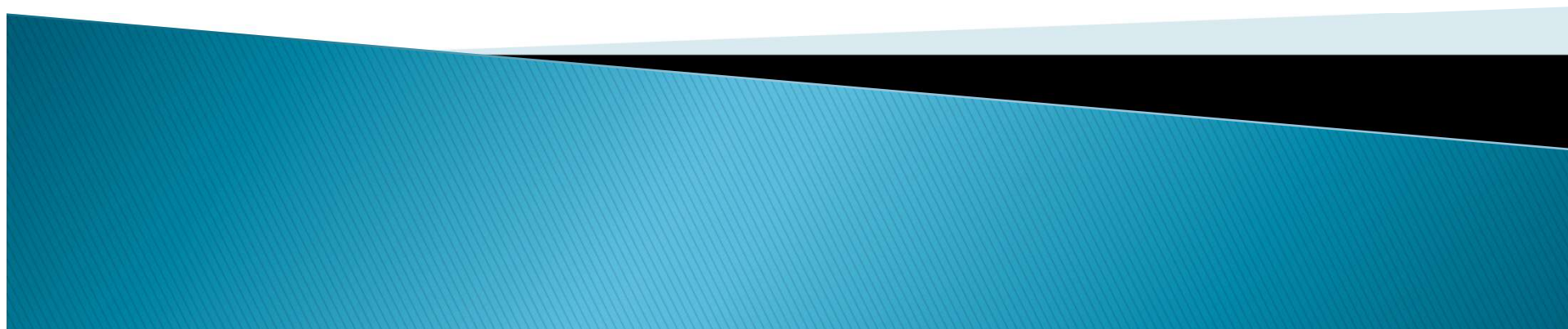


The Analysis of Polychlorinated Dibenzo-p-dioxins, Furans and Biphenyls in River Sediment with Automated Extraction and Clean Up

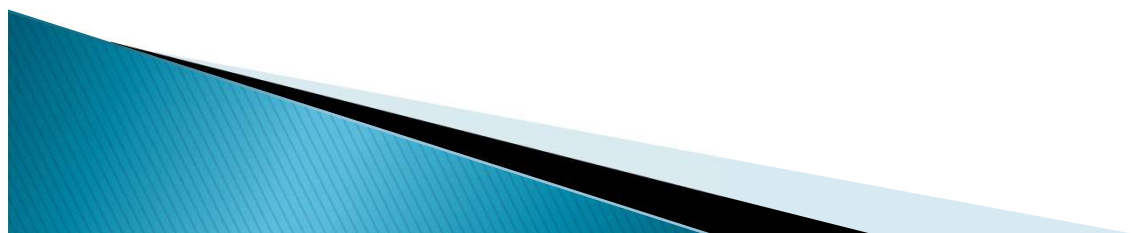
Ruud Addink and Matt Falkenstein

Toxic Report
Watertown MA



Introduction

- ▶ Stockholm Convention on Persistent Organics Pollutants 2001.
- ▶ Compounds of interest: polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxins (PCDDs), and furans (PCDFs).
- ▶ Known toxicity.
- ▶ Strict environmental regulations in force in most countries.



PCBs

- ▶ PCBs were intentionally produced 1920-1970s.
- ▶ Used in capacitors and transformers, also as flame retardants, hydraulic fluids, sealants, and vacuum pump fluids.
- ▶ Total production estimated worldwide 1.5 million metric tons. Produced as Aroclor in North-America.
- ▶ Levels are now dropping.
- ▶ Still at significant concentrations to pose danger.



PCDD/Fs

- ▶ PCDD/Fs are always unwanted byproducts.
- ▶ PCDD/F sources: combustion, incineration, metallurgical industry, pulp and paper bleaching/ production; low natural background (Trace Chemistries of Fire).
- ▶ Levels also dropping.
- ▶ Still at significant concentrations to pose danger.



