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DETERMINATION OF POLYCHLORINATED BIPHENYLS USING LIMITED MASS SCAN GAS CHROMATOGRAPHY–MASS SPECTROMETRY*

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SUMMARY

In time-programmed limited mass scan gas chromatography–mass spectrometry, discrete portions of the mass range are selected to monitor the presence of characteristic groups of ions. The selection of the mass ranges monitored is adjusted automatically during chromatography to match the elution times of compounds of interest.

This report describes the application of automated limited mass scan gas chromatography–mass spectrometry in conjunction with glass capillary gas chromatography for determination of polychlorinated biphenyls (PCBs) in process streams and environmental samples. The approach provides an optimal trade-off of sensitivity and selectivity for determination of (PCBs) with electron impact ionization or negative ion chemical ionization mass spectrometry. The reduction of interferences may allow less rigorous sample pretreatment and concentration steps and increase the confidence of peak assignments.

INTRODUCTION

In May, 1979, the United States Environmental Protection Agency set a limit of 50 ppm on polychlorinated biphenyls (PCBs) in process streams and products[1]. In addition, the method of disposal of matrices containing PCBs is regulated by the level of these contaminants[2]. There are 209 possible chlorinated biphenyls containing from one to ten chlorine atoms. Most PCBs were intentionally produced for uses such as transformer oil; however, PCBs can be formed unintentionally as by-products of process trace chemistries. This is especially true where chlorinated aromatics are used as solvents. For example, PCBs containing four to seven chlorines and decachlorobiphenyl were often found in copper phthalocyanine blue and green pigments when trichlorobenzene was used as a solvent in their manufacture[3]. The number of PCBs and the complex matrices presented to the analyst make high-resolution chro-

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matography with selective detection necessary to discriminate PCBs from other components of the sample matrix.

Sample preparation often involves dissolving the sample in concentrated sulfuric acid, extraction of PCBs with *n*-hexane, and concentration of the extract. When a total PCB number is desired, perchlorination techniques can be used to form decachlorobiphenyl plus chlorinated matrix by-products[4]. Only the decachlorobiphenyl needs to be quantitated and it usually elutes much farther from common interferences than partially chlorinated PCBs. The sensitivity of the measurement is also increased by converting all PCBs into a single, easily measured species. However, biphenyl is a positive interference in this procedure. An electron-capture detector is normally used to enhance sensitivity and selectivity, as can the more expensive, less often used, negative ion chemical ionization (NICI) mass spectrometry (MS).

Tindall and Wininger[5] have used a limited mass scan technique for PCB analysis. We extended their work by using high resolution capillary gas chromatography (GC) in conjunction with automated time-programmed limited mass scanning. In this technique, only three 11-amu windows are scanned instead of a continuous 50–550 a.m.u. full scan range or single ions. The data system controls selection of three mass windows out of the total of ten (corresponding to one to ten chlorines) mass windows monitored at a particular instant during the chromatogram. The selection of the group of mass windows monitored at a particular time is based upon the expected span of retention times for each molecular weight family of PCBs. As the chromatographic run progresses, the mass window for the lowest-molecular-weight family is dropped and the mass window for the next higher-molecular-weight family of PCBs is added.

The use of time-programmed limited mass scan is intended to provide an optimized trade-off between qualitative power and raw sensitivity. The limited mass scan spectra are somewhat more vulnerable to misinterpretation than are full scan spectra and the technique has less raw sensitivity than single ion monitoring of the most intense ion. However, this technique provides much better signal-to-noise ratio (S/N) than the full scan approach, and substantially higher qualitative information than the single ion monitoring (SIM) approach. Some of the S/N advantage lost by scanning over a total of 33 a.m.u. is "regained" by only interrogating the molecular ion region corresponding to those species expected to elute during that time and by using the sum of the three most intense ions in the chlorine isotope cluster. Other polychlorinated species (or electron-capturing non-chlorinated species) such as polychlorinated naphthalenes, polychlorinated terphenyls, pesticides, chlorinated benzenes, polychlorodibenzofurans and dibenzo-*p*-dioxins as well as halogenated analogues or alternation products are less likely to interfere[6]. This may also result in less rigorous sample workup than for conventional PCB analysis.

