Pyrrolidinedithiocarbamate AS A Reagent for Gc Analysis of Metal Ions

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Abstract: Dithiocarbamates have been extensively studied and reported as complexing reagents for a large number of metal ions for the solvent extraction, spectrophotometric and high performance liquid chromatographic (HPLC) determination of metal ions. They form coordinatively saturated, neutral metal chelates, which are easily extractable in organic solvents. They also provide adequate shielding to the metal ions to enable them to eluate from a GC column. The GC of metal chelates of diethyl dithiocarbamate, di(trifluoroethyl)dithiocarbamate and pentamethylenedithiocarbamate from packed and capillary columns have been reported. Pyrrolidinedithiocarbamate (PDTC) has advantages as an analytical reagent for metal analyses because of its complexation in acidic media. A number of studies have been made for HPLC determination of metal ions using PDTC, but the GC is characterized by increased resolving power with respect to HPLC and GC involves less running cost than HPLC. The conversion of the analyte selectively to volatile product, could possibly remove a number of matrix effects. The present work focuses to extend the range of complexing reagents for GC separation and analysis of metal ions. Pyrrolidinedithiocarbamate (PDTC) chelates of Cu(II), Ni(II), Fe(III), Mn(II), were extracted in MIBK and subjected to capillary gas chromatography. The research work was carried out on the capillary column; DB-1701 column (30 m x 0.25 mm, id, film thickness 0.25 mm) installed in Network GC 6890 (Agilent Technologies, USA) coupled with FID detection system. The metal chelates were subjected to capillary GC for the determination of Cu(II), Ni(II) and Fe(III) from Pakistani currency 5 rupee coin and municipal waste water sample of Hyderabad (Sindh). The results were compared by AAS.

Key words: Capillary GC, PDTC, MIBK, FID, Coins, Water Samples.

INTRODUCTION

The reagent pyrrolidinedithiocarbamate (PDTC) has advantages as an analytical reagent for metal analyses because of its complexation in acidic media [Fig 1]. A number of studies have been made for HPLC determination of metal ions using PDTC. The present study investigates the use of PDTC for GC determination of metal ions. Arain et al determined metal ions in water and coal samples (Arain *et al.,* 2002a; 2002b). Laghari et al determined zinc, copper, nickel, iron, manganese, chromium, vanadium, cobalt and platinum from metal alloys, water and pharmaceutical preparations (Laghari *et al.,* 2007; 2008). Applications of the proposed method could possibly be extended to a variety of reagents and metals. Literature survey showed that dithiocarbamates have been reported as complexing reagents for metals regarding their solvent extraction, spectrophotometric as well as HPLC and GC determinations (Bond and Wallace, 1983; Wang *et al.,* 1997; Zhang *et al.,* 1994; Butt *et al.,* 1996; Sturgeon *et al.,* 1980; Silva *et al.,* 1997). Gas chromatography of metal chelates prepared from diethyldithiocarbamate, di (trifluoroethyl) dithiocarbamate and pentamethylenedithiocarbamate has been reported (Masaryk *et al.,* 1975; Cardwell and Desarro, 1976; Radecki *et al.,* 1980; Riekkola *et al.,* 1979; Zabairova *et al.,* 1981; Tavlaridis and R. Neeb, 1976; 1978; Meyer and R. Neeb, 1982; Sucre, W. Jennings, 1980; Chebotarev and Koval'chuk, 2000; Koval'chuk and Chebotarev, 2001). Radecki et al determined zinc, copper and nickel from marine sediments, sea sand and mud (Radecki 1978; 1980). Feldmann *et al* (1994) separated, identified and quantified metals and metalloids; Sn, Sb, Bi, As, Te and Hg from condensates of domestic waste materials at low temperature GC hyphenated with ICP-MS. Xinmin *et al.,* (1993) applied capillary GC for determination of metallic pollutants present in water so as to maintain the quality of potable water available in China. Lobinski, (1994) presented a review on separation of metals using capillary gas chromatography with citation of 67 references. He gave more attention to the

