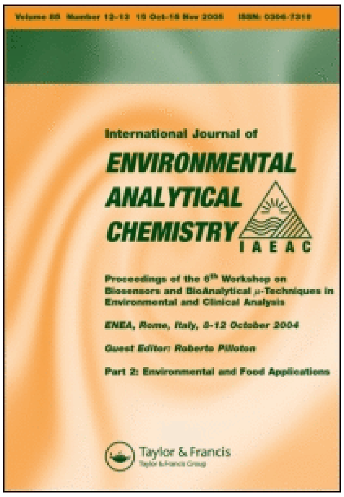

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Sensitive and Selective Spectrophotometric Determination of Hg(II), Ni(II), Cu(II) and Co(II) Using Iminodibenzyl and 3-Chloroiminodibenzyl as New Reagents and Their Applications to Industrial Effluents and Soil Samples

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SENSITIVE AND SELECTIVE SPECTROPHOTOMETRIC DETERMINATION OF Hg(II), Ni(II), Cu(II) AND Co(II) USING IMINODIBENZYL AND 3-CHLOROIMINODIBENZYL AS NEW REAGENTS AND THEIR APPLICATIONS TO INDUSTRIAL EFFLUENTS AND SOIL SAMPLES

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Iminodibenzyl (IDB) and 3-chloroiminodibenzyl (Cl-IDB) are proposed as a new class of spectrophotometric reagents for the determination of micro amounts of mercury(II), nickel(II), copper(II) and cobalt(II) in the presence of 3-methyl-2-benzothiazoline hydrazone hydrochloride hydrate (MBTH) or 4-aminoantipyrine (AAP) as electrophilic coupling reagents. The reaction is carried out in neutral aqueous medium. The blue colour formed shows maximum absorbance at 660 nm using MBTH and 630 nm with AAP. The methods obey Beer's law. The molar absorptivity and Sandell's sensitivity show different values with different metals and reagents. The blue colour can also be extracted quantitatively which can be exploited as an efficient extractive spectrophotometric technique for the separation of metal ion from other interfering species. As many as 15 cations and 12 anions and/or complexing agents listed do not interfere. Both the methods have good reproducibility and can be satisfactorily applied in the determination of metals in industrial effluents and soil samples.

Keywords: Spectrophotometry; New reagents; Dibenzazepines; Heavy metals; Industrial effluents; Soil samples

INTRODUCTION

Mercury, a heavy metal, well-known for its toxicity is distributed throughout the environment as a result of soil erosion and a broad spectrum of industrial and agricultural processes. This metal, in all the segments of the environment and in any form is a serious environmental pollutant [1]. Mercury, getting into the soil, has a negative effect upon the development of crop plants. Similarly copper is also acutely harmful to fish and its adverse effects depend on the hardness of water. Toxicity of nickel and cobalt

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to aquatic forms varies differently. Nevertheless, all these metals are cumulative poisons and affect human health [2]. This necessitates detailed studies on the composition and quantitation of toxic metals in environmental matrices.

Various optical methods, such as inductively coupled plasma atomic emission spectrometry [3], electron microprobe analysis [4], total-reflection X-ray fluorescence spectrometry [5], atomic absorption spectrophotometry and radioanalytical method such as neutron activation analysis have been extensively used for detection, quantitation and characterisation of these metals. However, the results obtained by the last two leave much to be desired for the analysis of small amounts of mercury [6]. Besides, these instruments are highly expensive, their day-to-day maintenance cost is high and are not free from various types of inherent interferences [7–9].

Visible spectrophotometry amongst the optical methods seems to be the most appropriate analytical approach for the determination of toxic metals, as it provides sensitive, precise and accurate measurements of suitable analytes, and offers practical and economical advantages over other methods. Besides, visible spectrophotometric detection is much more viable as a useful technique to develop a portable, on-line or at-line system.

Dithiazone has been unquestionably the most widely used spectrophotometric reagent [10] but, this highly sensitive reagent requires very careful handling and the determination of small amounts of mercury involves re-extraction of the reagent in excess (single-color method) [11]. However, in another communication [12] dithiazone was employed directly in aqueous media in the presence of a neutral surfactant. This procedure is reported to eliminate the need for an extraction step. During the last decade-and-a-half, a large number of chromogenic reagents have been reported for the determination of mercury, nickel and copper, but, only few of them have been used for their determination in environmental matrices [13–29]. These reagents and their spectral characteristics are enumerated in Table I. A survey of the literature revealed that most of the reported reagents lack simplicity, sensitivity and/or selectivity.

During the systematic studies on dibenzazepines [30–34], it was found that iminodibenzyl (IDB) and 3-chloroiminodibenzyl (Cl-IDB) react selectively with metal ions such as mercury(II), nickel(II), copper(II) and cobalt(II) in the presence of electrophilic coupling reagents, namely, 3-methyl-2-benzothiazoline hydrazone hydrochloride hydrate (MBTH) or 4-aminoantipyrine (AAP). Hence, chemistry aspects of the reactions have been studied, and procedure for the spectrophotometric determination of mercury(II), nickel(II), copper(II) and cobalt(II) in environmental matrices are proposed. The results show that IDB and Cl-IDB can be used for the selective spectrophotometric determination of aforesaid metal ions in the presence of MBTH or AAP and the method is simple, rapid and sensitive. Besides, the reagents offer clear advantages over most of the chromogenic reagents currently used for the purpose and the procedure shows positive features over existing methods.

