

THE SUPELCO “DIOXIN PREP SYSTEM - FLORISIL VERSION” : A MULTI-LAYER SILICA GEL COLUMN CONNECTED IN SERIES TO AN ACTIVATED FLORISIL MICRO-COLUMN FOR RAPID DETERMINATIONS OF PCDD/Fs AND PCBs IN ENVIRONMENTAL SAMPLES

Eric Aries¹, David R. Anderson¹, Nicholas Ordsmith², Lisa Fitzpatrick³ and Fiona Barclay³

¹CORUS R, D and T, Swinden Technology Centre, Rotherham, UK S60 3AR

²HALL ANALYTICAL LABORATORIES, Manchester, UK M23 9YJ

³SIGMA ALDRICH COMPANY Ltd., Poole, Dorset, UK BH12 4QH

Overview

- **Brief review on standard analytical procedures for PCDD/Fs and PCB analyses**
- **Collaboration between Corus / Hall Analytical / Supelco on the Dioxin Prep Systems**
- **Supelco Dioxin Prep Systems**
 - Dual Carbon Column Version
 - Florisil Version
 - Validation data
 - Sample throughput
- **Acknowledgements**

Standard analytical procedures for PCB and PCDD/F analyses

- **Method US EPA 1613 B** : PCDD/Fs in solids, waste waters and sediments
- **Method US EPA 23** : PCDD/Fs in stack emissions
- **Method EN1948** : European method for PCDD/Fs and PCBs in stack emissions
- **Method 1668A** : PCBs in water, soil sediment and tissue

ISOTOPE DILUTION : $^{13}\text{C}_{12}$ PCDD/F and PCB internal standards

**High Resolution Gas Chromatography / High Resolution Mass Spectrometry
HRGC / HRMS**

SEVERAL DAYS OF SAMPLE PREPARATION

- **Extraction (Soxhlet, Dionex ASE)**
- **Solvent concentration**
- **Successive clean-up steps (Silica, Florisil, Alumina, Activated Carbon)**
- **Data processing**

Supelco Dioxin Prep System

Collaboration Corus / Hall Analytical / Supelco



- 2002 :** Development and validation of the Dioxin Prep System – Dual Carbon Column Version in Japan for fast determinations of PCDD/Fs. *(Japan Quality Assurance Organisation and Kawajyu Techno Service)*
- 2003 :** Evaluation of the Dioxin Prep System – Dual Carbon Column Version by Corus and Hall Analytical prior to its UK commercial launch.
- 2004 :** A collaboration agreement is signed by Corus, Hall and Supelco to develop and validate an enhanced version of the Dioxin Prep System.
- 2005 :** Development and validation of the Supelco Dioxin Prep System - Florisil Version by Corus and Hall Analytical Laboratories.



Testing Laboratories

Trace Organic Analysis Laboratory (Corus R, D and T)
Hall Analytical Laboratories



Hall Analytical Laboratories

Manchester, UK

Contract laboratory

UKAS (ISO 17025) accreditation
for PCDD/F and PCB analyses

2 HRGC – HRMS instruments



Corus R, D & T

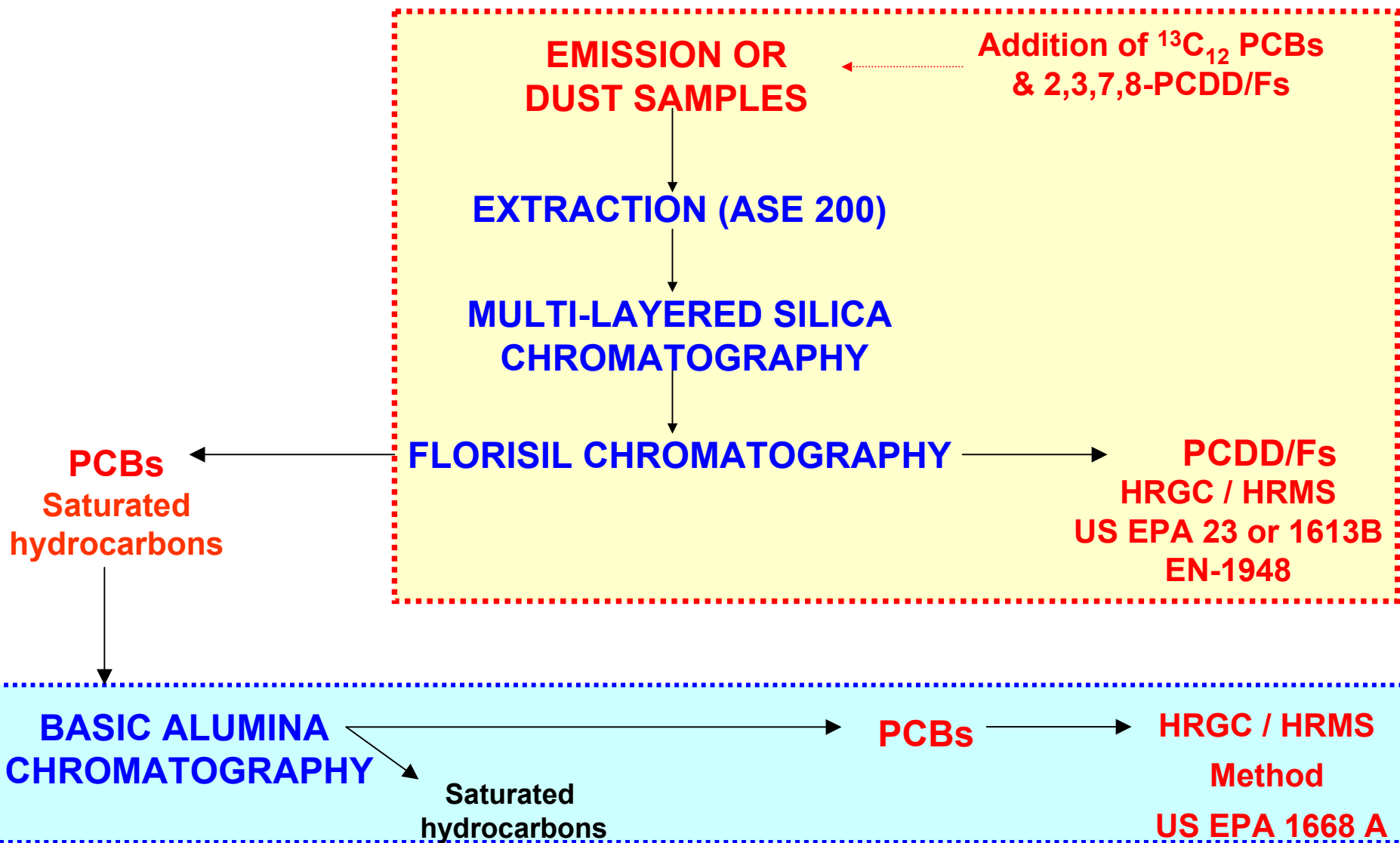
Swinden Technology Centre, Rotherham, UK

