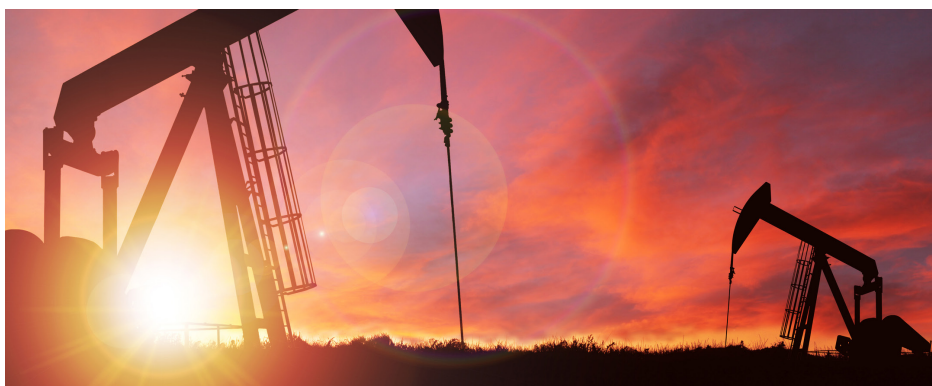**Agilent**

Trusted Answers

High-Throughput Multi-Elemental Analysis of Crude Oil

Accurate determination of Ni and V, using an Agilent 5110 VDV ICP-OES according to ASTM D5708-15 test method

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Introduction

Crude oil is one of the most actively traded commodities in the world. In North America, the West Texas Intermediate (WTI) crude, which trades on the New York Mercantile Exchange (NYMEX), is commonly used as a benchmark in oil pricing. In Europe, Africa and the Middle East, the benchmark is North Sea Brent crude, which trades on the Intercontinental Exchange (ICE). WTI is also known as Light Sweet crude oil because of its relatively low sulfur (S) content of 0.42% or less by weight. To ensure the quality of crude oil and acceptance of the oil into central storage hubs ready for trading, NYMEX set out quality specifications relating to S content, specific gravity, basic sediment and water (BSW), and pour point. However, in January 2019 (in collaboration with the industry), other quality standards were introduced relating to micro carbon residue (MCR), total acid number (TAN), and maximum concentration of nickel and vanadium content (1). Since both nickel and vanadium can de-activate

catalysts during oil processing, the specification for WTI crude was set at less than 8 ppm by weight for nickel and less than 15 ppm by weight for vanadium.

ASTM Standard D5708-15 Test Method B relates to the quantitative determination of nickel, vanadium, and iron in crude oils and residual fuels using inductively coupled plasma atomic emission spectrometry (ICP-AES) (2). The method is suitable for the analysis of Ni and V in WTI crude, in line with the latest quality standards. ICP-OES is a fast, multi-element technique that is widely used as a workhorse in the petroleum industry and many oil testing laboratories will be familiar with ASTM ICP-OES methods.

In this study, a fast and robust method was developed using the Agilent 5110 Vertical Dual View (VDV) ICP-OES fitted with a switching valve. The 5110 ICP-OES was used to quantify 23 elements, including Ni and V, in oil-related products according to D5708-15. The method is suitable for the accurate, high-throughput analysis of large numbers of samples over long runs.

Experimental

Instrumentation

The Agilent 5110 VDV ICP-OES fitted with the AVS 7 switching valve accessory and SPS 4 autosampler was used for the cost-effective analysis of crude oil samples. The 5110 was equipped with a Seaspray concentric glass nebulizer, a 1.4 mm i.d. organics torch, solvent resistant tubing, and a double-pass glass cyclonic spray chamber. The Easy-fit torch aligns automatically, enabling reproducible performance regardless of the operator. The vertical orientation of the torch and solid-state radio frequency (SSRF) system generate a robust, stable plasma that is suitable for the measurement of complex samples over extended periods (3). The system can rapidly adjust to changes in the plasma conditions arising from the varying composition of crude oils from different sources. The plasma's high tolerance to dissolved solids and organic solvents mean that less time is spent cleaning the sample introduction system and fewer replacement torches are needed.

