Journal of Advanced Chemical Sciences 2(1) (2016) 195–197

ISSN: 2394-5311

Contents List available at JACS Directory

Journal of Advanced Chemical Sciences

journal homepage: www.jacsdirectory.com/jacs

Sensing of Mercury(II) Using 1-(1*H*-Benzimidazol-2-yl)Guanidine As Chromophore

C.N. Sundaresan[1], D.K. Singh[2], A. Sunil[2,*]

[1]*Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Brindavan Campus, Kadugodi, Bangalore – 560067, Karnataka, India.*
[2]*Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Prasanthi Nilayam Campus, Puttaparthi, Anantapur – 515134, AP, India.*

ARTICLE DETAILS

Article history:
Received 30 October 2015
Accepted 05 December 2015
Available online 14 December 2015

Keywords:
1-(1*H*-Benzimidazol-2-yl)Guanidine
Mercury(II)
Spectrophotometry

ABSTRACT

The ligand, 1-(1*H*-benzimidazol-2-yl)guanidine (GBI) gives two absorbance peaks at 245 nm and 295 nm respectively. GBI complexes with mercury(II) to form a white coloured complex. The analytical parameters such as effect of pH, reagent dosage, reaction time, effect of mercuric ion concentration, effect of interfering ions have been studied. The range of detection was determined to be 0.01 – 1000 µg/mL. The minimum detection limit is 10 ng/mL. The method is fairly sensitive and does not involve any preconcentration procedures. The method was appropriately validated using analytical procedures.

1. Introduction

Mercury is considered to be one of the most toxic elements that pose harm to human health and ecosystem. It is widely spread in the atmosphere, lithosphere, and surface water. Mercury and its compounds are used in medicine for various purposes like an ingredient in dental amalgams, as a preservative in vaccines, as a topical antiseptic used for minor cuts and scrapes, in medical equipment like thermometers, etc. In industry, it is used for the production of chlorine and caustic soda, the chloro alkali process, for manufacturing of mercury vapour lamps, etc. In cosmetics, mercury is used as thiomersal, widely used in the manufacture of mascara. In agriculture, it is used as fungicides and herbicides. The anthropogenic emission of mercury into the environment is rapidly increasing due to its usage in many fields. It was reported that more than 2500 tons of mercury is released into environment every year through global anthropogenic activities [1]. The improper disposal of mercury containing products is the main reason for the raise in mercury levels in water, soil and air, particularly in the more populated and industrial areas. The toxicity of mercury poses serious problems to human health, as the bioaccumulation of mercury in various parts of human body ultimately leads to neurological diseases. To control mercury pollution and reduce mercury damage to human health, its usage should be minimized and sensitive methods for determination of mercury is important. The aim of current research in this direction is to come up with novel reagents that can determine mercury. Variety of techniques such as cold vapour atomic fluorescence spectrometry, LC–ICP-MS, CV-AAS, ICP-AES, GFAAS, anodic stripping voltammetry, flow-injection, cloud point extraction, etc. [2-9] have been reported for the determination of mercury. Various chromogenic reagents [10-20] have been utilized for the determination, through which, micro level detection limits were achieved.

To add to the existing knowledge, the authors here report an organic ligand, GBI which complexes with mercury. The advantages of using this reagent are facile synthetic procedures, cost effectiveness, ambient reaction conditions and less toxicity. This method is based on simple instrumentation and normal laboratory conditions. The present study utilizes the unique ability of GBI in the detection of mercury. The main principle behind the sensing aspect is the interaction between the mercury(II) and GBI which acts as a borderline base.

Table 1 List of chromogenic reagents used for catalytic oxidation method

Reagents	Range of determination (µg/mL)	Ref.
2', 4'- dihydroxy propiophenone benzoic acid hydrazone	0.11 - 0.97	[10]
Resacetophenone hydrazone (RBAH)	0.81 - 8.14	[11]
Anthrone phenylhydrazone	0 - 6.5	[12]
4,4'-Bis(dimethylamino)thiobenzophenone	0 - 3.9	[13]
Thio-Michler's Ketone	5.00 - 80.00	[14]
6-Hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1,3-thiazin-4(3H)-one	0.20 - 2.00	[15]
2-(2-Benzothiazolylazo)-p-cresol	2.80 - 11.10	[16]
Dithiothreitol	0.001 - 0.050	[17]
1-(2-Pyridylazo)-2-naphthol (PAN)	0.010 - 1.000	[18]
4-(2-Thiazolylazo) resorcinol (TAR)	0.05 - 2.50	[18]
2-Acetylpyridine thiosemicarbazone	0.240 - 2.407	[19]
Rhodamine B	0.250 - 1.300	[20]
GBI	0.01 - 1000	Current reagent

2. Experimental Methods

2.1 Chemicals and Reagents

All chemical used in the current study were of analytical grade. 2-guanidinobenzimidazole (2-GBI), mercuric chloride, potassium hydrogen phthalate, potassium phosphate monobasic and sodium tetra borate were procured from Sigma Aldrich Ltd. All the buffer solutions were prepared as prescribed by Vogel [21].

