

Key Comparison CCQM - K35
Determination of Sulfur in Diesel Fuel

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Final Report
April, 2007

Abstract

The CCQM-K35 Key Comparison was organized by the Inorganic Analysis Working Group (IAWG) of the CCQM to test the capabilities of National Metrological Institutes (NMIs) to measure the sulfur content of diesel fuel at the $\approx 40 \mu\text{g/g}$ level. Four NMIs participated in the Key Comparison: the Federal Institute for Materials Research and Testing (BAM), the Institute for Reference Materials and Measurements (IRMM), the Laboratory of the Government Chemist (LGC), and the National Institute of Standards and Technology (NIST). NIST designed and coordinated the study. All four laboratories used isotope dilution mass spectrometric techniques, but two laboratories (BAM and NIST) used thermal ionization mass spectrometry (TIMS) and two laboratories (IRMM and LGC) used inductively coupled plasma mass spectrometry (ICP-MS). Both techniques require spiking and combustion of the sample prior to the instrumental determination to quantify the amount of sulfur in the fuels. The agreement among the laboratories was good as evidenced by the small values for both the equivalence statements ($D_i < 1 \mu\text{g/g}$) and the associated uncertainties ($u_i < 2.3 \mu\text{g/g}$).

A pilot study (P26.1) was performed concurrently on a kerosene sample at the $\approx 8 \mu\text{g/g}$ level and on the same diesel sample used in this K35 study by laboratories preferring to participate in the pilot study. The results of the pilot study are reported separately.

1 Introduction

The European Union (EU) and the United States (US) after June 2006 have both mandated the use of ultra-low sulfur diesel (ULSD) fuel for on-road use to make possible more efficient exhaust emission after-treatment technologies which will result in substantially reduced particulate emissions from diesel engines. The EU mandated a 10 µg/g sulfur limit in diesel starting in 2005, and the US will phase 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. Diesel fuel below 50 µg/g sulfur is commonly referred to as ULSD (Ultra-Low Sulfur Diesel) or near-zero diesel fuel. The production of ULSD is expensive for the petroleum industry, and is expected to result in an incremental increase in cost to the consumer. The sulfur content in ULSD will be monitored through the complete supply chain, and this will present a formidable measurement challenge.

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, and the two combined accounted for 46 % of the 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 "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 accounting for 87 % of the US 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 recently:

"...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) estimated the introduction of ULSD will

result in health and welfare benefits of about \$150 billion annually to the American public,⁷ and the *per capita* benefits in the EU should be similar. The national regulatory agencies and the petroleum industry look to the 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 future 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 content near the projected EU regulatory limit of 50 µg/g would be used as the Key Comparison material. A diesel sample was prepared by NIST at a sulfur level of approximately 40 µg/g for the K35 Key Comparison. A pilot study (P26.1) was performed concurrently on kerosene at the 8 µg/g level, and the results are presented in a separate report.

2 List of Participants

The Inorganic Analysis Working Group (IAWG) of the CCQM asked the US National Institute of Standards and Technology (NIST) to coordinate the pilot study. NIST designed the analytical protocol and compiled and analyzed the submitted data. NIST also procured, packaged, and distributed the fuel samples. On October 10, 2003, a letter of invitation to participate in the CCQM K35 Key Comparison was sent via Dr. Michael Sargent (LGC), Chairman of the Inorganic Analysis Working Group (IAWG), to its members (Annex A).

Four NMIs responded asking to participate in the K35 Key Comparison (Table 1). All four laboratories chose to use isotope dilution analysis mass spectrometry for the determinations. Laboratories 1 and 4 (BAM and NIST) used thermal ionization mass spectrometry (TIMS) and laboratories 2 and 3 (IRMM and LGC) used inductively coupled plasma mass spectrometry (ICP-MS).

Table 1. List of Participating National Metrology Institutes

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

3 Samples

Three NIST Standard Reference Materials (SRMs) were used in the K35 study. They are listed as the first two entries in Table 2. Two of the samples were diesel fuels, designated *K35 unknown* (SRM 2770) and *check sample* (SRM 1624d).

These two materials were candidate NIST SRMs which were to be certified using the data generated by NIST during the CCQM-K35 exercise. The third sample, SRM 3154, is a coulometrically titrated dilute sulfuric acid solution. It was included in the Key Comparison so that each laboratory could calibrate their sulfur spike against a common material. Details of these materials and their NIST certified values are listed in Table 2.

