EPA ULSD Qualification and Round Robin Test Program Results

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Outline

- Motivation for test program.
- Overview of instrument qualification process and results.
- Overview of round robin test program participation.
- Review of test program sample analysis.
- Review of test program data analysis.
- Review of test program results.
- Conclusions.

Motivation for ULSD Round Robin Program

- ULSD FRM allows for a 2 ppm downstream test tolerance on sulfur measurements.
- We heard concerns that actual reproducibility (R) may be > 2 ppm.
  - 4.4 ppm historically as published in ASTM D 5453-03a.
  - 3-4 ppm in 2004 and 2005 ASTM crosscheck program for D 5453.
- If real world reproducibility is higher, then industry feared it would force down pipeline standards and refinery production targets, impacting cost and supply.

Motivation for ULSD Round Robin Program cont.

- EPA was concerned that current data is not reflective of what is possible/likely in 2006.
  - If we set the tolerance based on historical reproducibility, and significant improvement occurred, it would have the effect of relaxing the 15 ppm standard in-use.
  - None of the labs in the ASTM ILCP were qualified for measuring sulfur in the 15 ppm range for precision and accuracy.
- Committed to conduct our own round-robin test program limited to just EPA qualified laboratories and adjust the test tolerance accordingly as necessary.
  - We developed the test program and analytical protocol with industry stakeholders and received their buy-in May 2005.
- This test program has been completed and the results will be presented here.

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 sulfur)
  - 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.
  - 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.
  - 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).

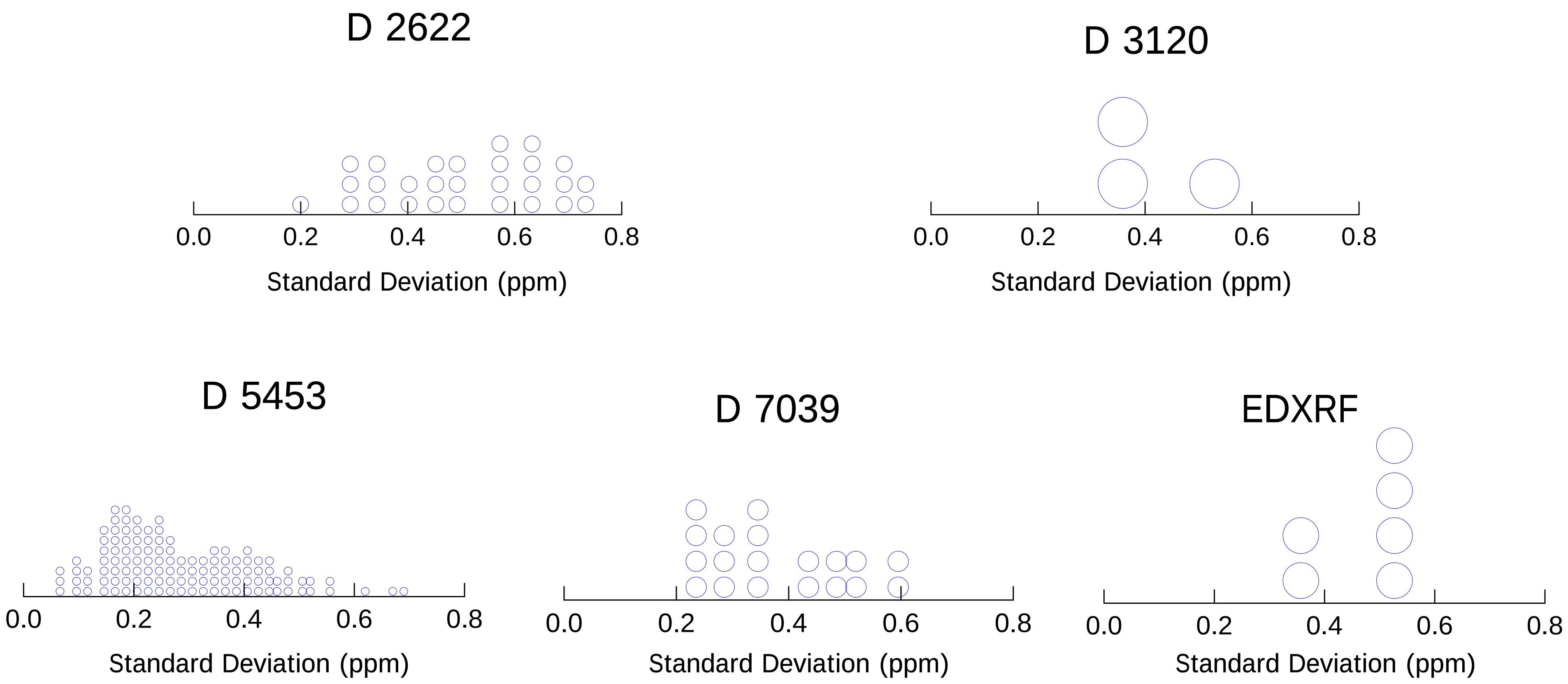
Qualification Results

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

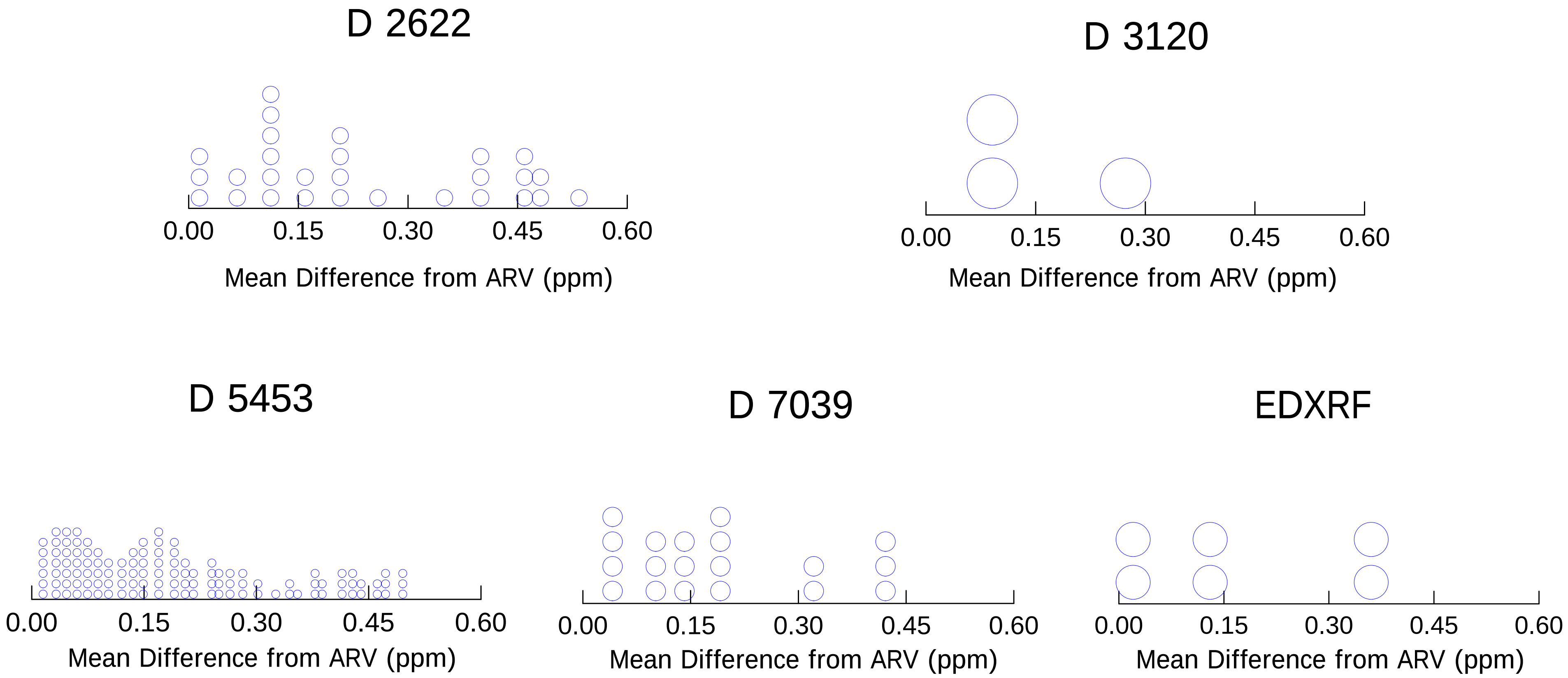
Test Method	D 5453	D 7039	D 2622	D 3120	EDXRF	Average Across Methods	**CFR Req.**
Number of Inst. (Total = 173)	116	19	28	3	6		
Average Precision	0.29	0.38	0.50	0.39	0.47	0.34	**0.72**
Average Accuracy (1 - 10 ppm)	0.20	0.18	0.24	0.14	0.16	0.20	**0.54**
Average Accuracy (10 - 20 ppm)	0.20	0.20	0.24	0.20	0.24	0.21	**0.54**

