The Determination of Vanadium in Heavy Industrial Fuel Oils Using the GTA-95

Application Note

Atomic Absorption

Author

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Introduction

The determination of vanadium in petroleum and petroleum products has been a continuing analytical requirement for the petroleum laboratory. The importance of vanadium in the processing of petroleum and petroleum products is discussed by Pradhan [1] and Hofstader et al [2]. The determination of vanadium has been conducted with many diverse approaches to methods of sample preparation and analytical instrumentation.

Atomic Absorption (AA) instrumentation is commonly used in the determination of metals in petroleum and petroleum products. McKenzie [3] refers to numerous papers on the analysis of petroleum and petroleum products by AA.

Sample preparation of oils for vanadium include dilution with a suitable organic solvent, wet ashing with acid followed by dilution into an aqueous medium, and dry ashing followed by dilution with acid. Atomic absorption analysis of oils include both flame and graphite furnace techniques. Calibration of the AA, for concentration determination, is performed by normal calibration (comparison with reference standards) and by the method of standard additions.

Scope

In this study, the Agilent Graphite Tube Atomizer-95 (GTA-95) was used for the determination of vanadium in a heavy #6 industrial fuel oil. The introduction of air as an ashing aid to reduce matrix interferences in the production of the vanadium atomic vapor was investigated. The method of standard additions was used to overcome any problems in the instrument calibration resulting from the complexity of the oily matrix.

The complete analytical system consisted of an Agilent AA-975 spectrophotometer, GTA-95, and a Hewlett Packard HP-85 computer.

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Analytical Procedure

One gram of #6 fuel oil sample was weighed into a 250 mL beaker and diluted to 100 mL [4]. Samples were diluted in reagent grade, odorless, kerosene (dilution factor 100).

An organometallic standard, Conostan C-21 Continental Oil Company [5] was diluted with kerosene from 500 mg/L to 1.0 mg/L for use as a standard to spike the sample. Addition concentrations were 0, 100, 300, and 500 µg/L. The procedure involved pipetting 5 mL of sample into each of 4 test tubes. Then 0, 1, 3 and 5 mL of standard was pipetted into the test tubes to prepare 0, 100, 300 and 500 µg/L additions, respectively. Each addition was brought to a final volume of 10 mL with kerosene. The test tubes were then stoppered to prevent evaporation of the samples. Kerosene was used as a blank in the calibration of the instrument and computer.

The AA-975 instrument parameters and GTA-95 temperature programs used are shown in Figures 1 and 2. Figure 1 shows that argon was used throughout the temperature program. In Figure 2, air (alternate gas) was used, as an ashing aid, in the dry and low temperature ash, up to 500 °C. Argon was used, after the air, in the completion of the temperature program. It should be noted that, when air is used, less time is required for drying and ashing the sample.

The samples were studied to determine if background correction was necessary. It was found that the oily matrix had been sufficiently removed by both temperature programs, therefore background correction was not necessary.

The samples were manually injected into the furnace because of the problem of settling of particulate matter in the #6 fuel oils. The samples were mixed prior to each injection of the sample. This allowed the most homogeneous sample possible to be injected into the furnace. An Oxford Micropipetting system with capillary tips was used aiding in the introduction of the oily samples. The sample volume was 5 µL.

```
PROGRAM ID       15.
INT TIME          1.0
WAVELENGTH     318.5
SLIT              0.2
LAMP NUMBER      10.
LAMP CURRENT     10.
EXPN FACTOR       1.0
STANDARD 1     0.100
STANDARD 2     0.300
STANDARD 3     0.500
ABS
BC OFF
PEAK HEIGHT

FURNACE OPERATING PARAMETERS.
```

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	80	10	3.0	NORMAL	
2	150	120	3.0	NORMAL	
3	180	20	3.0	NORMAL	
4	1400	10	3.0	NORMAL	
5	1400	40	3.0	NORMAL	
6	1400	2.0	.0	NORMAL	
7	2800	.7	.0	NORMAL	*
8	2800	2.0	.0	NORMAL	*
9	2800	2.0	3.0	NORMAL	
10	40	13	3.0	NORMAL	
11	2800	1.4	3.0	NORMAL	
12	2800	2.0	3.0	NORMAL	
13					
14					
15					
16					
17					
18					
19					
20					

Figure 1. Furnace operating parameters using argon.

```
PROGRAM ID       15.
INT TIME          1.0
WAVELENGTH     318.5
SLIT              0.2
LAMP NUMBER      10.
LAMP CURRENT     10.
EXPN FACTOR       1.0
STANDARD 1     0.100
STANDARD 2     0.300
STANDARD 3     0.500
ABS
BC OFF
PEAK HEIGHT

FURNACE OPERATING PARAMETERS.
```

