



Determination of Vanadium in Natural Gas using Graphite Furnace Atomic Absorption Spectrometry

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Abstract

Vanadium is recognized worldwide as the most abundant metallic constituent in petroleum. This has led to expect its existence in natural gas that is associated with oil as a trace amount in ppb concentration or less. For capturing the trace amount of vanadium in natural gas, the diluted acidic medium is used as adsorption collection, and the collection medium as a sample. Graphite furnace atomic absorption spectrometry (GFAAS) is the analytical method utilized in this study to determine nanoparticle of vanadium. The pyrolysis and the used atomization temperature are 1100 °C and 2700 °C, respectively. Employing such a procedure allows determining vanadium with a characteristic mass of 67 pg and a detection limit about 0.44 µg/L. The calibration graph is linear ranging at 40-120 µg/L with a correlation coefficient of 0.9980. The relative standard deviation (RSD%) is ranged between (0.83-6.13). The procedure accuracy is verified by determining vanadium in a newly prepared standard solution as unknown concentration. Finally, the range of vanadium amount in natural gas was supposed to range between 5-10 ng/L.

88

Key Words: Determination of Vanadium, Adsorption Collection Medium, GFAAS, Chemical Modifiers.

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Introduction

Vanadium is one of the important metals that received extensive attention for determining it in natural gas and crude oil. It is the most abundant metal found in petroleum. A careful evaluation has been applied to it for reducing problems during the process of industrial production due to being a catalyst poisoning and causing corrosion [1]. Vanadium in trace amount at (µ/L) levels represents an essential element for normal cell growth, but it can be toxic when existing in higher concentration [2]. The threshold limit values (TLV) reported are 0.5 mg/ m³ of air. The amount of vanadium above the TLV value is reported to cause dangerous diseases. Therefore, the determination of vanadium in environmental and biological samples is highly desirable [3]. The vanadium

concentration in natural gas is proposed to be in (ng/liter). It is not possible to collect and detect the trace element in natural gas because of limits related to sampling and methods of detection [4]. When carrying out the evaluation of ecological geochemistry for the important fields of natural gas, researchers applied adsorption collection to geo-gas survey originally for collecting the trace elements in natural gas. Hence, vanadium was revealed successfully as a trace element [5].

A review recently published has presented various methods for determining vanadium in products of petroleum and crude oil, including:

1. Inductively coupled plasma (ICP).
2. Optical emission spectrometry [6].

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3. ICP mass spectrometry [7].
4. X-ray fluorescence spectroscopy [8].
5. High-performance liquid chromatography with UV detection [9].

The graphite furnace atomic absorption technique, which has many advantages compared to other techniques, was employed. The outcomes obtained from a simple dilution with acidic medium-solvent and ashing were identical [10][11]. In a case where metal concentration is stable in sample and solutions of calibration, a serious problem might occur under this condition [12][13]. Utilization of modifiers has become a crucial part of electrothermal atomic absorption spectrometry (ETAAS). Modifiers have been used basically for having better control of conditions in ETAAS. When presented for the first time, a modifier was utilized for binding the analyte element (physically or chemically) in a form where high enough temperatures of pyrolysis can be employed for removing the matrix bulk by volatilization or decomposition before atomizing the analyte element ⁽¹⁴⁾. It is worth mentioning that this procedure is still used at present.

The remainder of this article is structured as follows. Section 2 presents the experimental parts. The results are discussed in Section 3. Finally, Section 4 concludes the paper.

Experimental Part

Apparatus

All measurements in this work were conducted

Table 1. The temperature of the graphite furnace for determining vanadium.