At the time these two diesel fuels were sent out to the participants, only approximate values of their sulfur concentrations were known by NIST. The check sample was a “No. 2-D” distillate fuel oil as defined by ASTM D 975-96a Standard Specification for Diesel Fuel Oils. This check sample was packaged in 100 mL amber bottles with screw caps. The K35 unknown was a custom blended sample prepared at NIST by gravimetry in a 55-gallon drum from a mixture of 0.8 % SRM 1624d (certified at $3882 \mu\text{g/g} \pm 20 \mu\text{g/g}$) and 99.2 % SRM 2723a (certified at $11.0 \mu\text{g/g} \pm 1.1 \mu\text{g/g}$) and packaged in 10 mL amber glass ampoules. The target value for the K35 unknown was $\approx 42 \mu\text{g/g}$ sulfur. Using the NIST certified values for the two end members, the predicted concentration for the K35 Unknown was calculated to be $41.99 \mu\text{g/g}$ with a 95 % confidence limit of $\pm 1.10 \mu\text{g/g}$.

Table 2. List of Samples Used in the K35 Comparison

| ¹ SRM | Mean ($\mu\text{g/g}$) | Uncertainty (U) ($\mu\text{g/g}$) | Sample Type |
|-------------------------------|--------------------------|-------------------------------------|-----------------------------|
| 2770 Sulfur in Diesel Fuel | 41.57 | 0.39 | K35 Unknown |
| 1624d Sulfur in Diesel Fuel | 3882 | 20 | Check Sample |
| Calibration Standard | | | |
| 3154 Sulfur Standard Solution | 10,300 | 30 | Calibration Standard |

¹ Dates of certification for SRMs were March 10, 2005 for SRM 2770 and April 26, 2005 for SRM 1624d.

All materials listed in Table 2 are assumed to be completely homogeneous because they are liquids, and there is no experimental evidence to suggest otherwise. The homogeneity of the parent material for the K35 unknown was verified by measuring the sulfur concentration of samples from the top, middle, and bottom of the 55-gallon drum before ampouling, and all three measurements were in excellent agreement. These samples are also considered to be stable during the time interval of the key comparison. Therefore, the uncertainty component for heterogeneity and stability is assumed to be zero.

4 Technical Protocol

The technical protocol is attached to this document as Annex B. The document, together with the Summary Sheet (Annex C) specified the manner in which the fuels were to be handled and when the specified measurement data were to be communicated to NIST.

The proposed time line for measurements and reporting was the following:

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

5 Methods of Measurement

The solicitation letter to IAWG members stated that “While the protocol focuses 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 other methods based on the combustion of fuel samples in oxygen to produce SO₂ which is then detected by UV or IR spectroscopy. All of these methods use external calibration as their accuracy base, and perform optimally when the matrices of the standards and unknown samples are matched exactly.

Four laboratories reported results by isotope dilution mass spectrometry. NIST and BAM used TIMS based on the well established arsenic sulfide technique.⁸ LGC and IRMM used a high resolution ICP mass spectrometric method (HR-ICPMS) similar to a technique originally described by LGC.⁹ All four laboratories used an enriched ³⁴S spike. Three calibrated their spike against the same calibration standard 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.

Table 3. Analytical Methods and Instrumentation

| Participant | Analytical Method | Instrumentation |
|-------------|-------------------|--------------------------|
| BAM | IDMS | TIMS – Multi-Collector |
| IRMM | IDMS | ICP-MS (Magnetic Sector) |
| LGC | IDMS | ICP-MS (Magnetic Sector) |
| NIST | IDMS | TIMS - Single Collector |

Table 4. Digestion Methods and Reagents

| Participant | Digestion Method | Reagents |
|-------------|---------------------|-------------------------------------------------|
| BAM | High-pressure asher | HNO ₃ /H ₂ O ₂ |
| IRMM | Microwave | HNO ₃ /H ₂ O ₂ |
| LGC | Microwave | HNO ₃ |
| NIST | Carius tube | HNO ₃ |

