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Synthesis, separation and determination of metal dithiocarbamates complexes by HPLC-ICP-MS.

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Abstract

A rapid, simple and reliable spectroscopic technique has been developed for the determination of metal cations using dithiocarbamates moiety as chelating agent by HPLC. The method is based on the formation of stable colored dithiocarbamate complexes by reaction metal salt and dithiocarbamate moiety, which is then extracted methanol and separated with acetonitrile water mobile phase. The different analytical parameters affecting the method such as pH for extraction, solvent for extraction, mobile phase and type of the column. After the column elution the sample was allow to passes in to UV detector and then into ICP-MS. The separate data have been observed from UV detector and ICP-MS for each sample and then from the help of both results the identification and determination of these complexes have been done. Satisfactory recovery from the spiked samples of standard metal ion suggests no interference of any excipients. The developed method was compared with other spectroscopic methods, no significant difference was observed.

Keywords:

Dithiocarbamate, Metal complexes, HPLC, ICP-MS

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1. Introduction

Determination of metals in the trace level from water and biological system is often made possible by the addition of complexing agent and analyzed by range of spectrophotometer techniques. In most of the separation method dithiocarbamates and dithiophosphate moiety have been used as complexing agent. Dithiocarbamate moieties are being used as chelating agent due to their unique property to remain intact under variety of the reaction [1]. Dithiocarbamate complexes are being investigated because of the structural interest, unidentate, bidentate and bridged coordination pattern of the dithiocarbamate moiety[2] are well known. Analysis of the metals as their dithiocarbamate complexes using Gas Chromatography[3], HPLC [3-5] and Atomic Absorption Spectrometry [6] (AAS) techniques have been done. Mostly chromatographic separations of metal dithiocarbamates complexes have been done by HPLC with UV spectrophotometeric detection and other techniques [7-11]. Some authors extracted of Fe, Ni, Cr and Mn metals by the complexation with pentamethylene dithiocarbamate and determined them by AAS [12, 13] from water.

2. Experimental

2.1. Instrumentation

Micro elemental analysis was carried out on a Vario El III Elemental analyzer. Sulfur was estimated by Messenger's methods. Nitrogen was estimated by the Kjeldahl method. Electronic absorption spectra in the range 200-1100 nm were recorded on Systronic 2201

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double beam UV-visible spectrophotometer in dichloromethane. IR spectra (4000-300 cm^{-1}) were recorded on an ABBomen FTLA-2000 spectrophotometer using KBr discs.

The instrument used in this research propramme is HPLC (1100 series, Agilent) coupled with ICP-MS (7500 series, Agilent Technologies). In the ICP-MS the spray chamber is peltier cooled to reduce the loading of the solvent on the plasma. After the elution from the column the samples passes through UV detector and then into the ICP-MS. The separate UV and ICP-MS results have been taken for each sample, which helps the peak identification and determination.

2.2. Chemicals and methods

All solvents and ammonium acetate buffer were used as such from E-merck. The stock solutions have been prepared from metal salt such as chloride, nitrate or sulfate. Distilled deionized water was prepared from Barnstead, E-pure purification system.

2.2.1. Synthesis of 2-Amino Pyridine Dithiocarbamate (APDTC)

APDTC have been synthesized using the reported method [14]. A solution of 2-amino pyridine (30 mmol) in 30 mL of methanol was taken in a round bottom flask and cooled in an ice bath. Carbon disulphide (30 mmol) was added dropwise in the above reaction with constant stirring. The light yellow precipitate was obtained. These compounds were filtered, washed with methanol and diethyl ether and dried under vacuum.

2.2.2. Preparation of Metal Dithiocarbamate Complexes

The Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) 2-amino pyridine dithiocarbamate complexes have been synthesized by taking 1 mL of the stoke solution of metal ion (10 ppm) in a glass beaker. The pH of the above solution has been adjusted with buffer solution. After that, 0.25 mL of 1% (w/v) APDC aqueous solution was added. The metal dithiocarbamate complexes were immediately formed.