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

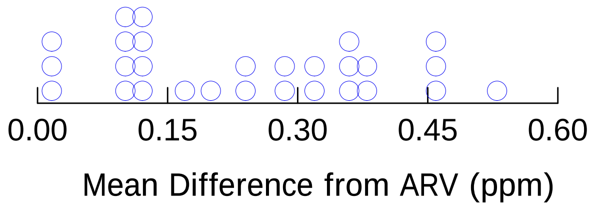
Dot Plot of Qualification Method Specific Precision Results

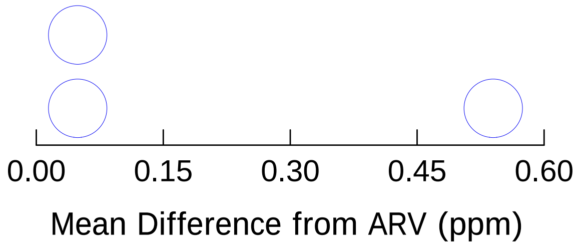


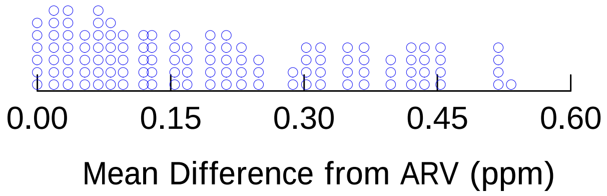
Dot Plot of Qualification Method Specific 1 to 10 ppm Accuracy Results

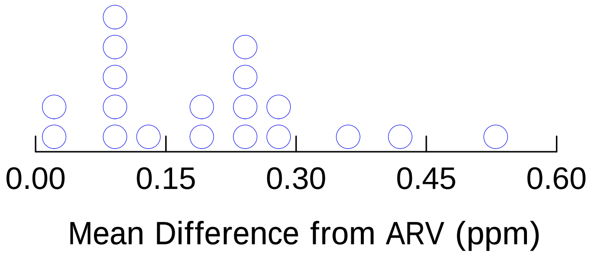


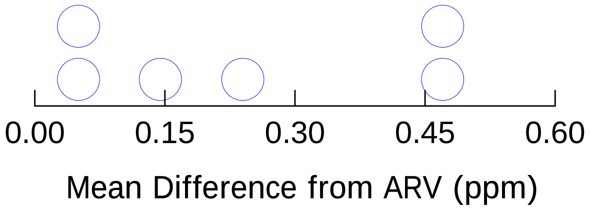
Dot Plot of Qualification Method Specific 10 to 20 ppm Accuracy Results


D 2622


D 3120

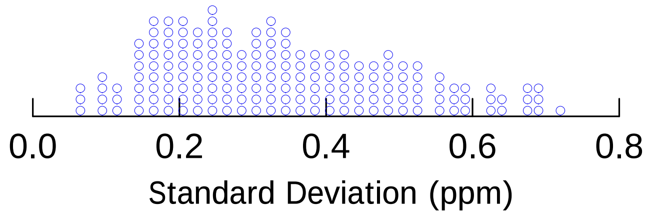

D 5453


D 7039

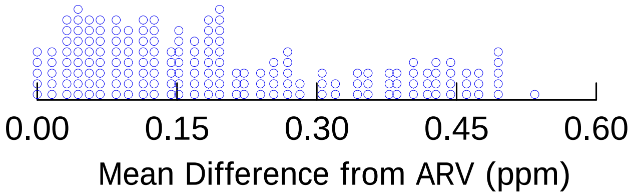

EDXRF

Dot Plot of Qualification Composite Precision and Accuracy Results

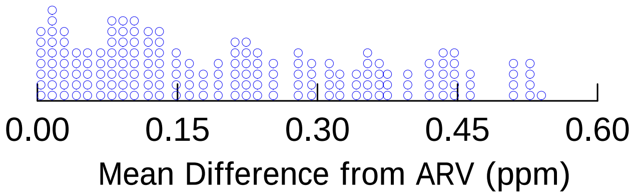
Precision



1-10 ppm Accuracy



10-20 ppm Accuracy



ULSD Round Robin Program Qualification Conclusions

- Qualification criteria easily met by the newest methods, D 5453 and D 7039.
- Precision means of 0.29 and 0.38 ppm for D 5453 and D 7039 respectively were well below the CFR limit of 0.72 ppm.
- Accuracy means for D 5453 and D 7039 respectively were well below the CFR limit of 0.54 ppm.
  - – 0.20 and 0.18 (1 to 10 ppm gravimetric std.)
  - – 0.20 and 0.20 (10 to 20 ppm gravimetric std)

ULSD Round Robin Test Program

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 cont.

Test Method	July 2005	August 2005	Dropped Out
D 5453	98	93	27
D 2622	25	24	23
D 7039	16	16	3
EDXRF	6	6	1
D 3120	3	3	3
D 7041	1	1	0
D 4294	0	0	2
Total Instruments	149	143	59
Total Labs	129	125	32

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.
- A blind gravimetric was sent out each month as fuel #4 - NIST SRM 1616b, 8.41 ppm sulfur in kerosene.

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 Sample Analysis

- 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.
  - – Based on their own individual in-house calibration standards (presumably used for qualification).
  - – Based on four EPA provided NIST SRMs.

ULSD Round Robin Program Sample Analysis 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 under contract by SwRI.
- Outliers were determined two ways.
  - Based on the results of the measurement of the blind gravimetric fuel sample (SRM check standard).
    - Analogous to the use of a calibration check standard in normal day-to-day test operations.
    - Possible when known gravimetric standards exist.
  - Using the two-stage robust procedure identical to that used in the ASTM inter-laboratory crosscheck program (ILCP).
    - It does not require known fuel sulfur values for any of the sample fuels.

Gravimetric Outlier Deletion Method

- Used the 8.41 ppm SRM as the calibration check standard.
  - This SRM was one of the same SRMs used to calibrate the instrument.
  - The SRM was dyed yellow to “blend in” with other samples.
  - Sulfur contribution of the dye to the SRM was 0.000516 ppm.

