Mercury Measurements for Solids Made Rapidly, Simply, and Inexpensively

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- Traditional methods for determining mercury in solid samples involve the use of aggressive chemicals to dissolve the matrix and the use of other chemicals to properly reduce the mercury to the volatile elemental form.

- In contrast, ***pyrolysis-based analyzers*** can be used by directly weighing the solid in a sampling boat and initiating the instrumental analysis for total mercury.

- Although not well suited for trace-level analyses of liquids because of the limited capacity (0.5 to 1.0 mL) of the sampling boat, such pyrolysis-based mercury analyzers (EPA Method 7473) have the following advantages:

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- *Throughput*: a measurement every 10-15 minutes (including the weighing and logging time)
- *Learning Curve*: operation simple enough for those with no prior analytical skill
- *Low Cost*: capital cost about $35K
- *Green*: generation of waste virtually eliminated
- *Sample Size Limit*: ca 500 mg or 0.5 mL (but use less if absorbance starts before 5 s)
- *Detection Limit*: 0.01 nanogram Hg

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- *Application Capabilities*:
  - non-lethal monitoring of fish (e.g., tissue biopsy)
  - longitudinal analysis of hair (to locate peak-exposure periods)
  - exposure assessments for other tissues (e.g., feathers, fur, toenails, botanicals)
  - near real-time monitoring of contaminated soil and sediment during remediations
  - coal-fired power plant emissions (from difference between coal Hg and solid waste Hg)
  - speciation for mercury in tissues (via suitable extracts of the methyl mercury)

Analyzer basics

- Sampling boat (ca 0.25 x 0.25 x 1.5 inch)
- Pyrolysis at ≥750 °C in air or oxygen flow
- Catalytic trap
- Amalgamator (one or more)
- Delay before amalgamator heat purged
- Atomic-absorption detection at 254 nm
- Method 7473 & instrument providers
  - (see links on “Additional Resources” page)

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Fish investigations

- Statistically equivalent results by blind analyses of freeze-dried whole-fish homogenates containing Hg between 0.10 and 2.26 ng/mg (ppm) Hg in collaboration with the USGS in Missouri (Dr. Brumbaugh)
- For fish from the National Park Service, fillet biopsy-plug Hg correlated with whole-fish homogenate Hg ($r^2 = 0.976$) with the latter between 64 & 80% of the former depending upon the fillet-Hg level
- EMAP whole-fish homogenates were analyzed in collaboration with EPA-CIN (SETAC 2002 Abstracts, P647, p. 287, Salt Lake City, Utah)

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Fish investigations

- Lake Mead fish reports (Dr. Cidziel first author)
  - Assess methodology (Water, Air, and Soil Pollut. **135**:355-370, 2002)
  - Fillet-Hg trends in 5 species (Arch. Environ. Contam. Tox. **43**:309-317, 2002)
  - Relationships between fish tissues (J. Environ. Monitoring **5**:802-807, 2003)

- Fillet Hg Higher in Skinnier Fish (poster at Jan 2004 National Forum on Contaminants in Fish)
  - Canadians have proposed including fish growth rates in walleye advisories (Simoneau et al. Environ. Res. Online Nov 2004)

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Fish investigations

- Non-lethal fillet biopsy sampling of fish has been successfully utilized for selenium (by NAA) in an endangered species (Waddell & May, Arch. Environ. Contam. Tox. **28**:321-326, 1995), and is feasible for Hg using a pyrolysis analyzer

- To remove an uncertainty in fish-Hg data, the wet-tissue basis (cited in EPA and FDA guidance) could be defined as a specified moisture percentage (such as 78.5% in The National Survey of Mercury Concentrations in Fish, Summary 1990 -1995, EPA-823-R-99-014)

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Hair Applications

- Accuracy for hair Hg verified by participation in Health Canada Mercury-in-Hair Interlaboratory Program
- Collaboration with State of Washington to assess exposure of ethnic groups (Dr. Marien)
- Longitudinal analysis can locate peak-exposure periods
  (and recommended by the NRC in Toxicological Effects of Methylmercury, 2000)
- Single–fiber segment analysis is feasible, but not practical, and weighing limitation requires expressing data per unit length

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Other tissue applications

- Feathers - detectable Hg levels found
- Fur – Collaboration with Alaska
- Toenails – cardio health study in Europe
- Botanicals – pine needles, leaves, bark

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Waste Applications

- Field application during soil remediation has been described by Boylan, Kingston, and Richter (Proceedings of the 14th Annual Waste Testing and Quality Assurance Symposium, Arlington, VA, July 1998)
- Mercury emissions from coal combustion via mass balance for the difference between Hg in the coal and in the captured solid waste (Boylan, Cain, and Kingston, J. Air & Waste Manage. Assoc. **53**:1318-1325, 2003)

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Mercury Speciation

- Methyl mercury results for KOH digests of fish tissues followed by partitioning into toluene agreed ($r^2 = 0.998$) with results from gas chromatography in collaboration with Steve Pyle in our branch (AOAC Method 983.20)

- Inorganic mercury values in Health Canada Mercury-in-Hair samples (via the difference between total Hg and the acid-extracted methyl mercury) have been within the acceptance ranges

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