Spectrophotometric Determination of Vanadium (V) in Different Rocks and some Vanadium Ores using 5-Bromo-2-(2-Pyridylazo)-5-Diethylaminophenol

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Summary: A selective and sensitive method for direct spectrophotometric determination of trace amounts of Vanadium (V) in several types of geological samples and industrial wastes is proposed. It depends on the formation of an orange-red colored complex between V(V) and 5-Bromo-2-(2-Pyridylazo)-5-Diethylaminophenol (5-Br-PADAP) in presence of hydrogen peroxide in sulfuric acid medium at pH (0.75-1.0). The formed complex shows maximum absorbance at 595 nm with molar absorptivity 6.12×10^4 $l\,mol^{-1}cm^{-1}$ and obeys Beer's law in V(V) concentration range 0.005-1.25 $\mu g\ ml^{-1}$. The parameters affecting the sensitivity are optimized and the effects of the foreign ions associated with each type of each sample are investigated. The effects of water miscible alcohols and acetone on the colorimetric determination of V(V) are studied and described. The absorbance of V(V)-Br-PADAP-H_2O_2 is enhanced by 30-38% using these solvents. The suggested method is successfully applied for determination of V(V) in reference standard silicate and phosphate rocks with high precision and accuracy (R.S.D $\leq 0.32\%$). The concentrations of V(V) obtained by the suggested method are in good agreement with their certified values.

Introduction

Vanadium is widely distributed in earth's crust. It is emitted into the environment through the combustion of fossil fuels. It is present in various amounts in different rocks and soils. Vanadium is an essential element of geological interest due to its variations and its abundance ratio to some other trace elements[1]. It has different industrial applications especially in steel alloys and petrochemical industries. Vanadium is recognized as very dangerous pollutant and very toxic at higher concentrations[2]. Its toxicity is depend on its oxidation state[3]. Vanadium in trace amounts is an essential element for cell growth. Hence, its accurate determination is receiving increasing attention.

A variety of methods has been used for determination of V(V). These include fluorometry[4,5], voltammetry[6], potentiometry[7], gas chromatography[8], neutron activation analysis[9,10], X-ray fluorescence

spectroscopy[11], emission spectro-scopy[12], atomic absorption spectroscopy[13] and colorimetry[14,15]. Some of these methods need special requirements few other having poor sensitivity due to matrix effects. ICP-AES[16] is also used for determination of V(V) with high sensitivity and high sample throughput; however, the cost may limit its use for routine analysis.

Spectrophotometric methods for V(V) analysis are more suited in routine analysis. However, the direct determination of V(V) in rocks is rarely possible because inadequate specificity, separation procedures, or using masking agents to overcome interferences before final spectrophotometric determination are needed[17]. Number of reagents have been introduced for spectrophotometric determination of V(V) in rocks. Among them are phosphotungestate[18], PAR[19], N-benzoyl-o-tolylhydroxylamine[20], N-phenyl-benzohydroxamic acid[21] and 2-(5-nitro-2-pyridyl-azo)-5-dimethylaminophenol[22].

Gusev and Shalamova[23] have investigated 2-(2-pyridylazo)-5-diethyl aminophenol (PADAP) and its bromo derivatives for spectrophotometric determination of V(V), but once more several elements are interfere. Me-bromo-PADAP has been used for determination of V(V) in rock samples after separation with chloroform. 5-Br-PADAP has been reported for the determination of some elements.[24] Previously, determination of V(V) using ICP-ES[25], ion chromatography[26] and adsorption voltammetry[26] were reported. The present study aims to develop fast, simple, cost-effective and low interference effects method for direct determination of V(V). It discusses a new application of 5-Br-PADAP reagent for direct determination of V(V) in rock solutions and some ore materials.

Experimental

Chemicals and reagents

Vanadium (V) stock standard solution, 1000 μg l^{-1} is prepared by dissolving 2.2966 g of ammonium metavanadate (99.9% Merck) in a slight excess NaOH. The solution is diluted to 1000 ml with double distilled water;

working standard solutions are obtained by appropriate dilutions. 1.431×10^{-3} M 5-Br-PADAP; (99% Aldrich) solution is prepared by dissolving 0.05 g reagent in pure ethanol in 100 ml measuring flask and stored in amber bottle. The solution is stable for several months. 3% v/v H_2O_2 is prepared by dilution from the 30 % v/v H_2O_2 (Adwic Co. Egypt) with double distilled water. Stock solutions of interfering ions are prepared by dissolving appropriate amounts of analytical grade salts in double distilled water.

