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Selective kinetic-spectrophotometric determination of trace amounts of As(III) based on an induction period

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Abstract

A new, selective, sensitive, and simple kinetic spectrophotometric method is proposed for the determination of As(III) in the presence of As(V) in alloys and water samples. This method is based upon the inhibiting effect of As(III) on the redox reaction between sodium periodate and meta-cresol purple (MCP) in acidic media. The reaction induction period is proportional to the concentration of As(III). The decolorization of MCP is used to monitor the reaction spectrophotometrically at 525 nm. As(III) can be determined in the range of 0.08–3.0 μg mL^{-1} under optimum conditions. The detection limit of the method with 3σ criteria is 0.08 μg mL^{-1}. The relative standard deviations for eight replicate determinations of 0.20, 0.60, and 0.80 μg mL^{-1} As(III) are 5.0%, 4.8%, and 1.9%, respectively. The recovery percentage ranges from 96.0% to 103.3%. The influence of various foreign species is also studied; As(V) does not interfere with the As(III) measurement even when present in1000-fold greater than As(III). This method can successfully be used to determine As(III) concentration in synthetic alloys and spiked water samples.

Keywords:

As(III); Meta-cresol purple (MCP); Induction period; Kinetic; Spectrophotometry

1. Introduction

Accurate determination of arsenic in environmental, biological, and food samples is of importance due to the toxicity of this element and its related compounds [1,2]. Arsenic is a ubiquitous element found in the environment and living organisms. It is mobilized though a combination of natural processes such as biological activities, weathering reactions, and volcanic emissions as well as through a range of anthropogenic activities namely, combustion of fossil fuels, wood preservation, mining activity, and use of arsenical pesticides among others [3,5].

Arsenic occurs naturally in several chemical forms. The toxicity of these various species varies widely [6]. In general, inorganic arsenic compounds are much more hazardous than organic ones. On the other hand, it has been reported that As(III) is 25-60 times more toxic than As(V), and several hundred times as toxic as organic arsenicals [7]. There is some evidence indicating that arsenic is also carcinogenic [8]. Arsenic contamination in natural water is a worldwide problem. Inorganic As(III) and As(V) have been distinguished as the dominant species in natural water with concentrations ranging from 0.02 to over 4000 μg L^{-1}, but methylated forms have also been found [9].

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With the exception of occupational exposure by inhalation, arsenic is generally introduced to the body through the ingestion of food and water. Ingestion of large doses leads to gastrointestinal cardiovascular and nervous system dysfunction and eventually death [9]. The human exposure to arsenic compounds can be estimated by determining their concentration in the urine [10]. For drinking water, the United States Public Health Service has recommended 10 μg L^{-1}, with a maximum permissible concentration of 50 μg L^{-1} [11]. Therefore, accurate, highly sensitive, rapid, and simple methods are required for the determination of trace amounts of As(III) in various samples. Different methods have been used for determination of arsenic. These include chemiluminescence [12,13], titrimetry [14], polarography and stripping voltammetry [15-20], chromatography [21], spectrophotometry [22-24], hydride generation atomic absorption spectrometry [25-27], hydride generation atomic fluorescence spectrometry [28,29], inductively coupled plasma atomic emission spectrometry [30], inductively coupled plasma mass spectrometry [31,32] and stripping potentiometry [33]. Some of these methods are either not sensitive enough or require complicated procedures and expensive instruments. Besides, most of these methods are essentially sensitive to total arsenic.

Using kinetic methods for the determination of trace amounts of arsenic are attractive alternatives. These techniques offer different advantages namely, high sensitivity, being simple, requiring inexpensive and simple apparatus, requiring low cost reagents, and having excellent selectivity, which allows diversifying the oxidation states of arsenic featuring different levels of toxicity. As(III) has been determined based on its accelerating effect on the Os(VIII)-catalyzed reaction between iodide and bromate in micellar media [34]. Stoytcheva et al. have determined As(III) based on its inhibition action on the enzyme acethylcholinesterase [35]. Afkhami et al. have determined As(III) based on its inhibition effect on the redox reaction between bromate and hydrochloric acid [36].

