ANALELE UNIVERSITATII BUCUREŞTI

Department of Physical Chemistry
4-12 Regina Elisabeta Blvd, District 3, Bucharest
phone: +40-21-3143508; fax: +40-21-3159249
*p*ISSN: 1220-871X *e*ISSN: 1844-0401

ARS DOCENDI PUBLISHING HOUSE
Sos. Panduri 90, District 5 Bucharest
phone/fax: +40-21-4102575
e-mail: arsdocendi@yahoo.com

A NOVEL SPECTROPHOTOMETRIC METHOD FOR THE MICRO DETERMINATION OF MERCURY (II)

V. Veeranna *, A. Raghavendra Guru Prasad ** and V. Suryanarayana Rao ***

abstract: The authors reported a new reagent namely Anthrone phenylhydrazone (APH) for the analytical determination of mercury (II) in water samples. Mercury (II) forms a yellow colored complex with APH in a media of *p*H 7. The method can be conveniently used for the determination of mercury (II) in the concentration range 0.8146-8.1456 μg mL^{-1}. The molar absorptivity and Sandell`s sensitivity were found to be 1.267×10^4 L moL^{-1} cm^{-1} and 0.00789 μg cm^2 respectively. The proposed method was found to be selective, linear ($R > 0.99$), accurate (recovery = <99.6%) and precise (RSD < 1.1%) in the reported linear concentration range.

key words: Spectrophotometric method; mercury (II); Anthrone phenylhydrazone; spiked water sample.

received: March 22, 2011 *accepted*: May 11, 2011

1. Introduction

Elemental mercury and all of its compounds are highly toxic. Exposure to inorganic mercury compounds can cause severe renal and gastrointestinal damage. Despite the well known fact that they are highly toxic, they have been widely used in agricultural, medicinal, electrolytic and electrical appliances industries. Mercury loading into the ecosystems is inexorable as the compounds of mercury are highly reactive, extremely volatile and highly soluble in water. Hence there has been a growing interest to develop the analytical procedures for the determination of trace amounts of mercury.

2. Experimental

Double-distilled water was used for preparation of solutions. The buffer solutions were prepared by mixing hydrochloric acid and sodium acetate (*p*H 1.0-3.0), acetic acid and sodium acetate (*p*H 3.5-7.0) and ammonium chloride and ammonium hydroxide (8-12). All chemicals and solvents used were of analytical reagent grade. Working solutions were prepared by appropriate dilutions of the stock solution.

* A.M.C Engineering College, Bangalore, Karnataka, India.
corresponding author e-mail: veeraug@gmail.com
** ICFAI Foundation for Higher Education, Hyderabad, A. P., India.
*** Sri Krishnadevaraya Universtity, Anantapur, A.P. India.

Table 1 A comparison to reveal the advantages of the proposed method.

S.No	Method	Detection Limit	Remark	Ref. No.
1	In situ single-drop micro extraction method by a miniaturized spectro-photometer	0.2 µg/L	Though sensitive, involve complicated procedures employing expensive equipment	1
2	Cold vapor atomic absorption spectrometry coupled to a flow injection	3 ng/L		2
3	Xylene microextraction combined with electrothermal vaporization atomic absorption spectroscopy	0.01µg/L		3
4	Square wave voltammetric deter-mination	3 nM	Highly complicated and require skilled analysts	4
5	Anodic stripping voltammetric assay	0.008 ppb		6
6	Polythymine oligonucleotide-modified gold electrode for voltammetric determination	60 pM	Though sensitive, involve complicated procedures employing expensive equipment	5
7	Reversed phase high performance liquid chromatography	1.6 ppb	Expensive and involve tedious preconcentration step	7
8	Liquid chromatographic method coupled with inductively coupled plasma mass spectrometry	0.75 µg/L		8
9	Photometric procedure	Microgram levels	Product to be estimated is fairly stable for only 10 minutes	9
10	Preconcentration of mercury followed by spectrophotometric determination.	2 µg/L	Involves complicated adsorption and desorption steps where there can be a inexorable scope for human errors	10
11	Spectrophotometric determination of mercury in water samples after cloud point extraction using nonionic surfactant	0.83 ng/mL	Involves complicated and extraction step	11
12	*β*-correction spectrophotometric method	0.026 µg/mL	Involve complicated and tedious steps. Has narrow calibration range	12
13	Solid phase extraction of the complex followed by spectrophotometric determination	0.001 µg/mL	Involves preconcentration and extraction steps	13
14	Extraction spectrophotometric determi-nation of Hg(II) with dithizone after its flotation as ion-associate using iodide and ferroin	0.14 ng/mL	Involves separation and preconcen-tration steps	14
15	Spectrophotometric method based on the formation of ion-pair complex	Microgram levels	Involves extraction step	15
16	Kinetic method for the determination of mercury (II) based on the catalytic effect of mercury (II) on ligand substitution	4.01 ng/mL	Time sensitive procedure	16
17	An indirect spectrophotometric procedure	0.4 $\mu g.L^{-1}$	Involves complicated procedure as reagent is a mixture of dithizone, CDTA (1,2-cyclohexylene-dinitrilo-tetraacetic acid), thiourea, ethylic alcohol and glycine	17

