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DEVELOPMENT OF SEDIMENT EXTRACT REFERENCE SAMPLES FOR SELECTED TOXIC ORGANIC CONTAMINANTS
Part I. Total PCBs, Chlorobenzenes and Polynuclear Aromatic Hydrocarbons

by

A.S.Y. Chau, W.C. Li and H.B. Lee

Research and Applications Branch
National Water Research Institute
Canada Centre for Inland Waters
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario, L7R 4A6

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MANAGEMENT PERSPECTIVE

Concern about toxic organic contaminants in environment has resulted in the monitoring of a wide variety of samples such as water , sediment and fish samples for total PCBs, chlorobenzenes and polynuclear aromatic hydrocarbons. Routine analysis of sediment samples for these toxic organic contaminants is particularly important , since the sediments are considered as a sink as well as a source for toxic organics in water.

From previous quality assurance/quality control (QA/QC) studies, it was noted that many variations in extraction, cleanup and quantification of toxic organic contaminants existed in sediment analysis. To eliminate the variation of various extraction procedures, a sediment extract reference sample was developed to be used as QC sample to evaluate the variation of cleanup procedures in interlaboratory comparison studies.

The quality of the sediment extract reference sample stored in ampules was determined through verification of the homogeneity of subsamples and their stability under various storage conditions.

Dr. Robert Bisson
A/Director
Research and Applications Branch

RÉSUMÉ ADMINISTRATIF

L'inquiétude au sujet de la présence de contaminants organiques toxiques dans l'environnement a entraîné le contrôle d'une grande variété d'échantillons - échantillons d'eau, de sédiments et de poissons - pour mesurer les PCB, les chlorobenzènes et les hydrocarbures aromatiques polycycliques totaux. L'analyse courante des échantillons de sédiments destinée à détecter la présence de ces contaminants est particulièrement importante, car on considère que les contaminants qui se trouvent dans l'eau s'accumulent dans les sédiments ou en proviennent.

Au cours d'études précédentes sur le contrôle et l'assurance de la qualité (CQ et AQ), on a remarqué que les méthodes d'extraction, de purification et de quantification des contaminants organiques toxiques utilisées dans l'analyse des sédiments variaient beaucoup. De façon à éliminer les variations causées par les diverses méthodes d'extraction, on a élaboré un échantillon de sédiment de comparaison qui servira d'échantillon du CQ dans l'évaluation des différences existant dans les méthodes de purification en usage dans les études de comparaison interlaboratoires.

On a déterminé la qualité de l'échantillon de sédiment de comparaison conservé dans des ampoules, en vérifiant l'homogénéité de sous-échantillons ainsi que leur stabilité dans diverses conditions d'entreposage.

Robert Bisson

Directeur p. i.

Direction de la recherche et des applications

ABSTRACT

This paper describes a simple and rapid method for the preparation of a large quantity of sediment extract reference sample in ampules for selected toxic organic contaminants. The homogeneity of subsamples was verified and their short-term stability for up to one month under various storage conditions was also monitored.

RÉSUMÉ

La présente étude décrit une méthode simple et rapide pour préparer, dans des ampoules, une grande quantité d'échantillons de sédiment de comparaison à utiliser pour des contaminants organiques toxiques sélectionnés. On a vérifié l'homogénéité de sous-échantillons ainsi que leur stabilité à court terme pendant une période pouvant aller jusqu'à un mois et dans des conditions d'entreposage variées.

1.0 INTRODUCTION

The Quality Assurance Project of the Research and Applications Branch is involved in many studies in support of the Canadian Environmental Protection Act (CEPA). These include various quality assurance programs designed for regional and national monitoring and assessment activities of toxic contaminants in the environment. The scientific literature contains very little information on the subject of quality assurance for toxic organic contaminants. Therefore considerable in-house investigation is required before interlaboratory round-robin studies in this area can be initiated. To determine accuracy, various reference samples of different characteristics and of known concentration are also required. We have developed and prepared a series of reference materials (RMs) for water analysis, and certified reference materials (CRMs) for sediment analysis. These materials include several of the world's first Great Lakes sediment CRMs for polynuclear aromatic hydrocarbons (PAHs)[1], chlorobenzenes (CBs)[2], total PCBs[3] and selenium[4]. These RMs and CRMs were developed to serve our various international, national, and interdepartmental laboratory performance assessment programs and to assist laboratories in obtaining more reliable and compatible data for trace elements and trace organic chemicals in sediments and waters.

As part of our QA project for the CEPA progam, we continue to develop the required reference samples of different characteristics to be used in various interlaboratory comparison

studies. A new program for the development of a new type of sediment extract reference samples with native contaminants or spiked target contaminants is now underway. From previous QA/QC studies, it was noted that many variations existed in procedures such as the extraction, cleanup and quantification of toxic organic contaminants as part of sediment analyses. To eliminate the variation of various extraction procedures, sediment extract reference samples can be used as QC samples to evaluate the variation of cleanup procedures in interlaboratory comparison studies.

This report presents our first developed protocol to prepare several hundred QC subsamples of sediment extract in ampules for three classes of toxic organic contaminants: total PCBs, chlorobenzenes (CBs) and polynuclear aromatic hydrocarbons (PAHs). In addition, the report provides information on the quality of the ampules prepared on the basis of the monitoring of the homogeneity and stability of reference samples.

2.0 EXPERIMENTAL

2.1 Selection of Sediments

Two sediment portions were taken from the leftover fractions of CRM SC-1 and LE-1 previously collected from Lake St. Clair and Lake Erie, respectively. Preliminary analysis of these two sediment portions indicated that they contained various concentrations of total PCBs, CBs and PAHs. While SC-1 had

relatively low levels of total PCBs and high levels of CBs, the reverse situtation was observed in the case of LE-1.

Approximately 1.5 kg each of -200 mesh, freeze-dried sediments (SC-1 and LE-1) were used for the preparation of a mixed sediment extract (SE-1) in ampules for toxic organic contaminants (total PCBs, CBs and PAHs).

2.2 Extraction

A total of 3.0 kg sediment portions including 1.5 kg each of SC-1 and LE-1 was extracted in the following manner. A 200 g subsample was placed into a 2 L Erlenmeyer flask with a large magnetic bar and 500 mL of acetone was added. The sample was extracted for 2 h by stirring vigorously with a magnetic stirrer. After the suspension settled, the supernatant solution was filtered through a solvent-washed celite 545 column under vacuum and the eluate was collected in a 500 mL round-bottomed flask. The extraction was repeated once with another 500 mL portion of acetone. After the last extraction, as much solvent as possible was removed from the sediment by filtration under vacuum through the same celite 545 column.

