard list. Response factors were calculated using m/z values of reference [1] relative to the base peak of the closest eluting internal standard.

2.2 Packed Column GC/MS

Packed column GC/MS data were acquired in accordance with Federal Register Method 625 [1]. A Dupont Model 321 mass spectrometer was interfaced via a glass jet separator to the appropriate chromatographic column [1] for acquisition of packed column priority pollutant data. The mass spectrometer scan time was 2.0 s from 45 to 450 amu. Ionization, chromatographic, and detector parameters were established to meet the specifications of reference [1].

2.3 Reagents

Standards were prepared gravimetrically from neat in-house materials of known purity in pestiquality methylene chloride. All internal standard compounds utilized, phenol-d_5, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and benzo[a]pyrene-d_{12} were purchased from Merck, Sharp and Dohme, Stable Isotope Division, Quebec, Canada. For early experiments, priority pollutant standards were purchased from Supelco, Inc., Bellefonte, Pennsylvania and diluted with methylene chloride.

Extracts of hazardous materials employed in the packed column/FSCC comparison were prepared by a solvent extraction procedure under development at Oak Ridge National Laboratory [5]. The extraction solvent in all cases was methylene chloride. Stock methylene chloride solutions of standards used for GC/MS calibration were also employed for the solution spiking. Composites of acid and base/neutral extracts of solid materials were prepared by transferring equal volumes of the acid and base/neutral extract to Pierce vials with Teflon lined septa or equivalent with subsequent addition of internal standards. The samples were then injected immediately (1.0 µl) into the GC/MS system.

3 Results and Discussion

Initial FSCC GC/MS experiments performed by Laboratory I on standard solutions of acid extractable priority pollutants gave excellent qualitative and quantitative results. For example, **Figure 1** shows a total ion current chromatogram for 50 ng of selected acid-extractable priority pollutant phenols. **Table 1** presents the percent relative standard deviation (RSD) for five consecutive single level 50 ng determinations. Even for the acidic dinitrophenols and the highly chlorinated phenols, narrow response factor variation (i.e., precision) was observed. We suspected fused silica capillary columns to be an important new inert column for priority pollutant analysis and a significant advance in the state of the art of gas chromatography. These observations led us to examine whether the acid, base/neutral, and pesticide priority pollutant fractions could be analyzed simultaneously. acqui-

Figure 2 shows a total ion current chromatogram for a standard containing 15 pesticides, 11 phenols, and 49 base/neutral extractable priority pollutants at the 140 or 200 ng level acquired on a narrow bore SE-54 FSCC. These data illustrate the utility of FSCC for the simultaneous analysis of acidic and basic species. The peaks labeled 1, 2, and 3 are dimethylnitrosamine, pentachlorophenol, and endrin, respectively. The compounds were readily detected and most of the compounds exhibited good peak shape (i.e., minimal or no tailing). Also, excellent response factor precision was observed for acidic and basic priority pollutants analyzed in composited standards [3].

Table 1

Relative standard deviation response factors for five consecutive injections of selected "acid extractable priority pollutant" phenols for W_x = 50 ng and W_{IS} = 40 ng.

Compound	m/z Employed for EICP relative to anthracene-d_{10} (m/z 188)	Relative std. deviation [%]
Phenol	94	4.8
2-Chlorophenol	128	6.3
2-Nitrophenol	139	10.0
4-Chloro-3-cresol	142	8.3
2,4-Dinitrophenol	184	7.7
4-Nitrophenol	139	8.5
2,4-Dinitro-o-cresol	198	2.5
Pentachlorophenol	266	4.8

3.1 Gas Chromatography

A multiple internal standard quantification strategy was employed to minimize the relative retention time (RRT) and response factor variation. The mean retention time and RRT values calculated using naphthalene-d_8, anthracene-d_{10}, and chrysene-d_{12}, for FSCC GC/MS analysis of standard (100 ng) solutions are presented in **Table 2**. The last six columns present the ±3 standard deviation (SD) windows for the retention time (RT) and the RRT calculated using the three previously-mentioned internal standards individually, and collectively (RRT_c). The relative retention time ±3 SD windows for five labeled/unlabeled analyte pairs (RRT_L) is shown in the last column. All of the data were acquired during one working day, and are therefore representative of short-term or best-case RRT precision.

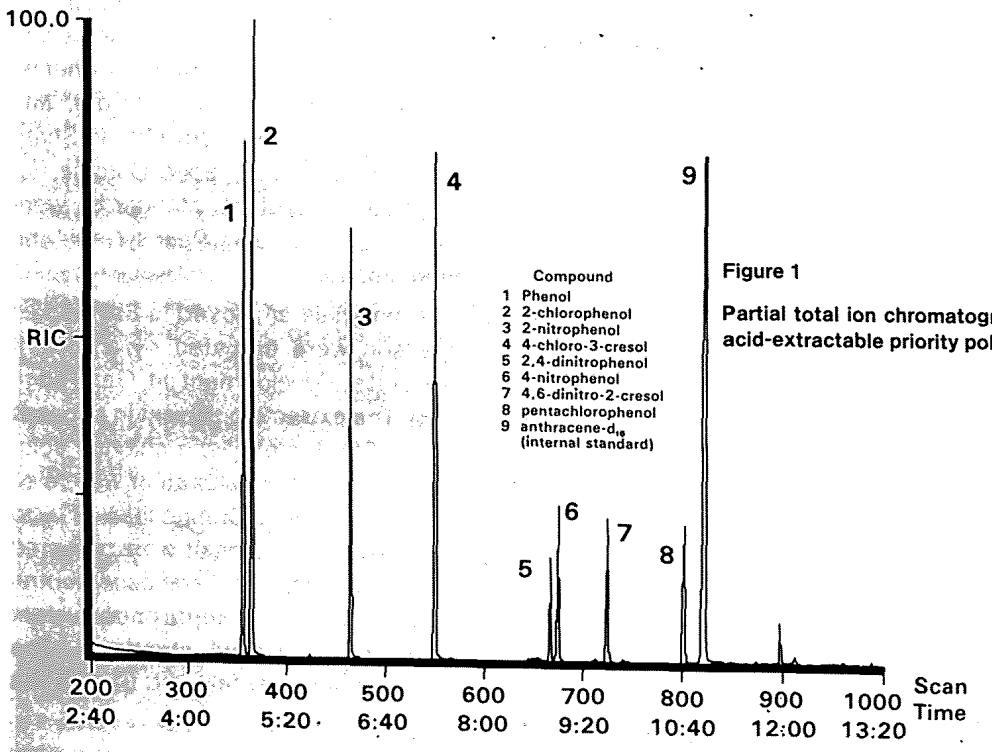

Figure 1

Partial total ion chromatogram for FSCC GC/MS analysis of selected acid-extractable priority pollutants (0.25 mm i.d. x 30 m SE-54).

Table 2[a)]

Retention time and relative retention time data and ±3 standard deviation windows [s].

Compound	Retention time and relative retention time data				±3 standard deviation windows [s]					
	RT [s]	RRT_{d8}	RRT_{d10}	RRT_{d12}	RT	RRT_{d8}	RRT_{d10}	RRT_{d12}	RRT_c	RRT_L
1,2-Dichlorobenzene-d_4	620	0.7978	0.4836	0.3668	16.65	11.13	12.86	15.03	11.13	–
1,2-Dichlorobenzene	620	0.7986	0.4845	0.3672	17.28	10.21	17.69	16.65	10.21	0.20
4-Methylphenol	658	0.8468	0.5138	0.3894	16.97	6.91	12.62	13.60	6.91	–
Naphthalene-d_8	777	-1-	0.6066	0.4600	13.68	–	10.31	10.13	–	–
2,4,6-Trichlorophenol-d_2	931	1.199	0.7276	0.5512	12.30	6.07	8.76	9.06	6.07	–
2,4,6-Trichlorophenol	932	1.200	0.7284	0.5518	12.73	7.07	6.87	18.13	7.07	2.49
1,4-Naphthoquinone	985	1.268	0.7696	0.5834	13.01	11.13	8.76	9.06	11.13	–
4-Chlorophenyl phenyl ether-d_5	1130	1.455	0.8828	0.6690	10.04	10.93	6.43	0.00	6.43	–
4-Chlorophenyl phenyl ether	1132	1.457	0.8840	0.6698	15.65	12.06	5.43	8.48	5.43	6.57
n-Nitrosodiphenylamine-d_6	1150	1.480	0.8980	0.6808	12.72	11.70	5.43	4.53	5.43	–
n-Nitrosodiphenylamine	1150	1.481	0.3988	0.6810	10.90	14.14	3.44	0.00	3.44	3.02
Lindane	1260	1.622	0.9838	0.7462	13.68	14.14	3.44	11.10	3.44	–
Phenanthrene-d_{10}	1272	1.637	0.9936	0.7532	12.30	12.15	6.87	4.53	6.87	–
Phenanthrene	1274	1.641	0.9954	0.7544	10.04	14.51	6.87	5.55	6.87	2.09
Anthracene-d_{10}	1281	1.649	-1-	0.7580	10.03	14.14	–	0.00	–	–
Triphenyl phosphate	1635	2.105	1.277	0.9680	14.07	21.51	5.43	7.17	7.17	–
Chrysene-d_{12}	1689	2.174	1.319	-1-	12.72	18.47	3.44	–	–	–
Mean					13.2	12.2	7.8	8.3	7.4	2.9
SD					2.3	4.0	3.9	5.8	2.9	2.3

[a)] The first four columns refer to the retention time (RT), and relative retention time (RRT) for the analytes listed relative to naphthalene-d_8, anthracene-d_{10}, and chrysene-d_{12}. The remaining six columns present the ±3 SD windows [s] for the retention time, and the RRT values in columns 2 through 4, as well as the ±3 SD windows for the internal standard which eluted nearest to the analyte and the ±3 SD windows for unlabeled to labeled analogues. The data (n = 5, 1, 100 ng) was generated by Laboratory III with 0.25 mm i.d. SE-54 FSCC programmed from 50 °C after 2-min hold to 265 °C at 10 °C/min with a 12-min final hold.

