Surfactant Mediated Cadmium Determination with Dithizone in Aqueous Solution

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ABSTRACT

Cadmium is a toxic and hazardous trace metal that has become a serious environmental pollutant since industrialization and intensive farming began in late 19th century. Although there are many established wet-chemical and instrumental methods for qualitative and quantitative determination of cadmium, most involve the formation of the Cd-dithizone complex in the presence of the highly toxic potassium cyanide which is then extracted into carcinogenic chlorinated organic solvents such as chloroform or carbon tetrachloride. The main purpose of this study was to see if a sensitive, simple, quick spectro-chemical method that utilizes safer and less toxic chemicals for cadmium analysis using dithizone could be developed. The results found so far are promising and indicate that in the presence of a chelating surfactant such as Deriphat-160C, the cadmium-dithizone complex in alkaline aqueous medium remains soluble and obeys Beers law in the micro molar Cd concentration range studied. The solutions prepared for spectroscopic measurement did not require KCN nor was it necessary to extract the complex in to chlorinated organic solvents.

Keywords: Dithizone, Cadmium, surfactant, spectrophotometric, Deriphat 160C

ÖZ

Kadmiyum zehirli ve zararlı bir ağır metal olarak 19. Yüzyılın başlarında sanayileşme ve yoğun tarıma geçiş ile etrafa yayılarak ciddi bir çevre kirleticisi haline gelmiştir. Kadmiyumunnitel ve nicel tayini için birçok kimyasal ve enstrümantal yöntemler olmasına rağmen, çoğu zaman bu yöntemlerde çok zehirli potasyum siyanür içeren ortamda kadmiyumun-dithizone kompleksinin oluşması ve bu kompleksin kloroform ve karbon tetraklorür gibi kanserojen klorlu organik çözücü içine alınmaları gerekmektedir. Bu çalışmanın temel amacı kadmiyumu dithizone kullanarak tayin etmek için hassas, basit, hızlı güvenli ve daha az zehirli ve zararlı kimyasallar maddelerin kullanıldığı bir spektroskopi-kimyasal yöntem geliştirmekti. Burada rapor edilen sonuçlar ümit verici olup, Deriphat-160 isimli yüzey aktif madde içeren bazik sulu bir ortamda kadmiyum-dithizonekompleksinin çökmeden oluşturulabildiğini ve incelenen Cdmikromolarderişim aralığında kompleksin Beer'syasasına uyduğunu göstermektedir. Spektroskopik ölçümü için hazırlanan çözeltilerde ne siyanür kullanılmasına gerek olmuş ne de oluşan kompleksi klorlanmış organik çözücüler için alınmaları gerekmemiştir.

Anahtar kelimeler: dithizone, kadmiyum, yüzeyaktif, spektrofotometrik, Deriphat-160C

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First of all I am grateful to the almighty God for establish me to complete this thesis, after foremost I offer my sincerest gratitude to my supervisor, Asst. Prof. Dr. Mehmet Garip who has supported me throughout my thesis with his patience and knowledge whilst allowing me the room to work in my own way. I attribute the level of my Master's degree to his encouragement and effort and without him this thesis, too, would not have been completed or written. One simply could not wish for a better or friendlier supervisor.

I have to mention,Dr. Zülal Yalınca and many others that I could not mention here who gave me helpful suggestions for the improvement of research and moral support.

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LIST OF SYMBOLS/ABBREVIATION

AC   Activated Carbon

MLC   Maximum level contaminate

ε The molar absorptivity with units of $L \cdot mol^{-1} \cdot cm^{-1}$

Chapter 1

INTRODUCTION

Several analytical methods to determine Cd exist which include HPLC, potentiomretic striping analysis, enzymatic determination, ion selectivity electrodes [1], flame atomic absorption spectrometry (FAAS)[2] and spectrometry. All of these methods, except for the last, have the disadvantage that they are relatively expensive and cannot be used on-site in field analysis [3].

Cadmium is a toxic and hazardous trace metal that has become a serious environmental pollutant since industrialization and intensive farming began in late 19th century. The main activities that have brought cadmium that was once buried beneath the earth for millions of years to the environment are mining and processing of metals; mining of phosphate fertilizers and their widespread use in intensive agriculture and more recently by their use in Ni-Cd batteries for modern electronic goods that end up in waste bins! It is also present in cigarette smoke which is probably the main source for human exposure. Cadmium is carcinogenic and it has been associated with kidney damage, anemia, loss of smell, and more seriously with damage to the reproductive system and birth defects [4]. Although there are many established wet-chemical and instrumental methods for quantitative determination of cadmium, most involve the formation of the Cd-dithizone complex in the presence of the highly toxic potassium cyanide which is then extracted into carcinogenic chlorinated organic solvents such as chloroform or carbon tetrachloride.

Spectrophotometric determination is essential as inexpensive Complexes that can be determinate photometric. Many of these photometric determinations were adaptedto FIA system- even those that needed an extraction step as part of the producer. Photometric determination include kinetic method or indirect determinations where for instance the inhibitor effect in the catalytic action of iodides on the as $-$ Ce reaction measured [5].

The main purpose of this study was to see if a sensitive, simple and quick spectro-chemical method that utilizes safer and less toxic chemicals for cadmium analysis using dithizone could be developed.

To achieve our goal, we needed to investigate and provide answers to the following questions:

1. Is it possible to make a stable Cd-dithizone complex without using toxic or hazardous chemicals or reagents and keep it dissolved in an aqueous environment? What are the conditions necessary to achieve this?

2. If such a water-soluble Cd-dithizone complex could be made, would it have high absorptivity and follow Beer's law so that its concentration could be determined by spectrophotometric measurements.

3. What range of Cd concentration can be measured with reasonable accuracy and precision by this method? What would be the detection limit?

4. What other factors must be studied further so as to verify the applicability of this method and develop it into an acceptable safe analytical method?

1.1 Trace Metals as Environmental Pollutants

From years past, it has being observed that the concentration of metals present in the coastal regions has been on the high side [6].A good amount of toxic metal ions are found in the environment today [7] which leads to the pollution of water, air and soil and serve as organic and inorganic pollutants[8]. An increase in the amount of metals and chemical reagents used for industrial processes led to an increase in the amount of wastes that contain a high level of toxic heavy metal ions in them [9].

Due to its non-degradable nature and its threat to man and the environment, the presence of these heavy metals is of paramount concern [10]. Waste water from many industries has dissolved heavy metals present in them. These toxic metals include cadmium, lead, copper, mercury etc. Discharge of this waste water without treatment will have a negative impact on the environment. Due to the increased awareness of the harmful impacts of these discharged heavy/toxic metals and the ease through which it enters into the food chain, it has become essential for industries to treat this effluents before it is released into water bodies thus leading to a lot of research on how best to effectively remove these heavy metals from industrial wastes [11]. Water serves as a habitat for aquatic animals and is also one of the most essential resources that man needs to survive thereby making it of great importance that the quality of water is easily controlled through rapid and sensitive means [12]. Heavy metals have a density that is greater than ($5g/cm^3$) and even though a lot of elements have this same characteristic, the list of elements with *maximum contaminant leve*l (MCL) in Table 1 comprises those elements that are of concern to the environment. Although arsenic is a semi-metal, it is usually present in the category of the hazardous heavy metals. Due to being easily soluble in water heavy

metals have the tendency to easily integrate themselves into the food chain [13]. Heavy metals pose serious adverse effects on human health such as; cancer, organ and nervous system damages, reduced growth and development and in worst case scenarios, death [14].

Table 1: List of Maximum Contaminant Level (MCL) Tolerable for the Following Metals That are Considered Very Hazardous

Name	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system,	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system	0.00003

1.2 Main Source of Metal Pollution; Industrial Waste Waters

Electroplating industries are one of the most hazardous chemical industries because of the high amount of metal contaminated waste water that they produce [15]. A significant amount of toxic metal ions are present in the waste water discharged from textile, leather, tannery, electroplating, galvanizing, pigment and dye, refineries and metal processing industries. All of these toxic metals do not only result in human health defects but are also harmful to other organism (e.g. marine animals) [16]. Surface treatment and electroplating of metals result in a high concentration of heavy metals (such as cadmium, chromium, copper, lead, nickel, platinum, silver, titanium,

vanadium and zinc) present in waste water bodies as they are used for a wide number of applications in these industries.

