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Rapid Extraction of Chlorobiphenyls from Sediment Grab Samples Using a Ball-Mill Extractor

by

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ABSTRACT

A rapid, simple, inexpensive analytical procedure allowing accurate quantification of chlorobiphenyls at $ng \cdot g^{-1}$ dry mass in sediment grab samples is described. The method is based on the use of a Ball-Mill apparatus which involves extraction into dichloromethane and copper treatment, followed by purification using a Florisil column, and measurement using capillary gas chromatography-low resolution mass spectrometry with selected ion monitoring to eliminate many interfering compounds. Recoveries of chlorobiphenyls (2-70 $ng \cdot g^{-1}$ dry mass) averaged 91.0 ± 5.2 % for the Ball-Mill procedure compared to 94 ± 17 % for the Soxhlet procedure. The analytical procedure has been validated on reference material sediment (NIST SRM 1944). The procedure was then applied to the study of chlorobiphenyl contamination of marine sediments collected in Sydney Harbour, Nova Scotia, Canada. The Ball-Mill procedure gave results for chlorobiphenyls in sediment grab samples comparable to those obtained by the conventional method of Soxhlet extraction.

RÉSUMÉ

Une procédure analytique rapide, simple, bon marchée permettant la quantification exacte de chlorobiphenyls à $ng \bullet g^{-1}$ se sèche la masse dans les échantillons de geste vif de sédiment est décrite. La méthode est fondée sur l'utilisation d'un appareil de Broyeur à boulets qui implique l'extraction dans dichloromethane et le traitement couleur cuivre, suivi par la purification en utilisant une colonne Florisil et une mesure en utilisant la masse de résolution chromatography-basse capillaire du gaz spectrometry avec l'ion choisi surveillant pour éliminer beaucoup d'enceintes se mêlant. Les récupérations de chlorobiphenyls (2-70 $ng \bullet g^{-1}$ sèchent la masse) ont fait en moyenne 91.0 5.2 % ± pour la procédure de Broyeur à boulets comparée à 94 ± 17% pour la procédure Soxhlet. La procédure analytique a été validée sur le sédiment de matière de référence (NIST SRM 1944). La procédure a été alors appliquée à l'étude de contamination chlorobiphenyl de sédiments marins recueillis dans le Port de Sydney, Nova Scotia, le Canada. La procédure de Broyeur à boulets a donné des résultats pour chlorobiphenyls dans les échantillons de geste vif de sédiment comparables avec ceux obtenus par la méthode conventionnelle pour l'extraction Soxhlet.

1.0 INTRODUCTION

Chlorobiphenyls (CBs) do not occur naturally, but were produced commercially by the direct chlorination of biphenyl. There are two hundred and nine congeners. Chlorobiphenyls are non-flammable, relatively insoluble in water, have high boiling points, low electrical conductivity and are chemically and thermally stable. These properties made them very desirable for a number of industrial applications including carriers of inks and dyes, dielectric heat transfer agents, hydraulic fluid, flame retardants, plasticizers in paints and adhesives (Nimii et. al 1989). Most of the polychlorinated biphenyls (PCBs) in these processes were marketed and sold by Monsanto under the brand name Aroclors. PCBs were banned in the 1970's. During that time, PCBs were measured as total PCB rather than as individual chlorobiphenyls. In the past decade more attention was paid to the specific identity of CB congeners. This was due to the fact that these individual compounds were placed on a list of priority pollutants by the environmental agencies of USA and Europe (Quintana et. al 2003). Despite the fact that these compounds were banned, interest still remains because of their persistence in the environment, sources for them besides Aroclors (King et. al 2002), and toxicological studies that demonstrated toxicity was dependent on the structure of the congeners (Nimii et. al 1989; De Voogt et. al 1990). There are a number of analytical procedures for extracting CBs from various sample matrices. EPA method 3540C is a Soxhlet extraction procedure commonly used to remove organic compounds from sediments and soils. This method requires use of expensive glassware, large volumes of solvent, running water to cool the condensers during operation, and extraction times of 18 hours or more. Removal of interfering sulfur from the extracts using this procedure proves to be a difficult task. There is the requirement to concentrate large volume extracts to a small volume that can be purified and handled effectively by gas chromatography coupled to mass spectrometry.

We describe a method that is less expensive, simple, sensitive, effective at removing sulfur, rapid and specific for measuring individual CBs in sediments. The Ball-Mill procedure was used in the past to extract organochlorine compounds from biological tissues (Muir et. al 1988). In that particular study there was no spike and recovery data available for the Ball-Mill procedure and it was applied to only biological tissues. The Ball-Mill procedure has been validated based on extensive fortification studies and extraction of reference material sediments. The procedure was applied to extract CBs from marine sediment grabs collected in Sydney Harbour, Nova Scotia, Canada. The Ball-Mill procedure was further validated by running a batch of sediment grab samples and comparing the results to previous results completed on the same samples using the Soxhlet extraction procedure. Also, this study will discuss how the employment of different analysts to prepare and extract samples for CBs using the same techniques will affect the final results.

2.0 MATERIALS AND METHODS

2.1 Reagents and Solvents

The solvents were: hexane (VWR-Canlab, Mont-Royal, Québec, Canada, Omnisolve, distilled in glass, lot no. 41297); acetone (Caledon, Georgetown, Ontario, Canada, distilled

in glass, lot no. 43895); dichloromethane (Caledon, Georgetown, Ontario, Canada, distilled in glass, lot no. 43346); 2,2,4-trimethylpentane (VWR-Canlab, Mont-Royal, Québec, Canada, Omnisolve, distilled in glass, lot no. 41234) Florisil (J.T. BakerPhillipsburg, NJ, USA, 60-200 mesh, cat no. 1343-88-0); Silica Gel (Whatman Laboratory Division, Clifton, NJ, USA, 60A 70-230 mesh ASTM for HPLC, cat no. 4791-010); Copper (J.T. Baker, Phillipsburg, New Jersey, USA, 20-30 mesh cat no. 1720-5); Sodium Sulphate (VWR-Canlab, Mont-Royal, Québec, Canada, 10-60 mesh, cat no. SX0760E-3); Cellulose Extraction Thimbles (Whatman International Ltd., England, double thickness, 33 mm x 94 mm, cat no. 2810339); Teflon boiling chips (VWR/Canlab, Mont-Royal, Québec, Canada, cat no. 26397-103); Glass wool (VWR-Canlab, Mont-Royal, Québec, Canada, Pyrex brand, cat no. 32848-003)

