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A simple spectrophotometric method for the determination of arsenic in industrial and environmental samples using 2,4-Dihydroxy benzophenone-2-amino thiophenol

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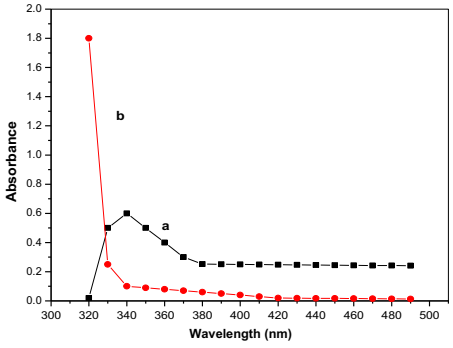
HIGHLIGHTS

- The synthesis and characterization and chromogenic properties of ligand.
- The ligand is stable more than 6 months and it is more sensitivity and selectivity.
- BPBT method, it was applied for determination of AS in some environmental samples.
- As (III) – BPBT complex showed maximum absorbance at 343 nm.

GRAPHICAL ABSTRACT

Absorption spectra of (a) AS (III)–BPBT complex (λ_{max} = 343 nm) in aqueous solution and (b) BPBT vs Water blank (1×10^{-4} M).



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ABSTRACT

2,4-Dihydroxy benzophenone-2-amino thiophenol (BPBT) has been proposed as new analytical reagent for the direct non-extractive spectrophotometric determination of arsenic. The reagent reacts with arsenic in acidic medium (pH = 6.0, sodium acetate–acetic acid buffer) to form light greenish yellow colored 1:1 (M:L) complex. Maximum absorbance was obtained at 343 nm and remains constant for over 24 h. The molar absorptivity and Sandell's sensitivity of BPBT are found to be 6.01×10^4 L mol^{-1}cm^{-1} and 0.0016 μg cm^{-2} respectively. The system obeys Beer's law in the range of 0.125–2.637 μg/ml of As (III). Since BPBT method is more sensitive, it was applied for the determination of arsenic in some environmental water samples.

Introduction

Arsenic compounds are widely used and have long been recognized as toxicants [1–3]. Arsenic is widely distributed in the nature. It occurs as inorganic and organic compounds as trivalent. Animals vary in their arsenic accumulation depending upon the type of food they consume [5,6]. Acute arsenic exposure can give symptoms with rapid onset of headache, nausea and severe gastrointestinal irritation [7]. Due to increased industrialization more and more industrial waste get accumulated in various regions and make their passage through soil cause severe environmental pollution and wide life toxicity [4] and also enter into animal body especially in their liver, kidney and lean meat.

Arsenic occurs naturally in the Earth's crust in its inorganic form, trivalent (arsenite) or pentavalent (arsenate) form. Erosion

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of arsenic containing surface rocks probably accounts for a significant amount of arsenic in water supplies. It is a ubiquitous element in water, soil and sediments. The occurrence of arsenic in plants and animals generally reflects its accumulation from the environment. The presence of arsenic in drinking water has reached calamitous proportions in many parts of the world. There are numerous reports in the literature based on past and ongoing experience in various countries in Asia and South America concerning the higher risks of skin, bladder, lung, liver, and kidney cancer that result from continued consumption of elevated levels of arsenic in drinking water [8]. Consumption of even low levels of arsenic over a long period can cause a multitude of diseases. The maximum permissible limit for As (III) drinking water is 0.05 mg/L as recommended by WHO [9]. In certain areas in India, Bangladesh,

China, and Mongolia [10], arsenic levels in groundwater exceed 1 ng/mL. Regarding inorganic arsenic, As (III) is appreciably more toxic than As (V). Usually these species of arsenic in natural water are found at the trace levels [10].

There are only a few analytical techniques available, which have sufficient sensitivity and selectivity to directly determine arsenic at the trace levels in natural water. Therefore, the development of sensitive and accurate methods for speciation and preconcentration of trace amounts of As (III) and As (V) is necessary. Recently many kinds of conventional analytical techniques such as hydride generatively coupled plasma atomic emission spectrometry (HG-ICP-AES) [5], capillary electrophoresis inductively coupled plasma mass spectrometry (CE-ICP-MS) [4], high performance liquid chromatography–inductively coupled plasma mass spectroscopy [11], electro thermal atomic absorption spectrometry (ETAAS) [12], hydride generation – atomic absorption spectrometry [13], hydride generation – atomic fluorescence spectrometry [14], cathodic stripping Voltammetry [15], anodic stripping voltammetry [16], neutron activation analysis [17], photometric analysis [18], ion selective electrodes [19] and energy dispersive X-ray fluorescence spectrometry [20] have been used for the determination of low concentrations of arsenic. But all these techniques are costly and require trained staff. Recently most of the spectrophotometric methods have been developed as an alternative for the determination of arsenic instead of conventional techniques.

