

Standard References Materials

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NIST

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

UNIVERSITY OF
Southampton

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

SRM 2779 Gulf of Mexico Crude Oil



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.”



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2779

Gulf of Mexico Crude Oil

This Standard Reference Material (SRM) 2779 is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), hopanes, and steranes in a crude oil matrix. All of the constituents for which certified, reference, and information values are provided are naturally present in the oil. A unit of SRM 2779 consists of five ampoules each containing 1.2 mL of crude oil.

Certified Mass Fraction Values: Certified mass fraction values for 21 PAHs are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1]. The certified values are based on the agreement of results obtained at NIST using multiple analytical techniques.

Reference Mass Fraction Values: Reference mass fraction values are provided for an additional 22 PAHs (Table 2), alkylated PAHs (Table 3), and hopanes and steranes (Table 4). Reference values are noncertified values that are estimates of the true value. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

Expiration of Certification: The certification of SRM 2779 is valid, within the measurement uncertainties specified, until **30 September 2020**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see “Instructions for Handling, Storage, and Use”). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall direction and coordination of technical measurements leading to certification were performed by M.M. Schantz and L.C. Sander of the NIST Analytical Chemistry Division.

Evaluation of the data was provided by N.A. Heckert, S.D. Leigh, and A.L. Pintar of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

Analytical measurements were performed by B.A. Benner, Jr., J.R. Kucklick, and M.M. Schantz of the NIST Analytical Chemistry Division. Additional results for PAHs, hopanes, and steranes were used from 24 laboratories that participated in an interlaboratory study coordinated by M.M. Schantz.

Partial funding support for the preparation and certification of this SRM was provided by the National Oceanic and Atmospheric Administration and ultimately paid by BP Corporation North America, Inc. as part of the natural resource damage assessment for the 2010 Deepwater Horizon oil spill.

Stephen A. Wise, Chief
Analytical Chemistry Division

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Gaithersburg, MD 20899
Certificate Issue Date: 04 June 2012
Certificate Revision History on Last Page

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Are NIST SRMs Expensive?

The Times-Picayune Greater New Orleans

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](mailto: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
- For use in determining response factors for ASTM Method D7363-11 “Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water using Solid-Phase Microextraction and GC/MS”

SRM 1991 Mixed Coal Tar/Petroleum Extract in Methylene Chloride



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1991

Mixed Coal Tar/Petroleum Extract in Methylene Chloride

This Standard Reference Material (SRM) is intended for use in evaluating analytical methods for the determination of selected polycyclic aromatic hydrocarbons (PAHs), particularly in determining relative response factors for ASTM Method D7363-11 "Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode" [1]. All of the constituents for which certified, reference, and information values are provided are naturally present in the extract. A unit of SRM 1991 consists of five ampoules each containing 1.2 mL of a methylene chloride solution.

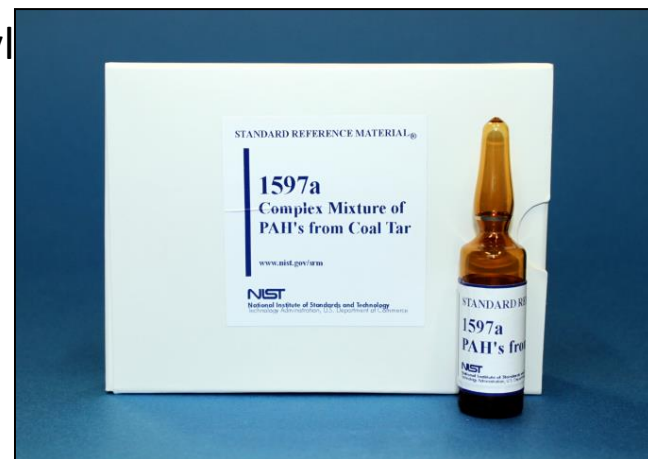
Certified Mass Fraction Values: Certified mass fraction values for PAHs are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of uncertainty have been investigated or taken into account [2]. The certified values are based on the agreement of results obtained at NIST and the Energy and Environmental Research Center (EERC) at the University of North Dakota (Grand Forks, ND) using multiple analytical techniques.

Reference Mass Fraction Values: Reference mass fraction values are provided in Table 2 for additional PAHs and in Table 3 for groups of alkylated PAHs. Reference values are noncertified values that are estimates of the true values. The values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [2].

