Chapter I

Introduction

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There are many analytical methods that are used in analytical determination of metal ions. These methods involve, high performance liquid chromatography, ion exchange, flow injection, flotation, extraction, catalytic and kinetic procedures and different reagents are used for this porpose, but her we concerned in spectrophotometric method that is the most important and common tool for determination of transition metal ions. The importance of spectrophotometric determination of metal ions was returned to, it is simple, little cost, rapid, sensitive, has higher accuracy and precision.

1.1. Literature survey for determination of cobalt

Spectrophotometric determination method for Co(II) was devolped by ***Wang, et al***[1]. The method was based on the complexation reaction of Co(II) with [2,6-dichloro-4-sulfonylphenyldiazoaminoazobenzene] in the presence of Triton X-100. Test solution containing 8.0 μg of Co(II) was mixed with 5.0 ml of buffer solution, 2.0 ml of 4.0% Triton X-100, 4.0 ml ethanolic 0.04% reagent and completed with water to 25 ml. After 5.0 min the absorbance was measured at 537 nm *vs.* a reagent blank. Beer's law was obeyed up to 0.32 μg/ml. The method was applied for tea and cyanocobalamin injection with recovery range from 99-103% and coefficient of variation of ≤ 2.0%.

Spectrophotometric determination of Co(II) was carried out by ***Han*** and ***He***[2]. The method was based on the reaction of Co(II) with 2-(3,5-dichloro-2-pyridylazo)-5-dimethylaminoaniline. Sample was digested and the digest evaporated to near dryness. The residue was dissolved in water and a portion of the solution was treated with 5.0% $Na_2B_4O_7$-acetate buffer of pH 4.88 and

ethanolic 1.0 x 10^{-3} M of reagent before heating for 2.0 min. The mixture was treated with 6.0 M HCl, diluted with water and the absorbance was measured at 612 nm (ε = 1.16 x 10^5 l mol^{-1} cm^{-1}) *vs* a reagent blank. Beer's law was obeyed up to 0.6 μg/ml Co(II) and the coefficient of variation was 0.6%. The method was applied to the analysis of ore and steel samples.

Tong, et al[3] described a spectrophotometric method for determination of Co(II). The method was based on the complexation reaction of Co(II) with 2-(5-nitro-2-pyridylazo)-5-dimethylaminobenzoic acid. Sample solution was mixed with sodium acetate/acetic acid buffer of pH 6.0, aqueous 0.05% of reagent and water. The absorbance was measured at 650 nm (ε = 3.1 x 10^4 l mol^{-1} cm^{-1}) *vs* a reagent blank. Beer's law was obeyed up to 0.56 μg/ml Co(II). The method was used in assay of organometallic compounds and vitamin B_{12} injection with recoveries of 98-104%.

Spectrophotometric determination of Co(II) was investigated by ***Amin, et al***[4]. The method was based on the reaction of Co(II) with 1-(2-arsenitophenyl-azo)-2-naphthol (I) or its 3-carboxylic derivative (II). A solution of Co(II) was adjusted to pH 7.5 or 9.0 using theil buffer (depending on reagent) and mixed with 4.0 ml ethanol and 3.5 ml of 2.0 x 10^{-3} M reagent. The solution was diluted with water to 25 ml. After 3.0 min, the absorbance was measured at 580 or 582 nm for (I) and (II), respectively. Beer's law was obeyed for 0.1-3.6 and 0.1-4.0 μg/ml Co(II) for the studied reagents. The RSD for 0.5 μg/ml Co(II) were 4.3% and 3.7%.

Spectrophotometric determination of Co(II), Cu(II) and Pd(II) was carried out by ***Issa, et al***[5]. The method was based on the reaction of Co(II), Cu(II) and Pd(II) with 1-(*o*-carboxyphenyl)-5-phenyl-3-benzoylformazan. The solutions containing 2.36-4.13, 0.95-3.18 and 2.75-7.45 μg/ml of Co(II), Cu(II) and Pd(II) ions, respectively, were mixed with 1.0 ml of 1.0 x 10^{-3} M reagent solution [2.0 ml in case of Co(II)]. The solution was diluted to 10 ml with 50% ethanolic universal buffers of pH 6.1, 4.1 and 4.0 for Co(II), Cu(II) and Pd(II), respectively. The absorbance was measured at 630 and 538 nm. Beer's law was obeyed up to 4.71, 5.08 and 8.5 μg/ml for Co(II), Cu(II) and Pd(II), respectively. The method was used to determine Cu(II) in brass and copper-nickel alloy samples.

