# ASTM D5453

## FITNESS FOR USE STUDY

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# UPDATE: May, 1999

Since the completion of this report, the U.S. EPA has announced its proposed rulemaking for Tier 2 Legislation concerning gasoline and diesel specifications. This Tier 2 Legislation has lowered the sulfur levels in fuels from their previously regulated specifications. **Due to these new levels, the estimates in Table 5B on page 8 of this D 5453/SWRI document can now be updated to read as follows**:

**Table 5B: Auto Fuels Directive (North America)**

Preliminary regulatory sulfur limits for future fuels in mg/kg;
(California position figures in brackets)

| | Year 2000 | Year 2004 | Year 2008 |
|---|---|---|---|
| RFG/GC | 150* (30) | 30 (<5) | <5 (<5) |
| Diesel | 150* (300) | 30 (30) | <5 (<5) |
| | estimated | estimated | estimated |

* 150 ppm or less to earn credits in the ABT system

These motor fuels sulfur reductions are significant! However, the EPA believes they are obtainable, and it will enforce their compliance. To accomplish this, the U.S. EPA is investigating better and more accurate ways to measure these lower sulfur specification. The current primary EPA sulfur enforcement method, ASTM Method D 2622, is not capable of measuring accurately in the lower ranges (determined by the EPA and CARB 1996 in the California fuels market). The U.S. EPA is currently requesting comments on whether ASTM Method D 5453 (sulfur by UV) should become the primary test method for the analysis of sulfur in gasoline and diesel fuels. The accuracy, efficiency and cost savings of D5453 can in itself benefit the users and their organizations. Refiners, blenders and importers that participate in the Averaging, Banking and Trading (ABT) system can use D 5453 capabilities to earn credits as lower sulfur content in motor fuels continue to be mandated.

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## EXECUTIVE SUMMARY


Mandatory production of very low sulfur content motor fuels is forcing refiners and regulators to reevaluate sulfur measurement technology. Regulators are considering a "performance based testing" approach[1] which requires that a "fitness for use" or an "equivalency" criterion be established for report and control analysis. This report provides an extensive examination of the three dominant ASTM total sulfur technologies used for regulatory purposes in petroleum sulfur testing, D 5453 ultraviolet fluorescence[2], D 2622 wavelength dispersive X-ray[3], and D 4294 energy dispersive X-ray[4]. Each method is examined in fuels at less than 0.0500 mass %, or 500 mg/kg sulfur.

**Report findings:**

1. All three ASTM sulfur test methods demonstrate equivalence for measurements in the 150-500 mg/kg (ppm wt/wt) range. D 5453 and D 2622 demonstrate an equivalent fitness for use down to 20 mg/kg. After a rigorous examination of level of detection (LOD) and level of quantification (LOQ) capabilities, strong evidence was found that D 5453 can be fit-for-use in multi-laboratory situations down to 1.0 mg/kg. Evidence was also developed which indicates that a single laboratory can use the D 5453 methodology for sulfur determinations less than 1.0 mg/kg.
2. A single isooctane matrix was used to minimize the well-known carbon to hydrogen ratio interference for the X-ray based test methods. All three test methods were then evaluated for any bias with regard to 24 commonly occurring compounds. No bias (accuracy was within the precision limits for each of the test methods) was found.

Of the three test methods, the best low-level precision and accuracy capabilities were found in D 5453 and D 2622. **Of these two, D 5453 generates better data in the lowest levels, below 50 mg/kg.**


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## INTRODUCTION

The fitness-for-use of analytical methods for the determination of sulfur content is increasingly at issue as the production and use of low-sulfur fuels is regulated. In this study, the ASTM test methods D 2622, D 4294, and D 5453 were evaluated for use in hydrocarbon fuels containing sulfur less than 500 mg/kg. The sulfur limits considered here include the motor fuel limits for California and for years 2000 and 2005 in the European community. Lower sulfur measurement levels needed for successful blending and transport were also considered. Sulfur, at levels less than fifty (50) mg/kg, is already regulated in gasoline and diesel fuels used within certain areas of Europe, North America, and other parts of the world.

**Sulfur in Hydrocarbon Fuels**

- **D5453**
- D2622
- D4294

• **EQUIVALENCY** – Each test method was evaluated for analytical range by concentration. Examination of recent ASTM laboratory cross-check program results and data generated from analysis of gravimetrically prepared materials found that all three ASTM sulfur test methods demonstrate equivalence for measurements in the 150-500 mg/kg (ppm wt/wt) range. D 5453 and D 2622 demonstrate an equivalent fitness for use down to 20 mg/kg. D 5453 was found fit for use down to 1.0 mg/kg. These new stringent sulfur content fuel requirements mean that the dispersive X-ray methods, D 4294 and D 2622, may no longer be useful for certain regulated fuel species.

• **BIAS** – Each of the above test methods was also evaluated for any bias with regard to common sulfur-containing compounds. The compounds used for the study included sulfides, disulfides, thiols, thiophenes, benzothiophenes, and a thionaphthene. The well-known carbon to hydrogen ratio interference, for the X-ray based test methods, was minimized by the use of a single isooctane matrix. No bias (accuracy was within the precision limits for each of the test methods) was found.

• **FITNESS-FOR-USE** – Further evaluation of the ASTM cross-check program and the gravimetric bias study revealed that the best low-level precision and accuracy capabilities were found in the D 5453 and D 2622 test methods. Of these, D 5453 had the better data in the lowest levels, below 50 mg/kg.

• **PRECISION STATEMENTS & POOLED DATA**– To further evaluate sulfur test method performance in a multi-laboratory situation, an analysis of ASTM precision statements published by D 02.03 (Elemental Analysis) was performed. After treatment of the data, using ASTM Practice D 6259 and D 6300, a pooled limit of detection (PLOD) of less than 0.6 mg/kg and a pooled limit of quantification (PLOQ) of less than 1.0 mg/kg can be derived from a recently completed round robin.

• **LOD/LOQ** – To evaluate D 5453 single instrument/single laboratory performance, data was generated and analyzed using ACS/IUPAC guidelines to establish a minimum detectable limit (MDL). Further study, using techniques described by Taylor[5], revealed a limit of detection (three standard deviations) of about 1mg/kg, and a LOQ of about 3 mg/kg when calculated based on a 5.6 mg/kg standard. When based on the lowest standard analyzed, at a level of 0.59 mg/kg, the limit of detection was calculated to be about 0.5 mg/kg, and the LOQ about 1.5 mg/kg. Using an IUPAC calculation based on lowest standard counts and background counts, a lowest LOD of 0.18 mg/kg was calculated.

Variations caused by instrument condition and actual laboratory application can make any attempt to develop a "universal" LOD/LOQ statement seem non-conclusive. However, **this report finds strong evidence that D 5453 can be routinely applied to the determination of sulfur in liquid hydrocarbons at levels less than 1 mg/kg**.

# EQUIVALENCY

The ASTM test methods commonly used in regulatory information for fuels, ASTM D 2622, ASTM D 4294, and ASTM D 5453 have been evaluated for analytical range by concentration using recent ASTM laboratory cross-check data and data generated from analysis of gravimetrically prepared materials. The data below provides a general equivalence evaluation. D 5453 and D 2622 demonstrate an equivalent fitness for use down to 20 mg/kg. D 5453 was found fit for use down to 1.0 mg/kg. Based on the low sulfur values mentioned in planned sulfur regulations in Europe, North America, and other areas of the world, and on large standard deviations at lower sulfur concentrations, dispersive X-ray methods, **D 4294 and D 2622 may no longer be useful for certain regulated fuel species**.

Investigations have been conducted using ASTM cross-check program information on gasoline, jet fuel, and diesel fuel with sulfur values less than 500 mg/kg. **Table 1** shows the robust means and standard deviations for 49 fuels with available data for the three test procedures. Methods D 2622, D 4294, and D 5453 are run in the ASTM RFG (reformulated gasoline) monthly program and the quarterly motor gas program (MG), as well as the diesel (DL) and jet fuel (JF) programs. The results are in mg/kg(ppm wt/wt) units.

