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DETERMINATION OF ARSENIC (III AND V) BY ANODIC STRIPPING VOLTAMMETRY ON GOLD FILM ELECTRODE

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ABSTRACT

The method of determination of As^{III} and As^{V} by differential pulse anodic stripping voltammetry (DP-ASV) using glassy carbon rotating disk electrode pre-plated with gold film was described. Influences of factors on sensitivity and precision such as concentration of supporting solution, deposition time and potential, electrode rotating rate and potential scan rate...were investigated. Electroinactive As^{V} was reduced to As^{III} by iodide (KI) in HCl solution prior to DP-ASV determination. The concentration of KI and HCl was studied. For a deposition time of 120 s the detection limit of the determination was approximately 1.2 ppb (≈ 16 nM). Reproducibility of the method was good (RSD = 2.1% ($n = 18$) at 3.7 ppb As^{III}). Linearity was good in the range of 4 – 75 ppb ($R = 0.999$). Influence of interferences (Cu^{II} , Pb^{II}) was assessed.

Keywords: Anodic stripping voltammetry; Arsenic; Gold film.

Introduction

The adverse impact of arsenic (As^{III} and As^{V}) to public health is of much concern (Smith et al., 2000). Since the toxicological, physiological, and geochemical properties of arsenic depends on its states, the speciation of arsenic in environmental samples is of considerable interest. Because the concentration of arsenic in natural waters is at the level of ppb or sub-ppb, it is essential to develop sensitive and reliable methods to determine not only trace-to-ultratrace levels of arsenic but also their respective speciation.

Atomic absorption spectrometry in combination with hydride generation techniques and inductive-coupled plasma emission spectrometry have been widely used for determination of trace arsenic (Fresenius et al., 1988; Gomez-Ariza et al., 2000; Yan et al., 1998). Since high analysis costs and instrumental complexity for the spectrometry may restrict their use in not-well-equipped laboratories. On the contrary, electrochemical methods have relative simple instrumentation and costs far less than that required for spectrometry. In addition, the electrochemical analysis, typically stripping voltammetry, not only attain a great sensitivity but also can distinguish between the different oxidation states of arsenic. Arsenic determinations have been carried out by cathodic stripping voltammetry (CSV) (Adeloju et al., 1999; Feeney and Kounaves, 2000; Greulich and Henze, 1995; Li and Smart, 1996; Locatelli and Torsi, 2000) and anodic stripping voltammetry (ASV) (Forsberg et al., 1975; Bodewig et al., 1982; Sun et al., 1997; Kopanica and Novotny, 1998; Gründler and Flechsig, 1998; Huang and Dasgupta, 1999). The application of differential pulse cathodic/anodic stripping voltammetry (DP-CSV/ DP-ASV) enhance sensitivity and precision of trace arsenic determinations in various matrices. Electroinactive As^{V} was determined by its reduction to As^{III} with a reductant in acid media and then CSV/ASV measurement of electroactive As^{III} . Common reductants used were SO_2 (Sun et al., 1997; Bodewig et al., 1982), Na_2SO_3 (Forsberg et al., 1975), NaHSO_3 (Huang and Dasgupta, 1999) and in some case, L – cysteine (Adeloju et al., 1999) and mannitol (Greulich and Henze, 1995) were also used.

In CSV application for arsenic analysis, mercury electrodes are widely used, namely hanging mercury drop electrode (Greulich and Henze, 1995; Li and Smart, 1996), static mercury drop electrode (Locatelli and Torsi, 2000), and mercury film electrode (Adeloju et al., 1999). Meanwhile, gold electrodes are usually used in ASV determination of arsenic, including gold disk electrode (Forsberg et al., 1975; Bodewig et al., 1982; Kopanica and Novotny, 1998), microfabricated gold ultramicroelectrode array (Feeney and Kounaves, 2000). Mercury

electrodes are of environmental concern and high price, while gold disk electrode is rather complex in preparation and high price as well. Because of high sensitivity and simple preparation, glassy carbon rotating disk gold-film electrode (AuFE) are also used for ASV determination of arsenic (Sun et al., 1997; Huang and Dasgupta, 1999). In this work, we studied application of DP-ASV using AuFE prepared ex situ for determination of arsenic (III & V). As^{V} was reduced to As^{III} with KI in boiling HCl solution prior to be determined by ASV.