- Compute the average (AVG) of the three repeat tests taken on the 8.41 ppm SRM for a given month by a given lab.
  - Fuel #4 in both July and August.

- Obtain the accepted reference value (ARV) of the standard fuel.
  - ARV=8.41 ppm in this study.

- Classify the data collected on all five sample fuels for a given month by a given lab as outliers and delete the entire set of lab data if

$$|AVG - 8.41| > 0.90.$$

Gravimetric Outlier Deletion Method cont.

- We allowed a ±0.90 ppm deviation since it was an average of three measurements.
  - Instead of 0.54 ppm qualification accuracy criteria over 10 measurements.
  - This compares to the actual means of 0.20 and 0.21 from the actual qualification results.
- 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).

$$= 0.54 - 95\%\ CL_{10\text{-}1} + 95\%\ CL_{3\text{-}1} + GSU$$
$$= (0.54 – 0.298 + 0.543 + 0.12) = 0.905$$

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

Robust Outlier Deletion Method

- Follows the procedure used in the ASTM inter-laboratory crosscheck program.
- Compute robust mean, RM, and robust standard deviation, RSD, for each combination of fuel sample, test method and calibration curve using a procedure that limits the influence of unusually large or small values.
- Classify an individual lab repeat value, Y, as an outlier and delete the value if

$$|Y - RM| > 3*RSD.$$

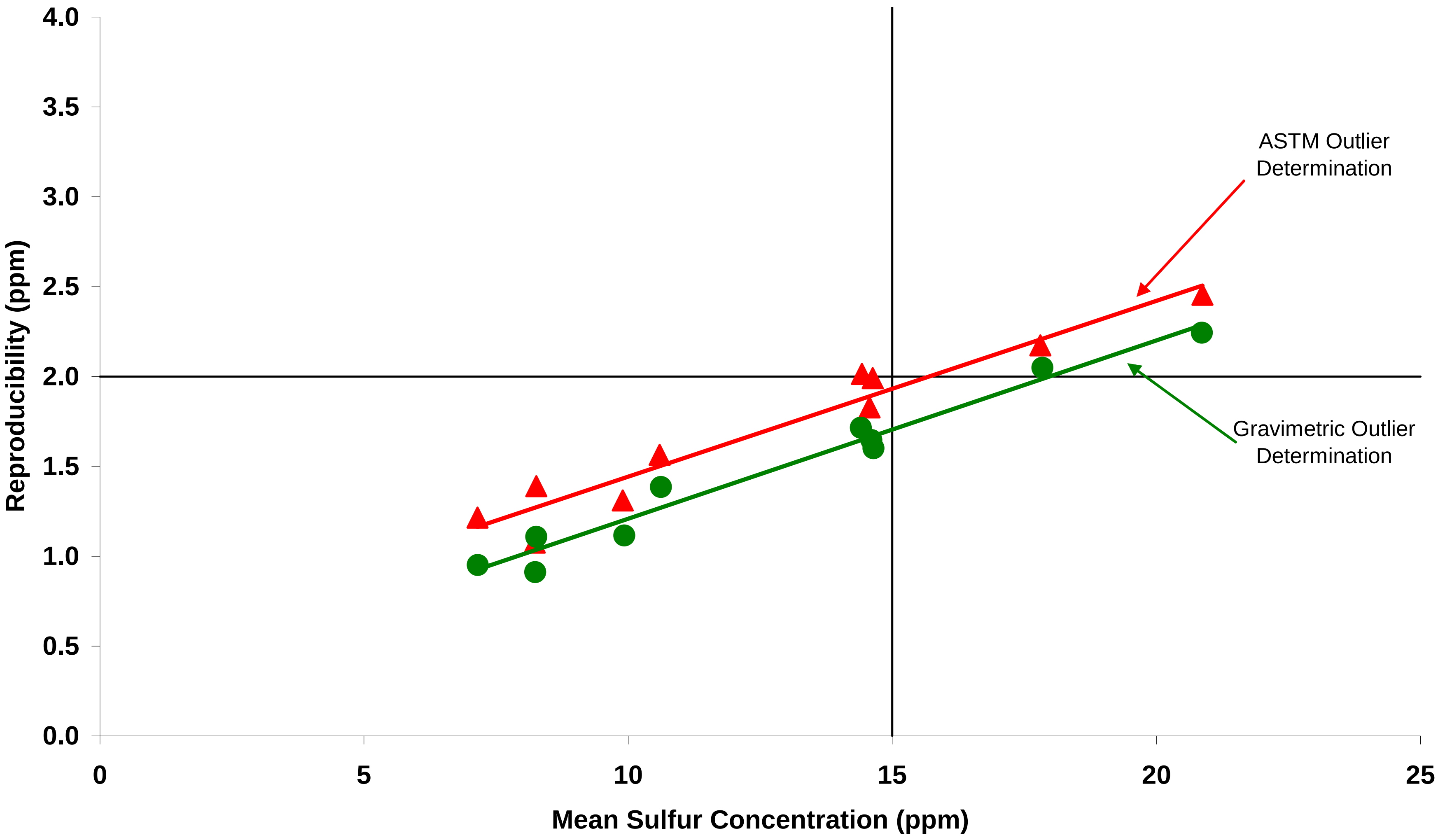
R&r Analysis Methods

- Calculate R and r in two ways
  - Robust calculation identical to the ASTM crosscheck program.
  - Analysis of Variance (ANOVA) method.
- ANOVA results were different, but no clear advantage/disadvantage was evident.
- Therefore, only results using the robust ASTM calculation will be presented here.

