better analysis counts

S, Ni, V, and Fe Analysis of Crude Oil Using HDXRF®

BACKGROUND

Test methods for measuring sulfur content, like ASTM D4294 and ISO 8754, have become critical for assessing the value of crude oil. 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.

A rapid measurement technique for sulfur compliance and simultaneous analysis of Ni, V, and Fe is necessary to meet the needs of refiners, pipelines, terminals, and other petroleum test labs.

ABSTRACT

Petra MAX™ delivers advanced D4294 sulfur analysis in addition to 12 elements from P to Zn including Ni, V, and Fe. This robust benchtop analyzer complies with ASTM D4294 and ISO 8754 for measuring sulfur in hydrocarbons. Petra MAX is powered by HDXRF, utilizing XOS patented doubly curved crystal optics coupled with a high-performance silicon drift detector and an intense monochromatic excitation beam. This industry-leading technology reduces background noise and increases signal-to-noise output, enabling low detection limits and high precision without the need for consumable helium gas, a vacuum pump, or extensive sample preparation.

APPLICATION STUDY

In each study, ten separate aliquots were prepared and analyzed for 5 minutes each. Their individual measurement results and average are reported. Samples were prepared by transferring 6 mL to a 43 mm XRF sample cup and sealed with an Etnom film.

Table A: Common Pipeline Feed Specifications

Element	Specification (ppm)
V	< 5
Ni	< 5
V & Ni	< 5
Fe	< 7

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.

ACCURACY STUDY

To study the accuracy of Petra MAX, ten repeat measurements were performed on a commercially-available mineral oil reference material containing 10,000 ppm of S, and 10 ppm of V, Fe, and Ni. See Table 1 for results.

Table 1: S, V, Fe, & Ni in Mineral Oil (ppm)				
Expected (ppm)	10,000	10	10	10
Repeats	S	V	Fe	Ni
1	9,867	11.1	9.3	10.2
2	9,854	11.3	9.2	10.1
3	9,707	11.2	9.0	10.0
4	9,662	10.8	9.1	10.0
5	9,739	10.9	9.0	10.1
6	9,727	11.1	9.0	10.1
7	9,656	11.1	9.0	10.1
8	9,634	10.9	9.0	10.1
9	9,636	10.8	9.0	10.0
10	9,671	11.0	8.9	10.2
Average	9,715	11.0	9.1	10.1
Standard Deviation	84.5	0.17	0.12	0.07
RSD%	0.9%	1.5%	1.3%	0.7%

LIMIT OF DETECTION

By incorporating patented doubly curved crystal optics to monochromate and focus the excitation beam, the Petra MAX is able to achieve low limits of detection without the assistance of a vacuum pump or consumable helium.

Petra MAX LOD ppm (600 second analysis time)			
S	V	Fe	Ni
5.70	0.10	0.07	0.04

CONCLUSION

In response to the increased blending of sweet crude oil with crude containing higher levels of metals and S, petroleum labs are beginning to see the need to measure other elements, in addition to S, as a part of their crude assay. This study demonstrates that Petra MAX delivers simultaneous trace metals and ASTM D4294 or ISO 8754 analysis of S, in a single measurement.

Petra MAX performs this analysis without the difficult ashing sample preparation that makes the analysis of metals like V, Ni, and Fe in crude oil so difficult today.

PRECISION STUDY

To study the precision of Petra MAX, ten repeat measurements were performed on two different crude oil samples containing S, V, Fe and Ni. 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 simply do not meet specification.

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%

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