Chapter – 9

SUMMERY OF THE PRESENT INVESTIGATIONS

Metal ions in general and transition metal ions in particular are found to play an important role in industry, agriculture, plant nutrition, biological activity of living beings and in medicine. Hence, their determination in micro quantities is still a challenging field of research in the context of increasing hazards of environmental pollution. Generally, spectrophotometric methods require less expensive instrumentation than atomic absorption or atomic emission methods and give greater sensitivity. Though hundreds of spectrophotometric methods, either direct or extractive, are reported in the literature for the determination of almost every metal ion in the periodic table, the increasing complexity of the analyzing matrices of the real samples still need more sensitive and particularly more selective methods.

The analytical results derived in the direct and derivative spectrophotometric determination of manganese, nickel, molybdenum, iron, employing a chromophore 2-amino acetophenone isonicotinoyl hydrazone is presented in the present thesis. The results regarding the application of the proposed direct and derivative methods in the analysis of complex materials are also included. The developed methods are found to be simple, rapid, highly sensitive and reasonably selective with good precision and accuracy.

The thesis is divided into **nine** chapters

CHAPTER 1 is divided into four sections

Section i deals with the importance of nitrogen and oxygen containing chelating agents, especially isonicotinoylhydrazones in analytical chemistry. A brief review of the past spectrophotometric analytical work reported with hydrazones was presented at the end of this section.

A brief introduction to the basic principles of derivative spectrophotometry is presented in ***Section ii.***

In ***Section iii*** the importance of the present investigations has been discussed.

Section iv consists of the objectives of the present investigations.

CHAPTER 2 is divided into three sections

Section i deals with synthesis of 2-amino acetophenone isonicotinoyl hydrazone (2-AAINH) and its characterization by IR, NMR spectral studies.

Preparation of the reagent solution and other experimental solutions employed in the studies are listed in ***Section ii.***

Section iii describes various instruments employed in the present investigations.

CHAPTER 3 describes the experimental procedure and preparation of sample solutions of direct and derivative methods.

CHAPTER 4 is divided into two sections.

Section i describes the zero order spectrophotometric determination of manganese (II) with 2-AAINH. Manganese (II) forms greenish coloured soluble complex with 2-AAINH. The complex shows maximum absorbance at 435 nm, where the reagent shows negligible absorbance. Hence, 435 nm is chosen for further studies. Beer's law is obeyed in the range of 0.1373-2.746 μg mL^{-1} of Mn (II). The Molar absorptivity is found to be 1.49 $x10^4$ L mol^{-1} cm^{-1}. The composition of the complex is found to be 1:1. The method developed is applied for the determination of Mn (II) in tap water and diverse samples.

Section ii deals with first and second order derivative spectrophotometric methods developed for the determination of Manganese(II). The derivative spectrophotometric methods are found to be more sensitive than the zero order method. The second order derivative spectrophotometric method is successfully applied for the determination of Manganese(II) in some steel alloys and plant samples.

CHAPTER 5 is divided into two sections

Section i describes zero order spectrophotometric determination of Nickel (II) with 2-AAINH. Nickel (II) forms yellow coloured soluble complex with the reagent. The complex exhibits absorption maximum at 470 nm, where the reagent shows negligible absorbance. Hence, 470 nm is chosen for further studies. Beer's law is obeyed in the range 0.29 - 6.16 μg mL^{-1}. The Molar absorbtivity and Stability constant of the complex were 1.05 x 10^4 L mol^{-1} cm^{-1} and 5.747 × 10^9 respectively. The stoichiometry of the complex is found to be 1:1. The method developed is applied for the determination of Ni (II) in drinking water and in aluminum based alloys.

Section ii deals with first and second order derivative spectrophotometric determination of Nickel (II). The tolerance limits of various diverse ions are higher than those of the zero order determination of Nickel (II). The second order derivative method is applied for the determination of Ni (II) in alloy steels and vegetable (groundnut) oil samples.

CHAPTER 6 is divided in to two sections

Section i describes the zero order spectrophotometric determination of Molybdenum (VI) with 2-AAINH. Molybdenum (VI) forms yellow coloured soluble complex with the reagent. The complex shows maximum absorbance at 385 nm, where the reagent shows negligible absorbance. Hence, 385 nm is chosen for further studies. Beer's law is obeyed in the range of 0.49 - 7.34 µg mL^{-1} of molybdenum(VI). The Molar absorptivity is found to be 1.21×10^4 L mol^{-1} cm^{-1}. The composition of the complex is 1:1. The present method developed is applied for the determination of Molybdenum (VI) in food stuffs and some alloy steels.

Section ii deals with first and second order derivative spectrophotometric determination of Mo (VI) . The first order derivative method of determination of Mo (VI) is more sensitive than zero order determination of Mo (VI). Further Beer's law range is improved. The tolerance limits of various diverse ions are 20 fold higher than those of the zero order determination of Mo (VI). The second order derivative method is applied for the determination of Mo (VI) in alloy steels

CHAPTER 7 The results obtained in the determination of iron (III) by direct and derivative spectrophotometric method are presented in this chapter, which is divided into two sections.