STEP NO.	TEMPERATURE °C.	TIME SEC.	GAS FLOW	GAS TYPE	READ COMMAND
1	80	10	3.0	ALT.	
2	150	60	3.0	ALT.	
3	180	20	3.0	ALT.	
4	500	10	3.0	ALT.	
5	500	20	3.0	ALT.	
6	500	2.0	3.0	NORMAL	
7	1400	10	3.0	NORMAL	
8	1400	20	3.0	NORMAL	
9	1400	2.0	.0	NORMAL	
10	2800	.7	.0	NORMAL	*
11	2800	2.0	.0	NORMAL	*
12	2800	2.0	3.0	NORMAL	
13	40	13	3.0	NORMAL	
14	2800	1.4	3.0	NORMAL	
15	2800	2.0	3.0	NORMAL	
16					
17					
18					
19					
20					

Figure 2. Furnace operating parameters using air.

Results

The video display on the GTA-95 allows the operator to observe the real-time analytical signal superimposed on the temperature profile as shown in Figures 3 and 4. In Figure 3 the entire temperature program is observed, from the beginning of the dry step (Step 1) through the completion of the tube cleaning step (Step 12). The analytical signal shows that the sample is properly dried and ashed prior to atomization. The use of the video is beneficial in the development of furnace methods because the time and temperature of background/matrix and sample evolution can be readily observed. Figure 3 shows the drying and ashing of the sample prior to atomization.

Figure 4 shows an additional benefit of the GTA-95. Figure 4 is an injection using air in the dry and low temperature ash steps. The low temperature ash steps necessitate an increase from 12 to 15 steps in the total temperature program — refer to the operating parameters in Figure 2. The step numbers observed were changed to view only steps 9 through 11. The absorbance scale was also changed to 0.5 Abs full scale from 1.0 Abs full scale. This allowed better observation of the peak and the peak's shape.

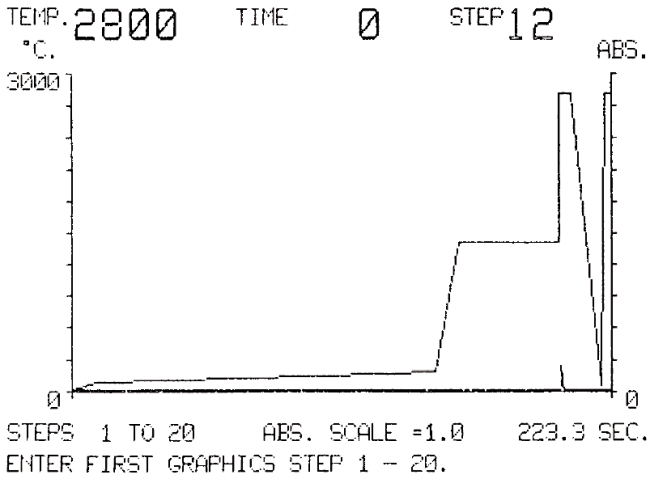

Figure 3. Entire temperature program, steps 1–12.

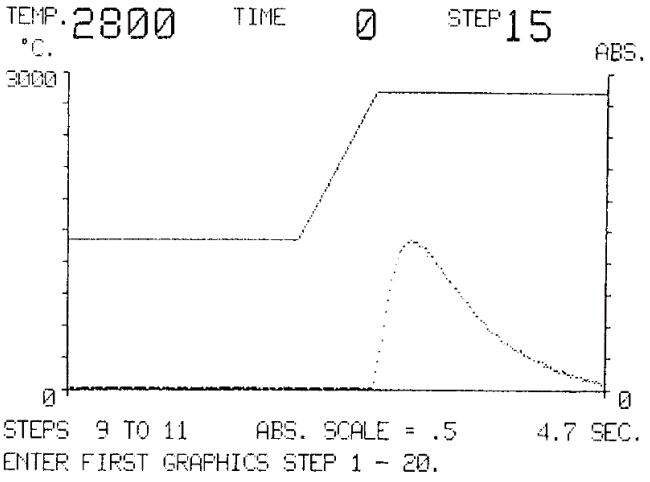

Figure 4. Selective temperature program, steps 9 –11.

Analytical results are shown in Figures 5 and 6. The results in Figure 5 are from the determination of vanadium when argon is used throughout the temperature program. Figure 6 shows the results of using air as an ashing aid. Note also the calibration curves for both analyses, plotted by the HP-85 computer.

The results from both methods agree very well with each other. The values reported should be multiplied by 100 to account for the dilution factor. The use of air, in Figure 6, exhibits poorer precision (% RSD) than the use of argon exclusively. Although determinations with air show poorer precision, these values are still acceptable for manual injections.

Two factors could contribute to the poorer precision. First, the use of air may lead to the formation of stable vanadium oxides in the furnace which would inhibit the formation rate of ground state vanadium atoms. The rate, or any changes in the rate, at which the ground state atom is formed in the furnace will affect the analytical precision.