Their applications include anodizing-cleaning, conversion-coating, etching, electro-depositions, electroplating and milling. Another industry responsible for a high amount of heavy metals discharge in industrial waste is the printed circuit board (PCB) manufacturers. Tin, lead and nickel soldering plates are mostly used as resistant over plates. Several other sources of metal wastes are; a) wood processing industries which make use of a chromate copper arsenate wood treating process that results in the production of wastes that contain arsenic b) Inorganic pigment producing industries apply compounds containing chromium and cadmium supplied c) Petroleum refineries whose catalyst used for treating crude oil contain nickel, vanadium and chromium and lastly d) Photographic processes that produce films having high concentrations of silver and ferrocyanide. All of these industries generate a huge amount of effluents, residues and sludge that are considered to be hazardous and require treatment. Consequently effective and efficient removal of these heavy metals from effluents is very important [14].

1.3 Cadmium

Cadmium is released into the environment by human activities such as the use of phosphate fertilizers, disposal of household, municipal and industrial wastes such example: metal coatings, plastics, pigments, and batteries, [17].

Cadmium occurs in nature at low levels and makes up only 0.00005% of earth's crust. It is listed as being dangerous to the environmental by UNEP/WHO.

Due to its low concentrations and matrix interferences along with such metals as lead, mercury, copper, zinc, chromium, tin and silver it poses a risk of disturbing the balance in the ecosystems [18]. One characteristic feature of cadmium is its high stability in environment. It is accumulated in soil and living organisms [19, 20, 21]. It is easily absorbed by plants, both through their root systems and by leaves, usually in proportion to its concentration in the environment. Acid reaction of soil increases its mobility and availability [22].

1.3.1 Sources of Cadmium

In the lithosphere cadmium appears mainly in the form of sulphides and its presence is connected with the deposits of zinc and copper. Therefore, emissions of zinc and copper works contribute the highest proportion of industrial cadmium pollution, accounting for 60% of all anthropogenic sources of pollution with cadmium [22].

The amount of cadmium in the environment may also be increased locally by the burning of solid waste. These processes cause pollution of underground and surface water, and cause the soil to be contaminated. The content of cadmium in soil increases as a result of the application of artificial fertilizers. Its amount is 0.1-17.0 mg/kg in phosphate fertilizers and0.5-8.0 mg /kg in nitrogenous fertilizers. Data accumulated over the years show that in most parts of the world, the mean content of cadmium in soil varies from 0.2 to 1.0 mg/kg of soil, whereas in Poland it is 0.2-0.3 mg/kg soil. Availability of cadmium to plants depends not only on its content in the soil, but also on its form, the strength by which it is bounded with the soil components and the kind of plant. Investigations show that contamination of fruit by harmful metals, including cadmium, is considerably lower than of other agricultural products, especially grain and root vegetables. Cadmium content in plants generally increases proportionally with its content in soil [23, 18].

1.3.2 Human Exposure

Because it is easily absorbed by humans and animals, it remains in tissues for a relatively long time and is accumulated in vital organs, especially in kidneys and liver [24]. Its biological half-life is 10-30 years. It is not found in the organs of children, its total amount varies from 30 to 40 mg in 45-year old people and increases up to the age of 60, when it begins to decrease [20]. A lethal dose of cadmium is 2 mg per 1 kg of body weight and is much lower than that of other toxic metals [17].

1.4 Methods for Determination of Cadmium

Several analytical method to determined Cd exist which include cold vapor AAS, chromatography (GC and HPLC) potentiomretic striping analysis enzymatic determination ion selectivity electrodes, ICP – AES and spectrometry. All of these methods, except for the last, have the disadvantage that they are relatively expensive and cannot be used on-site in the field analysis. Spectrophotometric determinations are therefore essential as inexpensive methods that can determine colored complexes. Many of these photometric determinations were adapted to FIA system- even those that needed an extraction step as part of the producer. Photometric determination include kinetic method or indirect determinations where for instance the inhibitor effect in the catalytic action of iodides on the as – Ce reaction measured [25].

The determination of Cadmium at low concentration which may be of toxicological significance requires a highly sensitivity method.

Dithizone is the preferred reagent for photometric determination of cadmium, although this reagent is not specific and numerous other heavy metals also form

dithizonates. The cadmium-dithizone complex has a pinkish color and is very stable in the strong alkaline range although Cd-dithizone is easily decomposed by weak acids, it experiences no interference from HCl, H_2SO_4 and HNO_3 [26].

1.5 Dithizone

Dithizone ($C_{13}H_{12}N_4S$) is an efficient and important chelating agent useful in extracting trace metal elements [27], the chemical structure of dithizone is shown in Figure 1.
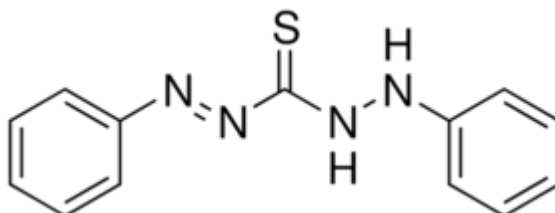
Figure 1: Chemical Structure of Dithizone

Dithiocarbamate compounds possess sulphur atoms as part of their structure and this sulphur present acts as electron donors. Uncharged chelation occurs when metal ions interact with ligands possessing more than one functional group such as Dithiocarbamates, dithizone, oxine etc. Metals that produce insoluble or slightly soluble sulphides can be easily separated as complexes with ligands that they form bonds with through the sulphur atoms present in the ligands e.g. dithizone and dithiocarbamate [28]. The structure of the complex of Cd with two dithizone molecules is shown n Figures 2 and a 3D model of the complex is shown in Figure 3. Also due to the high absorptivity of metal dithiocarbamate complexes, they are important spectrophotometric reagents used for the determination and analysis of trace metals. Generally, dithiocarbamate compounds have been used to pre concentrate the trace metals using various methods [29]. Using dithiocarbamate for chelating and liquid-liquid extraction procedures has been reported in literature

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whereby the analyte was effectively removed from the matrix. Coupling the above method with AAS or ICPAES significantly improves the selectivity and makes the process more sensitive. The use of toxic organic solvents for separating the complex formed by the analyte and the chelating agent from the sample matrix cannot be avoided in the liquid-liquid extraction process. This is disadvantageous because these organic solvents are harmful to organisms and the environment at large. Recently, several new materials such as; silica and modified silica gel, ion imprinted polymers, resins, carbon nanotubes, zeolite, bio adsorbents, metal oxides and polytetrafluoroethylene (PTFE) are now used for solid phase extraction techniques and this eliminates the need for organic solvents in the extraction process for analyzing metals . Mineral acids are then used to recover the metal species from the adsorbent [30].
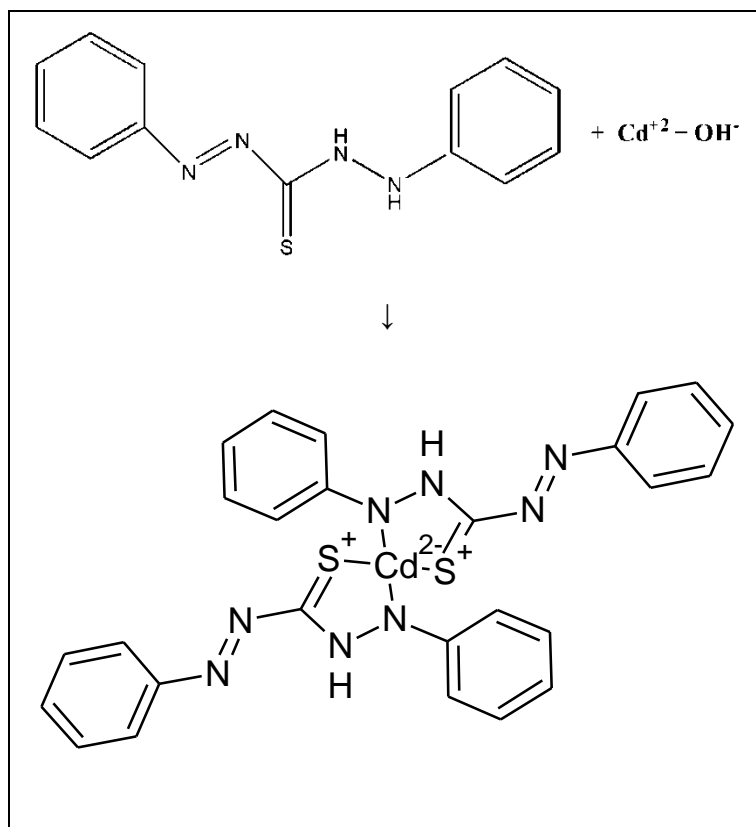
Figure 2: Reaction of Dithizone with Cd^{2+} in Alkaline Aqueous Solution Giving the Neutral Complex Cd (Dithizone)$_2$. However There is Internal Charge Separation Because of the Sulfur Atoms' sp^2 Hybridization State
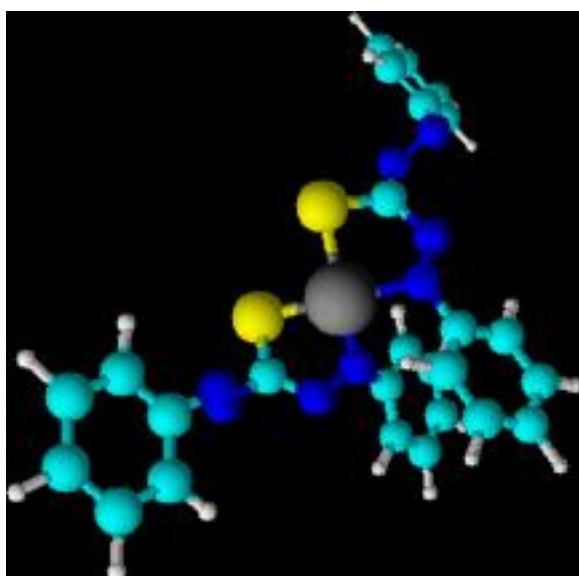
Figure 3: A Three Dimensional Model of the Cd(Dithizone)$_2$ Complex Showing the (almost) Square Planar Arrangement of Cd.