EXPERIMENTAL

Apparatus

Jasco US-VIS spectrophotometer UVIDEC-610 type with 1.0 cm matched cell was employed for measuring the absorbance.

TABLE 1 Comparison of visible spectrophotometric methods for the determination of mercury(II), nickel(II) and copper(II) in environmental samples

Reagent	λ_{max} (nm)	ε ($L\,mol^{-1}\,cm^{-1}$)	*Environmental matrice(s)*	*Method employed*	*Ref*
Mercury					
p-sulfamoylbenzenediazoaminoazobenzene	470	8.80×10^4	waste water	DS	13
p-azobenzenediazoaminoazobenzene sulfonic acid	528	1.76×10^5	waste water	DS	14
triphenyltetrazolium chloride	255	6.45×10^4	soil samples	ES	15
2-(2-thienyl)benzothiazoline (TBT)	375	1.70×10^5	liquid samples	ES	16
Rhodamine 6G	528	8.20×10^4	sea water	DS	17
p-phenolazo-3-aminorhodamine	510	2.00×10^4	industrial effluents	DS	18
Michler's thioketone	540	1.62×10^5	industrial effluents	DS	19
thiocyanate and Rhodamine B	610	1.10×10^5	air samples	DS	20
N-(*p*-chlorophenyl)benzohydroxamic acid	388	6.00×10^2	industrial effluents	DS	21
Nickel					
1-(2-pyridylazo)-2-naphthol	568	4.80×10^4	gasoline	DS	22
2,2′-dipyridyl ketone picolinoylhydrazone	385	5.17×10^3	industrial effluents	DS	23
Diethyldithiocarbamate	325	3.58×10^4	waste water	DS	24
2-hydroxyhydroquinonephthalein	545	1.26×10^5	waste water	DS	25
5-(2′-carboxyphenyl)azo-8-quinolinol	540	5.50×10^4	geological matrices	ES	26
bathophenanthroline, phloxine and polyoxyethyleneglycol	566	4.70×10^4	industrial effluents	DS	27
Copper					
(4-sulfophenyl) prophine dimer	489	5.00×10^5	tap water	DS	28
Diethyldithiocarbamate	520	1.22×10^5	tap water	ES	29

DS: Direct Spectrophotometry; ES: Extractive Spectrophotometry.

Chemicals

Mercury(II) Solution

Stock solution of mercury(II) ($1000\,\mu g\,ml^{-1}$) was prepared by dissolving known amounts of mercury(II) nitrate (BDH Chemicals) in 1 L of water to which a few drops of nitric acid was added to prevent hydrolysis. The mercury solution was standardised with standard EDTA solution using xylenol orange as indicator [35]. Solutions of the required strength were prepared by diluting this stock solution with distilled water.

Nickel(II) Solution

Stock solution of nickel(II) ($1000\,\mu g\,ml^{-1}$) was prepared by dissolving 1.0 g of pure metallic nickel in 10 ml of 1 : 1 hydrochloric acid and evaporating to dryness. It was further dissolved in distilled water with a little warming and finally made upto 1 L with distilled water. Working standards were prepared by appropriate dilution of the stock solution.

Copper(II) Solution

Copper(II) solution ($1000\,\mu g\,ml^{-1}$) was prepared by dissolving a known amount of copper(II) sulphate pentahydrate in distilled water, adjusting the pH of the solution to 1.0 with dilute sulphuric acid and diluting to 1 L with distilled water. The concentration was determined by EDTA titration using 1-(2-pyridylazo)-2-napthol (PAN) as indicator. Working solutions were prepared by appropriate dilution of the standardised solution.

Cobalt(II) Solution

Stock solution of cobalt(II) (1000 µg ml^{-1}) was prepared from cobalt(II) sulphate heptahydrate and was standardised by EDTA titration [36]. Working solutions were prepared by appropriate dilution of the standardised solution.

Solutions of diverse ions and complexing agents were prepared by dissolving their corresponding salts. Chloroform (Ranbaxy) was used as such. Alcohol was distilled before use.

IDB was procured from NR Chem., India and CI-IDB was a gift from Max Pharma, India. Fresh solutions of IDB and Cl-IDB (0.1% w/v) were prepared by dissolving 100 mg of sample in 100 ml distilled alcohol.

Aqueous solutions of (0.1% w/v) of MBTH and AAP were prepared and stored in amber bottles to protect from the sunlight.

Procedure

Method A: MBTH

Appropriate volumes of standard solutions of metal ion, 1 ml of 0.1% w/v MBTH and 1 ml of 0.1% w/v, IDB or Cl-IDB were added to a series of 25-ml calibrated flasks. The contents were mixed thoroughly and the flask was kept in a boiling water bath for 5 min and cooled. The solutions were made up to the volume with distilled alcohol. The absorbance was measured against the corresponding reagent blank, and calibration graphs were constructed. The concentration of metal ions, determined using IDB or Cl-IDB and MBTH are detailed in Table II.

Method B: AAP

The above procedure was repeated with 2.0 ml of 0.2% (w/v) AAP instead of MBTH. The metal ions concentration range and optical characteristics are shown in Table II.

