The Next-Generation of Elemental Analysis

INTRODUCTION

With tightening sulfur regulations across the globe, petroleum professionals have the unique challenge of certifying their products as efficiently as possible. In addition, there is an increasing need to test critical elements in various matrices to protect valuable equipment and avoid downtime. Petra MAX delivers D4294 sulfur analysis in addition to 12 elements in matrices like hydrocarbon, water and catalysts. Petra MAX is also available with a new autosampler design, delivering continuous sample loading and sample tracking capabilities. This analyzer was designed to save time for refineries, terminals, and third-party labs. Throughout this paper, we will review some of the features that make Petra MAX so unique compared to its counterparts in the market.

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D4294 SULFUR ANALYSIS

Petra MAX complies with ASTM D4294 and ISO 8754 for sulfur analysis in various hydrocarbon matrices, delivering an LOD as low as 5.7 ppm. To demonstrate the precision of Petra MAX, various hydrocarbon samples, including heating oil, kerosene, jet A, vacuum gas oil (VGO), and crude oil were analyzed. The analyses were performed at separate laboratories with unique instruments and users. The results shown in **Table 1** demonstrate that Petra MAX delivers precise measurements across a wide range of hydrocarbon sample types. In addition, Petra MAX is a valuable tool to monitor trends and identify materials that simply do not meet specification.

Table 1: S in Hydrocarbons (ppm)

	Sample Type	Crude Oil	VGO	Kerosene	Heating Oil	Jet A
Analyzer 1	User 1	16,553	6,754	146	391	930
		16,509	6,851	148	405	906
Analyzer 2	User 2	16,353	7,003	148	410	976
		16,751	7,017	152	428	974
Analyzer 3	User 3	17,666	7,002	161	436	987
		17,415	7,202	157	430	1,023
Analyzer 4	User 4	17,219	7,284	157	435	1,028
		17,382	7,308	138	434	1,017
	Average	16,981	7,053	151	421	980
	Standard Deviation	497	199	7	17	44
	RSD%	2.9%	2.8%	4.9%	4.0%	4.5%

ELEMENTAL ANALYSIS OF NI, V, AND FE

The blending of crude oils from different sources has become more commonplace within the industry to meet specifications for the classification of sweet crude oil. The introduction of new crudes brings new challenges, like higher concentrations of metals such as nickel (Ni), vanadium (V), and iron (Fe). Ni and V are known to rapidly deactivate process catalysts in the catalytic cracker (FCC) and hydrotreaters. In response, many refiners have incorporated Ni and V analysis into their routine crude assay, and pipelines have set specifications for Ni and V in their common stream sweet crude. Fe is introduced into crude oil from corrosion byproducts during transportation and can lead to pump and exchanger fouling, and off-specification coke.

Each refinery or pipeline location has their own specifications for specific elements like S, V, Ni and Fe. The desired level or limit for each heavy metal may vary depending on the detriment its presence causes to the equipment, process, or finished product. But in the case of V, Ni, and Fe, current methods can take a significant amount of time to prepare (including hours for ashing), analyze, and if outsourced, can be quite costly. **Table A** outlines common pipeline feed specifications.

Table A: Common Pipeline Feed Specifications	
Element	Specification (ppm)
V	< 5
Ni	< 5
V & Ni	< 5
Fe	< 7

To study the precision of Petra MAX for simultaneous measurement of S, Ni, V, and Fe, ten repeat measurements were performed on two different crude oil samples containing these elements. The results shown in **Tables 2 and 3** demonstrate that Petra MAX delivers precise measurement results well below desired specifications, and therefore is a valuable tool for monitoring trends as well as identifying materials that do not meet specification. Please see **Table 4** for Petra MAX's dynamic range, LODs, and applications.