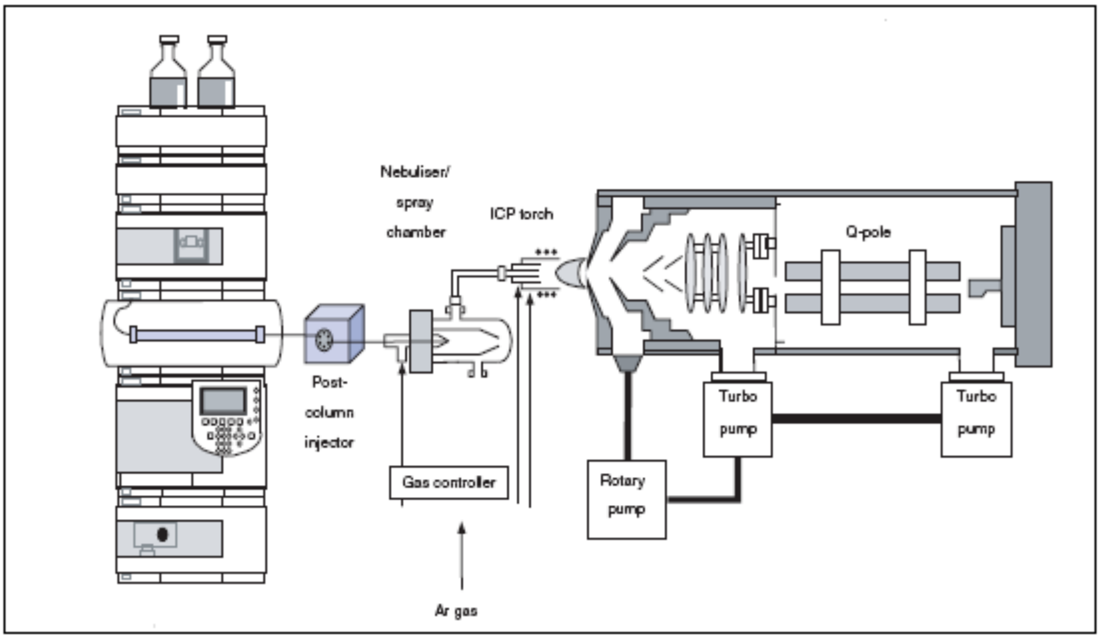
2.3. Solid Phase Extraction

The C_{18} SPE cartridge was conditioned with methanol to activate the packing before the sample is extracted. The complexes were passed through a column containing solid-phase and the complexes retained in the solid-phase were eluted with acetonitrile. The retention parameter for each metal complex was recorded and compared with standard metal complexes.

2.4. Analytical Procedure

150 mL of aqueous solution of the stoke solution containing chromium, manganese, iron, cobalt, nickel, copper zinc (20-30 ppm) was transferred to separating funnel. The methanolic solution of APDTC (5 mL, 0.1% w/v) and acetate buffer were added to adjust the pH 3. The reaction mixture then injected into HPLC. The chromatograph was run with the mobile phase contains 70/30 acetonitrile/water. The separation was achieved in 12 minute with excellent base line.

HPLC Conditions		ICP-MS Conditions	
Column	C-18 reversed-phase (15 cm× 2.1 mm i.d.; 3µm particale size)	Cones	Platinum
Mobile Phase	70/30 acetonitrile/ water	Plasma Gas Flow	14.4-14.8 L min^{-1}
Flow rate	0.2 mL min^{-1}	Carrier Gas Flow	0.62-0.73 L Min^{-1}
		Make-up Gas Flow	0.17-0.28 L min^{-1}
		RF power	1550 W



3. Result and Discussion

3.1. Characterization of APDTC

APDTC ligand has been characterized by infra-red spectroscopy. The band at 1509 cm^{-1} is intermediate between ν(C=N) (1691-1640 cm^{-1}) and ν(C-N) (1360-1250 cm^{-1}), which suggested the partial double bond character in the carbon and nitrogen bond [15]. The in band at 1040 cm^{-1} characteristic for dithiocarbamate moiety [16].

The dithiocarbamate moiety reacts metal ion to form color complexes, the complexsation is occurs at pH 3. These metal dithiocarbamates are extracted in methanol. These complexes are examined for preconcentration, extraction and determinations simultaneously as their metal ions. HPLC and ICP-MS were calibrated with standards. The instrument was recalibrated at the mean of the determination and was found 96-100 % recovery, with the coefficient of variation up to 3.6 %.

During the metal dithiocarbamate complexes preparations the pH 3 was adjusted which is one of the important variables; the complex formation and extraction of these complexes depend very strongly. The literature survey revealed that the complex formation and extraction ability from the aqueous solutions varies with metals and ligand[7]. Some author suggested that the peak area in HPLC was varied with pH.

The result of the Mn is found with less recovery that is probably due to less tend to form complexes and extract in organic phase at the lower pH range said 3. The said complex show the maximum complexes formation and having maximum peak area during the HPLC analysis at higher pH 7 due the formation of hydroxo complexes of certain metals.[13]

3.2. Selection of UV Detector Wavelength

The high molar absorptivity of the metal-PDC complexes lends itself to spectrophotometeric detection. The UV-VIS spectra of metal-PDC complexes were determined. The maximum UV absorption spectra differ from metal to metal and within the range of 203 nm to 284 nm. In the absence of common wavelength of maximum absorbance for all the metal-PDC under study, it was decided to use 254 nm as the detection wavelength, to make the method easily applicable to chromatographic system equipped with fixed UV wavelength detector.

4. Conclusions

The optimum results, in terms of selectivity, sensitivity and precision were obtained using HPLC-IPC-MS. The proposed method provided determination of dithiocarbamate complexes and heavy metals separation and analysis water and biological systems. The main advantages of this method are the small solvent quantity, speed, low cost, and the satisfactory recoveries having good precision. The interferences due to the other metal ion in the ICP, are reduced by the separation by HPLC and then the complexes were analyzed by UV detector and ICP-MS. The results obtained from the HPLC-ICP-MS are more informative than separate ICP and HPLC Unit.

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