TOPIC 2: What options exist for fundamental and traceable OC and EC Standards?

L.A. Currie (NIST Fellow Emeritus) – March 2003

- Metrological Nomenclature and Standards
- EC Standards (RMs), Sources, User Communities
- The Special Role of ^{14}C: standards and isotopic speciation
- SRM 1649a (urban dust): international comparison/certification
- Outstanding Issues

Metrological Nomenclature and Standards

EC, OC, TC, TOC, SC, Char, Soot, … [this workshop]

Reference Materials, SRMs, CRMs

- Certified-, Reference-, Information-Values

International Metrological Standards (and NMIs)

- Traceability
- Measurement Process (MP) Capabilities
  detection, quantification limits (IUPAC, ISO)
- Measurement Results (MR) Reporting
  standard/expanded uncertainty (ISO, NIST: u_i, u_c, U)
- Reporting of low-level data
  virtual reality; the special problem of the blank

Certified, Reference, and Information Values for SRM 1649a

Certified Concentration Values: Certified values for the concentrations, expressed as mass fractions, for 22 PAHs, 35 PCB congeners (some in combination), and 8 chlorinated pesticides are provided in Tables 1, 2, and 3, and for total carbon in Table 12. *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 accounted for by NIST.* The certified values for the PAHs, PCB congeners, and chlorinated pesticides are based on the agreement of results obtained from two or more chemically independent analytical techniques performed at NIST.

Reference Concentration Values: Reference values for concentrations, expressed as mass fractions, are provided for 22 additional PAHs in Tables 4 and 5 and for one additional chlorinated pesticide in Table 6. Reference values are provided in Table 7 for the seventeen 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners and total, tetra-, penta-, hexa-, and hepta-substituted congeners of polychlorinated dibenzo- *p*-dioxin and dibenzofuran. Reference values for 32 selected inorganic constituents are provided in Table 8. Reference values for mutagenic activity are provided in Table 9. Reference values for particle-size characteristics and total extractable mass are provided in Tables 10 and 11, respectively. Reference values for chemical carbon and isotopic carbon (^{14}C) composition are summarized in Tables 12 and 13, respectively. *Reference values are noncertified values that are the best estimate 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.* Explanations in support of each reference value are given as a note in Tables 4 through 13.

Information Concentration Values: Information concentration values, expressed as mass fractions, for selected components of the chemical and isotopic carbon composition are provided in Tables 12 and 13. *An information value is considered to be a value that will be of use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed.* Explanations in support of the information values are provided in the footnotes for Tables 12 and 13.

EC Standards, Sources, User Communities*

- NIST Standard Reference Materials
  [www.nist.gov/srm]
- The International Steering Committee for Black Carbon Reference Materials
  [www.du.edu/~dwismith/bcsteer.htm]
- Reference Materials for Ocean Science
  [www.nap.edu]

*for comparability of measurements in the atmosphere, cryosphere, soil, and sediment with applications ranging from health to climate to the global BC cycle.

NIST Standard Reference Materials

SRM	Name	TC	EC	^{14}C	
4990b	Oxalic acid			+	
1649a	Urban dust	+	+	+	
1650b	Diesel particulate matter	(+)	(+)		Gustafsson 2001
1941b	Organics in marine sediment	(+)	(+)	(+)	Reddy 2002 [1941a]
1944	NY/NJ waterway sediment	(+)	(+)	(+)	Reddy 2002
2783	Air particulate matter on polycarbonate filter media				Trace elements
2784	Air particulate matter on quartz filter media	(+)	(+)		Klouda 2003
2975	Diesel particulate matter (forklift truck emissions)	(+)	(+)		Gustafsson 2001

International Steering Committee for Black Carbon Reference Materials

- Black Carbon Reference Materials
  - n-hexane soot
  - lignocellulosic chars
  - soils
  - marine sediments (NIST SRM 1941a)
  - aerosol (NIST SRM 1649a)
- Interfering Materials
  - shale
  - natural organic matter
  - melanoidin
  - coals (lignite, low-volatile bituminous)

The Special Role of ^{14}C

- Standards (dating, environmental RMs)
- Fossil - biomass source apportionment
- C-cycle: global circulation, deposition (age)
  - EC-^{14}C: tracer of fire (soil, sediment, ice cores)
- Isotopic speciation
  - sources, transport, transformation: of *individual compounds* (advanced AMS: 'µg dating')
  - isotopic-mass balance; 'isotopic consistency'