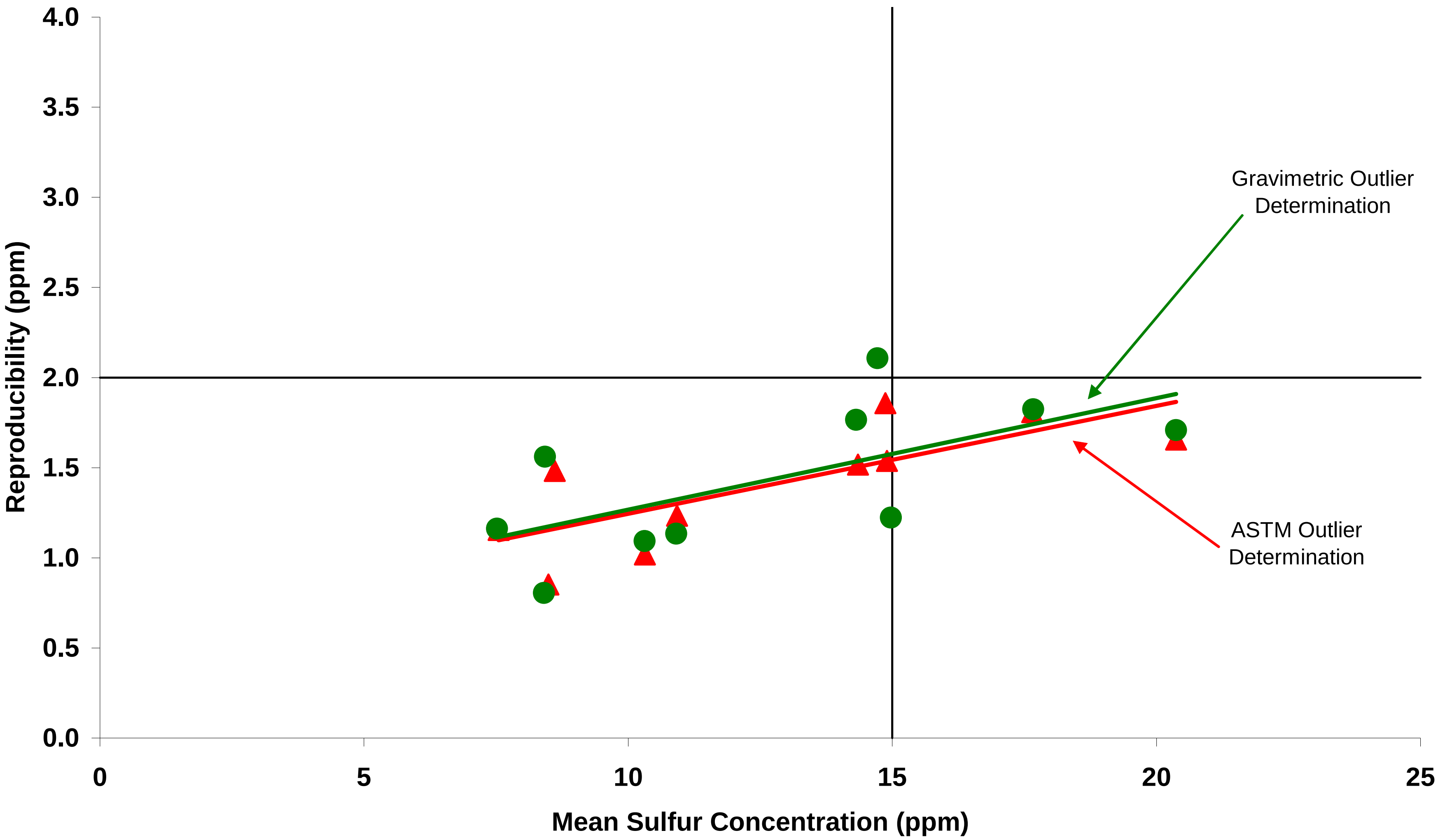
Results

ASTM Robust Outlier Determination vs. Gravimetric Outlier Determination - Using ASTM Reproducibility Calculation

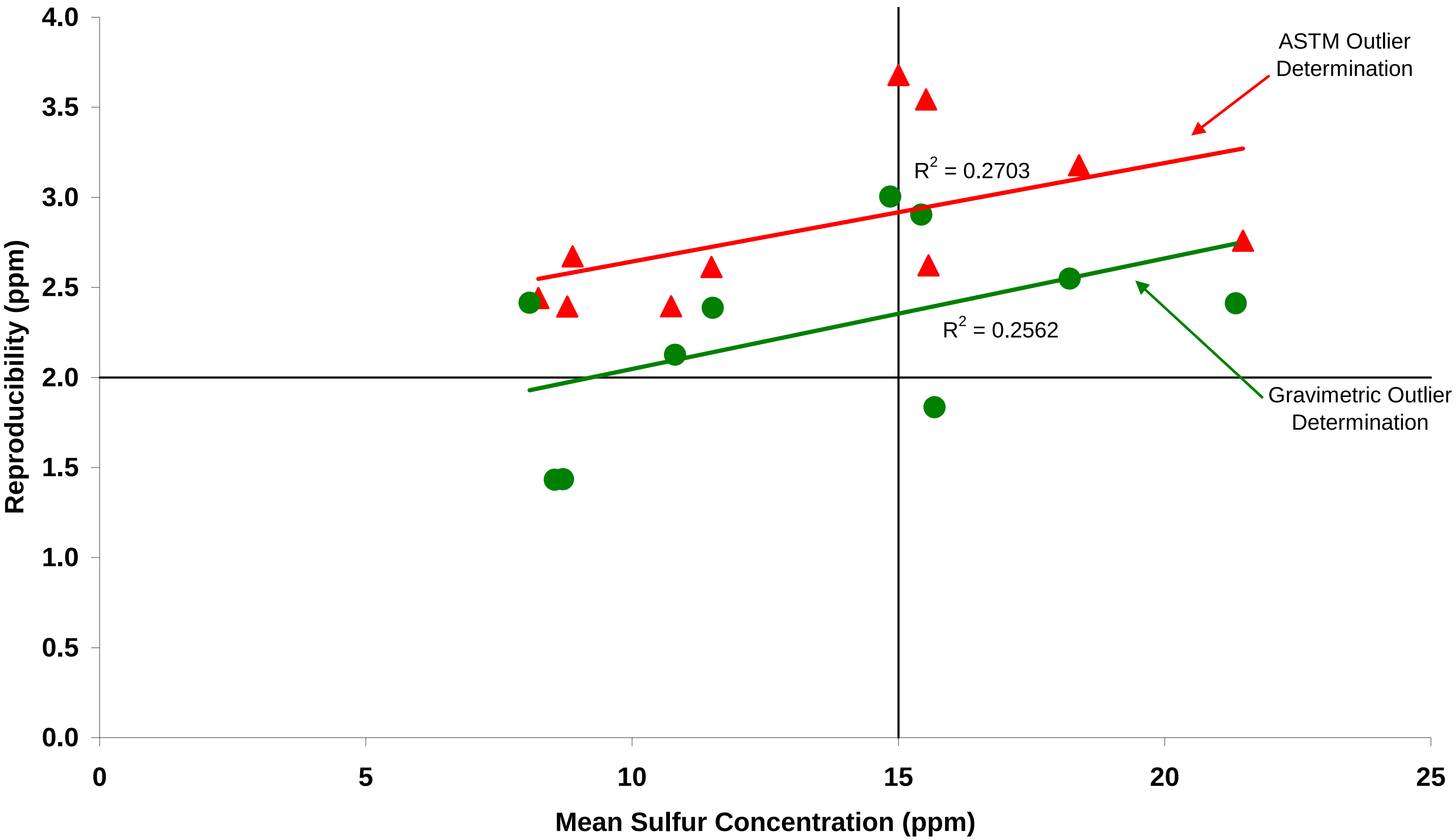
D 5453 Results: ASTM vs. Gravimetric Outlier Deletion
Using ASTM Calculations for Reproducibility and NIST SRM Calibration Curve



D 7039 Results: ASTM vs. Gravimetric Outlier Deletion
Using ASTM Calculations for Reproducibility and NIST SRM Calibration Curve



D 2622 Results: ASTM vs. Gravimetric Outlier Deletion
Using ASTM Calculations for Reproducibility and NIST SRM Calibration Curve

