

## Capillary Gas Chromatographic Separation of Copper, Mercury, Lead and Cadmium as Complexes of Pyrrolidine Dithiocarbamate.

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**Abstract:** Detection and separation of metals from fresh water and industrial effluents has become a pre-requisite for any nation in the world. In and around the city of Hyderabad (Sindh), Pakistan, the home as well as cottage industry which consumes chemicals containing the copper, mercury, cadmium and lead are freely dumped into local ravines and canals unchecked for many years. The process is polluting the underground aqueous system and depleting fertile local soil. There are many techniques available to detect these metals, in present work copper, mercury, lead and cadmium as complexes of pyrrolidinedithiocarbamates were isolated from aqueous samples, extracted in methyl isobutyl ketone (MIBK) and separated by capillary gas chromatography coupled with flame ionization detection (FID) system.

**Key words:** PDTC, Capillary GC, MIBK, FID.

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### INTRODUCTION

Metals if present in aqueous system pollutes the pond eco system because many a metals are toxic in nature like lead and cadmium, as the same metals are considered carcinogenic as well. Therefore check on such metals is very important, when dumped into aqueous systems. There are techniques like gravimetric, titrimetric, spectrophotometric available in order to keep check on the fresh waters as well as industrial effluents containing many pollutants being dumped into ravines and canals. The mercury, cadmium and lead are used in automobile parts in large quantities. The area of Hyderabad (Pakistan) under study is thronged with automobile workshops repairing and washing the used machine parts, ultimately the waste is discharged into drains. During present study the metals; lead and cadmium were selectively extracted after complexing them with pyrrolidine dithiocarbamate (Pyrrolidine-1-carbodithioic acid (IUPAC)) [Fig. 1] and separated by capillary gas chromatography. The extraction of the metals reported and their separation is restricted to volatile metal chelates (Uden, P.C., 1984). Among these metal chelates the GC of  $\beta$ -diketones, monothioacetylacone and its derivatives, bis and tetradentate ketoamine Schiff bases, dialkyldithiocarbamates (DDTC), penatmethylene dithiocarbamate, dialkyl dithiophosphate and metalloporphyrins is possible (Khuhawar, M.Y., 1991; Zeng, Y., 1995; Khuhawar, M.Y., 1993; Khuhawar, M.Y., 1995; Khuhawar, M.Y., 1997; Khuhawar, M.Y., 1998; Khuhawar, M.Y., 1999; Arain, M.A., 2002; Arain, M.A., 2002). Dithiocarbamates have been extensively studied and reported as complexing reagents for a large number of metal ions for the solvent extraction, spectrophotometric and liquid chromatographic determination of metal ions (Zheng, Y., 1994; Zheng, Y., 1994; Bond, A.M., 1983; Wang, P., 1997; Zhang, X.S., 1994). Laghari *et al* (2007, 2008, 2010) have worked on selective extraction of metals; Cu, Zn, Ni, Co, Mn, Cr, V and Pt by complexing with pyrrolidine dithiocarbamate and separated using capillary gas chromatography coupled with FID detection system.

### 2. Experimental

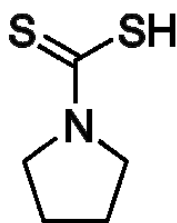
#### 2.1. Equipments:

##### Desktop pH:

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

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**Fig. 1:** Pyrrolidine dithiocarbamate (PDTC).

**Network GC:**

Computer controlled Chemstation software network GC 6890 of Agilent Technologies (USA), coupled with FID detection system, Split/splitless 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). Air compressor Hitachi (Japan) and hydrogen generator H2-90 Parker Balston (USA) for FID detection system. Extra pure nitrogen gas (99.99%) purchased with certification from BOC (Pakistan) was used as carrier gas. The elution was carried out at column temperature of 180 °C with programmed heating rate of 8 °C/min up to 260 °C with total run time 10 minutes. The nitrogen gas flow rate was maintained at 3.5 ml/min. Injection port and flame ionization detector temperatures were kept at 260 °C and 280 °C respectively. The split ratio was maintained at 10:1. Nitrogen was used as make-up gas. Hydrogen and airflow rates for FID were maintained at 45 ml/min and 450 ml/min respectively.