MCP is a dye that has been used in the past not only as an acid-base indicator but also as a reagent in the determination of nitrite, nitrate [37], bromide [38], and thiocyanate [39].

In the present report, a new, sensitive, and selective kinetic spectrophotometric method is proposed for the determination of As(III) based on the induction period associated with As(III) in the catalytic oxidation of MCP by periodate. As(III) acts as an inhibitor for the catalytic effect of bromide ion. The reaction induction period at 525 nm is proportional to the As(III) concentration.

2. Experimental

2.1. Reagents and chemicals

All chemicals used were of analytical reagent grade. All solutions were prepared with doubly distilled water. As(III) stock standard solution (1000 μg mL^{-1}) was prepared by dissolving 0.3290 g AS_2O_3 (Merck) in 50 ml of a 2 mol L^{-1} solution of sodium hydroxide (Merck) and diluting with doubly distilled water to the mark in a 250-mL volumetric flask. Working solutions were prepared by appropriately diluting the stock standard solution. A 100 mL potassium bromide solution (0.022 mol L^{-1}) was prepared by dissolving 0.0.2618 g of KBr (Merck) in distilled water and diluting to the mark in a 100-mL volumetric flask. A 2.6×10^{-4} mol L^{-1} solution of MCP was prepared directly by dissolving 0.010 g of MCP (Merck) in 20 mL ethanol and diluting with distilled water in a 100-mL volumetric flask. A 100-mL periodate solution (0.020 mol L^{-1} mol L^{-1}) was prepared by dissolving 0.4278 g of $NaIO_4$ (Merck). Diluted solutions were prepared by appropriately diluting the stock solution. Hydrochloric acid solution (1.0 mol L^{-1}) was prepared by diluting a known volume of concentrated solution (Merck), and was standardized against sodium carbonate.

2.2. Apparatus

For recording the UV-visible spectra and measuring the absorbance at a fixed wavelength, a Shimadzu UV-160 spectrophotometer with a 1.0-cm quartz cell pairs was used. A water bath thermostat (n-BIOTEK, INC, model NB-301) was employed to control the reaction temperature. A stopwatch was used for recording the reaction time.

2.3. Procedure

All solutions and doubly water were equilibrated at 20 °C in the thermostatic water bath for 30 min before the beginning of the reaction. The inhibited reaction was followed spectrophotometrically by monitoring the change in absorbance at 525 nm. A suitable aliquot of sample solution containing 0.8-30 μg As(III) was transferred into a 10-mL volumetric flask, and then, in sequence, 1.0 mL of MCP (2.6×10^{-4} mol L^{-1}), 1.0 mL of hydrochloric acid solution (1.0 mol L^{-1}), and 1.0 mL of potassium bromide solution (0.022 mol L^{-1}) were added. The mixture was diluted to the mark with doubly distilled water. Exactly 2.0 mL of this reaction mixture was transferred to a spectrophotometer cell, and then 100 μl of $NaIO_4$ solution (0.035 mol L^{-1}) was added to the cell using a calibrated micropipette. The stopwatch was started, and the solution in the cell was mixed within 10 s, and then absorbance change at 525 nm was recorded against water for the first 10-150 s from the beginning of the reaction. A blank solution (without arsenic) was prepared and measured in a similar way. Detailed operating conditions were summarized in Table 1. A calibration curve was constructed by plotting reaction induction period (t_{ip}) against As(III) concentration in a series of working standard solutions.

Table 1: Optimum conditions of the proposed method.

