



ARE YOU READY FOR THE NEW ASTM D8252 NI & V METHOD USING XRF?

ASTM D8252 METHOD HIGHLIGHTS

ASTM D8252 allows for multiple XRF technologies to be used to provide immediate method compliance to those who have historically used XRF as a prescreen for Inductively Coupled Plasma Mass Spectroscopy (ICP) (ASTM D5708B). ASTM D8252 includes both wavelength dispersive XRF (WDXRF) and energy dispersive XRF (EDXRF) (Section 1.3), as well as polychromatic or monochromatic excitation (Sections 4.5.1 and 4.6.1)¹. The Petra analyzers used in the study below utilize EDXRF with monochromatic excitation, also known as HDXRF[®]-XOS' branded technology, which allows for increased precision and superior performance over traditional EDXRF analyzers.

In **Table 1** of this paper and the method, we can see the method range is from the pooled limit of quantification (PLOQ), 1.9 ppm vanadium and 2.2 ppm nickel, to 50 ppm. The PLOQ is the "numerical limit at or above which the test results are considered to be quantitatively meaningful for commerce or regulatory activities"². Therefore, D8252 aligns well with the NYMEX amended rule maximums of 8 ppm for nickel and 15 ppm for vanadium. It should be noted that the PLOQs for this method are below the precision concentration ranges listed in the precision section of the ICP D5708 test method, which are 50-500 ppm and 10-100 ppm for vanadium and nickel, respectively³. Note also that these ICP concentration ranges are above the NYMEX amended rule maximums.

Element	PLOQ (ppm)	Max Concentration (ppm)
Vanadium	1.9	50
Nickel	2.2	50

Why XRF?

Historically, quantification of nickel and vanadium was performed by ICP analysis. ICP analysis can be demanding on the lab environment not only regarding time consumption, but also operator skill level. ICP analysis by ASTM D5708B requires rigorous sample preparation involving acid digestion and can take anywhere from 6 to 12 hours to complete a measurement. With an increasing demand for timely results alongside crude processing capacity, as well as the need to quickly onboard new and existing lab talent, refineries have looked to streamline their measurement processes to reduce time and lower the expertise threshold to

meet their unique needs. Petra MAX analysis is well equipped to meet these needs as measurement takes as little as 5 minutes and sample preparation being quick to master. This measurement process is detailed in D8252 under Section 13 Procedure, and we will review this in more detail further into the paper.

Method Precision

As with other ASTM methods, the precision statement in the method is a result of the Interlaboratory Study (ILS), which is detailed in Section 16.1: "The ILS was conducted in 2017 and included 15 laboratories analyzing 22 samples in duplicate for nickel and 10 laboratories analyzing 16 samples in duplicate for vanadium.

Concentration	V (ppm)	Ni (ppm)
3.0	0.8	0.8
5.0	1.0	1.1
10.0	1.5	1.5
25.0	2.4	2.5
50.0	3.5	3.6

Concentration	V (ppm)	Ni (ppm)
3.0	3.1	2.6
5.0	4.0	3.4
10.0	5.8	4.8
25.0	9.3	7.8
50.0	13.4	11.3

The participating laboratories used a combination of best-fit regression calibration and matrix effects corrections based on best-fit regression, FP or theoretical alphas³. Calculated values from the resulting precision are detailed in **Tables 2 and 3** of this paper.

Visit xos.com/resource-petroleum to find more XOS technical papers, like *HDXRF vs ICP for Ni & V in Crude Oil*. Read a short summary about this paper at the end of this method brief.

HDXRF Precision & Ensuring Compliance

To assess the precision of Petra MAX powered by HDXRF, two studies were performed:

- **repeatability** and **accuracy** study of Petra MAX at 10 ppm using a known Ni and V in mineral oil check sample
- **reproducibility** and **accuracy** of multiple Petra MAX analyzers using known and unknown Ni and V in crude oil samples

Table 4 contains repeatability data run for a mineral oil check sample—we ran this data to showcase not only repeatability but also the accuracy of Petra MAX analyzer using a 10 ppm Ni and V in mineral oil sample. Ten separate aliquots were prepared using the sample preparation procedure outlined below in the reproducibility study, and each aliquot was measured for 300s each using the Petra MAX Autosampler.

The average of ten determinations of the 10 ppm sample was 9.98 ppm and 9.63 ppm for Ni and V respectively. The standard deviations were 0.07 ppm for Ni and 0.09 ppm for V. If a guideline of 2.8 times the standard deviation is used, repeatability for this Petra MAX analyzer can be estimated as 0.20 ppm for Ni and 0.25 ppm for V, which is well within D8252 calculated repeatability of 1.5 ppm.

To purchase the new ASTM D8252 test method, please visit www.astm.org

Table 4 – 10 ppm in Mineral Oil Repeatability Study Results

Determination	Ni (ppm)	V (ppm)
1	9.97	9.64
2	9.84	9.60
3	10.00	9.69
4	10.06	9.81
5	9.95	9.64
6	9.96	9.51
7	9.93	9.60
8	10.05	9.60
9	10.05	9.51
10	9.96	9.66
Average	9.98	9.63
Std Dev	0.07	0.09
%RSD	0.67%	0.91%

In the reproducibility study, four crude oil samples were analyzed:

A Custom doped crude oil standard from VHG Labs containing 8 ppm Ni and 14 ppm V

B Sour crude oil retain from Intertek

C Medium sour crude retain from Crude monitor.ca

D Heavy sour crude retain from Crudemonitor.ca

Three independent laboratories analyzed the sample set using different Petra MAX analyzers. Each participant received two randomized sample sets packaged in blind duplicate for analysis. Samples were prepared by first shaking the sample to homogenize it. Using a disposable pipette, 7 to 10 mL of sample is transferred to a disposable plastic sample cup designed for XRF analysis. An X-ray transparent film is then placed over the opening of the cup and affixed using a snap-on ring. Finally, the sample is placed in the instrument and is ready for analysis. This process, from sample preparation to results, takes about 6 minutes. The resulting raw data sample means and standard deviations can be seen in **Table 5**.