The combined extract for each subsample (200 g) was evaporated to about 100 mL with a 3-stage Snyder column. The concentrated extracts from the all (15) subsamples were combined in a 2 L volumetric flask and the final volume of extract was made up to 1.5 L with acetone. One mL of the extract is equivalent to

approximately 2 g of sediment.

The sediment extract was stored in a freezer at -20°C for at least one week. The extract was then filtered through a 0.45 μm filter to remove any particulates and precipitates formed during cold storage. The clear sediment extract was made up to 1.5 L with additional acetone to compensate for any losses of sovent during the filtration steps. The extract was then stored in the dark in a refrigerator at 4°C until ready for the preparation of ampules.

2.3 Preparation of Ampules

Aliquots of approximately 2.5 to 3 mL of the refrigerated extract were transferred into 5 mL precleaned glass ampules. The ampules were placed in groups of 20 or so and covered with aluminun foil while being cooled in a freezer at -10°C for at least 30 min. The ampules were sealed with a glass blowing torch immediately after being removed from the freezer.

All the ampules prepared (about 500) were colour-coded and stored in the dark in a refrigerator at 4°C. For stability studies, a portion of about 50 ampules was stored separately in the dark at room temperature (25°C).

2.4 Reference Values and Stability of Toxic Organic Contaminants of Sediment Extract in Ampules.

An important task of this study was to generate the

reference values for toxic organic contaminants of sediment extract in ampules and to monitor their stability. Portions of the subsamples from the bulk sediment extract were analyzed before the ampules were prepared. Several subsamples of the extract stored in ampules were analyzed for selected toxic organic contaminants after storage periods of storage in the dark of 2 weeks and 1 month, at 4°C or at 25°C.

In-house reference standard solutions were used for the quantitative determination the levels of toxic organic contaminants in the sediment extract samples.

2.5 Analytical Procedures

2.5.1 Cleanup of Sediment Extract in Ampules

The subsamples (bulk sediment extract and the sealed ampules) were allowed to reach room temperature. In the case of the ampules, after breaking the seal, their content (2 to 2.5 mL) was quantitatively transferred into a 15 mL centrifuge tube and the solvent replaced through successive addition of 5 mL portions of hexane and evaporation to about 1 mL by blowing a nitrogen stream in the centrifuge tube immersed in a water bath kept at 35°C. The processs was carried out twice to ensure the complete solvent exchange from acetone to hexane. The concentrated extract was made up to 2 mL with hexane for cleanup. The cleanup for this extract was as follows: a 400 x 10 mm i.d. glass column with a coarse fritted disc was filled with a freshly prepared slurry of 10.0 g

of silica gel (Davison grade 923, 100-200 mesh, activated at 130°C for 18 h before use) in hexane and a 1 cm layer anhydrous Na_2SO_4 placed on top. The concentrated sediment extract in hexane was quantitatively transferred onto the column and drained just into the Na_2SO_4 layer. The sample tube was rinsed with 2 mL of hexane and the rinsing was again applied to the column. This process was repeated twice. Then the column was eluted with 50 mL petroleum ether and the eluate was collected as fraction A for analysis of total PCBs and CBs. The column was further eluted with 50 mL v/v dichloromethane/hexane (40:60%). This fraction was collected as fraction B for analysis of PAHs.

The fractions A and B were collected in 250 mL round-bottomed flasks and evaporated to about 5 mL using a 3-stage Snyder column. After quantitative transfer of the concentrated extract into a 15 mL centrifuge tube, a 2 mL portion of iso-octane was added and the extract was then evaporated to < 1 mL under a nitrogen stream while the tube was immersed in a 60°C water bath. The final concentrate was made up to exactly 1 mL with iso-octane. The extract was than analyzed for the selected toxic organic contaminants by using the analytical methods described below.

2.5.2 Quantification

A Hewlett-Packard 5880A gas chromatograph equipped with a Ni-63 electron capature detector (GC/ECD), a split/splitless injection port, a Model 7671A autosampler and Level IV terminal was

used. Helium was used as the carrier gas, at a linear velocity of 25 cm/sec. A 2 μL aliquot was injected in splitless mode by an autosampler with the splitless valve on for 0.5 min.

For the analysis of total PCBs in fraction A, a 30 m x 0.25 mm i.d. DB-5 fused silica capillary column of 0.25 μm film thickness (J and W Scientific) was used. The GC conditions were as follows: injection port temperature, 250°C; detector temperature, 300°C; initial column temperature, 70°C; initial time, 2.0 min; oven temperature programming rate 1, 25°C/min (70° to 170°C); programming rate 2, 1°C/min (170° to 260°C), oven held at 260°C for 15 min. The working standard was a mixture of Aroclors 1242,1254,1260 (1:1:1) in iso-octane with a total PCB concentration of 375 pg/μL.

For the analysis of CBs in fraction A, a 30 m x 0.2 mm i.d. wall-coated open tubular fused-silica capillary column OV-1 was used, as manufactured by Hewlett-Packard. The GC conditions were as follows: injector port temperature, 250°C; detector temperature, 300°C; initial column temperature, 40°C; initial time, 0.5 min; temperature programming rate 1, 30°C/min (40° to 70°C), oven temperature held at 70°C for 5 min; programming rate 2, 8°C/min (70° to 220°C); oven held at 220°C for 10 min; post value at 260°C for 10 min.