Determination of Co(II) in water by spectrophotometric method was carried out by ***Zhu***[6]. The method was based on the reaction of Co(II) with methylene blue. A sample (20 ml) was treated with 6.1 ml of 0.56 M methylene blue/0.5 M aqueous NH_3/5.0% H_2O_2/1.0% polyvinyl alcohol (20:5:6:30) and completed to 25 ml. After heating at ≤ 100 °C for 40 min and cooling for 5.0 min, the absorbance was measured at 600 nm. Calibration graph was linear up to 1.0 μg/ml Co(II) with detection limit of 50 pg/ml Co(II). The method was used to the analysis of tape, river, mineral and waste water with RSD of 4.88-5.83%.

Jin, et al[7] proposed a spectrophotometric method for determination of Co(II). The method was based on the complexation of Co(II) with 4,4-diazo-benzenediazoaminoazobenzene in surfactant medium. A sample was mixed with 3.0 ml sodium tetraborate buffer of pH 10.2 followed by 1.0 ml of 2.0% Triton X-100 and 2.5 ml of 0.05% of reagent in DMF. The solution was diluted to 25 ml with water and the absorbance was measured at 540 nm (ε = 1.72 x

10^5 l mol^{-1} cm^{-1}). The colour was stable for at least 24 h. The calibration graph was linear up to 7.0 μg/ml Co(II). The method was applied to the analysis of soil and vitamin B_{12} injection with RSD of 2.2-5.1% with recoveries of 95-104%.

Issa, et al[8] investigated a spectrophotometric method for determination of Co(II), Cu(II), and Pd(II). The procedure was based on the reaction of the above metals with 1,5-diaryl-3-cyanoformazan. In the determination of Co(II), Cu(II), and Pd(II) with 2,2-(3-cyanoformazan-1,5-diyl) dibenzoic acid (I) and Cu(II), and Pd(II) with 1,5-bis-(2-hydroxyphenyl) formazan-3-carbonitrile (II). The optimum pH values were 8.2, 5.6, 5.5, 8.3 and 8.5. Beer's law ranges were 0.18-5.3, 0-4.45, 0-8.51 μg/ml of Co(II), Cu(II), and Pd(II) on using reagent (I) and 0-4.45 and 0-0.58 μg/ml for Cu(II), and Pd(II) on using reagent (II), respectively.

Spectrophotometric determination of Co(II) was investigated by ***Zhao, et al***[9]. The method was based on the complexation reaction of Co(II) with (2-imidazolylazo)phenol-4-sulfonic acid in universal buffer. Portions of a standard Co(II) solution were treated with 5.0 ml of 0.04 M acetic acid/0.04 M phosphoric acid and 0.04 boric acid buffer of pH 8.5 and 2.0 ml of 2.0×10^{-3} M (2-imidazolylazo)phenol-4-sulfonic acid. The solution was diluted to 25 ml with water and after 2.0 min the absorbance was measured at 578 nm ($\varepsilon = 2.3 \times 10^4$ l mol^{-1} cm^{-1}) *vs* a reagent blank. Beer's law was obeyed up to 3.2 μg/ml Co(II). The method was applied to the analysis of Co(II) in a mixture of Ni(II) with recoveries of 98-99%.

