

FINAL REPORT
Report of the CCQM Pilot P26.1
Determination of Sulfur in Diesel Fuel

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Abstract

The European Union and the United States have set new lower limits on sulfur in diesel transport fuel of 10 $\mu\text{g/g}$ and 15 $\mu\text{g/g}$, respectively. Implementation of these regulations will require the production of high-accuracy standards at these and lower levels by National Metrology Institutes (NMIs). A CCQM-Pilot Comparison was organized by the Inorganic Analysis Working Group (IAWG) of CCQM to test the capabilities of NMIs to measure the sulfur content in diesel fuel at the 8 $\mu\text{g/g}$ (P26.1) level. In addition, a pilot study was performed concurrently using a Key Comparison (KC) sample at the 40 $\mu\text{g/g}$ level for laboratories preferring to participate in a pilot study rather than in the KC. Four NMIs participated in both the Key Comparison and the Pilot Comparison: the Federal Institute for Materials Research and Testing (BAM), Institute for Reference Materials and Measurements (IRMM), Laboratory of the Government Chemist (LGC), and the National Institute of Standards and Technology (NIST). Three other laboratories agreed to participate, but only on the condition that they be permitted to analyze both materials as a Pilot Study. They were the National Center of Metrology of Mexico (CENAM), NIST, and a second laboratory within BAM. NIST designed and coordinated the study. The four KC participants used isotope dilution methodology. The agreement among these laboratories was good for the K35 sample as evidenced by 1) the small values for both the *degrees of equivalence*, D_i , which is the absolute difference between a laboratory and the Key Comparison Reference Value (KCRV), and 2) their small associated uncertainties (U_i). The four values determined by isotope dilution yielded D_i values less than 0.8 $\mu\text{g/g}$ and U_i values of 2.2 in one case and 1.4 in three cases. The same four participants had even better agreement for the designated P26.1 Pilot Study sample. The *degrees of equivalence*, D_i and the associated uncertainties, U_i , were both less than 1 $\mu\text{g/g}$. The three laboratories that used non-isotope dilution methods also exhibited good agreement with the reference values. At the 8 $\mu\text{g/g}$ and 40 $\mu\text{g/g}$ sulfur levels the *degree of equivalence*, D_i , was less than 1 $\mu\text{g/g}$ in 5 out of 6 cases.

1 Introduction

The European Union (EU) and the United States (US) now mandate the use of ultra-low sulfur diesel (ULSD) fuel for on-road use to enable more efficient exhaust emission after treatment technologies which will result in substantially reduced particulate emissions from diesel engines. Diesel fuel with a sulfur concentration below 50 µg/g is commonly referred to as ULSD (Ultra-Low Sulfur Diesel) or near-zero diesel. The EU mandated a 10 µg/g sulfur upper limit in diesel starting in 2005, and the US phased in a 15 µg/g limit starting June 2006. These are substantial reductions in sulfur content from the previous regulatory limit of 500 µg/g. The measurement challenges increase non-linearly as sulfur concentrations decrease from 500 µg/g to near-zero levels. As the sulfur levels drop, the demand for calibration standards will increase in number and tighter limits on absolute accuracy will be required. For example, at the 500 µg/g regulatory level, most refineries in the US desulfurize between 300 µg/g and 400 µg/g and routinely measure this level with an uncertainty of ∇ 50 µg/g. At the 10 µg/g and 15 µg/g levels, the uncertainty requirements will be a factor of 25 more stringent because petroleum refineries will need to ensure they are in compliance with regulations, while avoiding excessive reduction of the sulfur content. ULSD is expensive for the petroleum industry to produce, and the need for sulfur determinations through the complete supply chain present a formidable measurement challenge.

Even though the 10 µg/g and 15 µg/g limits for Europe and the US appear to be very different, functionally they are equivalent. In the US unlike in the EU, about 60 % of the diesel fuel travels through pipelines where it can be contaminated by adjacent fuels or the valving system; therefore, petroleum refiners expect they will have to produce diesel at 7 µg/g or 8 µg/g to ensure that they meet the 15 µg/g specification at the retail pump. In the EU, refiners also project that they will need to produce at 7 µg/g or 8 µg/g to meet the 10 µg/g specification. It is thus probable that refineries in both the EU and the US will need to desulfurize to about the same sulfur level.

The consumption of distillate fuel oil by the EU and the US in 2003 was almost identical at 2.41 and 2.22 billion barrels each, and the combined consumption accounts for 46 % of world=s total.¹ Diesel fuel has been the premier transportation fuel in Europe since 1998 when it surpassed gasoline consumption, and the gap continues to widen. In 2004, the transport fuel mix in Western Europe was 40 % gasoline and 60 % diesel, the exact reverse of what it was in 1985. Diesel automobiles have heavily penetrated the European market during the last 20 years, accounting for 44 % of passenger car registrations in 2003 compared to only 16 % in 1985.² In the US, the market for light-duty diesel vehicles is less than 1 %, in effect Δ practically nonexistent.³ Nevertheless, diesel fuel is extremely important to the US economy because almost all of it is consumed by the trucking industry, which hauls 68 % of the nation=s freight thereby accounting for 87 % of the US=s freight bill in 2002.⁴

Reduction of the sulfur content in diesel and gasoline motor fuels is the single most important factor in efforts to reduce primary and secondary air pollution from existing and future diesel and gasoline engines. The International Council on Clean Transportation (ICCT)⁵ recently stated the following:

It is impossible to clean the air, or in particular to reduce air pollution from the transportation sector, without getting the sulfur out of fuels. Sulfur is a pollutant directly, but more importantly, sulfur prevents the adoption of all major pollution control technologies. No significant air pollution reduction strategy can work without reducing sulfur to near-zero levels.

Additional statements, similar to the one above, have been made by numerous international organizations such as the World Wide Fuel Charter⁶ which stated in its 2002 edition:

A...automobile and engine manufacturers have concluded from existing research that the sulfur levels of both gasoline and diesel fuel must be dramatically lowered to enable advanced and future motor vehicle technologies...@

The US Environmental Protection Agency (EPA) estimates the implementation of ULSD will result in health and welfare benefits of about \$150 billion annually to the American public.⁷ *Per capita* benefits in the EU should be similar to those of the US based on the approximately equal consumption rates.

The national regulatory agencies and the petroleum industry look to the National Metrology Institutes (NMIs) to produce calibration standards and check standards with certified concentrations and uncertainties for sulfur that will ensure a smooth and cost-effective transition to low sulfur diesel fuel. Because the pending regulations on sulfur in diesel fuel were already known in both the EU and the US, the design of this CCQM exercise could be highly focused. After discussing possible designs, it was decided that a diesel fuel with a sulfur value near the current EU regulatory limit of 50 µg/g would be used as the Key Comparison (KC) material, and a diesel with approximately 10 µg/g sulfur would be analyzed as a Pilot study. A diesel was prepared by blending two existing NIST SRMs to a sulfur level of approximately 42 µg/g for the K35 Key Comparison. The material used for the P26.1 Pilot Study was SRM 1616b, a low-sulfur kerosene (No. 1-K), with a sulfur concentration of 8 µg/g.

This pilot study (P26.1) actually consisted of both samples. The kerosene at the 8 µg/g level was the primary sample and the K35 sample at the 42 µg/g level was analyzed concurrently as a Pilot sample by laboratories preferring to participate in a pilot study rather than in the KC study. The results of the K35 study are reported separately, but are also reported here.

2 List of Participants

The participating NMIs are listed by name and abbreviation in Table 1. It was decided at a CCQM meeting in 2002 that the US National Institute of Standards and Technology (NIST) would be the coordinating laboratory for this study. NIST would design the analytical protocol and compile the submitted data. NIST would also procure, package, and send out the test samples. On October 10, 2003, a letter of invitation to participate in the CCQM K35 Key Comparison and the P26.1 Pilot Study was sent via Dr. Michael Sargent (LGC), Chairman of the Inorganic Analysis Working Group (IAWG), to all members of the IAWG under the signature of Dr. Robert D. Vocke of NIST. Four NMIs responded asking to participate in the K35 Key Comparison and in the P26.1 Pilot Comparison. All four laboratories possessed the capability of using the isotope dilution method for the determinations, and this was considered the only method with proven performance to measure sulfur accurately with an uncertainty of less than 1 µg/g at these low levels. Although this is not a specific requirement for sulfur measurements, this level of precision will be required for standards to be useful to the petroleum industry at the 15 µg/g level and below.