The amount 0.015 g of 2-GBI was weighed and dissolved in solvent mixture consisting of 95:5 water and dimethyl sulfoxide (DMSO) in a 100-mL volumetric flask to prepare a stock solution of 150.0 µg/mL. Working solutions were prepared by appropriate dilutions from the stock solution. Other working concentrations were prepared from the above stock solution by appropriate dilutions.

Mercury(II) stock solution was prepared by weighing 50.0132 g of mercuric chloride and dissolving it in a 50 mL volumetric flask using millipore water resulting in 1 mg/mL concentration of stock solution. The stock solution was standardized by titrating with standard NaCl solution (standardised with KI solution) using bromophenol blue as an indicator [21]. The working solutions were prepared by dilution from the stock.

*Corresponding Author
Email Address: asunil@sssihl.edu.in (A. Sunil)

Cite this Article as: C.N. Sundaresan, D.K. Singh, A. Sunil, Sensing of mercury(II) using 1-(1*H*-benzimidazol-2-yl)guanidine as chromophore, J. Adv. Chem. Sci. 2(1) (2016) 195–197.

The test sample was prepared by taking 1.004 g of the standard reference material (SRM-1515) apple leaves was appropriately weighed and digested using nitric acid and perchloric acid. After the digestion was completed, the mixture was cooled and preserved using a 100 mL stopper flask.

2.2 Instrumentation

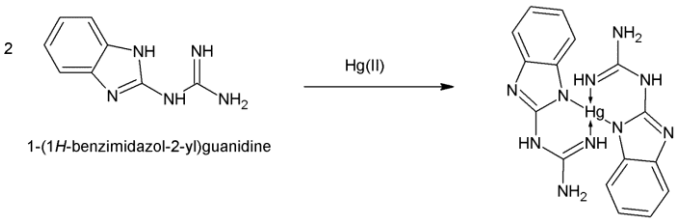
HitachiU-2001 UV-Visible spectrophotometer was used at all stages of the investigation. Quartz cells (HELLMA) of 10 mm path length and 3500 µL capacity were used for photometric and fluorometric measurements.

2.3 Recommended Procedure

Into 10 mL standard volumetric flasks, suitable aliquots of mercury(II) solution was transferred along with 2.0 mg/mL of GBI solution. The 1000 µL of hydrogen peroxide (30% w/v) was added to the metal-ligand mixture to initiate the reaction. The quartz cells of spectrophotometer were rinsed thoroughly and filled with the prepared solution. The absorbance measurements were monitored at 245 nm and 295 nm respectively.

3. Results and Discussion

GBI reacts with mercuric ion to form a white colored complex in an acidic pH range of 4.0-5.0 as described in Scheme 1. GBI gives a strong absorbance peak at 295 nm and 245 nm respectively. Upon complication with mercury(II), the absorbance decreases with increase in mercuric ion concentration. This phenomena gives us a good analytical strategy to sense mercury(II).



Scheme 1 Proposed reaction for the formation of GBI-Hg(II) complex

3.1 Effect of pH

The trend in pH studies is quiet unique and can be divided into three sub categories: one at lower or acidic pH, higher or basic pH and other at extremely acidic conditions like pH~2. Firstly under basic condition ranging from pH 7 to pH 11 the absorbance values are nearly same with an average value of 0.21 while that of pure ligand is that of 1.807, on the other hand the same value for mercury ligand solution is 0.428. Hence we can conclude from this that the under basic pH conditions the value of absorbance is reduced to 49.06% of the mercury ligand component. For the pH range between 3 and 5 the average value of the absorbance is 2.350 which is about 5.4 times the value observed for the mercuric ion ligand mixture having the absorbance value of 0.428. This is a case of hyperchromic shift. For the extremely acidic pH of 2 the absorbance value is 0.573 which is almost 1.21 times to that of the value obtained for the mercuric-ligand combination. Andrade et al investigated the protonation of 2-GBI by NMR [22]. The shift to low energy of the ^{13}CMR signals were observed. This infers that this ligand coordinates protons and the metal ions. X –ray diffraction analysis of the protonated ligand revealed that the molecule has a strong internal hydrogen bond which triggers the protonation at N10 rather than N3.

