

Development of Paper Strip Based Detection for Selected Heavy Metals Using Metal Ion Chromatography

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Abstract: In this research we have attempted to develop a paper strip based chromatography technique for the on-site detection of heavy metals. Various heavy metal ions such as Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Fe³⁺, Mn²⁺ and Co²⁺ were chromatographed on paper strips impregnated with sodium diethyl- dithiocarbamate (NADDC) and its admixture with Na₂CO₃, NaCl, CaNO₃, NH₄Cl, EDTA, H₃PO₄, CaCO₃, Na₂HPO₄, H₃PO₄ and NaOH. Common solvents viz. acetone, acetonitrile, carbon tetrachloride, benzene, and isopropyl alcohol, aqueous NADDC and distilled water were employed as mobile phases. Semi quantitative and qualitative determination of selected heavy metals by visual comparison of colour intensities on the TLC plates as well as by measurement of developed spot area has been experimentally accomplished. Appropriate onsite paper strip sensors have been developed for binary and multiple separations of selected heavy metals for different industrial wastewater.

Keywords: Industrial Waste Water, Metal Ion Chromatography, Sodium diethyldithiocarbamate,

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I. Introduction

Water pollution is a global problem disturbing both developed and developing countries. Of the contaminants, heavy metals are one predominant type of water pollutants. Numerous sources lead to heavy metal pollution problem. Ex. Lead can be observed as a consequence of lead solder in copper piping. Mercury and cadmium could be due to power plant emissions¹. The establishment of small quantities of heavy metals such as Cu, Cd, Hg, and Zn in the environment is imperative due to their high toxicity, increasing levels in the environmental and due to their bioaccumulation in living organisms. Metals are regularly estimated after digestion with strong acids. Common analytical techniques used are ion chromatography, inductively coupled plasma, polarography, ion-selective electrodes, and AAS etc.

Progress has been achieved in the biosensor development depending on whole cells of bacteria for monitoring toxic metals contamination. Both nonspecific and specific biosensors based on whole cells have been developed. Nonspecific microbial biosensors, being used for several years, measure only general toxicity. Additionally, heavy metals are acclaimed to inhibit the enzymes activity, and utilization of this aspect for the detection of these hazardous toxic elements offers several advantages such as simplicity and sensitivity. Besides, the metal inhibition of enzymes has been related to its biological toxicity². Paper-based detection system is a new unconventional technology with a low-cost, portable, simple and disposable analytical devices for multiple applications including diagnostics, food quality control and environmental monitoring.

The beneficial distinctive properties of paper embrace allowance of passive liquid transport and rapport with chemicals/biochemical. Current paper-based sensors are based on microfluidic delivery of solution to the detection zone while more progressive designs include complex 3-D geometries deployed on the equivalent microfluidic principles. Even though paper-based sensors are very propitious, they are still racked with some limitations such as sensitivity and accuracy. Thus, it is imperative to develop rapid and inexpensive, specific and sensitive on-site detection system using a portable, low-cost, and fast heavy metal analysis system for initial on-site/in-situ screening of heavy metal-contaminated sites³.

In this report we present rapid and inexpensive, specific, sensitive, chromatography based on-site detection system for heavy metal analysis in simulated and actual industrial waste waters.

II. Materials and Methods

Sodium diethyldithiocarbamide, sodium sulphide and dithiozone, Cobalt chloride, Mercuric chloride, Zinc chloride, Ferric chloride, Cadmium sulphate, Lead nitrate and Manganous chloride, NaCl, EDTA, NaOH, Na₂CO₃, H₃PO₄, CaNO₃, NH₄Cl, Na₂HPO₄ and CaCO₃ were purchased from SD fine chemicals, E.Merck and

Qualigens. All other chemicals and reagents used were of analytical grade and were obtained from standard chemical companies. AAS standards were procured from Sigma Aldrich.

