EUROPEAN COMMISSION

NIST

INMETRO

2nd International Conference on Biofuels Standards

Measurement Standards to Support Global Trade of Biofuels

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Suggestions for Moving Forward

from Tripartite Leaders and International Biofuels Forum

1) **Expanded Engagement of the IBF in this International Process through the Codes and Standards Working Group**

2) **Continued Engagement of Biofuels Technical Experts**

To facilitate expanded biofuels trade, the metrology community proposes that:

An internationally-accepted measurement infrastructure can provide a mechanism to:

- **"honor" and accommodate differences**
- **harmonize differences due to analytical bias and error**
- **underpin development and use of new test methods**
- **support the development of new specifications**

Planned Supportive Activities of the Governments
through their National Metrology Institutes

NIST (U.S.), and **INMETRO** (Brazil) have established plans for cooperative development of

Certified Reference Materials:

- **Anhydrous and Hydrated bioethanol**
- **Soy and Animal-based biodiesel**

  - for **calibrating** measurement instruments to a known and internationally accepted reference
  - for **validating** the accuracy of measurement results and measurement platforms, space and time.

Reference Measurement Methods:

- Chemical pattern recognition to identify feedstock source of biodiesel (e.g. soy, rapeseed, animal fat)
- Isotope metrology to distinguish between renewable/nonrenewable fuels

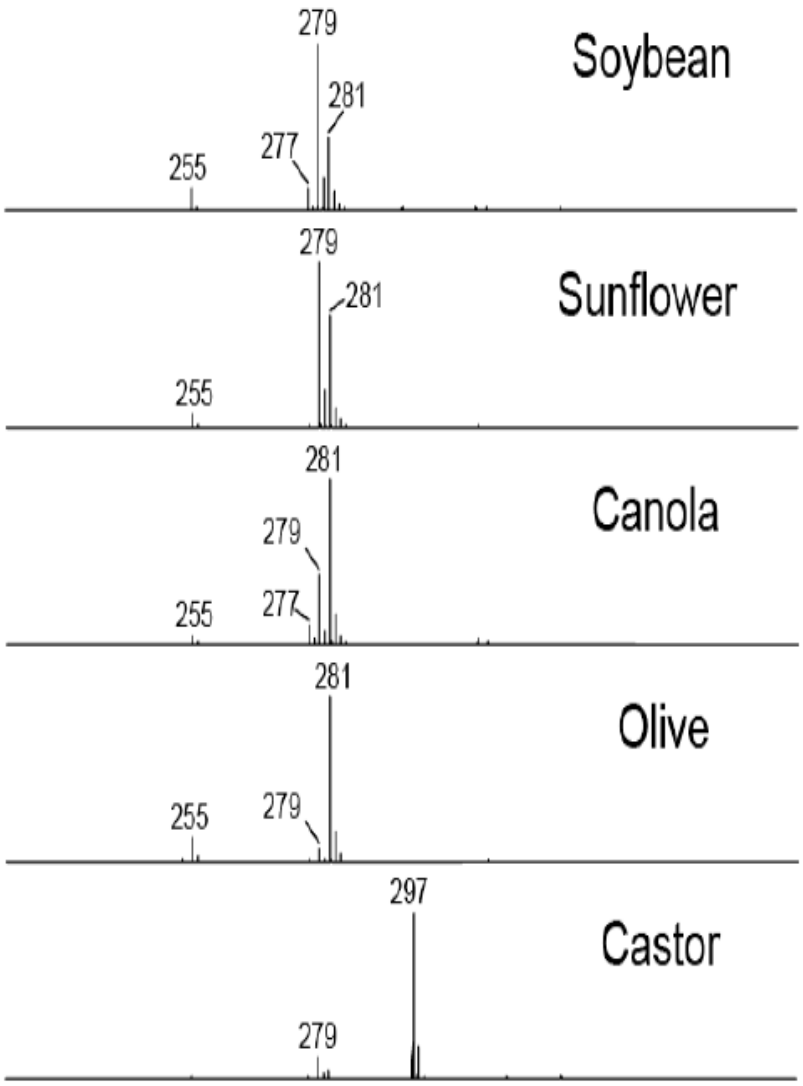
Advanced Isotope Ratio Measurements to Establish Source-type of Ethanol