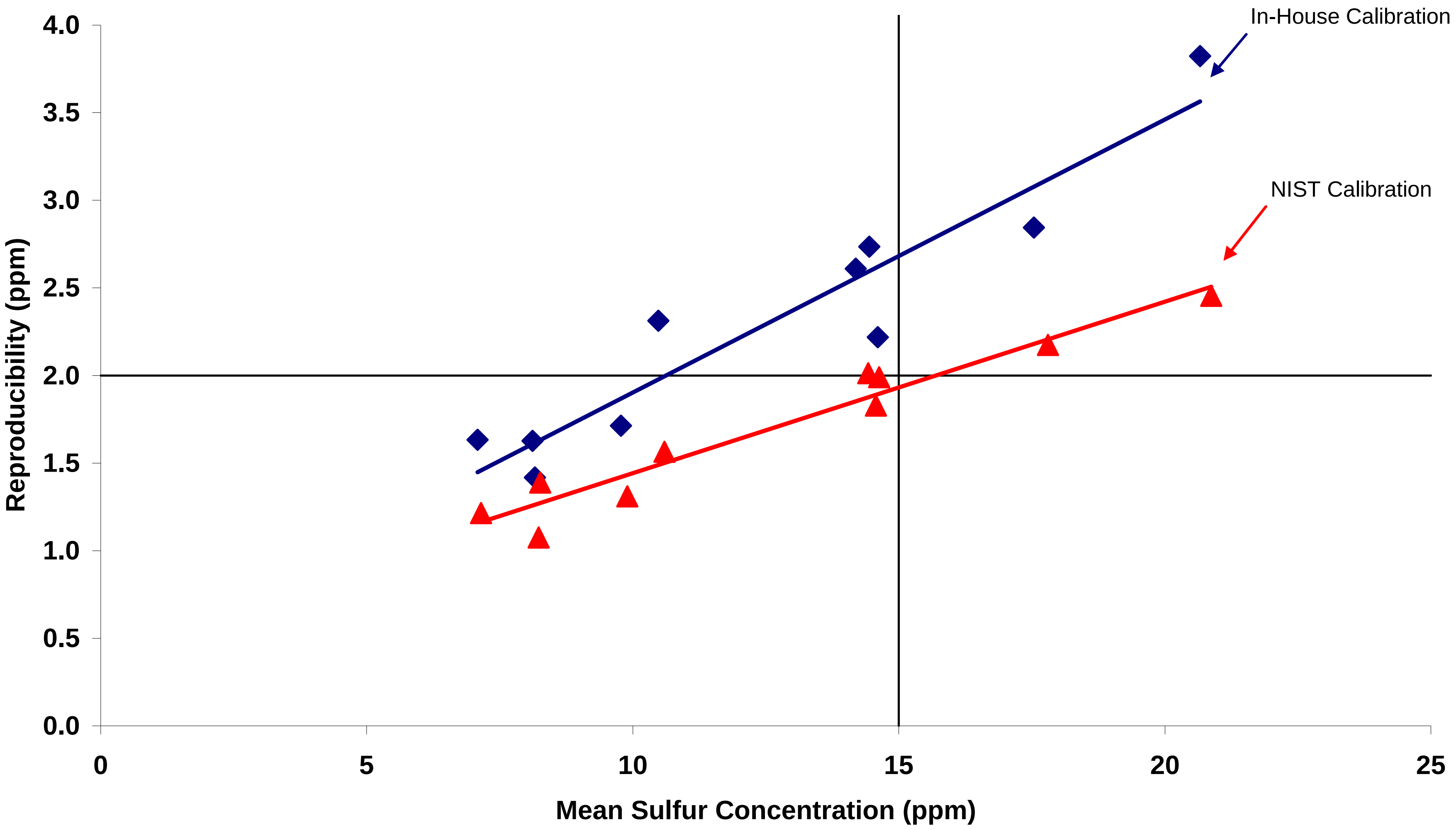


Conclusions

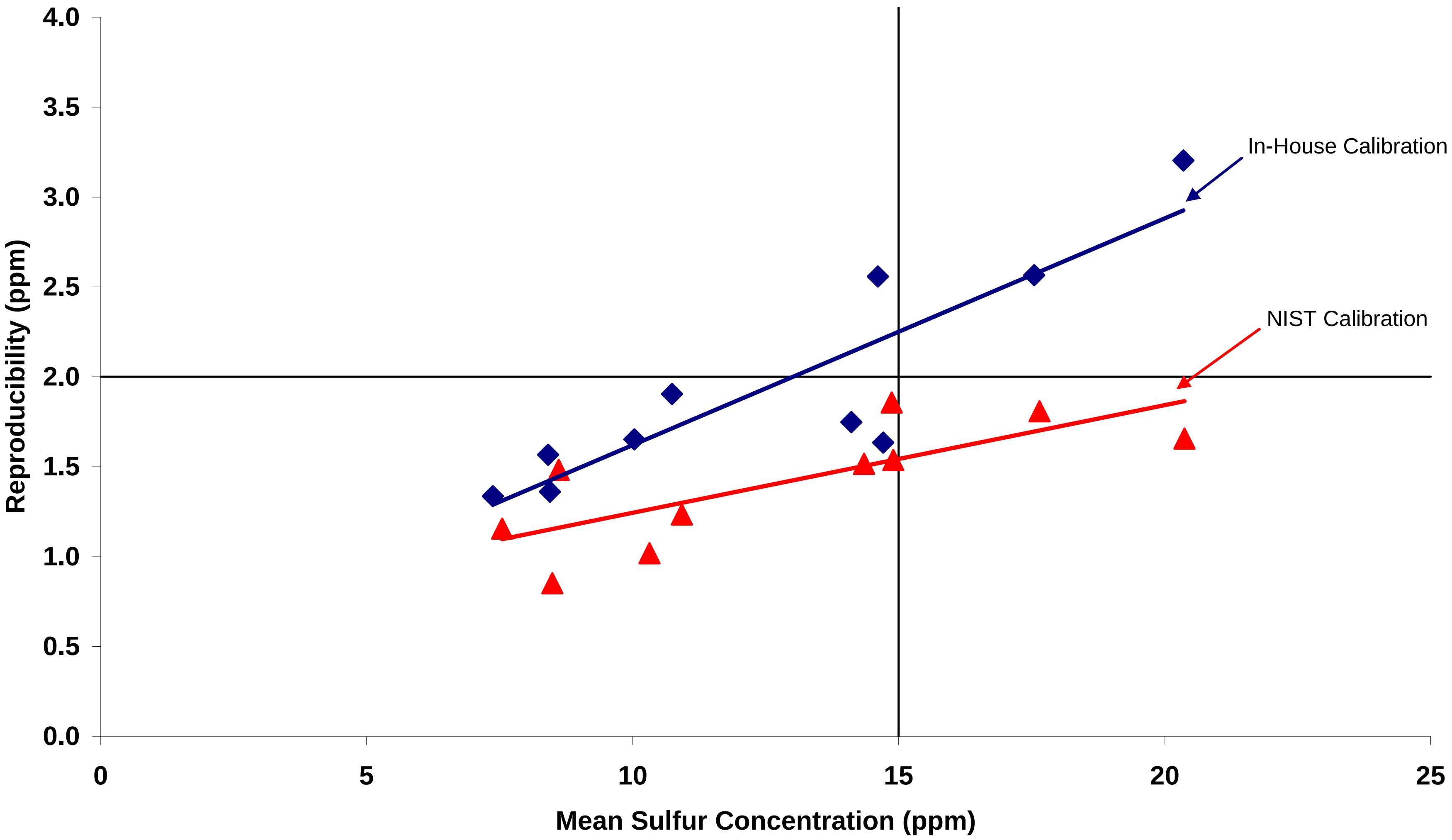
- The gravimetric deletion method produces lower R-values than the ASTM robust deletion method.
- For labs that can pass a calibration check standard, R is well below 2.0 ppm for D 5453 and D 7039.
- Oldest test method (D 2622) apparently not up to the challenge.
  - High R
  - Poor R^2
  - High variability may be due to wide range in instrument ages and capabilities of different instruments being used today.