2.2 Standards

Chlorobiphenyl standards: IUPAC Nos. 1-16, 18-22, 24-31, 33-40, 42, 44, 47-50, 52-55, 58, 60-62, 65-66, 69-70, 72, 74-75, 77-82, 86-87, 89, 93, 95, 97-106, 108-110, 112, 114-119, 121-124, 126-129, 131-134, 136-145, 147, 149, 151-154, 156-158, 160-162, 165-171, 173, 180-192, 194-196, 199-202, 204-209 (all CB standards purchased from Ultra Scientific, North Kingstown, RI, USA); Ottawa Sand Standard (016858, 20-30 mesh) (Fisher Scientific, Fair Lawn, New Jersey, USA); Standard Reference Material (1944 New York-New Jersey Waterway Sediment) (National Institute Standards and Technology, Gaithersburg, MD, USA); ^{13}C-IUPAC No. 77, ^{13}C-IUPAC No. 153, ^{13}C-IUPAC No. 194, ^{13}C-IUPAC No. 138 (all ^{13}C standards purchased from Cambridge Isotope Laboratories, Andover, MA, USA)

2.3 Apparatus

The following apparatus were used: Turbo Vap II Concentrator (Zymark, Hopkinton, Massachusetts, USA,); Combination heating mantels for soxhlet extractors (Fisher Scientific, Model RJ, Nepean, Ontario, Canada); Combo series power controls for heating mantels (Fisher Scientific model RL4312, Nepean, Ontario, Canada); Acculab balance (Canadawide Scientific, model VI 350, Ottawa, Ontario, Canada); Programmable Electronic Controller (VWR-Canlab, Mont-Royal, Québec, Canada) Soxhlet glassware (Fisher Scientific, Nepean, Ontario, Canada, cat no. 09-556C); Chromatography columns (VWR-Canlab, Mont-Royal, Quebec, Canada, 300 mL reservoir, 22 mm id x 350 mm L, cat no. KT420280-0232) Ball-Mill apparatus (customized, 50 mL stainless steel centrifuge tube 27 mm id x 90 mm long, stainless steel restraining strap, two stainless steel balls with a circumference of 56 mm and stainless steel cap 33 mm od x 26 mm id inside lip teflon lined, National Research Council of Canada, Halifax, Nova Scotia, Canada); Wrist Action Shaker (Burrell Corporation, model 75, Pittsburgh, PA, USA); Van Veen grab sampler (AGC, Dartmouth, Nova Scotia, Canada); SPE Vacuum Manifold (VWR-Canlab, Mont-Royal, Québec, Canada, cat no. BJ9400); Glass columns for sample preparation (VWR-Canlab, Mont-Royal, Québec, Canada, cat no. EM-19828-1); Gas Chromatograph-Mass Spectrometry (Agilent Technologies, 6890 Series GC and 5973N network mass spectrometer, Willmington, DE, USA) and fitted with a cool on-column inlet and a chromatographic column (30 m x 0.25 mm id fused silica, coated with MDN-5S, film thickness 0.25 µm, Supelco Sigma-Aldrich Canada Ltd., Oakville, Ontario, Canada).

2.4 Sampling

Sediment sampling was carried out in July 1999, July and October 2000 and October 2001at a total of 36, 54, and 20 stations respectively. Selected samples collected in 1999 were used in this method study. Sediments were collected using a Van Veen grab (~ 1 kg) sampler which was deployed from both a barge and a ship.

On the barge, the sampler was deployed from a fixed A-frame mounted on the rear of the barge, while sampling on the ship used the main crane, and was carried out on the aft starboard. A given sampling event included taking several grab samples to supply adequate material for various program components. Sediments were placed in a 20-L bucket lined with a clean polyethylene bag for each station, and were homogenized by stirring with a stainless steel potato masher or spoon. Sediments for analysis were placed in 1 L acetone-rinsed mason jars.

2.5 Sample Preparation

Marine sediment samples, once received by the lab, are mixed and sub-sampled. The sub-samples (60 grams of wet sediments) are air dried in a fume hood for 48 hours. The dried sample mass is recorded. Moisture content can be determined on the samples using the air-drying technique or samples can be dried in an oven at 110 °C for 24 hours and massed to constant weight. The air-dried samples are crushed lightly, sieved through a 1mm-mesh sieve and stored in a cleaned glass vial prior to extraction.

2.6 Ball-Mill Extraction

See Figure 1, which illustrates the Ball-Mill apparatus. Weigh 1.000-2.000 grams (g) of dried sediment into ball-mill tube (modified stainless steel centrifuge tube 50 mL). Add two stainless steel balls (56 mm), taking care not to splash sample out. Add surrogate recovery standards (^{13}C-CB-77, CB-153, and CB-194) to the extract tubes. Add 20 g clean anhydrous sodium sulfate and 2.0 g copper metal (to remove interfering sulfur) to the tubes. Add 20.0 ml dichloromethane (DCM) to the centrifuge tube. Cap the tube and clamp it horizontally on the Burrell wrist action shaker at minimum displacement for 30 minutes for sediment samples. A duplicate, certified reference material (NIST 1944 New York-New Jersey Waterway Sediment) and operational blank must be performed with each batch of 10 samples.

