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One Step Extraction-Clean Up for PCBs and Automated Column Chromatography for PCDD/Fs in Sediment and Soil

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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.

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PCBs

- PCBs were intentionally produced 1920-1970s.
- Used in capacitators 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.

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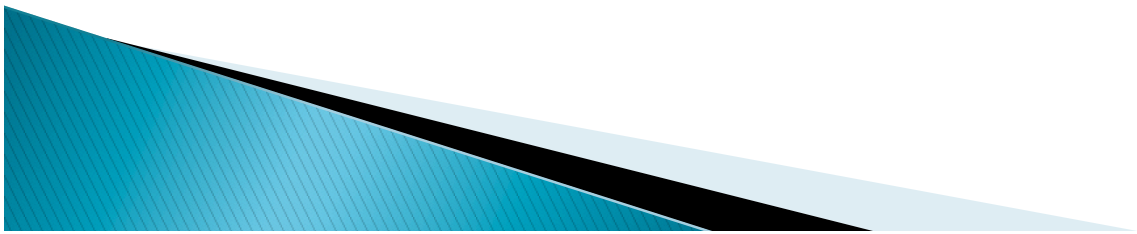
PCDD/Fs

- 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.



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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.

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Properties/Analysis

- 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.

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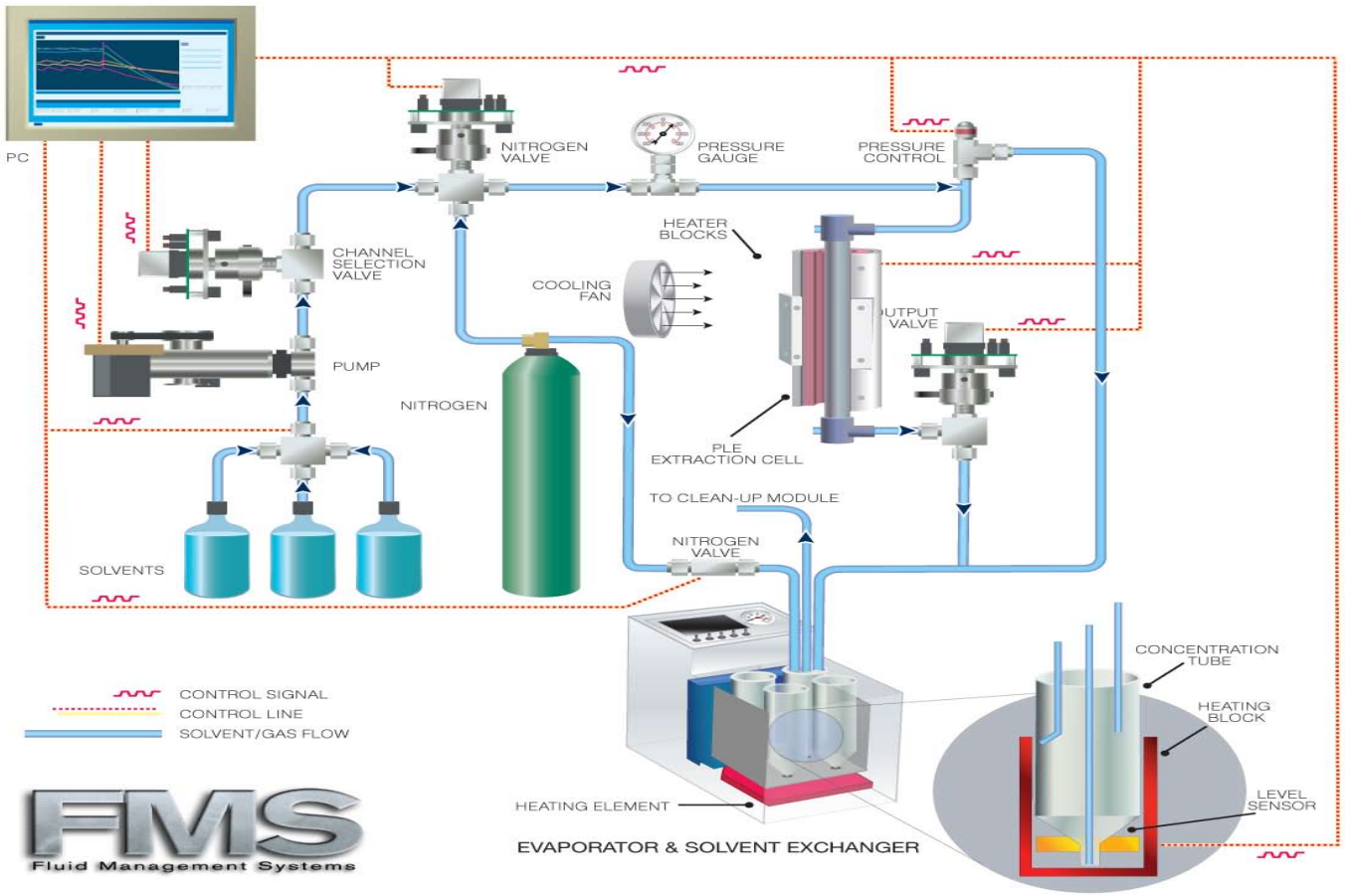
One Step Extraction + Clean Up