Methods

Reagents

Working solutions of As^{III} were prepared daily from 1000 ppm As^{III} standard solutions (atomic absorption standard, Kanto, Japan) and double-distilled water (water distiller Fistream Cyclon, England). Working solutions of As^{V} were prepared daily from As^{V} standard solution, that was made up by dissolving $(\text{NH}_4)_3\text{AsO}_4$ (Prolabo, France) with water and then re-determining its concentration by iodo-thiosulfate titration. Au^{III} standard solution (pH = 2) were made up by dissolving Au (99.99%, commercial grade) in the minimum amount of aqua regia, drying up to remove NO_2 , dissolving dried residue with HCl diluted solution, and storing at 4°C. HNO_3 , HCl and H_2SO_4 solutions were Suprapur (Merck, Germany). Other reagents (KI, ascorbic acid, Cu^{II} , Pb^{II} ...) were prepared from the chemicals of analytical reagent grade (Merck, Prolabo, Kanto).

Instrumental

A polarographic analyzer consisting of a 694 VA Stand and a 693 VA processor (Metrohm). The 694 VA Stand consists of three-electrode configuration with a graphite working electrode (2.8 ± 0.1 mm diameter), an Ag/AgCl (KCl sat.) reference electrode and a platinum wire auxiliary electrode. The instrument was also fitted with a Teflon purge tube for deaeration of solution with prepurified nitrogen (99.999 % nitrogen generator, Whatman, USA). The 693 VA processor is operated by the software available with this instrument, which enable the development of complete analytical procedures including control of electrolysis potentials, deposition time and rotating speed of working electrode, recording voltammograms...

Preparation of ex situ gold film electrode (AuFE)

The successively polished electrode was rinsed with acetone and water. Gold film was plated from the 5 mM Au^{III} solution for 2 min on the graphite working electrode at + 400 mV (vs. Ag/AgCl) and at a rotation speed of 2000 rpm. After that, cleaning the electrode was made by scanning anodic potential from -300 to + 750 mV to strip trace metals (Cu, Ag, Hg...), that may accumulated on the surface of the electrode, into solution and then soaking the electrode in 1 M H_2SO_4 for 5 min. The electrode was carefully rinsed with water and was then ready for use. After a series of 14-16 measurements cleaning the electrode from the gold film was made by wiping the rotating electrode with a wet tissue and then, if necessary, a new AuFE was re-prepared by the same way above.

Determination of As^{III}

An AuFE prepared was put into the cell filled with the analytical solution containing 1M HCl, 0.2 mM ascorbic acid, and As^{III} . The final volume of the solution was 10 ml. The solution was de-aerated with pure nitrogen for 5 min. Deposition of arsenic onto the surface of the electrode was carried out at -100 mV and the rotating rate of 2000 rpm (ω). After that, the rotation of the electrode was turned off and left for 30 s at -100 mV that the solution became quiescent. During the deposition step, As^{III} was preconcentrated by the way forming intermetallic compounds on the electrode (Forsberg et al., 1975; Li and Smart, 1996; Adeloju et al., 1999; Huang and Dasgupta, 1999). Stripping was made in differential pulse mode starting from -100 mV to + 250 mV with a scan rate of 20 mV/s in positive direction. Parameters of differential pulse voltammetry included a pulse width of 40 ms (t_{pulse}), a pulse height of 50 mV (U_{pulse}), sampling time of 20 ms (t_{meas}), and an

increment of 6 mV (U_{step}). Duplicate determinations were performed on each analytical solution before standard addition. The analytical current - potential response recorded is peak form.