Remove tubes from shaker and let stand a few minutes before opening. Decant solvent slowly into a clean 100 mL round bottom flask. Repeat the extraction two more times with the addition of 10.0 mL dichloromethane. Reduce solvents from the flask on a Turbo Vap II concentrator or a rotary evaporator with water bath at 35 °C, taking care to remove the flask from the evaporator as soon as the solvents have been evaporated to within 1 to 2 mL.

2.7 Florisil Column Cleanup Following Ball-Mill Extraction

Florisil column purification step was a modification of Nortstrom and Won 1985. Florisil was activated at 450 °C for 17 hours and deactivated (100:1, Florisil:water, w/v). Standardize Florisil using the Mill's Lauric Acid number procedure (Mills 1968). Plug the bottom of a clean glass chromatography column, (22 mm i.d.x 350 mm length) which has a Teflon stopcock, with solvent cleaned glass wool. Place (dry pack) 25.0 g of deactivated Florisil into the column and place approximately 1 cm depth of clean anhydrous sodium sulfate on top of the Florisil in the column.

Wash column with 60.0 ml DCM, which has been dried for 24 hours over clean anhydrous sodium sulphate. Allow DCM to just drain into the surface of the sodium sulphate in the top of the column and discard the DCM, which has drained from the column. Place a 250 mL turbovap tube under the column to collect the eluate.

Apply a 2.0 mL sediment extract (DCM) to the column. Allow the DCM solution to drain to the surface of the column. Quantitatively rinse the tube containing the extract into the column with three additional 2.0 mL DCM rinses, allowing DCM to drain to the top of the sodium sulfate each time. Add an additional 150 ml DCM to the column without disturbing the surface of the sodium sulfate, set the flow rate to 2-4 mL/minute and collect the eluate until the last bit of solvent in the column just enters the surface of the sodium sulfate. This fraction contains the PCBs.

2.8 Soxhlet Extraction

Prior to extraction all glassware must be soap and water washed and rinsed with organic solvents (i.e. 3 rinsings of each acetone followed by hexane). Cellulose extraction thimbles must be pre-extracted or soaked with dichloromethane prior to use to avoid background contamination.

Dry sediment (1.000 g) is weighed into a clean beaker. Add 20-30 g of anhydrous sodium sulphate. Mix the sediment with the sodium sulphate. This mixture helps the solvent to pass more freely through the sediment during extraction. Place the mixture of dry sediment and sodium sulphate into an extraction thimble and cover with clean glass wool. Place the thimble into a Soxhlet tube and add surrogate recovery standards (^{13}C-CB-77, CB-153, and CB-194). Add Teflon boiling chips to a 500 mL round-bottom flask. Add 300 mL of DCM. Attach the flask to the Soxhlet tube and condenser on the Soxhlet extraction apparatus. Soxhlet extract the samples for 18 hours using a programmed timer.

After 18 hours, remove flask from apparatus. Transfer the extracts to the Turbo Vap concentrator tubes. Place the tubes in the Turbo Vap Concentrator (Zymar) and concentrate to 1 to 2 mL. The extracts are now ready for purification.

2.9 Solid-phase Extraction Using Silica Gel Following Soxhlet

Activate Silica Gel at 200 °C in a muffle furnace overnight (17 hours). Remove the Silica Gel while "hot" into a clean pre-weighed round-bottom flask. Caution must be taken at this stage! Allow the Silica Gel to cool and deactivate with HPLC grade water (20:1, Silica

Gel:water, w/v). Rotate the flask every 15 minutes for the next hour to allow the Silica Gel to come to equilibrium. The Silica Gel is now ready for use.

Place a small plug of glass wool into a solid-phase extraction column. Place 2.00 g of deactivated Silica Gel into column. Add 1cm of anhydrous sodium sulfate. Wash with 12 mL of hexane. Close stopper and column is ready for use.

Add 2 mL of the sediment extract to the silica gel column. Drain into a clean 15 mL graduated centrifuge tube. Rinse the extract tube twice more with 1.0 mL portions of hexane and add to the column. Add 10 mL of DCM:hexane (1:4 v/v) to the solid-phase extraction (SPE) column. Collect the purified extract and concentrate to 2.0 mL final volume. The 15 mL centrifuge tube must be weighed before and after extract purification. The specific gravity of 2,2,4-trimethylpentane is used to calculate a final volume from the mass of the extract.

2.10 Copper treatment to Remove Sulfur from Sediment Extracts

Note when using Soxhlet extraction, an additional purification step is needed to remove sulfur. After the extracts have been purified, internal standards are added and the extracts are made up to a final volume of 1.0 mL by mass. The specific gravity of 2,2,4-trimethylpentane is used to determine the amount of solvent to add to a final volume of 1.0 mL. The extracts are mixed and an aliquot (~1 mL) is removed and placed into an autosampler vial. At this stage, a few granules of copper metal is added to the vials and mixed by shaking. If sulfur is present the copper will turn black at this stage. The extracts are decanted, carefully not to disturb the residue generated during the reaction of copper with the sulfur, into clean vials prior to analysis.

2.11 Gas Chromatography-mass Spectrometry (GC-MS) Analysis

The GC operating conditions are: injector on-column, oven track mode sets the inlet 3 °C higher than the oven at all times to optimize the repeatability; column, initial, 80 °C, hold 2 min, ramp at 4 °C/min to 280 °C and hold 10 min. The total run is 62 min.

The mass spectrometry is operated in the selected ion monitoring (SIM) mode, using 3 to 5 ions [SIM-multiple ion (MI)] for a specified class of CBs (Table 1 The SIM method that employs all ions for CBs simultaneously is designed SIM-total ion (TI). The MS software allows for single ion (SI) view for individual CBs in a class. Tune the spectrometer using perfluorotributylamine by performing standard auto-tuning (*m/z* 69, 219, and 502). Set detection ions (Table 1) for CBs. Identify CBs detection ions (*m/z*) and retention times of peaks. The peak area ratio (monitoring ion:quantification ion) must be within ± 20% of the ratio obtained for the corresponding component in the quantitative standard [8]. Construct a calibration graph for each peak response (as determined by the GC-low resolution MS software) and calculate $ng \cdot g^{-1}$ concentrations for each compound identified.