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Procedure (EPA 8082)

- 10 g sample mixed with Hydromatrix™ to dry, transferred to extraction cells with InCell acid silica end cap.
- Spiked with native and PCBs standards.
- Void volume filled with Ottawa Sand.
- Sample Cells filled with 50% mixture Hexane/Methylene Chloride.
- Cells pressurized to 1500 PSI.
- Heated to 120 ºC.
- Temperature held for 20 minutes.
- Extraction cells cooled and flushed with 50% cell volume.
- Additional clean up of sample as extract passes thru acid silica in end cap.
- Extract collected in tubes with direct-to-GC-vial connections.
- PCB-209 added as internal standard.

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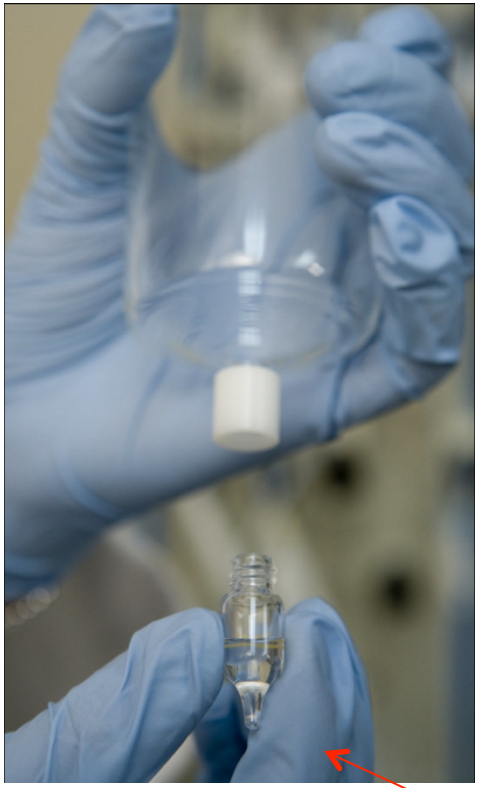
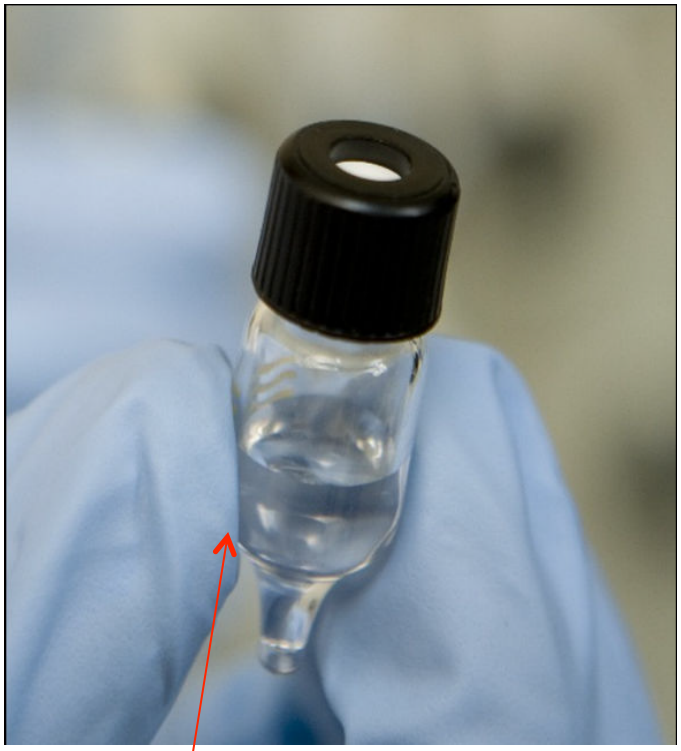
6 position evaporator