Table 5 – Reproducibility Study Results

Sample	Ni (ppm)	Ni Std Dev	V (ppm)	V Std Dev
A	8.7	0.1	14.3	0.3
B	5.6	0.1	16.7	0.3
C	12.7	0.1	29.9	0.2
D	45.3	0.1	100.4	1.2

The average Ni result on sample A was 8.7 ppm compared to the 8 ppm doped value, and 14.3 ppm V average as compared to the 14 ppm doped value, indicating good accuracy.

Samples B-D were unknown crude oil samples, and if we use the 2.8 times standard deviation guideline as before, we can see that samples B and C are well within D8252 method reproducibility, as is sample A. Sample D is outside the D8252 scope, but reproducibility on this sample is also very good.

Conclusion

With the ever-increasing need to measure incoming crudes as quickly and efficiently as possible, the industry has responded

with a new test method. To ensure compliance with the method and low levels of both nickel and vanadium, a highly precise XRF analyzer will become a critical piece of equipment in the lab environment. From the data shown in this study, Petra MAX analyzers demonstrate excellent analytical performance while ensuring compliance with ASTM Method D8252. In addition, sample preparation to results is typically 6 minutes or less, and non-technical users can learn how to use the analyzer quickly. Therefore, with minimal sample preparation and rapid results, Petra MAX is a viable solution for petroleum laboratories.

PetraMAX
Elemental Analyzer for Petroleum



Petra MAX delivers D4294 sulfur analysis alongside rapid measurement of 12 other elements including D8252 analysis of nickel and vanadium. Petra is powered by HDXRF which delivers higher performance over traditional EDXRF.

Petra MAX analyzers can provide lab professionals with ultra-low limits of detection for both nickel and vanadium by utilizing doubly curved crystal optics. This allows operators to detect low limits for critical elements without the assistance of a vacuum pump or the usage of consumable gasses. The detection limits for both elements as well as sulfur and iron are shown in **Table 6**.

Table 6 – Petra MAX Limits of Detection (600s)

Sulfur (ppm)	Nickel (ppm)	Vanadium (ppm)	Iron (ppm)
5.7	0.04	0.10	0.07

Additionally, Petra analyzers now come with the option for an autosampler add-on, utilizing a unique vertical sample slide that allows for one-of-a-kind continuous sample loading. Petra boasts updated software featuring customized measurement presets, several data output settings, on-screen averaging, and more. These analyzers also allow users to work within a wide variety of applications by measuring all 13 elements in hydrocarbon matrices including crude oil, naphtha, gasoline, and jet fuel, as well as water, catalyst, and petroleum coke samples.

HDXRF vs ICP Summary

In the paper *HDXRF vs ICP for Ni & V in Crude Oil*, a study is conducted to compare the precision of Petra MAX with ICP. This is the same study using samples A-D as mentioned above, and we will summarize the results.

First, let's review the ICP sample preparation process from the study. ICP performed by ASTM method D5708B requires extensive sample preparation when analyzing crude oil. The crude oil sample is digested with sulfuric acid and heat, using both an infrared lamp and a hotplate until the sample has been reduced to a carbonaceous ash. This ash is then carefully transferred to a muffle furnace and all of the carbon is burned away. The remaining material is then reconstituted with nitric acid, and the sample is then ready for analysis.

Users report that this process of sample preparation to results takes anywhere from 8 to 12 hours to complete.

The results show that HDXRF (Petra MAX) demonstrates good correlation with ICP for nickel and vanadium in crude oil with HDXRF delivering better precision and lower variability as shown in **Table 7** by HDXRF's lower standard deviation. In addition, HDXRF sample preparation to results can be completed in just minutes compared to the 8 to 12 hours for ICP.

REFERENCES:

- 1 ASTM D8252-19, Standard Test Method for Vanadium and Nickel in Crude and Residual Oil by X-ray Spectrometry, ASTM International, West Conshohocken, PA, 2019, www.astm.org
- 2 ASTM D6259-15(2019), Standard Practice for Determination of a Pooled Limit of Quantitation for a Test Method, ASTM International, West Conshohocken, PA, 2019, www.astm.org
- 3 ASTM D5708-15, Standard Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry, ASTM International, West Conshohocken, PA, 2015, www.astm.org

Table 7 – HDXRF vs ICP Reproducibility Study Results

Sample	HDXRF				ICP			
	Ni (ppm)	Ni Std Dev	V (ppm)	V Std Dev	Ni (ppm)	Ni Std Dev	V (ppm)	V Std Dev
A	8.7	0.1	14.3	0.3	7.4	3.2	14.2	3.8
B	5.6	0.1	16.7	0.3	5.2	3.1	17.9	8.2
C	12.7	0.1	29.9	0.2	12.4	4.4	31.5	9.9
D	45.3	0.1	100.4	1.2	30.5	23.0	73.9	45.1

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