2.12 Detection Limits

Detection limits (three times the noise levels) are: 1.0 ng·g^{-1} dry wt. for all chlorobiphenyls based on the analysis of 1.00 g dry mass and applies to both Ball-Mill and Soxhlet procedures.

2.13 Fortification Studies

Ottawa Sands (dried commercial sediment) was spiked at low (2-4 ng·g^{-1} dry wt), medium (10-35 ng·g^{-1} dry wt) and high (45-70 ng·g^{-1} dry wt), which covered most of the concentration ranges in our samples. A total of 3 to 5 spikes were prepared at each level for the Ball-Mill and Soxhlet procedures respectively.

3.0 RESULTS AND DISCUSSION

3.1 Interfering Compounds

Interfences are a possibility with any procedure, in particular other chlorinated compounds, that come through the purification step, co-elude with the compounds of interest and yield ions that cannot be distinguished from compounds of interest by low-resolution MS. Figure 2 shows SIM-TI chromatograms for A, a chlorobiphenyl standard; B, a sediment extract prepared using the Ball-Mill procedure; and C, the same sediment sample prepared using the Soxhlet procedure.

Retention times and detection ions are used to identify the individual chlorobiphenyls. Figure 3 shows SIM-SI chromatograms for A, a standard; B, a sediment sample prepared using the Ball-Mill procedure; and C, the same sample prepared using the Soxhlet procedure. Detection limits were established for confirming CBs: one quantifying ion with at least one confirmation ion, yielding the correct (20%) ratio with the quantifying ion (Table 1) (King et al. 1995). At least two of the ions in the SIM-MI method are used to give a final confirmation for CBs. The other remaining ions are useful for distinguishing CBs from other possible interferences, e.g., chlorinated naphthalenes, thiophenes and other co-eluting CBs. The NIST library of 130,000 mass spectra and SIM-MI (employing multiple ions) were used to distinguish co-eluding compounds, such as: polychlorinated naphthalenes, thiophenes, furans, and dioxins. No evidence of these compounds was found.

3.2 Purification Techniques

Two purifications techniques were employed. A Florisil column was prepared and used with extracts from the Ball-Mill procedure. The second used a SPE column of silica gel to purify extracts generated by the soxhlet procedure. These purification techniques had been previously employed in the lab to purify organic extracts. The SPE procedure was modified to include chlorobiphenyls. SPE is the more rapid and inexpensive of the two purification techniques, but is more acceptable to interference from other organochlorine type compounds. For this method comparison study, if we compare the chromatograms (Figures 2 and 3) produced by both procedures, the purfications steps preformed extremely well. Based on the results presented here, the purifications steps could be used with either/or extraction procedures.

3.3 Recoveries Studies

Fortifications studies yielded recoveries ranging 80 to 99 and 60 to 117 % for all CBs using the Ball-Mill and soxhlet procedures respectively (Table 2). The Ball-Mill procedure gave slightly higher recoveries for the lower chlorinated CBs and in some cases lower standard deviations compared to the soxhlet procedure. Recoveries of added PCB surrogates prior to Ball-Mill extraction averaged ^{13}C-CB77 (average ± standard deviation) 92±8%, 97±6%, 88±10%, ^{13}C-CB153 85±6%, 88±9%, 82±6%, and ^{13}C-CB194 90±7%, 89±7%, 82±8% for 1999, 2000, 2001 sediments respectively. Recoveries of added ^{13}C-CB77, 153, and 194 to sediments prior to Soxhlet extraction averaged 85±17%, 79±16%, and 74±19% for the 2001 data set. The surrogate recoveries were slightly better with a lower standard deviation for the Ball-Mill procedure. A duplicate, certified reference material (NIST 1944 New York-New Jersey Waterway Sediment) and operational blank must be performed with each batch of 10 samples.

3.4 Method Comparison

The two methods were tested by analysing sediment samples collected from Sydney Harbour, Nova Scotia, Canada and comparing the summed PCB results (Table 3). A correlation plot of CBs results for the Soxhlet versus Ball-Mill procedure gave an r^2=0.9888. Sediment data was not presented in this study for all sampling years. Only data that was used to evaluate the Ball-Mill procedure is presented. Individual CB concentrations in sediment grabs produced by both methods can be compared in Tables 4-6 for the Ball-Mill and Soxhlet procedures respectively. The individual CB results produced by both methods compared well with little variance.

The standard reference material results (Table 6) were valid for both methods (within 1 to 2 standard deviation of the mean). Although in some cases, the results may vary by more than two standard deviations due to the various analytical techniques available to quantify the results (Schantz et. Al 1993). For example, changing the gas chromatographic column may affect the order of elution causing different congeners to co-elute (chromatograph with the same retention times). As a result, this would change the elution pair as well as affect the quantitative results. This makes it difficult to compare our measurements with the reference material results, which are based on different analytical conditions. Our conditions are more sophisticated then those used to generate the SRM results, mostly because we are looking for a greater number of congeners and we used the more advance technique of mass spectrometry for detection compared to electron capture.

3.5 Employment of Different Analysts

Samples selected from the Sydney Harbour project and sediment reference material was used to test the variance between analysts. The comparison of results for analyst 1 and 2 are found in Tables 7-8. The certified reference material, running duplicates and triplicates of the sediments were used to test the analytical variance of our Ball-Mill procedure with two analysts. The variance between the analysts was greatest at the lower concentrations between 1-5 ng·g^{-1} as this was expected. The results produced by both analysts were within

1 to 2 standard deviations of the mean certified values for the NIST 1944. Based on our NIST 1944 and sample comparison results for Analyst 1 and Analyst 2 (Table 9, i.e., CB 5/8 was 23.3±3.4 and 24.2±0.6 for the NIST 1944 respectively), we were confident that changing analysts did not affect the results of the study.

