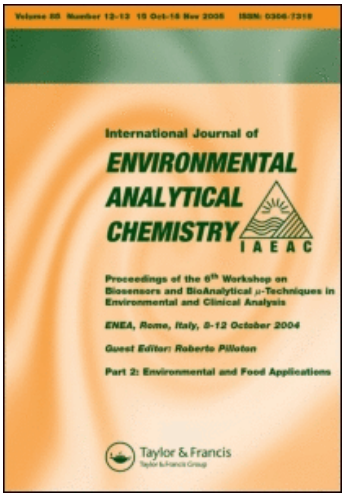

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Analysis of Polychlorinated Biphenyls and DDT and Related Isomers in Complex Samples using a small Volume of Organic Solvent in back extraction

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ANALYSIS OF POLYCHLORINATED BIPHENYLS AND DDT AND RELATED ISOMERS IN COMPLEX SAMPLES USING A SMALL VOLUME OF ORGANIC SOLVENT IN BACK EXTRACTION

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The traditional approach to the extraction of polychlorinated biphenyls, and of DDT and related compounds from complex liquid and solid substrates involves the use at some point, of several hundred millilitres of a hydrophobic solvent such as hexane. This step is required to partition the organic analytes of interest from an aqueous medium into an organic matrix for analysis by gas chromatography or some other technique.

This paper describes the effects on the recovery of PCBs and DDTs from complex substrates, of incorporating a liquid-liquid extraction step in the experimental protocol, using only a small volume(4–10 mL) of hexane. The procedure was applied successfully to the extraction of PCBs and DDTs in apple, orange and vegetable juices, milk, apples, green beans, mussels and finally, fish tissues. Percentage recoveries were usually better than 75% and coefficients of variation were usually below 10%. Results obtained using this modified procedure were compared with those obtained by other laboratories in an Interlaboratory Study of PCBs in fish tissues.

Keywords: PCBs; DDTs; extraction; juice; fruit; mussels; fish

INTRODUCTION

Even though the large-scale use of polychlorinated biphenyls(PCBs) and dichlorodiphenyltrichloroethanes(DDT and related isomers) in North America has subsided over the years, these chemicals are still omnipresent in our environment because of their great persistance[1,2]. Likewise, DDT and related compounds[3,4] are still in use in some parts of the world and eventually end-up in the environment through global air and water transportation. Consequently, chemical

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analyses for these chemicals are still required and we have to continue to improve on existing methods to render them more flexible and less costly.

Substantial progress has been made in recent years to improve existing methods of extraction of Priority Organic Pollutants(POPs) from environmental samples. For instance, the solid-phase microextraction approach, that is, the adsortion of analytes on a solid-phase followed by thermal desorption into a gas chromatograph, has gained widespread acceptance. Potter and Pawliszyn[5] and others[6] have determined polyaromatic hydrocarbons, polychlorinated biphenyls and pesticides[7] in water using solid-phase microextraction and GC-MS. Adsorption columns of Amberlite XAD resins, Florisil and Alumina are also used to concentrate analytes from aqueous samples[8]. The column is then eluted with a small volume of organic solvent, such as n-hexane, to recapture the desired analytes. The use of small adsortion columns, so-called solid-phase extraction[9] (SPE) is also very popular.

Reducing the quantity of organic solvent is important in terms of direct cost of the solvent but also in terms of the cost required for recycling or disposal. Also the use of a smaller quantity of solvent may facilitate automatic extraction techniques and considerably shorten the analysis time. In our case we have taken a different approach, concentrating our efforts upon the traditional liquid-liquid extraction technique but with the objective of using smaller amounts of solvent. In 1993[10] we developed a method for the analysis of organophosphorous pesticides in water at the 0.1 ng/L level using only 1-ml of solvent. We later perfected the technique to analyse PCBs and DDTs(40 ng/L) in tap water using only 2 ml of n-hexane[11]. We subsequently applied the technique to the analysis of chlorinated benzenes(CBs) and a selected group of organochlorine (OC) pesticides, in 1-litre water samples using 4 mL of n-hexane[12].

