Determination of Metals in Oils by ICP-OES

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers

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Introduction

The determination of metals in oils and petroleum products is important in many petroleum laboratories and manufacturing operations. The samples can be crude oils, lubricating oils, gas oils and fuel oils, to name a few. Fast, accurate and precise analytical results are required in this industry. The metals analyzed in the sample varys with the product, or its source or use, which is discussed by Johnson [1], McKenzie [2], Van Loon [3], Hofstader, Milner and Runnels [4], and Pradham [5].

The analysis of oils and petroleum products has been performed by flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry, arc-spark atomic emission spectrometry and ICP-OES. The ICP has many benefits for the analysis of oils. The samples are typically diluted, in kerosene or other suitable solvent, and aspirated directly into the ICP. The ICP analysis is very fast, and gives accurate, precise results.

The analysis of organic materials, using the ICP, can present difficult problems for the spectroscopist. The power requirements may be higher for many organic solvents and matrices used in the analysis of oils [6,7]. Additionally, it is necessary to reduce the sample uptake rate to minimize solvent loading of the plasma with some organics, which could cause the plasma to be extinguished.

The purpose of this study was to analyze 12 elements in a used lubricating oil, a gas oil (used as the feed stock for gasoline production) and a fuel oil #6 using the Liberty 200. The work determined the concentration of nickel, barium, silicon, iron, chromium, magnesium, vanadium, sodium, aluminium, calcium, zinc and lead in all three sample matrices.

The primary elements of interest in the used lube oil are Fe, Si, Al, Cu, Cr, and Pb. The elements of interest in the gas oil are Na, Fe, Ni, Cr, Cu, and Al. Finally, the prime elements for the fuel oil are Ca, Fe, Ni, V, and Na. The Ba, Si, Mg, and Zn are also of interest.

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Experimental

Instrumentation

The Agilent Liberty 200 ICP-OES was used in this study. The system was controlled with a Compaq 386/20e computer.

Analytical Procedures

The samples were analyzed after simple dilution using the weight-volume preparation. The samples were prepared by weighing 5 grams of oil and diluting with 5 mL analytical grade, deodorized kerosene as the solvent. The dilution ratio was 1:10. The standards were prepared with a 1:10 weight-volume dilution of kerosene with 10, 50 and 100 ppm Conostan [8] S-21 standards. A blank was prepared by diluting base oil 75, 1:10 weight-volume dilution with the kerosene.

During the analysis the 50 ppm standard was used as a QC Standard to check the accuracy and stability of the instrument and the analysis.

The dynamic mode of background correction was used to compensate for background and viewing height was optimized using intensity. The search and scan windows were optimized to eliminate any interference peaks and assist the instrument in the peak location for the lower concentration levels of the metals in the oil matrices. There were no spectral interferences encountered and therefore no corrections made.

A glass concentric K-type nebulizer was used for sample aspiration. The peristaltic pump was fitted with organic resistant tubing. The sample delivery tube was white/white and the drain tube was white/gray.

Because the fuel oil samples contained a high amount of particulate materials, the nebulizer-spray chamber system needed more frequent rinsing with the kerosene. The fuel oil did exhibit some carry over, but rinsing for 3 minutes with kerosene minimized the problem.

Results

The common parameters used for the analysis of all three matrices are found in Table 1. The analyses were performed with manual sample introduction.

Table 1. Liberty 200 Instrument Parameters

Nebulizer pressure (kPa)	150
Stabilization time (s)	15
Sample delay (s)	30
Rinse time (s)	10
Snout purge	OFF
Integration (s)	3
Replicates	3
PMT (V)	650
Power (kW)	1.50
Plasma (L/min)	13.5
Auxiliary (L/min)	2.25
Pump speed (rpm)	10
Nebulizer pressure (kPa)	150
Background mode	Dynamic
Standard 1	10
Standard 2	50
Standard 3	100
Units	mg/L
Max curve order	4
C.C. limit	0.9950

Table 2 shows the wavelength, viewing height, search window, scan window, filter and order which were optimized for each line in the program.

The results for the used lube oil, the gas oil and the fuel oil are given in Table 3.

