COQA Light Sweet Crude
Subcommittee Meeting - 03/04/20
San Antonio Meeting

Website address: crudemonitor.us

Light Sweet Crude subcommittee discussion and planning by the Oversight Committee.

Highlights:

- Member Attendees
    - Approximately 28 persons in attendance

- Welcome
    - Welcome to the meeting by Dennis S (COQA)
    - The schedule was reviewed with announcement of other meetings this afternoon
    - A description of the presentation for the Thursday sessions was discussed
    - It was noted that Aaron (Phillips 66) and Bill (Crude Quality Inc.) have headed up the Domestic Sweet Subcommittee for many years
    - The discussion was turned over to Aaron and Bill
    - Aaron noted that the minutes for the October 9, 2019 meeting are to be posted on the COQA website and that the minutes from today's meeting with presentations will also be made available
- 'DSW/WTI Committee Meeting' presentation material
    - Aaron reviewed the agenda from the presentation
        - Crude Quality Inc. is continuing efforts on follow up with shipper contacts for expanding data for crudemonitor.us
        - Other items (Bakken proposal and API creep and gap) to be also discussed
        - New discussion items, such as WTI exports quality monitoring and discussion on future direction, will be included in this meeting
        - Discussion turned over to Bill
    - Bill commented that he works for Crude Quality Inc. (CQI) and they do the monitoring for crudemonitor.ca. CQI also developed the crudemonitor.us
    - The program was started to persuade CME to expand specifications on DSW crude. This has been completed so now we are trying to redefine the project
    - Something that is being pursued is to get data from shippers (from pipelines, ports, etc.) to input in the exiting cruemonitor.us. Emphasis needs to be put on this activity. Need to follow up with individuals that have indicated support, and also looking for new persons for that want to be involved supplying data
    - There was a meeting regarding Bakken with Continental Resources in North Dakota in January, and hopefully more discussion from NDPC will happen tomorrow

- It was noted that CME set an upper API DSW limit of 42 and yet WTL came on with a lower set at 44. The question is if this gap is an issue or not.
- Dennis S clarified that in the specifications the CME adopted, there was not a change to the API or S. It was left alone
- The question was put to Terry (Enterprise) who responded that since they are shippers, they try to maintain what they are given, and so it is not an issue for them
- Gene (Enterprise) noted that it was not seen as an issue. Discussion on testing and reproducibility and such are on and on, but the API discussion is more a commercial point
- Bill commented that it is more of a commercial thing between shippers and receivers
- Rick (Phillips 66) stated that it would be nice if it at least met the Houston specification
- Bill responded that since one is set by CME and the other is proposed by Enterprise, they are two different things. Terry clarified that he was not sure who sets it
- Bill suggested that he was not sure there is anything this group could do about it, and so likely an end of the discussion for the room. Aaron agreed with the statement
- Bill moved on to the next discussion and commented the he would be looking into WTI and would like to be looking into WTL as well. Calling the project DSW at this time with the successful completion of objective now that the focus is changing may be something to reconsider since the DSW project is done and name complete
- Bill noted we have been getting updates for Ni and V

- Turned over to Satbir Nayar (XOS) for discussions on updating method D8252
  - This discussion is to be a quick update
  - This method has been in process for 4-5 years. Round robin was completed summer 2017
  - The original intent was to cover 5 elements, yet there was not consensus. The work did cover wide variety of XRF techniques
  - Satbir noted they changed the ranges going by element to element and scaled back to Ni and V. This was approved by the ASTM subcommittee 8 months ago
  - Presently, they are proposing task group formation to expand method scope and precision inclusive of looking at different XRF techniques
  - Right now they are in the process of collecting samples. The process has a 3rd party handling the samples. This work will kick off in about 3-4 months, and they are still getting participants. [There was a description of scope from the presentation]
  - Benefit of XRF methods is no sample prep as opposed to other methods which require sample prep (ICP 5708B)
  - ASTM PTP data was presented
  - Terry asked about calibration for the high value on the chart. Satbir indicated that calibration was not dependent on range
  - It was noted that when you have to prepare the sample, it adds variability; Sample D (nickel slide) is not representative
  - The method has been out for 8 months. Persons are starting to use it
  - More information will be posted online as addendum to meeting minutes on the COQA web site

- Turned back over to Bill for a discussion on test methods
    - Bill commented that he hoped Satbir's discussion segues into the following portion of the presentation that is about a potential go forward basis for the group. Could we or should we consider replacement test methods?
    - Would the committee consider every 2 years the possibility of composing a letter from the COQA as an industry group to CME NYMEX to include, for example, D8252 and D8045 in updating test methods? Or periodically sending updates to test methods lists for CME NYMEX so that the methods can be updated and improved. This would be a potential utility for the group in the future. Having multiple test methods causes question on what the referee is
    - Gene noted regarding D8252 that he finds it to be an advantage to be able to look at quality with the different tools. If this group says the method is ok, then it is easier to add it as an accepted method and then move it up to a referee method. They have been in contact to update to this method
    - Rick stated that internally, they already use the D8252 and D8045
    - Bill clarified for the group that it is not the accepted method for the CME
    - Rick responded that it is used as an internal method
    - Bill commented that we need to have a way as an industry to update
    - Rick responded that it could be similar to the way ASTM adds a date on the method for updates
    - Dennis S suggested that similar to digital density microcarbon discussion, if we were able to come to CME NYMEX similar to what we did in 2010, said we are not recommending numerical change to the value, but are recommending an improvement to the method; thinking of Dan Brusstar, the discussion would be likely accepted well. Since it is not changing values with economic implications, methods would be much easier accepted
    - Rick asked if the committee is looking for names from companies like Enterprise, Magellan, etc. to back these methods
    - Bill responded that with all the accessible pieces of information, as a group we could recommend methods that we are good. The ability to include COQA membership names (or just the working group) on a document to industry would improve its credibility and acceptance.
    - Ranzy (Choice Analytical) suggested the work could be based on 2 years of data to evaluate methods for candidates as referee methods
    - Dan W (VUV Analytics) asked if we have a standing invitation to COQA meetings for CME and other members
    - Dennis S stated 'yes', Dan Brusstar and others have invitations
    - Aaron commented with that, what we would like to do is formalize this idea and put some words around it to move forward so that when we meet again, we can get the path solidified
    - Since scope of the subcommittee is changing, we are looking for new members. If interested in joining, please send Bill or me (Aaron) an email
    - Before the next meeting, an email will be sent to Dan Brusstar
    - Good discussions since there have been several inquiries about old standards and why we don't use the new standards. Also, there is the point on name change of the project

    - Bill stated the we are looking for suggestions on the project name, and suggested 'Light Sweet Crude Subcommittee' as the recommended new name
    - Dennis S said it might be good for him to put a blurb on the COQA website to describe the name and content change so that others not able to attend can be informed. He stated he would draft a letter from the COQA and describe the purpose of the change so that companies involved would know about the change
- Closing Remarks
    - Aaron indicated he would put a new space on the website to add the new meeting minutes. He asked if there were any other questions
    - Aaron thanked all for attending the new subcommittee
    - The meeting was adjourned

<u>Appendices to the Minutes (attached)</u>

- Presentation: DSW/WTI Committee meeting (COQA Meeting, San Antonio, TX; March 4, 2020) [includes Agenda].
- Presentation: ASTM Method D8252 Update; Standard Test Method for Vanadium and Nickel in Crude and Residual Oil by X-ray Spectrometry (COQA Meeting, San Antonio, TX; March 4, 2020).
- Presentation: ASTM Method D8252 – More than you ever wanted to know (XOS, March 2020)

- Attendees
    - Aaron Dillard (Phillips 66)
    - Anna Morris (Marathon Pipeline)
    - Bill Lywood (Crude Quality Inc.)
    - Bob Ford (Horiba)
    - Brant Easterlins (Magellan)
    - Chandler Markovchik (Choice Analytical)
    - Clint Bram (Citgo)
    - Dan Carson (Core Lab/Saybolt)
    - Dan Wispinski (VUV Analytics)
    - Dennis Compton (Infineum)
    - Dennis Haynes (Nalco Water)
    - Dennis Sutton (COQA)
    - Divya Krishnan (Citgo)
    - Donn Bonnette (Horiba)
    - Gene Filipse (Enterprise Products)
    - Greg Gilbert (Bureau Veritas)
    - Jay Silvas (Citgo)
    - Jeff Bowifas (Halliburton)
    - Larry Kremer (Retired)
    - Nathan Wreyford (Horiba)
    - Raj Wadhwa (Phillips 66)
    - Ranzy Morgan (Choice Analytical Inc.)
    - Rick Dobies (Phillips 66)
    - Sam Lordo (Consultant)
    - Satbir Nayar (XOS)
    - Terry Thompson (FFPO)
    - Tyler Caughman (Magellan)
    - Umberto Cabarrocos (ASIKeco)

DSW/WTI COMMITTEE MEETING

CRUDE OIL QUALITY ASSOCIATION
SAN ANTONIO, TX
MARCH 4, 2020

AGENDA

- Review of past efforts
  - Crude Quality Inc has had limited follow up on shipper contacts for expanding data presented on crudemonitor.us
  - Bakken proposal to Continental Resources requires follow up, ND update pending tomorrow
  - Is API "creep" and "gap" still an issue? (API 42 upper limit – DSW, API 44 lower limit – WTL
- New ideas discussion
  - WTI exports quality monitoring
  - Open discussion on future direction