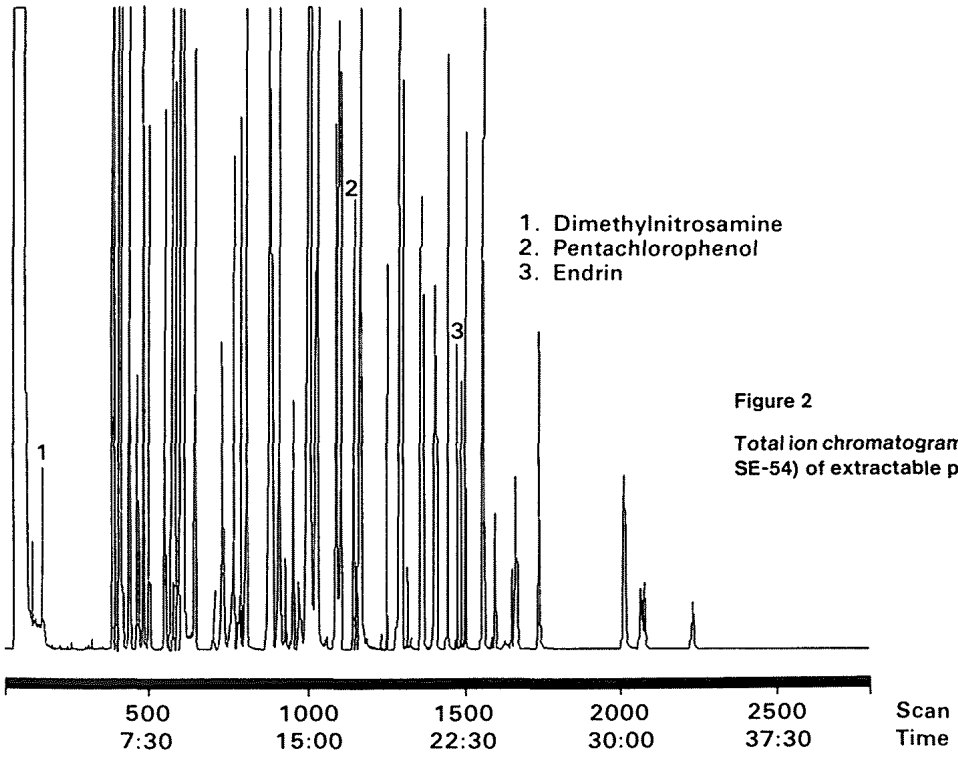

Figure 2

Total ion chromatogram for the one column analysis (0.25 mm i.d. x 30 m SE-54) of extractable priority pollutants.

These data show that the most precisely determined RRT value is that using the labeled/unlabeled pair (e.g., phenanthrene vs. phenanthrene-d_{10}). The mean ±3 SD window for the composite internal standard approach is not significantly narrower than the mean 3 SD RRT windows when chrysene-d_{12} or anthracene-d_{10} are used individually for RRT calculation. However, the SD using the multiple internal standards (RRT_c) is observed to be smaller and the ±3 SD range is approximately 5.5 seconds less. For these reasons, when the labeled analogue is not present, we suggest that RRT values should be assigned with multiple internal standards. Because of the apparent trend in 3 SD windows to larger values as the compound of interest elutes farther from the internal standard, it would appear that the internal standard should be spaced equally through a range of retention times.

The RRT statistics in Table 2 were generated over the short term, and represent best-case precision. RRT_c precision data were also acquired over six working days at 50 ng (n = 7) and are presented in **Table 3** for essentially all of the extractable priority pollutants. The mean, SD, and RSD calculated using the multiple internal standard approach demonstrated that the long-term, single-level RRT_c precision approximates that of the short-term experiments reported in Table 2. The mean RSD of the priority pollutants in Table 3 was 0.5%. For organic compounds with RRT_c values outside of the 0.85-1.25 range (n = 20) the mean

Table 3

Single-level long term RRT_c precision.

No.	Name	Quant. mass	Mean RRT	Std. dev. RRT	Rel. std. dev. RRT [%]
1	Naphthalene-d_8 (IS)	136	–	–	–
2	2-Chloroethyl vinyl ether	63	0.287	0.022	7.9
3	*N*-Nitrosodimethylamine	74	0.317	0.022	7.2
4	Phenol	94	0.724	0.009	1.2
5	Bis(2-chloroethyl) ether	93	0.734	0.008	1.1
6	2-Chlorophenol	128	0.733	0.008	1.1
7	1,3-Dichlorobenzene	146	0.757	0.007	0.9
8	1,4-Dichlorobenzene	146	0.767	0.007	0.9
9	1,2-Dichlorobenzene	146	0.800	0.006	0.7
10	Bis(2-chloroisopropyl) ether	121	0.830	0.005	0.6
11	Hexachloroethane	117	0.855	0.004	0.5
12	*N*-Nitroso-di-*n*-propylamine	70	0.856	0.004	0.5
13	Nitrobenzene	123	0.875	0.004	0.4
14	Isophorone	82	0.922	0.002	0.3
15	2-Nitrophenol	139	0.935	0.001	0.1
16	2,4-Dimethylphenol	122	0.952	0.001	0.1
17	Bis(2-chloroethoxy)methane	93	0.971	0.001	0.1
18	2,4-Dichlorophenol	162	0.980	0.001	0.1
19	1,2,4-Trichlorobenzene	180	0.994	0.001	0.1
20	Naphthalene	128	1.004	0.000	0.0
21	Hexachlorobutadiene	225	1.042	0.001	0.1
22	4-Chloro-3-methylphenol	142	1.121	0.003	0.3
23	Hexachlorocyclopentadiene	237	1.182	0.005	0.5
24	2,4,6-Trichlorophenol	196	1.199	0.006	0.5
25	2-Chloronaphthalene	162	1.229	0.007	0.5
26	Acenaphthylene	152	1.310	0.010	0.7
27	Dimethyl phthalate	163	1.309	0.010	0.7
28	2,6-Dinitrotoluene	63	1.320	0.010	0.7
29	4-Nitrophenol	139	1.324	0.010	0.7
30	Anthracene-d_{10} (IS)	188	–	–	–
31	Acenaphthene	154	0.823	0.003	0.4
32	2,4-Dinitrophenol	184	0.832	0.003	0.4
33	2,4-Dinitrotoluene	89	0.851	0.003	0.3
34	Fluorene	166	0.883	0.002	0.2
35	Diethyl phthalate	149	0.885	0.002	0.2
36	4-Chlorophenyl phenyl ether	204	0.887	0.002	0.2
37	4,6-Dinitro-*o*-cresol	198	0.899	0.002	0.2
38	*N*-Nitrosodiphenylamine	169	0.903	0.002	0.2
39	1,2-Diphenylhydrazine	77	0.906	0.002	0.2
40	4-Bromophenoxybenzene	248	0.944	0.001	0.1
41	alpha-BHC	181	0.950	0.001	0.1
42	Hexachlorobenzene	284	0.958	0.001	0.1
43	Pentachlorophenol	266	0.981	0.001	0.1
44	gamma-BHC	181	0.986	0.000	0.0
45	Phenanthrene	178	0.997	0.000	0.0
46	Anthracene	178	1.000	0.002	0.2
47	delta-BHC	181	1.010	0.000	0.0
48	Heptachlor	272	1.059	0.001	0.1
49	Di-*n*-butyl phthalate	149	1.081	0.001	0.1
50	Aldrin	66	1.095	0.001	0.1
51	Heptachlor epoxide	81	1.135	0.002	0.2
52	Fluoranthene	202	1.140	0.002	0.2
53	Benzidine	184	1.163	0.000	0.0
54	Pyrene	202	1.166	0.002	0.2
55	Chrysene-d_{12} (IS)	239	–	–	–
56	Endosulfan	195	0.879	0.001	0.2
57	DDE	246	0.894	0.001	0.1
58	Dieldrin	79	0.898	0.001	0.2
59	Endrin	81	0.914	0.001	0.1
60	DDD	235	0.924	0.001	0.1
61	Endosulfan sulfate	272	0.952	0.000	0.1
62	DDT	235	0.952	0.001	0.1
63	Endrin aldehyde	67	1.212	0.000	0.0
64	Butyl benzyl phthalate	149	0.948	0.000	0.0
65	Benzo[a]anthracene	228	0.998	0.002	0.2
66	3,3′-Dichlorobenzidine	252	1.000	0.000	0.0
67	Chrysene	228	1.002	0.002	0.2
68	Bis(2-ethylhexyl) phthalate	167	1.026	0.000	0.0
69	Di-*n*-octyl phthalate	149	1.137	0.001	0.1
70	Benzo[*b*]fluoranthene	252	1.182	0.003	0.3
71	Benzo[*k*]fluoranthene	252	1.184	0.003	0.3
72	Benzo[e]pyrene	252	1.185	0.003	0.3
73	Benzo[a]pyrene	252	1.253	0.003	0.2
74	Indeno[1,2,3-*cd*]pyrene	276	1.632	0.008	0.4
75	Dibenzo[*a,h*]anthracene	278	1.659	0.008	0.5
76	Benzo[*g,h,i*]perylene	276	1.744	0.009	0.5

Table 4

Relative retention times determined in spiked (50 ppm) industrial hazardous waste.

Compound Sample[a)]	1	2	3	4	5	6	7	8	9	Avg.±	SD (% SD)	Internal standard
1,2-Dichlorobenzene	0.806	0.808	0.809	0.809	0.809	0.808	0.808	0.805	0.807	0.8076±	0.0041 (0.17)	d_8
Hexachloroethane	0.857	0.859	0.859	0.860	0.859	0.858	0.859	0.858	0.858	0.8585±	0.0009 (0.10)	d_8
Bis(2-chloroisopropyl) ether	0.832	0.834	0.833	0.833	0.833	0.831	0.834	0.832	0.833	0.8328±	0.0009 (0.11)	d_8
Nitrobenzene	0.877	0.879	0.879	0.878	0.879	0.878	0.879	0.877	0.879	0.8783±	0.0009 (0.10)	d_8
Isophorone	0.935	0.923	0.923	0.923	0.923	0.922	0.924	0.924	0.923	0.9244±	0.0040 (0.43)	d_8
Naphthalene	1.003	1.004	1.002	1.002	1.002	1.002	1.003	1.002	1.004	1.0027±	0.0009 (0.09)	d_8
Phenanthrene	0.997	0.997	0.997	0.997	0.997	0.997	0.997	0.998	0.996	0.9970±	0.0005 (0.05)	d_{10}
Diethyl phthalate	0.884	0.884	0.884	0.885	0.884	0.884	0.884	0.888	0.884	0.8845±	0.0013 (0.15)	d_{10}
2,4-Dinitrotoluene	0.852	0.852	0.852	0.851	0.853	0.852	0.852	0.857	0.853	0.8527±	0.0017 (0.20)	d_{10}
Hexachlorobenzene	0.958	0.958	0.958	0.958	0.958	0.958	0.958	0.963	0.958	0.9585±	0.0017 (0.18)	d_{10}
Acenaphthylene	0.804	0.804	0.804	0.803	0.803	0.803	0.804	0.808	0.804	0.8041±	0.0015 (0.19)	d_{10}
2-Chloronaphthalene	1.221	1.221	1.221	1.222	1.221	1.222	1.222	1.221	1.222	1.2215±	0.0006 (0.05)	d_8
p-Cresol	0.855	0.857	0.856	0.855	0.855	0.854	0.857	0.855	0.856	0.8555±	0.0010 (0.12)	d_8
Naphthoquinone	0.777	0.778	0.778	0.778	0.778	0.777	0.778	0.782	0.778	0.7782±	0.0014 (0.18)	d_{10}
Pyridine	–	0.410	–	–	0.429	0.426	0.409	0.418	–	0.4184±	0.0086 (2.06)	d_8
Carbazole	1.022	1.023	1.023	1.023	1.023	1.023	1.023	1.028	1.024	1.0235±	0.0017 (0.17)	d_{10}
Tetrachlorobenzene	1.170	1.170	1.167	1.168	1.169	1.169	1.171	1.172	1.171	1.1697±	0.0016 (0.14)	d_8
2-Chlorophenol	0.742	0.747	0.748	0.747	0.747	0.747	0.747	0.745	0.744	0.7460±	0.0019 (0.25)	d_8
2,4,6-Trichlorophenol	1.192	1.189	1.190	1.190	1.191	1.191	1.192	1.192	1.192	1.1910±	0.0011 (0.09)	d_8
Phenol	0.729	0.733	0.734	0.733	0.732	0.731	0.733	0.731	0.731	0.7319±	0.0015 (0.20)	d_8
2-Nitrophenol	0.935	0.936	0.935	0.935	0.935	0.935	0.936	–	0.936	0.9352±	0.0004 (0.04)	d_8
Indole	1.126	1.126	1.126	1.124	1.125	1.125	1.127	1.125	1.129	1.1257±	0.0010 (0.09)	d_8
Quinoline	1.070	1.068	1.069	1.068	1.068	1.067	1.068	1.068	1.070	1.0684±	0.0010 (0.09)	d_8
Alpha-pinene	0.663	0.667	0.667	0.666	0.667	0.666	0.664	0.661	–	0.6650±	0.0021 (0.32)	d_8
Triphenyl phosphate	–	0.954	0.953	0.954	0.955	0.954	0.953	0.953	–	0.9537±	0.0007 (0.07)	d_{12}
Endrin	1.223	1.223	1.225	1.224	1.224	1.224	1.222	–	–	1.2233±	0.0016 (0.13)	d_{10}
Heptachlor	1.057	1.057	1.057	1.057	1.057	1.057	1.057	1.062	1.057	1.0575±	0.0017 (0.02)	d_{10}
Hexachlorobutadiene	1.037	1.038	1.038	1.037	1.038	1.038	1.039	1.038	1.039	1.0380±	0.0007 (0.07)	d_8
Lindane	0.985	0.984	0.985	0.985	0.986	0.985	0.985	–	0.984	0.9849±	0.0006 (0.06)	d_{10}
2,3,4,5-Tetrachlorobiphenyl	1.129	1.130	1.130	1.130	1.130	1.129	1.128	1.134	1.290	1.1299±	0.0017 (0.15)	d_{10}