TABLE II Spectral data for the determination of metal ions[†] using MBTH as electrophilic coupling reagent

	Mercury (II)		*Nickel (II)*		*Copper (II)*	
Parameters	*IDB*	*Cl-IDB*	*IDB*	*Cl-IDB*	*IDB*	*Cl-IDB*
Colour	Blue	Blue	Blue	Blue	Blue	Blue
λ_{max} (nm)	660	660	660	660	660	660
Stability (h)	> 24	> 24*	> 24	> 24*	> 24	> 24*
Beer's law (ng ml^{-1})	50–2000	50–2000	20–400	20–800	20–800	50–2000
Recommended metal ion concentration (ng ml^{-1})	500	500	200	300	200	800
(µg ml^{-1})	0.50	0.50	0.20	0.30	0.20	0.80
Molar absorptivity (L mol^{-1} cm^{-1})	9.74×10^4	6.34×10^4	9.22×10^4	4.75×10^4	7.87×10^4	1.95×10^4
Sensitivity	2.06×10^{-3}	3.17×10^{-3}	6.36×10^{-3}	1.24×10^{-3}	8.08×10^{-3}	3.26×10^{-3}
Regression equation:						
Slope	0.381	0.333	1.802	0.877	0.925	0.281
Intercept	0.041	−0.005	−0.031	0.004	0.030	0.030
Correlation coefficient	0.9969	0.9990	0.993	0.998	0.984	0.913

[†] Cobalt(II) gives unstable colour with MBTH and Cl-IDB.

*enhancement of the colour intensity observed after about 6 h.

RESULTS AND DISCUSSION

Iminodibenzyl (IDB) and 3-chloroiminodibenzyl (Cl-IDB) belong to dibenzazepine class of tricyclic compounds having a central ring constituted of seven atoms (Fig. 1a and b). Interest in the azepines encompasses a broad spectrum of theoretical [37,38] and applied disciplines [39,40]. At the theoretical level, chemists are fascinated by these compounds from the molecular orbital stand point. At the "applied" end of the spectrum, an enormous amount of research on depressive disorders has been conducted. The practical importance of dibenzazepine derivatives is by no means limited to pharmaceutical applications. For example, imipramine hydrochloride and desipramine hydrochloride, which are classified as benchmark antidepressant agents have been used as reagents for the detection of micro amounts of blood in faeces [33] and urine [34].

3-Methyl-2-benzothiazoline hydrazone hydrochloride hydrate (MBTH) or 4-amino-antipyrine (AAP) are electrophilic coupling reagents (Fig. 1d and c) MBTH was first introduced for the determination of aromatic amines and imino heteroatomic compounds and aliphatic aldehydes. Later, it was extended for the determination of a large number of organic compounds such as those containing methylene groups, as well as with carbonyl compounds, Schiff's bases, aromatic hydrocarbons, saccharides, steroids, olefins, phenols, furfural and heterocyclic bases. MBTH has often been applied in clinical, biochemical, pharmaceutical, insecticidal and in flow injection analysis.

Antipyrine is an important derivative of the 5-pyrazolone class and is used for the detection and determination of a number of compounds [41]. However, literature on the use of 4-amino-antipyrene (AAP) as a reagent in analytical chemistry is very scanty. The authors are the first to use IDB or Cl-IDB, the dibenzazepine class of compounds, which, coupled with electrophilic reagent such as MBTH or AAP, in the

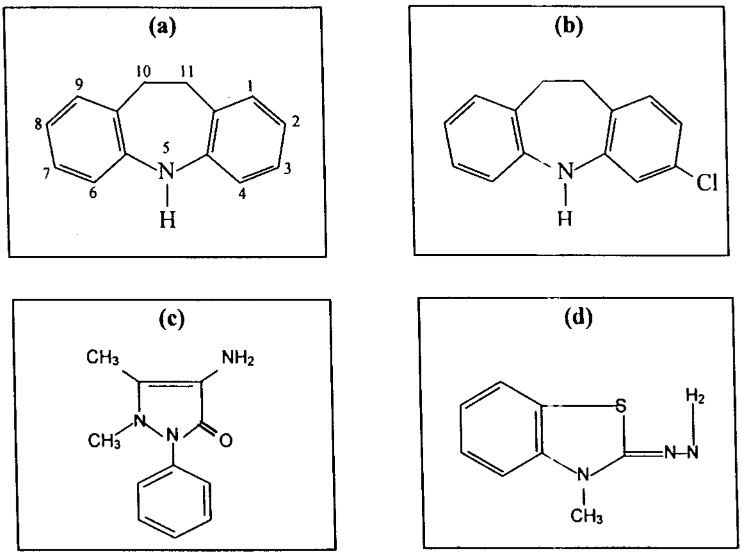


FIGURE 1 Structure of: (a) IDB, (b) Cl-IDB, (c) AAP and (d) MBTH.

spectrophotometric determination of mercury(II), nickel(II), copper(II) and cobalt(II) in soil and industrial effluents.

