

# Dioxin '97, Indianapolis, Indiana, USA

## CERTIFIED REFERENCE MATERIAL FOR POLYCHLORINATED DIBENZO-p-DIOXINS, DIBENZOFURANS AND POLYCHLORINATED BIPHENYLS

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### OBJECTIVES:

Development and certification of a reference material that is a naturally contaminated biological tissue for polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls are described. Certified reference materials (CRM) are universally important as analytical reference materials used in ensuring the accuracy and precision of analytical work carried out in laboratories. CRMs are also essential in developing analytical methodologies and techniques and monitoring quality control of analytical processes.

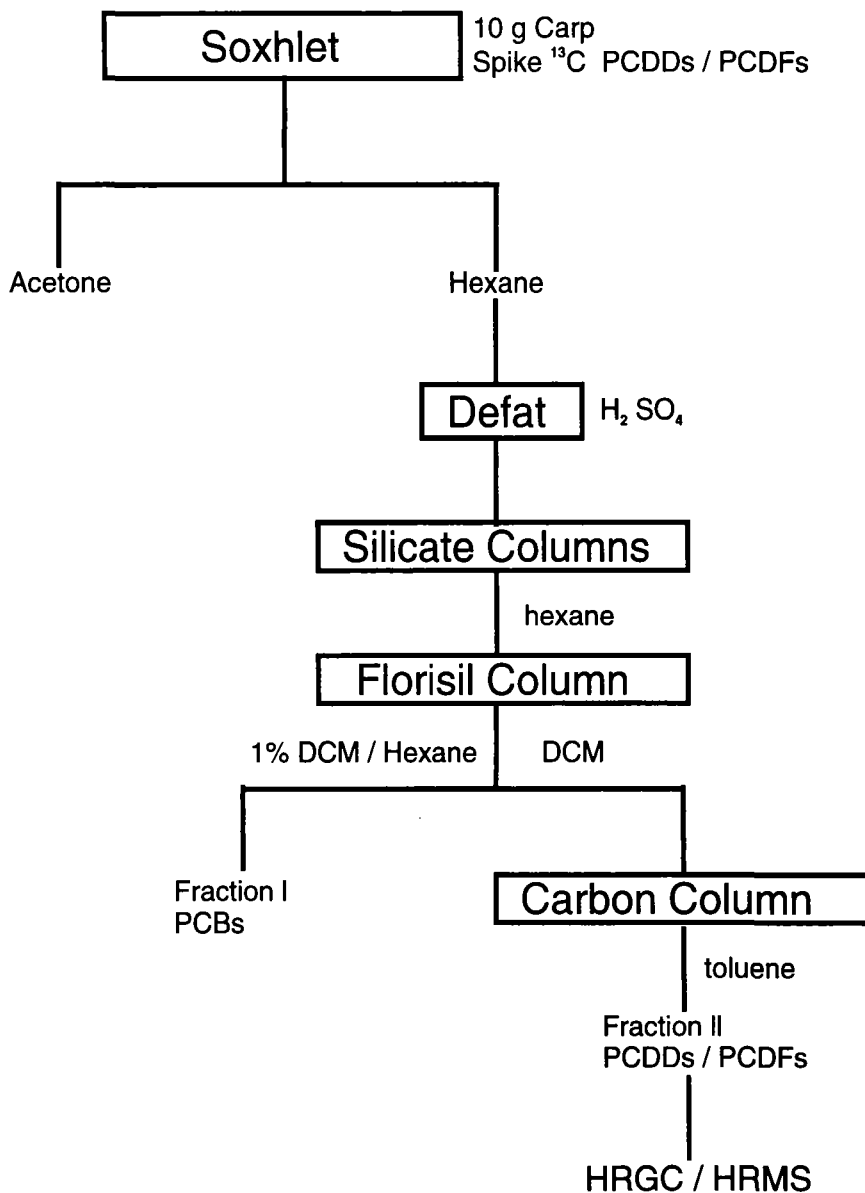
### WHY USE CARP-1 CERTIFIED REFERENCE MATERIAL:

- ◆ ensure accuracy of analytical process
- ◆ quality assurance of analyses
- ◆ maintain laboratory quality control
- ◆ method and research development aid
- ◆ usable sample size - 9 g X 6 ampoules per unit
- ◆ 18 polychlorinated compounds including nine EPA priority PCBs and nine 2,3,7,8-chlorinated dioxins and furans

### BACKGROUND:

CARP-1 was developed as a CRM by the National Research Council of Canada (NRCC) for nine 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, and nine EPA priority polychlorinated biphenyls. CARP-1 is a ground whole carp (*Cyprinus carpio*), harvested in 1988 from the warm water discharge of the Consumers Power Plant, Saginaw Bay, Lake Huron. The tissue was processed by the Technical University of Nova Scotia (TUNS) in Halifax, Nova Scotia, Canada. Thirty kilograms of the tissue was ground whole and stored at -20 C. The fish was comminuted four times in a food cutter, and an antioxidant, 9.5g ethoxyquin powder, was added to prevent rancidity. The moisture content was raised to 85% with deionized distilled water. The carp was homogenized and the slurry divided and bottled under nitrogen using an ampouling machine. Each ampoule contains approximately 9.0g of material, and is packaged and sold as a set of six. At NRCC, the analytical procedure for the dioxins and furans