In-House Calibration Curves vs. NIST Calibration Curves – ASTM Reproducibility and ASTM Robust Outlier Determination

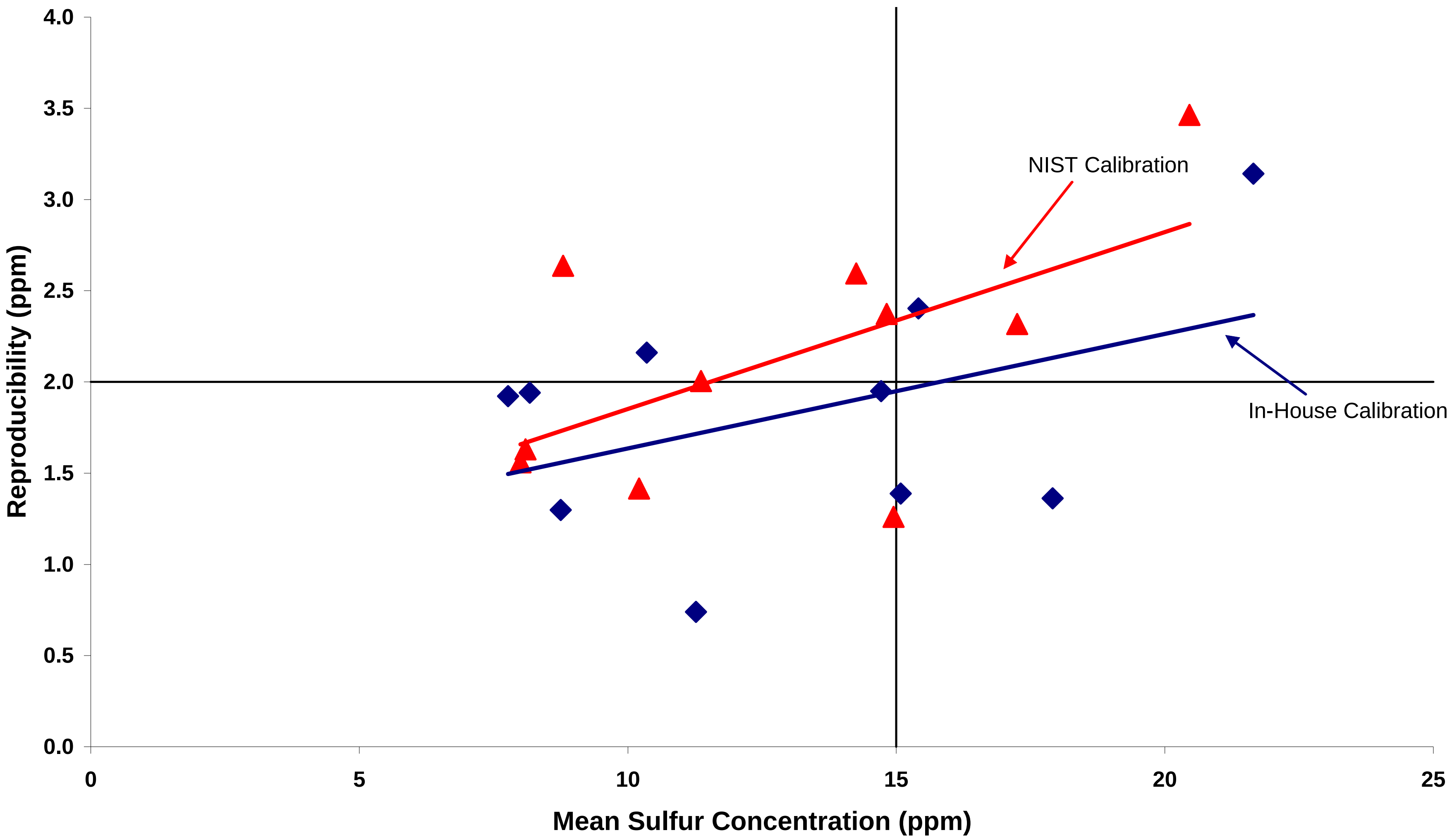
D 5453 Results: In-House vs. NIST SRM Calibrations Using ASTM Procedures to Calculate Reproducibility and Outliers



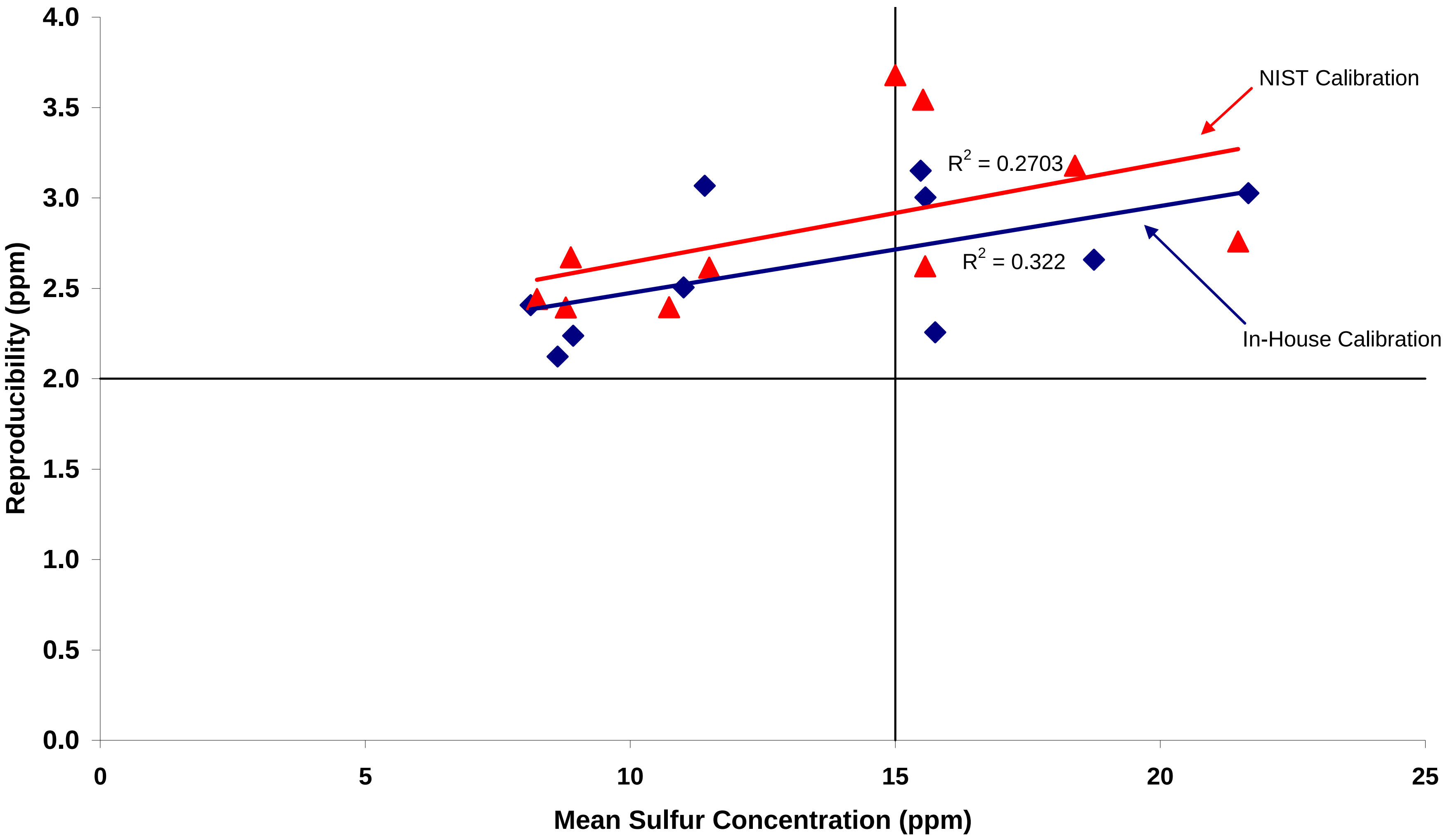
D 7039 Results: In-House vs. NIST SRM Calibrations Using ASTM Procedures to Calculate Reproducibility and Outliers



