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Applicability of phenylpiperazine dithiocarbamate in the determination of As(III) in natural water and biological samples by differential pulse anodic stripping voltammetry

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Abstract

A simple and rapid differential pulse anodic stripping voltammetric method was developed for the determination of As(III) in natural water and biological samples. As(III) was accumulated onto hanging mercury drop electrode using phenylpiperazine dithiocarbamate as selective complexing agent. The effects of various parameters, such as reagent concentration, effect of the pH of the medium, accumulation potential, accumulation time and the scan rate were investigated. Under the optimum conditions, a linear calibration graph was obtained in the concentration range of 0.05 to 60 μg mL^{-1} with a correlation coefficient of 0.9998 and detection limit of 0.024 μg mL^{-1}. The effects of interference ions were studied and it was found that the method was free from the interferences of some common cations. The proposed method was applied for the determination of As(III) in natural water and biological samples and the results according to the *t*-test and *f*-test for a 95% confidence level with a relative standard deviation lower than 2.7% showed good agreement with the reported methods.

Keywords: DPASV; As(III); Phenylpiperazine dithiocarbamate; Water and biological samples.

1. Introduction

Arsenic is the 20th most abundant element found in the earth's crust. It is a naturally occurring toxic and carcinogenic element. Arsenic containing pesticides and other agricultural products can lead to the accumulation of arsenic compounds in soils and plants and result in traceable amounts of arsenic in food and feedstuffs [1]. Its toxicological, physiological and geochemical behavior depends on its oxidation state. In general, inorganic arsenic is the more toxic than its organic forms and is readily absorbed in the animal and human body [2, 3] Living organisms are exposed to the toxic arsenic primarily through food and water. Exposure to arsenic can have a variety of adverse effects on health such as causing, dermal changes, respiratory, cardiovascular, gastrointestinal problems besides being geno-oxic, mutagenic and carcinogenic [4].

Arsenic can be determined by various analytical techniques such as atomic absorption spectrometry [5], graphite-furnace atomic absorption spectrometry (GFAAS), hydride generation atomic absorption spectrometry (HGAAS), inductively coupled plasma atomic emission

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spectrometry (ICP-AES) [6, 7], Mass spectrometer can also be used as a detector, coupled to plasma source (ICP-MS) [8] and neutron activation analysis [9]. These analytical techniques are expensive and need sophisticated instrumentation. Electroanalytical techniques on the other hand offer more economical approach.

There are several accepted analytical methods currently available for arsenic measurement in various samples such as polluted water [10, 11], beet sugar [12], natural waters [13, 14], bovine liver [14], biological digestion [15] and plant material [16]. However, in recent years the differential pulse anodic stripping voltammetry (DPASV) has attracted considerable attention for providing excellent sensitivity and good accuracy and precision [17-21].

In this work, a simple and selective differential pulse anodic stripping voltammetric procedure was developed for the determination of As(III) in water and biological samples using phenylpiperazine dithiocarbamate as complexing agent. A standard addition method was used in order to accounting for matrix interferences. The method was validated using biological CRM and the results were compared with those obtained from reported methods. The method, which is reasonably sensitive and selective, has been successfully applied in the determination of trace amount of As(III) in natural water and biological samples.

