

Determination of Arsenic in Environment by Spectrophotometric Technique using Hydroxamic Acids

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Abstract: A simple, rapid, stable and sensitive direct visible spectrophotometric method has been developed for the determination of trace amount of arsenic in environmental samples of Bhopal city using N-PBHA, N-p-CIPBHA and N-p-CIPCHA, Arsenic (III) reacts with different hydroxamic acids and forms light pink to violet colored complex in acidic medium which were extracted in n-hexane. The calibration graph was linear over the concentration range of 0.0003786-0.004164, 0.003786-0.06057 and 0.003786-0.04921 μgml^{-1} for N-Phenylbenzo-hydroxamic acid (N-PBHA), N-p-Chloro-phenyl-benzo-hydroxamic acid (N-p-CIPBHA) and N-p-Chloro-phenyl-cinnamohydroxamic acid (N-p-CIPCHA), respectively. The molar absorptivities were found to be 2.892×10^5 , 1.5973×10^4 and 2.0238×10^4 $\text{L mol}^{-1} \text{cm}^{-1}$ for the three hydroxamic acids. The optimum reaction condition and other analytical parameter were evaluated.

Key words: Arsenic, Environmental samples, N-PBHA, N-p-CIPBHA, N-p-CIPCHA and Spectrophotometric.

I. Introduction

Arsenic and its compounds are known as poisonous substances and are widely distributed in the earth crust. The compounds of arsenic in groundwater are found with both organic and inorganic moiety. The inorganic compounds of arsenic are about 100 times more toxic than the organic ones and are more prevalent in groundwater [1]. The major inorganic compounds of arsenic in natural water are pentavalent arsenate ions [As(V)] like H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-} and trivalent arsenite ions [As(III)]: H_3AsO_3 , H_2AsO_3^- and HAsO_3^{2-} with the later being more toxic [2]. Under oxygenated condition arsenate is more common in oxygenated water while arsenite is found in anaerobic or highly reducing conditions [3]. The toxicity of arsenic is dependent on its molecular forms with inorganic species being the most toxic forms. Various health problems due to their presence include stomach pain, nausea, vomiting, diarrhea, etc. The long-term exposure of arsenic in drinking water increases the risk of cancer of skin, kidney, liver, and prostate. Moreover, it also disturbs the functioning of nervous and cardiovascular system and eventually leads to death [4, 5].

Arsenic concentration in various water bodies is increasing day to day due to several reasons like use of arsenical pesticides, mineral dissolution, mine drainage, disposal of fly ash, and geothermal discharge [6]. Due to its high toxicity, World Health Organization (WHO) has lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50 to 10 μgL^{-1} [7].

There are several accepted analytical methods currently available for arsenic measurement in environmental samples. These include polarographic speciation [8], colorimetric analysis [9] multisyringe flow injection system with hydride generation-atomic fluorescence [10], atomic absorption spectroscopy [11, 12], HPLC coupled HG-AAS [13], dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry [14], electrothermal atomic absorption spectrometry [15], electrospray ionization mass spectrometry [16], electrochemical detection [17] and atomic fluorescence spectrometry [18].

Spectrophotometric determination of arsenic using hexamethylene ammonium-hexamethylenedithiocarbamate [19], silver diethylthiocarbamate [20], azure-B [21], molybdate-iodine tetrachloride [22], variamine blue [23], rhodamine-B [24] have also been reported. Studies have been also done on determination of arsenic from aqueous solution by electro coagulation method using Al-Fe electrodes [25]. PVC based 5, 10, 5, 20-tetrakis - (4-methoxyphenyl)-porphyrinatocobalt (II) membrane potentiometric sensor for arsenite has also been described [26]. MATLAB assisted disposable sensors for quantitative determination of arsenic was constructed by immobilizing reagents on TLC (thin layer chromatography) paper [27].

In the present investigation, the determination of trace arsenic in water by spectrophotometric method has been reported. This method is rapid, simple and based on use of non-toxic chemicals. Determination of trace amount of arsenic by this method is important because ground water, waste water and soil samples could be analysed in short period of time as compared to other spectrophotometric methods.