Table 2: S, V, Fe & Ni in Crude Oil Sample A (ppm)				
Repeats	S	V	Fe	Ni
1	1,057	1.03	0.37	0.09
2	1,082	1.04	0.42	0.16
3	1,071	1.10	0.35	0.17
4	1,067	1.10	0.41	0.08
5	1,059	1.10	0.38	0.15
6	1,062	1.04	0.37	0.13
7	1,081	1.07	0.33	0.17
8	1,083	1.08	0.42	0.11
9	1,085	0.96	0.48	0.10
10	1,047	1.06	0.33	0.16
Average	1,069	1.06	0.39	0.13
Standard Deviation	13.1	0.04	0.05	0.03
RSD%	1.2%	3.8%	12.8%	23.1%

Table 3: S, V, Fe & Ni in Crude Oil Sample B (ppm)				
Repeats	S	V	Fe	Ni
1	4,716	0.35	0.51	2.50
2	4,752	0.35	0.42	2.47
3	4,756	0.31	0.56	2.55
4	4,833	0.41	0.57	2.57
5	4,750	0.36	0.51	2.51
6	4,690	0.32	0.47	2.51
7	4,786	0.30	0.50	2.57
8	4,721	0.32	0.49	2.55
9	4,793	0.27	0.51	2.56
10	4,749	0.31	0.49	2.52
Average	4,755	0.33	0.50	2.53
Standard Deviation	41.4	0.04	0.04	0.03
RSD%	0.87%	12.1%	8%	1.2%

Table 4							
Petra MAX	Dynamic Range	Sulfur 5.7 ppm – 10 wt%					
	Limit of Detection (ppm @ 600 s)	Sulfur 5.7 ppm					
		P	Cl	K	Ca	V	Cr
		17	3	0.7	0.4	0.1	0.09
		Mn	Fe	Co	Ni	Cu	Zn
		0.07	0.07	0.07	0.04	0.1	0.1
	Applications	Hydrocarbons, water, and catalysts					

ELIMINATE THE NEED TO CENTRIFUGE

The X-ray fluorescence (XRF) testing method is known to have interferences. A common matrix effect interference involves particulates settling to the bottom of the sample cup and absorbing the X-ray signal. This matrix effect will ultimately influence the total sulfur measurement and lead to a biased result. Refineries and third-party certification companies using XRF for high-particulate samples have relied on centrifuging samples to ensure an accurate sulfur measurement – which involves a time-consuming sample preparation process.

Many D4294 analyzers are designed with the X-ray detector focused on the bottom of a sample cup where settling occurs, as depicted in **Diagram 1.** Since particulate solids and water settle over time, it is difficult to obtain accurate sulfur measurements due to the changing concentration of interferences. To combat the effects of settling in crude oil, Petra MAX delivers a new, innovative sample chamber that rotates the sample on its side, providing a clear measurement window for more accurate results. See **Diagram 2.**

To study the effects of particulate solids on sulfur measurements, a crude oil sample was analyzed using a traditional XRF analyzer and Petra MAX. The following sample analysis procedure was performed using both methods:

1. **A particulate-free certified reference standard of 2 wt% S in mineral oil sample was measured for 100-seconds to check instrument accuracy.**
2. **One-liter bottles of crude oil containing a high-level of particulates were shaken vigorously, and samples were prepared and measured immediately for 100-seconds.**
3. **Measurements were repeated 5 times with a 5-second pause in-between. The data was collected and compiled to evaluate the effect of particulate settling on sulfur analysis.**