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separation of metals from metalloids thereby coupling capillary GC with other techniques like optical and mass spectrometry as well. Discussion is also given about sample derivatization procedures using various organic reagents prior to their separations on capillary GC. Zeng (1993) separated metals selectively using gas chromatography coupled with atomic emission spectroscopy. Pretorius, *et al.,* (1993) reported to have developed high temperature GC- ICP-MS technique for the separation of metals from synthetic materials and metalloporphyrins. They also reported retention indices as well as detection limits of various metals separated. Liu, *et al.,* (1993) reported to have determined and separated metals from solid samples through complexation with bis(trifluoroethyl)dithiocarbamate (FDDC). The metals copper (II), cobalt(II), cadmium(II) and zinc(II) were complexed with FDDC, extracted with supercritical fluid extraction method and the same were determined through gas chromatography coupled with atomic emission detection system. Authors advocated this new method to economize the organic chemicals to determine inorganic metallic ions from solid substances. Hrouzek and Krupcik, (1993) have reviewed and reported a novel method for the determination and separation of inorganic substances and metals and metal chelates like dialkyldithiocarbamates (DDCs) and 2,2,2-trifluoroethyldithiocarbamates (TFDCs) using gas chromatography. The authors explored and cited 37 references for their work. Rucker *et al.,* (1992) determined and separated transition metals and organic substances present in denim jeans, using gas chromatography hyphenated with mass spectrometry. The metals Al, Cu, Fe, and Mn were separated along with alkaline earth metals like Ca and Mg present in the denim jeans. Zeng et al [31] reported to have developed new selective method for the determination of metals nonmetals and metalloids from different substances using capillary gas chromatography coupled with atomic emission detection system. The method was applied to selectively determine and separate B, Al, Ga, Ti, V, Ni, Fe, Cr, Mn, Rh, Pd and Pt. The authors separated selectively V, Ni and Fe in crude oil as metalloporphyrins, Mn as methylcyclopentadienylmanganesetricarbonyl (MMT) from gasoline and Ti from mixtures of titanium catalysis. In present study use of PDTC reagent coupled with extraction of metals in methyl isobutyl ketone (MIBK) and separation of metals by capillary GC with FID detection system is discussed.
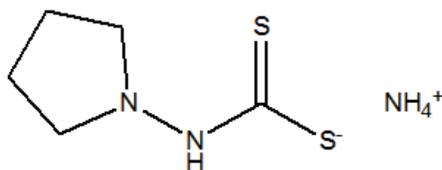

Fig. 1: Pyrrolidinedithiocarbamate (PDTC)

METHOD AND MATERIALS

Solutions of Metal Ions:

Aqueous solutions of metal ions were prepared from GR grade copper(II) sulphate hexahydrate, nickel(II) chloride, iron(II) chloride and manganese(II) chloride (E. Merck, Darmstadt, Germany). Solutions of lower concentrations were prepared by successive dilutions. Iron(II) was treated with aqua-regia for 10 min for conversion into iron(III) and diluted accordingly.

Pyrrolidinedithiocarbamate (PDTC) (BDH, UK) solution (1% w/v) was prepared in methanol-warer (1:1 v/v).

Buffer solutions were prepared between pH 3-9 at unit intervals as follows:
Acetic acid (1M) : Sodium acetate (1M)………………….…...pH 3-6.
Ammonia solution (1M) : Ammonium acetate (1M)……………pH 7.
Sodium bicarbonate (1M): Sodium carbonate (saturated)………pH 8-9.

Formation & Extraction of Metal Chelates:

Aqueous solutions (1-5 ml) of Cu(II), Ni(II), Fe(III) and Mn(II) were added to PDTC (1 ml, 1% w/v), acetate buffer pH 5 (1 ml) and extracted in methyl isobutyl ketone (MIBK). The solution (1 µl) was injected on the capillary column (DB-1701) and calibration curves were constructed using serial dilutions of stock solutions.