The analysis of more complex substrates such as fish or meat obviously implies a more complex series of steps. Usually, the sample is first extracted with a polar hydrophilic solvent such as acetonitrile or methanol to yield a primary extract. This extract contains many polar co-extractives and in order to retrieve PCBs or other similar POPs, a secondary extraction with a hydrophobic solvent is usually performed, sometimes preceded or followed by a column clean-up. Thus, in traditional methods still in use today, the secondary extraction step often involves the use of a large volume of organic solvent. The purpose of the present study was to determine whether a liquid-liquid microextraction step, that is, using a small volume of organic solvent, could be introduced into the analytical scheme without excessive loss in recovery. Large quantities of organic solvent are also used in current clean-up methods involving gel permeation and column chromatography, prior to GC-MS analysis[13].

EXPERIMENTAL

Chemicals and substrates

Individual analytical standards(99% pure) of PCBs, DDT, DDD, and DDE were obtained from Ultra Scientific. Stock solutions(1 ug/uL) of the individual congeners of STD-1 and STD-2, respectively, were prepared in ethyl acetate(Caledon Ltd) from pure standards. Aliquots containing the congeners were then mixed together in n-hexane to give a solution containing 200 ng/uL of each congener. Further dilutions were made in n-hexane or ethyl acetate. Thus, STD-1 contained the following congeners: PCB-10, 2,5-dichlorobiphenyl; PCB-21, 2,3,4-trichlorobiphenyl; PCB-26, 2,3′, 5-trichlorobiphenyl; PCB-49, 2,2′, 4,5′-tetrachlorobiphenyl; PCB-86, 2,2′, 3, 4, 5-pentachlorobiphenyl; PCB-116, 2, 3, 4, 5, 6,-pentachlorobiphenyl; and PCB-136, 2,2′, 3,3′, 6,6′-hexachlorobiphenyl. STD-2 contained the following congeners: PCB-28, 2, 4, 4′-trichlorobiphenyl; PCB-52, 2,2′, 5,5′tetrachlorobiphenyl; PCB-101, 2,2′, 4,4′, 6-pentachlorobiphenyl; PCB-118, 2,3′, 4,4′, 5-pentachlorobiphenyl; PCB-153, 2,2′, 4,4′, 5,5′-hexachlorobiphenyl; PCB-137, 2,2′, 3, 4, 4′, 5-hexachlorobiphenyl; PCB-138, 2,2′, 3, 4, 4′, 5′-hexachlorobiphenyl; PCB-180, 2,2′, 3, 4, 4′, 5, 5′-heptachlorobiphenyl; p,p′-DDT, p,p′-DDD, and p,p′-DDE.

All solvents were pesticide grade or equivalent: n-hexane(Burdick and Jackson), ethyl acetate(Anachemia) and acetonitrile(Caledon). Purified water was doubly distilled and deionized. Juices, apples, green beans and mussels were obtained from the local market.

Instrumentation[11]

A Perkin-Elmer 8700 gas chromatograph was equipped with an electron capture detector(ECD-Ni63) and a fused silica capillary column, 30 m × 0.32 mm (i.d.) containing 0.25 um DB-5(J.W. Scientific). A one-metre pre-column(0.53 mm., i.d.) of deactivated fused-silica was used. Instrument settings were: initial temp., 55°C, increased to 160°C at 25°C/min., increased to 180°C at 2.5°/min., increased to 214°C at 2.1°/min., increased to 240°C at 10°C/min. and kept there for 0.1 min. The injection port was set at 250°C and the detector at 350°C.

Analytical protocol

The following is a representative analytical protocol used in this study. Experimental conditions that differ are indicated below the data in each table.

(a) Fortification of samples

To 500 mL of purified(or environmental) water in a beaker was added 100uL of a standard solution containing 2 ng/uL of each analyte in ethyl acetate. 10 g of sodium chloride salt was added while stirring with a magnetic stirrer for 10 min. The solution was transferred to a 1-L volumetric flask which was then filled to the mark with purified water. Thus, the final concentration was 200 ng/L. For experiments with acetonitrile, 100 mL of this solvent was added in the beaker, diluted with 500 mL of purified water, salt added and the solution fortified at this point with 100 uL of the mixed standard of 2 ng/uL. With the difficult substrates, the primary extract containing 100 mL of acetonitrile was transferred in a beaker with a total of 500-mL of purified water and fortification was done at this time with 100 uL of the mixed standard of 2 ng/uL, while stirring. Salt was also added.

