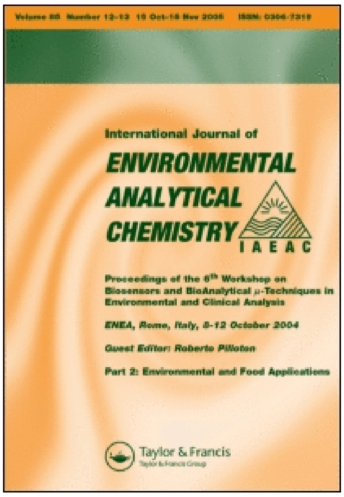

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# Spectrophotometric Determination of Vanadium in Complex Materials Using *N-m*-TMBHA and Thiocyanate

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**To cite this Article** Baveja, Anil K. and Gupta, V. K.(1984) 'Spectrophotometric Determination of Vanadium in Complex Materials Using *N-m*-TMBHA and Thiocyanate', International Journal of Environmental Analytical Chemistry, 17: 3, 299 — 306
**To link to this Article: DOI:** 10.1080/03067318408076982
**URL:** http://dx.doi.org/10.1080/03067318408076982

*Intern. J. Environ. Anal. Chem.*, 1984, Vol. 17, 299–306
0706-7319/84/1704-0299 \$18.50/0

Printed in Great Britain

# Spectrophotometric Determination of Vanadium in Complex Materials Using *N-m*-TMBHA and Thiocyanate

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(*Received August 11, 1983; in final form February 5, 1984*)

Vanadium(V) reacts with *N*-*m*-Tolyl-*p*-methoxy benzohydroxamic acid to form 1:2 (metal to ligand) complex containing a basic V=O group and an acidic V–OH group, which forms addition compounds with thiocyanate to give a hyper and bathochromic effect in chloroform. On the basis of this bathochromic effect of thiocyanate a rapid, selective and sensitive method for the spectrophotometric determination of vanadium(V) has been developed. The blue coloured complex of vanadium(V) is extractable in chloroform having absorption maxima at 580 nm and max $7100 \pm 50\ \mathrm{l.mole^{-1}\,cm^{-1}}$. The method is free from interferences of Mo(VI), W(VI), Zr(IV) and has been successfully applied for the analysis of steels and other complex materials.

KEY WORDS Vanadium, spectrophotometry, complex materials, *N*-*m*-TMBHA and Thiocyanate.

## INTRODUCTION

In recent years, research on analytical characterization of vanadium as contaminant has undergone an exponential growth because of its usefulness in modern science and technology. The concentration of

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vanadium in excess of TLV ($0.5\,mg/m^3$ of air and $0.1\,mg/m^3$ of fume)[2], is reported to cause anaemia, cough, emaciation, irritation of mucous membranes, gastro-intestinal disturbances and bronchopneumonia.[2] The amount of vanadium in blood and urine depends upon the intensity and duration of exposure,[1] however, in plants most of the vanadium accumulate in leaves and roots.[3]

*N*-Aryl-hydroxamic acids are the most popular reagents for the determination of vanadium in simple and complex materials.[4–6] Earlier methods, using cupferron[7] and 8-hydroxyquinoline[8] for colorimetric determination of vanadium are tedious and suffer from interference of iron. The present investigation deals with the determination of vanadium with *N*-*m*-Tolyl-*p*-methoxy benzohydroxamic acid in presence of thiocyanate. Vanadium(V) forms a 1:2 complex with the ligand. These complexes contain $V=O$ and $V-OH$ group in the same complex. The basic $V=O$ group reacts with acidic substances to give a hyper and bathochromic effect in organic solvent.[9] In this communication the sensitivity of *N*-*m*-tolyl-*p*-methoxy benzohydroxamic acid has been increased by extracting vanadium-*N*-*m*-TMBHA in presence of thiocyanate. The wavelength of maximum absorption shifts from 530 to 580 nm and the molar absorptivity increases from $5750 \pm 50$ to $7100 \pm 50\ l.mole^{-1}\,cm^{-1}$. The ratio of vanadium-*N*-*m*-TMBHA-$SC\bar{N}$ was found out by absorption-spectrometry to be 1:2:1 which is in agreement with that found by Saha and Bag.[10] The reaction has been optimized in terms of various analytical parameters and effect of diverse ions has been investigated. The method has been successfully applied for determination of vanadium in various steels and complex materials like blood, urine and plant materials.

## EXPERIMENTAL

### Apparatus

A Carl Zeiss UV VIS specord, recording spectrophotometer and ECIL spectrophotometer model GS-865 with 10 mm matched glass cells were used for all spectral measurements.

### Reagents

*N-m-Tolyl-p-methoxybenzohydroxamic Acid (N-m-TMBHA)* The reagent was prepared according to the method of Gupta and Tandon.[11] The melting point of the crystallized product was 113°C, reported 112.5°C.

