CHAPTER VIII

SUMMARY

The research in analytical chemistry envisages the development of new methods of estimation that are simple, rapid and precise over the methods already existing for the analysis of a variety of materials. Since the earliest days of analytical chemistry, several organic reagents have been employed in various ways to facilitate the detection and determination of chemical matrices. However, only during the last two or three decades these compounds have been extensively used in analytical procedures and research evaluation.

Carbonyl compounds and their derivatives have been extensively used by various researchers for the analytical determination of many metal ions. Among them thiosemicarbazones and phenylthiosemicarbazones occupy an important role. Hence, the researcher has attempted to prove the analytical potentiality of 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) for the spectrophotometric determination of copper (II) and for the extractive spectrophotometric determination of cobalt(II), cadmium(II), molybdenum(VI), palladium(II) and zinc(II).

The thesis incorporates the synthesis, spectral characterization of 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) and its analytical applications to the direct spectrophotometric determination of copper(II) and for the extractive spectrophotometric determination of cobalt(II), cadmium(II), molybdenum(VI), palladium(II) and zinc(II).

The thesis has been conveniently divided into eight chapters

The basic principles and techniques of solvent extraction and a brief review of the use of thiosemicarbazones in inorganic analysis with a particular reference to spectrophotometry are given in Section A and Section B, respectively of **Chapter I.** The synthesis of reagent 2,6-DAPBPTSC as well as inorganic salt solutions used in present investigation and the description of instruments are given in Section C of **Chapter I.**

Chapter II describes the spectrophotometric determination of copper(II) with 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone. The newly synthesized reagent, 2,6-diacetylpyridinebis- 4-phenyl-3-thiosemicarbazone (2,6-DAPBPTSC) was proposed as a selective analytical reagent for the spectrophotometric determination of

copper(II) at pH 3.0 to get a yellowish orange coloured 1:1 chelate complex. The complex has maximum absorbance at 370 nm. This method obeys Beer's law in the concentration range 0.63-6.30 μg mL^{-1}. The correlation coefficient of Cu(II)- 2,6-DAPBPTSC complex was 0.942, which indicates an adequate linearity between the two variables. The molar absorptivity and Sandell's sensitivity of the complex were calculated as 0.847×10^{4} lit mol^{-1} cm^{-1} and 0.0075 μg cm^{-2}, respectively. By using Asmus' method the instability constant of the complex is calculated as 1.415×10^{-4} at room temperature. The repeatability of the method was checked by finding the relative standard deviation (n = 5), which was 0.777% and the detection limit value is 0.0056 μg mL^{-1}. The interfering effect of various cations and anions has also been studied. The method is successfully applied for the determination of copper(II) in food, milk and water samples. The performance of the present method was evaluated in terms of student '*t*' test and variance '*f*' test. The results were compared with the results obtained from atomic absorption spectrophotometer which showed that the developed method was suitable for the spectrophotometric determination of copper(II).

Chapter III describes extractive spectrophotometric determination of cobalt(II) with 2, 6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone. 2,6-Diacetylpyridine bis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) was introduced as a sensitive and selective analytical reagent for the extractive spectrophotometric determination of cobalt(II). Cobalt(II) forms a reddish brown coloured complex with 2,6-DAPBPTSC, which can be easily extractable into isoamylalcohol, under optimum conditions. The complex has maximum absorbance at 400 nm. The complex obeys Beer's law in the concentration range 0.6-6.0 μg $mL^{-1}$of cobalt(II). The molar absorptivity and Sandell's sensitivity of the complex were calculated as 2.2×10^{4} lit $mol^{-1}cm^{-1}$ and 2.68×10^{-3} μg cm^{-2}, respectively. An adequate linearity with a correlation coefficient value of 0.969 was obtained for the Co(II)-2,6-DAPBPTSC complex. The instability constant of the complex calculated from Asmus' method was found to be 3.75×10^{-4} at room temperature. The repeatability of the method was checked by finding the relative standard deviation (n = 5), which was 0.388 % and the detection limit value is 0.0028 μg mL^{-1}. The method was successfully applied for the determination of cobalt(II) in vegetable, soil, water and standard alloy samples and the performance of the present method was evaluated in terms of student '*t*' test and variance '*f*' test. The results were compared with the results obtained

from atomic absorption spectrophotometer which showed that the developed method was suitable for the spectrophotometric determination of cobalt(II).