II. Experimental

2.1 Instruments

“Shimadzu spectrophotometer 1700” was used for electronic spectral measurements with 10 mm matched quartz cells. A Hanna 8521 model pH meter was used for pH measurements.

2.2 Reagents and chemicals

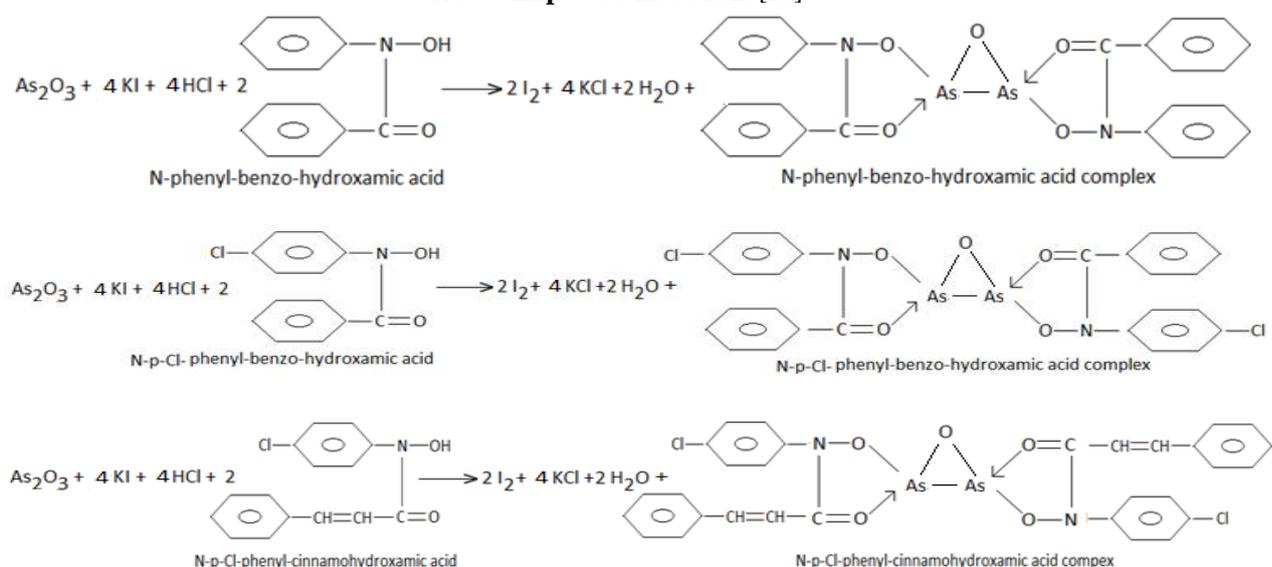
All the chemicals were of analytical grade. Stock standard solution of arsenic was made from arsenic tri-oxide. Working standard was prepared by appropriate dilution of stock solution. Aqueous solution of 2 % potassium iodide was prepared by dissolving 2g KI in 100 ml double distilled water. N-PBHA, N-p-CIPBHA and N-p-CIPCHA stock solutions were prepared by dissolving 0.1g of respective hydroxamic acid in 100 ml n-hexane. Double distilled de-ionized water was used for preparation of standard solutions, dilution and washing vessels.

III. Procedure

The calibration curve was obtained by the following method:

An aliquot of the sample solution containing 0.0003786 - 0.004164, 0.003786 - 0.06057 and 0.003786 - 0.04921 μgml^{-1} of arsenic for N-PBHA, N-p-CIPBHA and N-p-CIPCHA, respectively was transferred to a series of 25 ml calibrating flask. In this solution, 1.5 ml of 2 % potassium iodide and 1 ml of 1 M HCl were added and mixture was gently shaken until the appearance of yellow color which indicates the liberation of iodine. 1 ml of 2% EDTA was then added for masking the interfering ions. Finally, 1 ml of all the three hydroxamic acid solutions were added, light pink to violet colour was obtained immediately with different hydroxamic acids. The solution was kept for 2 minutes. A blank solution was prepared exactly in the same manner as test solution but without addition of arsenic. The absorbance of the sample solution was determined against the blank at 530 nm, 508 nm and 520 nm, respectively with three hydroxamic acids. The pH was maintained at 3.5 for N-PBHA, N-p-CIPBHA and N-p-CIPCHA with drop wise addition of buffer solution. The amount of the arsenic present in the volume taken was computed from the calibration graph.