Parameter	Optimum condition
Hydrochloric acid concentration	0.10 mol L^{-1}
Sodium periodate concentration	3.5×10^{-3} mol L^{-1}
Potassium bromide concentration	2.2×10^{-3} mol L^{-1}
Meta-cresol purple concentration	2.6×10^{-5} mol L^{-1}
Temperature	20.0 °C

3. Results and discussion

At room temperature, the oxidation of MCP by sodium periodate in an acidic medium is slow. In the presence of bromide ion, the reaction rate increases due to the catalytic effect of bromide ion. Periodate ion is reduced by bromide ion to produce Br_2. The Br_2 thus produced reacts with MCP, decolorizing it. As a result, absorption of MCP at λ_{max}= 525 nm decreased with time (Fig 1a). In the presence of As(III), the reaction rate decreases due to fact that As(III) reacts with Br_2 and/or periodate, and/or inhibits the reaction between bromide and periodate[39], causing an induction period (Fig 1b). It was found that the induction period increases linearly with increase in the arsenic concentration (Fig 2). The induction period was used as an analytical signal in the determination of arsenic. The induction period was measured from absorption-time curves of the reaction mixture at λ_{max} = 525 nm by extrapolation of the linear parts of each graph.

3.1. Optimization of variables

Various experimental parameters were studied in order to obtain the optimized system. In order to find the optimum conditions, the effect of different parameters on the absorbance change of the catalyzed (ΔA_c) and inhibited (ΔA_i) reaction was studied during a fixed time of 10-150 s after the beginning of the reaction. The difference between absorbance changes of the catalyzed and inhibited reactions ($\Delta A = \Delta A_c - \Delta A_i$) was used as the analytical signal in the one-at-a time optimization procedure.

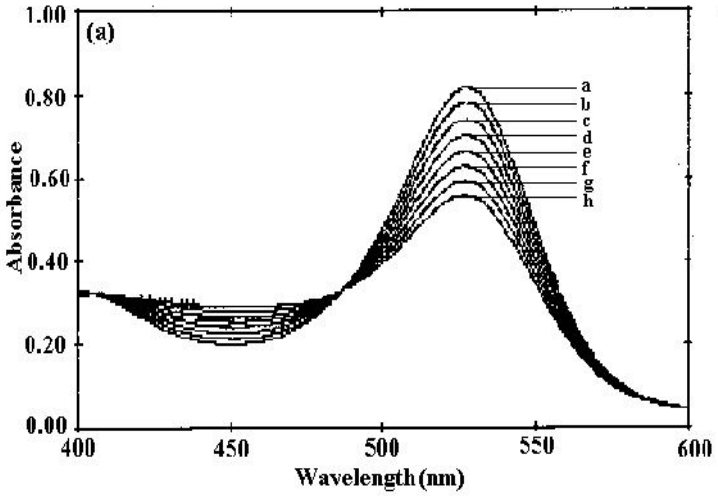

Fig 1a. Absorption spectra of reaction system in the absence of As(III). Conditions: HCl, 0.10 mol L^{-1}; MCP, 2.6×10^{-5} mol L^{-1}; NaIO4, 3.5×10^{-3} mol L^{-1}; KBr, 2.2×10^{-3} mol L^{-1} and temperature of 20.0 ^{o}C with scan time intervals of 15 s.

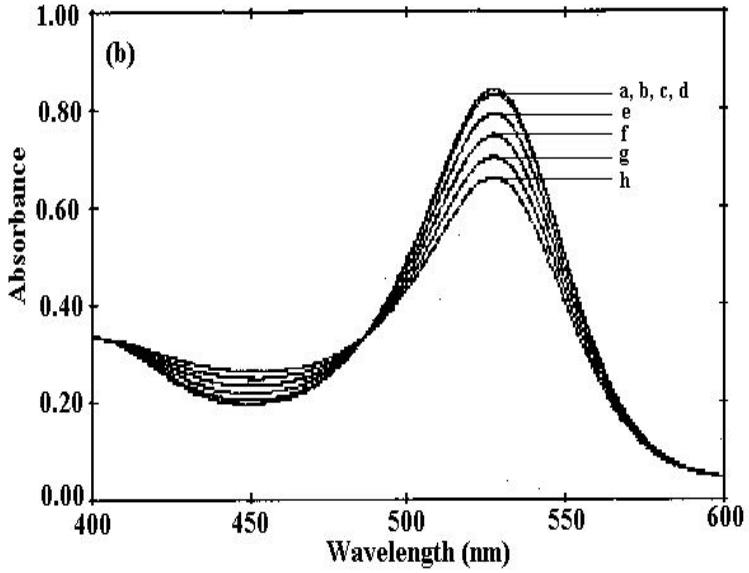

Fig 1b. Absorption spectra of reaction system in the presences of 1.0 μg mL^{-1} As(III). Conditions: same as Fig 1a.

