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ANALYSIS OF PCB CONGENERS IN FUELS

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ANALYSIS OF PCB CONGENERS IN FUELS

by

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MANAGEMENT PERSPECTIVE

This manuscript, intended for outside publication, is a
different perspective of the congener specific PCB analysis of
fuels. The internal government report, previously issued, listed
the results for all samples analyzed: duplicates, spiked samples,
standards and quality assurance samples. In the present report, the
authors have selected only results from the standards, spiked
samples, quality assurance aliquots and only one actual fuel
sample. This was done to show the PCB congener specific methodology
is reproducible and accurate both for standards and standards in
an oil matrix. By including the results for one sample, the
manuscript shows Environment Canada has the technology to detect
PCB contamination at the low ppb's, equivalent to 1L of PCB in a
large tanker truck.

Dr. J. Lawrence

Director

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PERSPECTIVE DE LA DIRECTION

Le présent manuscript, destiné à être publié à l'extérieur, offre une perspective différente du dosage des PCB spécifique des congénères dans les combustibles. Le rapport gouvernemental interne émis précédemment donnait les résultats obtenus pour tous les échantillons analysés : échantillons analysés en double, échantillons dopés, étalons et échantillons de contrôle de la qualité. Dans le présent rapport, les auteurs n'ont retenu que les résultats obtenus avec les étalons, les échantillons dopés, les échantillons de contrôle de la qualité et avec un seul vrai échantillon de combustible. Cette façon de procéder visait à montrer que la méthode spécifique des congénères de PCB est reproductible et exacte à la fois pour les étalons et pour les étalons dans une matrice d'huile. En incluant les résultats obtenus pour un échantillon, on démontre dans le manuscript qu'Environnement Canada possède la technologie nécessaire pour déceler une contamination par les PCB de l'ordre de quelques ppb, soit l'équivalent de 1 L de PCB dans un gros camion-citerne.

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ABSTRACT

A dual capillary column PCB congener method was used to determine PCB concentrations in fuels. The contribution from each congener present, denoted by its presence being detected on both columns, was summed so that the presence of PCBs could be detected well below the 1 ppm level. Standards were run frequently, and their results exhibited a high degree of reproducibility related to the injector and detectors during the study. Results from spiked fuel samples and quality control samples were consistent with the amount of added material.

RÉSUMÉ

Une méthode de dosage des congénères des PCB sur colonne capillaire double a été utilisée pour déterminer les concentrations de PCB dans des combustibles. On a fait la somme de la contribution de chaque congénère présent, c'est-à-dire dont la présence avait été décelée sur les deux colonnes, pour que les PCB puissent être décelés bien en-deçà de 1 ppm. Des étalons ont été analysés fréquemment et leurs résultats présentaient un degré élevé de reproductibilité pour ce qui est de l'injecteur et des détecteurs utilisés. Les résultats obtenus avec les échantillons de combustibles dopés et les échantillons de contrôle de la qualité concordaient avec la quantité de matière ajoutée.

INTRODUCTION

Previously a dual capillary column, EC detector method was reported to successfully analyze PCB concentrations in extracted sediment samples(1). Use of the dual columns, each connected to its own detector permits confirmation of the presence of the reported congeners as well as their concentrations. Previously, quantitation of PCBs by ECD analysis utilized packed column chromatography (2). With the synthesis and capillary column chromatography of all 209 PCB congeners by Mullin et al (3), the identification and quantitation of PCB congeners was made possible. This advance enhanced the analysis of Aroclor mixtures (e.g 4) and PCB congeners in environmental samples e.g.(5,6,7). It was the intent of using the simultaneous dual column method to enable routine analytical laboratories to accurately analyze samples for PCB congener content. A necessary extension of the dual column method was to apply this congener specific methodology to fuel samples that may contain PCBs.

Present regulations (8) require that no fuel shall contain more than 1 ppm total PCB. At this level it is possible to analyze PCBs in a hydrocarbon matrix by using capillary column GC/MS

although the method is still being developed, or capillary column ECD. Below this threshold the analysis is more difficult. Using GC/MS in the CI mode, contributing congeners of the possible Aroclors present would be interfered with by polynuclear aromatic compounds. Using a single ECD, the structural features of the hydrocarbon matrix of the fuel and additives, both of which elute in the PCB fraction of the cleanup stage (9), are susceptible to ECD activity resulting in considerable difficulty in assigning peak identification and recognizing Aroclor patterns.