2.1 Reagents and Chemicals

Solutions of metal salts (1%), sodium sulphide and sodium diethyldithiocarbamide (NaDDC) (0.01M) were formulated in distilled water. Aqueous solutions of metal salts were stabilized by the addition of the corresponding mineral acids (0.5ml of 4M) and ethanol (0.5ml). Solution of dithiozone (1%) was prepared in carbon tetrachloride. Pb^{2+} , Hg^{2+} , Cd^{2+} , Zn^{2+} , CO^{2+} , Fe^{3+} and Mn^{2+} were used as their $NO_3^- / Cl^- / SO_4^{2-}$ forms⁴.

2.2 Preparation of Impregnated Paper Strips

Solutions with desired concentration of impregnate with various additives $IM_1 = NADD C (20\%)$, $IM_2 = NADD C (20\%) + H_3PO_4(4\%)$, $IM_3 = NADD C (20\%) + CaNO_3$, $IM_4 = NADD C(20\%) + Na_2CO_3 (4\%)$, $IM_5 = NADD C (20\%) + NaCl (4\%)$, $IM_6 = NADD C (20\%) + NH_4Cl (4\%)$, $IM_7 = NADD C (20\%) + EDTA(4\%)$, $IM_8 = NADD C(20\%) + NaOH(4\%)$, $IM_9 = NADD C(20\%) + CaCO_3 (4\%)$ and $IM_{10} = NADD C (20\%) + Na_2HP O_4(4\%)$. NaDDC (20%) were prepared in distilled water.

Then these paper strips were dipped for 30 s in a watch glass containing these aqueous suspensions (separately). Then these paper strips were dipped for 30 s in a watch glass containing these aqueous suspensions (separately). Then the solvent was removed completely from the paper strips by suspending them to drained off the solvent. The paper strips were then dried at room temperature followed by an electric oven at 70°C for 5min. The dried strips were then stored in a polythene bags at room temperature till further use.

Mobile Phases used in this experiment were Acetone, Benzene, Carbon tetrachloride, Acetonitrile, Isopropanol, Aqueous NaDDC and distilled water⁴.

2.3 Thin Layer Chromatography

Thin layer chromatography was performed on two types of strips: silica based strips and whattman filter paper strips. Test solutions (1 μ l) were placed on impregnated strips using micropipettes at about 2 cm above the lower edge of the strips. Then the spot was dried at room temperature, and the strips were placed in chromatographic glass jar previously saturated with the mobile phase for the determination of R_F values of all individual metal ions, the solvent ascent was fixed to 10 cms. Ascending development was followed in a TLC chamber.

For separation of mixed metal salt solutions, the metal salt solution was spotted on the impregnated strip as given above and solvent was removed completely by air drying the strips. The metal salt solution was spotted. The plate was developed as given above.

Studies were also carried out for synthetic (mixture of metal salt solution) sample to check for any other interferences⁴.

2.4 Limit of Detection

The limits of detection of the metal ion were carried out by spotting different concentrations of metal ion onto the TLC plates, developing the plates using the method describe above, and then detecting the spots. The lowest concentration was the concentration where spots were not detected. The minimum detectable quantity on the TLC plates was considered as the limit of detection⁵.

2.5 The Simulated Metal Contaminated Waste Water

Different metal salt solutions were prepared at 1% level as mixture and used for analysis as given above

2.6 Real sample analysis

The tyre industry, textile industry, Aluminum Steel industry trade effluents and Natural Ground water samples were checked for the presence of heavy metals using these calibrated strips. For Industrial trade effluent samples, spotting of test solution was carried out in the same manner as said above. Visual comparison of colour intensities on TLC plates indicated the qualitative determination of selected metal salt solution.

The analytical performance of these strips were compared with Inductively Coupled Plasma (ICP - Horiba Jobinyvon, France) under the following conditions - With the help of Argon gas, flame ignited at 6kg/min at 5000 °C to 6000 °C.

