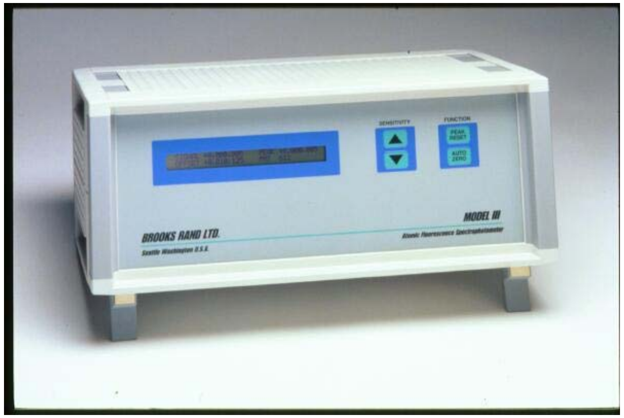
BROOKS RAND LABS

MEANINGFUL METALS DATA



Advances in Mercury Speciation Methodology

by Colin Davies

Overview

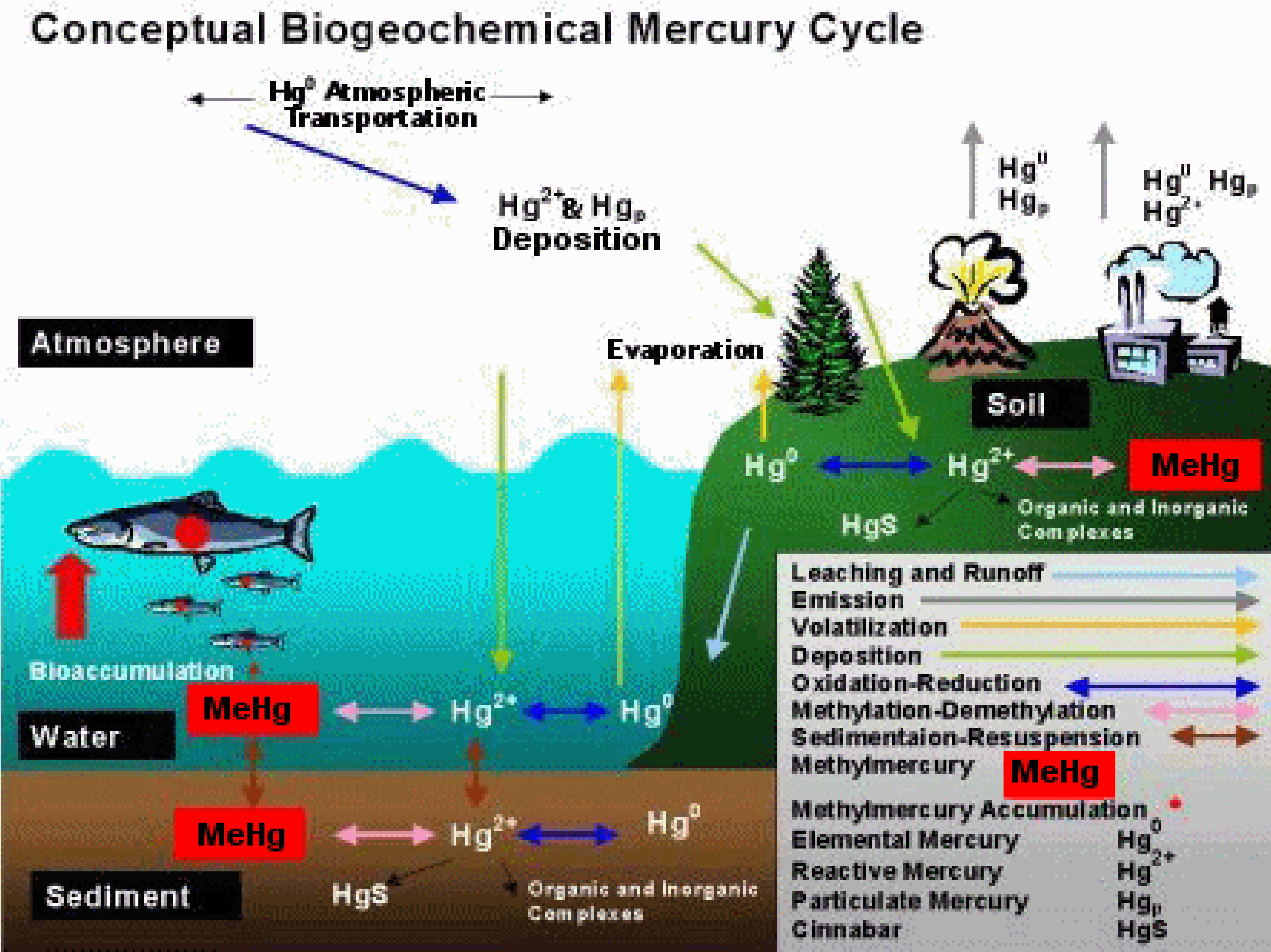
- Mercury Biogeochemical Cycle
- Physical Property Mercury Speciation
  - Total Mercury Method Review
  - Elemental Mercury
  - Reactive Mercury
  - Selective Extraction Techniques
- GC Based Mercury Speciation
  - Methyl Mercury Method Review
  - Automated Methyl Mercury
  - Dimethyl Mercury
  - Derivatization Techniques
- Summary