Apparatus

UV/VIS-100(UNICAM) double-beam spectrophotometer using quartz cells with 1.00 cm optical path length is used. pH meter (CG 820) is used for pH measurements.

Procedures

Sample preparation:

A 0.25 g of very fine powdered (200 mesh) rock or ore sample in a nickel crucible is fused with 2 g sodium peroxide and sodium hydroxide mixture for 20 minutes over bunzen flame. The obtained molten after cooling is re-dissolved with boiling water while stirring. After cooling, the solution is filtered into 100 ml measuring flask and completed up to the mark with double distilled water.

<div align="center">

Results and Discussion

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Optimum conditions for the color reaction.

Absorption spectra

Absorption spectra of 5-Br-PADAP dye, 0.25 µg ml^{-1} V(V) with 5-Br-PADAP only and in the presence of H_2O_2 in acidic medium are studied. The dye absorbed maximally at 595 nm. The formed complex between V(V) and 5-Br-PADAP solution without H_2O_2 absorbed at (λ_{max}) 595nm but the formed complex is not sensitive enough for determination of V(V) ($\varepsilon_{595nm}=7\times10^3$ l mol^{-1}cm^{-1}). The sensitivity of the complex is enhanced by addition H_2O_2 solution ($\varepsilon_{595nm} = 6.12\times10^4$ l mol^{-1} cm^{-1}), Fig.1

Fig. 1: Absorption spectra of the formed complexes
(a) V(V)-Br-PADAP, (b) V(V)-Br-PADAP-H_2O_2.
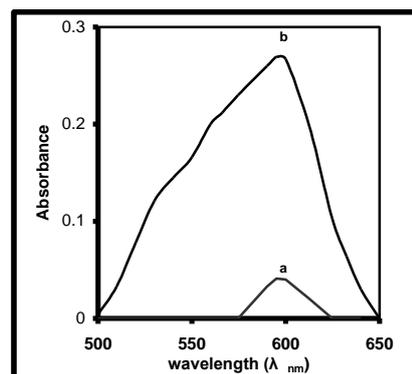
Effect of the acidity

An aliquot solutions containing 0.25 µg ml^{-1} V(V) are treated as in the recommended procedure except the pH is varied using sulfuric acid. It is found that the absorbance is highly dependent upon the pH of the solution. The maximum color development is obtained at pH range (0.75-1.0). The results are illustrated in Fig. 2.
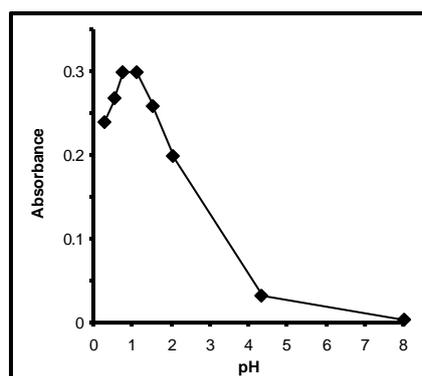

Fig. 2: Effect of pH on the color development of V(V)5-Br-PADAP-H_2O_2 complex.

The effect of acids (sulfuric, nitric and hydrochloric acid) on color intensity of the formed complex is studied. Results indicate that sulfuric acid the most reliable acid can be used in the preparation of sample solutions and pH adjustment. However, the absorbance is remarkably reduced by using nitric or hydrochloric acids, due to incomplete formation of complex. From the obtained results, we found that both type and concentration of acid have great influence on the complex formation.