Preliminary investigation showed that hydrochloric acid gives better sensitivity than sulfuric and nitric acid of the same concentration and therefore, hydrochloric acid was selected as the best reaction medium.

The effect of hydrochloric acid concentration on the sensitivity of the method was studied in the range of 0.020-0.12 mol L^{-1}. As Fig 3 shows, ΔA_i and ΔA_c increase with increase in the hydrochloric acid concentration due to the fact that with increase in the hydrochloric acid concentration, the oxidation ability of periodate increases. It can be seen that the analytical signal reaches a maximum value at 0.10 mol L^{-1} HCl. Therefore, the concentration of 0.10 mol L^{-1} HCl was selected as the optimum concentration.

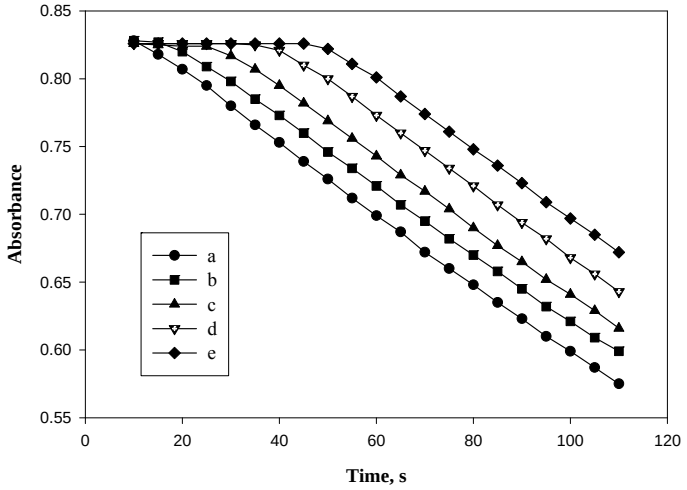

Fig 2. Absorbance change profile. Conditions: Same as Fig. 1a with As(III) concentrations of (a) 0.00, (b) 0.20, (c) 0.40, (d) 0.60 and (e) 0.80 μg mL^{-1}.

The dependence of sensitivity of the method on the sodium periodate concentration was studied in the range of 1.0×10^{-3} to 7.0×10^{-3} mol L^{-1}periodate. According to the results (Fig 4), ΔA_i and ΔA_c increase with increasing periodate concentration, due to increasing oxidation ability of periodate. Fig. 4 shows that the greatest difference (ΔA_c–ΔA_i) occurs at 3.5×10^{-3} mol L^{-1} and above this, decreases slightly. Thus this concentration was chosen for further work.

The effect of the potassium bromide concentration on the analytical signal is shown in Fig 5. This results show that with increasing bromide concentration, ΔA_c and ΔA_i increase due to the catalytic nature of the reaction in the presence of bromide ion as the catalyst. The difference between the absorbance changes of the catalyzed and inhibited reaction occurs at 2.2×10^{-3} mol L^{-1} of bromide. Therefore, 2.2×10^{-3} mol L^{-1} of KBr was chosen for the recommended procedure.

At the optimum conditions of HCl (1.0 mol L^{-1}), $NaIO_4$ (3.5×10^{-3} mol L^{-1}), and KBr (2.2×10^{-3}), at 20.0 ºC, the sensitivity increased as the concentration of MCP increased from 5.2×10^{-6} to 2.9×10^{-5} mol L^{-1} and then it remained constant. Thus MCP (2.6×10^{-5} mol L^{-1}) was chosen for further work.

