



Simultaneous Determination of V (V) and Co (II) as (S)-5-Methoxy-2-[[4-Methoxy-3, 5-Dimethyl-2-Pyridinyle-Methyle] Sulfinyle]-1H-Benzimidazole Using Derivative Spectrophotometry

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Abstract: The reagent (S)-5-methoxy-2-[[4-methoxy-3, 5-dimethyl-2-pyridinyle-methyle] sulfinyle]-1H-benzimidazole gives greenish yellow coloration with V (V) as well as Co (II) in basic medium. This observation is used for the simultaneous determination of both the metal ions using Zero and second order derivative spectrophotometry. Optimum conditions were established for this determination. Job's and mole-ratio methods are used for the determination of composition of the metal complexes. Determination of the metal ions was carried out in BAS alloys, and NTP ball bearings.

Keywords: Vanadium, Cobalt, ESMPZL, Derivative Spectrophotometry, Alloys, Steels and Synthetic Mixtures

1. Introduction

The chemical behavior of vanadium and cobalt is very similar. Cobalt is associated with vanadium as sulfides and arsenides and is found in minerals. It is used in medicine as an important radioactive tracer and as a cancer treatment agent as well as in biological activities such as vitamin B (cyanocobalamin). It is also used to make stainless steel and alloys highly resistive to oxidation at high temperatures when used as turbine blades and cutting tools [1]. Cobalt is known to be essential at trace levels to man, animals, and plants for metabolic processes. Even though cobalt is not considered to be as toxic as most of the heavy metals, it is an equally harmful element. Toxicological effects of large amounts of cobalt include vasodilation, flushing, and cardiomyopathy in humans and animals. The high consumption of nickel and cobalt-containing products in industry inevitably leads to environmental pollution at all stages of production, recycling, and disposal.

The industrial use of vanadium is widespread in the industry, catalyst industry, ceramic and electronic equipments. This element in trace amounts is an essential element for cell growth at $\mu\text{g} / \text{L}$ levels, but can be toxic at higher concentrations. The toxicity of vanadium is dependent on its

oxidation state [2], vanadium (V) being more toxic than vanadium (IV). Owing to its toxic and essential nature (e.g. to marine algae and green plants) in biological systems there has been considerable interest in the determination of vanadium in environmental samples [3].

Although some of these methods provide high sensitivity and specificity, they also have drawback such as high costs for equipment and assays, timeconsumption and complicated operation as well as being unsuitable for applications where mobility of the analytical equipment is of advantage. Among the most widely used analytical methods are those based on the UV-Vis spectrophotometry techniques, due to both the resulting experimental rapidity and simplicity and the wide application [4]. Spectrophotometric methods play a prominent role, but the selectivities of most spectrophotometric procedures are not satisfactory, owing to the close related properties, and separation procedures that must be introduced in most cases [5]. For achieving quantitative information from such systems without previous chemical separation several chemometric methods have been developed. H-point standard addition method, which is a modification of the standard addition method, is a simple two variable chemometric technique. The greatest advantage of HPSAM is that it can remove the presence of an interference

and reagent blank [6, 7]. This method has been applied in different analytical techniques, including spectrophotometry [8, 9, 10], spectrofluorimetry [11], kinetic spectrophotometry [12,13,14] and chromatographic techniques [15]. In order to apply HPSAM to resolve mixtures, the interferent(s) species should be known. Two methods namely Generalized H-Point Standard Addition Method (GHPSAM) [16, 17, and 18] and H-Point Curve Isolation Method (HPCIM) [19] were proposed to solve this problem.

S.N.Lanjuani, K.P.Mahar and A.K.Chamer *et al* [20] developed a simultaneous determination of Co, Fe, Cu and V in crude petroleum oils by HPLC. T.Kiriyama and R.Kuroda *et al* [21] developed a simultaneous determination of Vanadium and Cobalt in biological naturals. Bing Chan and Sandanobu Inoue *et al* [22] developed a simultaneous determination of Cobalt and Vanadium using 2-[5-Nitro-2-pyridylazo]-5-[N-n-propyl-N-(3-sulfoprpyl-) amino] phenol by reverse phase HPLC. A.Praveen Kumar and V.Krishna Reddy *et al* [23] developed a simultaneous determination of second order derivative spectrophotometric dermination of

Co, Ni and V using 2-Hydroxy-3-Methoxy benzaldehyde thiosemicarbazone.