Chapter IV describes extractive spectrophotometric determination of cadmium(II) with 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone. The newly synthesized reagent, 2,6-diacetylpyridinebis- 4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) was tried as a sensitive chromogenic reagent for the extractive spectrophotometric determination of cadmium(II) at pH 9.5 to form a yellowish orange colored 1:1 complex. The complex has maximum absorbance at 390 nm. This method obeys Beer's law in the range of 1.12 -11.20 μg mL^{-1} with 0.970 correlation coefficient of Cd(II)-2,6-DAPBPTSC complex, which indicates a good linearity between the two variables. The molar absorptivity and Sandell's sensitivity were found to be 6.088×10^{4} lit $mol^{-1}cm^{-1}$ and 0.0018 μg cm^{-2}, respectively. By using Asmus' method the instability constant of the complex was calculated as 1.447×10^{-4} at room temperature. The repeatability of the method was checked by finding the relative standard deviation (n = 5), which was 0.9289 % and the detection limit value was found to be 0.0060 μg mL^{-1}. The interfering effect of various cations and anions were also studied. The proposed method was successfully applied to the determination of cadmium(II) in food and water samples and the performance of the present method was evaluated in terms of student *'t'* test and variance *'f'* test. The results were compared with the results obtained from atomic absorption spectrophotometer which showed that the developed method was suitable for the spectrophotometric determination of cadmium(II).

Chapter V describes extractive spectrophotometric determination of molybdenium(VI) with 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone.The newly characterized 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone(2,6-DAPBPTSC) was introduced as a sensitive and selective analytical reagent for the extractive spectrophotometric determination of molybdenum(VI) at pH 3.5 to get a yellowish orange colored 1:1 chelate complex. The complex has maximum absorbance at 500 nm. This method obeys Beer's law in the concentration range 0.90-9.00 μg mL^{-1} and the correlation coefficient of Mo(VI)-2,6-DAPBPTSC complex was found to be 0.954, which indicates an adequate linearity between the two variables. The molar absorptivity and Sandell's sensitivity of the complex were found to be 1.212×10^{4} lit mol^{-1} cm^{-1} and 0.0079 μg cm^{-2}, respectively. The repeatability of the method was checked by finding the relative

standard deviation (n = 5), which was 0.894% and the detection limit value was 0.0056 μg mL^{-1}. The instability constant of the complex calculated from Asmus' method was found to be 6.476×10^{-5} at room temperature. The interfering effect of various cations and anions has also been studied. The method was successfully applied for the determination of molybdenum(VI) in food and water samples. The validity of the present method was evaluated in terms of student '*t*' test and variance '*f*' test. The results were compared with the results obtained from atomic absorption spectrophotometer which showed that the developed method was suitable for the spectrophotometric determination of molybdenum(VI).

Chapter VI describes extractive spectrophotometric determination of palladium(ii) with 2, 6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone. 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone (2,6-DAPBPTSC) was proposed as a chromogenic reagent for the extractive spectrophotometric determination of palladium(II). This reagent forms a yellowish orange colored 1:1 chelate complex with Pd(II) at pH 4.0. This complex can be extractable into isoamylalcohol and it has maximum absorbance at 410 nm. This method obeys Beer's law in the concentration upto 12.6 μg ml^{-1} of palladium(II) and the correlation coefficient of Pd(II)- 2,6-DAPBPTSC complex was 0.962. It indicates an adequate linearity between the two variables. The molar absorptivity and Sandell's sensitivity of the complex were found to be 1.156×10^{4} lit mol^{-1} cm^{-1} and 0.0092 μg cm^{-2}, respectively. By using Asmus' method the instability constant of the complex was calculated as 1.667×10^{-4} at room temperature. The repeatability of the method was checked by finding the relative standard deviation (n = 5), which was 0.371 % and the detection limit value was 0.0078 μg mL^{-1}. The method was successfully applied for the determination of palladium(II) in spiked samples. The performance of the present method was evaluated in terms of student'*t*' test and variance ratio '*f*' test. The results were compared with the results obtained from atomic absorption spectrophotometer which showed that the developed method was suitable for the spectrophotometric determination of palladium(II).

Chapter VII describes extractive spectrophotometric determination of zinc(ii) with 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone.Newly synthesized reagent 2,6-diacetylpyridinebis-4-phenyl-3-thiosemicarbazone (2,6-DAPBPTSC) was introduced as a selective analytical reagent for the extractive spectrophoto- metric determination of zinc(II) at pH 4.5 to form a greenish yellow colored 1:1 chelate complex, which was extracted in to

n-butanol. The complex has maximum absorbance at 490 nm. This method obeys Beer's law in the concentration range 1.36-13.60 μg ml^{-1} of zinc(II) and the correlation coefficient of Zn(II)-2,6-DAPBPTSC complex was 0.986, which indicates an adequate linearity between the two variables. The molar absorptivity and Sandell's sensitivity of the complex were found to be 4.707×10^{3} lit $mol^{-1}cm^{-1}$ and 0.0138 μg cm^{-2}, respectively. The repeatability of the method was checked by finding the relative standard deviation (n = 5), which was 0.697% and the detection limit value was found as 0.0081 μg mL^{-1}. The method was successfully applied for the determination of zinc(II) in biological and food samples. The performance of the present method was evaluated in terms of student '*t*' test and variance ratio '*f*' test. The results were compared with the results obtained from atomic absorption spectrophotometer which showed that the developed method was suitable for the spectrophotometric determination of zinc(II).

Chapter VIII This chapter comprises the summary of the work presented in the thesis. It describes the important results and also illustrates the significance of the work carried out in the field of direct and extractive spectrophotometric determination of transition metal ions.

The references are listed towards the end of every chapter