NEW INFORMATION

- Test methods update
  - Nickel & vanadium test method update – Satbir Nayar
- Updating and standardization of test methods generally
  - Could/should committee include focus on informing industry of new and/or replacement test methods?? Others that are better suited??
  - D8252 metals, D8045 TAN (for example) not in any contracts
    - Typically D5708B or latest version
  - Means of communicating – to whom, how often, format
  - Benefit – consistent, standardized reporting creates confidence in stream quality, allows more accurate stream comparisons

better analysis counts

ASTM Method D8252 Update

Standard Test Method for Vanadium and Nickel in Crude and Residual Oil by X-ray Spectrometry

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COQA – March 3, 2020

Satbir Nayar, Senior Product Manager

snayar@xos.com

Quick History Current Status of Method

WK57245 formed ~ 4 years ago

ILS 1292 completed summer 2017, 14 labs, 17 samples

Scope scaled back to Ni and V only

Published in September of 2019

Next ILS in 2020 – Expand Scope and Improve Precision

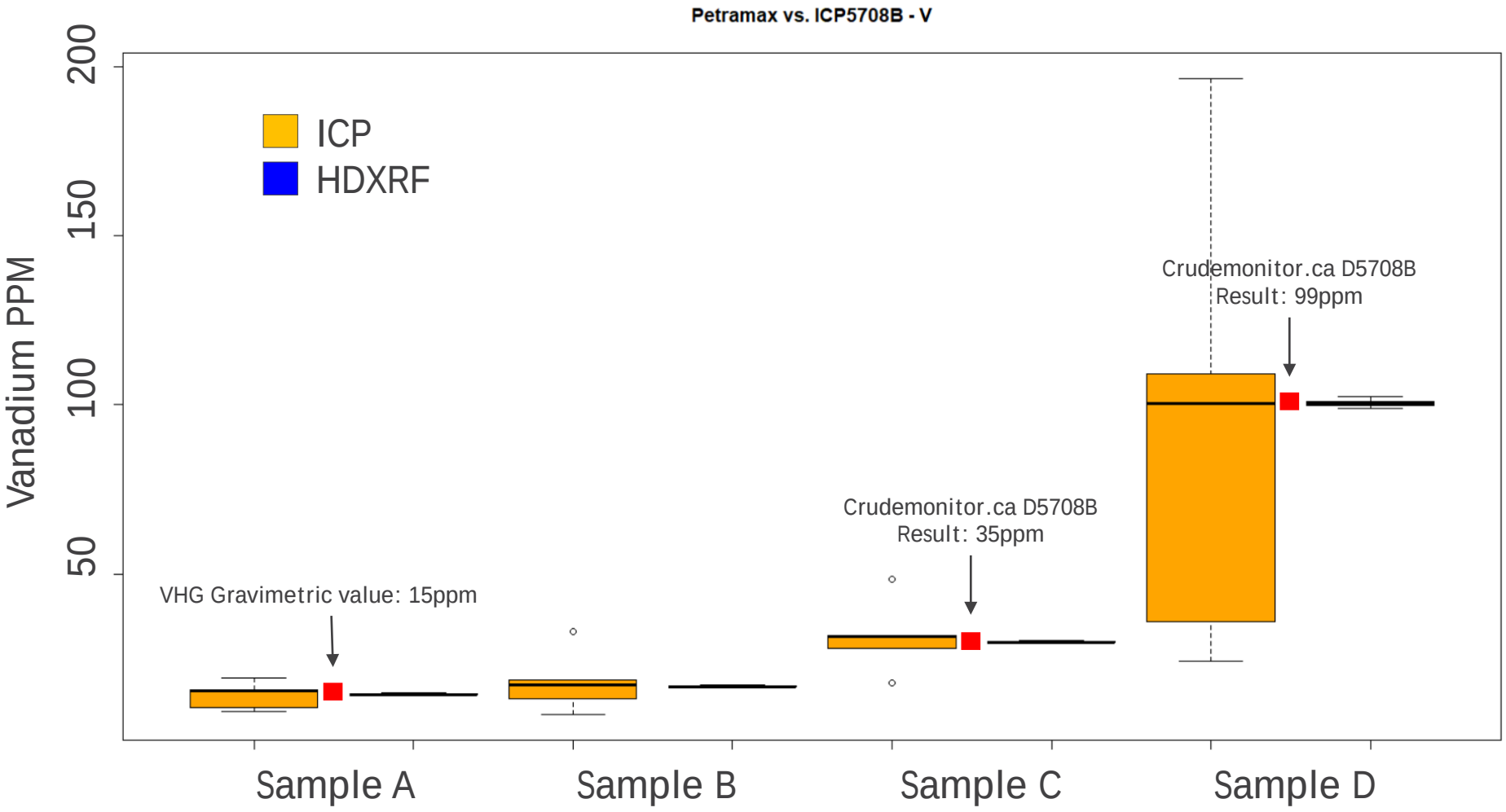
add Fe
increase Ni/V top end of scope

Element	D8252 Precision Statement Scope	D8252 "r" at 10ppm	D8252 "R" at 10ppm
Ni	2.2 to 50 ppm	1.5ppm	4.8ppm
V	1.9 to 50 ppm	1.5ppm	5.8ppm

ASTM PTP Correlation Data

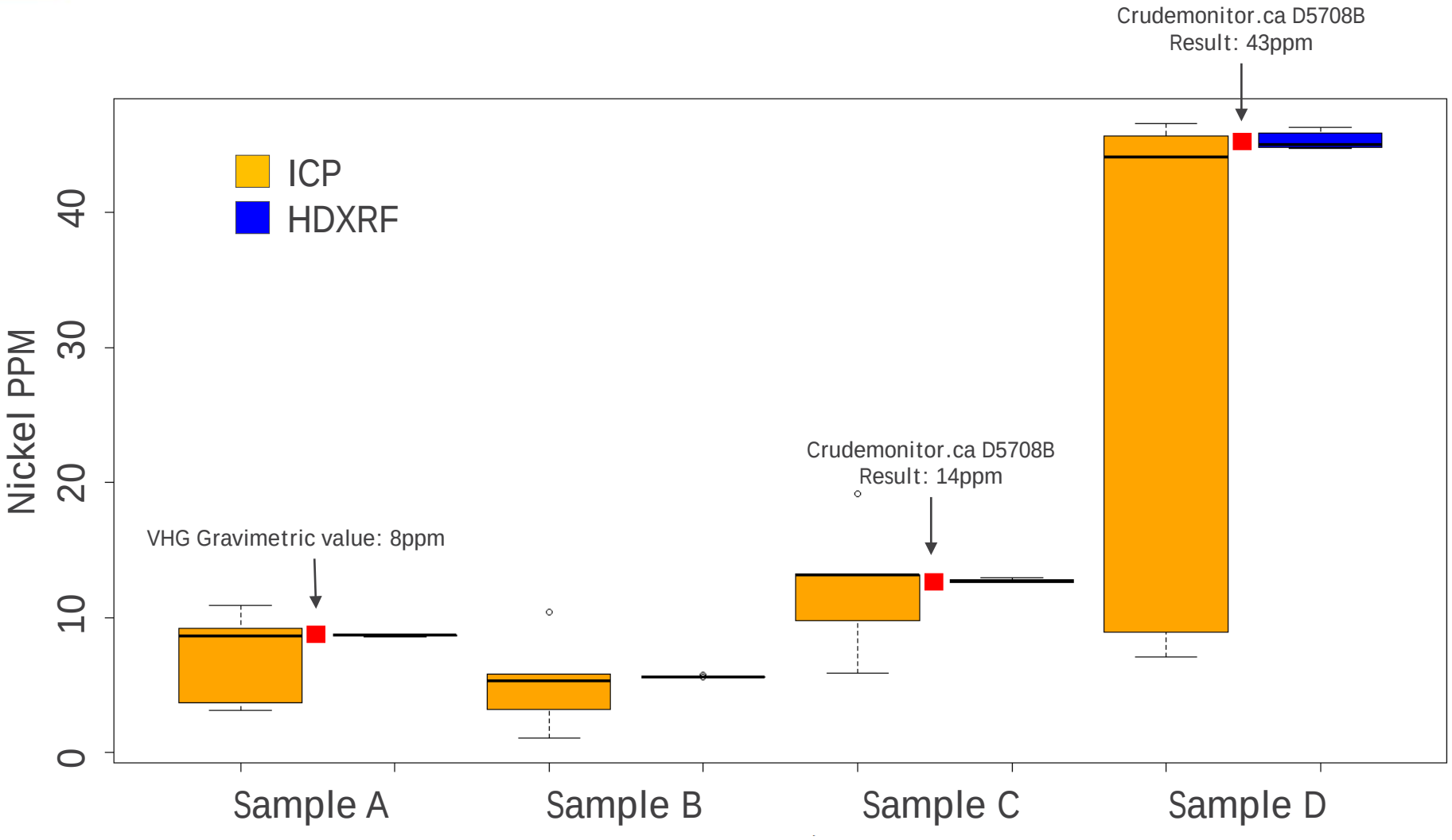
	Petra MAX (MEDXRF)				ICP 5708B			
ASTM PTP Sample	Vanadium		Nickel		Vanadium		Nickel	
	Average	STD	Average	STD	Average	R/STD	Average	R/STD
CO1411	0.4*		2		0.31		1.77	
CO1411	0.3*		2		0.31		1.77	
CO1503	27.3*		11.4		24.69		10.52	
CO1503	27*		11.3		24.69		10.52	
CO1507	319*		60.5		301.01	53.4/19.07	56.25	12.8/4/57
CO1507	317.7*		60.6		301.01	53.4/19.07	56.25	12.8/4.57
CO1511	**15.3****	**0.2**	**9.3**	**0.1**	**13.94**	**4.0/1.4**	**7.59**	**5.3/1.93**
CO1511	**15.2****	**0.2**	**9.3**	**0.1**	**13.94**	**4.0/1.4**	**7.59**	**5.3/1.93**
*Results are from single measurement each on 2 different instruments at one site								
**Results are from 2 separate instruments at one site, each sample measured 20 times.								
All values in mg/kg								

ICP vs HDXRF for Vanadium



HDXRF correlates well to ICP for Vanadium and has less variability

ICP vs HDXRF for Nickel



HDXRF correlates well to ICP for Nickel and has less variability

Questions?