A fifth NMI, CENAM, wished to analyze both materials, but not officially participate in the Key Comparison. Two additional laboratories within two Institutes (BAM and NIST) also wished to participant in the same manner as CENAM.

Table 1. List of Participating National Metrology Institutes

No.	Participating Laboratories	Country
1	BAM Federal Institute for Materials Research and Testing	Germany
2	CENAM National Center of Metrology	Mexico
3	IRMM Institute for Reference Materials and Measurements	European Union
4	LGC Laboratory of the Government Chemist	United Kingdom
5	NIST National Institute of Standards and Technology	United States of America

All participants are listed in Table 2 are separated based on their participation selection. The contact person and the analytical method employed is given in the right column.

The first four laboratories agreed to participate in the K35 Key Comparison and the P26.1 Pilot Study and all four submitted data for the three diesel materials listed in Table 3. The other three laboratories agreed to participate, but declined to participate in the Key Comparison; instead, they requested that they be permitted to measure both sets of test materials as part of the P26.1 Pilot Study.

Table 2. List of Contact Persons for Each National Metrology Institute

Participating Laboratory	Contact Person/Method
Laboratories Participating in K35 Key Comparison and Pilot Study P26.1	
BAM (I.42) Federal Institute for Materials Research and Testing	Jochen Vogl / ID-TIMS ¹
IRMM Institute for Reference Materials and Measurements	Philip Taylor / ID-HR-ICP-MS ¹
LGC Laboratory of the Government Chemist	Ruth Hearn / ID-HR-ICP-MS ¹
NIST National Institute of Standards and Technology	Robert Vocke / ID-TIMS ¹
Laboratories Participating in the Pilot Study P26.1 Only ²	
BAM (I.22) Federal Institute for Materials Research and Testing	Tin Win / Combustion-Fluorescence
CENAM National Center of Metrology	Antonio Salas / Wavelength X-Ray Fluorescence
NIST National Institute of Standards and Technology	John Sieber / Wavelength X-Ray Fluorescence

¹ ID-TIMS = Isotope Dilution – Thermal Ionization Mass Spectrometry, ID-HR-ICP-MS = Isotope Dilution-High Resolution-Inductively Coupled Plasma-Mass Spectrometry ² These laboratories elected to measure both the Key Comparison and Pilot Study materials as a Pilot Study.

3 Samples

Three sample materials were used in the Key and Pilot comparisons. These three materials were candidate Standard Reference Materials (SRMs) to be certified by NIST during the CCQM exercise and thereafter they would then be available for purchase. A fourth sample, SRM 3154, a coulometrically titrated dilute sulfuric acid solution, was

included in the comparison to enable each laboratory to calibrate their sulfur spike against a common material. A list of the four materials used and the NIST certified values are provided in Table 3. At the time the materials were sent out to the participants, no sulfur values were known precisely except for SRM 3154; NIST had not yet performed any measurements. The participants were given the following nominal sulfur concentrations: SRM 1616b - 10 µg/g, SRM 2770 - 40 µg/g, and SRM 1624d - 4000 µg/g. SRM 1616b is packaged in 100 mL amber glass bottles. SRM 2770 is a custom blended sample prepared at NIST from a mixture of 0.8 % SRM 1624d and 99.2 % SRM 2723a (certified at 11.0 µg/g ∓ 1.1 µg/g). SRM 2770 is packaged in 10 mL amber glass ampoules. SRM 1624d is also packaged in 10 mL amber glass ampoules.

Table 3. List of Samples Used in K35 and P26.1 Studies and NIST Certified Values

Study	Mean (µg/g)	Uncertainty (U) (µg/g)	NIST SRM Designation ¹
P26.1	8.41	0.12	1616b Sulfur in Kerosene
K35, P26.1 ²	41.57	0.39	2770 Sulfur in Diesel Fuel
Check Sample ³ K35, P26.1	3882	20	1624d Sulfur in Diesel Fuel
Calibration Standard			
Calibration Sample	10300	30	3154 Sulfur Standard Solution

¹ Dates of certification as SRMs were March 10, 2005 for SRMs 1616b and 2770, and April 26, 2005 for SRM 1624d. ² This sample was analyzed in both the Key and Pilot studies. ³ This sample was not officially part of either study, but analysis of this sample by all participants was requested.

4 Technical Protocol

The letter to the participants and the technical protocols are attached as Annex A and B. There is a protocol specific to each of the two exercises, K35 and P26.1. The high sulfur concentration sample did not have a protocol document, but other documents requested that one or both of the supplied ampoules be measured and the results submitted. Examples of the data reporting sheets are attached in Annex C.

The proposed time schedule was the following:

1. October 10, 2003: Letter of invitation to potential participants
2. November 14, 2003: Protocol letter sent to participants
3. November 2003: Samples distributed to participants in late November
4. March 31, 2004: Results submitted to NIST

5 Methods of Measurement

The solicitation letter to IAWG members did not prescribe a method of measurement, but stated "While the protocols focus on isotope dilution mass spectrometry as the assay method for sulfur, participation is open to any method participants wish to employ." The two most common methods used in the petroleum industry are XRF and a variety of methods based on combustion in oxygen to produce SO₂ and its subsequent detection by UV or IR spectroscopy.

Only four NMIs expressed interest in participating in the K35 Key Comparison. The small number of participants should not be taken as an indicator of the level of interest in ULSD. The nominal 40 µg/g and 10 µg/g samples are normally considered low and very low for traditional XRF techniques and NMIs would not normally use this technique to certify standards at these levels, and therefore they may have decided not to participate for this reason.

Four laboratories reported results by isotope dilution mass spectrometry (IDMS). NIST and BAM used thermal ionization mass spectrometry (TIMS) based on a well established NIST technique.⁸ It should be noted that BAM used a multi-collector instrument. LGC and IRMM used high resolution inductively coupled plasma mass spectrometry (ID-HR-ICPMS) based on a technique originally developed at LGC.⁹ All four laboratories used an enriched ³⁴S spike and three calibrated it as prescribed by the Technical Protocol (see Annex B) which removed a potential source of bias. The ³⁴S spike used by IRMM was a certified reference material IRMM-646.

The complete listing of methods used is given in Table 2, List of Participants.

6 Results

The results are reported in four sub-sections that give 1) the KC results for K35, 2) the results for K35 reported as a Pilot study, 3) the Pilot 26.1 study results for the 8 µg/g sample, and 4) the results on a high sulfur concentration (4000 µg/g) diesel fuel used as check sample in both exercises.

A Results of K35 as Reported as a Key Comparison

The details for the K35 Key Comparison are given in a separate report by the same authors. Some of the results are repeated here to serve as basis of comparison for those laboratories reporting on K35 as a pilot exercise.

Table 4 gives the results of the isotopic composition determinations reported by the four laboratories using mass spectrometric techniques on all samples used in the Key and Pilot studies. Because of the rather large variability of the sulfur isotopic composition resulting from mass fractionation in nature, isotopic dilution techniques must measure the isotopic composition of each sample and use it in the calculation of concentrations to obtain results of the highest accuracy. Sulfur has only one major isotope at mass 32; therefore, large variations in isotopic ratios have only a small effect on the atomic mass (see last column, Table 4).

The results on the K35 sample are presented graphically in Figure 1 and tabulated in Table 5. Descriptions of the various statistical methods are found in references 11 and 12. In general, the agreement among laboratories was good with expanded uncertainties that were less than 1 $\mu\text{g/g}$ in 3 out of 4 cases. Three problems were noted: 1) the mean value submitted by IRMM was higher than the other three, 2) the reported uncertainty by IRMM of 0.36 is smaller than that calculated from the standard deviation for $n=6$ and $k=2$, and 3) the reported uncertainties by LGC are larger than those reported by other NMIs whose data exhibit similar dispersion.