Researches into the emissions and the formation of PCDD/Fs and PCBs
from UK steel plants (iron ore sintering, EAF steel-making)

UKAS (ISO 17025) accreditation for PCDD/F and PCB analyses

Micromass Autospec Ultima HRGC - HRMS

Corus and Hall Analytical standard procedures for determination of PCDD/Fs and PCBs in environmental samples



Sample throughput at Trace Organic Analysis Laboratory (Corus) using standard analytical methods



1 fully trained technician / 8 samples

Extraction and concentration (ASE 200) = 1 to 2 days



Multi-layer silica clean-up = 1 day



Florisil step = 1 day



Basic Alumina step = 1 day



PCBs

**Analysis overnight
Data processing = 1 day**

PCDD/Fs

**Analysis overnight
Data processing = 1 day**

PCDD/Fs : 4 to 5 working days

PCBs : 5 to 6 working days

Additional Tasks : Packing and activation of columns

SUPELCO “DIOXIN PREP SYSTEMS”

The dual-carbon column version

Description

Analytical methods

Validation data

The Florisil version

Description

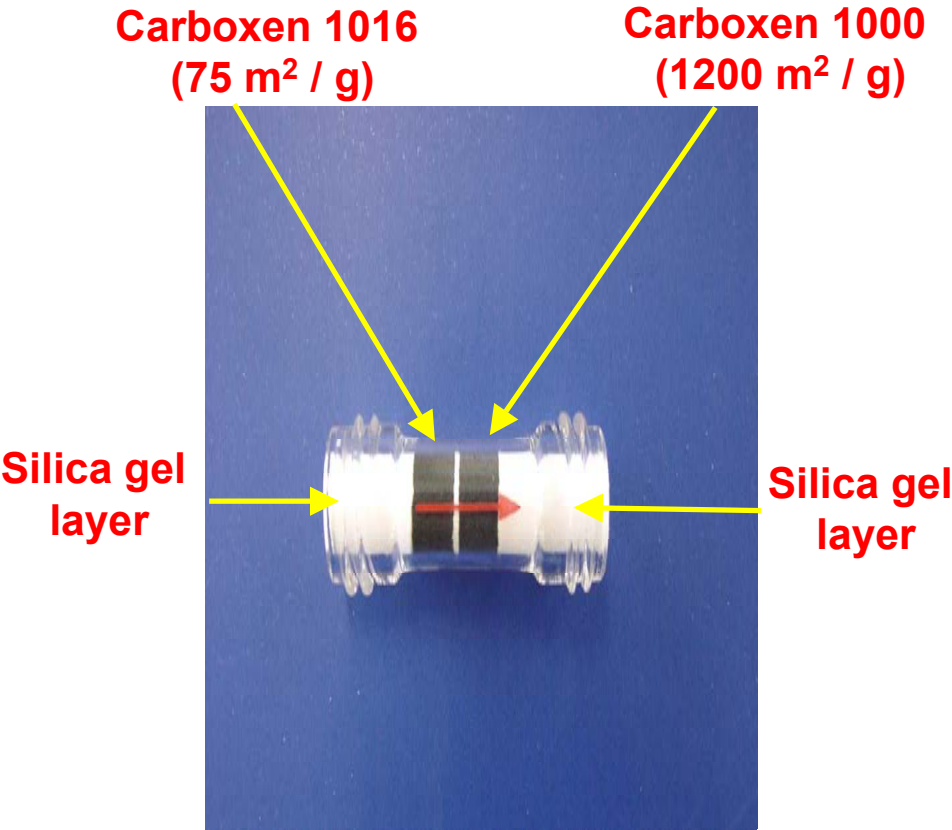
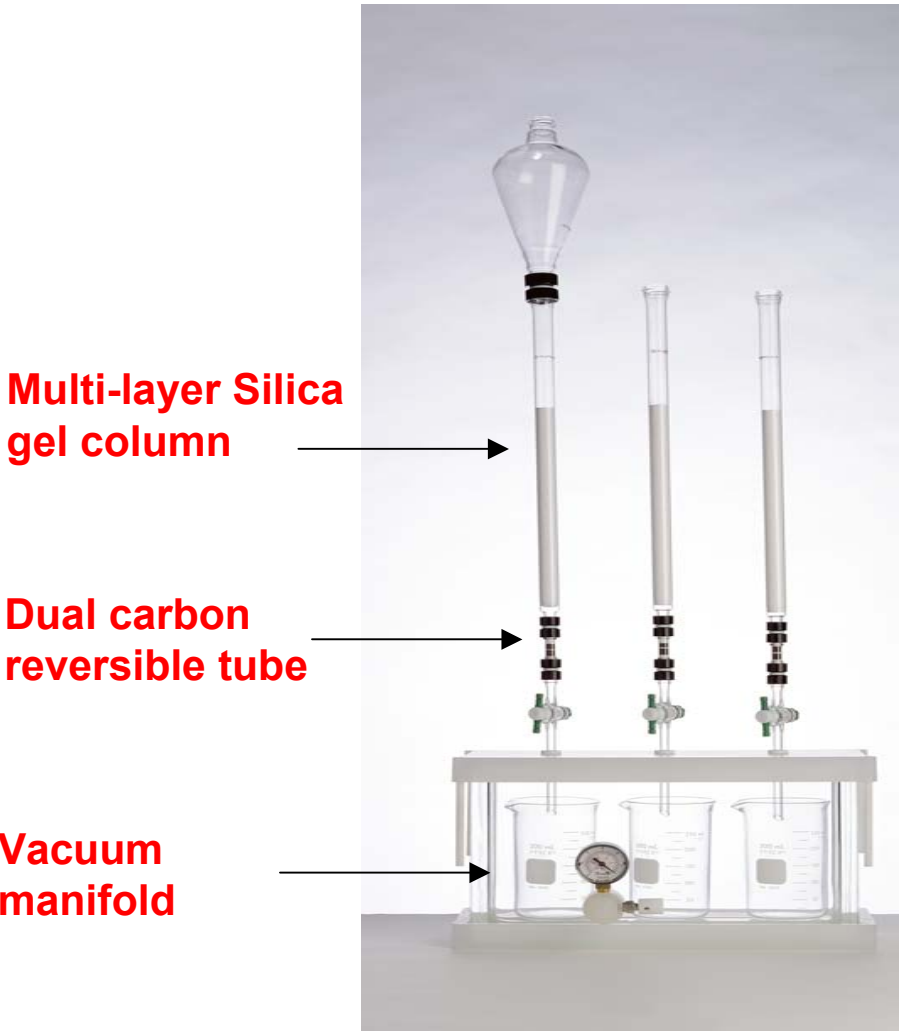
Analytical methods

