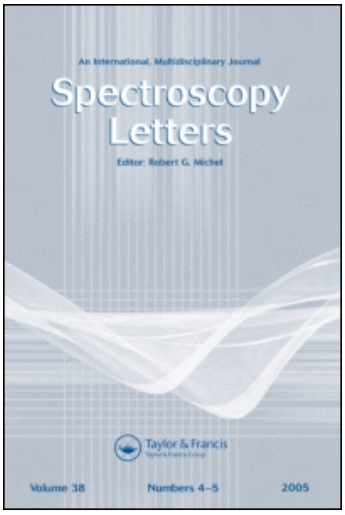

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Evaluation of Carbon Rod Atomizer for Routine Analysis of Vanadium in Crude Oil by Atomic Absorption Spectroscopy

C. L. Chakrabarti[a]; G. Hall[a]
[a] Department of Chemistry, Carleton University, Ottawa, Ontario, Canada

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EVALUATION OF CARBON ROD ATOMIZER FOR ROUTINE ANALYSIS OF VANADIUM IN CRUDE OIL BY ATOMIC ABSORPTION SPECTROSCOPY

Key Words: Carbon rod atomizer, atomic absorption spectroscopy, vanadium, crude oil.

C. L. Chakrabarti and G. Hall

Department of Chemistry, Carleton University,
Ottawa, Ontario, Canada, K1S 5B6

ABSTRACT

The Carbon Rod Atomizer (CRA) was evaluated for routine trace analysis of vanadium in crude oil by atomic absorption spectroscopy with a carbon (graphite) tube as a micro-furnace. Two crude oil samples were analyzed, both by standard addition and standard working curve methods, and the results confirmed by analysis with flame atomic absorption spectroscopy using a fuel-rich nitrous oxide-acetylene flame. Because of the relative involatility of vanadium at the temperature of the CRA, quantitative recoveries of vanadium in crude oil occur only when the vanadium content of the sample injected into the CRA does not exceed the limit of about 1×10^{-8} g. A sensitivity (weight/1% absorption) of 7.0×10^{-11}g and detection limit (signal-to-root-mean-square-noise equal to two) of 6.9×10^{-12} are reported.

INTRODUCTION

The objective of this study was to evaluate the Carbon Rod Atomizer (CRA), Model 63 (Varian Techtron Pty. Ltd., Melbourne, Victoria, Australia) using a carbon (graphite) tube for quantitative determination

of vanadium in crude oil. Vanadium is an important trace element in crude oil. Traces of vanadium poison the platinum catalyst of cracking plants for crude oil. The CRA has been evaluated for routine analysis[1,2] for silver, iron, nickel, and lead in lubricating oils and crude oils. Vanadium is less volatile than all these elements and has a melting point and a boiling point of 1900°C and 3450°C, respectively[3]. The latter figure is of interest because the maximum temperature obtained by the CRA[4] is ca. 3000°C; additionally the formation of carbides including a stable carbide[5], VC (melting point 2810°C, boiling point 3910°C) is well known. It may, therefore, be expected that vanadium would be more difficult to atomize in the CRA than more volatile elements, and that decreased sensitivity and poorer selectivity would be attained.

West[6] et al. recently reported determination of vanadium in titanium dioxide by ultramicro atomic absorption spectrometry on a carbon filament atom reservoir. Several other authors[7,8] reported the determination of vanadium by flame atomic absorption spectroscopy. However, the conventional flame technique does not have adequate sensitivity and detection limit for determining traces of vanadium. Also, it is desirable to have a faster and cleaner method of analysis for such a matrix as crude oil. The CRA gave improved sensitivity and detection limit for several elements[1,2] as well as requiring much smaller samples than the conventional flame technique, and seemed an attractive technique for the study of vanadium determination. This paper describes the results of this study.

Sensitivity and detection limit of vanadium as an organovanadium compound in organic solvents, and an inorganic salt of vanadium in aqueous solution were determined and compared. Two

crude oils, TV102 and Guanipa, were analyzed with the CRA using standard addition method and calibration curve method. The results were compared with those obtained using a fuel-rich nitrous oxide-acetylene flame. The results with the CRA compares extremely favourably in sensitivity with the flame atomization technique including the flame atomic-absorption-indirect amplification procedure[9], which is, as the title implies, also lengthy.

