BIOLOGY, MEDICINE, & NATURAL PRODUCT CHEMISTRY ISSN 2089-6514 (paper)
Volume 14, Number 2, October 2025 | Pages: 725-729 | DOI: 10.14421/biomedich.2025.142.725-729 ISSN 2540-9328 (online)

Sensitive and Selective Chromatographic Method to Determine Vanadium in Commercial Phosphoric Acid

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Manuscript received: 27 April, 2025. Revision accepted: 07 August, 2025. Published: 01 October, 2025.

Abstract

The spectrophotometric method based on N-Benzoyl-N-phenylhydroxylamine was executed for ascertaining vanadium in environmental samples. high performance liquid chromatography (HPLC) system equipped with a C18 RP column was used to determine vanadium in wet phosphoric acid and phosphate samples. A rapid pre-column response of vanadium with 5-Br-PADAP was used without prior separation or adding any masking agents. The results showed that, the chelates were detected after being injected through the column by UV- Vis detector at wavelength 585 nm. The molar absorptivity is 5.5 x10^4 and the retention time is 6.3 minutes. The sensitivity of this reagent is equal to twice as high as the use of (PAR) reagent. The RSD was 1.7% for weak concentrations to 0.22% for high concentrations and the relative error (RE) was between 3.21% and 1.07%. In conclusion the method of the currently study was found highly sensitive and selective and the results show a good accuracy and precision.

Keywords: HPLC system; Phosphoric acid; Spectrophotometric method; Vanadium.

INTRODUCTION

The extraction-spectrophotometric method is utilized with N-Benzoyl-N-phenylhydroxylamine was adopted to evaluate vanadium in environmental samples (Agarwal et al., 1990). Methods based on using of 4-(2-pyridylazo) resorcinol (PAR) which was generally was applied to determine vanadium in biological samples (Bag et al.,1982; Agnihotri et al., 1999), sewage (Buchberger, 2000), silicate rocks (Chakrabarti,1995), petroleum (Fasanmade, 1994) and titanium alloys (Fukasawa et al.,1981; Filik et al., 2008).

Vanadium traces in aluminum samples could be determined with a good accuracy. Vanadium was first isolated by organic solvent extraction and then, the absorption of the complex was measured at wavelength 585 nm (Geană, et al., 2019). Many methods that utilize vanadium chelating complexes have been used to determine vanadium such as pyrogallol for soils (George et al., 1990), Hydroxamic acid for steel and rocks (Guangyu et al., 2005; Gustafsson et al., 2019), Crown hydroxamic acid for body fluids (Iki et al., 2001) Phenylfluorone for steel alloys (Jamaluddin et al., 1999), 1,5-diphenylcarbazide for environmental samples and 6-chloro-3-hydroxy-7-methyl-2-(2-thienyl)-4H-chromen-4-1 for flue dust and waste water samples (Krasiejko et al., 1986; Kubinyi, 1995). These extraction-spectrophotometric methods with different chelating agents were accurate, but they lack selectivity and need prior extraction and separation or masking agent which must be added. Liquid chromatography has an important role in recent years due its use for separation and analysis of various metals such as Mn, Cd, Co, Ni, Zn, and Pb using post-column reaction and UV-V detector at different wavelengths, but they did not mention vanadium in their applications (Matsumiya et al., 2004; Michalski, 2018).

Sulfonylcalix[4]arenetetrasulfonate was used and checked for ultra-trace determination of different cations in river and tap water samples by HPLC with UV-Vis detector in an acetic buffer solution (pH4.7) (Pyrzyńska, 2005; Srivastav et al.,1996). Reversed phase liquid chromatography was developed to simultaneously determine of vanadium, copper and cobalt founding in electroplating baths (Vale et al., 2007).

This paper purposes a developed method to determine vanadium in phosphate industrial connecting parts by high performance liquid chromatography (HPLC) using the rapid reaction of vanadium with 5-Br-PADAP as a chelating agent in the pre-column system without prior separation or adding masking agents.

MATERIALS AND METHODS

Commercial wet phosphoric acid samples with 27% wt P_2O_5 and 1.26 g/cm^3 and other samples were supplied by the General Fertilizer Company (GFC) Homs /Syria. Methanol, acetonitrile, absolute ethanol and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) HPLC-grade, his formula as in Fig. 1. All other chemicals employed were of analytical grade.

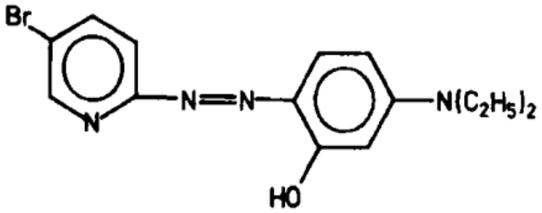

Figure 1. The structural formula of 5-Br-PADAP.