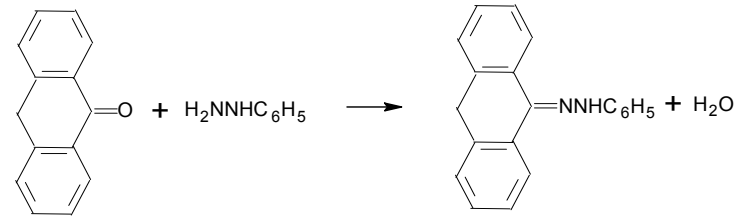
Very few methods are available which do not require expensive instrumentation and do not involve preconcentration and extraction steps [18]. The authors have proposed a simple and sensitive method for the determination of mercury (II). The method is based on the chromogenic reaction between Hg(II) and APH to give an yellow colored complex which has absorption maximum at 367 nm.

Required amount of mercurous chloride was taken in 100 mL standard flask. The salt was dissolved in distilled water and was diluted to 100 mL. This serves as a stock solution of mercury (II).

A Shimadzu UV-visible spectrophotometer (Model UV-160A) equipped with 1-cm matched quartz cells was used for absorbance measurements. An Elico digital pH meter was used for *p*H measurements.

2.1. Synthesis of Anthrone phenylhydrazone

Anthrone and phenyl hydrazine dissolved in 1:2 dilute dimethyl formamide were refluxed for 2 hours. The contents were cooled to room temperature. The crude orange colored product obtained was separated by filtration. The product obtained was washed with water, dried and recrystallysed from hot aqueous ethanol. APH solution of concentration 0.001M prepared in dimethyl formamdie serves as a stock solution.



Anthrone Phenyl hydrazine Anthrone phenylhydrazone

Fig. 1 *Synthesis of Anthrone phenylhydrazone.*

2.2. Characterization of Anthorne phenylhydrazone

2.2.1. IR spectral studies

The important bands in the infrared spectrum of APH (recorded in KBr pellet) and their assignments are given in the Table 2.

Table 2 IR spectral details.

Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment
3434.10	-(NH) Secondary	1463.87	Aromatic sketal stretching
3057.41	(=C-H) (Ar-H)	1479.80	Aromatic sketal stretching
1599.96	-(C=N)	1450.15	Aromatic sketal stretching
1310.79	-(C-N)		

The IR spectrum clearly indicates the presence NH and C=N in the aromatic nucleus.

2.2.2. ^{1}H-NMR spectral studies

The NMR spectrum of the compound was recorded in $CDCl_3$ and DMF using TMS as internal standard. The spectrum signified the presence of two different types of protons. The peak present at δ10.264 ppm indicates interaction of NH proton with aromatic protons.

2.2.3. Mass spectral studies

The mass spectrum of APH showed signal at 284.10 (m/z) corresponding to molecular ion peak.

Table 3 Mass spectral details.

m/z value	Source of fragment
284.10	$C_{14}H_{10}NNHC_6H_5$
195	$C_{14}H_{12}N^+$

Spectral details given above reveal that the compound contains –C=N, -(C-N), -(NH) and aromatic rings and confirm the structure shown in the Fig. 1.

2.2.4. General experimental procedure

5 mL of buffer solution of required *p*H, 3 mL of mercuric chloride of required concentration and 2 mL APH of required concentration were taken in a 10 mL volumetric flask. The contents of the flask were shaken well and absorption spectrum was recorded against reagent blank.

3. Results and Discussion

3.1. Effect of *p*H

The effect of pH on the complexation reaction is shown in the Fig. 3. The figure reveals that absorbance of the solution appreciably remains constant in the acidic media, it increases in the media of *p*H 7 and there is a decrease in the absorbance with the further raise in *p*H. Keeping in view the reproducibility and stability of the spectrum, a *p*H of 7 was considered optimum for further investigation. The absorption spectra showed the maximum absorbance at 367 nm and this fact was further substantiated by the Fig. 2 which revealed that complex formed between the Hg(II) and APH was responsible for the absorption spectra.

