



better analysis counts

# Sindie Best Practices – Improve Data Quality of Tier III Gasoline Measurements

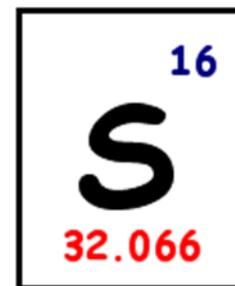
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*July 13, 2017 Webinar*

*Presented by Leslie Johnson, XOS Applications Engineer*

# Sulfur Limits in Gasoline

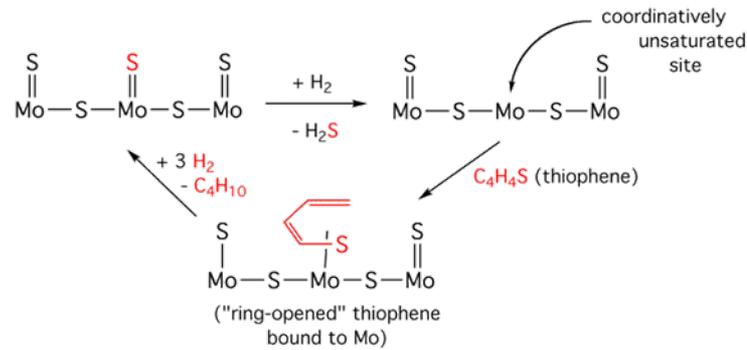
- In 2004, sulfur was limited to 120 ppm
  - In 2006, Tier 2 sulfur is capped at a 30 ppm annual average
  - In 2017, Tier 3 sulfur annual average dropped to 10 ppm
- Lowering sulfur levels lead to an increased emphasis on data quality...



# Data Quality Importance

Sulfur removal costs refineries MILLIONS per year in:

- Capital
- Hydrogen
- Catalyst
- Energy
- OCTANE



Reducing variability in sulfur measurements can contribute to reductions in removal costs!

# Today's Presentation – Improving Data Quality

1. Pick the right sulfur analyzer for your needs

-The XOS  has best in class precision!

2. Use Best Practices to reduce contamination and to obtain the best quality data

3. Maintain your analyzer at regular intervals

4. Calibration tips

Today's Focus

5. Sindie Tier III PBMS data

# Pick a Sulfur Solution That Meets Your Needs

## Good

LOD Diesel	0.7ppm 900s
r (10ppm)	0.9ppm
R (10ppm)	1.5ppm



ASTM D7039	Gas, diesel 3.2-2822ppm
ISO 20884	Gas, diesel 5- 500ppm



## Better

LOD Diesel	0.4ppm 300s
r (10ppm)	0.8ppm
R (10ppm)	1.4ppm



ASTM D7039	Gas, diesel 3.2-2822ppm
ISO 20884	Gas, diesel 5- 500ppm



ASTM D2622	Petroleum 3ppm-4.6wt%
ASTM D7039	Gas, diesel 3.2-2822ppm
ISO 20884	Gas, diesel 5-500ppm

## Best

LOD Diesel	0.15ppm 300s
r (10ppm)	0.6ppm
R (10ppm)	1.1ppm



ASTM D7039	Gas, diesel 3.2-2822ppm
ISO 20884	Gas, diesel 5- 500ppm



ASTM D2622	Petroleum 3ppm-4.6wt%
ASTM D7039	Gas, diesel 3.2-2822ppm
ISO 20884	Gas, diesel 5-500ppm



# ASTM Precision

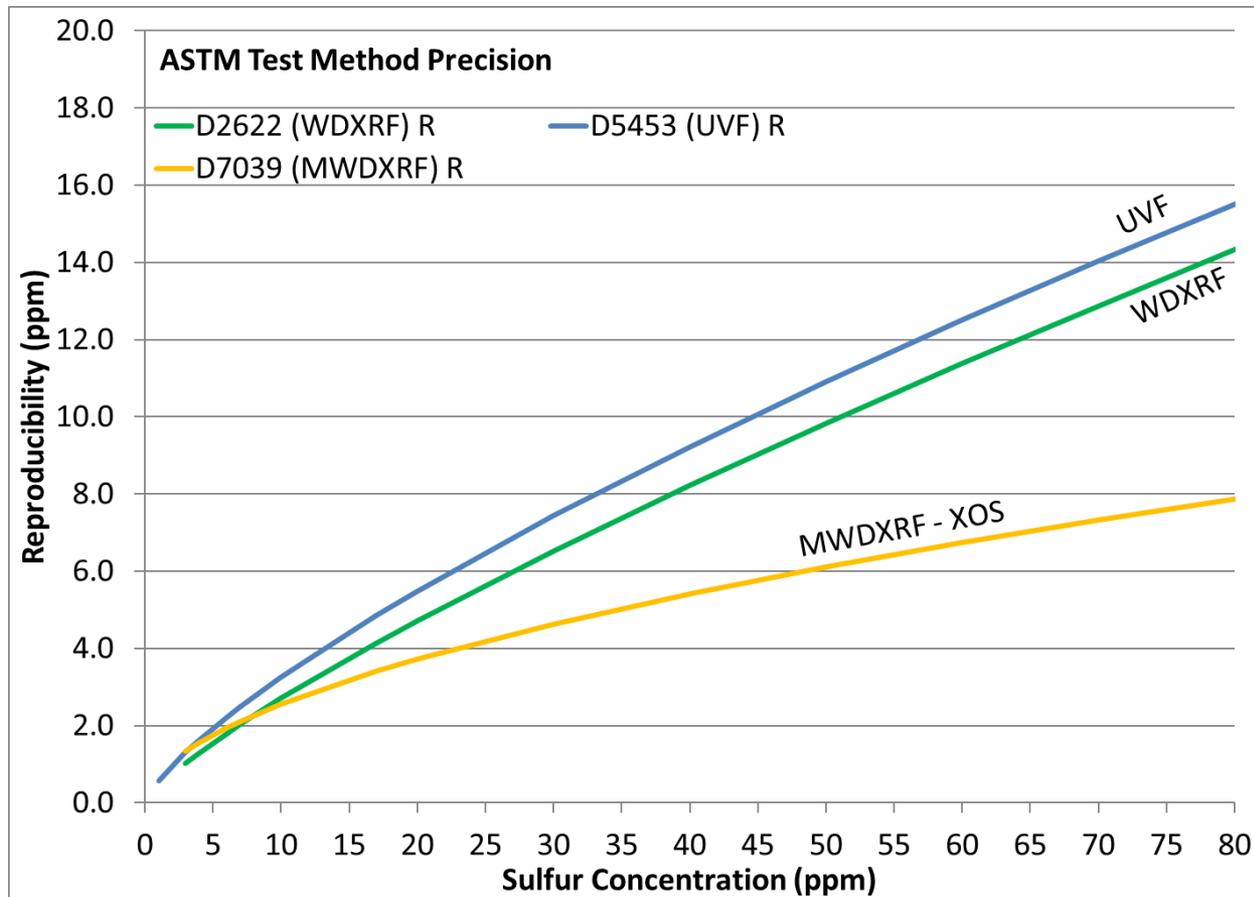
- **Reproducibility**—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20.