# ANALYSIS



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consisted of a 7.5 hour Soxhlet extraction using acetone and hexane, followed by a sulfuric acid defatting step. Cleanup was carried out by means of open multi-column chromatography consisting of acid and base silica, Florisil and carbon <sup>1</sup>. Quantification was by means of HRGC/HRMS. Similarly, the PCBs were extracted using a 7.5 hour Soxhlet extraction with acetone and hexane, and processed on Florisil and alumina cleanup columns. Quantification was carried out using GC/ECD and HRGC/HRMS. CARP-1 has been used as a sample for a NIST/NOAA interlaboratory comparison exercise <sup>2</sup>.

## RESULTS:

Certified values for dioxins/furans and PCBs in CARP-1. <sup>3</sup>

These values were derived from contributions of five expert laboratories for dioxins and furans, and 15 expert laboratories for PCBs. Each participating laboratory utilized its own preferred methodology.

## CARP-1

### Fish Reference Material for Dioxins, Furans and PCBs

CARP-1 is a ground whole fish reference material prepared from common carp (*Cyprinus carpio*). Certified concentrations are listed for two polychlorinated dibenzofurans, seven polychlorinated dibenzo-*p*-dioxins and nine polychlorinated biphenyls which are naturally present in the sample.

The carp was collected in Saginaw Bay, Lake Huron. The material was homogenized by comminution and an antioxidant was added. The water content was increased and the slurry was processed through a high pressure homogenizer. The material was bottled in 10 ml glass ampoules which were heat sealed, sterilized and individually packed in sealed trilaminate pouches.

A unit of CARP-1 contains six ampoules, each ampoule containing about 9 grams of slurry.

Certified concentrations are listed on a wet weight basis. The uncertainties are 95 percent confidence intervals based on the processing of the entire contents of one ampoule. That is, 95 per cent of the samples would be expected to have concentrations within the certified range.

Concentration (nanograms/kilogram)	
<b>Polychlorinated dibenzofurans</b>	
2,3,7,8-TCDF	11.9 ± 2.7
1,2,3,7,8-PCDF	5.0 ± 2.0
<b>Polychlorinated dibenzo-<i>p</i>-dioxins</b>	
2,3,7,8-TCDD	6.6 ± 0.6
1,2,3,7,8-PCDD	4.4 ± 1.1
1,2,3,4,7,8-HxCDD	1.9 ± 0.7
1,2,3,6,7,8-HxCDD	5.6 ± 1.3
1,2,3,7,8,9-HxCDD	0.7 ± 0.4
1,2,3,4,6,7,8-HpCDD	6.5 ± 1.8
OCDD	6.3 ± 1.9
Concentration (micrograms/kilogram)	
<b>Polychlorinated biphenyls</b>	
IUPAC	
52	124 ± 32
101/90	124 ± 37
105	54 ± 24
118	132 ± 60
138/163/164	102 ± 23
153	83 ± 39
170/190	22 ± 8
180	46 ± 14
187/182	36 ± 16

**WORK AHEAD:**

CARP-2 has already been produced and will be the replacement material for CARP-1, whose stock is depleting. CARP-2 is a very similar material to CARP-1 and was processed identically. CARP-2 has been used in our method development studies, including solid-phase extraction, supercritical fluid extraction, and column chromatographic work. All of its determined dioxin and furan concentrations fall within the 95% confidence interval of CARP-1, except for 2,3,7,8-TCDF. It is anticipated that CARP-2 will be certified for dioxin, furan and PCB congeners in addition to those that are certified in CARP-1.

**CARP-2**

Final Results, Summary	pg/g wet	RSD
2,3,7,8-TCDF	16.7	1.37
2,3,7,8-TCDD	7.3	0.73
1,2,3,7,8-PeCDF	5.6	0.48
2,3,4,7,8-PeCDF	23.9	7.84
1,2,3,7,8-PeCDD	4.8	0.64
1,2,3,4,7,8-HxCDD	1.5	0.17
1,2,3,6,7,8-HxCDD	5.2	0.64
1,2,3,7,8,9-HxCDD	0.7	0.22
1,2,3,4,6,7,8-HpCDD	6.2	0.42
OCDD	10.7	2.15

**CONCLUSION:**

CARP-1 is a naturally contaminated biological tissue reference material available from the National Research Council of Canada, Ottawa, Ontario, Canada. It is certified for eighteen polychlorinated congeners including nine 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins and dibenzofurans, and nine EPA priority polychlorinated biphenyls. The CRM is sold as a unit of 6 ampoules each containing approximately 9.0g of slurry. A replacement material has already been produced and will succeed CARP-1 once its stocks is depleted. CARP-2 is now being continuously monitored and is being used in in-house method development, including solid-phase extraction, supercritical fluid extraction and column chromatographic work.

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