Reference Materials for Biofuels

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Standard Reference Materials (SRMs)

- Standard Reference Materials (SRMs) are Certified Reference Materials (CRMs) issued by the National Institute of Standards and Technology (NIST)
- homogeneous, stable materials well-characterized for one or more chemical and/or physical properties
- assist laboratories worldwide in validating analytical measurements of chemical composition

NIST Standard Reference Materials

Chemical composition standards constitute about 65% of 1,500 NIST SRM types, and more than 24,000 of 32,000 NIST SRM units sold annually to 6,500 customers.

- **High Purity Neat Chemicals**
- **Organic Calibration Solutions**
- **Inorganic Calibration Solutions**
- **Gas Mixture Standards**

- **Complex Matrix Standards**
- **Advanced Materials**
- **Biological Fluids/Tissues**
- **Food/Botanicals**
- **Geologicals**
- **Metal Alloys**
- **Petroleum/Fossil Fuels**
- **Sediments/Soils/Particulates**

- **Optical Filter Standards**
- **Conductivity Standards**
- **Ion Activity Standards**

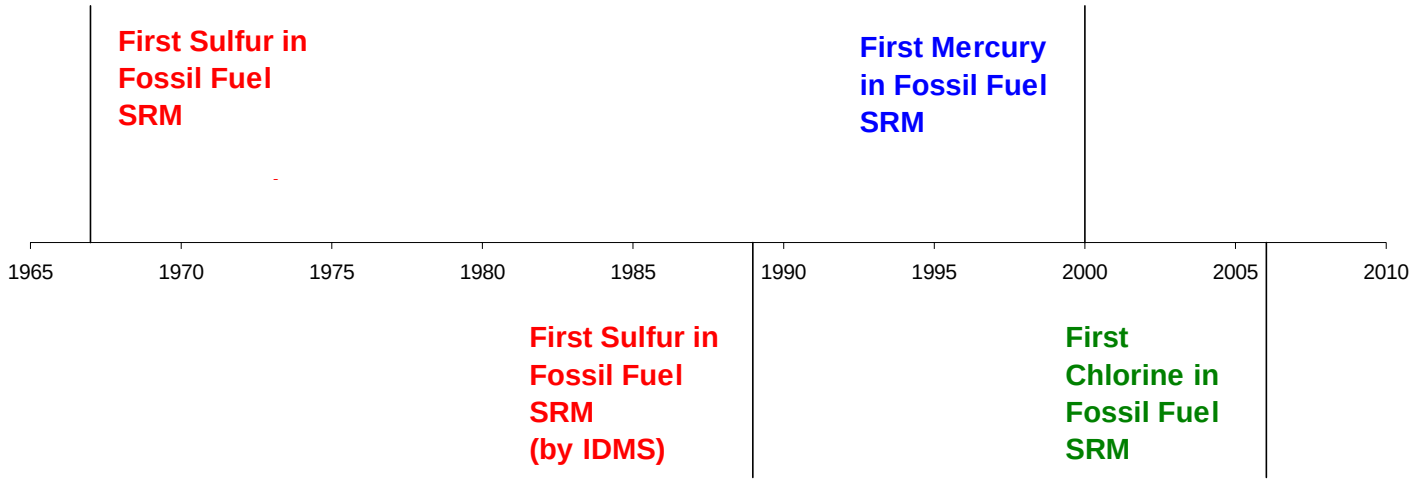
Fossil Fuel SRMs

Gasoline	16
Residual Fuel Oil	7
Diesel and Kerosene	6
Coal	2
Coal Fly Ash	8
Crude Oil	4
Coke	4
Total	47

First fossil fuel SRMs were issued in 1967 with certified values for sulfur content, SRM 1621 and SRM 1622 Sulfur in Residual Fuel Oil (1% and 2%, respectively).

Development of Fossil Fuel SRMs

HISTORY OF CERTIFIED ANALYTES IN NIST FOSSIL FUEL SRMs



Determination of Sulfur as Arsenic Mono-sulfidelon by Isotope Dilution Thermal Ionization Mass Spectrometry, P.J. Paulsen,and W.R. Kelly, *Anal. Chem.,* **1984**, 56, 708-713

Development of High Accuracy Vapor Generation Inductively Coupled Plasma Mass Spectrometry and its Application to the Certification of Mercury in Standard Reference Materials, S.J.Christopher, S.E.Long, M.S.Rearick and J.D.Fassett, *Anal. Chem*., **2001**, 73, 2190-2199.