[a)] 1 = Coal gasification tar waste; 2 = Still bottom (organic); 3 = Pulp and paper sludge; 4 = Electroplating sludge; 5 = Coke manufacturing sludge; 6 = Ink plant sludge; 7 = Latex paint sludge; 8 = Pharmaceutical sludge; 9 = Paint plant sludge.

RSD was 1.2%, whereas for eluants within the 0.85 to 1.25 RRT_c window, a significantly lower mean RSD of 0.2% was noted. (n = 52, endrin aldehyde was excluded because of elution problems). This observation underscores the importance of the internal standards eluting near in time to the analyte of interest.

To demonstrate the long-term RRT_c variation found in the analysis of actual hazardous waste sample extracts, Laboratory III analyzed spiked extracts of nine hazardous materials prepared by a recently developed isolation procedure [6]. These data (**Table 4**) were acquired over a 2-week period and demonstrate the excellent precision of RRT_c (mean RSD = 0.2%) in actual practice. It should be noted that 22 of the RRT_c values are in the 0.85-1.25 window and that the mean RSD for these analytes is comparable with the data previously reported for standards. Also note that Table 4 contains results for organic compounds which are not priority pollutants. Data is presented for concurrent composite analysis of a cresol, a quinone, nitrogen-containing heterocycles, a terpene, an organophosphate and a tetrachlorinated biphenyl. As the injected weight was approximately 25-30 ng per analyte, and because these compounds were located in data files by software in residence at Laboratory III, it is apparent that acids, bases, and polar aprotic analytes can be located precisely in FSCC GC/MS data files acquired on extracts of solid hazardous waste materials of diverse origin. Hence FSCC can withstand the assault of complex mixture analysis. Three initial experiments had therefore indicated that this chromatographic configuration is practical in application.

Table 5

Relative retention time standards (Lab II) versus samples (Lab III).

	Standards[a] Lab II		Hazardous[b] waste extracts Lab III	
Compound	RRT[c]	%SD	RRT[c]	%SD
1,2-Dichlorobenzene	0.800	0.7	0.808	0.2
Hexachloroethane	0.855	0.5	0.859	0.1
Bis(2-chloroisopropyl) ether	0.830	0.6	0.833	0.1
Nitrobenzene	0.875	0.4	0.878	0.1
Isophorone	0.922	0.3	0.924	0.4
Naphthalene	1.004	0.0	1.003	0.1
Phenanthrene	0.997	0.0	0.997	0.1
Diethyl phthalate	0.885	0.2	0.885	0.2
2,4-Dinitrotoluene	0.851	0.3	0.853	0.2
Hexachlorobenzene	0.958	0.1	0.959	0.2
Acenaphthylene	1.310[c]	0.7	0.804[c]	0.2
2-Chloronaphthalene	1.229	0.5	1.222	0.1
2-Chlorophenol	0.733	1.1	0.746	0.3
2,4,6-Trichlorophenol	1.199	0.5	1.191	0.1
Phenol	0.724	1.2	0.732	0.2
2-Nitrophenol	0.935	0.1	0.935	0.0
Endrin	0.914[c]	0.1	1.223[c]	0.1
Heptachlor	1.059	0.1	1.058	0.0
Hexachlorobutadiene	1.042	0.1	1.038	0.1
Lindane	0.968	0.1	0.984	0.1
Mean		0.4		0.2
SD		0.4		0.1

[a] n = 7, 50 ng/compound, acquired over 6-day period.
[b] n = 9, 25 ng/compound, acquired over 14-day period.
[c] Different internal standards employed.

To compare standard and sample RRT_c values and to demonstrate the excellent accuracy and precision of RRT_c determination when the composite internal standard and FSCC are employed, we have presented the intersection of Tables 3 and 4 in **Table 5**. The excellent RRT_c agreement between laboratories is apparent. We show the mean and RSD at the bottom of Table 4.

This treatment of RRT data has been somewhat laborious, but the results are nevertheless instructive. We have demonstrated that for the analysis of standards over the short and the long term, and for the analysis of spiked extracts of hazardous materials that have been analyzed over the long term, RRT_c values can be accurately and precisely determined even between laboratories. Although this work does not constitute a true interlaboratory comparison, the data acquired in the effort are encouraging in this regard. These RRT_c data demonstrate that this variable can be known to precision levels not previously thought possible between laboratories. For analytes with RRT_c values between 0.85 and 1.25, the ±3 SD RRT_c window corresponds in worst cases to approximately 15 seconds. Therefore, precise "location" of priority pollutants is a powerful property of the FSCC GC/MS method utilized herein.

Precision in RRT_c can improve the efficiency and reliability of qualitative GC/MS analysis. For example, fewer spectra have to be examined in target compound analysis strategies which utilize this descriptor to locate organic compounds in GC/MS data files [7]. This results in minimizing qualitative analysis data system I/O and, therefore, qualitative results can be obtained more quickly. As the location of given analytes can be precisely predicted, search results would be expected to be, in general, more reliable. Of course, isomer differentiation would be expected to be better for capillary columns, because of the increased resolution. In fact most of the isomeric priority pollutants are baseline resolved for the FSCC chromatographic configurations utilized in this work. However, experience has shown that such differentiation based on retention time and a mass spectral library search can still be problematical, i.e. the mean ±3 SD windows of RRT_c for isomers can overlap. Since the temperature programs utilized in this work were compromised to minimize the total data acquisition time while maintaining adequate chromatographic resolution for most of the priority pollutants, isomer differentiation via RRT_c is still problematical. If isomer differentiation is essential, slower temperature program rates could be used to provide better chromatographic resolution of isomers.

A recent report [7] provided a more definitive comparison of the qualitative improvement observed when data from a FSCC GC/MS configuration were compared with packed column GC/MS data generated in accordance with reference [1]. The recognition rate, the number of spectra automatically identified relative to the number of spectra detected [8], was increased by approximately a factor of two for the FSCC GC/MS configuration relative to the packed column GC/MS data acquired in accordance with reference [1] on extracts of industrial effluents. Based on this observation, the FSCC GC/MS analysis configuration apparently provides for better qualitative analysis results in addition to the aforementioned benefits.

3.2 Potential Gas Chromatographic Problems

In the course of this work two problems were encountered with the FSCC GC/MS configuration which in the best case would have limited routine application. The two chromatographic problems encountered in this work involved column overload and a phenomenon which we will call "double peaking".

3.2.1 Column Overload

Initially work performed at Laboratory I had shown that when high (hundreds) nanogram levels of priority pollutants were injected onto the FSCC, the RT values increased and

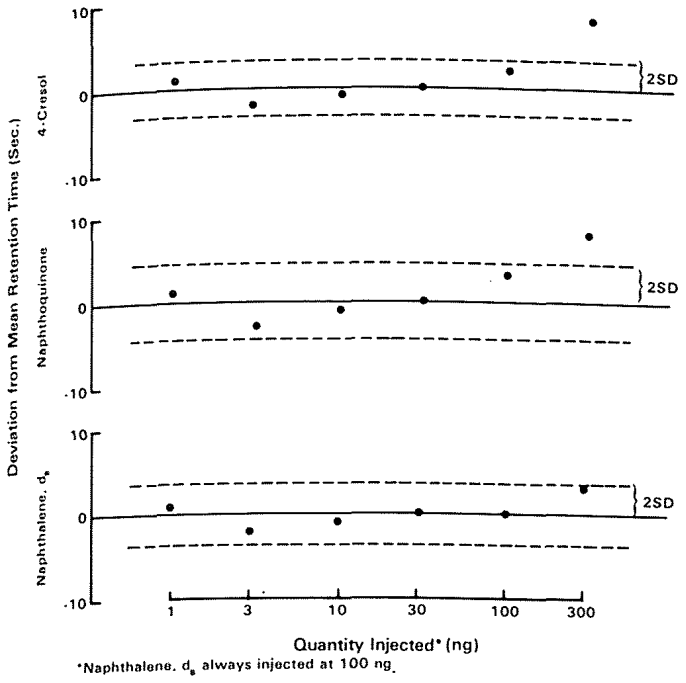

Figure 3

Retention time dependence on quantity of analyte injected.