EXPERIMENTAL

The organo-vanadium used as a standard was vanadium oxobis 1-phenyl-1,3-butanedionate (Eastman Organic Chemicals, Rochester, New York 10384). The inorganic vanadium salt used as a standard was vanadium pentoxide ('Baker Analyzed' reagent). Fresh dilutions of the 500 µg/ml stock solution of the standards were made up daily. All chemicals and solvents were of analytical reagents grade purity. Water used was freshly distilled water and then passed through a de-ionizing column immediately prior to its use. All chemicals and solvents (including water) were tested for their vanadium contents, and appropriate corrections made by using blanks.

The instrument was a Varian Techtron atomic absorption spectrophotometer, model AA-5, fitted with a Varian Techtron Carbon Rod Atomizer, model 63. Carbon (graphite) tubes supplied by Varian Techtron and having the following dimensions was used: internal diameter 3 mm, length 9 mm. Two Varian Techtron standard hollow-cathode lamps for vanadium and hydrogen (continuum), and a Hamamatsu R-106 photomultiplier tube were used. The analytical line used was a composite of the 318.40 nm doublet and 318.34 nm singlet and 318.54 nm singlet and was viewed with a spectral bandpass of 0.66 nm, which was wide enough to encompass the entire profiles of all these lines. These

experimental conditions were used for both the carbon tube atomization technique and the flame atomization technique.

Carbon Tube Atomization Technique

Calibration Curve Method. The sample preparation was as follows. 0.7 to 1.0 g of Guanipa crude oil samples and 0.2 to 0.5 g of T.V. 102 crude oil samples were separately and carefully weighed into 25 ml volumetric flasks and dissolved in methyl isobutyl ketone (or xylene) and diluted with the same solvent upto the mark.

Standard Addition Method. The sample preparation was as follows. About 8 g of Guanipa crude oil samples and about 3 g of T.V. 102 crude oil samples were separately and carefully weighed into 50 ml volumetric flasks and dissolved in methyl isobutyl ketone (or xylene) and diluted with the same solvent upto the mark. 2 ml aliquots of the above solution were pipetted into 25 ml volumetric flasks containing 0x, 1x, 2x, and 3x amounts of standard vanadium solution, where x equalled about 0.5 µg/ml of vanadium. Since vanadium occurs in crude oil predominantly as a porphyrin, best results are obtained by using a standard solution of vanadium porphyrin. A 2 µl sample volume was used and this was dispensed with a Hamilton graduated 5 µl syringe fitted with a platinum needle. This was chosen rather than the fixed-volume Eppendorf micropipette with disposable plastic tips usually recommended because the injection port of the graphite tube was too small for reproducible injection of the organic solution, which displayed a tendency to creep up the outside surface of the needle tip. The sheath nitrogen was used at its optimum flow rate of 4.0 l min^{-1}. The vanadium hollow-cathode lamp was operated at 8.0 mA current.

The dry, ash and atomize settings on the power unit were optimized for each sample studied. However, the maximum voltage across the electrodes (with unloaded graphite tube) was found to be about 12 volts and the maximum current about 150 amperes; the result was a rate of rise in temperature and a final temperature which were too low for the rapid and complete vaporization of vanadium. The consequence was broad drawn-out absorption peaks rather than narrow and sharp absorption peaks. When the CRA voltage was turned on again after the sample had been vaporized, an absorption peak was obtained, i.e., all of the vanadium was not removed from the graphite tube during the first firing, and thus, there was a memory effect. This memory effect persisted even after successive repetition of the above operation although its magnitude diminished continually with each repetition until a small, constant absorbance value was obtained. This observation together with the fact that the above absorption peak was not observed when the vanadium hollow-cathode lamp was replaced with a hydrogen hollow-cathode lamp (a continuum source) conclusively proved the absorption peak was due to memory effect and not to molecular absorption band nor to scattering of the radiation.

In order to remove the memory effect, a new transformer of larger capability and a new triac were installed in place of the existing transformer and triac in the power unit. Using the power unit thus modified, and the atomize setting of 9, the maximum voltage across the electrodes (with unloaded graphite tube) was found to be about 24 volts and the maximum current about 250 amperes; the result was a much faster rate of rise in temperature and a higher final temperature ($\sim 3500^{o}C$), and no memory effect

for vanadium content not exceeding 1 x 10^{-8} g. The modified power unit was therefore used throughout this study. The dry, ash, and atomize times used for the crude oil samples studies were 15 sec, 25 sec, and 3 sec, respectively.