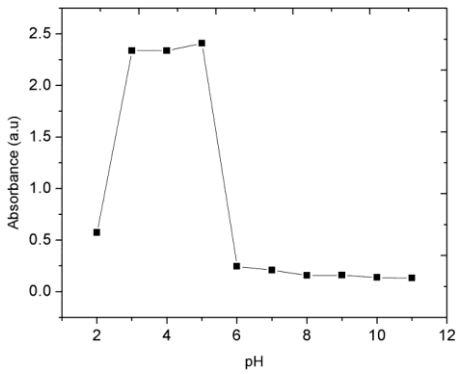


Fig. 1 Effect of pH on the GBI-Hg(II) reaction

With the data already available, the only possible reasoning that could be given is that the ligand contains the basic nitrogen atoms which might get protonated under the acidic conditions thereby interfering with the interaction between ligand and the metal ion. The conjugation possible in the unprotonated form gets disturbed thereby affecting the chromophore molecular energy separation thereby resulting in hyperchromic shift as compared to mercuric ligand combination. However when compared to the ligand the shift is in the hypochromic regime. Overall the ligand–metal ion shows unique behavior in each of these pH values, resulting in either hypochromic or hyperchromic shift depending upon the pH range which is different and distinct from mercury-ligand system, which indicates that such systems are versatile in the detection of mercuric ion.

3.2 Mercuric Ion Concentration

There is a plodding decrease in the intensity of the peak at 295 nm on interaction or more specifically with the complexation of the ligand with the mercuric salt as the concentration of mercuric ion increases from 10^{-12} g/mL to 10^{-3} g/mL. The sequential reduction in the intensity can be traced to the interaction of ligand with the mercuric ion as the concentration of the mercury ion increases; probably more of the coordination sites of ligand are occupied. The interaction probably inhibits the chromophore responsible for such peak. The molecular explanation may probably point towards the fact that the ability (efficiency) or more specifically probability of the chromophore to undergo transition decreases. Therefore in the presence of mercuric ion, behavior of the ligand changes thereby providing a hint for the presence of the mercuric ion. The data at 295 nm reveals the fact (Fig. 2).

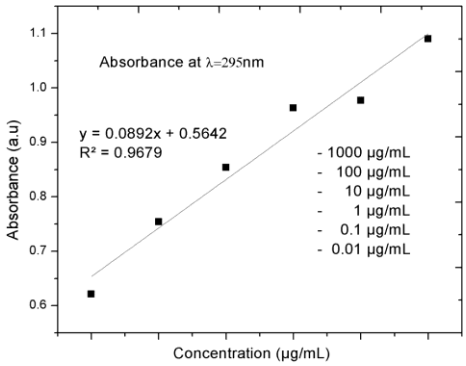


Fig. 2 Study of GBI-Hg(II) reaction at λ=295 nm

The data reveals that as the concentration of the mercury ion increases to the right there is almost linear decrease in the intensity of absorbance until at the concentration of 10^{-3} g/mL of mercuric ion concentration where the reduction in intensity is maximum. The point on the extreme is that of the ligand showing an absorbance value of 1.807 while the absorbance value of the mercuric ion having the concentration of 10^{-12} g/mL is 0.905, thereby showing a 50.08% reduction in intensity while the same value for the mercuric ion concentration of 10^{-3} g/mL is 34.36%, thereby demonstrating the capability of such kind of system to detect mercury even at pico level. Similar trends can also be traced to the behavior at 245 nm.

3.3 Effect of Temperature and Time on the Reaction

The reaction was studied by varying the temperature from 20 °C to 60 °C. Satisfactory results were recorded at room temperature itself and hence, the method was carried at normal laboratory temperature of 25 °C. The recorded values obtained at 30th minute of the reaction were stable and hence, various analytical parameters like pH, reagent concentration, etc., were studied at 30th minute.

3.4 Reagent Dosage

The experiment was carried out by varying the amount of GBI from 0.2-5.0 mg/mL and the absorbance values are recorded at 30th minute. The obtained data infers that the reaction was sufficiently fast when the concentration of GBI is 2.0 mg/mL and above hence this 2.0 mg of GBI was selected as the optimum amount of reagent required for the investigation.

3.5 Effect of Oxidizing Agent on the Reaction

Trends in the oxidation studies at higher concentrations of the oxidizing agent like hydrogen peroxide reveals that in case of oxidation studies at 245 nm, there a gradual increase in the absorbance values as the concentration of the hydrogen peroxide increases from 100 µL to 1000 µL

while the change in the absorbance value at 295 nm almost remains the same, the average value lies at 2.57. Therefore we can conclude that the prominent effect reflecting the changes can be monitored by studying the changes occurring at 245 nm.