Validation data

Sample throughput using Supelco Dioxin Prep system - Florisil Version

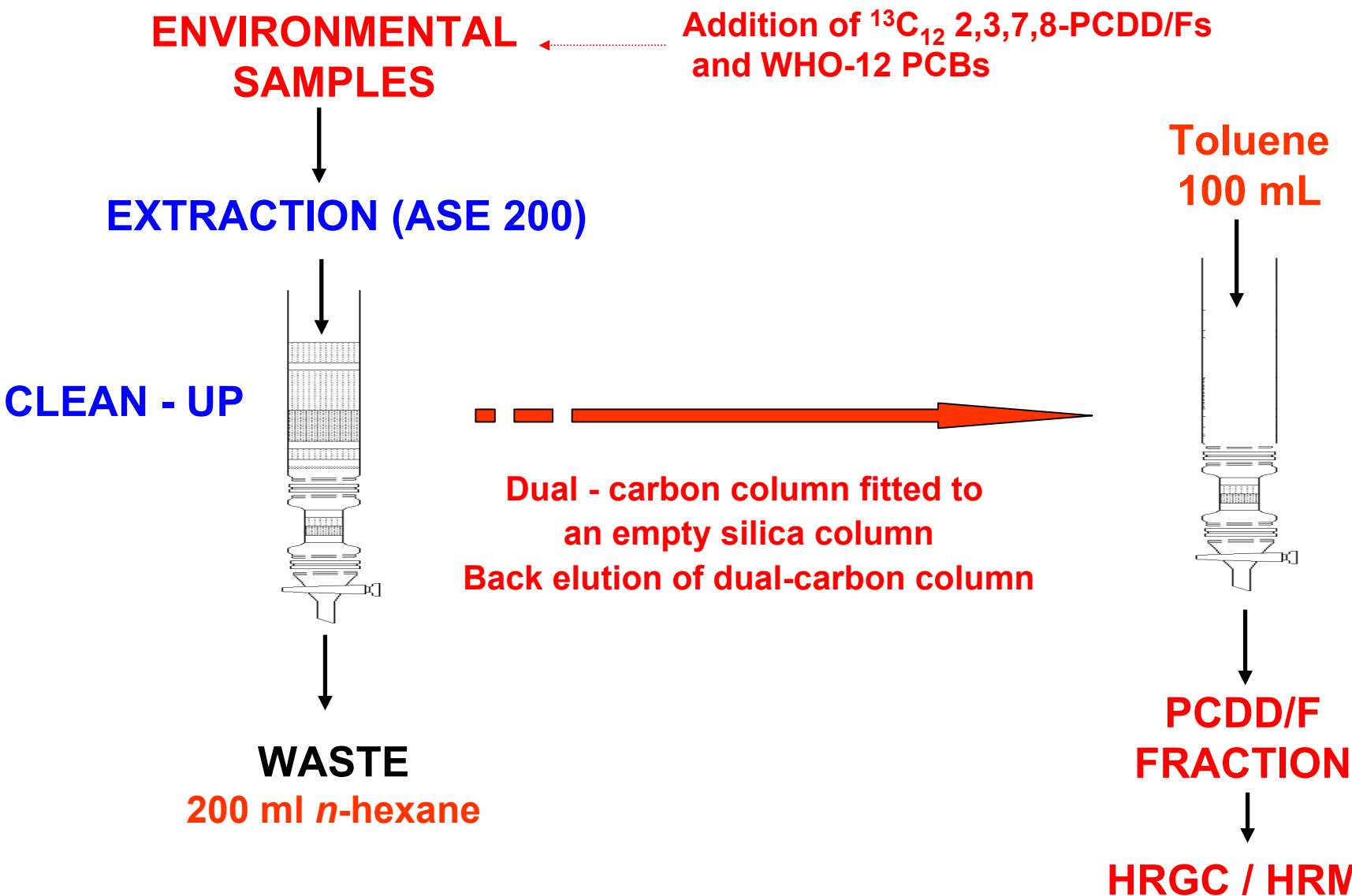


Supelco Dioxin Prep System - Dual Carbon Column Version

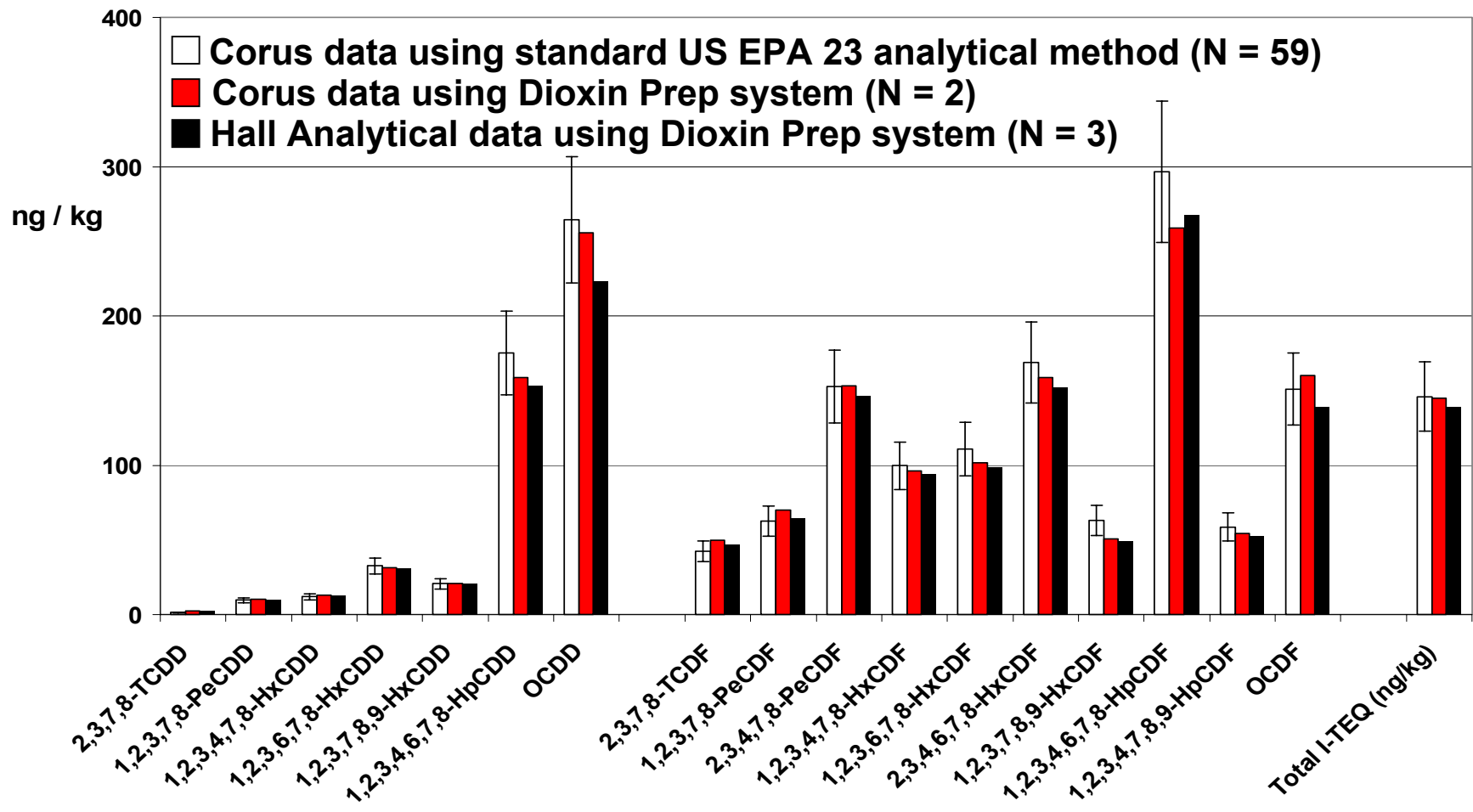


Analytical procedure

Dioxin Prep System – Dual Carbon Column Version

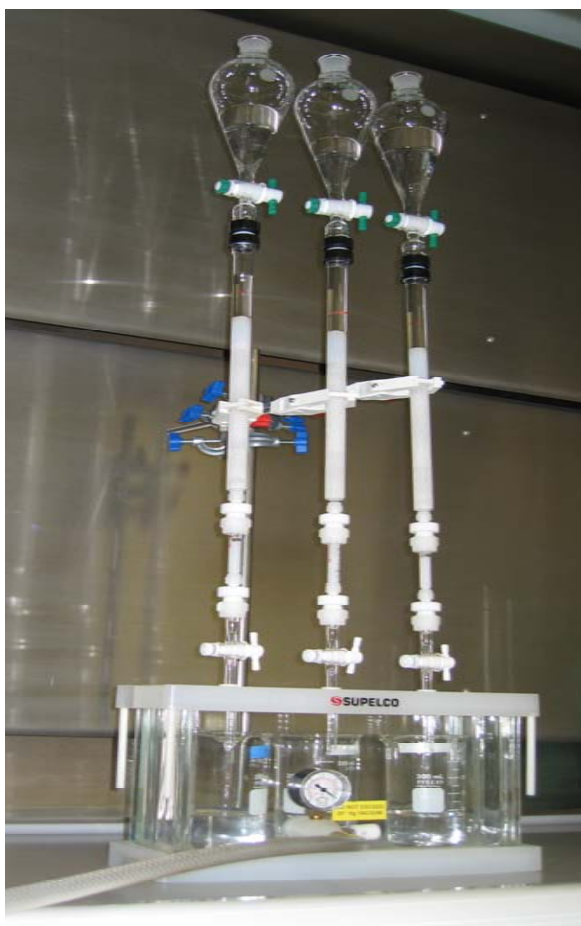


