Comparison of Priority Pollutant Response Factors for Triple and Single Quadrupole Mass Spectrometers

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Seventy-four percent of the electron impact GC/MS response factors (RF) determined on a triple quadrupole mass spectrometer for 53 extractable priority pollutants were found to be within ±15% of values determined in an independent interlaboratory single quadrupole GC/MS study. Furthermore, the RF values were shown to be independent of whether quadrupole Q1 or quadrupole Q3 was scanned. The precision of RF determinations for 53 extractable priority pollutants (mean relative standard deviation 11.9%) was found to be similar to that previously published for routine GC/MS multianalyte RF determinations.

Response factors are constants utilized in the internal standard quantitative analysis of organic compounds by electron impact GC/MS in environmental analysis (*1*). For comparable injected weights, the response factor of an analyte is simply a ratio of the ion current "area" of analyte and internal standard at their respective quantitation m/z values. A series of multianalyte, multilevel response factor precision determinations can be considered as a measure of the relative sensitivity and stability of a given instrument and, hence, its quantitative capabilities. Additionally, response factor determinations encode the entire laboratory standardization procedure from standard preparation to data transcription. Therefore, response factor monitoring is an important mechanism in establishing and maintaining control of multilaboratory programs which routinely employ GC/MS for the qualitative and quantitative analysis of organic compounds.

In an attempt to standardize the GC/MS determination of priority pollutants, the "Quality Control Protocol for the Fused Silica Capillary Column GC/MS Determination of Semivolatile Priority Pollutants" was written (*2*). Observance of this protocol has been shown to yield similar response factors for extractable priority pollutants on single quadrupole mass spectrometers in a recent interlaboratory study (*3*). An intralaboratory study which compared response factors on single quadrupole mass spectrometers of different design has shown that in many cases response factors were instrument independent (*4*). Response factor monitoring has been adopted as a quality control procedure in national U.S. EPA programs that utilize GC/MS for routine priority pollutant analysis (*5*).

A model to predict response factors has recently been proposed (*5*). Predicted and observed response factors were in general agreement even without consideration of ion abundance tune differences. For 41 of the extractable priority pollutants (excluding all nitrogen-containing analytes) a mean predicted/observed response factor ratio of 1.02 ± 0.27 was reported (*5*) when tested using the interlaboratory data cited previously (*3*). While the discussion of the proposed model is beyond the scope of this paper, the establishment of a set of true response factors is of interest for at least two reasons. Firstly, the ability to predict response factors would effectively establish accuracy criteria in programs that utilize GC/MS. Secondly, a scheme to predict response factors would be useful in providing a formal procedure to give quantitative results for organic compounds identified in complex mixtures by GC/MS for which standards are not readily available.

Concurrently, analytical applications of triple quadrupole mass spectrometry (TQMS) are becoming commonplace. The potential of TQMS for the direct analysis of mixtures with minimal sample preparation and without chromatographic separations has been shown (*6*). Others have indicated that TQMS mixture analysis can often benefit from prior chromatographic separations (*7*). Obviously, direct mixture analysis by TQMS affords significant logistical advantages over TQMS methods which employ chromatographic separations and is therefore preferred. Nevertheless, we anticipate that chromatographic TQMS configurations will be useful in minimizing sample matrix effects and in providing ancillary quantitative data to confirm assignments made by TQMS mixture screening schemes.

Because of our interest in standardizing and predicting GC/MS response factors, and as we are also evaluating the potential of TQMS for characterizing hazardous materials, it was of interest to compare response factors acquired on a TQMS system with response factors previously determined in an interlaboratory GC/MS study.

EXPERIMENTAL SECTION

Standards. The analytical standards of extractable priority pollutants were prepared by Radian Corp. under U.S. EPA Contract No. 68-03-2765 and have been described elsewhere (*8*). For this work a standard was prepared consisting of acid, base/neutral, and pesticide priority pollutants in methylene chloride at a nominal concentration of 150 ng μL^{-1} per analyte. This standard was diluted to give two additional standards containing 100 and 25 ng μL^{-1} per analyte. The internal standards, phenol-2,4,6-d_3, naphthalene-d_8, phenanthrene-d_{10}, chrysene-d_{12}, and benzo[a]pyrene-d_{12} were added to each standard prior to dilution to give nominal concentrations/internal standard of 20, 20, 26, 40, and 40 ng/μL, respectively, in each of the three composite standards. The ion abundance calibrant (decafluorotriphenyl)phosphine (DFTPP) was purchased from P.C.R. Inc., Gainesville, FL.