Mercury Biogeochemical Cycle

Biogeochemical Cycle

- Most naturally occurring mercury exists as Cinnabar (HgS)
  - Very Stable

- $HgS + O_2 \rightarrow (600°C)\ Hg^0 + SO_2$
- Volatile Hg^0 remains in atmosphere for 1+ years
- Hg^0 oxidizes to Hg^{2+} with light and Cl^- or Br^-
- Hg^{2+} enters water bodies
- $Hg^{2+} \rightarrow$ MeHg by sulfur reducing bacteria in anaerobic sediments
- MeHg bioaccumulates up the food chain



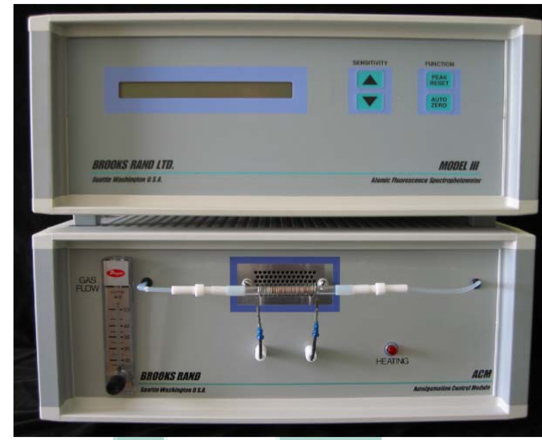
Conceptual Biogeochemical Mercury Cycle
Hg⁰ Atmospheric Transportation
Hg²⁺ & Hgp Deposition
Hg⁰ Hgp
Hg⁰ Hgp Hg²⁺
Atmosphere
Evaporation
Soil
Hg⁰
Hg²⁺
MeHg
HgS
Organic and Inorganic Complexes
Leaching and Runoff
Emission
Volatilization
Deposition
Oxidation-Reduction
Methylation-Demethylation
Sedimentaion-Resuspension
Methylmercury
MeHg
Methylmercury Accumulation
Elemental Mercury Hg⁰
Reactive Mercury Hg²⁺
Particulate Mercury Hgp
Cinnabar HgS
Bioaccumulation
MeHg
Hg²⁺
Hg⁰
Water
MeHg
Hg²⁺
Hg⁰
Sediment
HgS
Organic and Inorganic Complexes

PHYSICAL PROPERTY MERCURY SPECIATION

Total Mercury Method Review

- Total Mercury in Water, Sediments, Tissues
  - U.S. EPA Method 1631, 245.7, 7474,
  - Water Preparation: BrCl oxidation
  - Solids Prep.: HNO_3/HCl Digestion → BrCl Oxidation
  - Sample Analysis: $SnCl_2$ Reduction → Purge → Gold Amalgamation → CVAFS
- Total Gaseous Mercury
  - U.S. EPA Method IO-5
  - Collection & Analysis: Gold Amalgamation → CVAFS

Total Mercury
Method Review



Purge & Trap Module

$SnCl_2$ Reduction

N_2 Purge

Gold Amalgamation

TDM & Model III

Argon Carrier Gas

Trap Desorption

CVAFS Detection

Ultra-low level: IDL < 0.05 ng/L; MDL < 0.2 ng/L

Elemental Mercury (Hg^0)