Spectrophotometric determination of Co(II) was investigated by ***Ge***[10]. The method was based on the colour reaction of Co(II) with dibromo-hydroxyphenylfluorone. Sample solution containing 2.0 μg/ml of Co(II) was mixed with 1.0 ml NH_3/NH_4Cl buffer of pH 9.5, 1.5 ml of 0.6 x 10^{-3} M reagent solution in 50% ethanol, 1.0 ml of 1.3 x 10^{-2} M hexadecylpyridinium bromide solution in 50% ethanol and water to 25 ml. After 15 min, the absorbance was measured at 645 nm (ε = 1.76 x 10^5 l $mol^{-1}cm^{-1}$). Beer's law was obeyed up to 20-400 ng/ml Co(II). The method was used to determine Co(II) in water and food samples with recoveries of 96.7-104.5%.

Spectrophotometric determination of Co(II) was estimated by ***Winkler***[11]. The method was based on the reaction of Co(II) with phenylfluorone in the presence of Triton X-100. Borate buffer solution (3.0 ml) of pH 9.0 was mixed with 5.0 ml of 0.01 M Triton X-100, 1.5 ml of 0.01 M cetylpyridine chloride, 0.7 ml of 1.0 x 10^{-3} M phenylfluorone in ethanol and Co(II) nitrate solution containing 1.0-10 μg Co(II). The mixture was diluted to 25 ml with water, equilibrated for 30 min. The absorbance was measured at 635 nm (ε = 1.34 x 10^5 l mol^{-1} cm^{-1}). Beer's law was obeyed up to 0.40 μg/ml Co(II).

Spectrophotometric determination of Co(II) was carried out by ***Zhang,*** and ***Zhu***[12]. The method was based on the reaction of Co(II) with 7-(benzothiazolyl-2-azo)-8-hydroxyquinoline-5-sulfonic acid. Portions of Co(II) solution were mixed with 2.5 ml acetic acid/sodium acetate buffer of pH 3.94, 1.0 ml of 10 g/l OP and 3.0 ml of 0.2 g/l reagent in 95% methylated spirit, and water was added to 25 ml. The absorbance was measured at 582 nm (ε = 5.7 x 10^4 l mol^{-1} cm^{-1}) *vs* a reagent blank. Beer's law was obeyed up to 480 ng/ml

Co(II). The solution was stable for at least 3.0 h. The method was used to the analysis of steels alloys and cast iron alloys samples.

Spectrophotometric determination of Co(II) was described by ***Liang, et al***[13]. The method was based on the reaction of Co(II) with 2-(5-carboxy-1,3,4-triazolylazo)-5-diethylaminophenol. Portions of a standard Co(II) solution, containing 10 μg were treated with 5.0 ml ammonium acetate buffer of pH 7.0 and 2.0 ml of 1.0 x 10^{-3} M reagent solution. After 10 min, 2.0 ml HCl (1:1) was added and the mixture was diluted to 25 ml with water. The absorbance was measured at 540 nm (ε = 5.70 x 10^4 l mol^{-1} cm^{-1}) *vs.* a reagent blank. Beer's law was obeyed up to 800 ng/ml Co(II). Interference from Cu(II) was masked with addition of thiourea. The method was applied to determine Co(II) in vitamin B_{12} injection and industrial waste water samples with recoveries of 99.5-102.5% and RSD of 1.6-3.2%.

Determination of Co(II) by spectrophotometric method was studied by ***Ye, et al***[14]. The method was based on the reaction of Co(II) with 1-(1,3,4-triazol-2-ylazo)-2-naphthol. Portions of a standard Co(II) solution was treated with 2.5 ml acetic acid/sodium acetate, 2.0 ml of 20 g/l OP, 4.0 ml aqueous thiourea and 2.5 ml of 0.5 g/l reagent in 50% DMF. After 10 min, the mixture was diluted with water to 25 ml and the absorbance was measured at 578.2 nm (ε = 3.15 x 10^5 l mol^{-1} cm^{-1}) *vs.* a reagent blank. Beer's law was obeyed up to 1.0 μg/ml Co(II). The solution was stable for at least 24 h. Recoveries were 99.3-100% with RSD of 0.82-0.93%.

Determination of Co(II) using spectrophotometric method was illustrated by ***Pa, et al***[15]. The method was based on the complexation of Co(II) with 2-tetraazolylazo-5-diethylaminophenol. Portions of a standard Co(II) solution