Sample preparation

1 ml of 0.1M sodium acetate, 1 ml of 1% sodium dodecyl sulfate, 1 ml of 6 mM of (5-Br-PADAP) and three drops of 1% hydrogen peroxide were added to the sample and standard solutions.

Procedures and apparatus

A HPLC system connected to the C18 RP column from Shimadzu/Japan was used. The eluent solution consists of methanol, acetonitrile and water with a ratio of 84:12:4 respectively adjusted to pH=5.5 and degassed before use. As a comparison method the samples were diluted and analyzed by atomic absorption spectroscopy (AAS / Varian). The relative standard deviation (RSD%) and relative error (RE%) calculated as below:

$$RSD\% = (100 * SD)/X$$
$$RE\% = (X - X_0) * 100/X_0$$

Where:
SD : standard deviation.
X : mean value.
X_0 : reference value.

RESULTS AND DISCUSSION

Standard calibration curve:

To create standard calibration curve standard solutions, from one to 25 ppm in 40% pure phosphoric acid were pretreated as described in the experimental and injected through the column. The results are plotted in Fig. 2. in the form of the area versus concentration. The relationship is represented by straight line over studied range of concentration. The correlation factor is R= 0.9998. The correlation is represented by straight line equation: Area =188290 C + 3E+06

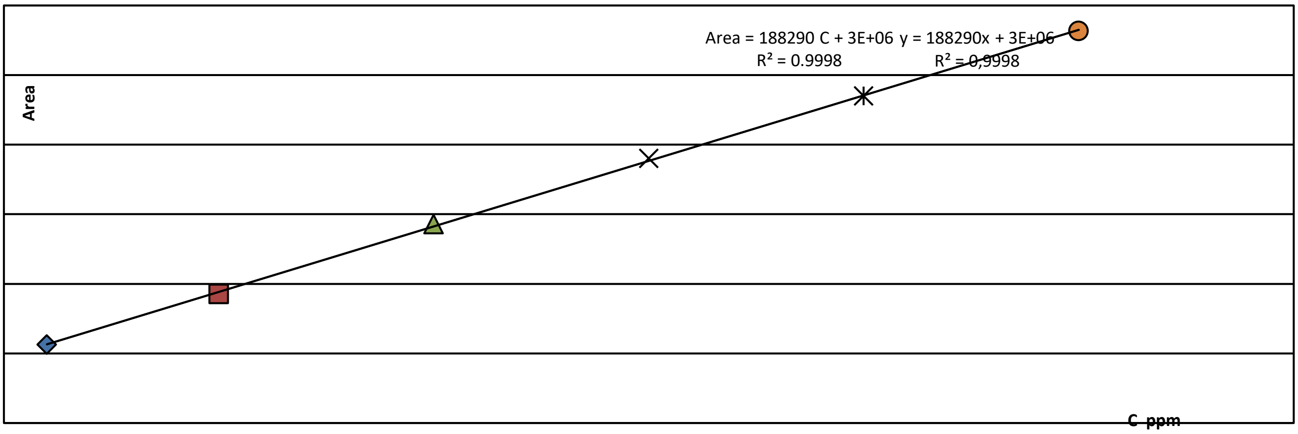

Figure 2. Standard calibration curve.

To determine the relative standard deviation (RSD), four samples of 40% pure phosphoric acid with predetermined concentration of vanadium (10- 25- 50- 100 ppm) were taken. Each sample was measured five times. The results are presented in Table 1. The RSD was of the order of 1.7 % for weak concentrations to 0.22% for high concentrations. The relative error (RE) was between 3.21% and 1.07%. This indicates that it is possible to use the standard calibration curve to determine vanadium concentration in phosphate derivative samples with an acceptable error. This result was similar to Filik et al. (2008).

Table 1. Evaluations of relative standard deviation.

Reference value [V] ppm	Measured value [V] ppm	X ± SD (ppm)	RE (%)	RSD (%)
10	9.78 10.43 10.51 9.88 10.25	10.17 ± 0.33	1.7	3.21
25	25.67 25.54 24.77 25.89 24.23	25.22 ± 0.69	0.88	2.76
50	49.21 50.76 49.51 50.93 50.34	50.15 ± 0.76	0.3	1.52
100	100.98 99.21 100.76 98.91 101.25	100.23 ± 1.08	0.22	1.07

The samples were also analyzed using the atomic absorption spectroscopy method for comparison. The results are presented in Table 2 showing a close approximation between the results of both methods. These results were in agreement with others (Krasiejko et al., 1986; Chakrabarti, 1995; Iki et al., 2001). An Attempt was made to inject samples containing metals such as Zn, Cd, Cr, Fe, Cu, Mn, Co, and U without vanadium (Pyrzyńska, 2005; Wen-yan et al., 2018). No peaks were obtained for chelates for these metals with 5-Br-PADAP because the chelates were unstable in the chromatographic system used in this study and they were decomposed in the mobile phase (Zaki, et al.,1991).