Step	Temp (°C)	Time (s)	Flow (L/min)	Gas Type	Read	Signal Storage
Dry	85	5	3	Normal	No	No
	95	25	3	Normal	No	No
	120	10	3	Normal	No	No
pyrolysis	1200	5	3	Normal	No	No
	1200	1.7	3	Normal	No	No
	1200	2	3	Normal	No	No
Cooling	200	8.8	3	Normal	No	Yes
	200	2	0	Normal	Yes	Yes
atomization	2700	1.2	0	Normal	Yes	Yes
	2700	2	0	Normal	Yes	Yes
	2700	2	3	Normal	No	Yes

Reagents

Throughout this study, we used analytical grade reagents. Distilled deionized water (DDW) with a specific resistivity of 0.07 μS/cm, from Milli-Q

using Varian AA240FS graphite furnace atomic absorption spectrometer (Mulgrave, Australia) equipped with a Varian GTA120 Atomizer unit and Varian programmable sample dispenser PSD 120 auto sampler was used for the introduction of solutions. Halo cathode lamp for vanadium furnished by Varian was utilized as a source of radiation with 20 mA current. With a spectral bandwidth of 0.2 nm, the basic analytical line at 318.4 nm was applied to all determinations. Deuterium lamp was used as background correction. All experiments were conducted using the pyrolytically coated graphite tube without platform (partition tube coated-GTA made in Germany). 99.999% of Argon was employed as a purge gas with the flow rate of 3 L/min during all stages except for atomization, where the flow was stopped. Peak height was employed entirely for evaluating and quantifying the signal. The optimized temperature program of graphite furnace applied to all determinations is shown in Table 1. If the chemical modifier is used, the solution of modifier is presented first. The dry steps of temperature program were implemented for drying and forming the modifier. After that, the program was stopped to allow cooling the furnace before presenting the sample. Then, the implementation of the entire program of temperature was done. The system was controlled by Spectra Atomic absorption software program from Agilent Technologies installed on windows XP operating system.

water purification system (TKA smart 2 pure, made in Germany) was utilized for preparing the standards. All glasses ware and containers were soaked in 10% of nitric acid for at least 24h. Then, they were washed three times using DDW before being utilized. The preparation of aqua stock



solution of vanadium (1000 mg/L) was based on ammonium mono-vanadate in 0.5 mol/L nitric acid (Density = 1.01g/cm³). The preparation of functioning standards was done by successive dilution of the stock solution with DDW. Finally, Table 2 illustrates chemical modifiers.

Table 2. Details of chemical modifiers.

Matrix modifier	Concentration	Dissolved in	Manufacturer
Palladium as Pd(NO ₃) ₂ ·2H ₂ O	1000 ppm, 3000 ppm	5M HNO ₃	BDH
Magnesium nitrate Mg(NO ₃) ₂ ·6H ₂ O	2000 ppm	0.6M HNO ₃	Merck
Palladium/magnesium nitrate	3000ppm Pd/2000ppm Mg(NO ₃) ₂	5M HNO ₃	BDH /Merck
L-(+)-ascorbic acid powder	10000 ppm	Deionized water	Merck

Preliminary analysis of the detection result of trace element in natural gas

Figure 1 shows the schematic diagram of the collection installation of natural gas. It was installed in one of the feed gas point (natural gas) in production unit related to North gas company, Kirkuk city, Iraq. It has 406 psi pressure of natural gas separated from all condensate associated with natural gas. The system consists of a 1200 psi regulator to control the high pressure of natural gas. It is supported by Millipore filter to prevent coarse particles passing through the regulator followed by flow meter that controls the flow rate of gas within 1.5 L/min through the adsorption liquid (3% nitric acid). Diluted nitric acid 3% was prepared from concentrated nitric acid (Wagtach, 1.42 gm/L) with ultrapure water. Nitric acid was favored over other liquid media as it collects the elements well, is easy to purify and an ideal medium for analysis directly by GFAAS, making the detection process more reliable and avoiding the annoying digestion used earlier for solid collector [15][16]. One liter of nitric acid was distributed to three glass scrubbers so that it could capture as much as possible amount of vanadium particles. After the scrubbers, there was a second flow meter supported with a counter to calculate the whole volume of natural gas in liter passing through the system. The total quantity was 1200 liter of natural

gas through the liquid medium. Each unit was linked with a clear polyvinyl laboratory tube.