1.6 The Surfactant: Deriphat 160C

Deriphat 160C is the trade name of the 30 % w/w aqueous solution of Sodium-N-lauryl-ß-iminodipropionate. It is also known as dodecyl iminobispropionate. Its structure is given in Figure 4. It is a non-toxic surfactant which is widely used in cosmetics preparations due to its amphoteric nature. As a result of the iminodipropionate group it exists as a zwitterion in aqueous solutions. It is soluble in both acidic and basic solutions and is therefore capable of being used together with anionic as well as cationic surfactants[31].Deriphat 160 C is a unique, multi-functional amphoteric surfactant. It can function as a foamer, cleaning agent, corrosion inhibitor, and a hydrotrope (solubilizes hydrophobic substances).

Benefits include:

- Solubilizer for cationic germicides
- Good emulsifier at low concentrations
- Foam not effected by pH or electrolytes
- Effective hydrotrope
- Stable in strong acid and alkaline solutions
- Easy to formulate ultra concentrates
- Listed on Clean Gredients (Approved cleaning ingredients by USA EPA in Design for the Environment Program)

Deriphat 160 C is especially valuable for its ability to produce and maintain stable emulsions at extremes of pH. It will function effectively at highly alkaline pH where most cationic, non-ionic and anionic emulsifiers are ineffective [32].

Our interest in this work results from the chelating/complexing functionality of Deriphat160C together with its ability to solubilize hydrophobic species, in other words its hydrotropic property. It is quite possible that Deriphat160C and dithizone

together may create mixed complexes (suggested structures in Figure 5) with cadmium cation that may be soluble in water. Alternatively, Deriphat forms micelles which solubilize the otherwise insoluble cadmium-dithizone complex.
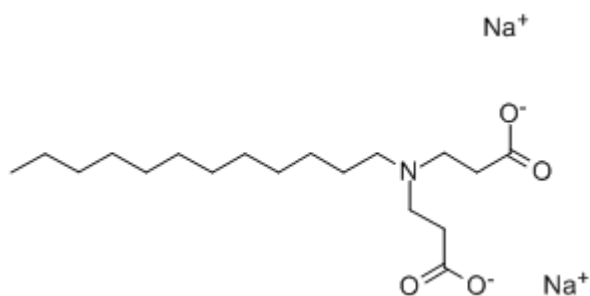
Figure 4: Structure of Deriphat 160 C Disodium Salt
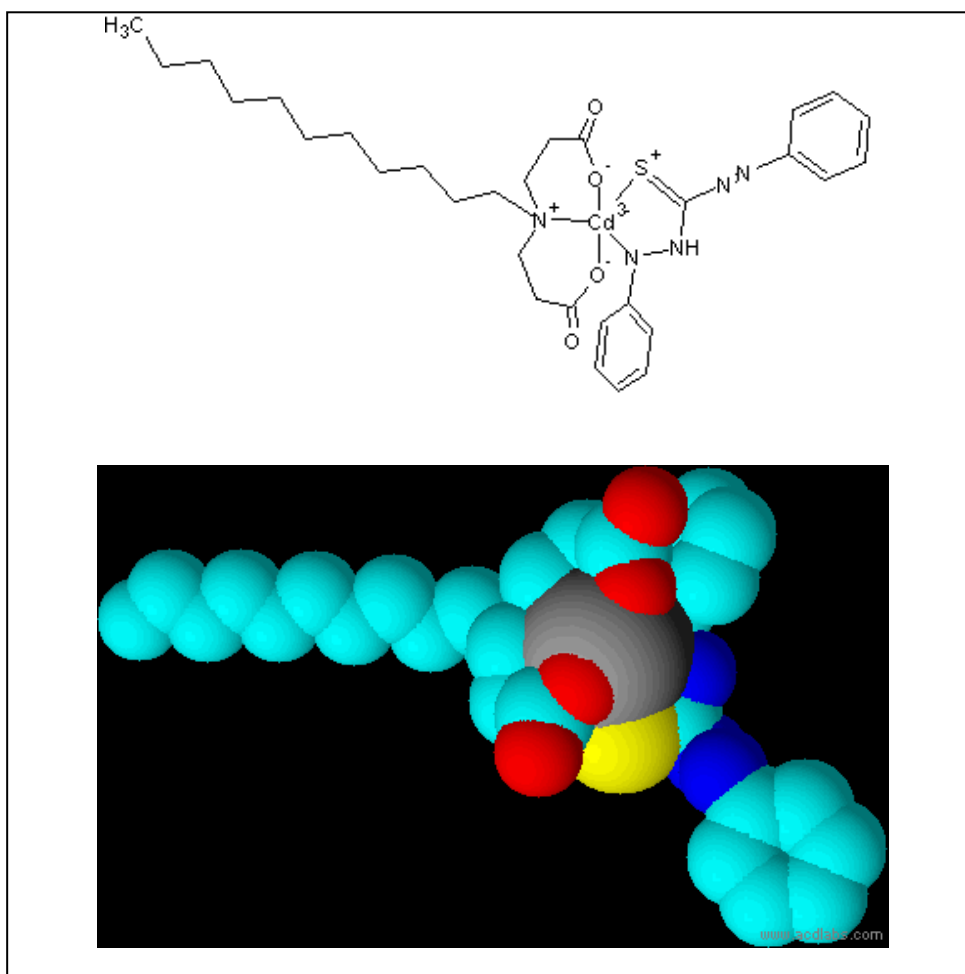
Figure 5: Postulated Mixed Complex Structure (Line Above and 3D Form Below) of Cd^{2+} Together with Deriphat and Dithizone Ligands

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1.7 Treatment Techniques for Wastewater Containing Heavy Metals

In the past, many treatment techniques for metal-polluted wastewaters have been developed. In all cases the aim of the treatment has been make the quality of the effluent better by removing the pollutants before discharge. The treatment techniques include filtration, adsorption and ion exchange, chemical precipitation, sedimentation, coagulation–flocculation, flotation [15], and electrochemical processes such as electrodepositing. Each has its own inherent advantages and limitations in application. For example, one of the most widely used techniques, especially for electroplating wastewater, in Thailand and Turkey is chemical precipitation [33, 34].

Coagulation–flocculation has also been employed for heavy metal removal from inorganic effluent in Thailand [33] and China [35]. Sorptive flotation has attracted interest in Greece [36] and the USA [37] for the removal of non-surface active metal ions from contaminated wastewater. In recent years [15], industry has used other methods such as ion-exchange to treat effluents in order to remove toxic metals. Most ion-exchangers used are synthetic in origin.

But there are disadvantage with this method. It is not suitable for concentrated solutions because of fouling of the resin by other particulate or organic contaminants in the effluent. Also this method is not very selective or specific and is affected by pH.

Recovery by electroextraction is also used for metal removal from wastewaters. In these methods, an electric current is passed through the wastewater and metal cations are deposited at the cathode. These deposited metals are then striped off the cathode

and collected. Main problem with this method is due to the corrosion of the electrodes which need to be changed frequently [14].

Activated carbon has also been used as an adsorbent but the costs are high. Many researchers continue to look for cheap and easily available adsorbents for the removal of heavy metals. Numerous published studies and reviews on the use of low-cost adsorbents utilizing natural substances, industrial and agricultural wastes or byproducts for heavy metal removal from effluents are available [39].

