Advances in the Analysis of Heavy Oils by High-Resolution ICP Optical Emission Spectrometry

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Control of impurities in heavy oils is of critical importance to the refining industry when inspecting incoming and outgoing goods as well as in the quality control of intermediate products. For example, when present in raw oils elements like Lead, Phosphorous or Silicium can act as poison to cracking catalysts. Elements like Arsenic, Mercury and Cadmium on the other hand are often penalty elements in final products as they are of environmental concern. Hence, trace contents of these elements are typically screened among other elements in crude oils using ICP techniques.

Trace analysis in refinery products

A limiting factor for the trace analysis of crude oils by ICP techniques is their high viscosity, but more so the high content of organic material to be submitted to the plasma. Here, a variety of organic solvents (e.g. kerosene, xylenes) are widely used for sample dilutions, which improve the plasma performance reducing plasma collapse, sooth formation, memory effects and high maintenance costs. However, for trace detectability in diluted oil samples sensitivity often becomes the most critical performance parameter, because sample dilution by factor 10 or 500 lowers the required detection limits accordingly. Hence, the quantification of Arsenic, Mercury and Phosphorous levels in the range from 10 to 50 µg/kg is usually rather problematic on many ICP optical emission spectrometers. In addition complex spectral signatures further complicate the quantification of many trace signals. Such unspecific spectral interferences impact on quality of the baseline fitting routines, the precision and the limits of detection. So, crude oil analysis by ICP-OES requires a finely tuned instrument that offers both excellent plasma performance and an exceptionally sensitive axial plasma view with high spectral resolution.

Pushing the boundaries of ICP-OES

The PlasmaQuant® PQ 9000 by Analytik Jena is well-suited for the cost-effective routine analysis of both trace elements (Al, As, Hg, P and Pb) and major constituents (Ca, K, Mg, Na, Ni, Si and V) in crude oil samples thanks to synergetic interactions of its four key components. Firstly, a fully re-designed, free-running High-Frequency Generator with a heavy-duty four-winding induction coil offers reliable plasma performance at 1300 W for crude oil samples that were diluted to 10 to 20 wt.-% with mixed xylenes. In addition, the vertical plasma geometry of the V Shuttle Torch makes sooth formation and memory effects a relic of the past, while a total argon consumption of less than 17 L/min set new standards in this industry. Equipped with an advanced Organic Kit that allows temperature controlled aspiration of organic samples using concentric standard nebulizers of normal flow rates (1.0 mL/min) the V Shuttle Torch technology does combine high ease of use with low maintenance costs.