Each sample was analyzed in triplicate. The used lube oil and gas oil required a rinse time of only 10 seconds between samples, but required a rinse time of 2 minutes between the samples and the QC standard. Because of the higher solids and particulate content of the fuel oil and problems with the particulates sticking to the pump tubes, nebulizer and spray chamber, a 3 minute rinse was used. The rinsing was performed with kerosene.

Figures 1, 2 and 3 are representative scans for nickel in the used oil and fuel oil, silicon in the gas oil and fuel oil and vanadium in the gas oil and fuel oil. The nickel and silicon exhibit some band structure, which is characteristic when analyzing hydrocarbon samples. The nickel peak is the middle peak. None of the high level scans show any band structures.

From the literature and experience in the analysis of these types of hydrocarbon samples, one would expect the gas oil to have the lowest concentration of metals, followed by the used lube oil with the fuel oil containing the highest concentration of metals. Indeed, the results follow the expected trend.

Recovery data for the quality control standard of 50 ppm is presented in Table 4.

Table 2. Measurement Parameters for the Liberty 200

Element	Wavelength nm	View height mm	Search window nm	Scan window nm	Filter	Order
Ni	231.604	5	0.030	0.060	6	2
Ba	233.527	8	0.040	0.060	6	2
Si	251.611	8	0.040	0.060	6	2
Fe	259.940	8	0.040	0.060	6	2
Cr	267.716	8	0.040	0.060	6	2
Mg	279.553	4	0.040	0.060	6	2
V	292.402	8	0.040	0.060	6	2
Na	589.592	8	0.080	0.120	7	1
Al	308.215	8	0.040	0.060	6	2
Ca	317.933	5	0.040	0.060	6	2
Zn	213.856	8	0.027	0.040	1	3
Pb	220.353	8	0.027	0.040	1	3

Table 3. Mean Results

	Used Lube Oil			Gas Oil			Fuel Oil		
Element	Mean mg/L	S.D. mg/L	%RSD	Mean mg/L	S.D. mg/L	%RSD	Mean mg/L	S.D. mg/L	%RSD
Ni	24.14	0.1	0.4	15.68	0.4	2.5	911.8	42.7	4.6
Ba	12.21	0.39	3.2	0.90	1.03	114.3	0.50	0.52	105.3
Si	33.22	2.89	9.6	3.01	1.58	52.7	156.9	3.91	2.5
Fe	10.51	0.27	2.5	3.72	0.09	2.3	34.88	0.93	2.7
Cr	0.23	0.13	57.0	0.41	0.2	49.7	1.39	0.3	21.6
Mg	2.48	0.1	4.2	0.43	0.02	4.6	3.01	0.13	4.3
V	0.55	N/A	N/A	22.08	0.39	1.8	1143.0	25.6	2.2
Na	12.86	8.51	66.2	3.78	N/A	N/A	27.36	1.62	5.9
Al	29.93	2.0	6.7	37.58	1.06	2.8	102.9	1.92	1.9
Ca	217.7	3.08	1.4	<0.01	0.0	0.0	4.93	0.5	10.1
Zn	73.11	0.68	0.9	2.28	0.15	6.8	5.12	0.59	11.5
Pb	<0.25	N/A	N/A	4.98	3.83	76.9	14.02	2.09	14.9

Table 4. Recovery for 50 ppm QC Standard

Metal	Concentration mg/L	% Recovery
Ni	51.44	102.9
Ba	52.42	104.8
Si	50.93	101.9
Fe	52.88	105.8
Cr	53.74	107.5
Mg	52.46	104.9
V	52.86	105.7
Na	51.60	103.2
Al	52.43	104.9
Ca	54.22	108.4
Zn	53.49	107.0
Pb	53.38	106.8

