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Determination of lead (II) in some water sample collected from Kamal Pokhari of Kathmandu using dithizone ligand

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Abstract

The Kathmandu Valley historically known as Nepal Valley lies at the crossroads of ancient civilizations of the Indian subcontinent and the broader Asian continent, and has at least 130 important monuments, including several pilgrimage sites for Hindus and Buddhists. There are seven World Heritage Sites within the valley. Kamal Pokhari is a gorgeous pond situated in the Hattisar region of Kathmandu, Nepal. Lead is a toxic element that can be found throughout our environment. It used to be an ingredient in gasoline and paint, though both uses were banned many years ago. Experts consider lead so toxic that there is no safe level of exposure. Thus a very simple, ultra-sensitive and fairly selective non-extractive spectrophotometric method is presented for the rapid determination of lead (II) at ultra-trace level using dithizone (1, 5-diphenylthiocarbazone) as a new spectrophotometric reagent (λmax = 490 nm) in a slightly acidic (0.07-0.17 M H_2SO_4) aqueous solution. The average molar absorption coefficient was found to be 3.99×10^5 L mol^{-1} cm^{-1} and Sandell's sensitivity was 30ng cm–2 of Pb. The method was successfully applied to a number of collected water samples from Kamal Pokhari contained lead (II).The method has high precision and accuracy (σ =±0.01 for 0.5 mg L^{-1}).

Keywords: heavy metals, lead, UV-VIS spectrophotometer, Kamal Pokhari, Nepal

1. Introduction

Kathmandu is an exotic destination with a rich history and culture, but underneath all this is a busy Nepalese life. Kamal Pokhari is a gorgeous pond situated in the Hattisar region of Kathmandu, Nepal [1]. For a long period of time, the Nepalese authorities didn't attend to this pond and it almost it was dried out. However, the people of the area and other socially responsible Nepalese restored the pond. Now, the locals enjoy taking long walks along Kamal Pokhari [2]. Besides supplying water for general purposes, the ponds had another important function they served as water reservoirs to fight fires as well. This was wise thinking as most of the houses constructed in those days were that of wood. And although there once were numerous ponds in the valley serving such important purposes, encroachments due to urbanization have resulted in only a few still surviving. One of Kathmandu's biggest ponds, Lainchaur Pokhari, has long disappeared. Now, in its place stands the Nepal Scouts building [3].

Contamination of water bodies with heavy metals occur worldwide as a result of increasing urbanization, extensive agricultural activities and industrial expansion and a consequence of which many rivers and ponds have been polluted [4]. Heavy metals constitute an important group of the environmentally hazardous substances [5]. Their toxicity has been reported to affect human health as they are not known to be easily disintegrated and decomposed for a very long period of time. This may be a reason why heavy metal contamination in water bodies is of primary concern [6]. Although some heavy metals such as iron and manganese are required for metabolic activities, others like zinc, lead, mercury, nickel and cobalt exhibit toxicity effects in living organisms [7]. Occurrence of toxic metals in ponds, ditch, and river water affect the lives of local people that depend upon the water body for their daily survival. Consumption of aquatic food enriched with toxic metals may cause serious health hazards through magnification of food chain [8].

Heavy metals are generally the elements heavier than ferrum in the periodic table. Some of them are necessary for human metabolism, such as organic compounds of iron, lead, cobalt, copper, and zinc [9]. Lead is a toxic element that can be found throughout our environment. It used to be an ingredient in gasoline and paint, though both uses were banned many years ago [10]. Experts consider lead so toxic that there is no safe level of exposure. Unlike many elements, such as copper and zinc, this heavy metal offers absolutely no benefit to human health. Ongoing environmental exposure to lead may damage organs, harm the nervous and reproductive systems, or even cause anemia [11]. In pregnant women, infants and young children, exposure may cause a number of health issues, as we'll explain further down below. In extreme cases, lead poisoning may even be fatal. Acute lead poisoning in humans causes severe damage in the kidneys, liver, brain, reproductive system, and central nervous system, and sometimes causes death [12]. All of these findings cause great concern regarding public health, demanding the accurate determination of this metal ion at trace and sub-trace levels.

Dithizone (1, 5-Diphenylthiocarbazone) is one of the most widely used photometric reagents and forms colored water insoluble complexes with a larger number of metal ions [13]. Metal-dithizone complexes are water insoluble and thus their determination requires a prior solvent extraction step into chloroform or carbon tetrachloride8 followed by spectrophotometric measurements [14]. Since these methods involve solvent extractions, they are lengthy and time consuming and lack selectivity due to much interference [15]. Carbon tetrachloride and chloroform have already been listed as carcinogens by the EPA. This problem has been overcome in recent years by introducing a hydrophobic micellar system generated by a surfactant similar to that employed in phase transfer reactions [16].