As the PCBs in any industrial waste added to refined petroleum products would be in the form of Aroclors (10), the identification and confirmation of a few PCB congeners would not be sufficient to identify the product as a tainted fuel. Instead the basic premise of this work was that there must be at least 20 confirmed congeners present and no more than 5 of the congeners could have concentrations differing by a factor greater than 3 from the results of the two columns.

Preliminary studies were conducted on the linear response of the EC detectors to the PCBs which encompassed the concentration range of the congeners analyzed for in the present work (11). A computer program that compares the result files originating from the two columns was created on the data-collecting mini computer and this program also separated the PCB congeners into degree of substitution. The contributions of the individual congeners were

summed to provide the final result. Standards composed of four Aroclors (4) were analyzed frequently during the analysis of the samples to ensure the calibration of the retention times and concentrations had not altered. Analysis of the results from the standards also provided a measure of the degree of the system reproducibility. In addition spiked samples were analyzed, as was the spiking solution and quality control samples. These latter samples were composed of an Aroclor mixture added to a standard fuel. All samples were also analyzed for other organochlorines which are included in the analysis using this PCB method. This work was carried out using splitless injection.

METHOD

An HP 5890 gas chromatograph equipped with dual EC Ni63 detectors, each connected to a separate HP3392A integrator, and a split/splitless injector was used exclusively for this work. Each injection of 1 uL per column was performed by an HP7235A automatic sampler. In the splitless mode, a purge time of 0.75 min was found to provide optimum response. The chromatographic configuration was controlled by the Laboratory Automated System (LAS) software of the Real Time Executive (RTE-A) operating system of an HP 1000 computer. The calibration table contained 112 entries, of which 90 are related to PCBs and 22 to other organochlorines(OCs).

Columns were supplied by HIRESCO (Mississauga, Ont.), one having a OV-1 liquid phase and the other an SE-52 liquid phase. All columns were 30 m long and had an internal diameter of 0.25 mm, with a liquid phase thickness of 0.25 u. With H2 used as carrier gas, a constant column head pressure of 17 psi was utilized. The Ar/Me(95/5) make-up gas was used at a flow rate of 45 mL/min. The detectors were maintained at 3000C. After an initial 2 min. at 800C, the oven temperature was programmed to increase at 100C/min to 1400C, at which time the rate was reduced to 20C/min until the upper temperature limit of 2550C was reached. The oven was then cooled. Isooctane was injected as every third sample to reduce the possibility of carry over. The chromatograms of the standards, obtained from the response of each of the two detectors was examined over the course of the study to ensure that the chromatography was as good during the study as at its beginning.

All standards were obtained from the National Depository of the National Bureau of Standards (USA). These include the Aroclors 1221,1016, 1254 and 1262 as well as the organochlorines of Aldrin, heptachlor, octachlorostyrene, p,p'-DDE, o,p'-DDT, p,p'-DDT, photomirex, mirex, and hexa-, penta-, 1,2,3,4-tetra-, 1,2,3-,1,3,5-, 1,2,4-tri-, and the three di-chlorobenzenes. The calibration standard for the PCBs was prepared by combining 1000 parts of Aroclor 1221, 500 parts of Aroclor 1016, 350 parts of Aroclor 1254 and 300 parts of Aroclor 1262 according to Onuska et

al (4). All standards were made up to the appropriate concentrations in isooctane.

For the fuel samples, a 1.5 to 3.0 g aliquot of the fuel was dissolved in 7 mL of hexane. A glass column (12mm id X 350 mm) was prepared by plugging one end with silanized glass wool on top of which was placed 25 mm of Na2SO4, then 80 mm of dried silica gel deactivated with 3% H2O, and then another 25 mm of Na2SO4. This was washed with 30 mL of hexane. The hexane solution containing the fuel sample was transferred to the top of the column with an additional 3 washes of 5 mL of hexane, then the sample was eluted with 20 mL of hexane which was collected. 3 mL of isooctane was added to the eluate and the volume was reduced to 3 mL using a Snyder column at a temperature of 350C. An aliquot was quantitatively transferred to a vial ready for injection on a gas chromatograph. If the ECD response was too high, the sample was diluted. Spiked samples were prepared by taking a known weight of the original sample and adding a known amount of a standard Aroclor mixture. This was cleaned up by the method outlined above. Standards for spikes and for quality control were supplied by the Quality Control Unit of Research and Applications Branch, NWRI (Burlington, Canada). To 3 g of the sample, 1.0mL of the standard was added and treated as above but with the final volume being 10mL.