SuperVap Evaporation

- System pre-heated to 45-60 ºC.
- 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

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Analysis: Polaris Q

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Results 8082 mix

	spiked ug/kg	Sand Mean Rec ug/kg	Sediment Mean Rec ug/kg
pcb-1	100	114	75
pcb-5	100	125	81
pcb-18	100	119	93
pcb-31	100	121	85
pcb-44	100	119	85
pcb-52	100	119	91
pcb-66	100	144	89
pcb-87	100	125	85
pcb-101	100	123	90
pcb-110	100	112	85
pcb-138	100	109	87
pcb-141	100	106	93
pcb-151	100	113	91
pcb-153	100	113	91
pcb-170	100	121	86
pcb-180	100	101	95
pcb-183	100	100	95
pcb-187	100	104	88
pcb-206	100	103	79

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PCDD/F sediment (1613)

- Analyzed 1 g of NIST-1944 sediment.
- Spiked with ^{13}C labeled standards.
- PLE extraction as above (no InCell clean up).
- Volume reduction and solvent exchange to hexane.
- PowerPrep automated clean up.

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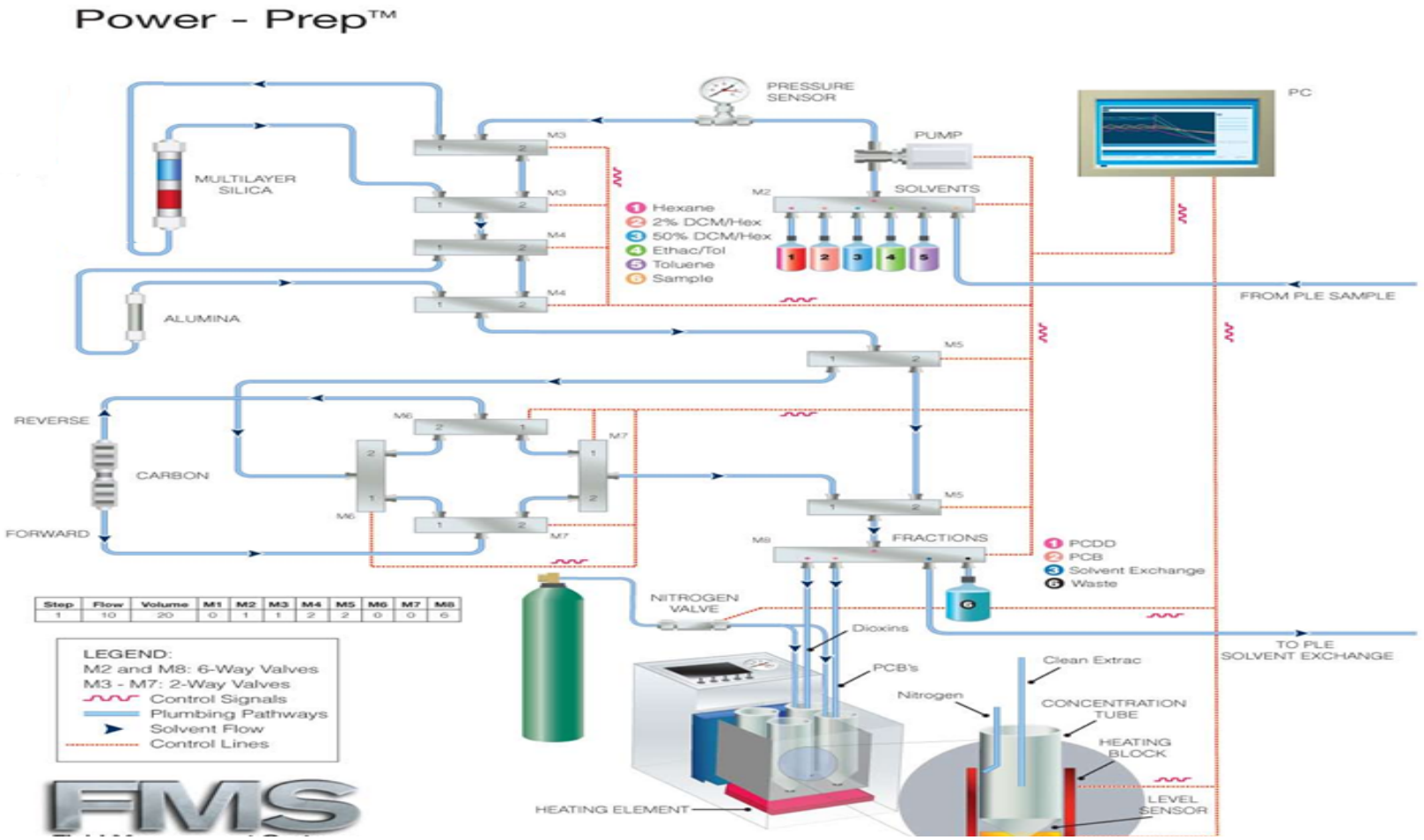
PowerPrep CleanUp System