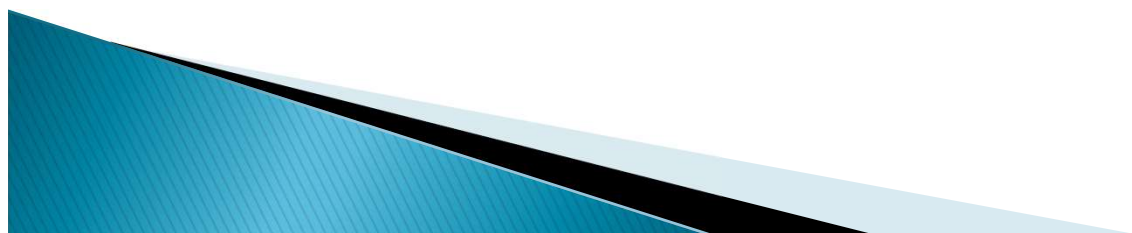
Health Effects

- Endocrine disruptors.
- Immune system.
- Nervous system.
- Reproductive functions.
- Carcinogenic.
- Chloracne.
- Main exposure (> 90%) is through dietary intake: meat, dairy, fish.
- Non-ortho and mono-ortho congeners (WHO-12) most toxic plus 17 laterally substituted PCDD/Fs.