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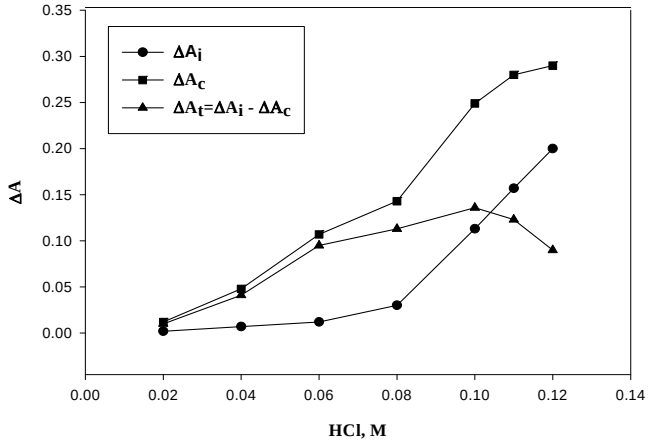

Fig 3. Effect of HCl concentration. Conditions: MCP, 2.6×10^{-5} mol L^{-1}; NaIO4, 2.5×10^{-3} mol L^{-1}; KBr, 2.00×10^{-3}; As(III), 1.0 μg mL^{-1} and temperature of 20.0 ºC.

The effect of temperature on the rates of the catalyzed and inhibited reactions was investigated in the range of 5.0–30.0 ºC. The results showed that the absorbance change for both reactions increases with increasing temperature. Thus 20.0 ºC was chosen and used throughout the study.

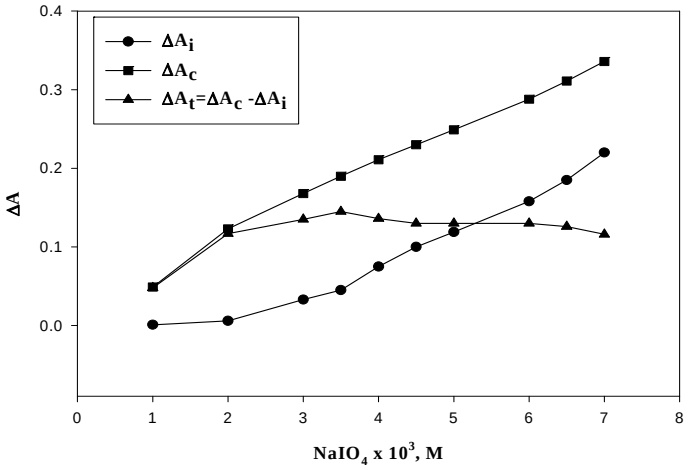

Fig 4. Effect of sodium periodate concentration. Conditions: HCl, 0.10 mol L^{-1}; MCP, 2.6×10^{-5} mol L^{-1}; KBr, 2.00×10^{-3} mol L^{-1}; As(III), 1.0 μg mL^{-1} and temperature of 20.0 ºC

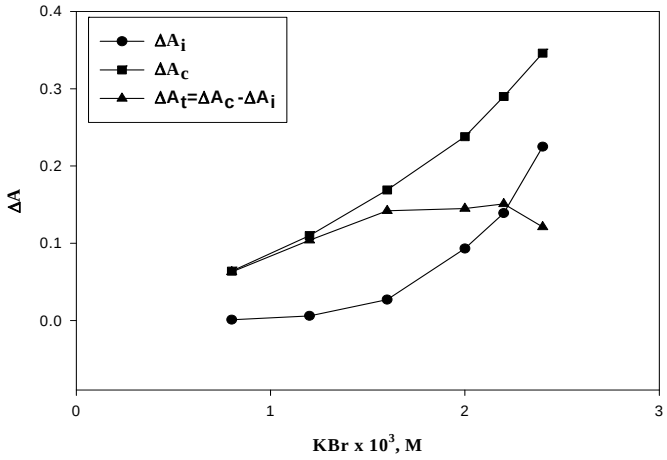

Fig 5. Effect of potassium bromide concentration. Conditions: HCl, 0.10 mol L^{-1}; MCP, 2.6×10^{-5} mol L^{-1}; $NaIO_4$, 3.5×10^{-3} mol L^{-1}; As(III), 1.0 μg mL^{-1} and temperature of 20.0 °C.