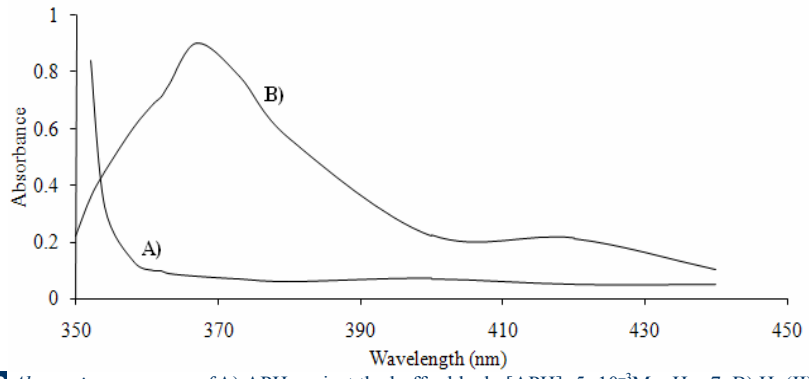


Fig. 2 *Absorption spectrum of* A) APH against the buffer blank. [APH]=5×10^{-3}M, *p*H = 7; B) Hg(II)-APH complex against the reagent blank. [Hg(II)] = 2.7×10^{-5}M, [APH]= 5×10^{-3}M, *p*H = 7.

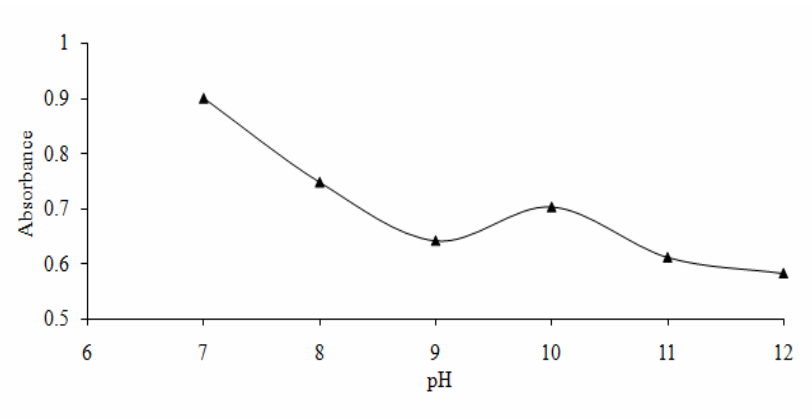


Fig. 3 *Effect of pH on absorbance*
[Hg(II)] = 2.7×10^{-5}M, [APH]= 5×10^{-3}M, λ_{max} = 367 nm.

3.2. Effect of APH on absorbance

In order to fix the concentration APH, the absorbance of the solution containing fixed concentration of metal ion and varying concentration of APH was recorded in a media of *p*H 7. It was found that an optimum reagent concentration of 5 fold was sufficient for the complexation. The presence of excess of the reagent does not alter the absorbance of the color reaction.

3.3. Effect of time on the color reaction

To study the effect of time on the color reaction, the absorbance values of the solution containing fixed amount of Hg(II) was measured at regular intervals of time (10 minutes). It was found that the color formation was instantaneous and absorbance remained constant for more than an hour. This suggests that the complex was stable for a reasonable period of time.

3.4. Composition of the complex

The stoichiometry of the Hg(II)-APH complex was determined by two methods namely, Job`s method continuous variation and molar ratio method.

In Job's method [19], a series of solutions containing varying amounts of the metal ion and APH solution of required concentration were taken in 10 mL volumetric flask. The absorbance values of these solutions were recoded in each case and the data is presented in the Fig. 4. It is clear from the figure that mercury forms 1:2 complex with the reagent. The stability constant of the complex was found to be 9.096×10^{5}. The stoichiometry was further confirmed by mole ratio method [20]. In mole ratio method, absorbance of the solutions containing fixed concentration of metal and varying concentration of the reagent was recorded at 367 nm.