6 Results

The laboratories were sent eight ampoules and were asked to analyze at least six. Three laboratories submitted 6 determinations each and LGC submitted 11 determinations by taking duplicate samples from each ampoule (one datum was not reported). The isotopic ratios as determined by each laboratory are given in Table 5. The last entry is an absolute determination of the sulfur isotopic ratios based on a new double spike procedure.¹⁰

The results for the K35 unknown and the check sample are given in Tables 6 and 7. Table 9 gives a summary of the results for K35. The individual data together with the mean value and associated expanded uncertainty for each lab are shown in Figure 1. While the agreement among the laboratories was good, the mean value submitted by IRMM was marginally higher than the other three. The ³²S/³⁴S natural ratio reported by BAM for the K35 unknown was much lower than laboratories (see first entry in Table 5). Two other noteworthy observations on the reported uncertainties are: 1) The expanded uncertainty (U) reported by IRMM was smaller than the standard deviation for their data, and 2) the expanded uncertainty (U) reported by LGC appears to be much larger, even taking their data spread into account, than the other NMIs (see Figure 1).

Table 5. Natural Isotopic Ratios in Samples and Calculated Atomic Masses

| Key Comparison K35 Unknown | | | | |
|------------------------------|-------------------------------|-------------------------------|---------------------------------|-------------|
| Laboratory | $^{32}\text{S}/^{34}\text{S}$ | $^{33}\text{S}/^{34}\text{S}$ | $^{36}\text{S}/^{34}\text{S}^1$ | Atomic Mass |
| 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 Standard | | | | |
| BAM | 22.555 | 0.17779 | 0.0035 | 32.0642 |
| IRMM | Not Reported | | | |
| LGC | Not Reported | | | |
| NIST | 22.5528 | 0.17693 | 0.015 % | 32.0642 |
| ² NIST (Absolute) | 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).

Table 6. Results for Sulfur in K35 by Isotope Dilution Mass Spectrometry

| Participant | Method | Reported Value ($\mu\text{g/g}$) | Expanded Uncertainty ($\mu\text{g/g}$) | k Value |
|-------------|----------|------------------------------------|------------------------------------------|---------|
| BAM | 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 |

CCQM K35

Key Comparison Reference Value computed using Labs 1-4.