- Water
  - N_2 purged from water to gold amalgamation trap[1]
  - Trap desorption → CVAFS
  - MDL 0.005 ng/L
- Sediment/Soil (still in development)
  - Soil + DI Water → N_2 purge to trap
  - Research Questions
    - Efficiency of release of Hg^0
    - Species Conversion
    - Sample storage and stability

Reactive Mercury

- Primarily for ionic Hg(II)
- Mercury available for methylation
- "Acid-Labile" mercury
  - HCl Preserve (pH < 2)
- "Reactive" mercury
  - Flash freeze ; thaw in O_2 free environment
- Analysis:

$SnCl_2$ reduction → Gold amalgamation → CVAFS

↓

Just like total Hg analysis

Selective Extraction
5-step SSE

BROOKS RAND METHOD BR-0013 - Mercury 5-step Selective Sequential Extraction Procedure

Fraction	Description	Extractant	typical compounds
F1	water soluble	DI water	$HgCl_2$ $HgSO_4$
F2	weak acid soluble/"stomach acid"	pH 2 HCl/HOAc	HgO
F3	organo complexed	1N KOH	Hg-humics Hg_2Cl_2 CH_3Hg
F4	strong complexed	12N HNO_3	mineral lattice Hg_2Cl_2 Hg^0
F5	mineral bound/cinnabar	aqua regia	HgS m-HgS HgSe HgAu

Notes

All fractions are oxidixed with BrCl after extraction and prior to analysis

Selective Extraction
EPA Method 3200

EPA METHOD 3200 (Extraction) & 1631 (Analysis) - Mercury Species by Selective Solvent Extraction and Acid Digestion

Operationally-Defined Mercury Fractions		Extractant	Individual Mercury Species
Total Mercury			All mercury-containing species
Extractable Mercury	Extractable Organic Mercury	HCl/ethanol followed by Solid Phase Extraction	CH_3HgCl CH_3CH_2HgCl
	Extractable Inorganic Mercury	HCl/ethanol followed by Solid Phase Extraction	$HgCl_2$ $Hg(OH)_2$ $Hg(NO_3)_2$ $HgSO_4$ HgO Hg^{2+} complexes[a]
Non-extractable Mercury	Semi-mobile Mercury	HNO_3/H_2O	Hg^0 or Hg^0-M[b] Hg^{2+} complexes[a] Hg_2Cl_2 (minor)
	Non-mobile Mercury	$HCl/HNO_3/H_2O$	Hg_2Cl_2 (major) HgS HgSe

Notes

a Certain inorganic mercury complexes may be present in both fractions

b This represents a mercury-metal amalgam

All fractions are oxidixed with BrCl after extraction and prior to analysis

GC BASED MERCURY SPECIATION

Methyl Mercury Method Review

- Methyl Mercury in Water
  - U.S. EPA Method 1630; USGS File 01-445
  - Preparation: Distillation
- Methyl Mercury in Sediment & Biota
  - USGS 5 A-7
  - Preparation: KBr & $CuSO_4$ Leach → CH_2Cl_2 Extraction → Back Extract into DI Water
- Analysis Method for all Matrices:

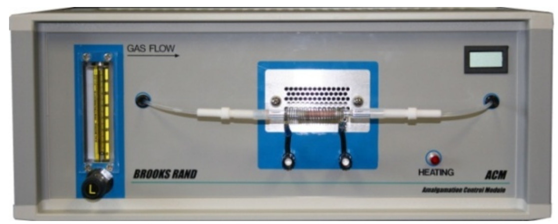
  Ethylation → Purge & Trap → GC Separation → Thermal Reduction → CVAFS