Limited mass scan has a definite qualitative advantage over techniques which employ SIM for quantitation. Using an 11-a.m.u. window enables the entire isotope cluster of a specific PCB to be scrutinized for the isotopic abundances characteristic of a given number of chlorine atoms, leading to fewer false positive assignments of PCBs. Three mass ranges are monitored "simultaneously" owing to the non-sequential and overlapping elution of some PCBs with differing numbers of chlorine atoms[9,10]. In addition, the exact mass chromatograms (± 0.5 of the exact isotopic mass) of the three most intense ions in the molecular ion region are summed to make

up some of the sensitivity lost by not scanning a single ion. Use of the exact mass chromatogram also reduces uncertainties which may result from the substantial negative mass defect of the more highly chlorinated PCBs, *i.e.*, the discontinuities in mass chromatograms mentioned by other investigators[5] are reduced. Thus, this technique has sensitivity similar to, but less than, that of GC–electron-capture detection (ECD) and SIM due to increased ion statistics (limited mass scan range) and quantitation based on ion summation, while being much more selective (fewer false positives) in true assignments of PCBs than the aforementioned, commonly used techniques.

EXPERIMENTAL

Reagents

The chromatographic solvent used was HPLC-grade, distilled-in-glass *n*-hexane (Fisher). Concentrated sulfuric acid was reagent grade (Fisher). Individual PCBs were purchased from Ultra Scientific (Hope, RI) and standards prepared from them in *n*-hexane at *ca.* 2 ppm per individual species. Dilutions were made with the same grade *n*-hexane. Decafluorotriphenylphosphine (DFTPP) from Aldrich was made at 10 ppm in *n*-hexane for internal standard use. Ultrapure methane (Matheson) was used in NICI experiments and Grade A Helium (Liquid Carbonic) as the GC carrier gas.

Extraction method

A 1-g portion of sample is dissolved in 150 ml of concentrated sulfuric acid and 20 ml of *n*-hexane added and stirred for 0.25 h. The hexane layer is concentrated in a Kuderna–Danish evaporator to 1 ml final volume. In the case of samples which are perchlorinated, trichlorotrifluoroethane ("Freon" 113) saturated with chlorine gas with a ferric chloride catalyst is used in the procedure described by Goldberg and Buchta[4]. DFTPP can be added at the 10-ppm level as an internal standard if desired. (Samples in non-polar solvents may be dissolved in hexane and concentrated without undergoing the sulfuric acid dissolution step.)

Apparatus

The gas chromatograph–mass spectrometer used is a Finnigan Model 4023 microprocessor-controlled, quadrupole GC–MS instrument equipped with the pulsed positive, negative ion chemical ionization accessory and a dual terminal Incos 2300 series data system. The normal analytical column was a 50 m × 0.4 mm I.D. Chrompack CP-SIL-5 glass capillary column (methyl silicone stationary phase) with a 0.4-μm film thickness. Operating conditions are as follows: temperature program, 165°C to 290°C at 6°C/min with a final 8-min hold at the maximum temperature; head pressure, 15 p.s.i.; linear velocity, 40 cm/sec; septum purge, 3 ml/min; split flow-rate, 45 ml/min; splitless time for Grob injection, 48 sec; sample injection volume, 2 μl; injector temperature, 250°C; separator temperature, 225°C; ionizer temperature, 300°C. The interface to the mass spectrometer is a jet separator with helium makeup gas for the wide bore capillary or direct connection to the ion source with fused silica columns.