- Mass Fraction Values assigned for:
 - 50 PAHs (31 certified, 15 reference, 4 information)
 - 17 Alkyl-PAH groups

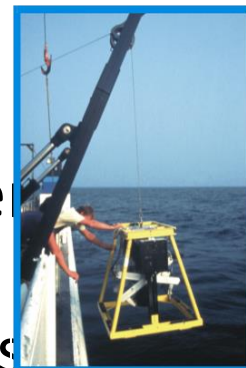
SRM 1597a Complex Mixture of PAHs from Coal Tar

- **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



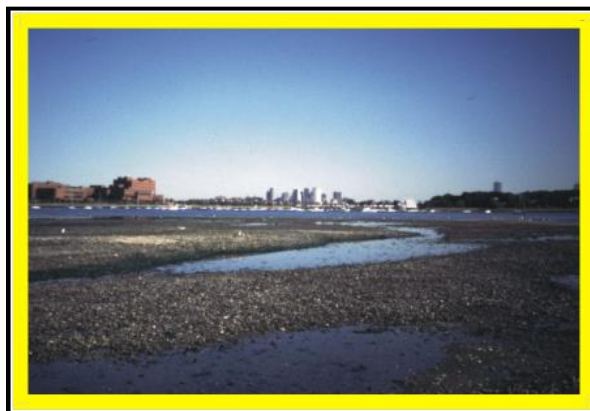
SRM 1941b Organic Contaminants in Marine Sediment

- 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)



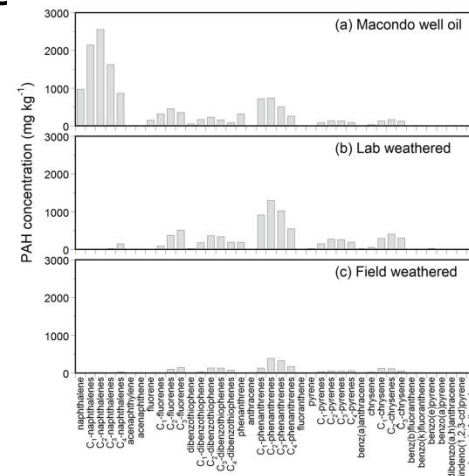
SRM 2777 Weathered Gulf of Mexico Oil – Why?

- 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)

Element	Laboratory-weathered oil (% composition)	Field-weathered oil (% composition)
C	87.4	81.3
H	12.2	10.8
N	None found	0.22
S	0.62	0.91
O	None found	7.31

Elemental analysis of laboratory vs. field-weathered oil



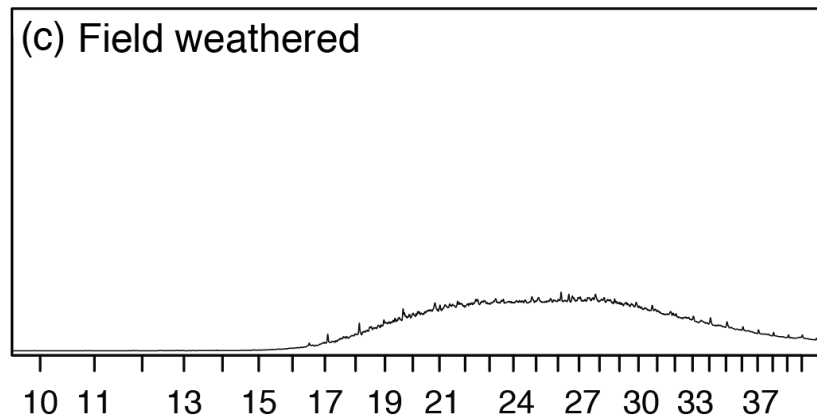
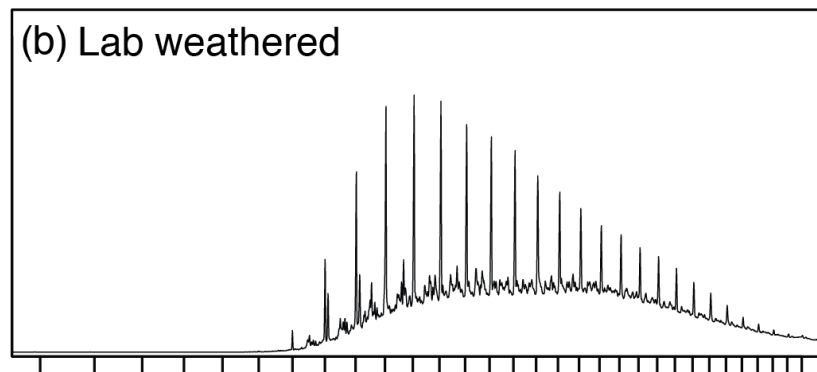
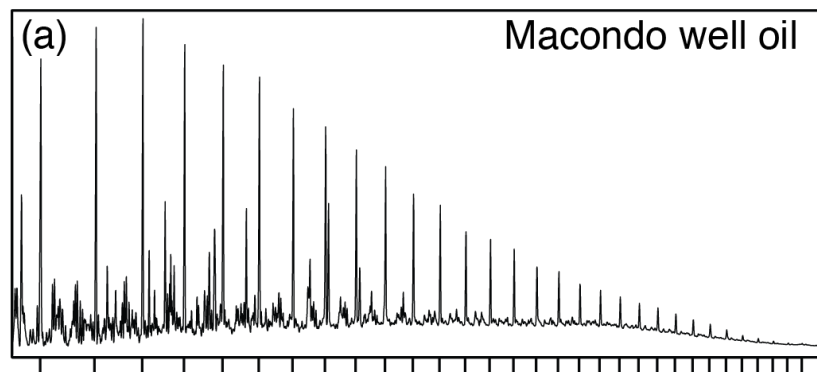
Concentration of PAHs in Macondo well oil, laboratory-weathered oil, and field-weathered oil