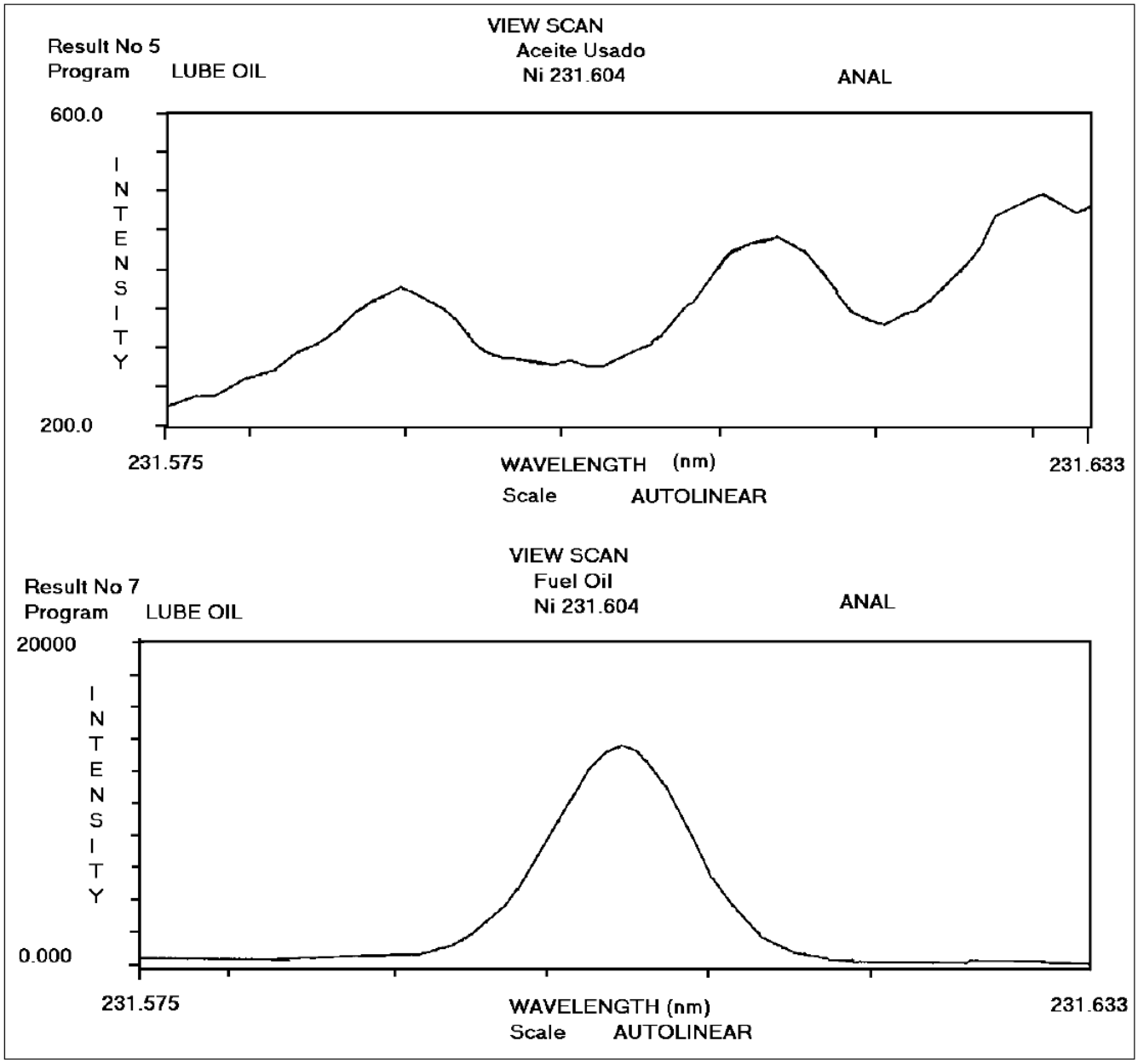

Figure 1. Nickel scans for used lube oil and fuel oil.