Step	Flow	Volume	M1	M2	M3	M4	M5	M6	M7	M8
1	10	20	0	1	1	2	2	0	0	6

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Clean Up (1)

- Silica - High Capacity PCB-free multilayer ABN silica gel column
- Alumina – PCB-free basic alumina column
- Carbon – PCB-free carbon/celite column

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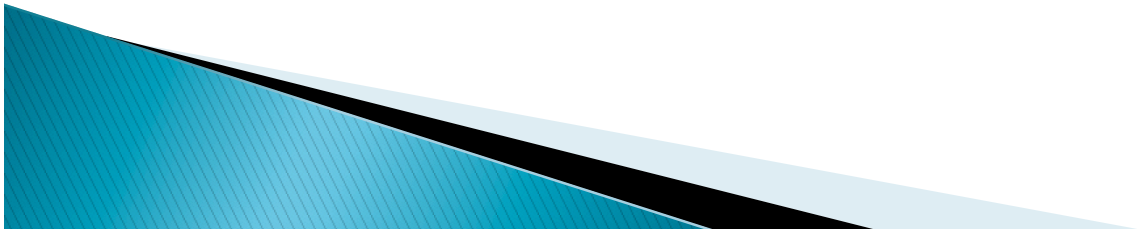
Clean Up (2)

- Condition columns 10 mLs or 40 (silica) mLs each.
- Sample loaded onto silica column in hexane.
- Elute silica and alumina with hexane (140 mLs), then 10% DCM/hexane (70 mLs, collect PCBs if present).
- Elute alumina with 50 mLs DCM to get PCDD/F onto carbon.
- Back elute carbon with 35 mLs toluene, collect PCDD/F. Total volume is ~ 375 mLs of solvent.