(b) Extraction of PCBs and DDTs from water(also with acetonitrile)

Unless otherwise stated, 1 mL of n-hexane was added to the aqueous sample in a one-litre volumetric flask while stirring for 10 min. After equilibration the n-hexane was recovered with a Pasteur pipette and put into a 2-mL volumetric flask. If there was an emulsion, it was broken by adding a few drops of acetone to the supernatent. The extraction was repeated once more and the volume of the combined extracts was made-up to 2-mL with a slight amount of n-hexane. No drying was carried out.

(c) Extraction of PCBs and DDTs from complex substrates

A 10 g sample of substrate, such as apples, green beans or mussels, was homogenized in a Waring blender for 5 min. with 70 mL of acetonitrile. The mixture was filtered through a Whatman #1 filter paper in a 500-mL beaker. A total volume of 30 mL of acetonitrile was used to wash the filter paper and the container.

The 100-mL acetonitrile extract was diluted with 500 mL of purified water and fortified at this point(see (a)). 10 g of sodium chloride were added and the mixture was homogenized for 10 min. Afterwards the mixture was transferred into a 1-L volumetric flask and purified water added to the mark. With a real sample the acetonitrile would be filtered directly into the volumetric flask, salt and then water added to the mark. The sample in the volumetric flask was then extracted with n-hexane as in (b).

With more difficult substrates such as mussels and fish, the acetonitrile extract in the volumetric flask was extracted with two 5-mL portions of n-hexane instead of two one-mL, each time the mixing was carried out for 10 min. as above. The hexane extract had to be cleaned-up. First it was reduced to a small volume using a nitrogen stream and passed through a neutral alumina column(4 cm $\times$ 1 cm

i.d.)previously washed with n-hexane. The column was then eluted under suction with 10 mL of n-hexane. The volume of the eluate was first reduced to less than 2 mL using a nitrogen stream, and finally adjusted to 2 mL with n-hexane.

(d) Quantitation

A 1-uL aliquot of the extract was injected into the gas chromatograph manually and in the splitless mode via a narrow bore injection liner using a 2-uL Hamilton microsyringe. Quantitation of analytes was achieved by comparing peak heights with those of an external standard of corresponding concentration.

RESULTS AND DISCUSSION

Quality control

In this study, the analysis of PCBs, DDT and related isomers was carried out using a GC-ECD and this instrumentation has proven to be very sensitive and precise in past experiments[11]. However, we recognize that in practice, a gas chromatograph with a mass spectrometric detector(GC-MS system) would be quite helpful since it also provides confirmation of the presence of particular analytes[14]. For the purpose of this study we have also found that quantitation with an external standard was sufficient to provide good precision. In terms of repeatability of retention times, less than 0.5% relative error was observed in this study. Typical chromatograms showing the separation of all the analytes in a standard solution were presented in an earlier study[11].

In terms of quantitative reproducibility we have also found that the results compared favorably with those reported in a previous study, that is, the coefficients of variation for individual congeners from repeated injections of analytical standards(10–1000pg), were usually around 2% but could be as high as 10%. Therefore, standards were injected every 10th injection to ensure that the relative error remained under 10%. The response of all analytes was considered to be linear between 1000–10 pg and typical calibration curves for PCB-21, PCB-52, PCB-138 and p, p′-DDT, yielded correlation coefficients at or near 0.999. However, we also recognize that in practice the use of an internal standard is recommended to compensate for matrix effects.

Preliminary experiments

It has been shown in an earlier study[11] that PCBs may be extracted quantitatively from one litre of water using one to two mL of n-hexane and that the pro-

cedure is both cost-saving and time-saving. The challenge in this study was to try to incorporate this microextraction step in a more complex procedure, such as the one used for a more complex substrate as was the case with mussels. In a typical analysis of a complex substrate, the sample is first extracted with an aqueous solvent such as acetonitrile or methanol. Thus, is it possible to use a small volume of solvent to partition the primary extract and improve on current procedures which require a lot of solvent and are more time-consuming[13].

Therefore, the plan was to attempt the primary extraction with 70 mL of acetonitrile, then transfer the acetonitrile extract and washings, for a total of 100 mL of acetronitrile, into a one-litre volumetric flask, dilute to one litre and extract with a small volume of n-hexane. Before doing this, however, it was necessary to determine whether PCBs and DDTs could be extracted from a 10% aqueous solution of acetonitrile.