Analysis of a waste sinter dust (QC material) for PCDD/Fs using the Dioxin Prep System- Dual Carbon Column Version



Supelco Dioxin Prep System - Florisil Version

Schematic



250 mL solvent reservoir
(28449-U)

24/24mm PP Connector
(21216-U)

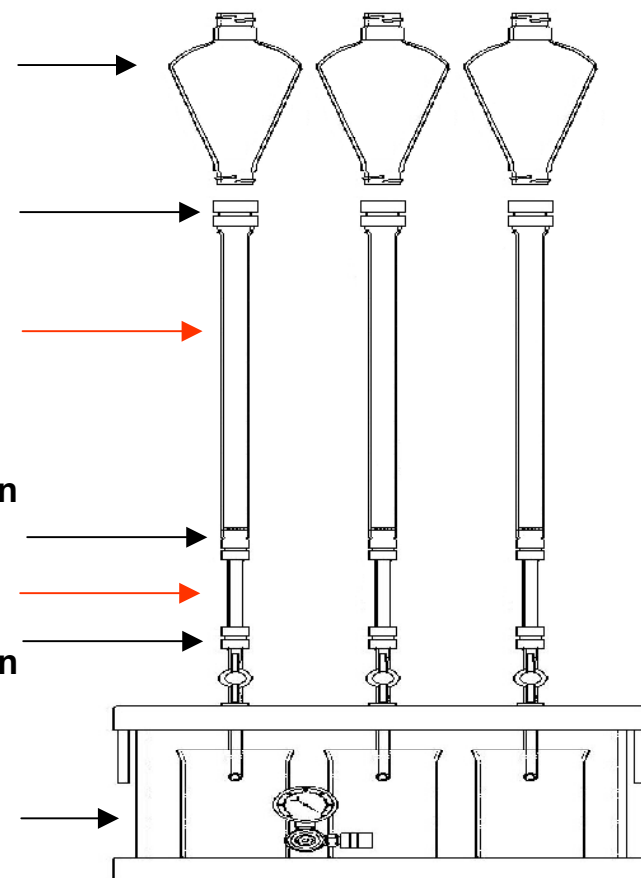
Multi-layered silica tube
(28397-U)