Fossil - Biomass Source Apportionment (*IACP*)

Carbonaceous Aerosols -- Albuquerque, New Mexico

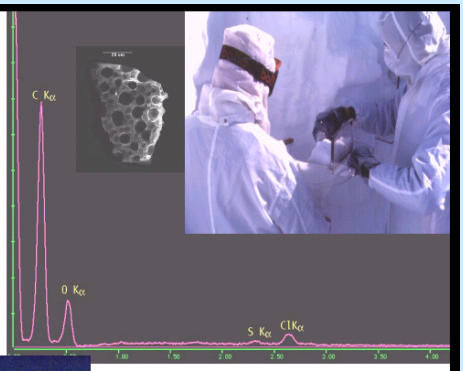
Impacts: health, visibility, climate (11-variate study)

^{14}C showed: motor vehicle soot, 2-11 µg/m^3
woodburning soot, 8-62 µg/m^3

Potency results: fossil particles more mutagenic (3 x)

Summit, Greenland

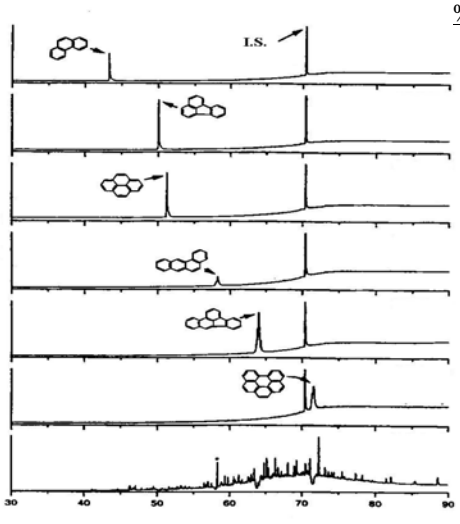
- Particle (90% C) from 1994 fire horizon
- Biomass aerosol seasonal cycle reported (2003) [9 to 49 μg C/kg snow]



Mt. Sonnblick
Austria (3106 m)
[CARBOSOL]

^{14}C 'dating' of atmospheric soot, cellulose, humates, pollen, … (≤ 2002)

GC/AMS -- 'dating' individual PAH



SRM 1649a Intercomparison/Certification
Non-isotopic Carbon Data

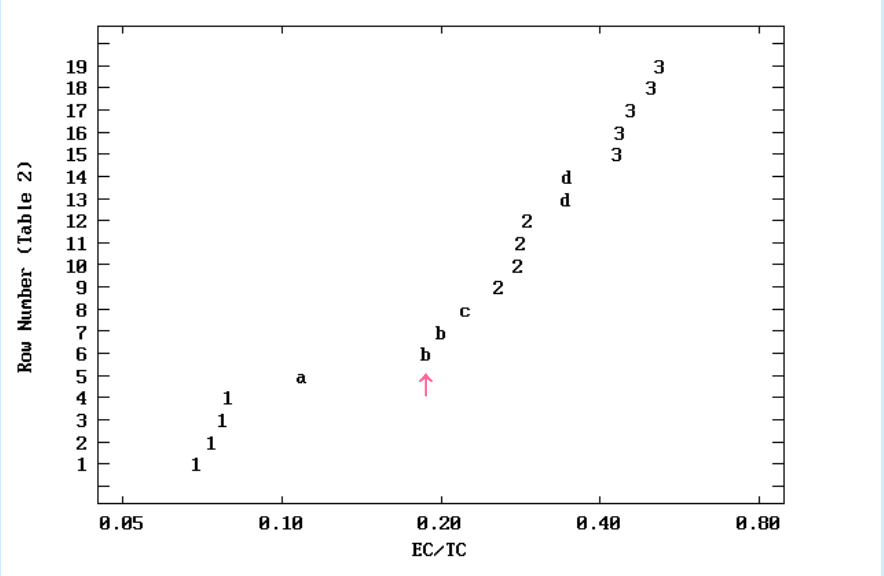
Total Carbon (TC) 0.1768 ± 0.0019 g/g (n = 7)

Insoluble Carbon	0.152 g/g	(n = 2)
Carbonate Carbon	0.00118 g/g	(n = 2)
Extractable Mass	0.044 ± 0.006 g/g	(n = 3)