EDXRF Results: In-House vs. NIST SRM Calibrations Using ASTM Procedures to Calculate Reproducibility and Outliers



D 2622 Results: In-House vs. NIST SRM Calibrations Using ASTM Procedures to Calculate Reproducibility and Outliers



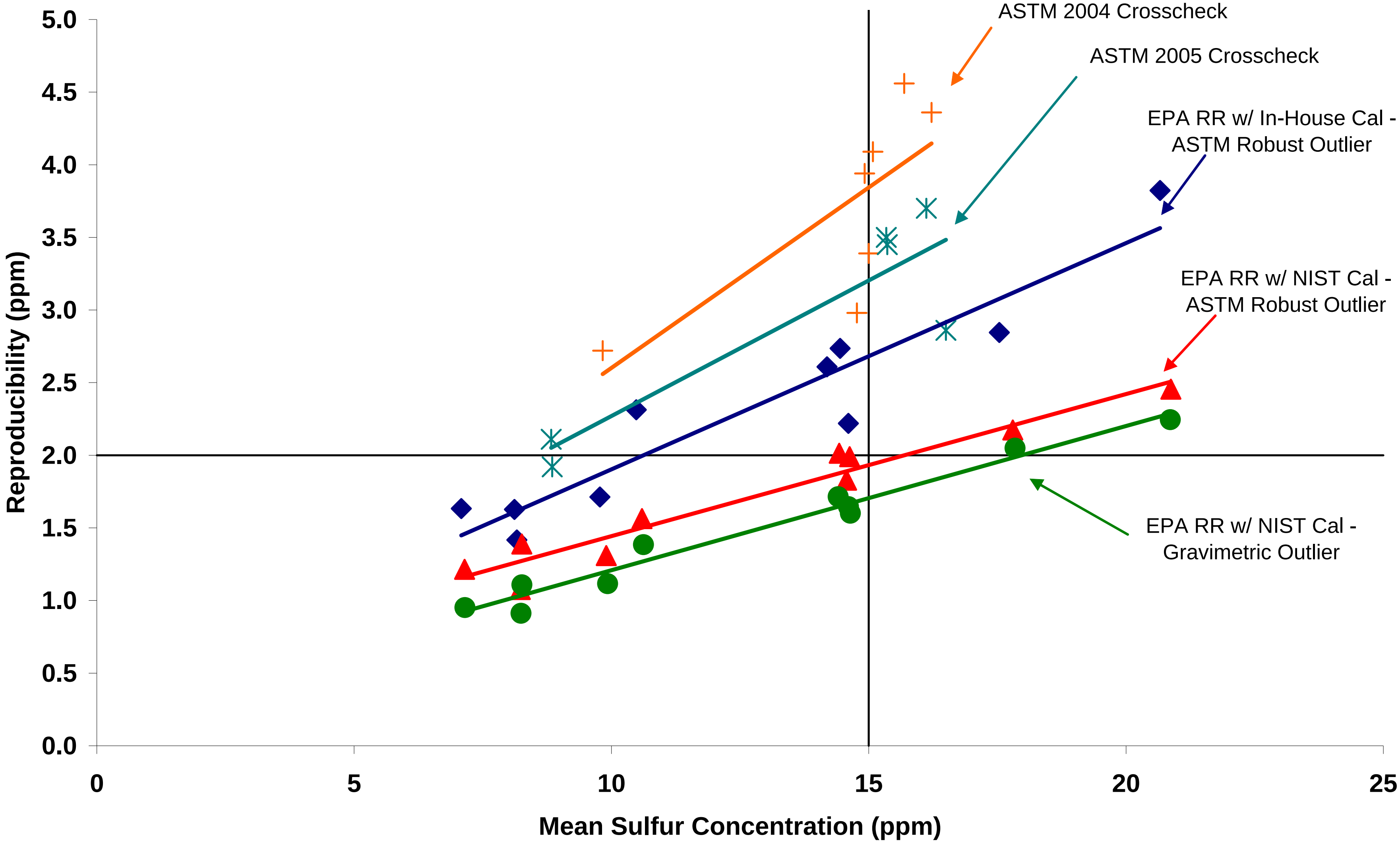
Conclusions

- The R-values for D 5453 and D 7039 are always less using the NIST calibration curves compared to the in-house calibration curves.
- The R-value results for D 2622 and EDXRF are mixed.

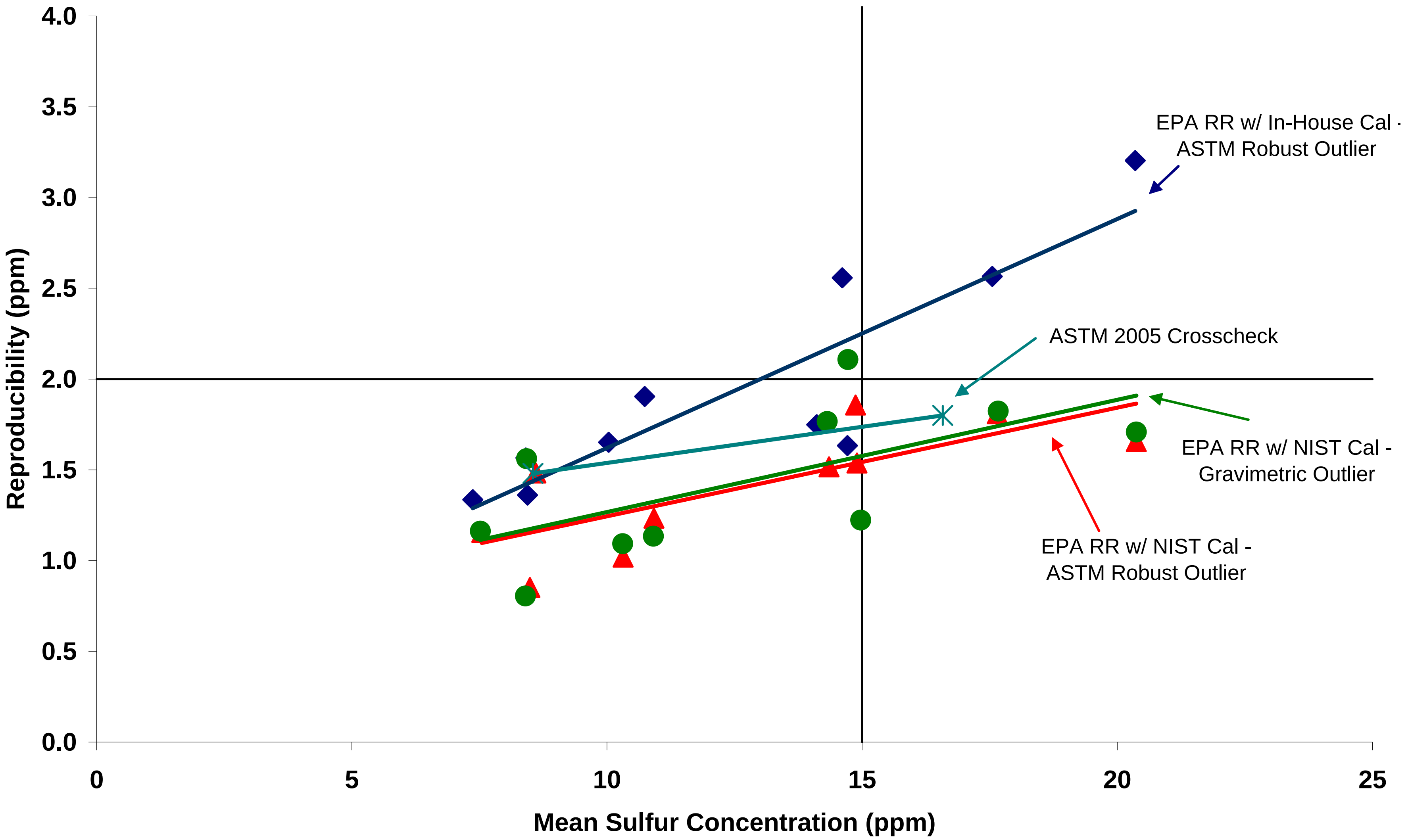
2004 and 2005 ASTM ULSD Crosscheck Results Comparison to EPA RR Results