THANK YOU

better analysis counts

Metals in Crude Oil
ICP (ASTM D5708B) vs. HDXRF

Presented at the Crude Oil Quality Association meeting; San Antonio, TX; Feb 22, 2018

By Leslie Johnson, XOS Applications Scientist

Today's Presentation

- Growing importance of metals in crude oil
- Metals in crude oil test method overview
- Nickel and Vanadium ICP vs. HDXRF Pilot study
  - Study outline and objectives
  - ICP vs. HDXRF correlation
  - ICP vs. HDXRF precision
- HDXRF results ASTM crude PTP sample CO1511

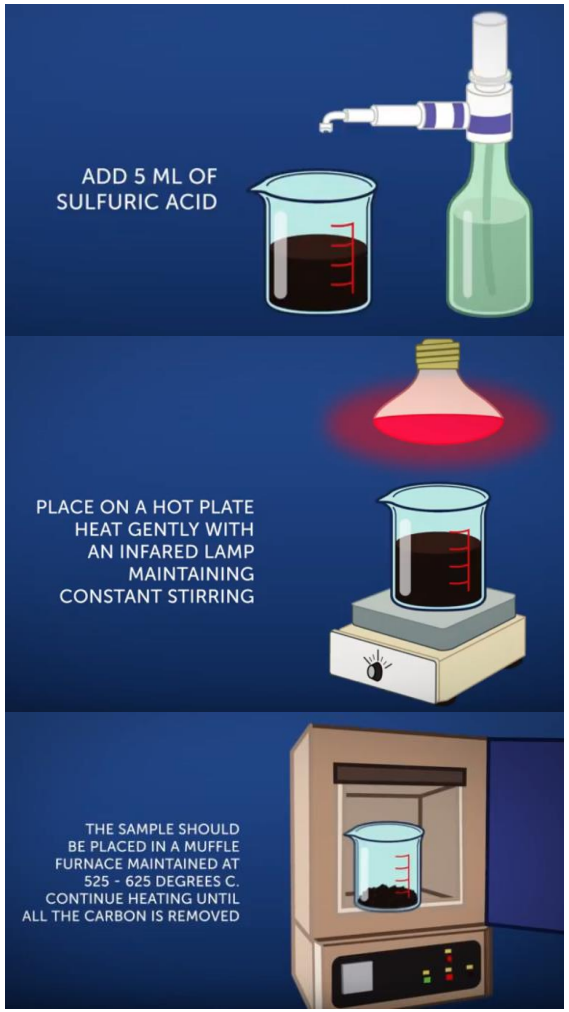
NYMEX Amended Rule 200101

Light Sweet Crude Oil Futures contract for January 2019 and beyond includes five additional quality test parameters:

- Micro method carbon residue (ASTM D4530): 2.40% max
- Total acid number (D664): 0.28 mg KOH/g max
- High-temperature simulated distillation (D7169): light ends 19% max, 50% point 470-570°F, vacuum residuum 16% max
- Nickel (D5708B): 8 ppm max
- Vanadium (D5708B): 15 ppm max

Metals in Crude Test Method and Technology Overview

D5708B Test Methodology



- Digest sample with sulfuric acid -
- Heat gently and maintain constant stirring until sample is reduced to a carbonaceous ash
- Burn off carbon in a muffle furnace
- Reconstitute sample with nitric acid
- Analyze sample by ICP

➢Users report sample preparation and analysis takes **6-12 hours** and requires **many steps** to obtain results

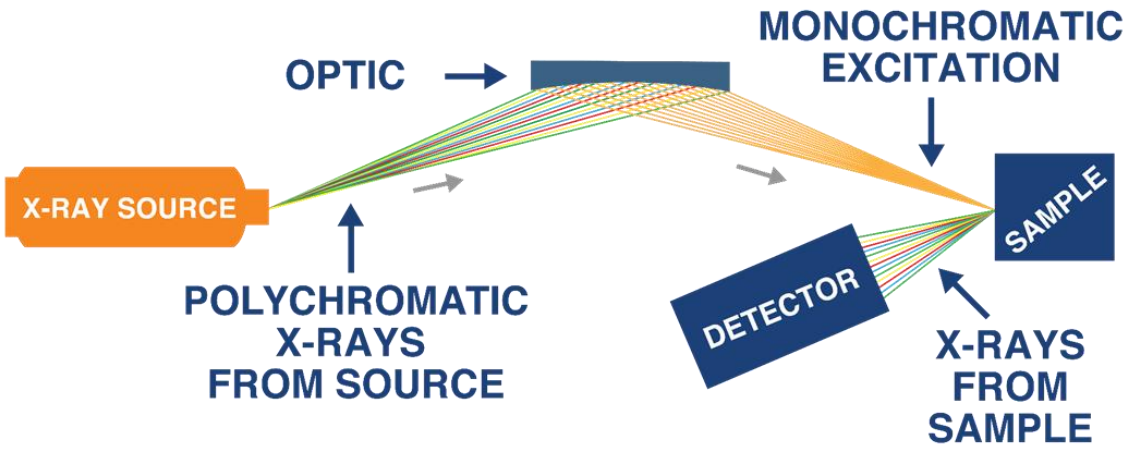
➢What if there were an easier way?

New HDXRF Solution from XOS

- Combines ASTM D4294 sulfur compliance with simultaneous measurement of:
  - Nickel
  - Vanadium
  - 10 other elements
- Minimal sample preparation
- Measurement results in minutes

Petra MAX
Elemental Analyzer for Petroleum

HDXRF Technology



- The polychromatic x-rays from the x-ray tube are monochromated by a doubly curved crystal optic prior to sample excitation
- Resulting sample XRF is directed to the detector
- Ambient air optical path (no vacuum or helium needed)
- Fundamental Parameters calibration is used for multi-element analysis

➢Very similar to D7751 (Additive Elements in Lube Oil by EDXRF) apparatus

Nickel and Vanadium
ICP vs. HDXRF Pilot Study

ICP vs. HDXRF Pilot Study Design

- Approximate range Ni: 7-45 ppm, V: 14-100 ppm
- Four crude oil samples:
  - A: Custom doped crude oil standard from VHG Labs
  - B: Sour crude retain from Intertek
  - C: Medium sour crude retain from Crudemonitor.ca
  - D: Heavy sour crude retain from Crudemonitor.ca
- Three independent laboratory participants using two techniques:
  - ICP: ASTM D5708B (ICP after acid digestion and ashing)
  - HDXRF: Petra Max demo analyzer
- Each participant received two randomized sample sets, with samples packaged in blind duplicate
- Key pilot study questions:

1. Does HDXRF correlate with ICP?
2. How does the precision of HDXRF compare to ICP?

Study Results – Raw Data Sample Means

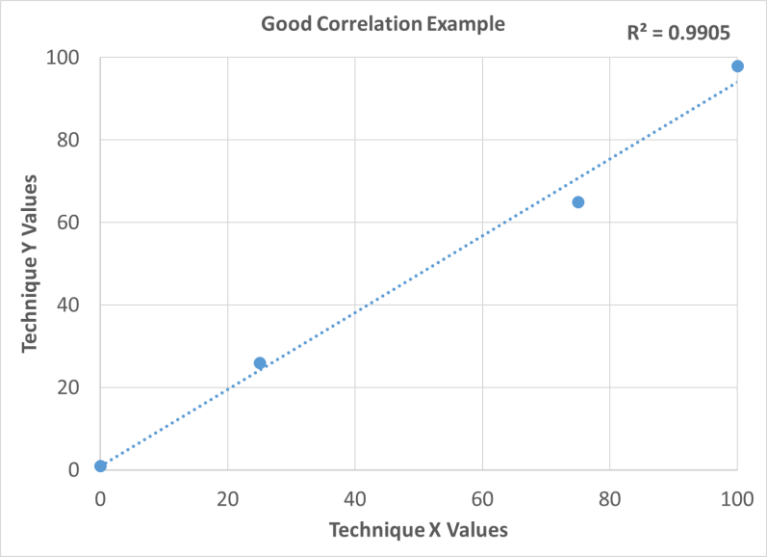
Sample	ICP - D5708B		HDXRF Petra MAX		ICP Crudemonitor.ca*	
	Ni (ppm)	V (ppm)	Ni (ppm)	V (ppm)	Ni (ppm)	V (ppm)
A	7.36	14.23	8.69	14.32	----	----
B	5.19	17.89	5.64	16.68	----	----
C	12.40	31.51	12.73	29.92	14	35
D	30.49	73.90	45.31	100.37	43	99

