

Fish Certified Reference Materials for Chlorinated Dibenzo-p-dioxins, Chlorinated Dibenzofurans, and Coplanar PCBs. Part II. Use as Reference Materials for Organohalogenes

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Certified reference materials (CRMs) of fish were not available until recently, but were needed for quality control (QC) and quality assurance of analyses of chlorinated dibenzo-p-dioxins (dioxins) and chlorinated dibenzofurans (furans) in samples related to pulp and paper mill emissions. With numerous government and contract laboratories (private sector) performing these analyses it was necessary to have a ruler against which data comparison could be made. The precision and accuracy of data from diverse sources could then be assessed by scientists and regulatory officials. Problems with accuracy and precision would be evident and could be addressed. To satisfy these needs 3 fish CRMs were developed and validated for dioxin and furan analyses ^{1),2)}.

Since analytical trends at that time indicated there would be a future need for coplanar PCB CRMs, these were included in the above project. CRMs were produced and validated for a naturally contaminated fish (lake trout), a spiked fish (salmon, artificially contaminated with dioxins, furans and coplanar PCBs), and a clean fish (herring).

Reference materials (RMs) are another way to address the QA/QC of analytical data. Their values are not necessarily as rigorously determined as for CRMs, with sometimes only one laboratory performing the analyses to characterize the material. Fish RMs were also not available for the organochlorine pesticides (OCs), total polychlorinated biphenyls (PCBs), congener specific PCBs, chlorinated diphenyl ethers (CDPEs), toxaphene, and octachlorostyrene, which were routinely analyzed by Fisheries and Oceans Canada (DFO). Since the 3 CRMs were already available they were analyzed at N=6 for these compounds. Their utility as RMs for these contaminants could then be assessed.

The methodology used was DFO's routine method for analysis of halogenated contaminants ³⁾. This comprised extraction of the fish tissue with dichloromethane; lipid removal by gel permeation chromatography; fractionation by silica gel column chromatography; and analysis using dual column gas chromatography (60m DB-5 and DB-1701 capillary columns) with electron capture detection. Detection limits were 0.002 µgKg⁻¹ for all compounds except toxaphene which was 0.030 µgKg⁻¹.

REF/QC

The results of the OC analyses are presented in Table 1. Examination of the data showed that the lake trout contained the greatest number of contaminants and that they were also at the highest levels of the 3 CRMs. An identical trend was observed for the PCB congeners (PCB28,52,101,118,153,137,138,180,170) and the CDPEs. In fact all the PCB congeners were present in the lake trout. CDPEs were absent from both the salmon and herring CRMs. It was concluded that the lake trout CRM was a useful RM for assessing the data quality of a wide variety of organohalogenes studied. The other 2 materials would be more useful as checks on low level PCB analyses or as indicators of sample cross-contamination during sample preparation. Use of the lake trout as a RM was implemented in the DFO laboratory as a result of this study.

Control charts are an effective way of displaying QA/QC data collected from RM and CRM analyses over time for the selected contaminants. Laboratory performance can be tracked by analyzing the RM or CRM frequently, although not necessarily with each batch of samples. Figure 1 gives an example of such a control chart for total PCBs in the lake trout RM. Results were within 1 standard deviation of the mean for most determinations. Similar charts can be constructed for other contaminants and retained on file as an indication of method and laboratory performance.

In conclusion, the lake trout dioxin/furan CRM was found to be a good RM for the analysis of OCs, total PCBs, PCB congeners, toxaphene, and octachlorostyrene. The herring and salmon CRMs were found to be of lesser use as RMs. However, due to the very low levels of contaminants in them, they can be used as matrix blanks or spiked and used as method evaluation materials. CRMs and RMs, where available, should be analyzed and reported along with samples to ensure that data are accurate, precise and defensible.

