A PBMS Response to Regulatory ICR Measurement Quality Objectives

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1) SGS Analytical Perspectives
2) USEPA-OAQPS

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Outline

- Information Collection Request (ICR)
- Target Analytes & Available Methods
- EPA's Measurement Objectives
- Specific Configurations
- Illustration
  - ✓ Optimization of Sampling & Analytical Costs
  - ✓ Enhanced Data Reliability
    - ➢ Dioxins/Furans & 12 PCBs
    - ➢ PAHs

*Though EPA has contributed technical input to this discussion, it does not imply EPA endorsement.

Information Collection Request

- 2007 Legal decision precipitated EPA issuance of many ICRs to collect additional air emissions data
- Support development of Maximum Achievable Control Technology (MACT) standards
- Hazardous Air Pollutants (HAPs)
- Each Targeted Source Category

Information Collection Request

- ICR = Tool to collect emissions-related data using authority under Section 114 CAA
- Includes reporting, emission testing, survey, & other information collection requirements
- 2010
  - ✓ OAQPS initiated a number of source category specific ICRs
  - ✓ Collect information related to facility emissions and controls for HAP
  - ✓ To develop standards and/or evaluate the residual risk for these source categories

Target Analytes & Available Methods

- Matrix: Flue Gases from Stacks
- **136 Dioxins/Furans Congeners & TEQs (Toxic Equivalents)**
  EPA Methods 8290/23/1613
- **12 coplanar PCBs** — **EPA Method 1668**
- **19 PAHs** — **CARB Method 429 or**
  EPA Method 8270
- **Semivolatile Organics** — **EPA Method 8270**

Measurement Objectives

1. Detection Limits — Lowest Achievable
2. Costs — Best Quality with Reasonable Costs
3. Response Time — Fast (ICR deadlines)
   - Planning
   - Sampling
   - Analysis
   - Reporting

Measurement Objectives

Low Detection Limits

Measurement Objectives

TEQ-Based Detection Limits for Dioxins/Furans

Year	N	**EDL**$_{TEQ}$ pg/train	**LOD**$_{TEQ}$ pg/train
2008	1,319	**8.47**	**19**
2009	930	**8.33**	**20.7**
2010	1,882	**6.59**	**16.2**

Measurement Objectives

WHO-2005 TEQ-Based Detection Limits for PCBs

Year	N	**EDL**$_{TEQ}$ pg/train	**LOD**$_{TEQ}$ pg/train
2008	63	**0.579**	**1.29**

Measurement Objectives

EPA 1993 RPQ-Based Detection Limits for PAHs

Year	N	EDL_{RPQ} ng/train	LOD_{RPQ} ng/train
2008	140	**1.42**	**4.19**

Measurement Objectives

Costs

standard approach

- Dioxins/Furans, PCBs, PAHs, Semivolatiles = 4 Sets of Target Compounds
- Field Test: 3 Runs + Blank = 16 Field Samples $16,000
- Analytical Runs

✓ 4 for Dioxins/Furans + 3 QA/QC = 7 runs	$7,000
✓ 4 for PCBs + 3 QA/QC = 7 runs	$6,300
✓ 4 for PAHs + 3 QA/QC = 7 runs	$5,600
✓ 12 for Semivolatiles + 9 QA/QC = 21 runs	$8,400
Total	**$43,300**