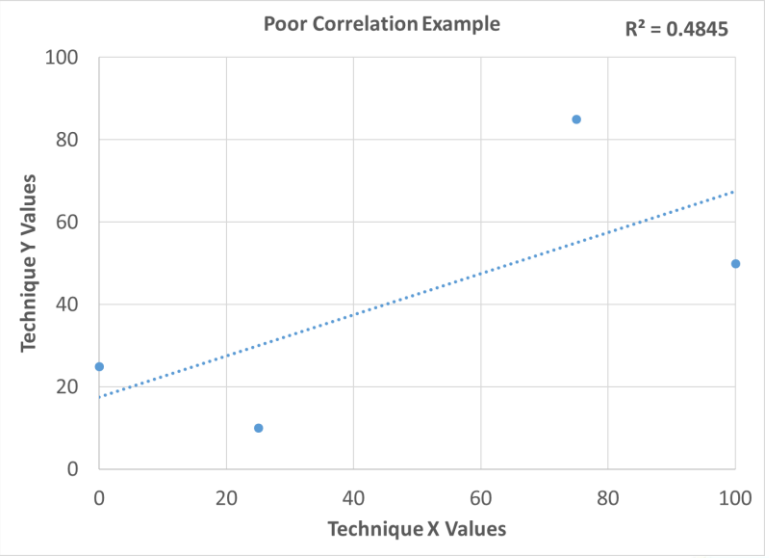
* For reference only

Correlation

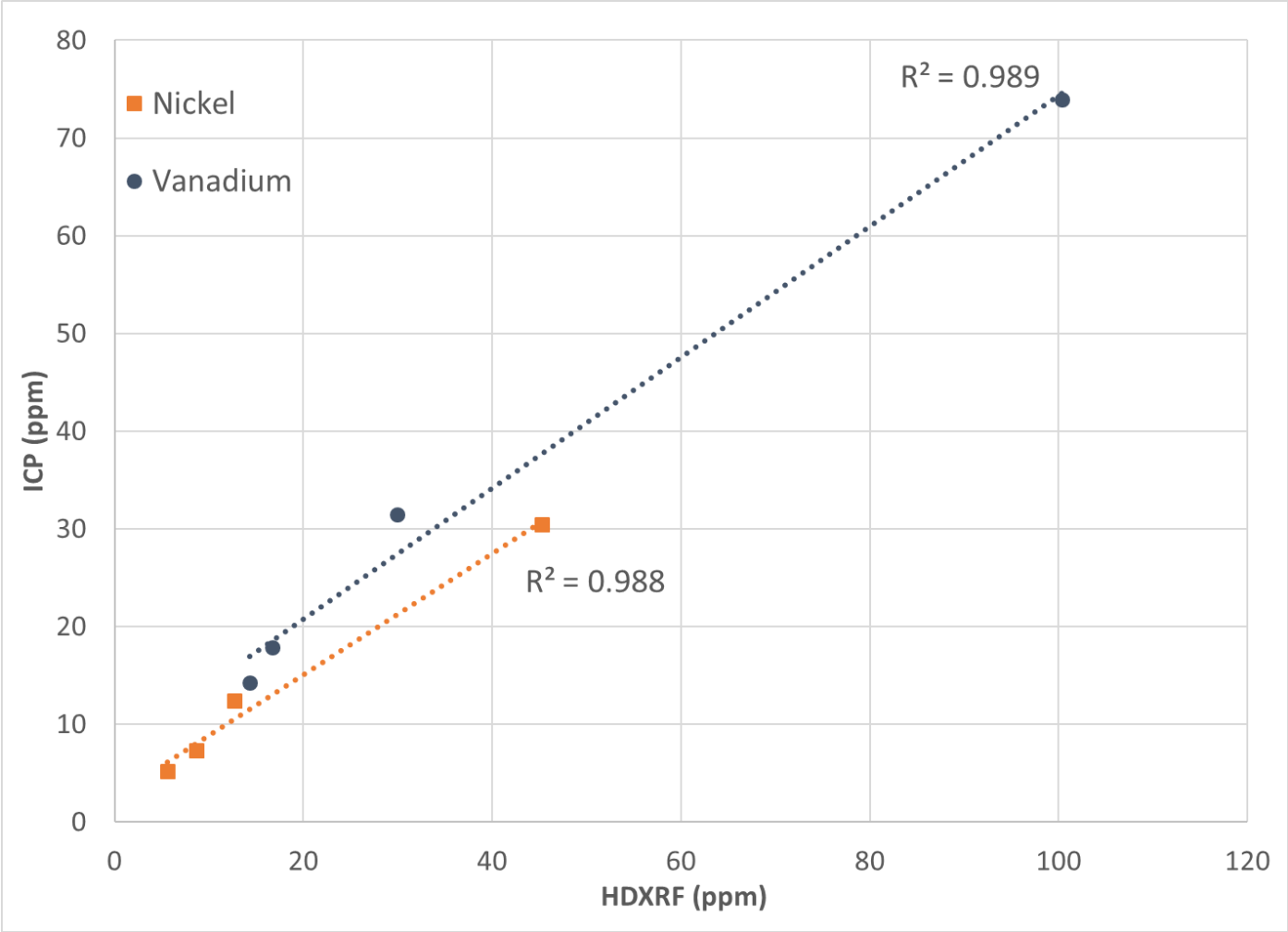
A simple way to show correlation between two techniques:

- Measure a sample set spanning a range using two techniques
- Scatter plot the results, technique Y on one axis, technique X on the other axis
- Plot the trendline with R-squared value
- If techniques display good correlation, the plotted points will be on or near the trendline. If the techniques display poor correlation, the plotted points will not be near the trendline.
- R-squared is the coefficient of determination. This is a value between 0 and 1, and the better the correlation, the closer to 1 this value will be.





ICP vs. HDXRF Correlation



HDXRF shows excellent correlation with ICP Method D5708B for both nickel and vanadium

ASTM Precision Definitions

- 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

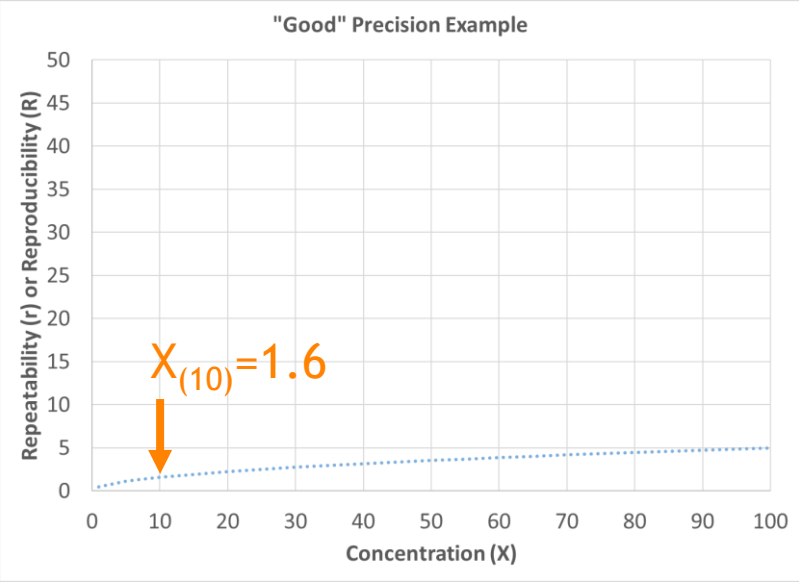
  - Repeatability (r) → Within lab difference

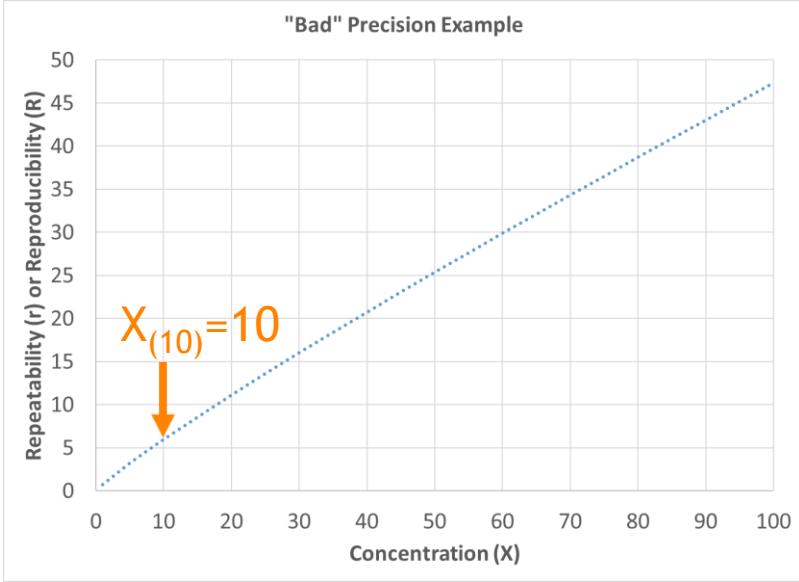
- Reproducibility—The difference between two single and independent results obtained by different operators applying the same test method in different laboratories using different apparatus on identical test material would, in the long run, in the normal and correct operation of the test method, exceed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

  - Reproducibility (R) → Between lab difference

Precision

- Precision is often dependent on concentration and in ASTM test methods is often presented in equation format such as:
  - Linear precision example: (r) or (R) = X * 0.1234
  - Exponential precision example: (r) or (R) = X^0.123 * 4.567
  - Where X is the mean value or concentration of interest
- This relationship can be graphed for an easier, visual representation
- The lower the repeatability or reproducibility value (y in the plots below) for a given concentration, the better the precision





