Sensors and Actuators B 182 (2013) 87–94

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Highly sensitive and selective spectrophotometric detection of trace amounts of Hg^{2+} in environmental and biological samples based on 2,4,7-triamino-6-phenylpteridine

Ahmed S. Al-Kady[a,b,*], Fatehia I. Abdelmonem[c]

[a] Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt
[b] Forensic Medicine Authority, Ministry of Justice, Tanta, Egypt
[c] Chemistry Department, Faculty of Women for Arts, Science, and Education, Ain Shams University, Asma Fahmy Street, Heliopolis-11341, Cairo, Egypt

ARTICLE INFO

Article history:
Received 6 October 2012
Received in revised form 20 February 2013
Accepted 26 February 2013
Available online 6 March 2013

Keywords:
2,4,7-Triamino-6-phenylpteridine
Hg^{2+} ion
Chemosensor
UV–vis

ABSTRACT

In this article, a simple, selective and sensitive spectrophotometric method for the direct determination of trace amounts of Hg^{2+} in aqueous samples was performed, based on complexation reaction between Hg^{2+} and 2,4,7-triamino-6-phenylpteridine (triamterene) with maximum absorbance at 415 nm. The important analytical parameters and their effects on the reported system were investigated. Beer's law was found to obey for Hg^{2+} in the concentration range 0.1–4.2 μg/mL with molar absorptivity of 5.32×10^4 l mol^{-1} cm^{-1} and Sandell's sensitivity of 8.532 ng cm^{-2}. The interference effect of some anions and cations on the determination was described. Most importantly, the method was applied for determination of trace amount of Hg^{2+} in water samples, biological, plant leaves and soil samples with satisfactory results. The performance of the proposed method was evaluated in terms of student's *t*-test and variance ratio *F*-test, which indicated the significance of proposed method over the reference method.

1. Introduction

The development of sensitive chemosensor has been receiving much attention in recent years because of the potential application in clinical biochemistry and environment. Mercury is a dangerous and widespread global pollutant. The long atmospheric residence time of mercury vapor and its oxidation to soluble inorganic Hg^{2+} provides a pathway for contamination vast amount of water and soil. Mercury can accumulate in animals and plants and also enters into human body through the food chain causing damage to central nervous system [1]. Due to the toxicological effects and potential accumulation of mercury onto human bodies and aquatic organisms, the determination of Hg^{2+} from biological and environment samples has seen an upsurge of interest in the last few years [2]

Numerous analytical and sophisticated techniques have been used for the determination of mercury in real samples. These include atomic absorption spectrometry [3,4], inductively coupled plasma-mass spectroscopy [5–9], spectrophotometry [10], neutron activation analysis [11], anodic stripping voltammetry [12], X-ray fluorescence spectrometry [13], electrothermal atomic absorption spectrometry [14], atomic fluorescence spectrometry [15], cold vapor atomic absorption spectrometry [16] and potentiometric ion-selective electrodes for Hg^{2+} ion detection [17–19]. Some Hg^{2+} sensors based on fluorescence enhancement or fluorescence quenching were reported [20,21]. Each of the mentioned techniques has its own merits, but each method also offers some problems such as poor reproducibility, limited sample adaptability, high cost, well-controlled experimental conditions, complicated sample-pretreatment, some inherent interference and time consuming procedures involving the use of sophisticated instrumentation, the wide utilization of these methods is largely limited.

Spectrophotometric methods are widely used due to their simplicity, rapidity, low costs and wide applications. Because of the availability of good number of chromogenic reagents with high sensitivities, spectrophotometry is still indispensable method for trace mercury determinations. The chromogenic reagents commonly used for the determination of mercury are 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one [22], phenanthroline and eosin [23], thiobenzoylacetone [24], variamine blue B [25], thiacrown ethers and bromocresol green [26], diphenylthiocarbazone [27], 1,5-diphenylthiocarbazone [28,29], methyl orange [30] and 1,3,5-triarylpent-2-en-1,5-diones [31].

Nowadays, in the development of new analytical methods, the amount and toxicity of the reagents used and of wastes produced

* Corresponding author at: Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt. Tel.: +20 405322083.
E-mail address: ahsaelkady@yahoo.com (A.S. Al-Kady).

0925-4005/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2013.02.102

are as important as any other analytical feature. Some of analytical methods use reagents or generate chemical wastes which are more toxic than the species being monitored. Hence, there is a great need to develop methods which are less harmful to human health and are environment friendly.

2,4,7-Triamino-6-phenylpteridine (triamterene) is a potassium-sparing diuretic used in combination with hydrochlorothiazide for treatment of hypertension (high blood pressure) and edema (water retention). This combination is in a class of medications called diuretics or water pills, and causes the kidneys to get rid of the body's unneeded water and sodium through the urine [32].

This paper describes a simple and selective spectrophotometric method for the determination of trace amounts of Hg^{2+} in aqueous samples in the presence of some other anions and cations. The proposed method was based on the reaction of Hg^{2+} with 2,4,7-triamino-6-phenylpteridine (triamterene) to form complex which absorb maximally at 415 nm. The method is sensitive, environment friendly, requires no control of temperature and does not suffer from most of the potential interferences. The proposed method was applied to determine of trace amounts of Hg^{2+} in water samples, biological, plant leaves and soil samples.