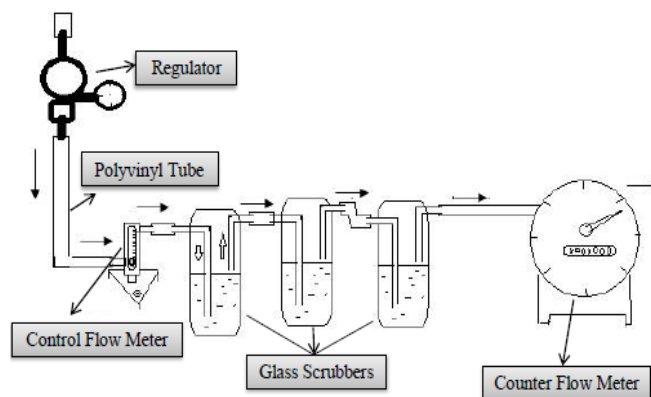


Figure 1. Schematic diagram of the collection installation of natural gas.

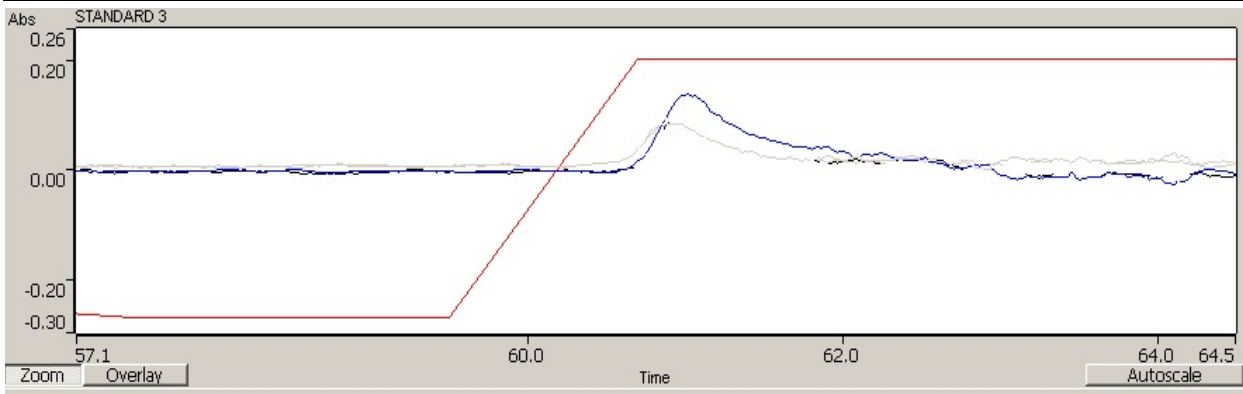
Chemical Modifiers

Three kinds of chemical modifiers were used to choose the maximum permissible pyrolysis temperature. Magnesium nitrate is considered a chemical modifier for vanadium [17][18]. This modifier was employed with a volume equal to that of the sample, namely, 15 µl of magnesium nitrate with 15 µL of the sample. 2ml of ascorbic acid (10g/L) was added to 10ml of the sample as a reduced agent. By using these two modifiers, the results were not desirable as magnesium nitrate shows relatively low signals compared to Palladium.