2. Experimental

2.1. Reagents and Solutions

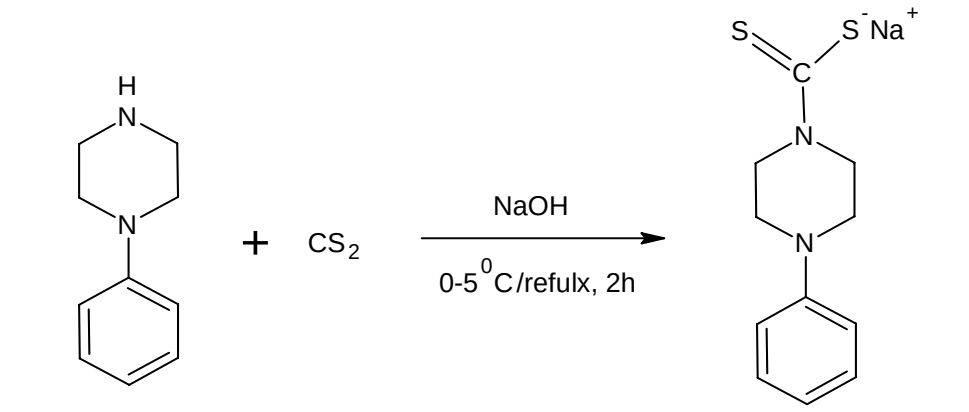
Triple distilled water and high-purity reagents were used throughout the experimental work. All chemicals were purchased from Merck chemicals, Mumbai, India. The 1.0×10^{-3} mol L^{-1} aliquot solution of phenylpiperazine dithiocarbamate was made by dissolving 0.0219 g of ligand in 100 mL of deionised triple distilled water in a volumetric flask. The buffer solution was prepared by mixing the appropriate ratios of 0.5 mol L^{-1} CH_3COOH and 0.5 mol L^{-1} CH_3COONa. The 1000 μg mL^{-1} of As(III) stock solution was prepared by dissolving 0.1320 g of arsenic trioxide in 1.0 mL of 25% NaOH, then acidified immediately with 2 mL of concentrated HCl and diluted to 100 mL with MilliQ water. The working standards were achieved by successive dilution of the stock solution as required.

2.2. Apparatus

The measurements were taken using an Elico Model CL-362 polarographic analyzer. A conventional three electrode system consisting of a HMDE as the working electrode, an Ag/AgCl reference electrode and platinum counter electrode were used in all the experiments. It was outfitted with a Model EPSON LX-300^+ X–Y recorder. Solutions were deoxygenated with high-purity nitrogen for 600 min prior to each experiment and all experiments were performed under a nitrogen atmosphere. An Elico Li-129 Model glass calomel combined-electrode was employed for measuring pH values.

2.3. Synthesis of Sodium salts of Phenylpiperazine dithiocarbamate

Stoichiometric amounts of the Phenylpiperazine (0.1 mol in 100 mL of diethyl ether), NaOH (0.1 mol in 100 mL of deionized water) and 0.1 mol in 100 mL of CS_2 were mixed, and refluxed for 2 hrs at 0-5 °C. After the separation of phases the water phase was taken and evaporated. The reaction product was checked by TLC and purified by recrystallisation and was washed with diethyl ether and dried at 80 °C as described in literature [22] and shown in Scheme.1.



1-phenylpiperazine phenylpiperazine dithiocarbamate

Scheme 1 Preparation of sodium salts of phenylpiperazine dithiocarbamate.

2.4. General procedure

All the containers and voltammetric cell were carefully cleaned subsequentially, first with detergent, then by rinsing with water and by soaking with 2.0M nitric acid and finally through rinsing with triple distilled water. The experiments were performed as follows; 10.0 mL of sodium acetate buffer solution (0.05 mol L^{-1}), pH=4.0, 2.0 mL of 0.2×10^{-3} mol L^{-1} phenylpiperazine dithiocarbamate solution, 6.0 µg mL^{-1} As(III) metal solution and 4.0 mL of 0.002% Triton X-100 were pipetted into the voltammetric cell and purged with nitrogen gas for 600 sec. After 80 sec of accumulation at – 0.60 V, the differential pulse anodic stripping voltammogram was recorded from –500 to –1600 mV with a potential scan rate of 12 mV sec^{-1} and pulse amplitude 50 mV. A blank solution without As(III) was used to obtain the blank current, aliquots of the As(III) standard solution were added into the cell and the voltammogram was also recorded. All data were obtained at room temperature 25-30 °C.

3. Results and Discussion

Fig. 1 shows differential pulse anodic stripping voltammogram of As(III)- phenylpiperazine dithiocarbamate of a blank solution. For the blank system, no current peak was observed between –500 and –1600 mV. The voltammogram of As(III) in presence of phenylpiperazine dithiocarbamate at pH 4.0 showed one stripping peak at about -640.0 mV. But, the peak current increased with the increasing arsenic concentration with limit of detection 0.028 µg mL^{-1}. The peak current increased with increasing accumulation time before the potential scan. In addition, the influence of scan rate shows that the peak currents decrease with potential scan rate from 12 to 30 mV sec^{-1}. These three phenomena, point out that the complex was strongly adsorbed on mercury electrode surface.