Measurement Objectives

Costs

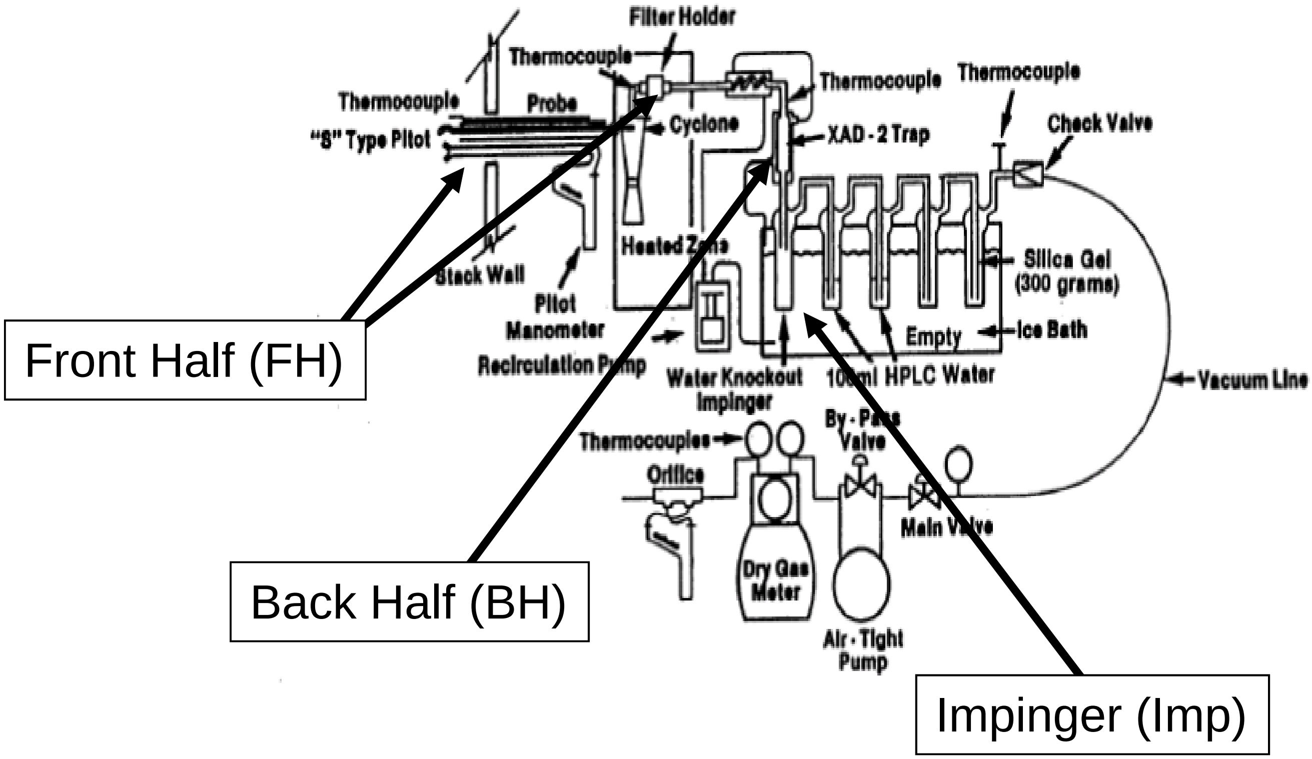
PBMS

- Dioxins/Furans, PCBs, PAHs, Semivolatiles = 4 Sets of Target Compounds
- Field Test: 3 Runs + Blank = 4 Field Samples $4,000 **(-$12K)**
- Analytical Runs
  - 4 for Dioxins/Furans & PCBs + 3 QA/QC = 7 runs $8,400 **(-$4.9K)**
  - 4 for PAHs + 3 QA/QC = 7 runs $4,900 **(-$0.7K)**
  - 12 for Semivolatiles + 9 QA/QC = 21 runs $8,400