(EC/TC):	median	[inter-quartile range]	
Cluster-1 ('soot')	0.075	[0.071, 0.078]	(n = 4)
Cluster-2 ('char')	0.28	[0.27, 0.29]	(n = 4)
Cluster-3	0.46	[0.44, 0.50]	(n = 5)

Complete range: [0.069, 0.520] (n = 19)

SRM 1649a -- EC/TC Data



Urban Particle Reference Material (SRM 1649a)

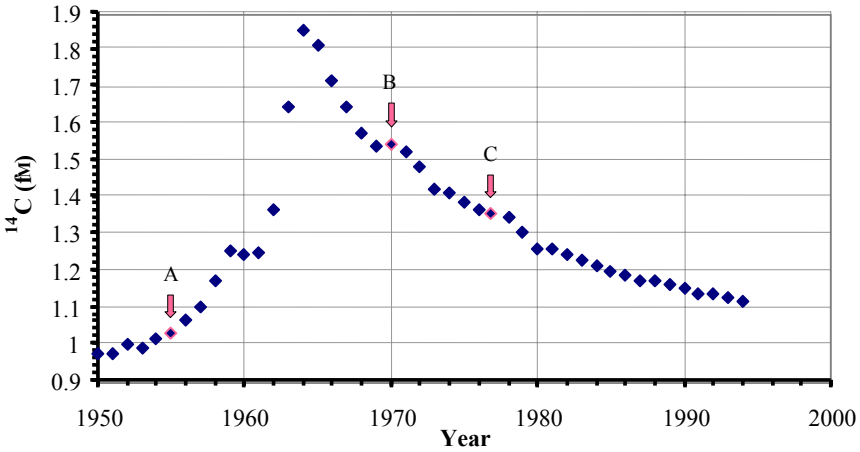
(prototypical isotopic-chemical aerosol reference/QA material)

^{14}C SPECIATION

CARBON	BIOMASS-C (%)
total	38
polar	32
elemental	
"char"	11
"soot"	4
aromatic	13
aliphatic	2
Fluoranthene	5
Benzo(*ghi*)perylene	6

(U = 6 [aromatic]; others <1)

Biomass ^{14}C (nuclear testing)



Standards: A=HOxI, B=IAEA C6, C=SRM 1649a

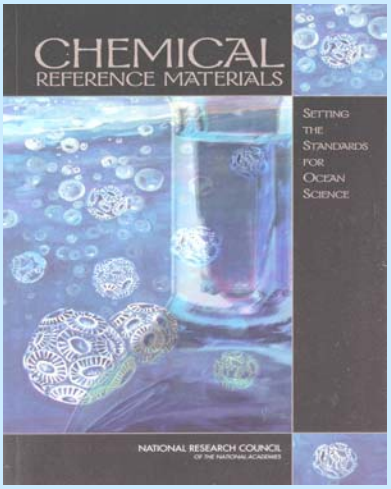
Some Intercomparison Perspectives

- **SRM 1649a:** prototypical isotopic-BC atmospheric RM; *ATTRIBUTES:* isotopic heterogeneity, charring potential, mineral residue
- **Diverse methods (EC):** Optical, Thermal ("dry" oxidation), Chemical ("wet"); *HYBRID:* T-O, T-C
- **Diverse results (EC):** partial confounding of method artifacts and probing different parts of the "BC spectrum"
- **Prospect for EC Reference Values** ("soot," "char");
  - Demonstrated importance (team-6)
- **^{14}C Speciation:**
  - Full source range: biomass ("missing link") to fossil (aliphatic-C)
  - Impossibility of isotopic-mass balance (extant data)
  - Isotopic consistency:

    "soot-C" (96 % fossil) vs PAH-C (95 % fossil)

Setting the Standards for Ocean Science*

(NSF/NRC Workshop, Islamorada, Sept. 2001)



SOME NUGGETS

-RM requirements & recommended types
-Carbonate caution
-Steps for RM preparation
-Key research areas
-Matrix perturbation (OC,^{13,14}C)
-Glossary (App. C)
-RMs (App. E)
NIST, IAEA, NRC-Canada, Atm, hydrosphere,sediment, ...

*Major (LAC) concern: *finite supply of specific natural matrix RMs*