CHAPTER-5

EXPERIMENTAL RESULTS

5.1 Synthesis of new organic reagent α-Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH)

The novel reagent α-Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) was synthesised by simple condensation method, the yield of the compound is 78% and M.P is 250-252^{0}C. The structure of the reagent was characterized and confirmed from IR, NMR and Mass spectral data. The structure of the reagent ACINH is shown in Fig.5.1.

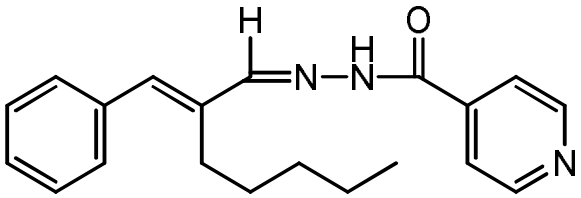

Fig: 5.1 Structure of ACINH

The α-Amyl Cinnamaldehyde Isonicotinoyl Hydrazone reagent is used for the spectrophotometric determination of Mercury (II) and Cadmium (II) for the present investigation.

5.2 Direct spectrophotometric determination of Mercury (II) using ACINH

The reagent α-Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) reacts with Mercury (II) to give water soluble yellow coloured specie in basic buffer (pH10.0) medium. The absorbance of the complex was stable for five hours. For the determination of Mercury (II), Hg (II)-ACINH complex was studied systematically and developed a direct spectrophotometric method in aqueous medium.

5.2.1 Absorption spectra of reagent solution and Mercury (II)-ACINH complex

The absorption spectra of Mercury (II)-ACINH complex and reagent solution was recorded in wavelength region 300-650nm region. From the Spectra (Fig.4.2.1) at 391nm the wavelength maximum was fixed for the determination Mercury (II) with ACINH by zero order spectrophotometric determination method.

5.2.2 Effect of pH on the absorbance of Mercury (II)-ACINH complex

The complex shows (Fig.4.2.2) constant absorbance and maximum absorbance in the pH range 10.0. Therefore, buffer solution having pH 10.0 was selected for entire studies.

5.2.3 Effect of reagent on the absorbance of the metal complex

The amount of reagent necessary for full colour development was established, for full colour development a ten-fold molar excess of reagent was sufficient.

5.2.4 Effect of time on the absorbance of Hg (II)-ACINH complex

Effect of time on the absorbance of Mercury (II)-ACINH was studied and the result shows that complex was stable for five hours.

5.2.5 Order of addition

The order of addition of metal solution, buffer solution and reagent solution has no adverse effect on the absorbance of reaction mixture.

5.2.6 Applicability of Beer's law

A calibration plot (Fig.4.2.3) drawn between the quantity of Mercury (II) and the absorbance. System obeyed the Beer's law in the concentration range of 1.0029-10.029 µg/ml from Ringbom's plot. The Molar absorptivity is 2.01×10^4 $L.mol^{-1}.cm^{-1}$ and Sandell's sensitivity is 0.0099 $\mu g.cm^2$, the straight line obeys the equation $A_{391nm}=0.0924X+0.0042$.

5.2.7 Tolerance limit of foreign ions

By employing the established optimum conditions the effect of various foreign ions were studied with a view to examine the selectivity of reagent. This experiment was also intended for the determination of tolerance limit of different associated ions.

By using 5.01475 µg/ml of Hg (II) the interference of different ions was studied. In the determination of Hg (II) using ACINH reagent no ions were interfere.

5.2.8 Applications

The Mercury (II) was estimated in water samples and the present method results were compared with certified values. The certified results and the results of the present investigation were closely resemble each other. The results are presented in Table 4.2.3.

5.2.9 Job's continuous variation method

The stability constant of the Mercury (II)-ACINH was found to be $6.45x10^5$ from the Job's variation method. From the value it is found that the complex was more stable during the investigation.

5.2.9.1 Molar ratio method

The molar ratio graph suggest the formation of 1:1 complexes (M:L)

5.3 Derivative first order spectra of Mercury (II)–ACINH complex

At 440nm the first order derivative spectrum (Fig.4.3.1) shows maximum amplitude. Therefore at 440nm first order derivative spectrophotometric determination of Mercury (II) was carried out at 440nm.

5.3.1 First order derivative method (Verification of Beer's law)

By using different concentrations of Mercury (II) the first order derivative spectra of the Mercury (II)–ACINH was recorded and shown in Fig.4.3.2. For the determination of the amount of Mercury (II) at 440nm a calibration plot (Fig.4.3.3) was constructed between the derivative amplitude and amount of Mercury. The plot was obeyed and linear the equation $A_{440nm}=0.1053X+0.0064$. The calibration graph suggests that the system obeys Beer's law in the range 1.0029-10.029 µg/ml of Mercury (II).