Reaction Mechanism

The chemical reaction in the procedure described for the spectrophotometric determination of mercury(II), nickel(II), copper(II) or cobalt(II) in aqueous neutral medium involves reduction of the metal ions by MBTH or AAP which subsequently couples with IDB or Cl-IDB to form a blue product having λ_{max} for MBTH at 660 nm and λ_{max} for AAP at 630 nm. The colour intensity remains constant for over 24 h. A representative absorption spectra of the system (1) Hg^{2+} + MBTH + IDB and (2) Hg^{2+} AAP + IDB and (3) MBTH + IDB (blank) are shown in Fig. 2. Similarly absorption spectra is observed for all the systems. The factors affecting the colour development, reproducibility, sensitivity and adherence to Beer's Law were investigated. The reaction mechanisms are depicted in Schemes 1 and 2.

Optimisation of MBTH Method

Effect of Reagent Concentration

IDB or Cl-IDB For a fixed concentration of metal ion and MBTH the colour intensity remains constant with 0.5–4.0 ml of 0.1% (w/v) IDB solution. Similar results

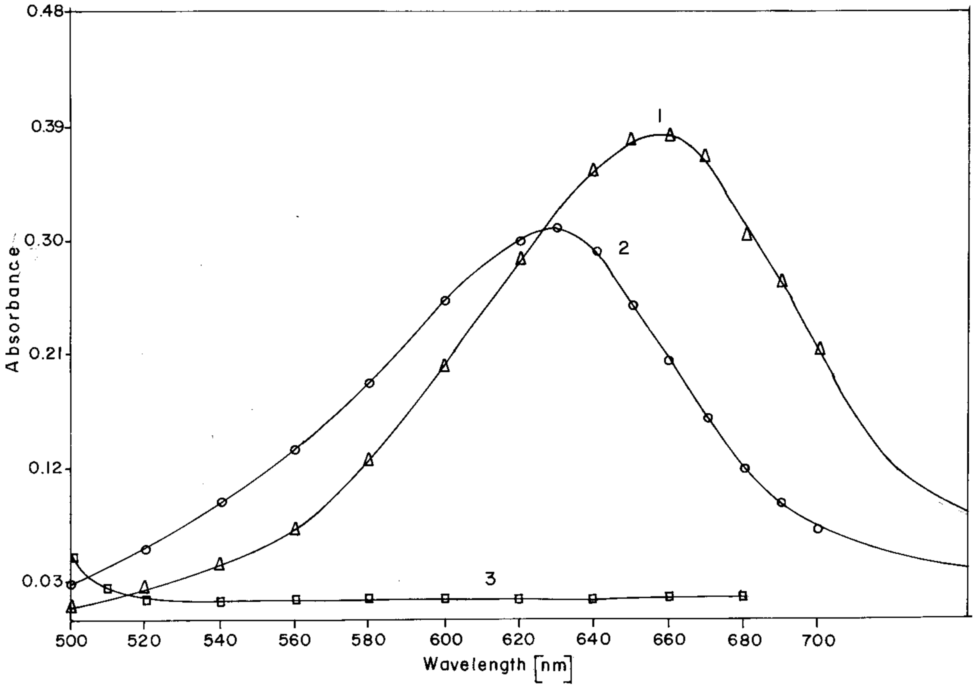
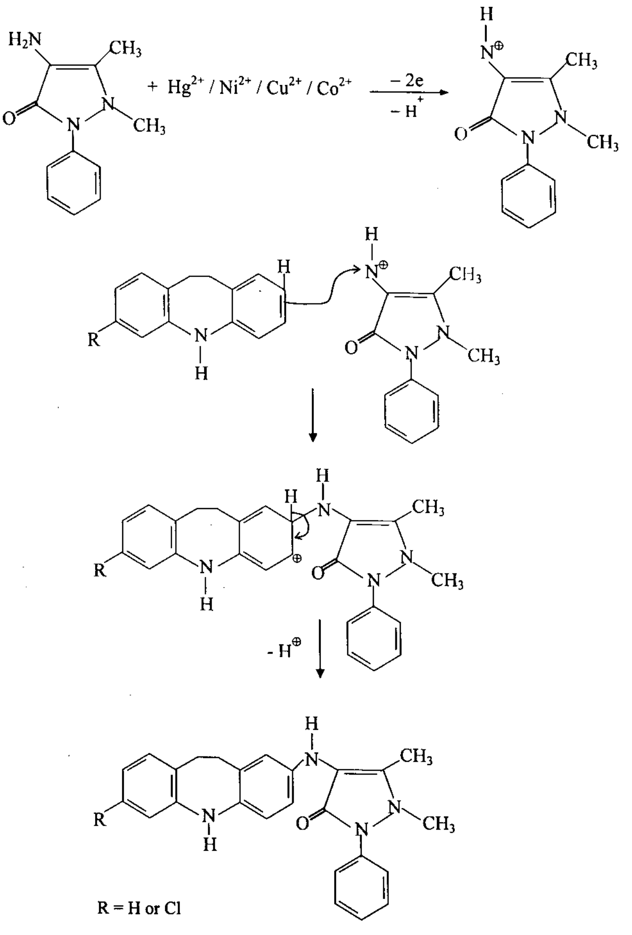


FIGURE 2 Absorption spectra of the reaction product of (1) Hg^{2+} (250 ng ml^{-1}) + MBTH + IDB, (2) Hg^{2+} (3.5 μg ml^{-1}) + AAP + IDB and (3) Reagent blank.