Chromatographic peaks identified as specific target compounds by the LAS software (HP) from the results derived from each detector were correlated by a specifically created program on the HP 1000 mini computer. Only when the compound was present in both chromatograms was it considered to be present in the sample. Also only if the concentrations of a particular compound agreed within a factor of 3, was it considered a positive identification. Using this methodology, we have found it convenient to use the results from one column after the presence of the target compounds (PCBs) have been confirmed on both columns. Therefore the results cited are from the OV-1 column with the concentrations reported agreeing with the results of the second column. As the object was to detect fuels tainted with waste PCBs, only those sample containing more than 20 congeners were considered to contain waste PCBs.

RESULTS

Listed in Table 1 are the results derived from the OV-1 capillary column for the standard PCB solution measured during the analysis of the fuel samples as well as results measured before and after the study. Included in the table are the total number of peaks whose area is 400 and above. Also included are the number of

contributing congeners whose concentrations were added to provide the total concentration. The average number of contributing congeners found in the standard is 76, with 81 being the maximum determined. The mean concentration of total PCB in the solution is 2185 pg/uL impinging on the detector, with a standard deviation of 74.29, which gives a relative standard deviation of 3%. The congeners which are not included in the lower measured values are at concentrations of sub pg/uL impinging on the detector and are at the instrumental detection limit. The mean value of 2185 pg/uL is the sum of over 75 individual entries and the reproducibility is excellent.

A concentration of 789.6 ug/uL of PCB was calculated for the Quality Assurance stock solution. When a known amount of this stock solution was added to a non-contaminated fuel which was subjected to the clean up, values of 979.1 and 1008 pg/uL were analyzed for two separate samples. The solutions were prepared to yield a value of 1000 pg/uL or 65.3 and 67.2 ug/g of fuel respectively. These analyzed values are within 1% of the anticipated values. For these calculations 76 and 80 congeners contributed to the total.

As noted for the Quality Assurance samples, the total PCB concentrations were calculated by summing the contributions of 76 and 80 congeners detected in these samples. From one analysis of a fuel sample, 19 of 120 peaks were identified on the OV-1 column as PCB congeners. These were {1}, {3}, {4+10}, {6}, {7}, {12+13},

{18}, {19}, {29}, {32}, {33+53}, {40}, {41}, {42}, {44}, {48}, {49}, {52}, {66}, {97}, {110}, {114+134}, {135}, {136}, {147}, {151}, {153}, {170}, {177}, {197} and {205}. From the SE-52 column, the following congeners were identified: {3}, {4+10}, {5}, {6}, {7}, {16+32}, {17}, {24}, {25}, {33+53}, {44}, {46}, {49}, {56+60}, {82}, {83}, {89}, {91}, {128}, {136}, {137}, {141}, {146}, {151}, {156+171}, {157+200}, {158}, {170}, {175}, {180}, {183}, {191}, {196} and {199}. Comparison of the two sets of results will show that there are only seven congeners common to both lists. Obviously this sample does not contain any contamination by Aroclor mixtures. The total concentration of the PCBs in this sample, using the results from the OV-1 column only is 34.3 pg/uL of sample impinging on the detector. OILTEST022b006

Table 2 contains the results for the samples spiked with PCBs at the 1 ppm level, as well as the results for the unspiked samples. Also included in Table 2 are the results for a sample spiked at the 0.5 ppm level(#25). In the results for the unspiked samples, the number of peaks identified as confirmed congeners on the OV-1 column is less than 12. These samples would not be considered as being contaminated. The first four spiked samples have greater than 30 confirmed congeners and the calculated concentration of total PCB is about 980 ppb, the anticipated value. The final entry has a PCB concentration of 680 ppb, slightly more than one half of the nominal minimal detectable level determined by other means. However the peaks representing the congeners are minor

peaks in the chromatogram of the sample and are difficult to recognize as an Aroclor mixture. In all cases the total number of peaks on the chromatogram whose areas are greater than 100 and between the retention times of dichlorobenzene and decachlorobiphenyl are listed. It is within these two retention times, that any peaks related to the PCBs or other organochlorines would be expected. The cut-off value of 100 for the area is commonly used by this laboratory to avoid interference from noisy baseline. Using these criteria, the isooctane solvent and injection blanks contain 4 to 7 peaks which do not coincide with any of the PCB or other OC peaks. The final two entries in Table 2 are the results for the solution used for spiking the samples. The anticipated result is 1000 pg/uL.

The results from sample 5 are shown in Table 3, which includes all identified congeners and their concentrations on both columns. When only the confirmed congeners are considered, a value of 62pg/uL impinging on the detector is the calculated concentration. This is converted to 48 ngPCB/g of sample which is 1/40 of the legal limit. No other organo chlorines were detected in this or other samples.