IV. Expected Reactions[28]



V. Results and discussion

5.1 Absorption spectrum and calibration curve

After reaction, complex present in organic phase was scanned from 400 nm to 600 nm against reagent blank (Fig.1). Maximum absorption values were observed at 530 nm, 508 nm and 520 nm for arsenic complex with N-PBHA, N-p-CIPBHA and N-p-CIPCHA, respectively. Therefore, 530 nm, 508nm and 520 nm were selected with N-PBHA, N-p-CIPBHA and N-p-CIPCHA, respectively for the absorbance measurement throughout the experiments.

A calibration plot of absorbance against concentration of N-PBHA, N-p-CIPBHA and N-p-CIPCHA complexes at the absorption maxima gave a linear and reproducible graph in the concentration range of 0.0003786-0.004164, 0.003786-0.06057 and 0.003786-0.04921 μgml^{-1} , respectively (Fig.2). The Beer's law is obeyed in this range. Optical characteristics, precision and accuracy of the proposed method are summarized in Table 1.

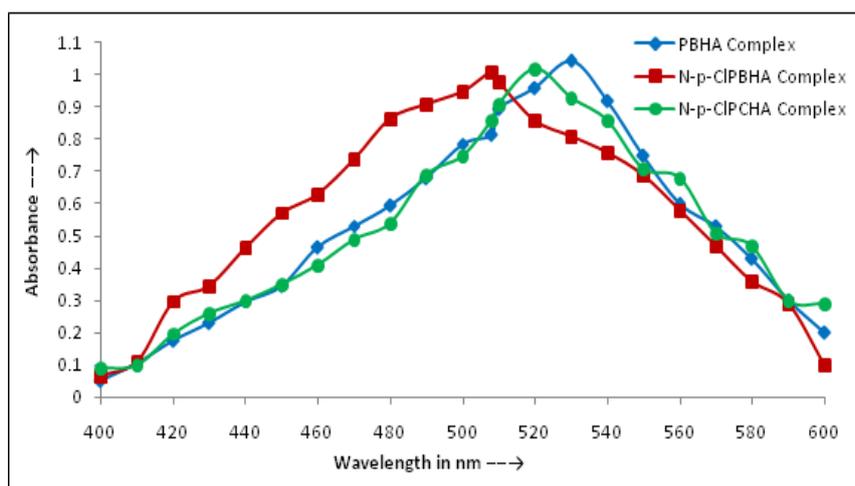


Figure1. Absorption spectra of arsenic complexes with hydroxamic acids

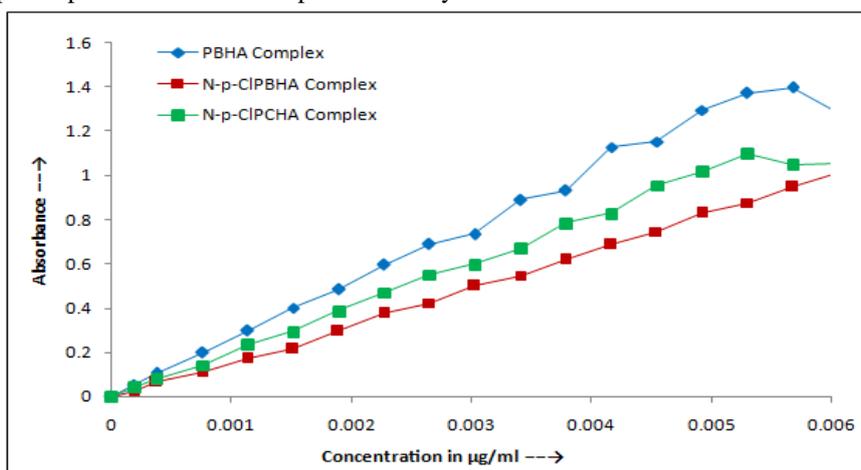


Figure2: Calibration plot for arsenic complexes with N-PBHA, N-p-CIPBHA and N-p-CIPCHA

