Research Article

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Metal ligand complexes of alpha nitroso beta naphthol

Abstract

Alpha nitroso beta naphthol complexes of transition metal ions were synthesized and then analyzed using flow system. It was found that the detection of cobalt was highly sensitive. Chromatographic studies revealed the presence of isomeric forms of cobalt chelate.

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Introduction

Alpha nitroso beta naphthol is a well known gravimetric reagent and can also be used for extractive spectrophotometric determination of metal ions.[1] The foremost advantages of the method are its high sensitivity and reproducibility but it suffers from sensitivity towards ammonia concentration and the low solubility of cobalt-nitrosonaphtholate. Modification of the gravimetry methodology was carried out by Chatterjee et al.,[2] wherein precipitation was carried out in acidic solution with a reagent prepared by heating alpha-nitroso-beta-naphthol in a mixture of glacial acetic acid, hydrogen peroxide and syrupy phosphoric acid. The complex of cobalt was ignited and weighed. There was no interferences from ions like iron(III), copper, chromium(III), vanadium(V), tungsten(VI), aluminium, molybdenum, nickel, titanium, zirconium, uranium(VI) and cerium.

The composition of cobalt complex is uncertain and therefore the determination of cobalt is carried out by the ignition of the chelate and weighed as such. Since the cobalt chelate is not water soluble, the studies were carried out by the formation of the precipitation of the chelate. In solution, the ligand tends to oxidize the cobalt (II) ions to its trivalent state and precipitates as its tris complex. The separation of α-nitroso-β- and β-nitroso-α-naphthols by ligand-exchange chromatography was studied. The best results were obtained by use of a strong acid type resin in the Fe^{3+} form as a stationary phase and a 50 %v/v ethanolic ammonia solution (pH 9.5 and 12.0) as the mobile phase for stepwise elution. In view of the slow adsorption rate of both isomers to the resin, the Fe(III)-nitrosonaphthol complex formed in the resin phase seems to be a low-spin 1:1 complex for which the oxygen of the hydroxyl group and the nitrogen of the nitroso group are both responsible.[3] The potential removal and preconcentration of lead (II), copper (II), chromium (III) and iron (III) from wastewaters were investigated and explored. Three new alumina adsorbents of acidic, neutral and basic nature (I–III) were synthesized via physical adsorption and surface loading of 1-nitroso-2-naphthol as a possible chelating ion-exchanger. The modified alumina adsorbents are characterized by strong thermal stability as well as resistance to acidic medium leaching processes. High metal up-take was found providing this order: Cu(II) > Cr(III) > Pb(II) owing to the strong contribution of surface loaded 1-nitroso-2-naphthol. The outlined results from the distribution coefficient and separation factor evaluations (low metal ion concentration levels) were found to denote to a different selectivity order: Pb(II) >Cu(II) >Cr(III)) due to the strong contribution of alumina matrix in the metal binding processes. The potential applications of alumina adsorbents for removal and preconcentration of Pb(II), Cu(II), Cr(III

) from wastewaters as well as drinking tap water samples were successfully accomplished giving recovery values of (89–100±1–3%) and (93–99±3–4%), respectively without any noticeable interference of the wastewater or drinking tap water matrices.[4] In this work, an on-line system for preconcentration and determination of cobalt at µg l level is proposed. Amberlite XAD-2 functionalized with α-nitroso-β-naphthol (NN-XAD) packed in a minicolumn was used as sorbent. Cobalt (II) ions were sorbed in the minicolumn, from which it could be eluted by hydrochloric acid solution. This eluate reacted with Nitroso Salt R and the absorbance of the complex was read at 510nm in a spectrophotometer. Signals were measured as peak height by using instrument software. Achieved sampling rate was 45samples per hour. Analytical parameters were evaluated and the results demonstrated that cobalt can be determined, with sample pH in the range of 7.0–8.5, preconcentration time of 60s with a sample flow rate of 5.0mLmin. The detection limit (3s) was 6.0µg l and the precision (assessed as the relative standard deviation) reached values of 6.1 to 1.9% in cobalt solutions of 10 to 300µg l concentration, respectively. The proposed procedure was applied in natural waters. Recoveries of spike additions (10, 25, or 50µg l) to natural water samples were quantitative (92–106%).[5] The composition of cobalt complexes with 1-Nitroso-2-naphthol has been established quite well.[6] A heterometric method[7] for the determination of cobalt in solutions or other metals has been reported. The cobalt comprises 0.1–3% of the total metal content. The titration generally takes 10–20minutes at room temperature, and the error is 0–3%. In this paper, studies of the metal chelates of alpha nitroso beta naphthol have been attempted using both flow injection analysis and liquid chromatographic systems.