Total **$25,700** **(-41%)**

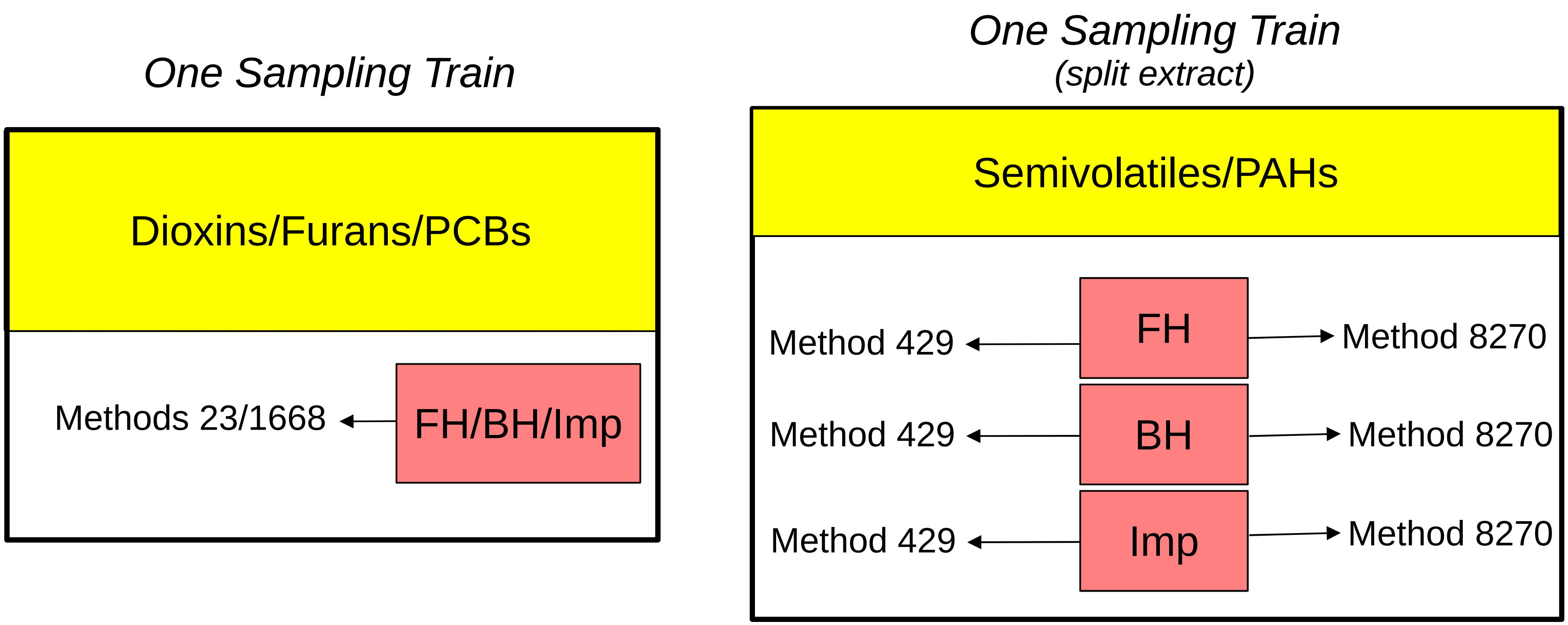
Methods 0010 & 23

Sampling Train



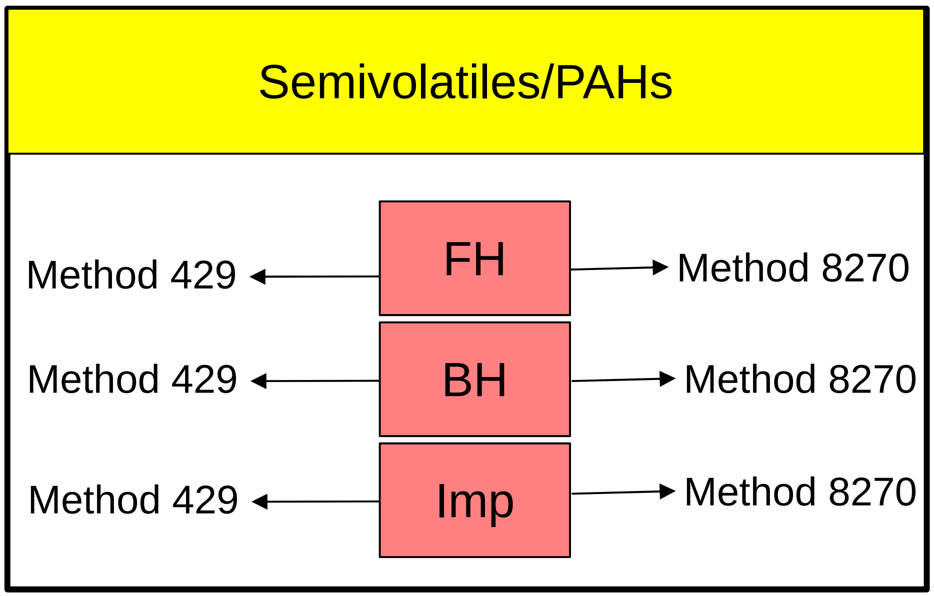
Dioxins/Furans	PCBs	Semivolatiles/PAHs
17 Congeners with Toxic Equivalency Factors (TEF) + Totals (homologue groups)	12 Congeners with Toxic Equivalency Factors (TEF)	EPA Method 8270 “List”
		CARB Method 429 – 19 PAHs (SIM – LRMS or HRMS)