2.7 AAS Studies

The analytical performance of these strips was also compared by AAS (GBC Scientific equipment, Australia). The metal samples in the strip were scraped, dissolved in concentrated HNO_3 . Two drops of HCl were added, volume was made up to 25mL with distilled water and subjected to digestion at 80°C for 1h. The solution was filtered using Whatman No. 1 filter paper and volume was made up to 25mL before AAS

analysis. The AAS conditions were: Acetylene gas (Acetylene in Acetone 300:1 by volume at 1100 KPa), Flame - Air-Acetylene Flame, Flame temperature: 1800°C to 2300°C, Radiation Source - Hollow Cathode Lamp.

2.8 Detection of the Analyte

To visualize the metal ion, the developed and dried strips were dipped in a watch glass containing the following detectors:

- (1) NADDC solution was used for Mn²⁺ (violet), Fe³⁺ (Black), CO²⁺ (light green).
- (2) Sodium sulphide solution was used for Cd²⁺ (yellow), Hg²⁺ (light black) and Pb²⁺ (brown).
- (3) Dithiozone solution was used for Zn²⁺ (pink).

2.9 Measurement of the Metal

The following expressions were used to calculate the aforesaid parameters:

$$R_F(\text{Compact Spot}) = \frac{\text{Distance travelled by the solute (cm)}}{\text{Distance travelled by the solvent (cm)}}$$

R_L(Tailing) = Distance travelled by the Lower edge of a tailing spot in cm

R_T(Tailing) = Distance travelled by the upper edge of a tailing spot in cm

R_M(Tailing) = Avg of R_L and R_T⁴.

III. Results and Discussion

The study was attempted by chromatography of seven metal ions (Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Co²⁺, Fe³⁺ and Mn²⁺) on paper strips impregnated with ten adsorbent (NaDDC, H₃PO₄, CaNO₃, Na₂CO₃, NaCl, NH₄Cl, EDTA, NaOH, CaCO₃, Na₂HPO₄ and seven different mobile phase (Acetone, Benzene, Carbon tetrachloride, Acetonitrile, Isopropanol, aqueous NaDDC and distilled water). The performance of the developed strips was done by AAS and ICP. The quantitative measure of metal ion concentration in developed strips was done by scraping band from developed strips and quantifying by AAS. Analysis of real water samples and effluent samples was also done by the developed methods.

3.1 Effect of Mobile Phase

The movement of metals as determined by R_F values depended on the type of solvent used. The R_F values were observed to be zero with water as mobile phase. That is to say, the dithiocarbamates of metal ions with atomic numbers less than 20 are water insoluble⁴.

The R_F values with different mobile phases were different (Table 1). This is because of change in dielectric constant. Thus it is evident from the results that the R_F values of metal dithiocarbamates depends on their solubility in the mobile phase, the adsorption affinity and pH of the impregnation material^{4, 5}.

The best separation was observed in CCl₄ and isopropanol mobile phase. Thus CCl₄ and isopropanol were observed to be good mobile phases for metal ion chromatography on NaDDC.

