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UV-VIS Spectrophotometric Determination of Mercury (II) Metal using 2-Acetylpyridine Thiosemicarbazone (APT) as New Analytical Reagent in Waste Water Samples collected from Rani Pokhari of Kathmandu, Nepal

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Abstract

The presence of heavy metals in the wastewater is harmful for human being. The waste water containing metal ions can contaminate water resources. These metals enter human bodies through food and water. In order to understand the heavy metal concentration from wastewater, it is desired to have effective, accurate but simpler and low cost method for heavy metals. Various methods such as atomic absorption spectroscopy, X-ray diffraction, chromatography and other advanced analysis techniques are available for this purpose. U.V. Spectrophotometer promises cost effective solution to the analysis of heavy metals. Thus 2-Acetylpyridine thiosemicarbazone (APT) is used as new analytical reagent for the direct non-extractive spectrophotometric determination of Hg (II) Metal. The method is successfully applied for the determination of mercury in a number of water samples (potable and polluted) collected from different points of Rani Pokhari of Kathmandu, Nepal.

Keywords: 2-Acetylpyridine Thiosemicarbazone (APT), spectrophotometry, mercury (II), Nepal

1. Introduction

Nowadays, in such an industrial world one of the most important concerns is securing the health of human race. The harmful effects of mercury and organomercury species are well known. Disastrous effects, both on personal levels and large population levels, have resulted from exposure to certain mercury species. Mercury exists in a variety of inorganic and organic forms [1]. The environmental chemistry of mercury is complex and difficult to predict because it is controlled by a multitude of environmental processes which includes photochemical reactions, chemical oxidation and reduction, microbial transformation, and physiological fractionation leading to complex and highly mobile cycles of transitions between molecular forms, each with varying degrees of toxicity [2]. In aquatic environments, mercury is methylated through a microbially-mediated process primarily involving sulfate-reducing bacteria. Methyl mercury is of great concern in aquatic environments because of its ability to bio-concentrate and biomagnify through trophic webs. More direct anthropogenic mercury contributions come from municipal wastewater treatment plants and a number of industrial processes [3]. Chronic exposure to mercury results in toxicity to the central nervous system, and the extensive use of mercury in the fur, felt and hat industry in the eighteenth century was the cause of “mad hatters disease,” a condition characterized by delirium and hallucinations [4]. At least two epidemiological studies have linked methyl mercury exposure to deaths from leukemia. Therefore this paper describes the non-extractive spectrophotometric determination of Hg (II) as its APT complex in aqueous medium. A close literature survey reveals that APT has so far not been employed for the spectrophotometric determination of mercury (II). This method does not require a solvent extraction step; hence the use of carbon tetrachloride or chloroform as solvent is avoided which are reported as toxic and environmental pollutants and carcinogens. Compared to even some recently published spectrophotometric methods for the determination of Hg (II) the present method offers several distinct advantages.

2. Materials and methods

2.1 Apparatus

Absorption spectra and absorbance measurements were made by a Shimadzu UV-1800, UV–Vis spectrophotometer using 1 cm quartz cells (1.0 mL). A Metrohm digital pH meter (model 691) with a combined glass electrode was applied to measure pH values. A Hettich universal 320 centrifuge was used to hasten the phase separation.

2.2 Standard solutions and reagents

Unless otherwise stated, all commercial reagents used were of analytical grades without further purification. The stock solution of Hg^{2+} (1000μg mL^{-1}) was prepared by dissolving suitable amount of $HgCl_2$ in ultrapure water with several drops of concentrated hydrochloric acid (HCl). A working solution was prepared by suitable dilution. A 1.0×10-4 mol L-1 solution Xylidyl Blue was prepared by dissolving appropriate amount of this reagent (Sigma) in freshly double distillated water and diluting to the mark in a 100 mL volumetric flask. Stock solution was prepared by dissolving 0.0364 g of this reagent (Merck) in bi-distilled water and diluting to the mark in a 100 mL volumetric flask. Stock solution of NaCl (1.0×10-1) was prepared by dissolving 0.584 g NaCl in distilled water and diluting to 100 mL in a flask.

The reagent (APT) was prepared by simple condensation of

1mol of 2-acetylpyridine and 1 mol of thiosemicarbazide. In a 250-ml Erlenmeyer flask, a hot methanolic solution of 2-acetylpyridine (5ml, 0.0438mol in 5ml of methanol), thiosemicarbazide (4g, 0.0438 mol, dissolved in10 ml of hot water) were taken in 250- ml round bottom flask. Suitable quantity (~2ml) of glacial acetic acid was added to the reaction mixture and refluxed for 3 hours. On cooling the reaction mixture, light brown coloured product was separated out. It was collected by filtration and washed several times with hot water and 50 percent cold methanol. This compound was recrystallised from ethanol and dried in vacuo, 60% yield 4.2 g; m.p. 175° C. The reagent solution (0.01M) was prepared by dissolving 50 mg of the compound in dimethylformamide (DMF) in 25-ml standard flask. The reagent solution is stable for at least 12h. Hydrochloric acid (1M) sodium acetate (1 M) (pH 0.5-3.5);0.2 M NaOAc-0.2 M AcOH (pH 4-6) and 2 M NH4Cl-2 M NH4OH (pH7-10) solutions were used.