For the analysis of PAHs in fraction B, a gas chromatograph with mass-selective detector (GC/MSD) was used. The system consisted of a Hewlett-Packard 5880A gas chromatograph equipped with a 5970B mass-selective detector, a series 300

computer and a 9133H disc drive. A 30 m x 0.25 mm i.d. SPB-5 capillary column was directly interfaced with the electron impact ion source (70 eV) for maximum sensitivity. The GC conditions were as follows: injection port temperature, 250°C; initial column temperature, 70°C; initial time, 0.75 min; oven temperature programming rate 1, 30°C/min (70° to 180°C); programming temperature rate 2, 3.0°C/min (180° to 280°C), oven held at 280°C for 20 min. Helium was used as the carrier gas, at a linear velocity of 25 cm/min. A 2.0 μL aliquot was injected in splitless mode by an autosampler with the splitless valve on for 0.5 min. Before GC/MSD analysis, an aliquot (20 μL) of mixed internal standards containing naphthalene-d_8, phenanthrene-d_{10}, chrysene-d_{12} and benzo[ghi]perylene-$^{13}C_{12}$ was added to the final extract to calibrate the MSD response. For quantitative purpose, the MSD was operated in the selected ion monitoring mode. The following molecular ions characteristic of PAHs were monitored: m/z 128 for naphthalene (Nap); m/z 152 for acenaphthylene (Ac-thyl); m/z 154 for acenaphthene (Ac-the); m/z 166 for fluorene (Fl); m/z 178 for phenanthrene (Phen) and anthracene (Anth); m/z 202 for fluoranthene (F) and pyrene(Py); m/z 228 for benzo[a]anthracene (B[a]A) and chrysene (Ch); m/z 252 for benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F) and benzo[a]pyrene (B[a]P); m/z 276 for indeno[123cd]pyrene (I[cd]P) and benzo[ghi]perylene (B[ghi]P) and m/z 278 for dibenz[ah]anthracene (D[ah]A).

3.0 RESULTS AND DISCUSSION

3.1 Homogeneity Study

Analysis of subsamples from the bulk sediment extract provided some information on the preliminary reference values of the selected toxic organic contaminants as well as the precison (relative standard deviation) for the analytical methods used. By comparing the results obtained from the bulk sediment extract (before the ampules were prepared) with those obtained from the sealed ampules (after the ampules were prepared), it is then possible to evaluate whether the procedure of filling and sealing the ampules causes any loss of solvent and/or analytes of interest. The results of the analysis of the selected toxic organic contaminants in subsamples of the bulk sediment extract are summarized in Tables 1a,1b and 1c for total PCBs, CBs and PAHs, respectively. The total PCBs analyzed were the sum of Aroclor 1242, 1254 and 1260; the CBs analyzed were 1,3,5-trichlorobenzene (TCB), 1,2,4-TCB, 1,2,4,5-tetrachlorobenzene(TeCB), 1,2,3,4-TeCB, pentachlorobenzene(PeCB), hexachlorobenzene(HCB), along with hexachlorobutadiene(HCBD) and octachlorostyrene(OCS); the PAHs analyzed were naphthalene(Nap), acenaphthylene(Ac-thyl), acenaphthene(Ac-the), fluorene(Fl), phenanthrene(Phen), anthracene (Anth), fluoranthene(F), pyrene(Py), benzo[a]anthracene(B[a]A), chrysene(Ch), benzo[b]fluoranthene(B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene(B[a]P), indeno[123cd]pyrene(I[cd]P), dibenz[ah]anthracene(D[ah]A) and benzo[ghi]perylene(B[ghi]P). The

relative standard deviations (RSDs) for five replicates were 5.6% for total PCBs, from 7.8% to 19.3% for CBs except for 1,2,3,4-TeCB (40.0%), and from 5.0% to 20.7% for PAHs except for naphthalene (38.8%). Overall, RSDs for most parameters of the organic contaminants were satisfactory, with the exception of a few parameters in CBs and PAHs which had high RSDs because of their low concentrations in the sediment extract.

After the ampules were prepared, four replicates of random subsamples (the sealed ampules) were analyzed for the same parameters as those analyzed for the bulk sediment extract. The results of these analyses are summarized in Tables 2a, 2b and 2c for total PCBs, CBs and PAHs, respectively. The relative standard deviations (RSDs) were 6.2% for total PCBs, from 3.3% to 16.9% for CBs, except for 1,2,3,4-TeCB (30.8%), and from 3.2% to 23.1% for PAHs except for D[ah]A (33.9%). These results being comparable to those obtained with the bulk sediment extract, the subsamples obtained from the sealed ampules can be considered to be homogeneous.

A comparison of the total PCBs results obtained with the bulk sediment extract and the sealed ampules indicates that the difference is better than 1% (Table 1a and Table 2a). To facilitate the easy inspection of the differences in CBs and PAHs concentrations between the bulk sediment extract and the sealed ampules, paired sample plots were made. As can be seen from Fig.1a, all the points of CB parameters are lying on or very close to the theoretical straight line (45 degree). This suggests that

there is no detectable loss of CBs of interest and/or solvent (acetone) during ampule filling and sealing process. As shown in Fig. 1b, similar results were observed for the PAHs except for a few parameters such as B[b]F + B[k]F and B[a]P. The difference observed with these parameters may be due to the random experimental error of the analytical procedure employed. GC/MSD was used for PAHs analysis. Although B[b]F + B[k]F and B[a]P actually had higher concentrations than other PAHs, they are less sensitive by this MSD analysis and thus the results are less precise. In addition, B[b]F and B[k]F were not resolved by the GC conditions employed.

In conclusion, the subsamples obtained from the sealed ampules are homogeneous and the ampule filling and sealing procedure described above is adequate.

3.2 Stability Study

The stability of the sealed ampules under common storage condition, that is in the dark in a refrigerator at 4°C, was monitored for up to one month after the ampules were sealed. Results for total PCBs, CBs and PAHs are summarized in Tables 2a, 2b, and 2c, respectively. The relative standard deviations (RSDs) for all the parameters were comparable with those obtained upon analysis of the bulk sediment extract and the sealed ampules after a 2 weeks storage period. This result provides further confirmation that the sealed ampules are homogeneous. Results for

total PCBs showed that no degradation occur for up to one month storage (Table 2a). Similar conclusions for CBs and PAHs can be drawn from the results shown in Figs. 2a and 2b. It is therefore evident that, at least for this sediment extract, no degradation occurred for the total PCBs, CBs and PAHs during the storage period for up to one month under the specified storage condition. These results also provide additional substantiation that the subsamples of the sealed ampules are in fact homogeneous.

In this study, the content of the sealed ampules stored in the dark at 25°C was also monitored for stability after a one month period along with ampules stored in the dark at 4°C. Results of total PCBs, CBs and PAHs are summarized in Tables 2a, 2b, and 2c, respectively. As can be seen from Table 2a, the total PCBs were comparable for the two sets of storage conditions and similar situation was observed for CBs and PAHs, as shown in Figs. 3a and 3b. While it should be preferable and safer to store the sediment extract in the dark at 4°C, no signs of degradation was detected in the ampules stored in the dark at 25°C for up to one month. The total PCBs, CBs and PAHs mean concentrations obtained by in-house analysis of sediment extract samples kept under various storage conditions are summarized in Tables 3a, 3b and 3c, respectively.