A 0.1 w/v solution of *N*-*m*-tolyl-*p*-methoxybenzohydroxamic acid was prepared in ethanol free chloroform.

*Standard ammonium metavanadate solution* Standard ammonium metavanadate solution was prepared as reported earlier.[6] A working standard of 5 $\mu$g/ml was prepared by appropriate dilution of the stock.

*Ammonium thiocyanate solution* A 1 M solution of ammonium thiocyanate was prepared by dissolving pre-dried ammonium thiocycnate in glass distilled water.

All reagents used were of AnalaR grade and solutions of diverse ions were prepared by method of West.[12]

*General procedure* An aliquot of the sample solution, containing 20 to 120 $\mu$g of oxidised vanadium was taken in a separatory funnel and the acidity was adjusted to 4 M with hydrochloric acid and water. 8 to 10 ml of reagent solution was added and the separatory funnel was shaken vigorously for 2 minutes and subsequently 5 ml of aqueous ammonium thiocyanate were added. The contents were then shaken for 10 minutes. The chloroform layer was collected in a 25 ml beaker containing 1 to 1.5 g of sodium sulphate. The aqueous layer was washed 2–3 times with chloroform and the washings were collected in the same beaker. The contents were transferred to 25 ml volumetric flask and diluted to the mark. The absorbance was measured at 580 nm against chloroform and the amount of vanadium was calculated from a calibration curve prepared in a similar manner. Samples containing high vanadium content were diluted prior to the determination.

## RESULTS AND DISCUSSIONS

Chloroform solutions of *N*-*m*-TMBHA extracts vanadium(V) from strong hydrochloric acid medium. The wavelength of maximum absorbance of the violet complex is 530 nm. When this is extracted in presence of thiocyanate the wavelength of maximum absorption shifts to 580 nm and the molar absorptivity increases from 5750 ± 50 to 7100 ± 50 lit. mole$^{-1}$ cm$^{-1}$.

## Effect of varying reaction conditions

The effect of following parameters were studied:

*Acidity* Constant absorbance values were obtained over the acidity range of 2.8 M to 7.5 M hydrochloric acid prior to the addition of thiocyanate. After addition of thiocyanate, an acidity range of 3.5 to 6 M hydrochloric acid was found to be the most suitable. At 1 to 3 M acidities, nearly 1 to 2 hour shaking time was needed and the colour intensity and stability were found to be low as turbidity appeared after 10 minutes.

*Amount of reagent* At least 1:8 molar ratio of vanadium to *N*-*m*-TMBHA was required for full colour development while higher ratios had no effect on the colour intensity. With increasing concentration of thiocyanate to vanadium-*N*-*m*-TMBHA complex, the wavelength shifts to longer wavelength with increase in absorption. At the concentration range of 0.2 M to 1 M, maximum colour intensity was observed. At higher concentrations of thyocyanate (above 2 M) the chloroform extract becomes turbid after 5 minutes of extraction.

*Order of addition* The order of addition of reagents is critical. If thiocyanate was added prior to the addition of the reagent *N*-*m*-TMBHA during procedure then no colour was observed. This may be attributed to the probable formation of vanadium thiocyanate complex.

## Beer's law, molar absorptivity, Sandell's sensitivity and reproducibility

The colour system obeys Beer's law over the range 0 to 4.8 ppm of vanadium. The regression of absorbance on concentration gave a regression coefficient of 0.056 with a correlation coefficient of 0.999 and an intercept of 0.00 respectively. The molar absorptivity and

Sandell's sensitivity as calculated from Beer's law were found to be $7100 \pm 50$ lit. mole$^{-1}$ cm$^{-1}$ at 580 nm and 0.00723 $\mu$g. Reproducibility of the method was checked by replicate analysis of standard vanadium solution over a period of 10 days. The data were employed to compute standard deviation and relative standard deviation which were found to be ±0.0033 and ±0.59% respectively.

## Effect of diverse ions

Tolerance limits of Mo(V), W(VI) and Zr(IV) which are common interferents in the determination of vanadium by *N*-arylhydroxamic acid are improved. The elements do not interfere up to concentrations of 500 ppm. Fe(III), which is the main interferent in the other methods,[7, 8] does not interfere. This can be attributed to the fact that Mo(VI), W(VI), Zr(IV) and Fe(III) form complexes with thiocyanate which are not extracted in chloroform. Their presence in aqueous phase was tested by reported methods.[13] The large excess of Al(II), Ba(II), Be(II), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mg(II), Hg(II), Mn(II), Ni(II), Sn(IV), Sr(II), Th(II), Zr(II), acetate, chlorate, phosphate, sulphate, oxalate, nitrate and fluoride do not interfere.

## Analytical application of the method in the determination of vanadium in steel samples and complex materials

In order to evaluate the analytical applicability of the method, vanadium in alloy steels and complex materials such as blood, plant leaves and soil samples was determined. The general method for treating vanadium containing materials depends upon the nature and composition of the sample.