Results obtained with STD-1 at a concentration of 200 ng/L and under conditions specified, are presented in Table I. In a typical case such as this one, the experiment was repeated six times such that representative averages and coefficients of variation could be calculated for each analyte present in the standard. This allowed for comparison between the % recoveries of the various analytes. In this case the conclusion was that all of the analytes may be recovered quantitatively from a 10% aqueous solution of acetonitrile under the specified conditions.

Unfortunately this type of reporting generates a tremendous amount of results and for the purpose of this paper, where we want to compare the impact of many sets of conditions on the % recoveries, it was found sufficient to display only the average recoveries, for each analyte along with the respective coefficients of variation. Furthermore, taking the average of these averages, so-called Averaged recoveries, allows for comparison between the different experimental conditions. Thus, the results in Table I may be summarized by saying that the Averaged recovery(AR) was 88.0%, which is very good, and the Averaged coefficient of variation(ACV) was 6.99%, which is also very good.

This is further exemplified in Table II where we compare the results obtained with STD-1 with those obtained with STD-2. Thus with STD-2, the Average recovery at 84.5% with an ACV of 6.25%, is slightly less than the averaged values obtained for STD-1. This drop may be attributed to the unexplained lower average recoveries obtained with PCB-180 in this particular set of experiments.

Another set of experiments was conducted to determine any effect on the recoveries of using 2×5 mL of n-hexane instead of 2×1 mL. The results shown in Table III indicate no significant impact on the AR for STD-1 but a better AR for STD-2. In fact the % recoveries of the individual congeners of STD-2 are all above 90% when using 2×5 mL of n-hexane and this volume of solvent was preferred with complex substrates, as shown later.

TABLE I Replicate Recoveries of PCBs and DDTs in 10% aqueous acetonitrile

Chemical	*Experiment #*						*Average recoveries (%)*	*Standard deviation (S)*	*Coefficient of variation (CV)*
	1	*2*	*3*	*4*	*5*	*6*			
BPC-10	90.3	115	94.4	89.2	103	83.3	95.9	11.4	11.9%
BPC-26	71.4	76.1	95.9	88.9	95.5	86.6	85.7	10.1	11.8%
BPC-21	95.7	96.0	86.6	84.2	90.5	86.4	89.9	5.04	5.60%
BPC-49	84.3	83.6	84.0	81.5	87.9	84.3	84.3	2.07	2.45%
BPC-86	92.9	87.9	83.7	85.7	78.9	88.1	86.2	4.72	5.47%
BPC-116	83.6	86.1	86.7	81.4	77.7	81.6	82.9	3.35	4.04%
p, p′-DDE	85.9	81.4	83.6	80.5	74.3	77.6	80.6	4.16	5.16%
BPC-136	89.2	80.0	71.6	88.9	78.6	85.1	82.2	6.82	8.29%
p, p′-DDT	105	95.0	91.2	101	93.0	96.4	96.9	5.18	5.34%
p, p′-DDD	89.0	82.5	94.4	108	95.7	104	95.6	9.39	9.82%
Averaged recovery and Averaged coefficient of variation							88.0	6.22	6.99%

Legend: concentration, 200ng/L; method, 100 mL of acetonitrile in one litre of purified water, extracted with 2 × 1 mL of n-hexane for 2 × 10 min.; 10 g of NaCl added.

TABLE II Recoveries of PCBs and DDTs from 10% aqueous acetonitrile using 2 × 1 mL of n-hexane

STD-1	*%R(CV)*	*STD-2*	*%R(CV)*
BPC-10	95.9% (11.9%)	BPC-28	88.3% (5.86%)
BPC-26	85.7% (11.8%)	BPC-101	83.0% (5.14%)
BPC-21	89.9% (5.60%)	BPC-52	90.8% (6.93%)
BPC-49	84.3% (2.45%)	BPC-118	86.2% (5.47%)
BPC-86	86.2% (5.47%)	BPC-153	84.4% (7.87%)
BPC-116	82.9% (4.04%)	BPC-137	82.6% (7.30%)
p, p′-DDE	80.6% (5.16%)	BPC-138	83.0% (5.31%)
BPC-136	82.2% (8.29%)	BPC-180	78.6% (8.05%)
p, p′-DDT	96.9% (5.34%)		
p, p′-DDD	95.6% (9.82%)		
Average	88.0% (6.99%)		84.6% (6.49%)

Legend: concentration: 200ng/L; method:100 nL of acetonitrile in one litre of purified water, extracted with 2 × 1 mL of n-hexane for 2 × 10 min.; 10g of NaCl added. The % recoveries are averages of 6 replicate analyses.

