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Quantitative determination and development of sensing devices via a new reagent system for arsenic

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ABSTRACT

Determination of arsenic through a new reagent system has been described here. The method is based on reduction of sulfanilic acid by arsenic and subsequent coupling with N-(1-naphthyl) Ethylene diamine dihydrochloride (NEDA) in aqueous medium. The dye formed shows maximum absorbance at 550nm. The detection limit of arsenic is 0.015ppm, the method obeys Beer's Law in the range 0.1-0.6ppm. The molar absorptivity was found to be $2.53x10^4 Lmol^{-1}cm^{-1}$. Sandell's sensitivity, standard deviation and relative standard deviation were found $5.24x10^{-4}$, 0.023 and 1.48 % respectively. The method is free from most of the interferences. The method was successfully applied for the determination of arsenic in various environmental samples, plant, pharmaceutical tablet and biological samples. The method is utilized for developing sensing devices for detection of arsenic.

KEYWORDS

Sensing devices;
Determination;
Coupling;
NEDA;
Azo dye;
Analytical method.

INTRODUCTION

Arsenic occurs in the environment as a result of several inputs that contain it in organic and inorganic forms. Arsenic and its compounds are used in medicine, manufacture of glass, production of pigments, rodenticide, insecticide, fungicide, textile printing, tanning, taxidermy preservatives etc. Element and its compounds are reported to be carcinogenic, mutagenic and teratogenic in nature. Peoples having arsenical skin manifestations and drinking contaminated water have high levels of arsenic in hair, nail, urine, and skin scales causing melanosis, leucomelanosis, keratosis, non pitting swelling, gangrene etc. Its chronic contamination leads to skin cancer and cancer of bladder and lungs. The TLV for arsenic by ACGIH is $0.5mg^{-3}$[1-3].

Various methods for the analysis of arsenic have been reported. Analytical techniques based on FIA with hydride generation AAS, GF-AAS, ICP-AES, XRF; AFS and spectrophotometry etc. are available[4-12]. GF-AAS is not too selective and is time consuming. The AAS methods are characterized by high efficiency, low sample volume, reagent consumption and improved tolerance to interferences[4-6]. Instrumental methods are costly and require trained staff.

The present work aims to develop a rapid, low cost, accurate, sensitive and simple analytical method for the determination of arsenic and development of sensing devices using the same method for on spot detection of arsenic. The method is based on reduction of sulfanilic acid by arsenic and subsequent coupling with NEDA in aqueous medium. The magenta colored dye is formed which shows maximum absorbance at 550 nm Figure 1. The method is sufficiently selective as compared to other method, very rapid and low cost.

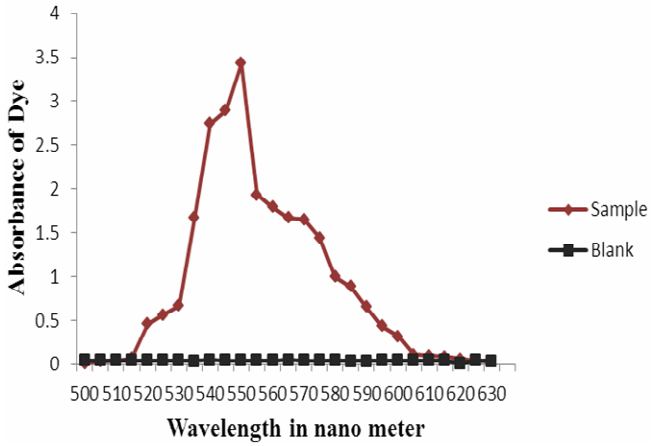

Figure 1 : Spectra of Dye with respect to blank.

EXPERIMENTAL

Apparatus

All spectral measurements have been carried on digital UV-VISIBLE Spectrophotometer 2201.

Reagents

All reagents used were analytical grade chemicals. Double distilled water is used throughout the experiment.

Arsenic solution: 1000 µg/ml stock solution of Arsenic was prepared by dissolving 264 mg of As_2O_3 in 100 ml of 5% concentrated HCl. 1 µg mL^{-1} (1ppm) working standard was prepared by appropriate dilution of stock daily.

Sulfanilic acid (SA): 1% Sulfanilic acid was prepared by dissolving 1g SA in hot water.

N-(1-naphthyl) Ethylene diamine dihydrochloride (NEDA): 1% NEDA was prepared by dissolving 1g NEDA in 2ml HCl and then made up to 100 ml by distilled water.

Procedure

1-3 ml of sample is taken in 10 ml graduated tube; 2.5 ml of 1% Sulfanilic acid were added to it. The solutions are shaken and kept for few seconds, then, 1ml of 1% NEDA are added and diluted to 10 ml by water & the absorbance is measured at 550 nm. The reagent blank prepared in the same fashion shows negligible absorbance at 550 nm Figure 1.