4.0 CONCLUSION

An assessment of the two methods used to extract CBs was completed. Based on our results the two methods were highly correlated and we are able to substitute one method for the other with slight differences in our data. The traditional EPA method of soxhlet extraction is time-consuming, requires handling of expensive glassware and heating apparatus, and uses large volumes of solvent. The Ball-Mill procedure is rapid, uses less solvent, requires the use of very durable unbreakable stainless steel centrifuge tubes, and a wrist action shaker. The Ball- Mill works well for PCBs, is quick (3 extractions at 30 minutes each compared to 18 hours by soxhlet), and requires less solvent (40 mL compared to 300 using soxhlet). The Ball-Mill procedure is more effective at removing sulfur with the addition of copper in the extraction step due to the shaking action. The soxhlet procedure is inadequate at removing sulfur during the extraction stage. Additional copper is required after the purification step in order to remove sulfur effectively from the extracts.

The Ball-Mill apparatus can be easily constructed in a machine shop using stainless steel and some teflon. The initial cost maybe great, but the apparatus will be very durable and can last for many years with little maintenance. The only maintenance required is to replace worn out Teflon liner on the Ball-Mill cap. The Ball-Mill apparatus is cleaned and cared for similar to glassware. The Ball-Mill procedure was used in the past to isolate organochlorine compounds from biological tissues and now can be applied to sediments making it very versatile.

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TABLES

Table 1. Ions used for detection (SIM-MI) of CBs (ions in bold were used for quantification, those in italics for confirmation). ^{13}C standards were used as surrogate internal standards.

Class	Ions				
Mono	**188**	*190*	*126*		
Di	**222**	*224*	*226*		
Tri	**256**	*258*	*260*		
Tetra	**292**	*290*	*294*		
Penta	**326**	*328*	*324*	*330*	
Hexa	**360**	*362*	*292*	*294*	*364*
Hepta	**394**	*396*	*324*	*322*	
Octa	**430**	*432*	*358*	*356*	
Nona	**464**	*466*	*394*	*392*	
Deca	**498**	*500*	*430*	*356*	
^{13}C-CB 138	**372**				
^{13}C-CB 77	**304**				
^{13}C-CB 153	**372**				
^{13}C-CB 194	**442**				

Table 2. Percent recoveries (average ± standard deviation) of added CBs to sediments. Ottawa Sands (dried commercial sediments) were spiked at low (2-4 ng·g-1 dry wt.), medium (10-35 ng·g-1 dry wt.) and high (45-70 ng·g-1 dry wt.). A total of 3 to 5 spikes were prepared at each level for the Ball-Mill and Soxhlet procedures respectively.

Class	Ball- Mill			Soxhlet		
(n= # isomers)	low	medium	high	low	medium	high
Mono (n=3)	81±5%	87±13%	80±3%	65±4%	60±9%	67±6%
Di (n=12)	87±8%	89±12%	89±5%	74±8%	69±8%	75±6%
Tri (n=21)	83±7%	94±13%	94±5%	85±5%	83±9%	83±8%
Tetra (n=27)	83±6%	92±9%	88±5%	92±5%	84±11%	88±5%
Penta (n=32)	87±10%	94±8%	93±3%	96±4%	92±12%	95±4%
Hexa (n=35)	88±9%	92±7%	97±5%	102±5%	96±13%	99±3%
Hepta (n=16)	92±5%	94±7%	99±4%	107±5%	100±14%	104±3%
Octa (n=9)	91±7%	94±6%	98±5%	111±5%	103±14%	107±3%
Nona (n=3)	92±9%	93±4	97±4	115±6%	109±16%	114±3%
Deca (n=1)	91±9%	97±8%	97±9%	117±8%	112±17%	117±4%

Table 3. Method comparison $\sum$CB results for sediment samples collect in 2001.

Station	Soxhlet $\sum$CB (ng·g^{-1} dry wt.)	Ball-Mill $\sum$CB (ng·g^{-1} dry wt.)
1	519	264
2	1524	1312
3	2180	1992
4	2294	1975
5		
6	383	338
7		
8	58	56
9	5261	5049
10	4782	4198
11	3080	3060
11	NA	3132
12	79	67
12	80	70
13	2710	NA
14	695	722
15	1489	1299
16	1230	1262
17	91	81
18		
19	77	61
19	62	55
20		

NA-not analyzed.

Table 4. CBs (ng·g^{-1} dry wt.) in sediment grabs collected in Sydney Harbour in 2001.

	BM	BM	Sox	BM	Sox	BM	Sox	BM	Sox	BM	Sox
Station	1	2	2	3	3	4	4	5	5	6	6
CB No.											
8/5											
18											
28/31											
52											
49											
44											
66/80											
95/121/88	7.0	27	35	58	69	52	66			8.0	9.0
101	8.6	37	49	63	75	67	84			11	13
99		11	8.7								
116/115		5.8	4.5								
110	9.1	37	36	55	63	55	57			11	13
118/106	5.1	13	13	18	18					4.1	4.0
105											
136		22	27			40	46			4.6	6.6
151	6.1	30	33	51	57	60	55			8.6	11
144		29	35	50	35	47	42			8.9	12
149/139	26	132	152	222	262	199	250			34	40
161	5.2	13	21	27	36	30	33			6.6	5.7
153/132	30	142	170	246	264	210	264			39	43
168	6.0	34	42	68	75	68	71			7.3	9.3
137/138/ 163/158	34	142	175	266	272	227	268			46	49
128		17	19			21	22				
156		13	8.2	15	15						
187/182	19	100	110	146	175	123	164			26	29
183	6.6	33	40	58	65	45	56			8.3	9.5
185	4.0	12	13	17	17	15	16				
181	14	74	84			112	111			20	24
171	5.0	19	23	27	40	30	30			4.8	5.7
180	32	161	189	276	291	237	266			41	46
191											
170/190	17	63	69	100	104	85	108			14	19
189											
202		7.4	10	13	14	17	20				
200/201		6.4	12	12	14	11	18				
199		5.0	6.4	6.0	8.5						
196	8.3	49	52	76	84	72	79			12	14
195	6.0	21	21	31	29	25	24			7.5	5.3
194	7.0	38	38	57	61	49	57			9.8	10
205						40	42				
208											
206		8.7	15	18	20	15	23				
209											
$\sum CB$ ng·g^{-1}	256	1273	1524	1926	2180	1905	2294			324	383

Table 5. CBs (ng·g^{-1} dry wt.) in sediment grabs collected in Sydney Harbour in 2001.

