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Spectrophotometric Determination of Hg (II) in Cosmetics

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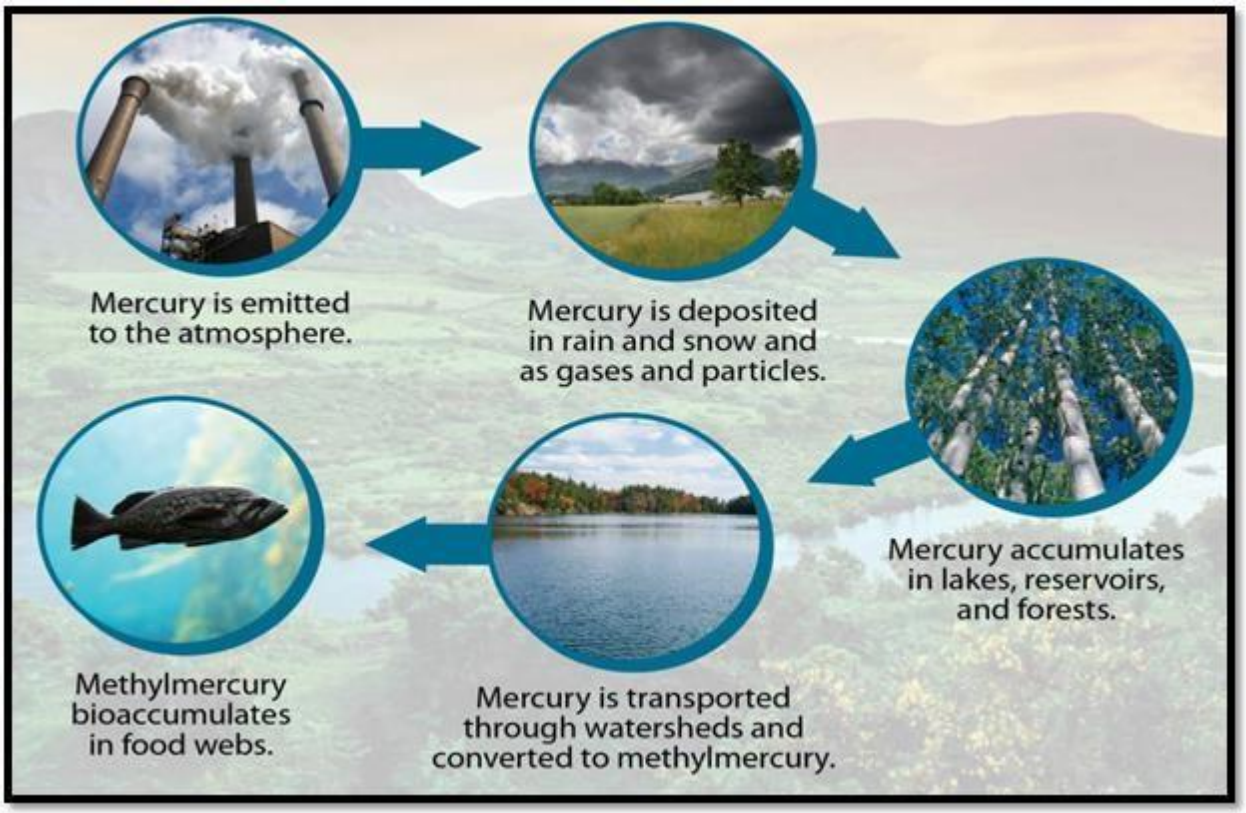
Abstract:

Natural sources of mercury come from volcanoes, forest fires and the weathering of mercury-bearing rocks. However, this is small compared to the vast amount of mercury which is generated from anthropogenic sources (human activities), such as fossil fuel combustion, solid waste incineration, mining and smelting, manufacture of cement and the use of mercury cells in the commercial production of chlorine.[24] Of all the anthropogenic activities, by far the largest polluters are coal-fired power plants, which release approximately 50 tons of elemental mercury into the atmosphere each year via the effluent generated by the combustion process[5]. Once released, the mercury particulates fall back down to the ground and get absorbed by soils, where they eventually get into commercial farming crops and vegetables. Mercury also enters surface waters, such as lakes, rivers, wetlands, estuaries and the open ocean, where it is converted to organic mercury (mainly methyl mercury – CH3Hg+) by the action of anaerobic organisms. The methyl mercury biomagnifies up the aquatic food chain as it is passed from a lower food chain to a subsequently higher food chain level through feeding and eventually finds its way into the fish we eat.