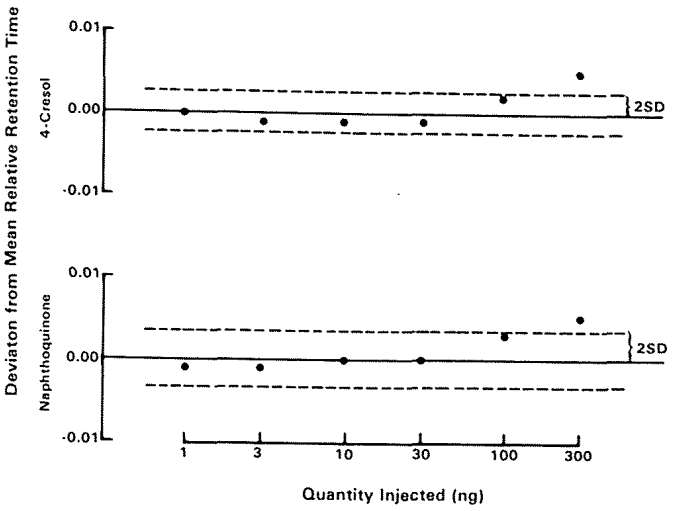

Figure 5

Relative retention time dependence on quantity of analyte injected.

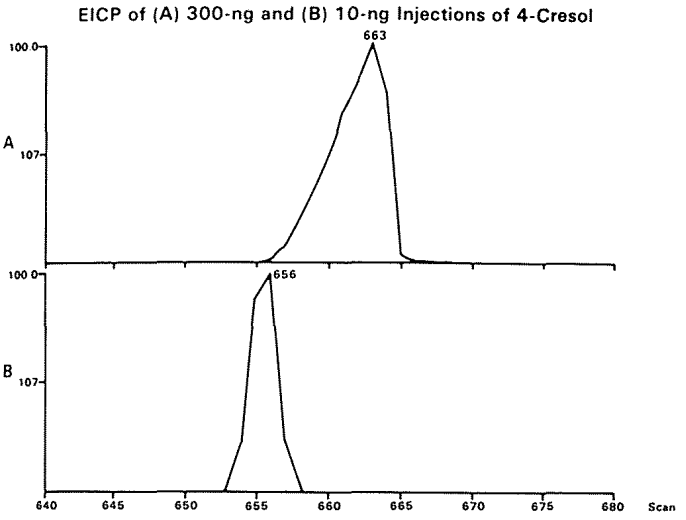

Figure 4

Extracted ion current profiles for 300 ng (top) and 10 ng (bottom) injections of *p*-cresol.

the peak shape degraded. For data acquired at Laboratory III on a narrow bore SE-54 FSCC under conditions identical to those used for the generation of the data presented in Table 2, the mean RT is plotted versus the quantity injected for 4-cresol and naphthoquinone in **Figure 3**. The RT and SD calculated for this figure do *not* include the point at 300 nanograms. Note that the deviation for the 300 nanogram level injection in both cases is greater than the mean value.

Even the naphthalene-d_8 RT value was greater than the mean value at 300 ng although this internal standard was injected at a single level (100 ng). In addition, severe peak "fronting" was noted at the 300 ng level. This is illustrated in **Figure 4** which presents the extracted ion current profiles (EICP) for two separate acquisitions of naphthoquinone (top 300 ng, lower 10 ng). **Figure 5** presents the dependence of RRT_c on injected quantity. Again the values at 300 nanograms were not included in the calculation of mean and SD. Figure 4A shows the peak shape (positive peak skew) observed when high nanogram levels of material were injected on column. As shown in Figure 5, the RRT_c value at the 300 ng level was greater than the mean value (calculated for the 1 through 100 ng injected quantities), but because of the increased RT of the internal standard (see Figure 3) at 300 ng the relative retention time increase was minimal. There can be no doubt that such anomalies are of concern when setting RRT_c windows for automated qualitative and quantitative data processing programs, as well as the parameters for "peaking finding" or eluent detecting programs. The effect of "fronting" on quantitation will be discussed separately in a later section. For the current discussion, we have reported that "fronting" was observed in temperature programmed data acquired with narrow bore columns when the injected weight of analyte approached 300 ng. Wide bore columns were not readily available at the time of the early work reported herein, but similar results were noted with wider bore (0.32 mm i.d.) columns. Of course, capillary column overload is a consideration which could limit the usefulness of FSCC GC/

MS; therefore, quantitative results at higher levels should be considered carefully. For these results, data processing programs were employed to identify and quantify even higher levels (500 ng) of priority pollutants, so that the poor peak shape shown in Figure 4 has not been a limiting aspect of detection (as the compound detecting software utilized in this work can readily detect eluents with such geometry). Furthermore, column overload does not severely affect the RRT_c value as the internal standard aids in correction. However, it is important to note such effects in highly contaminated samples. The monitoring of RT for internal standards could be employed as a quality control device for this problem.

3.2.2 Double Peaking

The most distressing chromatographic anomaly, noted and experienced to some degree by all three laboratories in early work, was an intermittent phenomenon which was dubbed "double peaking". This phenomenon was characterized by the occurrence of two peaks with identical mass spectra at adjacent retention times. Generally, the area of the first peak was of 5 to 10 percent of the area of the later eluting peak. This was observed for analytes with no geometrical isomers (e.g. phenol) so that compound impurities were not a likely source of the precursor peak. Experiments conducted at Laboratory II demonstrated a correlation between the percentage of methanol in methylene chloride and the area of the precursor peak. The higher the percentage of methanol, the larger the precursor peak area. As the initial standards utilized in this work were purchased from a commercial supplier in methanol, a percentage of the solvent (methanol) in the methylene chloride diluent was unavoidable, especially for higher concentrated standards. Subsequently all standards were prepared in methylene chloride from neat in-house materials because "double peaking" was rarely observed when this solvent was used.

Experiments at Laboratory III had indicated that an injection port modification was required to eliminate "double peaking" [6]. Experiments at Laboratory I had also shown that interruption of initial temperature program hold could cause "double peaking" even with methylene chloride as the solvent, so that thermal considerations were noted to cause the phenomenon. Injection port modifications, establishment of thermal equilibrium, accurate temperature reproduction, and use of methylene chloride as the solvent worked together to eliminate "double peaking". This description does not explain the cause of this phenomenon; nevertheless, once the aforementioned changes were implemented double peaking was eliminated in all three laboratories.

3.3 Quantitative FSCC GC/MS

The quantitative aspects of FSCC GC/MS analysis of composited standards of the organic priority pollutants

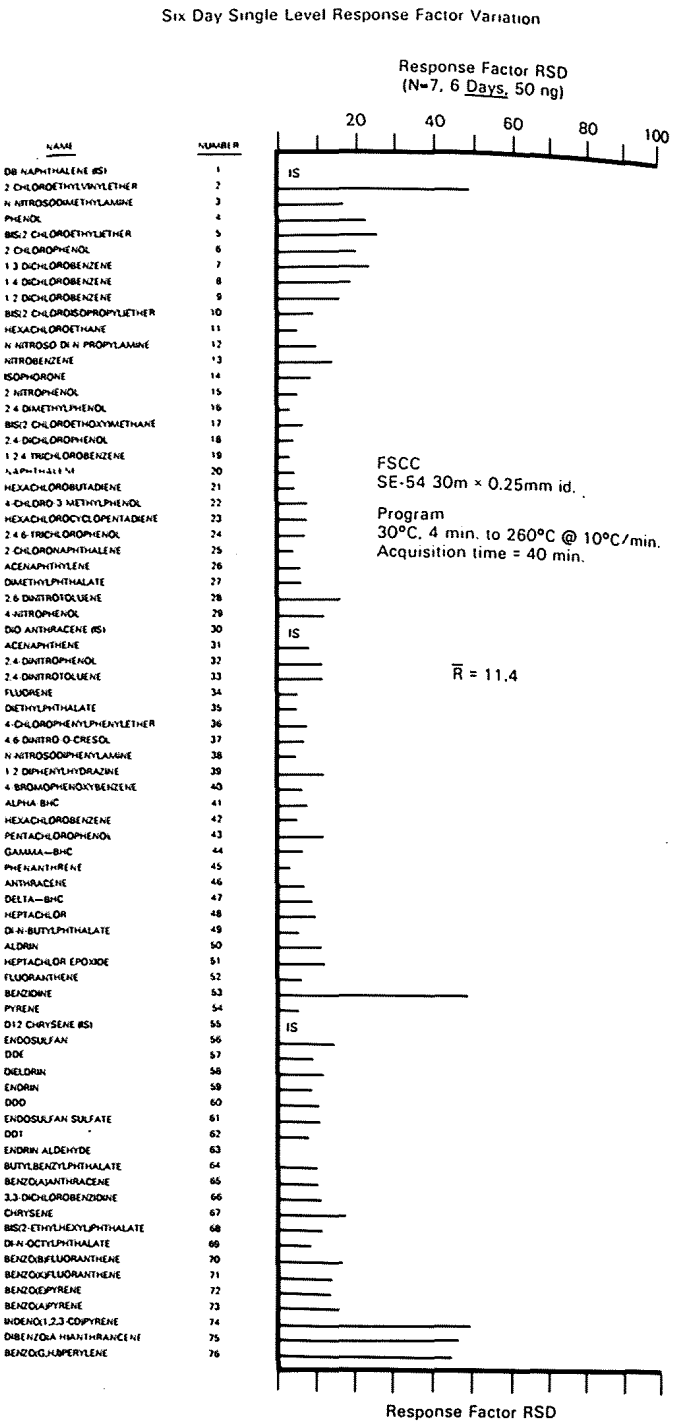

Figure 6

Single level (50 ng, n = 7), long-term (six day) response factor relative standard deviations for 72 priority pollutants.

(excluding those analytes generally isolated by the Bellar Lichtenberg, see reference [1], p. 69532, purge and trap technique) were investigated at single and multiple levels to test the feasibility of composite extract analysis, as well as to test the practical aspects of composite standard analysis. The results are reported and discussed below.

3.3.1 Single-Level Calibration Precision

Presented in **Figure 6** are the relative standard deviations of single level response factors (RF) for essentially

all of the extractable priority pollutants determined in a composite standard. This data was acquired at Laboratory II on a narrow bore SE-54 FSCC using a temperature starting at 30 °C (4-minute hold) and ramping at 10 °C/min to 260 °C with a final hold of 13 minutes. Seven data points were employed to calculate the mean, SD, and RSD for each response factor calculated as shown below:

$$RF = \frac{A_x \; W_{IS}}{A_{IS} \; W_x} \qquad (1)$$

where W is the injected quantity of internal standard (IS) or analyte (x), and A_{IS} is the summed area of the ion current for the base peak of the internal standard eluting nearest in time to the analyte, x. A_x is, of course, the summed ion current for analyte x for a characteristic m/z value. For two analytes, endrin aldehyde and benzidine, the data reported above differed. For the former compound, RF could not be calculated because this compound was not detected below 250 ng in these experiments. In the case of benzidine, this analyte could be detected in only five of the seven data files, resulting in n = 5 for this compound. Apparently, results with FSCC GC/MS configurations for these analytes should be assessed carefully. Additional discussion on this point will be presented later in this section.