SAMPLE INTRODUCTION METHODS

Diagram 1: Traditional XRF

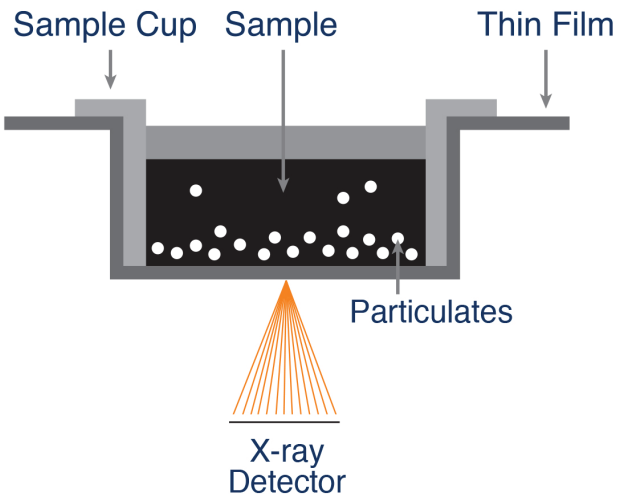
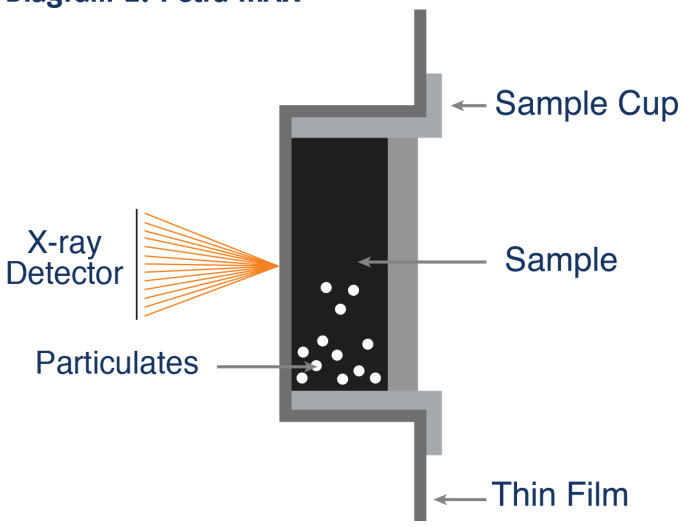
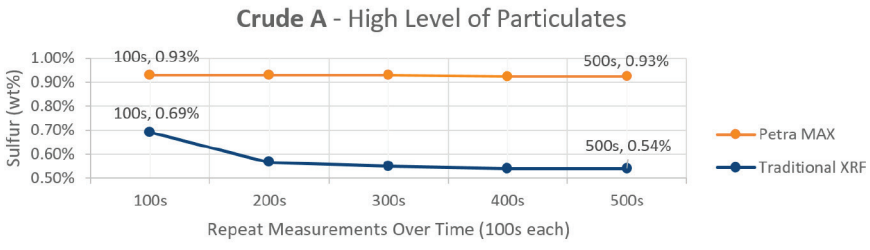


Diagram 2: Petra MAX™



The results are shown in **Graph 1.** While the traditional XRF results show a rapid drift in sulfur concentration due to particulate settling, the results from Petra MAX remain stable for each repeat measurement. This demonstrates that, even with high levels of particulates, Petra MAX delivers accurate and precise sulfur measurements in crude oil for ASTM D4294 and ISO 8754 methodology.

Graph 1: Crude A Results



PRECISION COMPARE BETWEEN HDXRF VS. ICP FOR NI, FE, AND V

As petroleum professionals continue to refine their production processes, products such as crude oil can contain higher concentrations of problematic metals like nickel (Ni), iron (Fe), and vanadium (V). In the face of tightening regulations and increased demand for sweeter crudes, refiners are looking to buy lower cost oils that contain these metals, with the intent of assessing their concentration levels throughout the refining process. To compound the challenge of attaining a sweet crude and mitigating risk of damages from metals, refineries and other petroleum certification sites, such as terminals and third-party labs, must adhere to regulations that require them to utilize D5708B methodology, which specifies ICP analysis. There is, however, an option for users to screen samples before ICP using XRF analysis.

High Definition X-ray Fluorescence (HDXRF®), XOS' patented technology, is an improved version of the

XRF technique, and a cost-effective alternative to ICP. While some may utilize an in-house ICP setup, many professionals, such as those working at pipelines, must send samples out. This is yet another necessary burden these professionals must deal with as the costs and downtime will ramp up significantly when products come back from ICP analysis out of spec. By testing in-house and getting results in less than five minutes, refineries, terminals, and labs will be able to make real-time decisions when products are off-spec and can improve their overall processes when products are within spec.