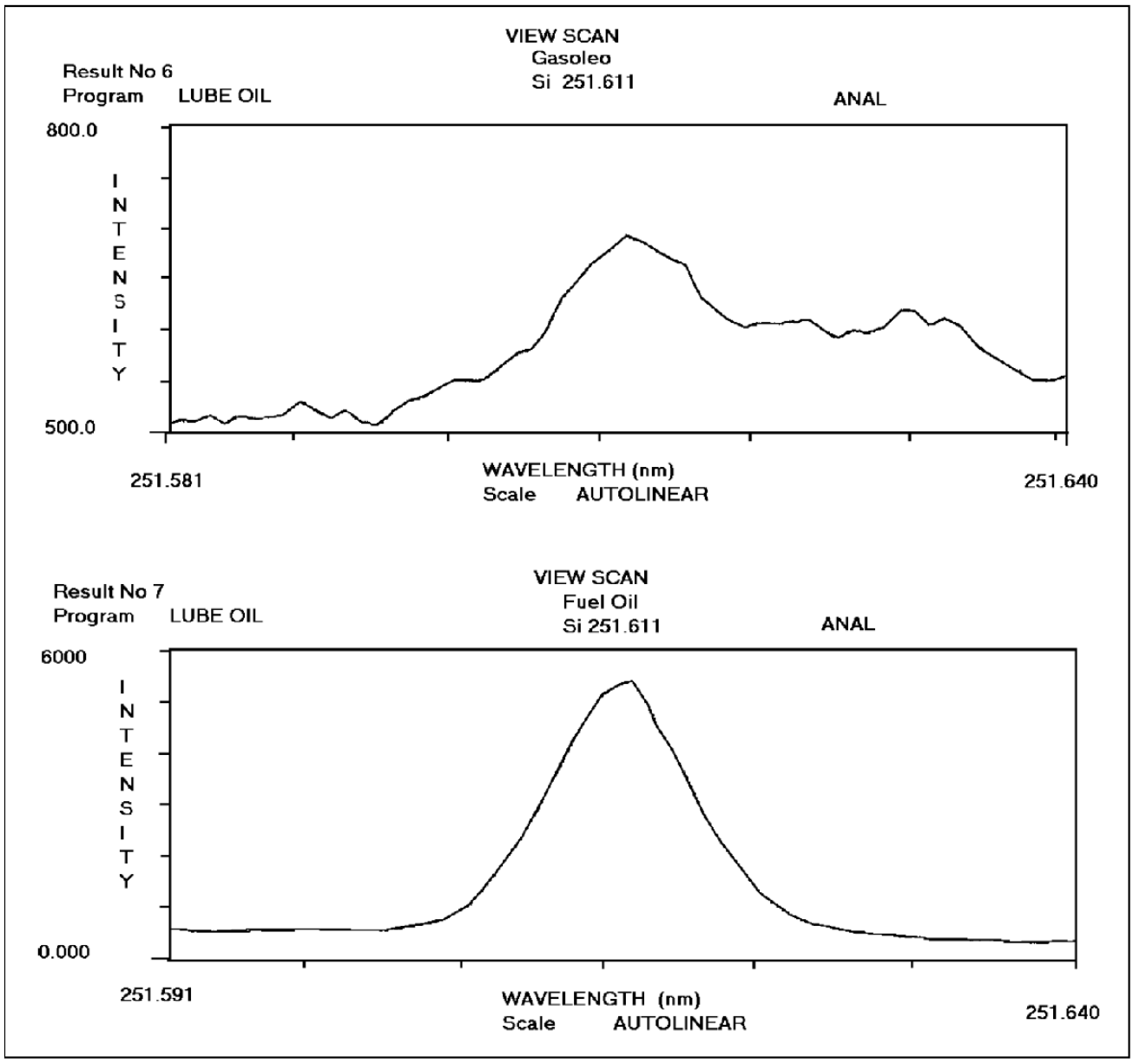

Figure 2. Silicon scans for gas oil and fuel oil.