➤ Reproducibility (R) → Between lab difference

- **Repeatability**—The difference between repetitive results obtained by the same operator in a given laboratory applying the same test method with the same apparatus under constant operating conditions on identical test material within short intervals of time would in the long run, in the normal and correct operation of the test method, exceed the following vs only in one case in 20

➤ Repeatability (r) → Within lab difference

# ASTM Test Method Reproducibility



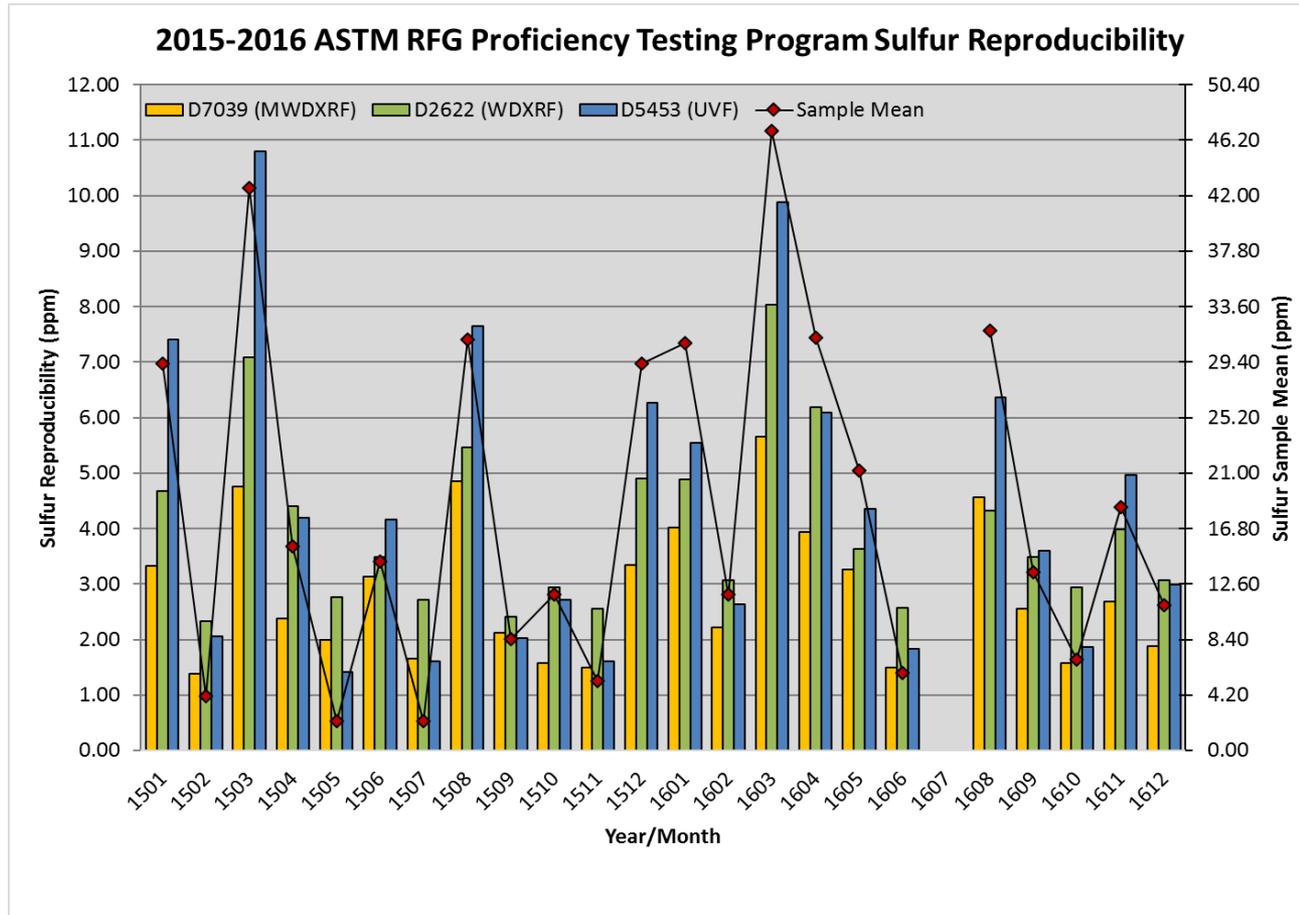
Graphed reproducibility statements from D2622, D5453, and D7039