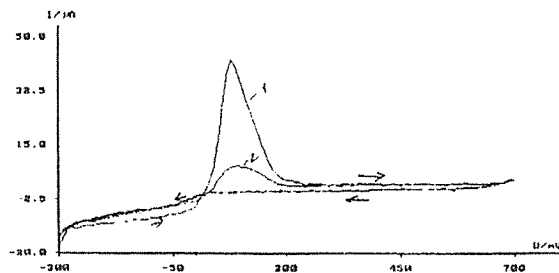


Fig1. Two cyclic voltammograms for a solution containing 5 μM of As^{III} (1). with deposition step on an AuFE; (2). without deposition step. Conditions: deposition time (t_{dep}), 20s; deposition potential (E_{dep}), -100 mV; range of potential scan (E_{range}), +300 mV \div -700 mV; scan rate (v), 100 mV/s; supporting electrolyte, 0.4M HCL; [AA] = 0.1mM.

Determination of As^{V}

As^{V} was reduced to As^{III} with KI (mole ratio of $\text{I}^-/\text{As}^{\text{V}}$ was about 2.5) in the solution of 4 M HCL. The solution was boiled at 150°C for 10 min that removed up I_2 from the analytical solution. After the solution cooled, As^{III} was determined by the same way mentioned above.

Results and discussion

Voltammetric characteristics of As^{III} on AuFE

From cyclic voltammetry study of AuFE in As^{III} solution acidified with HCl and ascorbic acid (AA), shown in Fig.1, a relatively well-defined peak occurred at +90 \div +100 mV in the run with depotion step indicating the possibility of using a such AuFE for As^{III} determination. Ascorbic acid (AA) was added into the solution as a consitituent decreasing the background signal of the voltammograms and increasing the reproducibility of the measurements. This was also confirmed by G. Bodewig et al. (1982).

Reproducibility of the stripping response on a AuFE

A series of 19 runs carried out on an AuFE (see Fig.2) shown that except the first run (not shown in Fig.2) having bad (or unstable) stripping voltammetric response, the reproducibility of the responses was good: RSD = 2.1% ($n = 18$). This confirmed that AuFE can be used for determination of arsenic.

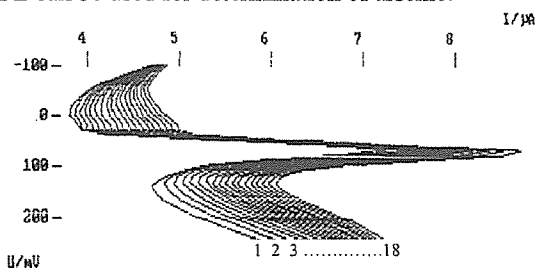


Fig. 2. A series of 18 stripping voltammograms was recorded on an AuFE. Conditions: the concentration of As^{III} , [As^{III}] = 50nM (\approx 3.7 ppb); [HCL] = 0.4 M; [AA] = 0.1M; E_{dep} = -100mV; t_{dep} = 60s; ω = 2000 rpm; U_{pulse} = 50 mV; t_{pulse} = 40 ms; t_{meas} = 20 ms; U_{step} = 6 mV; v = 30 mV/s; E_{range} = -100 \div +250 mV.

Effect of the concentration of AA and HCl

Several of tests indicated that the peak current of arsenic decreased rapidly if AA was absent in the analytical solution, but for the solution contained AA, the current gained relatively good reproducibility. Effect of the concentration of AA on the stripping current of arsenic (I_p) was shown in Fig.3. The height of the peak current was almost unchanged in the range of AA concentration of $0.1 \div 1.0$ mM and gained good reproducibility ($RSD < 1.2\%$, $n = 2$). The concentration of AA was chosen for the next experiment was 0.2 mM. According to Bodewig et al. (1982), the suitable concentration of AA was 5.7 mM and AA prevented the oxidation As^{III} to As^V , and decreased the slope of the rear side of arsenic stripping response, even in the solution of high chloride concentration such as seawater. However, he did not know the reason for that.