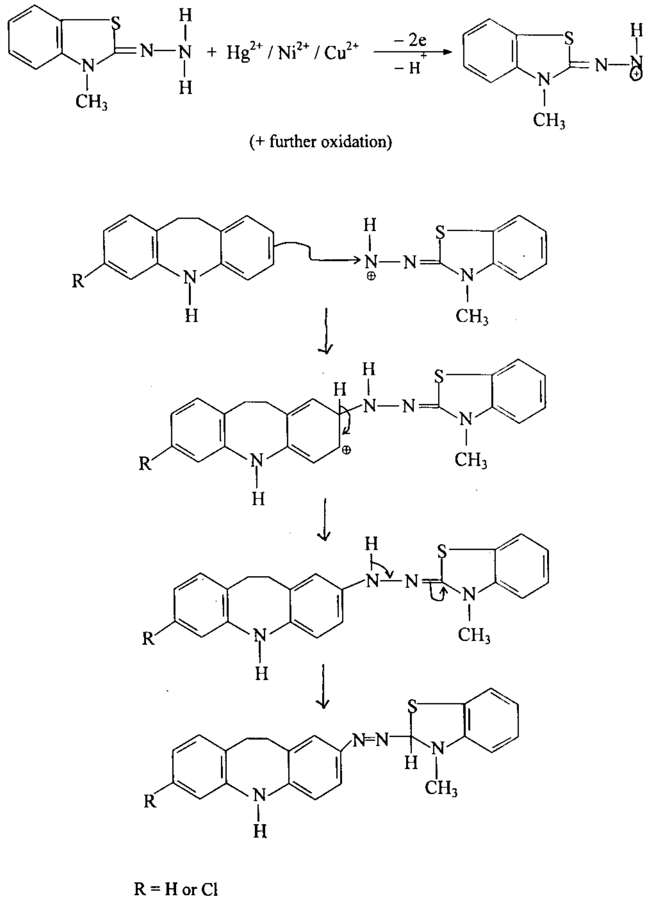
SCHEME 1 Proposed mechanism of the reaction between dibenzazepine and AAP.

were observed for Cl-IDB. Therefore, 1 ml of 0.1% (w/v) IDB or Cl-IDB is sufficient for routine analysis.

Similar procedures were adopted to know the amount of MBTH required for the constant colour intensity. It was found that 1.0 ml of 0.1% (w/v) MBTH solution is sufficient to get reproducible results.

Order of Addition

The study indicated that the sequence of addition of reactants had profound influence on the intensity and the stability of the colour; for example (i) IDB/Cl-IDB – metal ion – MBTH and (ii) metal ion – IDB/Cl-IDB – MBTH gave less intensive and unstable colour. While, the order; (iii) metal ion – MBTH – IDB/Cl-IDB and (iv) MBTH – metal ion – IDB/Cl-IDB gave more intense and stable blue colour. This is expected as the reactions (i) and (ii) produce radical cation, while (iii) and (iv) involve electrophilic substitution reactions.



SCHEME 2 Proposed mechanism of the reaction between dibenzazepine and MBTH.

Temperature and Stability

Development of blue colour at room temperature takes longer time. However, heating in a boiling water bath for about 5 min yields an intense blue colour and this intensity when diluted with water decreases rapidly, but ethyl alcohol stabilises the colour for over 24 h.

Acids like hydrochloric, sulphuric, nitric and perchloric: bases, such as sodium hydroxide, ammonia; and solvents like acetone, acetic acid, acetonitrile etc. were not effective in stabilising the blue colour. Conversely, methyl alcohol and ethyl alcohol have profound influence on the stability of colour and for routine analysis, ethyl alcohol is preferred as it is nontoxic and is cost-effective.

Calibration and Spectral Data

The blue colour obeyed Beer's Law. The optical characteristics, such as optimum range for the determination of metals, as evaluation from a Rigbom plot, molar absorptivity, Sandell's sensitivity, slope, intercept, correlation coefficient are shown in Tables II and III.

Sandell's sensitivity (S) represents the number of micrograms of the determinant per millilitre of a solution having an absorbance (A) of 0.001 for a path length (1) of 1 cm. Thus $S = 10^{-3}/a = \mu g\,cm^{-2}$ where a is the specific absorptivity, and its value (in $ml\,g^{-1}\,cm^{-1}$) corresponds to the determinant in a cuvette with an optical length of 1 cm. Also,

$$a = \frac{\varepsilon}{\text{at. wt. of the metal} \times 1000}$$

ε = molar absorptivity = A/cl where c is the molar concentration of the determinant and $l = 1$ cm.