A Closed System Digestion and Purification Procedure for the Accurate Assay of Chlorine in Fossil Fuels, M.E. Howard and R.C. Vocke, J. Anal. At. Spectrom., **2004**, 19, 1423-1427

Fossil Fuel SRMs

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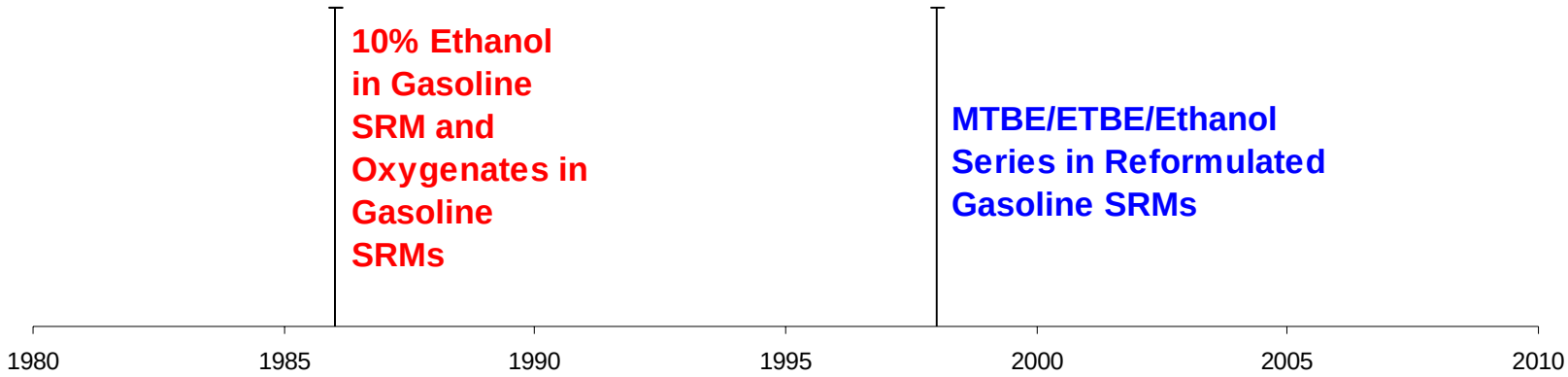
SRM	Matrix	S (ppm)	U 95% CI	U (% rel.)
1624d	#2 Diesel	3882	20	0.52
1617a	#1 Kerosene	1730.7	3.4	0.20
2724b	#2 Diesel	426.5	5.7	1.3
1616a	#1 Kerosene	146.2	1.8	1.2
2770	#2 Diesel	41.57	0.39	0.94
2723a	#2 Diesel	11.0	1.1	10
1616b	#1 Kerosene	8.41	0.12	1.4
RM 8771	#2 Diesel	0.071	0.014	20

New regulations will require on-road diesel to contain <15 ppm sulfur and gasoline to contain <30 ppm sulfur. Because of potential for contamination during transfer in pipelines, sulfur at refineries must be near 7 ppm.

Development of SRMs for Oxygenates in Fuels

HISTORY OF CERTIFIED ANALYTES IN NIST REFORMULATED GASOLINE



1979: 10% ethanol / 90% gasoline blends available to U.S. consumers.
1992: EPA's Oxygenated Fuel Program requires use of gasoline with 2.7% oxygen (by mass) in areas with high CO during fall and winter, i.e., 15% MTBE or 7.3% ethanol (by volume).
1995: EPA's Reformulated Gasoline Program requires use of gasoline containing 2% oxygen (by mass) year round, i.e., 11% MTBE or 5.4% ethanol (by volume).