1- Introduction

1.1 Mercury (occurrence and toxicity)

Mercury is distributed throughout the environment in a number of different forms. It is found as elemental mercury vapor in the atmosphere, while most of the mercury in water, sediments, soil, plants, and animals is found as inorganic and organic forms of the element[1]. Natural sources of mercury come from volcanoes, forest fires and the weathering of mercury-bearing rocks. However, this is small compared to the vast amount of mercury which is generated from anthropogenic sources (human activities), such as fossil fuel combustion, solid waste incineration, mining and smelting, manufacture of cement and the use of mercury cells in the commercial production of chlorine.**[24]** Of all the anthropogenic activities, by far the largest polluters are coal-fired power plants, which release approximately 50 tons of elemental mercury into the atmosphere each year via the effluent generated by the combustion process[5]. Once released, the mercury particulates fall back down to the ground and get absorbed by soils, where they eventually get into commercial farming crops and vegetables. Mercury also enters surface waters, such as lakes, rivers, wetlands, estuaries and the open ocean, where it is converted to organic mercury (mainly methyl mercury – CH_3Hg+) by the action of anaerobic organisms. The methyl mercury biomagnifies up the aquatic food chain as it is passed from a lower food chain to a subsequently higher food chain level through feeding and eventually finds its way into the fish we eat[6-10]. Several studies indicate that methylmercury is linked to subtle developmental deficits in children exposed *in utero* such as loss of IQ points, and decreased performance in tests of language skills, memory function and attention deficits. Methylmercury exposure in adults has also been linked to increased risk of cardiovascular disease including heart attack[11]. methylmercury found complexed with free cysteine and with proteins and peptides containing that amino acid. The methylmercuric-cysteinyl complex is recognized as and/or by amino acids transporting proteins in the body as methionine, another essential amino acid[12] Because of this mimicry, it is transported freely throughout the body including across the blood–brain barrier and across the placenta, where it is absorbed by the developing fetus. Also for this reason as well as its strong binding to proteins, methylmercury is not readily eliminated. Methylmercury has a half-life in human blood of about 50 days.[13]



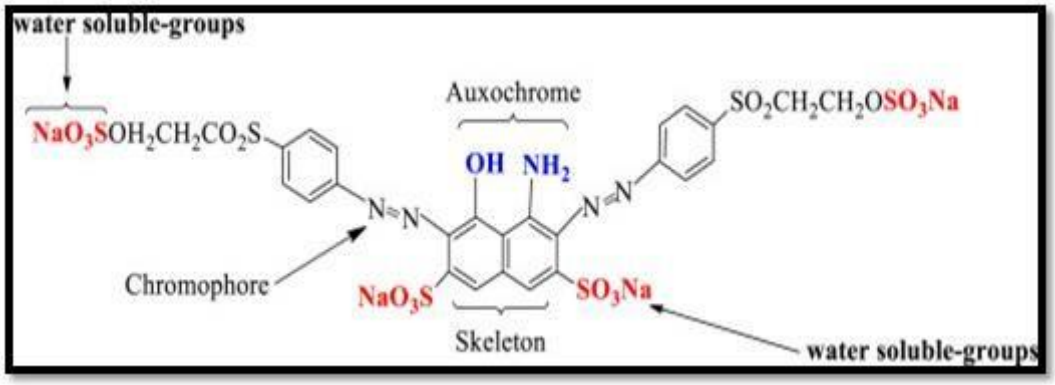
Elemental and methylmercury are toxic to the central and peripheral nervous system . The in halation of mercury vapour can produce harmful effects on the nervous , digestive and immune

systems , lungs and kidneys , and may be fatal .[14] The inorganic salts of mercury are corrosive to the skin , eyes and gastrointestinal tract , and may induce kidney toxicity if ingested . " Neurological and behavioural disorders may be observed after inhalation , ingestion or dermal application of different mercury compounds . Symptoms include tremors , insomnia , memory loss , neuromuscular effects , headaches and cognitive and motor dysfunction [15]. Mild subclinical signs of central nervous system toxicity can be seen in workers exposed to an elemental mercury level in the air of 20g / m ' or more for several years . Kidney and immune effects have been reported .