3.2. Selectivity

In order to investigate the selectivity of the proposed method, the effect of various species on the determination of 0.50 μg mL^{-1} As(III) was studied under the optimum conditions. The maximum tolerable concentration was taken as the concentration of a foreign species that produces a change in the induction period more than ±5%. The results are given in Table 2. This table shows that As(V) and most cations and anions did not interfere even when present in1000-fold greater than As(III). Therefore, this method has a good selectivity, and is suitable for distinction between the As(III) and As(V) species. Inhibitory effects of NO_2^- and I^- were observed; they could also inhibit the indicator reaction.

Table 2: Interferences for the determination of As(III) (0.50 μg mL^{-1}).

Foreign species	Tolerated ratio $W_{species}/W_{As}$
Na^+, K^+, NH_4^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Co^{2+}, Al^{3+}, Ni^{2+}, Li^+, Sr^{2+}, Mg^{2+}, SO_4^{2-}, Sn^{2+}, Zn^{2+}, Mn^{2+}, CH_3COO^-, CN^-, NO_3^-, F^-, As(V)	1000[a]
Al^{3+}	600
Fe^{3+}	100
Ag^+	20
NO_2^-	8
I^-	2

a) Maximum ratio tested

3.3. Analytical parameters

At the optimum conditions (Table 1) the calibration graph is linear in the ranges of 0.080-1.0 and 1.0-3.0 μg mL^{-1} with regression equations of t_{ip}= 49.2C_{As}+4.92 (r= 0.9980, n= 10), and t_{ip}= 10.05C_{As}+44.4 (r= 0.9996, n= 6), respectively; C_{As} is the As(III) concentration in μg mL^{-1} and t_{ip} is the reaction induction period in seconds.

In order to evaluate the precision and accuracy of the method, standard solutions of 0.20, 0.60, and 0.80 μg mL^{-1} of As(III) were analyzed using the recommended procedure. Eight replicate determinations of each concentration gave the relative standard deviations (RSDs) of 5.0%, 4.8%, and 1.9%, respectively. The 3σ experimental limit of detection was 0.080 μg mL^{-1}.

3.4. Analysis of real samples

To evaluate the analytical applicability of the method, it was applied to the determination of As(III) concentration in synthetic alloys and spiked water samples using the standard addition technique according to the procedure described in the experimental section. The results were tabulated in Table 3 and 4. The calculated recoveries of arsenic show that the proposed method is applicable and valid for analysis of real samples.

Table 3: Analysis of spiked water samples by the proposed method.

Sample	added (μg mL^{-1})	Found (μg mL^{-1})	Recovery (%)
Tap water	0.500	0.490 (±0.020)[a]	98.0
Tap water	0.300	0.310 (±0.011)	103.3
Mineral water	0.500	0.496 (±0.020)	99.2
Mineral water	0.200	0.192 (±0.009)	96.0
Spring water	-	< LOD	-
Spring water	0.200	0.194 (±0.008)	97.0
Spring water	0.600	0.613(±0.022)	102.2

a) ± Standard deviation (n= 6)

Table 4: Results for the determination of As(III) in the synthetic alloy samples.

Sample[a]	Found (%)[b]	Recovery (%)
Alloy (1)	0.103 (±0.004)	103.0
Alloy (2)	0.272 (±0.010)	98.9

a) The alloy composition (%):
Alloy (1): Cu(70.45), Sn(28.18), Sn(1.208), Pb(0.068), As(0.100).
Alloy (2): Pb(92.50), Sn(6.607), Cu(0.551), Cd(0.055), Zn(0.00551), Al(0.00551), As(0.275)
b)± Standard deviation (n= 6)

4. Conclusion

A new reaction system was suggested for the kinetic spectrophotometric determination of As(III) in alloys and water samples. This method offers several distinct advantages namely, high selectivity and sensitivity, requiring cheap reagents, simple and inexpensive instruments, ease of operation, and rapidity. The proposed method is suitable for distinction between the

As(III) and As(V) species. The validity and simplicity of this method allows the analysis of alloys and water samples with satisfactory results.