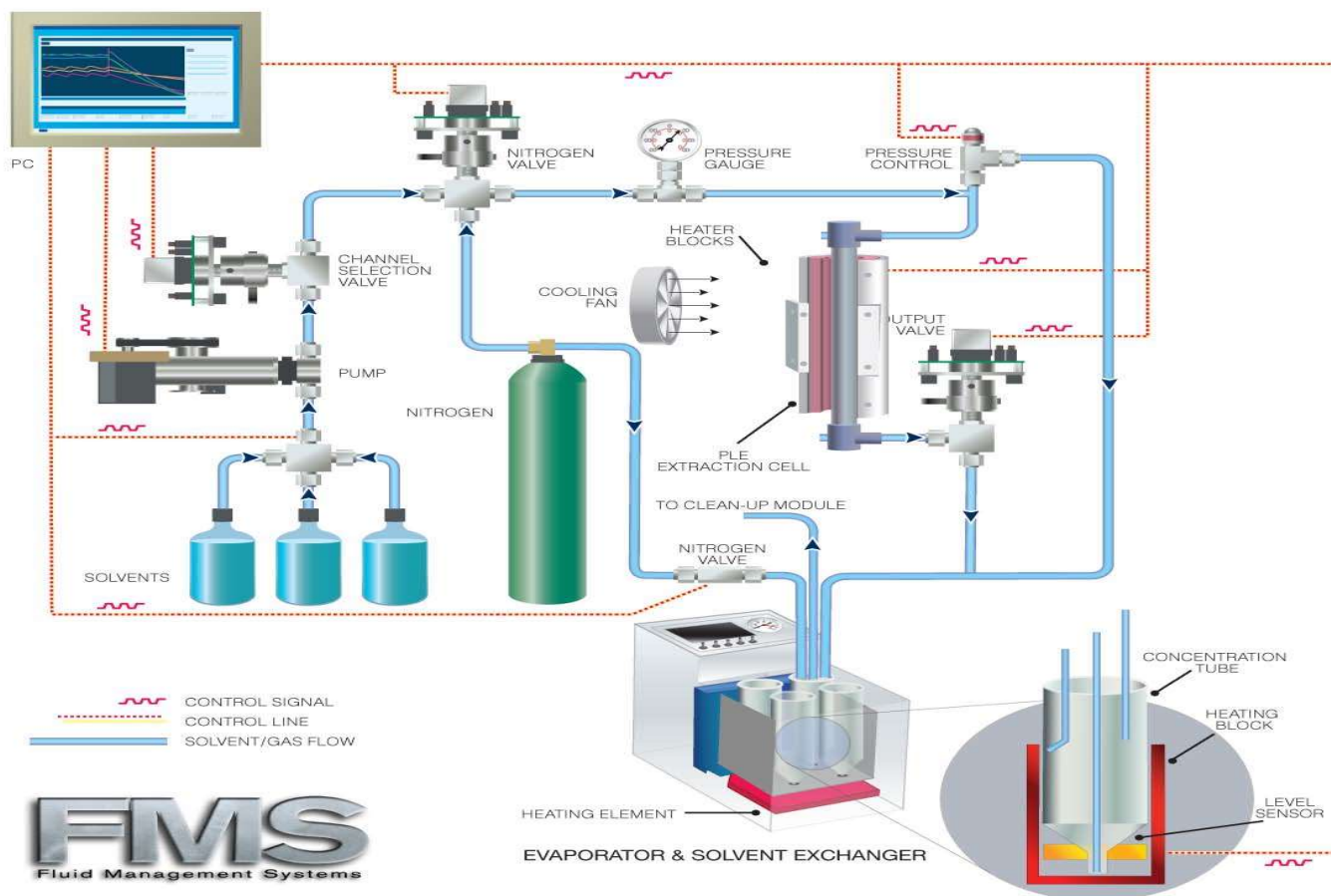
Scope

- ▶ Low solubility in water and chemically inert.
- ▶ Resist environmental degradation.
- ▶ Both PCBs and PCDD/Fs accumulate in soil and river sediment.
- ▶ Traditional extraction methods: up to 24-36 h Soxhlet and manual clean up.
- ▶ Manual methods are time-consuming; can have poor accuracy and reproducibility.
- ▶ Analyze 1 g river sediment for PCDD/Fs, PCBs with automated equipment.



Pressurized Liquid Extraction

PLE® Fast Extraction & Concentration System



Extraction Procedure

- ▶ 1 g sample mixed with Hydromatrix™ to dry, transferred to extraction cells
- ▶ Spiked with ^{13}C PCDD/Fs and PCBs standards.
- ▶ Void volume filled with Hydromatrix™.
- ▶ Sample Cells filled with 50% mixture Hexane/Methylene Chloride.
- ▶ Cells pressurized to 1500 PSI and heated to 120 °C.
- ▶ Temperature held for 20 minutes.
- ▶ Extraction cells cooled, flushed with solvent (50% cell volume), and nitrogen; collected in 250 mL tubes.