- **Figure 1** shows ASTM D 5453 versus ASTM D 2622 mean values from cross-check data
- **Figure 2** shows ASTM D 5453 versus ASTM D 4294 mean values from cross-check data

Figures 1 and 2 include a line showing where the data points would fall for an exact correlation. That would be a case where a mean value of 100 mg/kg for the first procedure would also be 100 mg/kg for the second procedure, and a mean value of 200 mg/kg for the first procedure would also be 200 mg/kg for the second procedure.

- **Figure 3** shows standard deviation in mg/kg for ASTM D 5453 across concentration ranges using ASTM cross-check data. See inset for < 50 mg/kg evaluation.
- **Figure 4** shows standard deviation in mg/kg for ASTM D 2622 across concentration ranges using ASTM cross-check data. See inset for < 50 mg/kg evaluation.
- **Figure 5** shows standard deviation in mg/kg for ASTM D 4294 across concentration ranges using ASTM cross-check data. See inset for < 50 mg/kg evaluation.

**ASTM D 2622 has the lowest standard deviation across the higher concentration ranges, and ASTM D 5453 at the lower (below 50 mg/kg) ranges.**

**Figure 1**

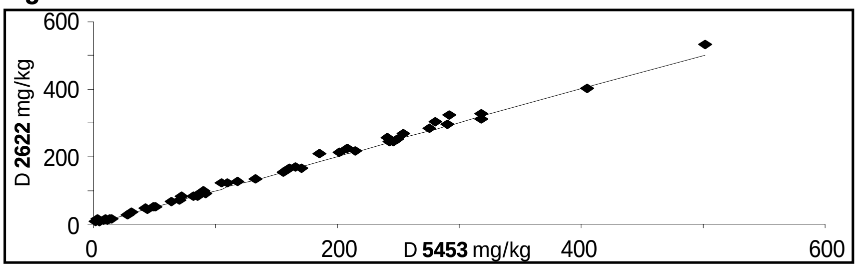


**Figure 2**

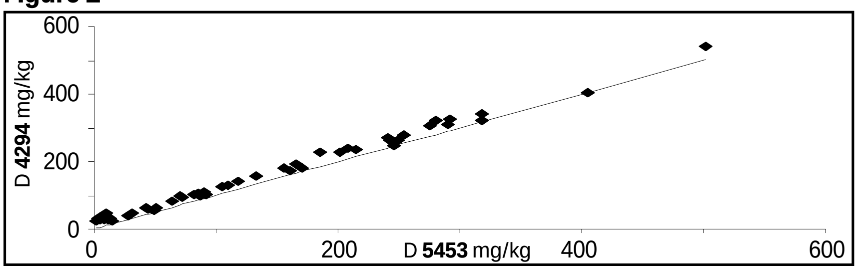


**Figure 3**

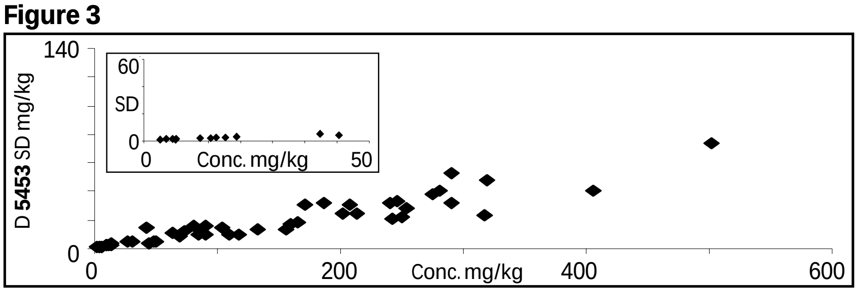


**Figure 4**

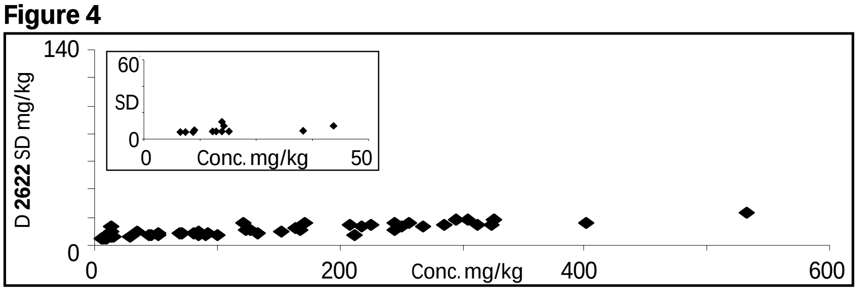


**Figure 5**

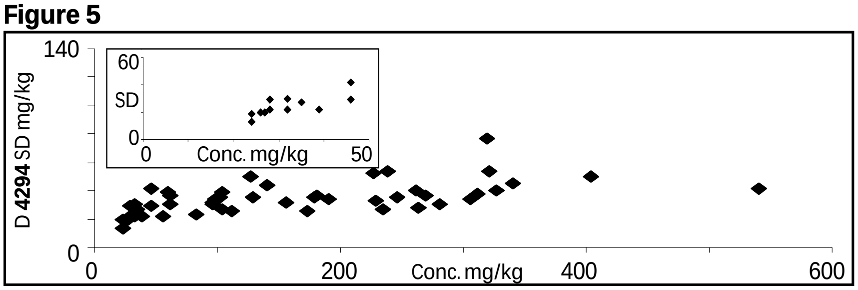

**Table 1: ASTM cross-check program data (<500 mg/kg)** for each sulfur method, showing mean values in mg/kg, standard deviations, and number of participants running each procedure