There is no conclusive evidence linking mercury exposure to cancer in humans . - Children are especially vulnerable and may be exposed directly by eating contaminated fish . Methylmercury bioaccumulated in fish and consumed by pregnant women may lead to neurodevelopmental problems in the developing fetus . Transplacental exposure is the most dangerous , as the fetal brain is very sensitive . Neurological symptoms include mental retardation , seizures , vision and hearing loss , delayed development , language disorders and memory loss . In children , a syndrome characterized by red and painful extremities called acrodynia has been reported to result from chronic mercury exposure . Biological measurement of mercury , for example in hair and blood , allows exposure to be quantified and linked to possible health effects.[16]

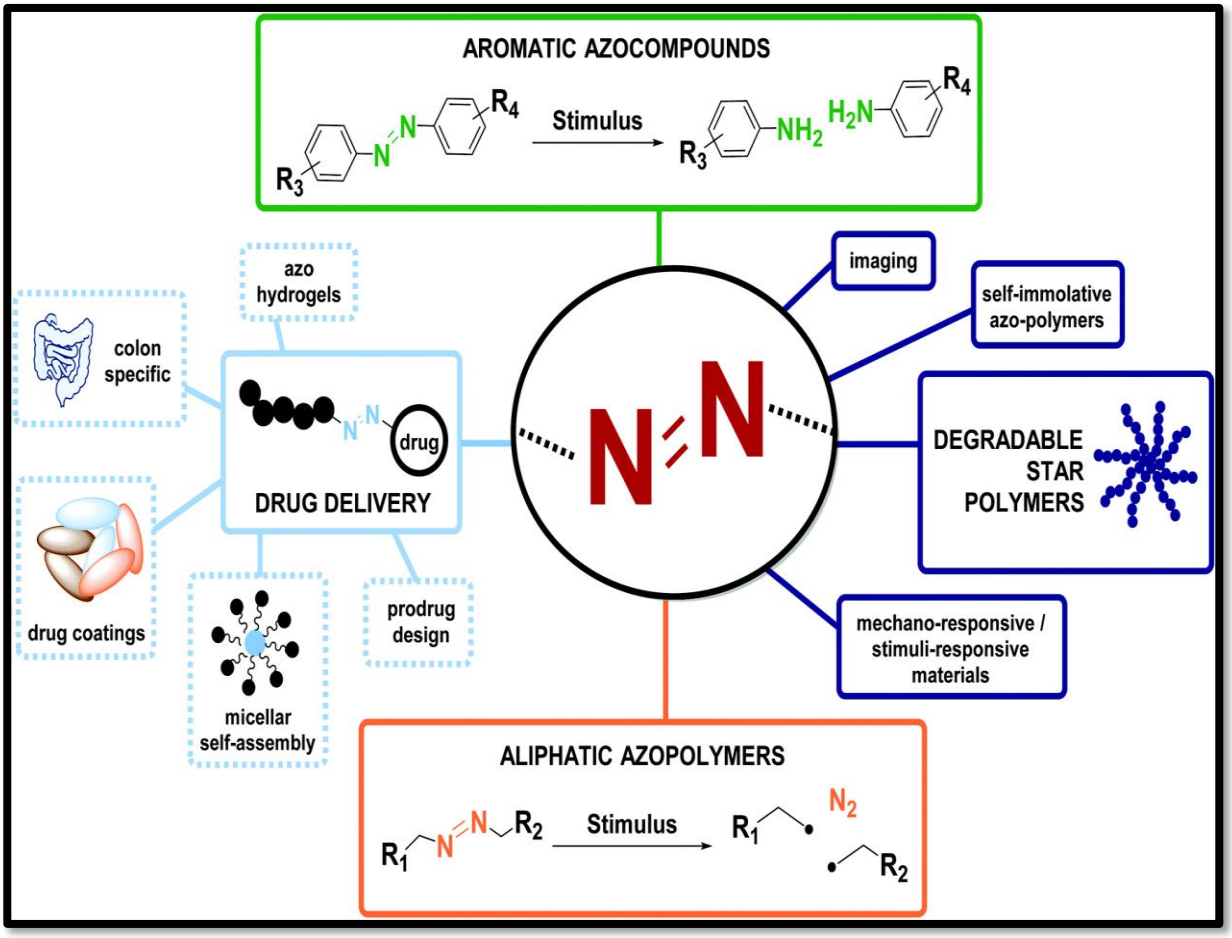
1.2 Azo compound

Azo dyes contain at least one nitrogen-nitrogen double bond (N=N); however many different structures are possible1. Mono-azo dyes have only one N=N double bond, while diazo and tri-azo dyes contain two and three N=N double bonds, respectively[17]. The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups. These side groups are necessary for imparting the color of the dye, with many different shades and intensities being possible. A common example of an azo dye is shown in Figure below[18]. When



describing a dye molecule, nucleophiles are referred to as *auxochromes*, while the aromatic groups are called *chromophores*. Together, the dye molecule is often described as a *chromogen*. Synthesis of most azo dyes involves diazotization of a primary aromatic amine, followed by coupling with one or more nucleophiles. Amino- and hydroxy- groups are commonly used coupling components1. Because of the diversity of dye components available for synthesis, a large number of structurally different azo dyes exist and are used in industry2. World wide production of organic dyes is currently estimated at nearly 450,000 tons, with 50,000 tons being lost in effluents during application and manufacture.['19-21]