“Gasohol” SRMs

SRM	Name	Methanol, % mass fraction	Ethanol, % mass fraction	*t*-Butanol, % mass fraction	Oxygenate, % mass fraction	Oxygen, % mass fraction
1829	Alcohols in Reference Fuels	Single ampoule of each of SRMs 1837 through 1839				
1837	Methanol and *t*-Butanol (in Gasoline)	10.33 ± 0.09		6.63 ± 0.02		
1838	Ethanol (in Gasoline)		11.39 ± 0.04			
1839	Methanol (in Gasoline)	0.335 ± 0.014				
2286	Ethanol in Gasoline				5.73 ± 0.06	2.02 ± 0.04
2287	Ethanol in Gasoline				10.07 ± 0.10	3.53 ± 0.04

Oxygenates-in-Gasoline SRMs

SRM	Name	Oxygenate, % mass fraction	Oxygen, % mass fraction
2288	*t*-Amyl Methyl Ether in Gasoline	12.78 ± 0.18	2.02 ± 0.04
2289	*t*-Amyl Methyl Ether in Gasoline	17.30 ± 0.20	2.73 ± 0.04
2290	Ethyl *t*-Butyl Ether in Gasoline	12.78 ± 0.28	2.01 ± 0.04
2291	Ethyl *t*-Butyl Ether in Gasoline	17.18 ± 0.18	2.70 ± 0.04
2293	Methyl *t*-Butyl Ether in Gasoline	14.86 ± 0.20	2.71 ± 0.04

Reformulated Gasoline SRMs

SRM	Name	Sulfur, mg/kg	Toluene, % mass fraction	Benzene, % mass fraction	Oxygenate, % mass fraction	Oxygen, % mass fraction
2294	Reformulated Gasoline (nominal 11% MTBE)	40.9 ± 0.1	8.29 ± 0.16	1.03 ± 0.02	10.97 ± 0.46	2.01 ± 0.01
2295	Reformulated Gasoline (nominal 15% MTBE)	308 ± 2	7.89 ± 0.12	0.99 ± 0.01	14.54 ± 0.24	2.66 ± 0.05
2296	Reformulated Gasoline (nominal 13% ETBE)	40.0 ± 0.4	8.02 ± 0.09	1.00 ± 0.02	13.02 ± 0.15	2.06 ± 0.06
2297	Reformulated Gasoline (10% Ethanol)	303.7 ± 1.5	8.27 ± 0.14	1.04 ± 0.01	9.91 ± 0.12	3.50 ± 0.07

SRM 2900 Ethanol-Water Solution (Nominal 95.6% by mass)