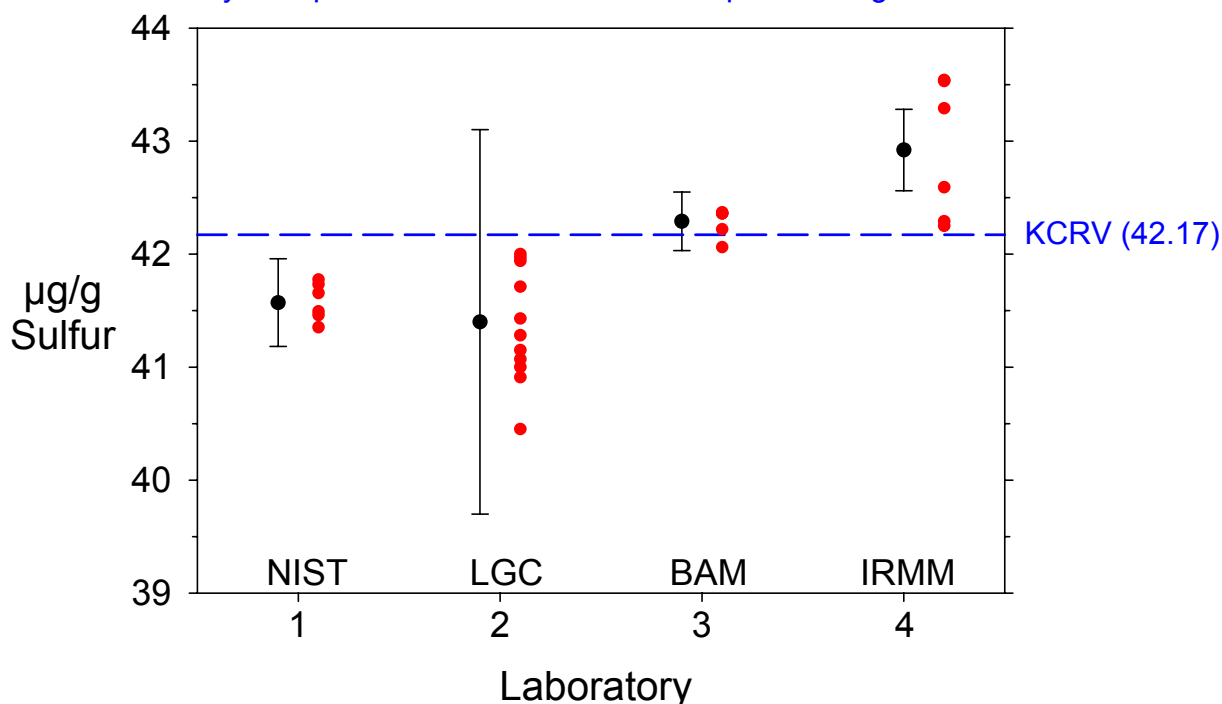


Figure 1. Plot of the individual determinations for K35 together with the means and reported expanded uncertainties from the four Key Comparison participants. The dashed horizontal line represents the mixture model median of the four laboratories.

The results for the check sample are given in Table 7 and plotted in Figure 2. Each laboratory received two bottles containing 100 mL of diesel fuel with a nominal sulfur concentration of 4000 µg/g. Due to the high level of sulfur in this sample, it was essentially insensitive to variations in blank and instrumental background and could therefore serve as a check on differences in calibration, chemical processing, and measurement. The last report of measurements on this material was received at the end of September 2004. There is good agreement among the first three laboratories, but IRMM is about 2 % higher than the mean of the other three. However, the IRMM mean value passes the Grubbs¹¹ outlier test at a rejection level of 95 % ($\alpha=0.05$).

Table 7. Results for Check Sample by IDMS

| Participant | Method | Reported Value (µg/g) | One standard deviation µg/g (n) |
|-------------|----------|-----------------------|---------------------------------|
| BAM | ID-TIMS | 3895 | 6 (2) |
| IRMM | ID-ICPMS | 3976 | 22 (4) |
| LGC | ID-ICPMS | 3908 | 34 (4) |
| NIST | ID-TIMS | 3882 | 17 (6) |

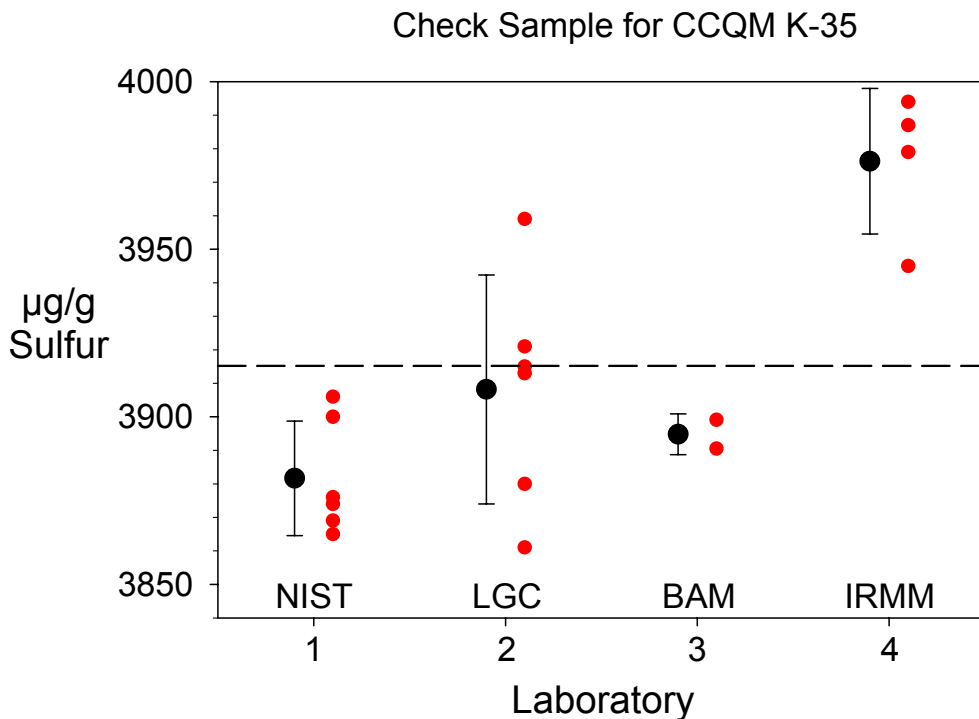


Figure 2. Plot of the individual data for high sulfur check sample together with the means and the standard deviations from the four Key Comparison participants. The dashed horizontal line is the mean (3915 µg/g) calculated from the reported means (black filled circles) of the four laboratories.