EPA Method 23	EPA Methods 0010 and 1668	SIM = Selected Ion Monitoring LRMS = Low-Resolution MS HRMS = High-Resolution MS

One Possible Alternate Approach – Two Sampling Trains



One Sampling Train

(split extract)



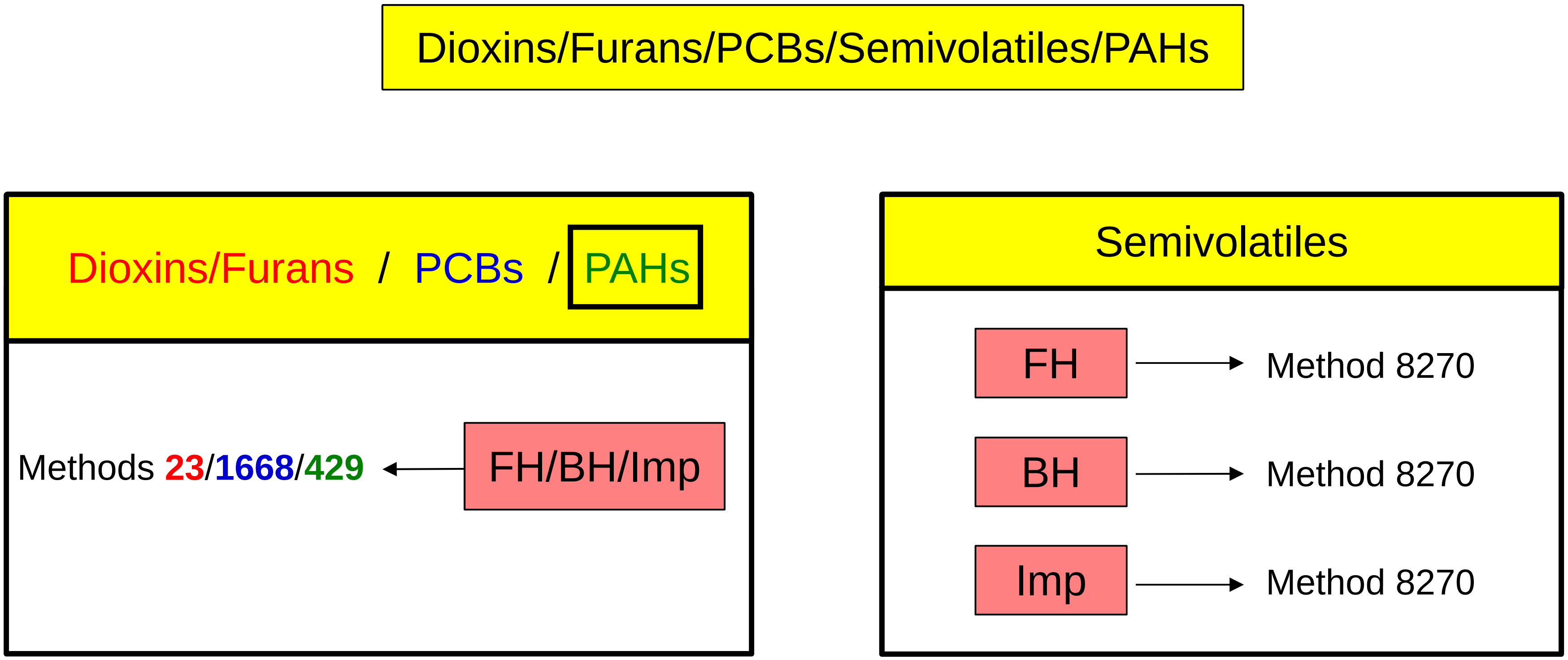
Splitting extracts between LRMS & HRMS results in many conflicts (e.g., standards); thus, this configuration is not recommended.