Effect of hydrogen peroxide concentration

The influence of the presence of H_2O_2 on the developing of the color complex of 0.25 µg ml^{-1} V(V) with 5-Br-PADAP is investigated.
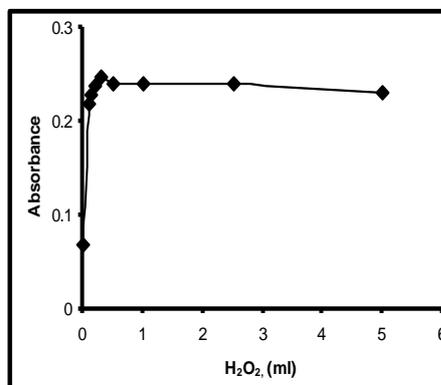

Fig. 3: Effect of H_2O_2 on V(V)-Br-PADAP-H_2O_2 complex

Maximum absorbance is obtained at 0.25 ml from 3% (v/v) H_2O_2 solution. Increasing amounts of H_2O_2 have no effect on the absorbance measured Fig. 3.

Effect of 5-Br-PADAP concentration.

The effect of varying concentrations of 5-Br-PADAP dye on the color intensity of (V)-Br-PADAP-H_2O_2 complex is studied Fig. 4. Maximum absorbance takes place at 0.5 ml of (1.431×10^{-3} M) 5-Br-PADAP solution. The molar ratio of V(V)-Br-PADAP-H_2O_2 ternary complex is established using the molar ratio and Job's methods and is found 1:1:1 V(V):5-Br-PADAP:H_2O_2.
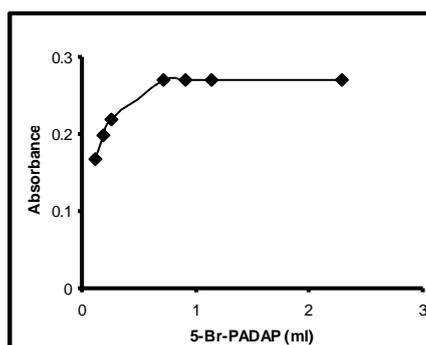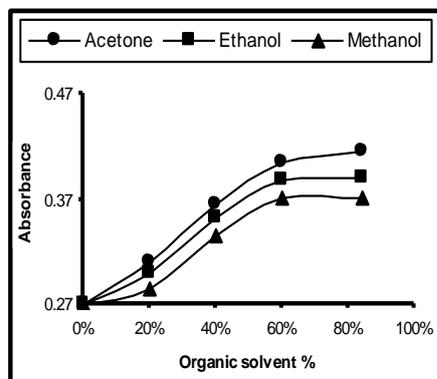

Fig.4: Effect of 5-Br-PADAP concentration on the color reaction

Effect of water miscible alcohols and acetone ratio.

The effect of organic solvents on the intensity of absorption spectra of V(V)-Br-PADAP-H_2O_2 complex is studied under the optimum conditions. Addition of organic solvents does not impart change in the maximum

wavelength absorption of the formed complexes; but it enhances the color intensity of the formed complex 30-38% more than in the aqueous medium based on type and polarity of the solvent used.

Fig.5: Effect of organic solvents ratio on the color development
of V(V)-Br-PADAP-H_2O_2 complex

Water miscible alcohols and acetone addition is used for determination low V(V) concentrations can not be detect in aqueous medium The color intensity is increased as in the respective order (acetone > ethanol > methanol > water). The best results are achieved with 60% organic solvent, and remain constant over this percent. The results are shown in Fig.5.

Calibration curve.

Straight-line calibration curve Fig.6 shows the applicability of Beer's law in the concentration range (0.005-1.25 µg ml^{-1}) V(V) in aqueous medium and (0.0005-1.25 µg ml^{-1}) in acetone medium. For testing the precision of the analytical procedure, two concentration levels of V(V) are chosen and three determinations are made at each level. The absorbance of each solution is measured at least 3 times and averaged. The calibration curves are linear and relative standard deviations (R.S.D) calculated is 0.32% in aqueous medium and 0.215% in acetone medium for 0.25 µg ml^{-1} of V(V).

Effect of interfering ions.