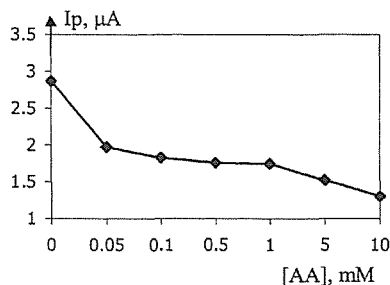


Fig. 3. Effect of AA concentration on the peak current of arsenic (I_p). Conditions as in Fig. 2.

HCl was accepted to be a suitable supporting electrolyte for anodic stripping voltammetric determination of arsenic (Forsberg et al.,1975; Sun et al.,1997; Huang and Dasgupta,1999). Some authors found that the suitable concentration of HCl was 2 M (Sun et al.,1997), 4.5 M (Huang and Dasgupta,1999). However, on using gold disk electrodes, the mixed solution of $HClO_4 + HCl$ (Forsberg et al.,1975) and $H_2SO_4 + HCl$ (Bodewig et al.,1982; Kopanica and Novotny, 1988) were used as supporting electrolytes. Investigation of the effect of HCl concentration on the stripping current of arsenic (see Fig.4) shown that for analytical purposes the optimum HCl concentration was ca. 1 M. At the concentration of 1 M HCl the stripping peak potential of arsenic was approximately $160 \div 170$ mV.

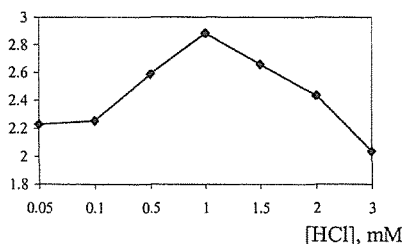


Fig. 4. Effect of HCl concentration on the peak current of arsenic; $[AA] = 0.2$ mM; other conditions as in Fig. 2.

Effect of the deposition potential and time

The peak current of arsenic decreased at the deposition potentials more positive than -50 mV (shown in Fig.5). Because the potentials are quite near to the stripping potential of arsenic, the preconcentration of arsenic on AuFE was bad. At the deposition potentials more negative than -150 mV, the formation of H_2 may be occurred and so that the deposition step was inefficient. The suitable deposition potential was -100 mV.

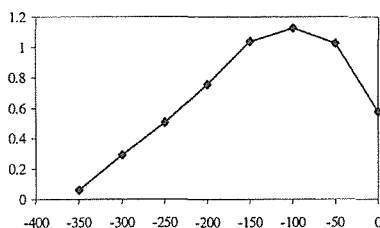


Fig. 5. Effect of E_{dep} on the peak current of arsenic; $[AA] = 0.2$ mM; $[HCl] = 1$ M; other conditions as in Fig. 2.

Since elemental arsenic is a very poor conductor of electricity, the peak current of arsenic was found to be limited when the active surface of the electrode was fully covered with elemental arsenic (Sun et al.,1997). The dependence of peak current on deposition time for the solution containing 50 nM arsenic was shown in Fig. 6. The peak reached a limiting height indicated that the electrode surface was saturated with arsenic at the deposition time greater than 120 s. The saturation of the electrode surface with arsenic depends on the length of the deposition time, the deposition potential, the stirring efficiency, the surface area of the electrode and the concentration of As^{III} ,... In this study, a deposition time of 120 s was used.

Effect of rotating rate

The sensitivity of stripping voltammetry depends on the amount of substance accumulated at the electrode and therefore, it depends on the rate of the substance flux from the bulk of the solution to the electrode (i.e. hydrodynamic conditions) (Armališ et al.,1996). The results obtained in this work indicated that stripping peak current increased with increasing the rotating rate of the electrode, but was unchange when the rotating rate greater than 2200 rpm. The rate chosen was 2000 rpm.