Experimental

The metal chelates were prepared by adding a slight excess of the reagent solution in glacial acetic acid to the metal salt solution in dilute acid. The solution was warmed and the chelates precipitated were filtered, washed and dried. A known accurately weighed amount of the metal chelate ligand was dissolved in Acetonitrile and made into

solution. Further dilutions were carried out using acetonitrile prior to injection. The solutions were injected into a single flow system which consists of a pump (for pushing the carrier through a narrow tube), an injection port (for reproducible injection of a fixed volume of 20uL of a sample solution chelate dissolved in acetonitrile) and detector (JASCO UV 2070 Plus flow detector at a fixed appropriate wavelength) and output recorder. The chromatographic studies were carried out using C18 ODS filled column to bring about separation.

Results and discussion

The solubility of the metal chelate is not very high in acetonitrile. However for our present studies, the amount of chelate taken was quite less and hence there was no solubility issues. It is to be mentioned that in the flow analysis studies of single ions, the elution peaks for all the metal ions except for Co(II) were quite sharp but in the case of cobalt, the peak was broad. Figure 1 shows the variation of detector response with respect to the varying concentrations for different cations in the flow injection analysis system.

It is seen that calibration shows excellent linearity for Co with a R^2 value of 0.9978 while for others the values are nearly 0.95. Moreover it is seen that the sensitivity is maximum for Co(II) as compared to the other cations as seen from the slope. In order to understand the further aspects, the chromatographic studies of single ions as well as mixture was carried out. For single ions, mobile phase of acetonitrile: water (80:20) was used. It was seen that for cobalt there were two well defined peaks. When the mixture of cations was studied, the mobile

phase had to be varied and optimized to a mixture of acetonitrile, methanol and water (40:40:20) to enable good resolution and fast analysis. The results are given in Figure 2. It is seen that even in the case of mixture, cobalt showed two independent well resolved peaks indicating the formation and simultaneous existence of two different stable species. The two different species could arise due to two possibilities of (i) presence of Co(III) (formed by oxidation of Co(II) by the ligand) along with Co(II); or (ii) the cobalt existing in a single oxidation phase but the chelate formed is present in two isomeric forms.

In order to confirm the reason for the above observation, the first approach was to first oxidize the Co (II) to Co (III) using hydrogen peroxide resulting in the formation of black cobalt (III) hydroxide. The black precipitate was dissolved in glacial acetic acid and to it was added the alpha nitroso beta naphthol reagent solution. The tris-chelate was dissolved in acetonitirle and analyzed. It was seen that the chelate showed two peaks at 16.8 and 18 min and this matched with the result obtained for Co (II) chelate. Thus it is understood that the ligand first oxidizes the Co (II) to Co(III) and then results in the formation of two isomeric forms of the chelate (in the ratio of 1:2 for cis: trans) which elute at different timings resulting in two different peaks. In order to test the labile nature of the chelates and also the presence of thermodynamic equilibrium between the two forms, chromatograms were recorded at different temperatures and it was seen that with increase in temperature there was no change in the ratio but the peak resolution became poorer. This indicates that the isomeric forms of the chelates are quite stable.
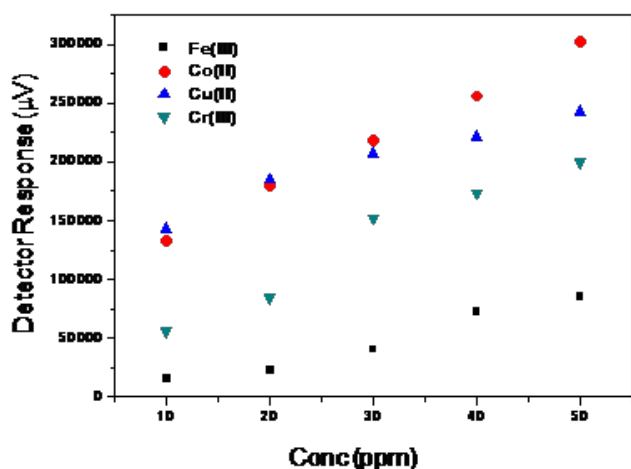

Figure 1 Calibration curve for different cations.

Figure 2 Chromatogram of mixture.

Conclusion

The ligand alpha nitroso beta naphthol formed chelates with most of the transition metal ions. However, for cobalt it was understood that two stable forms of the chelate were present and they are in equilibrium with each other.
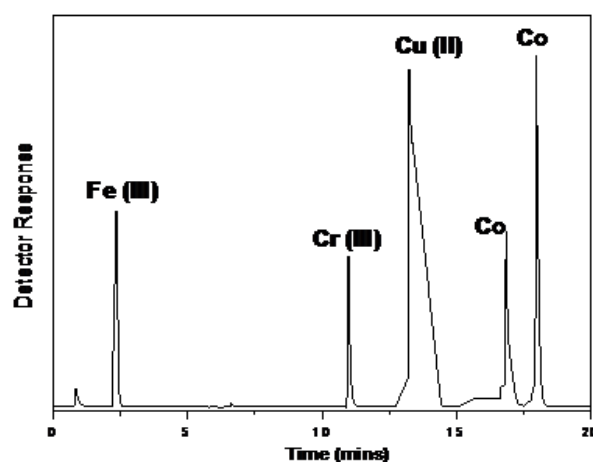
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None.

Conflict of interest

Author declares that there is no conflict of interest.

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