Table 4. Isotopic Ratios Determined on CCQM K35 and P26.1 Test Materials by Mass Spectrometry

Laboratory	$^{32}\text{S}/^{34}\text{S}$	$^{33}\text{S}/^{34}\text{S}$	$^{36}\text{S}/^{34}\text{S}^1$	Atomic Mass
Pilot Sample P26.1				
BAM	22.351	0.17647	0.0235	32.0648
IRMM	22.38	0.1768	0.02 %	32.0651
LGC	Not Reported			
NIST	22.6297	0.1773	0.015 %	32.0639
Key Comparison K35				
BAM	20.396	0.1616	0.0086	32.0737
IRMM	22.46	0.1777	0.02 %	32.0648
LGC	Not Reported			
NIST	22.6422	0.18717	0.015 %	32.0641
Check Sample				
BAM	22.428	0.17756	0.00444	32.0649
IRMM	22.49	0.1776	0.02 %	32.0647
LGC	Not Reported			
NIST	22.588	0.17835	0.015 %	32.0641
Calibration Sample				
BAM	22.555	0.17779	0.0035	32.0642
IRMM	Not Reported			
LGC	Not Reported			
NIST	22.5528	0.17693	0.015 %	32.0642
NIST ²	22.5667	0.178102	0.003487	32.0642

¹ The $^{36}\text{S}/^{34}\text{S}$ column gives the assumed isotopic abundance if the value is followed by a percent sign; otherwise, it is the actual measured ratio. ² Based on double spike determination described by Mann and Kelly (see ref. 10).

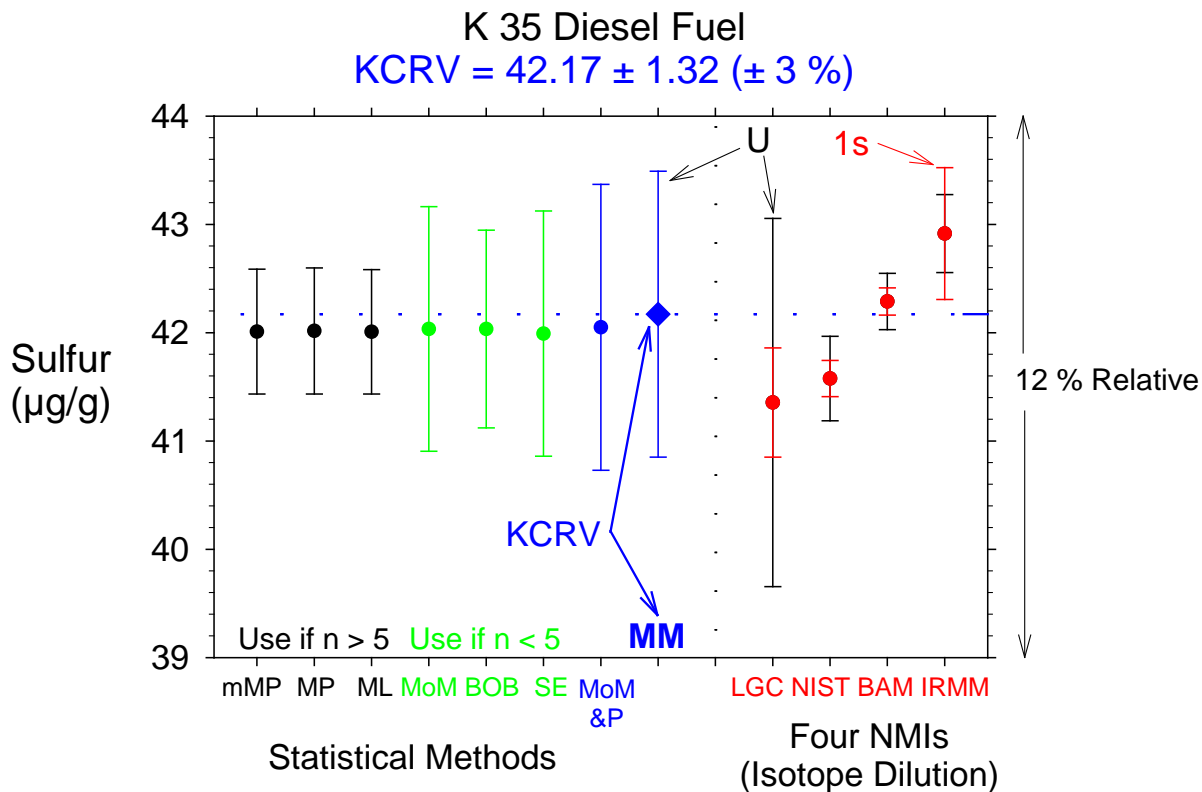


Fig. 1. Plot of Key Comparison Reference Value (KCRV) as determined by different models. To the right of dashed line are the submitted mean values with attached expanded uncertainties (U) and 1s calculated from the submitted data.

Table 5. Results for Sulfur in K35 by Isotope Dilution Mass Spectrometry

Participant	Method	Reported Value (µg/g)	Expanded Uncertainty (µg/g)	k Value
BAM (1.42)	ID-TIMS	42.29	0.26	2
IRMM	ID-ICPMS	42.92	0.36	2
LGC	ID-ICPMS	41.36	1.7	2
NIST	ID-TIMS	41.57	0.39	2.31

B Results of K35 as Reported as a Pilot Study

The results reported by three laboratories using techniques other than isotope dilution are tabulated in Table 6. Their results are comparable in precision to those by isotope dilution presented in Table 5 above. The XRF values submitted by CENAM and NIST are essentially identical and are also in good agreement with the KCRV as shown in Figure 2. They are also in good agreement with the certified value as shown in Tables 6 and 3.

Table 6. Results for Sulfur in K35 Sample as Determined in the Pilot Study

Participant	Method	Reported Value (µg/g)	Expanded Uncertainty (µg/g)	k Value
BAM (I.22)	Combustion/ Fluorescence	40.21	0.86	2
CENAM	WDXRF	42.44	1.05	2.23
NIST	WDXRF	42.46	0.67	2

CCQM K35 (NIST SRM 2770)

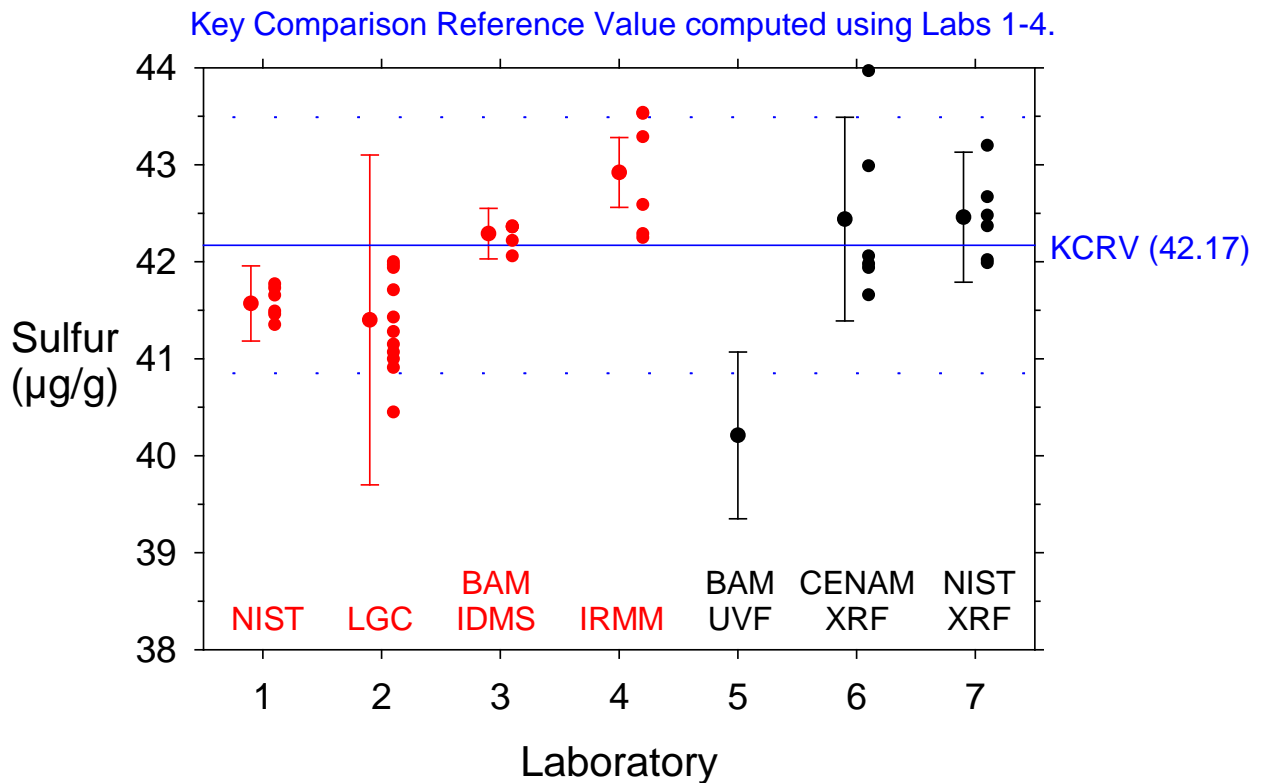


Figure 2. Plot of all results received for the K35 sample. Isotope dilution results are shown in red. The horizontal dashed line is the uncertainty on the KCRV value.