We note that the data presented in Figure 6 were acquired over six working days, and are therefore representative of relatively long-term, single-level RF variation. The mean value of the RF RSD was 11.4%, which approaches the single level value of 7.0% considered acceptable [9] in GC/MS instrument evaluation tests. We note that the mean value of 11.4% is high because of the data shown for entries 2 through 9 and 74 through 76 in Figure 6. Data for these entries exhibited wider variation than possible, in part, because the RT values are considerably different from unity and because of other factors to be discussed later. We and others have reported the empirical dependence of RF precision on RRT value [3,10]. For example, if the RF RSD for 2-chlorophenol is calculated relative to phenol (phenol being designated as the internal standard for the sake of argument), the RSD for this analyte is reduced from 18.1% to 5.0%.

It is our opinion that the apparent empirical dependence of response factor precision on the elution choice of internal standard is caused at least in part by the relative number of data points acquired across the analyte and internal standard. The ion current ratio term in eq. (1) is actually a sum of intensity values [eq. (2)] where the ion current for the analyte x and the internal standard are summed over N and M values, respectively. If the ratio of data points differs for any series of determinations, the response factor can differ. We imply that internal standards which elute near to analytes of interest will better mirror elution of a compound and maintain a more precise M/N value. Additionally, the use of multiple internal standards decreases the difference in m/z value for analyte vs. m/z value for internal standard compared to reference [1] for many of the priority pollutants. When the m/z analyte, m/z internal standard difference is small, comparable ion sensitivities would be expected because ion transmission and resolution are similar for adjacent m/z values. As a result, we would expect that the effect of the instrument tune would be smaller for adjacent m/z values. For these reasons and because of observations reported in the chromatographic section of this paper we have suggested the application of five internal standards, one early and one later eluter. We are currently using phenol-d_5 and benzo[a]pyrene-d_{12} as early and late eluting internal standards in addition to the perdeuterated aromatic hydrocarbons cited previously.

$$\frac{A_x}{A_{IS}} = \frac{\sum_{i=1}^{i=N} I_{xi}}{\sum_{j=1}^{j=M} I_{ISj}} \qquad (2)$$

Despite a few anomalies, we cite the data in Figure 6 as supportive of our contention that composite analysis of extractable priority pollutant is possible, and, as importantly, is practical for essentially all of the extractable priority pollutants. Problems which had concerned us initially, such as chemical reactions between the numerous organic compounds of different functionality, are by inference not precision limiting when samples are composited just prior to injection and analyzed as indicated.

The data in Figure 6 also support a 1-second scan time as quantitatively adequate, although we would indicate that faster scan times may aid the precision and the detection of the early eluters. Because of the convenience of the 1-second scan time and because of data file length considerations, it is our opinion that precision problems for early eluters are better remedied by the addition of an early eluting internal standard rather than by using faster scan times.

These data were acquired over the long term (6 days) using the internal standard quantification strategy. Other quantification strategies for priority pollutants exist, most notably, isotope dilution (ID), see references [11] and [12]. The ID approach is obviously preferred for benzidine because of the qualitative and quantitative difficulties discussed previously. However, we found, in experiments conducted at Laboratory I using the identical standard employed to acquire the RF RSD reported in Figure 6 and a similar FSCC GC/MS analysis configuration, a short-term (n = 3, 50 ng) RSD of 3.5% for benzidine. Therefore, excellent short-term single-level precision for benzidine can be obtained when the internal standard approach is used, although the results have been found to be erratic for this analyte.

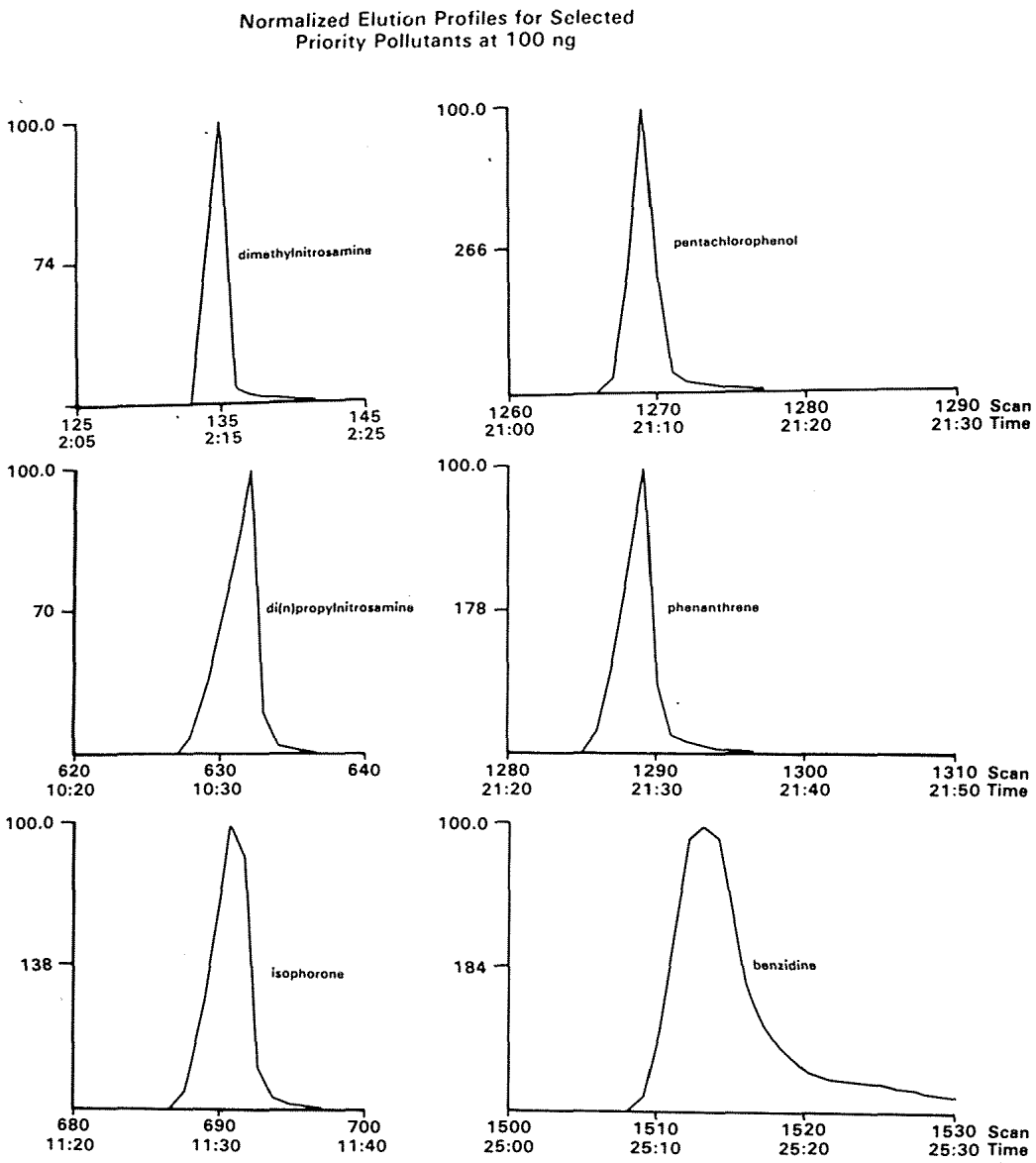

Figure 7

Normalized elution profiles for six priority pollutants at 100 ng.

Figure 7 shows the elution profile for six priority pollutants acquired (SE-54, 0.25 mm i.d. x approx. 25 m) at Laboratory I for the FSCC GC/MS analysis of a composite standard containing 30 of the extractable priority pollutants. The EICP axes have been expanded to present the peak shape of the analytes, dimethylnitrosamine, di-*n*-propylnitrosamine, isophorone, pentachlorophenol, phenanthrene, and benzidine. With the exception of benzidine, minimal "tailing" is observed. The tailing shown for benzidine, whatever the cause, is indicative of interaction other than gas/liquid partitioning. Unless this tailing is reproduced from injection to injection, wide response factor variability will be noted (the relative number of data points, N/M ratio, will differ). On some occasions we observed good or symmetrical peak shape for this analyte, but the elution profile was erratic. For these reasons, qualitative and quantitative measurements for benzidine should be accomplished by ID. For most of the priority pollutants, however, the internal standard quantification strategy is satisfactory, and for many of these compounds the internal standard quantification strategy provides precision which approaches the ID quantification technique.

3.3.2 *Multiple Level Calibration Data*

Ion current ratio plots (i.e., A_x/A_{IS} versus nanograms injected) are shown for three priority pollutants in **Figure 8**. These data were acquired by Laboratory II on a narrow bore SE-54 FSCC under conditions identical to those for which we have previously reported single level response factor variation in Figure 6. Ion current ratio plots for pentachlorophenol, heptachlor, and 1,2-diphenylhydrazine (detected as azobenzene) are presented along with the multilevel least squares line and 2.9 times the standard deviation multiplier (SDM) as determined from simultaneous injection in composited multiple level standards. Graphic representations and calculations were performed via the software in residence at Laboratory II. Correlation coefficients for each ion current ratio plot are presented to demonstrate the degree of correlation observed for these priority pollutants over the 5 to 500 nanogram injected weight range.

Table 6

Correlation coefficient for ion current ratio plots for selected priority pollutants calculated from multilevel injection (n = 6, range = 5, 500 ng).

Compound	Mean RF	Correlation coefficient
2-Chlorophenol	0.35	0.999
1,3-Dichlorobenzene	0.35	0.999
Isophorone	1.00	0.994
Bis(2-chloroethoxy)methane	0.55	0.995
Naphthalene	1.17	1.000
2,4-Dinitrotoluene	0.19	0.999
1,2-Diphenylhydrazine	1.05	0.995
Hexachlorobenzene	0.15	0.997
Phenanthrene	1.02	0.997
DDT	1.13	0.999
Benzo[a]pyrene	0.68	0.999

Although the higher injected levels were noted to "front" as discussed in the chromatographic section of this work, reasonable correlations were attained over the 5 to 500 ng range. These data suggest that quantitation over two orders of magnitude is possible despite chromatographic column overload. For many compounds, linearity over three orders of magnitude is possible; however, caution should be exercised when ion current ratios approach 25-30, (utilizing 20 ng of the internal standards), because saturation can be observed. Additional correlation coefficients calculated for selected analytes are presented in **Table 6**. A variety of functionalities are presented over a range of mean response factors and retention times.

For analytes with relatively high RF values saturation can be potentially problematical. Alternatively, for analytes with low RF values, detection at lower injected levels must be verified. The detection, saturation problems for analytes of greatly differing sensitivity (approximately a factor of 20 for the range of the extractable priority pollutants) are important if FSCC GC/MS is to be a practical analysis configuration.

In **Table 7** the naphthalene versus naphthalene-d_8 RF value at different electron multiplier (EM) voltages is shown. At higher EM voltages a decrease in the naphthalene response factor is apparent due to saturation of the m/z 128 EICP used for quantitation. Saturation must be avoided, but because of the large numbers of analytes, it can be difficult in practice to determine saturation in all cases. Compounds with high RF values can be employed to test for saturation. Alternatively, compounds with low response factors can be utilized to test for detection at relatively low injection levels.