National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 2900

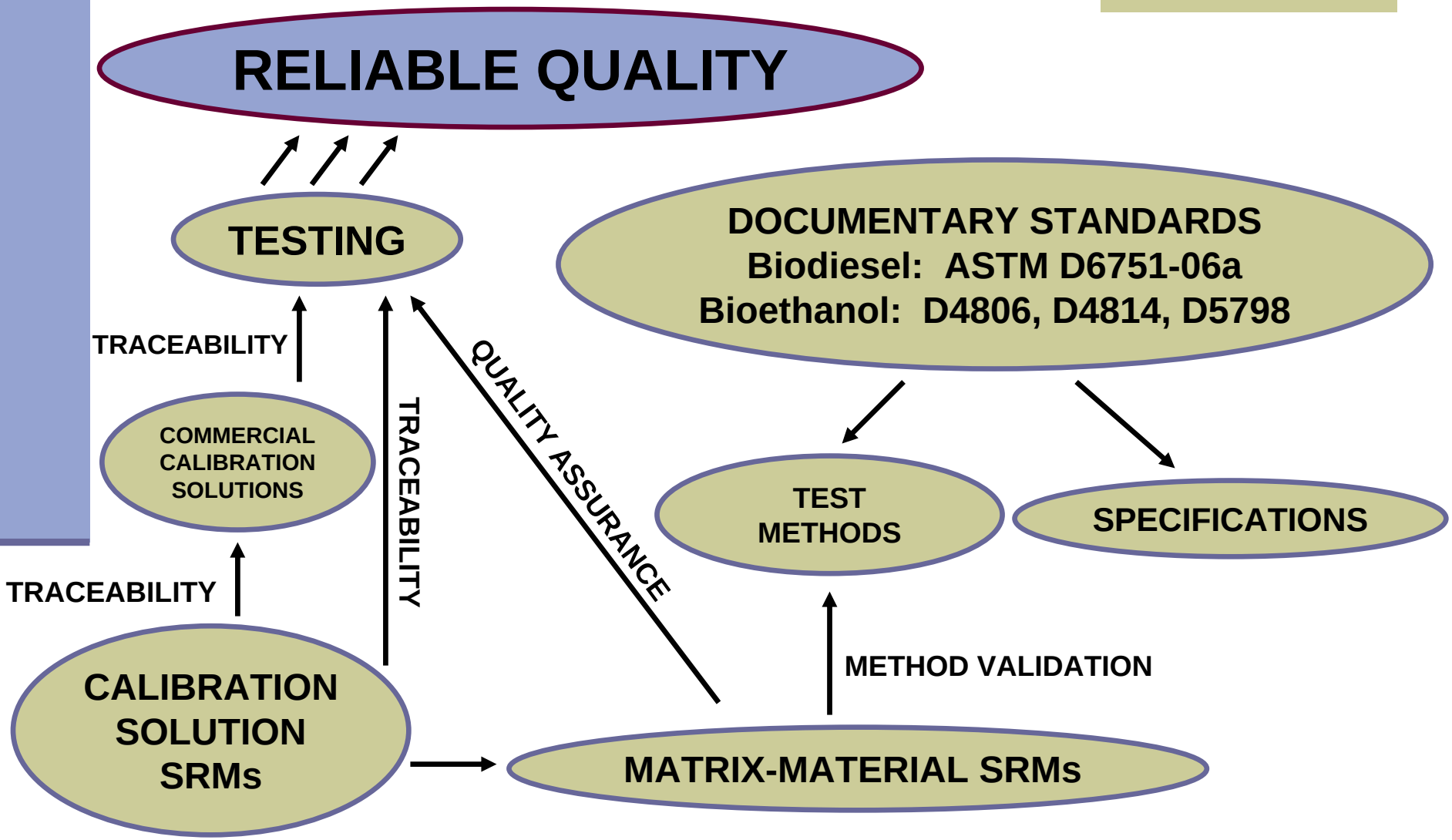
Ethanol-Water Solution (nominal 95.6 % by mass)

This Standard Reference Material (SRM) is a solution of ethanol (ethyl alcohol - Chemical Abstracts Service [CAS] Registry Number 64-17-5) in water at a nominal concentration of 95.6 % by mass. This SRM is intended primarily for use in the calibration of instruments and techniques used for the determination of ethanol in water-based media. SRM 2900 consists of five 10-milliliter ampoules (nominal concentration of 95.6 % by mass), each containing approximately 10 mL of solution.

Certified Concentration of Ethanol: 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 [1]. The certified concentration value given below is based on results obtained from the gravimetric preparation of the solution and from the analytical results determined using gas chromatography.

Ethanol Certified Concentration Value: 95.6 % ± 1.9 % (mass fraction)