3.1. Effect of pH

It was found that a well-defined and sensitive anodic stripping peak current appeared at -0.60V when sodium acetate buffer was used as the supporting electrolyte. The effect of pH on the peak current was studied with 0.2×10^{-3} mol L^{-1} phenylpiperazine dithiocarbamate and 6.0 µg mL^{-1} of As(III) (Fig. 2). Variation of pH produced a maximum peak current obtained at pH 4.0. A substantial decrease in peak current was observed at higher pH values. This effect is due to the interaction of As(III) with hydroxyl ion. On the other hand, at low pH values (pH<4.0), As(III) does not completely complexed with phenylpiperazine dithiocarbamate. Therefore, the sodium acetate buffer with a pH of 4.0 was selected as the supporting electrolyte.

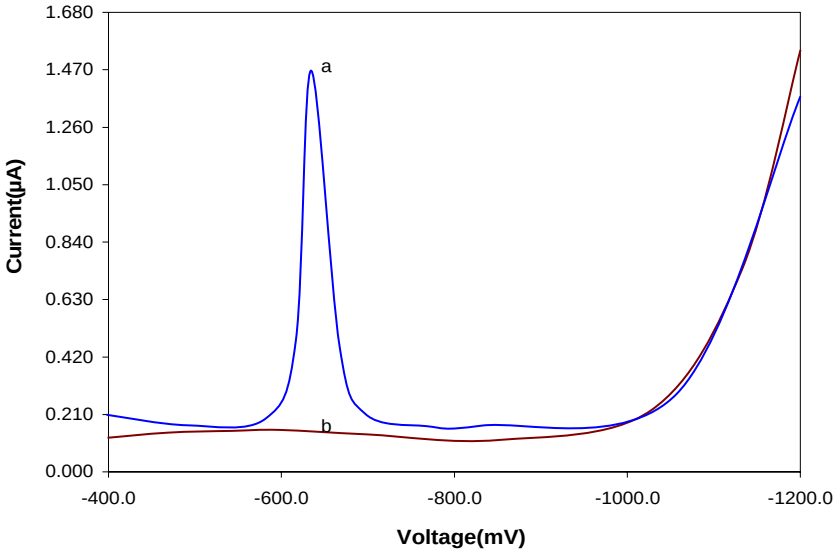


Fig. 1. Anodic stripping voltammogram of As(III) peak at -640.0 mV: (a) 0.2×10^{-3} mol L^{-1} of phenylpiperazine dithiocarbamate + 0.05 mol L^{-1} of sodium acetate buffer (pH 4.0) with experimental conditions(b) blank..

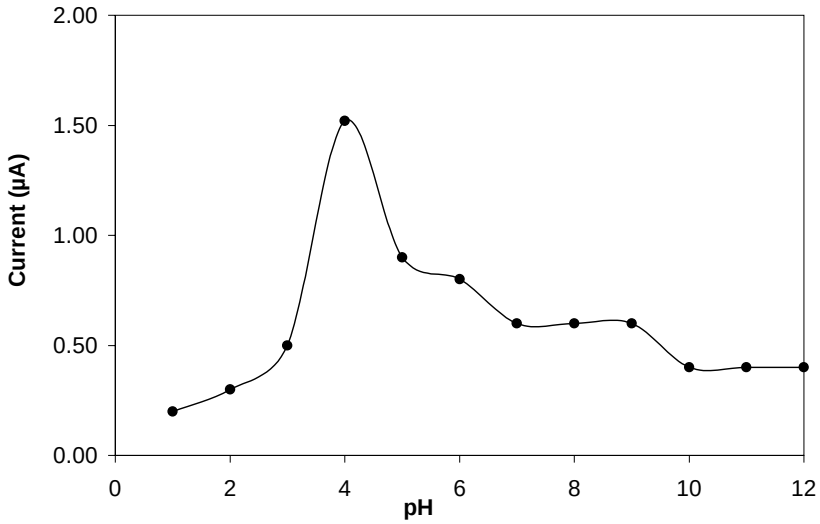


Fig. 2. Effect of pH on DPASV peak current of As(III); Conditions; 6.0 µg mL^{-1} of As(III) concentration, accumulation potential -0.64 V, sodium acetate buffer (pH 4.0); accumulation time 80 Sec.