# ASTM Proficiency Testing Programs (PTP)

Reformulated gasoline (RFG) program - 1 L sample distributed monthly to ILCP participants for the following tests:

- V/L and vapor pressure
- API gravity
- Aromatics and olefins
- Density
- Distillation
- Gum
- Hydrocarbon type
- Oxygenates
- Sulfur: D2622, D5453, D7039

# 2015-16 ASTM RFG PTP Sulfur Data



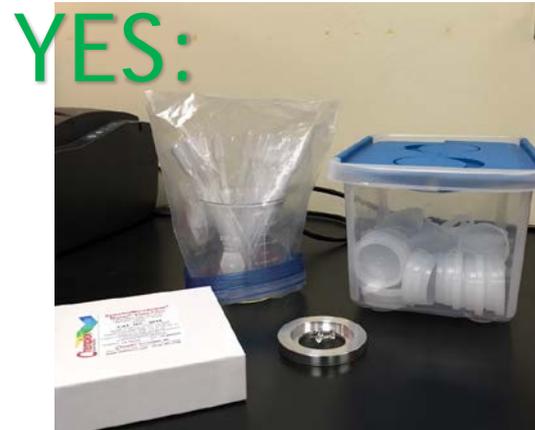
MWDXRF has, on average, the best reproducibility for sulfur in gasoline

# Best Practices Summary

1. Cleanliness is key!
2. Use canned air to reduce contamination
3. Prepare samples correctly
4. Use correct measurement time
5. Check for sample leaks
6. Prepare a new sample when doing repeat measurements
7. Perform routine analyzer maintenance
8. Calibrate correctly and maintain analyzer calibrations properly

# Cleanliness is Key!

- Keep your sample preparation area clean
- A vented hood can be beneficial for low concentration samples
- Store materials in sealed containers in a dust-free area
- Do not leave pipettes and cups out on the open bench
- Promptly cover sample film after use to prevent contamination



# Clean the Sample Chamber

- Daily cleaning with reagent-grade isopropyl alcohol (IPA) goes a long way to ensuring optimal performance
- Use to clean:
  - Sample weight/plunger
  - Primary window
  - Sample basket
- Wipe sample weight with Kimwipe to remove residue whenever contaminated; clean with IPA daily or as needed

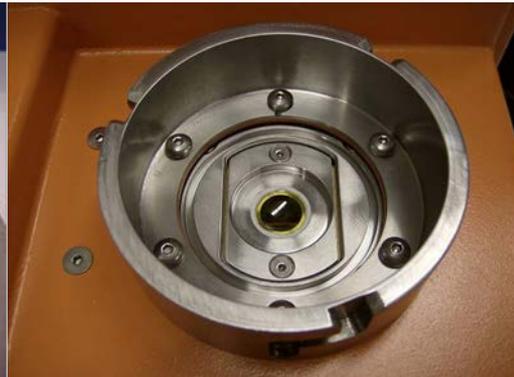


# Clean the Primary Window

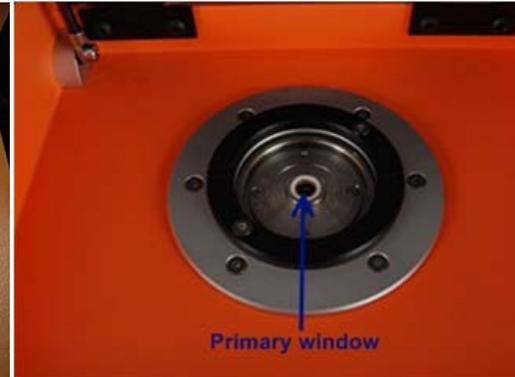
- The primary window is a stainless steel disc with a thin Kapton<sup>®</sup> (polyimide) film
- Clean daily for optimal performance, especially if regularly measuring samples <1 ppm
- Soak a foam-tipped swab in reagent-grade IPA and shake excess IPA off swab.
  - Excess alcohol may leave a residue on the primary window