Table 2: Vanadium concentrations in phosphate industrial derivatives.

Sample	HPLC value (ppm)	Spectrometric value (ppm)
Strong green phosphoric acid	123.7	125
Weak green phosphoric acid	86.5	88.2
Phosphate	110.8	111.5

Determination of vanadium in phosphate industrial derivatives

Phosphate and green phosphoric acid samples were pretreated as described in the experiment and injected through the column. A typical chromatogram for these samples has two sharp and resolved peaks (Fig. 3). This result was in the same line with Zhao and Fu (Zhao et al., 1991). The first peak showed at retention time of 6.3 minutes which indicates to vanadium chelate and another peak appeared at retention time of 10.3 minutes which indicates 5-Br-PADAP reagent (Zhao et al.,1991).

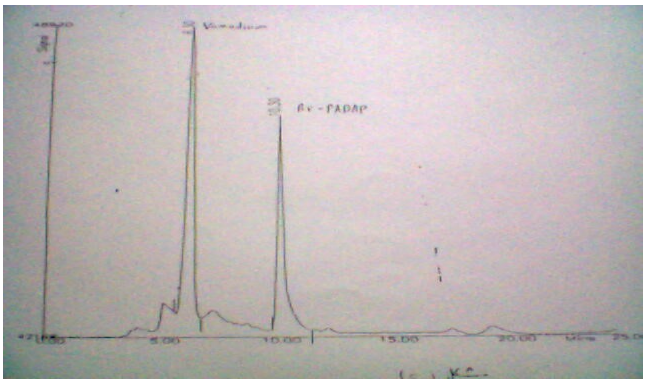

Figure 3. Typical sample chromatogram.

CONCLUSIONS

The proposal method was applied for a wide range of concentrations of phosphate industrial derivatives and different aqueous media without any need to use masking agent or prior separation of metal ions. The method doesn't consume rather expensive post column reagents like the other method but the sample needs only simple pretreatment. Clearly, proposed method is practical and selective for vanadium, and the sensitivity is double as high as in the use of (PAR) reagents. The results show good accuracy and high precision.

Acknowledgment: The authors are indebted to Hadhramout University for their valuable help, also would like to express their thanks and appreciation to General Fertilizer Company (GFC) for supplying catalyst samples.

Competing Interests: All authors state that there are no competing interests.

REFERENCES

Agarwal C., M. Deb & Mishra, R.(1990). Sensitive spectrophotometric determination of vanadium in environmental samples at PPB levels. Anal. Lett., 23: 2063-2075. DOI: 10.1080/00032719008052550.

Agnihotri, N., R. Das & Mehta, J. (1999). A Highly sensitive and selective spectrophotometric determination of vanadium (V) using 6-Chloro-3-hydroxy-7-methyl-2- (2-thienyl)-4H-chromen-4-one. Analytical Sciences, 15: 1261-1264. https://doi.org/10.2116/analsci.15.1261.

Bag, S., A. Chatterjee, A. Chakrabarti & Chakraborty, P. (1982). Extraction of vanadium(V) chelates with N-benzohydroxamic acid (BHA) and ammonium thiocyanate and its application in steel and rock analyses. Talanta, 29: 526-528. DOI: 10.1016/0039-9140(82)80209-9.

Buchberger, W. (2000). Detection techniques in ion analysis: What are our choices?. Journal of chromatography A. 884: 3-22. DOI: 10.1016/S0021-9673(00)00283-1

Chakrabarti, A. (1995). Selective extraction and photometric determination of trace vanadium with cinnamohydroxamic acid in MIBK and its application to steel and rock ore analysis. Talanta, 42: 1279-1283. DOI: 10.1016/0039-9140(95)01574-U.

Fasanmade, A. (1994). Ultraviolet spectral features affecting computer-aided multiwavelength quantitation of multicomponent mixtures using phenothiazines as model. Analytical Letters, 27: 1955-1977. DOI: 10.1080/00032719408002644.

Filik, H., Y. Zeynep & Reşat, A. (2008). Selective determination of total vanadium in water samples by cloud point extraction of its ternary complex. Analytica chimica acta, 620: 27-33. DOI: 10.1016/j.aca.2008.05.024.