	BM	Sox	BM	Sox	BM	Sox	BM	Sox	BM	Sox	BM
Station	7	7	8	8	9	9	10	10	11	11	20
CB No.											
8/5											
18											
28/31											
52											
49											
44											
66/80											
95/121/88					145	122	138	162	90	77	
101					287	183	142	186	140	131	
99											
116/115											
110			4.0	5.0	168	123	184	171	159	97	
118/106											
105											
136					102	117	81	109	83	64	
151					133	127	107	129	78	76	
144											
149/139			6.5	9.0	527	535	479	571	315	372	
161					77	98	68	71	56	59	
153/132			12	9.2	554	584	501	562	329	363	
168					149	164	158	164	119	102	
137/138/											
163/158			11	11	528	595	445	607	411	361	
128											
156											
187/182			5.6	4.6	350	374	294	383	198	236	
183					162	124	115	155	79	92	
185					59	50	46	49			
181			4.0	4.6	321	231	264	334	197	220	
171					56	98	92	61	44	51	
180			9.4	9.5	628	591	528	687	408	412	
191											
170/190			5.0	5.0	242	289	203	263	143	197	
189											
202											
200/201											
199											
196					173	185	148	181	121	90	
195					73	83					
194					140	135	146	158	92	78	
205											
208											
206											
209											
∑CB ng·g^{-1}			58	58	5001	4782	4139	5261	3062	3080	

Table 6. CBs (ng·g^{-1} dry wt.) in sediment grabs collected in Sydney Harbour in 2001.

CB No.	Sox 20	BM Blk reagent	Sox Blk reagent	BM Blk Ott Sands	Sox Blk Ott Sands	BM NIST 1944 (n=2)	Sox NIST 1944 (n=4)	Cert Values
8/5						24	25	22.3±2.3
18						48	44	51.0±2.6
28/31						140	135	159.5±3.6
52						84	77	71.9±4.3
49						67	56	53.0±1.7
44						77	64	60.2±2.0
66/80						66	57	71.9±4.3
95/121/88						40	35	65.0±8.9
101						56	51	73.4±2.5
99						32	26	37.5±2.4
116/115								
110						74	68	63.5±4.7
118/106						44	39	58.0±4.3
105						22	19	24.5±1.1
136								
151								
144								
149/139						49	43	49.7±1.2
161								
153/132						65	53	74.0±2.9
168								
137/138/163/158						80	68	62.1±3.0
128						13	8.4	8.47±0.28
156						5.8	5.5	6.52±0.66
187/182						23	19	25.1±1.0
183						9.1	7.0	12.19±0.57
185								
181								
171								
180						37	33	44.3±1.2
191								
170/190						30	15	22.6±1.4
189								
202								
200/201								
199								
196								
195								3.75±0.39
194						9.1	6.8	11.2±1.4
205								
208								
206						8.2	5.9	9.21±0.51
209						7.6	5.2	6.81±0.33
ΣCB ng·g^{-1}								

Table 7. CBs (ng·g^{-1} dry wt.) in blanks, Ottawa sands and NIST sediments. INF-interference.

Station	1	1	2	2	3	3	4	4	4	4	5	5
CB No.	An-1	An-1	An-1	An-1	An-1	An-1	An-1	An-2	An-2	An-2	An-1	An-2
8/5												
18												
28/31												
52												
49												
44												
66/80												
95/121/88	29	32	99	96	13	22	21	29	31	23	29	31
101	35	43	130	120	24	25	50	36	36	30	53	43
99	5.9	4.6	17	13	4.3	3.0	INF	5.4	6.9	5.6	11	INF
116/115			18	23							7.0	6.9
110	33	34	120	110	19	23	31	30	30	25	34	40
118/106												
105												
136	24	27	68	74	11	13	17	20	21	19	25	28
151	32	37	98	100	13	16	22	25	27	22	31	33
144	30	33	75	94	13	10	24	24	27	22	31	34
149/139	140	170	430	470	64	80	110	130	140	120	160	170
161	20	17	54	41			14	11	15	13	15	19
153/132	120	130	380	340	50	60	89	120	140	110	130	170
168	40	37	130	110	19	24	36	35	35	32	40	41
137/138/											180	170
163/158	190	190	580	580	70	88	120	130	140	120		
128							4.6	5.1	5.6	3.1	8.8	7.4
156			19	24			11	11	15	9.7		
187/182	100	120	320	330	49	53	79	86	92	78	110	120
183	33	39	102	93	22	20	29	30	31	26	36	39
185	19	26	37	31	5.8	7.0	10	11	11	10	12	14
181	77	97	250	260	40	43	64	69	79	63	93	92
171	48	56	140	51	10	12	15	18	20	16	23	23
180	29	29	56	15	81	94	130	140	170	130	190	210
191												
170/190	79	110	260	270	31	39	65	57	70	52	90	81
189												
202	7.5	10	28	24			7.4	10	11	6.3	8.8	11
200/201	6.2	7.0	23	21			5.4	6.8	6.9	7.7	7.0	9.1
199	7.5	8.9	INF	22			4.3	7.3	15	5.4	7.1	11
196	45	61	170	170	31	30	42	46	52	40	54	61
195	20	28	55	63	9.3	13	20	18	23	17	19	24
194	44	48	130	130	18	22	30	37	40	31	42	46
205	36	39										
208			12	8.0			3.5	3.5	4.0	3.1	6.8	5.2
206	13	16	49	31	6.5	8.5	9.9	8.9	8.1	7.1	12	12
209												
ΣCB ng·g-1	1263	1450	3850	3714	604	706	1064	1160	1303	1047	1466	1552