| | D 2622 | | | D 4294 | | | D 5453 | | |
|---|---|---|---|---|---|---|---|---|---|
| **Sample** | **Mean*** | **Std Dev** | **n** | **Mean*** | **Std Dev** | **n** | **Mean*** | **Std Dev** | **n** |
| RFG9601 | 257 | 16 | 61 | 269 | 36 | 32 | 241 | 32 | 13 |
| RFG9603 | 84 | 8 | 67 | 102 | 35 | 34 | 82 | 16 | 18 |
| RFG9604 | 153 | 10 | 68 | 179 | 35 | 38 | 155 | 14 | 18 |
| RFG9605 | 82 | 9 | 69 | 96 | 31 | 36 | 73 | 12 | 17 |
| RFG9606 | 269 | 14 | 66 | 280 | 30 | 40 | 255 | 29 | 18 |
| RFG9607 | 100 | 7 | 66 | 111 | 25 | 40 | 90 | 16 | 17 |
| RFG9608 | 285 | 14 | 68 | 306 | 34 | 38 | 276 | 38 | 21 |
| RFG9609 | 15 | 6 | 67 | 24 | 13 | 30 | 14 | 3 | 22 |
| RFG9610 | 133 | 9 | 68 | 155 | 32 | 37 | 132 | 14 | 22 |
| RFG9611 | 209 | 15 | 68 | 229 | 33 | 39 | 186 | 31 | 16 |
| RFG9612 | 12 | 6 | 61 | 26 | 20 | 29 | 9 | 2 | 24 |
| RFG9701 | 123 | 11 | 71 | 128 | 35 | 45 | 110 | 9 | 21 |
| RFG9702 | 52 | 9 | 71 | 62 | 30 | 37 | 51 | 5 | 22 |
| RFG9703 | 28 | 6 | 75 | 39 | 22 | 36 | 27 | 5 | 21 |
| RFG9704 | 295 | 19 | 72 | 311 | 38 | 40 | 291 | 32 | 19 |
| RFG9705 | 172 | 16 | 73 | 191 | 34 | 42 | 165 | 18 | 21 |
| RFG9706 | 7 | 5 | 69 | 28 | 29 | 32 | 5 | 1 | 20 |
| RFG9708 | 85 | 9 | 77 | 104 | 39 | 37 | 85 | 9 | 18 |
| RFG9709 | 14 | 6 | 74 | 32 | 22 | 35 | 13 | 3 | 21 |
| RFG9710 | 44 | 8 | 72 | 59 | 39 | 36 | 45 | 4 | 21 |
| RFG9711 | 92 | 8 | 73 | 103 | 27 | 41 | 91 | 9 | 21 |
| RFG9712 | 9 | 5 | 68 | 35 | 27 | 35 | 5 | 1 | 21 |
| RFG9802 | 91 | 7 | 78 | 98 | 34 | 40 | 86 | 13 | 22 |
| RFG9803 | 34 | 10 | 77 | 46 | 29 | 41 | 30 | 4 | 21 |
| RFG9804 | 251 | 14 | 75 | 263 | 28 | 42 | 249 | 22 | 23 |
| RG9805 | 69 | 9 | 78 | 82 | 23 | 42 | 64 | 11 | 22 |
| RFG9806 | 9 | 7 | 75 | 27 | 20 | 37 | 4 | 1 | 19 |
| RFG9807 | 13 | 6 | 70 | 28 | 22 | 36 | 11 | 2 | 21 |
| RFG9808 | 52 | 8 | 71 | 56 | 22 | 36 | 49 | 5 | 21 |
| RFG9809 | 165 | 12 | 73 | 174 | 25 | 50 | 160 | 17 | 22 |
| RFG9810 | 7 | 6 | 55 | 24 | 19 | 31 | 2 | 1 | 18 |
| RFG9811 | 218 | 14 | 69 | 235 | 27 | 42 | 214 | 25 | 20 |
| MG9608 | 127 | 11 | 33 | 141 | 44 | 50 | 118 | 9 | 12 |
| MG9612 | 14 | 10 | 30 | 46 | 42 | 41 | 10 | 2 | 10 |
| MG9704 | 71 | 8 | 23 | 97 | 32 | 43 | 70 | 9 | 12 |
| MG9708 | 304 | 19 | 32 | 320 | 77 | 49 | 280 | 40 | 14 |
| MG9712 | 226 | 14 | 32 | 239 | 54 | 47 | 208 | 31 | 16 |
| MG9804 | 122 | 16 | 34 | 126 | 50 | 47 | 104 | 15 | 13 |
| MG9808 | 46 | 7 | 32 | 62 | 36 | 42 | 43 | 15 | 14 |
| DL9602 | 401 | 16 | 47 | 403 | 50 | 118 | 405 | 40 | 15 |
| DL9606 | 313 | 15 | 50 | 322 | 54 | 118 | 318 | 23 | 16 |
| DL9706 | 326 | 19 | 60 | 340 | 45 | 130 | 319 | 48 | 17 |
| DL9802 | 167 | 11 | 67 | 180 | 36 | 142 | 171 | 31 | 16 |
| DL9806 | 244 | 11 | 63 | 261 | 40 | 143 | 243 | 21 | 14 |
| JF9603 | 533 | 23 | 45 | 541 | 42 | 85 | 501 | 74 | 16 |
| JF9611 | 323 | 14 | 45 | 326 | 40 | 87 | 291 | 53 | 18 |
| JF9707 | 213 | 8 | 43 | 226 | 52 | 91 | 201 | 25 | 18 |
| JF9711 | 14 | 13 | 38 | 32 | 30 | 78 | 4 | 2 | 15 |
| JF9803 | 245 | 15 | 55 | 247 | 35 | 103 | 245 | 33 | 15 |

* mg/kg

# BIAS

This portion of the study set out to determine and document any bias that these dominant sulfur measurement technologies exhibit in the measurement of sulfur bearing compounds. Also investigated was whether different common sulfur bearing compounds produce different recov- eries, making calibration with one compound inaccurate for the determination of another. Both X-ray based methods (D 2622 and D 4294) can experience interference caused by variations in carbon to hydrogen ratios between analyzed samples and calibration materials. These potential bias-causing interferences were minimized by the use of a single isooctane matrix for all the gravimetrically prepared samples.

Based on expected levels of sulfur in fuels for the next ten years, concentrations of 200, 100, 50, and 25, and 10 mg/kg sulfur were selected for consideration in the bias study. A group of sulfur compounds was selected to include all the common types of sulfur that would be anticipated in gasoline and diesel fuels. The compounds were selected based on literature, experience of ASTM members, and availability of the products. Included are sulfides, aryl and alkyl thiols, aryl and alkyl thiophenes, and a thionaphthene.

Bias can be identified when accuracy deviates beyond accepted precision limits for a given test method (see pages 8–9). **With allowances for the expected variation, the data at right demonstrates that no bias can be determined for any of these methods**.

A stock solution of 2900 to 4100 mg/kg (ppm w/w) sulfur in isooctane was made from each compound, and that stock was used to make each of the individual 10, 25, 50, 100, and 200 mg/kg target concentrations, by dilution with isooctane.

- **Table 2** *gives an overall summary of the standard deviations for each of the three methods across the group of compounds*
- **Table 3** *gives an overall summary of the % relative standard deviations for each method over the group of compounds*
- **Table 4** *shows sulfur compounds used and the:*

  *— target concentrations that were made up for testing using each of the three methods*

  *— ASTM D 5453 results and deviations from gravimetric values*

  *— ASTM D 2622 results and deviations from gravimetric values*

  *— ASTM D 4294 results and deviations from gravimetric values*

ASTM D 2622, ASTM D 4294, and ASTM D 5453 were performed at Southwest Research Institute. ASTM D 2622 was run on an ARL instrument, calibrated using di-*n*-butyl sulfide in mineral oil, with standards made up as instructed in the ASTM procedure. No sample dilutions were used. Two standard curves were used, one for the 0–200 mg/kg range, and one for the 50–1000 range. The 10, 25, and 50 mg/kg samples were run on the low curve, and the 100 and 200 on the higher curve. Each sample was a single run, and results were calculated in mg/kg.

ASTM D 4294 was run on a Kevex 770 analyzer, also calibrated using di-*n*-butyl sulfide. These sample results are from single runs. One standard curve was used over the whole range. No sample dilutions were made. Results were calculated in mg/kg.

The ASTM D 5453 was run on an Antek 9000 Sulfur Analyzer, calibrated with butyl sulfide. Samples were measured versus standards in micrograms/mL, converted to micrograms/g by dividing by sample density in g/mL. Three 10 or 15 microliter injections per sample were made, and an average value reported. No sample dilutions were made. Two calibration curves were used, one to cover 0–50 micrograms/mL, the other 20–200 micrograms/mL.

The deviation values shown for each of the data points in Table 4 are produced by the sulfur test value less the gravimetric value for each compound concentration. The standard deviations shown in Table 2 are calculated using the Excel formula for STDEV for the concentration deviations. The % relative standard deviation shown in Table 3 is the standard deviation value, divided by the target concentration, times 100. Figures 6 and 7, which illustrate deviations versus concentrations, can be used to show concentration dependent precision. Each of the test methods has a standard deviation which, in general, increases with concentration, as seen in Table 2 and Figure 6. This concentration dependence is also illustrated with increasing relative standard deviation values for lower concentrations, shown in Table 3 and Figure 7. The method D 4294 shows an unusual pattern in the figures because of its quantitation limit.

The common isooctane matrix and gravimetric preparation of the analyzed materials supports the conclusion that any bias that is shown by this testing would be attributed to sulfur compound bias for a method. None of the test procedures exhibited compound-type bias toward these materials, as evidenced by the lack of any consistent high or low deviations across concentration ranges for any of the compounds studied. Table 4 lists the individual deviations for the compounds.