ASTM runs a Proficiency Testing Program (PTP) where they send out samples of crude oil several times per year to be tested at independent labs and refineries around the world. The results are then published which includes statistics on many test results, such as the average concentration values for Ni, V and Fe by ICP - see **Table 5**. XOS obtained sample retains from eight different PTPs and tested these samples on different Petra MAX analyzers. Each crude oil sample was homogenized and then pipetted into a sample cup. The cup was sealed with a sample film and then vented before analysis with Petra MAX. Analysis time for each sample was five minutes, and the results were averaged - see **Table 5**.

HDXRF delivers comparable results to ICP in five minutes or less. In addition, users have minimal sample preparation and can achieve results with the push of a button. Those looking to save time and money in elemental quantification by screening samples before ICP analysis can achieve comparable results with Petra MAX.

Table 5: ASTM PTP – ICP vs Petra MAX (results in ppm)

Sample Name	Analysis Type	V	Ni	Fe
CO1407B	ICP	0.3	0.2	2.0
	Petra MAX	ND<0.2	ND<0.1	2.1
CO1411	ICP	0.4	2.1	3.4
	Petra MAX	0.4	2.0	3.4
CO1503	ICP	26.9	11.4	0.8
	Petra MAX	26.9	11.4	0.8
CO1507	ICP	313.9	55.2	1.2
	Petra MAX	314.8	60.3	0.8
CO1511	ICP	15.7	9.6	10.4
	Petra MAX	15.1	9.2	19.5
CO1611	ICP	0.2	0.1	3.8
	Petra MAX	ND<0.2	ND<0.1	12.0
CO1703	ICP	0.1	0.1	7.5
	Petra MAX	ND<0.2	ND<0.1	22.7
CO1707	ICP	0.1	0.3	3.8
	Petra MAX	ND<0.2	ND<0.1	6.6

AUTOSAMPLER

Petra MAX Autosampler boasts a truly unique design with a vertical sample slide that delivers continuous sample loading. The sample slide can accommodate up to 8 samples at one time and users can add samples without interrupting the current measurement. In addition to its unique sample introduction, Petra MAX Autosampler couples this improved workflow with optional sample tracking. X-ID sample cups come with a unique QR-code to identify each sample. Users simply scan the QR-coded sample cup with a handheld scanner and the analyzer scans the sample again when it reaches the measurement chamber, ensuring the correct sample name and measurement parameters are paired with results. Users can eliminate data errors and add urgent samples to the queue as needed. The sample tracking is accomplished by using an internal camera that matches the QR-code on the sample cup with the saved scan information logged in the interface. By using a QR-code, the user can fully integrate with their LIMS system while also removing the need to manually transcribe their sample ID. The Autosampler is an optional add-on feature and users have the option to use X-ID Sample Cups (QR-coded) or standard XRF cups.

How it Works

1. Use integrated scanner or onscreen keyboard to enter sample name
2. Scan sample QR-code
3. Select preset measurement configuration and insert sample into autosampler
4. QR-code is scanned in measurement chamber to retrieve sample name and measurement configuration
5. Measurement begins automatically. Upon completion, sample is ejected and next in queue is measured

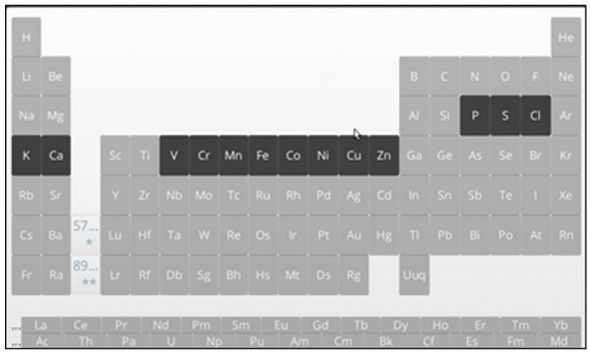
GEN 4 SOFTWARE HIGHLIGHTS

The Petra Series Gen 4 software release contains new features to help deliver a more efficient workflow for the user. A new application feature is the ability to analyze new matrices: aqueous samples and catalysts. To support this new feature, the user interface includes an on-screen table of elements that delivers both a visual and effortless process for setting up a calibration standard as well as creating a calibration curve - see **Figures 1 and 2.** For instances when a calibration is interrupted, the new software will detect which standards were run and allow the users to resume their calibration from where they left off – saving users many hours over time in re-run calibration standards.