The 5110's Vista Chip II CCD detector facilitates the analysis of samples much faster than other ICP-OES instrumentation (4). The performance is due to the detector's 1 MHz pixel processing speed and ability to measure the full wavelength range in a single exposure without the need for multiple detectors or slits. The Vista Chip II can actively adapt using integration times ranging from 1 to 100 s, providing a full eight orders of dynamic range.

The detector allows access to multiple wavelengths per element, so the user is not limited to wavelengths that may be susceptible to interferences. This feature is especially important for the analysis of samples with a complex matrix such as crude oil, where spectral interferences can be problematic. In addition, simple and complex background structures can be corrected by modeling the background to each analyte peak. Corrections can be done automatically using the Fitted Background Correction (FBC) technique included in the Agilent ICP Expert software (5).

The high-speed Vista Chip II detector also enables IntelliQuant—a fast, single scan screening mode used for the rapid identification and semi-quantification of analytes in a sample (6). IntelliQuant is also useful for method development, such as identifying interferences or checking the calibration range of elements present in a sample. IntelliQuant results are presented visually using a color-coded heat map of the periodic table. The color-coding concentration levels are user-customizable, allowing laboratories to set the high concentration limit as the maximum regulated concentration for a specific element. This set up ensures that any noncompliant samples will be flagged automatically on the periodic table heat map.

The Agilent AVS 7 switching valve allows labs to improve their sample throughput and reduce argon consumption by at least 50% per sample (7). The switching valve is fully integrated with the 5110 ICP-OES hardware and software, making it easy to set up and operate. It uses a high-speed positive displacement pump to speed up the sample uptake time. Argon bubble injection between sample and rinse solution prevents mixing of the sample and rinse allowing a longer read time and minimal carry over. The fast, efficient analysis provided with by AVS 7 also extends the lifetime of consumables, further reducing operating costs.

If needed, operation of the 5110 ICP-OES can be simplified using an ICP Expert Applet software—a limited-access interface that allows less-experienced users to run an analysis without having access to method parameters. They simply select the appropriate applet, enter sample details, ignite the plasma, and click 'Start' (8). An example screenshot of the Applet software is shown in Figure 1.
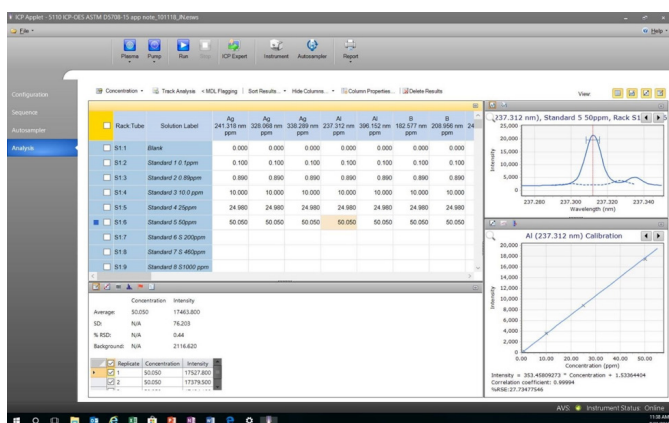
Figure 1. ICP Expert Applet browser-based software interface that is suitable for the routine operation of the 5110 ICP-OES.

The instrument and method parameters for the 5110 VDV ICP-OES are given in Table 1 with the AVS 7 settings given in Table 2.

Table 1. 5110 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Viewing Mode	Radial
Read Time (s)	8
Replicates	3
Stabilization (s)	15
Rinse Time (s)	0
Pump Speed (rpm)	12
RF Power (kW)	1.3
Aux Flow (L/min)	1.3
Ar/O_2 Addition (%)	20
Plasma Flow (L/min)	12
Nebulizer Flow (L/min)	0.60
Viewing Height (mm)	10
Sample Pump Tubing	Black/black*
Internal Standard Tubing	Orange/green*
Waste Pump Tubing	Blue/blue*
Internal Standard	Yttrium

Solvent-resistant tubing.

Table 2. AVS 7 switching valve settings.