Methyl Mercury Preparation

- Requires:
  - Temperature Control to within 1°C
  - Complete Encapsulation

Direct distillation with no refluxing

Methyl Mercury Analysis



Purge and Trap

Ethylation

N_2 Purge

Tenax Trapping

TDM

Argon Carrier Gas

Trap Desorption

GC & Pyro Module

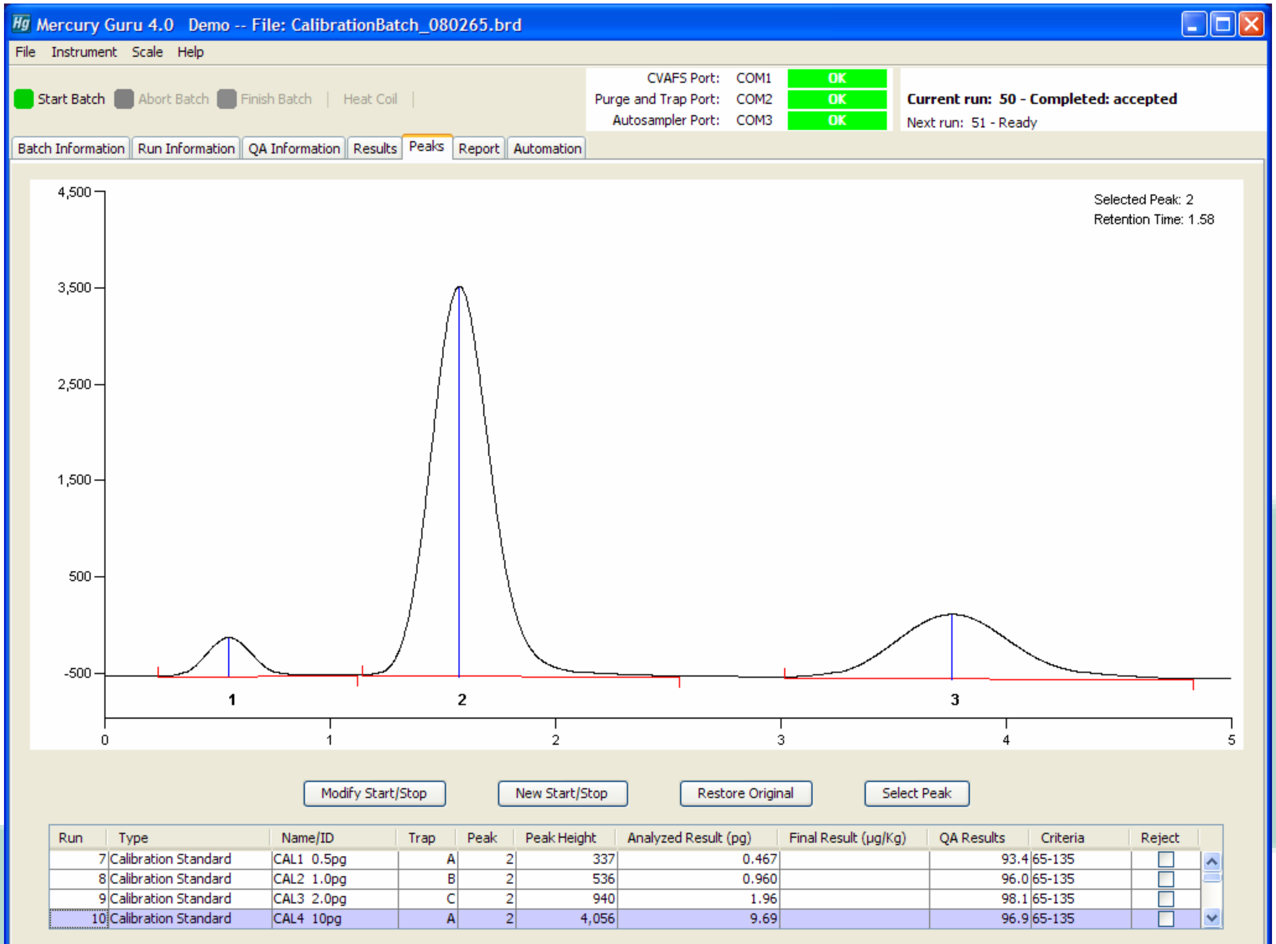
Argon Carrier Gas