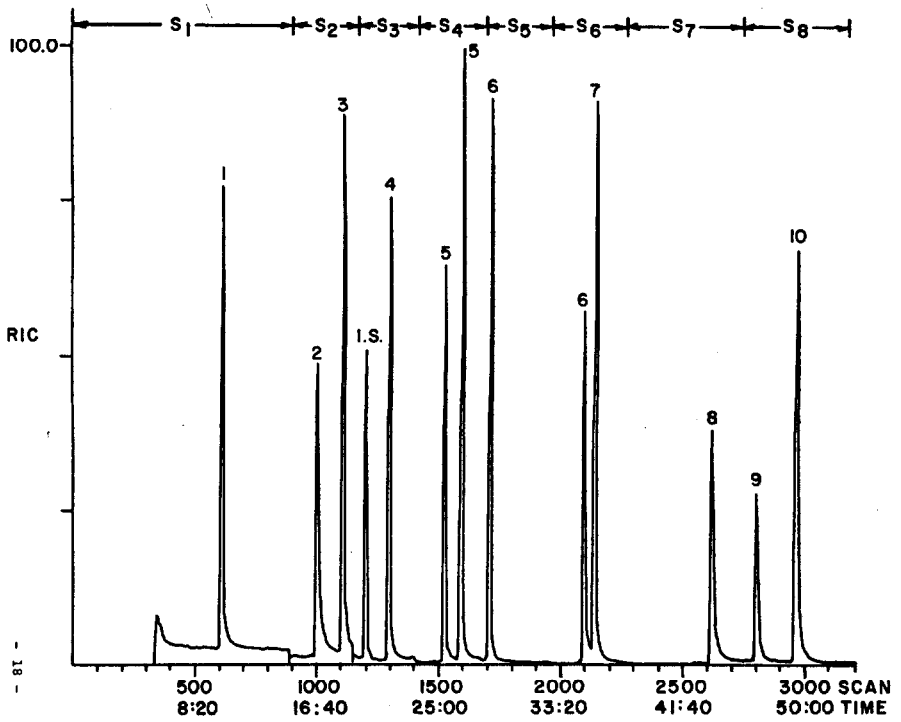

Fig. 1. Reconstructed ion chromatogram (RIC) of twelve-component PCB standard mixture (*ca.* 1 ppm each) by electron impact ionization and limited mass scanning technique. Chromatographic conditions are given in text. Internal standard (I.S.) is DFTPP at 10 ppm. The "S" regions refer to scan descriptors in Table I. Time in min:sec.

Calibration procedure

Calibration is performed daily using a 12-component PCB standard containing 0.6–1.0 ppm of each species or the 12-component standard spiked with 10-ppm DFTPP internal standard (see Fig. 1). A chromatogram is obtained using the mass window groups listed in Table I. Fig. 1 shows the selection of window groups during the chromatographic run. The areas of the mass chromatograms for the three most intense ions in the chlorine isotope cluster corresponding to the molecular ion for each PCB are summed (except for monochlorobiphenyl where only the two most intense ions were used). The same injection volume is used for both standards and samples. A subset of the descriptors listed in Table I can be used for samples which are known to contain only a known range of chlorines per PCB molecule.

RESULTS

Detection limits

Table II shows typical lower limits of detection for PCBs as determined from two times the average peak-to-peak noise value for electron impact (EI) mass scan and NICI operation. Despite the limited mass scan operation, peaks other than PCBs can influence the minimum detectable limits for the PCBs if they fall into the mass spectral scan range.

TABLE I

LIMITED MASS SCAN GROUPS FOR MONOCHLORO- TO DECACHLOROBIPHENYLS

Total scan time of 1.000 sec is used for each group. The actual scan time for each mass window within the group is 0.290 to 0.292 sec. MW = Molecular weight.

Group	*Mass window*	*Begin mass*	*End mass*	*Comments*
S1	1	185.500	196.500	Mono MW 188
	2	219.500	230.500	Di MW 222
	3	253.500	264.500	Tri MW 256
S2	1	219.500	230.500	Di MW 222
	2	253.500	264.500	Tri MW 256
	3	287.500	298.500	Tetra MW 290
S3	1	253.500	264.500	Tri MW 256
	2	287.500	298.500	Tetra MW 290
	3	321.500	332.500	Penta MW 324
S4	1	287.500	298.500	Tetra MW 290
	2	321.500	332.500	Penta MW 324
	3	355.500	366.500	Hexa MW 358
S5	1	321.500	332.500	Penta MW 324
	2	355.500	366.500	Hexa MW 358
	3	389.500	400.500	Hepta MW 392
S6	1	355.500	366.500	Hexa MW 358
	2	389.500	400.500	Hepta MW 392
	3	423.500	434.500	Octa MW 426
S7	1	389.500	400.500	Hepta MW 392
	2	423.500	434.500	Octa MW 426
	3	457.500	468.500	Nona MW 460
S8	1	423.500	434.500	Octa MW 426
	2	457.500	468.500	Nona MW 460
	3	491.500	502.500	Deca MW 494