To accommodate users that run similar sample types on a frequent basis, Petra now allows users to set unique preset measurements with adjustable parameters for quick access to pre-determined measurement types. For example, a terminal frequently running crude oil samples can set their measurement time to 300s using a hydrocarbon curve. Other parameters include matrix type, number of repeats, and the ability to toggle a preset as a default – see **Figure 3**. The presets can be set directly after users scan their QR-coded cup or sample bottle with a single push of a button before loading the sample into the analyzer. This information can be found on the main scan screen to reinforce the high throughput and efficient workflow that the Petra offers - see **Figure 4.**

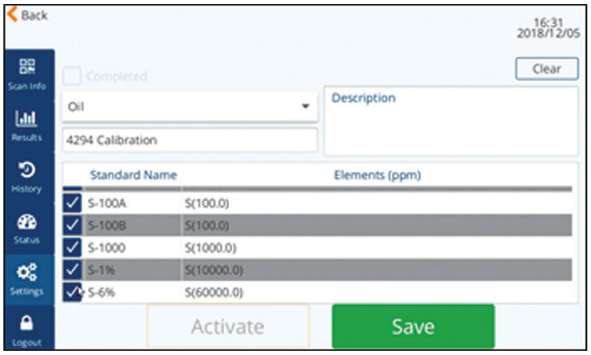
Once a sample completes its measurement, results will populate for the elements of interest. Users can continue to load samples, work with a different instrument, or view their historical results. When a sample is not being measured, completed measurements can be averaged on-screen using the built-in averaging function – see **Figure 5.** Those looking to export their data can do so either through their network, as a printable CSV or PDF, or through a USB thumb drive.

Figure 1: Elements Selector Screen



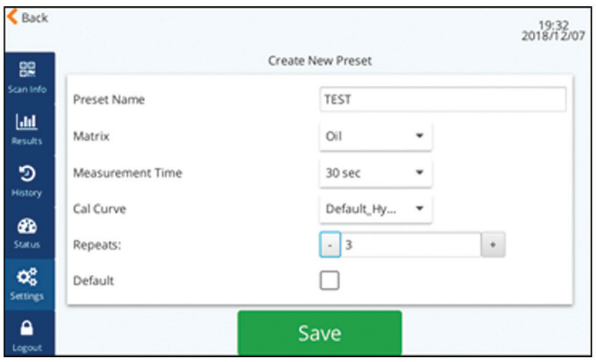
An on-screen table of elements makes creating calibration standards easy and foolproof. For standards with multiple elements, Petra's software enables quick selection, so users can have their calibrations running quicker than ever before.

Figure 2: Calibration Curve Screen



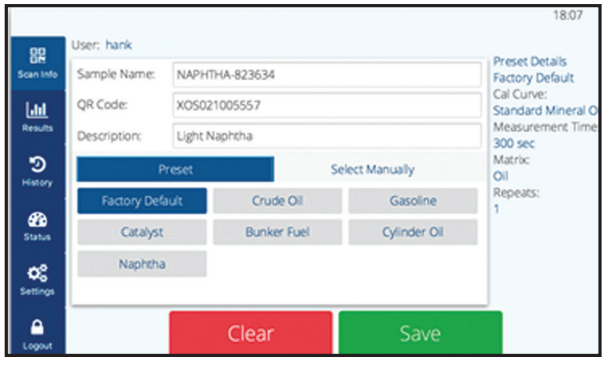
Creating a calibration curve is simple and intuitive with the new Petra series software. Users simply select their matrix and then toggle which calibration standards they need to create the curve. The system will then prompt the user to run the appropriate samples in the right order.