Flame Atomization Technique

The carbon rod (tube) atomizer was replaced with a Varian Techtron, model AB40, 50 mm, single-slot, nitrous oxide-acetylene burner. The atomic-absorption measurements were made using the nitrous oxide-acetylene flame and the vanadium hollow-cathode lamp operated at 10 mA current. The hydrogen hollow-cathode lamp was used to correct for any absorption due to molecular bands and scattering of the incident radiation.

Standard Addition Method. The sample preparation was as follows. About 12 g of Guanipa crude oil samples and about 9 g of T.V.102 crude oil samples were separately and carefully weighed into 50 ml volumetric flasks and dissolved in methyl isobutyl ketone (or xylene) and diluted with the same solvent upto the mark. 10 ml aliquots of the above solution were pipetted into 25 ml volumetric flasks containing 0x, 1x, 2x, and 3x amounts of standard vanadium solution (preferably made of vanadium porphyrin), where x equalled about 10 μg/ml of vanadium.

The instrumental conditions were optimized as follows. The flow rates were 5.0 l min^{-1} for nitrous oxide and 4.7 l min^{-1} for acetylene. The burner height was adjusted so that the incident radiation passed through the red, reducing, interconal zone of the flame (5 mm above the burner top).

RESULTS AND DISCUSSION

Sensitivity (defined as the amount in gram/1% absorption) and detection limit (defined as the amount in gram equal to twice the signal-to-root-mean-square-noise ratio) for the two vanadium standards in various solvents are presented in Table 1. The solvents

Table 1

Sensitivity and Detection Limit of Vanadium. Sensitivity in Grams for 1% Absorption

Vanadium Compound	Solvent	Sensitivity, g	Detection Limit, g	Precision at 3×10^{-9} g level
Vanadium oxobis 1-phenyl-1,3-butanedionate	Xylene	7.1×10^{-11}	6.8×10^{-12}	4.4%
	MIBK	7.4×10^{-11}	-	4.3%
Vanadium pentoxide	20%(v/v) NH_4OH	7.1×10^{-11}	-	4.3%
Vanadium pentoxide	10%(v/v) HNO_3	7.0×10^{-11}	-	4.3%

were tested for vanadium contamination prior to their use but none was found. Use of a hydrogen diffusion flame made absolutely no difference to the sensitivity of any of these systems. Below the optimum nitrogen flow rate of 4.0 l min^{-1}, the sensitivity gradually dropped and the precision became poor. Replacement of nitrogen with argon as the purge gas did not alter the sensitivity. It is evident that the form in which the vanadium is bound up does not sensibly affect the sensitivity, nor the solvent in which the compound is dissolved. In all these systems a memory signal appears at the point corresponding to 9-10 ng vanadium, below which analysis must be carried out when using the calibration curve method.

Results of analysis of the two crude oils, TV102 and Guanipa, using both nonflame and flame atomization, are presented in Tables 2 and 3.

Table 2

Results of Analysis by Carbon Tube Atomization Technique

Crude Oil	Vanadium Concentration (µg/g) found by Standard (Calibration) Curve Method	Standard Addition Curve Method	Dilution (g/ml)*
TV 102	278 ± 10		1:34
	280		1:35
	299		1:83
	298		1:111
	303		1:115
	304		1:208
TV 102		299 ± 10	1:50
		298	1:100
		298	1:205
Guanipa	64 ± 4		1:10
	74		1:20
	82		1:50
	83		1:51
	85		1:70
	82		1:95
Guanipa		82 ± 4	1:52
		84	1:65
		83	1:80

* The ratio 1:34 means that 1 gram of the crude oil was diluted with 34 ml of methyl isobutyl ketone.