The importance of differences in instrumentation linearity cannot be overemphasized. For example, the naphthalene RF calculated at Laboratory II for six multiple level injections (5, 500 ng range) was found to be 1.17 ± 0.10. The value at

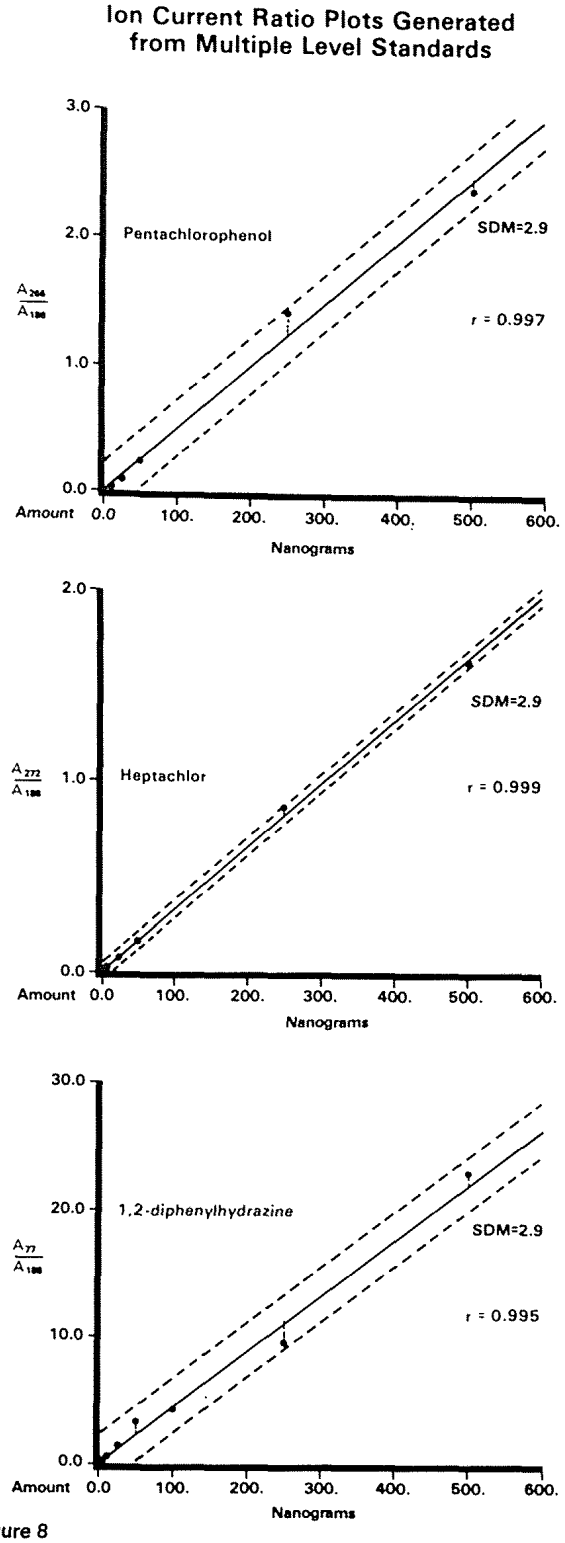

Figure 8

Multilevel (5, 500 ng) ion current ratio plots and correlation coefficients for pentachlorophenol, heptachlor, and 1,2-diphenylhydrazine (detected as azobenzene) acquired from composite standard.

500 ng was within 1 SD, 1.08, although it was below the mean value determined by multiple level injections. We observed that the data acquired at Laboratory I (Table 7) had demonstrated a significantly larger degree of saturation. Assuming that no major differences were caused by

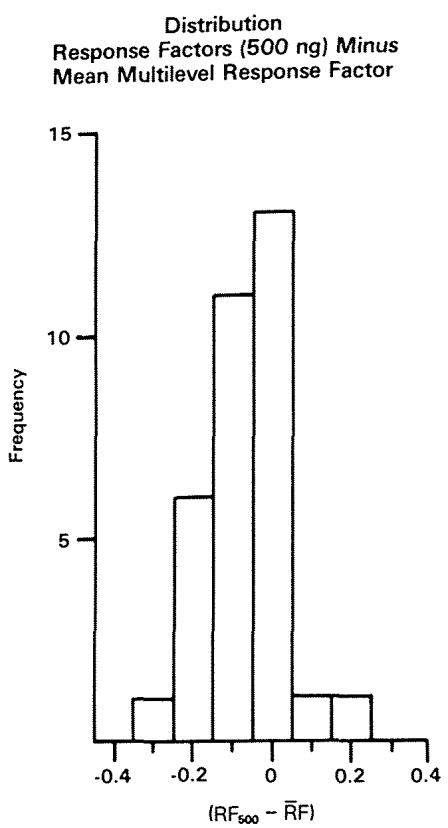

Figure 9

Distribution of 500 ng response factors minus the mean response factor determined at multiple levels (5, 500 ng).

"purity", which we regard as unlikely because of the similarity in the absolute RF value, we suspected that instrumental differences were the cause of this phenomena. Data from Laboratory I were acquired on a GC/MS system equipped with the positive ion conversion dynode maintained at −3.0 kV. The use of lower multiplier voltages is possible for instruments with this modification because these dynodes improve the electron multiplier gain [13]. We suspect therefore that the instrumental differences in ion detection at Laboratory I were the major factor responsible for this saturation relative to Laboratory II. It is apparent that FSCC GC/MS work requires linearity verification to ensure optimal analysis results, and that RF values at the upper quantitation limit should be compared with values found at lower levels.

With this in mind, we reviewed the initial multiple level data acquired at Laboratory II. For multiple level response factor data acquired by Laboratory II, 34 compounds had 500 ng Rf values reported [14]. **Figure 9** shows a ranged distribution of the residuals at 500 ng (i.e. $RF_{500} - \bar{RF}$). Seventy-six percent of the points in this distribution were below zero. The positive skew of the distribution and the apparent negative bias of the 500 ng response factor (RF_{500}) caused concern, for it appeared that these data (unmodified continuous dynode EM) were saturated. We would indicate that while the negative bias was apparent in the 500 ng response factor data, 76% of all RF values at 500 ng were

Table 7

Multiplier voltage effect on response factor. Naphthalene.

Nanogram injected	W_{IS}/W_x	Response factor at different EM voltages		
		−1 250V	−1 400V	−1 500V
5.0	8.00	0.86	1.05	1.04
50.0	0.80	1.00	–[a]	1.01
100.0	0.40	1.03	1.08	0.81
250.0	0.16	0.97	–[a]	0.81
500.0	0.08	1.00	0.77	0.53
Mean	–	0.97	0.97	0.84
SD	–	0.07	0.17	0.20

[a] Data not acquired for these concentrations.

Table 8

Ion current ratio correlation coefficient.

	EM voltage	
Compound	−1 250V	−1 500V[a]
Naphthalene	0.999	0.971
Phenanthrene	0.999	0.995
Chrysene	0.999	0.996

[a] If the 500 ng value is excluded from the correlation coefficient calculation, the values for naphthalene, phenanthrene, and chrysene become 0.997, 0.999, and 0.997.

Table 9

Single and multiple level response factor statistics for selected chlorinated phenols.

		Laboratory II		
		Multiple-level RF results		Single-level RF results
Analyte	IS[a]	ng n, range, RF±σ		n = 7,50 ng, 6 day RF±σ
2-Chlorophenol	d_8	6.5–500	0.35±0.07	0.38±0.07
2,4-Dichlorophenol	d_8	5.5–500	0.24±0.02	0.24±0.01
2,4,6-Trichlorophenol	d_8	5.5–250	0.17±0.02	0.15±0.01
Pentachlorophenol	d_{10}	6.5–500	0.09±0.02	0.08±0.01

[a] d_8 = naphthalene-d_8; d_{10} = anthracene-d_{10}.

±0.1 RRF units of the multilevel mean value. Subsequently, experiments were conducted at Laboratory I to investigate linearity for compounds with relatively high RF values (ca. 1.00). Multilevel RF data acquired for naphthalene, phenanthrene, and chrysene were determined at seven levels over a range from 5 to 500 nanograms. Table 7 presents the correlation coefficients for the ion current ratio plots at two different electron multiplier voltages.

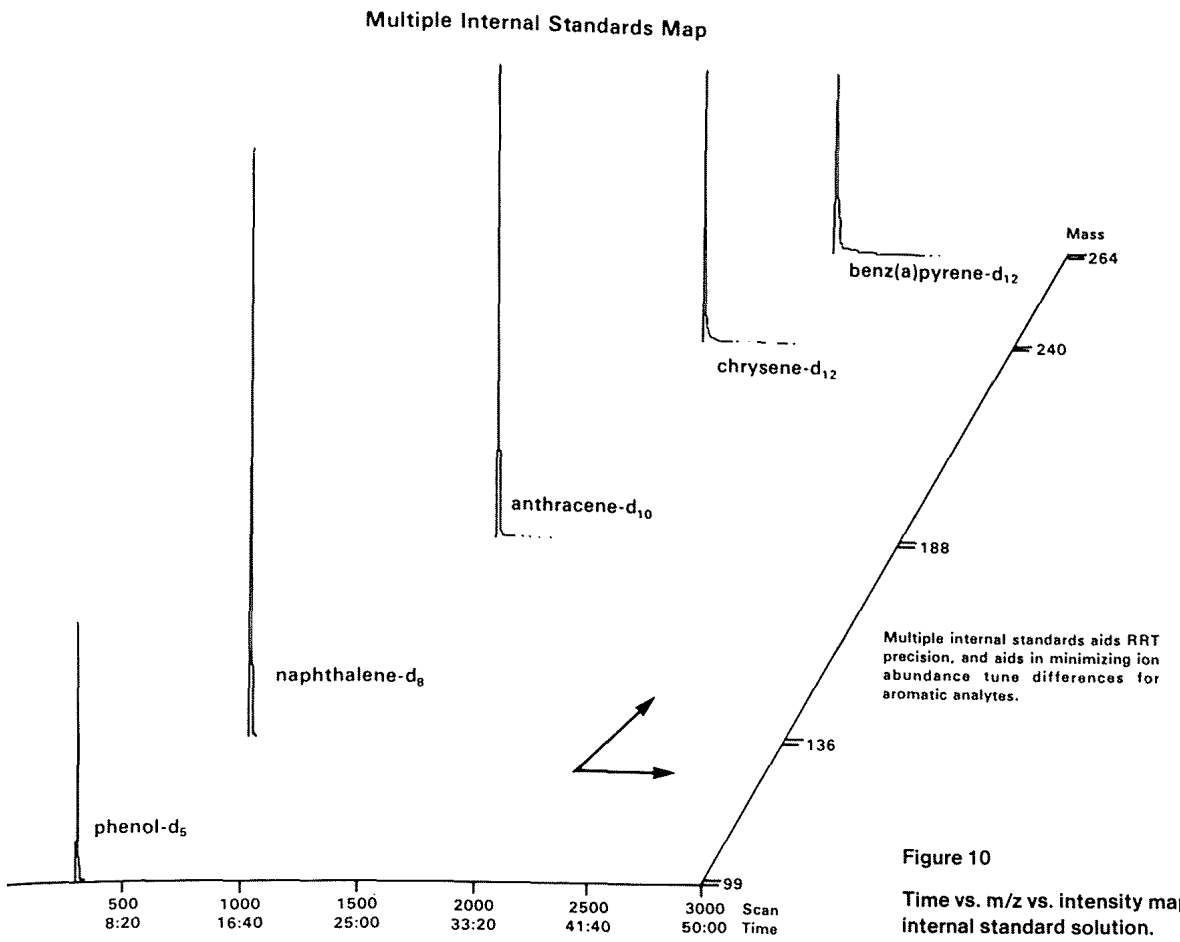

Figure 10

Time vs. m/z vs. intensity map for base peaks of five internal standard solution.