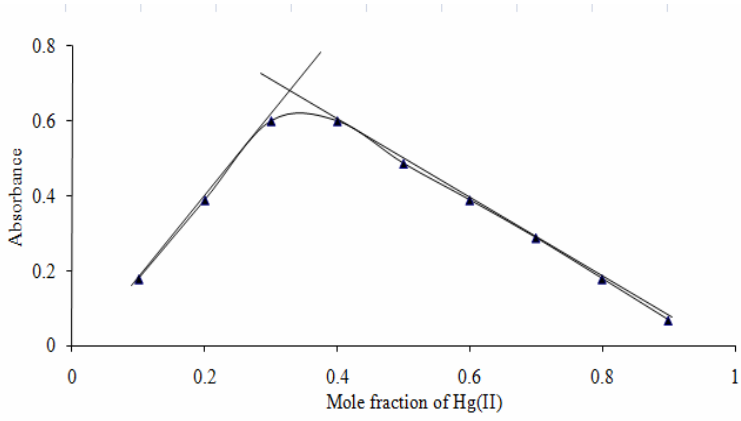


Fig. 4 *Stochiometry of the complex by Job`s method continuous variation*
[Hg(II)] = [APH]= 6×10^{-4}M, *p*H = 7, λ_{max} = 367 nm.

3.5. Analytical determination of Hg(II)

In order to determine the amount of Hg(II), a series of solutions containing fixed concentration of the reagent and varying concentration of metal ion in the appropriate *p*H media was prepared. The absorbance values were measured at 367 nm in each case against respective reagent blank solution. Linear calibration plot shown in the Fig. 5 indicates that mercury (II) can be determined in the concentration range 0.8146-8.1456 µg mL^{-1}.

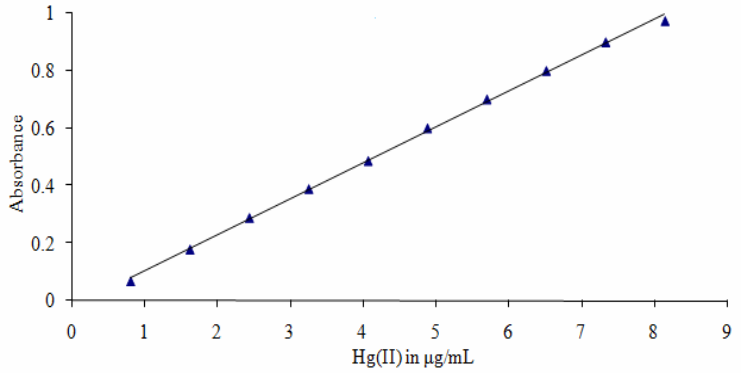


Fig. 5 *Analytical determination of Hg(II)*
[APH]=5×10^{-3}M, *p*H = 7, λ_{max} = 367 nm.

3.6. Analytical parameters and sensitivity

The calibration plot for the analytical determination mercury (II) can be fitted into the equation $A_{367\ nm}$ = 0.125C-0.022 (A is absorbance and C is concentration in µg mL^{-1}). The correlation coefficient was 0.998. The molar absorptivity and Sandell`s sensitivity were found to be 1.267×10^4 L $mol^{-1}cm^{-1}$ and 0.00789 µg cm^{-2} respectively. The relative standard deviation was found to be around 1.1%. The corresponding method detection limit and limit of quantification were found to be 0.0939 and 0.1879 µg mL^{-1} respectively.

3.7. Effect of diverse ions

The effect of interfering ion on the determination of mercury (II) was investigated by adding known concentration each ion to a solution containing 4.100 µg mL^{-1} of Hg(II) and determining the latter by the general experimental procedure mentioned above. The tolerance limit of each ion was taken as the concentration of foreign ion which caused less than ±1% deviation in absorbance value. It is evident from Table 4 that except Pd(II), Cu(II), Co(II), and Ni(II), all other ions were tolerated at significant levels.

Table 4 Effect of diverse ions in presence of Hg(II)]. [Hg(II)] = 4.100 µg mL^{-1}.

Anion	Tolerance limit (µg mL^{-1})	Cation	Tolerance limit (µg mL^{-1})
Thiourea	104	Co(II)	0.51
Tartrate	219	U(VI)	84.21
Sulfate	855	Ru(III)	13.20
Phosphate	193	Ni(II)	0.612
Fluoride	20	Sr(II)	12.54
Chloride	54.21	Cd(II)	0.845
Iodide	253.8	Zr(IV)	10.23
Nitrate	130.23	Ti(IV)	6.98
Oxalate	8.57	Sn(II)	14.12
EDTA	1664	Mg(II)	32.4
Thiosulfate	15.23	Al(III)	13.49
Bromide	640	W(VI)	198
Citrate	841	Pd(II)	0.13
Acetate	44.3	Cr(VI)	5.19
		Cu(II)	0.45
		Mo(VI)	19.25

3.8. Determination of mercury (II) in spiked tap water samples

The water samples were spiked with several known amounts of Hg(II). The analytical determination of mercury was carried out by the general experimental procedure mentioned in 2.2.4. The results presented in Table 5 indicate the applicability of the method to tap water samples.