Table no 1 : Separation of metals with different mobile phases

Stationary Phase Separations R _F or (R _L -R _T)	
Mobile Phase – Acetone	
IM ₁	Cd ²⁺ (0.80 cm) from CO ²⁺ (1.8 to 5.8 cm)
IM ₃	Cd ²⁺ (1.20 cm) from Zn ²⁺ (1.6 to 5.1 cm)
IM ₄	Zn ²⁺ (0.5 cm) from CO ²⁺ (2.0 to 5.6 cm)
IM ₅	Hg ²⁺ (0 cm) from Fe ²⁺ (0 cm)
IM ₆	Co ²⁺ (0 cm) from Cd ²⁺ (2.3 to 5.5 cm)
IM ₈	Hg ²⁺ (0 cm) from Pb ²⁺ (0 cm)
IM ₉	Pb ²⁺ (0 cm) from Zn ²⁺ (1.9 to 5.0 cm)
Mobile Phase – Isopropanol	
IM ₁	Mn ²⁺ (0 cm) from Cd ²⁺ (2.0 to 4.0 cm)
IM ₃	Cd ²⁺ (0 cm) from Hg ²⁺ (2.3 to 4.6 cm)
IM ₄	Fe ²⁺ (0.3 cm) from Zn ²⁺ (2.0 to 4.0 cm)
IM ₅	CO ²⁺ (0 cm) from Cd ²⁺ (2.0 to 4.3 cm)
IM ₆	CO ²⁺ (0 cm) from Cd ²⁺ (2.3 to 4.0 cm)
IM ₇	Hg ²⁺ (0 cm) from Cd ²⁺ (2.0 to 4.0 cm)
IM ₈	Pb ²⁺ (0 cm) from Cd ²⁺ (0 cm)
IM ₉	Fe ²⁺ (0 cm) from Pb ²⁺ (2.0 to 2.6 cm)
Mobile Phase – Carbon Tetrachloride	
IM ₁	Hg ²⁺ (0 cm) from CO ²⁺ (2.1 to 4.2 cm)
IM ₃	Cd ²⁺ (0 cm) from Hg ²⁺ (2.1 to 3.7 cm)
IM ₄	Cd ²⁺ (0 cm) from Hg ²⁺ (2.5 to 4.2 cm)
IM ₅	Cd ²⁺ (0.6 cm) from Zn ²⁺ (2.8 to 5.0 cm)
IM ₆	Fe ²⁺ (0 cm) from Cd ²⁺ (0 cm)
IM ₇	Cd ²⁺ (0 cm) from Hg ²⁺ (2.6 to 4.0 cm)

IM ₉	Cd ²⁺ (0.5 cm) from Zn ²⁺ (2.6 to 4.7 cm)
Mobile Phase – Benzene	
IM ₁	Mn ²⁺ (0 cm) from Cd ²⁺ (1.8 to 3.7 cm)
IM ₃	Cd ²⁺ (0 cm) from Pb ²⁺ (1.8 to 5.2 cm)
IM ₄	Cd ²⁺ (0.6 cm) from Hg ²⁺ (2.3 to 5.6 cm)
IM ₆	Mn ²⁺ (0 cm) from Pb ²⁺ (2.0 to 5.5 cm)
IM ₈	Hg ²⁺ (0 cm) from Cd ²⁺ (0 cm)
IM ₁₀	Cd ²⁺ (0 cm) from Pb ²⁺ (1.9 to 3.4 cm)
Mobile Phase – Acetonitrile	
IM ₁	Hg ²⁺ (0 cm) from Cd ²⁺ (0 cm)
IM ₃	Hg ²⁺ (0 cm) from Pb ²⁺ (0 cm)
IM ₅	Fe ²⁺ (0 cm) from Pb ²⁺ (0 to 0.2 cm)
IM ₇	Hg ²⁺ (0 cm) from Cd ²⁺ (2.0 to 3.1 cm)

- IM = Impregnations materials listed in experimental section.
 R_L (tailing) = distance (cm) travelled by the lower edge of a tailing spot.
 R_T (tailing) = distance (cm) travelled by the upper edge of a tailing spot.

3.2 Quantitative analysis of developed method in simulated water

An attempt has been made to determine the recovery of Pb²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Co²⁺, Fe³⁺ and Mn²⁺ metals spiked into different water using spot area measurement method by using impregnated plates and carbon tetrachloride as a mobile phase.

A linear relationship was achieved when the quantity of sample spotted was plotted against area of the spot (data not shown). The linearity is maintained from 1000 to 3500 µg/spot. At higher concentrations a positive deviation from linear line was observed⁵. The analysis compared well with AAS analysis

3.3 Quantitative analysis of developed method in real samples

In the real sample analysis the metals were identified based on colour and R_F value. Table 2 gives the analysis of different waste water effluents and quantitative comparison using AAS and ICP. In silk weaving industry effluent Co²⁺, Cd²⁺ and Zn²⁺ metals, in Tyre Manufacturing industry effluent Co²⁺, Cd²⁺ and Zn²⁺ metals, Aluminium Steel Industry Zn²⁺, Cd²⁺, Hg²⁺ and Pb²⁺ and in borewells (groundwater), heavy metals such as Pb²⁺ and Cd²⁺ were determined.