3.2. Effect of reagent concentration

The effect of phenylpiperazine dithiocarbamate concentration on the peak current was studied at pH 4.0 and 6.0 µg mL^{-1} of As(III). Fig. 3 shows that by increasing the ligand concentration up to 0.2×10^{-3} mol L^{-1}, the peak current can be increased, where as greater amounts of the ligand concentration decrease the peak current. This effect may be due to the competitive adsorption of phenylpiperazine dithiocarbamate in HMDE. Thus, the 0.2×10^{-3} mol L^{-1} phenylpiperazine dithiocarbamate concentration was selected.

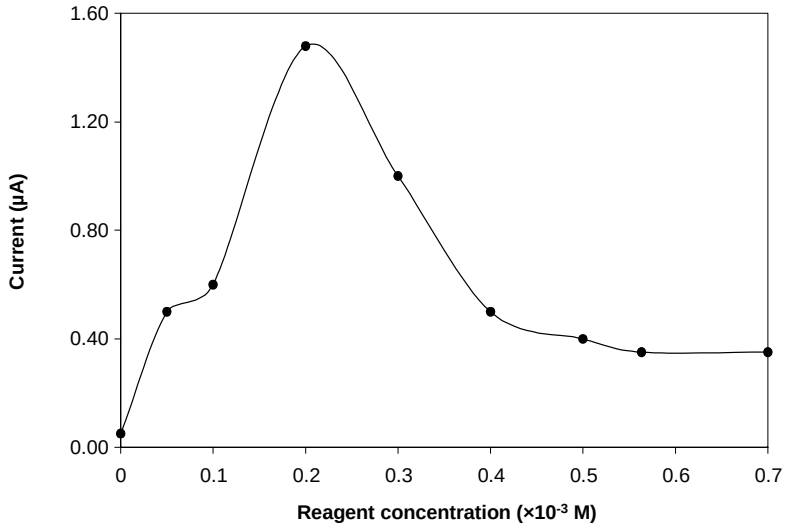


Fig. 3. Effect of the reagent concentration on DPASV peak current of As(III). Conditions; 6.0 µg mL^{-1} of As(III) concentration, scan rate 12 mVs^{-1}; accumulation potential -0.64 V, sodium acetate buffer (pH 4.0); accumulation time 80 Sec.

3.3. Effect of accumulation potential

The effect of accumulation potential on the stripping peak current of the complex was examined over the range -0.0 to 1.2 V. As illustrated in Fig. 4, the peak current increased gradually with a changing potential from -0.0 to -0.60 V, probably due to the increased accumulation of complex on the surface of the electrode. The peak current decreased at a potential more negative than -0.6 V. Therefore, -0.64 V was chosen as the optimum accumulation potential in our measurement.