C Results of Pilot Study P26.1

The isotope dilution results for the P26.1 Pilot kerosene sample are given in Table 7. Each laboratory received two 100 mL bottles and were told the concentration was approximately 10 µg/g. Each laboratory was asked to take three independent samples from each bottle. The number of reported determinations is given in parentheses in column four. NIST used different bottles for each because their data were to be used for certification of the material as an SRM. Two points are immediately obvious from Table 7: 1) the reported means are in good agreement, and 2) the expanded

uncertainties are Δ small@ - all are less than 1 $\mu\text{g/g}$. These two observations are encouraging because the EU laboratories had not previously demonstrated their capability at this level.

Table 7. Results for the P26.1 Pilot Study Sample (SRM 1616b)
(Nominal Δ 10 $\mu\text{g/g}$ @ Sulfur in Kerosene)

Participant	Method	Reported Value S in $\mu\text{g/g}$	Expanded Uncertainty S in $\mu\text{g/g}$ (n)	k Value
BAM (I.42)	ID-TIMS	9.03	0.62 (6)	2
IRMM	ID-ICPMS	8.91	0.36 (5)	2
LGC	ID-ICPMS	8.49	0.54 (8)	2
NIST	ID-TIMS	8.41	0.12 (8) ¹	2.23
CENAM	WDXRF	8.68	0.78 (6)	2.23
NIST	WDXRF	8.47	0.22 (6)	2
BAM (I.22)	Combustion/ Fluorescence	8.17	0.44 (8)	2

¹ NIST used 8 different bottles because these data were used for SRM certification.

CCQM P26.1
(NIST SRM 1616b)

Pilot Study Reference Value computed using Labs 1-4.

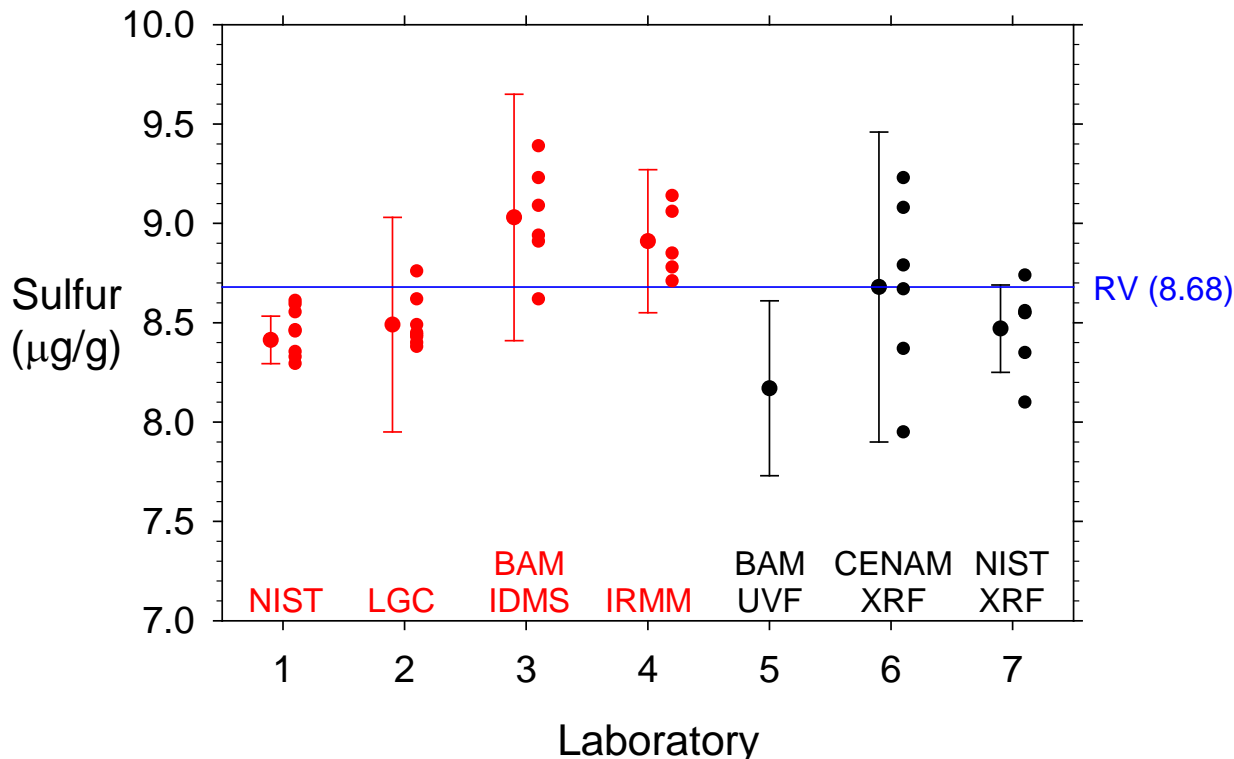


Figure 3. Plot of all results received for the Pilot 26.1 sample. Results from isotope dilution determinations are plotted in red. Uncertainty bars represent 95 % confidence intervals. Individual determinations are shown as solid circles to the right of the mean values.

D Results of High Sulfur Diesel Δ Check@ Sample

The results for the check sample are given in Table 8. Each laboratory received two 100 mL bottles of this material and were told that it had an approximate sulfur concentration of 4000 $\mu\text{g/g}$. The rationale for including this sample in a study designed to test measurement capability at very low levels is the following. It was assumed that K35 at 40 $\mu\text{g/g}$ and P26.1 at 10 $\mu\text{g/g}$ were near or approaching the limit of quantitation for techniques other than isotope dilution. In the case of isotope dilution, it was assumed that although the individual measurements might be highly precise, the expanded uncertainty (U) might be degraded considerably by fluctuations in chemical blank during chemical digestion and processing of the sample. Therefore, this high sulfur sample was included in the analysis suite because it would be essentially

insensitive to variations in blank, and it could also be measured with sufficient precision to check for differences in calibration. After some initial reluctance to measure a material with such a high sulfur content, five of the seven laboratories complied, and the last report on this material was received at the end of September 2004. The results presented in Table 8 are in fairly good agreement. BAM (I.42) did not report an expanded uncertainty; an estimated expanded uncertainty was calculated from their two reported determinations. This value does not include all sources of uncertainty, and two determinations do not necessarily yield a good estimate for the true standard deviation.

Table 8. Results for Check Sample by Isotope Dilution and Other Methods

Participant	Method	Reported Value µg/g	Expanded Uncertainty µg/g (n)	k Value
BAM (I.42)	ID-TIMS	3895	9 (2) ¹	2
IRMM	ID-ICPMS	3976	42 (4)	2
LGC	ID-ICPMS	3908	72 (6)	2
NIST	ID-TIMS	3882	20 (6)	2.12
Laboratories Not Included in Key Comparison				
NIST	WDXRF	3969	79 (6)	2
BAM (I.22) ²	Combustion/ Fluorescence			
CENAM ²	WDXRF			

¹ An approximate U was calculated by multiplying s by k=2 and dividing by \sqrt{n} . ² BAM (I.22) and CENAM did not submit results.

7 Estimation of Key Comparison Reference Value (KCRV) for K35 and Reference Value for P26.1

A Key Comparison Reference Value (KCRV) for K35

A summary of three different estimates of the KCRV and their associated uncertainties are listed in Table 9. At the fall 2004 IAWG meeting at CENAM (Mexico) it was decided

by the K35 participants to use the Mixture Median (MM) model¹² for the final KCRV value. In this particular study the values from the three different models are essentially identical, and there are only small differences in the calculated uncertainties.