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Table 1a. Analytical results of total PCBs (ng/mL) on the bulk sediment extract.

Replicate No.	Total PCBs
1	190
2	193
3	213
4	198
5	183
Mean	195
SD	11
RSD, %	5.6

Table 1b. Analytical results of CBs (ng/mL) on the bulk sediment extract.

Parameter	Replicate No.							
	1	2	3	4	5	Mean	SD	RSD,%
1,3,5-TCB	12.6	15.0	15.8	13.6	9.8	13.4	2.3	17.2
1,2,4-TCB	5.1	6.0	6.5	5.7	4.4	5.5	0.8	14.5
1,2,4,5-TeCB	14.8	17.3	17.2	14.7	13.1	15.4	1.8	11.7
1,2,3,4-TeCB	0.9	0.9	2.4	1.7	1.5	1.5	0.6	40.0
PeCB	9.4	10.5	9.6	9.8	8.4	9.5	0.8	8.4
HCB	49.4	55.3	44.0	41.7	41.6	46.4	5.9	12.7
HCBD	5.6	6.9	6.4	5.4	4.1	5.7	1.1	19.3
OCS	16.5	15.1	18.6	16.4	16.6	16.6	1.3	7.8

Table 1c. Analytical results of PAHs (μg/mL) on the bulk sediment extract.

Parameter	Replicate No.							
	1	2	3	4	5	Mean	SD	RSD,%
Nap	0.069	0.074	0.026	0.064	0.039	0.054	0.021	38.8
Ac-thyl	0.028	0.036	0.030	0.032	0.019	0.029	0.006	20.7
Ac-the	0.008	0.011	0.011	0.011	0.010	0.010	0.001	10.0
Fl	0.028	0.027	0.041	0.032	0.027	0.031	0.036	19.0
Phen	0.298	0.304	0.304	0.288	0.259	0.291	0.019	6.5
Anth	0.037	0.045	0.039	0.039	0.037	0.039	0.003	7.7
F	0.483	0.479	0.425	0.407	0.366	0.432	0.050	11.6
Py	0.597	0.633	0.509	0.506	0.466	0.542	0.070	12.9
B[a]A	0.256	0.248	0.257	0.245	0.222	0.246	0.014	5.7
Ch	0.383	0.381	0.350	0.348	0.352	0.363	0.018	5.0
B[b]F + B[k]F	0.575	0.616	0.510	0.537	0.535	0.555	0.041	7.4
B[a]P	0.404	0.436	0.340	0.349	0.339	0.373	0.044	11.8
I[cd]P	0.196	0.181	0.188	0.169	0.216	0.190	0.018	9.5
D[ah]A	0.057	0.052	0.076	0.067	0.082	0.067	0.013	19.4
B[ghi]P	0.234	0.211	0.188	0.182	0.219	0.207	0.022	10.6

Table 2a. Stability of total PCBs (ng/mL) at various storage conditions in the sealed ampules of sediment extract.

Time	Storage Conditions	Mean*	SD	RSD,%
2 weeks	4°C in dark	194	12	6.2
1 month	4°C in dark	197	2	1.0
1 month	25°C in dark	206	9	4.4

Note: * Mean is average of 4 replicates.

Table 2b. Stability of CBs (ng/mL) at various storage conditions in the sealed ampules of sediment extract.

Parameter	4°C , 2 weeks			4°C, 1 month			25°C, 1 month		
	Mean+	SD	RSD,%	Mean+	SD	RSD,%	Mean+	SD	RSD,%
1,3,5-TCB	16.6	2.8	16.9	15.5	1.1	7.1	15.3	3.2	20.9
1,2,4-TCB	6.9	0.7	10.1	6.9	0.6	8.7	7.2	1.6	22.2
1,2,4,5-TeCB	16.9	2.4	14.2	17.4	1.0	5.7	16.7	1.3	7.8
1,2,3,4-TeCB	1.3	0.4	30.8	2.5	0.5	20.0	2.7	1.3	48.1
PeCB	9.1	1.0	11.0	9.4	0.5	5.3	8.8	0.3	3.4
HCB	46.5	3.3	7.1	49.4	1.0	2.0	49.5	1.5	3.0
HCBD	6.1	1.0	16.4	6.5	0.2	3.1	6.3	0.3	4.8
OCS	15.2	0.5	3.3	20.6	1.6	7.8	20.9	2.1	10.0

Note: + Mean is average of 4 replicates.

Table 2c. Stability of PAHs (ug/mL) at various storage conditions in the sealed ampules of sediment extract.

Parameter	4°C , 2 weeks			4°C, 1 month			25°C, 1 month		
	Mean+	SD	RSD,%	Mean+	SD	RSD,%	Mean+	SD	RSD,%
Nap	0.051	0.003	5.9	0.042	0.005	11.9	0.035	0.015	42.9
Ac-thyl	0.020	0.003	15.0	0.033	0.003	9.1	0.022	0.004	18.2
Ac-the	0.010	0.002	20.0	0.010	0.001	10.0	0.010	0.001	10.0
Fl	0.026	0.006	23.1	0.024	0.002	8.3	0.025	0.005	20.0
Phen	0.245	0.016	6.5	0.274	0.010	3.6	0.279	0.026	9.3
Anth	0.048	0.003	6.3	0.049	0.005	10.2	0.035	0.008	22.9
F	0.411	0.030	7.3	0.395	0.026	6.6	0.402	0.021	5.2
Py	0.551	0.027	4.9	0.549	0.033	6.0	0.547	0.032	5.9
B[a]A	0.223	0.023	10.3	0.200	0.006	3.0	0.231	0.015	6.5
Ch	0.441	0.029	6.6	0.358	0.010	2.8	0.379	0.039	10.3
B[b]F } B[k]F	0.750	0.024	3.2	0.667	0.013	1.9	0.741	0.057	7.7
B[a]P	0.519	0.024	4.6	0.451	0.008	1.8	0.556	0.045	8.1
I[cd]P	0.218	0.026	11.9	0.142	0.008	5.6	0.164	0.010	6.1
D[ah]A	0.062	0.021	33.9	0.050	0.003	6.0	0.064	0.006	9.4
B[ghi]P	0.214	0.020	9.3	0.206	0.004	1.9	0.218	0.001	0.5

Note: + Mean is average of 4 replicates.

Table 3a. Summary of analytical results of total PCBs (ng/mL) on sediment extract reference sample (SE-1) in ampules.