Table 8. CBs (ng·g^{-1} dry wt.) in sediment generated by two different Analysts.

| Station	5	21	21	56	56	Blk	Blk	1944	1944	Cert
CB No.	An-2	An-1	An-2	An-2	An-2	An-1 (n=4)	An-2 (n=5)	An-1 (n=3)	An-2 (n=4)	NIST 1944
8/5								23.3±3.4	24.2±0.6	22.3±2.3
18								43.9±2.8	42.8±1.9	51.0±2.6
28/31								126.7±7.5	129.7±14.3	159.5±3.6
52								72.2±10.1	79.4±2.1	71.9±4.3
49								41.6±3.1	41.6±4.2	53.0±1.7
44								61.9±4.6	67.2±4.2	60.2±2.0
66/80								63.0±4.3	53.9±8.0	71.9±4.3
95/121/88	27	86	63		4.2			35.3±1.9	47.1±5.1	65.0±8.9
101	39	82	67		6.1			49.3±4.4	55.5±4.7	73.4±2.5
99	9.2	6.9	13					24.9±3.1	34.5±6.5	37.5±2.4
116/115	3.0									
110	32	61	52		4.9			78.4±5.6	86.5±3.3	63.5±4.7
118/106								43.0±2.0	45.2±2.0	58.0±4.3
105								22.2±2.0	20.4±1.5	24.5±1.1
136	20	48	43							
151	28	56	49		4.5					
144	27	52	47							
149/139	160	310	300	18	23			44.3±3.5	42.7±2.5	49.7±1.2
161	14	26	23							
153/132	160	210	260	22	27			50.5±7.2	65.6±2.4	74.0±2.9
168	39	77	72	4.9						
137/138/			240	21	24			69.3±0.7	62.1±4.0	62.1±3.0
163/158	160	290								
128	6.1							7.6±1.0	7.5±0.8	8.47±0.28
156		17	16					5.3±1.0	6.0±1.3	6.52±0.66
187/182	110	190	160	15	18			21.3±1.9	24.8±3.8	25.1±1.0
183	34	64	53	4.0	5.2			9.4±0.9	8.2±0.9	12.19±0.57
185	12	21	20							
181	86	160	120	8.0	9.3					
171	16	39	38	2.2						
180	180	320	270	15	22			38.5±1.4	37.9±4.3	44.3±1.2
191		6.9	26							
170/190	74	130	120	9.0	10			19.9±2.1	18.3±1.6	22.6±1.4
189										
202	10	15	11							
200/201	6.4	12	12							
199	10	13	14							
196	56	100	91	5.9	6.7					
195	24	33	27					4.5±0.8	3.7±0.8	3.75±0.39
194	47	71	63		7.2			9.0±0.2	12.5±2.8	11.2±1.4
205										
208	3.0									
206	8.3	20	17					9.1±2.1	9.1±0.9	9.21±0.51
209								6.9±0.3	7.1±0.3	6.81±0.33
ΣCB ng·g^{-1}	1401	2517	2287	125	172					