2. Experimental

2.1. Apparatus

UV–vis absorption spectra were measured in 1 cm quartz cells using a Shimadzu UV-1601PC spectrophotometer. The equipment permits multiple expansions in both absorbance and wavelength, and an accuracy of (±0.001) in absorbance readings. ^{1}H NMR spectra were measured on a Varian Gemini 200 spectrometer at 200 MHz in DMSO-d_6.

Measurement of pH was performed using a Metrohm-digital model 713 pH meter with a combined glass-calomel electrode of sensitivity (±0.001) pH units. All measurements were performed at room temperature (25 ± 0.01 °C).

2.2. Reagents and solutions

All reagents were of analytical grade and distilled water was used throughout the experiments. Mercuric acetate $Hg(CH_3COO)_2$ was purchased from Aldrich. The solute triamterene was purchased from parish chemical.

Standard stock solutions (1.0×10^{-3} M) of Hg^{2+} was prepared by dissolving appropriate amounts of $Hg(CH_3COO)_2$ in water. A stock solution of triamterene reagent of concentration 1.0×10^{-3} M was prepared by dissolving an accurately weighed amount of the reagent in pure methanol. Working solutions were prepared by adequate dilution of the stock solution. Stock solutions of diverse elements were prepared from the high purity salts of anions and cations.

2.3. Determination of stoichiometry

The experiments for the determination of the stoichiometry of Hg^{2+}–triamterene complex was conducted using a UV–vis spectrometry. Job's method of continuous variation [33] was applied to establish the components ratio of the complex. For this, different volumes (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0 mL) of 1.0×10^{-5} M Hg^{2+} was added with different volumes (2.0, 1.8, 1.6, 1.4, 1.2, 1.0, 0.8, 0.6, 0.4, 0.2, 0 mL) of 1.0×10^{-5} M triamterene and diluted to the volume with double distilled water in 10 mL standard volumetric flask. The absorbance was recorded at λ_{max} of the complex and plotted against the mole fraction of Hg^{2+}. Further confirmation of this ratio was ascertained by applying the molar ratio method [34]. For this, different volumes (0.1–2.0 mL) of 1.0×10^{-4} M triamterene was added to constant volume 5 mL of 1.0×10^{-5} M Hg^{2+} and diluted to the volume with double distilled water in 10 mL standard volumetric flask. The absorbance was recorded at λ_{max} of the metal complex and plotted against the molar ratio [triamterene]/[Hg^{2+}]. The complex stoichiometry was found from the graphs obtained and the conditional stability constant of that complex was calculated using the Harvey and Manning method [35].

2.4. Recommended procedure for spectrophotometric determination of Hg^{2+}

Into a 10 mL calibrated flask, a suitable aliquot containing between 1 and 42 μg of Hg^{2+}, 2.0 mL of 1.0×10^{-5} M triamterene solution, and 5 mL universal buffer solution of pH 8.0 were added and completed to the mark with doubly distilled water. The contents of each flask was mixed well at room temperature (25 ± 5 °C) and the absorbance was measured at 415 nm against the reagent blank prepared similarly in 10 mm reference cell within the stability time period of 48 h. The concentration of Hg^{2+} was calculated either from a calibration curve or regression equation.

2.5. Procedure for reference method [22]

A solution containing no more than 20.0 μg of Hg^{2+} was transferred into a 10.0 mL volumetric flask and 1.5 mL of 0.05% 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one solution was added. To the test solution, an approximate volume (5 mL) of Britton–Robinson buffer of pH 4–5 was added and finally the solution was made up to the mark with distilled water. The solution mixtures were allowed to stand at room temperature for 5 min before measuring the absorbance at 336 nm (λ_1) and λ_2 505 nm.

2.6. Determination in water samples

The proposed method was applied to determine of trace amounts of Hg^{2+} in several water samples including well-water, spring water, synthetic wastewater [36] and a synthetic laboratory seawater [37]. Water samples were collected without adding any preservative in polyethylene bottles and analyzed within 6 h. Water samples were filtered through a Whatman No. 41 filter paper, then an aliquot of the filtrate was taken for analysis. They tested negative. To these samples known amount of Hg^{2+} (2.0 μg) was added and analyzed for Hg^{2+} by recommended method and reference method [22].

2.7. Determination in biological samples and in plant leaves

Three deproteinized human blood samples (5 mL) and three samples of dried plant leaves (5 gm) were spiked with known amount of Hg^{2+} (2.0 μg). These were mixed with nitric acid (5 mL) and potassium sulphate (0.5 gm) and then heated to dryness in Kjeldahl's flask. The process was repeated 2–3 times, and then 25 mL nitric acid (1:3) was added to the residue and digested on a water bath for 30 min. The contents were again evaporated to dryness and residue was dissolved in distilled water filtered and cooled. Similarly three deproteinized samples of urine (each 50 mL) were concentrated to 5 mL before treatment as described above and analyzed by recommended method and reference method [22].

2.8. Determination in soil

Three soil samples (each 1 g) which were found to contain negligible amount of vanadium were spiked with known amount of Hg^{2+} (2.0 μg) and fused with 5 g of anhydrous sodium carbonate.