Fukasawa, T., S. Miyata & Matsunaga, S. (1981). Rapid and sensitive determination of total vanadium inairborne particulates by an extraction-spectrometric method with N-benzoyl-N-phenylhydroxylamine. Analytica Chimica Acta, 130: 353-360. DOI:10.1016/S0003-2670(01)93013-2.

Geană, E., C. Ciucure, C. Apetrei & Artem, V. (2019). Application of Spectroscopic UV-Vis and FT-IR Screening Techniques Coupled with Multivariate Statistical Analysis for Red Wine Authentication: Varietal and Vintage Year Discrimination. Molecules, 24: 4166; DOI: 10.3390/molecules24224166.

George, W.O. & Willis, H. (1990). Computer methods in UV-VIS and IR spectroscopy. Royal Society of Chemistry, Cambridge. ISBN-10: 085186323X.

Guangyu, Y., H. Qiufen, H. Zhangjie & Jiayuan, Y. (2005). Study on the determination of lead, cadmium, mercury, nickel and zinc by a rapid column high-performance liquid chromatography, J. Braz. Chem. Soc., 6:1154-1159. DOI: 10.1590/S0103-50532005000700011

Gustafsson, J. (2019). Vanadium geochemistry in the biogeosphere - speciation, solid-solution interactions, and ecotoxicity, Applied Geochemistry. 102: 1-25. DOI: 10.1016/j.apgeochem.2018.12.027

Iki, N., T. Horiuchi, H. Oka, K. Koyama, N. Morohashi, C. Kabuto & Miyano, S. (2001). Energy transfer luminescence of Tb3+ ion complexed with calix[4]arenetetrasulfonate and the thia and sulfonyl analogue. The effect of bridging groups. Journal of the Chemical Society-Perkin Transactions, 2. 2219-2225. DOI: 10.1039/b009151k

Jamaluddin, M. & Banoo, S. (1999). Spectrophotometric method for determination of vanadium and its application to industrial, environmental, biological and soil samples. Talanta, 48: 1085. 1085-1094. DOI: 10.1016/s0039-9140(98)00329-4.

Krasiejko, M. & Zygmunt, M. (1986). Sensitive spectrophotometric determination of vanadium with 2-(5-bromo-2-pyridylazo)-5-diethyl-aminophenol (5-Br-PADAP). Mikrochim Acta, 90: 89-94. https://doi.org/10.1007/BF01196823

Kubinyi H. (1995). Spectrophotometric analysis of multicomponent systems. Trends in Analytical Chemistry, 14: 199-201. https://doi.org/10.1016/0165-9936(95)91370-8

Matsumiya, H., N. Iki & Miyano, S. (2004). Sulfonylcalix[4]arenetetrasulfonate as pre-column chelating reagent for selective determination of aluminum(III), iron(III), and titanium (IV) by ion-pair reversed-phase high-performance liquid chromatography with spectrophotometric detection. Talanta, 62: 337-342. DOI: 10.1016/j.talanta.2003.08.001.

Michalski, R. (2018). Ion chromatography applications in wastewater analysis. Separations. 5:16-27. DOI: 10.3390/separations5010016

Pyrzyńska, K. (2005). Recent Developments in spectrophotometric methods for determination of vanadium. Microchimica Acta, 149: 159-164. DOI: 10.1007/s00604-004-0304-5.

Srivastav, P. & Agrawal, Y. (1996). Solvent extraction, spectrophotometric and inductively coupled plasma atomic emission spectroscopic (ICP-AES) determination of vanadium (V) with crown hydroxamic acid. Analusis: 24, 13-16. ISSN 0365-4877

Vale, M., F. Amorim, B. Welz, A. Costa, F. Lepri & Ferreira, S. (2007). Determination of vanadium in petroleum and petroleum products using atomic spectrometric techniques. Talanta,72: 349-359. DOI: 10.1016/j.talanta.2006.12.015.

Wen-yan, H., W. Kun-peng & Jin-yan, Y. (2018). Spectrophotometric methods for determination of vanadium: a review. Toxicological & Environmental Chemistry, 100:1, 20-31, DOI: 10.1080/02772248.2018.1428325

Zaki, M., S. Abuo-Zeid & Tarek, M. (1991). Determination of vanadium in steels using phenylfluorone and cetylpyridinium bromide, Journal of Chemical Technology & Biotechnology. 51: 507-513. DOI: 10.1002/jctb.280510408

Zhao, Y. & Fu, C. (1991). Liquid chromatographic behaviour of chelates of vanadium (V), copper (II), cobalt (III) and chromium (III) with 2-(3,5-dibromo-2-pyridylazo) diethylaminophenol. Analyst, 116: 621.