Illustration

PBMS response

Optimization of Sampling & Analytical Costs

Two Sampling Trains



Enhanced Data Reliability

1 Sampling Train

(FH, BH and impinger **combined**)

- Dioxins Furans
- co-planar PCB
- HR-PAH

M429

ID-SIM-MS*

WHO-2 PLUS

2 vials = 1 GC/MS = 1 report

M23 / **M1668** with ID-SIM-MS*

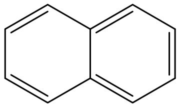
* Comprehensive Stable **I**sotope-**D**ilution **S**elected **I**on **M**onitoring **M**ass **S**pectrometry

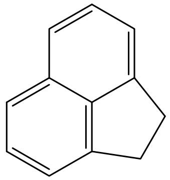
1 Sample Train

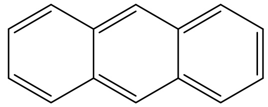
(FH, BH & impinger **separate**)

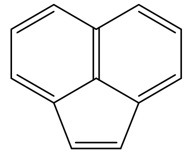
Methods 8270D / 3542
plus
7,12-dimethylbenz(a)anthracene

No false positives for Furans


naphthalene


acenaphthene


anthracene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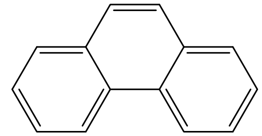
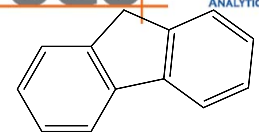
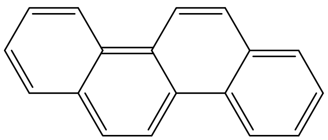
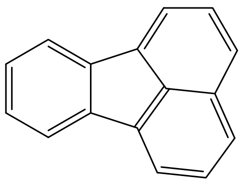