Here in we report the simultaneous Zero and second order derivative spectrophotometric determination of vanadium (V) and cobalt (II) using (S)-5-methoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyle-methyle] sulfinyle]-1H-benzimidazole [ESMPZL]. The proposed simultaneous method involves the applications of alloy samples, synthetic mixture and steel samples.

2. Experimental

2.1. Preparation of ESMPZL

Esomeprazole is 5-methoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyl] methyl] sulfinyl]-1H-benzimidazole. It is white crystalline powder freely soluble in water and its molecular formula is C₁₇H₁₉N₃O₃S. (M.Wt:345.11).

Conversion of omeprazole to esomeprazole:

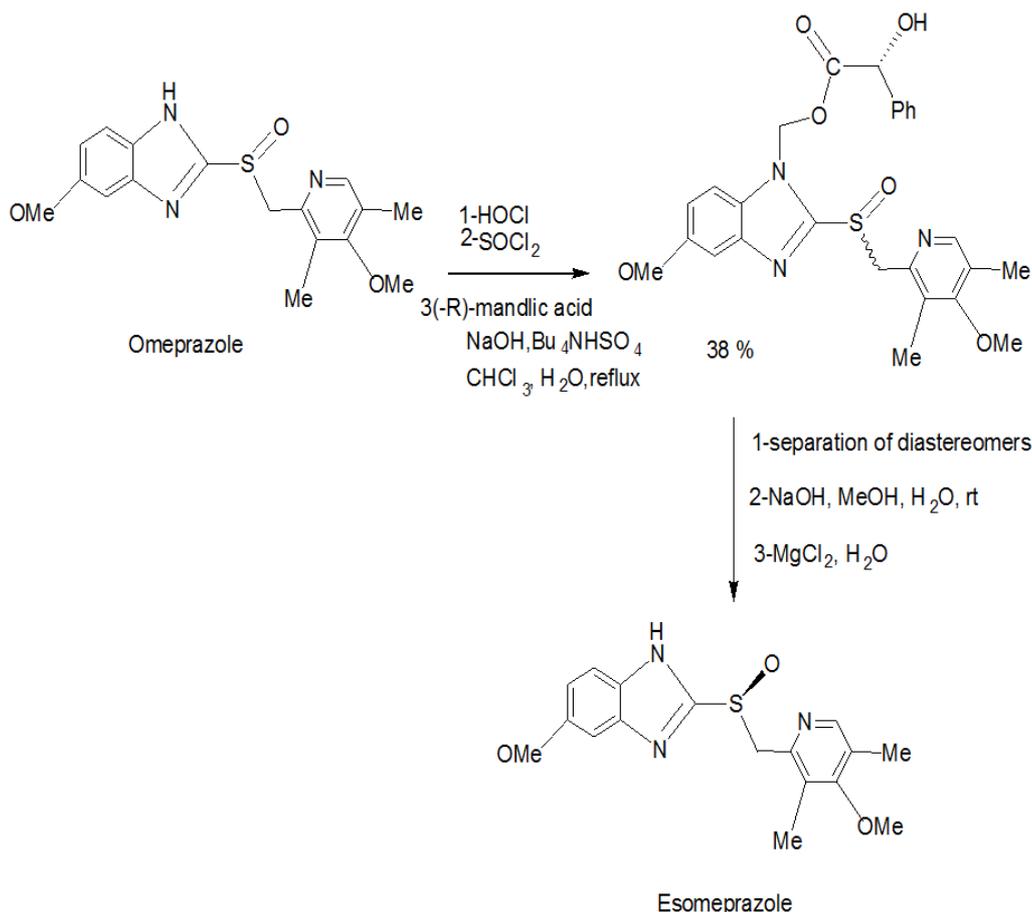


Fig. 1. Esomeprazole was characterized by IR, ¹H-NMR and Mass spectral data.

