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Stability of Residual Levels of Polychlorinated Biphenyls in Cold-Extracted Herring Oil

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The measurement of residual concentrations of polychlorinated biphenyl (PCB) in a variety of foodstuffs and other biological materials has been characterised by a large (up to 50%) interlaboratory variation (bias) (Tuinstra et al. 1985, Holden et al. 1983, Musial and Uthe 1983). An interlaboratory coefficient of variation of 14% was reported by Tuinstra et al. (1985) for their study in which exact methodological details and quantitative standard solutions were supplied to participants who were asked to determine the levels of a suite of six chlorobiphenyls (CB) present at trace levels in eel fat. Following the completion of our earlier study (Musial and Uthe 1983), remaining vials of fortified (approximately 1 mg Aroclor 1254/kg herring oil) and control oils were stored and analyzed sporadically to determine if any changes in measured PCB concentrations in the oils resulted from changes in PCB and the oil during storage of approximately eight years.

MATERIALS AND METHODS

Preparation and fortification of herring oils have been described in detail (Musial and Uthe 1983). In summary, fresh frozen herring (Clupea harengus harengus) fillets were extracted three times at room temperature with high-purity acetone, water was added to the acetone filtrate, the oil was partitioned into high-purity hexane and the solvent removed by flash evaporation. Fortification was performed with Aroclor 1254 (Monsanto Co. Ltd, St. Louis, MO) and the oils (5-10 mL) placed in solvent-washed borosilicate glass ampuls and flame-sealed under nitrogen. The sealed ampuls were stored at -20 C. No antioxidants were added to the oil, and a fresh ampul was used for each sample time. Herring oil has been reported to contain alpha-tocopherol, a natural antioxidant, at a concentration of 14-16 mk/kg (Braekkan et al. 1963).

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PCB was separated from the oil (0.2-0.3 g in 2 mL hexane, 3 x 2 mL wash) and many other co-contaminants by chromatography on Florisil activated at 450 C overnight and deactivated with 1% water. The Florisil was washed in the chromatography column with 60 mL hexane (dried over sodium sulfate), and PCB residues were eluted with 107 mL dried hexane. Various batches of Florisil and solvents were used over the course of the experiment. The Florisil was standardized by using a modified Mills (1968) procedure and the amounts of the adsorbent were adjusted as required.

Gas chromatography was performed isothermally at 200 C with a 4 mm i.d. x 182 cm long silanized glass column packed with 3% SP -2100 on 80/100 mesh Supelcoport, using argon/methane:95/5 at a flow rate of 25 mL/min, an electron capture detector at 350 C and the Aroclor 1254 used to fortify the oil as a standard (Musial et al. 1979). A total of 3 resolved peaks, eluting after p,p'-DDE, were used for quantification (Musial and Uthe 1983). The same batch of Aroclor 1254 was employed throughout the experiment.

RESULTS AND DISCUSSION

PCB concentrations in both the fortified and control oils did not change appreciably during the first sixteen months of storage (Table 1). Concentrations varied somewhat in both oils thereafter although the magnitude of the variation was not large. However, recovery of added Aroclor 1254 was constant and essentially quantitative. The observed drop in PCB concentrations in the two oils resulted from either changes in the oils themselves (elimination of materials interfering positively in the PCB determination) or variations in the different batches of Florisil used throughout this study. Because the various batches of Florisil were standardized according to the Mills (1968) procedure and the elution profile checked with reference organochlorine standards and fortified samples, the contribution of Florisil variation to the intralaboratory variance should be negligible. Therefore it is possible that the adsorbent varied in its behaviour toward the various other components in the oil which were themselves affecting the quantitative measurement of PCB. Evidence for this was obtained from visual examination of the chromatograms obtained for both fortified and control oil PCB-fractions from the various batches of Florisil employed over the course of the experiment. Chromatograms from different batches showed variations in the size of negative peaks (interferences) in particular in the early part (pre-p,p'-DDE) of the chromatograms, which unfortunately could not be quantitated under the existing chromatographic

conditions. The non-uniform removal of materials responsible for negative peaks in the chromatograms would result in an apparent changes in the PCB concentrations. It is also possible that the batch of coated support and age of the packed column used in the gas chromatographic step of the analysis contributed to these observations. The dependence of PCB quantitation on the nature of the silicone stationary phase used in the gas chromatographic step of the analysis has been described by Musial and Uthe (1983) so that it would not be surprising to observe more subtle changes in the chromatograms over the lifetime of a packed column or use of different batches of the same coated support.

Table 1. PCB concentrations (mg Aroclor 1254 equivalents/kg oil) and average percent recovery of added Aroclor 1254 of replicate analysis performed at each period on spiked and unspiked acetone-extracted herring fillet oil.

Storage Time (Months)	PCB Concentration		Spike Recovery
	Unspiked	Spiked	
1	1.44	2.55	104
	1.39	2.31	
	1.38	2.42	
9	1.71	2.49	102
	1.22	2.42	
	1.32	2.37	
16	1.33	2.33	97
	1.38	2.29	
	-	2.36	
41	1.12	-	-
	1.14	-	-
49	1.11	2.20	100
	1.20	2.10	
82	1.32	2.42	110
	1.41	2.51	
	1.39	2.49	
94	1.23	2.27	104

Because precautions were taken to prevent oxidation of the oil and no evidence of gross oxidation was observed (ring at surface of oil) the stability of PCB described here cannot simply be applied to PCB stability in materials undergoing oxidation. Hesselberg and Northrup (1986) reported an increase (3%) in the measured concentrations of PCB and other organochlorines in frozen (-40 C) composite lake trout (Salvelinus namaycush) and a decrease (3%) in the measured fat content of the tissue over four years. However our results show the feasibility of preparing reference oils containing certified concentrations of PCB or CBs (Guevremont 1986) with stability for at least eight years. The results of comparative studies reported to date support the preparation and use of appropriate reference materials by all analysts. Results of the current study also indicate that further cleanup of fish oils, for example, by gel-permeation chromatography or appropriate chemical means such as saponification, is necessary to remove interferences which coelute from Florisil to achieve the true value of PCB contents. Analysts are also urged to run a parallel ECD-FID or ECD-MS scan on their cleaned up extracts as a check on the efficacy of their cleanup.

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