**Figure 6**
**Standard Deviations vs Concentration**

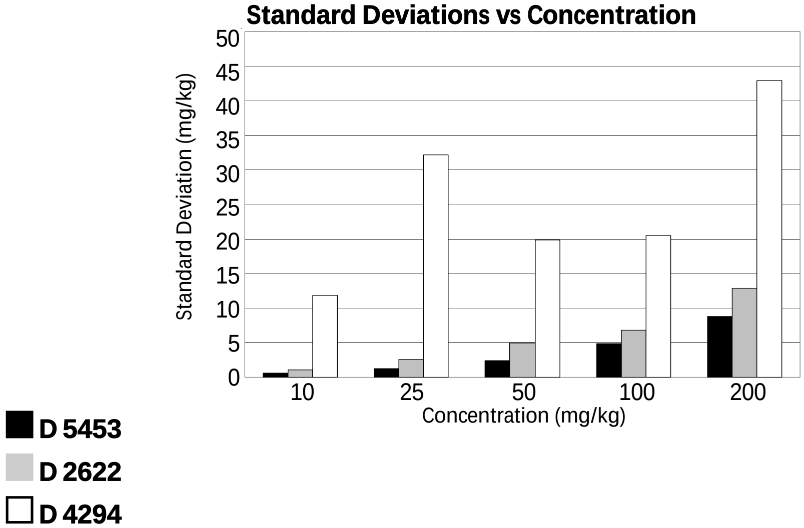


**Table 2**
**STANDARD DEVIATION**

| Concentration | **D 5453** | D 2622 | D 4294 |
|---|---|---|---|
| 10 mg/kg | 0.66 | 1.08 | 11.92 |
| 25 mg/kg | 1.23 | 2.64 | 32.16 |
| 50 mg/kg | 2.42 | 4.91 | 19.86 |
| 100 mg/kg | 4.82 | 6.82 | 20.53 |
| 200 mg/kg | 8.84 | 12.89 | 42.90 |

**Figure 7**
**% Relative Standard Deviation vs Concentration**

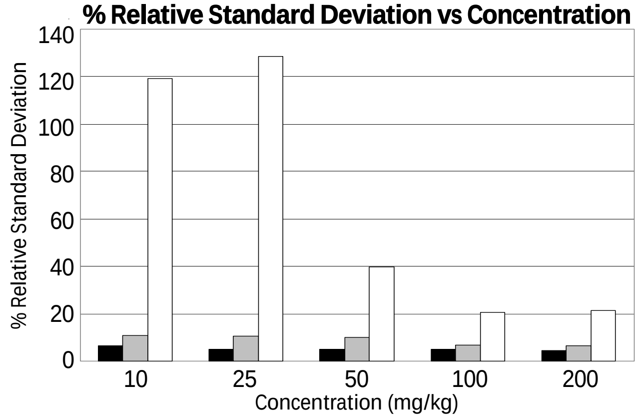


**Table 3**
**% RELATIVE STANDARD DEVIATION**

| Concentration | **D 5453** | D 2622 | D 4294 |
|---|---|---|---|
| 10 mg/kg | 6.55 | 10.75 | 119.15 |
| 25 mg/kg | 4.92 | 10.56 | 128.64 |
| 50 mg/kg | 4.84 | 9.82 | 39.73 |
| 100 mg/kg | 4.82 | 6.82 | 20.54 |
| 200 mg/kg | 4.42 | 6.44 | 21.45 |