The effect of various cations and anions on the determination of V(V) is studied and the results are summarized in Table (1). Among of tested anions (sulfate, oxalate, acetate, etc…) these anions below $5.6×10^3$ fold have no

interference effect. Only the chloride anion up to 1.19×10^2 fold decreases the absorbance intensity. An excess of chloride ion in the medium is destroy the formed complexes. Mg^{2+}, Sc^{2+}, Cu^{2+}, and Ni^{2+} species up to 4.5×10^2 fold have a positive interference effect during V(V) determination, however, K^+ has negative interference action by the same ratio. Si^{4+}, Th^{4+}, Ba^{2+} and Al^{3+} ions up to 2.9×10^3 fold have little positive interference effects on the complex formation. Fe^{3+}, Fe^{2+} and Ca^{2+} ions up to 80 fold are increasing the absorbance of the formed complex. Li^+ and Co^{2+} ions up to 9 fold have a positive interfering action while TiO^{2+} ion up to 9 fold is bleach the formed colored complex. Mo^{VI}, Cr^{3+} and Ce^{4+} species up to 25 fold are enhance the color development of the formed complexes. Pb^{2+}, Na^+, Mn^{2+} and Zr^{4+} ions do not interfere.
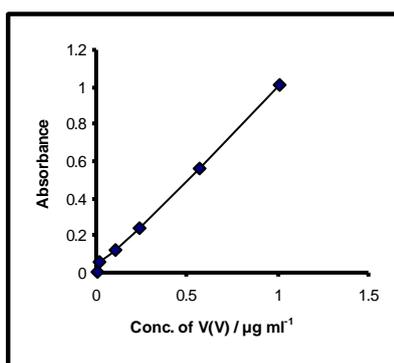

Fig.6: Calibration curve of V(V)-Br-PADAP-H_2O_2 complex

Using the alkaline dissolution method of the samples (as explained above) leads to removing the most cations that cause interfering effects during V(V) measurements.

Application.

The wide applicability of the method is tested by analyzing different international standard samples. The results obtained are accepted with the published values with high accuracy and precision Table (2).

Table 1: Effects of foreign ions on determination of 0.25 µg ml^{-1} V(V).

Foreign ions	Tolerance ratio (w ion/w V)
Si^{4+}, Th^{4+}, Ba^{2+}, Al^{3+}	2900
SO_4^{2-}, NO_3^-, ClO_4^-, CH_3OO^-, CrO_4^{2-}, EDTA, Taretrate, Citrate, Oxalate, CO_3^{2-}, F^-, PO_4^{3-}, SCN^-.	5619
Cl^-	119
UO_2^{2+}, La^{3+}	802
Sc^{+2}, Cu^{2+}, K^+, Mg^{2+}, Ni^{2+}	450
Fe^{3+}, Fe^{2+}, Ca^{2+}	80
Mo^{VI}, Cr^{3+}, Ce^{4+}	25
Li^+, TiO^{2+}, Co^{2+}	9
Pb^{2+}, Na^+, Mn^{2+}, Zr^{4+}	Not interfere

* The tolerance ratio is defined as that ratio causing a relative error of ≤ 5%

Conclusion

The proposed method using 5-Bromo-PADAP in presence of hydrogen peroxide in sulfuric acid medium is not only one of the most sensitive methods for determination of micro amount of V(V) but also is excellent in terms of selectivity and simplicity. The method is free from most interfering ions especially (TiO^{2+}, Cr^{6+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mo^{6+}, W^{6+}, Zr^{4+} and Fe^{3+}) due to a selective dissolution procedure as explained in experimental part. The developed method is reasonable to direct determination of V(V) in different samples that would be useful in routine analysis.

Table 2: Determination of vanadium in international standard rock samples.

Sample	Description and Locality	Present work ($\mu g\ ml^{-1}$)	Published values ($\mu g\ ml^{-1}$)
JG-1	Granite, Japan.	26.0, 25.0	24.9[28], 24.8[29]
BCR-1	Basalt, Washington, U.S.A.	387.5	399.0[27]
DTS-1	Dunite, Washington, U.S.A.	30.4	31.0[27]
Phosphate (1)	Phosphate, Egypt.	83.7	88.6[30]
Phosphate (2)	Phosphate, Egypt.	193.2	195.7[31]
Ilmenite (mineral)	Ilmenite (SARM 60), South Africa.	2677.5	2700[32]

Table 3: Determination of vanadium in some different samples.

