



Procedures involving reduction with thiourea. Rapid potentiometric method for determination of vanadium alone or in binary mixtures, alloys, ores and glass

^aKh. Elgendy, ^bA. Bokhzam and ^{*b}A. Benhmid

^aZagazig University, Faculty of Science, Chemistry Department, Zagazig, Egypt

^bBenghazi University, Faculty of Science, Chemistry Department, Benghazi, Libya

ABSTRACT

A new rapid, reliable and accurate method is suggested for determination of small amounts of vanadium based on its reduction with excess of thiourea in slightly acidic medium whereupon the yellow vanadium (V) is determined. The unreacted thiourea is determined with Hg (II) potentiometrically in presence of Ag / amalgam as indicator electrode coupled with S.C.E. The method finds application for the determination of vanadium in some industrially important products .

Keywords: Potentiometry; vanadium determination; binary mixtures; thiourea

INTRODUCTION

Vanadium and its compounds have occupied a dominant position in modern science and technology because of their versatile and diverse chemical, mechanical and electrical properties[1]. Vanadium as a metal and as a form of complex exhibits biological properties [2,3], it has been used as a catalyst [4]. The importance of vanadium as a minor or a major constituent in various industrial products created renewed interest in methods for its determination, especially when it is associated with other elements or when present in alloys. Babko [5] determined the element by direct potentiometric titration of V^{5+} with $FeSO_4$ in glycerol-KOH medium. Pribiland and Vasely [6] suggested a complexometric method for its determination in steel. Galliford [7] stated that tetravalent vanadium can be determined in 0.01 M H_2SO_4 photometrically with periodate. Korkisch and Steffan [8] determined vanadium in presence of Mo and U using Fe (II) and barium diphenyl- amine sulphonate as an indicator. Khalifa et al [9] determined V (IV) using $KBrO_3$ as oxidising agent. Sahuand and Tando [10] used N-benzyl-2-naphthohydroxamic acid as a highly selective reagent for solvent extraction and spectrophotometric determination of vanadium. Zaky et al [11] determined vanadium in ore using hydroxylamine as reducing agent. Thiourea and its *derivatives* have been reported to possess various activities such as *anticonvulsant activity*. [14]

EXPERIMENTAL SECTION

All reagents were of analytical *grade* except the solvents, which were distilled before use, and the solutions were prepared in deionized distilled water. 0.0202 M V^{5+} solution was prepared by dissolving the calculated amount of NH_4VO_3 (M.wt =116.98) in appropriate volume of water, it was standardized potentiometrically by the method involving back titration of excess EDTA with Hg (II). 1% iodine solution was prepared by dissolving previously sublimed solid iodine in ethanol. Hg (II) and EDTA solutions were 0.047 and 0.046 M respectively. 0.0497 M of thiourea was prepared and standardized following recommended methods [12]

Equipment

The titration cell consist of a 100 ml Pyrex beaker, magnetic stirrer, a 5 ml burette (1 division = 0.02 ml), silver amalgam indicator electrode in junction with a reference saturated calomel electrode as the other half cell. The two electrodes were fitted to the pH meter (model CG 701 Schöutgeratte).

Procedures

I- for Vanadium only

To a 150 ml Pyrex beaker, add 0.4-3 ml V (v) solution, add 20 ml H₂O followed by 1 ml 10% H₂SO₄, 5 ml thiourea, the mixture was heated for about 3 minutes to ensure complete reduction of V (V) to V (IV), then titrate the excess thiourea against Hg (II)

Find out thiourea \equiv V (IV).

II- Analysis of Binary Mixtures

a) 1 ml V (V) + 0.5 ml Fe (III)

Dilute the mixture with 20 ml H₂O, add 5 ml thiourea and proceed as following (I) to obtain thiourea = V and Fe

b) To another identical mixture add 3 ml EDTA, 8 ml 10% urotropine buffer, titrated against Hg (II). Find out the concentration of EDTA \equiv Fe. Calculate the concentration of V by difference.

2) 1 ml V (v) + 0.5 ml Cr (III) or Mn (II).

a) dilute the mixture with 20 ml water, add 5 ml thiourea and proceed as under (I) to obtain thiourea \equiv V (v).

b) To another identical mixture add 3 ml EDTA, buffer with 8 ml 10% urotropine, and titrated with Hg (II) to obtain EDTA \equiv Cr or Mn.

3) Determination of Vanadium in

a) Ferrovandium alloy (1.56 % Al, 34.8 % V)

Dissolve 0.5 g sample in a mixture of 30 ml 30% H₂SO₄ and 10 ml 50% HNO₃, add few drops of HF to enhance dissolution, evaporate until SO₃ begins to fume off, cool, add 30 ml H₂O, few drops of H₂O₂, and then cool, filter from SiO₂ and carbon (542 Whatmann), wash throughly with hot water and add water up to 500 ml.