DISCUSSION

The values presented in Table 1, show that the dual column PCB congener specific method provides very reproducible results. A measure of this is the relative standard deviation which is less than 5% for splitless injection. Also the mean value of 2185 pg/uL is within 3% of the concentration of the standard solution which is 2250 pg/uL. In preliminary studies (11), the response of each of the congeners is linear down to 18 pg/uL total PCB and the relative standard deviations for each congener were generally less than 5%. That is to say that for each congener in the solution, its response was determined to be linear down to that concentration at which its response was less than the interference from the noise at baseline. At the low concentrations, analysis for PCB congeners is not different from analyzing a sample for trace amounts of other organochlorines. Over 120 individual analyses were made including samples, internal standards, quality assurance samples, spiked samples and duplicates. The samples included light jet fuels and heavy oils such as #6 fuel. Yet no deterioration of the system occurred as shown by a comparison of the results for the standards over the duration of the study. This indicates that with a properly maintained system, the method is quite rugged. The results in Table 2 show that the method, properly calibrated, provides results that are consistent and within experimental error of the anticipated

concentration. The fuel matrix gave rise to chromatograms that are as complicated as other environmental samples analyzed by the EC detector.

With the capability of measuring each congener at the trace level of 1 pg/uL, low concentrations of Aroclors can be detected. The results presented in Table 3 illustrate this. With the many peaks caused by the interaction between the fuel and the EC detector, some spurious peaks may be identified as a PCB congener. For this reason at least 20 peaks identified and confirmed on both columns is necessary before the sample is considered to contain any Aroclor contamination. The low concentration measured in this sample was difficult to confirm by GC/MS as it does not have the desired sensitivity and the trace for the PCBs are imbedded in the carbon trace.

Each analysis cited here required 1.5 hr, from time of injection to the final report from the computer. If the baseline of the chromatogram had to be adjusted because of negative peaks, an additional half hour may be required. Even so, the method is reasonably fast and capable of measuring 1L of Aroclor contamination in a large tanker truck used to haul fuels.

ACKNOWEDGEMENTS

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TABLE 1

STANDARD PCB SOLUTION

Sample I.D.	sequence1 #12	sequence2 #7	sequence3 #2	sequence4 #2	sequence4 #13
# peaks in chromat.	139	142	138	139	143
Total (pg/uL)	2254.1	2231.4	2102.4	2039.6	2217.3
# congeners	74	76	75	77	74

Sample I.D.	sequence5 #19	prior to study	with stand.	after study
# peaks in Chromat.	138	127	140	144
Total (pg/uL)	2205.6	2229.4	2206.4	2289.9
# congeners	81	79	77	80

Mean (pg/uL)	Std Dev	Relative Standard Deviation
2197.35	77.80	3.5%

TABLE 2

CONCENTRATIONS AND NUMBERS OF PEAKS IN SPIKED AND UNSPIKED FUEL SAMPLES

Sample	#3	#3 spiked	#9	#9 spiked	#22	#22 spiked
Total No. of Peaks	139	155	198	168	206	155
# of Congeners	11	57	10	60	12	59
Conc. (pg/uL)	20.8	1128	59.2	1241	107	710

Sample	#25	#25 spiked	External Stand(1)	External Stand(2)
Total No. of Peaks	108	129		
# of Congeners	13	30	57	55
Conc. (pg/uL)	207	887	1110	1048

TABLE 3.

SAMPLE 5

CONGENER NUMBER AND CONCENTRATION (pg) in SUSPECTED FUEL SAMPLE

Congener #	OV-1	SE-52	Congener #	OV-1	SE-52
3	15.52	15.52	128+182+187	0.57	1.21
Mono Total	15.52	15.52	138	1.00	1.72
4+10	2.99	5.25	149		2.73
5+8	6.83	10.49	156+171	0.7	1.05
6	(7.51)	1.44	Hex Total	2.27	6.71
7	0.96	0.96	170	0.33	(2.86)
12+13	0.53	0.53	174	0.37	1.04
Di Total	12.75	18.67	175	0.45	0.60
16+32	0.88	(3.86)	177	0.24	0.53
17	1.67	2.24	180	0.93	1.61
18	4.42	5.33	182+187		0.95
22	0.82	1.65	189	0.16	0.22
26	0.64	1.54	Hepta Total	2.48	5.28
			195	0.41	1.18
Tri Total	8.43	11.64	196+203	0.43	0.73
40	0.58	1.83	201	0.37	0.83
41+64+71	1.83	3.93	Octa Total	1.21	2.74
44	3.84	6.57	206	0.38	0.23
45	0.67	1.49	Nona Total	0.38	0.23
49	1.19	2.44			
52	1.91	3.44			
66+95	0.61	0.61	Total =	62.22	91.62
Tetra Total	10.63	20.31			
87	0.86	1.34	# peaks	164	212
101	3.57	3.53	in chromatogram		
105	1.29	2.42			
110	1.32	2.28			
118+149	1.51	0.95			
PentaTotal	8.55	10.52			