	Total PCBs
Mean	199
SD	9.8
No. of determination	12

Table 3b. Summary of analytical results of CBs (ng/mL) on sediment extract reference sample (SE-1) in ampules.

Parameter	Mean	SD	No. of determination
1,3,5-TCB	15.8	2.4	12
1,2,4-TCB	7.0	1.0	12
1,2,4,5-TeCB	17.0	1.5	12
1,2,3,4-TeCB	2.2	1.0	12
PeCB	9.1	0.6	12
HCB	48.5	2.4	12
HCBD	6.3	0.6	12
OCS	19.9	4.0	12

Table 3c. Summary of analytical results of PAHs (μg/mL) on sediment extract reference sample (SE-1) in ampules.

Parameter	Mean	SD	No. of determination
Nap	0.042	0.011	12
Ac-thyl	0.025	0.006	12
Ac-the	0.010	0.001	12
Fl	0.025	0.004	12
Phen	0.266	0.023	12
Anth	0.043	0.009	12
F	0.403	0.025	12
Py	0.549	0.028	12
B[a]A	0.218	0.020	12
Ch	0.392	0.045	12
B[b]F } B[k]F	0.717	0.052	12
B[a]P	0.509	0.053	12
I[cd]P	0.174	0.037	12
D[ah]A	0.059	0.013	12
B[ghi]P	0.213	0.012	12

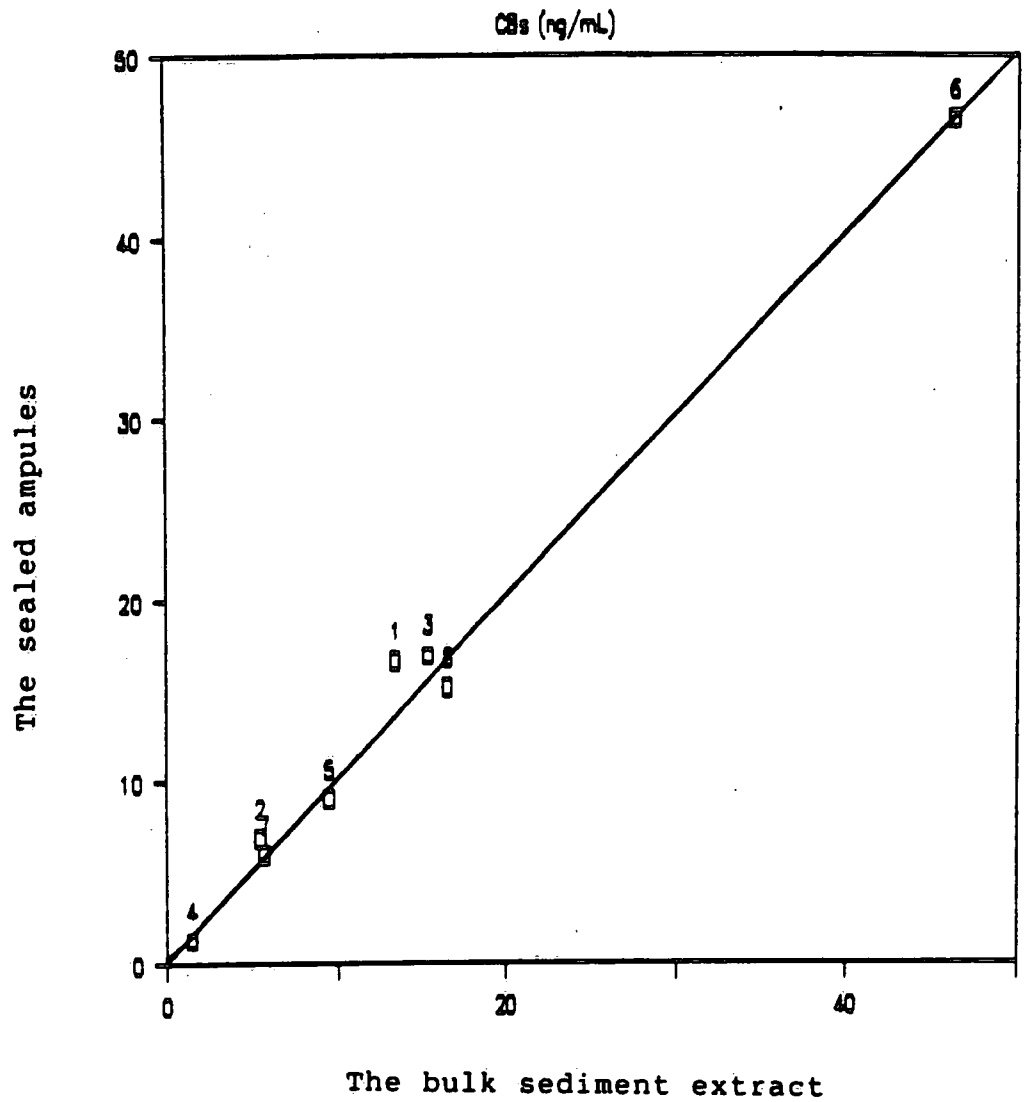

Fig. 1a. Comparison of analytical results of CBs (ng/mL) between the bulk sediment extract and the sealed ampules. 1: 1,3,5-TCB; 2: 1,2,4-TCB; 3: 1,2,4,5-TeCB; 4: 1,2,3,4-TeCB; 5: PeCB; 6: HCB; 7: HCBD; and 8: OCS.