Section i describes the zero order spectrophotometric determination of iron (III) with 2-AAINH. Iron (III) forms dark brown coloured water soluble complex with the reagent at pH 4.0 with absorption maximum at 400 nm. Beer's law is obeyed over the range of 0.25 -2.25 µg mL^{-1} of iron (III). The Molar absorptivity is found to be 8.82×10^4 L mol^{-1} cm^{-1}. The dark brown coloured solution showed a stoichiometry of 1:1. The method developed is applied for the determination of iron (III) in alloy, pharmaceutical and surface soil samples.

Section ii deals with first and second order derivative spectrophotometric determination of iron (III). The derivative methods are most sensitive than the zero order method. The tolerance limits of various ions are found to be higher than those in the zero order determination of Fe (III).

CHAPTER 8 is divided into five sections.

Section i describes the simultaneous first derivative spectrophotometric determination of manganese (II) and nickel (II). The first derivative spectrum of Mn (II) shows zero amplitude at 437 nm and considerably large amplitude at 447 nm. On the other hand, Ni (II) shows sufficient derivative amplitude at 485 nm and zero amplitude at 447 nm. Further Mn(II) and Ni (II) obey Beer's law at 447 nm and 485 nm respectively. Hence, Mn (II) and Ni (II) can be determined simultaneously in a mixture without separation by measuring the first order derivative amplitudes at 447 nm and 485 nm respectively. The developed method was applied for the determination of Mn (II) and Ni (II) in some aluminum based samples.

Section ii describes the simultaneous first derivative determination of Nickel (II) and cobalt (II). The first derivative spectrum of Ni (II)complex shows maximum amplitude at 480 nm, while Co (II) complex shows zero amplitude. On the other hand Co (II) complex shows maximum absorbance at 530 nm, while Ni (II) complex shows low amplitude. Further, the derivative amplitudes obey Beer's law at 480 nm and 530 nm for Ni (II) and Co (II) respectively. Hence Ni (II) and Co (II) can be determined simultaneously in a mixture without separation by measuring the first order derivative amplitudes at 480 nm and 530 nm respectively.

Section iii describes the simultaneous first derivative spectrophotometric determination of Molybdenum (VI) and Vanadium (V). The first derivative spectra of Mo (VI) and V (V) complexes show maximum amplitude at 422 and 465 nm respectively. Whereas V (V) show zero at 435 nm and Mo (VI) at 495 nm. Studies are therefore carried out for the simultaneous determination of Mo (VI) and V (V) by first derivative spectrophotometric by measuring the derivative amplitudes at 422 and 465 nm respectively. Hence, Mo (VI) and V (V) can be determined simultaneously in a mixture without separation by measuring the first order derivative amplitudes at 422 nm and 465 nm respectively. The developed method was applied for the determination of Mo (VI) and V (V) in some alloy steel samples.

Section IV describes the simultaneous second derivative spectrophotometric determination of manganese (II) and nickel (II). The second derivative spectrum of Mn (II) shows zero amplitude at 445 and 490 nm and considerably large amplitude at 462 nm. On the other hand, Ni (II) shows sufficient amplitude at 445 nm (valley), 482 nm (peak) and zero amplitude at 462 nm. Further derivative amplitudes obey Beer's law at 462 and 445 nm or 482 nm for Mn(II) and Ni (II), respectively. Hence, Mn (II) and Ni (II) can be determined simultaneously in a mixture without separation by measuring the second order derivative amplitudes at 445nm and 462 nm respectively. The developed method was applied for the determination of Mn (II) and Ni (II) in some aluminum based samples.

Section V describes the simultaneous second derivative spectrophotometric determination of nickel(II) and cobalt (II). The second derivative spectrum of Ni (II) shows zero amplitude at 435 and 540 nm and considerably large amplitude at 450 nm with zero crossing at 465 nm. On the other hand, Co (II) complex shows sufficient amplitude at 540 nm (peak), 480 nm (valley) and zero amplitude at 450 nm with zero crossing at 520 nm.

Further derivative amplitudes obey Beer's law at 450 and 540 nm for Ni (II) and Co (II), respectively. Hence, Mn (II) and Ni (II) can be determined simultaneously in a mixture without separation by measuring the second order derivative amplitudes at 450 nm and 540nm respectively. The developed method was applied for the determination of Ni (II) and Co (II) in some alloy steel samples and soil samples.

CHAPTER 9 summarizes the results obtained from the present investigation.

List of Research papers Published

1. “Direct and Second Derivative Spectrophotometric Determination of Manganese (II) in Tap Water, Alloy Steels and Plant samples **Satyanarayana Rao M**, Swetha M, and Raveendra Reddy P., July - August 2014, Research Journal of Pharmaceutical, Biological and Chemical Sciences, 5(4), 975-982.

2. “Spectrophotometric determination of nickel (II) with aminoacetophenone isonicotinoylhydrazone”, **M. Sathyanarayana Rao**, P. Saifulla Khan and P. Raveendra Reddy Der Pharmacia Lettre, 2015, 7 (7):281-286.