References

- 1) Sergeant, D.B. Development and Validation of Fortified and Unfortified Fish CRMs for Chlorinated Dioxins, Chlorinated Dibenzofurans, and Coplanar PCBs. Presented at 76th Canadian Society for Chemistry Conference and Exhibition, Symposium on Reference Materials for Environmental Analysis: Making and Using Them. Sherbrooke, Quebec, Canada, May 30-June 3, 1993.
- 2) Sergeant, D.B., Bolt, D.L., Re, M.A. Fish Tissue Performance Evaluation Standards For PCDD, PCDF, And Coplanar PCB Analysis From An International, Interlaboratory Study. Extended Abstracts, DIOXIN '93, 11: 185-186.
- 3) Huestis, S.Y., Servos, M.R., Sergeant, D.B., Leggett, M., Dixon, D.G. 1995. Methods for Determination of Organochlorine Pesticides. Polychlorinated Biphenyl Congeners and Chlorinated Dibenzo-p-dioxins and furans in Fish. Can. Tech. Rep. Fish. Aquat. Sci. 2044:30p.

TABLE 1 ORGANOCHLORINE PESTICIDES, TOTAL PCBs, and CDPEs CONCENTRATIONS (mgKg⁻¹)IN THREE CRMs

COMPOUND	EDF-2524 (HERRING)	EDF-2525 (LAKE TROUT)	EDF-2526 (SALMON)
alpha-BHC	ND	0.005±0.001	0.002±0.000
HCB	0.003±0.001	0.031±0.001	0.003±0.001
beta-BHC	ND	ND	ND
gamma-BHC	ND	ND	ND
delta-BHC	ND	ND	ND
HEPTACHLOR	ND	ND	ND
ALDRIN	ND	ND	ND
OCS	ND	0.030±0.002	ND
HEPT. EPOX.	ND	0.020±0.002	ND
gamma- CHLORDANE	ND	0.022±0.001	ND
alpha-CHLORDANE	0.002±0.000	0.058±0.001	0.002±0.000
pp'-DDE	0.022±0.003	0.597±0.035	0.006±0.001
DIELDRIN	0.002±0.000	0.086±0.002	ND
ENDRIN	ND	0.009±0.001	ND
beta-ENDOSULFAN	ND	ND	ND
pp'-TDE	0.004±0.001	0.181±0.007	0.003±0.000
op'-DDT	ND	0.014±0.004	ND
pp'-DDT	ND	0.007±0.003	ND
PHOTOMIREX	ND	0.156±0.011	ND
pp'- METHOXYCHLOR	ND	ND	ND
MIREX	ND	0.239±0.024	ND
TOXAPHENE	ND	0.132±0.027	ND
TOTAL PCBs	0.134±0.188	2.563±0.141	0.034±0.006

TOTAL PCB RESULTS for LAKE TROUT RM , 1993-94

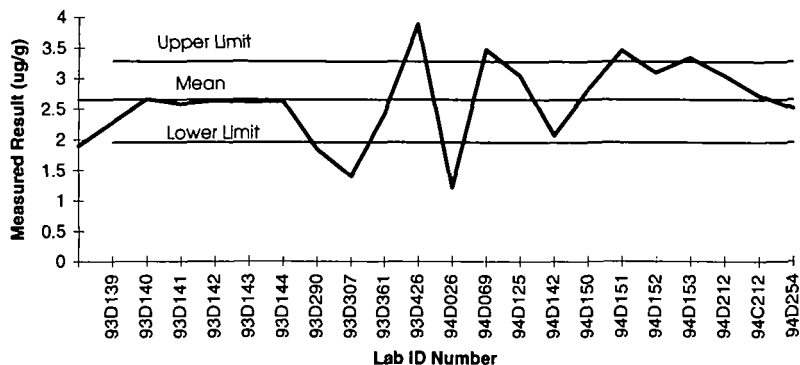


Figure 1: Concentration of total PCBs in lake trout RM versus laboratory number for 1993-94. Upper and lower limits represent 1 standard deviation from the mean and are shown as an indication of the precision of the data.