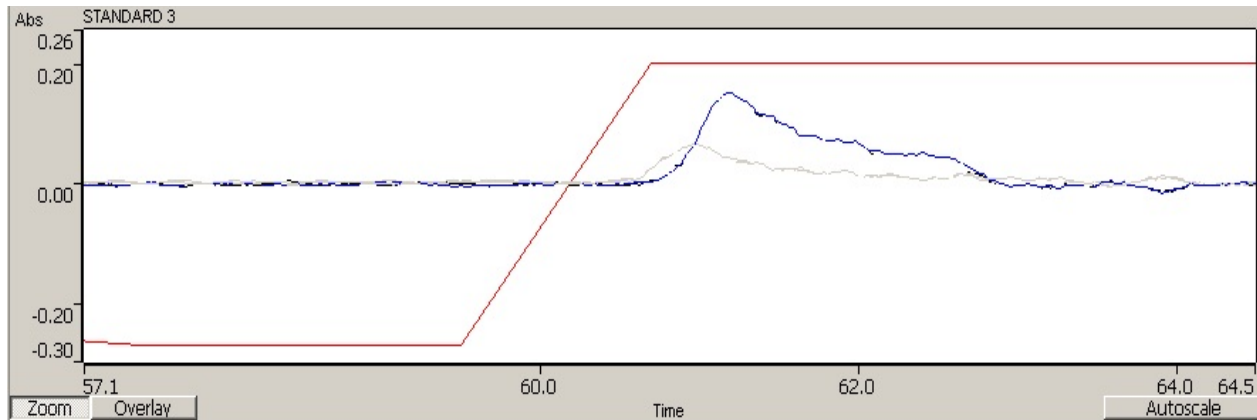
Palladium is also considered a chemical modifier for vanadium [19-21] due to its successful application to a large number of elements. 15 µL of the Palladium solution was dispensed into the graphite tub, followed by 15µL of the vanadium solution. The calibration curve was constructed using a standard solution containing (40, 60, 80,100 and 120 ppb) of vanadium stock solution.

By using the mixture containing equal volumes of both palladium modifier 3000 µg/L and magnesium nitrate 2000 µg/L, the results were reasonable, and the mixture modifier solution could be reliable. Figure 2 shows the signal graphics for 120 ppb vanadium stock solution when using modifier in the three states mentioned earlier.

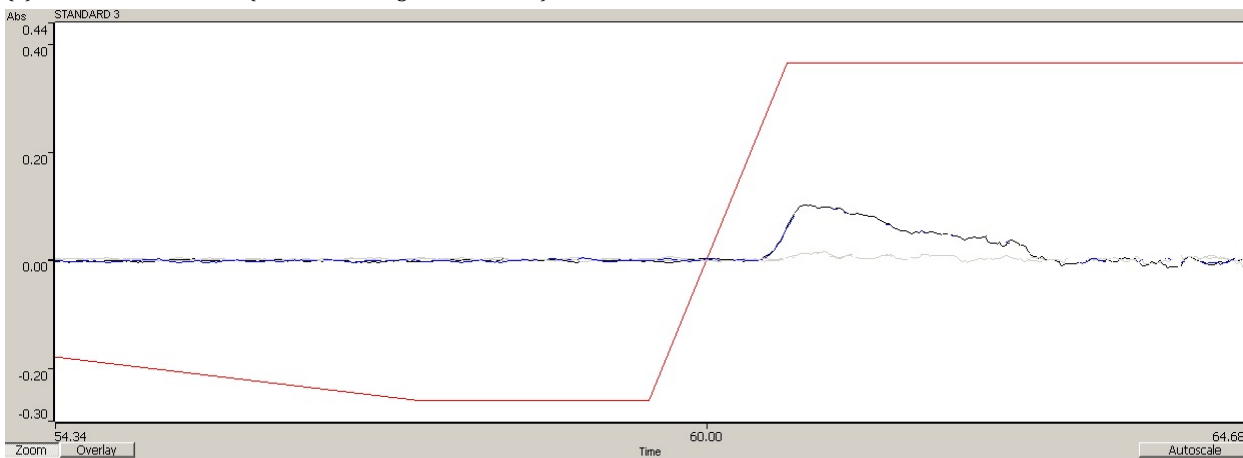




(a) With Palladium modifier.



(b) With mixture modifier (Palladium + Magnesium nitrate).



(c) With Magnesium nitrate.

Figure 2. Signal graphic for 120 ppb vanadium with different modifiers.