Solution of Coin:

Five-Rupee denomination coin, unit of Pakistan currency (Cupro-nickel in composition) weighing 6.51 g was dissolved in aqua-regia by heating gently and diluting to 250 ml as stock solution. The sample solution was again diluted to 250m ml by taking 1 ml from stock solution. The metal chelates were prepared and extracted in MIBK as mentioned the procedure in above section (formation & extraction of metal chelates) and were run on capillary GC with FID detection system. The chromatograms of copper, nickel and iron were obtained and quantified with external calibration curves of standard solutions. The copper, nickel and iron metals from the coin were further examined and compared by AAS.

Solution of Muncipal Waste Water Sample:

A municipal waste water sample was collected from pumping site off Phuleli canal near Liaquat Colony area of Hyderabad. Exactly 100 ml was filtered and treated with aqua-regia. The sample was digested and concentrated to 5 ml. The pH value was adjusted to 5 with acetate buffer and added PDTC solution and extracted in MIBK. The sample was injected and run on to capillary GC with FID detection system. The waste water sample results were compared by AAS.

Instruments and Equipments:

Desktop pH:

meter, 420A Orion (USA) coupled with glass membrane combined electrode properly calibrated unit selected for measurements of pH scale.

3.2. Network gc:

6890 (Agilent Technologies, USA), FID detection system, Split mode injection port facility and capillary column DB-1701 (30 m x 0.25 mm id. film thickness 0.25 mm) (J & W Scientific GC Columns, USA) were installed in the GC system. The complete GC system was controlled through Chemstation Software installed in and run by computer. Hydrogen generator (H2-90 Parker Balston, USA) was used for FID detection system. Extra pure nitrogen gas (BOC- Pakistan) was used as carrier gas. The elution was carried out at column temperature of $180^{\circ}C$ with programmed heating rate of 8 oC/min up to $260^{\circ}C$ with total run time 12 minutes. The nitrogen gas flow rate was 3.5 ml/min. Injection port and detector temperatures were $260^{\circ}C$ and $280^{\circ}C$ respectively. The split ratio was maintained at 10:1. Detection was by FID. Nitrogen was used as make-up gas for FID. Hydrogen and airflow rates for FID were maintained at 45 ml/min and 450ml/min respectively.

3.3. Atomic Absorption:

Spectrophotometer of Varian Spectr AA-20 model (Australia) with air-acetylene flame head burner and standard HCL lamps as a source was used according to the conditions set by manufacturer. The analyses were carried out in triplicate with an integration time of 3s and delay time 3s, for Cu, Ni, Fe and Mn at 324.8nm, 232nm, 248.3nm and 279.48nm respectively.

RESULTS AND DISCUSSION

The water soluble reagent pyrrolidinedithiocarbamate (PDTC) reacts with many metal ions in acidic medium, including Cu(II), Ni(II), Fe(III) and Mn(II). PDTC serves as derivatizing reagent. The neutral metal chelates are extractable in non-aqueous solvents. The solution of the metal chelates in organic solvent, when injected on capillary column DB-1701, the metal chelates eluted from the column as separate peaks from the derivatizing reagent. The reaction conditions for the simultaneous determination of four metal ions were examined. The effects of pH [Fig. 2], derivatizing reagent concentration and extracting solvents were examined. Constant amount (1μl) of metal chelate was injected and average response (peak height) (n=4) was noted [Fig 3]. For the simultaneous determination of metal ions sodium acetate buffer pH 5 was selected. The calibration curves were attained in the "1-20 μg ml^{-1}" range for Cu(II), Ni(II), Fe(III), Mn(II), corresponding to 0.1-2.0 ng reaching to the detector. The coefficients of determinations (R^2) for calibrations were obtained within the range 0.9994-0.9997 [Fig 4]. The detection limits measured as signal to noise ratio 3:1 were obtained within "0.15-0.2 μg ml^{-1}" corresponding to Cu(15 pg), Ni(20 pg), Fe(16 pg) and Mn(18 pg) reaching to the detector. The analytical method was examined for the determination of metal ions from metal alloys. The contents of Cu, Ni and Fe were determined from Pakistani coin of Rupees five denominations [Fig 5]. The % Cu, Ni and Fe found in the coin is summarized [Table 1] and indicated RSD 2.2 – 4.1% and 1.7 – 5.9% respectively. The