Parameter	Setting
Valve Uptake Delay (s)	7.0
Pump Rate - Uptake (mL/min)	25.0
Pump Rate - Inject (mL/min)	6.0
Sample Loop Size (mL)	1.0
Preemptive Rinse Time (s)	1.8
Bubble Inject Time (s)	1.8

Standards and sample preparation

Calibration standards containing the following elements: Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, and Zn were prepared at 0.1, 1, 10, 25, and 50 mg/kg. The S calibration standard was prepared at 200, 450, 1000, and 2000 mg/kg using an Agilent single element standard (part number: 5190-8784). The other calibration standards were prepared by weight by adding Agilent A21+K wear metal standard (9, part number 5190-8713) into a pre-prepared o-xylene diluent (Fisher Scientific). The o-xylene diluent, which included a matrix modifier and yttrium internal standard (ISTD) was added to the sample line before the nebulizer using a mixing tee-connector. The standards and a quality control (QC) sample prepared by ASI Standards (Oak Ridge North, Texas, USA) were matrix matched to a constant viscosity to give a total oil concentration of 10% (w/w) in each solution. A 5 ppm multi-element standard was used as a Continuing Calibration Verification (CCV) solution.

Crude oil samples covering a wide range of API gravity and density were analyzed in this study. The samples were prepared according to the ASTM D5708-19 method, which is an expansion of ASTM D5708-15. The samples were all diluted from 1:10 up to 1:20 in o-xylene by weight. The more viscous samples that did not readily flow at room temperature were heated in a hot block at 60 °C and shaken before being weighed and diluted with o-xylene.

Two National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) standard reference materials (SRMs) were used to validate the method for the certified elements Ni and V. NIST 1634c Trace Elements in Fuel Oil and NIST 8505 Vanadium in Oil SRMs were diluted approximately 1:60 in the o-xylene diluent before analysis.

Table 3. Wavelength and working calibration range.

Element and Wavelength (nm)	Background Correction	Correlation Coefficient	Calibration Fit	Calibration Range, mg/kg
Ag 328.068	Fitted	0.9999	Linear	0.1−50
Ag 338.289	Fitted	0.9999	Linear	0.1−50
Al 237.312	Fitted	0.9999	Linear	0.1−50
Al 396.152	Fitted	0.9999	Linear	0.1−50
B 249.678	Fitted	0.999	Linear	0.1−50
B 249.772	Fitted	0.999	Linear	0.1−50
Ba 455.403	Fitted	0.9999	Linear	0.1−50
Ba 493.408	Fitted	1	Linear	0.1−50
Ca 315.887	Fitted	0.9999	Linear	0.1−50
Ca 422.673	Fitted	0.9999	Linear	0.1−50
Cd 214.439	Fitted	0.9999	Linear	0.1−50
Cd 226.502	Fitted	0.9999	Linear	0.1−50
Cr 205.560	Fitted	1	Linear	0.1−50
Cr 267.716	Fitted	1	Linear	0.1−50
Cu 324.754	Fitted	0.9999	Linear	0.1−50
Cu 327.395	Fitted	0.9999	Linear	0.1−50
Fe 234.350	Fitted	1	Linear	0.1−50
Fe 238.204	Fitted	1	Linear	0.1−50
K 766.491	Fitted	0.9999	Linear	0.1−50
K 769.897	Fitted	0.9999	Linear	0.1−50
Mg 279.553	Fitted	0.999	Linear	0.1−50
Mg 285.213	Fitted	0.9999	Linear	0.1−50
Mn 257.610	Fitted	1	Linear	0.1−50
Mn 259.372	Fitted	1	Linear	0.1−50
Mo 202.032	Fitted	1	Linear	0.1−50
Mo 204.598	Fitted	1	Linear	0.1−50
Na 588.995	Fitted	0.9999	Linear	0.1−50
Na 589.592	Fitted	0.9999	Linear	0.1−50
Ni 216.555	Fitted	0.9999	Linear	0.1−50
Ni 231.604	Fitted	0.9999	Linear	0.1−50
P 178.222	Fitted	0.9999	Linear	0.1−50
P 213.618	Fitted	0.9999	Linear	0.1−50
Pb 182.143	Fitted	0.9999	Linear	0.1−50
Pb 220.353	Fitted	0.9999	Linear	0.1−50
S 181.972	Fitted	0.9999	Linear	200−2000
S 182.562	Fitted	0.9999	Linear	200−2000
Si 251.611	Fitted	0.9999	Linear	0.1−50
Si 288.158	Fitted	1	Linear	0.1−50