The aim of the present study is to develop a simpler direct spectrophotometric method for the trace determination of lead with dithizone in the presence of cetyltrimethylammonium bromide (CTAB), in aqueous solutions. This method does not require a solvent-extraction step; hence, the use of chloroform is avoided. The method described here has recorded for the first time the non-extractive direct spectrophotometric determination of lead (II) in aqueous media without the recourse of any “clean-up” step. This method is far more selective, non-extractive, simple and rapid than all of the existing spectrophotometric methods. The method is based on the reaction of slightly absorbent dithizone in acidic solution to produce a highly absorbent violet-chelate product, followed by the direct measurement of the absorbance in aqueous solution.

2. Experimental

2.1 Instrumentation

Shimadzu (Kyoto, Japan) (Model-1800) double beam UV/VIS the recording spectrophotometer and a Jenway (England, U.K) (Model-30100) pH meter with a combination of electrodes were used for the measurements of absorbance and pH, respectively. A Varian (Australia) ICP-MS spectrophotometer was used for comparing the results [17].

2.2 Chemicals and Reagents

All chemicals used were of analytical reagent grade or the highest purity available. Doubly distilled deionized water, which is non-absorbent under ultraviolet radiation, was used throughout. Glass vessels were cleaned by soaking in acidified solutions of KMnO4, followed by washing with concentrated HNO3 and rinsing several times with deionized water. Stock solutions and water samples (1000 mL each) collected from Kamal Pokhari were kept in polypropylene bottles containing 1 mL of concentrated nitric acid and immediately after collection; they were stored in a salt–ice mixture and later, at the laboratory, were kept at –20˚C. More rigorous contamination control was used when one lead levels in the specimens were low [18].

2.2.1 Lead (II) Standard Solutions (4.83 × 10^{-3} M)

A 100 mL stock solution (1 mg mL–1) of divalent lead was prepared by dissolving 159.9 mg of lead nitrate (Merck, Germany) in deionized water. Aliquots of this solution were standardized with EDTA using xylenol orange as an indicator. The working standard of silver solution was prepared by suitable dilutions of this stock solution [19].

2.2.2 Sodium dodecyl sulfate (SDS) solution (1%)

A 100 mL of SDS solution was prepared by dissolving 1g of pure sodium dodecyl sulfate (SDS) (E. Merck, Darmstadt, Germany) in doubly distilled de-ionised water using ultrasonic bath [20].

2.2.3 Dithizone or 1,5-Diphenylthiocarbazone (1.95×10-4 M)

Dithizone prepared by dissolving the requisite amount (0.005%) of diphenylthiocarbazone (E. Merck, Darmstadt) in a known volume of 2 propanol (Fluka, Germany). More dilute solutions of the reagent were prepared as required [21].

2.2.4 Tartrate solution

A 100 mL stock solution of tartrate (0.1% w/v) was prepared by dissolving 100 mg of potassium sodium tartrate tetrahydrate (E. Merck, Germany) in (100 mL) deionized water [22].

2.2.5 Dilute ammonium hydroxide solution (NH4OH)

A 100-mL solution of dilute ammonium hydroxide was prepared by diluting 10-mL concentration. NH4OH (28-30% A.C.S. grade) to 100-mL with deionized water. The solution was stored in a polypropylene bottle [23].

2.2.6 1, 10-Phenanthrolin solution

A 0.1% 1, 10-phenanthrolin solution was prepared by dissolving 0.1 gm amount in 100-mL slightly hot deionized water [24].

2.2.7 Sodium azide solution

A 100-mL sodium azide solution (2.5 % w/v) (Fluka purity > 99%) was freshly prepared by dissolving 2.5 gm in 100-mL of deionized water [25].

2.2.8 EDTA solution

A 100-mL stock solution of EDTA (0.01%) was prepared by dissolving 10 mg of A.C.S. grade (≥90%) ethylenediaminetetraacetic acid, disodium salt dehydrate in (100-mL) deionized water [26].

2.2.9 Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their analytical grade or equivalent grade, water soluble salts. In the case of insoluble substances, special dissolution methods were adopted [27].

2.3 General Procedure

To 0.1-1.0 mL of a slightly acidic solution containing 0.7-100 μ g of lead (II) in a 10-mL volumetric flask was mixed with 1.0-4.0 (preferably 1.0 mL) of 1% sodium dodecyle sulfate (SDS) and 1.0– 4.0 (preferably 1.0 mL) of 1 M sulfuric acid followed by the addition of a 25 - 80 fold molar excess of a dithizone solution (preferably 1.0-mL of 1 x 10-3 M). The mixture was diluted up to the mark with de-ionized water. The absorbance was measured at 495 nm against a corresponding reagent blank. The lead content in an unknown sample was determined using a concurrently prepared calibration graph.