( ) indicates that the value obtained from other capillary column was used in summation
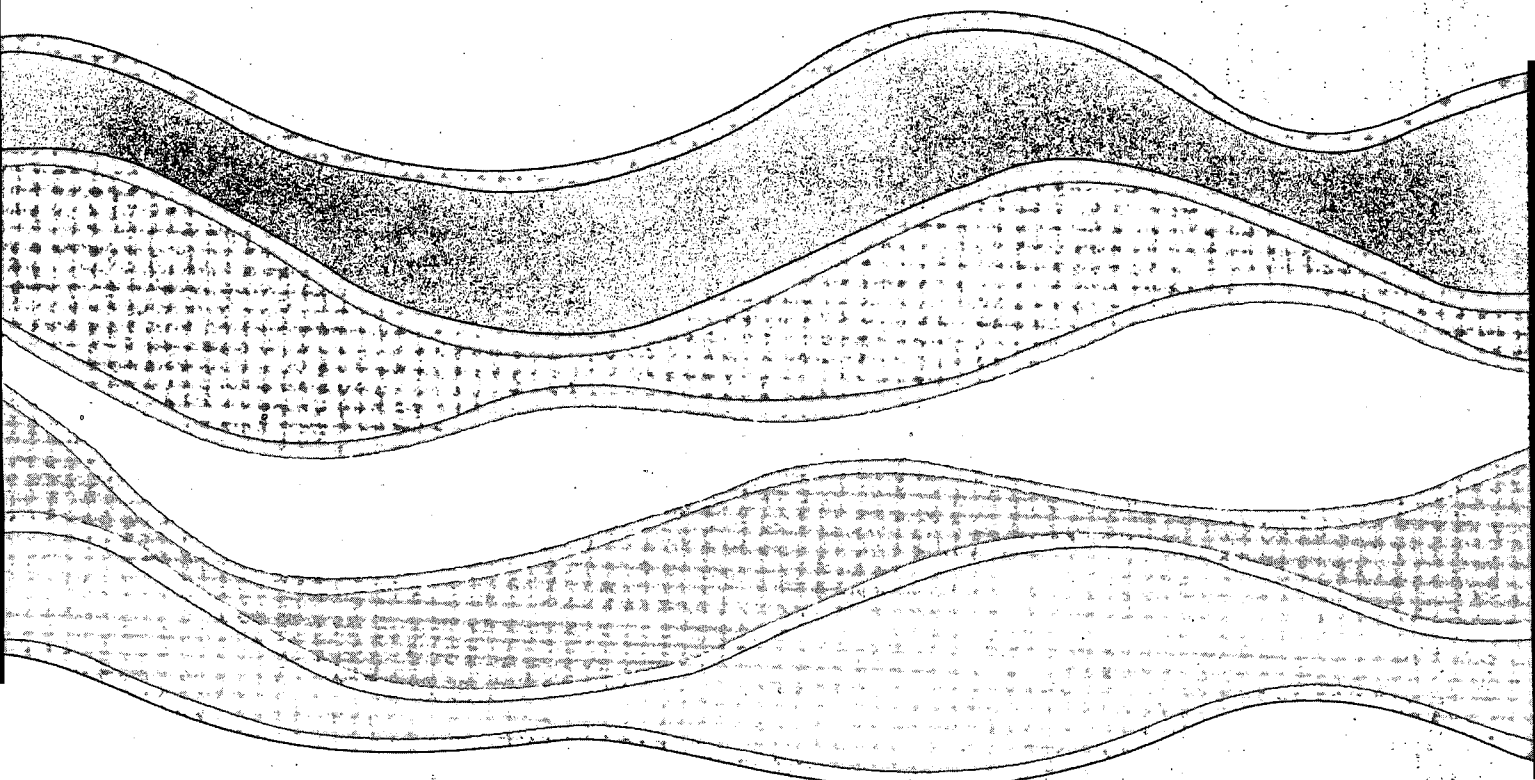
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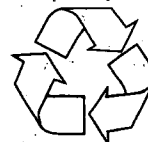P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

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