

EPA ULSD Round Robin Program Overview

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November 1, 2005

Outline

- Overview of instrument qualification process and results.
- Overview of round robin test program participation.
- Review of test program sample analysis.
- Brief review of test program data analysis.
- Upcoming data presentation and publication.



ULSD Round Robin Program Qualification

- All laboratories participating in this round robin test program were required to qualify their sulfur measurement methods with EPA.
- This meant that the labs must meet the precision and accuracy requirements per 40 CFR 80.580 - 80.585.



ULSD Round Robin Program Qualification cont.

- Any VCSB or non-VCSB method that meets specified performance criteria under 40 CFR 80.584 and 80.585 can be used.
- For 15 ppm ULSD, just using a designated “approved” method is not sufficient.
- Lab has to qualify each individual method it wants to use on lab specific basis using the Qualification Criteria in 40 CFR 80.584.
- Non-VCSB method good for only 5 years unless VCSB acceptance is obtained.
- Allows for greater flexibility in instrument selection and encourages the development and use of better instrumentation.



ULSD Round Robin Program Qualification cont.

- **Qualification criteria** (P&A criteria were based on 2002 ASTM Round Robin results using ASTM D 3120-03 @ 15 ppm)
 - Precision
 - 20 repeat tests over at least 20 days on samples taken from a single commercially available diesel fuel (5 – 15 ppm range).
 - Standard deviation must be less than
 - » 0.72 ppm for 15 ppm sulfur diesel fuel.
 - » 0.72 ppm is equal to 1.5 times standard deviation of D 3120.
 - » Where the standard deviation (SD) is equal to the repeatability (r) of D 3120 at 15 ppm divided by 2.77.
 - » $r = 0.08520(x + 0.65758)$; $r = 1.33$; $SD = 0.48$



ULSD Round Robin Program Qualification cont.

- Accuracy
 - Two continuous series of 10 repeat tests on two commercially-available gravimetric sulfur standards.
 - Mean of test results may not deviate from the Accepted Reference Value of the standard by more than.
 - » 0.54 ppm for 15 ppm sulfur diesel fuel.
 - » 0.54 ppm is equal to 0.75 times the precision value (0.72 ppm).
 - 10 tests are required on each of two sulfur levels as follows;
 - » 1-10 ppm and 10-20 ppm for 15 ppm sulfur diesel fuel.



Qualification Results

- The qualification results by method are as follows (as of 10/13/05)*:

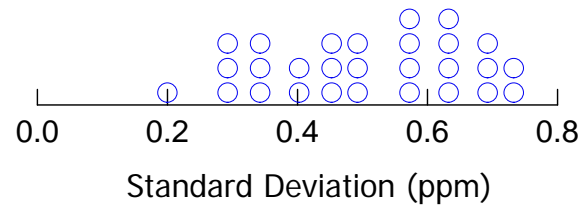
Test Method	D 5453	D 7039	D 2622	D 3120	Average Across Methods	CFR Req.
Number of Inst.	116	19	28	3		
Average Precision	0.29	0.38	0.50	0.39	0.34	0.72
Average Accuracy (1 - 10 ppm)	0.20	0.18	0.24	0.14	0.20	0.54
Average Accuracy (10 - 20 ppm)	0.20	0.20	0.24	0.20	0.21	0.54

*Not all of the qualified labs participated in the RR test program.