Anionic surfactant adsorption from water has also been studied extensively. Many adsorbent materials have been investigated [40].

Chapter 2

MATERIALS AND METHODS

2.1 Materials

The chemicals used in this work and their manufacturers are listed in Table 2.

Table 2: Materials and Their Manufacturers

No	Chemicals	Manufacturer, Country
1	Dithizone (DTZ)(Analar)	BDH, England
2	Deriphat 160C	Henkel, Germany
3	Cadmium (acetate)$_2$.H$_2$O(Analar)	BDH, England
4	Sodium hydroxide(Analar)	BDH, England
5	Ethanol (Puriss)	Riedal- de Häen, Germany
6	Hydrochloric acid (Puriss)	Riedal- de Häen, Germany

All glassware used in this work were borosilicate glass and were first washed with detergent; rinsed with tap water; washed with 2 M Hydrochloric acid and then rinsed with distilled water.

The UV-Visible measurements were done one a double beam PG Instruments T80 UV-Visible Spectrophotometer. Matched 1 cm quartz cells were used.

Infrared spectrums were obtained on a Perkin Elmer Spectrum-65 FT-IR spectrometer.

2.2 Methods

2.2.1 Preparation of Dithizone

Two dithizone stock solutions with different compositions were prepared and used.

The first solution was prepared by dissolving 0.0256 g of dithizone (MM = 256.33g/mol) in AR grade ethanol in a 100 mL volumetric flask. The resulting solution was 1.00×10^{-3} M in dithizone and was one of the stock solutions used in the experiments. This solution had a very dark blue/black color and was opaque. It also appeared to be somewhat heterogeneous (possibly due to some undissolved or re-precipitated dithizone

The second solution was prepared by first dissolving 0.0512 g of dithizone in about 60 ml of ethanol in a 100 mL volumetric flask. In a separate beaker, 2.000 g of sodium hydroxide was dissolved in 30.0 ml of distilled water. Once all the sodium hydroxide dissolved, the solution was allowed to cool and was then quantitatively transferred to the 100 mL volumetric flask containing the alcoholicdithizone solution. The final volume was made up to 100mL with distilled water. This solution was 2.00×10^{-3} M in dithizone and 0.500 M in NaOH.

Both solutions were kept in refrigerator when they were not being used.

2.2.2 Preparation of Deriphat 160C

Deriphat 160C is the trade name of the 30($\pm$1) % w/w aqueous solution of Sodium-N-lauryl-ß-iminodipropionate (also known as dodecyl iminobispropionate. MM = 373.44 g/mol). A 0.10 % (w/v) stock solution of Deriphat 160C was prepared in

double distilled water by dissolving 3.111 grams of the as received material in 250 mL volumetric flask and made up to volume. This corresponds to a calculated concentration of 1.0×10^{-2} M of the active compound.

2.2.3 Preparation of Cd Stock Solution

The cadmium Cd^{2+} stock solution was prepared by dissolving 0.0267 g of Cadmium $(acetate)_2.H_2O$ (MM = 266.5g/mol) in distilled water in a 100 mL volumetric flask which gave a 1.00×10^{-3} M solution of Cd^{2+}. Working solution with a concentration of 1.00×10^{-4} M Cd^{2+} was prepared by tenfold dilution of the stock in a 100 mL volumetric flask with water. Subsequent experimental solutions were prepared by taking appropriate volumes of this working solution.

2.2.4 Preparation of NaOH Solution

A 1 M stock solution of NaOH was prepared by dissolving 4 g of NaOH in distilled water in a 100 mL volumetric flask. This solution was used in the preparation of all subsequent experimental solutions.

2.2.5 FT-IR Analysis

The FT-IR spectra of the dithizone and of its Cd-dithizone complex were recorded on a Perkin Elmer Spectrum-65 FT-IR spectrometer. The spectra obtained are reproduced and discussed in Chapter 3.

2.2.6 UV-Visible Absorbance and Spectrum Measurements

The spectrums of all the trial solutions were measured between 200 and 800 nm using a PG Instruments T80+ model double beam UV-Visible spectrophotometer with matched quartz cells. The spectra obtained and the absorbance measurements made at selected wavelengths are reproduced and discussed in Chapter 3.

2.3 Trial Solution Sets of Cd with Dithizone and/or Deriphat 160C

A number of solution sets were prepared containing varying concentrations of Cd, dithizone and Deriphat. The concentration of Cd was varied from 0 to about 10^{-5} M. In all solutions the amount of dithizone was always more than Cd^{2+} so as to ensure complexation of all the Cadmium. All measurements were done spectrophotometrically by recording the UV-Visible spectrum of the prepared solutions. After some trials, it was found that water was the most appropriate reference solution.

A summary of the sets of solutions that were prepared and measured are tabulated below in Table 3. In some cases the solutions precipitated almost immediately and therefore no further measurements were made. These failed trials are labeled as "**unsuitable for measurement**". All other solutions that appeared to be soluble and homogeneous were measured and their results are given in chapter 4.

These solutions were prepared by mixing together appropriate volumes of the stock or diluted stock solution of each species in a 25 mL volumetric flask and made up to volume with distilled water. Then having mixed the solution well, those with precipitate were noted and the solution discarded, and those without precipitate were scanned on the UV-Visible spectrophotometer for their absorption spectrum.

Table 3: Composition of the Alkaline Cd-dithizone (-Deriphat) Test Solutions Used

[Cd^{2+}] M range	[Dithizone] M	[NaOH] M	[Deriphat] M	Comments
0 to 5×10^{-6}	8×10^{-5}	4×10^{-2}	0	Clear solution
8×10^{-6} to 32×10^{-6}	8×10^{-5}	4×10^{-2}	0	Precipitates. Unsuitable for measurement
0 to 40×10^{-6}	3.2×10^{-5}	8×10^{-2}	24×10^{-4}	Clear solution
None	3.2×10^{-5}	8×10^{-2}	24×10^{-4}	Clear solution

Chapter 3

RESULTS AND DISCUSSION

Various sets of Cd^{2+} solutions containing dithizone, NaOH and in some trials, the surfactant Deriphat 160Cthat we prepared were measured spectrophotometrically. All data and observation about these solutions are presented here. The concentrations are in units of mol/L (also M), and the absorbance values are in milliabsorbance units, mAU.

3.1 Solutions Tested for Cd^{2+} Determination.

Those solutions containing greater than about 5 to 10×10^{-6} M Cd^{2+} and no Deriphat 160C either precipitated immediately as the dithizonecomplex or did so gradually within 5 to 15 minutes after preparation. These solutions gave erratic and non-reproducible absorbance measurements when we tried to measure them. On the other hand, the precipitation rate was observed to be much slower for solutions with less that 5-10 $\times 10^{-6}$ M Cd^{2+}. Although during the first one hour we could obtain reproducible results, absorbance measurements after standing for one or more hours became erratic and non-reproducible. In fact the next day we could even detect the red Cd-dithizone complex precipitate with the naked eye.

It may be useful to investigate this precipitation behavior further because these solutions had very low concentrations of Cd^{2+} (around 10^{-6} M) yet they were able to precipitate and come out of solution quantitatively. The precipitate that formed slowly consisted of sufficiently large particles that they settled to the bottom of the

flask. They could also be easily filtered through a Whatman No 41 ashless filter paper. Since these properties are amongst the most desired properties for gravimetric analysis this process may be developed into a gravimetric method of Cd^{2+} analysis or the filtered precipitate may be re-dissolved quantitatively in a less toxic solvent such as acetone or ethanol and determined spectrophotometrically!

When Deriphat 160C was also included in the test solutions containing Cd^{2+} with dithizone and NaOH, these solutions were clear and homogeneous, and remained free of any precipitate even after 24 hours.

The range of Cd^{2+} concentration that were tested was from 0 to 40×10^{-6} M which corresponds for dilute aqueous solutions to a concentration of 0 to 4.5 mg/L or *ppm*.

3.1.1 Determination of Optimum Conditions for the Method

The first procedure followed for preparing the test solutions resulted in precipitate formation very quickly. These solutions were prepared by pipetting 0.500, 1.00, 2.00, 4.00 and 8.00 mL of 1.00×10^{-4} M Cd^{2+} in to the volumetric flasks first, followed by 2 mL of 1.00×10^{-3} M ethanolicdithizone solution and then 1.00 mL of 1.00 M NaOH solution. The mixture in the volumetric flask was shaken and then made up to volume with double distilled water. The results obtained are shown in Table 4. The solution with the highest Cd concentration precipitated almost immediately. The two lesser concentrated ones precipitated more slowly, but actual red precipitate could be seen after about 15-20 minutes. The least concentrated solutions appeared to be clear, and free from precipitate. Absorbance (in mAU) at 600 nm for all except the last solution were measured and are given in Table 4 and plotted in Figure 6. It can be seen that Beers Law is not obeyed well because we do not get a linear relationship between absorbance and concentration.