Effect of Diverse Ions

The effect of various anions and cations on the determination of mercury(II), nickel(II), copper(II) and cobalt (II) was studied as per the proposed procedures and the results are present in Tables IV and V. In general, 100 mg of salt of the anions and an amount of salt equivalent to 500 µg of metal ions were added individually to aliquots containing 0.60 µg ml^{-1} of mercury(II), 0.20 µg ml^{-1} of nickel(II) and 0.25 µg ml^{-1} of copper(II) for MBTH method; and 4.0 µg ml^{-1} of mercury(II), 2.0 µg ml^{-1} of nickel(II), 1.20 µg ml^{-1} of copper(II) and 6.0 µg ml^{-1} of cobalt(II) for AAP method. Among the anions examined, thiosulphate interfered seriously with copper(II) and fluoride interfered with cobalt(II). EDTA interfered in the determination of mercury(II) and nickel(II). Chloride did not interfere, but free chlorine did. The metal ions that interfered in the determination of mercury(II) were Ni^{2+}, Cu^{2+} and Co^{2+}. Among the three, Cu^{2+} and Co^{2+} can be masked by sodium thiosulfate and sodium fluoride respectively. Conversely, in the determination of copper(II) and cobalt(II); Hg^{2+} and Ni^{2+} can be masked using EDTA. Only Ce^{4+} and Ni^{2+} interfered in the determination of mercury(II), while Fe^{3+} interfered in the determination of all

TABLE III Spectral data for the determination of metal ions using 4-aminoantipyrine (AAP) and iminodibenzyl (IDB)* as electrophilic coupling reagent

Parameters	*Mercury(II)*	*Nickel(II)*	*Copper(II)*	*Cobalt(II)*
Colour	Blue	Blue	Blue	Blue
λ_{max} (nm)	630	630	630	630
Stability (h)	~6 h	~6 h	~6 h	~6 h
Beer's law (µg ml^{-1})	1–8	0.1–4	0.1–2	0.5–20
Recommended metal ion concentration (µg ml^{-1})	4.0	1.5	1.0	10.0
Molar absorptivity (L mol^{-1} cm^{-1})	1.45×10^4	1.50×10^4	2.13×10^4	0.21×10^4
Sensitivity	1.38×10^{-2}	3.92×10^{-3}	3.00×10^{-3}	2.84×10^{-2}
Regression equation:				
Slope	0.082	0.211	0.346	0.025
Intercept	−0.011	0.054	−0.007	0.051
Correlation coefficient	0.996	0.9801	0.9893	0.976

*Cl-IDB was not used as the colour was stable only for less than a minute.

TABLE IV Effect of anions on the determination of mercury(II), nickel (II) copper(II) and cobalt(II) in the visible region. MBTH-IDB/CI-IDB method: medium, neutral; 0.1% MBTH, 1 ml; IDB or CI-IDB, 0.5 ml and Hg, 0.60 μg ml^{-1}. Ni, 0.20 μg ml^{-1}, or Cu, 0.25 μg ml^{-1}; λ_{max} 660 nm. AAP-IDB/Cl-IDB method: medium, neutral; 0.1% AAP, 2 ml; 0.1% IDB, 1 ml and Hg, 4.00μg ml^{-1}; Ni, 2.00 μg ml^{-1}; Cu, 1.20 μg ml^{-1} or Co, 6.00 μg ml^{-1}; λ_{max}, 630 nm.

Salt of the anion added	*Salt added* (mg)	*Absorbance*						
		Mercury		*Nickel*		*Copper*		*Cobalt*
		*MBTH (0.301)**	*AAP (0.285)**	*MBTH (0.280)**	*AAP (0.447)**	*MBTH (0.319)**	*AAP (0.511)**	*AAP (0.194)**
Ammonium tartarate	100	0.298	0.284	0.281	0.448	0.321	0.512	0.193
Disodium EDTA	100	MA	MA	MA	MA	0.323	0.512	0.195
Potassium bromate	100	0.301	0.285	0.279	0.447	0.320	0.510	0.193
Potassium chloride	100	0.300	0.286	0.280	0.446	0.321	0.514	0.191
Potassium iodate	100	0.298	0.286	0.281	0.448	0.318	0.512	0.193
Potassium sulphite	100	0.299	0.284	0.274	0.447	0.321	0.510	0.193
Sodium sulphite	100	0.303	0.283	0.280	0.446	0.320	0.511	0.195
Sodium fluoride	100	0.301	0.285	0.282	0.445	0.322	0.512	MA
Sodium nitrate	100	0.300	0.283	0.279	0.447	0.319	0.513	0.193
Sodium nitrate	100	0.304	0.282	0.278	0.448	0.318	0.514	0.192
Sodium phospate	100	0.300	0.283	0.279	0.449	0.319	0.510	0.193
Sodium thiosulphate	100	0.302	0.282	0.279	0.447	MA	MA	0.193

*Values of absorbance without foreign ion. MA: Masking Agent.

TABLE V Effect of cation on the determination of mercury(II), nickel(II), copper(II) and cobalt(II) as given in Table IV