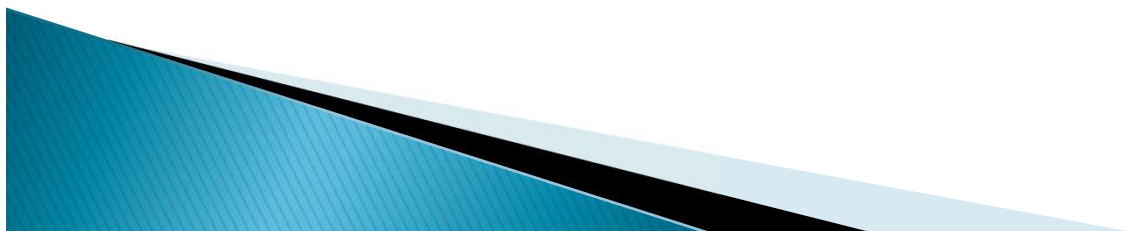


6 position evaporator

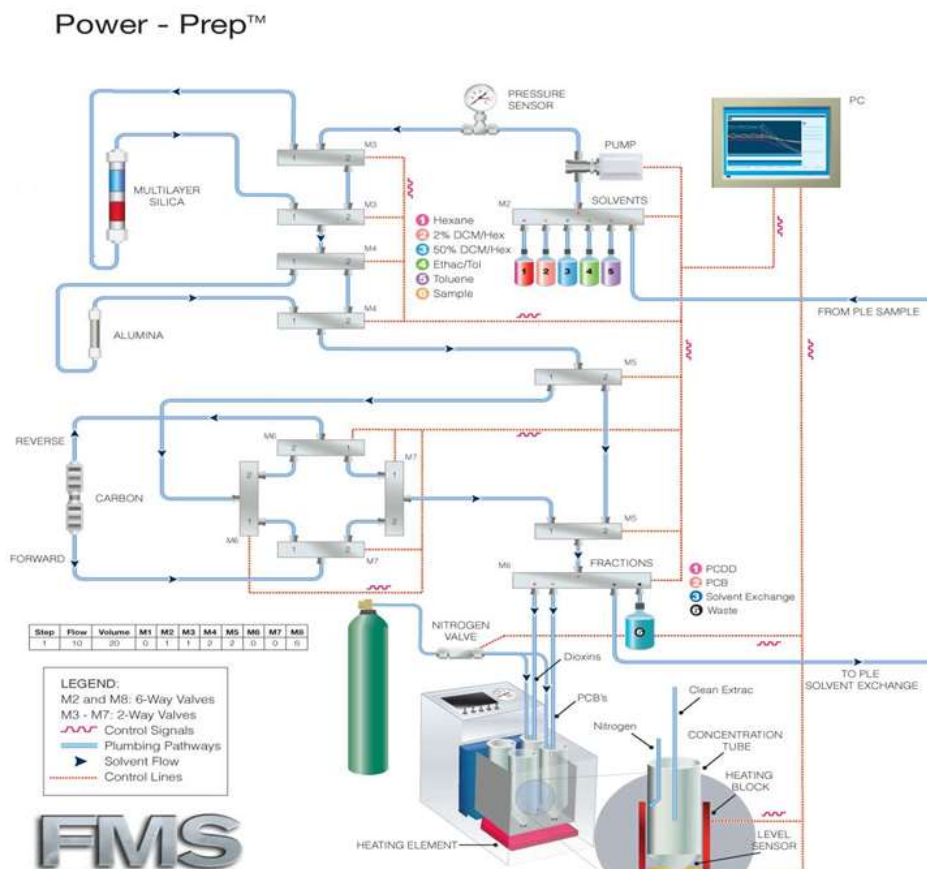


SuperVap Evaporation

- ▶ System pre-heated to 45-60 °C.
- ▶ Extracts evaporated at stable temperature under 5-6 psi nitrogen.
- ▶ Solvent exchange with hexane to eliminate dichloromethane.
- ▶ Dichloromethane would interfere with subsequent sample clean up.
- ▶ Extracts reduced to a few mLs.

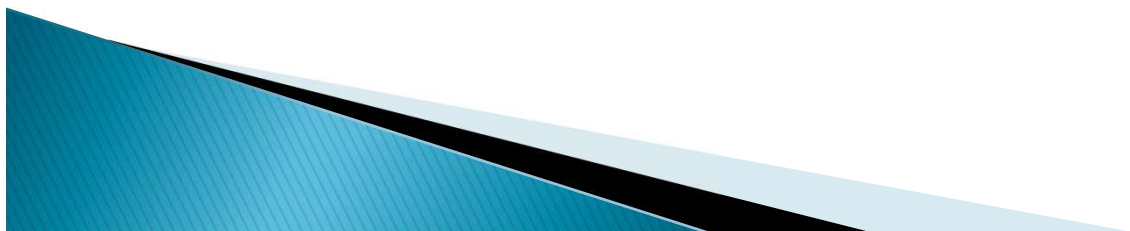


PowerPrep CleanUp System



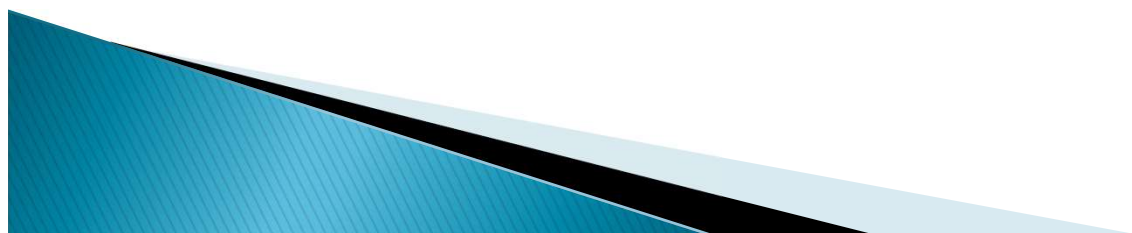
System Characteristics

- ▶ Control module that pilots valve drive modules connected to a pump and pressure modules responsible for solvent flow in the valve module.
- ▶ Built in computer that does not need a stand-alone pc.
- ▶ Easy programming and software editing provides custom made sequences of events that drive the required solvent at the right place at the right moment.
- ▶ Low pressure (5-30 psi). Flow rates of up to 5-15 mL/min are used.