Table 4: Different Cd^{2+} Concentrations with Constant Dithizone and NaOH Concentration and no Deriphat 160C Present

[Cd] M	[Dithizone] M	[NaOH] M	mAU
0	8.0×10^{-5}	4×10^{-2}	0
2.00×10^{-6}	8.0×10^{-5}	4×10^{-2}	4
4.00×10^{-6}	8.0×10^{-5}	4×10^{-2}	9
8.00×10^{-6}	8.0×10^{-5}	4×10^{-2}	12 Slowly precipitated
16.0×10^{-6}	8.0×10^{-5}	4×10^{-2}	16 Slowly precipitated
32.0×10^{-6}	8.0×10^{-5}	4×10^{-2}	Precipitated

Figure 6: Absorbance (at 600 nm) Versus Concentration of Cd-Dithizonecomplex in NaOH Solution. Order of Mixing: Cd^{2+}, Dithizone, NaOH (aq), Water.

Next we changed the order of reagent mixing to see if it would make any difference. We added dithizone first, then NaOH solution and then Cd^{2+}. The mixture was shaken and then made up to volume with double distilled water. There was no visible precipitate formation at first up until the 16×10^{-6} M Cd solution which gave a precipitate fairly quickly. The absorbance values of the lower concentration solutions were however measured without any problems. But upon standing for one hour, the solutions began to become cloudy. When left overnight, all the solutions had precipitated the red Cd-dithizone complex. The absorbance measurements made

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before any precipitation is shown in Table 5and are plotted in Figure 7. In the concentration range tested Cd (2.00 to 8.00 $\times 10^{-6}$M) the absorbance measurements at 600 nm gave a linear plot indicating that Beer-Lambert law is valid and that absorbance is directly proportional to concentration. But increasing the concentration of Cd above 8×10^{-6} M was lead to the formation of precipitate.

Table 5: Different Cd^{2+}Concentrations with Constant Dithizone and NaOH Concentration. Order of Mixing the Reagents is Different From That in Table 4.

Cd / M	Dithizone/ M	NaOH/ M	mAU
0	8.0×10^{-5}	4×10^{-2}	0
2.00×10^{-6}	8.0×10^{-5}	4×10^{-2}	15
3.20×10^{-6}	8.0×10^{-5}	4×10^{-2}	29
4.00×10^{-6}	8.0×10^{-5}	4×10^{-2}	34
8.00×10^{-6}	8.0×10^{-5}	4×10^{-2}	69
16.0×10^{-6}	8.0×10^{-5}	4×10^{-2}	Ppt, not measured

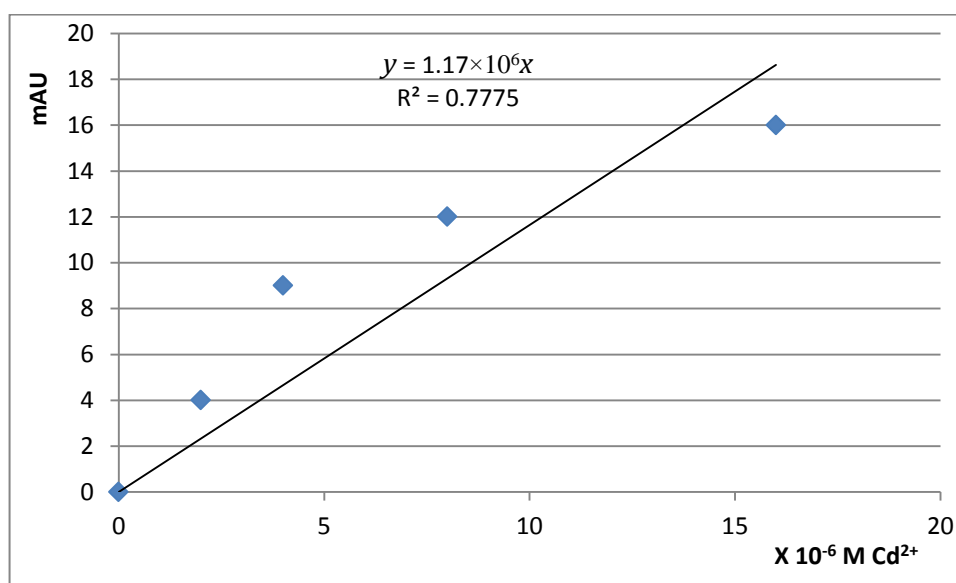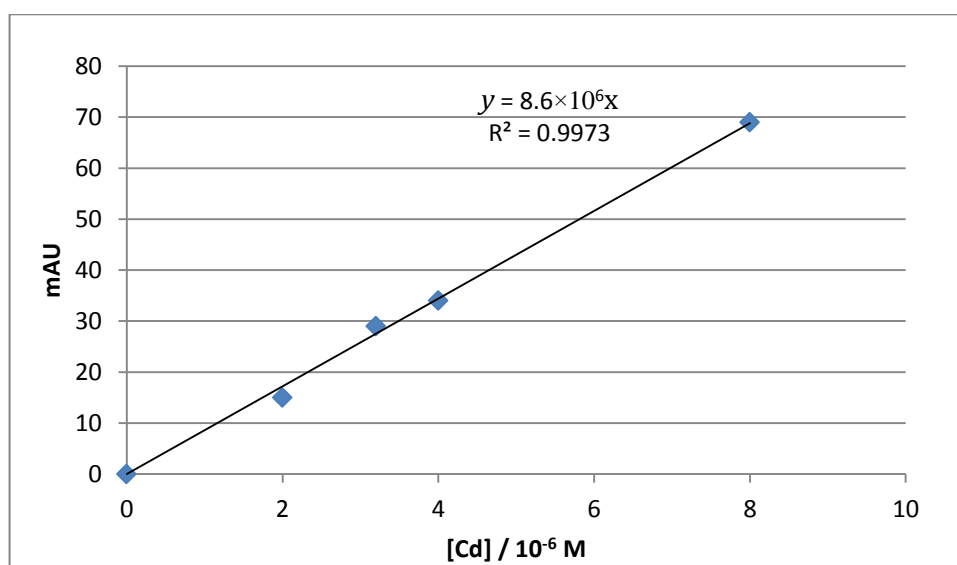**Figure 7:** Absorbance (at 600 nm) Versus Concentration of Cd-dithizone Complex in NaOH Solution. Order of Mixing: Dithizone, NaOH (aq), Cd^{2+}, Water.

We then tried to replicate this particular set of results by preparing and testing the following solutions given in Table 6. Irrespective of the solution condition all solutions were measured for their absorbance at 600 nm. It is obvious from the data

below that the solutions with Cd concentration above 8 µM gave erratic results. However when the data for the lower concentrations are plotted as in Figure 8, there is a fairly linear relationship and the absorbance values are close to the previous values.

Table 6: Absorbance of Cd^{2+} Solutions Containing Constant Dithizone and NaOH Concentrations

Cd / M	Dithizone / M	NaOH / M	mAU	Comment
0	8×10^{-5}	4×10^{-2}	0	Clear
2.00×10^{-6}	8×10^{-5}	4×10^{-2}	15	Clear
4.00×10^{-6}	8×10^{-5}	4×10^{-2}	25	Clear
8.00×10^{-6}	8×10^{-5}	4×10^{-2}	80	Hazy
16.0×10^{-6}	8×10^{-5}	4×10^{-2}	95	Precipitate
32.0×10^{-6}	8×10^{-5}	4×10^{-2}	106	Precipitate
64.0×10^{-6}	8×10^{-5}	4×10^{-2}	100	Precipitate