GC Separation

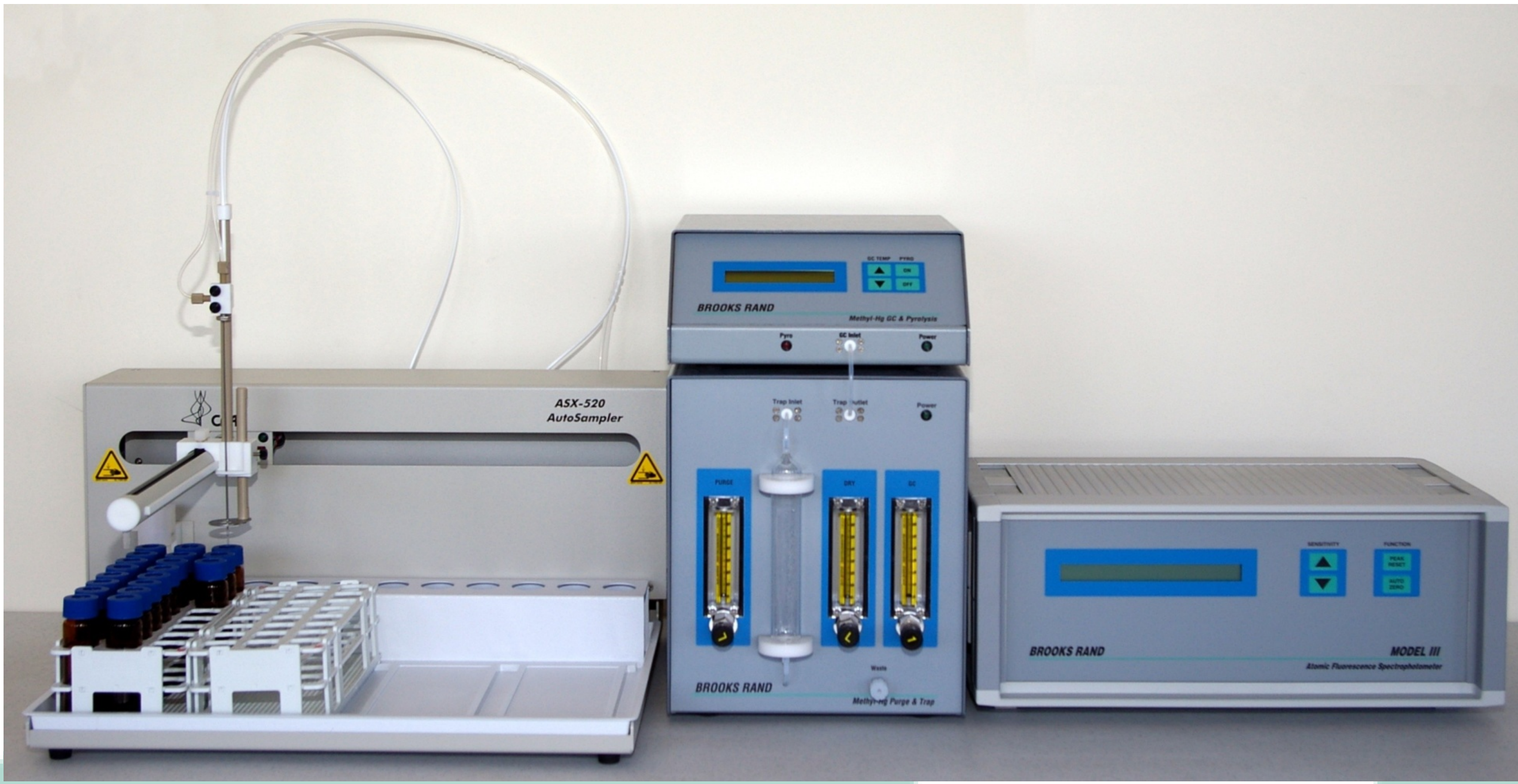
Thermal Reduction

Ultra-low level: IDL < 0.01 ng/L, MDL < 0.02 ng/L

Methyl Mercury Chromatography

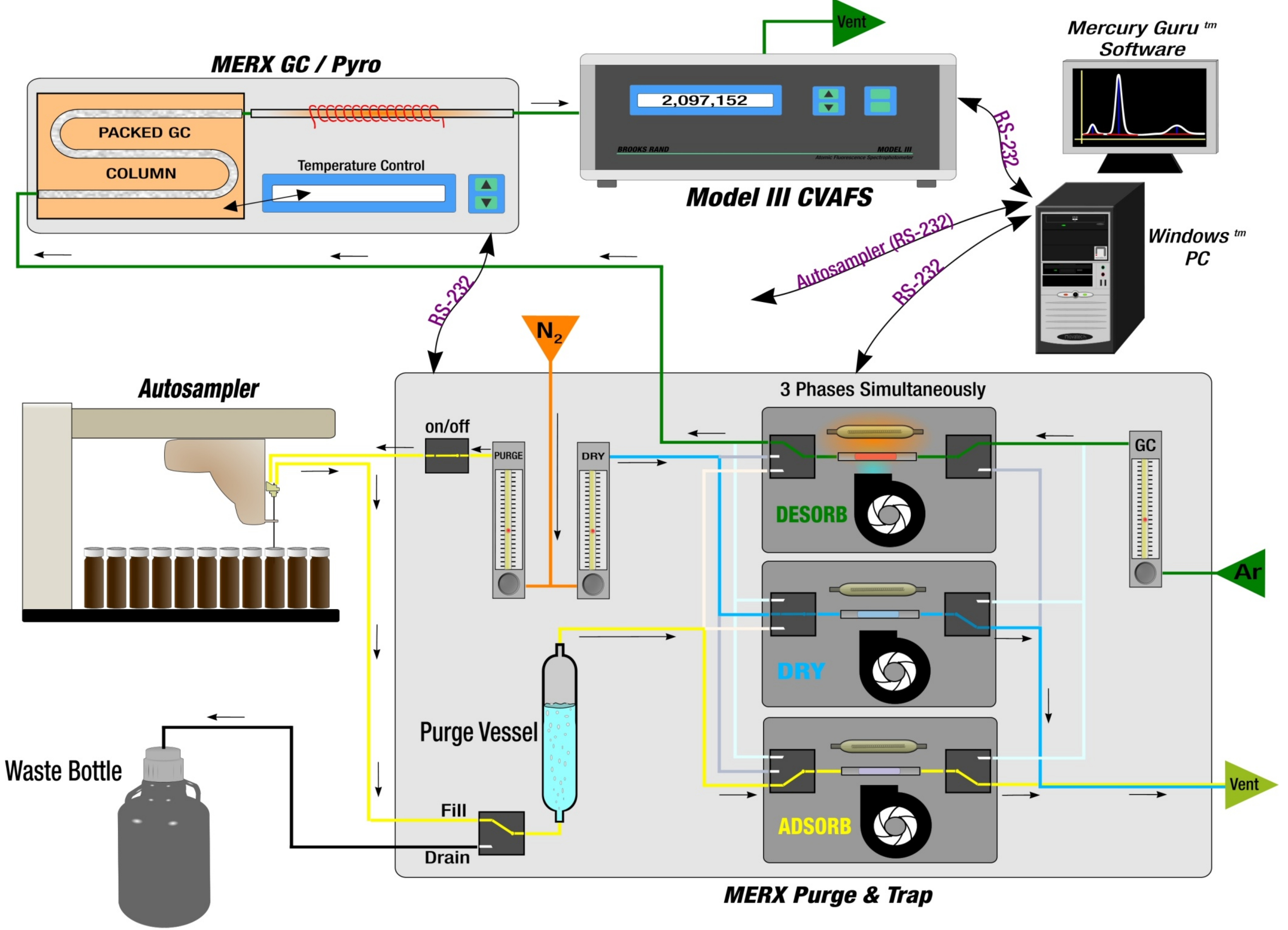


Automated Methyl Mercury System (MERX)



Automated Methyl Mercury System (MERX)

- Gas Pressurized Liquid Handling System
  - Patent Pending
  - Eliminates maintenance intensive pumps
  - Reduced carryover contamination
- Rapid Infrared Trap Heating
  - Patent Pending
  - Results in better chromatography & sharper peaks
- Wide linear range of 5000x
  - Calibrate from 0.005 ng/L to 25 ng/L



Brooks Rand Labs - MERX Mercury Speciation Analytical System

Automated Methyl Mercury System (MERX)