Again evidence is shown for saturation at the higher injected values at the highest EM voltage; however, excellent correlation is shown for three compounds with relatively high response factors at the lower EM voltage. It is apparent that linearity is attainable over at least two orders of magnitude using even the narrow bore (0.25 mm i.d. × 30 m) FSCC and GC/MS conditions as outlined in the experimental section of this paper. Caution is indicated because of the potential for saturation. We advise that linearity and detection criteria be demonstrated in quality assurance experiments when analyzing for priority pollutants.

3.3.3 Multiple versus Single-Level Response Factors

Response factors determined at single levels should be the same as response factors determined at multiple levels if eq. (1) applies. For the sake of this discussion, we have separated the compounds listed into two groups, those compounds with RF values calculated relative to naphthalene-d_8 and anthracene-d_{10} (Group I) and those compounds with RF factors calculated relative to chrysene-d_{12} (Group II). For Group I compounds (n = 52, see Figure 6), response factors determined at multiple levels (generally 5 through 500 ng) often agreed with single level determinations. Sixty-five percent of the compounds in Group I had multiple level mean RF values within 2 SD (single level) of the single level RF values (Figure 6). Therefore, the Group I compounds listed in Figure 6 had single and multiple level RF factors in fair agreement. The compounds in Group II showed considerably poorer agreement in single and multiple level determinations. We will address this point later.

In certain cases, we noted excellent agreement between single and multiple level RF values. For example, **Table 9** presents the response factors determined for chlorinated phenols at Laboratory II for single level (50 ng) and multiple level (5, 500 ng) experiments. This agreement was especially noteworthy in that these data were acquired in experiments at Laboratory II separated in time by one month.

3.3.4 Interlaboratory Response Factor Agreement

These experiments were repeated at Laboratory I utilizing similar FSCC GC/MS conditions, as well as the same analytical standard utilized for the data reported in Table 9. Response factors for selected Group I aromatic priority pollutants determined at both laboratories are presented in **Table 10** along with the standard deviations. Similar response factor values were observed.

Additionally, interclass trends were apparent. For example, as the degree of chlorination increased, RF values decreased for the chlorinated phenols and benzenes listed in Table 10. Moreover, for analytes with the RF values calculated from molecular ions, a RF value clustering was noted (see the nitroaromatics).

Table 10

Interlaboratory mean response factors for selected Group I aromatic priority pollutants.

m/z	Compounds	Lab I n = 3, 50 ng RF ± σ	Lab II n = 7, 50 ng, 6 day, RF ± σ
128	Naphthalene	1.05 (0.02)	1.17 (0.06)
94	Phenol	0.44 (0.05)	0.60 (0.12)
128	2-Chlorophenol	0.35 (0.04)	0.38 (0.07)
162	2,4-Dichlorophenol	0.28 (0.01)	0.24 (0.01)
196	2,4,6-Trichlorophenol	0.18 (0.01)	0.15 (0.01)
266	Pentachlorophenol	0.14 (0.01)	0.08 (0.01)
146	1,2-Dichlorobenzene	0.37 (0.04)	0.35 (0.06)
146	1,4-Dichlorobenzene	0.39 (0.05)	0.41 (0.08)
146	1,3-Dichlorobenzene	0.42 (0.05)	0.37 (0.07)
180	1,2,4-Trichlorobenzene	0.30 (0.02)	0.24 (0.01)
284	Hexachlorobenzene	0.29 (0.03)	0.12 (0.00)
123	Nitrobenzene	0.20 (0.01)	0.22 (0.01)
139	2-Nitrophenol	0.22 (0.01)	0.23 (0.01)
139	4-Nitrophenol	0.19 (0.01)	0.16 (0.02)
184	2,4-Dinitrophenol	0.09 (0.01)	0.09 (0.01)
198	2,4-Dinitro[o]cresol	0.11 (0.01)	0.11 (0.01)
89	2,4-Dinitrotoluene	0.33 (0.03)	0.20 (0.02)
63	2,6-Dinitrotoluene	0.15 (0.01)	0.14 (0.02)

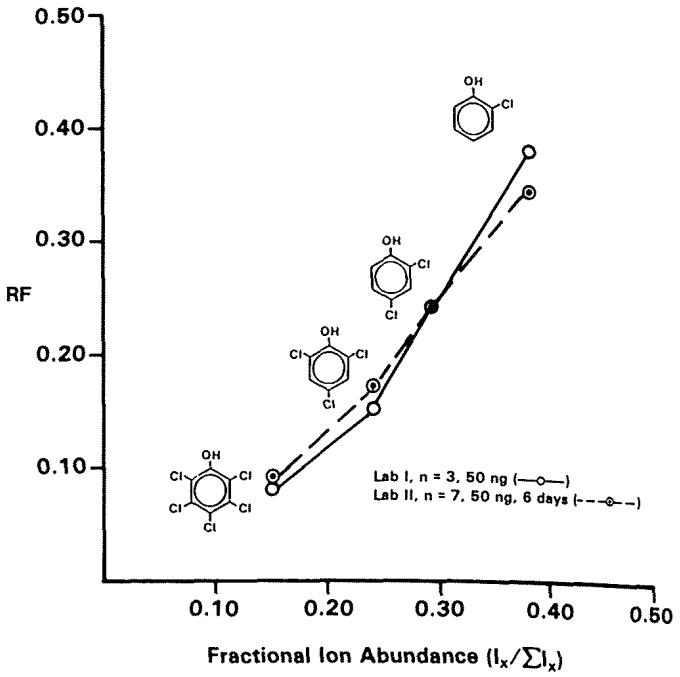

Figure 11

Fractional ion abundance vs. response factor plot for selected priority pollutant phenols.

For compounds whose interlaboratory RF agreement was poorest (e.g. phenol, pentachlorophenol, and hexachlorobenzene), it was noted that the difference (I m/z analyte – m/z internal standard I) was relatively large. Differences in ion abundance calibration could account for this trend. We suspect that this factor is the principal cause of this difference.

Figure 10 presents a three-dimensional (retention time vs. m/z vs. intensity) plot of a FSCC GC/MS acquisition for the internal standards phenol-d_5, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and benz[*a*]pyrene-d_{12}. Note that at later times the internal standard molecular ions (m/z = 99, 136, 188, 240, and 264) are at higher m/z values as are the molecular weights of analytes eluting near in time to these internal standards. This property of the multiple internal standard technique is helpful in minimizing inter- and intralaboratory RF variation for aromatic priority pollutants, presumably because the relative sensitivity is similar for adjacent m/z values. We concede that this contention is not proven by these data. These data do suggest, however, that the summation of standardization criteria employed in this work (mass calibration; ion abundance calibration via decafluorotriphenylphosphine, DFTPP [9]; multiple internal standards; and standardized ion source and FSCC parameters can generate numerically similar interlaboratory RF values even for instrumentation with significantly different hardware, as in the difference in ion detection between laboratory I and II. Any agreement in interlaboratory RF values is limited, of course, by the ion abundance calibration differences.

We forward that because FSCC are inert and can be easily coupled to the ion source, phenomena which degrade chromatographic performance are minimized. Furthermore, the multiple internal standard approach can reduce ion abundance calibration differences for aromatic priority pollutants because the difference in quantitation masses are smaller relative to the single internal standard packed column GC/MS methods of reference [1] and therefore less susceptible to ion abundance calibration differences between similar instruments. The multiple internal standard FSCC GC/MS configuration presented in this work could significantly aid in standardizing GC/MS response factors. This potential is perhaps the most noteworthy property of FSCC GC/MS. We are continuing investigations in this area.

3.3.5 Empirical Response Factor Prediction

In **Figure 11** mean RF values for chlorinated phenols acquired at Laboratories I and II are plotted versus the fractional ion abundance of the quantitation ion (determined experimentally at Laboratory I). In all cases the quantitation ion was the lowest m/z value in the molecular ion cluster.

These plots can reflect numerous factors [1) "ion abundance tune"; 2) the molar differences of analytes injected at constant weight; 3) the obvious decrease in the percentage of the ion current carried by the quantitation ion for analytes of higher degrees of chlorination; 4) substituent effects [15], 5) chromatographic and other effects].

In one set of experiments conducted at Laboratory I, mean RF values were determined for 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, and hexachlorobenzene relative to naphthalene-d_8 from 3, 50 ng/analyte injections. A quantity of 1,2,4,5-tetrachlorobenzene unknown to the analyst added to this standard (75 ng), was determined as 73 ng utilizing this approach. A straight least squares line calculated from a plot similar to Figure 11 gave a correlation coefficient of 0.9995, which allowed for calculation of concentration without employing the exact analytical standard, but rather by using other chlorinated benzenes. We do not mean to infer that all such correlations are linear, as positional isomer effects on fragmentation would be expected to degrade correlations, as might the variety of other factors presented earlier. Rather we have forwarded this empirical observation because the value of predictive capabilities in this regard is considerable and could be of great advantage in complex mixture or environmental analysis.

For example, it is impossible to standardize GC/MS systems adequately for all possible analytes of interest in complex mixture analysis. We suggest that this approach could be employed to quantitate isomeric analytes for which specific RF values were not obtained due to the lack of the appropriate standard. Moreover, we would expect that such an approach could be employed to predict RF values for highly toxic/carcinogenic materials, so that human exposure to especially hazardous organic analytes could be minimized to less hazardous positional isomers. Furthermore, for materials which are complex mixtures (e.g., polychlorinated biphenyls), such plots could be employed to estimate the quantity of individual isomeric species when standards are not readily available and when adequate mass and chromatographic resolution is demonstrated. These empirical observations are indicative of the robust nature of the FSCC GC/MS analysis configuration.