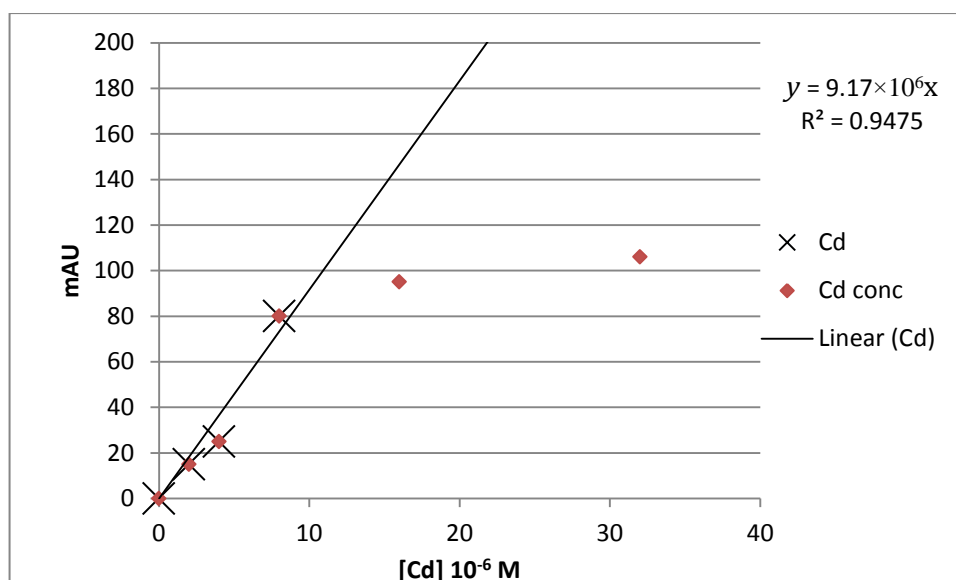Figure 8: Absorbance (at 600 nm) Versus Concentration of Cd-dithizone Complex in NaOH Solution. Order of Mixing: Dithizone, NaOH (aq), Cd^{2+}, Water. Precipitation Occurs Above 8.00 µM Cd^{2+} Concentration

The preceding two sets, in the concentration range of 0 to 8.00 µM Cd^{2+} give fairly linear absorbance with concentration. However even these solutions precipitate upon prolonged standing.

In another trial, we decided to see how changing solution concentrations of Dithizone and NaOH, either together or separately, would affect the results. However, we were unable to improve upon the results we had gotten so far, and precipitation of the complex was still occurring as soon as the Cd concentration became greater than about 8.00 µM. Therefore we decided to include the surface active agent, Deriphat 160C in our test solutions. The reasoning behind our choice of Deriphat was twofold:

1. Surfactants are hydrotropes which help solubilize hydrophobic materials in aqueous solutions.

2. Deriphat is a tridentate ligand which may form mixed complexes with the Cadmium and dithizone as depicted in Figure 5.

Hence we reformulated some of our stock solutions as follows:

- Cd^{2+} working solution was 1.00×10^{-4} M, as before. In other words we did not change the cadmium working solution.

- Dithizone and NaOH solutions were prepared as a mixture in a mixed solvent system of 60% ethanol and 40 % water. The concentration of dithizone was 2.00×10^{-3} M and the NaOH concentration was 0.500 M.

- The Deriphat 160C solution was 1.0×10^{-2} M.

The test solutions were prepared by first mixing 2.00 mL of Deriphat 160C solution and 4.00 mL of the Dithizone-NaOH solution in a 25 mL volumetric flask, and then adding the appropriate volume of Cd^{2+} working solution. The flasks were then filled up to the mark with double distilled water and their absorbance measured at 600 nm on the UV-Visible spectrophotometer. The data is tabulated in Table 7 and plotted in Figure 9.

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Table 7: Absorbance of Cd^{2+} Solutions Containing Constant Dithizone, Deriphat 160C and NaOH Concentrations

$[Cd^{2+}]$	[Dithizone]	[NaOH]	[Deriphat 160C] M	Abs
0	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	0
2.00×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	51
4.00×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	96
8.00×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	178
16.0×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	389
32.0×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	735

Figure 9: Absorbance (at 600 nm) Versus Concentration of Cd-dithizone Complex in Deriphat 160C and NaOH Solution. Order of Mixing: Dithizone, NaOH (aq), Cd^{2+}, Water

When these solutions were inspected a few hours later, no precipitate could be seen. All the solutions appeared very clear and homogeneous. To test the stability of these solutions, they were kept in the fume cupboard for 24 hours at room temperature and their UV-visible absorbance spectrums recorded again the following day. No visible precipitation of Cd-dithizone could be detected. This was also confirmed by the absorbance data given in Table 8and Figure 10 showing that there is almost no difference in the absorbance values of the solutions after 24 hours.

Table 8: Absorbance Data for the Same Solutions in Table 7 Measured 24 hours Later

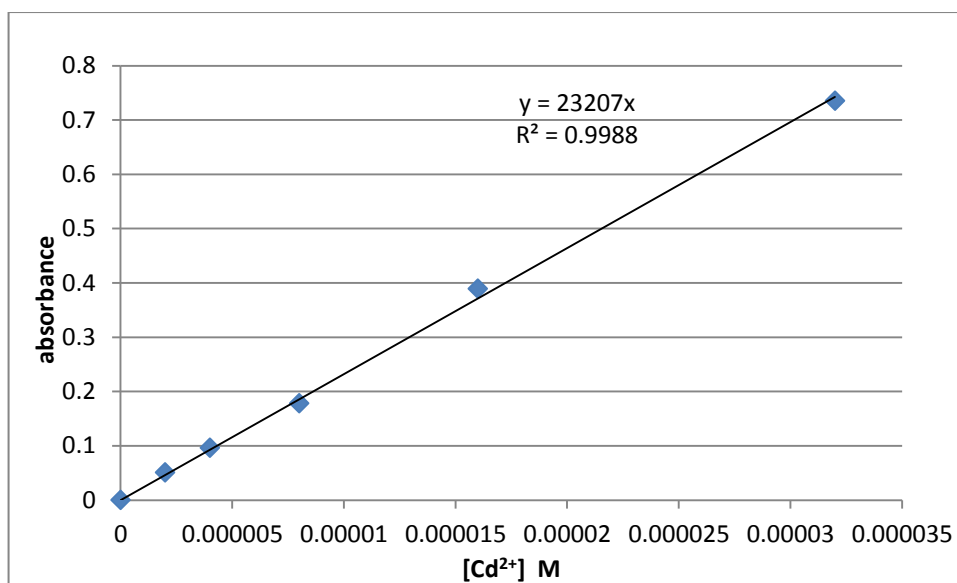| $[Cd^{2+}]$	[Dithizone]	[NaOH]	[Deriphat 160C] M	Abs
0	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	0
2.00×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	51
4.00×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	96
8.00×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	178
16.0×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	389
32.0×10^{-6}	3.2×10^{-4}	8.0×10^{-2}	8.0×10^{-4}	738

Figure 10: Calibration Curve for Cd (II)-dithizone Complex at 600 nm

3.1.2 Absorbance of Free Dithizone-Deriphat 160C in NaOH Solutions.

In the solutions we were working with, the amount of dithizone was not in a very large excess. Therefore when we add Cd^{2+} to these solutions, a significant proportion of the dithizone complexes and only a small amount/concentration remain free. Since the absorbance of free and complexed dithizone is different, we wanted to see if this would cause problems or interfere in obtaining a linear calibration curve. Therefore we prepared Cd free solutions of varying concentrations of dithizone in the presence of Deriphat 160C and NaOH, and measured their absorbance at 600 nm. Results are given in Table 9 and plotted in Figure 11.

Although there is a linear relationship between the concentration of free dithizone and absorbance at 600, the equation for the least squares line shows that the absorbance will change at a slow rate. Therefore, as long as we prepare our Cd containing test and standard solutions with an excess of dithizone, the dithizone concentration will remain nearly constant, and hence the absorbance measurements will measure the Cd-dithizone complex as opposed to free dithizone.

Table 9: Absorbance of Dithizone (with zero Cd) at 600 nm

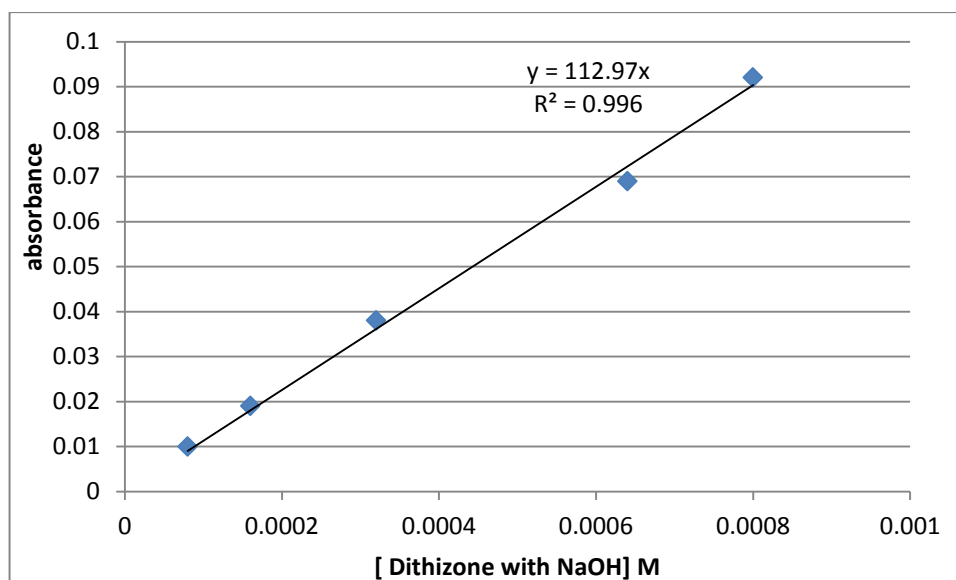| [Dithizone] M	NaOH M	Deriphat 160C M	mAU
0	0.00	8.0×10^{-4}	0
8.0×10^{-5}	0.020	8.0×10^{-4}	10
16×10^{-5}	0.040	8.0×10^{-4}	19
24×10^{-5}	0.080	8.0×10^{-4}	34
64×10^{-5}	0.16	8.0×10^{-4}	69
80×10^{-5}	0.20	8.0×10^{-4}	92