**Atomic Absorption:**

Varian Spectr AA-20 model (Australia) atomic absorption spectrophotometer with air-acetylene flame head burner and standard HCL lamp 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 Cd, and Pb at 228.8nm and 217nm respectively.

**2.2. Reagent Solutions and Procedure:**

**Stock solutions** containing metal ions were prepared in water from GR grade copper(II) chloride, mercury(II) acetate, lead(II) chloride, and cadmium(II) chloride salts (E. Merck Darmstadt Germany). Solutions of lower concentrations were prepared by successive dilutions.

Pyrrolidinedithiocarbamate (BDH, UK) solution (1.3% w/v) was prepared in methanol-water (1:1 v/v).

Acetate buffer (pH-5) prepared .....Acetic acid (1M) : Sodium acetate (1M).

**Formation of Metal Chelates:**

Stock solutions 2 ml diluted to 10 ml and then 1 ml solution of Cu(II), Hg(II), Pb(II) and Cd(II) were added to PDTC (1.5 ml, 1.3 % w/v), acetate buffer pH 5 (1.5 ml) and extracted in methyl isobutyl ketone (MIBK). The organic layer of MIBK was pipetted out to screw capped sample vial. The solution (1 µl) was injected on the capillary column (DB-1701) and calibration curves were constructed using serial dilutions of stock solutions. Average peak height (n=5) for cadmium and lead were recorded.

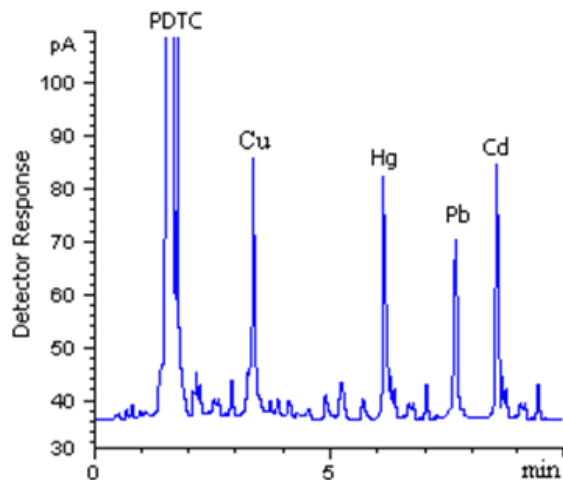
**Waste Water Sample:**

2.0 L waste water sample was collected from new bridge off Qazi Qayoom road area of Hyderabad. Exactly 150 ml was filtered, digested and concentrated to 5 ml. The pH 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 sample results were compared with AAS.

## RESULTS AND DISCUSSION

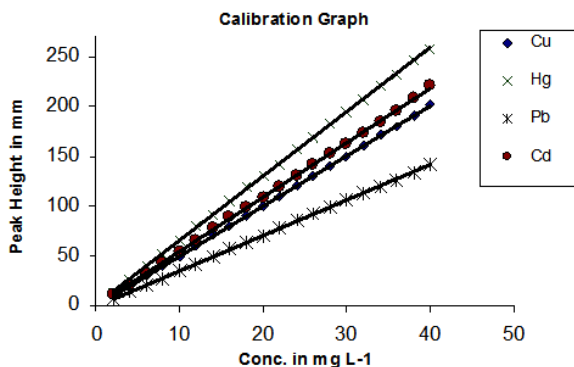
Derivatizing organic reagent PDTC is a water soluble reagent and has ability to complex in slightly acidic medium with number of metal ions including copper, mercury, cadmium and lead. The standards of the metals treated with PDTC to form complex and extracted in MIBK at pH 5 were subjected to capillary GC installed with capillary column DB-1701 and coupled with FID detection system, the metal chelates were thus eluted simultaneously as separate peaks from PDTC. An amount (1µl) of metal chelate was injected consistently and