TABLE II

LIMITS OF DETECTION FOR PCBs

PCB isomer	*MW*	*EI MDL* (ppb)*	*NICI MDL* (ppb)*
2-Monochlorobiphenyl	188	1.3	>10
4,4′-Dichlorobiphenyl	222	3.1	>10
2,4,5-Trichlorobiphenyl	256	2.6	>10
2,2′,4,4′-Tetrachlorobiphenyl	290	2.0	>10
2,3′,4,5′,6-Pentachlorobiphenyl	324	1.2	>10
2,2′,4,5,5′-Pentachlorobiphenyl	324	1.9	>10
2,2′,3,3′,6,6′-Hexachlorobiphenyl	358	1.3	3.5
2,2′,3,3′,4,4′-Hexachlorobiphenyl	358	2.8	1.8
2,2′,3,4,5,5′,6-Heptachlorobiphenyl	392	2.2	0.16
2,2′,3,3′,4,4′,5,5′-Octachlorobiphenyl	426	3.2	0.09
2,2′,3,3′,4,4′,5,5′,6-Nonachlorobiphenyl	460	4.5	0.13
2,2′,3,3′,4,4′,5,5′,6,6′-Decachlorobiphenyl	494	4.3	0.10

* MDL = amount which corresponds to a peak height of twice the average noise level above baseline.

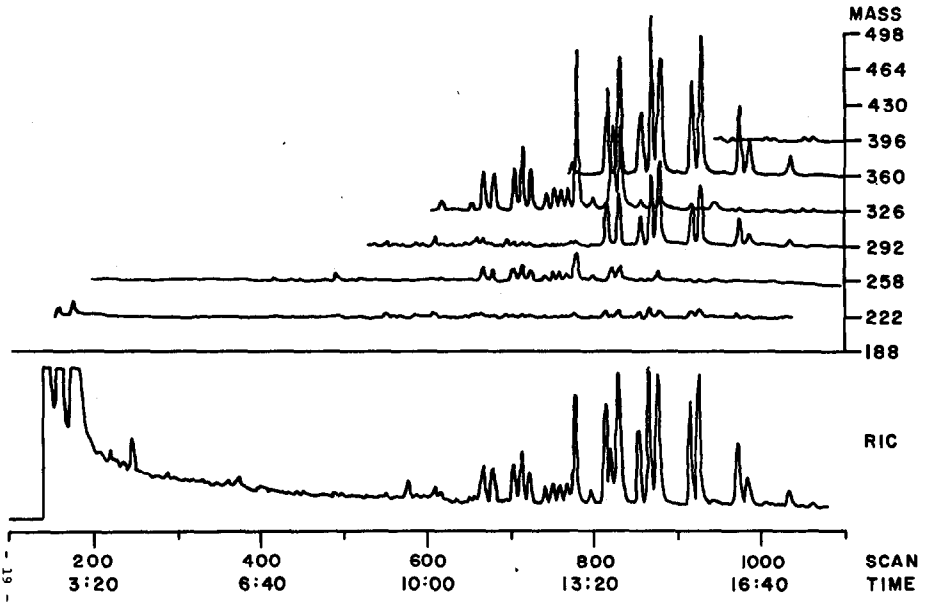

Fig. 2. RIC and mass chromatograms for PCBs in an extract of copper phthalocyanine blue pigment with trichlorobenzene as solvent.