IR (KBr) ν_{max} : 3346, 3168, 2961, 2928, 2683, 1657, 1597, 1449, 1255, 1218, 1092, 876, 710 cm⁻¹

¹H NMR (DMSO-d₆, 500 MHz) : δ 2.20 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 3.73 (s, 3H, OCH₃), 3.88 (s, 3H, OCH₃), 4.60 (d, 1H), 4.77(d, 1H), 6.97, 6.99 (m, 2H, Ar-H), 7.65 (m, 1H, Ar-H), 8.25 (s, 1H, Pyridine ring), 9.57 (s, 1H, NH) ppm. MS

m/z: found 345.11 [M⁺]; calcd. 345. Anal C₁₇H₁₉N₃O₃S.

2.2. Solutions Preparation

Buffer solutions are prepared using HCl, CH₃COOH and NaOAc in acidic medium and NH₄OH, NH₄Cl in basic medium.

2.3. Preparation of Metal Solutions and Reagent solution

The standard V (V) solution and Co (II) solutions were prepared using analytical reagent grade samples. Appropriate quantity of is (S)-5-methoxy-2-[[[4-methoxy-3, 5-dimethyl-2-pyridinyle-methyle] sulfinyle]-1H-benzimidazole dissolved in DMF for making 0.1M reagent solution.

2.4. Zero Order Spectrums of Cadmium and Copper

A Solution containing 1ml 1×10^{-3} M ammonium vanadate and 1ml of 1×10^{-3} M cobalt chloride are taken in a 25ml volumetric flask. 10ml of a buffer solution of pH 8.5 is added. The contents of the flask are made up to the mark with distilled water. The solution is shaken well for uniform concentration. A blank solution is prepared on the same lines but without containing the metal ions.

2.5. Simultaneous Determination of V (VI) and Co (II)- Present Method

By keeping reagent concentration constant, the author varied the concentrations of both the metal ions. Blank solution is also prepared on the same lines containing no metal ions. The second order derivative spectrum is recorded for each of the solution. These are shown in figures 6. Graphs are plotted between the concentration of V (VI) and peak amplitude as well as valley amplitude. Linear plots are obtained in the case of vanadium as well as cobalt when graphs are plotted between concentration and peak amplitude, valley amplitude and sum of peak and valley amplitudes. These are shown in figures 7. For V (VI) and 8 for Co (II).

Thus the second order derivative spectrophotometric method is very useful to make simultaneous determination of V (VI) and Co (II) in microgram quantities. Greater sensitivities can be achieved by using the sum of the amplitudes of peak and valley for drawing calibration plots. V (VI) can be determined in the range 4.0 - 24 $\mu\text{g/ml}$ and Co (II) can be determined in the range 0.472 - 2.829 $\mu\text{g/ml}$ using this method. No prior separation of the two metals is required in this determination. This method can be used for the analysis of alloys or simulated mixtures containing both the metal ions.

3. Results and Discussion

Studies carried out with various metal ions with the present reagent revealed that ESMPZL gives a greenish yellow colored solution with V (V) and yellow colored solution with Co (II). The authors have carried out the effect of pH on the color reaction in presence of V (V) as well as Co (II). The color development is maximum in the pH range 7 – 9 with both the metal ions taken individually. In view of this a solution of pH 8.5 is fixed for further investigations. Studies relating to the effect of metal ion concentration, reagent concentration, time, organic solvent are carried out to establish the optimum conditions for maximum color development. The order of addition of various components of the reaction system has no influence on the color reaction. It

is also observed that a minimum of 10 times excess of the reagent is essential for the complete formation of color either with individual metal ion (or) an admixture. The color is quite stable for one hour; hence the absorbance measurements can be made from various solutions even after one hour.

Job's continuous variation method and mole ratio method are performed to determine the composition and stability constants of the complexes. Both the metal ions form 1:2 (M:L) complexes with the reagent. The stability constants are 5.89×10^{10} and 2.74×10^{11} for cadmium and copper respectively.