Sample	Description and Locality	Present work ($\mu g\ ml^{-1}$)
Phosphate rock	Abou-Tartour, Egypt.	68
Standard (4)[33]	Granite, Cairo, Egypt.	25.3
Standard (6)[33]	Basalt, Cairo, Egypt.	176
Ilmenite (mineral)	Ilmenite, Egypt.	1510

References

1. R. David Lide, CRC *Handbook of Chemistry and Physics*, 78TH Edition (1998).

2. M. Taylor and J. Van Staden, *Analyst*, 119, 1263 (1994).

3. B. Patel, S. Hasell , K. Grzeskowiak and G. Henderson, *Analyst,* 115, 1063 (1990).

4. L. S. Xian Dizhi, *Xueyuan. Xuebo*, 17, 83 (1995).

5. Y. Yu, C. Hong, Z. Wo, J. Huang and R. Wang, *Fenxi. Huaxue*, 24, 479 (1996).

6. A. Ensafi, B. Naderi, Fresenius, *J. Anal. Chem.*, 358 480 (1997).

7. H. Zhu, C. Zhu and J. Lihua, *Huoxue Fence,* 31, 217 (1995).

8. R. Sievers, B. Ponder, M. Morris and R. Moshier, *Inorg. Chem.*, 2, 693 (1963).

9. E. A. Eissa, N. Rofail, R. Ali and A. Hassan, *Radiat. phys. Chem.*, 47, 705 (1996).

10. J. Kucera, J. Lener L. Soukol and J. Horakova, *J. Trace Micro probe-Tech*; 14, 191 (1996).

11. D. Wildhagen, V. Krivan, B. Gerchen and J. Pavel, *J. Anal. At. Spectrum.*, 11, 371 (1996).

12. D. Lander, R. Steiner, D. Anderson and R. Dehm, *Appl. Spectrosc.*, 25, 270 (1971).

13. T. Yanashige, M. Yananoto, H. Sunahara, *Analyst,* 114, 1071 (1989).

14. K Murty, R. Devi and R. Naidu, *Chem. Environ. Res.,* 3, 129 (1994).

15. M. Zhuang and F. Jiang, *Yejn Fenxi*, 15, 39, (1995).

16. G. Wuilloud, A. Salonia, A. Olsina and D.Martinez, *Spectrochimica Acta*, 55, 671-680 (2000).

17. M. Jamaluddin, S. Banoo, *Talanta*, 48, 1085-1094 (1973).

18. W. Wallace W. Gerald and M. Mellon, *Anal. Chem.*, 32, 207 (1960).

19. V. Rossi, T. Matthieu and X. He, Anal. Chem. Acta, 389, 275-280 (1999).

20. P.Jeffery and G. Kerr, *Analyst,* 92, 763-765 (1967).

21. M. Donaldson, *Talanta*, 17, 583, (1970).

22. H. Wang, H. Zhang and H. Cheng, *J. Anal. Chem.*, 351, 683-685 (1995).

23. Gusev and G. Shalamova, *Zh. Anal. Khim.*, 23, 686 (1968).

24. H.Wang, H. Miao, Y. Zhang, H. Cheng, *Talanta*, 41, 685-689 (1994).

25.G. Wuilloud, A. Salonia, A. Olsina and D. Martinez, *Spectrochimica. Acta*, 55, 671-680, (2000).

26. J. Wenrui, S. Shengli and J. Wang, *J. Electro anal. Chim.*, 291, 41-47 (1990).

27. F. Flanagan, *Geochim. Acta*, 31, 289 (1967).

28. A. Ando and Bunseki, *Geochem. Journal,* 9, 151 (1971).

29. *Geostanderds Newsletter*, 20 (1996).

30. M. M. Ali, *Spectrochimica Acta,* 41B, No 8, 837-845 (1986).

31. M. M. Ali, *National Research Center*, 3-6 November (1985).

32. *SA Bureau of Standards*, Republic of South Africa (1996).

33. Standard silicate rocks, personal communication of Prof. M. M. Ali. (*Nuclear Materials Authority, Cairo, Egypt)* (2006).