Legacy Primary Window



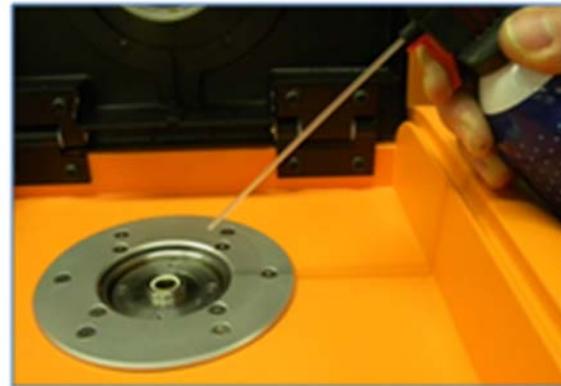
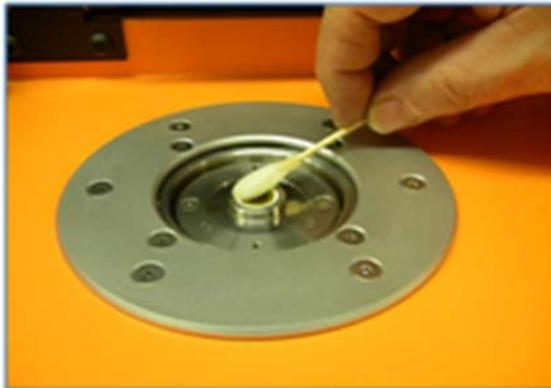
OTG Primary Window



M-Series Primary Window

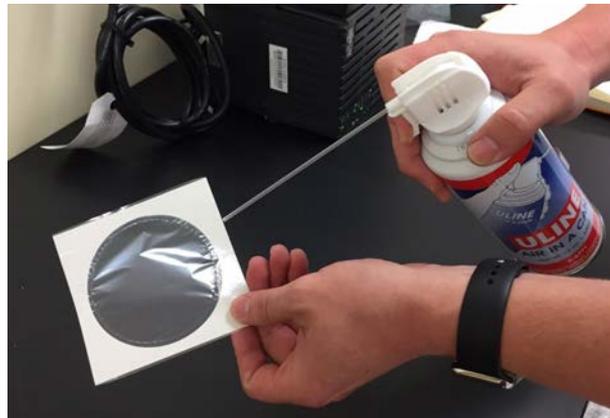
# Clean the Primary Window (cont.)

- Gently clean the window by keeping the swab parallel to the window. Avoid excess force which may puncture the window.
- Always keep a spare primary window on hand!
- Alternatively, use a wetted Kimwipe.
- Dry the window using canned air.
  - If propellant is visible when drying the window, repeat the cleaning procedure.



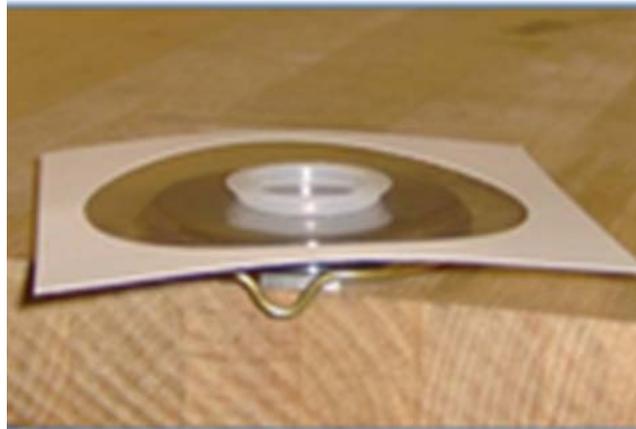
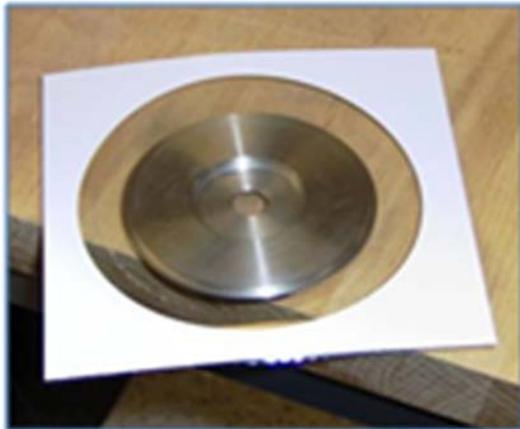
# Prepare the Sample Basket

- For optimal results, change secondary window daily
  - Remove the sample basket from the analyzer
  - Remove the secondary window and clean the metal sample basket with IPA
  - Use canned air to blow off a single piece of new Mylar<sup>®</sup> film on both sides (Prolene<sup>®</sup> for OTG)



# Prepare the Sample Basket (cont.)

- With the basket upside down, place the film on the sample basket
- Place the capture ring onto the window film
  - Avoid touching the window film. Fingerprints can affect measurements!
- Press the ring firmly using four fingers.
  - If window is wrinkled, remove and replace with new film



# Use Best Laboratory Practices

- Don't reuse!
  - Sample cups\*
  - Disposable pipettes
  
- Don't wait!
  - Analyze sample as soon as possible after transferring sample to measurement cup

\*For best results, use a new sample and new cup each time - even for sample repeats. Samples measured repeatedly in the same cup will give erratic results over time due to film effects, sample evaporation, etc.