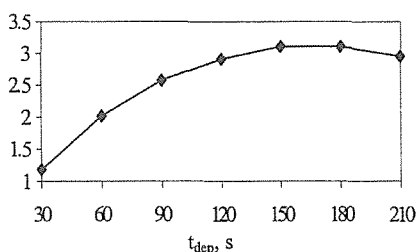


Fig. 6. Effect of t_{dep} on the peak current of arsenic; $[AA] = 0.2$ mM; $[HCl] = 1$ M; $E_{dep} = -100$ mV; other conditions as in Fig. 2.

Effect of scan rate

It is expected to result in an increase of the stripping response as the scan rate is increased. However, increase of the scan rate also results in a broader of the stripping peak and a lift of the slope of the voltammogram background. The scan rate of 20 mV/s was considered suitable.

Detection limit, sensitivity, and linearity

Detection limit, sensitivity, and linear range depends on the deposition time. The results obtained from three experiments on three gold films indicated that for 120 s preconcentration the calibration graph was linear up to 1000 nM (75 ppb) As^{III} ($R = 0.998$); the detection limit (3σ level) and sensitivity for arsenic under the conditions used in this study was (16.1 ± 1.9) nM $\approx (1.21 \pm 0.14)$ ppb and (16 ± 4) nA/nM, respectively. The stripping voltammograms of the one of the 3 experiments was shown in Fig.7. Such a low detection limit indicated the possibility of ASV with AuFE for the determination of arsenic in natural waters.

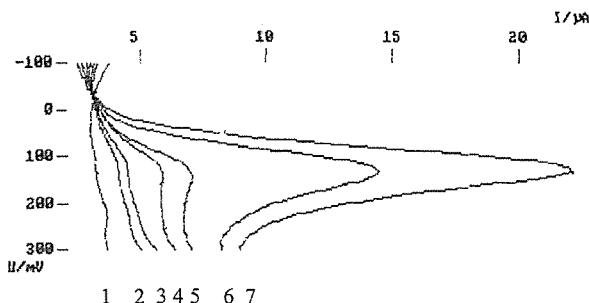


Fig.7. The stripping voltammograms of arsenic: 1. blank; 2,3,4,5,6,7. $[\text{As}^{\text{III}}] = 5, 10, 50, 100, 500, 1000 \text{ nM}$, respectively. Conditions: $[\text{AA}] = 0.2 \text{ mM}$; $[\text{HCl}] = 1 \text{ M}$; $E_{\text{dep}} = -100 \text{ mV}$; $t_{\text{dep}} = 120 \text{ s}$; $\omega = 2000 \text{ rpm}$; other conditions as in Fig. 2.

Interferences

Copper and lead commonly occurred in environmental samples and were found to be most serious interference when gold electrode was used to determine arsenic (Kopanica,1998; Forsberg,1975; Huang,1999). According to Huang et al. (1999), intermetallic compound Cu_3As can be formed at the AuFE and that can show a decrease of 50% in the stripping signal of arsenic when Cu is present in 20-fold excess; but lead caused no significant change upon adding 2 – fold excess of lead (at the concentration of 50 ppb As^{III}).

In this work, it can be seen that when the ratio (mole /mole) of $\text{Cu}^{\text{II}}/\text{As}^{\text{III}}$ and $\text{Pb}^{\text{II}}/\text{As}^{\text{III}}$ was greater than 10 (at the concentration of 200 nM $\approx 15 \text{ ppb As}^{\text{III}}$), the stripping peak of arsenic could be decreased more than 30% of its height.

Reduction of As^{V} with iodide

Since the reaction of reduction of As^{V} to As^{III} with iodide in HCL solution is reversible (Skoog,1994), the efficiency of the reduction of As^{V} is increased with the level of the removal of iodine formed from the solution. In this study, the removal of iodine was carried out by boiling the solution at 150°C for 7 - 8 min (for the volume of 5ml solution). On finishing the boiling, the final volume of the solution was approximately 2 ml. The solution was neutralized with diluted NaOH solution to $\text{pH} \approx 2 - 3$ (tetsted with pH indicator paper). After the reduction of As^{V} to As^{III} , the stripping voltammetric determination of As^{III} was made under the optimum conditions found above.