The reported blanks are listed in Table 8 below. The number of blanks to be determined was not specified in the protocol.

Table 8. Chemical Blanks Determined by Each Participant

| Participant | Blanks (µg/g S) | Comments |
|-------------|-------------------------------|-----------------------------------------------------------------|
| BAM | Mean = 0.082 n = 5 | Individual values were not reported |
| IRMM | Mean = 0.112 | 2 blanks were determined with each batch of 4 samples |
| LGC | No values reported | Unspiked blanks prepared and raw counts subtracted from samples |
| NIST | Set 1 = 0.097 Set 2 = 0.17 | One blank determined with each set of 3 samples |

7 Estimation of Key Comparison Reference Value (KCRV) for K35

Candidate Key Comparison Reference Values were calculated by a variety of statistical methods and are displayed in Figure 3. The first six (black and green color) were calculated using Dataplot.¹² The first three estimators should not be used unless the number of laboratories is greater than 5. The two estimates in blue were calculated using a statistical approach developed by Duewer.¹³ The submitted data are plotted to the right of the dashed line. 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. For n=6 the expanded uncertainty (black bar), expressed as a 95 % confidence interval, must be equal to or greater than one standard deviation (red bar). How much greater it is depends on the relative magnitude of the type B uncertainty components.

Three different estimates of the KCRV and the associated uncertainties are listed in Table 9. At the Fall 2004 IAWG meeting at CENAM (Mexico), it was decided to use the Mixture Model (MM) median¹³ for the final KCRV value. The values from the three