Table 3

Results of Analysis by the Flame Atomization Technique

Crude Oil Sample	Vanadium Concentration (µg/g) found by Standard Addition Method
T.V. 102	303 ± 10
T.V. 102	301 ± 10
Guanipa	84.5 ± 4.0
Guanipa	84.7 ± 4.0

Analysis by the Standard Addition Method using the carbon tube atomization and the nitrous oxide-acetylene flame atomization gave the same, constant result for the vanadium concentration of both crude oils. Since the dilution factor appears to be extremely significant (as shown below), it is also listed in Table 2. Results with the carbon tube atomization technique employing the Standard Addition Method and the Calibration Curve Method agree well at high dilution (any dilution shown below the horizontal dashed line in Table 2). With the carbon tube atomization technique, low values for the vanadium content were obtained if a calibration curve was used at absorbance values above about 0.40 for TV 102 crude oil and 0.30 for Guanipa crude oil. Thus, it seems that with the carbon tube atomization technique, the degree of dilution is an extremely important factor and, for these particular crude oils, the analysis must be carried out at a dilution greater than about 1 gram of crude oil to 40 ml of methyl isobutyl ketone in order to avoid interference by the oil matrix. Now, this point, at about 0.30-0.40 absorbance units, is the level at which a memory signal appears (as is shown later on). There is always another signal of about 0.02 absorbance unit which is due to the incandescent carbon tube but this in no way interferes with the atomic absorption peak as it merely forms a shoulder after the analytical signal has been recorded. The signal due to the incandescent carbon tube is constant whereas a memory signal decreases gradually as the tube is repeatedly fired (as is shown later on).

The two working curves prepared with solutions of standard vanadium oxobis 1-phenyl-1,3-butanedionate and crude oil, TV 102 (the vanadium content of which has been pre-determined), are presented in Fig. 1.

These curves were obtained by using various dilutions of the above solutions. Each experimental point in Fig. 1 represents the mean of the readings obtained from four discrete and consecutive samplings. It can be seen that the curves begin to separate at about 0.4 absorbance unit, where the memory effect is first encountered. It can also be seen from the Fig. that the absorbance signal given by greater than 10 ng of vanadium in the crude oil matrix is smaller than that given by standard vanadium oxobis 1-phenyl-1,3-butanedionate in MIBK. Hence, a knowledge of this crucial position where the two working curves begin to separate is of the utmost importance. It is evident that analysis or crude oils using a standard such as vanadium oxobis 1-phenyl-1,3-butanedionate must be performed at concentrations below 5 µg/ml (= 10 ng of vanadium using a 2 µl sample volume).

Figure 2 presents memory effect shown by 1.2×10^{-8} g of vanadium in various matrices as a function of the number of firings of the carbon tube. It can be seen that the memory effect is shown by both the standard and the crude oil samples but in varying degrees, the standard showing the least, and that the memory effect decreases gradually with each firing, and after several firings finally reaches almost a plateau having small absorbance values but does not reach zero values. This can be explained as follows. The residual vanadium probably combines with carbon at high temperature forming vanadium carbide, which is not completely vaporized at the temperature attained by the carbon tube.

The crude oils were also tested for particulate vanadium as follows. A quantity of the crude oil sample was filtered through a close filter paper (Whatman No. 42), washed with MIBK, and the particulate vanadium retained by the filter paper was then dissolved by digesting