Instrumentation. The GC/TQMS data were acquired on a Finnigan triple stage quadrupole mass spectrometer (TSQ) equipped with 4500 series ion source and a continuous dynode electron multiplier with the conversion dynode maintained at −3.0 kV. Gas chromatography was performed on a fused silica capillary column (30 m × 0.24 mm i.d., 0.25 μm thick SE-54 phase; J. and W. Scientific Inc., Rancho Cordova, CA) coupled directly to the ion source. A Finnigan 9610 gas chromatograph with Grob-type split/splitless injector under data system control was used to provide splitless injections. After 30 s the split and sweep valves were opened. The carrier gas was helium at a column head pressure of 26 psig. The split and septum sweep flow rates were 35 and 10 mL min^{-1}, respectively, and carrier gas linear velocity was 60 cm s^{-1} at 30 °C. Initial column temperature was held at

Table II. Response Factor, Relative Standard Deviation Values Determined on Q3 Scanned TQMS[a]

	% RSD		% RSD
N-nitrosodimethylamine	19.5	acenaphthene	8.2
bis(2-chloroethyl) ether	9.7	2,4-dinitrophenol	44.0
2-chlorophenol	12.5	2,4-dinitrotoluene	9.8
phenol	9.2	4-nitrophenol	12.0
1,3-dichlorobenzene	6.2	fluorene	9.9
1,4-dichlorobenzene	11.4	4-chlorophenyl phenyl ether	8.9
1,2-dichlorobenzene	9.1	diethyl phthalate	8.3
bis(2-chloroisopropyl) ether	9.0	4,6-dinitro-*o*-cresol	19.9
hexachloroethane	13.0	*N*-nitrosodiphenylamine	11.6
N-nitrosodi-*n*-propylamine	8.5	4-bromophenyl phenyl ether	13.3
nitrobenzene	17.5	hexachlorobenzene	10.1
isophorone	11.7	pentachlorophenol	11.2
2-nitrophenol	10.6	phenanthrene	4.5
2,4-dimethyl phenol	16.1	anthracene	7.6
bis(2-chloroethoxy)methane	10.7	dibutyl phthalate	7.7
2,4-dichlorophenol	6.9	fluoranthene	15.0
1,2,4-trichlorobenzene	11.1	pyrene	9.8
naphthalene	13.2	benzidine	10.5
hexachlorobutadiene	12.6	butyl benzyl phthalate	4.7
4-chloro-*m*-cresol	5.4	benz[*a*]anthracene	5.3
hexachlorocyclopentadiene	11.7	chrysene	8.5
2,4,6-trichlorophenol	8.9	3,3'-dichlorobenzidine	4.0
2-chloronaphthalene	15.8	bis(2-ethylhexyl) phthalate	19.7
acenaphthylene	13.3	di-*n*-octyl phthalate	24.8
dimethyl phthalate	18.0	benzo[*a*]pyrene	8.9
2,6-dinitrotoluene	19.0	dibenz[*a,h*]anthracene	11.2
		benzo[*g,h,i*]perylene	10.0

[a] $N = 9$, triplicate determinations at 25, 100, and 150 ng over a 3-day acquisition period.

origin. Despite this anomaly these data indicate that RF values acquired within the criteria of the QC protocol are not greatly affected by the additional ion optics of the TQMS. Interlaboratory and intralaboratory comparisons of this type are complicated by the higher average variance of the former data set. For analytes of equal variance, instrumental sensitivity differences can cause RF values to be formally nonequivalent. For example, the RF values determined for bis(2-chloroethyl) ether by GC/MS and GC/TQMS were 1.01 ± 0.10 and 0.87 ± 0.08, respectively. At the 95% confidence level these mean values are statistically nonequivalent, and an argument could be made that chromatographic and/or spectroscopic sensitivity differences were observed. The fact that the mean RF values for this compound are not greatly different indicates that the relative sensitivity differences were not large. The observation that the difference in mean values is often not large can be seen by inspection of Table I. It should be noted that these RF values were calculated with reference internal standards which had been selected to minimize the relative retention time and the quantitation mass difference between analyte and internal standard. Therefore, many of the compounds with small quantitation mass differences would quite likely be poor indicators of relative sensitivity differences between single and triple quadrupole mass spectrometers. However, reviewing selected analytes from Table I with relatively wide differences in quantitation mass between analyte and internal standard, e.g., the dichlorobenzenes (m/z 146 vs. phenol-2,4,6-d_3, m/z 97), hexachlorobutadiene (m/z 225 vs. naphthalene-d_8, m/z 136), and hexachlorobenzene (m/z 284 vs. phenanthrene-d_{10}, m/z 188), it can be seen that no major relative sensitivity differences were observed which could not be accounted for by ion abundance tune differences. Also, because the TQMS-generated RF values were acquired in triplicate at 25, 100, and 150 ng μL^{-1} per analyte and the RF determinations for these analytes at multiple levels were precise (i.e., 6.2, 11.4, 9.1, 12.6, and 10.1 percent relative standard deviation), significant sensitivity differences were not observed over the mass and injected weight range of these experiments. In fact, the integrated ion currents for these analytes were of similar magnitude to those obtained in routine GC/MS analysis using similar detection apparatus. This observation suggested that significantly lower quantities of these analytes could have been readily detected and quantified. Because the objective was to compare the TQMS data to data acquired in a previous interlaboratory GC/MS study, lower analyte concentrations were not examined.