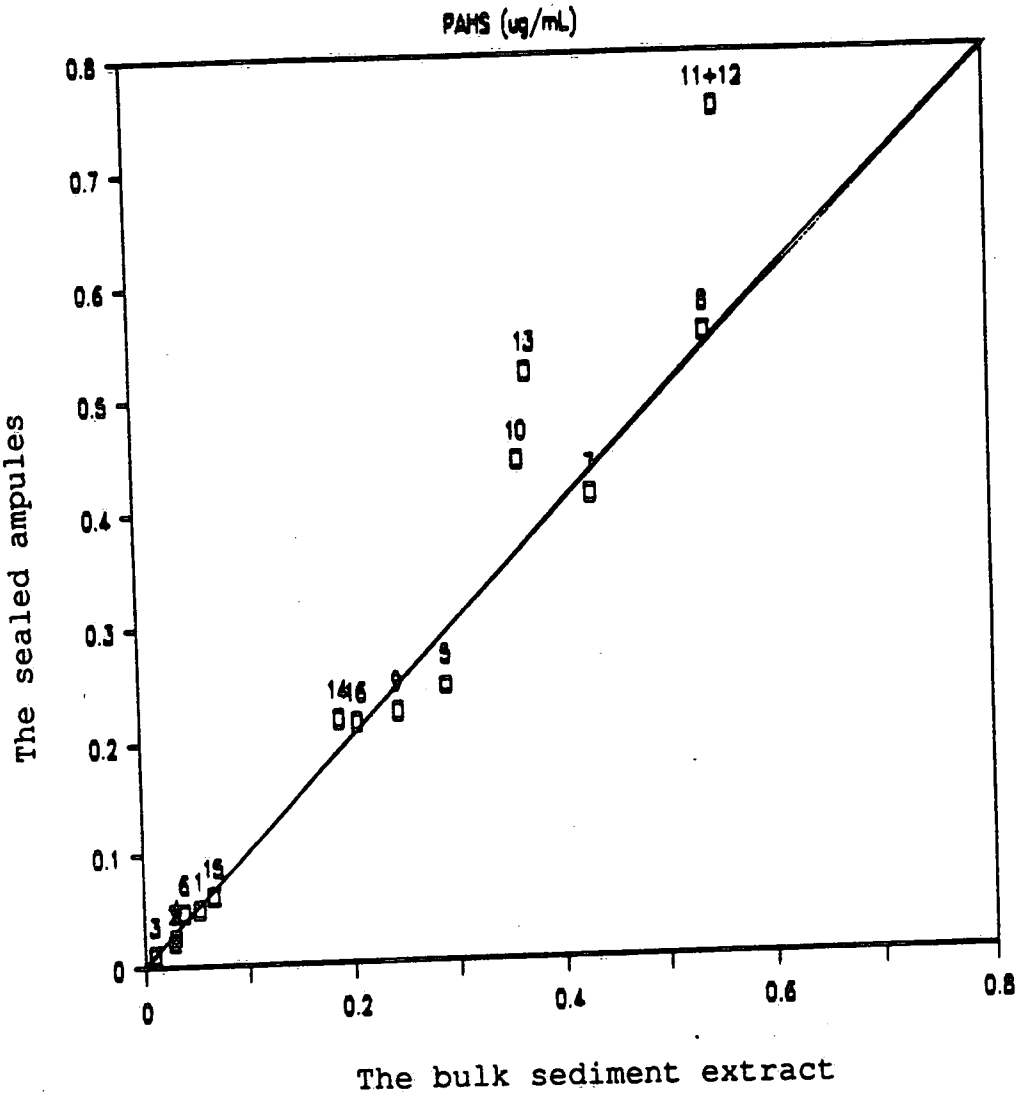

Fig. 1b. Comparison of analytical results of PAHs (ug/mL) between the bulk sediment extract and the sealed ampules. 1: Nap; 2: AC-thyl; 3: Ac-the; 4: Fl; 5: Phen; 6: Anth; 7: F; 8: Py; 9: B[a]A; 10: Ch; 11: B[b]F; 12: B[k]F; 13: B[a]P; 14: I[cd]P; 15: D[ah]A; and 16: B[ghi]P.

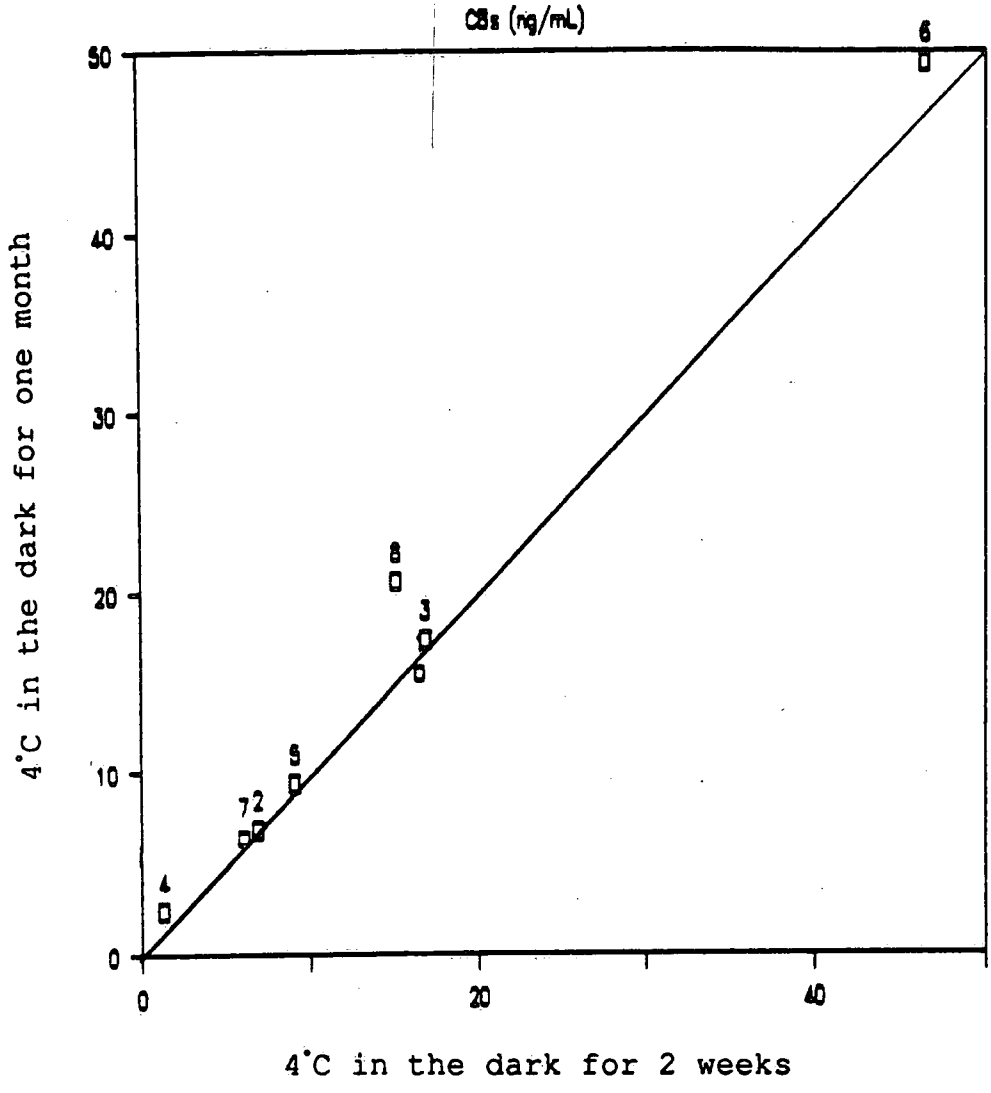

Fig. 2a. Comparison of analytical results of CBs (ng/mL) in the sealed ampules stored at 4°C in the dark for 2 weeks and one month. 1: 1,3,5-TCB; 2: 1,2,4-TCB; 3: 1,2,4,5-TeCB; 4: 1,2,3,4-TeCB; 5: PeCB; 6: HCB; 7: HCBD and 8: OCS.