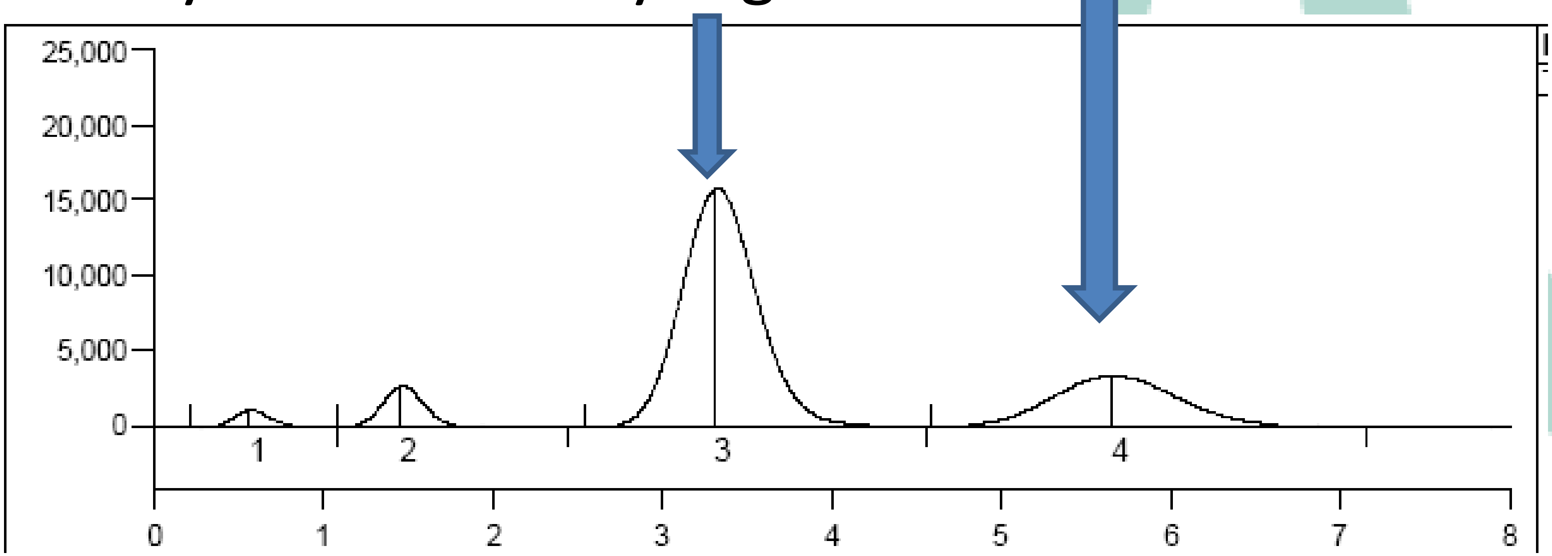
- Benefits
  - Easy-to-use: Learn to use in only hours
  - Fast: Runs every 6.5 minutes or less
  - Great Performance: IDL of 0.002 ng/L
  - Low Operating Costs
    - Less than 1/4th the labor compared to manual systems
    - Minimal reagent use and very low maintenance

Dimethyl Mercury

- Water and Soil
  - Purged from water to Tenax or CarboTrap
  - Trap desorption → GC → Pyrolysis → CVAFS
  - Analysis same as Methyl Hg except
    - No preparation or ethylation
  - Automated (water only)
  - MDL < 0.01 ng/L
  - Peak retention after Hg^0 before Methyl Hg

Derivatization Techniques: Ethylation ($NaBEt_4$)