SRM 2777 Weathered Gulf of Mexico Oil

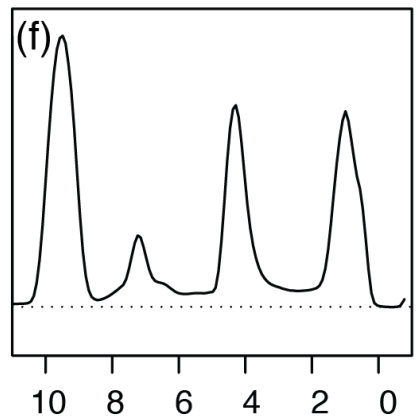
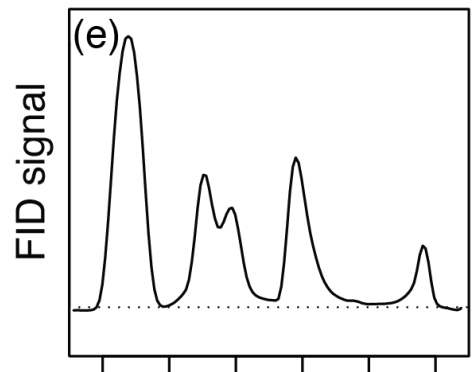
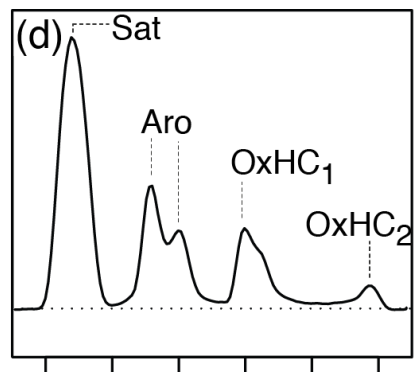
- Weathered oil sample
- Weathered oil sample extracted from 1.7 kg of sand patties collected in August 2012 from Gulf Shores Beach, Alabama, which was impacted by DWH spill
 - 200 g of oil was isolated at WHOI and a subsampled (≈ 120 g) provided to NIST
- Solution of oil in toluene prepared at level 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



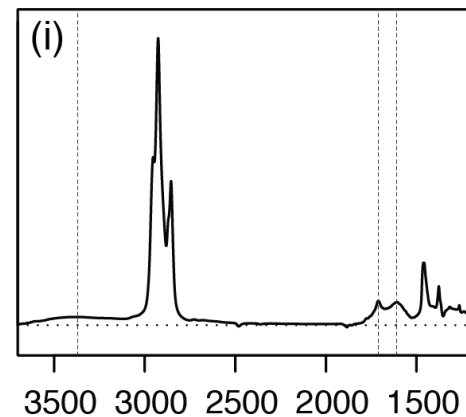
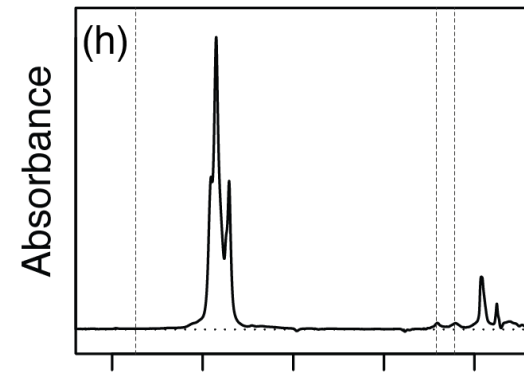
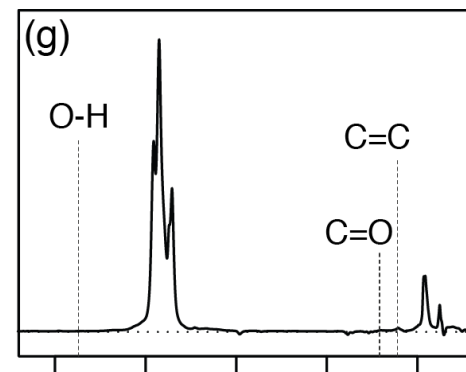
Photos from C. Reddy