Table 9. KCRV and Uncertainty for the Sulfur Concentration from Three Statistical Models in $\mu\text{g/g}$

Statistical Model	KCRV	U
Mean of Means (MoM)	42.05	1.11
MoM and Pooled U	42.05	1.32
Mixture Median Model	42.17	1.32

B Reference Value for P26.1

The isotope dilution determinations on Pilot sample P26.1 are displayed graphically to the right of the vertical dashed line in Figure 4. The black error bars are the expanded uncertainties (U) submitted by the participants and the red error bars are the standard deviations calculated from the individual determinations. One noteworthy observation in the LGC data is the very large difference between the expanded uncertainty, U, and the standard deviation, s.

Reference Values were calculated by a variety of statistical methods and are displayed in Figure 4 to the left of the vertical dashed line. The first six (black and green color) were calculated using DataPlot.¹¹ DataPlot suggests that the first three not be used unless the number of laboratories is greater than 5. The next two values in blue were calculated using the procedure developed by Duewer.¹² The Mixture Median Model Reference Value was $8.68 \mu\text{g/g}$ with a combined uncertainty of $0.64 \mu\text{g/g}$. This uncertainty is quite small considering it is a mean of results generated by four different laboratories.

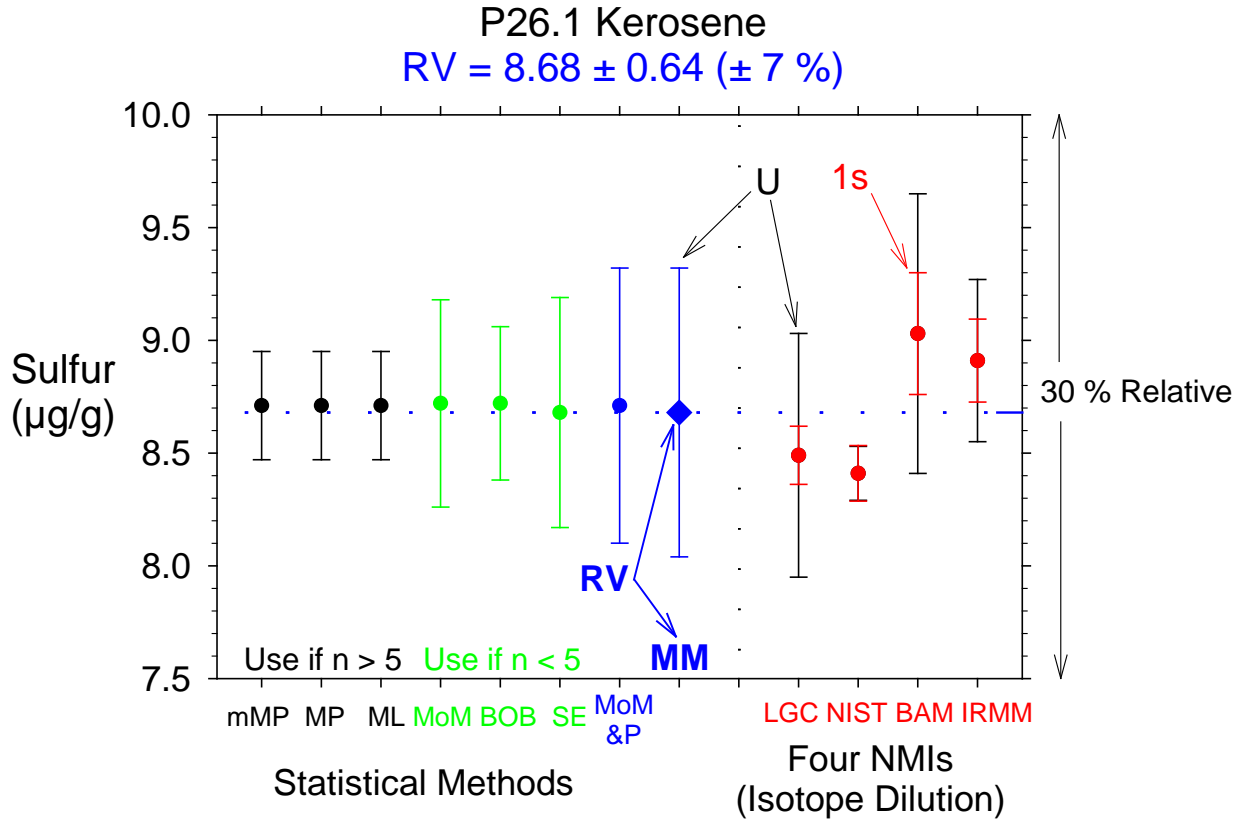


Figure 4. Plot of reference values as determined by different models. To the right of the dashed line are the submitted mean values with attached expanded uncertainties (U) and 1s calculated from the submitted data.

8 Degrees of Equivalence

Degrees of equivalence were calculated using the following equations where D_i is the difference in $\mu\text{g/g}$ between the laboratory, x_i , and the KCRV, x_R . The degree of equivalence uncertainty, U_i , for each laboratory is the combined uncertainty of the

$$D_i = (x_i - x_R)$$

$$U_i^2 = (k_i^2 u_i^2 + k_R^2 u_R^2)$$

KCRV with that for each laboratory. The u_i for each laboratory was calculated by dividing U by the appropriate k value which was 2 for all laboratories except NIST. A k_i and k_R of 2 were used for all calculations so that all laboratories could be compared on the same basis.

A Equivalence Statements for Key Comparison K35 Participants

The degrees of equivalence for the K35 Key Comparison are summarized in Table 10. It is noteworthy that D_i is less than 1 $\mu\text{g./g}$ in all four cases and that U_i is 1.4 $\mu\text{g/g}$ for three NMIs and is 2.2 for LGC. The U_i values for last three laboratories in the table, which are equal to 1.4, are dominated by the kU_R contributions which are equal to 1.3.

Table 10. Degree of Equivalence Statements for Key Comparison K35

Participant	Mean ($\mu\text{g/g}$)	Expanded Uncertainty (U)		D_i ($\mu\text{g/g}$)	U_i ($\mu\text{g/g}$)
Four Isotope Dilution Participants					
LGC	41.36	1.7	k = 2	-0.81	2.2
NIST	41.57	0.39	k = 2.31	-0.6	1.4
BAM (I.42)	42.29	0.26	k = 2	0.12	1.4
IRMM	42.92	0.36	k = 2	0.75	1.4
Key Comparison Reference Value (KCRV) by Mixture Median Model					
KCRV	42.17	1.32	k = 2		

B Equivalence Statements for Pilot Sample as Determined by Isotope Dilution

The *degrees of equivalence* for the P26.1 results are presented in Table 11. The metrics were calculated even though they should not be used to establish laboratory capability because this is a pilot study. It is remarkable that results for this 8 $\mu\text{g/g}$ sample are almost as good as those for K35, which is a factor of 5 higher in concentration.

Table 11. Degree of Equivalence for Pilot P26.1 by Isotope Dilution Mass Spectrometry

Participant	Mean ($\mu\text{g/g}$)	Expanded Uncertainty (U)	D_i ($\mu\text{g/g}$)	u_i ($\mu\text{g/g}$)	
Four Isotope Dilution Participants					
LGC	8.49	0.54	k = 2	-0.19	0.81
NIST	8.41	0.12	k = 2.23	-0.27	0.62
BAM (I.42)	9.03	0.62	k = 2	0.35	0.87
IRMM	8.91	0.36	k = 2	0.23	0.71
Reference Value (RV) by Mixture Median Model					
RV	8.68	0.61	k = 2		

C Equivalence Statements for Laboratories Participating in Pilot Study Only

The degrees of equivalence were also calculated for the methods other than isotope dilution in Table 12 for both the K35 and P26.1 samples. The reference values for comparison were taken to be the values determined by isotope dilution.