Reaction mechanism: The color reaction for the proposed system is based on reducing property of As (III) which reduces sulfanilic acid and subsequent coupling takes between NEDA & reduced SA, thus forming a stable magenta dye.

RESULTS AND DISCUSSION

Spectral characteristics

The magenta colored dye formed exhibit maximum absorbance at 550nm. Reagent blank shows negligible absorbance in this range.

Reaction conditions

Temperature: The reaction was studied for 0^0C-100^0C for 1µg mL^{-1} of arsenic. Absorbance decreases below room temperature & no remarkable change is observed above the room temperature (Figure 2), thus reaction is carried out at room temperature. The dye was found stable for more than 2 days.

Time: Absorbance was measured instantly and at

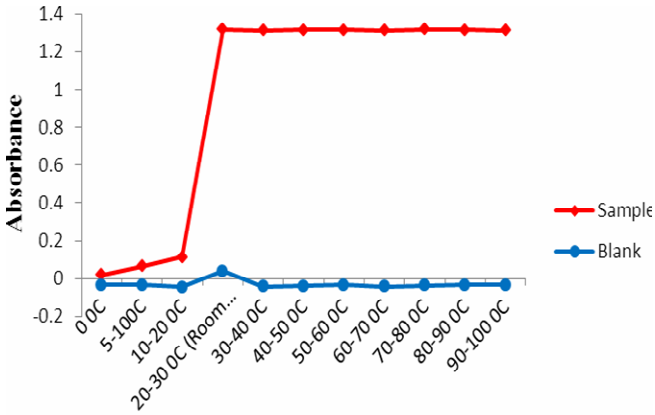

Figure 2 : Effect of temperature on absorbance of dye.

intervals of 5 minutes, 10 minute, 15 minute, 20 minute and 25 minute for 1 µg mL^{-1} of arsenic. It was found that full color development of dye re-

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quires minimum 5 minute and reaches maximum after 10 minute then decreases continuously after 15 minute. Thus 10-15 minute time was found optimum Figure 3.

Reagent concentrations : 2.5 ml of 1% Sulfanilic acid (SA) and 1 ml of 1% NEDA were found optimum when reaction was studied for 1-6 ml of each reagent.

Effect of Co-pollutants: The method has been

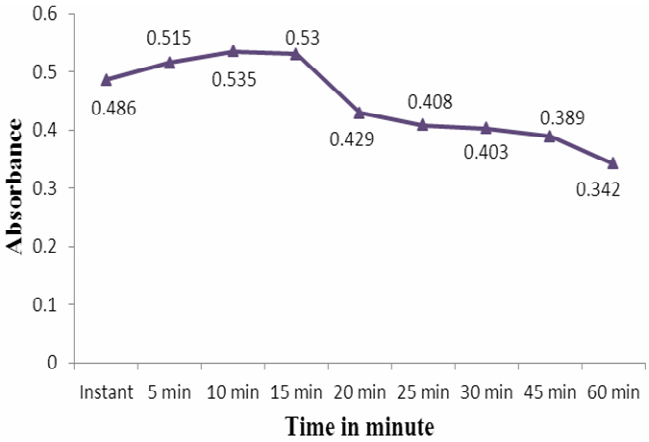

Figure 3 : Effect of time on absorbance of dye.

checked for its validity in presence of various co-pollutants and other foreign species for 1µg mL^{-1} of arsenic. Nitrite may interfere; hence, its interference is masked by addition of sulphamic acid prior to analysis. The method was found to be free from most of the co-pollutants. The results obtained were given in TABLE 1.

TABLE 1 : Concentration of Interfering Ions in (µg mL^{-1})

S.No.	Interfering ions (co-pollutant species)	Tolerance limit (µg mL^{-1})
1	K^+, Cr^+	6×10^5
2	Mn^{++}, Ca^{++}, Mg^{++}, Na^+ ,Cl^- , $CO3^{--}$	2×10^5
3	Al^{+++}	1×10^5
4	NH_3	2.5×10^5
5	Zn^{++}	2×10^5
6	Fe^{+++}, NH_4^+ , SO_4^{--}	5×10^5
7	Cu^{++}	6×10^6
8	Hydrazine	1×10^3
9	Se^{+++}	1×10^2

Application

Tube well water: Water samples were collected from tube wells (bore wells) in polyethylene bottles pre-washed with nitric acid-water (1+1) and after collection ascorbic acid (100 mg mL^{-1}) was added as a preservative. After filtration the samples were analyzed as described above and shown in TABLE 2. To check the validity of the method, a known amount of samples were added to arsenic free tap water. The recoveries were found to be 93.1-94.4% (TABLE 2).