The fractional ion abundance (the ratio of the quantitation m/z "area" to the total ion "area") of the quantitation m/z value is an indicator of mass dependent relative sensitivity differences. The fractional ion abundance of the quantitation mass of hexachlorobenzene (m/z 284) was determined for each acquisition of the GC/MS data (three acquisitions in each of four laboratories) and found to be 14.6 ± 1.3%. For the nine RF acquisitions with the TQMS (Q3 scanned), the fractional ion abundance of m/z 284 of hexachlorobenzene was found to be similar, i.e., 13.4 ± 1.1%; the fragmentation pattern did not show any mass dependent spectral skewing. TQMS-generated electron impact mass spectra were found to be similar to spectra acquired on a single quadrupole mass spectrometer when both were tuned to meet DFTPP ion abundance criteria.

GC/TQMS Precision. To examine the stability of the TQMS, we calculated the relative standard deviation of the response factors in the nine Q3-scanned acquisitions taken over a 3-day period. These data are presented in Table II for 53 extractable priority pollutants. The average relative standard deviation, 11.9%, is similar to the multiday RF determination precision (mean RSD 11.4%) previously published for similar GC/MS determinations (*1*). This precision level approaches the short-term consecutive injection precision, RSD 7.0%, considered acceptable in GC/MS instrument evaluation tests (*12*). It is noteworthy that the combination of rapid (1.0 s, 40–475 amu) scanning and sample introduction (via FSCC) and the additional ion optics of the TQMS do not appear to affect the RF values. Furthermore, as the relative standard deviation for many of the analytes studied was low, the stability of the TQMS in practice was found to be excellent. On the basis of these results, the utilization of the TQMS for routine multianalyte quantitative and qualitative

Table I. Mean Response Factor Comparison of GC/TQMS to Interlaboratory GC/MS Values

	IS[a]	GC/TQMS[b]	GC/MS[c]		IS[a]	GC/TQMS[b]	GC/MS[c]
N-nitrosodimethylamine	d3	0.43	0.42	acenaphthene	d10	0.94	0.81
bis(2-chloroethyl) ether	d3	0.87	1.01	2,4-dinitrophenol	d10	0.11	0.07
2-chlorophenol	d3	0.72	0.79	2,4-dinitrotoluene	d10	0.30	0.23
phenol	d3	1.02	1.10	4-nitrophenol	d10	0.17	0.10
1,3-dichlorobenzene	d3	0.64	0.72	fluorene	d10	1.15	0.96
1,4-dichlorobenzene	d3	0.77	0.90	4-chlorophenyl phenyl ether	d10	0.53	0.47
1,2-dichlorobenzene	d3	0.62	0.75	diethyl phthalate	d10	0.85	0.91
bis(2-chloroisopropyl) ether	d3	0.19	0.22	4,6-dinitro-*o*-cresol	d10	0.13	0.10
hexachloroethane	d3	0.37	0.35	*N*-nitrosodiphenylamine	d10	0.65	0.58
N-nitrosodi-*n*-propylamine	d8	0.08	0.05	4-bromophenyl phenyl ether	d10	0.25	0.24
nitrobenzene	d8	0.18	0.19	hexachlorobenzene	d10	0.27	0.24
isophorone	d8	0.76	0.84	pentachlorophenol	d10	0.14	0.13
2-nitrophenol	d8	0.21	0.22	phenanthrene	d10	1.32	1.16
2,4-dimethylphenol	d8	0.35	0.32	anthracene	d10	1.21	1.15
bis(2-chloroethoxy)methane	d8	0.44	0.51	dibutyl phthalate	d10	1.29	1.28
2,4-dichlorophenol	d8	0.29	0.30	fluoranthene	d10	1.05	1.07
1,2,4-trichlorobenzene	d8	0.30	0.32	pyrene	d10	1.13	1.08
naphthalene	d8	1.13	1.08	benzidine	d12	0.81	0.24
hexachlorobutadiene	d8	0.13	0.13	butyl benzyl phthalate	d12	0.70	0.84
4-chloro-*m*-cresol	d8	0.28	0.26	benz[*a*]anthracene	d12	1.17	1.11
hexachlorocyclopentadiene	d8	0.15	0.15	chrysene	d12	1.03	1.02
2,4,6-trichlorophenol	d8	0.19	0.19	3,3'-dichlorobenzidine	d12	0.40	0.28
2-chloronaphthalene	d8	0.65	0.63	bis(2-ethylhexyl) phthalate	d12	0.73	0.88
acenaphthylene	d8	0.42	0.72	di-*n*-octyl phthalate	d12	1.00	1.34
dimethyl phthalate	d8	0.59	0.62	benzo[*a*]pyrene	d12B	1.06	1.00
2,6-dinitrotoluene	d8	0.15	0.15	dibenz[*a,h*]anthracene	d12B	0.56	0.58
				benzo[*g,h,i*]perylene	d12B	0.59	0.64

