better analysis counts

Best Practices for Measuring Sulfur in Gasoline to Meet PBMS and SQC Tier 3 Requirements Using Monochromatic WDXRF

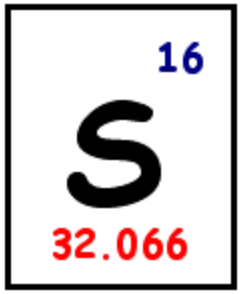
Kyle Kuwitzky

Product Manager

12/15/16

Sulfur Limits on Gasoline

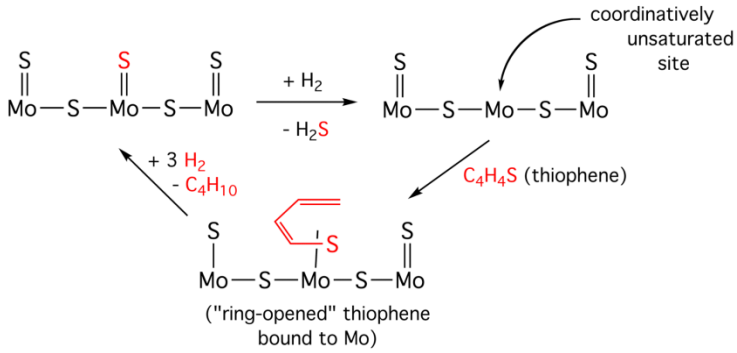
- In 2004, sulfur was limited to 120 ppm
- In 2006, Tier 2 was introduced dropping sulfur levels to 30 ppm
- In 2017, sulfur in gasoline will drop to 10 ppm
  - About 30 small refiners can wait until 2020



Data Quality Importance

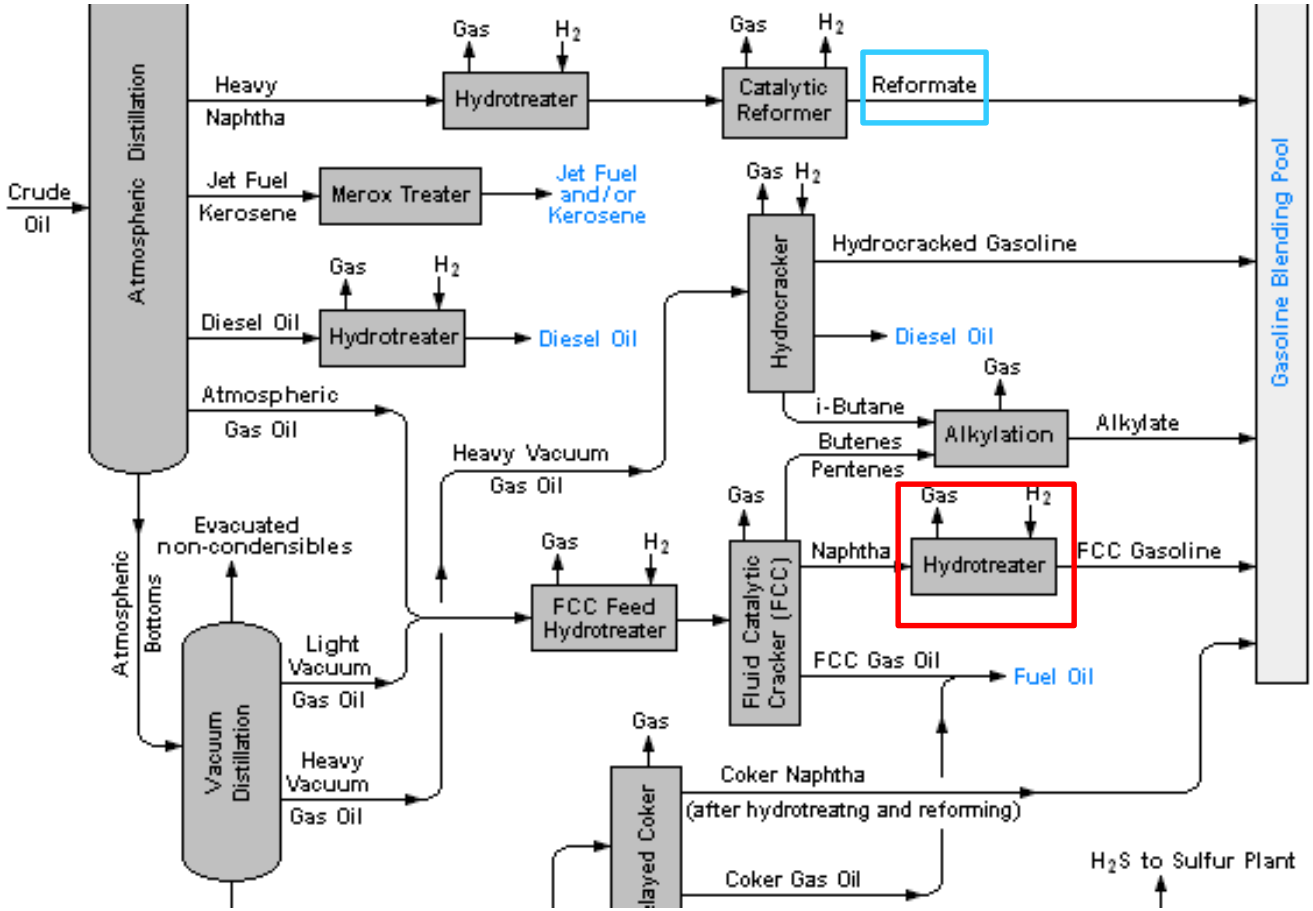
Sulfur Removal Costs Refineries MILLIONS per Year in:

- Capital
- Hydrogen
- Catalyst
- Energy
- OCTANE



Reducing variability in Sulfur measurement can contribute to reductions in removal costs!