Repeatability & Reproducibility

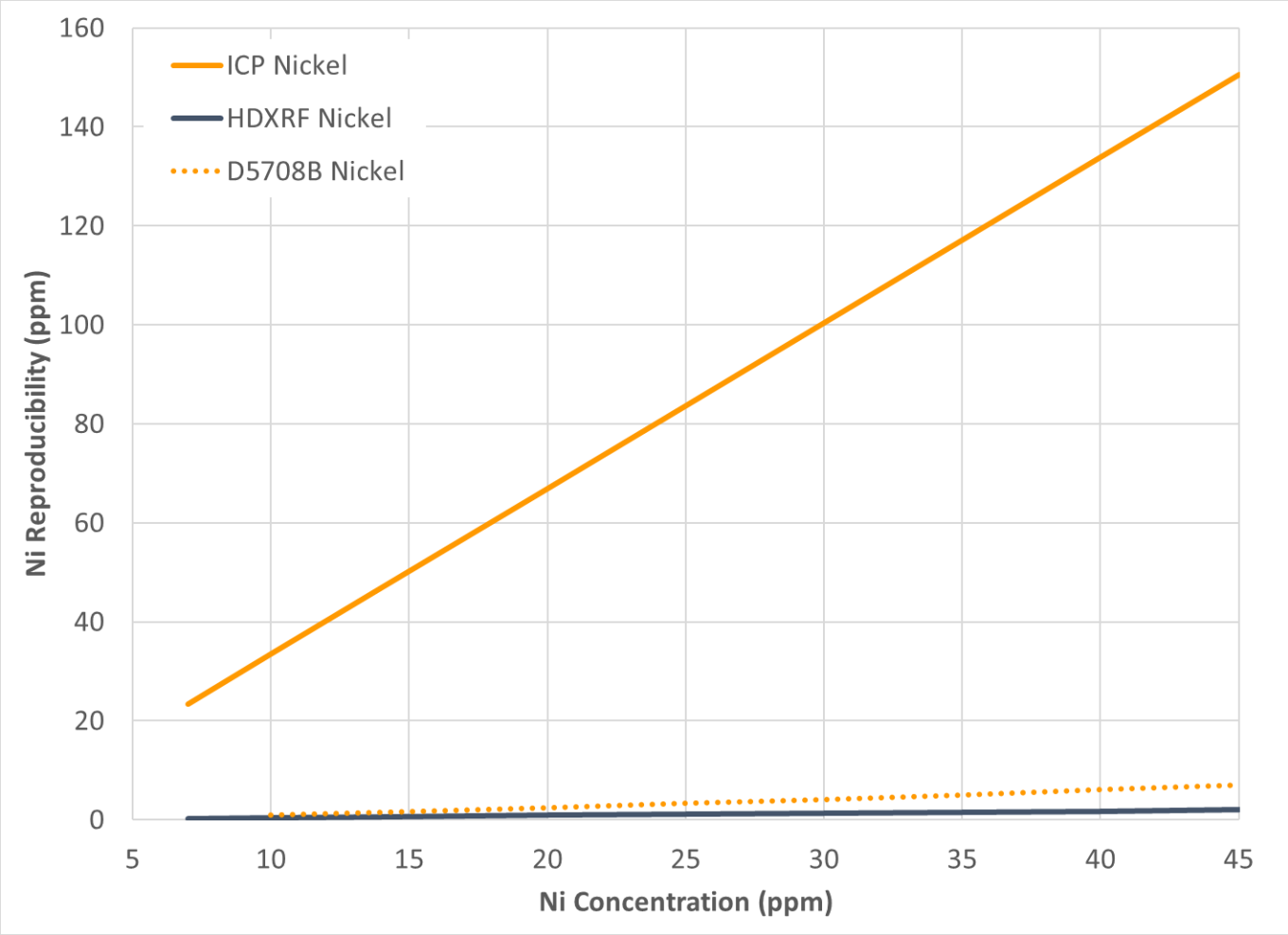
Study statistics were performed according to ASTM D6300 – Standard Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

	Reproducibility	
	Ni (ppm)	V (ppm)
HDXRF Data‡	0.04428*X	0.1359*X^0.646
ICP Data‡	3.3477*X	1.9288*X
D5708B (Method)	0.05*X^1.3	0.10*X^1.1

	Repeatability	
	Ni (ppm)	V (ppm)
HDXRF Data‡	0.02716*X	0.1373*X^0.646
ICP Data‡	0.9536*X	0.7101*X
D5708B (Method)	0.02*X^1.2	0.02*X^1.1

‡<30 degrees of freedom

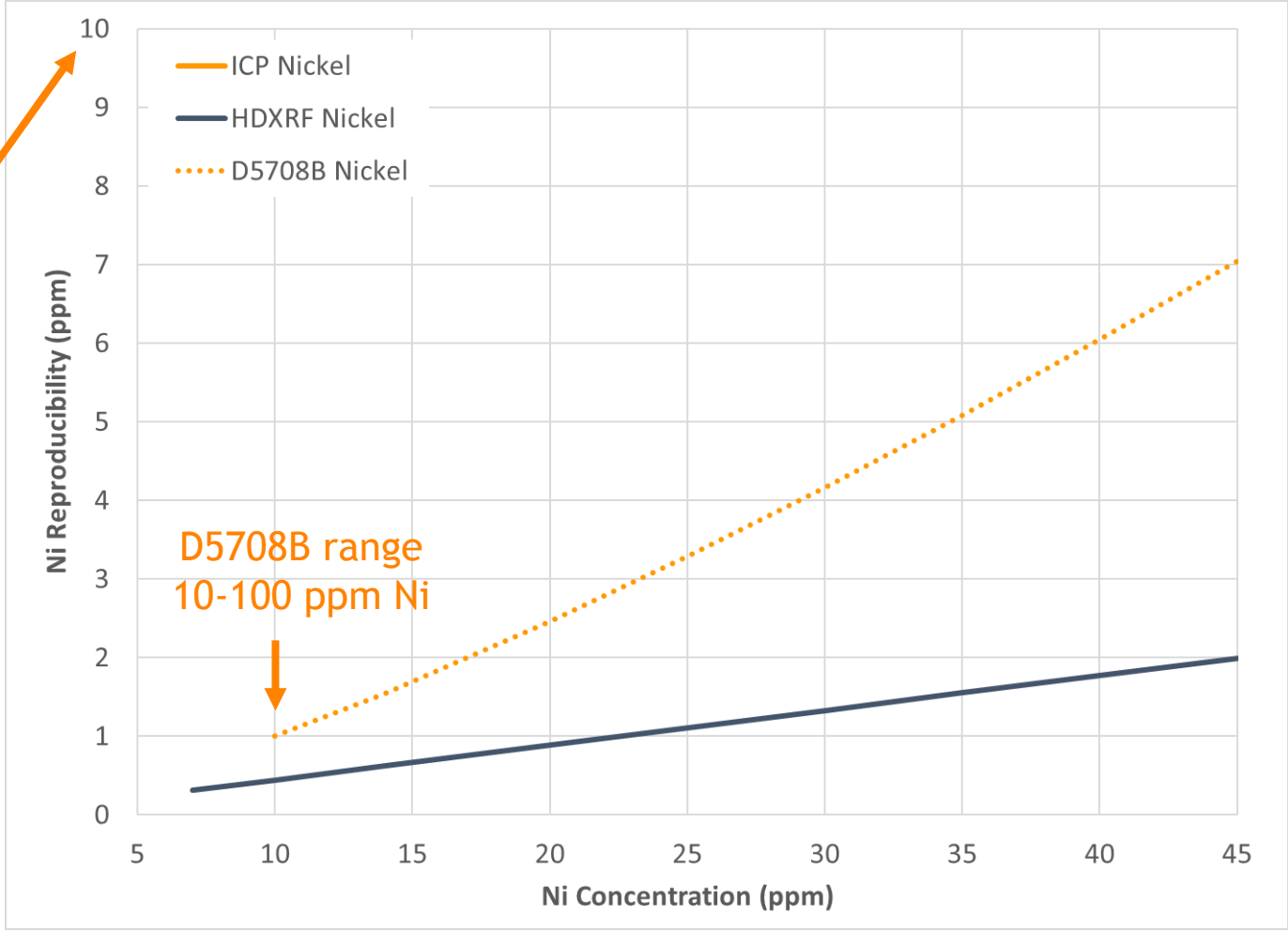
Nickel Reproducibility (7- 45 ppm)



ICP study data for nickel exhibited poor precision when compared with HDXRF and D5708B method precision