6.35/10 mm Reducing union
(28398-U)

Florisil micro-column

6.35/10 mm Reducing union
(28398-U)

Vacuum Manifold
(28403-U)



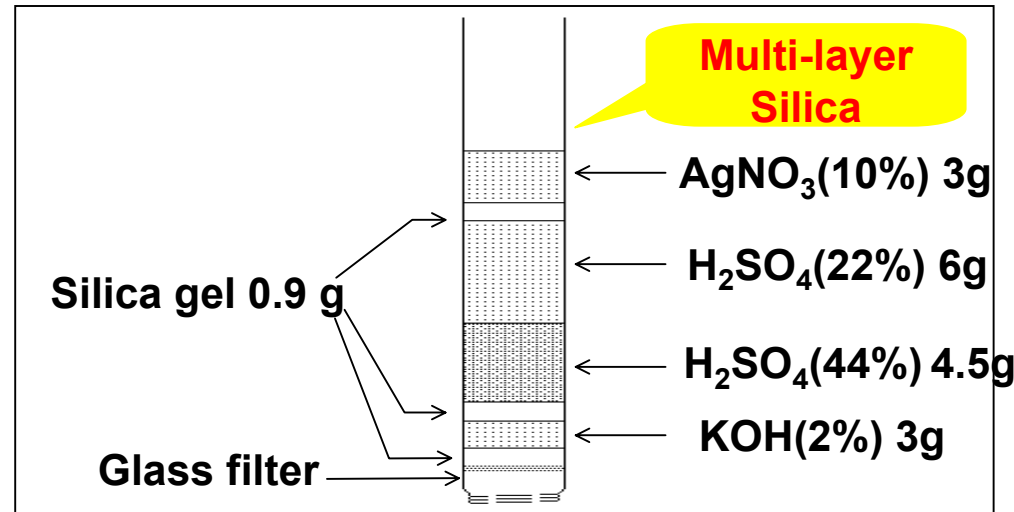
Supelco Dioxin Prep System - Florisil Version

Multi-layer silica and activated Florisil



MULTI - LAYER SILICA

Designed to meet requirements of
Japanese Industrial Standard
Methods K- 0311 / K - 0312



ACTIVATED FLORISIL

Empty Florisil tubes and connectors.

Flame sealed ampoules containing
1g activated Florisil (60/100 mesh)