Element and Wavelength (nm)	Background Correction	Correlation Coefficient	Calibration Fit	Calibration Range, mg/kg
Sn 189.925	Fitted	0.9999	Linear	0.1−50
Sn 283.998	Fitted	0.9999	Linear	0.1−50
Ti 334.941	Fitted	1	Linear	0.1−50
Ti 336.122	Fitted	0.9999	Linear	0.1−50
V 292.401	Fitted	0.9999	Linear	0.1−50
V 309.310	Fitted	0.9999	Linear	0.1−50
Zn 206.200	Fitted	0.9999	Linear	0.1−50
Zn 213.857	Fitted	0.9999	Linear	0.1−50

Results and discussion

Detection limits

The Method Detection Limits (MDLs) shown in Table 4 are based on three sigma measurements of 10 replicate measurements of blank *o*-xylene solutions taken during the analytical run. The results were multiplied by 10 (the sample dilution factor) to give the MDL in the original sample.

Table 4. MDLs based on the sample weight (1 g in 10 g) per the ASTM method.

Element and Wavelength (nm)	MDL, mg/kg	Element and Wavelength (nm)	MDL, mg/kg
Ag 328.068	0.0170	Mo 202.032	0.3424
Al 396.152	0.2725	Na 588.995	1.1116
B 249.772	0.0202	Ni 216.555	0.2641
Ba 455.403	0.0084	P 213.618	0.7740
Ca 422.673	0.0499	Pb 220.353	1.4314
Cd 226.502	0.0145	S 181.972	1.4170
Cr 267.716	0.0158	Si 288.158	0.0491
Cu 324.754	0.0126	Sn 189.925	2.9423
Fe 238.204	0.0359	Ti 334.188	0.0424
K 766.491	0.3968	V 292.401	0.0425
Mg 279.553	0.0059	Zn 213.857	0.0580
Mn 257.610	0.0049		

SRM analysis

To validate the method for the analysis of Ni and V (and S) in oil, both elements were determined in duplicate samples of the NIST 1634c fuel oil SRM. V was also measured 10 times in duplicate samples of NIST 8505 SRM. The recoveries of Ni and V (and S) were all within ±10% of the certified values, as shown in Table 5. There was good agreement between the concentration measurements for multiple wavelengths of the same element (within ±10%).

Table 5. Analysis of Ni, V, and S in oil SRMs.

Element and Wavelength (nm)	NIST 1634c (n=10)			NIST 8505 (n=10)		
	Measured Value (mg/kg)	Certified Value (mg/kg)	Recovery (%)	Measured Value (mg/kg)	Certified Value (mg/kg)	Recovery (%)
Ni 216.555	17.67 ± 0.26	17.54	101			
V 292.401	27.39 ± 0.38	28.19	97	363.07 ± 7.34	390.00	93
V 309.310	28.18 ± 0.37	28.19	100	375.97 ± 7.64	390.00	96
V 311.837	26.79 ± 0.35	28.19	95	355.93 ± 6.79	390.00	91
S 181.972	20465 ± 290	20000[IV]	102			
S 182.562	20613 + 302	20000[IV]	103			

IV = Information value.

QC solution

Since the range of elements in crude oil RMs is limited, a solution from ASI Standards containing known concentrations of Ca, K, Na, Ni, and V was used as a QC test solution.

The measured concentrations obtained by the 5110 VDV ICP-OES and the reference values are given in Table 6. Recoveries of Ca, K, Na, Ni, and V were within 10% of the expected values, with good agreement between the different wavelengths of the same element (Table 6).

Quantitative results

Quantitative results for 23 elements in 20 crude oil samples were acquired using the 5110 VDV ICP-OES. The results in Table 7 show the results for three representative samples. The results show that most elements were present in the crude oil samples at low concentrations (< 1 ppm). There was some variation in the concentrations of Ca, Fe, K, Na, Ni, S, and V in the representative samples. Two of the three samples met the WTI crude oil specifications for Ni (8 ppm) and V (15 ppm). Overall, nine of the 20 samples analyzed in this study met the WTI specifications for Ni and V (not all data is shown).