3.6 Interference Studies

The effect of various anions and cations on the determination of mercury(II) under the optimum conditions was studied. It was clear from the interference studies that anions such as nitrate, suphate, oxalate, phosphate, fluoride, citrate, bromide, chloride, and borate did not interfere even when present in more than 1000 fold excess. Cations such as sodium(I), potassium(I), barium(II), magnesium(II), aluminium(III), lead(II), arsenic(III), antimony(III), bismuth(III) did not interfere even above 1000 fold excess. Scandium(III), zirconium(IV), rhenium(II), zinc(II), cobalt(III), osmium(IV) and tungsten(VI) can be tolerated up to 800 folds. Vanadium(V), manganese(II), chromium(VI), nickel(II), silver(I), gold(III), rhodium(III), ruthenium(III), cadmium(II), nickel(II), platinum(II), palladium(II) and iron(III) can be tolerated up to 500 folds. Copper(II), iron(II) and cobalt(II) can be tolerated up to 50 folds. Cobalt(II) showed no interference at pH of 4.0. A slight interference of copper(II) and Iron(II) was noted, which was masked by using thiosulphate and tratarate respectively.

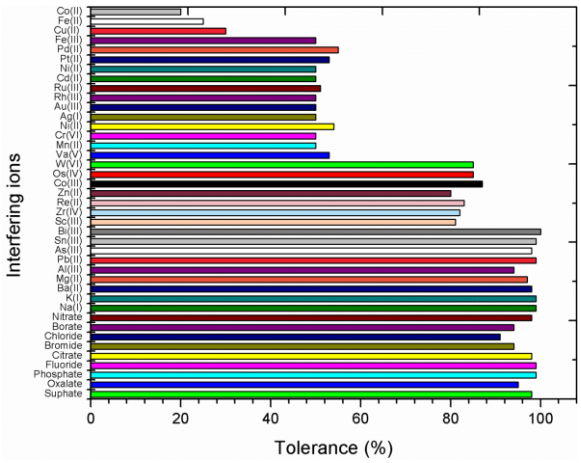


Fig. 3 Interference of various anions and cations on the determination of mercury(II)

3.7 Applicability of the Method

The current method can be utilized for determining mercury up to 0.01 µg/mL. In order to validate the method, the determination of mercury in SRM-1515 was done using the developed technique. The amount of mercury determined was 0.039 µg, which is in agreement with the amount reported. This method proves to be simple, accurate and acceptable in terms of mercury determination in real time samples.

Table 2 Determination of mercury in SRM-1515

Sample taken	Certified amount of mercury reported (µg/g)	Amount of mercury determined (µg) (n=4)
SRM-1515	0.044 ± 0.004	0.039 ± 0.017

4. Conclusion

The determination of mercuric ion using GBI was reported for the first time using the current developed method. The reaction was monitored at 295 nm using the technique of spectrophotometry. The minimum detection limit achieved was 10 ng/mL. The method was a facile one with no stringent laboratory conditions. There are no pre-concentration procedures involved. Overall this work is novel with respect to the branch of spectrophotometric methods for the determination of mercury.

Acknowledgments

Authors are thankful to the founder, chancellor, Bhagawan Sri Sathya Sai Baba, and authorities of Sri Sathya Sai Institute of Higher Learning for the support and guidance.