# Prepare Sample

- Use canned air to blow any dust particles out of the inside of the Chemplex sample cup\*
  - This is especially important with low level (<1 ppm) samples which are more susceptible to contamination

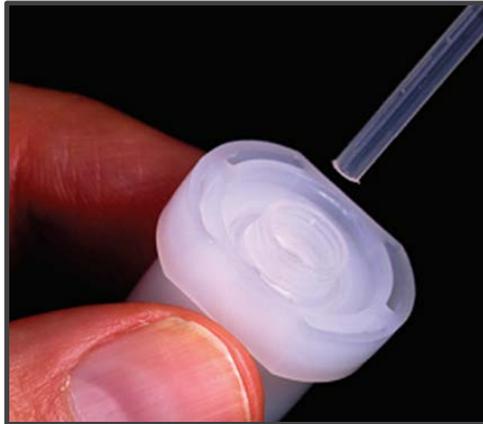
\*not necessary if using Accu-Cells

- Thoroughly swirl the sample bottle before removing a sample to ensure homogeneity



# Prepare Sample (cont.)

- Use a new, disposable transfer pipette to obtain the sample rather than pouring directly from the bottle
- Fill the Chemplex sample cup until sample is level with the center cup well, approximately halfway full
  - It is not necessary to fill the cup completely, which can lead to spills and analyzer contamination
- Fill Accu-Cell with 1 ml of sample



# Assemble Chemplex Sample Cup

- Gently blow off dust particles from a new Mylar<sup>®</sup> sample film using canned air
  - Always use the same film type as was used for instrument calibration
- Place the film over the half-filled sample cup and install the collar of the sample cup
- Check the sample film
  - Film should be tight with no wrinkles or swelling apparent
  - The sample cup should not leak, even if shaken



Correctly prepared sample cup – **CAN USE**



Incorrectly prepared sample cups – **CANNOT USE**



# Assemble Chemplex Sample Cup (cont.)

- Use canned air to blow dust off the film
- Turn the sample cup over and place on stand
  - Never place filled sample cup face-down on the benchtop
- Vent the sample using a push pin
  - Use a new push pin (or clean push pin with IPA)
  - Recommend **TWO** vent holes
  - Vent all sample types
  - **Avoid** venting in the center
- Analyze sample as soon as possible after preparation
  - Do not prepare multiple Chemplex samples at once



# Sample Measurement

- Use the correct measurement time:
  - 300s for Sindre 7039 and Sindre 2622 for samples >1 ppm
  - 600s for samples <1ppm on Sindre 7039/2622
  - 900s for OTG samples <500 ppm (to consistently meet D7039 precision)
- Remove sample promptly after measurement
- Check sample cup and analyzer for leaks
  - If a leak is detected: clean analyzer, change secondary window, and clean primary window if necessary
- Wipe off sample weight on underside of lid
- Prepare a new sample when doing repeat measurements

# Analyzer Maintenance

- Use Best Practices to maintain analyzer cleanliness
- Routinely check fan filter and clean when necessary (keeps analyzer from overheating)
- Run SQC checks to maintain quality control of analyzer
- Recalibrate when SQC chart is out of control
- Perform routine maintenance as needed
  - Consider an XOS Service contract for ultimate peace of mind  
Contact [support@xos.com](mailto:support@xos.com) for more information

# Sindie Calibration Do's and Don'ts

- **DO** calibrate the analyzer when needed:
  - When your control chart is out of range
  - After major analyzer changes, such as replacement of the x-beam
  - Periodic calibration, though not harmful, is not necessary if your analyzer is in statistical control (see ASTM D6299 for setting up a control chart).
  
- **DO** start with a clean analyzer:
  - Clean primary window
  - Change secondary window
  - Canned air is highly recommended for cleaning and prep

# Sindie Calibration Do's and Don'ts (cont.)

- **DO** use matrix matching or correction factors for Tier 3 gasoline calibrations to improve accuracy
  - Gasoline has a small (~1%) high bias when run on mineral oil calibrations

**TABLE 3 Correction Factors for Gasoline-ethanol Blends**

NOTE 1—Determine the correction factor in the table below by finding the known sum of the value in the first column and the value in the first row (for example, 15 (for example, 1.0881). Apply the correction according to 12.5.

Ethanol, vol %	0 %	1 %	2 %	3 %	4 %
0 %	0.9895	0.9962	1.0029	1.0095	1.0161

- **DON'T** tightly bracket your calibration range
  - 0-500 ppm is still recommended for <10 ppm gasoline
  - Sindie uses a weighted calibration which is extremely linear, and so the high points anchor the calibration slope

# Sindie Calibration Do's and Don'ts (cont.)

- **DO** use Auto Calibration for best results
  - the Sindie uses a weighted calibration in Auto Cal
- **DO** make sure you have a good calibration blank
  - A bad blank will cause high calibration offset, leading to bad precision at the lower end

Analyzer Type	Typical Blank Counts/300s	
	7039 Mode:	2622 Mode:
Sindie Gen 2 (Chemplex cups)*	<300	<150
Sindie Gen 3 (Accu-Cell cups)*	<200	<100
Sindie OTG	<125	N/A

\*A note on Autosamplers (Accu-Cell cups): Sindie 2622 Autosamplers are Gen 2,  
Sindie 7039 Autosamplers are Gen3

- For Sindie Gen3 analyzers, use DI water for the blank
- **DO** read the user manual for more information

# Sindie Advanced Calibration Tips

- Use the Stats and Replace features (on newer M-Series analyzers) to improve calibration fit.