Table 1: Optical characteristics, precision and accuracy of the proposed method

	N-PBHA	N-p-CIPBHA	N-p-CIPCHA
λ_{max} , nm	530	508	520
Beer's law limits in concentration range $\mu\text{g ml}^{-1}$	0.0003786-0.004164	0.003786-0.06057	0.003786-0.04921
Molar absorptivity, $\text{L mol}^{-1} \text{cm}^{-1}$	2.892×10^5	1.5973×10^4	2.0238×10^4
Sandell's sensitivity, $\mu\text{g cm}^{-2}$ per 0.001 absorbance unit	3.60×10^{-6}	6.76×10^{-5}	5.40×10^{-5}
Limit of detection, $\mu\text{g ml}^{-1}$	8.432×10^{-5}	8.956×10^{-4}	9.585×10^{-4}
Relative standard deviation %	1.5	1.9	1.6
Quantitation limit $\mu\text{g ml}^{-1}$	2.55×10^{-4}	2.714×10^{-3}	2.904×10^{-3}

5.2 Effect of iodide concentration and acidity

The effect of iodide concentration and acidity on the color intensity was studied with given concentration range of arsenic solution. The appearance of yellow color indicates the liberation of iodine. Although any excess of iodine in the solution will not interfere. It is found that 1 ml of 2 % potassium iodide and 1 ml of 1 M HCl are sufficient for completion of reaction. In order to obtain the optimum condition for the determination of arsenic, absorbance was measured at the pH range 1.0 -10.0. Constant and maximum absorbance values were obtained at the $\text{pH}=3.5 \pm 0.2$. Hence, the pH of the reaction system is maintained at 3.5 ± 0.2 throughout the study. This could be achieved by the addition of 2 ml of 1 M sodium acetate solution in a total volume of 25 ml (Fig. 3.)

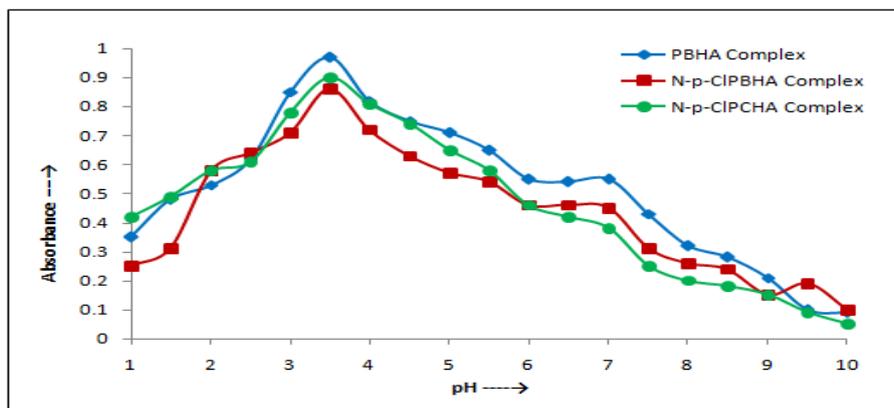


Figure3: Effect of pH on absorbance of complexes

5.3 Effect of different solvent

Different organic solvents like ethanol, n-butanol, diethyl ether, ethyl-methyl ketone, ethyl acetate, chloroform, toluene, n- hexane and carbon tetrachloride were used for determination. n- hexane was found to be most suitable solvent as it gave better and quick phase separation. Therefore, n- hexane was selected.

5.4 Effect of reagent concentration

Optimal concentration of hydroxamic acids were investigated by varying the amount of hydroxamic acids used as a reagent. To a series of arsenic standard solution, varying concentration of various hydroxamic acids solutions were added and mixed. It was observed that the absorbance increases with increasing the concentration of hydroxamic acids .It is found that maximum absorbance was observed at 1.5 ml, 2ml and 3ml of 0.0001% of N-PBHA, N-p-CIPBHA and N-p-CIPCHA hydroxamic acids solutions, respectively. After which it decreases rapidly. Therefore, the above mentioned volume was selected for these hydroxamic acids for all experiments (Fig. 4).