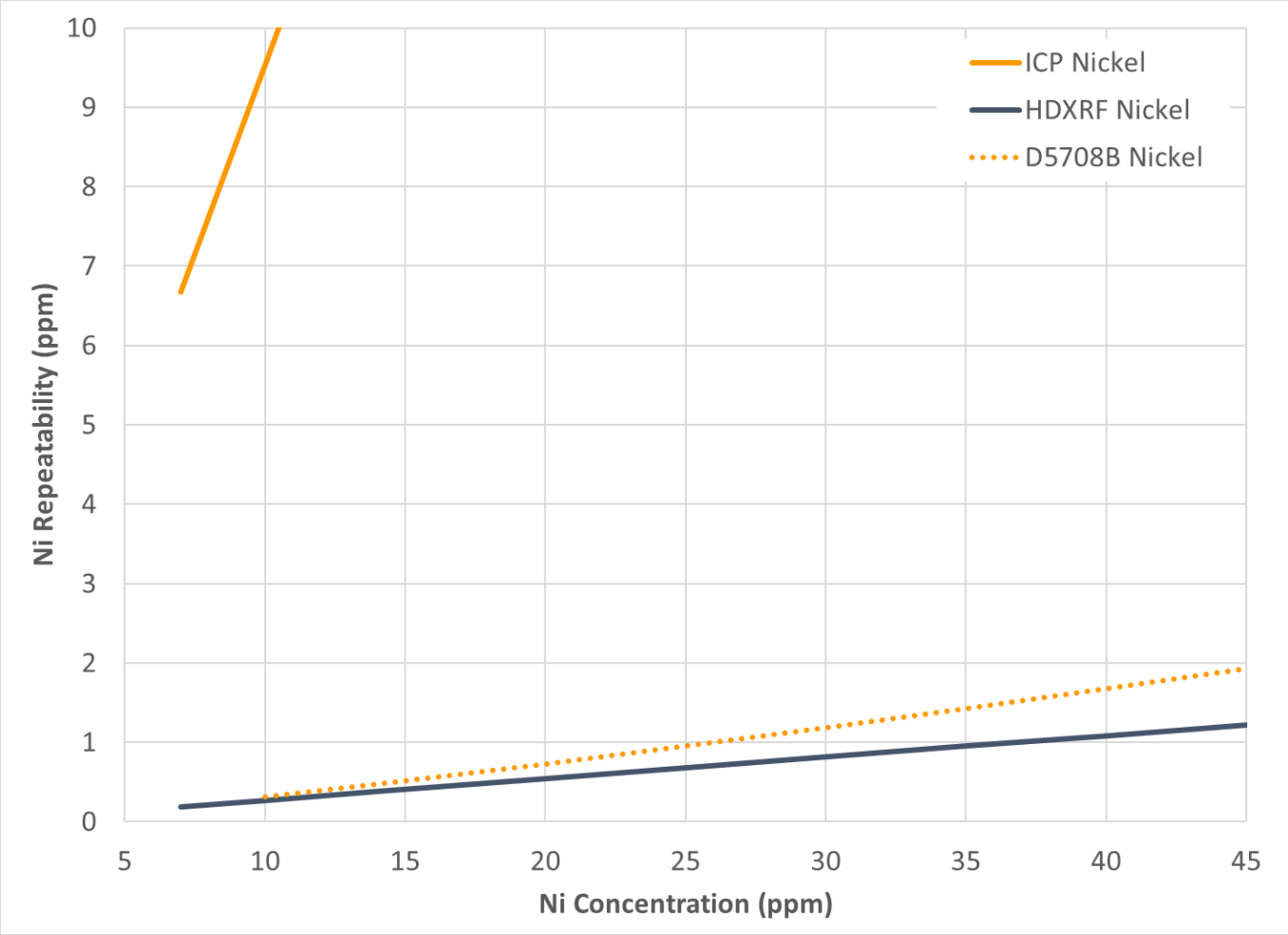
Nickel Reproducibility (cont.)

Zoomed in



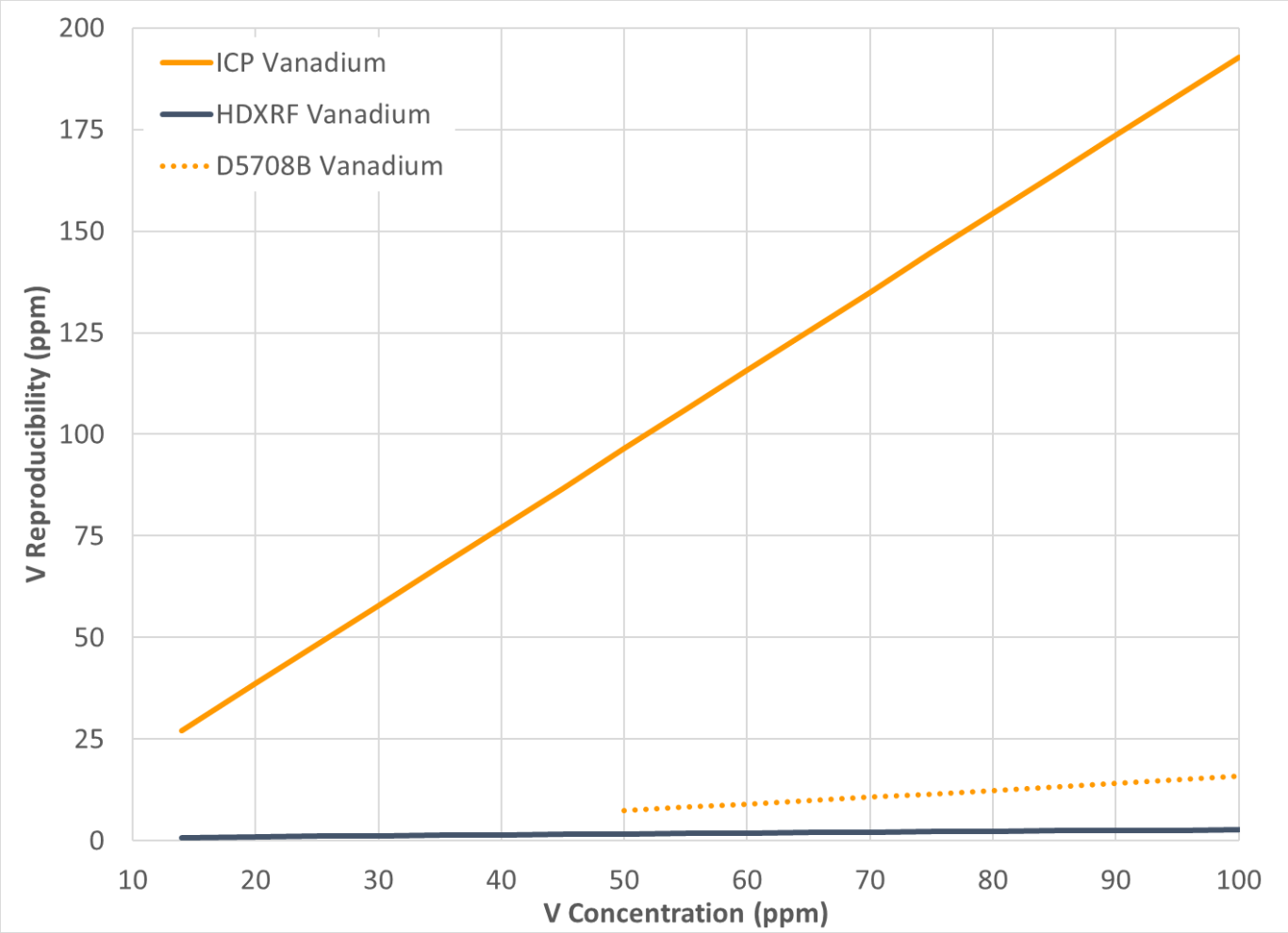
HDXRF exhibits better reproducibility for nickel as compared to both the ICP study data and D5708B method precision

Nickel Repeatability (7- 45 ppm)



HDXRF exhibits similar or better repeatability for nickel as compared to D5708B method precision and better repeatability than the ICP study data

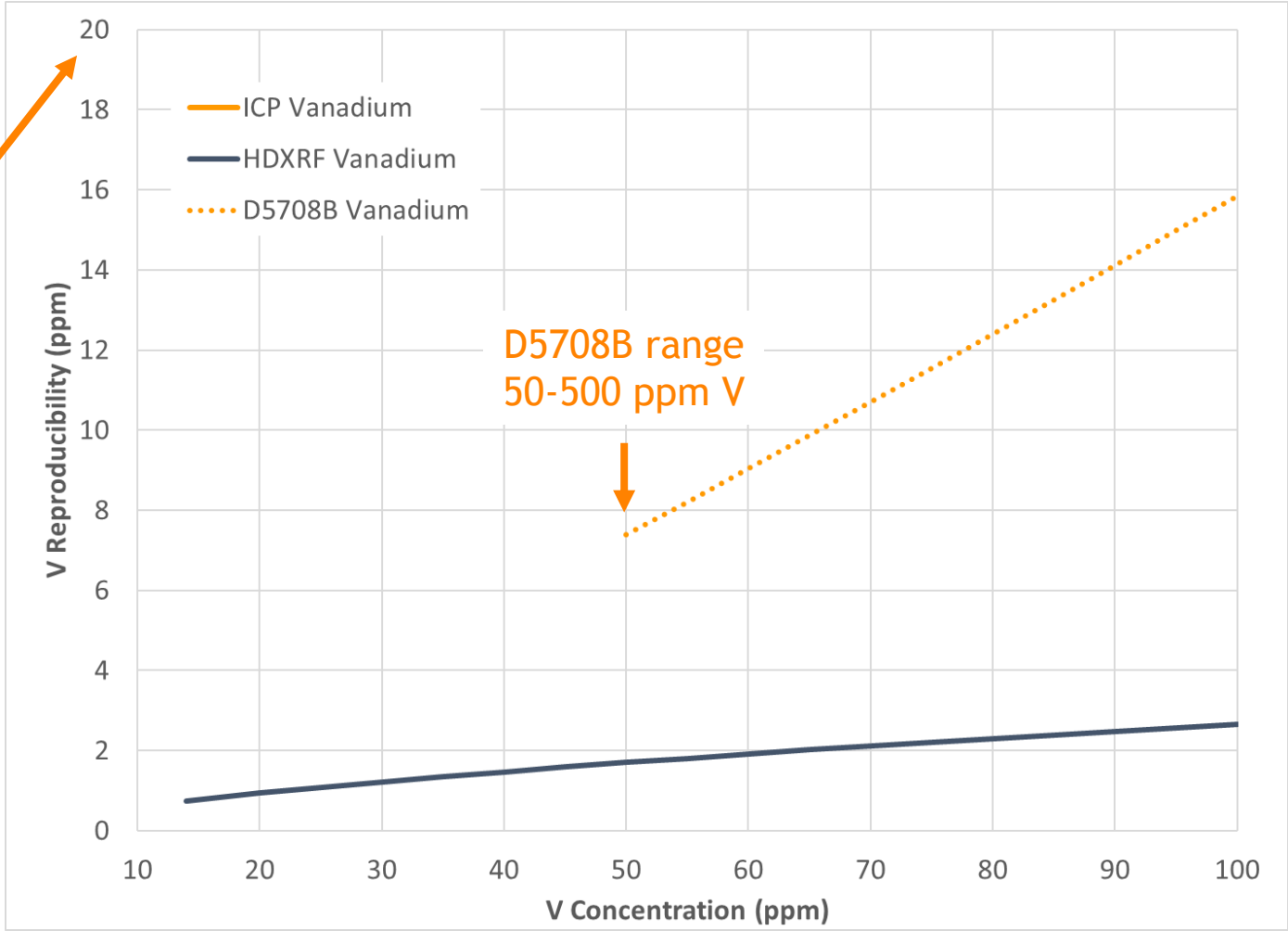
Vanadium Reproducibility (14 - 100 ppm)