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DFS HRGC/HRMS

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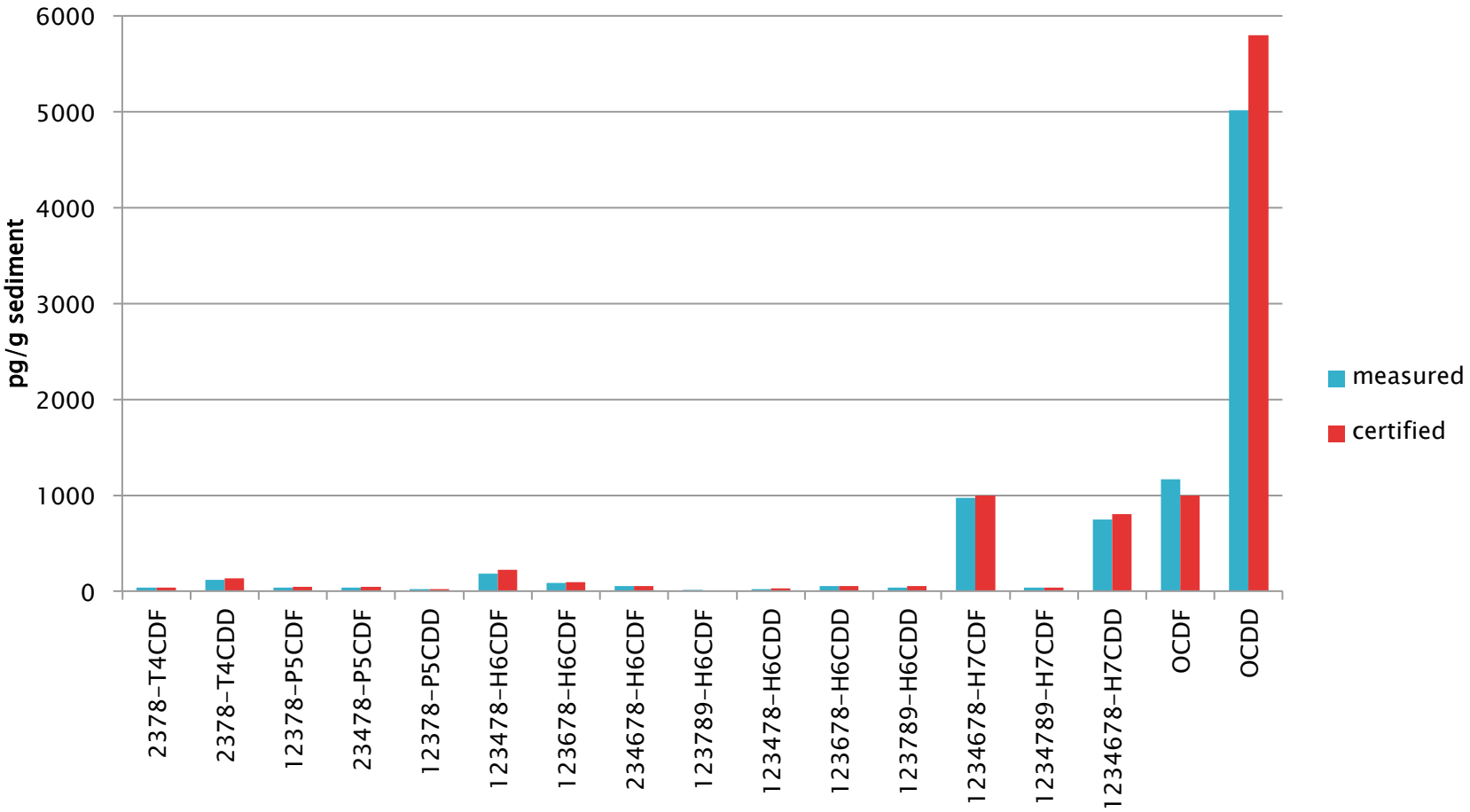
NIST 1944 sediment analysis (1)



