

A Simple Extraction Method for Polychlorinated Biphenyls in Sediment with Fast Analysis by Gas Chromatography— Time-of-Flight Mass Spectrometry

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1. Introduction

The trend towards congener-specific analysis of polychlorinated biphenyls (PCBs) and faster Gas Chromatography (GC) has led to the use of 0.10 mm ID columns. These columns can be highly efficient, producing peak widths on the order of 1 or 2 seconds, which mandates the use of very fast recording detectors. When mass spectrometry is selected for detection, scanning instruments fall short; only Time-of-Flight Mass Spectrometry (TOFMS) can provide the necessary spectral collection rate to define such narrow peaks with full-mass range data.

To match fast instrumental methods, faster sample preparation methods are desirable. This note describes the results from an attempt to devise a fast and simple extraction method for PCBs from sediment. GC-TOFMS was used to quantify PCBs in the sediment extract.

2. Experimental Conditions

Sediment

Sediment EC-1, certified for 22 specific PCB congeners, was obtained from Wellington Laboratories. The sediment was a freeze-dried composite from the Great Lakes basin.

Standards

PCB stock solutions were obtained from AccuStandard, and were diluted in hexane to cover a calibration range of 2.5, 10, 50, 100, 500, and 1000 pg/ μ l.

Gas Chromatography/Mass Spectrometry

Instrumental conditions are listed below. A Vacuum Vu-Union connector (Restek Corporation) was used to connect the retention gap and analytical column.

Instrumentation

Gas Chromatography: Agilent 6890

Retention Gap:

4 m x 0.10 mm IP-deactivated guard column (Restek)

Column:

40 m x 0.10 mm x 0.10 μ m DB-XLB (J&W Scientific)

Carrier:

Hydrogen at 0.7 ml/minute, constant flow

Injection:

1 or 0.25 μ l splitless at 260°C

Oven Program:

75°C (1 minute), 50°/minute to 125°,

20°/minute to 335° (1 minute)

Total Run Time: 13 minutes

Mass Spectrometry: LECO Pegasus III GC-TOFMS
Ionization: Electron ionization at 70eV
Source Temperature: 225°C
Stored Mass Range: 120 to 520 u
Acquisition rate: 20 spectra/second

Data Processing

LECO ChromaTOF software with Automated Peak Find and Deconvolution

Extraction of Sediment

Five grams of sediment was weighed into a 15 ml bottle with a PTFE-lined cap. 10 ml of hexane was added; the vial was capped, and shaken vigorously to disperse the sediment. The vial was submerged in an ultrasonic bath (Branson) at 55°C for 15 minutes. After the ultrasound extraction, the vial was removed from the bath and allowed to rest for 30 minutes to permit the sediment to settle. Then the solvent was pipetted from the top of the sediment into a clean, glass bottle. This process was repeated two additional times with 7 and 6.5 ml portions of hexane. All three extracts were combined prior to the next level of processing.

The extract was passed through a small amount of anhydrous sodium sulfate, concentrated to approximately 0.5 ml with gentle heat and dry nitrogen gas, and then adjusted to exactly 1.0 ml with hexane. A 4 g copper treatment was used to remove sulfur from the extract.

Cleanup of Sediment Extract

A Supelco "champagne" cleanup column (125 mm long x 6 mm ID) was tap-packed with fully activated silica gel (100 to 200 mesh) and eluted with 10 ml hexane wash (discard). 0.25 ml of the sediment extract was added to the top of the column. The column was eluted as follows.

30 ml hexane (PCB fraction)

15 ml 90:10 hexane:methylene chloride (PAH fraction)

15 ml 50:50 hexane:methylene chloride (intermediate polars)

The PCB fraction was concentrated just to dryness with gentle heat and dry nitrogen gas, and diluted to exactly 0.25 ml with hexane. This fraction was analyzed by GC-TOFMS.

3. Results

The goal of the present work was to measure as many PCBs as possible, in the shortest time possible. An Aroclor mix containing at least 129 congeners was used to test the system. The chromatogram of hexachlorobiphenyls in Figure 1 demonstrates two important points: the high efficiency of the 0.10 mm ID DB-XLB column, and the TOFMS ability to acquire data for peaks that are approximately 1.5 seconds wide.