As mentioned above, series of solutions are prepared containing varying concentrations of the two metal ions. Blank solutions are also prepared on the same lines, but without containing metal ions. For each of the solution, the second order derivative spectrum is recorded. These are shown in figures 5. Graphs are plotted between the concentration of V (V) and peak amplitude as well as valley amplitude. Similar linear plots are obtained even in the case of cobalt when graphs are plotted between concentration and peak or valley amplitude.

It may be mentioned here that straight line plots are obtained even with the sum of peak and valley amplitudes. These linear plots are shown in figs. 6 and 7 for V (V) and Co (II) separately.

Thus the second order derivative spectrophotometric method is very useful to make simultaneous determination of V (V) and Co (II) in microgram quantities. Greater sensitivities can be achieved by using the sum of the amplitudes of peak and valley for drawing calibration plots. V (V) can be determined in the range 2.131 – 12.772 $\mu\text{g/ml}$ and Co (II) can be determined in the range 1.269 - 7.629 $\mu\text{g/ml}$ using this method. No prior separation of the two metals is required in this determination. This method can be used for the analysis of alloys or simulated mixtures containing both the metal ions.

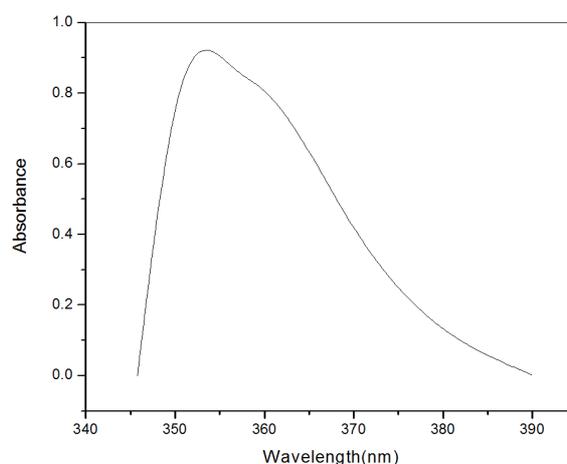


Fig. 2. Zero order spectrum of V (VI) in presence of ESMPRZL .

[Co (II)] = 4×10^{-5} M;
 [ESMPRZL] = 5.6×10^{-4} M;
 Ph = 8.5

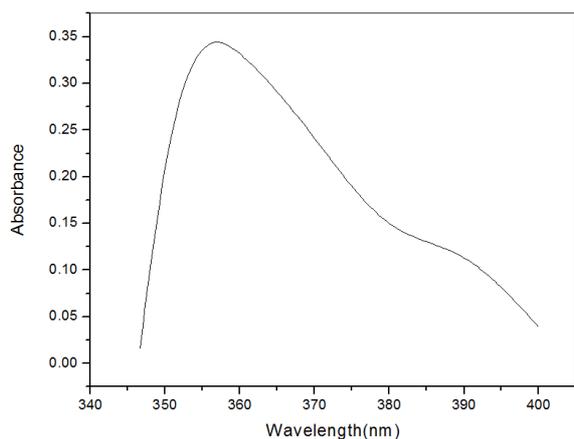


Fig. 3. Zero order spectrum of Co (II) in presence of ESMPRZL.

[Co (II)] = 1.6×10^{-5} M;
[ESMPRZL] = 5.6×10^{-4} M;
pH = 8.5

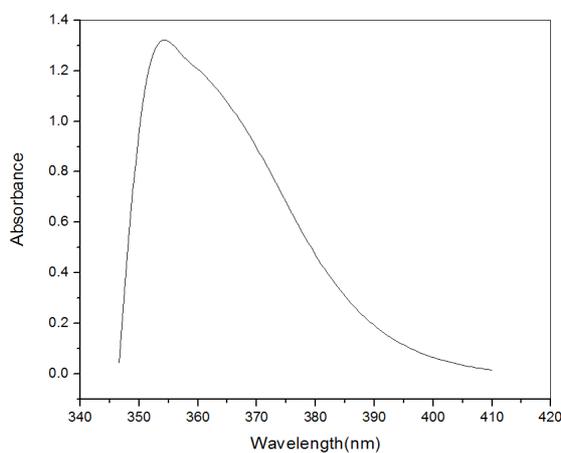


Fig. 4. Zero order spectrum of V (VI) + Co (II) in the presence of ESMPRZL.