Figure 11: Dithizone Concentration Versus Absorbance

3.1.3 Molar Absorptivity of the Dithizone and Cd-Dithizone Complex at 600 nm

From the calibration curves in Figures 9 (or 10 because they are almost identical) and 11 we can calculate the molar absorptivity at 600 nm of the Cd-dithizone and the free dithizone.

The least squares equation with an R^2 value of 0.999 for the Cd-dithizone complex in Figure 9 gives

$$y = 23{,}207 \cdot x$$

Where y is the measured absorbance and x is the concentration of the absorbing species. Since the quartz cells used had a path length of 1 cm, by comparison of the above equation with Beer's equation for absorbance, namely, $A = \varepsilon \cdot c \cdot \ell$, in its rearranged form:

$$\varepsilon = A / c \cdot \ell = y/x$$

(ε is the molar absorptivity with units of $\mathbf{L \cdot mol^{-1} \cdot cm^{-1}}$)

We see that the slope of the least squares line in Figure 9 is the molar absorptivity of Cd bound dithizone at 600 nm, ε_{600}. In other words for:

$$\varepsilon_{600} = 23{,}200 \ \mathbf{L \cdot mol^{-1} \cdot cm^{-1}}$$

On the other hand, from the least squares line in Figure 11 (with an R^2 value of 0.996) for the free dithizone we find the molar absorptivity at 600 nm to be 113 $L \cdot mol^{-1} \cdot cm^{-1}$.

Thus, the huge difference between the molar absorptivities of the two species at 600 nm (113 against 23,200, $L \cdot mol^{-1} \cdot cm^{-1}$) means that free dithizone will not cause any significant systematic errors in the absorbance values of the Cd-dithizone complex.

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3.2 Potential Concentration Range and Detection Limit of Cadmium with the Present Method

Although further research is necessary to refine and validate this method, preliminary work presented here indicates that the concentration range for the determination of Cadmium is between zero to 30 µM which corresponds to a about 4 mg/L (4 ppm) for dilute aqueous solutions. More concentrated solutions can be handled by further dilution to bring the concentration to within the range.

For the detection limit, what we can say is that test solutions with a Cd concentration 1.00×10^{-6} M failed to provide a measurable absorbance at 600 nm. Therefore in the absence of more information we must conclude that present detection limit will be 1.00×10^{-6} M.

3.3 FTIR Analysis

The infrared spectra of azo reagent Dithizone and its complex with Cd^{2+} are given in Figures12 and 13. The spectra are complex because of many bonds γ(C=N),(N=N), (C=S),(C=C) and other bonds for thiazole and phenyl rings in the sub 1700 cm^{-1} overlap with each other position shift and/or changes in shapes of the bonds in the metal-ligand complex , and the associated interpretations are given below :

The FTIR spectrum shows the following characteristic bands: aromatic C-H stretch at 3118 cm^{-1}, anhydride C=O stretch at 1772 cm^{-1} and 1739 cm^{-1}, aromatic C=C stretch at 1594 cm^{-1} and C-O stretch at 1024 cm^{-1}.

The FTIR spectrum of Dithizone shows the following characteristic bands: aromatic C=C stretch at 1593 cm^{-1}, anhydride N=N stretch at 1441 cm^{-1}, aromatic C-N stretch

at 1212 cm^{-1}, C=S stretch at 1141 cm^{-1} and aromatic C-H bending at 745 cm^{-1}, 712 cm^{-1}and 680 cm^{-1}.
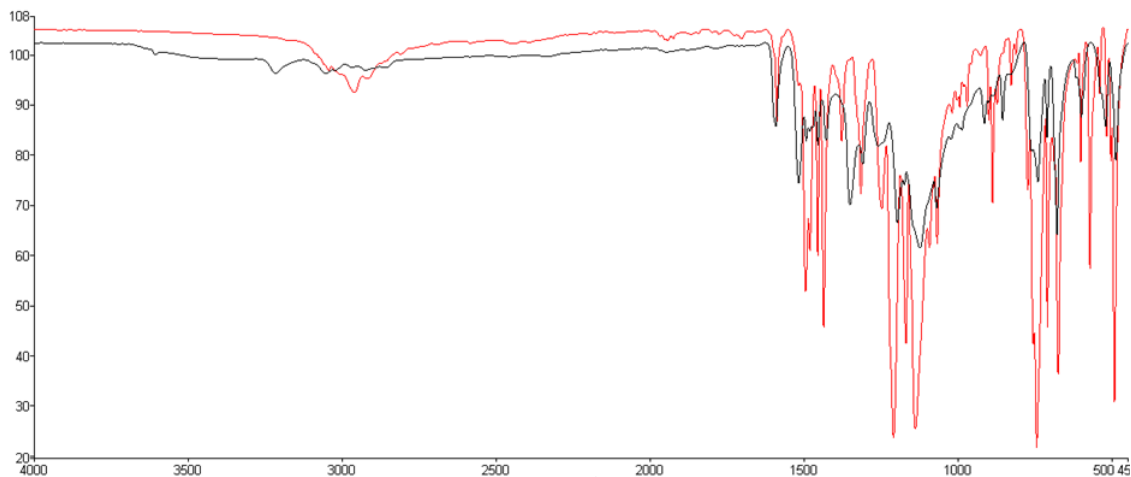
Figure 12: Overlapping Infrared Spectra of Dithizone (red line) and Dithizone-Cd Complex (black line)

Figure 13: Overlapping Infrared Spectra Between 1700 and 400 cm^{-1} of Dithizone (Red line) and Dithizone-Cd Complex (Black line)

3.4 UV-Visible Absorption Spectrum of the Test Solutions.

The absorption spectrums of some of the test solutions are reproduced below to illustrate the dependence of absorbance on solution compositions. Figure 14 shows

the absorbance spectrum of 40 µM dithizone in aqueous NaOH solution. Absence of

any absorption at the 600 nm wavelength is clearly visible.

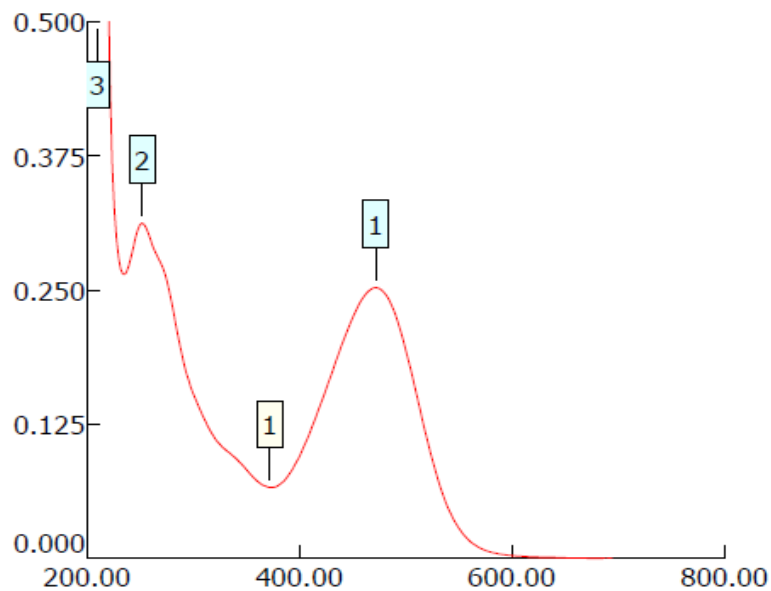Figure 14: Absorption Spectrum of 40µM Dithizone in 0.04 M NaOH Solution with
no Cadmium or Deriphat 160C