**Table 4** next page →

**Table 4**

| | 1-Decanethiol | 2-Propanethiol | Ethyl Sulfide | 2-Methyl-1-Propanethiol | Butyl Sulfide | Thiophene | Phenyl Sulfide | Carbon Disulfide | Ethyl Disulfide | 1-Methyl-1-Propanethiol | Propyl Disulfide | Ethyl Methyl Sulfide | Methyl Disulfide | Benzenethiol | 2-Methyl-2-Propanethiol | 1-Butanethiol | Methyl Sulfide | 2-Ethylthiophene | Dibenzothiophene, white | Ethanethiol | 3-Methyl-Thiophene | Thianaphthene | Propyl Sulfide | Isopropyl Disulfide | SD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **A. Actual Gravimetric Sulfur Content (mg/kg)** | | | | | | | | | | | | | | | | | | | | | | | | | |
| **• 10 range** : | 10.13 | 9.97 | 9.88 | 10.11 | 10.05 | 10.05 | 9.95 | 10.06 | 10.01 | 9.99 | 10.02 | 10.04 | 9.99 | 10.12 | 9.98 | 10.18 | 10.04 | 10.20 | 10.08 | 10.06 | 13.07 | 9.97 | 10.03 | 10.13 | |
| **• 25** : | 25.33 | 25.44 | 24.83 | 25.07 | 25.04 | 24.81 | 24.84 | 25.10 | 25.08 | 25.02 | 25.00 | 25.03 | 25.02 | 25.21 | 24.98 | 24.97 | 25.17 | 25.06 | 25.02 | 25.04 | 26.09 | 25.00 | 25.07 | 25.34 | |
| **• 50** : | 50.42 | 50.00 | 49.99 | 49.97 | 50.00 | 50.14 | 50.05 | 50.05 | 50.07 | 50.36 | 50.11 | 50.07 | 50.07 | 50.25 | 50.05 | 50.00 | 49.98 | 50.05 | 49.87 | 50.05 | 52.15 | 50.06 | 50.07 | 50.05 | |
| **• 100** : | 100.13 | 100.10 | 100.06 | 100.09 | 100.01 | 99.95 | 100.02 | 100.08 | 100.03 | 99.85 | 100.26 | 100.04 | 100.10 | 100.14 | 99.98 | 99.98 | 100.05 | 100.07 | 100.01 | 99.99 | 104.28 | 100.01 | 99.93 | 100.19 | |
| **• 200** : | 200.07 | 200.01 | 199.96 | 199.96 | 199.95 | 199.98 | 199.99 | 199.93 | 199.53 | 197.34 | 199.97 | 200.02 | 200.01 | 200.09 | 200.12 | 200.08 | 199.72 | 196.83 | 198.83 | 200.07 | — | 200.04 | 200.03 | 199.99 | |
| **B. D 5453 – Results & Deviations*** | | | | | | | | | | | | | | | | | | | | | | | | | |
| **• 10 range** : | 10.92 | 9.20 | 9.57 | 9.56 | 10.38 | 9.92 | 9.47 | 8.51 | 9.92 | 9.61 | 10.06 | 9.63 | 10.12 | 9.56 | 8.80 | 9.73 | 9.00 | 9.73 | 9.49 | 8.72 | 12.39 | 11.33 | 9.34 | 10.48 | |
| Deviation: | 0.79 | -0.77 | -0.31 | -0.55 | 0.33 | -0.13 | -0.48 | -1.55 | -0.09 | -0.38 | 0.04 | -0.41 | 0.13 | -0.56 | -1.18 | -0.45 | -1.04 | -0.47 | -0.59 | -1.34 | -0.68 | 1.36 | -0.69 | 0.38 | 0.66 |
| **• 25** : | 25.52 | 23.70 | 24.27 | 24.16 | 25.35 | 24.07 | 23.79 | 23.54 | 25.06 | 25.35 | 25.64 | 24.95 | 24.30 | 24.62 | 23.71 | 23.79 | 23.04 | 24.25 | 24.32 | 22.20 | 24.82 | 28.64 | 23.81 | 25.55 | |
| Deviation: | 0.19 | -1.74 | -0.56 | -0.91 | 0.31 | -0.74 | -1.05 | -1.56 | -0.02 | 0.33 | 0.64 | -0.08 | -0.72 | -0.59 | -1.27 | -1.18 | -2.13 | -0.81 | -0.70 | -2.84 | -1.27 | 3.64 | -1.26 | 0.21 | 1.23 |
| **• 50** : | 52.00 | 49.37 | 49.91 | 49.80 | 49.93 | 48.58 | 51.67 | 47.66 | 50.59 | 51.15 | 51.60 | 50.32 | 49.43 | 49.38 | 48.62 | 49.37 | 47.04 | 49.57 | 49.02 | 46.23 | 48.76 | 58.78 | 47.90 | 49.97 | |
| Deviation: | 1.58 | -0.63 | -0.08 | -0.17 | -0.07 | -1.56 | 1.62 | -2.39 | 0.52 | 0.79 | 1.49 | 0.25 | -0.64 | -0.87 | -1.43 | -0.63 | -2.94 | -0.48 | -0.85 | -3.82 | -3.39 | 8.72 | -2.17 | -0.08 | 2.42 |
| **• 100** : | 101.21 | 98.33 | 99.05 | 98.23 | 99.90 | 97.31 | 98.05 | 93.43 | 99.17 | 98.03 | 97.34 | 95.30 | 95.50 | 101.78 | 88.40 | 97.61 | 91.05 | 99.66 | 98.02 | 90.24 | 99.43 | 113.31 | 96.68 | 103.13 | |
| Deviation: | 1.08 | -1.77 | -1.01 | -1.86 | -0.11 | -2.64 | -1.97 | -6.65 | -0.86 | -1.82 | -2.92 | -4.74 | -4.60 | 1.64 | -11.58 | -2.37 | -9.00 | -0.41 | -1.99 | -9.75 | -4.85 | 13.30 | -3.25 | 2.94 | 4.82 |
| **• 200** : | 203.12 | 189.38 | 198.13 | 194.67 | 201.77 | 193.99 | 198.32 | 185.83 | 198.49 | 194.55 | 198.13 | 230.74 | 191.55 | 201.21 | 191.28 | 195.92 | 188.90 | 196.34 | 194.09 | 188.23 | — | 193.45 | 195.26 | 205.40 | |
| Deviation: | 3.05 | -10.63 | -1.83 | -5.29 | 1.82 | -5.99 | -1.67 | -14.10 | -1.04 | -2.79 | -1.84 | 30.72 | -8.64 | 1.12 | -8.84 | -4.16 | -10.82 | -0.49 | -4.74 | -11.84 | — | -6.59 | -4.77 | 5.41 | 8.84 |
| **C. D 2622 – Results & Deviations*** | | | | | | | | | | | | | | | | | | | | | | | | | |
| **• 10 range** : | 9.80 | 9.60 | 10.60 | 9.50 | 10.20 | 9.50 | 9.50 | 7.00 | 10.50 | 9.60 | 9.50 | 9.00 | 9.20 | 11.30 | 8.10 | 9.80 | 7.30 | 9.30 | 8.70 | 7.70 | 12.10 | 11.20 | 9.40 | 9.40 | |
| Deviation: | -0.30 | -0.40 | 0.70 | -0.60 | 0.10 | -0.60 | -0.40 | -3.10 | 0.50 | -0.40 | -0.50 | -1.00 | -0.80 | 1.20 | -1.90 | -0.40 | -2.70 | -0.90 | -1.40 | -2.40 | -1.00 | 1.20 | -0.60 | -0.70 | 1.08 |
| **• 25** : | 33.30 | 24.50 | 25.20 | 26.00 | 26.40 | 23.50 | 25.40 | 22.80 | 26.20 | 26.10 | 26.00 | 25.10 | 24.90 | 33.20 | 24.30 | 27.20 | 23.00 | 25.70 | 24.40 | 23.80 | 25.00 | 29.70 | 25.50 | 26.20 | |
| Deviation: | 8.00 | -0.90 | 0.40 | 0.90 | 1.40 | -1.30 | 0.60 | -2.30 | 1.10 | 1.10 | 1.00 | 0.10 | -0.10 | 8.00 | -0.70 | 2.20 | -2.20 | 0.60 | -0.60 | -1.20 | -1.10 | 4.70 | 0.40 | 0.90 | 2.64 |
| **• 50** : | 52.70 | 50.80 | 52.70 | 53.40 | 52.90 | 49.20 | 50.90 | 47.40 | 51.20 | 50.40 | 53.70 | 52.30 | 52.10 | 68.60 | 48.10 | 53.10 | 46.60 | 52.00 | 50.90 | 50.80 | 43.00 | 60.50 | 51.10 | 52.30 | |
| Deviation: | 2.30 | 0.80 | 2.70 | 3.40 | 2.90 | -0.90 | 0.90 | -2.70 | 1.10 | 0.00 | 3.60 | 2.20 | 2.00 | 18.40 | -2.00 | 3.10 | -3.40 | 2.00 | 1.00 | 0.80 | -9.20 | 10.40 | 1.00 | 2.30 | 4.91 |
| **• 100** : | 96.00 | 86.00 | 93.00 | 91.00 | 97.00 | 93.00 | 93.00 | 89.00 | 92.00 | 92.00 | 94.00 | 94.00 | 92.00 | 114.00 | 89.00 | 98.00 | 83.00 | 95.00 | 93.00 | 90.00 | 96.00 | 112.00 | 92.00 | 100.00 | |
| Deviation: | -4.10 | -14.10 | -7.10 | -9.10 | -3.00 | -7.00 | -7.00 | -11.10 | -8.00 | -7.80 | -6.30 | -6.00 | -8.10 | 13.90 | -11.00 | -2.00 | -17.10 | -5.10 | -7.00 | -10.00 | -8.30 | 12.00 | -7.90 | -0.20 | 6.82 |
| **• 200** : | 209.00 | 190.00 | 194.00 | 195.00 | 206.00 | 193.00 | 191.00 | 184.00 | 198.00 | 185.00 | 198.00 | 192.00 | 191.00 | 226.00 | 196.00 | 195.00 | 177.00 | 192.00 | 190.00 | 180.00 | — | 233.00 | 184.00 | 199.00 | |
| Deviation: | 8.90 | -10.00 | -6.00 | -5.00 | 6.10 | -7.00 | -9.00 | -15.90 | -1.50 | -12.30 | -2.00 | -8.00 | -9.00 | 25.90 | -4.10 | -5.10 | -22.70 | -4.80 | -8.80 | -20.10 | — | 33.00 | -16.00 | -1.00 | 12.89 |
| **D. D4294 – Results & Deviations*** | | | | | | | | | | | | | | | | | | | | | | | | | |
| **• 10 range** : | 4.00 | 4.00 | 17.00 | 20.00 | 4.00 | 4.00 | 22.00 | 4.00 | 35.00 | 4.00 | 4.00 | 4.00 | 15.00 | 4.00 | 20.00 | 4.00 | 20.00 | 10.00 | 13.00 | 4.00 | 4.00 | 48.00 | 24.00 | 4.00 | |
| Deviation: | -6.50 | -6.40 | 7.00 | 10.10 | -6.50 | -6.50 | 12.20 | -6.50 | 24.80 | -6.40 | -6.40 | -6.50 | 5.30 | -6.50 | 10.00 | -6.60 | 9.60 | -0.60 | 2.90 | -6.10 | -9.10 | 38.00 | 14.00 | -6.10 | 11.92 |
| **• 25** : | 15.00 | 4.00 | 27.00 | 4.00 | 15.00 | 38.00 | 39.00 | 14.00 | 30.00 | 46.00 | 34.00 | 14.00 | 143.00 | 62.00 | 4.00 | 4.00 | 35.00 | 14.00 | 44.00 | 4.00 | 13.00 | 4.00 | 73.00 | 74.00 | |
| Deviation: | -10.60 | -21.90 | 2.10 | -21.50 | -10.00 | 13.60 | 13.70 | -11.00 | 4.80 | 21.50 | 9.40 | -10.60 | 117.50 | 37.10 | -21.40 | -21.40 | 10.10 | -11.00 | 19.00 | -21.00 | -13.10 | -21.00 | 47.90 | 48.70 | 32.16 |
| **• 50** : | 64.00 | 57.00 | 95.00 | 62.00 | 56.00 | 64.00 | 57.00 | 20.00 | 84.00 | 70.00 | 54.00 | 52.00 | 51.00 | 56.00 | 90.00 | 65.00 | 47.00 | 35.00 | 41.00 | 4.00 | 45.00 | 54.00 | 53.00 | 68.00 | |
| Deviation: | 14.10 | 6.60 | 45.40 | 11.90 | 6.30 | 14.30 | 6.90 | -30.50 | 33.90 | 20.00 | 4.40 | 2.30 | 0.80 | 6.10 | 40.20 | 14.80 | -2.80 | -14.60 | -8.60 | -46.10 | -7.20 | 3.90 | 2.90 | 18.00 | 19.86 |
| **• 100** : | 103.00 | 90.00 | 96.00 | 102.00 | 108.00 | 104.00 | 101.00 | 101.00 | 130.00 | 91.00 | 97.00 | 105.00 | 86.00 | 95.00 | 115.00 | 39.00 | 53.00 | 113.00 | 98.00 | 67.00 | 99.00 | 118.00 | 120.00 | 115.00 | |
| Deviation: | 2.60 | -9.60 | -3.60 | 1.70 | 7.70 | 3.60 | 1.50 | 1.10 | 29.60 | -9.00 | -2.80 | 4.90 | -14.50 | -5.00 | 14.90 | -60.90 | -47.50 | 12.80 | -2.10 | -33.00 | -5.30 | 18.00 | 20.10 | 14.80 | 20.53 |
| **• 200** : | 202.00 | 136.00 | 190.00 | 180.00 | 244.00 | 141.00 | 234.00 | 197.00 | 236.00 | 193.00 | 252.00 | 181.00 | 203.00 | 198.00 | 187.00 | 201.00 | 124.00 | 229.00 | 162.00 | 143.00 | — | 301.00 | 213.00 | 255.00 | |
| Deviation: | 2.30 | -63.70 | -9.60 | -19.50 | 43.90 | -58.80 | 34.50 | -3.00 | 36.40 | -4.10 | 51.80 | -18.70 | 2.90 | -1.90 | -13.60 | 0.80 | -76.10 | 32.00 | -36.80 | -57.10 | — | 101.00 | 13.00 | 55.00 | 42.90 |