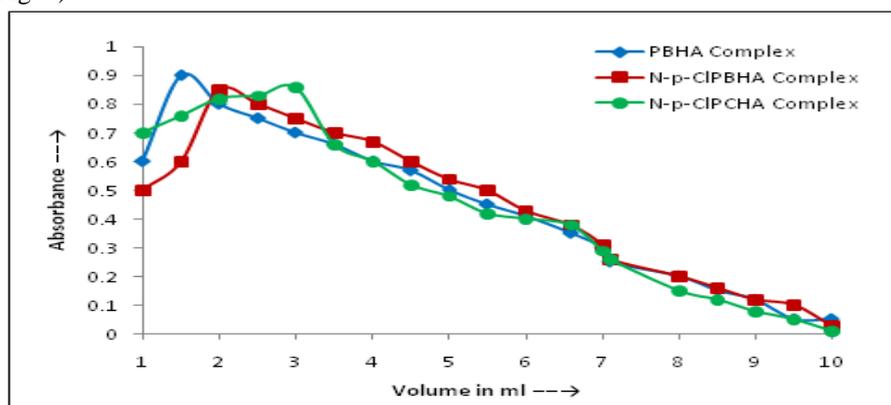


Figure4: Effect of reagent concentration on absorbance of complexes

5.5 Effect of temperature

The effect of temperature on absorbance of the complex was studied over the temperature range of 1^oC – 60^oC. It was observed that reaction becomes very fast at the room temperature and formed complexes gives maximum and stable absorption at the temperature of 30^oC, 25^oC and 22^oC for N-PBHA, N-p-CIPBHA and N-p-CIPCHA, respectively. Therefore, all experiments performed at the above temperature (Fig.5).

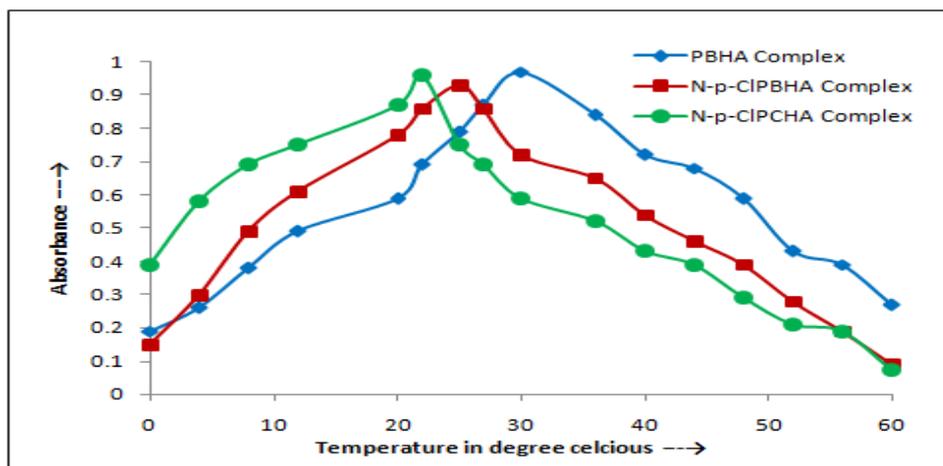


Figure5: Effect of temperature on absorbance of complexes

5.6 Effect of stirring time and rest time

Effect of stirring time and rest time was also studied. For studying the effect of stirring time, the absorbance of formed complex was studied and compared. The stirring time was varied from 0-90seconds. As it is clear, after about 40, 55, 64 seconds of stirring and 10seconds of rest time, the formed complex gives maximum absorption. Therefore above stirring and rest time selected in subsequent studies (Fig. 6).