5.3.2 Effect of foreign ions

In the determination of 5.01475 µg/ml of Mercury (II), interference of various ions was studied. For each solution the first order derivative spectrum was recorded against reagent blank solution and amplitudes measured selected wavelength at 440nm from which the foreign ions tolerance limits were determined. It was observed that in determination of Mercury (II) (see Table 4.2.2) no ions were interfere in zero order and first order investigation.

5.3.3 Applications

In water samples the mercury (II) was estimated and the results are presented. By the certified values the first order derivative method was compared. The results of the verified values and present investigation values were closely resemble each other. The results are incorporated in Table 4.3.2.

5.4 Direct spectrophotometric determination of Cadmium (II) using ACINH

The reagent α-Amyl Cinnamaldehyde Isonicotinoyl Hydrazone (ACINH) reacts with Cadmium (II) to give water soluble yellow coloured specie in basic buffer (pH 9.0) medium. The absorbance of the complex was stable for five hours. For the determination of Cadmium (II), Cd (II)-ACINH complex was studied systematically and developed a direct spectrophotometric method in aqueous medium.

5.4.1 Absorption spectra of reagent solution and Cadmium (II)-ACINH complex

The absorption spectra of Cadmium (II)-ACINH complex and reagent solution was recorded in wavelength region 300-650nm region. From the Spectra (Fig.4.4.1) at 380nm the wavelength maximum was fixed for the determination Cadmium (II) with ACINH by zero order spectrophotometric determination method.

5.4.2 Effect of pH on the absorbance of Cadmium (II)-ACINH complex

The complex shows (Fig.4.4.2) constant absorbance and maximum absorbance in the pH range 9.0. Therefore, buffer solution having pH 9.0 was selected for entire studies.

5.4.3 Effect of reagent on the absorbance of the metal complex

The amount of reagent necessary for full colour development was established. For full colour development a ten-fold molar excess of reagent was sufficient.

5.4.4 Effect of time on the absorbance of Cadmium (II)-ACINH complex

Effect of time on the absorbance of Cadmium (II)-ACINH was studied and the result shows that complex was stable for five hours.

5.4.5 Order of addition

The order of addition of metal solution, buffer solution and reagent solution has no adverse effect on the absorbance of reaction mixture.

5.4.6 Applicability of Beer's law

A calibration plot (Fig.4.4.3) drawn between the amount of Cadmium (II) and the absorbance. System obeyed the Beer's law in the concentration range of 0.5031-5.0531 µg/ml from Ringbom's plot. The Molar absorptivity is 2.94×10^4 $L.mol^{-1}.cm^{-1}$ and Sandell's sensitivity is 0.0034 $\mu g.cm^2$ the straight line obeys the equation $A_{380nm}= 0.1243X+0.0132$.

5.4.7 Tolerance limit of foreign ions

By employing the established optimum conditions the effect of various foreign ions were studied with a view to examine the selectivity of reagent. This experiment was also intended for the determination of tolerance limit of various associated ions. By using 1.5888 µg/ml of Cd (II) the interference of different ions was studied. In the determination of Cd (II) using ACINH reagent no ions were interfere.

5.4.8 Applications

The Cadmium (II) was estimated in soil samples and the present method results were compared with certified values. The certified results and the results of the present investigation were closely resembling each other. The result are presented in Table 4.4.3.

5.4.9 Job's continuous variation method

The stability constant of the Cadmium (II)-ACINH was found to be $8.58x10^7$ from the Job's variation method. From the value it is found that the complex was more stable during the investigation.

5.4.9.1 Molar ratio method

The molar ratio graph suggest the formation of 1:1 complexes (M:L)

5.5 Derivative first order spectra of Cadmium (II)–ACINH complex

At 435nm the first order derivative spectrum (Fig.4.5.1) shows maximum amplitude. Therefore, at 435nm first order derivative spectrophotometric method determination of Cadmium (II) was carried out at 435nm.

5.5.1 First order derivative method (Verification of Beer's law)

By using different concentrations of Cadmium (II) the first order derivative spectra of the Cadmium (II)–ACINH was recorded and shown in Fig 4.5.1. For the determination of the amount of Cadmium (II) at 435nm, a calibration plot (Fig.4.5.3) was constructed between the derivative amplitude and amount of Cadmium. The plot was obeyed and linear the equation A_{435nm}=0.1426X+0.0248. The calibration graph suggests that the system obeys Beer's law in the range 0.5031-5.0531 µg/ml of Cadmium (II).

5.5.2 Effect of foreign ions

In the determination of 1.5888 µg/ml of Cadmium (II), interference of various ions was studied. For each solution the first order derivative spectrum was recorded against reagent blank solution and amplitudes measured selected wavelength at 435nm from which the foreign ions tolerance limits were determined. It was observed that in determination of Cadmium (II) (see Table 4.4.2) no ions were interfere in zero order, also do not interference in first order investigation.

5.5.3 Applications

In Soil samples the Cadmium (II) was estimated and the results are presented. By the certified values the first order derivative method was compared. The results of the verified values and present investigation values were nearly resemble each other. The results are incorporated in Table 4.5.2.