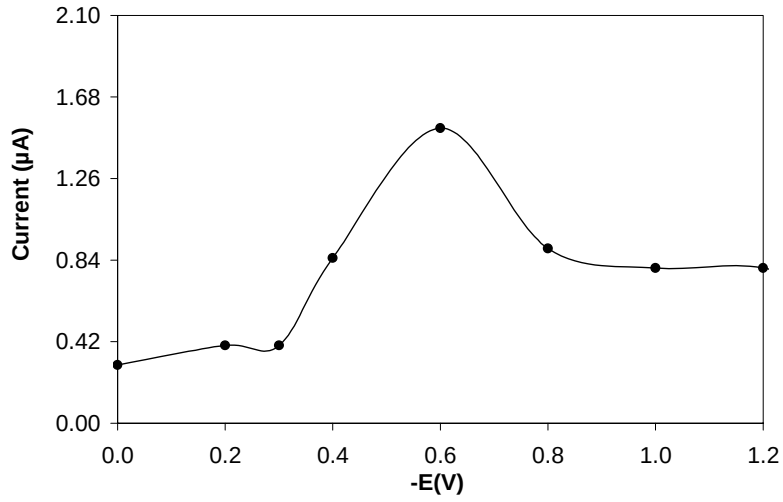


Fig. 4. Effect of accumulation potential on DPASV peak current of As(III). Conditions; 6.0 µg mL^{-1} of As(III) concentration, 0.2×10^{-3} mol L^{-1} of phenylpiperazine dithiocarbamate; scan rate 12 mVs^{-1}; sodium acetate buffer (pH 4.0); accumulation time 80 Sec.

3.4. Effect of accumulation time

The effect of accumulation time on peak current was also studied for the 6.0 µg mL^{-1} of As(III) and 0.2×10^{-3} mol L^{-1} phenylpiperazine dithiocarbamate solution with the other variables at the optimum conditions (Fig. 5). The results showed that the peak current increased with the increase in accumulation time of up to 80 sec. Therefore, 80sec was chosen as optimum accumulation time in our measurement.

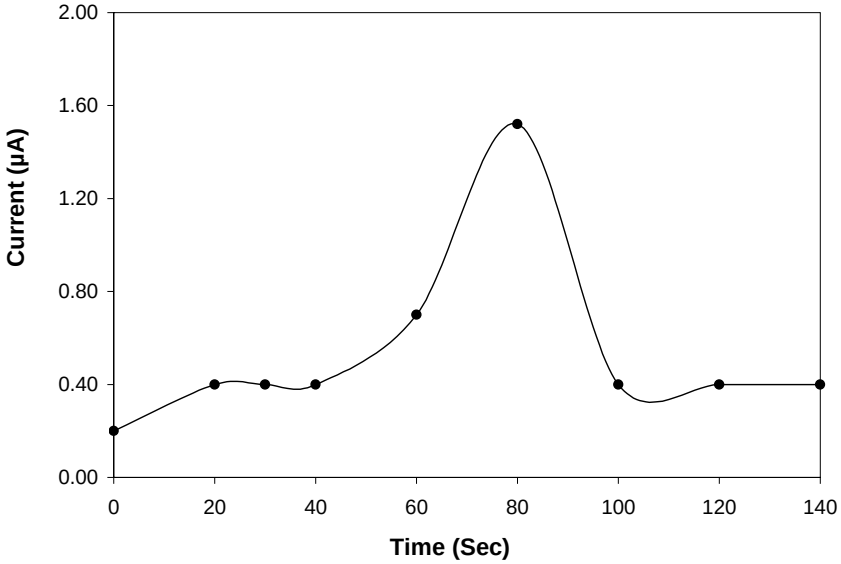


Fig. 5. Effect of accumulation time on DPASV peak current of As(III).Conditions; 6.0 µg mL^{-1} of As(III) concentration, 0.2×10^{-3} mol L^{-1} of phenylpiperazine dithiocarbamate;scan rate 12 mV s^{-1}; accumulation potential -0.64 V, sodium acetate buffer (pH 4.0).

3.5. Effect of scan rate

The effect of scan rate on the stripping peak current was examined. For this purpose, the stripping voltammograms were recorded for 6.0 µg mL^{-1} of As(III) and 0.2×10^{-3} mol L^{-1} phenylpiperazine dithiocarbamate solution with various scan rates of electrode potential, ranging between 4 and 18 mV sec^{-1} (Fig. 6).