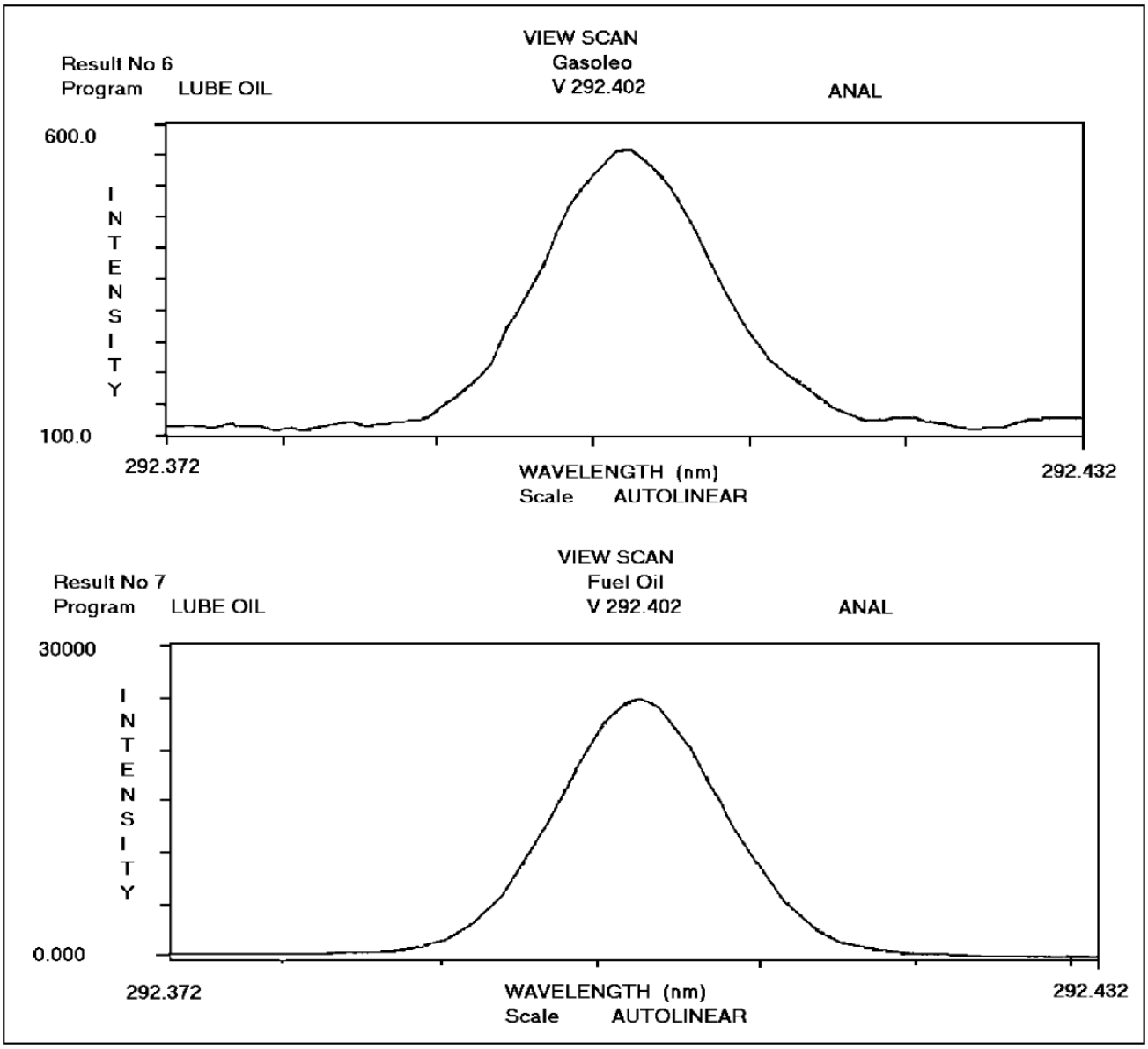

Figure 3. Vanadium scans for gas oil and fuel oil.

The QC data indicates the analysis and instrument are performing well. The data was accumulated over a two day period. The QC check after the analysis of the fuel oil samples was generally higher and in the range approximately 120% recovery. These results, after the fuel oil analysis, were used in overall recovery calculations. The overall recoveries are excellent, ranging from 101.9–108.

Conclusion

The Liberty ICP-OES instruments offer a fast, accurate and precise method for the determination of metal constituents in oil matrices. The simple dilution method provides an easy sample preparation scheme for the analysis, with accurate results for trend analysis.

The Liberty's 40.68 MHz RF generator easily handles the hydrocarbon matrices resulting in stable, precise results. Dynamic background correction and the instrument's high resolution compensate for background problems and minimize spectral interferences.

The Liberty could analyze the 12 metals with 3 replicates in the samples in approximately 6 minutes 30 seconds. Coupled with the ability to analyze QC samples periodically, it gives the analyst assurance of fast, accurate results.

Acknowledgments

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