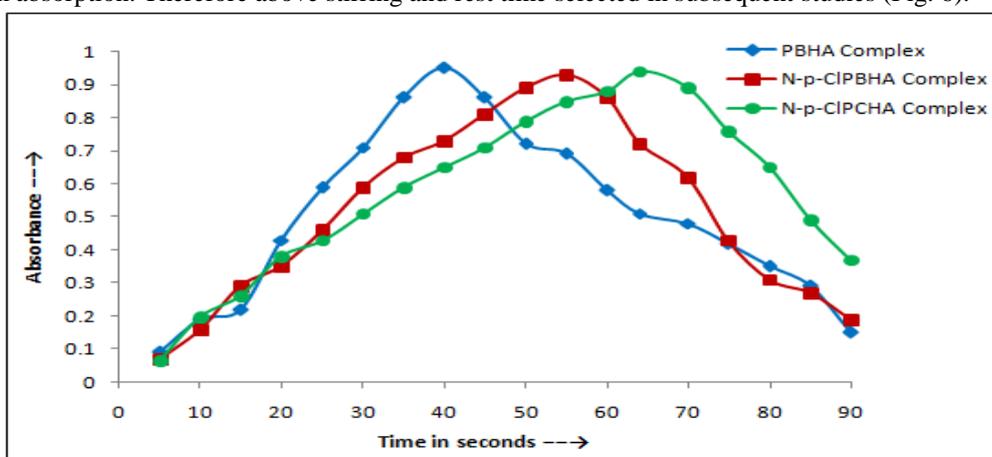


Figure6: Effect of reaction time on absorbance of complexes

5.7 Effect of foreign ions

The effect of various foreign ions at microgram levels on the determination of arsenic using different hydroxamic acids were studied. The tolerance limits of interfering species were established at the concentration that do not cause more than $\pm 1.0\%$ error in absorbance values for arsenic(III) at 0.0003786-0.004164, 0.003786-0.06057 and 0.003786-0.04921 μgml^{-1} for N-PBHA, N-p-CIPBHA and N-p-CIPCHA, respectively. The results indicated that most of the common ions did not interfere Table 2.

Table2: Effect of foreign ions on the determination of arsenic

S No	Diverse ions	Tolerance limit (μgL^{-1})		
		N-PBHA	N-p-CIPBHA	N-p-CIPCHA
1	Al^{3+}	600	400	370
2	Ba^{2+}	900	850	700
3	Ca^{2+}	420	390	300
4	Cd^{2+}	550	610	520
5	Co^{2+}	170	168	150
6	V^{5+}	150	146	140
7	Zn^{2+}	1050	900	850
8	Cu^{2+*}	140	100	90
9	Fe^{3+*}	120	105	111
10	Bi^{3+}	950	1000	750
11	PO_4^{3-}	1000	960	700
12	Mg^{2+}	160	163	155

13	Mn ²⁺	120	105	110
14	Na ⁺	500	450	430
15	K ⁺	800	810	797
16	SO ₄ ²⁻	900	820	760
17	C ₂ O ₄ ²⁻	1050	1105	1000
18	Ni ²⁺	120	80	75
19	NO ₃ ⁻	700	680	650
20	C ₄ H ₄ O ₆ ²⁻	1300	1225	1000

* Masked by EDTA

Table 3: Determination and recovery of arsenic in water and soil samples

S No.	Locations in Bhopal	As ³⁺ added (µg L ⁻¹)	As ³⁺ found			Recovery %		
			N-PBHA	N-p-CIPBHA	N-p-CIPCHA	N-PBHA	N-p-CIPBHA	N-p-CIPCHA
1	GI	0.00	3.7	3.3	2.9	-----	-----	-----
		2.00	5.68	5.26	4.80	99.6	99.2	97.9
2	MI	0.00	3.9	3.2	3.7	-----	-----	-----
		2.00	5.75	5.18	5.68	97.4	99.6	99.6
3	SL	0.00	2.7	2.6	2.4	-----	-----	-----
		2.00	4.69	4.55	4.37	99.7	98.9	98.3
4	UL	0.00	2.6	2.4	2.3	-----	-----	-----
		2.00	4.58	4.35	4.24	99.5	98.8	98.6
5	LL	0.00	2.3	1.8	2.1	-----	-----	-----
		2.00	4.29	3.68	4.05	99.7	96.8	98.7
6	ANUC	0.00	2.5	1.8	1.6	-----	-----	-----
		2.00	4.44	3.70	3.48	98.6	97.3	96.6
7	KD	0.00	1.3	1.1	1.2	-----	-----	-----
		2.00	3.28	3.05	3.14	99.3	98.3	98.12
8	Soil Samples	0.00	1.46	1.55	1.48	-----	-----	-----
		2.00	3.42	3.51	3.4	98.84	98.87	97.7