Second, oxidation of the graphite furnace may occur during analysis using air and this could also contribute to poorer precision. Oxidation of the graphite causes the furnace to become porous, and solvents (with the analyte atoms) tend to soak into the graphite. Consequently, ground state atoms are evolved from the graphite at differing rates from firing to firing. Again with the differing evolution rates of the ground state atoms the precision will degrade as the graphite oxidizes and becomes porous.

When using air in the temperature program the analysis time was decreased from that when argon was used exclusively. The total analysis time was decreased by 49.2 seconds when using air. The shorter analysis time would allow a higher throughput of samples.

OPERATOR = DEEN JOHNSON
DATE = 12/20/1982
BATCH = #6 Fuel Oil DEMONSTRATION!

AUTO-PROGRAM 15 V in #6 Fuel Oil

SOLUTION	CONC mg/L	RSD	MEAN ABS	ABSORBANCE READINGS		
BLANK	0.000	16.7%	0.018	0.022	0.018	0.016
ADDITION 1	0.100	7.2%	0.181	0.171	0.177	0.197
ADDITION 2	0.300	2.0%	0.299	0.294	0.306	0.299
ADDITION 3	0.500	1.0%	0.392	0.394	0.395	0.387
SAMPLE 1	0.320	3.8%	0.157	0.156	0.152	0.164
SAMPLE 2	0.314	1.3%	0.154	0.157	0.153	0.152

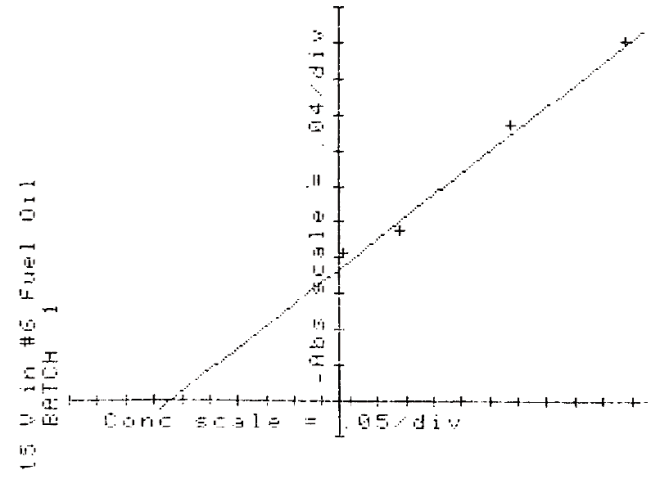

Figure 5. Analytical results when using argon.

OPERATOR = DEEN JOHNSON
DATE = 12/21/1982
BATCH = #6 Fuel Oil DEMONSTRATION!

AUTO-PROGRAM 15 V in #6 Fuel Oil

SOLUTION	CONC mg/L	RSD	MEAN ABS	ABSORBANCE READINGS		
BLANK	0.000	23.5%	0.017	0.023	0.015	0.014
ADDITION 1	0.100	0.8%	0.250	0.248	0.252	0.252
ADDITION 2	0.300	3.1%	0.381	0.368	0.386	0.391
ADDITION 3	0.500	2.8%	0.502	0.519	0.498	0.490
SAMPLE 1	0.297	4.8%	0.188	0.178	0.196	0.191
SAMPLE 2	0.293	4.9%	0.185	0.186	0.194	0.176

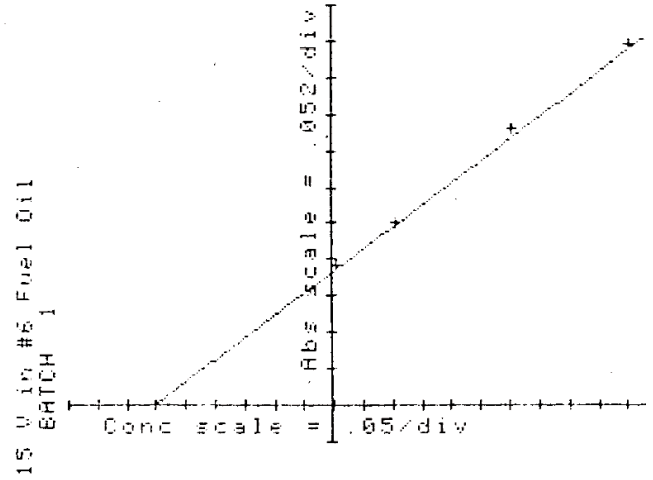

Figure 6. Analytical results when using air.

Conclusions

The use of air as an ashing aid on oily matrices, such as #6 fuel oils, is an acceptable method when conducting oils analysis. Results are comparable to those obtained using an inert gas exclusively in the temperature program of the furnace. Slightly poorer precision is observed when using air, but greater sample throughput is achieved. Vanadium responses were found to be about 25% higher when using air as an ashing aid.

References

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Printed in the USA
November 1, 2010
AA036

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