We used an ICP-OES machine which converts all arsenic forms into inorganic arsenic. Inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) are very feasible techniques for quantitative determination of the As (III). The most important advantages of these techniques are high sample throughput, simplicity and good sensitivity in comparison to other techniques [21,22] used for As (III) determination.

Nowadays, due to the higher sensitivity achieved with axially viewed plasma and better spectral resolution given by high-resolution monochromators, it is expected that low concentrations of all naturally occurring arsenic may be directly quantified by ICP OES. Furthermore, depending on the nebulizer used to introduce the sample solution in the plasma, sensitivity improves.

This paper describes synthesis, characterization and analytical properties of new reagent viz., 2,4-dihydroxy benzophenone-2-amino thiophenol (BPBT). Since the reagent is more sensitive, it is used for the determination of arsenic in various water samples.

Experimental

Apparatus

A Shimadzu (Model-1601) UV–VIS spectrophotometer (Perkin Elmer Singapore Private Limited, Singapore) and ELICO model Li-610 pH meter (M/s ELICO private limited, Hyderabad, India) with combination electrodes were used for measurements of absorbance and pH respectively. ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry Model-7000) methods were used for the quantitative analysis of As (III). To determine the As (III), AOAC methods were used (AOAC 1986, 2003; Jorhem 1993). In this method, the samples were dissolved at 190 °C and 400 psi pressure in Mars 5 apparatus (Vessel Type XKP 1500, CEM, Matthews, USA). As (III) was analyzed by inductively coupled plasma-optical emission Spectrometry (Varian Vista-MPX CCD Simultaneous Spectrophotometer, Mug rave-Victoria, Australia) [23,24].

Reagent and solutions

All chemicals used were of analytical-reagent grade of the highest purity available procured from Merck. Doubly distilled de-ionized water was used throughout the experiment. Glass vessels were cleaned soaking in acidified solutions of $K_2Cr_2O_7$ followed by washing with conc. HNO_3 and were rinsed several times with high purity de-ionized water. Stock solutions and environmental water samples were kept in polypropylene bottle containing 1 ml of conc. HNO_3.

Preparation of reagent (BPBT)

2,4-Dihydroxy benzophenone (5 g, 0.0233 mol) dissolved in 20 ml of methanol, 2-amino thiophenol (2.5 ml, 0.0233 mol) dissolved in 20 ml of methanol were taken in 250 ml round bottom flask. Suitable quantity (10 ml) of 1 M sodium acetate was added to the reaction mixture and refluxed for 12 h. On cooling the reaction mixture brown colored product was separated out. It was collected by filtration and washed several times with hot water followed by n-hexane. This compound was recrystallised from methanol and dried in vacuum. The ligand is stable for more than 6 months. Yield is 8.48 g; m.p. 118–120 °C. The structure of BPBT is shown in (Fig. 1).

Characterization of BPBT

The reagent has been characterized by IR, ^{1}H NMR and Mass spectral data. Infrared spectrum (Fig. 2) of BPBT shows bands at 3374, 3063, 2593, 1628, 1598, 1584, 1220, 1122, 699 cm^{-1} respectively corresponding to ν (O—H) symmetric stretch, ν (C—H) Aromatic stretch (sp^2---C—H), ν (S—H) stretch (weak) (δ), ν (C=C) Aromatic stretch, ν (C=N) Schiff base, Aromatic ring ν (C—C) stretch, ν (C—O) stretch, ν (C—N) stretch, ν (C—S) stretch. H^1NMR spectrum of BPBT ($CDCl_3$ + DMSO-d_6) showed signals at 6.30–7.54 (12H), 3.30 (1H) due to benzene or aromatic protons, −SH (thiolic protons) (Fig. 3). Mass spectrum of BPBT (Fig. 4) shows signal at 322 (M + 1) corresponding to its molecular ion peak. The molecular formula of the reagent is $C_{19}H_{15}NSO_2$ (M.Wt, 321).

pKa values of reagents

The pKa values were determined by recording the UV–Visible spectra of 1×10^{-4} M solutions of the reagent at various pH values using Phillips and Merrit method. The values of deprotonation obtained for BPBT were 6.86 (pK_1) and 6.86 (pK_2).

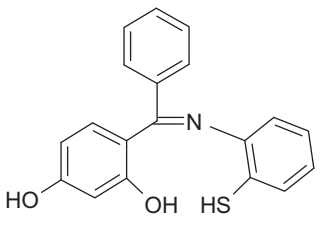

Fig. 1. BPBT-structure.