[a] The internal standards employed for response factor calculation were phenol-$2,4,6$-d_3 (d3), naphthalene-d_8 (d8), phenanthrene-d_{10} (d10), chrysene-d_{12} (d12), and benzo[*a*]pyrene-d_{12} (d12B). [b] RF values determined in triplicate at 25, 100, and 150 ng/μL using TQMS (Q3 scanned). [c] RF values determined in interlaboratory GC/MS study using single quadrupole MS device.

30 °C for 4 min and then raised at 10 °C min^{-1} and maintained at 270 °C until all components had eluted. Total GC run time was ca. 38 min.

The conditions for electron impact ionization mass spectrometry were as follows: electron energy, 70 eV; emission current, 0.40 mA; source temperature, 90 °C. For the RF determinations, two adjacent quadrupoles (Q1 and Q2; Q2 and Q3) were operated in the all-pass (radio-frequency-only) mode while the third quadrupole (Q3 or Q1, respectively) repetitively scanned the range m/z 40–475 in 0.95 s. The instrument was tuned to meet DFTPP ion abundance criteria (*9*).

Data System. Data acquisition was performed under control of Finnigan MAT TSQ Rev. B software with a Data General NOVA-4 minicomputer and a Control Data Corp. cartridge module disk drive. Computer generated areas were used for quantitation of analytes and internal standards. Subsequent calculations for RF, mean RF, and relative standard deviation were performed via calculators.

Qualitative identification of analytes was accomplished by reference to published relative retention times and library (EPA/NIH Mass Spectral Data Base) matches via resident software together with manual interpretation and verification.

RESULTS AND DISCUSSION

In early work with triple quadrupole mass spectrometers, it was reported that large ion signal losses can occur in systems with aperture separated, independently driven rod systems (*10*). The highest ion transmission was reported for closely spaced rod systems where the radio frequency component of each rod set was synchronized in frequency and phase. It has recently been reported that theoretical and experimental data indicate that "properly designed" instruments provide high ion transmission (*11*). However, the same study has indicated that for instruments where ions leave and reenter the quadrupole field through restrictive apertures, ion transmission can be reduced.

Relative ion transmission is encoded in multianalyte, multilevel response factors. Response factor precision determinations provide information about instrument stability and performance. However, as these factors are relative measures, fundamental ion transmission characteristics are largely obscured. Nevertheless, response factor determinations acquired under rapid source introduction and scanning modes provide useful experimental insight into the quantitative properties of TQMS.

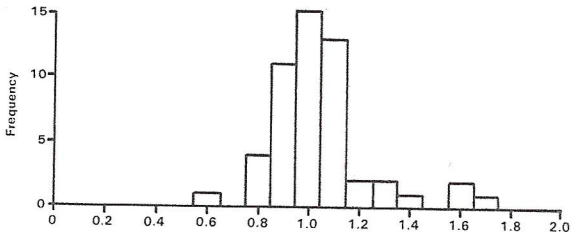

Figure 1. Distribution of response factor ratios, TQMS (Q-3 scan)/Interlaboratory GC/MS, does not include benzidine (3.38).