Calibration Curves - Low Range

Current : FHR.H20      0.680      0.300  
   9 / 30 / 11      10:08

Select # : \*

	Name	Offset	Slope	Date	Time
1	FHR.H20	0.680	0.300	9/30/11	10:08
2	FHR.HYDR	0.697	0.737	9/30/11	11:03
3	DEMS	0.589	0.200	7/13/11	10:55
4	M3T	0.569	0.150	6/30/11	12:24
5	WATER4	0.655	0.299	5/17/11	11:10
6	WATER3	0.544	0.255	1/30/11	18:16
7	WATER2	0.574	0.259	1/30/11	17:02
8	WATER1	0.675	0.256	1/30/11	15:24

Print    Delete    **Select**    Stats    Done

- View the Stats of any calibration curve by first selecting it as the Current calibration curve (press asterisk, enter curve number, press Select)
- Press the Stats button to view statistics

# Sindie Advanced Calibration Tips (cont.)

- Standardized residuals must be between -3 and +3 (or  $<|3|$ ) or will be removed as an outlier. Should be  $<|2|$  for better results, but even better if  $<|1|$ .
- 'r' is the correlation coefficient, and it should be very close to 1. (i.e. 0.999 = okay, 0.9999 = good, 0.99999 = best)
- Consider replacing/removing calibration points to improve fit

Statistics -		Low Range	
Curve :		0.700	0.455
# Standardized Residuals		1/26/12	11:44
1	-0.33		
2	0.32		
3	1.07	r =	0.999101
4	-0.30		
5	1.14		
6	-1.11		

Done

# Sindie Advanced Calibration Tips (cont.)

- Before running any new samples, you can remove or replace bad points
  - To remove points, press Clear to remove all calibration values
  - Re-enter the good calibration values in the PPM fields.
  - Leave out any point by leaving asterisks in the PPM field.
  - Do not remove more than 2 calibration points (4 point minimum)

The screenshot displays the 'Auto Calibration - Low Range' interface. It features a table with columns for '#', 'PPM', and 'cps'. The PPM column contains asterisks for all points. To the right of the table, there is a 'Replace #' button with an asterisk, a 'Clear' button, and 'Abort' and 'Next' buttons at the bottom.

#	PPM	cps	Enter the PPM values for each measurement
1	*****	372.5	<input type="button" value="Replace # *"/> <input type="button" value="Clear"/> <input type="button" value="Abort"/> <input type="button" value="Next"/>
2	*****	168.0	
3	*****	43.0	
4	*****	14.5	
5	*****	5.0	
6	*****	0.8	

# Sindie Advanced Calibration Tips (cont.)

- To replace bad calibration points:
  - Touch red asterisk and enter the calibration point you would like to replace (remember they are in reverse order!)
  - Press Replace # to exit calibration screen, then Done to return to the Ready to Measure Screen
  - Measure calibration sample. The cps of the next measured result will be replaced in the Auto Calibration screen
  - Return to Auto Cal to finish calibration or to replace other calibration points
  - Check Stats when finished

The screenshot shows the 'Auto Calibration - Low Range' interface. It features a table with columns for '#', 'PPM', and 'cps'. The PPM column contains red asterisks, and the cps column contains numerical values. To the right of the table, there is a text prompt 'Enter the PPM values for each measurement' and a 'Replace #' button with a red asterisk. At the bottom right, there are 'Clear', 'Abort', and 'Next' buttons.

#	PPM	cps	Enter the PPM values for each measurement
1	*****	372.5	<input type="button" value="Replace # *"/>
2	*****	168.0	
3	*****	43.0	
4	*****	14.5	
5	*****	5.0	
6	*****	0.8	

# Sindie Advanced Calibration Tips (cont.)

- For those without Stats and Replace buttons use Low Range Calibration Rev D (Excel) and enter Sindie calibration manually

Serial Number: Sindie		Calibration Curve Sindie		
Number of Stds:	5	Slope	0.4142	CPS/PPM
Measurement Time:	300 Seconds	Offset	0.7088	CPS
		R	0.99996	
Standard Values	Measured Counts	Standard Values	Measured Counts	R/σ
0 PPM	211 Counts	0 PPM	211 Counts	-0.113
25 PPM	3321 Counts	25 PPM	3321 Counts	0.02801
100 PPM	12656 Counts	100 PPM	12656 Counts	0.14563
500 PPM	63123 Counts	500 PPM	63123 Counts	3.08659
1000 PPM	123705 Counts	1000 PPM	123705 Counts	-2.2103
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!
PPM	Counts	0 PPM	0 Counts	#DIV/0!

**Instructions:**  
 Cells Highlighted In Yellow Are For User Inputed Data  
 Standards Do Not Have To Be Put In Numerical Order  
 A Calibration Curve Is Automatically Generated When Data Is Entered  
 Only To Be Used For Low Range Calibrations (0-3000ppm)  
 Values R, R/σ and Standard Values Will Flag Red If They Are Out Of Range  
 Useable For 2 To 9 Standards To Create A Calibration  
 Any Unused Slots For Standards Must Be At The Bottom Of The Table  
 Measured Number Of Counts Must Be In The Same Row As The Standard



# Run a Calibration Check

- Finally, when calibration is complete - don't forget to run a calibration check
- Acceptable check sample limits are often already established by existing SQC charts
- Alternatively:
  - Use a NIST SRM
  - 40 CFR § 80.47(n)(1)(i) - accuracy SQC should be  $\leq 0.75 \cdot R$
  - D7039 Section 10.5: The determined value shall be in the range defined by the certified concentration plus or minus the repeatability of this test method.
  - D2622 Section 9.5: The differences between two measured values shall be within the repeatability of this test method.