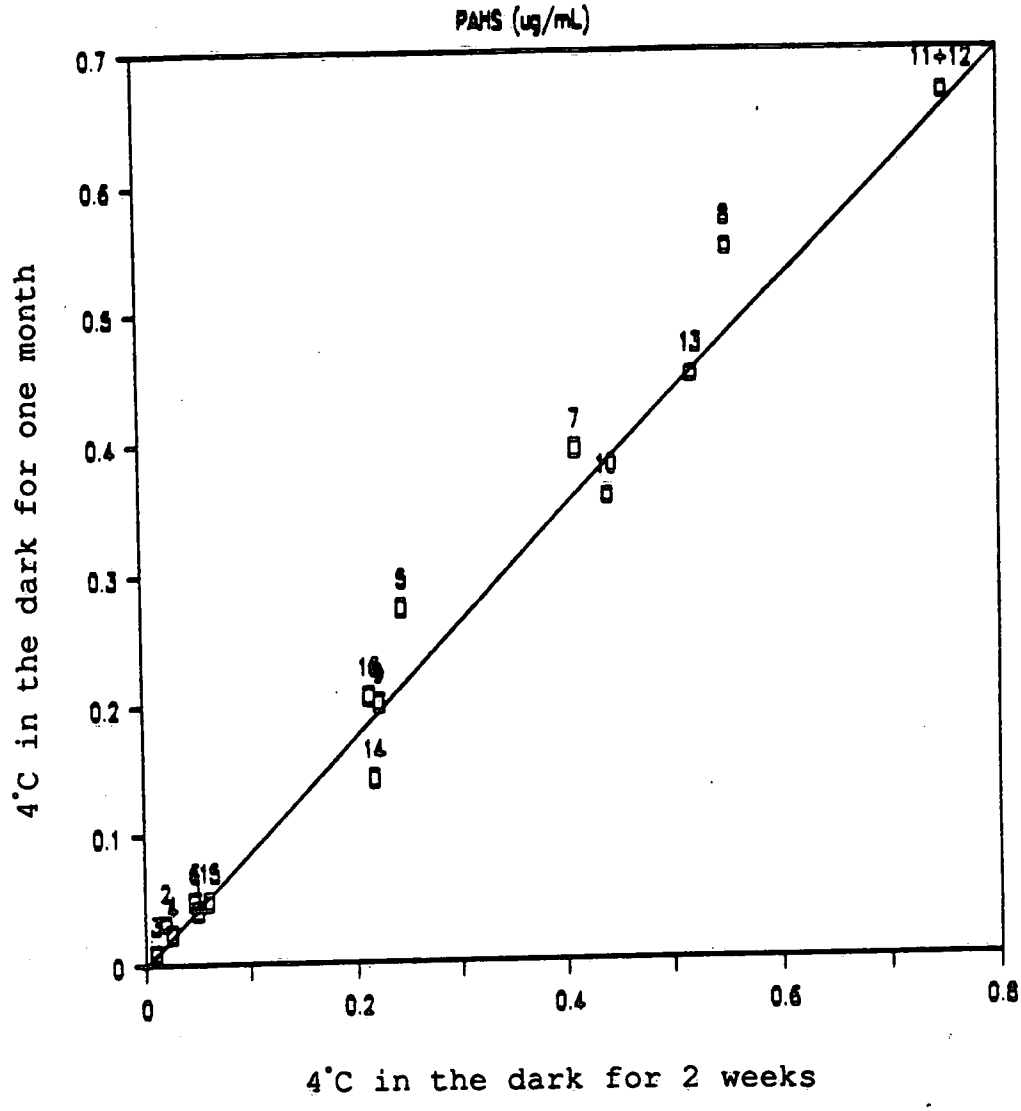

Fig. 2b. Comparison of analytical results of PAHs (ug/mL) in the sealed ampules store at 4°C in the dark for 2 weeks and one month. 1: Nap; 2: AC-thyl; 3: Ac-the; 4: Fl; 5: Phen; 6: Anth; 7: F; 8: Py; 9: B[a]A; 10: Ch; 11: B[b]F; 12: B[k]F; 13: B[a]P; 14: I[cd]P; 15: D[ah]A; and 16: B[ghi]P.