Results and Discussion

1-Pyrolysis and Atomization Temperature

The pyrolysis and atomization temperature curves are illustrated in Figure 3. They were constructed by using 15 μ L vanadium standard solution 80 ppb and palladium nitrate as modifier solution. In the

case where the chemical modifier is absent, more than 70% of the total concentration could be lost. This was examined by injecting 80 ppb vanadium standard solution, and the instrument reading was just 25 ppb.



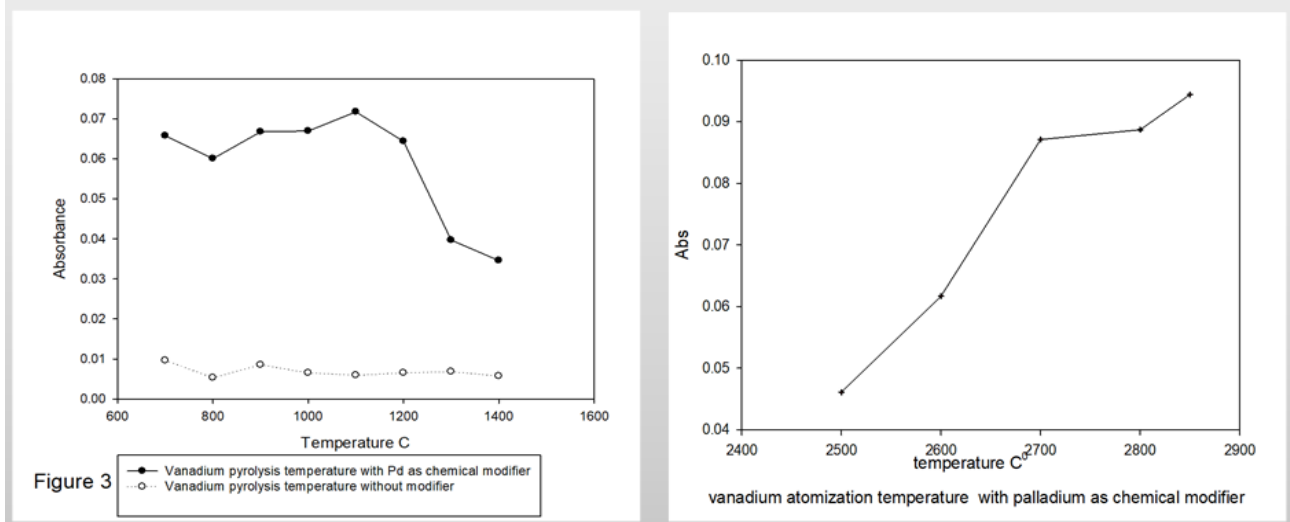


Figure 3. Vanadium atomization with palladium as a chemical modifier

Figure of Merits

A linear calibration graph was obtained (Figure 4) for concentrations (40-120) µg/L of vanadium stock solution with the existence of Pd modifier. The detection limit of vanadium was found to be about 0.44µg/L. The calibration graph has a correlation coefficient of 0.9985 and an RSD% between (0.83-6.13) (Table 3).

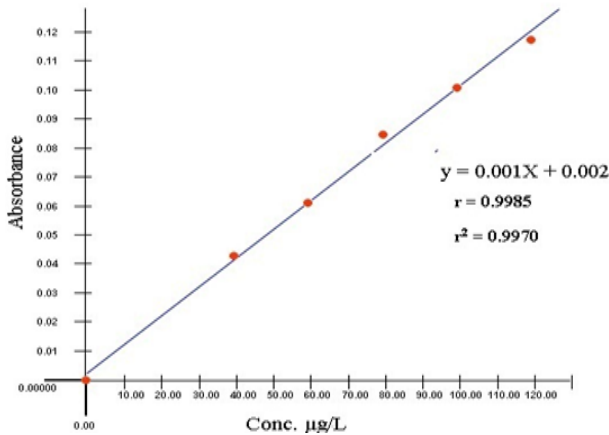


Figure 4. Calibration curve for vanadium.

Table 3. Analytical characteristics of vanadium calibrant solution for the proposed method.