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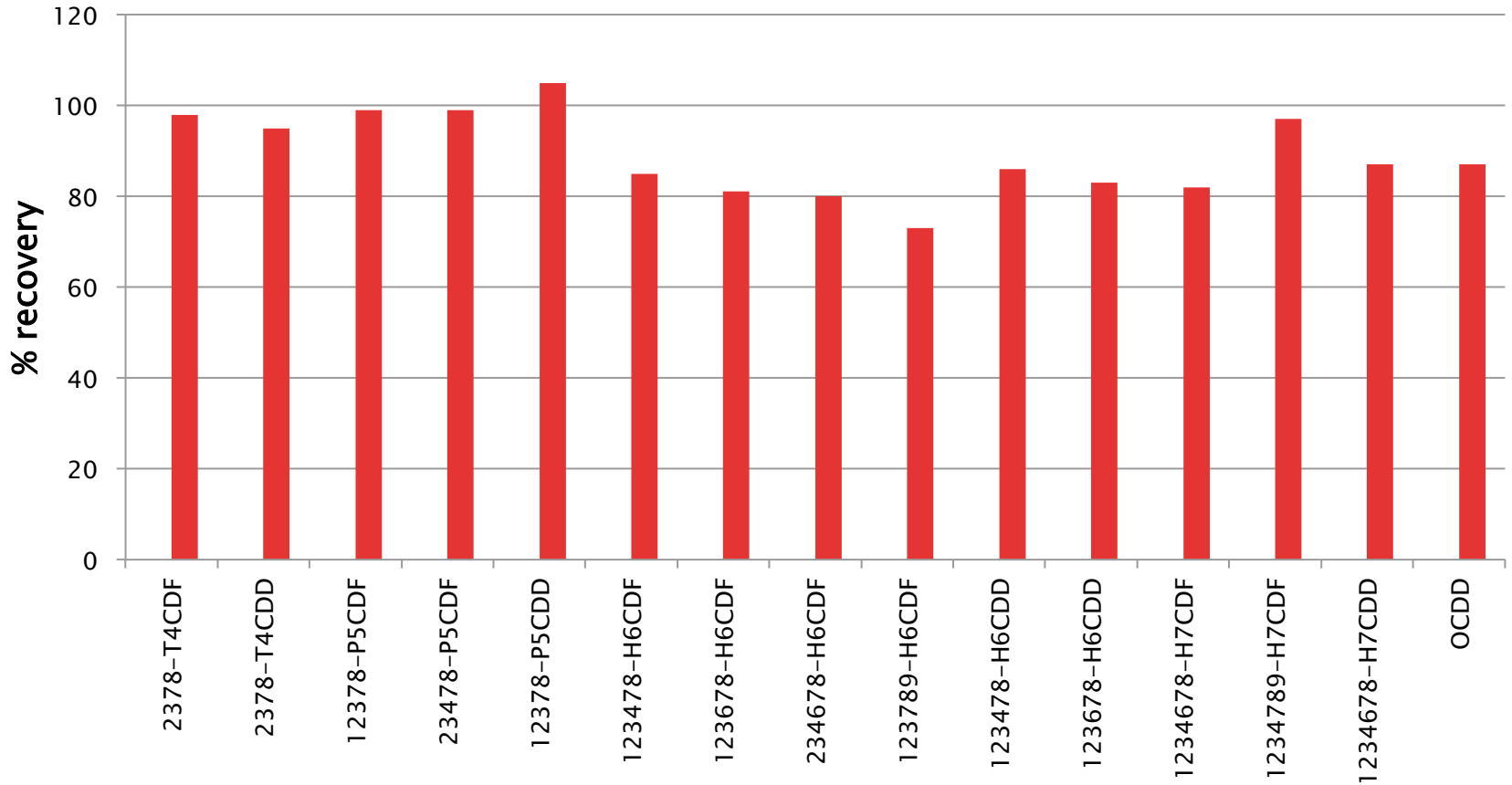
NIST 1944 sediment analysis (2)



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Conclusions (1)

- Pressurized Liquid Extraction combined with InCell acid silica clean up gives fast and reliable technique for extraction of PCBs in sediments and soils under the 8082 method.
- Up to six position PLE can extract samples in under one hour.
- When analyzing PCDD/Fs under 1613 method, PLE combined with automated multi column silica, alumina, and carbon clean up delivers clean samples ready for analysis.

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Conclusions (2)

- Same technique can be used for PCBs (1668) in sediments and soils.
- Same day sample processing and analysis (HRGC/HRMS or other techniques if desired) is now possible.