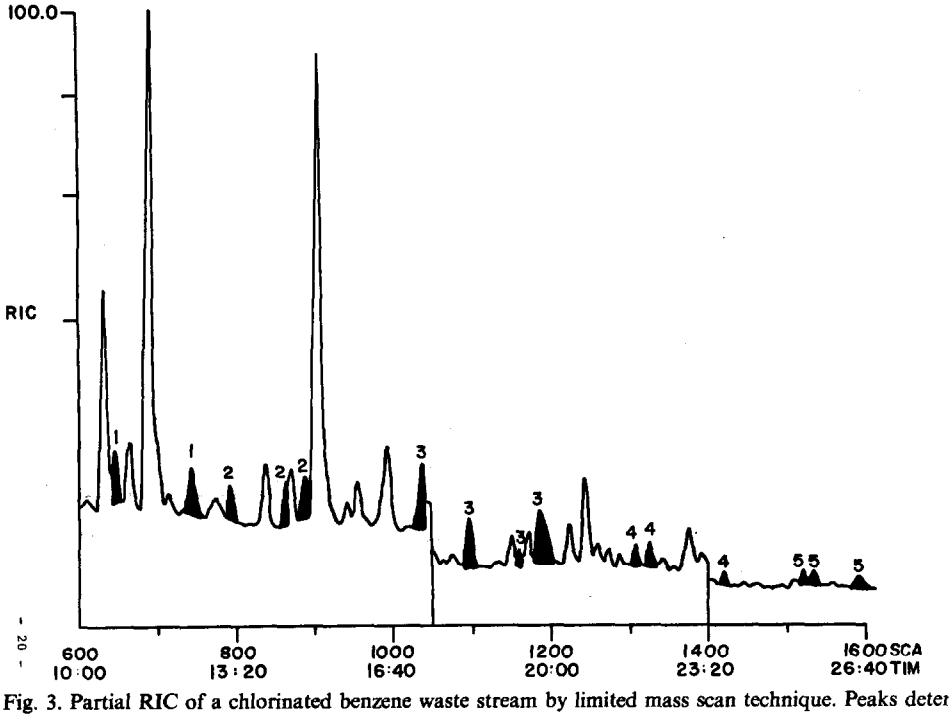

Fig. 3. Partial RIC of a chlorinated benzene waste stream by limited mass scan technique. Peaks determined to be PCBs are darkened.

The ability of the data system to plot reconstructed ion chromatograms and individual ions in the limited mass scan range simultaneously is useful in real-time screening the regions of the chromatogram for possible PCBs as they elute. Figs. 2 and 3 show partial mass chromatographic displays for a pigment extract and a chlorinated benzene waste stream using characteristic ions for chlorinated biphenyls.

As previously noted, the 11-a.m.u. limited mass scan filter eliminates many interferences in the matrix leaving a reconstructed ion chromatogram which must be visually scrutinized to determine the molecular ion and chlorine isotope pattern. After manually classifying the peaks according to the number of chlorine atoms, each isomer group is quantitated using the response factor generated by the sum of the intensities of the three largest ions in the 11-a.m.u. region around the species' exact masses. Individual PCB isomers are not delineated.

The repeatability of the procedure for samples containing large amounts of chlorinated benzenes is given in Table III. Recovery studies of PCBs spiked into concentrated extracts of the same samples are given in Table IV. The relative standard deviations of these experiments reflect the imprecision in the extraction procedure as well as the GC–EI-MS processes.

This laboratory participated in a round robin experiment for analysis of PCBs generated "incidentally" in process streams (sponsored by the Chemical Manufac-

TABLE III

REPEATABILITY OF EXTRACTION AND INJECTION PROCEDURE BY ELECTRON IMPACT

Values in ppm.

	Sample B		*Sample B*	*Sample C*
Injection 1	67.0	Extraction 1	12.1	60.7
2	67.6	2	9.4	53.6
3	71.9	3	8.7	68.8
Average	68.8	Average	10.1	61.0
R.S.D. (%)	3.9	R.S.D. (%)	17.8	12.5

TABLE IV

RECOVERY OF PCBs SPIKED INTO CONCENTRATED EXTRACTS BY ELECTRON IMPACT

Values in ppm.