Figure 1: PlasmaQuant® PQ 9000 by Analytik Jena

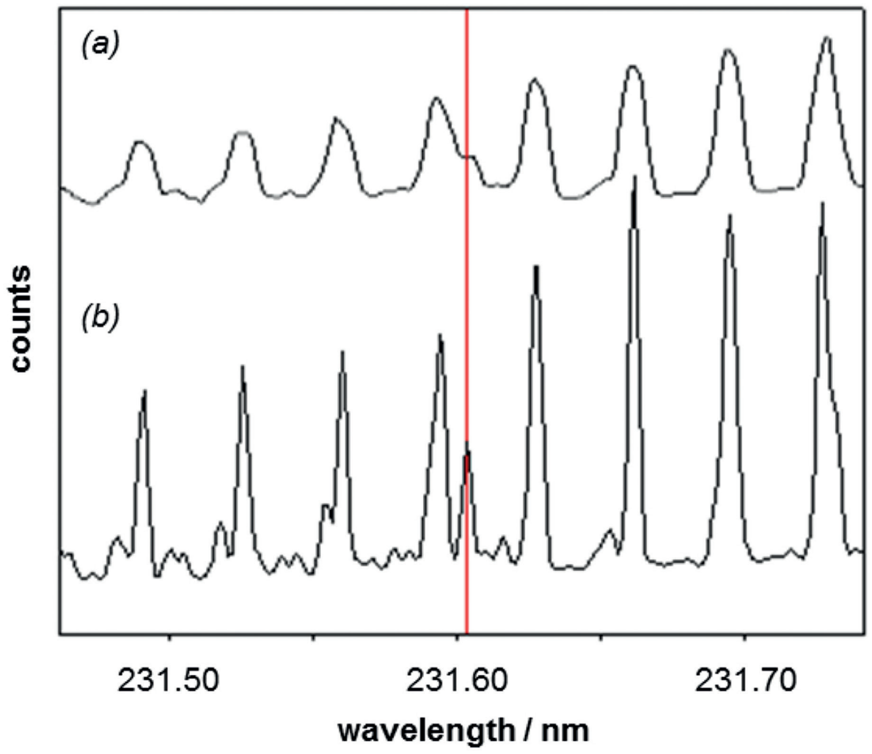

Figure 2: Comparison of Ni 231.603 nm (1 ppm, red line) in an oil-kerosene mixture recorded on ICP-OES instruments with (a) conventional and (b) high spectral resolution

Thirdly, the high sensitivity of the axial plasma views of the High-Resolution Optics proved to be particularly beneficial for Arsenic, Mercury and Phosphorous trace detection in matrix-rich crude oil samples. Aided by the usage of recycled argon as counter gas in PlasmaQuant® PQ 9000, their sensitive emission lines that are located in the UV-range (e.g. Hg 184.668 nm) are less likely to sensitivity losses in the absence of oxygen, air or nitrogen. Actually, argon counter gas technology only provides a highly transparent optical path that translates to lowest detection limits and best RSD values.

In addition, the high spectral resolution of the High-Resolution Optics is an authority in the field of ICP-OES. For example when comparing the appearance of the Ni 231.603 nm line as-recorded in an oil-kerosene mixture on an ICP-OES instrument with average and high spectral resolution the advantage of the latter become very clear (see Figure 2). On the conventional instrument the Ni 231.603 nm line appears as a shoulder on top of the spectral signature of the oil-kerosene matrix, but the spectrum obtained on PlasmaQuant® PQ 9000 shows a well-resolved Ni 231.603 nm line instead. The HR spectrum of PlasmaQuant® PQ 9000 allows for Ni 231.603 nm to be used in standard calibration routines, which increases productivity, while for the conventional instrument it is recommended to use an alternative line or standard addition calibration routines. That is even more relevant since the Ni 231.603 nm line (FWHM = 3.5 pm) is among the most sensitive Nickel line, and thus a likely candidate for the lowest detection limits.

Cost-effective routine analysis

Lastly, the DualView PLUS plasma observation will improve in the productivity of crude oil analysis significantly, because trace elements and major constituents can now be quantified from one sample measurement. Trace levels of Cadmium, Lead and Mercury are analyzed by axial plasma observation, while elevated contents of Calcium, Potassium or Sodium are measured from radial plasma view. So, tedious sample preparation and/or repetitive measurements can be avoided.

The results obtained for limit control analysis (according to ASTM D7697-11) of three typical heavy oils from a refinery plant are summarized in Table 1. Here, a matrix-matched calibration was established using commercial blank oil and mixed-xylenes, while the total analysis time including rinse and read delays was optimized to about 3 minutes per sample allowing for both best precision and competitive speed.

Table 1: Results from limit control analysis on PlasmaQuant® PQ 9000 according to ASTM D7697-11