References

[1] Graham, I.P. Thompson, Treatment of waste metalworking fluid by a hybrid ozone-biological process, J. Hazard. Mater. 244 (2013) 394–402.
[2] N. Lubick, Funding struggle for mercury monitoring, Nature News 459 (2009) 620-621.
[3] D.G. Da Silva, L.A. Portugal, A.M. Serra, S.L. Ferreira, V. Cerda, Determination of mercury in rice by MSFIA and cold vapour atomic fluorescence spectrometry, Food Chem. 137 (2013) 159-163.
[4] B.L. Batista, J.L. Rodrigues, S.S. De Souza, V.C.O. Souza, F. Barbosa, Mercury speciation in seafood samples by LC–ICP-MS with a rapid ultrasound-assisted extraction procedure: Application to the determination of mercury in Brazilian seafood samples, Food Chem. 126 (2011) 2000-2004.
[5] G. Jarzyńska, J. Falandysz, The determination of mercury in mushrooms by CV-AAS and ICP-AES techniques, Jour. Env. Sci. Health Part A 46 (2011) 569-573.
[6] P.M. Moraes, F.A. Santos, B. Cavecci, C.C. Padilha, J.C. Vieira, P.S. Roldan, P.D.M. Padilha, GFAAS determination of mercury in muscle samples of fish from Amazon, Brazil, Food Chem. 141 (2013) 2614-2617.
[7] E. Bernalte, C.M. Sánchez, E.P. Gil, Determination of mercury in ambient water samples by anodic stripping voltammetry on screen-printed gold electrodes, Anal. Chim. Acta 689 (2011) 60-64.
[8] R.S. Picoloto, H. Wiltsche, G. Knapp, J.S. Barin, E.M. Flores, Mercury determination in soil by CVG-ICP-MS after volatilization using microwave-induced combustion, Anal. Methods 4 (2012) 630-636.
[9] V. Angeli, S. Biagi, S. Ghimenti, M. Onor, A. D'Ulivo, E. Bramanti, Flow injection-chemical vapor generation atomic fluorescence spectrometry hyphenated system for organic mercury determination: A step forward, Spectrochim. Acta Part B: Atomic Spect. 66 (2011) 799-804.
[10] M.D.M. Abadi, M. Chamsaz, M.H. Arbab-Zavar, S.A. Taheri, Preconcentration of Mercury in water samples by cloud point extraction and its determination by electrothermal atomic absorption spectrometry, Asian Jour. Chem. 24 (2012) 4277-4280.
[11] A.R.G. Prasad, V. Seshagiri, L.K. Ravindranath, A catalytic spectrophotometric method for the analytical determination of trace amounts of mercury(II), Chem. Sci. Jour. 2010 (2010) 1-8.
[12] V. Veeranna, A.R.G. Prasad, V.S. Rao, A novel spectrophotometric method for the micro determination of mercury(II), An. Univ. Bucuresti. 20 (2011) 57-64.
[13] J. Hongbo, Study on mensurating trace mercury in the environmental water sample using synergistic catalytic spectrophotometry, Jour. Northeast Agri. Univ. 12 (2010) 029-032.
[14] M. Gharehbaghi, F. Shemirani, M. Baghdadi, Dispersive liquid–liquid microextraction based on ionic liquid and spectrophotometric determination of mercury in water samples, In. J. Env. Anal. Chem. 89 (2009) 21-33.
[15] A. Niazi, T. Momeni-Isfahani, Z. Ahmari, Spectrophotometric determination of mercury in water samples after cloud point extraction using nonionic surfactant Triton X-114, J. Hazard. Mater. 165 (2009) 1200-1203.
[16] A. Hamza, A.S. Bashammakh, A.A. Al-Sibaai, H.M. Al-Saidi, M.S. El-Shahawi, Spectrophotometric determination of trace mercury(II) in dental-unit wastewater and fertilizer samples using the novel reagent 6-hydroxy-3-(2-oxoindolin-3-ylideneamino)-2-thioxo-2H-1, 3-thiazin-4 (3H)-one and the dual-wavelength correction spectrophotometry, J. Hazard. Mater. 178 (2010) 287-292.
[17] V. A.Lemos, L.O.D. Santos, E.D.S. Silva, E.V.D.S. Vieira, Spectrophotometric determination of mercury in water samples after preconcentration using dispersive liquidliquid microextraction, Jour. AOAC Int. 95 (2012) 227-231.
[18] N. Bi, Y. Chen, H. Qi, X. Zheng, Y. Chen, X. Liao, Y. Tian, Spectrophotometric determination of mercury(II) ion using gold nanorod as probe, Sensors Actuat. B: Chem. 166 (2012) 766-771.
[19] H.I. Ulusoy, R. Gürkan, S. Ulusoy, Cloud point extraction and spectrophotometric determination of mercury species at trace levels in environmental samples, Talanta 88 (2012) 516-523.
[20] S.V. Babu, K.H. Reddy, Direct spectrophotometric determination of mercury (ii) using 2-acetylpyridine thiosemicarbazone in environmental samples, Ind. J. Adv. Chem. Sci. 1 (2012) 65-72.
[21] A.Y.Y. Loo, Y. LAY, M.G. Kutty, O. Timpe, Spectrophotometric determination of mercury with iodide and Rhodamine B, Sains Malaysiana 41 (2012) 213-218.
[22] A.I. Vogel, Text-book of quantitative inorganic analysis including elementary instrumental analysis, Longmans, Green, London, 1961.
[23] N.A. Lopez, A. Ariza-Castolo, R. Contreras, A.V. Olmos, N.B. Behrens, H. Tlahuext, Versatile behavior of 2-guanidinobenzimidazole nitrogen atoms toward protonation, coordination and methylation, Heteroatom Chem. 8 (1997) 397-410.