Of 129 Aroclor congeners, 119 could be measured individually, based on either chromatographic separation or differentiation by mass spectrometry. Important PCBs such as 153/132 (pentachlorobiphenyls) and 138/163 (hexachlorobiphenyls)—which typically coelute on 5%

phenyl columns—are separated enough for quantitative estimates (if they do not differ drastically in concentration), in approximately 8.5 minutes. Decachlorobiphenyl elutes at approximately 10.5 minutes.

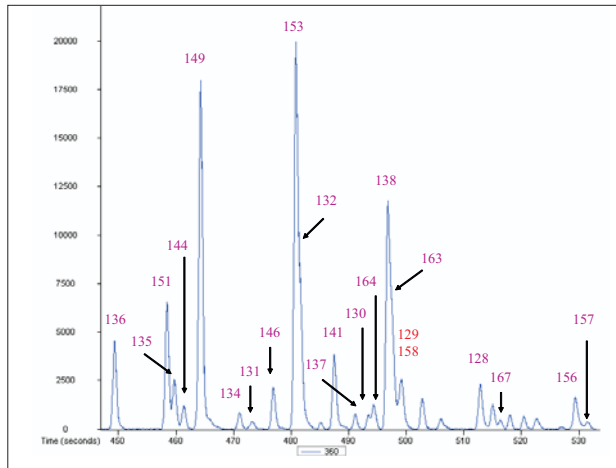


Figure 1. GC-TOFMS extracted ion chromatogram of hexachlorobiphenyls on DB-XLB. The numbers are the IUPAC names for the specific PCB congeners.

Unfortunately, sediment extracts are not as clean as Aroclor mixes, and in this case coextractives from the sediment severely overloaded the 0.10 mm x 0.10 μm column, resulting in peak splitting and retention time shifts (Figure 2). Adjusting the injection volume to 0.25 μl from 1 μl permitted successful analysis of the extracts (Figure 3), even though the matrix background was overwhelming (Figure 4).

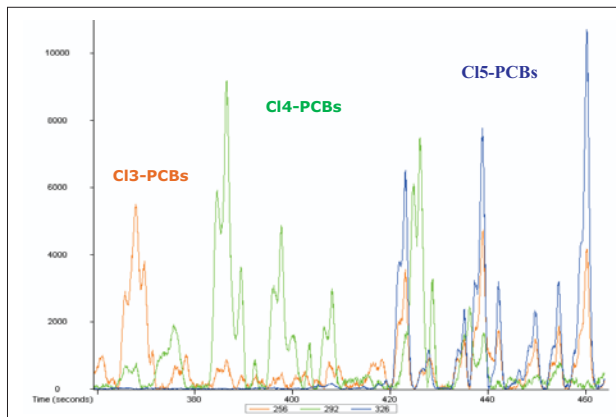


Figure 2. Overload of 0.10 mm x 0.10 μm GC column by sediment matrix components resulting in split PCB peaks. Extracted molecular ions are plotted for trichloro- (256), tetrachloro- (292), and pentachloro- (326) biphenyls.

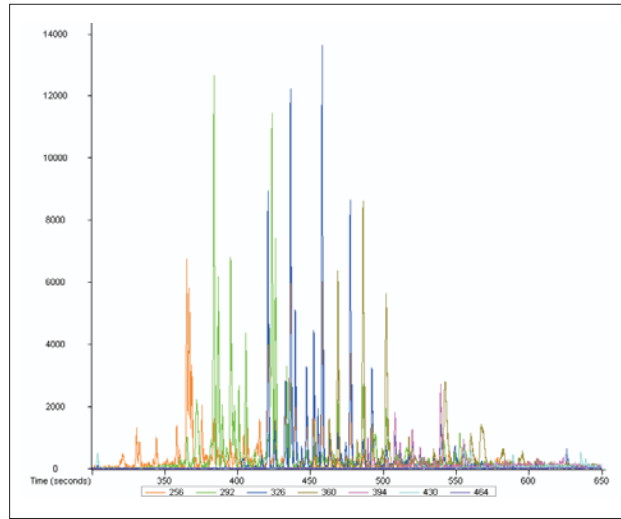


Figure 3. Extracted molecular ion chromatograms of PCBs in a sediment extract, showing narrow peaks from 0.25 μl injection. Trichloro- (256), tetrachloro- (292), pentachloro- (326), hexachloro- (360), heptachloro- (394), octachloro- (430), and nonachloro- (464) biphenyls are shown.