phenanthrene

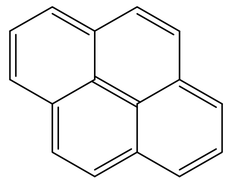

fluorene

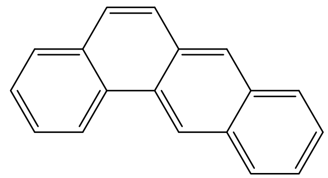
2-ring

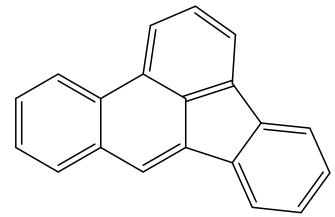
3-ring


chrysene


fluoranthene


pyrene

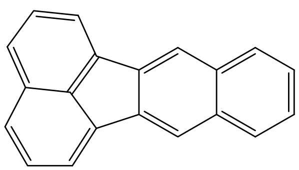

benzo[a]anthracene

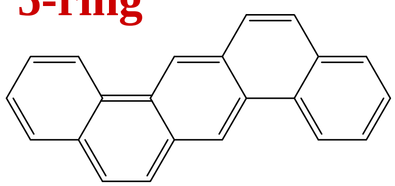

benzo[b]fluoranthene

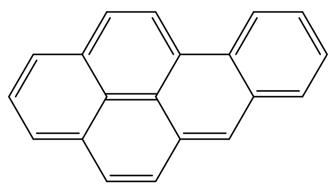
4-ring

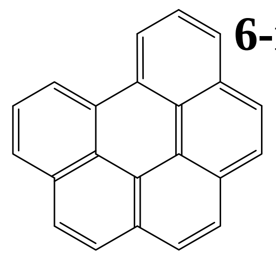
5-ring

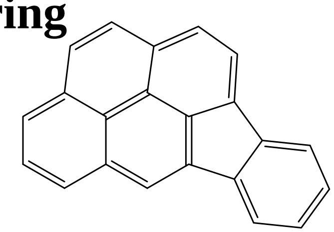
6-ring


benzo[k]fluoranthene


dibenz[a,h]anthracene


benzo[a]pyrene

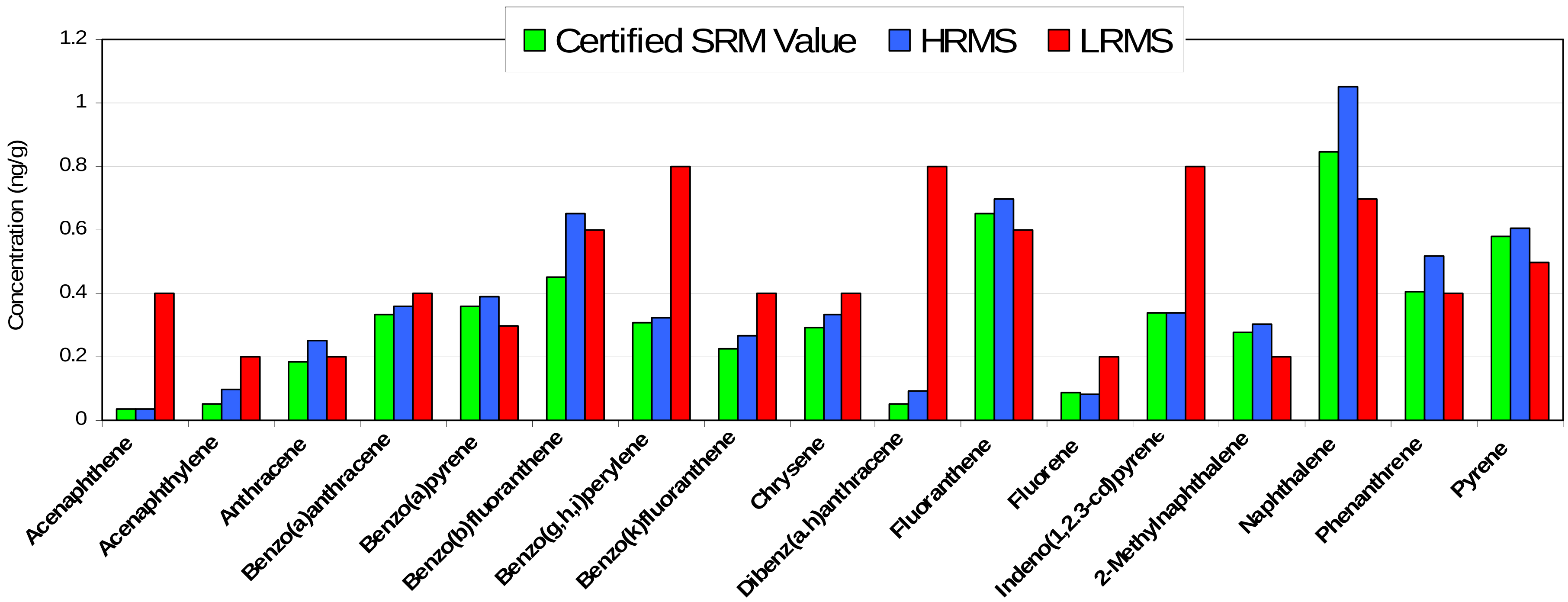

benzo[ghi]perylene


indeno[1,2,3-cd]pyrene

Court D. Sandau, PhD

Method **8270** *vs.* Method **429** with Isotope-Dilution Selected Ion Monitoring High-Resolution Mass Spectrometry

- Samples from 5 Locations
- Homogenized & Split
- Sent 5 for Routine PAH by **M8270** to **Lab X**
- Sent 5 for ID-HRMS **M429** / ID-SIM-HRMS to **Lab Y**
- SRM – Accuracy
- Blind Duplicate – Precision (Field Duplicate - includes sampling error)


Certified SRM Value
HRMS
LRMS
Concentration (ng/g)
1.2
1
0.8
0.6
0.4
0.2
0
Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(g,h,i)perylene
Benzo(k)fluoranthene
Chrysene
Dibenz(a,h)anthracene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
2-Methylnaphthalene
Naphthalene
Phenanthrene
Pyrene