- **Petroleum-derived ethanol is chemically identical to bio-ethanol**
- **Measurement strategy needed to distinguish non-renewable sources from renewable sources for:**
  - **Establishment of appropriate tax credits**
  - **Metrics to support assessment of achieving national/international fuel composition targets**
  - **Verification of meeting customer criteria as to source of ethanol,**
  - **Etc.**
- ***Carbon-14 and carbon-13 measurements provide a means to authenticate ethanol source***

non-renewable	*renewable*
C 14/12 = 10^{-12}	C 14/12 ~ 10^{-15}
C 13/12 = 0.0111	C 13/12 = 0.0109

Chemical pattern recognition to identify feedstock source of biodiesel

An ESI-MS (electrospray ionization mass spectrometry) technique being developed at Inmetro in Brazil and NIST for providing a fingerprint for categorizing biodiesel by source



Certified Reference Materials for Biodiesel

SRM 2772 B100 Biodiesel (Soy-based)

- Received from a farmer-owned cooperative in Nebraska (US)
- Produced from refined, bleached, and deodorized soy oil
- 10 mL amber ampoules evacuated with argon prior to filling with 10 mL of biodiesel and flame-sealing

SRM 2773 B100 Biodiesel (Animal-based)

- Received from a bioenergy firm
- 85% animal fat (sources – 65% pork, 20% beef, and 15% poultry) and 15% soy oil
- Same lot of material used in an ASTM Biodiesel Cross Check Program
- 10 mL amber ampoules evacuated with argon prior to filling with 10 mL of biodiesel and flame-sealing

Classification of Biodiesel Specifications from White Paper

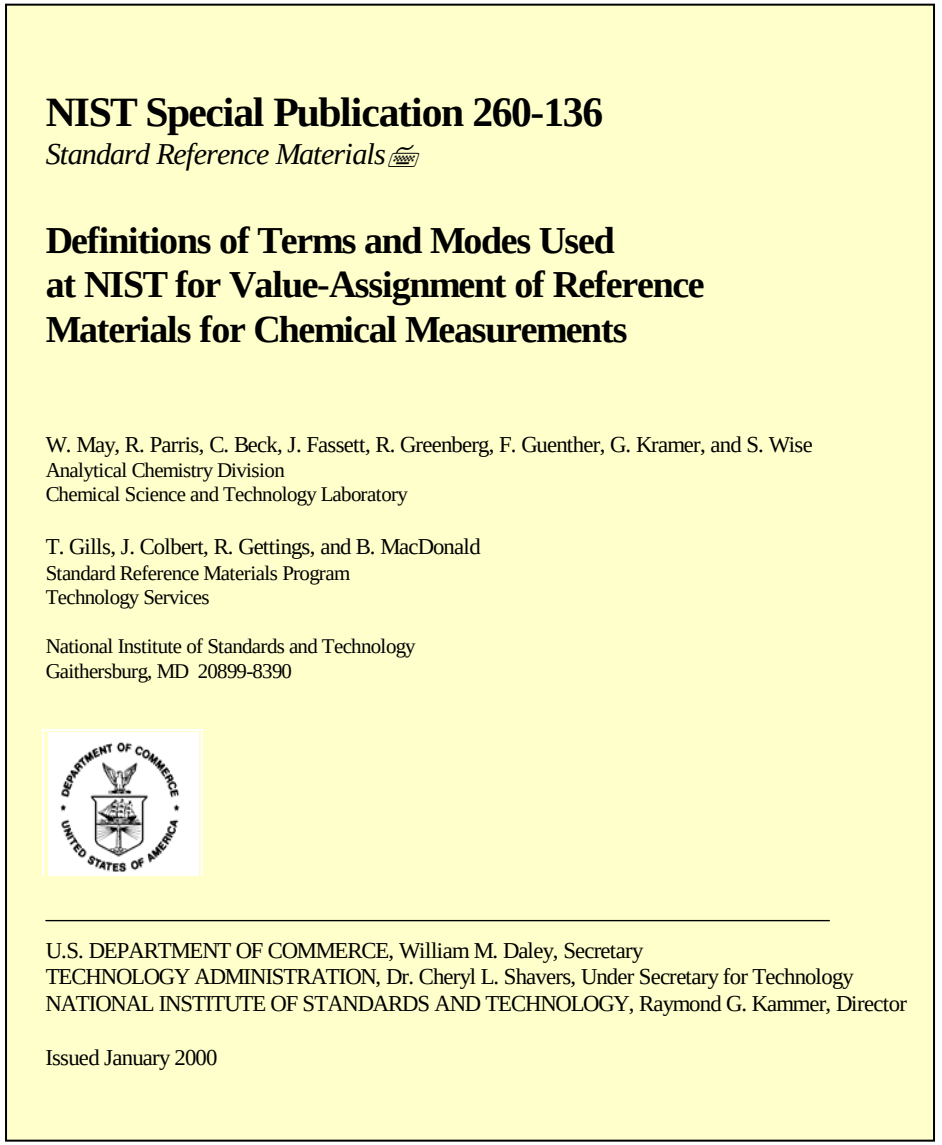
Category A *similar*	Category B *significant differences*	Category C *fundamental differences*
sulfated ash	total glycerol content[a,b]	sulfur content[a]
alkali and alkaline earth metal content[a,b]	phosphorus content[a,b]	cold climate operability
free glycerol content[a,b]	carbon residue	cetane number
copper strip corrosion	ester content[a,b]	oxidation stability[b]
methanol and ethanol content[a]	distillation temperature	mono, di-, tri-acylglycerides[a,b]
acid number[b]	flash point[b]	density[a,b]
	total contamination	kinematic viscosity[a,b]
	water content[a,b] and sediment	iodine number
		linolenic acid content[a,b]
		polyunsaturated methyl ester[a,b]

[a]Measurements at NIST

[b]Measurements at Inmetro

To define terms and criteria for NIST CRMs for chemical measurements - as a CRM Provider, NIST has provided SP 260-136 to the public:

- describes seven modes currently used at NIST for value-assigning SRMs and RMs for chemical measurements
- defines data quality descriptors used at NIST for these SRMs and RMs
  - NIST Certified Value
  - NIST Reference Value
  - NIST Information Value
- links these modes to these three data quality descriptors



NIST Special Publication 260-136
Standard Reference Materials

Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements

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NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, Raymond G. Kammer, Director

Issued January 2000

View/download from: http://ts.nist.gov/MeasurementServices/ReferenceMaterials/upload/SP260-136.PDF

Summary

	SRM 2772 B100 Biodiesel (Soy-based)	SRM 2773* B100 Biodiesel (Animal-based)
Certified	9 FAME, water, density, viscosity at 40 °C	13 FAME, water, sulfur, density, viscosity at 40 °C
Reference	3 FAME, acid #, viscosity at 20 and 30 °C, oxidation stability, gross heating value, methanol, individual glycerides	5 FAME, acid #, viscosity at 20 and 30 °C, oxidation stability, gross heating value, methanol, individual glycerides
Information	Trace elements and summed glycerides	Trace elements and summed glycerides

* data also provided from ASTM Committee D-2 Interlaboratory Crosscheck Program

Certified and Reference Concentration Values (g/kg) for FAMEs

	SRM 2772	SRM 2773
Lauric (C12:0)	<0.1	0.470 ± 0.017
Myristic (C14:0)	0.755 ± 0.089	9.20 ± 0.42
Pentadecanoic (C15:0)	*0.104 ± 0.008*	0.305 ± 0.009
Palmitic (C16:0)	107 ± 2	184 ± 5
Palmitoleic (C16:1 n-7)	1.32 ± 0.18	23.3 ± 0.6
Stearic (C18:0)	43.0 ± 1.8	87.8 ± 2.8
Oleic (C18:1 n-9)	233 ± 6	343 ± 8
cis-Vaccenic (C18:1 n-7)	14.3 ± 1.0	19.4 ± 0.5
Linoleic (C18:2 n-6)	770 ± 17	297 ± 4
Linolenic (C18:3 n-3)	204 ± 3	80.3 ± 1.7
Arachidic (C20:0)	3.66 ± 0.52	2.28 ± 0.08
Arachidonic (C20:4 n-6)	Not reported (<0.1)	2.53 ± 0.09
Behenic (C22:0)	*3.7 ± 1.1*	1.66 ± 0.06

Reference Concentration Values (g/kg) for FAMEs

	SRM 2772	SRM 2773
Capric (C10:0)	(<0.1)	0.20 ± 0.02
Heptadecanoic (C17:0)	1.03 ± 0.02	Not reported (<0.5)
trans-Vaccenic (tC18:1 n-7)	(<0.1)	0.78 ± 0.05
Nonadecanoic (C19:0)	(<0.1)	0.42 ± 0.03
Heneicosanoic (C21:0)	(<0.1)	0.077 ± 0.005
Tricosanoic (C23:0)	(<0.1)	0.130 ± 0.007

Additional Certified Values

	SRM 2772	SRM 2773	units
Water	0.018 ± 0.002	0.046 ± 0.002	Mass fraction (%)
Sulfur	Will be added as reference (<0.5)	7.39 ± 0.39	Mass fraction (mg/kg)
Density at 20 °C*	0.8813 ± 0.0001	0.8763 ± 0.0001	g/cm^3
Viscosity at 40 °C*	4.082 ± 0.005	4.425 ± 0.005	mm^2/s

*Will be updated (additional set of data) before release

Reference Values for Additional Chemical and Physical Properties

	SRM 2772	SRM 2773	units
Acid number	0.180 ± 0.007	0.207 ± 0.007	mg/g KOH
Oxidation Stability of FAME at 110 °C	4.41± 0.27	4.46 ± 0.04	g/cm^3
Viscosity at 20 °C	6.425 ± 0.008	7.129 ± 0.008	mm^2/s
Viscosity at 30 °C	5.049 ± 0.006	5.534 ± 0.006	mm^2/s
Gross Heating Value	9465 ± 3	9479 ± 4	cal/g
Methanol	587 ± 44	401 ± 34	mg/kg
Free glycerin	164 ± 16	12.1 ± 0.6	mg/kg
Monopalmitin	29.7 ± 2.3	141 ± 3	mg/kg
Monolein, monolinolein, monolinolenin	1994 ± 98	2668 ± 14	mg/kg
Diolein, diolinolein	707 ± 31	1030 ± 23	mg/kg
Tripalmitin	Not reported (<20)	91.2 ± 3.4	mg/kg
Triolein	241 ± 17	495 ± 38	mg/kg

Information Concentration Values (mg/kg) for Trace Elements, Glycerides, and Ethanol

	SRM 2772	SRM 2773
Sodium	0.07	0.9
Potassium	<0.1	<0.1
Calcium	0.5	0.1
Magnesium	<0.2	0.05
Phosphorous	<0.4	<0.4
Iron	<0.2	<0.2
Copper	<0.008	<0.01
Monoglycerides	3620	4110
Diglycerides	1960	2970
Triglycerides	1230	1350
Total glycerin	1520	1660
Ethanol	<0.2	<5

SRM 2773 B100 Biodiesel (Animal-based)
Appendix with following data from
ASTM Committee D-2 Interlaboratory Crosscheck Program

- Distillation – IBP, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, FBP
- Cloud point
- Flashpoint
- Kinematic Viscosity at 40 °C
- Carbon residue – micro and ramsbottom
- Ash
- Sulfur
- Lubricity by HFRR
- Total particulate contamination
- Water by KF
- Cold filter plugging point
- Acid number
- Free glycerin
- Total glycerin
- Thermal stability (90 min)
- Methanol content
- Ca, Mg by ICP/OES
- Mg, K by ICP/OES
- FAME: oxidation stability at 110 °C

Classification of Bioethanol Specifications

Category A *similar*	Category B *significant differences*	Category C *fundamental differences*
color	ethanol content	water content*
appearance	acidity	
density	phosphorus content	
sulfate content	pHe	
sulfur content	gum / evaporation residue	
copper content	chloride content	
iron content		
sodium content		
electrolytic conductivity		

Certification Plan for Bioethanol

Parameter	NIST	INMETRO
Elements (other than sulfur)	X	X
Sulfur	X	
EtOH	X	X
Acidity		X
Water	X	X
Density	X	X
Electrolytic conductivity	X	X

Thanks for Your Attention

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Questions and Comments Welcome

"We're from the Government and we're here to help !!!!