b) Egyptain ilumenite (36.7% TiO₂, 47.3 % Fe₂O₃, 1.72 % Al₂O₃, 0.41 % V₂O₅, 3.83 % MgO and 1.12 % CaO) to 0.50 g pulverized ilumenite (passing 200 mesh B.Bs) add 40 ml 1:1 H₂SO₄, boil for 1 hour, cool, dilute with water and then filter using 542 Whatmann filter. Fuse the thoroughly washed residue with KHSO₄, cool and dissolve the melt in the filtrate. Evaporate until SO₃ begin to fume off, cool, add 50 ml H₂O filter from SiO₂, which is always associated with the ore as impurity, wash it thoroughly with water and volatilize it as SiF₄ (HF – H₂SO₄). Fuse the occluded impurities with solid KHSO₄, dissolve the melt in the silica free solution and make it with water up to 500 ml. Take a 5 ml aliquot portion from 3(A) or 25 ml from 3(B), add few mg of (NH₄)₂S₂O₈, boil it for 10 minutes to oxidize V(IV) to V(v), Fe(II) – if present to Fe (III) and to decompose excess persulphate, cool, add few drops of 10 % HF to form the more stable fluoride complexes Fe(III) in 3(A) or Fe(III) and Ti (IV) in 3(B) which resist reduction, 5 ml thiourea then continue as given under (1). The results obtained by this method amounts to 0.41% compared with 0.42% for the conventional method.

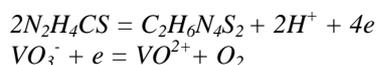
Determination of vanadium in glass (1% V₂O₃)

Dissolve 0.5 g sample in 20 ml HF, evaporate, then add 30 ml of 30% H₂SO₄ and 10 ml 50% HNO₃, boil it for 10 min., evaporate, cool, add 30 ml H₂O, few drops of H₂O₂, boil for 10 min, to obtain V(IV) and to decompose excess H₂O₂, cool, water up to 500 ml. then follow as above.

RESULTS AND DISCUSSION

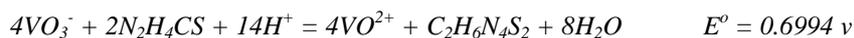
Thiourea used in analytical chemistry in different purposes firstly complexation, which is either insoluble in the available medium such as Hg, Cu, Ag, Bi, Cd and lead. Secondly as masking agent especially to bind with Bi, Cu and Cd finally as a reducing agent with Mo, Rh, Pd, Pt, Se and Te.

Representative results for the determination of vanadium using thiourea in slightly acidic medium, the stoichiometry of the redox reaction can be presented by the following redox equations [13]



$$E^o = - 0.30 \text{ v}$$

$$E^o = 0.9994 \text{ v}$$



Using the relation $E^o = 0.0591 / n \log K$ where E^o is the standard potential of the net reaction and equal to (2.7976v), n is the number of electrons required to reduce one mole of V (v) to V (IV), and K is the equilibrium constant

$$2.7876 = 0.0591 \log K$$

$$\log K = 48.222335$$

this value indicates that the above reaction should proceed quantitatively to completion, also from the relation $\log \infty = \log K / n_1 + n_2$ where n_1 and n_2 are the number of the electrons involved in the two half reactions, $\log(\infty)$ is calculated to be (9.64445) which shows the quantitativness of the method.

Table 1, 2. list the results of determining vanadium alone or in binary mixtures using thiourea as a reductant, which show high accuracy, precision indicate that procedures described for such estimation are extremely reliable.

Table 3. shows the results of vanadium determination in ferrovanadium alloy and ilumenite.

Table 4.shows the results of vanadium determination in a colored glass.

Table 1. Determination of Vanadium

Taken(mg)	Found(mg)	Error %	Recovery %
0.182	0.181	0.549	99.45
0.366	0.362	0.82	99.178
0.549	0.544	0.91	99.69
0.736	0.733	0.40	100.40
0.918	0.917	0.11	99.89
1.100	1.104	0.36	100.36
1.367	1.361	0.44	99.56
1.650	1.646	0.24	99.76
1.831	1.829	0.11	99.84
2.205	2.198	0.32	99.68
2.487	2.483	0.16	99.84
2.657	2.650	0.44	99.66

Table 2. Analysis of binary mixtures

Taken (mg)	Found (mg)	Error%	Metal taken	Found	Error %
0.921	0.917	0.43	0.642 Fe(III)	0.641	0.16
0.921	0.916	0.54	0.709 Co(II)	0.703	0.85
0.921	0.916	0.54	0.808 Cr (III)	0.801	0.87
0.921	0.914	0.86	0.932 Mn(II)	0.924	0.86

Table 3. Determination of vanadium in

A) Ferrovanadium, B) Ilmenite

A	B
34.8%	0.41
35.4%*	0.43*

* by conventional method

Table 4. Determination of vanadium in glass containing V₂O₅

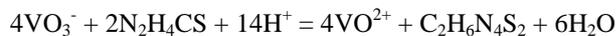
A	B
0.25%	0.248%
0.25%*	0.249%*

*by conventional method

CONCLUSION

Thiourea used in analytical chemistry in different purposes firstly interaction with many heavy metals to form complexes e.g Hg, Cu, Ag, Bi, Cd and lead. Secondly as masking agent especially to bind with Bi, Cu and Cd,

finally as a reducing agent with Mo, Rh, Pd, Pt, Se and Te. In our method thiourea can be used for vanadium determination, based on reduction with excess of thiourea in slightly acidic medium where upon the fellow vanadium (v) is determined through oxidation with iodine dissolved in ethanol to produce iodide which is subsequently titrated with Hg (II) potentiometrically in presence of Ag / amalgam as an indicator electrode coupled with S.C.E. The method finds wide applications to the determination of the element in some industrially important products.



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