TABLE III Recoveries of PCBs and DDTs from 10% aqueous acetonitrile using 2 × 5 mL of n-hexane

STD-1	*%R(CV)*	*STD-2*	*%R(CV)*
BPC-10	81.0% (10.6%)	BPC-28	94.5% (7.87%)
BPC-26	83.5% (9.50%)	BPC-101	91.5% (3.89%)
BPC-21	89.3% (8.14%)	BPC-52	90.3% (4.52%)
BPC-49	89.9% (6.37%)	BPC-118	97.6% (6.19%)
BPC-86	88.5% (8.55%)	BPC-153	101% (9.95%)
BPC-116	90.7% (5.48%)	BPC-137	96.1% (5.84%)
p, p′-DDE	88.9% (6.91%)	BPC-138	97.0% (4.33%)
BPC-136	87.8% (6.49%)	BPC-180	105% (7.39%)
p, p′-DDT	87.6% (5.08%)		
p, p′-DDD	87.8% (6.63%)		
Averaged	87.5% (7.37%)		96.5% (6.25%)

Legend: concentration: 200ng/L; method:100 nL of acetonitrile in one litre of purified water, extracted with 2 × 5 mL of n-hexane for 2 × 10 min.; 10g of NaCl added. The % recoveries are averages of 6 replicate analyses.

Before applying the method to very complex substrates such as mussels, several attempts were made to quantify the analytes in selected simpler matrices. One set of experiments was conducted with apple juice. The data shown in Table IV give an AR of 86.8%(ACV 12.1%) for STD-1 in 100 mL of apple juice(no acetonitrile was used here). Although the average %recoveries for the individual analytes were good, there was a greater variation in the data as expressed by some values of ACV near 15%. A similar experiment carried out with orange juice(data not shown) gave only 23% AR for STD-1 and therefore another approach was sought for these substrates.

TABLE IV Recoveries of PCBs and DDTs in Various Liquid Substrates

STD-1	*Apple juice*[1] *%R(CV)*	*Vegetable juice*[2] *STD-2*	*Milk*[3] *%R(CV)*
BPC-10	95.8% (5.60%)	90.6% (6.89%)	71.5% (7.92%)
BPC-26	92.9% (7.90%)	74.2% (10.4%)	65.3% (11.7%)
BPC-21	91.9% (14.6%)	77.7% (9.11%)	77.6% (7.67%)
BPC-49	87.8% (14.7%)	64.9% (7.04%)	73.5% (10.1%)
BPC-86	85.5% (13.4%)	63.5% (12.5%)	71.4% (6.76%)
BPC-116	86.2% (16.3%)	67.5% (10.2%)	68.1% (7.92%)
p, p'-DDE	85.8% (15.9%)	69.7% (7.20%)	64.4% (8.19%)
BPC-136	85.6% (10.6%)	70.0% (6.60%)	69.6% (4.70%)
p, p'-DDT	80.4% (12.1%)	95.7% (14.4%)	83.9% (16.9%)
p, p'-DDD	76.5% (9.67%)	70.2% (13.8%)	78.2% (14.9%)
Averaged	86.8% (12.1%)	74.4% (9.80%)	72.3% (9.70%)

1) 100 mL of apple juice extracted with 2 × 1 mL of n-hexane for 2 × 10 min, 10g of NaCl added; 2) 10g of vegetable juice in 100 mL of acetonitrile, diluted to one litre and extracted with 2 × 5 mL of n-hexane for 2 × 10 min, 10g of NaCl added; 3) 10g of milk, otherwise as in 2). The % recoveries are averages of 6 replicate analyses.

Further experiments with liquid substrates were carried out using 10g of sample, to which was added 100 mL of acetonitrile followed by dilution to one litre in a 1-L volumetric flask and extraction with 2 × 1 mL of n-hexane. The results with orange juice (not shown here) were good(greater than 75% average recoveries obtained for some analytes of STD-1, namely BPC-10, BPC-26, BPC-21 and BPC-49 and p, p'-DDT). A sample of vegetable juice gave similar results for the same congeners. We had very little success with whole milk under the same con-

ditions, presumably because of the high fat content. However, when 2 × 5 mL of n-hexane were used the results were much improved as shown in Table IV with an AR of 74.4% (ACV 7.36%) for vegetable juice and 72.3% (ACV 9.7%) for milk, respectively.