Table 5 Application to spiked tap water samples [APH]= 5×10^{-3}M, *p*H = 7, λ_{max} = 367 nm.

Sample	Hg(II) added	Found(µg/ml)		Recovery (%)	RSD (%)
		AAS method	Present method*		
Tap water	3.0	2.981	2.9810±0.0224	99.37	1.05
	4.8	4.782	4.7793±0.0317	99.57	0.93
	7.0	6.948	6.9665±0.0459	99.52	0.92

*The value of *t* at 95% confidence level is 2.26.

4. Conclusion

The proposed procedure was simple, sensitive and rapid. The molar absorptivity and Sandell`s sensitivity of the proposed method were reported to be 1.267×10^4 L $mol^{-1}cm^{-1}$ and 0.00789 µg cm^{-2} respectively. The selectivity of the proposed method was excellent. The proposed method can be used directly to determine trace mercury in various water samples without separation, preconcetration or extraction steps.

REFERENCES

1. Fangwen Yang, Rui Liu, Zhiqiang Tan, Xiaodong Wen, Chengbin Zheng and Yi Lv. (2010) *Journal of Hazardous Materials* **183,** 549-553.
2. Zavvar Mousavi, H., Alireza Asghari and Hamid Shirkhanloo. (2010) *Journal of Analytical Chemistry* **65,** 935-9.
3. Habib Bagheri and Mehrnoush Nader. (2009) *Journal of Hazardous Materials* **165,** 353-8.
4. Wenfang Deng, Yueming Tan, Yunyong Li, Yanqing Wen, Zhaohong Su, Zhao Huang, Suqing Huang, Yue Meng, Qingji Xie and Yueping Luo. (2010) *Microchimica Acta* **169,** 367-74.
5. Jikui Wu, Lanying Li, Bijun Shen, Guifang Cheng, Pingang He and Yuzhi Fang. (2010) *Electroanalysis* **22**, 479-82.
6. Jingming Gong, Ting Zhou, Dandan Song, Lizhi Zhang† and Xianluo Hu. (2010) *Anal. Chem*. **82**, 567-73.
7. Susumu Ichinoki, Masashi Kodani, Youichi Fujii. (2009) *Journal of Liquid Chromatography & Related Technologies* **32**, 1463-74.
8. Bloxham, M. J., Anthony Gachanja, Hill S. J. and Worsfold, P. J. (1996) *J. Anal. At. Spectrom*., **11**, 145-8.
9. Khabarov, Y.G. and Veshnyakov, V.A. (2009) *Zhurnal Analiticheskoi Khimii* **64**, 254-6.
10. Rajesh, N. and Hari, M. S. (2008) *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **70**, 1104-8.
11. Niazi, A., Momeni-Isfahani, T. and Ahmari, Z. (2009) *Journal of Hazardous Materials* **165**, 1200-3.
12. Hamza, A., Bashammakh, A. S., Al-Sibaai, A. A., Al-Saidi, H.M. and El-Shahawi, M.S. (2010) *Journal of Hazardous Materials* **178**, 287-92.
13. Mohammad Saber-Tehrani, Hamid Hashemi-Moghaddam, S. Waqif Husain, Karim Zare. (2007) *Annali di Chimica* **97**, 675-83.
14. Hosseini, M. S. and Hashemi, M, H. (2004) *Talanta* **67**, 555-9.
15. Perez-Ruiz, T., Ortuno, J. A. and Torrecillas M. C. (1984) *Analytica Chimica Acta* **165**, 275-9.
16. Radhey Mohan Naik, Pradeep Kumar. (2007) *Annali di Chimica* **97**, 1169-79.
17. Frederic Theraulaz and Thomas, O. P. (1994) *Microchimica Acta* **113**, 53-59.
18. Jamaluddin Ahmed, M. and Shah Alam, Md. (2003) *Spectroscopy* **17**, 45-52.
19. Job, P. (1928) *Ann. Chim*. (Paris) **9**, 113-203.
20. Yoe, J. H. and Jones, A. L. (1944) *Ind. Eng. Chem. Anal. Ed*. **16**, 111-5.