Table I shows the response factors for 53 acid and base/neutral extractable priority pollutants determined by GC/TQMS (Q3 scanned) and RF values previously determined in an interlaboratory GC/MS study (*3*). Figure 1 shows the distribution of TQMS/GCMS response factor ratios. Seventy-four percent of the RF values determined on the TQMS were within ±15% of the mean RF values determined in the interlaboratory single quadrupole GC/MS study. The RF value for benzidine differed greatly from the interlaboratory GC/MS value. As this analyte had the second highest interlaboratory GC/MS RF RSD (47.0%), the RF value for this compound was imprecisely determined in the GC/MS work. We were not surprised at this discrepancy because we have previously encountered and discussed GC/MS analysis problems with this analyte (*1*, *3*). Also, because other analyte, internal standard pairs had similar RF values for comparable mass ranges, the difference in GC/MS and GC/TQMS RF values for benzidine was thought to be of nonspectroscopic

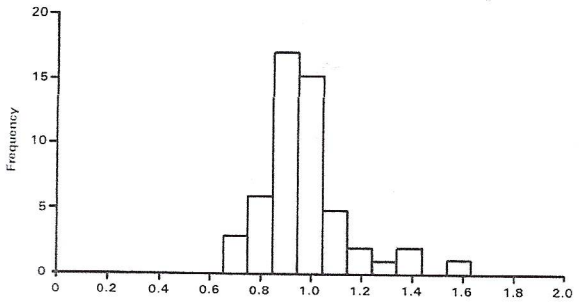

Figure 2. Distribution of response factor ratios, TQMS (Q3-scan)/TQMS (Q1-scan), does not include dibenz[*a*,*h*]anthracene (2.07).

FSCC GC/MS determinations of organic compounds, if required, is viable.

Q1-Scanned GC/TQMS Response Factors. In those instruments with interquadrupole lenses the ion beam leaves and reenters the quadrupole field and is therefore susceptible to fringe field effects (*10*, *11*). Hunt et al. (*13*) have reported decreased negative ion sensitivity at m/z 614 when Q1 rather than Q3 was scanned on an instrument of this type and attributed this result to fringe field effects. Dawson has also indicated that the highest absolute sensitivity of a triple quadrupole mass spectrometer is obtained when Q3 is scanned, with Q1 and Q2 in the radio-frequency-only mode (*14*). To determine if RF values were dependent on which quadrupole was scanned, we acquired the RF values for priority pollutants as before except that Q1 was scanned with Q2 and Q3 in the all-pass radio-frequency-only mode. Many values determined in this acquisition mode were in close agreement with Q3 values. For 48 of the extractable priority pollutants (excluding 4-nitrophenol, 2,4-dinitrophenol, 4,6-dinitro-*o*-cresol, benzidine, and 3,3′-dichlorobenzidine, analytes with high interlaboratory GC/MS RF relative standard deviations) the Q3/Q1 mean RF ratio was 1.02 with a relative standard deviation of 17.2% (Figure 2). Within the mass and injected weight ranges and ion abundance tune of this study, the relative sensitivities of analyte and internal standard are independent of which quadrupole (Q1 or Q3) is scanned. These observations are thought to arise because the multiple internal standards tend to minimize spectroscopic and chromatographic sensitivity differences between analyte and internal standard. While fundamental ion transmission characteristics are obscured by this approach, the practical observation that TQMS response factors and response factor precision are similar to routine GC/MS determinations is valuable. These data indicate that multianalyte, multilevel quantitative TQMS determinations in mixture analysis should be comparable to quantitative GC/MS data.

Since the RF values determined with the TQMS are shown to be in general agreement with values determined with single quadrupole instruments, it is apparent that the predictive response factor scheme (*5*) is applicable to the TQMS. Therefore, for analytes which can be introduced via FSCC, the ability to provide quantitative estimates for analytes whose structure has been determined via collision activated dissociation techniques is anticipated. Such results are of considerable potential in the qualitative and quantitative deconvolution of complex mixtures by triple quadrupole mass spectrometry. We further expect that with a LC/TQMS QC protocol of similar design, the predictive scheme should be applicable to organic analytes which are not amenable to analysis by gas chromatography.