The heterocyclic azo compounds are considered very active toward metal ions because they have active donor group and contain atoms such as oxygen, nitrogen and sulfur, to form chelatic coordination complexes and make it important in the biological field. The azo dye are used in the electronic industry, like nonlinear optical (NLO) devices, colorimetric sensors, and liquid crystalline displays (LCDs).[22] The nitrogen atom in the imidazol ring has biological activities such as antibacterial, anti-inflammatory, antimycotic, antitumor, and powerful antifungal agents. Azo compounds show a highly pharmacological activity, whereas the drug become very active when administered as metal complexes.[23] Azo compound includes some biological reactions like inhibition of RNA, DNA, and protein synthesis, carcinogenesis and nitrogen fixation. Metal complexs of hetrocyclic azo compounds are useful in the redox responsive, and pH-sensitive through azo group.[24]



Azo dyes acquired wide interest in application to biological system and indicator in complexometric titration of analytical chemistry. Azo dyes are the most important group of synthetic colorants.[25] They are generally considered as xenobiotic compounds that are very recalcitrant against biodegradative processes. Aromatic azo compounds especially are used as acid-base indicators, also used in biological strains and commercial colorants for clothing, plastics, cosmetics and food beverages. Color changes are caused by change in extent of delocalization of electrons. More delocalization shifts the absorption max to longer wave lengths and makes the light absorbed redder, while less delocalization shifts the absorption max to shorter wavelengths.[26-30]

Aim of research

Synthesis a new imidazole-azo for spectrophotometric determination of Hg (II) in cosmetics.