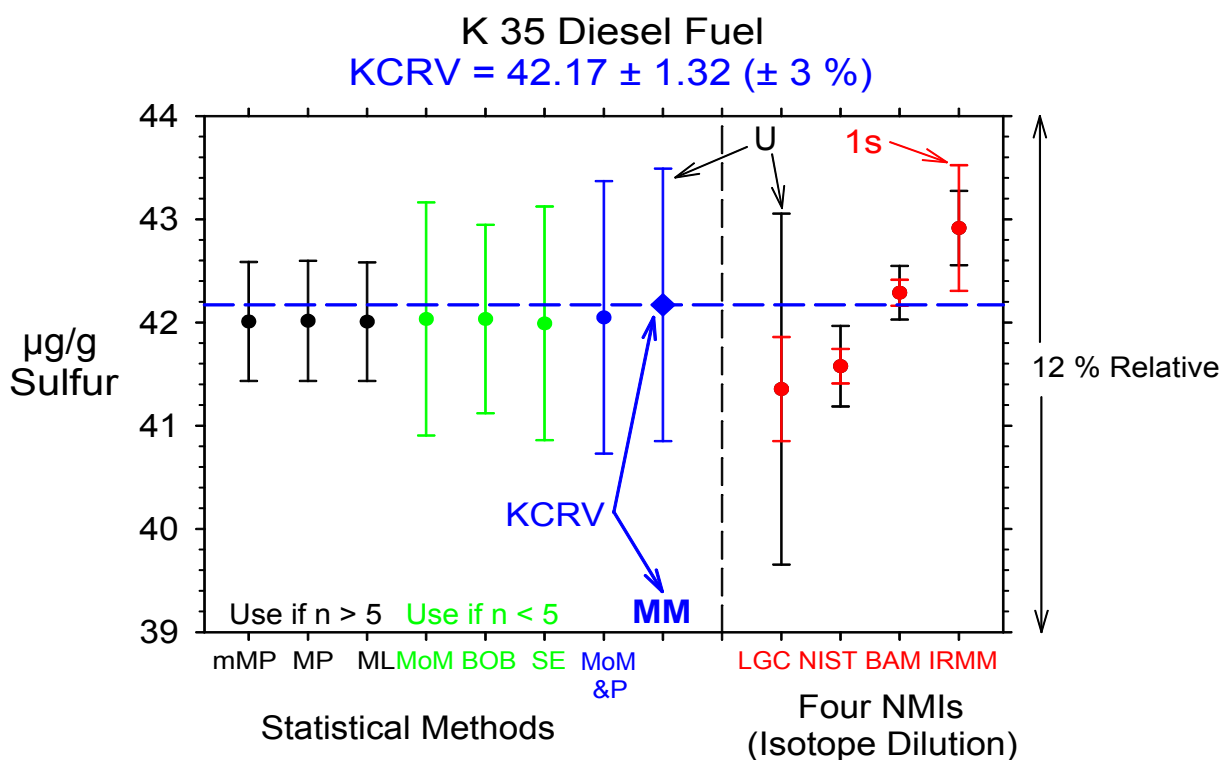


Figure 3. Plot of different model approaches for the estimation of the KCRV. To the right of the vertical dashed line are the means and associated uncertainties (U) submitted by the four laboratories. The 1s error bars were calculated from the individual measurements. mMP = Modified Mandel Paule, MP = Mandel Paule, ML = Ruhkin Vangel Maximum Likelihood, MoM = Mean of Means, BOB = Type B on Bias, SE = Schiller Eberhardt, MoM&P = Mean of Means & Pooled uncertainties, MM = Mixture Model median.

different models are essentially identical, and there are only small differences in uncertainties.

Table 9. KCRV and Uncertainty from Three Statistical Models

| Statistical Model | KCRV µg/g | U µg/g |
|----------------------------------|--------------|-------------|
| Mean of Means (MoM) | 42.05 | 1.11 |
| MoM and Pooled U | 42.05 | 1.32 |
| Mixture Model (MM) median | 42.17 | 1.32 |

8 Equivalence Statements

Equivalence statements were calculated for each of the four laboratories that participated in the K35 according to the following expressions:

$$D_i = (x_i - x_R)$$

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

where D_i is the difference in µg/g between the laboratory mean value, x_i , and the KCRV, x_R . The degree of equivalence uncertainty, U_i , for each laboratory is the combined uncertainty of the KCRV with that for each laboratory. A value of 2 was used for both k_i and k_R in all calculations. Therefore, all laboratories are compared on an equal basis. The equivalence statements for K35 are presented in Table 10. It is noteworthy that D_i is less than 1 µg/g in all four cases and that u_i is 1.4 µg/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 contribution which is equal to 1.3. LGC's expanded uncertainty is suspected of being overestimated; it is substantially larger, about a factor of 5, than that of the other three participants.

Table 10. Degrees of Equivalence for Key Comparison K35

| Participant | Mean ($\mu\text{g/g}$) | Expanded Uncertainty (U) | | D_i ($\mu\text{g/g}$) | U_i ($\mu\text{g/g}$) |
|-------------------------------------------------------------------------------|--------------------------|--------------------------|------------|---------------------------|---------------------------|
| LGC | 41.36 | 1.7 | k=2 | -0.81 | 2.2 |
| NIST | 41.57 | 0.39 | k=2.31 | -0.60 | 1.4 |
| BAM | 42.29 | 0.26 | k=2 | 0.12 | 1.4 |
| IRMM | 42.92 | 0.18 | k=2 | 0.75 | 1.4 |
| Key Comparison Reference Value (KCRV) by the Mixture Model (MM) median | | | | | |
| KCRV | 42.17 | 1.32 | k=2 | | |

9 Discussion

The agreement among the results reported by all laboratories is quite good. This is corroborated by the equivalence data presented in Table 10. Degrees of equivalence less than 1 $\mu\text{g/g}$ or less than 2 % relative for all laboratories suggest that reproducible measurements of sulfur in distillate fuel can be achieved in the 42 $\mu\text{g/g}$ range by these laboratories.

Tables 11 and 12 give the relative differences between the four laboratories taken two at a time. For the K35 sample only LGC and NIST had agreement less than 1 %. For the check sample at a sulfur concentration about 10 times higher, three laboratories agreed to better than 1 %, while IRMM differed from the other three laboratories by about 2 %. These values for differences are relatively small compared to other techniques used in a recent European round-robin consisting of 69 laboratories in nine countries.¹⁴ The reproducibilities at 42 $\mu\text{g/g}$ for diesel fuel for the following four techniques, WDXRF, EDXRF, UV-fluorescence, and microcoulometry, were calculated to be 7 %, 3 %, 11 %, and 17 %, respectively (see Table 3 of Ref. 14). Essentially the same values are calculated at the 3900 $\mu\text{g/g}$ level.