Extraction of solid substrates

The above experiments have shown that the chances of getting higher recoveries with complex substrates are better when 2 × 5 mL of n-hexane were used. In fact with a 10g sample of apples the AR increased from 58.4%(ACV 7.77%) with 2 × 1 mL to 74.3%(ACV 8.91%) with 2 × 5 mL as shown in Table V. Similarly the AR for green beans increased from 58.4%(ACV 15.5%) to 76.6%(ACV 8.6%)(see Table V). This trend is also shown with individual congeners with the exception of BPC-10 in green beans, which shows a higher value with 2 × 1 mL of n-hexane. With apples and green beans further clean-up was not neccessary. However, this was not the case with mussels or fish tissue.

TABLE V Recoveries of PCBs and DDTs from solid substrates. Effect of volume of n-hexane

STD-1	*Substrate*			
	Apples		*Green Beans*	
	2 × 1 mL	*2 × 5 mL*	*2 × 1 mL*	*2 × 5 mL*
BPC-10	76.5% (6.83%)	75.9% (7.92%)	98.6% (6.01%)	88.4% (8.01%)
BPC-26	59.7% (8.83%)	83.7% (7.91%)	65.0% (6.41%)	68.8% (7.23%)
BPC-21	66.9% (9.44%)	86.6% (8.46%)	77.4% (7.68%)	78.4% (8.07%)
BPC-49	57. 9% (8.29%)	84.4% (2.82%)	63.8% (8.20%)	74.1% (10.5%)
BPC-86	59.8% (25.1%)	64.4% (5.97%)	41.7% (17.6%)	71.7% (10.2%)
BPC-116	49.3% (12.3%)	64.2% (12.9%)	39.1% (19.4%)	69.1% (9.41%)
p, p′-DDE	47.4% (14.1%)	66.9% (10.0%)	35.2% (24.3%)	80.2% (5.91%)
BPC-136	53.0% (17.6%)	67.2% (11.3%)	42.0% (17.7%)	80.4% (6.60%)
p, p′-DDT	73.3% (18.1%)	82.0% (11.4%)	80.5% (11.1%)	79.2% (10.0%)
p, p′-DDD	40.2% (14.4%)	67.3% (10.4%)	41.1% (36.1%)	75.5% (10.1%)
Averaged	58.4% (13.5%)	74.3% (8.91%)	58.4% (15.5 %)	76.6% (8.60%)

Legend: concentration: 200ng/L; method:100 nL of acetonitrile in one litre of purified water, extracted with 2 × 1 mL or 2 × 5 mL of n-hexane for 2 × 10 min.; 10g of NaCl added. The % recoveries are averages of 6 replicate analyses.

Therefore we verified several types of adsorbents for that purpose, namely, Florisil, RP-C18, neutral Alumina, basic Alumina, and Silica-gel. We finally opted for a small(4 cm × 1 cm i.d.)neutral alumina column which gave very high recoveries of all the analytes of both standards.

Using the procedure developed in this study, that is, primary extraction of 20 g of mussels with 100 mL of acetonitrile, dilution to one litre with water and back extraction with 2 × 5 mL of n-hexane followed by clean-up with a neutral alumina column, we have obtained the results shown in Table VI. At a concentration of 10 ng/g, the AR for the analytes of STD-1 was 86.6%(ACV 11.5%). The average %recovery for each of the congeners was above 80% with a coeff. of var. between 6% and 16%. With STD-2 the average recovery was 88.7%(ACV 5.02%). All of the recoveries for each of the congeners were above 80% and the coefficients of variation varied between 2% and 11% indicating better precision than was the case with STD-1. With this type of analysis using the electron capture detector, it was found the the precision varied quite a bit from one replicate experiment to the next, from a minimum of about 5% average coefficient of variation to a maximum of about 15%.