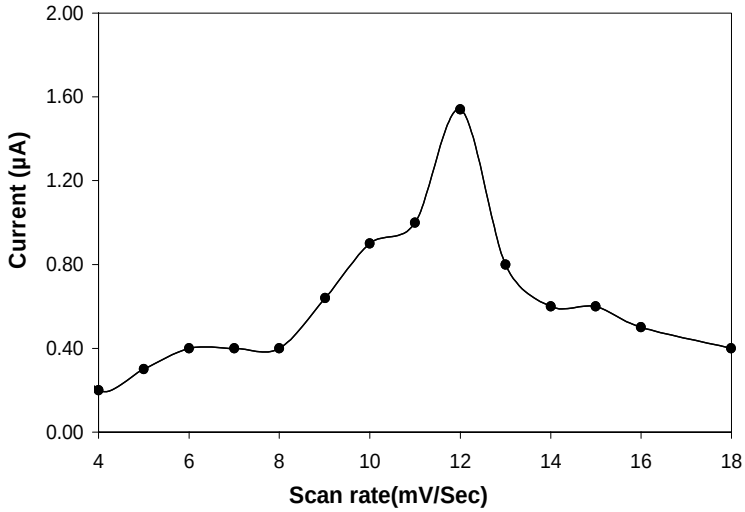


Fig. 6. Effect of scan rate on DPASV peak current of As(III); Conditions; 6.0 µg mL^{-1} of As(III) concentration, 0.2×10^{-3} mol L^{-1} of phenylpiperazine dithiocarbamate; accumulation potential -0.64 V, sodium acetate buffer (pH 4.0); accumulation time 80 Sec.

The peak current increased with increasing the scan rate, after that 12 mV/sec, the peak current decreased. For that reason, the maximum value for the analyte signal appeared at a scan rate of 12 mV sec^{-1}, so this scan rate was selected for further studies.

3.6. Effect of pulse amplitude

An increase in pulse amplitude leads to an increase in sensitivity but also a decrease in resolution. The experiment was conducted by varying the pulse amplitudes from 10 to 100 mV. Well defined peak was obtained at 50 mV of pulse amplitude; therefore, 50 mV was used in the present study.

3.7. Stirring speed of the solution

In order to increase the rate of deposition, the stirring of the solution during the deposition of analyte is required. To present an irregular and eddy diffusion of the analyte towards electrode, the optimization of stirring speed or rotational speed of mechanical stirrer is suggested. The plot of stirring peak current vs. $w^{1/2}$ is linear at the stirring speed range of 500-3000 rpm as indicated in Levich equation. However, by considering the stability of the hanging mercury drop electrode, a stirring speed of 2000 rpm may be found to the more suitable for this purpose.

3.8. Effect of Maximum Suppressor

To a solution containing 6.0 µg mL^{-1} of As(III), 0.2×10^{-3} mol L^{-1} phenylpiperazine dithiocarbamate, 0.05 mol L^{-1} of sodium acetate buffer at pH 4.0, scan rate 12 mV s^{-1}, drop time 0.5 sec, pulse amplitude 50 mV, gelatin in the range from 0.005 to 0.01% and Triton X-100 of 0.002 to 0.004 % were added and the effect was studied. It was found that the As(III) reduction peak of suppressed slightly when gelatin was added and the stripping peak reduced initially to about 10% and up to 0.005% and the decrease thereof was small above this concentration. The peak potential shifted towards the less negative potentials.

Triton X-100 has no effect on As(III) reduction as well as on the peak current and potential. But the presence of Triton X-100 improves the stripping peak currents to a well-defined and a symmetrical one with a clear base line. 0.002% Triton X-100 is, therefore, maintained for all studies.

3.9. Effect of foreign ions

The influence of various foreign species on the determination of 6.0 µg mL^{-1} arsenic was investigated. It was observed that Pb^{2+}, Al^{3+}, Zn^{2+}, Co^{2+}, Mg^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Ba^{2+}, Fe^{2+}, Fe^{3+}, Bi^{3+} did not interfere even when present 50 times in excess. Slight interference was observed from Cr^{6+} and V^{5+}. With increase in concentration of these ions, the peak current decreased. The peak current was found to reduce by about 15% when any of these ions were present 10 times in excess while about 60% reduction in peak current was observed when these ions were present 20 times in excess. This shows a fair degree of selectivity of the method.

3.10. Determination of arsenic in standard reference materials

A samples of 400 mg containing NIST SRM 1515 apple leaves, SRM 1570a spinach leaves, SRM 1573a tomato leaves, SRM 1547 peach leaves, GBW 07605 tea, was digested with 6.0mL of concentrated HNO_3 (65%) and 2.0 mL of concentration H_2O_2 (30%) in microwave system. After digestion, the volume of the sample was made upto 50mL with distilled water. Few drops of 10% KI were added to convert As (V) into As(III). The presence of any excess of iodine, indicated by light brown color was destroyed by adding few drops of ascorbic acid [23]. The

blanks were prepared in the same way as the sample, but omitting the sample. The procedures given above were applied to the samples and the results were summarized in Table 1.