The primary HCl concentration and ratio of $\text{I}^-/\text{As}^{\text{V}}$ are also of effect on the efficiency of As^{V} reduction (see Table 1 and 2). The trace amount of iodine present in the solution, which might be formed by the oxidation of iodide with oxygen, had no significant effect on the stripping response of arsenic. The high primary concentration of HCL and I^- may decreased the formal potential of couple $\text{As}^{\text{V}}/\text{As}^{\text{III}}$ and therefore, decreased the efficiency of As^{V} reduction. On the other hand, increase of I^- concentration can lengthen the time to remove iodine from the solution.

According to Horwits Function (Thomson and Lowthian,1995), on determining the concentrations of 16.5 ppb, the RSD of interlaboratory testing was 29.7% and so that within a laboratory, half of the RSD (i.e. approximately 15%) could be accepted to be an error for the detrmiation of the concentration. In this study, therefore, 15% error of the determination of As^{III} and the efficiency of As^{V} reduction as well can be satisfied. The low value of the efficiency can be explained due to the reversibility of the reaction of As^{V} reduction with

iodide. The results shown in Table 1 and 2 indicated that the suitable primary concentration of HCL and ratio of $\Gamma / \text{As}^{\text{V}}$ (mole/mole) in As^{V} reduction were 4.0 M and 2.5, respectively

Table 1. Effect of HCL concentration on the efficiency of As^{V} reduction (E)

C_{HCl}^* , M	1.0	2.0	3.0	4.0	5.0	6.0	7.0
E^{**} , %	52	50	81	85	75	43	20

* C_{HCl} : primary HCL concentration in As^{V} reduction;

** E (%) = $\{([As^{\text{V}}] - [As^{\text{III}}]) \times 100\} / [As^{\text{V}}]$; herein,

$[As^{\text{V}}]$: the primary concentration of As^{V} ;

$[As^{\text{III}}]$: As^{III} determined after the reduction of As^{V} to As^{III}

Conditions: $[As^{\text{V}}] = 220 \text{ nM}$ (16,5 ppb); $\Gamma / \text{As}^{\text{V}}$ (mol/mol) = 2.0;

$[AA] = 0.2 \text{ mM}$; $[HCl] = 1 \text{ M}$; $E_{\text{dep}} = -100 \text{ mV}$; $t_{\text{dep}} = 120 \text{ s}$; ω

= 2000 rpm; other conditions as in Fig. 2.

Table 2. Effect of the ratio of $\Gamma / \text{As}^{\text{V}}$ on the efficiency of As^{V} reduction (E)

Ratio $\Gamma / \text{As}^{\text{V}}$, mol/mol*	1.5	2.0	2.5	3.0
E^{**} , %	40	53	85	41

* Primary ratio of $\Gamma / \text{As}^{\text{V}}$ in the reduction of As^{V} ;

** E : as in Table 1.

Conditions: primary HCL concentration in As^{V} reduction, ($C_{\text{HCl}} = 4.0 \text{ M}$; other conditions as in Table 1.

Conclusion

Differential pulse anodic stripping voltammetry using gold film electrode prepared ex situ can be successfully used for determination of arsenic (III and V). This method has high sensitivity, good precision, and low detection limit and therefore, can be applied for the analysis of arsenic in environmental samples. For the application of this method, it needs to be tested with Certified Reference Materials and checked to compare with other methods such as AAS and ICP-AES or ICP-MS.

Acknowledgement

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References

1. Adeloju S. B., Young T. M., Jagner D., Batley G. E. (1999). *Constant current cathodic stripping potentiometric determination of arsenic on a mercury film electrode in the presence of copper ions*. Analytica Chimica Acta, 381, 207-213.
2. