Fossil Fuel SRMs Certified for Sulfur, Mercury, and Chlorine

NIST has produced a suite of eight coal SRMs that are certified for sulfur and mercury concentrations. Three coal SRMs were also certified for chlorine this past year. The mixing procedure mentioned above can also be used for these standards if they are used in combustion instruments. This will make possible multipoint calibration curves over narrow concentration ranges.

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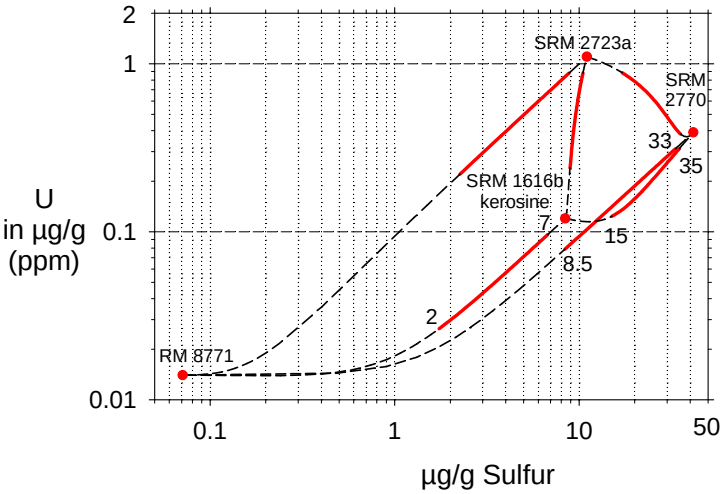
The U.S. Environmental Protection Agency (EPA) mandated ultra-low sulfur diesel fuel (ULSD, upper limit 15 µg/g) for on-road use starting June 2006 to make possible more efficient exhaust emission after-treatment technologies. This will result in substantially reduced particulate emissions from diesel engines. The accurate determination of sulfur in ULSD at low levels is a major measurement challenge with enormous economic consequences, mostly in avoided costs, for petroleum refineries and in every link in the distribution system. To meet this challenge in a cost-effective manner and with the least disruption in product availability, the industry must have highly accurate real-matrix sulfur standards. NIST responded in 2005 with the production of three low-level sulfur distillate fuel reference materials. This year we have described a procedure for the blending of distillate fuel SRMs that will enable the petroleum community to prepare standards at any sulfur level and be traceable to NIST values. The implementation of this procedure within the petroleum community will provide greater flexibility in preparing natural-matrix standards at any desired sulfur level and at the same time reduce the number of SRMs that NIST will need to produce.

NIST fossil fuel SRMs continue to be in high demand by the petroleum industry and the fossil fuel- based electric power industries as shown in ***Table 1***. The increase in demand for coal SRMs has been about 14 % per year, and last year the demand for coal SRMs was almost half (49 %) of the fossil fuel sales. The demand for diesel SRMs has doubled between FY 2004 and FY 2006 which is probably the effect of more restrictive limits by EPA on sulfur in diesel fuel. The high demand for diesel fuel SRMs in FY 2005 was the result of a large purchase by EPA for an interlaboratory comparison.

Table 1. ***Comparison of Sales of Coal and Diesel Fuel SRMs as Percentage of Total Fossil Fuel SRM Sales***

Sales by Fiscal Year	FY03	FY04	FY05	FY06
Total Fossil Fuels	2305	2578	3734	3243
Coal and Petroleum Coke	1081 47 %	1192 46 %	1387 37 %	1598 49 %
Diesel Fuel	287 17 %	358 15 %	1229 33 %	611 19 %

Figure 1. ***A log-log graph showing uncertainties and concentration of possible gravimetric mixes of four low-sulfur level distillate fuel oils. The red circles indicate the certified values for the SRMs. The red lines indicate the concentration range possible for binary mixtures assuming 4 to 1 mixing ratios.***



The U.S. and the European Union (EU) have mandated ULSD fuel for on-road use to reduce particulate emissions from diesel engines. The new U.S. limit is 30 times lower (15 µg/g versus 500 µg/g) than the current regulatory limit, although higher than the EU mandate of 10 µg/g. However, diesel fuel in the US is moved long distances by pipeline, which makes it more susceptible to contamination; therefore the sulfur concentration at refineries must be near 7 µg/g to ensure retail outlets meet regulatory requirements, which is essentially the same concentration level required for EU refineries.

The EPA estimates that the health and welfare benefits of this new regulation will be about $150 billion annually to the American public. *Per capita* benefits in the EU should be similar because their consumption of diesel is slightly greater than that of the US and their population is larger.

Three low-sulfur distillate fuel reference materials were certified last year, SRM 1616b, SRM 2770, and RM 8771. These certified reference materials complement the four existing distillate fuel SRMs at sulfur concentrations of 11 µg/g, 427 µg/g, 1731 µg/g, and 3882 µg/g. The four low-sulfur standards are plotted in Figure 1 and can be used in a binary mixing system to generate concentrations desired by an end-user. The possible mixtures are indicated by the solid red lines. The lines terminate at mixing ratios of 4 to 1 and vice versa. There is very good concentration coverage from 2 µg/g to 35 µg/g with expanded uncertainties less than 1 µg/g at the high end and less than 0.1 µg/g between 2 and 7 µg/g.

NIST has eight coal SRMs all of which are certified for sulfur and mercury. In recent years there has been increasing interest in the chlorine content of coal. The chlorine content of coal determines to a large degree the speciation of inorganic mercury emissions from coal-fired power plants. The fraction of mercury that is emitted as elemental mercury is inversely proportional to the chlorine content. Three coals were certified for chlorine this year and are listed in Table 2 along with the previously determined values for mercury and sulfur. An additional five coals will be certified in 2007. The chlorine was determined by isotope dilution negative thermal ionization mass spectrometry.

Table 2. ***New Chlorine Values by Isotope Dilution for Three SRM Coals***

SRM Coal	Cl µg/g	Hg ng/g	S %
SRM 2692b	1651 ± 28	133.3 ± 4.1	1.170 ± 0.020
SRM 2693	369.6 ± 5.7	37.3 ± 7.7	0.4571 ± 0.0067
SRM 2685b	517 ± 13	146 ± 11	4.730 ± 0.068

Impact: The combined impact of all NIST fossil fuel SRMs certified for sulfur has been studied in detail by Martin *et al.* (2000) in an economic impact report. The lower sulfur regulations in on-road diesel fuel compared to year 2000 logically mean that the environmental impacts are now even greater. The current lower sulfur limit of 15 µg/g compared to the former limit of 500 µg/g means that the petroleum industry must control diesel fuel quality in terms of sulfur content with much smaller tolerances. It will be very difficult and expensive to blend down streams of high sulfur concentration to pass the regulatory specification. For example, to blend a 20 µg/g product to 10 µg/g would require an equal volume of diesel fuel near zero concentration.

If the blending of liquid and solid fossil fuels is accepted widely in the fossil fuel community, this could reduce significantly the number of SRMs that NIST would produce and maintain in the future.

Future Plans: A number of states now require, or will require in the near future, that diesel fuel be sold as a mixture of petroleum diesel and bio-diesel. There is a clear need for a new pure (B100) bio-diesel SRM certified for both inorganic and organic constituents.

There are currently no NIST crude oil SRMs certified for mercury content at levels measurable by the petroleum industry. To address the critical need for this, a crude oil candidate SRM, having a relatively high level of mercury, will be developed in the coming year.

Publications:

Kelly, WR, MacDonald, BS, and Leigh, SD (2006) ***"Determination of Sulfur in Fossil Fuels: User Prepared Standards with Concentrations and Uncertainties Traceable to NIST Values,"*** accepted for publication in Journal of ASTM International.

Mann, JL and Kelly, WR (2005) ***"Measurement of sulfur isotope composition ($\delta^{34}S$) by multiple-collector thermal ionization mass spectrometry using a ^{33}S-^{36}S double spike,"*** Rapid Commun. Mass Spectrom.**19**, 3429-3441.

Martin, SA, Gallaher, MP, and O'Connor, AC (2000) **"Economic Impact of Standard Reference Materials for Sulfur in Fossil Fuels,"** 00-1 Planning Report, NIST.