	Found in unspiked	*Spiked amount*	*Found in spiked sample*	*Recovery**
Sample B				
2,2′,4,4′-Tetrachlorobiphenyl	0	1.10	1.17	106
2,2′,4,5,5′-Pentachlorobiphenyl	0.17	0.80	0.985	102
Sample C				
Spiked with twelve individual PCBs	2.66	3.538	6.09	96.9

* Recovery $= \frac{\text{(amount found in spiked sample} - \text{unspiked sample)}}{\text{actual and spiked}} \times 100\%.$

turers' Association). The data from eight larboratories using ten different methods on five samples containing PCBs in chlorinated matrices was interpreted statistically by Heiden, Pittaway Associates[7]. The trend of the data shows that limited mass scan capillary GC–EI-MS gives lower values for PCBs in interfering matrices than normal full scan of SIM acquisition (see Table V). Also, this technique resulted in one of the highest recoveries for PCBs (90%) from complex matrices where a known amount of was added.

When greater sensitivity is required, capillary GC–NICI-MS with methane carrier gas is employed. Fig. 4 shows a reconstructed ion chromatogram of a mixture of PCB standards at the 0.6–1.0-ppb* level. Using NICI-MS, under the conditions employed of the PCB examined, only PCBs with seven or more chlorines are enhanced in sensitivity relative to electron impact ionization. A limited comparison of the results of the analysis of two green pigment samples for decachlorobiphenyl by GC–ECD and GC–NICI-MS showed excellent agreement between the two techniques.

TABLE V

RESULTS OF PCBs IN SAMPLES A–E IN ROUND ROBIN EXPERIMENT BY ELECTRON IMPACT

Values in ppm.

	A	*B*	*C*	*D*	*E*
$\bar{X}$	283	24.3	64.2	129.5	9.0
Low	104	1	7	33	0.3
High	413	71	112	294	13.2
J.L.*	179	10.0	68.8	71.6	3.4

* Jackson Laboratory, DuPont.

DISCUSSION

At present, most attempts at quantitating PCBs are by GC–ECD[8,9]. The methods for determining response factors are quite subjective and the standard must be close to the same PCB distribution as the sample because of the disproportionate response between isomers and species with differing numbers of chlorine atoms. The fact that all PCBs with a given number of chlorine atoms do not elute as a group, but are mixed, makes quantitative analysis even more inexact, *e.g.*, trichlorobiphenyls can elute with pentachlorobiphenyls and tetrachlorobiphenyls[10,11]. The use of perchlorination techniques (where no biphenyl is present or is independently quantifiable) is more sensitive, probably just as accurate and much less subject to interferences[5]. The advantages of the limited mass scan GC–MS technique is that information concerning the exact number of chlorines present can be helpful in understanding chemical processes, degradation and formation mechanisms, etc.

Several papers have dealt with the use of single PCB congeners as represen-

* Throughout this article, the American billion (10^9) is meant.