2. Experimental

2.1. Apparatus

All the laboratory instrument and equipment that used are summarized in table (1)

Table (1) summery of laboratory instrument and equipment

1	**Instruments**
2	UV_1610 pc double spectrophotometer SHIMADZU(Japan) using 1cm quartz cells
3	WTW multi 740. pH-meter, Germany
4	Balance BP , 3015 Sartorius , Germany
5	Water bath and shaker M00/M01 – Memmert, Germany
10	Micropipette

11	Distillator
12	Hot plate
13	Oven

2.2 Materials

All the chemicals that used are summarized in table (2)

Table (2) summery of chemical compounds

ت	substances	formula	Purity or concentration	company
1	diphenylimidazole-4,5	$C_{15}H_{12}N_2$	98	Sigma-Aldrich
3	Acetone	C_3H_6O	99.9	B.D.H
4	Citric acid	$C_6H_8O_7$	99.5	B.D.H
5	Hydrochloric acid	HCl	%37	B.D.H
6	Sodium acetate	CH_3COONa	99	B.D.H
8	Ethanol	C_2H_5OH	absolute	J.T. Baker
9	Sodium hydroxide	NaOH	97	Fluka
11	Mercury nitrate	Hg(NO3)2	99.99	B.D.H

2.3. Synthesis of imidazole-azo ligand ((E)-3,5-dibromo-2-((4,5-diphenyl-1H-imidazol-2-yl)diazenyl)benzaldehyde) (DBPIAB)

2.79 gram (0.01 mole) of 2-amino-3,5-dibromobenzaldehyde was dissolved in acidic solution prepared by adding 3 ml of concentrated HCl to 20 ml distilled water in ice bath, then a cold solution of sodium nitrite ($NaNO_2$) was added very slowly to the previous solution. 10 minutes later, the product (diazonium salt) was added slowly to the solution prepared from mixing 2.2 gram (0.01 mole) of 4,5-diphenyl imidazole with NaOH in alcoholic media, an orange product was formed, washed many fold with distilled water and dried.

2.4. Preparation of standard solution of reagent (DBPIAB)

1. ($1 * 10^{-3}$ M) reagent solution

0.0456 gram of reagent was dissolved in ethanol in 100 ml volumetric flask and complete to the mark with the same solvent.

2. ($5 * 10^{-5}$ M) reagent solution

Five ml of solution (1) were transferred to 100 mL volumetric flask and complete to the mark with the same solvent.

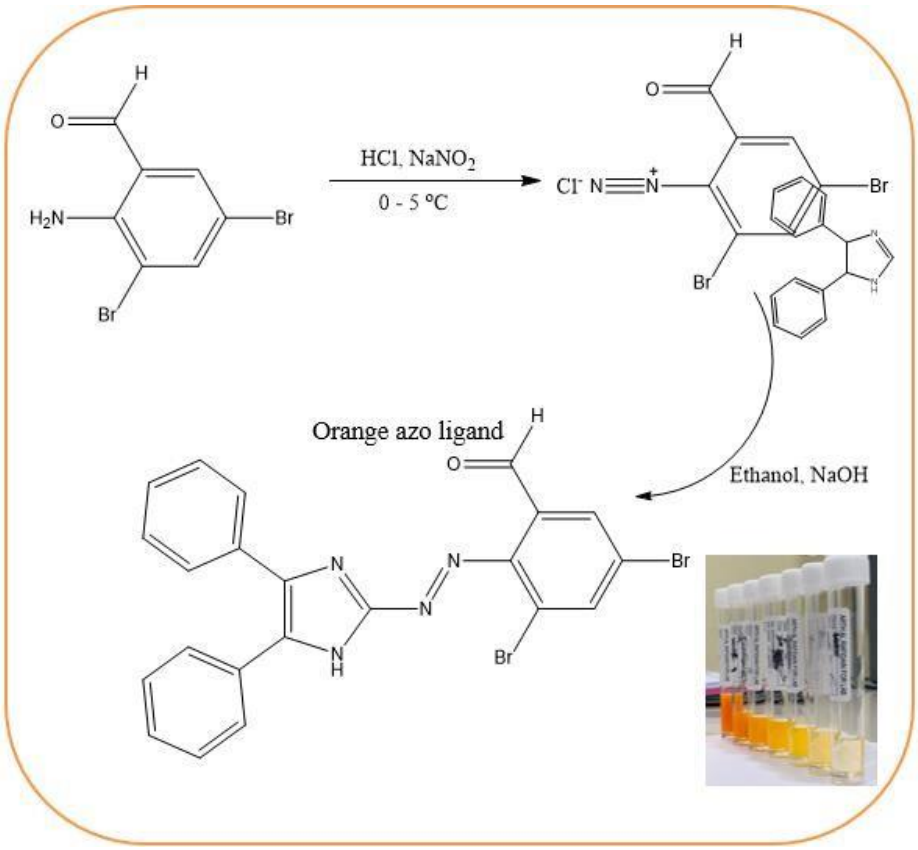
2.5. Standard solution of Hg (II) (500 ppm)