Consumer Acceptance of Biofuels



Biodiesel SRMs in Development

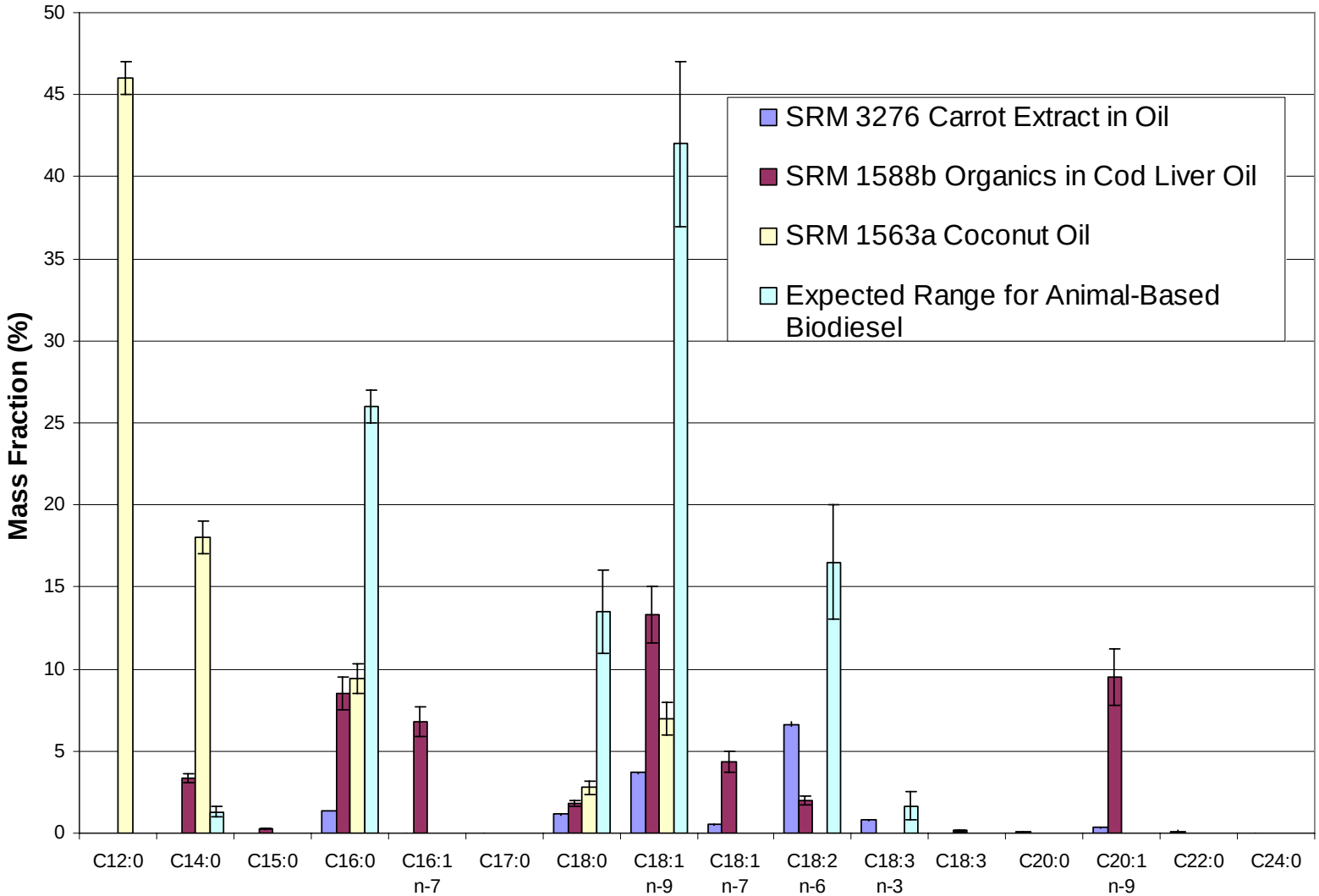
- Two materials:
  - SRM 2772 - soy-based B100
  - SRM 2773 - animal-fat-based B100 (approx. 70% choice white grease, 15% edible pork lard, and 15% soy)
- Packaged in 10 mL amber ampoules under argon
- Expect certification of sulfur, sodium, potassium, calcium, magnesium, phosphorus, glycerin, tryglycerides, and fatty acid methyl esters (FAMEs) (C_{12} to C_{24})

2008: Development of calibration solution SRMs containing FAMEs related to biofuels