[V (VI)] = 4×10^{-5} M [Co (II)] = 1.6×10^{-5} M;
[ESMPZL] = 5.6×10^{-4} M;
pH = 8.5

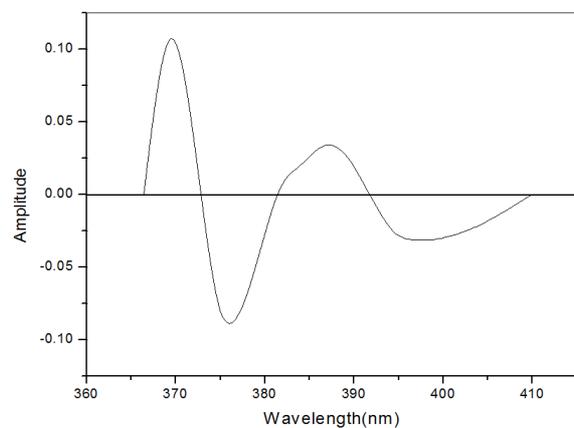


Fig. 5. Typical second order spectrum of V (V) + Co (II) in the presence of ESMPRZL.

[V (V)] = 4×10^{-5} M [Co (II)] = 1.6×10^{-5} M; pH = 8.5

[ESMPRZL] = 5.6×10^{-4} M;

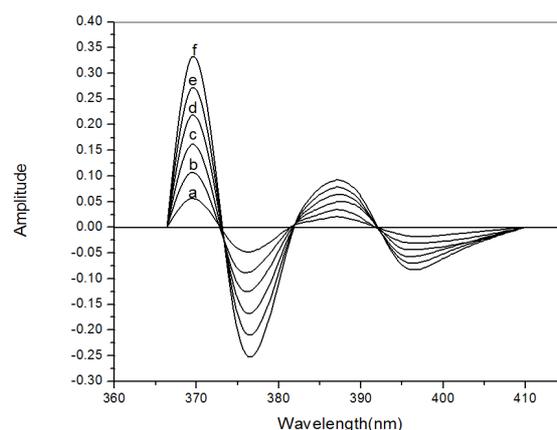


Fig. 6 Second order spectrum of V(VI) + Co(II) in the presence of ESMPRZL.

[V (VI)] = 4.0×10^{-5} M; [Co (II)] = 1.6×10^{-5} M
[ESMPRZL] = 5.6×10^{-4} M; pH = 8.5

- a) 0.5 ml of V(VI) and Co(II) each
- b) 1.0 ml ,,
- c) 1.5 ml ,,
- d) 2.0 ml ,,
- e) 2.5 ml ,,
- f) 3.0 ml ,,

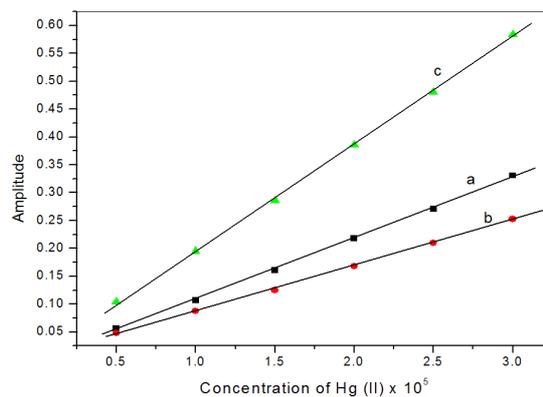


Fig. 7. Second derivative amplitude Vs Concentration of V(V).