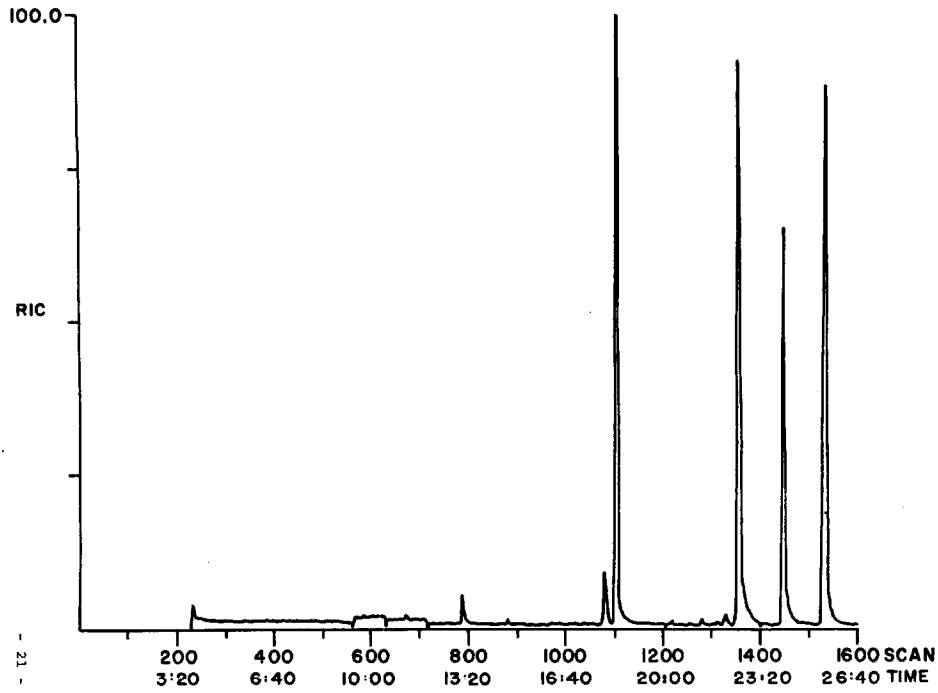

Fig. 4. RIC of twelve-component PCB mixture (*ca.* 1 ppm each) using limited mass scanning in conjunction with negative ion chemical ionization mass spectrometry. Note sensitivity enhancement relative to electron impact only for Cl $\geqslant$ 7.

tative species from each molecular weight group to quantitate all the isomers of their respective number of chlorines[5,12]. The response factors by GC–MS for PCBs within a single molecular weight group are generally free of the gross disproportionality observed by electron capture. In general, response factors have been reported as within $\pm$ 10% by GC–MS[5]. There is a trend of decreasing sensitivity with increasing molecular weight using EI ionization (unlike the great increase in sensitivity with GC–ECD) but it is relatively unimportant when quantitating using individual specific isomers.

The use of chemical ionization MS by Cairns and Siegmund[12] producing pseudomolecular ion peaks and $(M + 1 - 35)^+$ from loss of HCl which interfere with the isotopic patterns of the next lower homologue is not a problem with EI ionization. The use of high resolution capillary GC–MS demonstrated here has several advantages over packed column studies including previous application of limited mass scan detection[5]. In many instances, two entirely different columns or different programmed temperature runs have been required with packed columns to provide adequate sensitivity and spectral purity for accurate quantitation. The use of capillary columns and summation of the three most intense ions of the molecular ion isotope cluster increases the sensitivity for individual PCBs by an order of magnitude. The reduction in interferences afforded using capillary GC makes identification and quantitation of PCBs more accurate and precise. The same criteria as previous limited mass scan work[5], namely retention time range, molecular ion peak and isotope ratios,

are used for qualitative identification of individual PCB peaks.

The repeatability of our extraction and chromatographic procedure as determined by replicate extractions and injections of two chlorinated benzene waste streams is given in Table III. Replicate injections of samples consistently gives estimate coefficients of variation of less than 5% (relative). We assume that since replicate extractions followed by GC–MS analysis show more variability, that the sample cleanup procedure becomes the limiting factor in the precision and accuracy of the quantitation of PCBs when sample matrices contain large amounts of positive interferences. The values for recovery of PCBs spiked into concentrated extracts further indicate the ability of this procedure to accurately quantitate PCBs in complex matrices.

The use of NICI-MS in conjunction with capillary chromatography is a little used technique which shows promise for many electron-capturing species. Increased sensitivity has been observed for PCBs containing seven or more chlorine atoms using this approach. Again, the use of capillaries and summing multiple ions easily extends the detection limits for decachlorobiphenyl to *ca.* $5 \cdot 10^{-4}$ ng in solution. The similarity of detection limits for GC–NICI-MS and GC–ECD establishes GC–MS as a complementary technique to GC–ECD for determination of total PCB content by the perchlorination technique. GC–NICI-MS is a valuable reference method for GC–ECD which does not require any further concentration steps or sample handling.

CONCLUSIONS

High-resolution capillary GC–MS using limited mass scan multiple ion detection is a very sensitive technique for the qualitative and quantitative determination of PCBs in various commercial and environmental matrices. The determination of PCBs in chlorinated waste streams necessitates this approach for accurate qualitative and quantitative speciation of individual PCBs in matrices which show large positive interferences by non-GC–MS techniques. The limited mass scanning region (molecular ion cluster) for PCBs decreases interferences and increases the sensitivity of the analysis significantly.

Time programmed selection of mass windows further reduces interferences while modestly increasing sensitivity. The retention characteristics of the column employed dictate the choice of times particular mass windows are interrogated.

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