It is clear that the isotope dilution determination of sulfur in diesel fuel at the 42 $\mu\text{g/g}$ is superior to other techniques employed in both Europe and the US as evidenced by the experimental data in the above comparison. However, the differences between NMIs employing isotope dilution should be less than 1 %. The smaller differences among three of the NIMIs for the check sample (see Table 12) compared to the K35 sample (see Table 11) may be a result of the relatively large influence of chemical blank that exists at the lower level, but is negligible at the higher level. The large difference between IRMM and the other three NMIs for the check sample may indicate a differential bias in spike calibration.

Table 11. ¹Relative Differences between Laboratories in Relative % for the K35 Unknown at the 42 µg/g Sulfur Level

| | LGC | NIST | BAM | IRMM |
|------|------|------|------|------|
| LGC | | 0.5 | 2.2 | 3.7 |
| NIST | -0.5 | | 1.7 | 3.2 |
| BAM | -2.2 | -1.7 | | 1.5 |
| IRMM | -3.7 | -3.2 | -1.5 | |

¹ Differences of less than 1 % are indicated by green shading; differences greater than 1 % are indicated by yellow shading.

Table 12. ¹Relative Differences between Laboratories in Relative % for the Check Sample at the 3900 µg/g Sulfur Level

| | LGC | NIST | BAM | IRMM |
|------|------|------|------|------|
| LGC | | -0.7 | -0.3 | 1.7 |
| NIST | 0.7 | | 0.3 | 2.4 |
| BAM | 0.3 | -0.3 | | 2.1 |
| IRMM | -1.7 | -2.4 | -2.1 | |

¹ Differences of less than 1 % are indicated by green shading; differences greater than 1 % are indicated by yellow shading.

10 Acknowledgments

The authors would like 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.

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Annex B – Technical Protocol, Page 16

Annex C – Summary Sheet, Page 21

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Annex A – Protocol Letter of November 14, 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



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

| | | |
|-----|-------------------------------------------------------------------|------------------------------------------------|
| 1.0 | Spike Isotopic Ratios¹ | |
| 1.1 | Spike R-4 Measured $^{32}\text{S}/^{34}\text{S}$ | 0.001733 U |
| 1.2 | $^{33}\text{S}/^{34}\text{S}$ | 0.000054 U |
| 1.3 | $^{36}\text{S}/^{34}\text{S}$ | 0.000011 U |
| 2.0 | Spike Concentration² | 1.2212 $\mu\text{mol/g}$ ± 0.0010 , n=9 |
| 3.0 | Unspiked K35 Isotopic Ratios¹ | |
| 3.1 | $^{32}\text{S}/^{34}\text{S}$ | 22.6671 U |
| 3.2 | $^{33}\text{S}/^{34}\text{S}$ | 0.178311 U |
| 3.3 | <i>Not Meas. – Value assumed</i> $^{36}\text{S}/^{34}\text{S}$ | ^{36}S At% 0.00015 |
| 3.4 | Sulfur Atomic Weight K35 | 32.0638 |
| 4.0 | Unspiked SRM 3154 Isotopic Ratios¹ | |
| 4.1 | $^{32}\text{S}/^{34}\text{S}$ | 22.5528 U |
| 4.2 | $^{33}\text{S}/^{34}\text{S}$ | 0.176926 U |
| 4.3 | <i>Not Meas. – Value assumed</i> $^{36}\text{S}/^{34}\text{S}$ | ^{36}S At% 0.00015 |
| 4.4 | Sulfur Atomic Weight SRM 3154 | 32.0642 |
| 5.0 | Unspiked SRM 1624d Isotopic Ratios¹ | |
| 5.1 | $^{32}\text{S}/^{34}\text{S}$ | 21.8669 U |
| 5.2 | $^{33}\text{S}/^{34}\text{S}$ | 0.17219 U |
| 5.3 | <i>Not Meas. – Value assumed</i> $^{36}\text{S}/^{34}\text{S}$ | ^{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 | $\mu\text{g/g}$ | 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 | $\mu\text{g/g}$ | 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 $\mu\text{mol/g} \pm 1\text{sd}$, 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

| | |
|-----------------|-------------------------------------------|
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