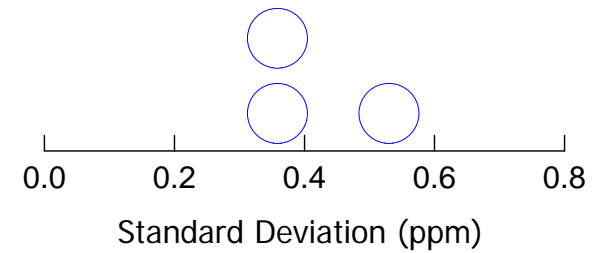


Dot Plot of Qualification Method Specific Precision Results

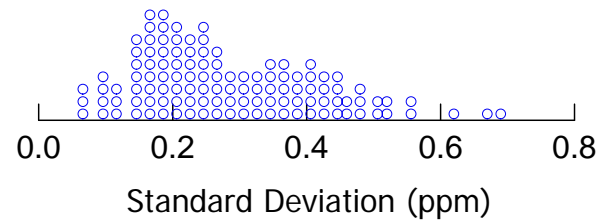
D 2622



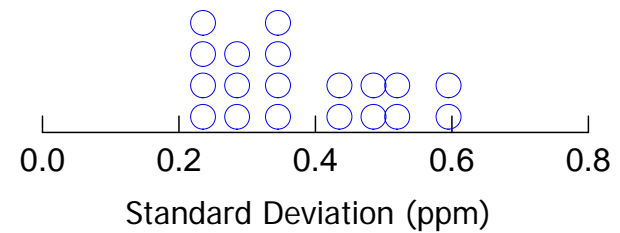
D 3120



D 5453

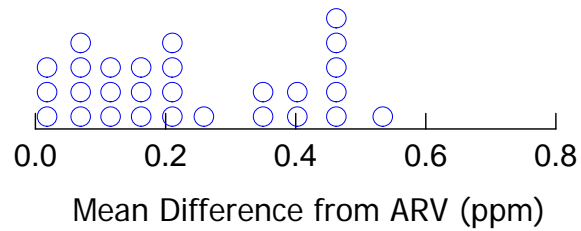


D 7039

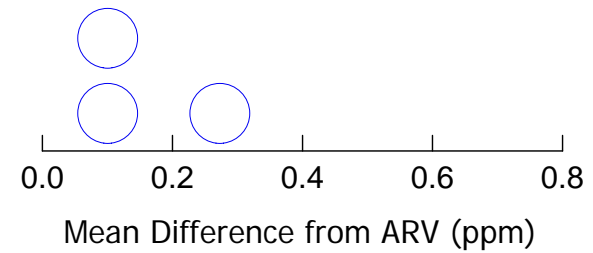


Dot Plot of Qualification Method Specific 1 to 10 ppm Accuracy Results

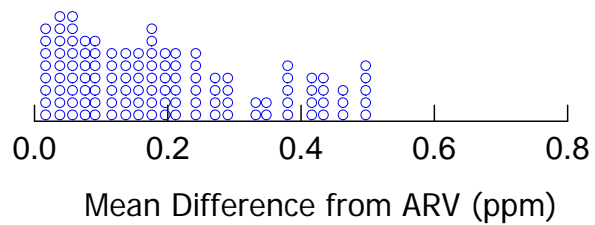
D 2622



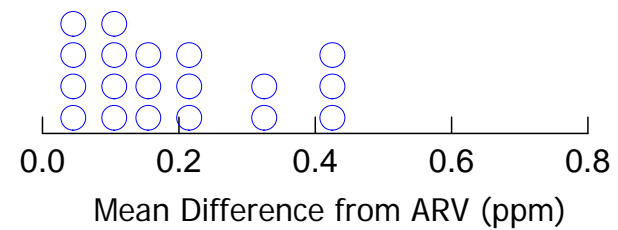
D 3120



D 5453

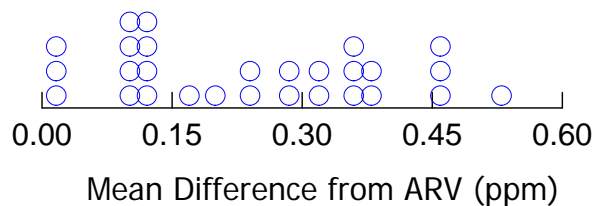


D 7039

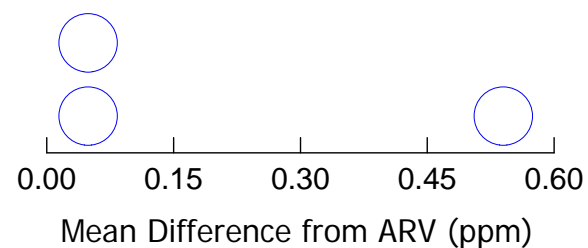


Dot Plot of Qualification Method Specific 10 to 20 ppm Accuracy Results

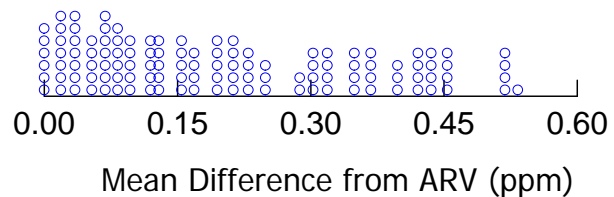
D 2622



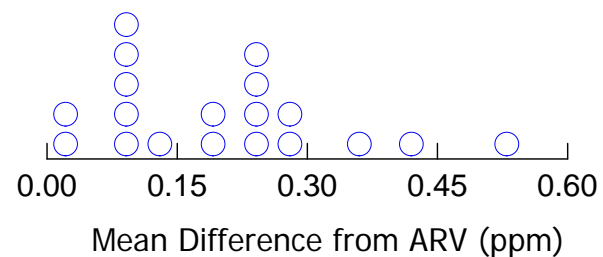
D 3120



D 5453

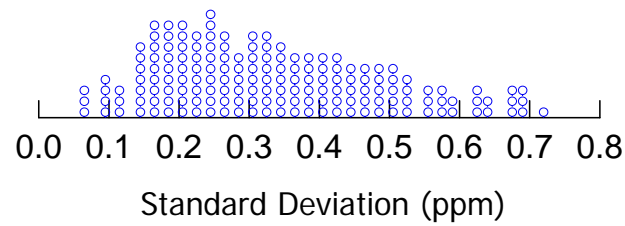


D 7039

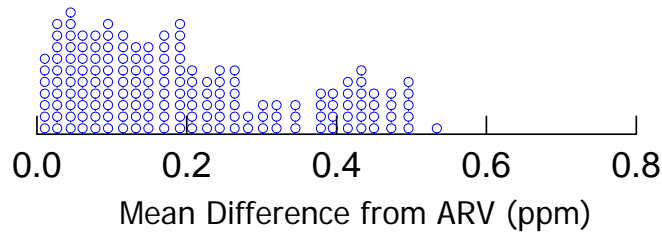


Dot Plot of Qualification Composite Precision and Accuracy Results

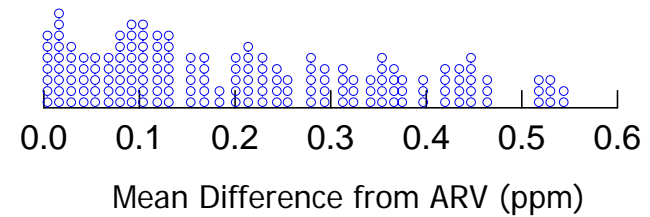
Precision



1-10 ppm
Accuracy



10-20 ppm
Accuracy



ULSD Round Robin Program Participation

- Initially 161 labs utilizing 208 instruments registered to participate in the program.
- Some labs failed to qualify (2).
- Others determined during the qualification process that they would not pass and abandoned testing.
- Most of these labs started looking into procuring new instrumentation.
- Overall, 59, or 28% of the instruments that registered for the program dropped out.
 - This left 129 labs participating with 149 instruments.



ULSD Round Robin Program Participation

- Final participant count for the program was as follows:
 - 129 labs using 149 instruments in July.
 - 125 labs using 143 instruments in August.
- We lost some labs in August due to hurricane Katrina.



ULSD Round Robin Program Fuel Samples

- Five fuel samples were sent out in the months of July and August 2005.
 - Fuel sample sulfur values were unknown to the test labs.
- EPA targeted blending samples in the 7 to 15 ppm range.
- The samples were not sent out for independent analysis.
- The actual concentrations turned out to be in the 7 to 21 ppm range.
- One blend was sent out both months as sample #5.
- The blind gravimetric sent out each month was NIST SRM 1616b (8.41 ppm sulfur in kerosene).
 - The SRM was dyed yellow to “blend in” with other samples.
 - Sulfur contribution of the dye to the SRM was 0.000516 ppm.



ULSD Round Robin Program Fuel Samples cont.

- The target fuel sample concentration and actual concentration based on composite robust mean are as follows:

	July Blend Target	July Composite Robust Mean*	August	August Composite Robust Mean*
Fuel #1	7	7.31	9	10.05
Fuel #2	11	10.71	13	14.42
Fuel #3	16	20.86	17	17.80
Fuel #4**	8.41	8.32	8.41	8.32
Fuel #5***	15	14.69	15	14.76

*This mean is the average of the two composite robust means taken from the In-House and NIST data.

** This fuel was the gravimetric both months and was actually NIST SRM 1616b.

*** This fuel blend was sent out both months as fuel #5.



ULSD Round Robin Program Measurement

- NIST SRMs were sent out each month with the blind fuel samples.
- Laboratories were required to measure the blind fuel samples in triplicate using two different calibration curves.
 - Historical, in-house curve (presumably used for qualification).
 - Curve generated using four EPA provided NIST SRMs.



ULSD Round Robin Program Measurement cont.

- SRMs used in 4-point calibration curve generation are as follows:
 - RM 8771 0.07 ± 0.014 ppm S in diesel fuel
 - SRM 1616b 8.41 ± 0.12 ppm S in kerosene
 - SRM 2723a 11.0 ± 1.1 ppm S in diesel fuel
 - SRM 2770 41.57 ± 0.39 ppm S in diesel fuel



ULSD Round Robin Program Data Analysis

- Data analysis was performed by SwRI.
- Repeatability and Reproducibility were calculated
 - On both a composite and method specific basis.
 - Using both the ASTM method and an Analysis of Variance method (ANOVA).
 - Using both in-house and NIST SRM calibration curves.
- Outliers were determined two ways.
 - Using a two-stage robust procedure identical to that used by ASTM.
 - Based on the results of the measurement of the blind gravimetric fuel sample (SRM check standard).



ULSD Round Robin Program

Gravimetric Limit Determination

- We allowed a ± 0.90 ppm deviation since it was an average of three measurements.
 - Instead of 0.54 ppm qualification accuracy criteria.
- The value takes into consideration the 95% two-sided confidence interval for three repeat measurements, as well as real bias and gravimetric standard uncertainty (GSU).

$$\begin{aligned} &= 0.54 - 95\% CL_{10-1} + 95\% CL_{3-1} + GSU \\ &= (0.54 - 0.298 + 0.543 + 0.12) = 0.905 \end{aligned}$$

95% CL calculations assume infinite degrees of freedom and use 0.48 as the std. dev. (0.48 is std. dev. of D 3120 @ 15 ppm). GSU = 0.12. 0.54 = accuracy limit in qualification criteria.



ULSD Round Robin Program Additional Presentation Dates

- Data will also be presented at the following conferences
 - 2005 ULSD Implementation Workshop on 11/10/05.
 - ASTM D02.SC3 meeting on 12/6/05.
- Final report due in late November.
- The data will be published in an SAE technical paper in 2006.