Table 12. Reproducibility for Laboratories Participating in Pilot Study Only

Participant	Mean ($\mu\text{g/g}$)	Expanded Uncertainty (U)	D_i ($\mu\text{g/g}$)	u_i ($\mu\text{g/g}$)	
K35 Key Comparison Reference Value (KCRV) by Mixture Median Model					
KCRV	42.17	1.32	k = 2		
BAM (I.22)	40.21	0.86	k = 2	-2	1.6
CENAM	42.44	1.05	k = 2.23	0.27	1.6
NIST	42.46	0.67	k = 2	0.29	1.5
P26.1 Reference Value (RV) by Mixture Median Model					
RV	8.68	0.61	k = 2		
BAM (I.22)	8.17	0.44	k = 2	-0.51	0.75
CENAM	8.68	0.78	k = 2.23	0.0	0.93
NIST	8.47	0.22	k = 2	-0.21	0.65

9 Discussion

The agreement among all laboratories, including the ones using methods other than isotope dilution, is very good as evidenced by the *degrees of equivalence* (Tables 10 and 11) and reproducibility (Table 12). A common calibration material for the isotope dilution determinations removed a potential source of bias, but this effect cannot be assessed without performing the same experiment devoid of a common calibration material. For all 14 cases presented in these three tables, D_i and reproducibility were better than 2 $\mu\text{g/g}$, in 13 cases it was better than 1 $\mu\text{g/g}$, and in 9 cases it was better than 0.5 $\mu\text{g/g}$. This degree of agreement (equivalence and reproducibility) indicates that reproducible measurements of sulfur in distillate fuel can be achieved in the 8 $\mu\text{g/g}$ to 42 $\mu\text{g/g}$ range by all these laboratories

The statement above is based on a 2004 presentation by the US EPA which stated Δ Current reproducibility of the test methods in ASTM (American Society for Testing and Materials) Ultra Low Sulfur Diesel (ULSD) Inter-laboratory Cross Check Program (ILP) is greater than 2 $\mu\text{g/g}$ for 15 $\mu\text{g/g}$ sample.¹³ The data from this EPA presentation has been tabulated in Table 13 along with the ranges of the data observed in this study. In all 14 cases the data from this study fall within the 2.57 value, which is the smallest value from the 2004 ILP study, and in 13 out of 14 cases the values are well within this ILP limit by a factor of 3 or better. The US EPA believes that diesel fuel certified reference materials with uncertainties less than 1 $\mu\text{g/g}$ are needed to implement the new sulfur regulations.^{7,13}

The two laboratories that used XRF techniques displayed uncertainties at least 7 times smaller than the 2.57 value. This indicates that the goal of the EPA to have reproducibility at 2 $\mu\text{g/g}$ or better in ULSD is realistic and achievable.¹³ Furthermore, the reproducibility of XRF for the P26.1 sample was better than 1 $\mu\text{g/g}$. A sulfur concentration of approximately 8 $\mu\text{g/g}$ is near the projected value that refineries in both the EU and the US will need to meet in order to be below the regulatory limit of 10 $\mu\text{g/g}$ and 15 $\mu\text{g/g}$ at the retail filling stations.

In Figures 1, 2, and 3 the means from the four laboratories using isotope dilution fall within the error bars for the KCRV and RV produced by the MM model suggesting excellent agreement among all participants within the limitations of the precision. This is, in fact, an artifact that results from the small number of determinations. The standard deviation of the four determinations for K35 in Figure 1 is 0.71 $\mu\text{g/g}$, and the uncertainty bar is 1.32 or equivalent in magnitude to 1.85 standard deviations. Likewise, the standard deviation of the four determinations for P26.1 is 0.29 $\mu\text{g/g}$ and the uncertainty bar is equivalent in magnitude to 2 standard deviations. The maximum z-score (or Grubb statistic) for $n=4$ is only 1.5^{14,15} which means no datum will be more than 1.5 standard deviations from the average value. Therefore, the inclusion of all four means within the uncertainty of the KCRV and RV is to be expected and does not

negate the possibility that an extreme value could be an outlier. What criterion to use in this case is for now an open question, but one that is being studied.¹⁵

Table 13. Reproducibility of Methods from ASTM Round Robin, Inter-Laboratory Cross Check Program, and CCQM Study (Units for numerical values are $\mu\text{g/g}$ sulfur)

Method	2002 RR	2004 ILP	2005 CCQM $\Delta 10 \mu\text{g/g@}$	2005 CCQM $\Delta 40 \mu\text{g/g@}$
Results from RR and ILP on $15 \mu\text{g/g}$ Diesel Fuel ¹				
D5453	6.26	3.94		
D3120	8.07	2.57		
2622-03		5.92		
Results from CCQM K35 and Pilot 26.1 ²				
IDMS			-0.27 to 0.35	-0.81 to 0.75
XRF, Combustion			-0.51 to 0.0	-2 to 0.29

¹ Data from reference 13. ² The range in reproducibility is given for the data in Tables 9-11. There were 4 IDMS determinations, 2 determinations by XRF, and 1 determination by a combustion technique.

Figure 5 is a presentation of all the D_i values for the isotope dilution data and the data from the three laboratories participating in the concurrent pilot study. Deviations from the KCRV and RV expressed in percent are plotted on the ordinate, and the concentrations of the test samples are plotted on a log scale along the abscissa. NIST and LGC track each other over a range of about three orders of magnitude of sulfur concentration. Three laboratories (NIST, LGC, and BAM) agree at the highest level where blank effects are negligible, but where a miss-calibration of their respective spikes should be resolvable. The data show an increasing divergence from the reference values as the sulfur level decreases and uncertainty in the blank becomes progressively bigger. The data from IRMM are consistently more elevated than all the other laboratories except at the lowest level. The three sets of data from the laboratories participating in the pilot study are plotted as open symbols to the right of the KCRV and RV values. These data are in good agreement with the reference values as evidenced by the fact that 6 of the 7 values fall within the uncertainties for the reference values.

Deviations of Means Relative to KCRV or RV as Determined by MM Model

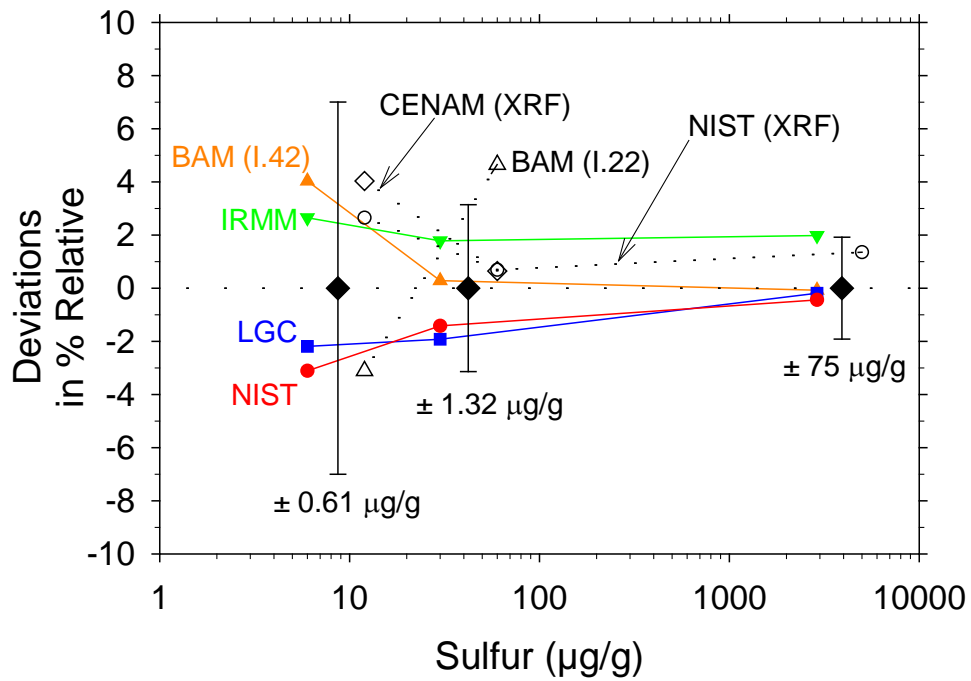


Fig. 5. Deviations of IDMS and pilot laboratory means in relative percent from the calculated KCRV and RV values as determined by the MM model. The IDMS deviations are plotted to the left and the pilot laboratory values (open circles) are plotted to the right of the KCRV and RV (filled diamonds) values for clarity. The absolute uncertainties as determined from the IDMS data for the three samples are below the lower tails of the relative uncertainties.