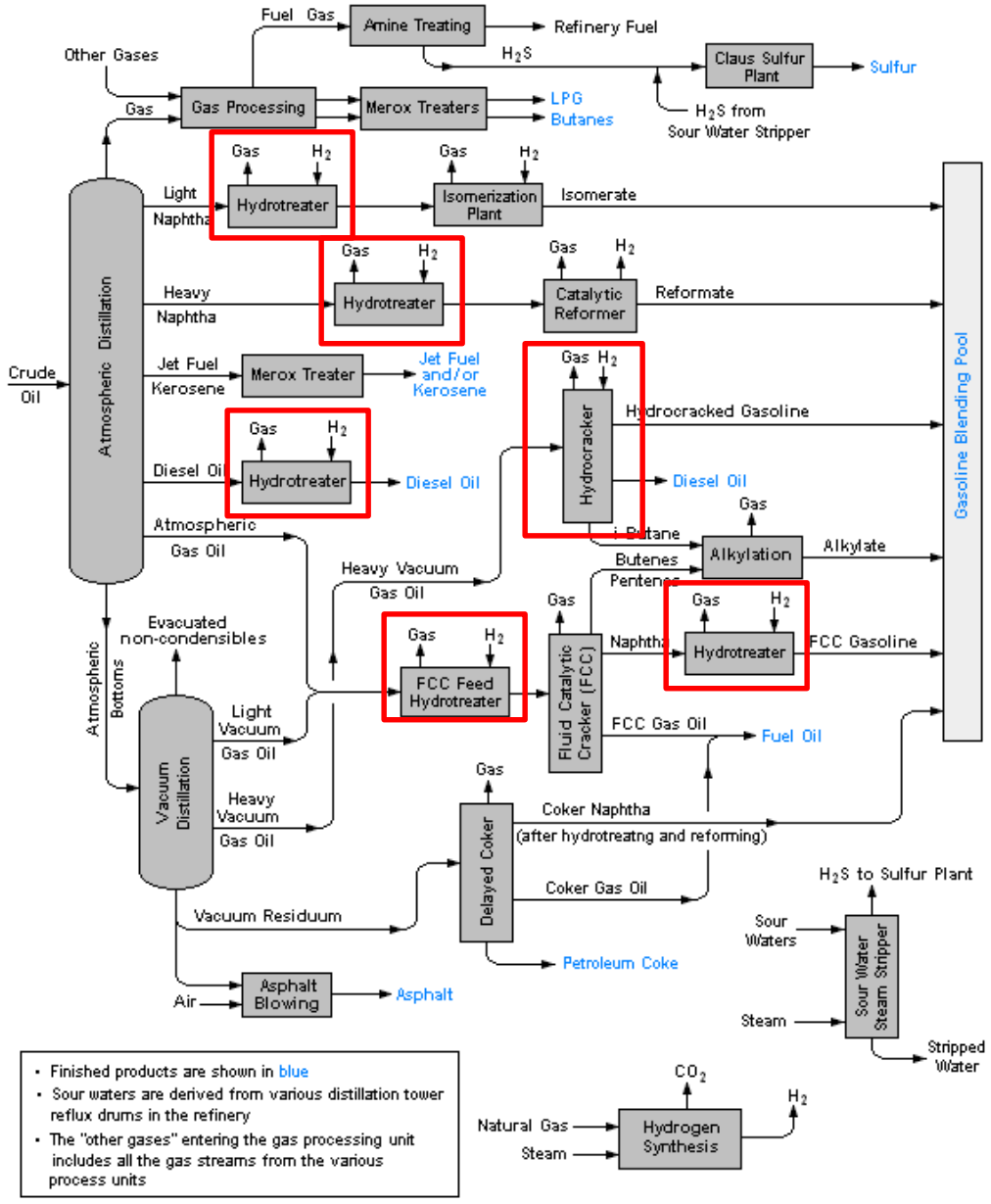
Loss of Octane



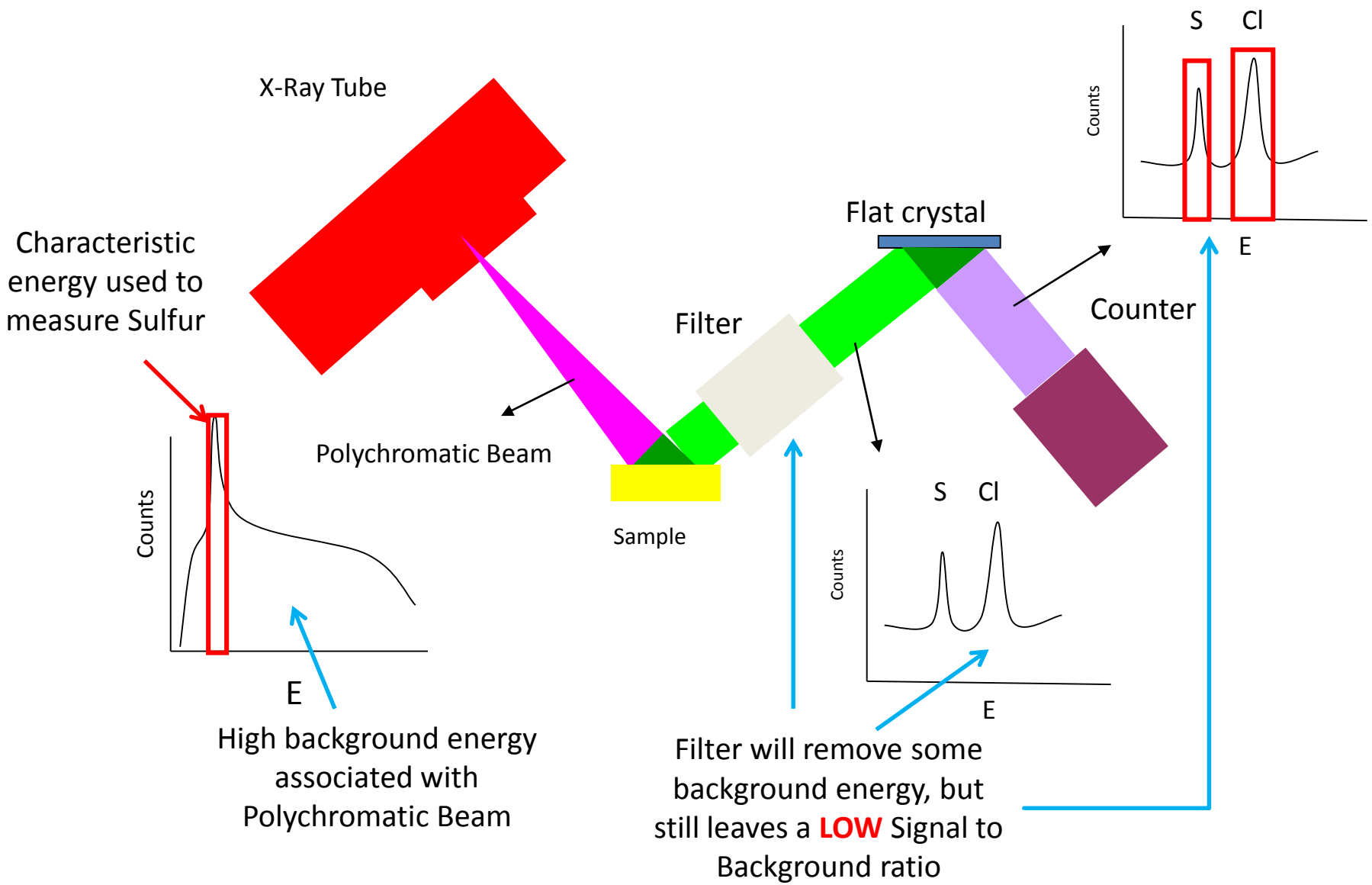
Post Treatment at FCC can convert Olefins, which contribute to Octane. This Octane must be replaced, typically with Reformate