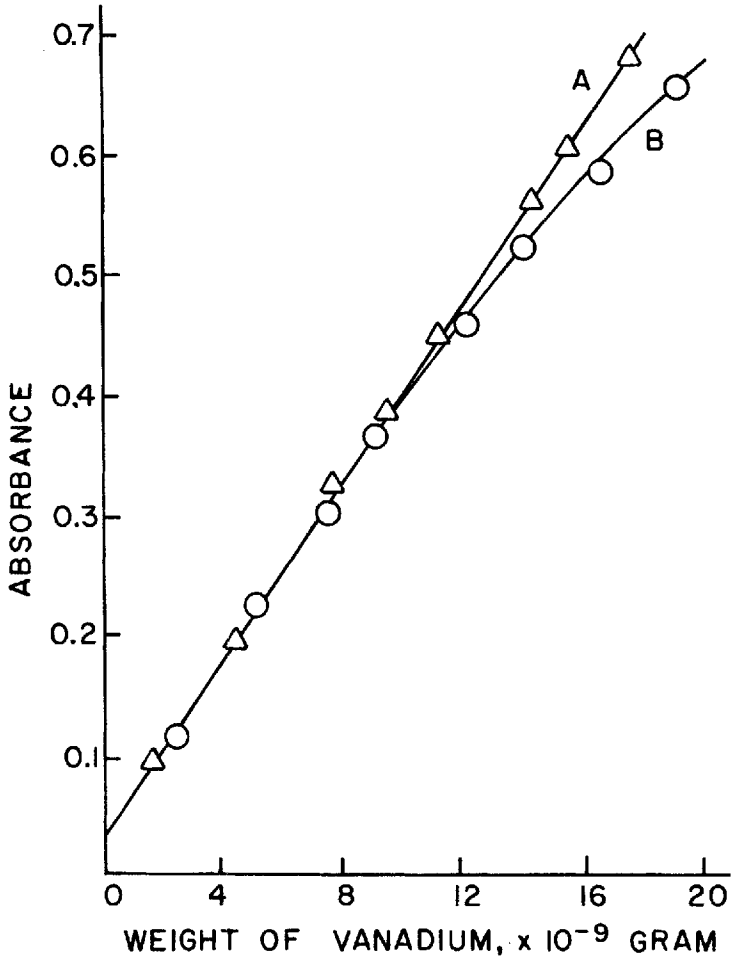

FIG. 1

Working curves for the determination of vanadium.
Curve A: vanadium oxobis 1-phenyl-1,3-butanedionate in methyl isobutyl ketone.
Curve B: crude oil, TV 102, in methyl isobutyl ketone.

it in a 40% (v/v) solution of nitric acid at an elevated temperature. This solution was then analyzed with the carbon tube atomizer using a calibration curve prepared with standard vanadium (taken as vanadium pentoxide) in nitric acid aqueous solution. A relatively

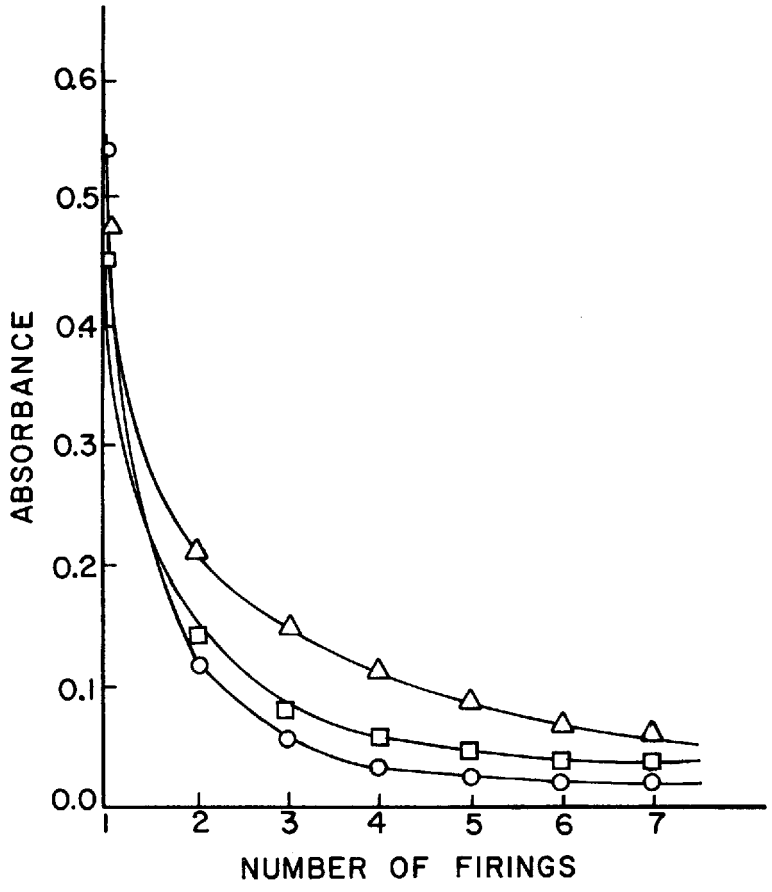

FIG. 2

Memory effect - absorbance by residual vanadium as a function of number of firings.

△ vanadium in crude oil, TV 102

□ vanadium in crude oil, Guanipa

○ vanadium oxobis 1-phenyl-1,3-butanedionate in methyl isobutyl ketone

low concentration of 1.5 ± 1.0 µg/g vanadium as particulate was found for both crude oils, based on five separate determinations each.

The carbon cup atomizer was not investigated for the following reason. Although it can accommodate a sample volume of 20 µl,

and hence, more dilute sample solutions, it was found that the rise in temperature was slower than that with the carbon tube atomizer. The rate of rise in temperature is an extremely important factor which determines the final temperature and the time taken to reach it, and therefore, the amount of vanadium that is vaporized.

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