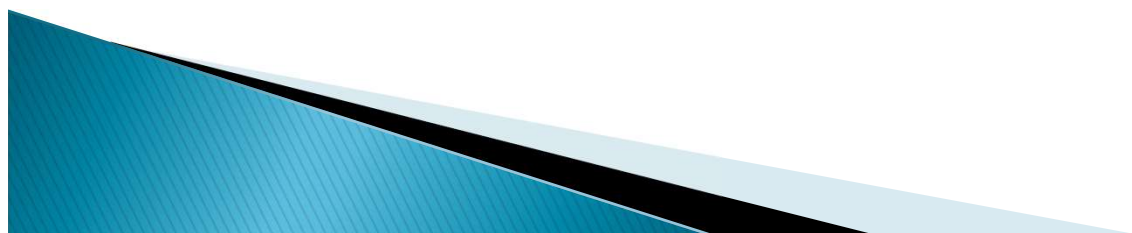
Clean Up (1)

- ▶ Jumbo Acidified Silica gel PCB-free column
- ▶ Silica - Classical PCB-free multilayer Acid-Base-Neutral silica gel column
- ▶ Alumina – PCB-free basic alumina column
- ▶ Carbon – PCB-free carbon/celite column



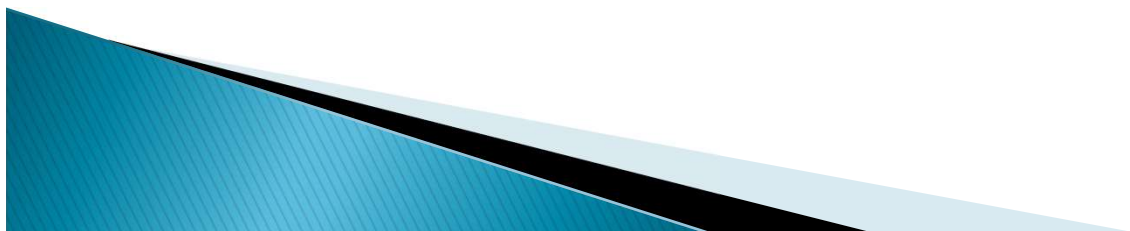
Clean Up (2)

- ▶ Standard 25-step program
- ▶ Install jumbo silica, classical ABN, alumina and carbon/celite columns
- ▶ Mixes used: hexane, 2%/98% dichloro methane/hexane, 50%/50% dichloromethane /hexane, 50%/50% ethylacetate/benzene, and toluene



Clean Up (3)

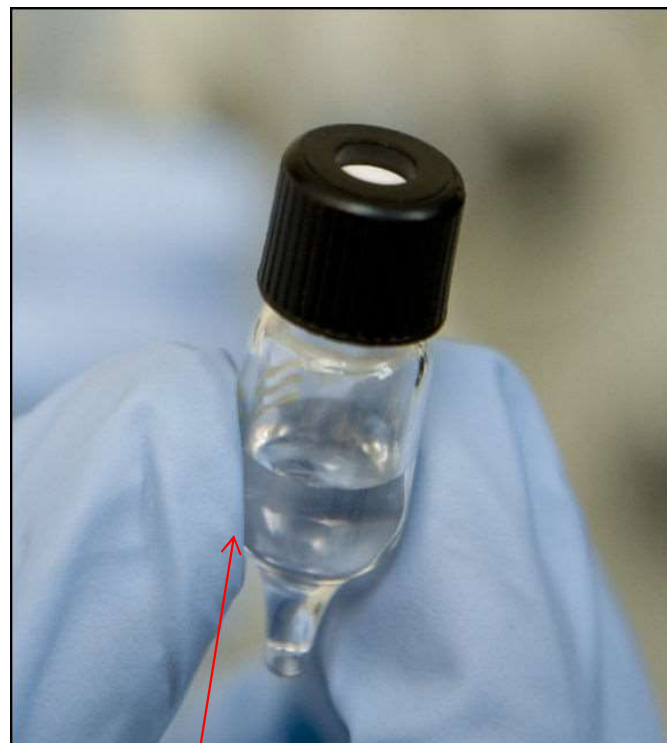
- ▶ Run conditioning steps 1-13 with columns in place
- ▶ Load sample (in hexane)
- ▶ Elute silica with 150 mLs hexane (waste)
- ▶ Elute alumina with 60 mLs 2%/98% DCM/ hexane (collect as F1; PCBs)
- ▶ Elute alumina with 120 mLs 50%/50% DCM/hexane (collect as F1; PCBs)
- ▶ Elute carbon with 4 mL 50%/50% ethyl-acetate/benzene (collect as F1; PCBs)
- ▶ Elute carbon with 75 mLs toluene (collect as F2; PCDD/F and co-planary PCBs)