Using ASTM Robust Outlier Determination and Gravimetric Outlier Determination – ASTM Reproducibility Calculation

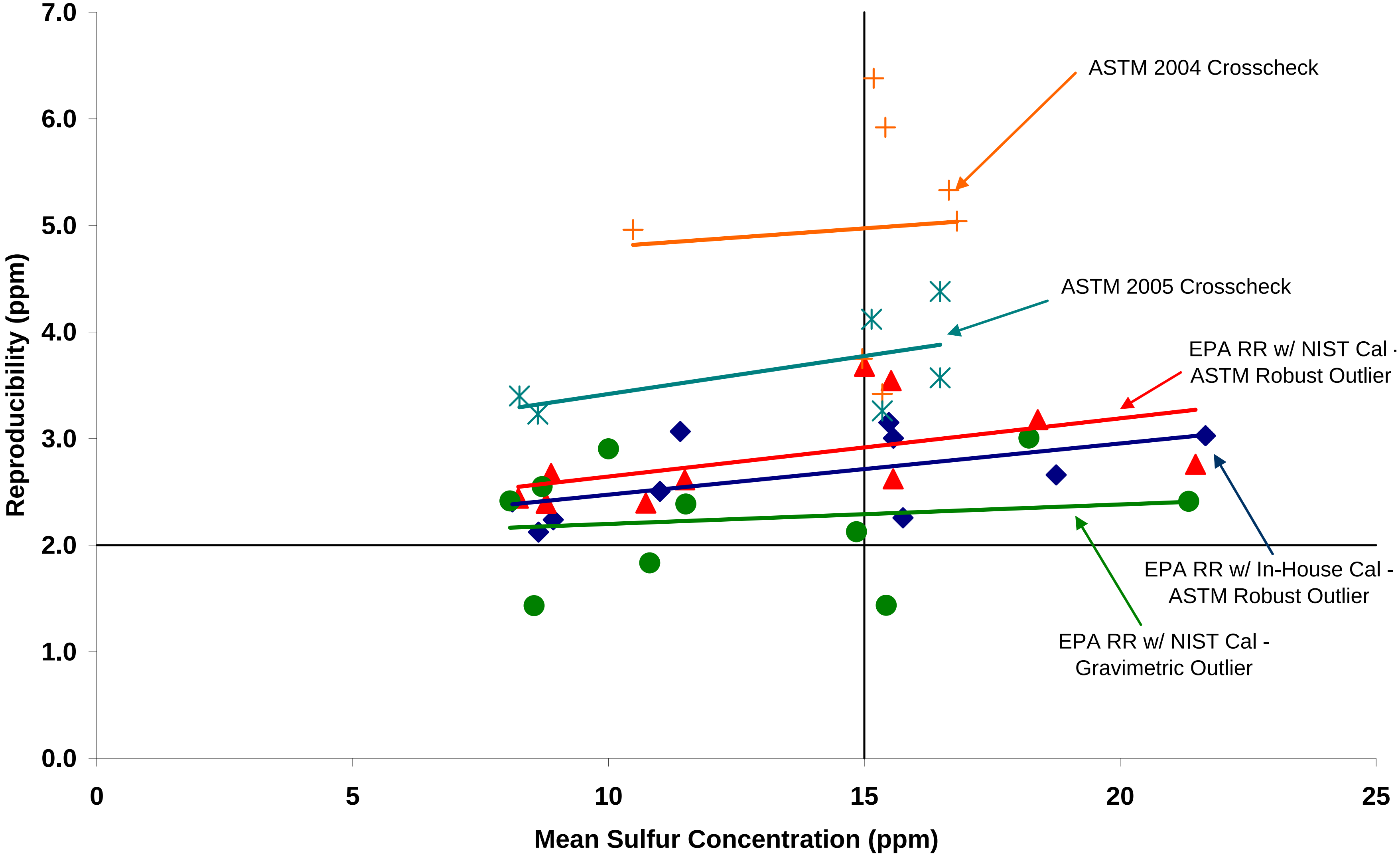
D 5453 Results: ASTM Crosscheck vs. EPA Round Robin Results



D 7039 Results: ASTM Crosscheck vs. EPA Round Robin Results



D 2622 Results: ASTM Crosscheck vs. EPA Round Robin Results



Conclusions

- Qualification process appears to have significantly improved R compared to ASTM crosscheck results.

Predicted Reproducibility at 15 ppm

Approach	Method	ASTM R Calculation
ASTM 2004 ILCP	D 2622	4.97
	D 5453	3.84
ASTM 2005 ILCP	D 2622	3.78
	D 5453	3.20
	D 7039	1.74
EPA RR Results NIST Calibration – Gravimetric Outlier Determination	D 2622	2.29
	D 5453	1.71
	D 7039	1.58
EPA RR Results NIST Calibration – ASTM Robust Outlier Determination	D 2622	2.91
	EDXRF	2.34
	D 5453	1.93
	D 7039	1.54
EPA RR Results In-House Calibration – ASTM Robust Outlier Determination	D 2622	2.71
	EDXRF	1.94
	D 5453	2.68
	D 7039	2.25

Conclusions Summary

- The regression equations produce lower predicted R-values (at 15 ppm) for the EPA RR results relative to the 2004 and 2005 ASTM CC results.
  - The data support the conclusion that limiting the RR participation to labs that have qualified their methods under 40 CFR 80.584 has had a favorable impact on lowering reproducibility.

Conclusions Summary

- The data also support the conclusion that using identical NIST calibration curves across participating labs reduces curve bias contributions to reproducibility.
  - A reduction in predicted R (at 15 ppm) over the predicted R-values obtained using the 2004 and 2005 ILCP data were apparent in all cases when using the NIST calibration curves.
  - The magnitude of the reduction in predicted R (at 15 ppm) from in-house to NIST under ASTM robust deletion was 0.73 ppm on average for D 5453 and D 7039.

- Using gravimetric outlier deletion further improves reproducibility.
  - Use of this method can be analogous to a calibration check standard.

- New test methods are producing results with lower R (D 5453 and especially D 7039).