Standard References Materials

Christopher Reddy
Woods Hole Oceanographic Institution
NIST SRMs to Address Petroleum Hydrocarbon Measurements

• Existing SRMs have been updated
  – SRM 1582 Petroleum Crude Oil
  – SRM 1941b Marine Sediment
  – SRM 1974c Mussel Tissue
• SRM 1597a Complex Mixture of PAHs from Coal Tar
• SRM 2779 Gulf of Mexico Crude Oil (NEW)
• SRM 1991 Coal Tar/Petroleum in Methylene Chloride (NEW)
• SRM 2777 Weathered Gulf of Mexico Oil (In Progress)
SRM 1582 Petroleum Crude Oil

- Originally issued in 1984 with values assigned for only 6 PAHs
- Recently updated with values assigned for:
  - 38 PAHs
  - 35 Alkyl-PAH groups
  - 15 Hopanes and Steranes
- Supply is nearly depleted
  - Bulk material is still available; therefore could be reissued
The Gulf of Mexico Research Initiative (GoMRI) Research Board was established by BP in May 2010 as an independent body to administer a 10 year $500 million commitment to research designed to study the impact of the oil spill on the environment and health of the Gulf of Mexico.

The first of these grants were awarded in 2011, and the GoMRI research board has requested that all GoMRI-funded investigators use SRM 2779 “for analytical chemistry primary calibration and primary reference against which secondary laboratory standards and reference materials, if used, can be calibrated.”
Are NIST SRMs Expensive?

Pricey samples from BP oil spill being sold to scientists

Published: Thursday, March 08, 2012, 10:15 PM    Updated: Thursday, March 08, 2012, 10:21 PM
By Mark Schleifstein, NOLA.com       The Times-Picayune mschleifstein@nola.com

It's likely to be one of the oddest ironies to emerge from the BP oil spill: the federal government is selling tiny containers of oil siphoned from the Macondo well at a price equal to $76.3 million a barrel. By comparison, a barrel of crude oil was selling for $106 on Wednesday.

Of course, the BP oil is not being sold by the barrel.

The National Institute of Standards and Technology, an agency of the U.S. Department of Commerce, is selling 1.2 milliliter bottles of the oil to scientists who need it for comparison with materials collected as part of the federal Natural Resources Damage Assessment process. The price: $480 for a set of five.
SRM 1991 Mixed Coal Tar/Petroleum Extract in Methylene Chloride

- Developed in conjunction with the Energy and Environmental Research Center (EERC), University of North Dakota
- Intended use is as a “common” calibration solution for quantifying alkyl-PAHs
SRM 1991 Mixed Coal Tar/Petroleum Extract in Methylene Chloride

- Mass Fraction Values assigned for:
  - 50 PAHs (31 certified, 15 reference, 4 information)
  - 17 Alkyl-PAH groups
SRM 1597a Complex Mixture of PAHs from Coal Tar

- **SRM 1597 issued in 1987**
  - Certified values for 12 PAHs
  - Reference values for 18 PAHs
  - Mutagenicity results added in 1992
  - Complex mixture of PAHs for direct analysis or minimal cleanup
- **Reissued in 2006 as SRM 1597a**
  - Certified values for 34 PAHs
  - Reference values for 36 PAHs
  - Reference values for 10 PASHs
  - Certified and reference values include 19 methyl PAHs and 17 302 MW isomers
  - Value assignment based on:
    - GC/MS on 3 different stationary phases
    - LC-Fluorescence
SRM 1941b Organic Contaminants in Marine Sediment

• Collected near Baltimore, MD (USA) in 1998
• Freeze-dried, sieved, radiation sterilized; 50 g per bottle
• Certified values for 24 PAHs and reference values for 44 PAHs
• Recently added reference values for 27 alkylated groups and 10 hopanes and steranes as petroleum hydrocarbon markers
• Additional values for:
  – PCB congeners (29 certified, 13 Reference)
  – Chlorinated pesticides (7 Certified and 2 Reference)
SRM 1974c Organics in Mussel Tissue (Mytilus edulis)

- Fourth collection of mussels from Dorchester Bay, near Boston MA
- Shucked, cryo-homogenized, bottled (10 g per bottle), and stored at -80 °C
- Values assigned for:
  - PAHs (22 certified, 18 reference)
  - PCB congeners (38 certified, 14 reference)
  - Chlorinated pesticides (11 certified, 2 reference)
  - PBDEs (5 certified)
- Alkyl PAH groups will be added as reference values
- Freeze-dried mussel tissue SRM from same collection (SRM 2974a)
SRM 2777 Weathered Gulf of Mexico Oil – Why?

- Assessing the impact of an oil spill in the environment requires information on the chemical composition and potential toxic effects of the remaining of “weathered” oil
  - 50% by mass of sample extracts from DWH consisted of oxygenated compounds not traditionally monitored after oil spill (Aeppli et al., ES&T 46:8799-8807, 2012)
- Laboratory weathered oil (generally produced by heating on hot plate) is significantly different from field weathered oil

Data in Table and Figure from C. Reddy and coworkers (WHOI)

<table>
<thead>
<tr>
<th>Element</th>
<th>Laboratory-weathered oil (% composition)</th>
<th>Field-weathered oil (% composition)</th>
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<tr>
<td>C</td>
<td>87.4</td>
<td>81.3</td>
</tr>
<tr>
<td>H</td>
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<td>S</td>
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<td>0.91</td>
</tr>
<tr>
<td>O</td>
<td>None found</td>
<td>7.31</td>
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</tbody>
</table>

Elemental analysis of laboratory vs. field-weathered oil

Concentration of PAHs in Macondo well oil, laboratory-weathered oil, and field-weathered oil
SRM 2777 Weathered Gulf of Mexico Oil

- Weathered oil sample
- Weathered oil sample extracted from 1.7 kg of sand patties collected in August 2012 from Gulf Shores Beach, Alabama, which was impacted by DWH spill
  - 200 g of oil was isolated at WHOI and a subsampled (≈ 120 g) provided to NIST
- Solution of oil in toluene prepared at level of ≈ 71 mg/g
- Ampouled with 1.2 mL solution in 2 mL ampoules filled with argon prior to filling
- Characterization of SRM 2777 will start in 2014

Photos from C. Reddy
Bottom line

• The NIST has a wide range of SRMs available for use and want to expand target list.
• Others are in the pipeline including a field-weathered oil.
• As much as it appears to be a hassle running these standards. They add confidence to you and your colleagues.
• Please feel free to contact Steve Wise (NIST) or me.
• Keen to perform intercalibration exercises.