This solution was prepared by dissolving (0.0404) grams of mercury nitrate in 5 ml distilled water and completed to the mark in 100 mL volumetric flask with the same solvent.

3. Result and discussion

3.1. Synthesis of ligand

The scheme below represents the reaction steps for synthesis of ligand.



3.2. Spectral study

The absorption spectra of the reagent (**DBPIAB**) and it's mercury complex under the optimum conditions are shown in fig (2):

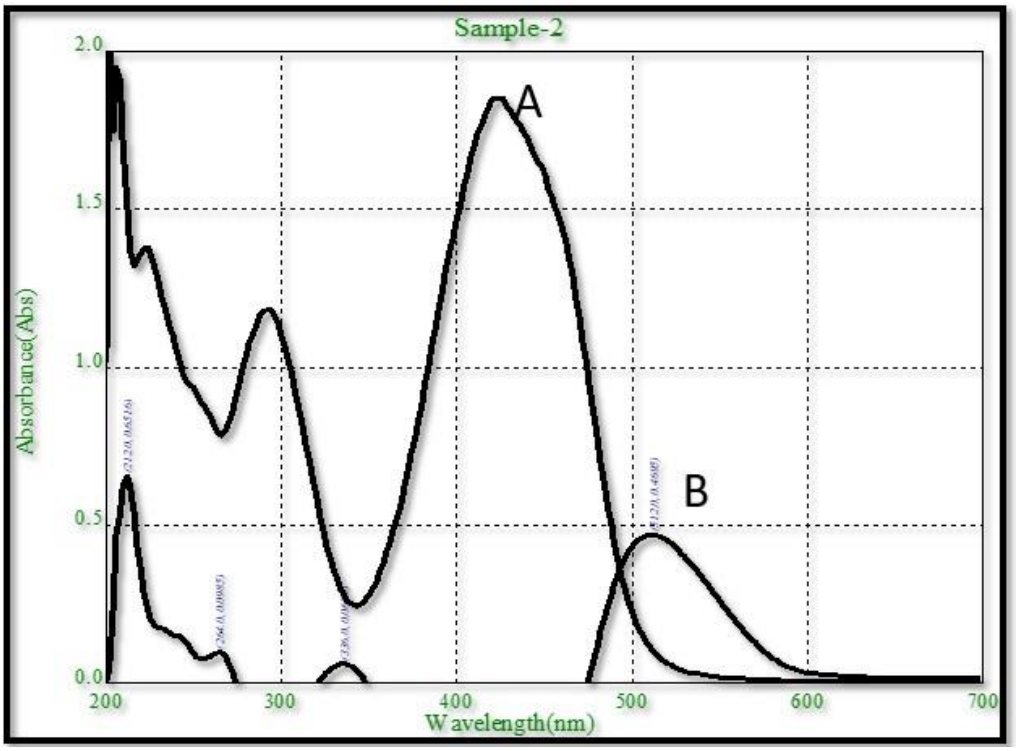


Fig. (2):-Absorption spectra of A: DBPIAB reagent ($5*10^{-5}$M), B: [Hg-DBPIAB] complex at pH=7