pH = 8.5
a = Peak; b = Valley; c = Peak + Valley

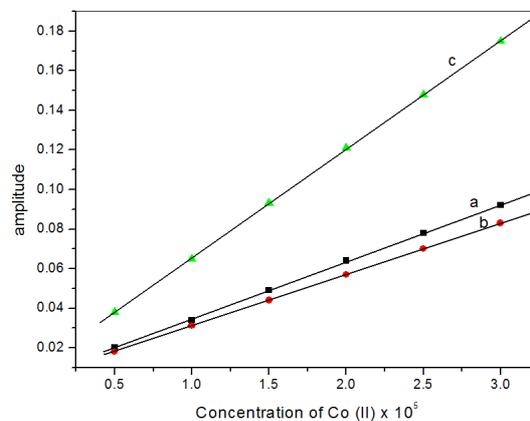


Fig. 8. Second derivative amplitude Vs Concentration of Co(II).

pH = 8.5s

a = Peak ; b = Valley ; c = Peak + Valley

APPLICATIONS: The simultaneous second derivative

spectrophotometric determination of V (V) & Co (II), some alloy steels and soil samples. The results are presented in Table 1, 2 &3 respectively.

Table 1. Simultaneous determination of V (V) and Co (II) in Alloy steel samples.

| Alloy sample | Certified (%) | | Amount found (%) | | Error (%) | |
|---------------------|---------------|---------|------------------|---------|-----------|---------|
| | V (V) | Co (II) | V (V) | Co (II) | V (V) | Co (II) |
| (a) Eligiloy M-1712 | 15.00 | 39.00 | 15.11 | 40.95 | +0.66 | -0.15 |
| (b) BCS 406/1 | 0.14 | 0.017 | 0.129 | 0.018 | -1.55 | +0.64 |
| (c) Alloy steel | 11.21 | 23.71 | 11.29 | 23.67 | +0.72 | -0.16 |

*Average of three determinations;

Table 2. Simultaneous Second-order derivative determination of V (V) and Co (II) in synthetic binary mixtures.

| Amount taken (µg/mL) | | Amount found (µg/mL) | | Error (%) | |
|----------------------|--------|----------------------|--------|-----------|--------|
| V(V) | Co(II) | V(V) | Co(II) | V(V) | Co(II) |
| 0.2347 | 0.2357 | 0.2340 | 0.2362 | -0.29 | +0.21 |
| 0.4694 | 0.2357 | 0.4685 | 0.2352 | -0.23 | -0.21 |
| 0.7041 | 0.2357 | 0.7049 | 0.2354 | +0.11 | -0.12 |
| 0.9388 | 0.2357 | 0.9382 | 0.2361 | -0.06 | +0.16 |
| 1.1785 | 0.2357 | 1.1780 | 0.2365 | -0.04 | +0.33 |
| 0.2347 | 0.2357 | 0.2352 | 0.2362 | +0.21 | +0.21 |

*Average of three determinations.

Table 3. Determination of V (V) and Co (II) in Soil samples.

| Sample and composition (ppm) | Amount in ppm | | | | Relative error (%) | |
|--|-----------------------------|--------|---------------------------------------|--------|--------------------|--------|
| | Certified (GSI) value (ppm) | | Amount found by present method* (ppm) | | V(V) | Co(II) |
| | V(V) | Co(II) | V(V) | Co(II) | | |
| S-18 20.20 Pb (II) 20.30 Zn (II) 88.85 Cu (II) | 50.50 | 40.35 | 50.84 | 39.98 | +0.67 | -0.92 |

* Average of best three among five determinations

4. Conclusions

(S)-5-methoxy-2-[[[(4-methoxy-3, 5-dimethyl-2-pyridinyle-methyle) sulfinyle]-1H-benzimidazole[ESMPZL] is a versatile chromogenic reagent used for the simultaneous determination of V(V) and Co(II) in basic medium in microgram quantities. The present second order derivative spectrophotometric method is simple, rapid, sensitive and selective and do not involve heating or filtration or separation. Foreign ions do not interfere in the determinations. The method precise and accurate determinations can be made. Hence simultaneous determination of V (V) and Co (II) can be carried out by using ESMPZL by the present method.

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