# Sindie Tier III PBMS Data

# Sindie PBMS Accuracy Data at 9 ppm

## §80.47 Performance-based Analytical Test Method Approach

(2) *Accuracy.* Beginning January 1, 2016, for motor vehicle gasoline, gasoline blendstock, and gasoline fuel additives subject to the gasoline sulfur standard at §§80.195 and 80.1603:

(i) The arithmetic average of a continuous series of at least 10 tests performed using good laboratory practices on a commercially available gravimetric sulfur standard in the range of 1-10 ppm, say 10 ppm, shall not differ from the accepted reference value (ARV) of the standard by more than 0.70 ppm sulfur;

(ii) The arithmetic average of a continuous series of at least 10 tests performed using good laboratory practices on a commercially available gravimetric sulfur standard in the range of 10-20 ppm, say 20 ppm, shall not differ from the ARV of the standard by more than 1.02 ppm sulfur; and

(iii) In applying the tests of paragraphs (b)(2)(i) and (ii) of this section, individual test results shall be compensated for any known chemical interferences using good laboratory practices.

Measurement #	Sulfur (ppm)
1	9.37
2	9.67
3	9.32
4	9.69
5	9.68
6	9.06
7	9.54
8	9.17
9	9.47
<u>10</u>	9.33
Average	9.43
St dev	0.22
%RSD	2.32%

Tier 3 Accuracy:	
ARV	9.0
ARV-Avg	0.43
Pass?	Yes

# Sindie PBMS Accuracy Data at 19 ppm

## §80.47 Performance-based Analytical Test Method Approach

(2) *Accuracy.* Beginning January 1, 2016, for motor vehicle gasoline, gasoline blendstock, and gasoline fuel additives subject to the gasoline sulfur standard at §§80.195 and 80.1603:

(i) The arithmetic average of a continuous series of at least 10 tests performed using good laboratory practices on a commercially available gravimetric sulfur standard in the range of 1-10 ppm, say 10 ppm, shall not differ from the accepted reference value (ARV) of the standard by more than 0.70 ppm sulfur;

(ii) The arithmetic average of a continuous series of at least 10 tests performed using good laboratory practices on a commercially available gravimetric sulfur standard in the range of 10-20 ppm, say 20 ppm, shall not differ from the ARV of the standard by more than 1.02 ppm sulfur; and

(iii) In applying the tests of paragraphs (b)(2)(i) and (ii) of this section, individual test results shall be compensated for any known chemical interferences using good laboratory practices

Measurement #	Sulfur (ppm)
1	19.70
2	19.47
3	19.24
4	19.47
5	18.87
6	19.06
7	18.81
8	19.61
9	19.55
<u>10</u>	19.52
Average	19.33
St dev	0.32
%RSD	1.64%

Tier 3 Accuracy:	
ARV	19.0
ARV-Avg	0.33
Pass?	Yes

# PBMS Precision Testing

## §80.47 Performance-based Analytical Test Method Approach

b) *Precision and accuracy criteria for approval for the absolute fuel parameter of gasoline sulfur.*

(1) *Precision.* Beginning January 1, 2016, for motor vehicle gasoline, gasoline blendstock, and gasoline fuel additives subject to the gasoline sulfur standard at §§80.195 and 80.1603, the maximum allowable standard deviation computed from the results of a minimum of 20 tests made over 20 days (tests may be arranged into no fewer than five batches of four or fewer tests each, with only one such batch allowed per day over the minimum of 20 days) on samples using good laboratory practices taken from a single homogeneous commercially available gasoline must be less than or equal to 1.5 times the repeatability “r” divided by 2.77, where “r” equals the ASTM repeatability of ASTM D7039 (Example: A 10ppm sulfur gasoline sample: Maximum allowable standard deviation of 20 tests  $\leq 1.5 * (1.73\text{ppm}/2.77) = 0.94 \text{ ppm}$ ). The 20 results must be a series of tests with a sequential record of analysis and no omissions. A laboratory facility may exclude a given sample or test result only if the exclusion is for a valid reason under good laboratory practices and it maintains records regarding the sample and test results and the reason for excluding them.