10 Acknowledgment

The authors wish to thank Bruce S. MacDonald of the NIST Standard Reference Materials Program for coordinating the production of K35 unknown and for supplying the other samples for this study. David L. Duewer of the NIST Analytical Chemistry Division generously shared data analysis techniques that he is developing. WRK thanks James J. Filliben of the NIST Statistical Engineering Division (SED) for several helpful discussions on both statistical and deterministic topics. Alan N. Heckert of SED gave invaluable help on the nuances of DATAPLOT.

Annex A - Protocol Letter

Annex B - Technical Protocol

Annex C - Summary Sheet

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Annex A – Protocol Letter of November 13, 2003



November 14th, 2003

**Ref: CCQM-K35 and P26.1
Laboratory Identification No. 2**

Dear CCQM-K35 and P26.1 Participant,

Enclosed are the comparison protocols and a combined set of samples for Key Comparison CCQM-K35 (Low Sulfur in Diesel Fuel) and pilot study CCQM-P26.1 (Very Low Sulfur in Kerosene). Both fuels are middle petroleum distillates and are, for the purpose of these exercises, identical except for their sulfur mass fractions. Two single page summary sheets are also included for reporting your results and should accompany your final report.

The K35 and P26.1 sample set consists of eight ampoules of the CCQM comparison sample, eight ampoules of the CCQM pilot sample, two ampoules of SRM 3154 (Sulfur Standard Solution) and two ampoules of SRM 1624d.

While the protocols focus on isotope dilution mass spectrometry as the analysis method for sulfur, participation is open to any method participants wish to employ. Please refer to the protocol sheets for reporting instructions applicable to all analysis methods.

This letter, the protocols and the summary reporting sheets have also been e-mailed to you as PDF files where possible. **Please, let me know promptly by FAX or e-mail when you have received the samples.** If the samples have not arrived within seven days of the aforementioned e-mail, please contact me without delay so that the sample shipment can be tracked and expedited to you.

Please return your summary sheet and the results report to me by post, e-mail or fax **no later than March 31st, 2004.**

Thank you for your participation in this CCQM exercise.

Yours sincerely,

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Annex B – Technical Protocol



CCQM-K35 – Low Sulfur in Fuel Key Comparison

Technical Protocol

Introduction

This key comparison is intended to document the capability of National Metrological Institutes (NMIs) to accurately meet the current and near-future regulatory limits on low sulfur concentrations in fuel, in particular the middle petroleum distillate products, diesel fuel (gas oil) and kerosene.

The sulfur content of diesel fuel is being lowered via a staged process by petroleum producers around the world to enable extremely efficient and long-lived after-treatment emission technologies, primarily catalytic converters. The need for these after-treatment systems is being nationally and internationally mandated by regulatory actions seeking to reduce the level of nitrogen oxides and non-methane organic gases which are the primary emission pollutants from internal combustion engines. Fuel sulfur is the principal poison affecting the sophisticated catalytic and on-board diagnostic systems that are central to this advanced technology. As the requirements for reducing these emissions become more severe, the EC, for example, will implement a $50 \mu\text{g g}^{-1}$ sulfur limit in fuel by 2005 to be followed by further reductions by 2009. The USA has called for a limit of $15 \mu\text{g g}^{-1}$ S by 2007.

These levels of S pose a significant analytical challenge and the $\approx 40 \mu\text{g g}^{-1}$ S samples will provide an important benchmark of national capabilities for accurate measurements at these low levels.

Samples

- *Distribution:* The participants will be informed by email/fax of the date of shipment. Participants are required to confirm the receipt of the sealed samples. In the event of any damage to the packaging or the samples, NIST should be informed immediately.
- *Materials:* Participants will be supplied with 3 sets of ampouled materials.

<u>Type of Material</u>	<u>Number of Ampoules</u>	<u>Approximate Concentrations</u>	<u>Remarks</u>
K35	8	$\approx 40 \mu\text{g g}^{-1}$	Unknown for Key Comparison
SRM 3154	2	$10.30 \pm 0.03 \text{ mg g}^{-1}$	Sulfur Spike calibrant
SRM 1624d	2	$\approx 4000 \mu\text{g g}^{-1}$	Blank insensitive check sample

- *Packaging, labelling, and opening of ampouled materials:* The following information is provided on the label of the Key Comparison solutions: **CCQM Key Comparison K35, S in Diesel Fuel ($\approx 40 \mu\text{g/g}$)**. Ampoules of SRM 3154 and SRM 1624d are identified by standard NIST labels. All materials have been sealed in amber glass ampoules with pre-scored necks to guard against sample loss due to volatility. To open an ampoule, first carefully wipe the necked section of the stem with a clean, damp cloth. Then wrap the body of the ampoule in a clean, absorbent material and, holding the body of the ampoule steady, grasp the stem with thumb and forefinger. Apply minimal thumb pressure to snap the stem at the scoring. The origin and purity of the material used for the preparation of CCQM-K35 and SRM 1624d will be provided in the final summary report at the conclusion of this exercise.
- *Handling and storing instructions:* Each ampoule should be opened for the minimum time required to dispense the material. Once an ampoule is opened, the material must be used within a period of 8 h to avoid any significant change in sulfur content. Unopened ampoules may be stored under normal laboratory conditions away from direct sunlight.

Methods of measurement

While participants are free to choose their method of measurement, isotope dilution mass spectrometry is the suggested method of analysis due to its high sensitivity and potential for highly accurate results.

The sulfur isotopic spikes (or any calibration solutions used in analyses by non-IDMS methodologies) should be calibrated to SRM 3154, a sulfur assay standard. Two ampoules are included for this purpose. If another assay material is used, please document the basis for its assay value.

Eight ampoules of K35 have been sent to each participant, however only six (6) need be analyzed. The two extra ampoules are to be held in reserve and can be used in the event of difficulties.

Two ampoules of SRM 1642d are also included as blank insensitive control samples. Only one set of two independent sample measurements of this material need be done in the context of the two CCQM exercises, Key Comparison K35 and the Pilot Study P26.1. The results of these measurements can be reported on either the K35 or the P26.1 summary sheets.

Reporting

In order to allow a detailed documentation and interpretation of the comparison data, all participants are requested to fill out the attached summary sheet as completely as possible. In particular, please note that you are requested to list, on the summary sheet, the six independent measurements made on K35 and the two independent

measurements of SRM 1624d. In order to avoid round-off errors, please supply a sufficient number of significant figures for these values that are commensurate with two significant figures in the uncertainty of the mean values as defined by one standard deviation of the six independent measurements. Thus, for example:

39 ± 1		Insufficient Significant Figures
38.7 ± 0.7		Insufficient Significant Figures
38.73 ± 0.71		This is a sufficient number of significant figures
38.7 ± 1.4		This is also a sufficient number of significant figures in the event of a larger standard deviation

In addition, a written report should be included, containing but not limited to:

- a detailed description of the method of measurement.
- information about sample preparation (e.g. acids used, digestion methods, spike origin and characterization, special sample handling procedures)
- a description of the analytical instrumentation used (e.g. type, technical specifications)
- information about the materials used for calibration of the analytical instrumentation (origin, purity, isotopic ratio if necessary) or any other material used during the analytical procedure
- a complete description of the data reduction process including all equations and corrections (e.g. blanks and interferences).
- the identification and quantification of all uncertainty sources (list or table)
- a description of the complete uncertainty budget. This must include the complete specification of the measurand.
- the calculation of the combined standard uncertainty u_c (complete formula) and information on the number of effective degrees of freedom

Key Comparison Reference Value (KCRV)

The KCRV value resulting from the IDMS measurements will be given in $\mu\text{g g}^{-1}$ and mol g^{-1} including an uncertainty statement.

Proposed time schedule

The samples will be distributed to participants towards the end of November 2003. The measurement results must be returned to NIST by March 31st, 2004. The results of this key comparison will be collated, analyzed and presented at the spring 2004 meeting of the Inorganic Working Group in Paris.

Participants

Participation in the CCQM Key Comparison is limited to institutes that are listed in Appendix A of the CIPM-MRA and are from countries which are members of the Metre Convention. The results of these institutes will appear in the BIPM key comparison database (KCDB).

In the very special case where an Appendix A listed institute underpins its measurement capabilities, which are within the scope of the comparison, by subcontracting measurements to a specialized institute within its country (namely one with INAA facilities), this specialized institute may participate in the Key Comparison along side its contracting Appendix A listed institute. Criteria related to sub-contracting are now being developed by the BIPM for approval by the JCRB and the CIPM.