Sulfur Measurement

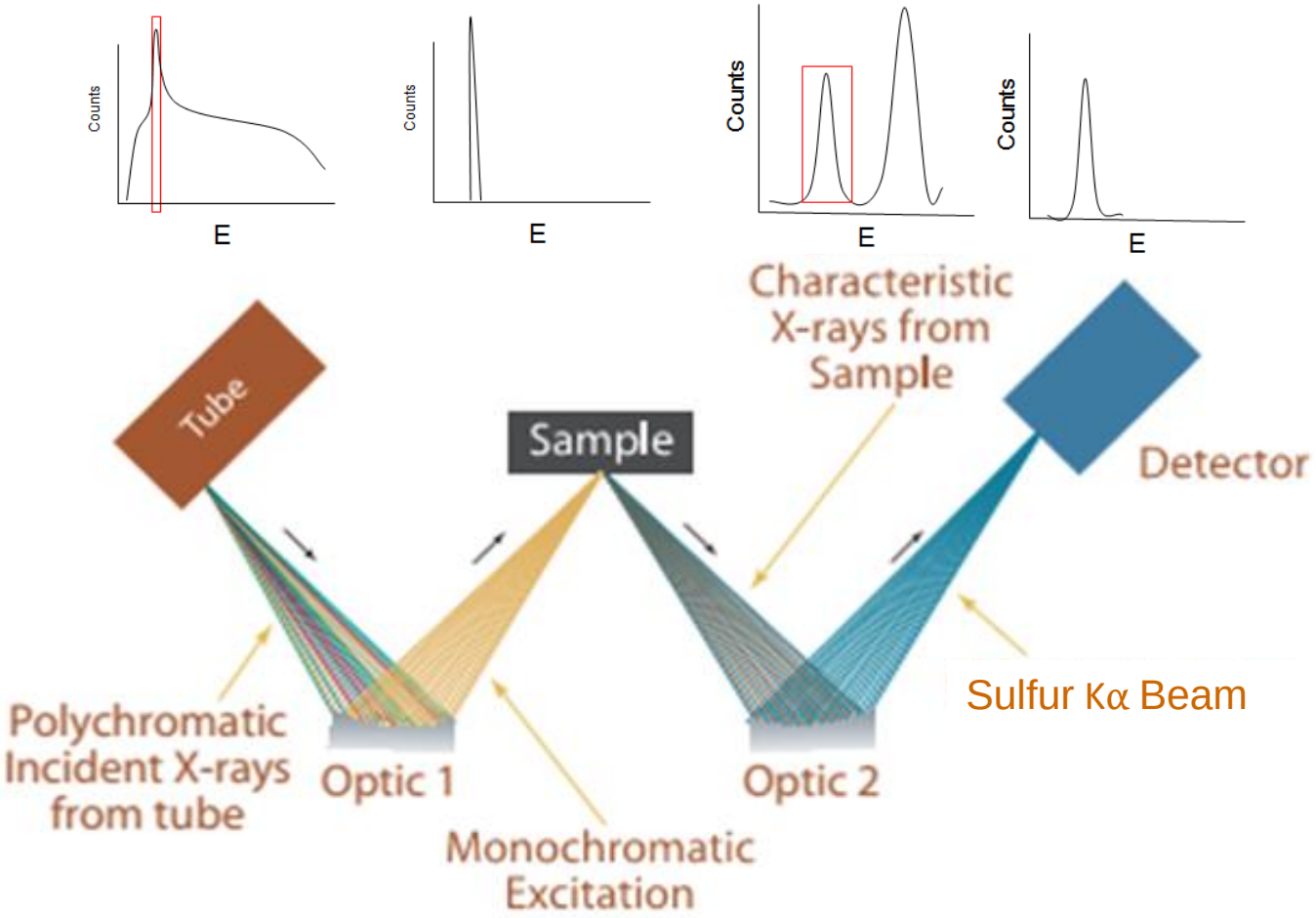
In order to optimize production, monitoring **must** be performed on unit sulfur levels. This can be done in a laboratory or online.



Typical Wavelength Dispersive XRF



Monochromatic WDXRF



Monochromatic WDXRF (MWDXRF) utilizes two doubly curved crystal monochromators to filter and focus x-ray excitation and collection creating a high signal to background ratio that results in the most reproducible measurement of sulfur in gasoline.

Sindie 7039 G3 Sulfur Analyzer

Sindie 7039 Sulfur Analyzer

Sindie 2622 Sulfur Analyzer

Sindie OTG Sulfur Analyzer

ASTM D7039 ISO 20884	Gas, diesel 3.2-2822ppm Gas, diesel 5-500ppm
LOD Diesel	0.15ppm 300s
r (10ppm)	0.6ppm
R (10ppm)	1.1ppm

ASTM D7039 ISO 20884	Gas, diesel 3.2-2822ppm Gas, diesel 5-500ppm
LOD Diesel	0.4ppm 300s
r (10ppm)	0.8ppm
R (10ppm)	1.4ppm

ASTM D2622 ASTM D7039 ISO 20884	Petroleum 3ppm-4.6wt% Gas, diesel 3.2-2822ppm Gas, diesel 5-500ppm
LOD Diesel	0.4ppm 300s
r (10ppm)	0.8ppm
R (10ppm)	1.4ppm

ASTM D7039 ISO 20884	Gas, diesel 3.2-2822ppm Gas, diesel 5-500ppm
LOD Diesel	0.7ppm 900s
r (10ppm)	0.9ppm
R (10ppm)	1.5ppm