Figure 3: Preset Editor Screen



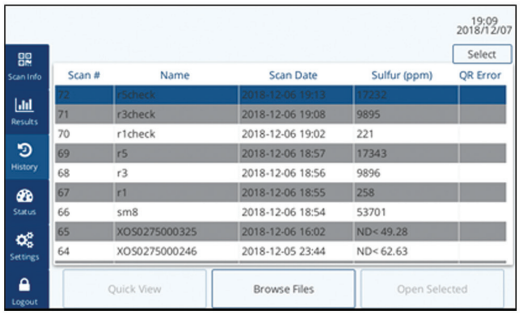
For users that run similar sample types frequently, creating a measurement preset can be done by selecting matrix type, measurement time, a calibration curve, and number of repeats. Users can save their new preset as a default and give it any name they choose.

Figure 4: Scan Info Screen



On the scan info screen, users will be able to input their sample data: QR Code (if running in QR-Mode), Sample Name, Description (optional), and a preset. For users not running a preset, they can select their measurement parameters manually by selecting their matrix, measurement time, calibration curve, and number of repeats. This same screen will also display the time and number of repeats remaining.

Figure 5: History Screen



While viewing the historical data, users can view and select up to 20 measurements. Similar sample measurements, such as repeats, can be averaged on-screen. The average will occur instantly and populate a new result in the history screen which will show an average of all selected data.

ONE LINEAR CALIBRATION CURVE

Many customers running samples using D4294 analysis commonly use three separate calibration curves to ensure linearity along a broader range of sample concentrations. Typically, this broader range is from the low end of sub-10 ppm sulfur all the way to the high end of 6 wt% sulfur (or 60,000 ppm). Setting up and maintaining three separate empirical curves can be a hassle for operators, particularly when samples in various ranges fail to pass a QC check.

Petra 4294 and Petra MAX analyzers accomplish the broad 0-6 wt% range of sulfur measurements all within a single calibration curve. As **Figure 6** shows, the established 4294 sulfur curve on the Petra MAX analyzer shows excellent linearity in sulfur concentrations from the low end all the way to the high end. The benefit to this is that when the curve goes out of control, operators only have to recalibrate one curve, and with the improved calibration processes detailed above, operators can simply re-run specific calibration standards and have their analyzer back in control.

CONCLUSION

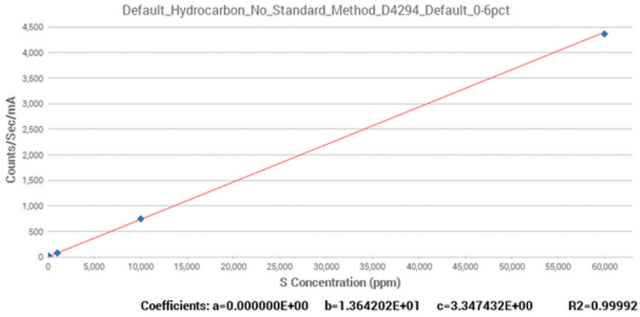
Petra MAX delivers ultra-low 4294 sulfur analysis, rapid measurement of 12 additional elements, advanced software upgrades, and a more efficient workflow with autosampler.

Most of the topics highlighted throughout this paper are available as separate whitepapers with much more information about that topic. These can be found by visiting xos.com/resource-petroleum.

AUTOMATIC MATRIX CORRECTION

As with any method, it is important to consider potential interferences. For ASTM D4294 and ISO 8754 analysis, Petra MAX software delivers an automatic correction for matrix differences due to differences in carbon to hydrogen (C/H) ratio of calibration samples (white oils) and measurement samples (such as fuel oil, automotive diesel and gasoline). The instrument uses information from the deconvolution of the elastic and inelastic X-ray scattering within the sample spectrum to determine the needed correction factor. This ensures that the C/H ratio differences between calibration materials and samples measured do not result in biased results. Users get accurate results without the need to set up and maintain multiple calibration curves to compensate for C/H ratio differences.

Figure 6: Petra MAX Sulfur Cal Curve



Petra MAX
Elemental Analyzer for Petroleum

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