Spinach leaves: Samples were collected from agriculture fields and about 1 g of sample was placed in a Kjeldahl's flask and 10 ml each of nitric acid and sulphuric acid were added and heated to 80-100^{0}C for 20 min. Then the solution was allowed to cool. 10 ml perchloric acid was added and again heated for 5 min. until dense fumes of sulphur dioxide appeared. The sample was cooled and 1 ml of HCl was added to complex heavy metal ions and reduce inter element interferences. The solution was heated for 15 min at near boiling and then allowed to cool to room temperature. The residue was washed with water and transferred to 25 ml volumetric flask and diluted to volume with water[13]. Aliquots were analyzed with proposed method (TABLE 2).

Urine: Arsenic is reported to be present in urine [1]. Several urine samples have been tested for arsenic but were found negative. Therefore, to check the validity of method, synthetic samples were prepared by adding known amount of arsenic to urine. Deprotienization of samples has been done with TCA as recommended and then analyzed by proposed procedure (TABLE 2).

Hair and nails: Hair samples mainly close to scalp were collected by using a ceramic blade cutter. The samples were spiked with arsenic. The samples were first washed with distilled water then deionized water and finally with acetone, as recommended by the International Atomic Energy [14]. The samples were dried in an oven at 50-60^{0}C temperature. Thereafter, 0.5-1.0 g of hair and nail samples were placed in a test tube and 3.0 mL of concentrated HNO_3 was added, the lid was closed and heated on a hot plate at 90-100^{0}C for 5 min, then heating was discontinued and the samples were allowed to stand overnight. Next morning the lid was opened and 1.0 mL of concentrated HNO_3 was added and evaporated at about 100^{0}C until 1 mL of solution is left. The sample is cooled and diluted to 5 mL and analyzed by proposed method (TABLE 2).

Detection and semi quantitative determination in water: The test papers had also been success-

fully used for water to detect minimum 0.125 µg arsenic. Semi quantitative determination had been done by comparing the color with standard samples prepared.

Indicator plates: Detection and semi quantitative determination of arsenic in water has been done using above method. Simple glass plates of size (2 x 6 cm) having uniform thickness were taken and a slurry of silica was pasted of about 1mm thickness. After drying the plate in oven at 100^0C for an hour it was impregnated with SA, dried at 40^0C-60^0C, finally impregnated with NEDA and again dried at the same temperature. These indicator plates were found to be stable for about10 days if kept in a well stoppered bottle. A single drop of water containing arsenic will indicate its presence on these plates in form of magenta color appearance. Minimum 0.1 µg of arsenic can be detected using these plates.

TABLE 2 : Determination of Arsenic in Environmental Samples.

Sample Mass/volume	Arsenic initially found*(µg)	Arsenic added (µg)	Arsenic Total found*(µg)	% Recovery
1.Water				
A. Ground Water[a]	0.51	1	1.44	95.36
	0.48	2	2.36	95.16
	0.53	3	3.2	90.65
B. Tap Water[b]	0.46	1	1.40	95.8
	Nil	1	0.95	95
	Nil	2	1.98	98
	Nil	3	2.8	93.3
2. Spinach Leaves[c]	0.8	1	1.7	94.4
	0.73	2	2.53	92.6
	0.76	3	2.57	93.1
3. Urine[c]	-	1	0.948	94.8
		2	1.96	98.0
		3	2.85	95.0
4. Nail[c]	-	1	0.957	95.7
		2	1.936	96.8
		3	2.87	95.6
5. Hair[c]	-	1	0.954	95.4
		2	1.886	94.3
		3	2.829	94.0

***Mean of three replicate analysis. [a,b] = 5 mL after treatment described in procedure section.**
[c] = 5 g, 2 mL aliquot of sample was analyzed, after treatment described in procedure.

CONCLUSION

The proposed method is cheap, rapid; environment friendly, sensitive and easily employable as compared with the methods based on same principle and can detect arsenic within its toxic limit (TABLE 3). Moreover, the indicator plates and strips developed can serve as an efficient and fast analytical tool for on spot and emergency detection of arsenic in various samples; hence the method is of commercial applicability.

TABLE 3 : Comparison with other methods.

S.no.	Reagent/Ref.	λmax (nm)	Range of determination (ppm)	Remarks
1	Ammonium molybdate + SDHA [15]	780	0.02-0.14	Phosophorus interferes, extraction required, time consuming
2	LCV [16]	592	0.004-0.04	Highly dependent on pH
3	Rhodamine B [17]	553	0.04-0.4	Sensitive but highly pH dependent
4	Variamine blue [18]	556	0.2-14	Less sensitive
5	Toludine blue [19]	628	1.2-10.5	Less sensitive
6	Safranine O [19]	532	0.4-11.5	Less sensitive
7	SA+NEDA [proposed]	550	0.1-0.6	Sensitive, rapid, low cost

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