NIST, as the coordinating laboratory and with the agreement of the CCQM Inorganic Analysis Working Group, has expanded this exercise and will run a CCQM pilot study on the same samples in parallel to the Key Comparison (see CCQM - P26.1 Protocols). CIPM-MRA Appendix A listed NMIs and designated institutes that are members of the Metre Convention may participate in the pilot study. Other expert institutes, from countries that are members of the Metre Convention, may participate in the pilot study if their contribution has added scientific value and is agreed by the coordinating laboratory and they have the agreement of their appropriate national institute listed in Appendix A of the CIPM-MRA. The process of nomination of expert laboratories for participation in the CCQM pilot study should be nationally coordinated. The results of the pilot study do not form part of the key comparison final report, but may be published separately provided all participants agree to this.

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Annex C – Summary Reporting Sheet



Summary Reporting Sheet for CCQM-K35 (Low Sulfur in Diesel Fuel)

1.0	Spike Isotopic Ratios¹	
1.1	$^{32}\text{S}/^{34}\text{S}$	
1.2	$^{33}\text{S}/^{34}\text{S}$	
1.3	$^{36}\text{S}/^{34}\text{S}$	
2.0	Spike Concentration²	
3.0	Unspiked K35 Isotopic Ratios¹	
3.1	$^{32}\text{S}/^{34}\text{S}$	
3.2	$^{33}\text{S}/^{34}\text{S}$	
3.3	$^{36}\text{S}/^{34}\text{S}$	
3.4	<i>Sulfur Atomic Weight K35</i>	
4.0	Unspiked SRM 3154 Isotopic Ratios¹	
4.1	$^{32}\text{S}/^{34}\text{S}$	
4.2	$^{33}\text{S}/^{34}\text{S}$	
4.3	$^{36}\text{S}/^{34}\text{S}$	
4.4	<i>Sulfur Atomic Weight SRM 3154</i>	
5.0	Unspiked SRM 1624d Isotopic Ratios¹	
5.1	$^{32}\text{S}/^{34}\text{S}$	
5.2	$^{33}\text{S}/^{34}\text{S}$	
5.3	$^{36}\text{S}/^{34}\text{S}$	
5.4	<i>Sulfur Atomic Weight SRM 1624d</i>	
6.0	Fractionation Correction Factor	

7.0	K35 Sample³ <i>Blank corrected</i>	$\mu\text{g/g}$	Sample Mass	Spike Mass
7.1	XX.XX Ampoule 1			
7.2	XX.XX Ampoule 2			
7.3	XX.XX Ampoule 3			
7.4	XX.XX Ampoule 4			
7.5	XX.XX Ampoule 5			
7.6	XX.XX Ampoule 6			
7.7	Measured blanks associated with K35			
8.0	SRM 1624d Sample³ <i>Blank corrected</i>	$\mu\text{g/g}$	Sample Mass	Spike Mass
8.1	XXXX.XX Ampoule 1			
8.2	XXXX.XX Ampoule 2			
8.3	Measured blanks associated with 1624d			
9.0	Mean value of K35			
9.1	Type A uncertainty⁴			
9.2	Type B uncertainty⁴			
9.3	Multiplier⁴			
9.4	Expanded Uncertainty⁴			
10.0	Mean value of 1624d			
10.1	1 sd			

Important Notes for filling out this table:

1. Indicate whether the measured isotopic ratios (Boxes 1.X, 3.X,4.X and 5.X) are corrected for a constant fractionation factor or not (C/U). If they are corrected, then indicate the factor in the Box 6.
2. Spike concentration values should be reported as $\mu\text{mol/g} \pm 1\text{sd}, n$; where n = the number of calibration measurements. Spike concentration values should be reported relative to the sulfur assay standard, SRM 3154
3. The number of significant figures to report for the sulfur concentration in each ampoule should be commensurate with two (2) significant figures in the uncertainty of the mean as defined by 1 standard deviation of the six independent measurements. See the written protocol for an example.
4. The values in boxes 9.0 through 9.4 summarize the result of the total uncertainty analysis which is itemized in the text of the report accompanying this summary sheet.

Participant Identification

name:
institute:
address:

country:
e-mail address:
telephone number:
fax number:

Signature: _____ Date: _____

Please return this sheet by fax no later than March 31st, 2004 to:

Dr. Robert Vocke
Spectrochemical Methods Group
Analytical Chemistry Division
National Institute of Standards and Technology
Fax: +01.301.869.0413



UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Gaithersburg, Maryland 20899-8391

Summary Reporting Sheet for CCQM-K35 (Low Sulfur in Diesel Fuel)

1.0	Spike Isotopic Ratios¹	
1.1	Spike R-4 Measured ³² S/ ³⁴ S	0.001733 U
1.2	³³ S/ ³⁴ S	0.000054 U
1.3	³⁶ S/ ³⁴ S	0.000011 U
2.0	Spike Concentration²	1.2212 μmol/g ±0.0010, n=9
3.0	Unspiked K35 Isotopic Ratios¹	
3.1	³² S/ ³⁴ S	22.6671 U
3.2	³³ S/ ³⁴ S	0.178311 U
3.3	<i>Not Meas. – Value assumed</i> ³⁶ S/ ³⁴ S	³⁶ S At% 0.00015
3.4	Sulfur Atomic Weight K35	32.0638
4.0	Unspiked SRM 3154 Isotopic Ratios¹	
4.1	³² S/ ³⁴ S	22.5528 U
4.2	³³ S/ ³⁴ S	0.176926 U
4.3	<i>Not Meas. – Value assumed</i> ³⁶ S/ ³⁴ S	³⁶ S At% 0.00015
4.4	Sulfur Atomic Weight SRM 3154	32.0642
5.0	Unspiked SRM 1624d Isotopic Ratios¹	
5.1	³² S/ ³⁴ S	21.8669 U
5.2	³³ S/ ³⁴ S	0.17219 U
5.3	<i>Not Meas. – Value assumed</i> ³⁶ S/ ³⁴ S	³⁶ S At% 0.00015
5.4	Sulfur Atomic Weight SRM 1624d	32.0668
6.0	Fractionation Correction Factor	Not measured but constant

7.0	K35 Sample³ Blank corrected	μg/g	Sample Mass	Spike Mass
7.1	XX.XX Ampoule 1	54.85	0.16288	0.16288
7.2	XX.XX Ampoule 2	54.84	0.26531	0.26531
7.3	XX.XX Ampoule 3	54.21	0.27326	0.27326
7.4	XX.XX Ampoule 4	54.26	0.23742	0.23742
7.5	XX.XX Ampoule 5	54.57	0.24820	0.24820
7.6	XX.XX Ampoule 6	54.77	0.26549	0.26549
7.7	Measured blanks associated with K35	0.073 μg 0.081 μg		0.30947 0.30113
8.0	SRM 1624d Sample³ Blank corrected	μg/g	Sample Mass	Spike Mass
8.1	XXXX.XX Ampoule 1	1453.85	0.14712	0.73256
8.2	XXXX.XX Ampoule 2	1454.84	0.18458	0.95301
8.3	Measured blanks associated with 1624d	0.132 μg 0.114 μg		0.10373 0.17869
9.0	Mean value of K35	54.58		
9.1	Type A uncertainty⁴	0.12		
9.2	Type B uncertainty⁴	0.08		
9.3	Multiplier⁴	2.18		
9.4	Expanded Uncertainty⁴	0.32		
10	Mean value of 1624d	1454.35		
10.1	1 sd	0.70		

Important Notes for filling out this table:

1. Indicate whether the measured isotopic ratios (Boxes 1.X, 3.X, 4.X and 5.X) are corrected for a constant fractionation factor or not (C/U). If they are corrected, then indicate the factor in the Box 6.
2. Spike concentration values should be reported as μmol/g ± 1sd, n where n= the number of calibration measurements. Spike concentration values should be reported relative to the sulfur assay standard, SRM 3154

3. The number of significant figures to report for the sulfur concentration in each ampoule should be commensurate with two (2) significant figures in the uncertainty of the mean as defined by 1 standard deviation of the six independent measurements. See the written protocol for an example.
4. The values in boxes 9.0 through 9.4 summarize the result of the total uncertainty analysis which is itemized in the text of the report accompanying this summary sheet.

Participant Identification

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