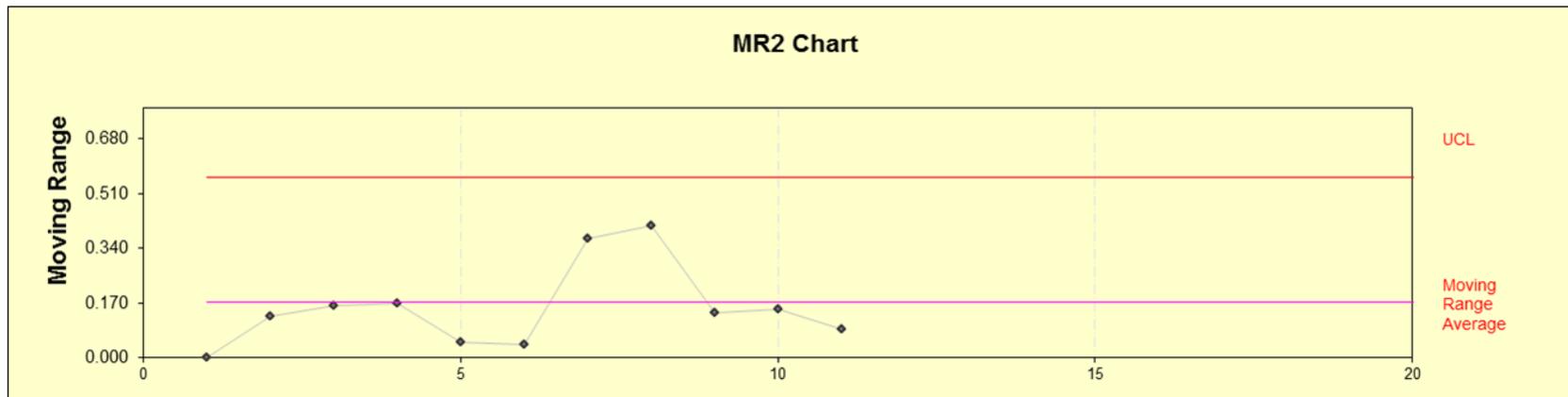
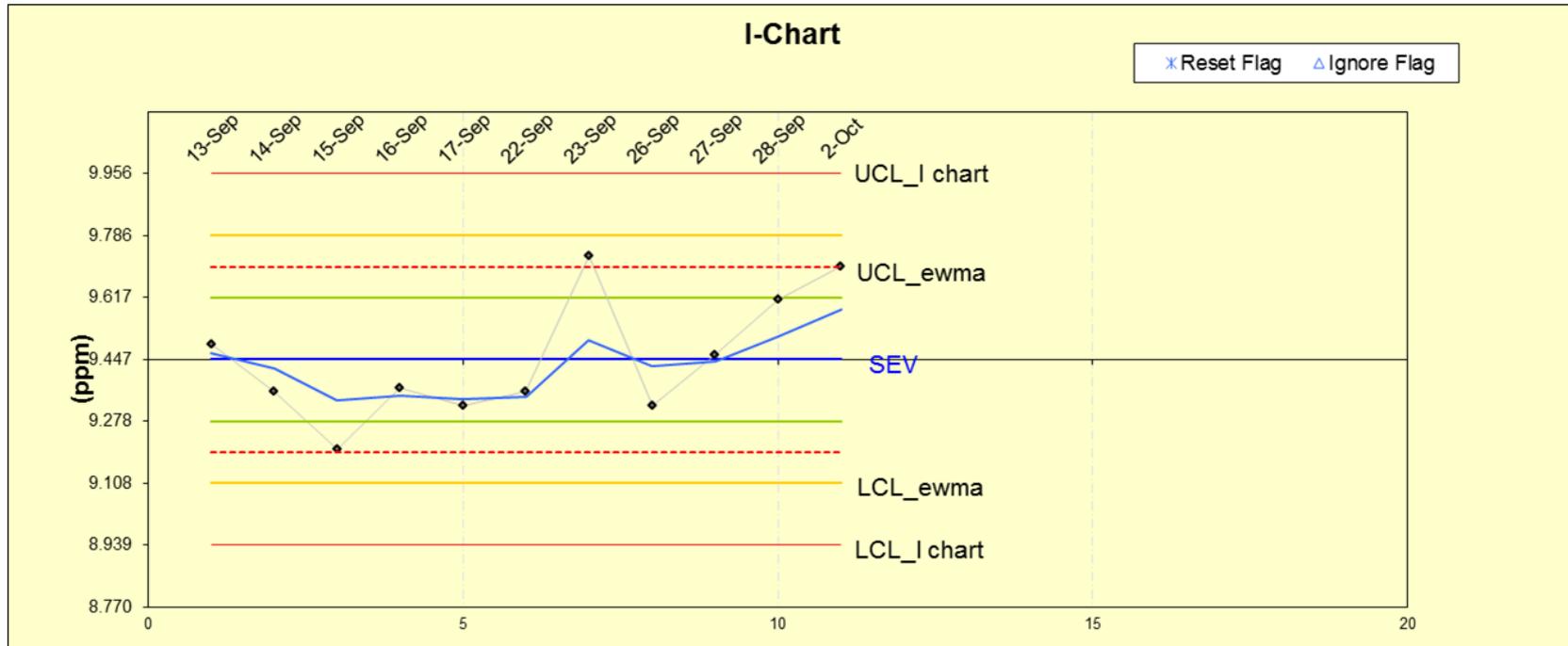
# Sindie 7039 PBMS Precision Data

Measurement #	Day	Sulfur (ppm)	Measurement #	Day	Sulfur (ppm)
1	1	10.88	21	10	11.13
2		10.38	22		10.97
3		10.71	23		10.94
4		10.89	24		12.00
5	2	11.01	25	14	11.19
6		10.42	26		11.50
7		10.60	27		10.89
8		11.12	28		10.93
9	3	11.14	29	16	11.31
10		11.29	30		11.35
11		10.54	31		11.62
12		11.18	32		10.76
13	4	10.86	33	20	11.16
14		11.29	34		11.30
15		10.52	35		11.40
16		10.60	36		11.12
17	5	10.86			
18		11.05			
19		10.91			
20		10.98			

### Tier 3 Precision:

Std Dev	0.36
$1.5*r/2.77$	0.99
Pass?	Yes

# D6299 Precision SQC – Gasoline Standard



Thank you for your time today. This concludes the presented material.

I will take a few questions as time permits.

If you have questions later, please do not hesitate to contact me.

**Leslie Johnson** | Applications Engineer

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# THANK YOU

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