3.3.6 *Group II Analysis*

For compounds in Group II, the multiple level and single level RF values acquired at Laboratory II were not in good agreement. We suspect that differences in standard preparation (e.g., solubility problems) have adversely affected this comparison. As we noted earlier, single level precision for the latest eluting aromatic priority pollutants was considerably poorer than for those analytes with RRT_c values closer to unity. In current work we recommend the use of a late eluting internal standard to increase precision. For single level RF determination at Laboratory I (n = 8,50 ng, 3 day) using a similar FSCC GC/MS configuration and benzo[a]pyrene-d_{12} as the internal standard for dibenz[a,h]anthracene, the relative standard deviation was found to be 5.4%. Multiple level RF determinations (5, 500 ng) performed (n = 6) for dibenz[a,h]anthracene were not in good agreement with single level determinations cited above (ML RF = 0.456±0.181 and SL RF = 0.837±0.045). Deleting the lower 3 W_X values (5, 20, and 50 ng) improves the multiple level and single level RF, comparison (n = 3, ML RF = 0.62±0.03). **Figure 12** presents the ion current ratio plot for all six data points.

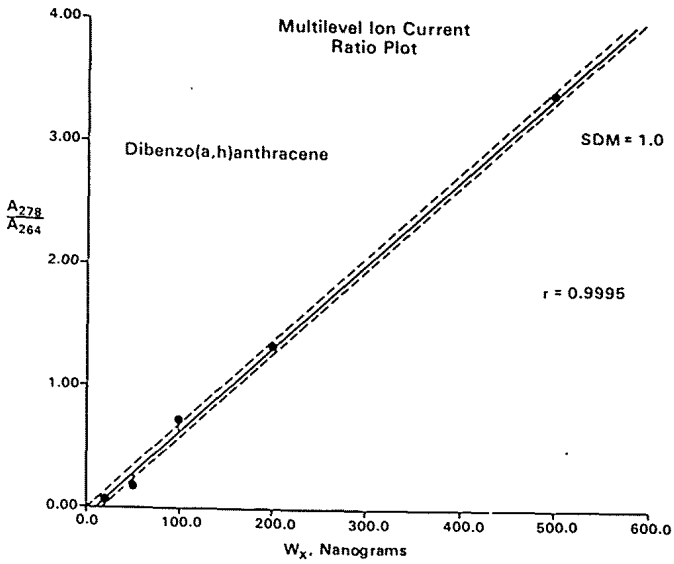

Figure 12

Ion current ratio plot of six-level dibenz[a,h]anthracene using benzo[a]-pyrene-d_{12} as internal standard.

Injector discrimination [16] could be partly responsible for this problem. Experiments increasing the septum sweep time did not increase response factors; however, response for late eluting Group II compounds have been noted to decrease when columns become contaminated presumably with residues from complex samples. Upon breaking off and discarding the first 15 cm of the column, sensitivity for the late eluting priority pollutants (see last entries in Figure 6) returns. We suggest that RF values for compounds such as dibenz[a,h]anthracene or the last internal standard can be utilized to monitor the need for column repair as a daily quality control check for routine priority pollutant analysis.

We are continuing to examine ways to minimize RF variation for late eluting polynuclear aromatic compounds. It is likely that newer capillary column injection techniques will aid single and multiple level precision for the late eluting priority pollutants. In the interim we have been employing a fifth internal standard. Initial work has utilized benz[a]pyrene-d_{12}, although we anticipate using a less carcinogenic and expensive compound which elutes nearer in time to the last three polynuclear aromatic priority pollutants in our final method.

3.3.7 Selected Packed vs. FSCC GC/MS Analysis Results

To this point we have demonstrated the properties of FSCC GC/MS analysis principally with standard solutions to describe in detail the qualitative and quantitative characteristics. It is important that FSCC GC/MS methods be equivalent to packed column methodology and practical in application. To this end, we have analyzed extracts of hazardous materials via packed column GC/MS methods [1] and the multiple internal standard FSCC GC/MS approach [3] for priority pollutant analysis of separate and composited acid and base/neutral extracts. Methylene chloride extracts of solid, potentially hazardous materials generated by a solvent extraction procedure [5] were spiked with 30 priority pollutants and analyzed three times by each configuration to examine the degree of data comparability, as well as practical considerations in an analysis of this type. Different GC/MS instrumentation was used at the participating laboratory for the packed column and FSCC GC/MS analysis so that extracts could be analyzed as close in time as possible to minimize effects of extract age. Ion abundance tuning with DFTPP was employed to minimize instrumental differences. The data acquired in this manner provide a useful comparison of packed column and the FSCC GC/MS analysis configuration.

Phenanthrene determination in the spiked base/neutral extract by Method 625 [1] and by FSCC GC/MS are presented in **Table 11**. Determinations made with the composited (acid and base/neutral extract spiked to the equivalent level) are also presented in the last row of the table. The values presented for the six samples are means of three determinations (18 acquisitions/configuration) with the standard deviations from which confidence intervals can be calculated in parenthesis. Samples 1/2 and 4/5 are duplicates. Analysis sequence was from left to right, and data were acquired at the same time for Method 625 and B/N FSCC results. Composite FSCC results were acquired as near in time to the previous data as logistically possible.

For phenanthrene, the mean of the means for each configuration was 110, 102, and 99 ng with mean SD of 9, 5, and 4 ng, respectively. Because this analyte is chemically similar to the single internal standard utilized in Method 625 (anthracene-d_{10}), this is a best case comparison of the packed column and capillary column GC/MS configurations. Within a given configuration, determinations for duplicate samples are in reasonable agreement with the exception of results for B/N FSCC for samples 4 and 5. However, the mean ± 3 SD for sample 5 for the packed column and B/N FSCC GC/MS determinations overlap (Method 625 = 106 ± 12 ng, B/N FSCC = 86 ± 15 ng). Determinations in the six samples for naphthalene are presented in **Table 12** for the same series of experiments. In accordance with Method 625, anthracene-d_{10} was employed as an internal standard for the packed column data (method 625). This configuration gave a mean SD of 15 ng. Because this extract had been spiked with multiple

Table 11

Phenanthrene results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	120(8)	116(2)	99(18)	110(4)	106(4)	102(7)
B/N FSCC	125(7)	107(4)	106(6)	106(3)	86(5)	83(6)
Composite FSCC	98(5)	97(2)	106(10)	96±(-)	94(2)	102(7)

Table 12

Naphthalene results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	95(8)	92(26)	81(17)	75(18)	81(6)	78(15)
B/N FSCC	105(4)	97(11)	92(11)	81(5)	71(2)	76(7)
Composite FSCC	91(8)	95(10)	114(16)	90(8)	102(2)	104(2)

Table 13

Dimethylnitrosamine results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	ND[a)]	ND	ND	ND	ND	ND
B/N FSCC	129(36)	56(7)	60(23)	77(3)	56(8)	53(5)
Composite FSCC	56(8)	66(11)	85(14)	52(2)	88(16)	77(3)

[a)] ND = not detected.

Table 14

Di-*n*-propylnitrosamine results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	110(16)	83(9)	49(18)	66(40)	93(29)	71(8)
B/N FSCC	99(11)	94(11)	101(5)	101(3)	99(14)	93(3)
Composite FSCC	96(4)	93(6)	88(26)	111(6)	93(6)	103(3)

Table 15

Benzidine results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	T[a)]	T	T	T	T	T
B/N FSCC	27(8)	20(7)	35(5)	36(4)	51(3)	46(2)
Composite FSCC	27(1)	27(2)	25(4)	27(1)	24(1)	28(3)

[a)] T = Trace

Table 16
Pentachlorophenol results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	60(6)	56(6)	65(12)	36(32)	58(12)	54(6)
ACI/FSCC	54(3)	52(3)	60(3)	51(1)	52(1)	77(1)
Composite FSCC	54(4)	53(3)	49(3)	54(1)	52(1)	46(8)

Table 17
Aldrin results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	42(4)	43(5)	40(8)	42(5)	46(2)	46(7)
B/N FSCC	50(5)	49(5)	46(4)	43(1)	37(4)	39(4)
Composite FSCC	61(3)	60(2)	54(2)	62(1)	62(2)	61(2)

Table 18
Dibenzo[*a,h*]anthracene results [ng].

GC/MS configuration	Sample					
	1	2	3	4	5	6
625	20(2)	17(2)	11(1)	18(6)	19(2)	18(2)
B/N FSCC	17(2)	19(1)	18(2)	17(3)	20(4)	22(6)
Composite FSCC	15(2)	17(1)	20(2)	18(1)	19(1)	24(2)

internal standards, we calculated the mean SD using the labeled analogue for the packed column experiments. The mean SD using naphthalene-d_8 was found to be 2 ng. We cite these data to point out that the use of multiple internal standards is an integral part of the FSCC GC/MS method used here. Multiple internal standards can obviously aid packed column GC/MS work as well [17].

Determinations of dimethylnitrosamine, di-*n*-propylnitrosamine and benzidine acquired in these experiments are presented in **Tables 13, 14, and 15**, respectively. Note that in eighteen packed column determinations, dimethylnitrosamine was not detected in the extract, whereas it was detected in all FSCC GC/MS experiments. Di-*n*-propylnitrosamine was detected in all the experiments; however, the mean SD was larger with the packed column experiments (Method 625 = 20 ng vs. B/N FSCC = 8 ng and composite FSCC = 9 ng). Results for benzidine are also quite poor by the packed column GC/MS method. These results are consistent with experience and demonstrate that Method 625 is prone to false negatives for the nitrogen containing priority pollutants. The occasional large standard deviations for FSCC determinations demonstrate that for these samples precision can be a problem for nitrogen-containing priority pollutants. However, false negatives were minimized.

Determinations of pentachlorophenol are presented in **Table 16**. The packed column (1% SP 1240-DA) and capillary data are in good agreement. Note, however, that the SD are generally greater for the packed column analysis of the acid extract.

Finally, **Tables 17 and 18** present the determinations of aldrin, a pesticide, and dibenzo[*a,h*]anthracene, a late eluting polynuclear aromatic priority pollutant. Inspection of these Tables shows that similar determinations were achieved with the packed and FSCC chromatographic configurations.

4 Conclusions

FSCC GC/MS analysis of composited standards and extracts has been shown to be a powerful technique for the analysis of extractable priority pollutants. The advantages of this GC/MS configuration include: reduced acquisition time for the determination of extractable priority pollutants; accurate and precise interlaboratory RRT values; low (i.e., generally less than 10%) response factor variation; a linear dynamic range of two orders of magnitude; the potential for interlaboratory RF agreement for aromatic priority pollutants; RF empirical predictive properties for chlorinated aromatic compounds; reduced quality control burden as compared to GC/MS methods which employ more than one GC column; and significantly improved data processing and data acquisition logistics, relative to reference [1]. This configuration was shown to be less likely to produce false negatives for nitrogen-containing priority pollutants. It is also practical in application, and we therefore forward that this analysis configuration is superior to the packed column method of reference [1], and consequently should be adopted for the characterization of environmental samples for extractable priority pollutants.

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