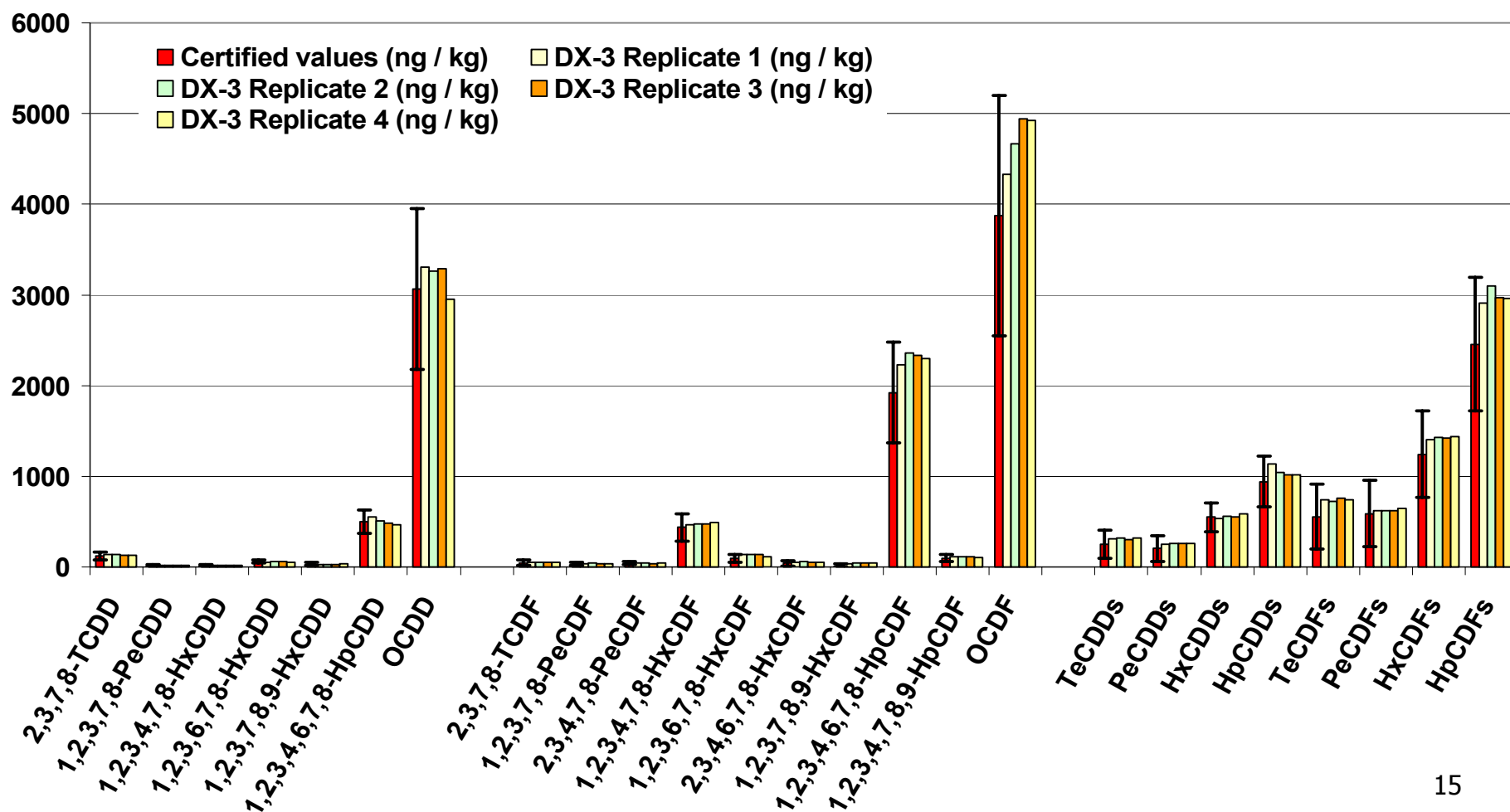




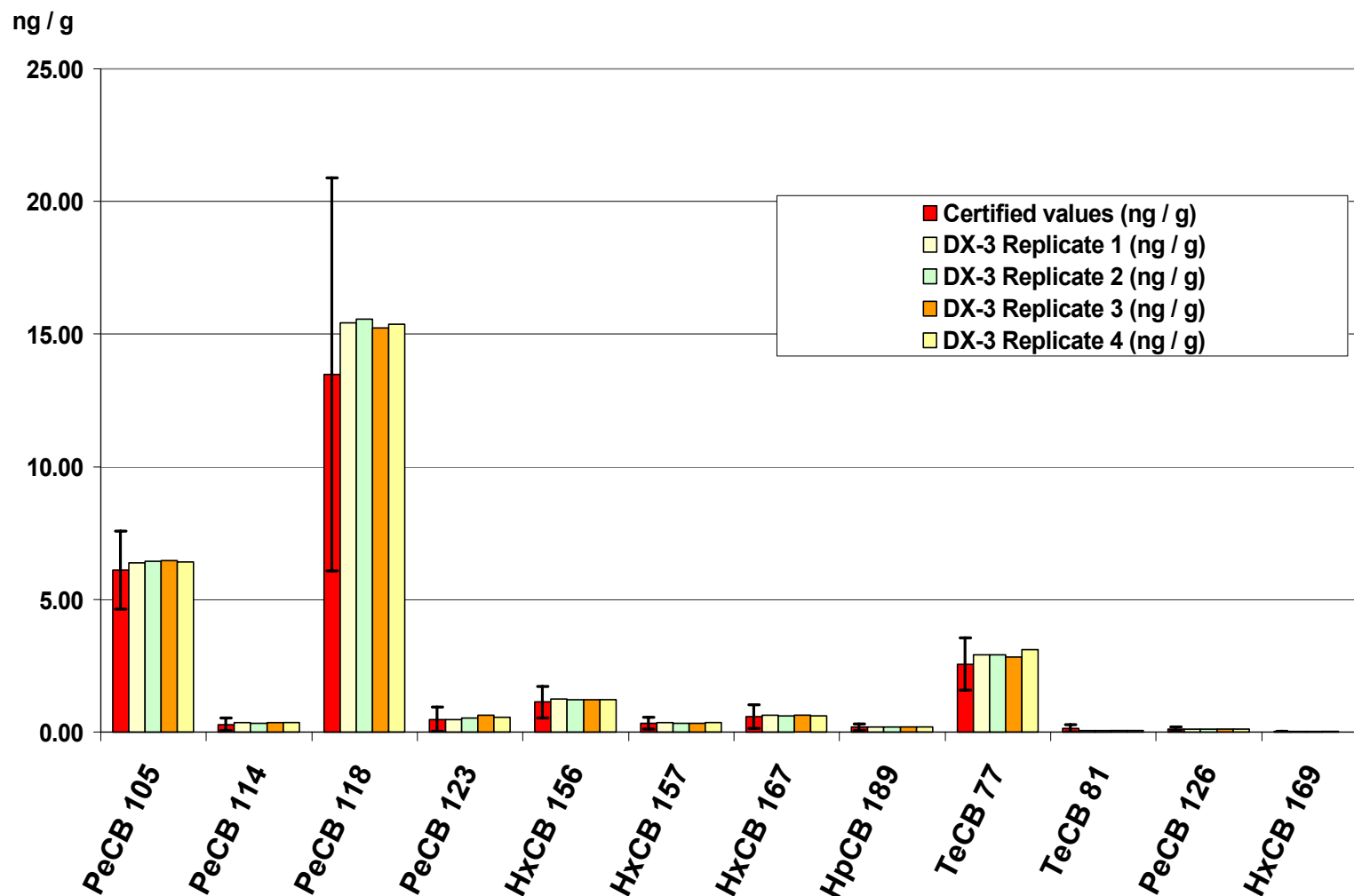
Determination of PCDD/Fs in DX-3 certified reference sediment using the Dioxin Prep System – Florisil Version