amount of Cu, Ni and Fe in coin was also analyzed by flame atomic absorption spectrometry and the results obtained agreed with the GC method. A sample of sewage water was collected from Kali Mori area Hyderabad, treated and analyzed. The analytical procedure was applied and the metal ions Cu(II), Ni(II) Fe(III) observed were quantified [Fig 6]. The results obtained agreed with flame atomic absorption spectrophotometry [Table 2].

Table 1: Copper(II), nickel(II) and iron(III) as PDTC complexes in 5- Rupee Coin by GC and AAS.

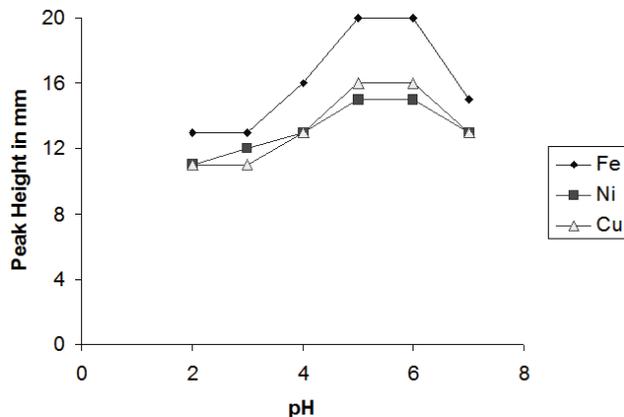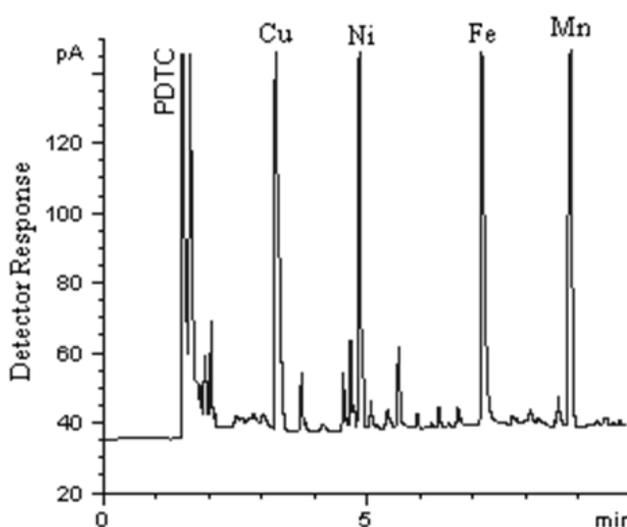| Sample	Wt of Coin	Analyzed by	%Cu	%Ni	%Fe
5-Rupee	6.51 g	GC	72.94 (2.2)	21.62 (1.7)	4.81 (1.9)
Coin		AAS	65.52 (4.1)	18.11 (5.6)	3.69 (4.3)

Fig. 2: Effect of pH on PDTC

Fig. 3:   Capillary GC separation of copper(II), nickel(II), iron(III) and manganese(II) as complexes of pyrrolidinedithiocarbamate (PDTC).