*Steel samples* Treat a known amount of steel containing about 1 mg of vanadium with 10–12 ml of 6 M sulphuric acid in a 250 ml beaker. Heat gently till all action ceases, adding more acid if necessary. Cautiously add concentrated nitric acid to oxidise vanadium to its highest oxidation state and to convert the tungsten into bright yellow tungstic acid. Heat gently at first and then strongly till all the particles disappear. Care should be taken not to evaporate the solution as appreciable amount of vanadium are carried down by tungstic acid. Cool and dilute to 25 $\mu$l and filter off the precipitate on a sintered glass crucible and wash several times with hot water and 0.1 M sulphuric acid. Dilute the filtrate to 100 ml into a volumetric flask.

In case of tungsten free steel filtration is not necessary.

*Soil samples* 1 gram of soil with 5 grams of anhydrous sodium carbonate was fused in a platinum crucible and after complete decomposition was allowed to cool to room temperature. The mass was then transferred to a beaker, to which 30 ml of water was added. It was then heated on a steam bath and the cake was crushed by means of a glass rod, when the residue was completely disintegrated. The solution was then filtered and washed with distilled water. The filtrate and washings were collected in a 50 ml volumetric flask and diluted to the mark. Since the normal content of vanadium in soil was negligible, an aliquot was added to it before fusion.

*Blood, urine and plant material samples* 5 grams of the sample (leaf samples were dried on an oven prior to the weighing) was taken in a 100 ml Kjeldahl's flask. Concentrated nitric acid with little potassium sulphate (1 ml of nitric acid and 0.1 gm of potassium sulphate for each gram of sample) were added to it and heated on a burner inside a fume cupboard. The samples were first heated charred and then dissolved in the acid mixture. The contents were evaporated to dryness and this process was repeated 2–3 times to ensure complete oxidation of the sample. The residual matter was treated with 25 ml of 1:3 dilute nitric acid and digested on a water bath for 30 minutes to hydrolyze any polyphosphate formed to orthophosphate. (This step is very necessary as polyphosphates formed during the wet oxidation have tendency to complex with vanadium which prevent the complete extraction). The contents were again evaporated to dryness and the residual matter was extracted with hot distilled water which was then filtered and cooled. The use of perchloric acid, which is more efficient for oxidation is avoided because of the attended hazards of its application. Since vanadium contents in blood, urine and plant samples is negligible, synthetic samples were prepared by the addition of known amount of vanadium to each sample prior to wet oxidation.

*Analysis of samples* An aliquot of the sample solution was taken and the vanadium content in it was determined as recommended in the procedure. The results of analysis of different steel samples, blood and plant samples are given in Tables I and II.

TABLE I

Analysis of synthetic samples of blood, urine and plant material

| Sample | Vanadium added μg | Vanadium[a] found μg | Error % |
|---|---|---|---|
| *Human blood* (5 gms) | | | |
| $B_1$ | 10.00 | 9.92 | 0.80 |
| $B_2$ | 10.00 | 9.96 | 0.40 |
| $B_3$ | 15.00 | 14.86 | 0.93 |
| $B_4$ | 20.00 | 19.79 | 1.05 |
| $B_5$ | 20.00 | 19.83 | 0.85 |
| *Urine, human* | | | |
| $U_1$ | 5.00 | 4.95 | 0.60 |
| $U_2$ | 10.00 | 9.90 | 1.00 |
| $U_3$ | 15.00 | 14.77 | 1.50 |
| *Plant material* (5 gms) | | | |
| $P_1$ | 15.00 | 14.82 | 1.20 |
| $P_2$ | 20.00 | 19.87 | 0.65 |
| $P_3$ | 20.00 | 19.73 | 1.35 |
| $P_4$ | 30.00 | 29.67 | 1.00 |
| $P_5$ | 40.00 | 39.54 | 1.15 |

[a]Mean of three repetitive analysis.

## CONCLUSION

Vanadium can be determined profitably with *N*-*m*-tolyl-*p*-methoxy benzohydroxamic acid in presence of thiocyanate. The method has been successfully applied for the analysis of vanadium in steel samples and complex materials such as blood and plant and soil samples. The method is simple, selective and sensitive as compared to the other commonly used methods.

TABLE II

Determination of vanadium in BCS steels and MRG-I samples

| Sample No. | Vanadium found % ppm | Certified value % ppm | Standard deviation |
|---|---|---|---|
| BCS No. 642 alloy steel | 1.56 | 1.57 | ±0.0048 |
| BCS 252 low alloy steel | 0.454 | 0.46 | ±0.0061 |
| BCS 241/1 high speed steel | 1.554 | 1.57 | ±0.0056 |
| BCS 224/I | 0.187 | 0.19 | ±0.0083 |
| BCS 220/I | 2.06 | 2.09 | ±0.0041 |
| MRG-I (Cabbro Ore sample, Canada) | 528±12 | 530±10 | — |

[a]Mean of three repetitive analysis.

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