The pKa values were determined by recording the UV-Visible spectra of micro molar (2x10-5 M) solutions of the reagent at various pH values and by taking the arithmetic mean of the values obtained from the measurements at different wavelengths determined spectrophotometrically using Phillips and Merrit method [5]. The values of deprotonation of APT are 5.46(pK1) and 8.56 (pK2).

Stock solution (1 x 10-2 M) of divalent mercury was prepared by dissolving 0.27 g of mercuric chloride (Merck Darmstadt) in deionized water containing few drops of concentrated hydrochloric acid and made up to the mark in a 100-mlvolumetric flask. Aliquots of this solution were standardized [6] with EDTA using xylenol orange as an indicator. Dilute solutions were prepared from this stock solution. Solutions of large number of inorganic ions and complexing agents were prepared form their Analar grade or equivalent grade water soluble salts [7]. In the case of insoluble substance, special dissolution methods were adopted.

2.3 Preparation of sample and Determination of mercury (II)

Rani Pokhari is situated in the heart of city and well known locally from historical point of view hence, water samples from different points from Rani Pokhari of Kathmandu, Nepal were collected and preconcentration by evaporation. All the collected samples were spiked with a suitable amount of standard solution of Hg^{2+}. All the aforementioned samples were filtered through a 0.22µm membrane to remove the suspended and floated particles. An aliquot of the solution containing 0.240-2.407 µg/ml (or ppm) of mercury(II),10 ml of Sodium Acetate Acetic Acid Buffer Solutions buffer solution (pH, 6.0) and 1.5 ml of 0.01 M APT were combined in a 25 ml volumetric flask and resulting solution was diluted to the mark with distilled water. The absorbance of this solution was read at 351nm against reagent blank. The measured absorbance is used to compute the amount of mercury form predetermined calibration plot. A sensitive derivative spectrophotometric method was developed for the determination of mercury (II). The derivative amplitudes were measured for different concentration of Hg (II) and plotted against the amount of Hg (II). The plots were linear and obeyed Beer's law in the range 0.664- 0.0286 µg ml^{-1} at 410 nm and 0.08-0.008 µg ml^{-1}. The absorbance of extracted colored ion associate was measured at 523 nm in 1 cm cells against a reagent blank.

3. Results and Discussion

The reagent, APT is easily obtained just as any mono thiosemicarbazone. A 0.01M solution of this reagent is stable for 12h. The bath chromic shift divalent metal ion as mono anion to give neutral complex of absorption band from 290 to 300 nm indicates that in solution on increasing the pH, the acid is neutralized and the>C=S groups is enolized and dissociated [8]. In basic medium (above pH 8.56) the ligand presumably exists in enolic form and coordinates the divalent metal ion as mono anion to give neutral complex.

Mercury (II) react with APT in acidic pH to give coloured complexes. The colour reaction is instantaneous at room temperature. The order of addition of metal ion, reagent, buffer has no effect on the absorbance of complex. The stoichiometry of the complex (M:L=1:2) was determined by well-known Job's continuous variation, molar ratio methods. Sodium acetate (0.2M)-acetic acid (0.2M) buffer solution (pH 6.0 µ, 0.2 and T=300K) and equimolar (4.8x10-5M) solution of Hg(II) and APT were used in these methods. The data obtained in Job's method were used in the calculation of stability constant of the complex [9]. Derivative spectrophotometry is a very useful technique in the sense that it decreases the interference i.e., increases the tolerance limit value of foreign ions and it may be adventageously used for the second derivative determination of metal ion having peak-valley method is more sensitive and hence is adopted for the determination of Hg(II).

4. Conclusion

The present method for the determination of mercury (II) is compared with other recently reported spectrophotomeric methods [17-26]. The present method seems to rank among highly sensitive method for the determination of mercury(II).The results obtained in the analysis of different samples using present method are comparable to the data obtained using dithizone method. The present ligand containing heterocyclic ring is found to be potential and cost effective for the determination of mercury(II) without the need for extraction using the toxic solvent. Further, the reagent is easy to synthesize using commercially available precursors. Moreover, the present method is simple, rapid and very sensitive for nonextractive spectrophotometric determination of mercury(II) in aqueous medium.

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