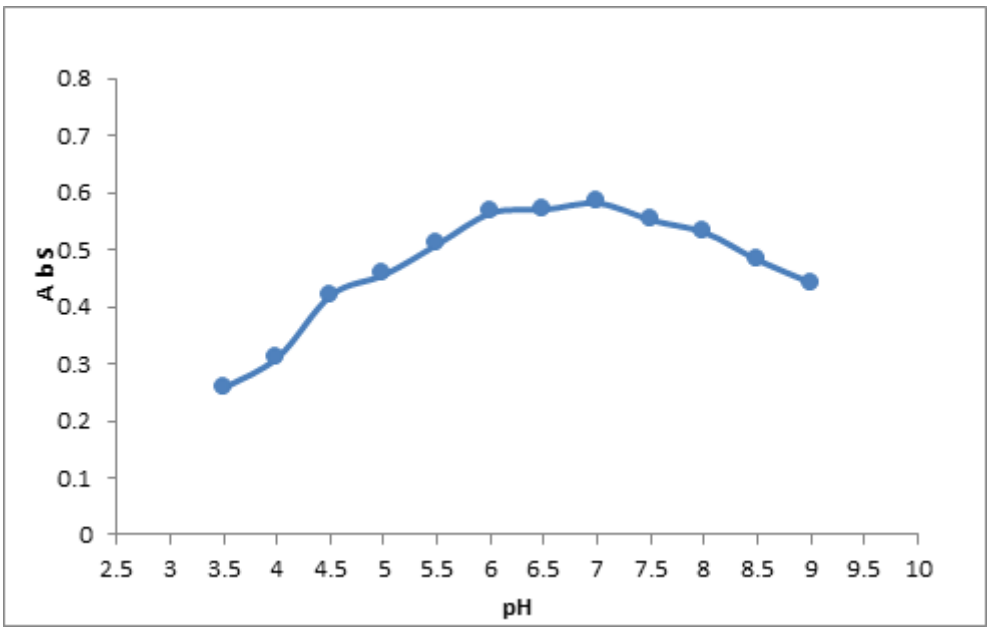
The electronic spectrum of the reagent shows three bands, the first two bands at (216,290) nm is related to the (π ===> π*) transition of the aromatic ring , wherease the third band at (422)nm is related to the (n ==> π*) transition of the non bonding electron pairs of the nitrogen atom . The mercurry complex with this reagent exhibits a maximum absorbance wavelength(λ_{max}) at 514 nm which differs from that for the reagent (**DBPIAB**), this indicates that a reaction take place between Hg (II) and the reagent and the complex Hg- DBPIAB is formed.

Effect of reagent concentration

The concentration of mercury (II) solution is remained constant for all conditions optimization, The concentration of reagent DBPIAB was studied at the range ($1*10^{-6}$-$1*10^{-3}$)M, on mixing with mercury solution, the reagent concentration range ($5*10^{-4}$-$1*10^{-3}$)M gives the metal complex as a precipitate, while the reagent concentrations ($8*10^{-5}$-$3*10^{-4}$)M show a high absorbance value, whereas for the reagent concentration ($1*10^{-6}$-$9*10^{-9}$)M exhibits a very low absorbance which are insufficient for measurement ,and the concentration between ($1*10^{-5}$-$5*10^{-5}$) M give the best absorbance, therefore the reagent concentration of $5*10^{-5}$M was chosen as the optimum value.