ASTM Precision Definitions

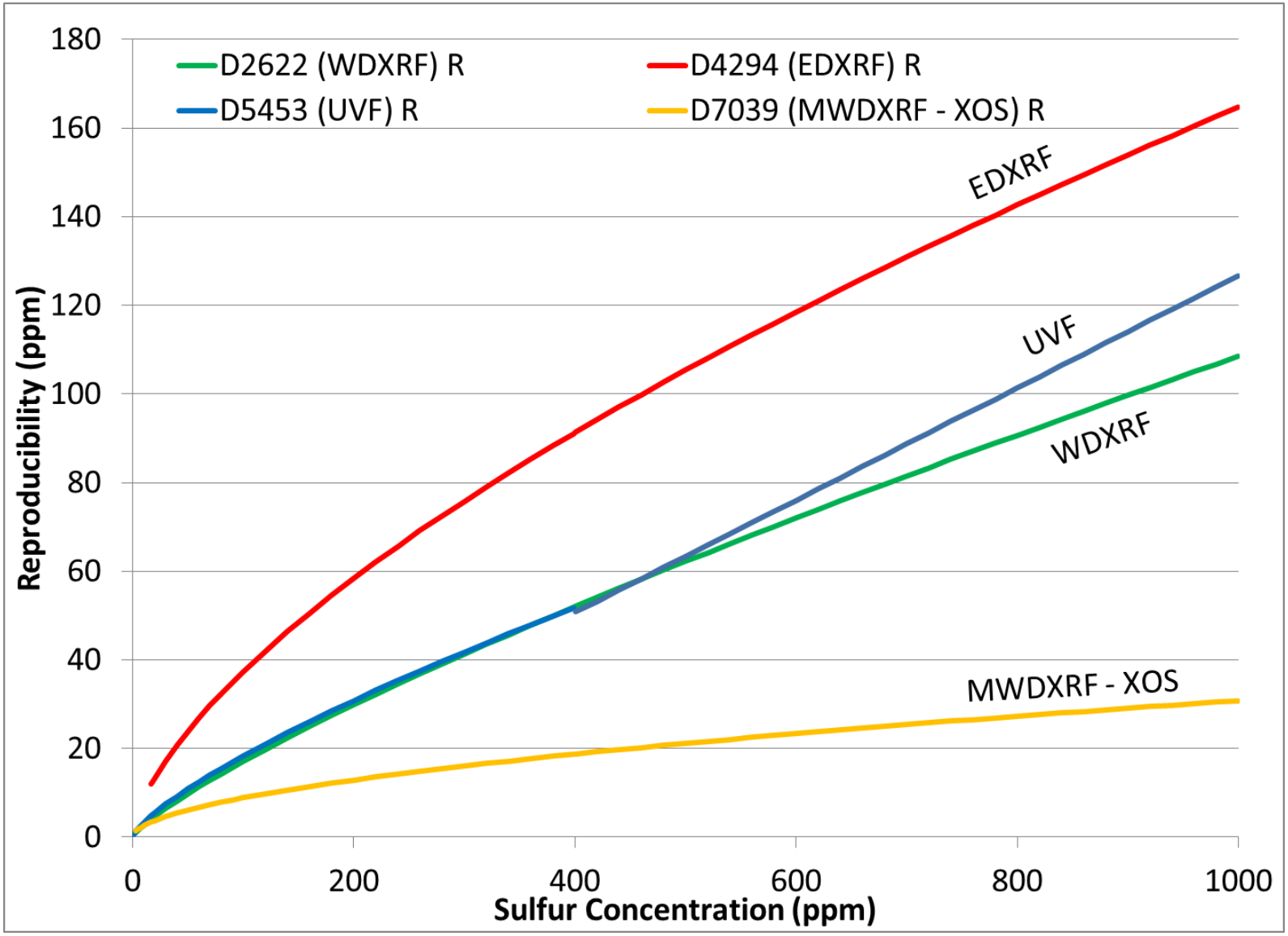
- Reproducibility—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed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

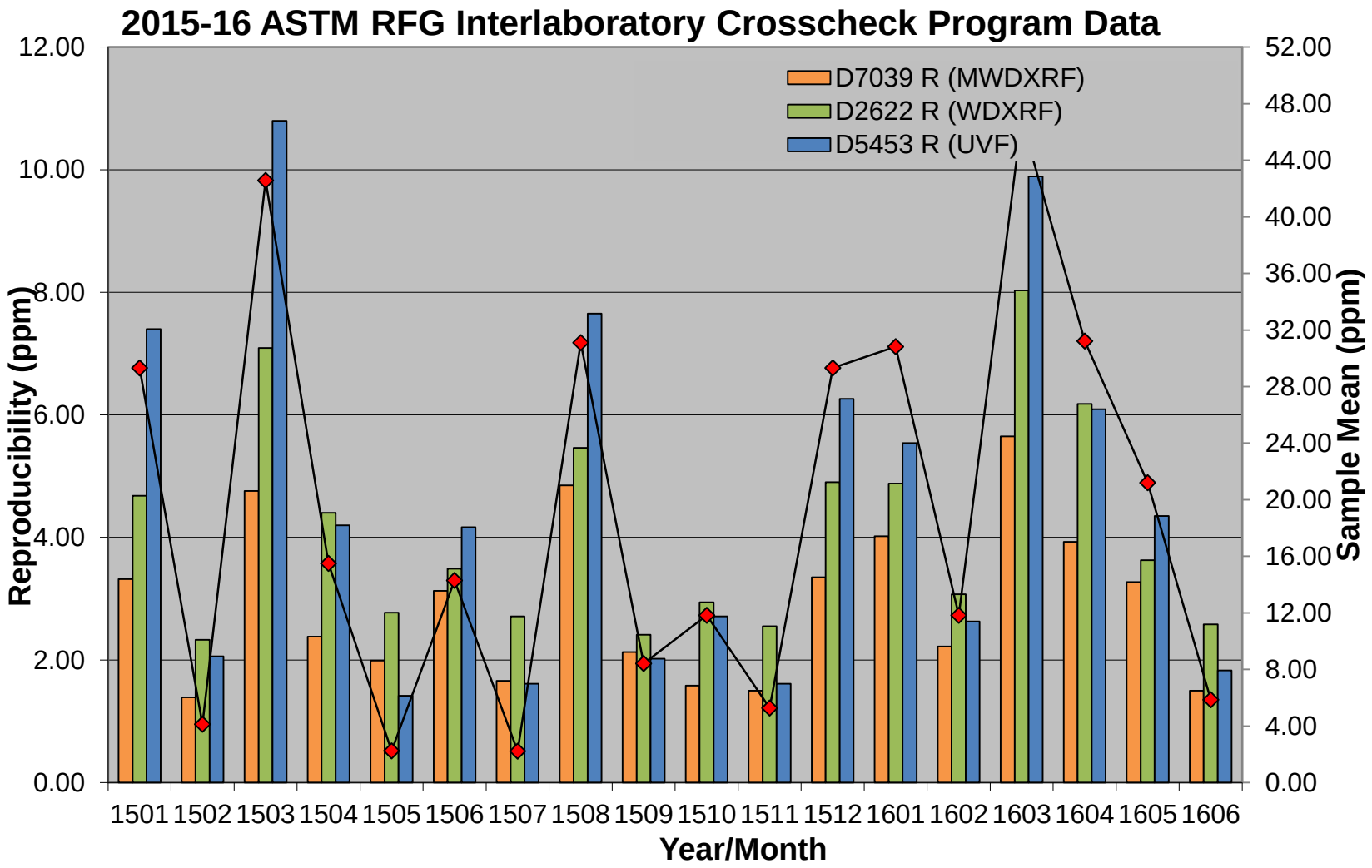
  – Repeatability (r) → Within lab difference