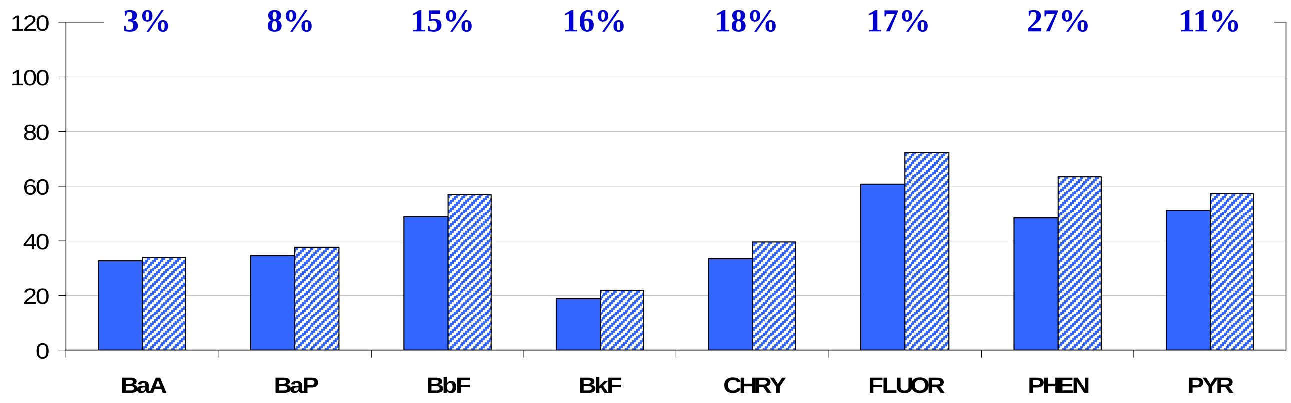
RPD

field duplicate

ID-SIM-MS

Isotope Dilution

Selected Ion Monitoring



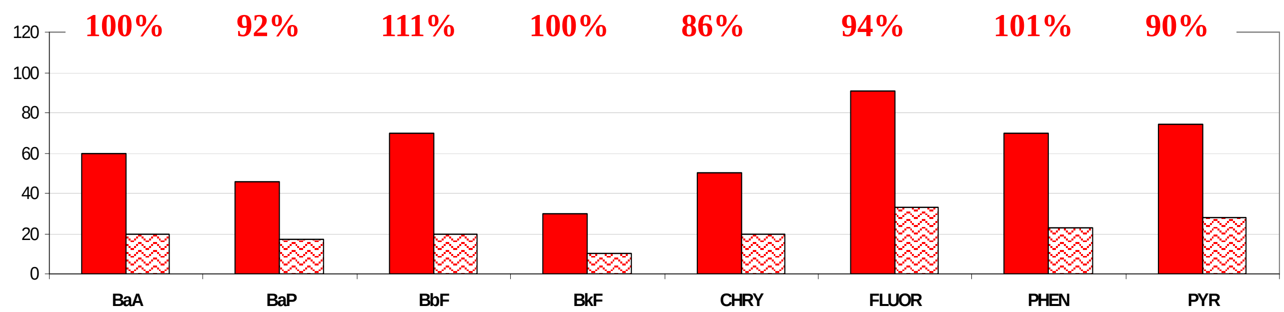
RPD

field duplicate

IS-FS-MS

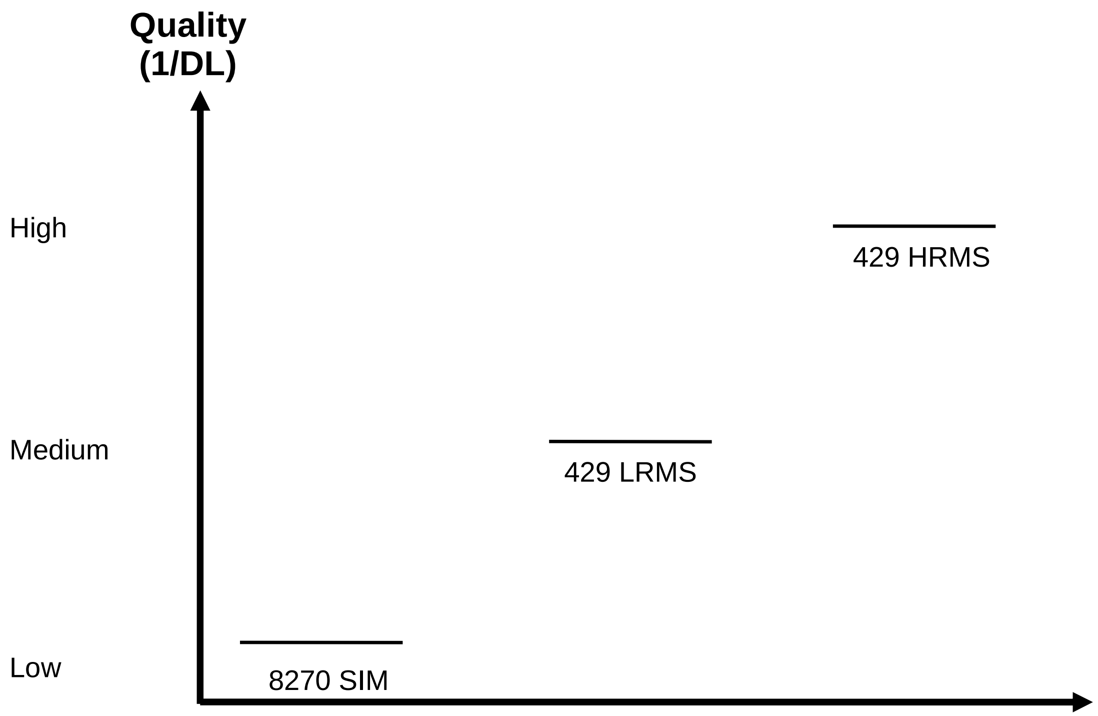
Internal Standard

Full Scan



Detection limits are 200x lower with ID-SIM-HRMS

PAH



Conclusions

Generation of Cost-Effective Quality Data

- ✓ Cooperation between Stakeholders (EPA / Stack Tester / Lab)
- ✓ Purposeful DQOs
- ✓ Understanding the Technology and its Limits
- ✓ Accurately Assessing Analytical Measurement's Performance

A PBMS Response to Regulatory ICR Measurement Quality Objectives