* deviation in mg/kg from actual gravimetric sulfur content as listed in portion A of the table

# FITNESS-FOR-USE

Further evaluation of the ASTM cross-check program and the gravimetric bias study data can be done to discover precision and accuracy tendencies. For low levels, D 5453 and D 2622 have the best data. **Of these, D 5453 had the better data in the lowest levels below 50 mg/kg**.

Using information shown in **Tables 5A and 5B**, a fitness-for-use evaluation of the three methods for the measurement of sulfur in regulated fuels can be made. For example, the first step in this evaluation can be to determine test method capability at the limit and half the limit required in Europe (CEN) for Year 2000 and Year 2005 gasoline and diesel fuels. A comparison of the standard deviations values determined for concentration levels at 25 mg/kg (Fig. 6) with the corresponding % relative standard deviations (Fig. 7) will give an indication of the fitness-for use for each test method.

**Table 5A: Auto Oil Fuels Directive (Europe)**

Preliminary regulatory sulfur limits for future fuels in mg/kg; (common position figures in brackets)

| | Year 2000 | Year 2005 |
|---|---|---|
| Mogas | 100 (150) | 30 (50) |
| Diesel | 200 (350) | 50 |

**Table 5B: Auto Fuels Directive (North America)**

Preliminary regulatory sulfur limits for future fuels in mg/kg; (California position figures in brackets)

| | Year 2000 | Year 2004 | Year 2008 |
|---|---|---|---|
| RFG | 150* (30) | 30 (<5) | <5 (<5) |
| Diesel | 150* (300) | 30 (30) | <5 (<5) |
| | estimated | estimated | estimated |

*150 ppm or less to earn credits in the ABT system

In mid-1997, the European Council adopted the "common position" shown in Table 5A. Other values are undergoing current voting. These levels are also covered in the cross-check data above. North American (US) sulfur levels are currently under US EPA regulatory review. Decreasing European, Canadian, and California sulfur specifications are also being considered.

Figures 3 through 5 show the standard deviation with relation to the concentration for each of the methods using cross-check data. Tables 2 and 3 show average standard deviation information for each of the three methods using the concentration data from the bias study.

To further evaluate the test methods at sulfur levels less than 10 mg/kg, five fuel samples were run by each procedure. Included was a biodiesel sample to assess use of each of the methods on that product. Data for these analyses are shown in **Table 6**. The method D 5453 has no trouble with analyzing these sample types in this range. The D 2622 X-ray method is at the limit of detection, and does not perform adequately in this range. The samples are all well below the detection limit of ASTM D 4294, so neither of the X-ray methods would be appropriate for motor fuels, very low level diesel samples, or biodiesel in the less than 10 mg/kg sulfur concentration range.

**Table 6: Sulfur data**

low level sulfur gasolines, an experimental diesel, and biodiesel; mg/kg

| Test Method | — gasolines — "A" | "B" | "C" | Diesel experimental | Biodiesel | |
|---|---|---|---|---|---|---|
| ASTM D 5453 | 4.4 | 4.9 | 2.4 | 1.2 | 3.3 | |
| ASTM D 2622 | <10 | <10 | <10 | <10 | <10 | : below precision range |
| ASTM D 4294 | <50 | <50 | <50 | <50 | <50 | : below method scope |

# PRECISION STATEMENTS & POOLED DATA

To estimate performance characteristics of a test method within the laboratory community, an interlaboratory study (ILS) or round robin can be performed. Many statistical estimates can be derived from such an exercise. Classic among these is an estimate of precision within a given lab (repeatability = r) and an estimate of the agreement between laboratories (reproducibility = R). **Table 7** shows the r and R precision statements available for each of the test methods found in 1999 Annual Book of ASTM Standards (volumes 5.02 and 5.03).

A practical way to view these precision statements is to create a table with representative X values through a concentration range of interest. By executing the calculation for each concentration, the user of the table can then gain an easy indication of the capability of test method for a given concentration. **Tables 8 and 9** compare the precision of the three methods for r and R at concentrations of 5, 10, 25, 50 and 100 mg/kg.

Using these tables, it is easy to compare method performance at a given concentration.

A recent motor fuel ILS conducted using D 5453 yielded the results shown in **Table 11** (next page). The original data included 13 labs and 13 samples. All results returned were treated using ASTM practices D 6259 and D 6300. This standard approach resulted in one sample being dropped. Using this data, R and r were found to be: $r = 0.1930(X)^{0.6667}$ and $R = 0.6867(X)^{0.6667}$. Using these equations, **Table 10** shows individual repeatability, or duplicate in-lab type test precision, and reproducibility, or between lab precision, for various low mg/kg ranges. The data in Table 10 is comparable to the r and R values in Tables 8 and 9.

Round robin data used to find the above estimates can be further examined to derive a Pooled Limit of Detection (PLOD) and Pooled Limit of Quantification (PLOQ). These pooled estimates can provide an evaluation of the variation in detection and measurement capability of a method in a multi-laboratory/multi-instrument situation. **A PLOD of less than 0.6 mg/kg and a PLOQ of 1.0 mg/kg can be derived from this data**.