ASTM Test Method Reproducibility



ASTM Interlaboratory Crosscheck Programs (ILCP)

- Reformulated gasoline (RFG) – 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**



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

- Gasoline producers and blenders don’t have to begin meeting the 10.00 ppm maximum average sulfur level until calendar year 2017.
  - Labs may not being seeing samples below 10 ppm sulfur until next year
  - Little things can have a much bigger impact on data quality at lower concentrations

Best Practices Summary

- Good Laboratory Practices
- Daily Activities
- Sample Preparation Tips

Good Laboratory Practices

- Cleanliness is key
  - Sample preparation area
    - Vented hood can be beneficial for low concentration samples
  - Store materials in sealed containers in a dust-free area

Good Laboratory Practices

- Don’t reuse!
  - Sample cups
  - Disposable pipettes

- Don’t wait
  - Analyze sample as soon as possible after transferring sample to measurement cup

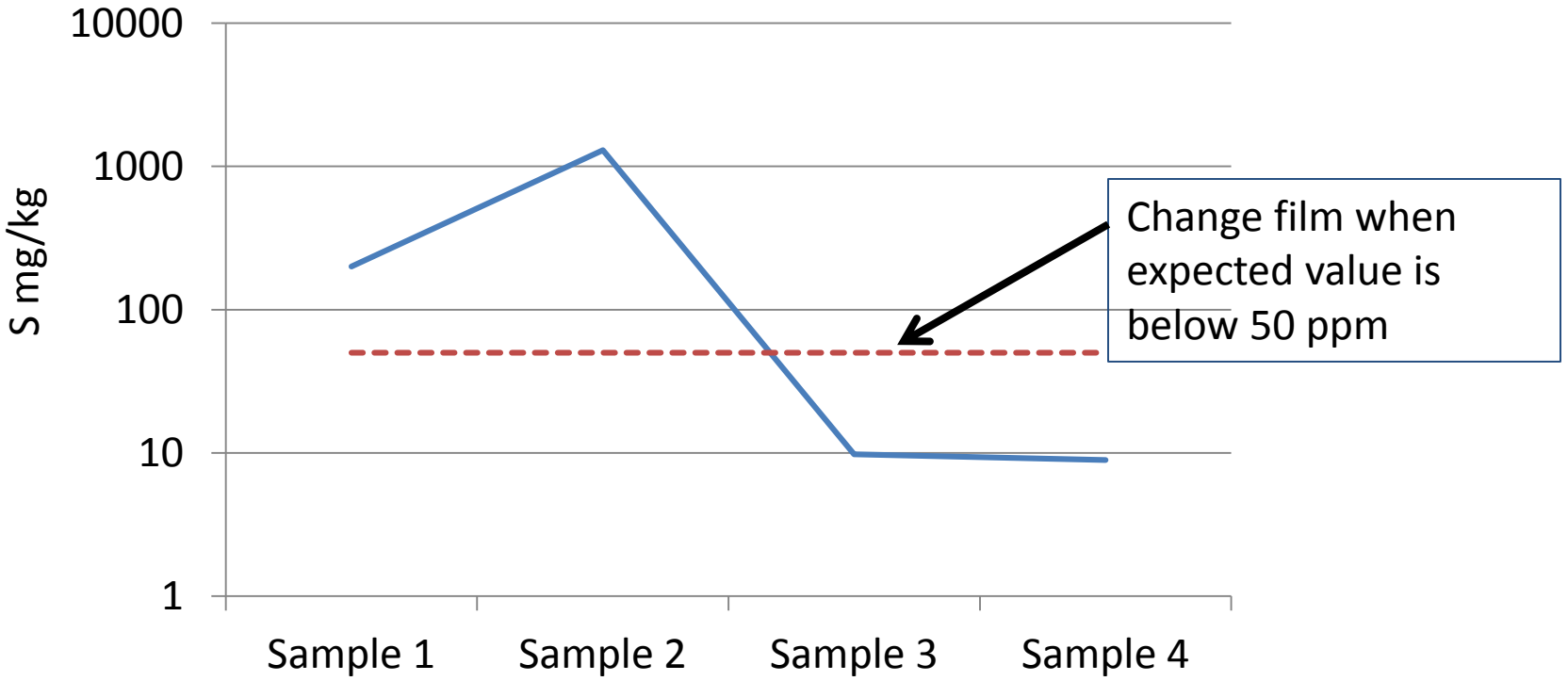
Clean Sample Chamber

- Daily cleaning goes a long way to ensuring optimal performance
  - Use reagent-grade isopropyl alcohol (IPA) to clean:
    - Sample basket
    - Primary Window
    - Sample Weight

- Change the secondary window with the recommended Mylar® film daily

Good Laboratory Practices

- Avoid contamination
  - Change secondary window film when switching from samples with high to low concentration

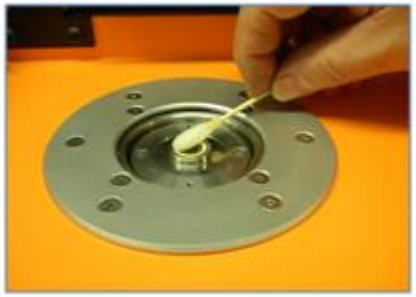


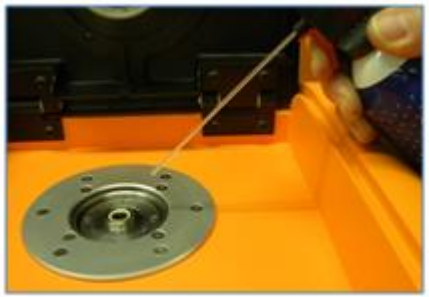
Clean Primary Window

- The primary window is a stainless steel disc with a thin Kapton® (polyimide) film
  - Needs to be cleaned daily

Clean Primary Window

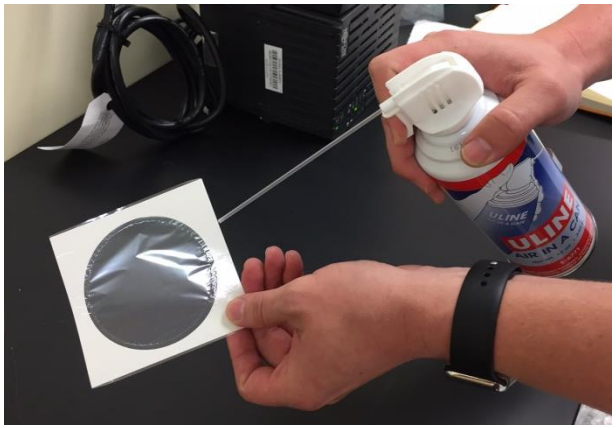
- Very easy to do
  - Soak a foam-tipped swab in reagent-grade IPA and shake excess off swab.
  - Gently clean the window by keeping the swab parallel to the window. Avoid excess force
  - Dry the window using canned air.
    - If propellant is visible on the window, repeat the cleaning procedure.