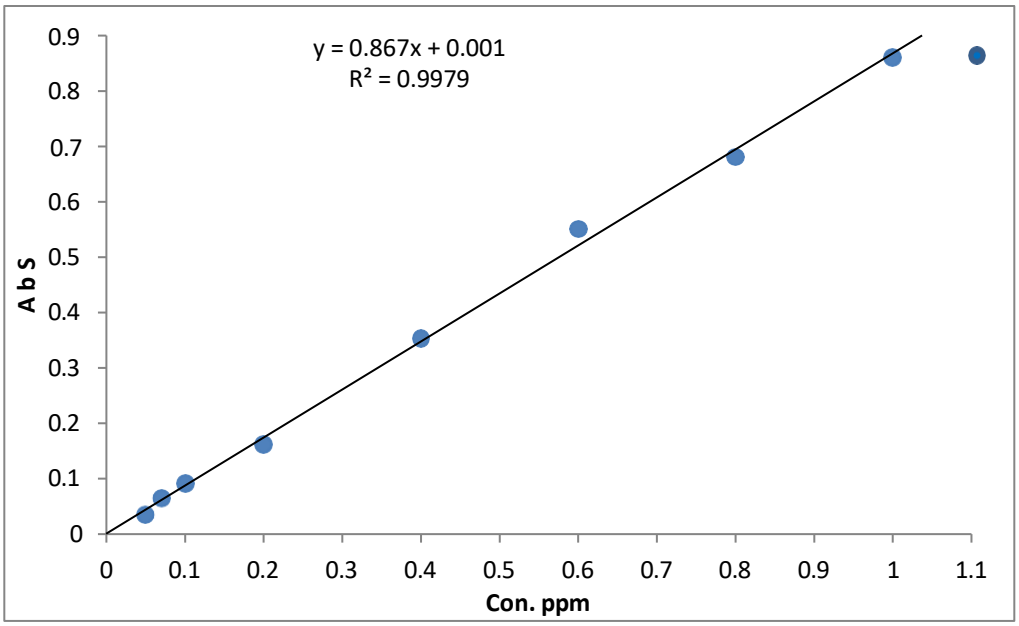
Effect of pH

The optimum pH range for the complex formation was examined fig (5), At the pH lower than 3.5 there is no complex formation takes place may be due to the protonation of the electrons pair of nitrogen atoms that prevent the mercury cations from coordination with the reagent. On increasing the pH, the mercury ions will compete with the hydrogen ions to occupy the electrons pair and form a coordination complex, showing a good absorbance value for the range (3.5 – 9), while for the pH value more than (9), the precipitate of mercury hydroxide $Hg(OH)_2$ will be formed. The optimum pH value chosen is 7. The pH was adjusted by addition of 0.2M NH_4OH and 0.2M HCl.



Calibration graphs and the some analytical parameters

Aliquots of Hg (II) within the concentration range cited in range (0.04-1 µg/mL) was placed in a 10 ml volumetric Flask. Then 2 mL of reagent solution was added to each flask. The absorbance was measured against blank solution prepared under the same condition without mercury solution. Beers Law was obeyed in the range of 0.04-1 µg/mL of mercury at 514 nm. The analytical parameters were summarized in table (1)



Precision and accuracy

The precision of the proposed analytical method was calculated by calculating both the relative error (E_{rel}%) and the recovery ratio (Re%) for (0.5) ppm of mercury ion.

Real value (μ) = 0.5 ppm

Analytical value (y) = 0.498 ppm

$E_{rel}\% = (y-\mu)/\mu * 100 \Rightarrow E_{rel}\% = [(0.5-0.498)/0.5] = -0.379$

Re%= 100 – 0.379 ===➔ Re%= 99.62%

The accuracy of the analytical method was studied by calculating the relative standard deviation (R.S.D%) for (0.5) ppm of mercury ion solution by performing seven replication of absorbance as shown in the following table:

Table (2): absorbance of 0.5 ppm Hg (II) for seven replication

X_i (Abs)	0.435	0.431	0.433	0.432	0.437	0.43
N = 7						

Table (3): Analytical parameters of the proposed procedure (N =number of determinations)

analytical parameter	value
Molar absorptivity (Ɛ)	$5.4*10^2$
Correlation coefficient (r^2)	0.9979
Detection Limit (D.L)	0.0083 ppm
Standard Deviation (S.D)	0.0024
Relative. Standard. Deviation (R.S.D)	0.556% (N=7)
Standard deviation	0.0024
Percentage Relative error	-0.37%
Percentage Recovery	99.62%

Analysis of samples

In order to illustrate the utility of the proposed method, it was used for the spectrophotometric determination of Hg (II) in the cosmetics. The mercury concentration was determined by the

proposed method and the results are compared with that obtained by atomic absorption Analysis method. The results are shown in Table (3).

Table (3) Concentration of Hg (II) µg/g in some local cosmetics

sample	Atomic absorption spectroscopy	Proposed method
Top Shirley (Taiwan)	6.63	6.55
Super Rose (Taiwan)	1.81	1.7
Norseen (Thailand)	26.5	27.3

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