Element/Line	**crude oil A**		**crude oil B**		**vacuum gas oil**		**DL**[2]
	mg/kg	**RSD**[1] **/ %**	**mg/kg**	**RSD / %**	**mg/kg**	**RSD / %**	**µg/kg**
Al 167.022 nm	0.49	0.16	< DL	-	< DL	-	1.3
As 193.698 nm	< DL	-	< DL	-	< DL	-	8.6
Ca 393.366 nm	0.50	1.51	0.15	0.2	< DL	-	0.2
Hg 184.668 nm	< DL	-	< DL	-	< DL	-	1.8
K 766.491 nm	< DL	-	< DL	-	< DL	-	5.7
Mg 279.553 nm	0.07	2.5	0.03	0.1	< DL	-	0.1
Na 589.590 nm	9.6	0.49	0.20	3.1	< DL	-	3.1
Ni 221.648 nm	18.2	0.19	9.85	1.7	6.98	0.39	1.7
P 177.434 nm	< DL	-	< DL	-	< DL	-	9.0
Pb 220.353 nm	< DL	-	< DL	-	< DL	-	8.0
Si 251.611 nm	1.111	2.23	0.2883	2.9	< DL	-	2.9
V 311.071 nm	60.2	0.15	35.9	0.5	15.1	0.05	0.5

1 … RSD from 3 replicate measurements; not given when content lower than detection limit
2 … detection limit obtain from 11xSD on QC blank

Alkali, earth alkali, Nickel, Silicium and Vanadium contents in the low ppm(w) range were found in both crude oils samples, while the vacuum gas oil only exhibited residual Nickel and Vanadium levels. Detection limits in the low ppb(w) range, achieved in these matrices, offer attractive limits of quantification of 2, 5 and 8 ppb(w) for Vanadium, Mercury and Silicium, respectively. However, the Phosphorous detection limit of 9 µg/kg is particularly noteworthy, as contents as low as 30 ppb(w) may be specified for crude oil products. Moreover, the P 177.436 nm line used here is a good example to illustrate the extra potential of the High-Resolution Optics. As evident from Figure 3, the P 177.436 nm emission is partly overlapped by a spectral contributions arising from the oil-kerosene matrix. Such unspecific spectral interferences may lead to overestimation of Phosphorous if gone unaccounted for; while global baseline fits like the automatic baseline correction (ABC, green lines) on PlasmaQuant® PQ 9000 might yield slightly higher RSD values. Yet, when undesired spectral interferences are subtracted using the CSI tool (Correction of Spectral Interferences) in the ASpect PQ Software package, the quality of the baseline fit improves significantly and, hence, RSD values and detection limits will be reduced.

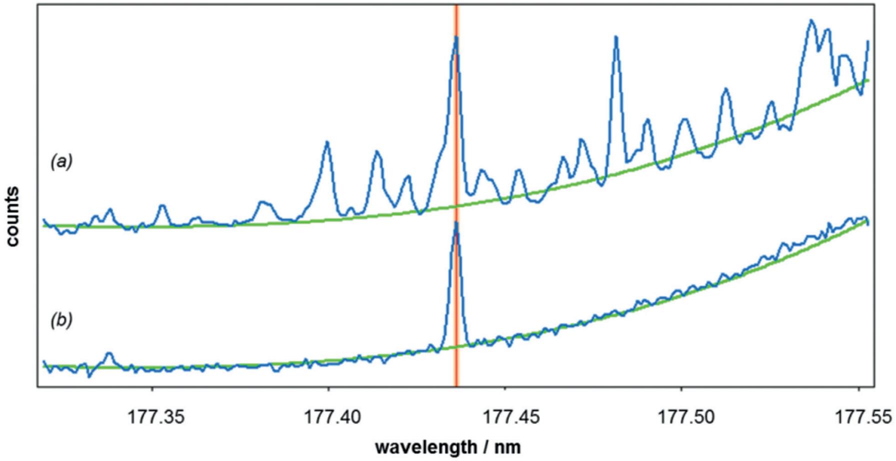

Figure 3: High resolution optical emission spectra of P 177.436 nm (orange line) recorded on PlasmaQuant® PQ 9000 in an oil-xylenes mixture (a) without and (b) with correction of spectral interferences (CSI)
Green lines represent the automatic baseline fitting (ABC).

Concerning the advances in sensitivity, spectral resolution and plasma performance presented here, the PlasmaQuant® PQ 9000 by Analytik Jena adds clarity, simplicity and confidence to cost-effective ICP-OES routines in the petrochemical industry.