TABLE VI Recoveries for PCBs and DDTs in mussels

STD-1	*%R(CV)*	*STD-2*	*%R(CV)*
BPC-10	96.4% (5.63%)	BPC-28	101% (4.71%)
BPC-26	82.8% (13.5%)	BPC-52	82.8% (11.3%)
BPC-21	84.6% (10.1%)	BPC-101	90.5% (5.75%)
BPC-49	86.2% (9.38%)	BPC-118	96.5% (3.13%)
BPC-86	90.6% (11.1%)	BPC-153	86.6% (5.27%)
BPC-116	83.8% (13.0%)	BPC-137	81.9% (2.05%)
p, p'-DDE	87.2% (15.9%)	BPC-138	87.0% (4.16%)
BPC-136	88.3% (12.4%)	BPC-180	83.7% (3.83%)
p, p'-DDT	85.4% (13.2%)		
p, p'-DDD	80.7% (11.0%)		
Average	86.6% (11.5%)		88.7% (5.02%)

Legend: 20g of mussels, fortified with 200 ng of each analyte; extracted with acetonitrile(70 mL + 30 mL), diluted to one litre with water and partitioned into n-hexane(2 × 5 mL for 2 × 10 min); 10 g of NaCL was added. The % recoveries are averages of 6 replicate analyses.

Thus, using the method described in this study, we analysed a sample of fish tissue provided to us by Fisheries and Oceans Canada as part of an Interlabora-

tory Study[15]. The results presented in Table VII show that our data(#34) compared reasonably well with those of laboratories, #4 and #12.

TABLE VII Interlaboratory Study for the Presence of PCB Congeners in Fish Tissue

Lab	*PCB Congeners (ng/g)*							
	28	*52*	*101*	*118*	*137*	*138*	*153*	*180*
1	1.5	12	72	114	4.0	75	127	66
4	9.4	15.6	35.2	55.5	4.1	76.0	79.6	33.4
6	16.7	30.3	103	93.4	13.5	135	162	84
7	7	20	62	82	---	126	136	69
10	14	41	112	230	9	240	227	125
12	6.1	28.6	47.2	50.1	2.8	64.2	86.4	35
14	6	22	74	72	6	140	148	78
16	N.D.	22	49	76	N.D.	141	108	34
17	13.2	26.2	58.5	104	2.2	152	118	70.8
19	10	36	104	90	12	152	157	74
20	13	35.4	123.8	148.9	4.4	140	136.6	64
22	10.8	15.0	50.5	58.8	7.5	90.0	75.6	32.4
30	11	24	69	124	N.D.	172	202	87
Average	9.9	25.3	73.9	89.0	6.6	122	128	60.6
S	4.3	8.8	28.1	29.8	3.88	36	37	21.0
C.V.	43%	35%	38%	33%	59%	35%	29%	35%
34 (Our data)	9.1	15.4	33.8	39.0	--	64.9	66.7	34.5

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Legend: (---), no data; N.D. not detected. The % recoveries from lab 34 are averages of two replicate analyses.

CONCLUSION

It has been demonstrated in past studies that extraction of an aqueous sample with a small volume(1–2mL) of n-hexane yielded good recoveries for various types of organic contaminants such as organochlorines and PCBs. The objective in this study was to determine whether a small volume of n-hexane could be used

to back-extract an aqueous primary extract from a more complex substrate using a small volume of n-hexane in order to recover quantitatively PCBs and other organic contaminants.

Initially we tried various aqueous substrates to determine whether they could be extracted directly with n-hexane. Satisfactory results were obtained with apple juice, vegetable juice and milk.

However, with more complex substrates, particularly solid ones, it is usually neccessary to carry out an initial extraction step using an aqueous solvent. In this study the solvent of choice was acetonitrile. Therefore, it was neccassary to evaluate the presence of this solvent on the back-extraction step. Thus, several experiments were carried out in the presence of acetonitrile. and it was shown that n-hexane could extract PCBs and DDTs from a 10% aqueous solution of acetonitrile.

The procedure developed in this study, that is, back extraction of the aqueous extract with a small volume of n-hexane, was then applied successfully to apples and green beans. Finally, the method was applied to the extraction of PCBs and DDTs in mussels, a rather complex substrate. Comparison of our data with those obtained by several other laboratories showed that our recoveries were generally lower. Nevertheless, our method was deemed valuable because most of the analytes were detected even though smaller volumes of organic solvents were used. What is lost in accuracy is gained by cost saving. However, our results are definitely on the low side when compared with those of the other laboratories, as reflected by the averaged values. Our low results can be explained by the fact that only 75 mL of acetonitrile was used for the primary extract. Not having any information on the procedures used by the other laboratories, it is impossible to know whether or not they used a larger volume of primary solvent than we did nor is it possible to speculate on the accuracy of their results.

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