Salt of the cation added	*Salt added* (mg)	*Absorbance*						
		Mercury		*Nickel*		*Copper*		*Cobalt*
		MBTH {0.301)*	*AAP (0.285)**	*MBTH (0.280)**	*AAP (0.447)**	*MBTH (0.319)**	*AAP (0.511)**	*AAP (0.194)**
Aluminium ammonium sulphate	100	0.301	0.285	0.279	0.447	0.319	0.5101	0.190
Ammonium molybdate	100	0.303	0.285	0.280	0.448	0.318	0.512	0.195
Barium sulphate	100	0.302	0.286	0.280	0.449	0.318	0.514	0.191
Cadmium sulphate	100	0.305	0.281	0.280	0.446	0.321	0.511	0.195
Ferric ammonium sulphate	100	0.304	0.285	0.281	0.450	0.318	0.510	0.190
Potassium chromate	100	0.310	0.281	0.279	0.439	0.320	0.512	0.191
Lead nitrate	100	0.305	0.284	0.286	0.450	0.319	0.512	0.192
Magnesium sulphate	100	0.306	0.280	0.280	0.446	0.318	0.515	0.195
Manganese sulphate	100	0.301	0.281	0.285	0.447	0.325	0.514	0.196
Selenium sulphate	100	0.300	0.284	0.283	0.443	0.318	0.511	0.193
Sodium arsenate	100	0.306	0.286	0.284	0.450	0.327	0.515	0.196
Sodium vanadate	100	0.305	0.286	0.284	0.446	0.320	0.513	0.195
Strontium nitrate	100	0.302	0.286	0.284	0.446	0.318	0.515	0.195
Tin chloride	100	0.300	0.286	0.280	0.441	0.319	0.516	0.191
Zinc sulphate	100	0.305	0.283	0.281	0.446	0.318	0.511	0.193

*Values of absorbance without foreign ion.

the metals. This interference was eliminated by the addition of sodium fluoride. The interference by other metallic ions was insignificant as they were within the limits of ±2% error. Cobalt(II) gives light blue colour with IDB/Cl-IDB and MBTH. As the system – metal ion–AAP-Cl-IDB – gives very unstable colour, further studies were not pursued.

Applications

Determination of Mercury in Industrial Effluents

The waste water generated by industrial operations comprised of both industrial and domestic effluents. The domestic effluent was first treated and mixed with industrial effluent, which results in the dilution of various constituents.

Two types of effluents (treated and untreated) collected from two different factories were analyzed for the content of mercury. One of the effluents(I) was from the industry manufacturing organic/polymer products such as rayon fabric and another effluent(II) was collected from the factory manufacturing inorganic products such as caustic soda and liquid chlorine.

The process of manufacture of caustic soda involves the use of an electrode consisting of brine and mercury. The waste water from this plant was an alkaline medium containing trace amounts of mercury. The specific parameter prescribed by the statutory agency for effluent I is mercury, whereas for effluent II the parameters are mercury and zinc.

Untreated effluent (I and II each 25 ml) and treated effluent (I and II each 25 ml) were evaporated to get about 5 ml of each. They were digested with 5 ml of 5 M nitric acid till the volume was reduced to about 1 ml (or until all the brown fumes of nitric acid subsided) and were diluted to 25 ml and used for the determination of mercury by the proposed method.

The use of nitric acid has the advantage over the reported concentrated sulphuric acid medium [42] for digestion as the former dissolves elemental mercury in a short span of time. Further, it has advantages over the wet oxidation method of Rolfe *et al.* [43] in which concentrated nitric acid and potassium permanganate are used. These reagents are also recommended by the Analytical Methods Committee for the destruction of organic matter [44]. However, these reagents are found unnecessary for effluent I. Certain organic matter which imparts colour (generally light brown colour) do not interfere seriously as the aliquot sample chosen for analysis is small and upon dilution gives almost no colour to the solution. Even particulate organic matter, if found can be eliminated by filtration. We have found that the results of our procedure are in accordance with the recommended procedure [45] within the acceptable range of ± 2% error (Table VI).

Determination of Mercury in Soils

The MBTH-IDB method was applied for the determination of micro quantities of mercury in soils collected about 0.5 km away from a scrap yard situated on the forested slopes around the factory. The factory manufactures thermometers and the broken or other discarded thermometers are dumped in the scrap yard. Though the scrap yard is cleared periodically, still considerable amounts of metallic species get into the soil. "Static" sampling procedure was adopted and six soil samples were collected at random from a depth of 0–20 cm with a distance of about 50 m between each sampling site.

Dissolution of Mercury Content of the Soil Sample

The soil sample was dried at 110°C for 4 h and cooled in a desiccator. Two grams of dried soil and 10 ml of 5 N HNO_3 were placed in a 100-ml conical flask and heated

TABLE VI Determination of mercury(II) in industrial effluents and soil samples

Sample	*Hg^{2+}added* $\mu g\,ml^{-1}$	*Hg^{2+} recovered by the proposed method*[a] $\mu g\,ml^{-1}$	*Hg^{2+} found in the effluent/soil sample by difference*[b] $\mu g\,ml^{-1}$	*RSD%*	*Hg^{2+} found in the effluent/soil sample by AAS method* $\mu g\,ml^{-1}$
1. Industrial effluent I[c]					
Treated	0.200	0.222	0.022	2.95	0.226
Untreated	0.200	0.262	0.062	3.85	0.265
2. Industrial effluent II[d]					
Treated	0.200	0.232	0.032	2.65	0.230
Untreated	0.200	0.262	0.062	4.31	0.266
3. Soil samples[e]					
Sample 1	0.100	0.352	0.255	2.42	0.341
Sample 2	0.100	0.618	0.518	1.87	0.624
Sample 3	0.100	0.178	0.078	3.16	0.192
Sample 4	0.100	0.192	0.092	4.05	0.194
Sample 5	0.100	0.414	0.314	2.65	0.416
Sample 6	0.100	0.318	0.218	2.85	0.323

[a] MBTH + IDB method.
[b] mean of six determinations.
[c] industry manufactures rayon (organic polymer).
[d] industry manufactures caustic soda and liquid chlorine.
[e] samples collected at random and distance between each sample site was about 50 m.

until the brown vapour was expelled. After cooling, 10 ml of distilled water was added. Iron was isolated by precipitation with 1 : 1 ammonia solution. After filtration, the filtrate was boiled to expel ammonia, cooled and transferred into a standard flask. The volume was brought to the mark with distilled water. Aliquots of this solution were analysed by MBTH-IDB method.