average response (peak height) (n=5) was noted [Fig 2]. The calibration curves were attained in the “1-40  $\mu\text{g ml}^{-1}$ ” range for Cu(II), Hg(II), Cd(II) and Pb(II), corresponding to 0.1-4.0 ng reaching to the detector. The coefficients of determinations ( $R^2$ ) for calibrations were obtained within the range 0.9997-0.9999 [Fig 3]. The detection limits measured as signal to noise ratio 3:1 were obtained within “0.09-0.43  $\mu\text{g ml}^{-1}$ ” corresponding to Cu(15 pg), Hg(09 pg), Cd(21 pg) and Pb(43 pg) reaching to the detector. The analytical method was examined for the determination of metal ions from water samples. The PDTC complexes of copper, mercury, cadmium and lead analyzed by capillary GC [Fig 4] quantified and compared with the amounts obtained by AAS [Table 1].



**Fig. 2:** GC chromatogram showing separation of (1) PDTC reagent in methanol (2) Cu(II) (3) Hg(II) (4) Pb(II) and (5) Cd(II).

Conditions  $\text{N}_2$  flow rate 3.5 ml/min column initial temp. 160 °C for 2 min. with programmed heating rate of 20 °C upto 260 °C, at final temp. 260 °C for 3 min. Total run time 10 minutes. Concentration 10 ppm (1 $\mu\text{L}$  injection) n = 5



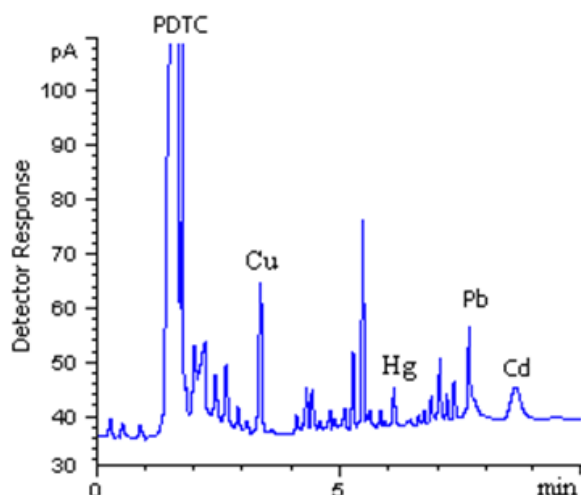
**Fig. 3:** GC calibration curves of (1) Cu(II) (2) Hg(II) (3) Pb(II) and (4) Cd(II).  
Conditions Same as in Fig. 2.

**Table 1:** Quantitation of copper, mercury, cadmium and lead as PTDC complexes by GC and AAS with n=5 (RSD%)

Sample	Analyzed by	Copper	Mercury	Cadmium	Lead
Water sample $\mu\text{g/mL}$	GC	264.0 (2.1)	24.3 (1.7)	208.2 (1.9)	233.0 (2.4)
	AAS	230.6 (6.5)	19.0 (4.3)	185.4 (5.6)	209.2 (5.5)

**Conclusion:**

A new method has been developed to monitor discharge of metals into open drains by means of complexation of copper, mercury, cadmium and lead as chelates of PDTC, extracted with MIBK solvent and analyzed by capillary GC with (n=5) RSD 1.7-2.4 % and results are compared with spectrophotometric technique AAS with RSD 4.3-6.5%.



**Fig. 4:** GC chromatogram of water sample showing separation of (1) PDTC reagent in methanol (2) Cu(II) (3) Hg(II) (4) Pb(II) and (5) Cd(II).  
Conditions Same as in Fig. 2.

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