SuperVap Evaporation

- ▶ System pre-heated to 45-60 °C.
- ▶ Samples evaporated at stable temperature under 5-6 psi nitrogen.
- ▶ 1 mL extract vial transferred directly to connected GC vial.
- ▶ Recovery standards added (nonane/dodecane).
- ▶ Extract taken 10 uL volume with a gentle stream of nitrogen at ambient temperature.





GC vial

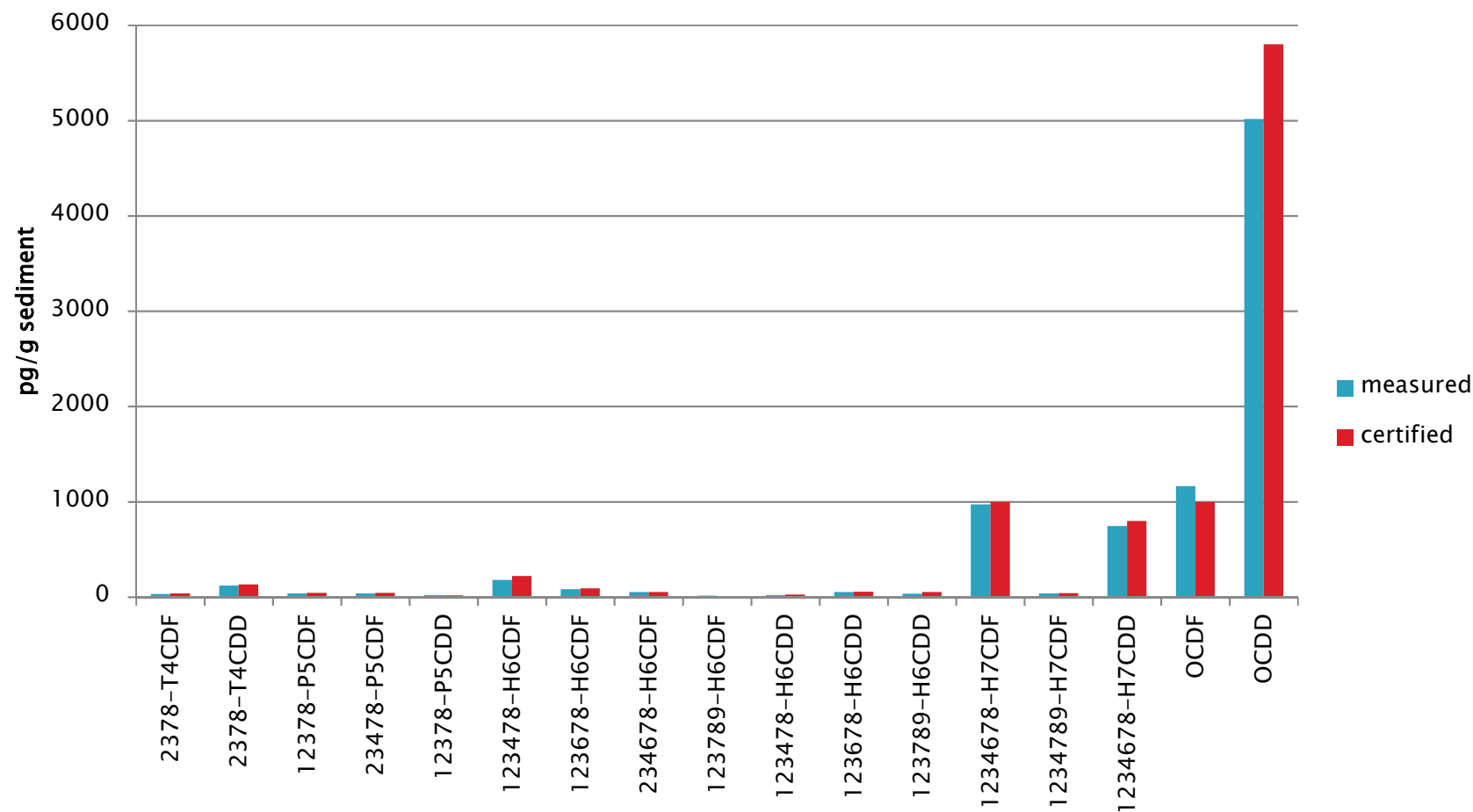
24 position Vial Evaporator



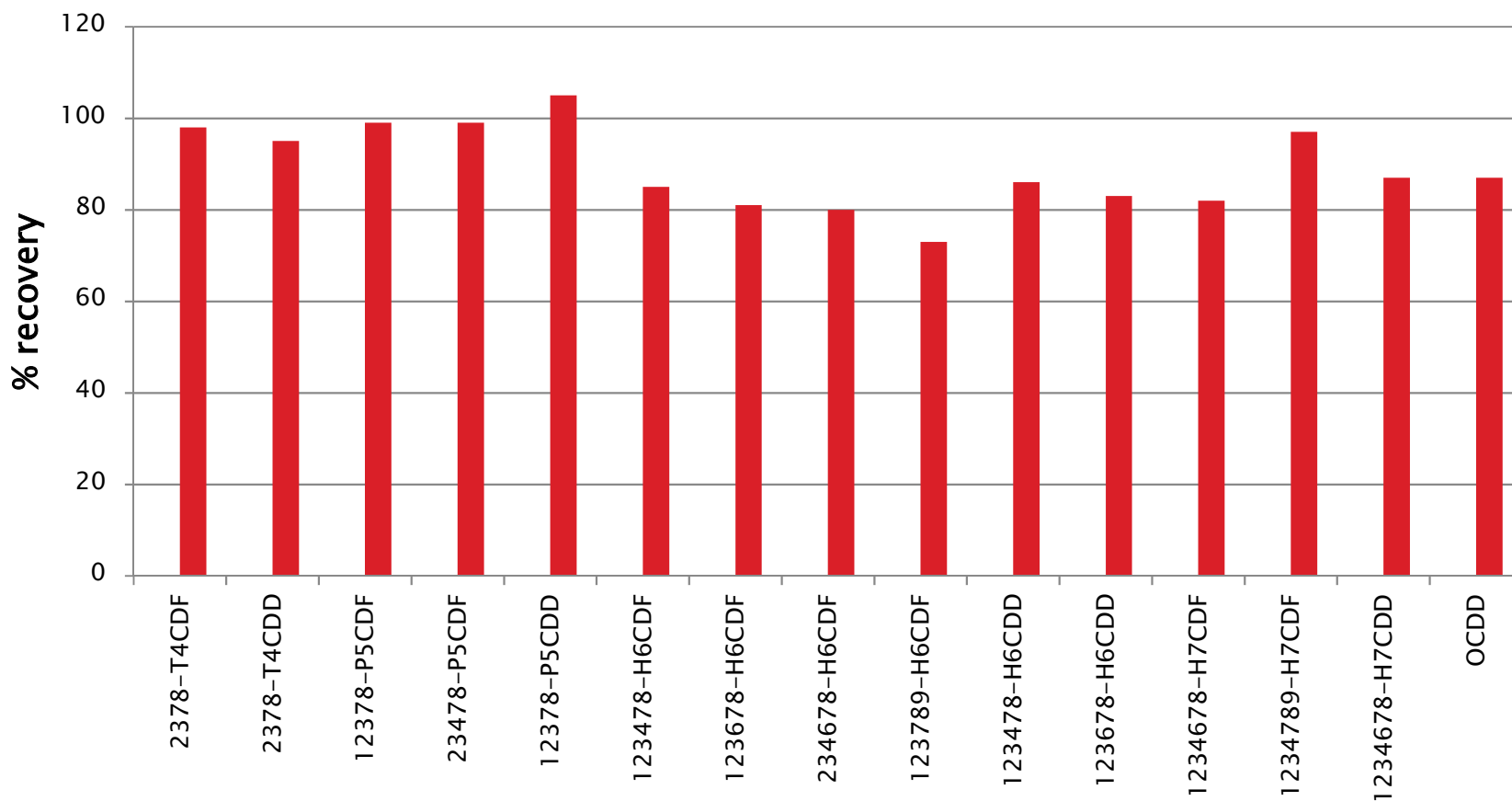
DFS HRGC/HRMS



NIST 1944 PCDD/Fs analysis (1)