Table no 2 : Analysis of different waste water effluents and quantitative comparison using AAS and ICP

Sample	Mobile Phase	Impregnation Material & Metal Detected	Analysis By		
			Metal Chromatography	AAS	ICP
Aluminium Steel Industry	Acetone	IM ₃ Zn ²⁺	100 %	98.12 %	96.10 %
	Isoproponal	IM ₂ Cd ²⁺	56.25 %	90.0%	90.01%
	Carbon tetrachloride	IM ₃ Hg ²⁺	56.25%	64%	69.25%
	Benzene	IM ₆ Pb ²⁺	100%	91.95%	94.48%
Ground Water	Acetone	IM ₆ Cd ²⁺	44.44 %	64.48%	58.4%
	Isoproponal	IM ₅ Cd ²⁺	44.44%	59.25%	42.0%
	Benzene	IM ₆ Pb ²⁺	100%	100%	100.05%
Tyre Industry	Acetone	IM ₁ Cd ²⁺	64%	49.4%	61.33%
		IM ₆ Cd ²⁺	56.25%	59%	50%
	Carbon tetrachloride	IM ₅ Zn ²⁺	56.25%	64.48%	61%
Silk weaving Industry	Acetone	IM ₁ Cd ²⁺	64%	29.65%	64.7%
		IM ₆ Cd ²⁺	44.44%	29.65%	64.7%
	Isoproponal	IM ₄ Zn ²⁺	44.44%	99.75%	44.81%

Similar results were determined using impregnated paper strips which clearly shows that the heavy metals are determined even in simple, low cost, portable and disposable analytical gadget for employment in environmental monitoring such as detection of heavy metals.

Table no 3 : Metals detected in different industrial effluents

Industrial Effluent	Metals identified from		
	Metal chromatography	AAS	ICP
Aluminium Steel Industry	Cd ²⁺	Cd ²⁺	Cd ²⁺
	Pb ²⁺	Pb ²⁺	Pb ²⁺
Ground Water	Cd ²⁺	Cd ²⁺	Cd ²⁺
	Zn ²⁺	Zn ²⁺	Zn ²⁺
Tyre Industry	Cd ²⁺	Cd ²⁺	Cd ²⁺
	Zn ²⁺	Zn ²⁺	Zn ²⁺
Silk weaving Industry	Zn ²⁺	Zn ²⁺	Zn ²⁺
	Cd ²⁺	Cd ²⁺	Cd ²⁺
	Hg ²⁺	Hg ²⁺	Hg ²⁺
	Pb ²⁺	Pb ²⁺	Pb ²⁺

IV. Conclusions

It is anticipated that in the future, with advances in fabrication and analytical techniques, that there will be more new and inventive advances in paper-based sensors.

These sensors could better fulfill the existing objectives of a viable low-cost and portable device besides contributing to selectivity, high sensitivity and multiple analyte discrimination. Sodium diethyldithiocarbamate is a promising chromatographic material for the separation of metal ions in organic mobile phases such as acetone, isopropanol, carbon tetrachloride, benzene and acetonitrile. However aqueous solutions and acidic solutions were not useful as mobile phase in chromatography on sodium diethyldithiocarbamate. The thin layer plate of Sodium diethyldithiocarbamate with CaNO₃ and NH₄Cl and carbon tetrachloride as mobile phase was identified as the most useful for the analysis of heavy metal ions^{4,5}. The results were comparable with AAS and ICP. Thus this would be an inexpensive technique for the analysis of metal ions. Studies on on-site method for metal ion detection is underway and this would facilitate the detection of type of contaminating metals in the polluted area.

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