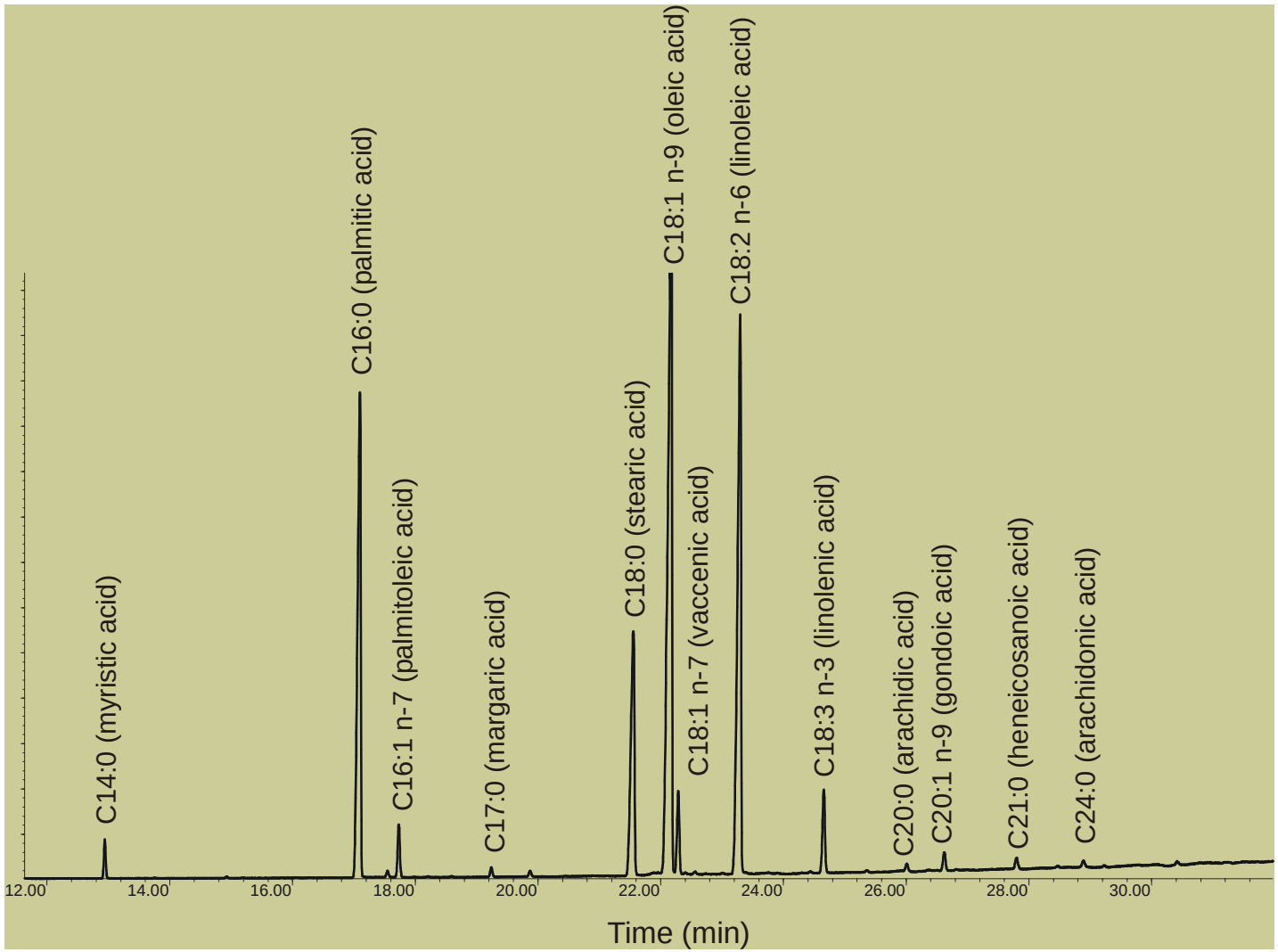
Calibration Solution SRMs for FAMEs

- Even-numbered saturated chains of C_6 through C_{24} in chloroform
- Concentrations will be high relative to actual concentrations in biodiesel so that the solutions can be diluted to prepare calibration curves
- Following discussion with potential users, some of the unsaturated fatty acids may be included or put in a separate solution for use by the food industry
- Ampouled in 2 mL ampoules (approximately 1.2 mL solution) under argon

Fatty Acids (as Triglycerides) in Three SRMs



Chromatogram of Animal-Based Biodiesel SRM



Animal-Based Biodiesel - Percent Composition

C12:0	0.1
C14:0	1.1
C15:0	0.1
C16:0 Palmitic Acid	21.6
C16:1 n-7	2.0
C17:0	0.4
C18:0 Stearic Acid	9.4
C18:1 n-9 Oleic Acid	34.0
C18:1 n-7	1.4
C18:2 n-6 Linoleic Acid	25.8
C18:3 n-3	3.3
C20:0	0.2
C20:1 n-9	0.1
C24:0	0.2
Total	99.7

Proposed SRM 2300 Bioethanol

- In development
- Will be packaged in 10 mL amber ampoules under argon
- Expect certification of ethanol, water, benzene and possibly other aromatic compounds, sulfur, other elements of interest

State of the Union Address

23 Jan 2007

"America is on the verge of technological breakthroughs that will enable us to live our lives less dependent on oil. And these technologies will help us be better stewards of the environment, and they will help us to confront the serious challenge of global climate change."