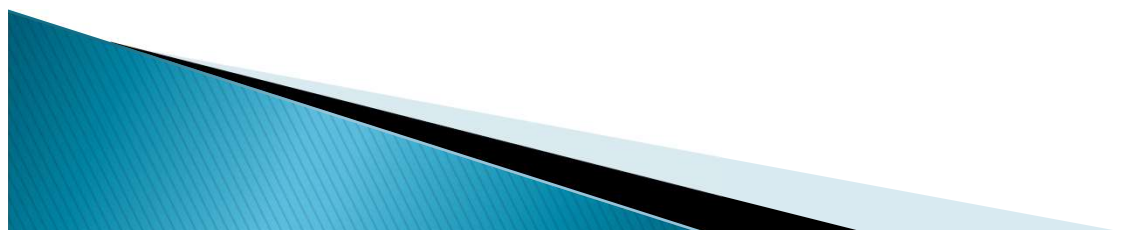


NIST 1944 PCDD/Fs analysis (2)



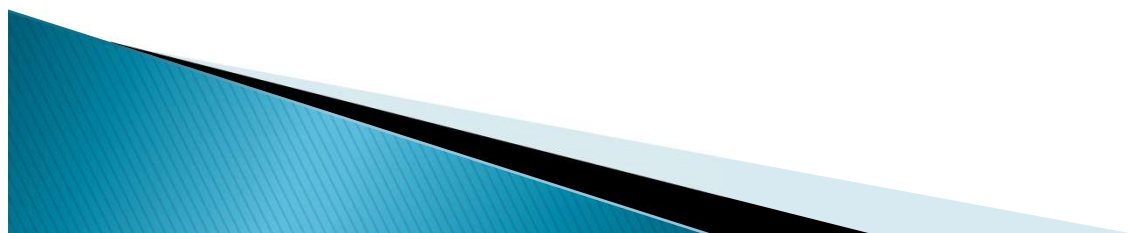
NIST 1944 PCBs analysis

		native pg/g	NIST1944 pg/g	recoveries %
33'44'-T4CB	77	5714.03		104%
344'5-T4CB	81	307.57		98%
233'44'-P5CB	105	20895.78	24500± 12250	109%
2344'5-P5CB	114	1196.34		106%
23'44'5-P5CB	118	56443.83	58000 ± 29000	102%
2'344'5-P5CB	123	4514.92		106%
33'44'5-P5CB	126	206.71		125%
233'44'5-H6CB	156	4936.21	6520 ± 3260	109%
233'44'5'-H6CB	157	941.96		109%
23'44'55'-H6CB	167	2421.59		93%
33'44'55'-H6CB	169	31.58		124%
233'44'55'-H7CB	170	15553.43	22600 ± 11300	100%
22'344'55'-H7CB	180	47244.50	44300 ± 22150	99%
233'44'55'-H7CB	189	532.65		115%



Conclusions (1)

- ▶ Pressurized Liquid Extraction combined with PowerPrep clean up gives fast and reliable technique for extraction of PCDD/Fs and PCBs in sediments under the 1613 and 1668 methods.
- ▶ Up to six position PLE can extract samples in under one hour.
- ▶ When analyzing POPs with PLE and automated open multi- column chromatography clean up - silica, alumina, carbon, samples are ready for analysis.



Conclusions (2)

- ▶ Excellent recoveries are obtained and very good agreement is found between NIST certified PCDD/Fs-PCBs native reference values and data obtained in our laboratory.
- ▶ Same day sample processing and analysis (HRGC/HRMS or other techniques if desired) is now possible.