Table 1
Determination of As(III) in certified reference materials.

Certified materials	Certified value ($\mu g\ g^{-1}$)	Found value ($\mu g\ g^{-1}$) [a]	Recovery (%)	RSD (%)
SRM 1570a Spinach leaves	0.068±0.012	0.069±0.001	101.40	1.4
SRM 1573a Tomato leaves	0.112±0.004	0.110±0.003	98.20	2.7
SRM 1547 Peach leaves	0.060±0.018	0.054±0.001	90.00	1.8
SRM 1515 Apple leaves	0.038±0.007	0.039±0.001	102.60	2.5
GBW 07605 Tea	0.28±0.014	0.28±0.002	100.00	0.7

[a] n=5 (Mean ± Standard deviation)

3.11. Determination of arsenic (III) in water samples

Natural water samples were collected around Tirupati and Nellore area. Tirupati is one of the well-known pilgrim centers in India and is generally known all over the world. Pollutants are mainly responsible for destroying the natural beauty of the holy town. Ultimately this rich pilgrim center was chosen as the collection area. The samples were collected from various places in and around Tirupati, A.P., India. The samples (150 mL) were stored at 0-5 °C in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper No.41 and clean solution was collected into a 250 mL beaker. The contents were diluted with deionised doubly distilled water up to the mark. Few drops of 10% KI were added to convert As (V) to As(III). The presence of any excess of iodine, indicated by light brown color was destroyed by adding few drops of ascorbic acid [23]. 20 mL of this solution was further diluted to get working solution for the determination of As(III) as described in the above procedure and the results were summarized in Table 2 and 3.

Table 2
Determination of As(III) in biological samples.

Samples	Present method			Reported method [25]		*t*-test	*F*-test
	Added ($\mu g\ mL^{-1}$)	Found ($\mu g\ mL^{-1}$) [a]	Recovery (%)	Found ($\mu g\ mL^{-1}$) [a]	Recovery (%)		
Serum	2.0	1.99±0.02	99.50	1.95±0.05	98.00	0.68	1.72
	4.0	4.01±0.05	100.2	3.85±0.03	96.30	0.88	2.25
	6.0	5.99±0.04	99.83	5.98±0.08	99.70	0.92	2.59
Urine	2.0	2.00±0.01	100.0	2.01±0.04	100.5	1.35	1.76
	4.0	3.99±0.02	99.75	3.93±0.06	98.30	0.57	1.42
	6.0	5.99±0.01	99.83	5.94±0.03	99.00	1.75	2.25
Hair	2.0	2.00±0.01	100.0	1.96±0.03	98.00	1.24	1.25
	3.0	2.98±0.03	99.33	2.99±0.03	99.70	0.89	1.74
	4.0	3.98±0.04	99.50	3.99±0.06	99.70	0.30	2.10

[a] n=5 (Mean ± Standard deviation).

3.12. Determination of arsenic in urine and serum

Arsenic was reported to be present in traceable amounts in normal urine and serum [24]. If a person was affected by arsenic poisoning, the amount of arsenic in urine and serum increases. To check the validity of the method, synthetic samples were prepared by adding known amounts of arsenic to serum and urine samples. The samples were deprotonised with trichloroacetic acid and filtered. Aliquots were then analyzed and checked for arsenic according to the described procedure and reported methods [25].

3.13. Determination of arsenic in hair

A bout 0.5 to 1.0 g of hair samples were placed in a tube containing 10 mL of nitric acid. The tube was closed and heated on a hot plate at 100 °C for 5 min. After 24 hrs the lid was opened and 1 mL of concentrated nitric acid was added and made to evaporate at 100 °C until 1 mL of solution remained. Few drops of 10 % KI were added to convert As (V) to As(III). The presence of any excess of iodine, indicated by light brown color was destroyed by adding few drops of ascorbic acid [23]. The sample was cooled, diluted to 5 mL and analysed according to the described procedure and the results are checked by reported method [25].