ICP study data for vanadium exhibited poor precision when compared with HDXRF and D5708B method precision

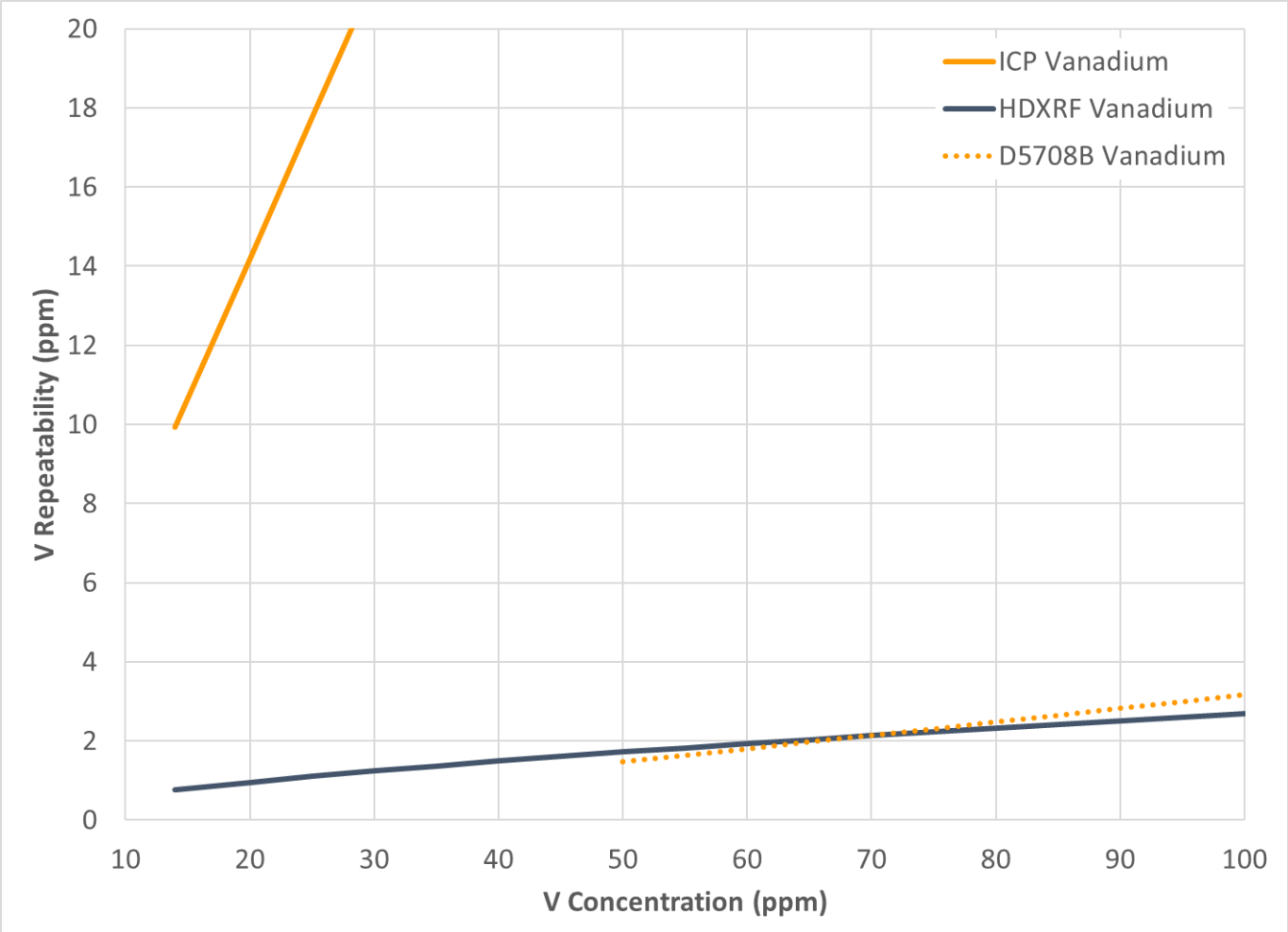
Vanadium Reproducibility (cont.)

Zoomed in



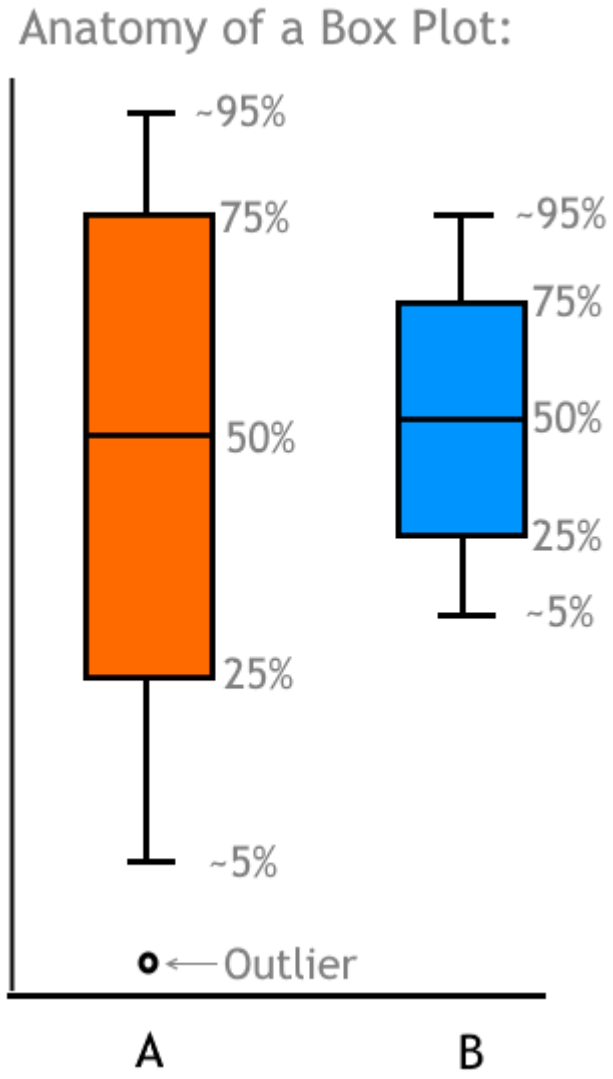
HDXRF exhibits better reproducibility for vanadium as compared to both the ICP study data and D5708B method precision