**Table 7: Precision Statements from ASTM Test Procedures**

| Test Method | repeatability = r | reproducibility =R |
|---|---|---|
| D 2622 for 0.0060-5.300 | $0.02651(x)^{0.9}$ | $0.0913(x)^{0.9}$ |
| D 2622 for 0.0003–0.093 | $0.00736(x+0.0002)^{0.4}$ | $0.0105(x+0.0002)^{0.4}$ |
| D 4294 | 0.02894(x+0.1691) | 0.1215(x+0.05555) |
| **D 5453** | $0.1867(x)^{(0.63)}$ | $0.2217(x)^{(0.92)}$ |

**Table 8: Repeatability = r**
in-lab precision for back-to-back duplicate analyses; test data point should differ by no more than this amount 19 times out of 20

| mg/kg | D 2622 | D 4294 | **D 5453** |
|---|---|---|---|
| 5 | 4 | below method scope | 0.5 |
| 10 | 5 | below method scope | 0.8 |
| 25 | 7 | below method scope | 1.4 |
| 50 | 9 | below method scope | 2.2 |
| 100 | 12 | below method scope | 3.4 |

**Table 9: Reproducibility = R**
between-lab precision; test data point should differ by no more than this amount 19 times out of 20

| mg/kg | D 2622 | D 4294 | **D 5453** |
|---|---|---|---|
| 5 | 6 | below method scope | 1.0 |
| 10 | 7 | below method scope | 1.8 |
| 25 | 10 | below method scope | 4.3 |
| 50 | 13 | below method scope | 8.1 |
| 100 | 17 | below method scope | 15.3 |

**Table 10: D 5453 r, R—from a 1998 13 lab x 13 sample ILS**

| **D 5453** mg/kg | repeatability = r | reproducibility =R |
|---|---|---|
| 5 | 0.56 | 2.01 |
| 10 | 0.90 | 3.19 |
| 25 | 1.65 | 5.87 |
| 50 | 2.62 | 9.32 |
| 100 | 4.16 | 14.80 |

Turn page to view **table 11** →

**Table 11**
**1998 D 5453 Motor Fuel Round Robin (mg/kg)**

| Lab | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **A** | 0.7 | 3.5 | 3.3 | 5.4 | 14.6 | 1.2 | 5.5 | 4.5 | 33.9 | 17.9 | 36.4 | 8.4 |
| **A** | 0.8 | 3.4 | 3.3 | 5.4 | 14.4 | 1.1 | 5.6 | 4.5 | 33.9 | 18.0 | 36.1 | 8.4 |
| **B** | 0.4 | 3.2 | 3.0 | 4.8 | 14.4 | 0.9 | 5.1 | 3.8 | 35.2 | 18.0 | 37.1 | 8.0 |
| **B** | 0.5 | 3.1 | 3.0 | 4.7 | 14.3 | 1.0 | 5.1 | 4.3 | 35.3 | 17.9 | 37.3 | 7.6 |
| **C** | 0.6 | 4.5 | 3.6 | 4.4 | 13.2 | 1.5 | 4.9 | 6.5 | 33.0 | 17.2 | 31.5 | 7.4 |
| **C** | 0.5 | 4.6 | 3.6 | 4.9 | 13.4 | 1.6 | 5.5 | 6.5 | 34.1 | 17.2 | 33.7 | 7.5 |
| **D** | 0.4 | 4.0 | 3.3 | 5.6 | 14.8 | 1.1 | 5.0 | 5.3 | 34.6 | 18.8 | 35.3 | 7.7 |
| **D** | 0.5 | 4.0 | 3.3 | 5.5 | 14.3 | 1.1 | 5.6 | 5.0 | 35.1 | 18.5 | 35.8 | 7.7 |
| **E** | 0.2 | 2.9 | 2.9 | 5.2 | 14.1 | 0.7 | 5.5 | 5.2 | 34.5 | 17.5 | 35.0 | 8.5 |
| **E** | 0.1 | 2.9 | 2.7 | 5.2 | 13.9 | 0.6 | 5.2 | 5.1 | 34.3 | 17.6 | 34.9 | 8.2 |
| **F** | 0.8 | 2.6 | 2.4 | 5.3 | 13.7 | 0.9 | 5.2 | 5.0 | 27.7 | 16.5 | 32.8 | 7.7 |
| **F** | 0.6 | 2.6 | 2.2 | 5.8 | 12.7 | 1.0 | 4.7 | 5.5 | 29.2 | 16.7 | 32.3 | 8.8 |
| **G** | 0.8 | 2.6 | 2.7 | 5.3 | 11.8 | 0.9 | 5.7 | 4.6 | 25.6 | 14.6 | 28.5 | 7.2 |
| **G** | 0.7 | 2.6 | 2.3 | 5.0 | 12.5 | 0.9 | 5.5 | 4.5 | 25.1 | 14.7 | 28.6 | 7.0 |
| **H** | 0.4 | 3.8 | 3.9 | 5.6 | 11.9 | 1.2 | 5.5 | 4.5 | 32.4 | 15.4 | 31.6 | 6.9 |
| **H** | 0.4 | 4.0 | 3.8 | 5.1 | 11.7 | 1.2 | 5.0 | 5.8 | 33.0 | 15.9 | 33.1 | 6.7 |
| **I** | 0.5 | 3.2 | 2.7 | 5.3 | 14.8 | 0.9 | 5.8 | 4.1 | 38.5 | 18.4 | 35.4 | 8.4 |
| **I** | 0.4 | 3.3 | 2.9 | 5.1 | 14.0 | 0.8 | 5.3 | 3.8 | 33.8 | 18.6 | 36.0 | 8.6 |
| **J** | 0.5 | 3.6 | 3.1 | 3.9 | 12.6 | 1.2 | 5.7 | 5.0 | 34.2 | 17.2 | 32.7 | 6.8 |
| **J** | 0.6 | 3.3 | 3.0 | 4.2 | 12.7 | 1.0 | 5.2 | 5.4 | 34.4 | 16.9 | 32.6 | 6.6 |
| **K** | 0.0 | 2.2 | 2.0 | 4.8 | 13.5 | 0.2 | 5.2 | 4.6 | 31.1 | 16.7 | 33.1 | 7.8 |
| **K** | 0.0 | 2.0 | 2.1 | 5.0 | 13.2 | 0.3 | 5.0 | 4.3 | 30.7 | 16.5 | 33.2 | 7.7 |
| **L** | 0.5 | 4.2 | 3.6 | 5.9 | 15.5 | 1.1 | 6.1 | 6.6 | 34.3 | 19.6 | 38.4 | 9.1 |
| **L** | 0.4 | 4.2 | 3.4 | 6.0 | 15.7 | 1.1 | 6.1 | 6.5 | 37.7 | 19.4 | 36.3 | 9.2 |
| **M** | 0.8 | 4.3 | 3.4 | 5.5 | 16.3 | 1.4 | 5.9 | 6.1 | 35.4 | 21.3 | 40.5 | 8.8 |
| **M** | 0.8 | 4.3 | 3.3 | 5.6 | 16.2 | 1.4 | 5.9 | 5.8 | | 20.5 | 40.5 | 8.7 |
| | | | | | | | | | | | | |
| Avg | 0.5 | 3.4 | 3.0 | 5.2 | 13.9 | 1.0 | 5.4 | 5.1 | 33.1 | 17.6 | 34.6 | 7.9 |
| SD | 0.2 | 0.7 | 0.5 | 0.5 | 1.3 | 0.3 | 0.4 | 0.8 | 3.3 | 1.6 | 3.0 | 0.8 |

## LOD & LOQ

As seen in the previous sections and especially the results for the individual compounds, **the method D 5453 shows the best precision and accuracy of the examined methods at the predicted future fuel sulfur levels**. To evaluate single instrument/single laboratory performance, techniques described by Taylor[5] were employed to examine the lowest level performance of this technique. Several samples were analyzed in replicate at levels below 10 mg/kg to establish the limit of detection (LOD) of the method, and the precision of the data to be expected at these low levels.

Samples of isooctane containing 0.589, 1.54, and 5.6 mg/kg sulfur (from butyl sulfide) were run ten times each on three days. These samples were all run using 15 microliter injections, with the detector voltage and gain optimized for low levels. Data for these studies are shown in **Tables 12–14**.