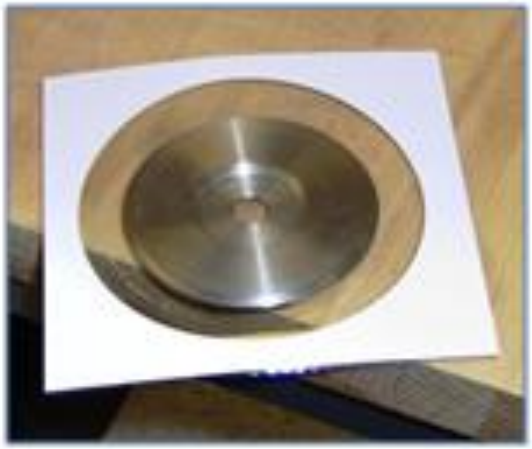
Prepare the sample basket

- Remove the sample basket from the analyzer
- Remove the secondary window and clean the metal sample basket with IPA
- Use canned air to blow of a single piece of new film on both sides



Prepare the sample basket

- 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



Transfer Sample

- Thoroughly swirl the sample bottle before removing a sample to ensure homogeneity
- Use canned air to blow any dust particles out of the inside of the sample cup

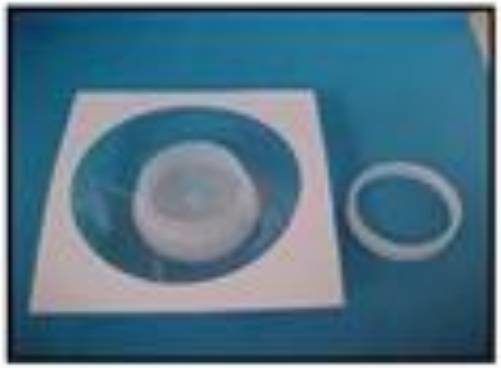
Transfer Sample

- Use a new, manual, disposable transfer pipette to prepare each sample
- Fill the sample cup halfway
  - Typically about three pipettes' worth of sample

Assemble Sample Cup

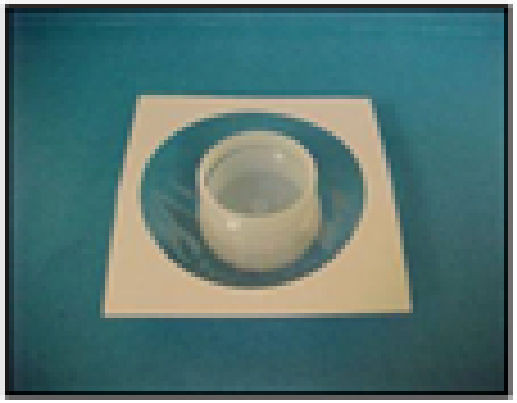
- Gently blow off dust particles from a new sample film using canned air
  - Always use the same film type as was used for instrument calibration

- Place the film over the half-filled sample cup



Assemble Sample Cup

- Install the collar of the sample cup
  - The bottom of the collar has a half round edge
  - Place the collar on the cup and press down firmly
  - Be sure not to touch the sample film



Assemble 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**

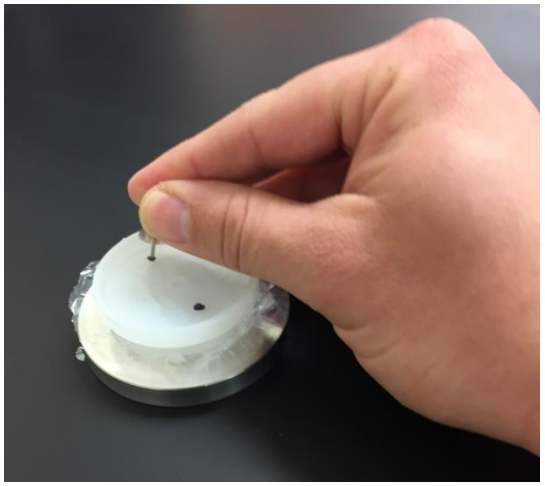
Assemble Sample Cups

- Use canned air to blow dust off the film

- Turn the sample cup over and place on stand

Assemble Sample Cups

- Vent the sample using a push pin
  - Use a new push pin or clean push pin with IPA in between samples
  - Recommend **TWO** vent holes
  - Vent all sample types
  - **Avoid** venting in the center



- Analyze sample as soon as possible after preparation

Sindie 7039 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
10	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 7039 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
10	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≤1.5*(1.73ppm/2.77) = 0.94 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.