Table 6. Results from the analysis of a crude oil QC solution, n=10.

| Element and Wavelength (nm)	Measured Value (mg/kg)	SD	Reference Value (mg/kg)	Recovery (%)
Ca 315.887	5.01	0.09	5.00	100
Ca 396.847	5.05	0.09	5.00	101
Ca 422.673	5.08	0.08	5.00	102
K 766.491	4.77	0.24	5.00	95
K 769.897	5.00	0.31	5.00	100
Na 588.995	5.25	0.23	5.00	105
Ni 216.555	5.07	0.25	5.00	101
Ni 231.604	4.71	0.30	5.00	94
V 292.401	5.33	0.26	5.00	107
V 309.310	5.49	0.27	5.00	110
V 311.837	5.34	0.26	5.00	107

Table 7. Averaged measured concentrations of multiple elements in representative crude oil samples, n=10.

Element and Wavelength (nm)	Sample 1 Measured Conc (mg/kg)	Sample 2 Measured Conc (mg/kg)	Sample 3 Measured Conc (mg/kg)
Ag 328.068	<LOQ	<LOQ	<LOQ
Al 396.152	<LOQ	0.60 ± 0.03	0.40 ± 0.05
B 249.772	5.34 ± 0.02	7.10 ± 0.32	6.64 ± 0.02
Ba 455.403	0.02 ± 0.01	0.03 ± 0.01	<LOQ
Ca 422.673	0.44 ± 0.01	46.97 ± 0.72	8.84 ± 0.94
Cd 226.502	0.10 ± 0.01	0.08 ± 0.01	0.08 ± 0.00
Cr 267.716	0.02 ± 0.01	0.04 ± 0.01	0.08 ± 0.01
Cu 324.754	0.04 ± 0.01	0.03 ± 0.01	0.03 ± 0.01
Fe 238.204	0.64 ± 0.00	21.91 ± 0.07	21.71 ± 0.30
K 766.491	0.55 ± 0.11	46.34 ± 2.12	1.97 ± 0.81
Mg 279.553	0.03 ± 0.00	0.51 ± 0.10	0.12 ± 0.01
Mn 257.610	0.01 ± 0.00	0.06 ± 0.03	0.01 ± 0.01
Mo 202.032	0.16 ± 0.29	0.09 ± 0.02	0.81 ± 0.04
Na 588.995	1.45 ± 0.24	48.54 ± 0.84	76.09 ± 2.91
Ni 216.555	0.42 ± 0.24	5.05 ± 0.05	21.56 ± 0.24
P 213.618	0.15 ± 0.55	<LOQ	47.53 ± 0.25
Pb 220.353	1.29 ± 0.63	0.06 ± 0.18	<LOQ
S 181.972	1146.39 ± 12.94	883.38 ± 4.39	19825.10 ± 317.60
Si 288.158	0.79 ± 0.01	0.55 ± 0.02	0.84 ± 0.03
Sn 189.925	4.55 ± 0.75	<LOQ	<LOQ
Ti 334.188	0.04 ± 0.01	0.05 ± 0.01	0.04 ± 0.01
V 292.401	1.17 ± 0.03	4.98 ± 0.03	100.39 ± 0.72
Zn 213.857	0.29 ± 0.02	0.16 ± 0.02	0.18 ± 0.00

Long-term stability

To demonstrate the robustness and precision of the 5110 VDV ICP OES over an extended period, approximately 400 crude oil samples were analyzed over six hours (Figure 2). QC solutions were measured every 10 samples. The results for all elements show recoveries within ±10% and %RSD less than 3%.