FIGURES

Figure 1. Ball-Mill Apparatus.
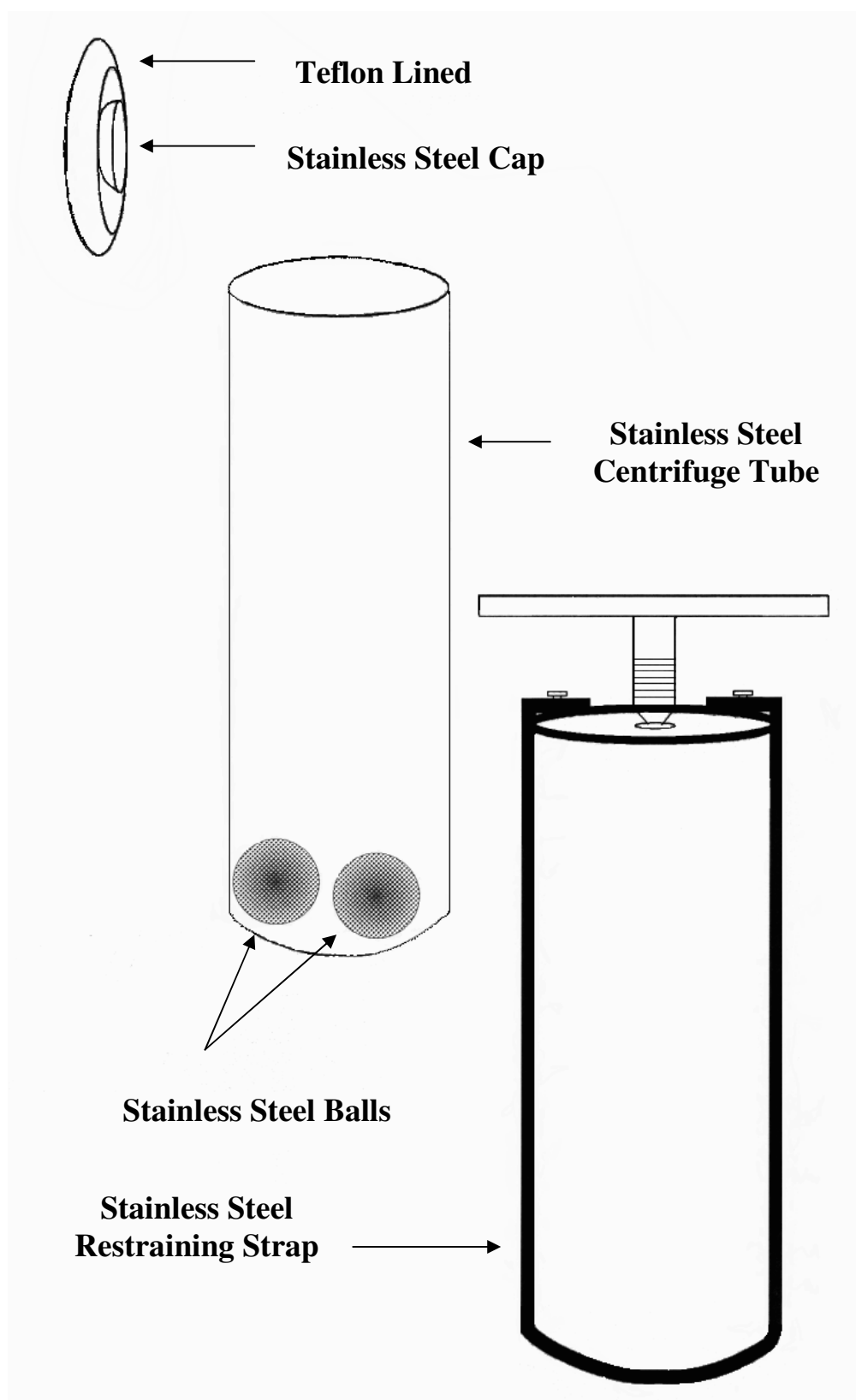
Figure 2. SIM-TI chromatograms for A, a chlorobiphenyl standard; B, a sediment extract prepared using the Ball-Mill procedure; and C, the same sediment sample prepared using the Soxhlet procedure.
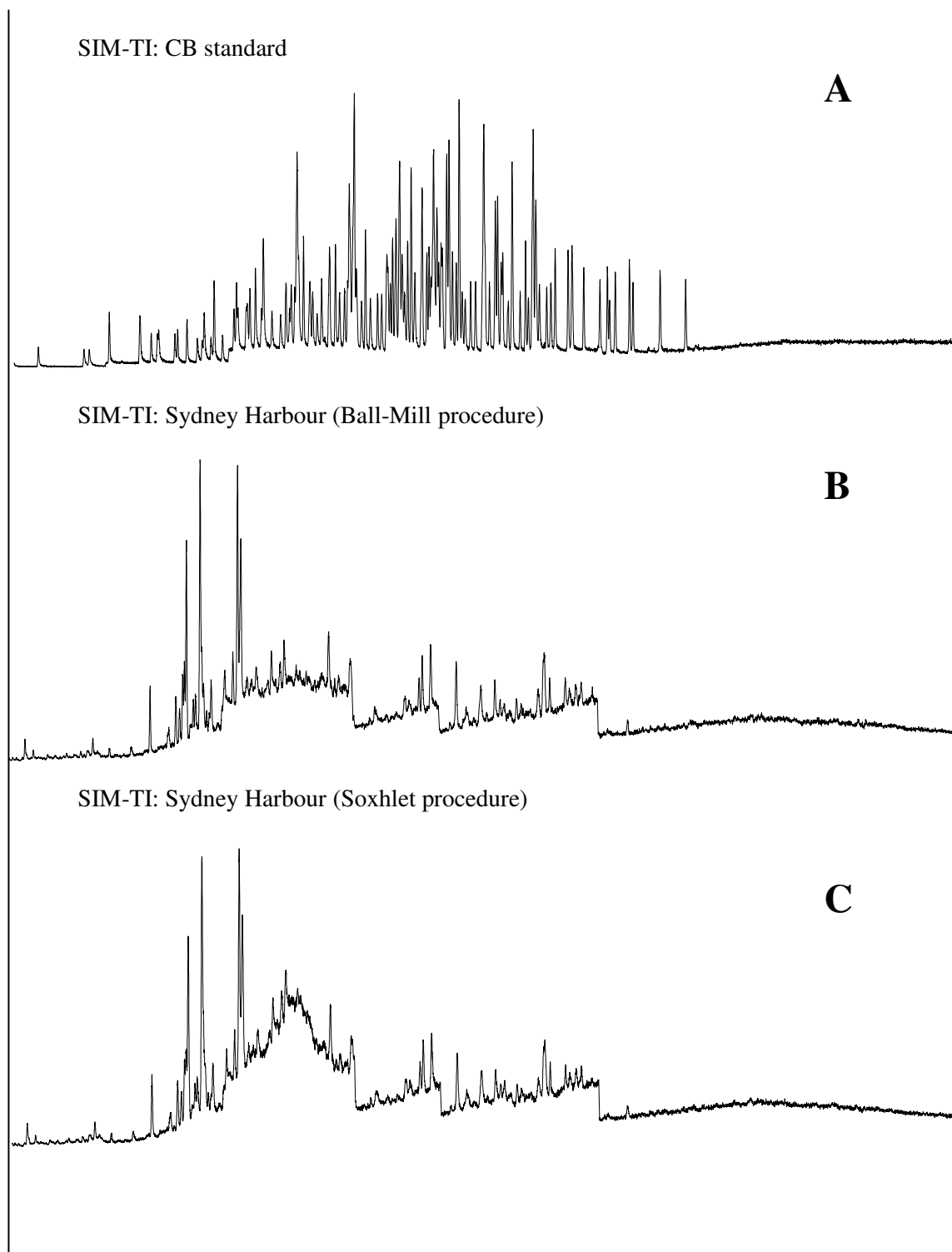

SIM-TI: CB standard

A

SIM-TI: Sydney Harbour (Ball-Mill procedure)

B

SIM-TI: Sydney Harbour (Soxhlet procedure)

C

Figure 3. SIM-SI chromatograms for A, a standard; B, a sediment sample extract prepared using the Ball-Mill procedure; and C, the same sample prepared using the Soxhlet procedure.

Ion 360 Hexachlorobiphenyl

SIM-SI: A CB standard

A

SIM-SI: Sediment extract from Ball-Mill procedure

B

SIM-SI: Same Sediment sample extract from Soxhlet procedure

C