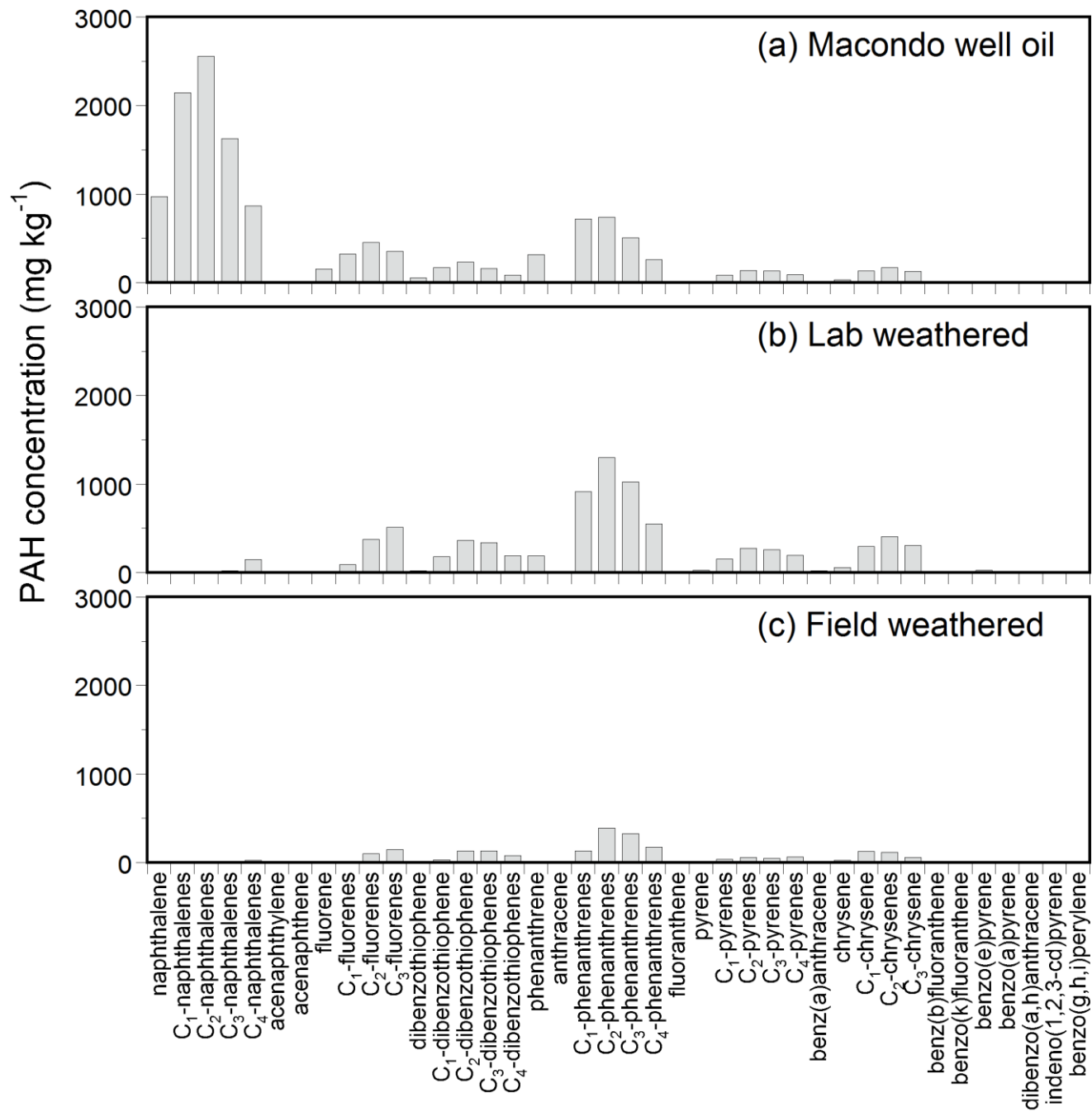
n-alkane carbon number



distance migrated (cm)



wavenumber (cm⁻¹)



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.