Iron which is commonly found in most of the soil interferes and its elimination is necessary. Methods reported in the literature for the elimination of iron(III) interference, are either precipitation as hydroxide or use of masking agents. The former method is extensively used [15]. However, no confirmation has been reported so far to ascertain the completion of precipitation process of iron(III). We have developed a simple spot test to know the presence of iron(III) in filtrate which involves the use of KSCN solution which gives red colour with iron(III). Absence of red colour is an indication that iron(III) precipitation process is almost complete.

The use of masking agent sodium fluoride (NaF) to eliminate the interference of iron(III) is simple and straightforward. Besides, in the proposed method, use of masking agent has the advantages of elimination of the laborious procedure of precipitation, filtration and washings. Detailed investigations indicate that NaF does not interfere in the experiment. Hence, for routine analysis of mercury in the soil samples by MBTH-IDB method, the use of NaF as masking agent for iron(III) is recommended.

Determination of Nickel(II) and Copper(II) in Industrial Effluents and Soil Samples

Industrial Effluents The procedure adopted for the determination of mercury(II) can also be employed for the determination of nickel(II) and copper(II). The industrial effluent samples were collected from an electroplating industry which contained both nickel and copper ions. In the determination of nickel(II), Cu^{2+} was masked using 2 ml of 0.2% of sodium thiosulphate solution, while, in the determination of

TABLE VII Determination of nickel(II) and copper(II) in industrial effluents ans soil samples

Sample	*Ni^{2+} recovered by proposed method*[a] $\mu g\,ml^{-1}$	*Ni^{2+} recovered by AAS method* $\mu g\,ml^{-1}$	*RSD%*	*Cu^{2+} recovered by proposed method* $\mu g\,ml^{-1}$	*Cu^{2+} recovered by bathcuprine method* $\mu g\,ml^{-1}$	*RSD%*[a]
1. Industrial effluent						
Untreated[b]						
Sample 1	8.62	8.51	1.63	28.65	29.13	1.86
Sample 2	8.70	8.62	1.41	33.16	33.41	1.38
Sample 3	8.42	8.44	1.92	24.32	24.51	1.42
Treated						
Sample 1	3.14	3.22	1.04	4.15	4.12	1.75
2. Soil samples (sediments)						
Sample 1	21.35	21.63	1.45	32.18	32.26	1.45
Sample 2	26.16	26.39	1.96	14.32	14.51	1.68
Sample 3	13.23	13.61	1.38	18.41	18.63	1.75

[a] mean of six determinations.
[b] The industry runs three shifts and untreated samples 1, 2 and 3 correspond to shifts 1.2 and 3.

copper(II), Ni^{2+} was masked using 2 ml of 0.1% of EDTA solution. The results compare favourably with the bathocuproine method [46] for the determination of copper and AAS method for the determination of nickel [47], (Table VII).

Soil Samples The treated industrial effluents are discharged in the open fields. Soil samples were collected as described earlier. Iron was masked by the addition of sodium fluoride solution as described. Aliquots of this solution were used for analysis by MBTH-IDB method. Masking agents were used similar to those described under the determination of copper(II) and nickel(II) in industrial effluents.

CONCLUSION

Iminodibenzyl (IDB) and 3-chloroiminodibenzyl (Cl-IDB) are attractive as a new class of spectrophotometric reagents for the determination of environmentally toxic divalent metals such as mercury(II), nickel(II), copper(II) and cobalt(II) as they exhibit better sensitivity and higher reproducibility. While using these compounds as spectrophotometric reagents it is essential to use either MBTH or AAP as electrophilic coupling reagent. The use of aqueous neutral medium and flexibility to extend the methods to extractive spectrophotometry make the procedure cost-effective and versatile.

The proposed method ($M^{2+}+MBTH+IDB$ system) has distinct advantages of simplicity, sensitivity, selectivity and reproducibility. Besides, it is superior to dithiazone method [10] for the determination of trace amounts of mercury which necessarily involves an extraction step. Also, the proposed simple spot test to ascertain the completion of precipitation process of iron(III) manifest the improvement over the existing methods. Furthermore, the use of MBTH or AAP as electrophilic reagents in the determination of divalent metals will open up new areas of research. A value-addition to this method can be achieved, if the procedure is combined with on-line or at-line system and this is currently under investigation.

In summary, among the three newer methods studied by us, the feasibility of the method for routine analysis is in the order: $M^{2+} + MBTH + IDB > M^{2+} + MBTH + Cl\text{-}IDB > M^{2+} + AAP + IDB$. Considering simplicity, sensitivity and minimum interference by cations and anions, we recommend the $M^{2+} + MBTH + IDB$ system for the routine analyses of mercury(II), nickel(II) and copper(II) in pure samples, in industrial effluents and in soil samples.

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