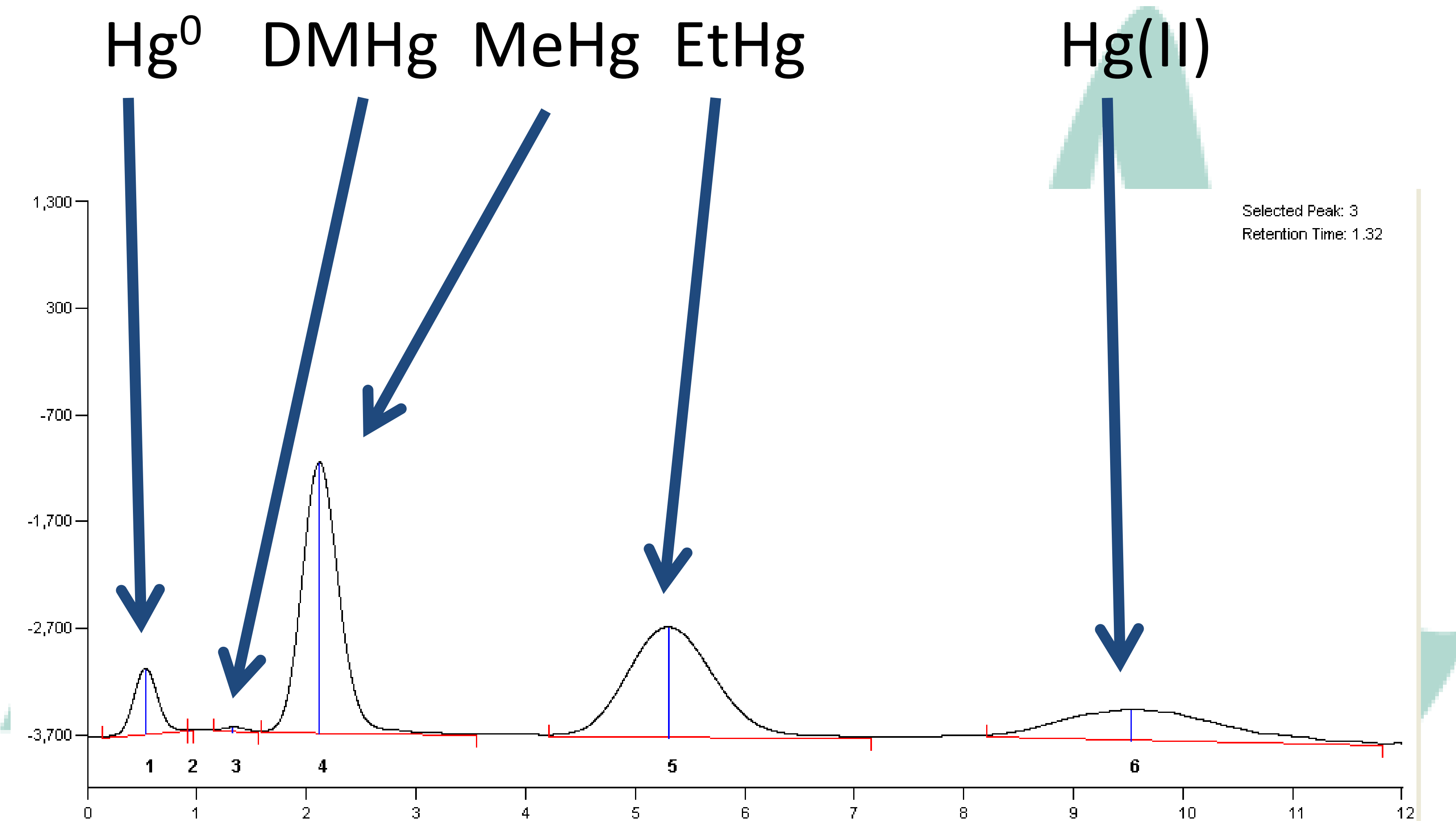
- Direct Ethylation
  - No Distillation
  - Works on most waters
  - N-propyl Hg surrogate
- Limitations
  - Hg(II) and Ethyl Hg both ethylated to Diethyl Hg



Derivitazation Techniques: Propylation ($NaBPr_4$)

- Pros
  - Allows differentiation between Hg(II) and Ethyl Mercury
  - Maybe more efficient reaction than ethylation
- Cons
  - Will require new surrogate Hg compound
  - Difficult to source (1 source in Europe)
- Works very well in water
- MeHg MDL 0.003 ng/L; EtHg MDL 0.005 ng/L

Derivitazation Techniques: Propylation ($NaBPr_4$)



Summary

- Speciation provides critical information on toxicity, mobility, and bioavailability of Hg.
- THg, Reactive Hg, Methyl Hg
  - methods well established for all water, sediment, tissues
- Dimethyl Hg and Elemental Hg well established in water, but methods need more R&D and validation in soil/sediment.

Summary

- Methyl Hg Automation and direct ethylation
  - Improved precision and MDLs
  - Improved efficency
- Propylation
  - Works great for methyl and ethyl Hg
  - Still needs some validation
  - Sediment/soil needs R&D

Acknowledgments

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  - Paul Danilchik - Engineering Director
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    - Research on alternate derivatization techniques
  - Citron Choice - Mercury Lead Analyst, and Misun Um – Mercury Analyst
    - Research on volatile mercury speciation

Questions

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