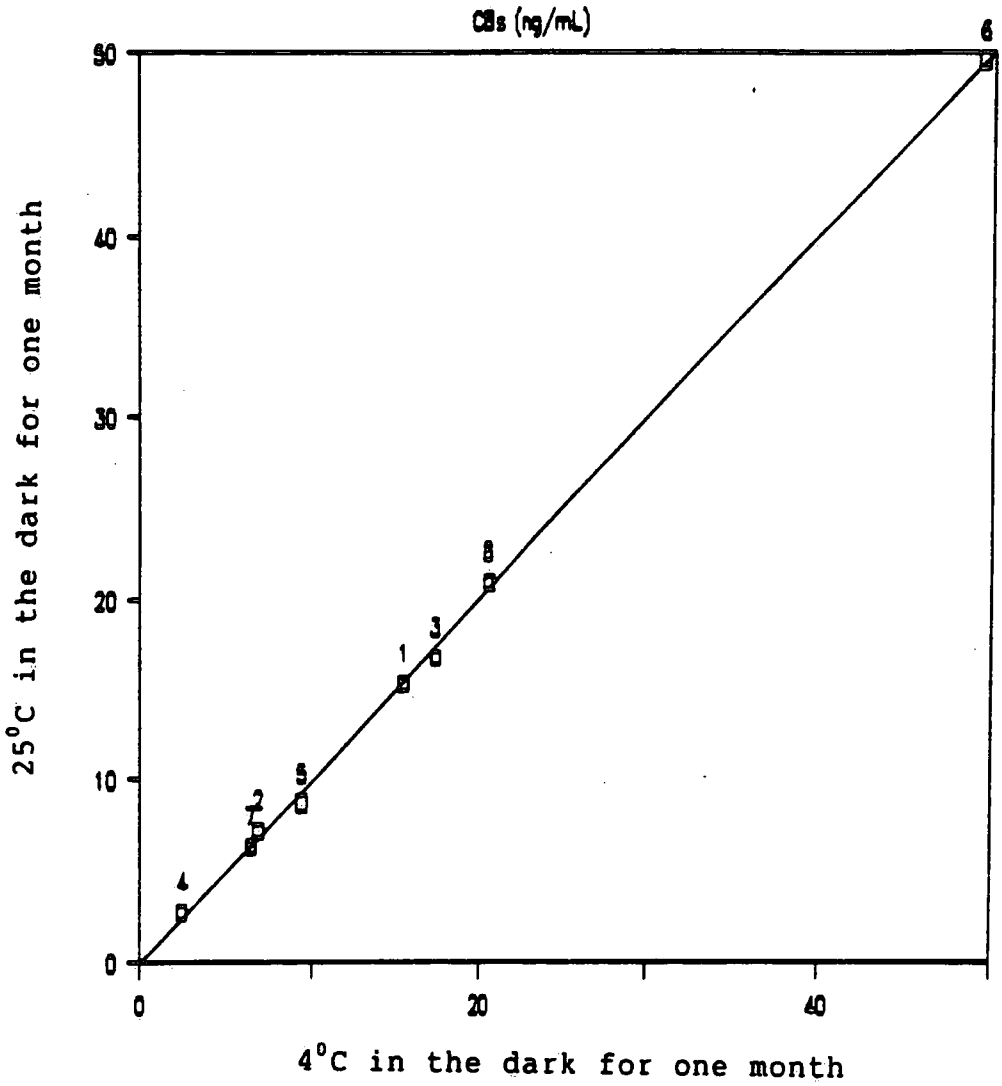

Fig. 3a. Comparison of analytical results of CBs (ng/mL) in the sealed ampules stored for one month at 4°C in dark and 25°C in the dark. 1: 1,3,5-TCB; 2: 1,2,4-TCB; 3: 1,2,4,5-TeCB; 4: 1,2,3,4-TeCB; 5: PeCB; 6: HCB; 7: HCBD; and 8: OCS.

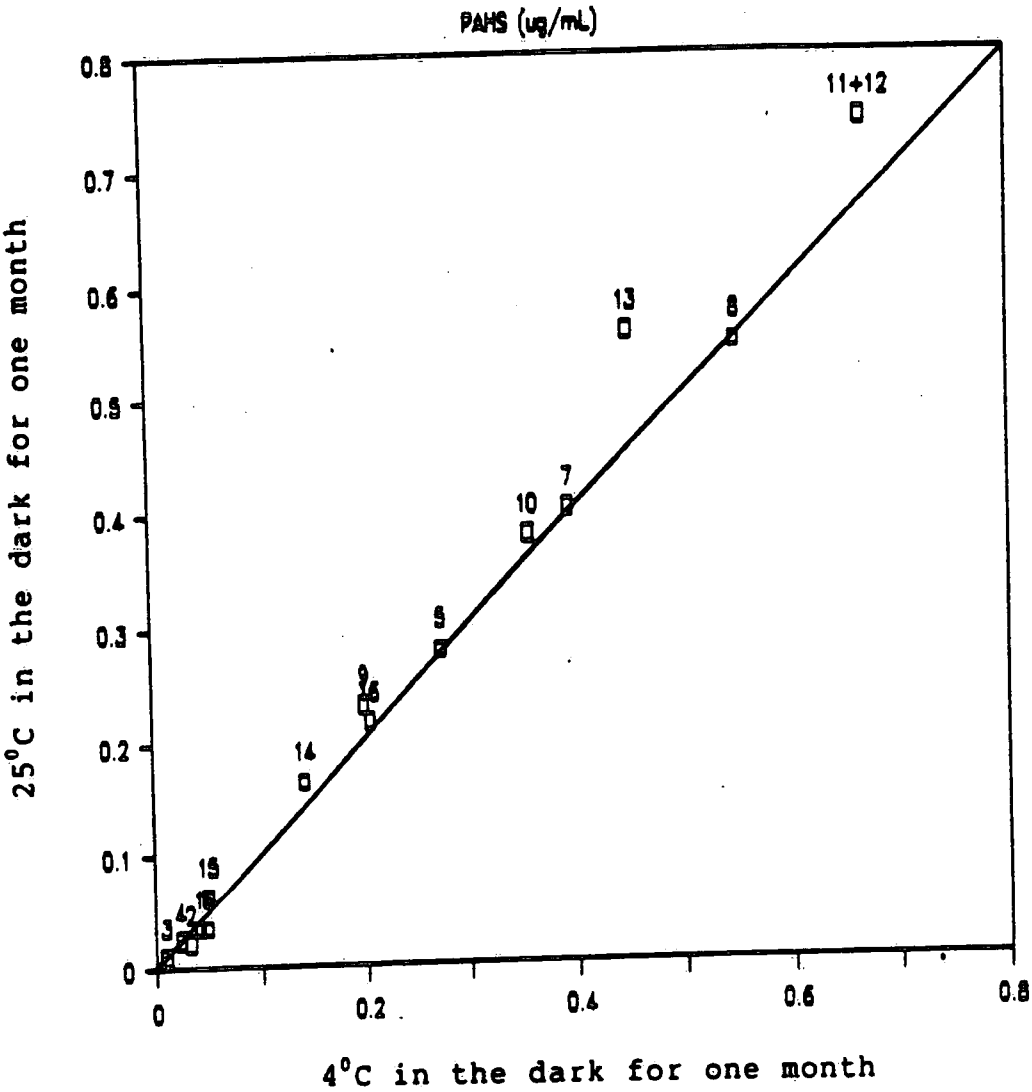

Fig. 3b. Comparison of analytical results of PAHs (ug/mL) in the sealed ampules stored for one month at 4°C in the dark and 25°C in the dark. 1: Nap; 2: AC-thyl; 3: Ac-the; 4: Fl; 5: Phen; 6: Anth; 7: F; 8: Py; 9: B[a]A; 10: Ch; 11: B[b]F; 12: B[k]F; 13: B[a]P; 14: I[cd]P; 15: D[ah]A; and 16: B[ghi]P.