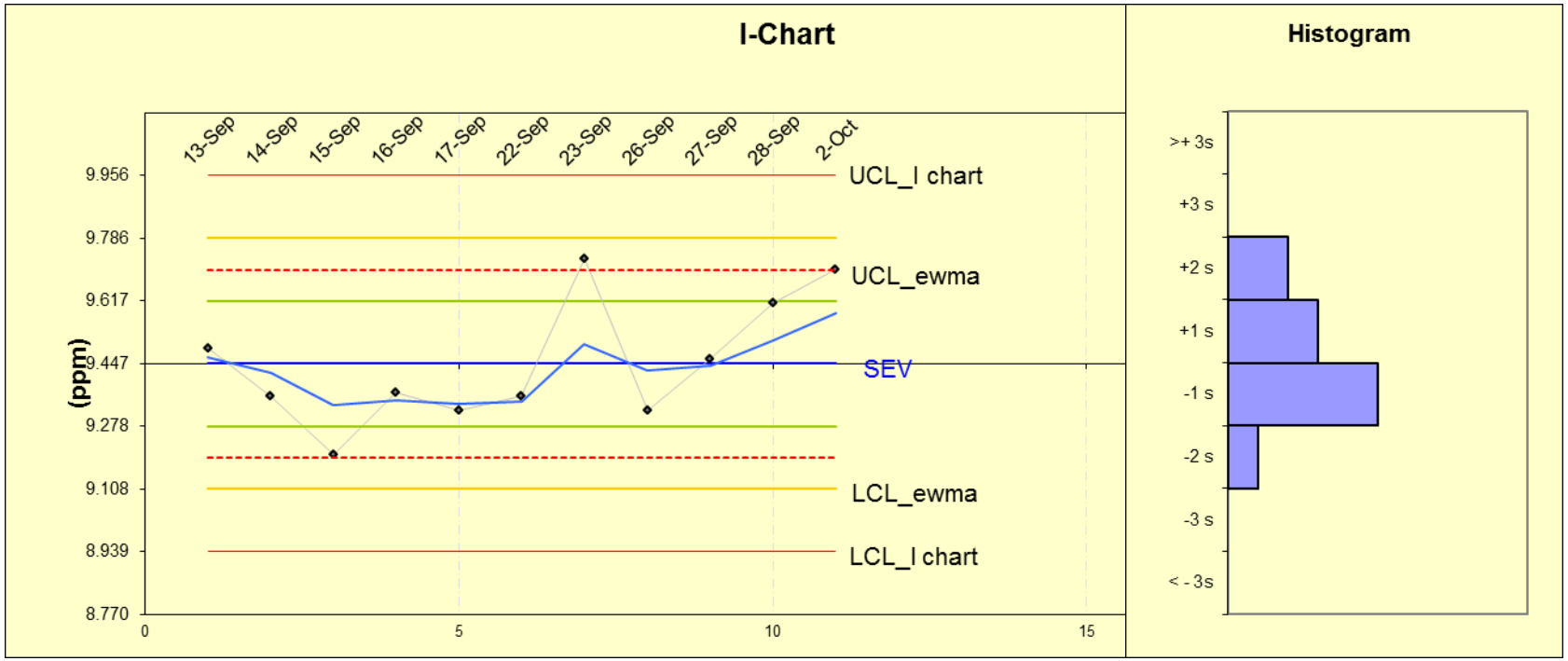
Sindie 7039 PBMS Precision Data

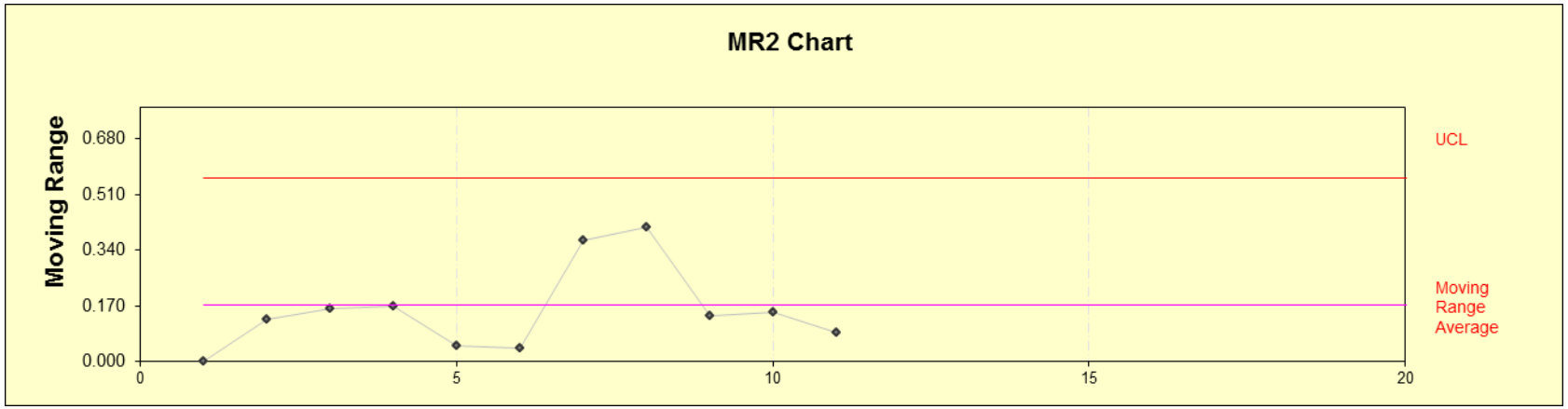
Measurement #	Day	Sulfur (ppm)	Measurement #	Day	Sulfur (ppm)
1	1	10.88	21	10	11.13
2		10.38	22		10.97
3		10.71	23		10.94
4		10.89	24		12.00
5	2	11.01	25	14	11.19
6		10.42	26		11.50
7		10.60	27		10.89
8		11.12	28		10.93
9	3	11.14	29	16	11.31
10		11.29	30		11.35
11		10.54	31		11.62
12		11.18	32		10.76
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