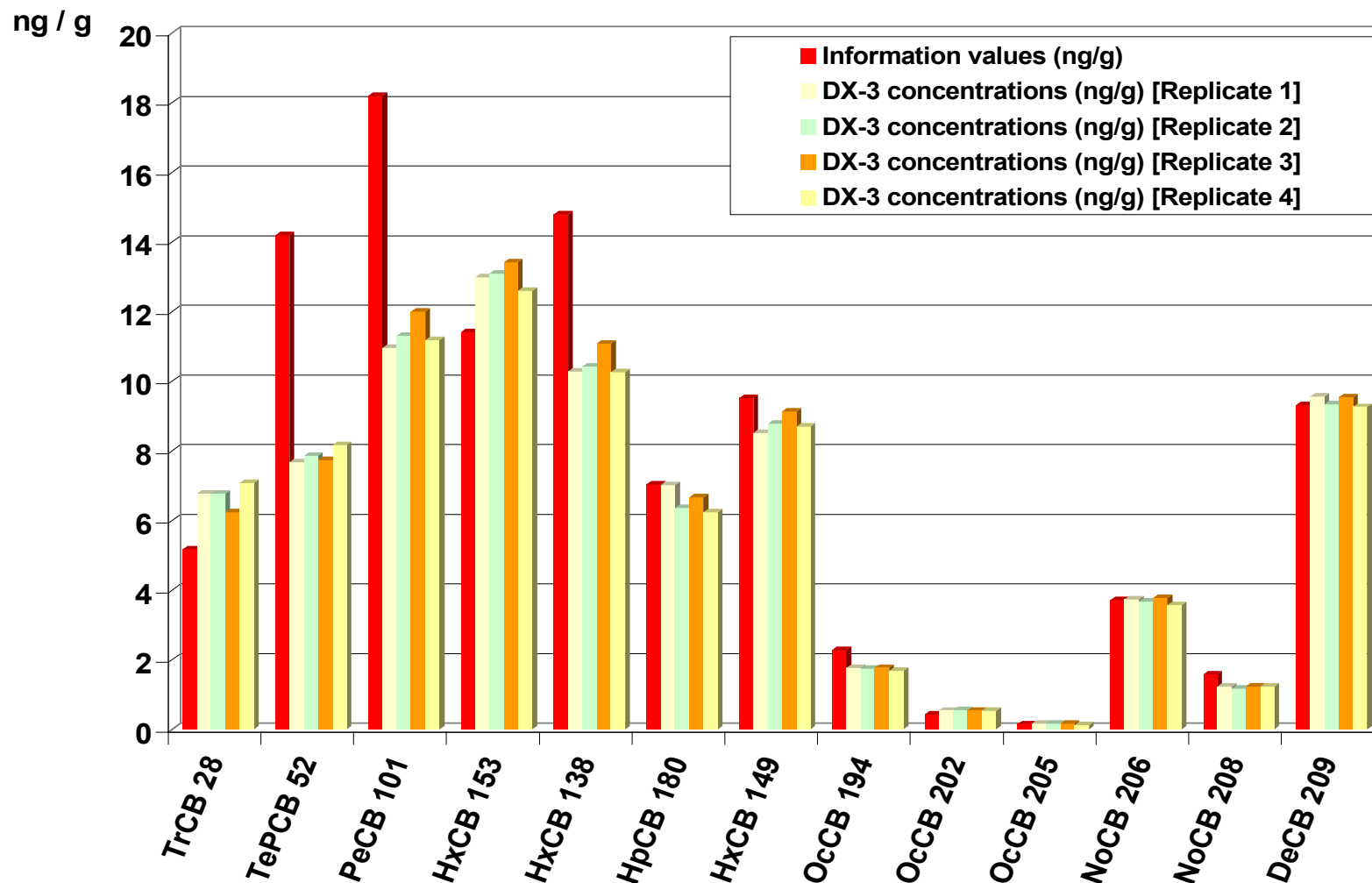
ng / kg



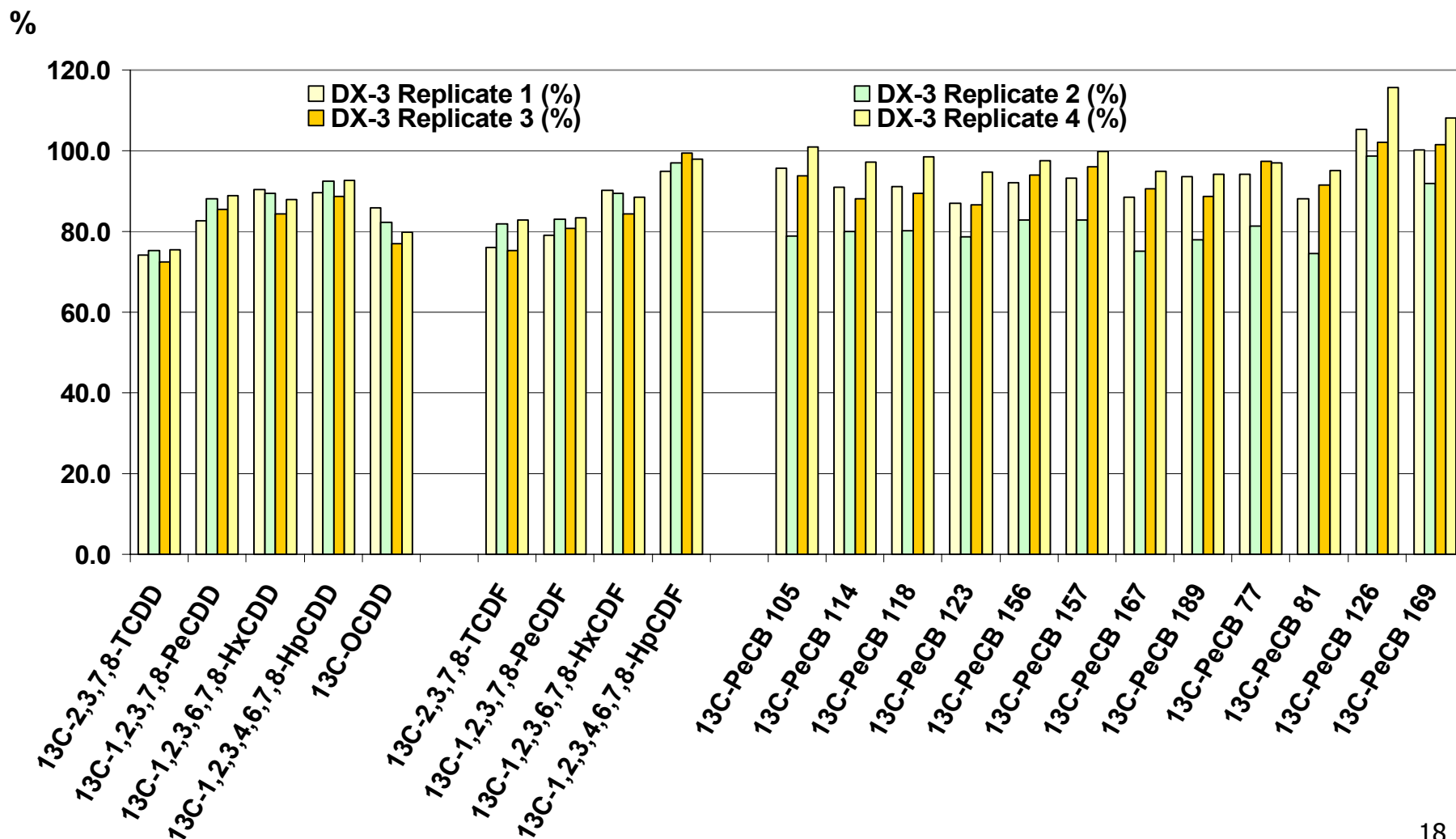
Determination of WHO-12 PCBs in DX-3 certified reference sediment using the Dioxin Prep System – Florisil Version