However when 4 µM Cd is added to this solution, the Cd-dithizone complex clearly

absorbs at 600 nm as seen from the spectrum of this solution in Figure 15.
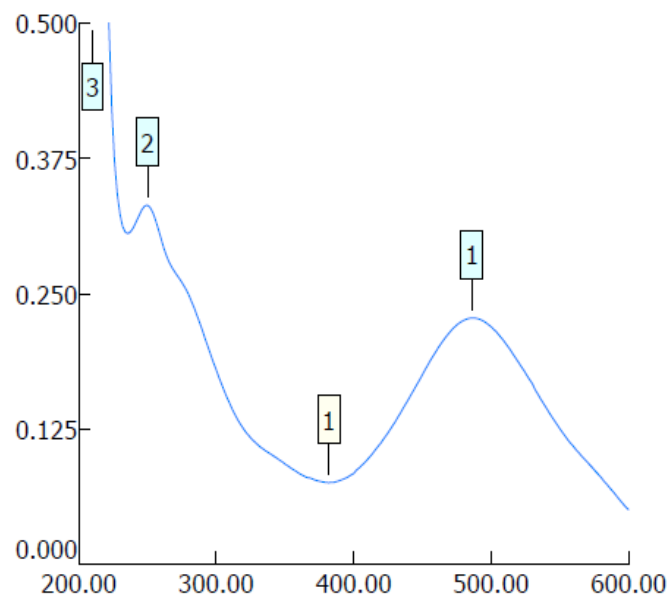
Figure 15: Absorption Spectrum of Dithizone-Cd Complex in NaOH Solution. Solution Composition is 4μM Cd, 40 μM Dithizone, 0.04 M NaOH and Zero Deriphat 160C.

A similar observation can be made for dithizone solutions without cadmium (Figure 16) and with cadmium (Figure 17) also containing Deriphat 160C. Because the concentration of NaOH and Dithizone are not the same as the previous two, direct comparison cannot be made. But nevertheless the spectrums show clearly that absorbance of the free dithizone solution at 600 nm is almost zero.

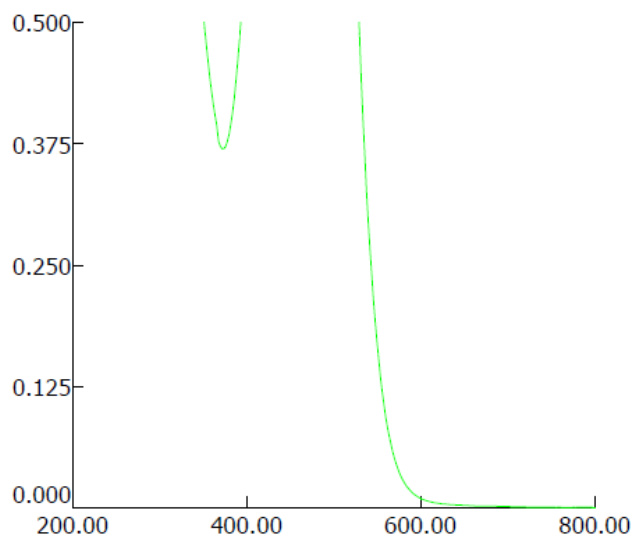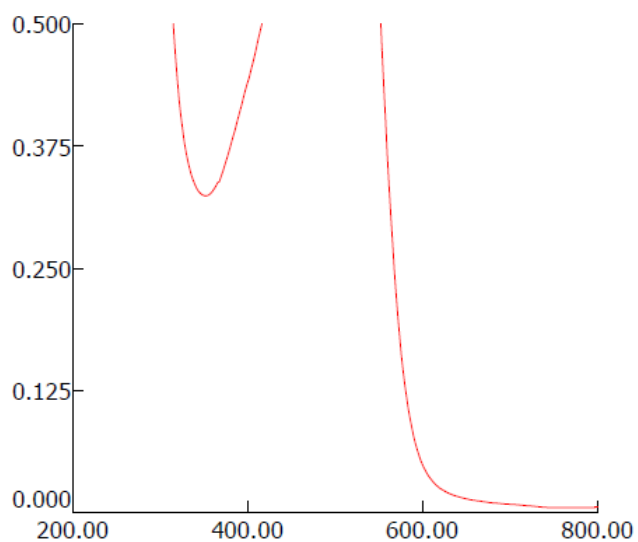Figure 16: Absorption Spectrum of 80µM Dithizone in 1.6 mM Deriphat 160C and 0.02 M NaOH no Cadmium.

Figure 17: Absorption Spectrum of Dithizone-Cd Complex in Deriphat 160C and NaOH Solution. Solution Composition is 4µM Cd, 80 µM Dithizone, 1.6 mM Deriphat 160C and 0.02 M NaOH

Chapter 4

CONCLUSION

In this study, we set out to investigate if sensitive, simple and quick method using reasonably safe and non-toxic chemicals for quantitative determination of cadmium with the colored complexing reagent dithizone could be developed. And to do this we broke it down to a set of questions to which we tried to find answers. From the results of our investigation we can provide the following answers and conclusions regarding our original goal and the questions.

1. *Is it possible to make a stable Cd-dithizone complex without using toxic or hazardous chemicals or reagents and keep it dissolved in an aqueous environment? What are the conditions necessary to achieve this?*

After a number of failed attempts which resulted with the precipitation of the Cd-dithizone complex, we eventually found that the Cd-dithizone complex made in basic aqueous solution (pH = 12.5) containing 8×10^{-4} M Deriphat 160C remains dissolved in the solution and it is stable for at least 24 hours as shown by its UV-visible absorbance spectrum taken at the beginning and after 24 hours. Thus we are able to prepare and measure absorbance of Cd-Dithizone complex containing solutions without using chloroform, carbon tetrachloride or potassium cyanide!

2. *If such a water-soluble Cd-dithizone complex could be made, would it have high absorptivity and follow Beer's law so that its concentration could be determined by spectrophotometric measurements.*

The absorbance of the Cd-dithizone complex in the solution described above has a molar absorptivity of 23,200 $M^{-1} \cdot cm^{-1}$. This means that a 1 µM solution of Cd in a 1 cm cell will give an absorbance of 0.023 or 23 mAU. This is sufficiently high so as to be measured fairly accurately. Therefore, the Cd-dithizone complex does have a good enough molar absorptivity to enable accurate photometric determination of Cd at µM levels.

3. *What range of Cd concentration can be measured with reasonable accuracy and precision by this method? What would be the detection limit?*

The results (so far) show that the Cd-dithizone complex obeys Beer's law in the range of 1.0×10^{-6} to 32×10^{-6} M with a molar absorptivity of 23,200 L/mol·cm.

Also, since the acceptable absorbance range for accurate photometric measurements is between 0 (corresponding to 100% transmittance) and 1 (corresponding to 10% transmittance), we can calculate an upper limit for Cd-dithizone complex of around 50 µM.

As for the detection limit, we can safely assume that for a good spectrophotometer the absorbance signal for blank will be within ± 0.002 of zero. Thus, by taking the usual definition of detection limit (real signal) as three times the standard deviation

of the blank signal (i.e., 3×0.002 = 0.006) we can calculate the limit of detection or this method.

LOD of Cd-Dithizone complex = $0.006/23,200 = 2.5 \times 10^{-7}$ M

4. What other factors must be studied further so as to verify the applicability of this method and develop it into an acceptable safe analytical method?

There is a need to investigate if other trace or heavy metal cations present in the solution will interfere with the analysis. And if there is interference, finds way to eliminate or minimise them.

The effect of pH should also be studied further. Although Dithizone normally works in basic solutions, we should still find and confirm the optimum pH for the analysis. The absorption spectrums given in Figures 14 to 17 indicate that pH also plays a significant role in the complexation and absorption behaviour.

Also, other surface active agents can also be tried out to evaluate their influence on the method. Surfactants that do not have chelating hydrophilic groups can also be tried out so as to shed light on the mechanism of solubilizing the Cd-dithizone complex.

To sum up, our results show that it is possible to determine Cd with dithizone in basic aqueous solution containing the surface active agent Deriphat 160C.

- The Cd-dithizone complex remains soluble;

- Its absorbance is sufficiently large enough so that it can be measured down to a concentration of 2×10^{-6} M;

- It obeys Beer's law in the concentration range of 2×10^{-6} M to 32×10^{-6} M.;

- Toxic or carcinogenic chemicals such as KCN, $CHCl_3$ and CCl_4 are NOT used in the analysis of the Cd-dithizone complex.

Thus, this work needs and deserves to be developed further in to a viable method with its accuracy, reproducibility, validity and applicability firmly established.

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