Conditions: Capillary column DB-1701 (30m x 0.25mm id, film thickness 0.25 m) (Agilent, USA) using split ratio of 10:1, column temperature was programmed from 180oC to 280oC at the rate of 8oC min-1 with oxygen free nitrogen flow rate of 3.5 ml min-1. Injection port and detector temperatures were maintained at 280oC and 320oC, respectively. Pure nitrogen was used as the make up gas. The detection was by FID.
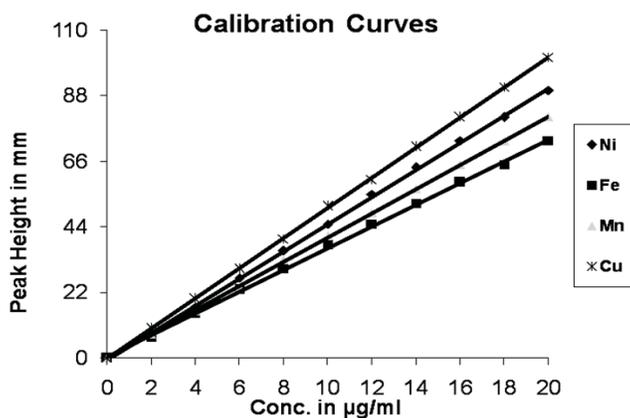
Fig. 4: Capillary GC Calibration Curves of copper(II), nickel(II), iron(III) and manganese(II) as complexes of pyrrolidinedithiocarbamate (PDTC).
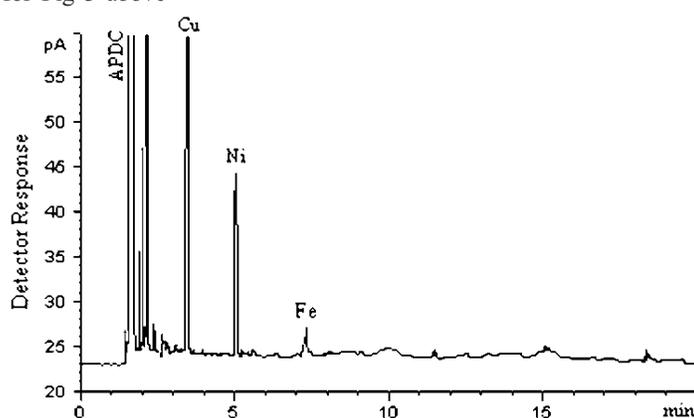
Conditions: Same as for Fig 3 above

Fig. 5: Capillary GC separation of copper(II), nickel(II) and iron(III) from 5 Rupee coin (Pakistani currency) as complexes of pyrrolidinedithiocarbamate (PDTC).
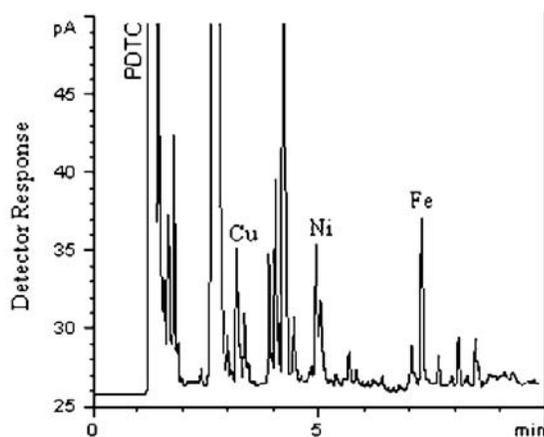
Conditions: Same as for Fig 3 above

Fig. 6: Capillary GC separation of copper(II), nickel(II) and iron(III) from sewage water sample as complexes of pyrrolidinedithiocarbamate (PDTC).

Conditions: Same as for Fig 3 above

Table 2: Copper(II), nickel(II) and iron(III) as PDTC complexes in sewage water samples, by GC and AAS

Sample	Analyzed by	Cu	Ni	Fe
Sewage water sample (μg ml^{-1})	GC	0.11 (1.5)	0.12 (2.2)	0.14 (2.5)
	AAS	0.08 (4.8)	0.09 (5.9)	0.11 (5.2)

Conclusion:

A new GC procedure has been developed for Cu, Ni, Fe and Mn with extensively used complexing reagent pyrrolidinedithiocarbamate (PDTC). Complete separation is obtained between the elements examined with detection of 15 -20 pg reaching up to FID detection. The method is applied for determination of metals from coin and water samples.

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