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References

1. Vandergrift G F, Reed D T and Tasker I R (1992) Environmental remediation removing organic and metal ion pollutants. American Chemical Society, Washington, DC, p 275.
2. Irgolic J K and Marttel A E (1985) Environmental Inorganic Chemistry. VCH, New York, p 654.
3. Smedley P L and Kinniburg D G (2002) Behavior and distribution of arsenic in natural waters. Appl Geochem 17: 517.
4. Gong Z, Lu X, Ma M, Watt C and Chrisle X (2002) Arsenic speciation analysis. Talanta 58: 77.
5. Mandal B K and Suzuki K T (2002) Arsenic round the world: a review. Talanta 58: 201.
6. Penrose W R (1974) Arsenic in the marine and aquatic environments: analysis, occurrence, and significance. Crit Rev Environ Contr 6: 1259.
7. Burguera M and Burguera J L (1997) Analytical methodology for speciation of arsenic in environmental and biological samples. Talanta 44: 1581.
8. Tamaki S and Frankenberger W T (1992) Environmental biochemistry of arsenic. Rev Environ Contam Toxicol 124: 79.
9. Cullen W R and Reimer K J (1989) Environmental arsenic chemistry. Chem Rev 89: 713.
10. Chatterjee A, Shibata Y, Yoshinaga J and Morita M (2000) Determination of arsenic compounds by high-performance liquid chromatography-ultrasonic nebulizer-high power nitrogen-microwave-induced plasma mass spectrometry: an accepted coupling. Anal Chem 72: 4402.
11. US public health service, Drinking water standards, US department of health, Education and welfare, Washington, DC (1962).
12. Sakai H, Fujiwara T and Kumamaru T (1994) Effect of arsenious and arsenic acids on the chemiluminescence of luminol in the absence of hydrogen peroxide and its analytical application. Bull Chem Soc Jpn 67: 2317.
13. Lomonte C, Currell M, Morrison R J S, McKelvie I D, and Kolev S D (2007) Sensitive and ultra-fast determination of arsenic(III) by gas-diffusion flow injection analysis with chemiluminescence detection. Anal Chim Acta 583: 72.
14. W. C. Purdy, E. A. Burns, L. B. Rogers, Sensitivity of Bromine-Bromide Potentiometric End Point. Anal Chem 27 (1955) 1988-1994.
15. Zima J and van den Berg C M G (1994) Determination of arsenic in sea water by cathodic stripping voltammetry in the presence of pyrrolidine dithiocarbamate. Anal Chim Acta 289: 291.