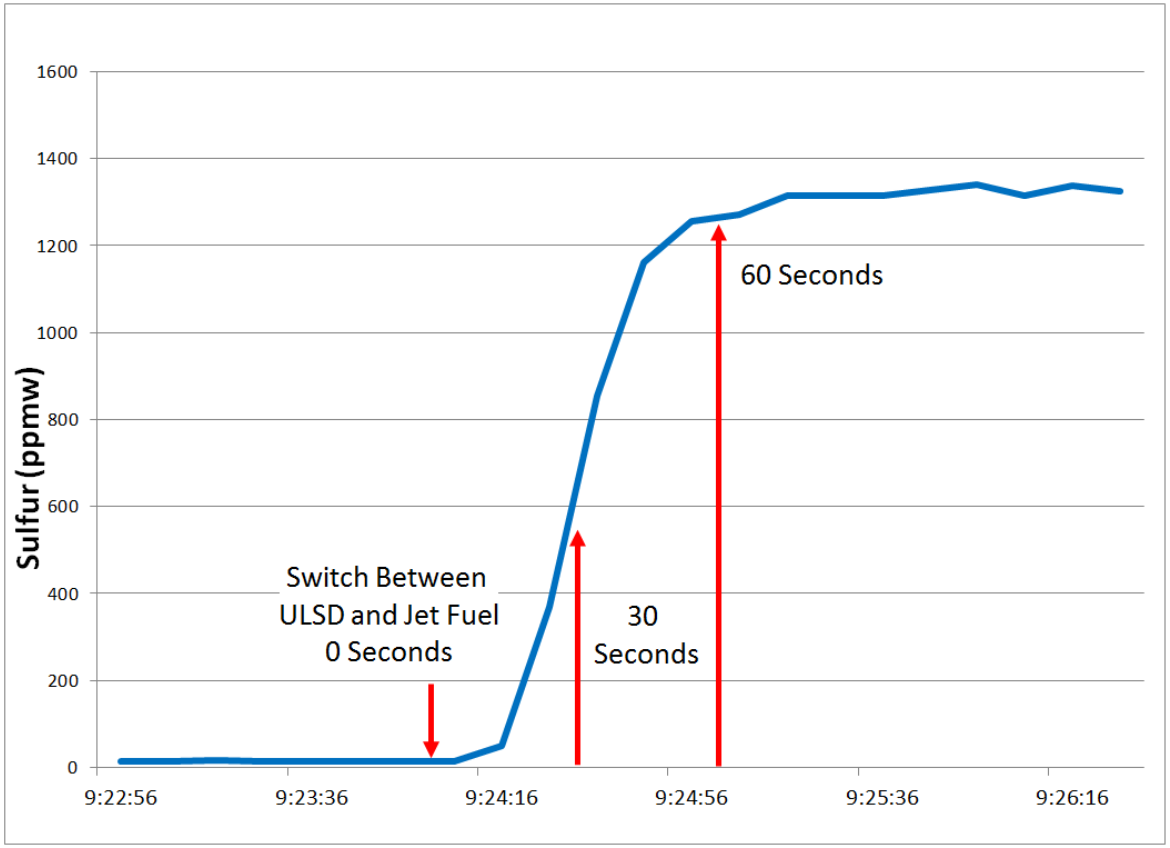




MWDXRF Online Measurement

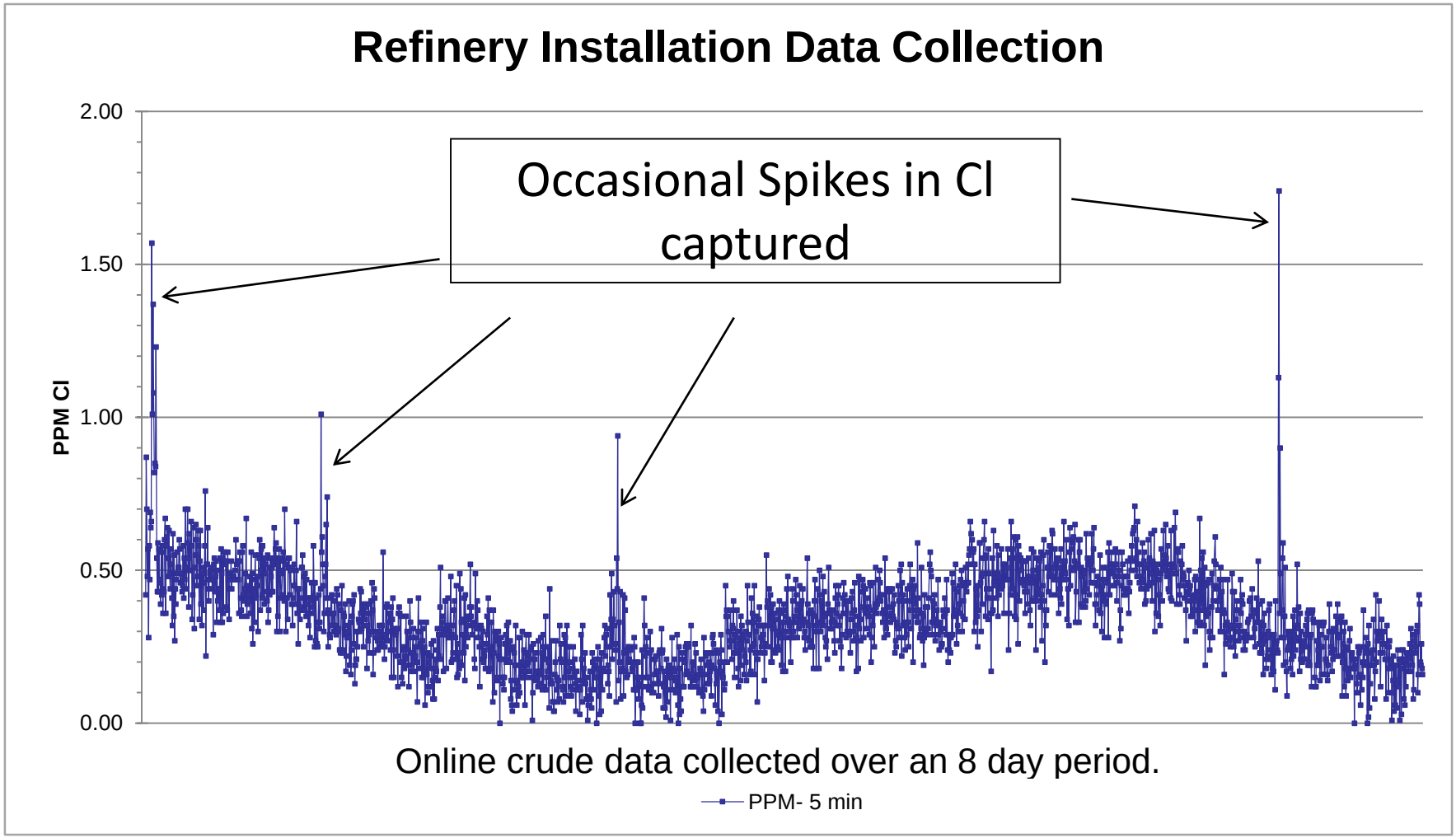
- Applications for Sulfur and Chlorine available
  - Direct measurement technique
    - No combustion gasses or high temperature furnace
  - Low maintenance
    - 3-6 month maintenance interval
  - Rapid instrument response to changes in concentration
    - Changes registered in seconds rather than minutes
  - Same technology used for both lab and online measurement

Rapid Instrument Response



- Online MWDXRF used in blending operations
- Precise fuel interface cuts to reduce transmix

Sub-ppm Chlorine Monitoring



- **Data collected from analysis of a domestic crude at a major North American refinery**
- **Online MDWXRF is able to monitor sub-ppm levels of chlorine in incoming crudes**

Summary

- Tier 3 maximum average sulfur level of 10.00 ppm begins calendar year 2017
- Monochromatic WDXRF (ASTM D7039) provides the most reproducible sulfur measurement in gasoline
- Data quality is important for meeting the Tier 3 requirements but help to lessen the impact of sulfur removal on refinery costs
- A few simple best practices will ensure optimal data quality

Thank you!

Kyle Kuwitzky
Product Manager

Phone: 518.880.1508

Email: kkuwitzky@xos.com

Web: https://xos.com/industries/petroleum/

Demo request: www.xos.com/request-information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