The robust plasma generated using the SSRF system and the vertically orientated torch ensure that the 5110 delivers excellent repeatable performance, even for complex crude oil samples.
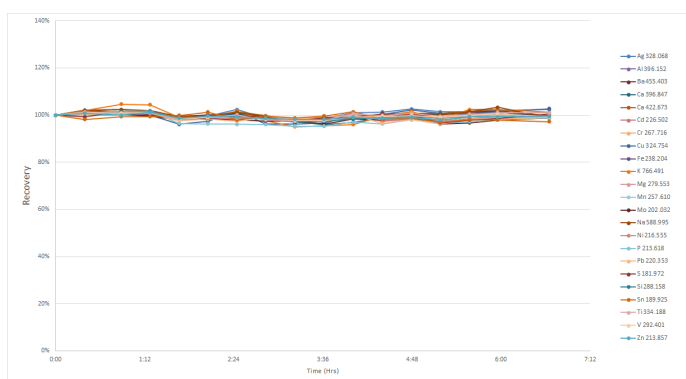
Figure 2. Long-term stability test results. Recovery of QC sample analyzed every 10 samples over approximately six hours. Boron was only measured for part of the six-hour run before a problem occurred, so no results for B have been included in the graph.
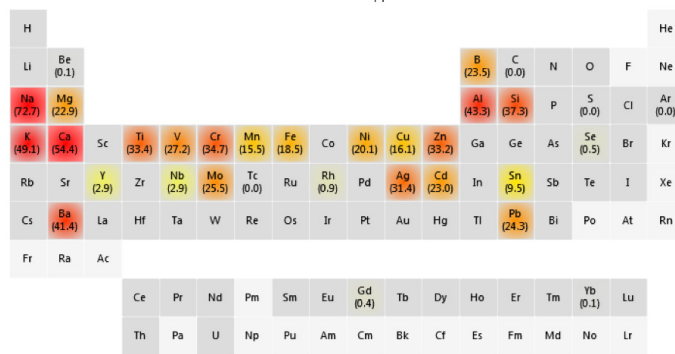
Sample analysis time

All 23 elements in each sample were determined in 52 seconds using the 5110 VDV ICP-OES fitted with the AVS 7. The fast analysis time was due to the high-speed Vista Chip II detector and integrated sampling valve. Total argon consumption per sample was 17.0 L.

Full spectrum scan using IntelliQuant

An IntelliQuant scan was performed during the routine analytical run to provide additional information on the samples. IntelliQuant rapidly scans for up to 70 elements in less than 15 seconds—an efficient way to identify and semiquantify elements that are not present in the calibration standards. The results for one of the crude oil samples are shown in Figure 3. The heat map shows that 23 elements were detected in the scan, as well as their approximate concentration (ppm). For the crude oil sample, the scan provided additional elemental information for Be, Se, Nb, Gd, and Rh.

Elements present at low concentrations are shown in yellow, medium concentrations are shown in orange, and high concentrations are shown in red. The concentration ranges are user adjustable.

Figure 3. Heat map generated by a rapid IntelliQuant analysis of a crude oil sample.

Conclusion

The Agilent 5110 VDV ICP-OES fitted with an AVS 7 switching valve was used for the analysis of 23 elements in crude oils following dilution in *o*-xylene. All elements were quantified in a 52 s run, requiring only 17 L of argon per sample.

The 5110 ICP-OES includes advanced hardware and software features to simplify operation and method development for the analysis of crude oil samples. The Vista Chip II detector allows analysis across a wide dynamic range eliminating the need for multiple dilutions. It also allows access to multiple wavelengths per element, so the user is not limited to wavelengths that may be susceptible to interferences. Within the ICP Expert software, fitted background correction automatically corrects the background without the analyst needing to intervene. Using these features, the method was shown to deliver excellent accuracy for the measurement of Ni and V in two NIST oil SRMs and good recoveries for Ca, K, Na, Ni, and V in a QC reference material. The robustness of the solid-state RF plasma system and the vertical torch orientation of the 5110 VDV ICP-OES provided excellent long-term stability during the analysis of organic oil samples over approximately six hours.

For the routine analysis of samples, including testing for Ni

and V in accordance with the latest specifications for WTI crude oil, the powerful ICP Expert software includes:

- ICP Applet mode – a simplified user interface that enables operators of all skill levels to carry out routine analysis of complex samples.

- IntelliQuant semiquantitative scan mode—a useful extra source of information for method development by identifying interferences and checking the calibration range. IntelliQuant also identifies and provides an estimation of the concentration of over 70 elements in the sample in less than 15 seconds, providing extra confidence in the analysis.

- Data reporting options—Report Designer enables users to configure reports to include only the data that is required, and to customize sample report templates with a company logo.

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