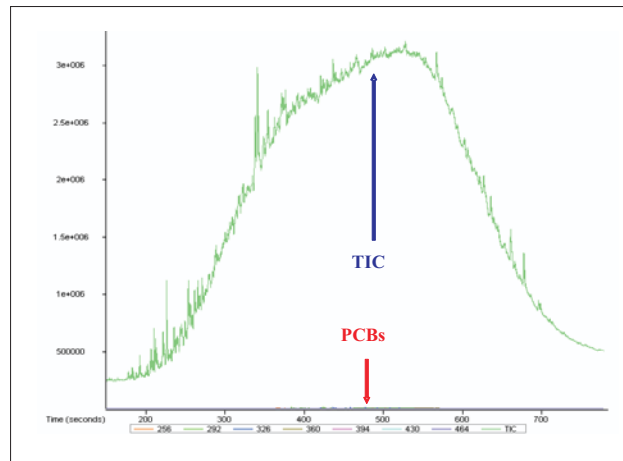


Figure 4. Total ion chromatogram (TIC) plotted versus extracted ion chromatograms of PCBs demonstrating the high matrix background of a sediment extract.

The sediment quantification serves two purposes, to demonstrate the utility of a GC-TOFMS for fast analysis, and to attempt to match fast analysis with a fast sample preparation method. PCBs were quantified on the basis of summed ions as shown in Table 1, with standard mixes ranging from 2.5 to 1000 pg/μl. Example calibration curves, using 2-fluorobiphenyl as an internal standard, are shown in Figures 5 and 6.

Table 1. Ion masses used for specific PCB congener quantification.

Cl#	Quantification Masses
3	256+258+260
4	290+292+294
5	324+326+328
6	358+360+362
7	394+396+398
8	428+430+432
9	462+464+466
10	496+498+500

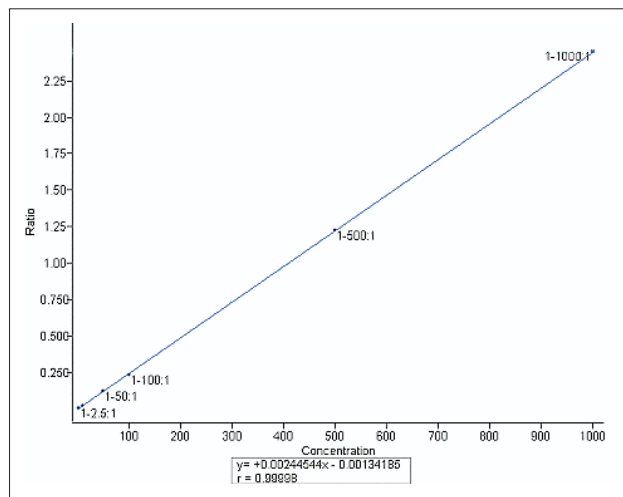


Figure 5. Calibration curve from 2.5 to 1000 pg/ μ L for PCB 52, a tetrachlorobiphenyl.