Determination of 'non dioxin-like' PCBs in DX-3 certified reference sediment using the Dioxin Prep System - Florisil Version



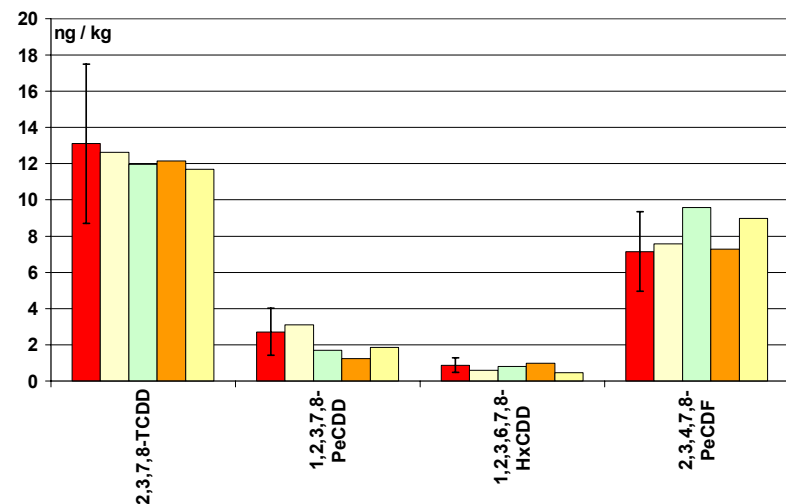
Typical recoveries of $^{13}\text{C}_{12}$ labelled PCDD/Fs and PCBs using the Dioxin Prep System - Florisil Version



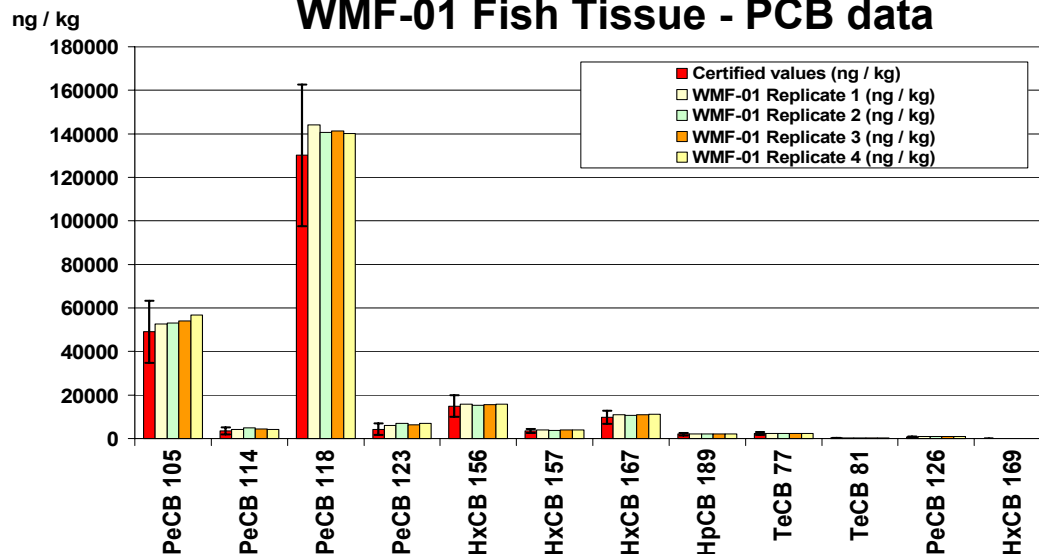
Fish tissue (WMF-01, Wellington Laboratories) and sandy soil (CRM 529, Supelco) – Validation data using the Dioxin Prep System - Florisil Version



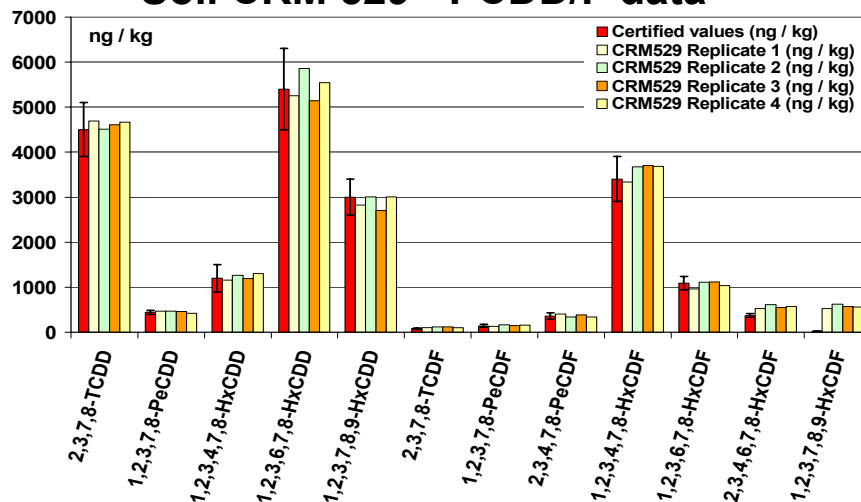
WMF-01 Fish Tissue - PCDD/F data



WMF-01 Fish Tissue - PCB data



Soil CRM 529 - PCDD/F data



Sample throughput at Trace Organic Analysis Laboratory (Corus) using the Supelco Dioxin Prep System – Florisil Version



1 fully trained technician / 9 samples

Extraction and concentration (ASE 200) = 1 to 2 days

Multi-layer silica clean-up + Florisil = 1 day

Basic Alumina step = 1 day

PCBs

Analysis overnight
Data processing = 1 day

PCDD/Fs

Analysis overnight
Data processing = 1 day

PCDD/Fs : 3 to 4 working days

PCBs : 4 to 5 working days

No additional tasks (column packing and activation)

Acknowledgements

- **Shelley Richardson**
Corus R, D & T
- **Laurent Ragava, Florian Mure**
University of Aix-Marseille III, France
- **Rasika Fernando**
University of Sheffield
- **Sue and Katie**
Hall Analytical Laboratories