Table 3
Determination of As(III) in water samples.

Sample	Proposed method (μg mL^{-1})		
	Added	Found	Recovery (%) [a]
Sea water collected from Bay of Bengal, Sullor peta, Nellore district,	-	0.380	-
	0.20	0.579	99.50±0.004
	0.40	0.779	99.75±0.016
	0.80	1.178	99.75±0.020
River water collected from, Swarnamuki belt, Srikalahati,	-	0.640	-
	0.20	0.838	99.00±0.012
	0.40	1.038	99.50±0.030
	0.80	1.437	99.62±0.010
Tap water collected from S.V.U.College of Sciences, Tirupati	-	0.310	-
	0.20	0.506	98.00±0.013
	0.40	0.708	99.50±0.010
	0.80	1.110	100.00±0.015

[a] Mean standard deviation (n=5).

3.14. Analytical Parameters

At the optimum parameters and the experimental procedure described above, the stripping peak current and the As(III) concentration was examined. The peak current increases linearly from 0.05 to 60 μg mL^{-1} with ($y=0.0163x-0.0288$) $r=0.9998$ for n=5 (Fig. 7). The relative standard deviation for five replicate measurements of As(III) was 2.7 %. The detection limit was calculated as three times the standard deviation of the blank and was found to be 0.028 μg mL^{-1} of As(III).

The precision of the present method was evaluated by determining different concentrations of arsenic (n=5). The analytical result that must be evaluated with regard to the validity of the analytical method was tested by recovery studies and several standard reference materials NIST SRM 1515 apple leaves, SRM 1570a spinach leaves, SRM 1573a tomato leaves, SRM 1547 peach leaves and GBW 07605 tea, (Table 1).

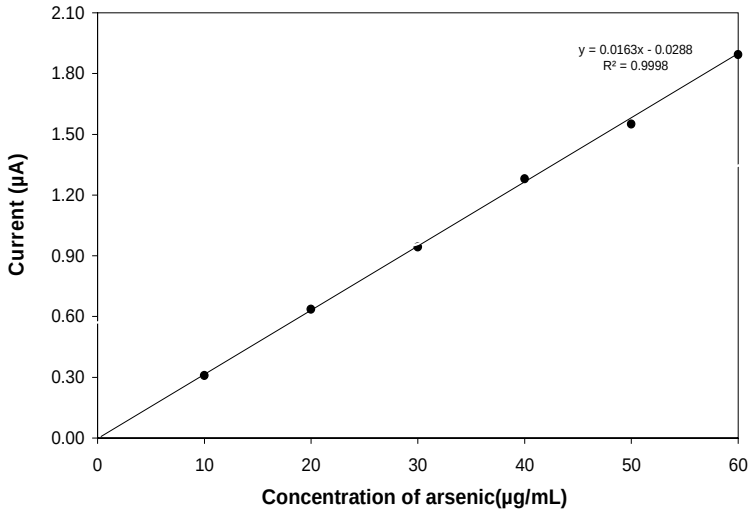


Fig. 7. Calibration plot for the DPASV determination of As(III). Conditions; 0.2×10^{-3} mol L^{-1} of phenylpiperazine dithiocarbamate; scan rate 12 mV s^{-1}; accumulation potential -0.64 V, sodium acetate buffer (pH 4.0); accumulation time 80 Sec.

A comparison of the results obtained both from the present method and the reported methods, varying natural water and biological samples is given in Tables 2 and 3.

4. Conclusion

The proposed differential pulse anodic stripping voltammeric method benefits from simplicity in performance and adequate accuracy and selectivity for the determination of arsenic in water and biological samples. It offers a very efficient procedure for speciation analysis. The statistical analysis shows that the data obtained from the proposed method are in good agreement with the reported methods. The low detection limit and the excellent selectivity show that this method is the most appropriate one for arsenic analysis in water and biological samples. It is an inexpensive, convenient and alternative to the very expensive techniques like AAS, ICP-AES and neutron activation analysis.

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