Species	V
Calibration	Absorbance = 0.001(±0.000028) [V] + 0.002 (±0.0022)
Linear analytical range (µg/l)	0.44-120 µg/l
RSD% N=3	(0.83-6.13)%
LOD (µg/l)	0.44

[V] Expressed in µg/l; N number of measurements
 The accuracy and precision of the used method are listed in Table 4. Besides, Table 5 summarizes the analytical condition for vanadium determination.

The correlation coefficient (R), characteristic mass in pigogram obtained for vanadium using the standard solution in 80ppb concentration and characteristic concentration in µg/L for all tests that deal with previous chemical modifiers are given in Table 6. The precision is expressed as the relative standard deviation of three replicate determinations of the stock solution. The prepared sample contained 7.50 ng/L of vanadium as average.

Table 4. Accuracy and precision of the method.

Conc. ppb	Abs in 3 replicates	RSD%	Erel. (%)	Recovery (%)
40	0.0423 0.0452 0.0400	6.13	7.00	107
60	0.0582 0.0610 0.0633	4.20	2.21	102.2
80	0.0840 0.0833 0.0847	0.83	5.6	105.6
100	0.0995 0.0986 0.1020	1.76	0.93	100.93
120	0.1172 0.1160 0.1152	0.87	-2.5	97.5

t- calculated at confidence level 95% = 1.23
 t- tabulated at confidence level 95% = 4.3

Table 5. Analytical condition for vanadium determination

Calibration Mode:	Concentration
Measurement Mode	Peak Height
Wavelength	318.5 nm
Slit Width	0.2 nm
Lamp Current	20.0 mA
Background Correction	BC On
Calibration Algorithm	Linear Origin



Table 6. The analytical figure of merits for determination of V in natural gas.

Analyte	Modifier	R	m° (pg)	Characteristic concentration µg/L
Vanadium stock solution	Pd + ascorbic acid	0.9980	67.6	4.429
Vanadium stock solution	Mg(NO ₃) ₂ +ascorbic acid	0.9991	87	5.433
Vanadium stock solution	Pd+ Mg(NO ₃) ₂ +ascorbic acid	0.9996	57	0.924

m°: Characteristic mass

The absorbance reading for 15ul sample was prepared by passing 1200 liter of natural gas in 1 liter of dilute nitric acid and with the use of Pd/ascorbic acid. The concentration for every signal is illustrated in Table 6. The amount of vanadium supposed to be 3% of nitric acid was approximately 2µg/L.

- 1. Characteristic Concentration:** it refers to the element concentration in milligrams for each liter (mg/L) necessary for producing a 1% absorption (0.0044 absorbance) signal.

$$\text{Char Conc. (mg/L)} = \frac{\text{Conc. of Std. (mg/L)} \times 0.0044}{\text{Measured absorbance}}$$

- 2. Characteristic Mass (m):** mass is in picogram of the analyte element that produces an integrated absorbance of 0.0044 signal. It represents a theoretical calculation of sensitivity.

Table 7. Instrument readings and concentration for the samples injected.

Concentration µg/L	Abs
8.00	0.0050
8.96	0.0088
12.1	0.0121
14.3	0.0140

So, the amount of vanadium in natural gas after abstracting the V amount in nitric acid is shown in Table 8.

Table 8. Vanadium concentration

Vanadium concentration in ng/L	
Maximum	10.00
Minimum	5.00
Average	7.50

Conclusion

By using graphite furnace atomic absorption spectrometry with deuterium lamp background, the correction was possible for determining the concentration of nanoparticle of vanadium in natural gas feeds found at the northern gas company, Kirkuk, Iraq. Due to considering vanadium as one of refractor elements that make refractory carbides in the graphite furnace, the pyrolytic coated tube was used to overcome this

problem. Moreover, the appropriate chemical modifier was utilized for more sensitivity and to suppress interferences. The study also compared several kinds of chemical modifiers to have appropriate signals for the target.

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