3. Results and discussions

3.1 Factors affecting the absorbance

3.1.1 Absorption spectra

The absorption spectra of the lead (II) dithizone system in a 1 M sulfuric acid medium were recorded using a spectrophotometer. The absorption spectra of the lead (II)-dithizone are a symmetric curve with the maximum absorbance at 490 nm and an average molar absorption coefficient of 5.02 × 104 L mol^{-1} cm^{-1}. The reagent blank exhibited negligible absorbance, despite having a wavelength in the same region. In all instances, measurements were made at 490 nm against a reagent blank. The reaction mechanism of the present method is as reported earlier.

3.1.2 Effect of surfactant

Different volumes of 1% SDS solutions were added to a fixed metal ion concentration, in a 10 mL volumetric flask a` the absorbance was measured according to the standard procedure. Effect of surfactant concentration was studied on the absorbance of 1 mg L^{-1} Pd- chelate complex, and 1.0-4.0 mL of 1% SDS solution produced a constant absorbance of the Pd-chelate. Outside this range of surfactant the absorbance decreased. The effect may be due to inadequate interactions of surfactant at lower concentrations, while the aquatic dilution effect is responsible for increasing in the absorbance at higher surfactant concentrations. For all subsequent measurements, 1-mL of 1% SDS solution was added.

3.1.3 Effect of acidity

Of the various acids (nitric, sulfuric, hydrochloric and phosphoric) studied, sulfuric acid was found to be the best acid for the system. The absorbance was at a maximum and constant when a 10 mL of solution (1 mg L–1; path length, 1) contained 0.7 – 1.7 mL of 1 M sulfuric acid (or pH 0.8 – 1.2) at room temperature (25 ± 5˚C). Outside this range of acidity, the absorbance decreased. For all subsequent measurements, 1 mL of 1 M sulfuric acid (or pH 1) was added.

3.1.4 Effect of time

The reaction is very fast. Constant maximum absorbance was obtained just after dilution to volume, and remained strictly unaltered for 24 h.

3.1.5 Effect of temperature

The absorbance at different temperatures, 0-70˚C, of a 10 mL solution (1 mg L^{-1}) was measured according to the standard procedure. The absorbance was found to be strictly unaltered throughout the temperature range of 5-60˚C. Therefore, all measurements were performed at room temperature (25 ± 5˚C).

3.1.6 Effect of the reagent concentration

Different molar excesses of dithizone were added to a fixed metal-ion concentration, and the absorbances were measured according to the standard procedure. It was observed that at 1 mg mL^{-1} lead metal (optical path length, 1 cm), reagent molar ratios 1:20 and 1:100 produced a constant absorbance of the Pd-chelate. A greater excess of the reagent was not studied. For all subsequent measurements, 1 ml of 1.95 × 10^{-4} M dithizone reagent was added.

3.1.7 Calibration graph (Beer's law and sensitivity)

The effect of metal (Pd) concentration was studied over 0.01-10 mg L$^{-1,}$ distributed in three different sets (0.01- 0.1, 0.1- 1, 1-10 mg L^{-1}) for convenience of the measurement. The absorbance was linear for 0.05-10 mg L^{-1} of mercury at 490 nm. From the slope of the calibration graph, the average molar absorption coefficient was found to be 5.02×104 L mol–1 cm–1. The Sandell's sensitivity (concentration for 0.001 absorbance unit) was found to be 10 ng cm^{-2}. Of these two calibration, the one showing the limit of the linearity range while next one was straight-line passing through the origin (R^2= 0.999).

3.1.8 Determination of lead in water samples collected from Kamal Pokhari

Each filtered (with Whatman No. 40) water sample (1000$^{\text{-mL}}$) was mixed with 10$^{\text{-mL}}$ of concentrated HNO3 and 1$^{\text{-mL}}$ of concentrated H_2SO_4 in a 2000$^{\text{-mL}}$ distillation flask. The sample was digested in the presence of an excess potassium permanganate solution following a method recommended by Greenberg *et al.* [30]. The solution was then cooled and neutralized with dilute NH_4OH solution. The resulting solution was then filtered and quantitatively transferred into a 25$^{\text{-mL}}$ calibrated flask and made up to the mark with deionized water. An aliquot (1-2$^{\text{-mL}}$) of this solution preconcentrated sampled water was pipetted into a 10 mL calibrated flask and the lead content was determined as described under the general procedure using EDTA or tartrate as a masking agent.

4. Conclusion

In the present work, a simple, sensitive, selective and inexpensive micellar method with the Pb(II)-dithizone complex was developed for the determination of lead in water samples collected from Kamal Pokhari. The molar absorptivities of the lead-dithizone complex formed in the presence of surfactants are almost the ten-times 3.99 × 105 L mol–1 cm–1 the value observed in the standard method (1.9 × 104 L mol–1 cm–1); the maxima of absorption is shifted by about 20 nm when compared with standard method, resulting in an increase in the sensitivity of the method. Therefore, this method will be successfully applied to the monitoring of trace amounts of lead in water samples.

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