Vanadium Repeatability



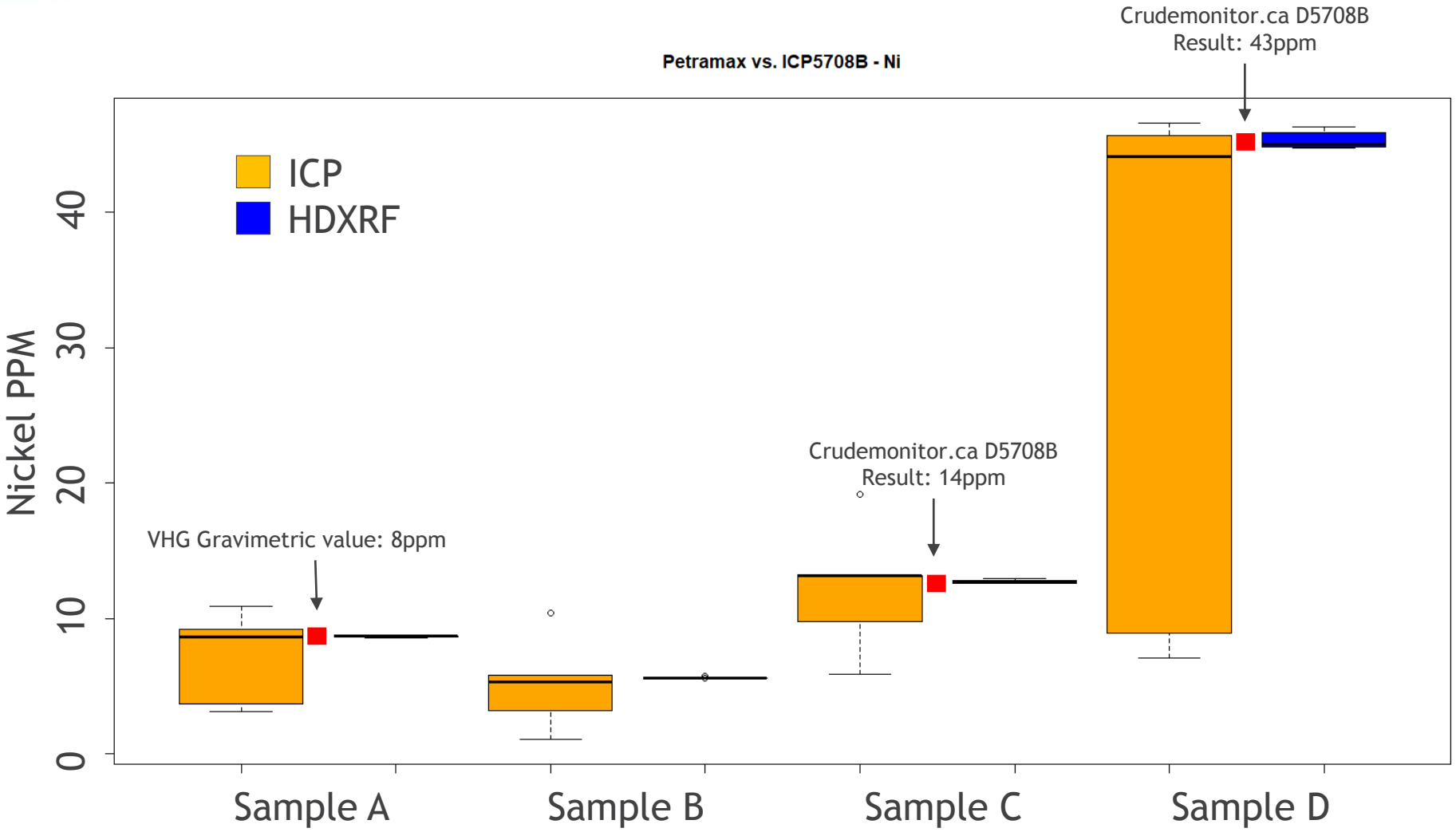
HDXRF exhibits similar repeatability for vanadium as compared to D5708B method precision and better repeatability than the ICP study data

Box and Whisker Plots



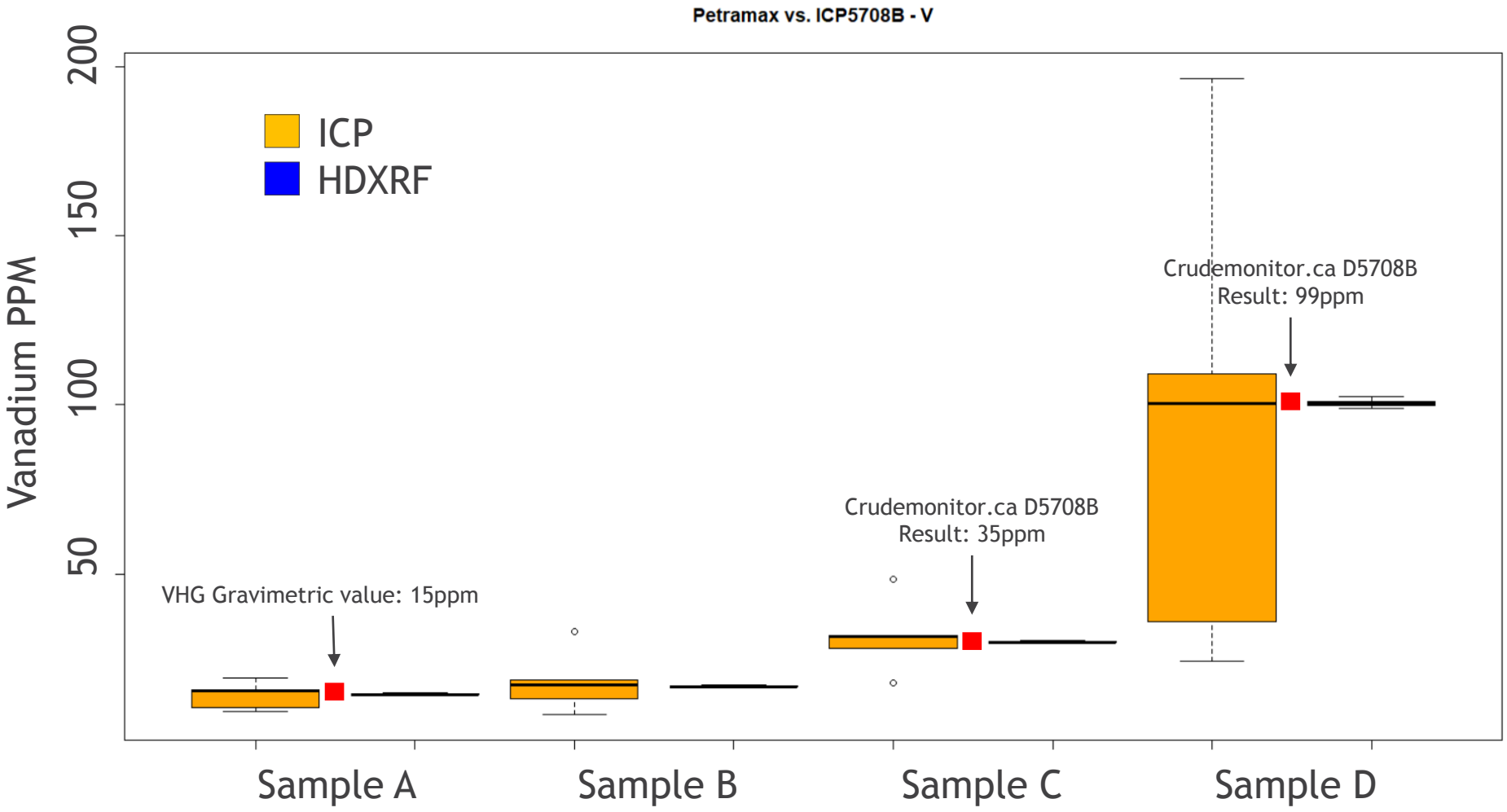
- Box and whisker plots show a quick graphical examination of sample distribution.
- The larger the box, the wider the distribution. A smaller box is indicative of tighter precision.
- If the 50% median bisects the center of the box, the distribution is normal (bell curve). If it is closer to one end, the distribution is skewed.
- If two test methods measuring the same sample are compared, box and whisker plots can be used to infer correlation (comparing the medians) and precision (comparing the size of the boxes)

Nickel Box and Whisker Plot



HDXRF correlates to and exhibits better precision than ICP for nickel.

Vanadium Box and Whisker Plot



HDXRF correlates to and exhibits better precision than ICP for vanadium.

ASTM Crude Oil Proficiency Testing Program (PTP)

ASTM Crude Oil PTP Program

- Samples distributed about three times per year for the following tests:

D664	Acid Number - Total
D6560	Asphaltenes
D1298, D5002, D287	Density, Relative Density or API Gravity
D7169	High Temperature Simulated Distillation
D5708, D5863	Metals (Vanadium, Nickel, Iron)
D4530	Micro Carbon Residue
D4629, D5762	Nitrogen, Total
D97, D5853	Pour Point
D323, D5191, D6377	Reid Vapor Pressure
D3230, D6470	Salt
D473, D4807	Sediment
D2622, D4294	Sulfur
D445	Viscosity, Kinematic
D4006, D4928, D4377, D4007	Water

ASTM CO1511 PTP Retain

ASTM INTERNATIONAL

Committee D-2
Proficiency Testing Program

Crude Oil
Sample ID: CO1511
November 2015

PetraMAX
Elemental Analyzer for Petroleum

Test Parameter	D5708B ICP Mean Results (ppm)	D5708 ICP Reproducibility (ppm)	HDXRF (ppm)
Nickel	7.6	5.3	9.4
Vanadium	13.9	4.0	15.3
Iron	16.8	17.7	17.5

CO1511 HDXRF Data

Sample Repeat	Ni (ppm)	V (ppm)	Fe (ppm)
1	9.3	15.2	17.5
2	9.4	15.2	17.2
3	9.2	15.1	16.4
4	9.4	15.4	16.7
5	9.4	15.2	17.3
6	9.3	15.2	20.0
7	9.4	15.5	17.0
8	9.3	15.2	17.5
9	9.4	15.6	17.9
10	9.4	15.7	17.7
Average	9.4	15.3	17.5
Std Dev	0.1	0.2	1.0
%RSD	0.72%	1.40%	5.65%

Conclusion

- In 2019, nickel and vanadium will be two additional required quality test parameters for light sweet crude oil
- HDXRF offers a precise, fast and easy to use alternative for crude oil, delivering D4294 compliant sulfur results plus nickel, vanadium, and 10 other elemental results in minutes
- In a three laboratory, four crude oil sample pilot study:
  - HDXRF demonstrated excellent correlation with ICP data for nickel and vanadium
  - HDXRF demonstrated better precision than the ICP data, and similar or better precision for test method D5708B for nickel and vanadium
- HDXRF nickel, vanadium, and iron results were similar to ICP test method D5708B results for ASTM crude oil retain CO1511

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.

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THANK YOU

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