GI-Govindpura industrial area, MI- Mandideep Industrial area, SL- Shahpura Lake, UL- Upper Lake, LL- Lower lake, ANUC- Area Near Union Carbide, KD- Kolar Dam

VI. Applications of the method

6.1 Determination of arsenic in polluted water samples

Environmental exposure to arsenic has an important public health concern and is receiving increasing attention. However, there is a scarcity of data available on arsenic geochemistry in Bhopal city. In order to investigate the applicability of this procedure to water and soil samples, the recoveries of known amounts of arsenic added to water samples were examined by the proposed procedure.

The water samples were collected from different areas of Bhopal district in polyethylene bottles, which were filtered through whatmann 42 filter paper. The arsenic levels found (1.1–3.9 µg L⁻¹) showed that high concentration (more than permissible limit) of arsenic is not present in the investigating areas. Arsenic recovery was measured using a standard addition method. The results are given in Table 3, EDTA was used to eliminate the interferences. Recovery of arsenic varied from 96.6 to 99.7%. These results summarized in Table 3 demonstrate that the proposed procedure is applicable for arsenic analysis in different water samples and soil with a satisfactory recovery.

6.2 Determination of arsenic in soil samples

A known weight (1 g) of a soil sludge sample was placed in a 50 ml beaker and extracted 4 times with a 5 ml portion of concentrated HCl. The solution was evaporated at a low temperature (<100°) for about 30 minutes. Because of a possible presence of organically bound arsenic, a digestion step must be included to ensure conversion of total arsenic to an inorganic form. The solution was cooled and diluted to 25 ml volumetric flask with distilled water. Suitable aliquot of the sample was analyzed by the proposed method.

The proposed method is compared with other spectrophotometric methods in Table 4

Table 4: Comparison with other methods

S. no	Reagents/reference	λmax, nm	Range of determination, mg L ⁻¹	Remarks
1	Hexamethylene Ammonium-Hexamethylenedithiocarbamate [19]	256	0.2–1.0	Sensitive, simple, rapid; free from common interference
2	Silver diethyldithiocarbamate - Triton-X[20]	540	0.05–2.80	non-ionic surfactant required
3	Azure- B [21]	664	0.2-10	Less sensitive

4	Variamine blue[23]	556	0.2-14	Less sensitive
5	Rhodamine-B[24]	553	0.04-0.4	Based on bleaching of dye i.e. (indirect method)
6	Ammonium molybdate + sodiummetavanadate [29]	460	1-30	Phosphorus, silicon, interfere; less sensitive
7	Oleic acid surfactant [30]	435	0.25-20	Indirect reaction
8	2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) [31]	560	0.1 – 2.0	Complexing reagent was formed within reaction so it is time taking method.
9	Different hydroxamic acids: N-PBHA, N-p-CIPBHA and N-p-CIPCHA (Proposed method)	530 nm, 508 nm 520 nm	0.0003786-0.004164, 0.003786-0.06057, 0.003786-0.04921	Sensitive, simple, rapid; free from common interference, colour is stable for several days.

VII. Conclusions

The proposed procedure provides a selective, accurate and precise method for the determination of arsenic in environmental samples. This suggested method could be used for rapid and simple determination of As (III) in water samples. The results of analysis of samples are very close to those obtained by the other common methods. Our method has enormous practical potential for simple detection of arsenic, including field conditions which require no complex equipment or skilled laboratory support. As seen in figures this method based on using various hydroxamic acids are very suitable for the analysis of natural samples. These chelating agents have been used before to determine other metals with different methods but this is their first application to determine arsenic in environment of Bhopal district.

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