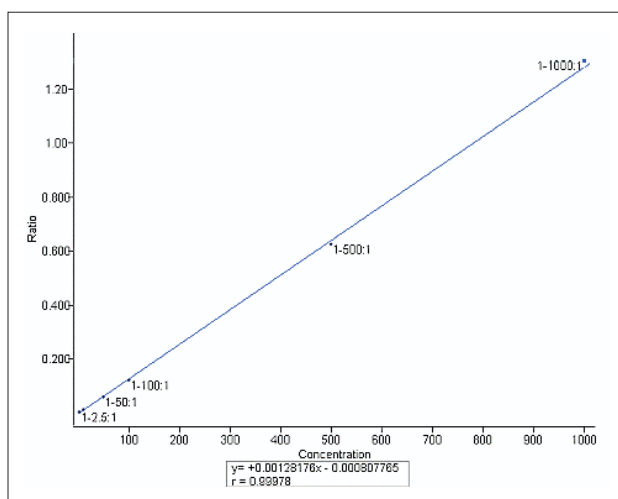


Figure 6. Calibration curve from 2.5 to 1000 pg/ μ L for PCB 180, a heptachlorobiphenyl.

Table 2 compares the GC-TOFMS results to the certified values for 22 PCB congeners. The Cert column contains the certified values calculated in pg/ μ L based on the extraction conditions. Ext 1, Ext 2, and Total are averages from triplicate extractions of sediment EC-1 (i.e. three different 5 g portions from the same bottle). Ext 1 and Ext 2 represent values from sequential extractions of the same sediment. The Total is the sum of these two extractions. Ext% defines the efficiency of the first extraction as a percentage of the measured total; if the Total represents all of the PCB that could be recovered by this extraction process. And Rec% is the percent recovery calculated by comparing the Total versus the Cert, or certified values.

The interpretation of Table 2 can be summarized as follows.

1. The first hexane extraction is relatively efficient with an average recovery of 86%.
2. The simple extraction method with fast GC-TOFMS produces numbers relatively close to the certified values for the majority of the PCB congeners. At the very least, the method would suffice for screening purposes.

Table 2. Specific PCB congener quantification for a Great Lakes basin sediment.

PCB#	Cl#	Cert	Ext 1	Ext 2	Total	Ext%	Rec%
18	3	237	64.3	19.2	83.1	77	35
22	3	244	173	32.7	204	84	84
44	4	324	298	53.9	350	85	109
52	4	497	428	69.7	494	86	100
87	5	225	199	29.8	228	87	102
101	5	547	578	81.2	656	88	121
105	5	171	146	39.3	185	78	108
110	5	601	476	70.1	543	87	91
118	5	399	497	76.1	570	87	144
128	6	72.5	102	18.7	120	85	167
137	6	19.0	19.0	2.4	21.3	89	113
138	6	360	471	49.3	517	90	144
141	6	97.0	127	15.5	142	89	147
151	6	83.0	112	20.3	132	85	159
153	6	341	504	70.0	571	88	168
170	7	84.0	136	19.8	154	87	185
180	7	225	246	35.1	280	87	125
183	7	76.0	70.4	9.0	78.9	89	104
194	8	65.5	48.1	8.6	56.4	84	87
201	8	36.5	13.2	3.5	16.5	79	46
206	8	35.0	20.9	4.1	24.9	83	71
209	8	7.0	7.8	1.0	8.7	90	125

The simple extraction method provides adequate results for the EC-1 sediment, but would be faster without the 30 minute time for phase separation. Centrifugation instead would produce a clear supernatant in only a minute or two. Even without centrifugation, as many as 60 samples can be extracted in one day. The other bottleneck is the cleanup method. Commercially available silica cartridges that will work on a vacuum extraction manifold did not have the capacity for good cleanup of sediment extracts. The "champagne" column cleanup is gravity flow only, and is very slow.

4. Conclusions

Fast GC with 0.10 mm columns mandates the use of TOFMS to adequately define narrow peaks. These columns are easily overloaded, so close attention to injected sample amount is necessary. A selective GC column and TOFMS allow highly efficient, congener-specific quantification of PCBs in sediment in less than 15 minutes. The TOFMS easily detected 2.5 pg of all PCBs measured for this application. Lower detection levels of PCBs are possible.

The simple extraction method could be improved by centrifugation instead of a rest period, and by using a silica cleanup column with the dimensions described in this note that will fit on a vacuum extraction manifold.

5. References

J.W. Cochran; Fast Gas Chromatography—Time-of-Flight Mass Spectrometry of polychlorinated biphenyls and other environmental contaminants; *J. Chromatogr. Sci.* 40 (2002) 254-268.

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