16. Sadana R S (1983) Determination of arsenic in the presence of copper by differential pulse cathodic stripping voltammetry at a hanging mercury drop electrode. Anal Chem 55: 304.
17. Viltchinskaia E A, Zeigman L L, Garcia D M and Santos P F (1997) Simultaneous determination of mercury and arsenic by anodic stripping voltammetry. Electroanalysis 9: 633.
18. Sun Y C, Mierzwa J and Yang M H (1997) New method of gold-film electrode preparation for anodic stripping voltammetric determination of arsenic (III and V) in seawater. Talanta 44: 1379.
19. Ferreira M A and Barros A A (2002) Determination of As(III) and arsenic(V) in natural waters by cathodic stripping voltammetry at a hanging mercury drop electrode. Anal Chim Acta 459: 151.
20. He Y, Zheng Y, Ramnaraine M and Locke D C (2004) Differential pulse cathodic stripping voltammetric speciation of trace level inorganic arsenic compounds in natural water samples. Anal Chim Acta 511: 55.
21. Chris Le X and Ma M (1998) Short-column liquid chromatography with hydride generation atomic fluorescence detection for the speciation of arsenic short-column liquid chromatography with hydride generation atomic fluorescence detection for the speciation of arsenic. Anal Chem 70: 1926.
22. Tamari Y, Yamamoto N, Tsuji H and Kusaka Y (1989) Thorium co-precipitation method for spectrophotometric determination of arsenic(III) and arsenic(V) in ground waters. Anal Sci 5: 481.
23. Cherian L, Raju and Gupta V K (1990) A simple extraction spectrophotometric method for the determination of arsenic in water and environmental samples. J Indian Chem Soc 67: 500.
24. Kolesnikova A M and Lazarev A I (1991) Spectrophotometric determination of arsenic in copper- and nickel-based alloys by using iodonitrotetrazolium. Zh Anal Khim 46: 169.
25. Geng W, Furuzono T, Nakajima T, Takanashi H and Ohki A (2010) Determination of total arsenic in coal and wood using oxygen flask combustion method followed by hydride generation atomic absorption spectrometry. J Hazard Mater 176: 356.
26. Nielsen S and Hansen E H (1997) Determination of As(III) and As(V) by flow injection-hydride generation atomic absorption spectrometry via on-line reduction of As(V) by KI. Anal Chim Acta 343: 5.
27. Näykki T, Perämäki P, Kujala J and Mikkonen A (2001) Optimization of a flow injection hydride generation atomic absorption spectrometric method for the determination of arsenic, antimony, and selenium in iron chloride/sulfate-based water treatment chemical. Anal Chim Acta 439: 229.
28. Leal L O, Semenova N V, Forteza R and Cerda V (2004) Determination of As(III) and As(V) in soils using sequential extraction combined with flow injection hydride generation atomic fluorescence detection. Talanta 64: 1335.
29. Karadjova I B, Lampugnani L, Onor M, D'Ulivo A and Tsalev D L (2005) Continuous flow hydride generation-atomic fluorescence spectrometric determination and speciation of arsenic in wine. Spectrochimica Acta Part B 60: 816.

30. de Oliveira E, McLaren J W and Berman S S (1983) Simultaneous determination of arsenic, antimony, and selenium in marine samples by inductively coupled plasma atomic emission spectrometry. Anal Chem 55: 2047.

31. Wang J, Tomlinson M J and Caruso J A (1995) Extraction of trace elements in coal fly ash and subsequent speciation by high-performance liquid chromatography with inductively coupled plasma mass spectrometry. J. Anal. At. Spetrom 10: 601.

32. Entwisle J and Hearn R (2006) Development of an accurate procedure for the determination of arsenic in fish tissues of marine origin by inductively coupled plasma mass spectrometry. Spectrochimica Acta Part B 61: 438.

33. Munoz E and Palmero S (2005) Analysis and speciation of arsenic by stripping potentiometry: a review. Talanta 65: 613.

34. Sicilia D, Rubio S and Perez-Bendito D (1992) Indirect kinetic determination of As(III) based on its accelerating effect on the Os(VIII)-catalyzed reaction between iodide and bromate in a micellar medium. J Anal Chem 342: 327.

35. Stoytcheva M, Sharkova V and Panayotova M (1998) Electrochemical approach in studying the inhibition of acetylcholinesterase by arsenate(III): analytical characterization and application for arsenic determination. Anal Chim Acta 364: 195.

36. Afkhami A, Madrakian T and Afshar Assl A (2001) Kinetic-spectrophotometric determination of trace amounts of As(III) based on its inhibitory effect on the redox reaction between bromate and hydrochloric acid. Talanta 55: 55.

37. Ensafi A A, Rezaei B and Nouroozi S (2004) Simultaneous spectrophotometric determination of nitrite and nitrate by flow injection analysis. Anal Sci 20: 1749.

38. Ensafi A A, Rezaei B and Nouroozi S (2004) Highly selective spectrophotometric flow-injection determination of trace amounts of bromide by catalytic effect on the oxidation of *m*-cresolsulfonephthalein by periodate. Spectrochim Acta Part A 60: 2053.

39. Arab Chamjangali M, Bagherian G and Salek-Gilani N (2007) Determination of trace amounts of thiocyanate by a new kinetic procedure based on an induction period. Spectrochimica Acta Part A 67: 1252.