Registry No. *N*-Nitrosodimethylamine, 62-75-9; bis(2-chloroethyl) ether, 111-44-4; 2-chlorophenol, 95-57-8; phenol, 108-95-2; 1,3-dichlorobenzene, 541-73-1; 1,4-dichlorobenzene, 106-46-7; 1,2-dichlorobenzene, 95-50-1; bis(2-chloroisopropyl) ether, 39638-32-9; hexachloroethane, 67-72-1; *N*-nitrosodi-*n*-propylamine, 621-64-7; nitrobenzene, 98-95-3; isophorone, 78-59-1; 2-nitrophenol, 88-75-5; 2,4-dimethylphenol, 105-67-9; bis(2-chloroethoxy)methane, 111-91-1; 2,4-dichlorophenol, 120-83-2; 1,2,4-trichlorobenzene, 120-82-1; naphthalene, 91-20-3; hexachlorobutadiene, 87-68-3; 4-chloro-*m*-cresol, 59-50-7; hexachlorocyclopentadiene, 77-47-4; 2,4,6-trichlorophenol, 88-06-2; 2-chloronaphthalene, 91-58-7; acenaphthylene, 208-96-8; dimethyl phthalate, 131-11-3; 2,6-dinitrotoluene, 606-20-2; acenaphthene, 83-32-9; 2,4-dinitrophenol, 51-28-5; 2,4-dinitrotoluene, 121-14-2; 4-nitrophenol, 100-02-7; fluorene, 86-73-7; 4-chlorophenyl phenyl ether, 7005-72-3; diethyl phthalate, 84-66-2; 4,6-dinitro-*o*-cresol, 534-52-1; *N*-nitrosodiphenylamine, 86-30-6; 4-bromophenyl phenyl ether, 101-55-3; hexachlorobenzene, 118-74-1; pentachlorophenol, 87-86-5; phenanthrene, 85-01-8; anthracene, 120-12-7; dibutyl phthalate, 84-74-2; fluoranthene, 206-44-0; pyrene, 129-00-0; benzidine, 92-87-5; butyl benzyl phthalate, 85-68-7; benz[*a*]anthracene, 56-55-3; chrysene, 218-01-9; 3,3′-dichlorobenzidine, 91-94-1; bis(2-ethylhexyl) phthalate, 117-81-7; di-*n*-octyl phthalate, 117-84-0; benzo[*a*]pyrene, 50-32-8; dibenz[*a*,*b*]anthracene, 53-70-3; benzo[*g*,*h*,*i*]perylene, 191-24-2.

LITERATURE CITED

(1) Sauter, A. D.; Betowski, L. D.; Smith, T. R.; Strickler, V. A.; Beimer, R. G.; Colby, B. N.; Wilkinson, J. E. *HRC CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1981**, *4*, 366–384.
(2) Lopez-Avila, V.; Sauter, A. D. Presented at the 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, HI, June 6–11, 1982.
(3) Sauter, A. D.; Mills, P. E.; Fitch, W. L.; Dyer, R. *HRC CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1982**, *5*, 27–30.
(4) Smith, T.; Mosesman, N. H.; Sauter, A. D. Presented at the 1982 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, Atlantic City, NJ, March 1982.
(5) Sauter, A. D.; Fitch, W. L.; Lopez-Avila, V. Presented at the 1982 American Chemical Society Meeting, Las Vegas, NV, March 1982.
(6) Hunt, D. F.; Shabanowitz, J.; Harvey, T. M.; Coates, M. Presented at the 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, HI, June 6–11, 1982.
(7) Henion, J. D.; Skrabalak, D. S.; Thomson, B. A. Presented at the 30th Annual Conference on Mass Spectrometry and Allied Topics, Honolulu, HI, June 6–11, 1982.
(8) "Repository Services for Priority Pollutants, Toxic Pollutants and Chromatographic Materials"; Progress Report for April–June 1981, Radian Corp.; U.S. EPA Contract No. 68-03-2765.
(9) Eichelberger, J. W.; Harris, L. E.; Budde, W. L. *Anal. Chem.* **1975**, *47*, 995–1000.
(10) Dawson, P. H. European Patent Application 80302635.0, 1980.
(11) Dawson, P. H.; Fulford, J. E. *Int. J. Mass. Spectrom. Ion Phys.* **1982**, *42*, 195.
(12) Budde, W. L.; Eichelberger, J. W. EPA-600/4-80-025. U.S. EPA, Cincinnati, OH, April 1980.
(13) Hunt, D. F.; Shabanowitz, J.; Giordani, A. B. *Anal. Chem.* **1980**, *52*, 386–390.
(14) Dawson, P. H.; French, J. B.; Buckley, J. A.; Douglas, D. J.; Simmons, D. *Org. Mass Spectrom.* **1982**, *17*, 205–211.

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