**Table 12:** Results & standard deviations on three standards, run 10 times each on 3 consecutive days, with LOD/LOQ values calculated from each data set

**0.589 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 0.92 | 1.19 | 0.89 | | |
| | 1.01 | 0.78 | 0.99 | | |
| | 0.66 | 0.91 | 0.79 | | |
| | 0.63 | 0.93 | 0.82 | | |
| | 0.92 | 0.63 | 0.75 | | |
| | 0.68 | 0.66 | 0.70 | | |
| | 0.89 | 0.70 | 0.43 | | |
| | 0.24 | 0.75 | 0.72 | | |
| | 0.55 | 0.76 | 0.59 | | |
| | 0.49 | 0.79 | 0.55 | | |
| Avg | 0.70 | 0.81 | 0.72 | | |
| SD | 0.24 | 0.16 | 0.17 | 0.57 | 1.90 |

**1.54 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 1.72 | 1.84 | 1.90 | | |
| | 1.71 | 2.11 | 1.84 | | |
| | 1.77 | 1.98 | 1.85 | | |
| | 1.65 | 1.78 | 1.65 | | |
| | 1.72 | 2.06 | 2.01 | | |
| | 2.01 | 2.13 | 1.90 | | |
| | 1.31 | 1.84 | 1.68 | | |
| | 1.49 | 1.97 | 1.49 | | |
| | 1.55 | 1.72 | 0.85 | | |
| | 2.10 | 1.75 | 1.21 | | |
| Avg | 1.70 | 1.92 | 1.64 | | |
| SD | 0.23 | 0.15 | 0.36 | 0.75 | 2.49 |

**5.60 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 6.58 | 6.80 | 6.25 | | |
| | 6.58 | 6.90 | 5.96 | | |
| | 6.24 | 6.87 | 6.31 | | |
| | 5.96 | 6.38 | 5.92 | | |
| | 6.05 | 6.68 | 6.22 | | |
| | 6.06 | 6.81 | 6.01 | | |
| | 6.34 | 6.17 | 5.03 | | |
| | 5.58 | 6.38 | 4.97 | | |
| | 5.62 | 5.76 | 3.95 | | |
| | 5.19 | 5.29 | 3.82 | | |
| Avg | 6.02 | 6.40 | 5.45 | | |
| SD | 0.45 | 0.53 | 0.95 | 1.93 | 6.44 |

The measured value is meaningful when it is larger than the method uncertainty. The point where this occurs is called the Method Detection Limit (MDL) and is defined as three times the standard deviation. The level when measurements become quantitatively meaningful is called the Limit of Quantification (LOQ), and is defined by the American Chemical Society Committee on Environmental Improvement as ten times the standard deviation. At this point, the relative uncertainty of the measurement is about ±30%. The standard deviation value can be estimated with sufficient confidence by repetitive measurements of a single sample or group of samples near the LOQ.[5]

When based on the lowest standard analyzed, at a level of 0.589 mg/kg, the limit of detection was calculated to be about 0.5mg/kg, and the limit of quantification about 1.5 mg/kg. Using the 5.6 mg/kg standard as the basis for calculations, the MDL for the method would be approximately 1 mg/kg, and the Limit of Quantification (LOQ) approximately 3 mg/kg. Repeatability of the measurements, as defined by the International Standards Organization guidelines, would be 2 times the square root of 2 times the short term standard deviation, or about 0.85 mg/kg.

Using IUPAC definitions of limit of detection, as specified by Long and Winefordner[6], the lowest standard used in the calibration curve and the blank value may be used to approximate a lowest limit of detection. This approach is based on how many standard deviation units exist between the blank and the lowest discernable analytical signal. **Using this approach, the LOD for these data would be 0.18 mg/kg**.

These data are not conclusive for all D 5453 instrumentation, but are the result of three days of data on three low-level standards. In fact, variations caused by instrument condition and actual laboratory application can make any attempt to generate “universal” LOD/LOQ data seem non-conclusive. However, **this report finds strong evidence that D 5453 can be routinely applied to the determination of sulfur in liquid hydrocarbons at levels less than 1 mg/kg**.

**Table 13:** Results & standard deviations on three standards, using the last 7 of 10 runs each on 3 consecutive days, with LOD/LOQ values calculated from each data set

**0.589 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 0.92 | 1.19 | 0.89 | | |
| | 1.01 | 0.78 | 0.99 | | |
| | 0.66 | 0.91 | 0.79 | | |
| | 0.63 | 0.93 | 0.82 | | |
| | 0.92 | 0.63 | 0.75 | | |
| | 0.68 | 0.66 | 0.70 | | |
| | 0.89 | 0.70 | 0.43 | | |
| Avg. | 0.82 | 0.83 | 0.77 | | |
| SD | 0.15 | 0.20 | 0.18 | 0.53 | 1.76 |

**1.54 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 1.72 | 1.84 | 1.90 | | |
| | 1.71 | 2.11 | 1.84 | | |
| | 1.77 | 1.98 | 1.85 | | |
| | 1.65 | 1.78 | 1.65 | | |
| | 1.72 | 2.06 | 2.01 | | |
| | 2.01 | 2.13 | 1.90 | | |
| | 1.31 | 1.84 | 1.68 | | |
| Avg. | 1.70 | 1.96 | 1.83 | | |
| SD | 0.21 | 0.14 | 0.13 | 0.48 | 1.59 |

**5.60 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 6.58 | 6.80 | 6.25 | | |
| | 6.58 | 6.90 | 5.96 | | |
| | 6.24 | 6.87 | 6.31 | | |
| | 5.96 | 6.38 | 5.92 | | |
| | 6.05 | 6.68 | 6.22 | | |
| | 6.06 | 6.81 | 6.01 | | |
| | 6.34 | 6.17 | 5.03 | | |
| Avg. | 6.26 | 6.66 | 5.96 | | |
| SD | 0.25 | 0.28 | 0.44 | 0.97 | 3.23 |

Turn page to view **table 14** →

**Table 14:** Results & standard deviations on three standards, using the first 7 of 10 runs each on 3 consecutive days, with LOD/LOQ values calculated from each data set

**0.589 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 0.63 | 0.93 | 0.82 | | |
| | 0.92 | 0.63 | 0.75 | | |
| | 0.68 | 0.66 | 0.70 | | |
| | 0.89 | 0.70 | 0.43 | | |
| | 0.24 | 0.75 | 0.72 | | |
| | 0.55 | 0.76 | 0.59 | | |
| | 0.49 | 0.79 | 0.55 | | |
| Avg. | 0.63 | 0.75 | 0.65 | | |
| SD | 0.23 | 0.10 | 0.13 | 0.47 | 1.56 |

**1.54 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 1.65 | 1.78 | 1.65 | | |
| | 1.72 | 2.06 | 2.01 | | |
| | 2.01 | 2.13 | 1.90 | | |
| | 1.31 | 1.84 | 1.68 | | |
| | 1.49 | 1.97 | 1.49 | | |
| | 1.55 | 1.72 | 0.85 | | |
| | 2.10 | 1.75 | 1.21 | | |
| Avg. | 1.69 | 1.89 | 1.54 | | |
| SD | 0.28 | 0.16 | 0.40 | 0.84 | 2.81 |

**5.60 mg/kg standard**

| | Day 1 | Day 2 | Day 3 | LOD | LOQ |
|---|---|---|---|---|---|
| | 5.96 | 6.38 | 5.92 | | |
| | 6.05 | 6.68 | 6.22 | | |
| | 6.06 | 6.81 | 6.01 | | |
| | 6.34 | 6.17 | 5.03 | | |
| | 5.58 | 6.38 | 4.97 | | |
| | 5.62 | 5.76 | 3.95 | | |
| | 5.19 | 5.29 | 3.82 | | |
| Avg. | 5.83 | 6.21 | 5.13 | | |
| SD | 0.39 | 0.53 | 0.98 | 1.90 | 6.32 |

## NOTES

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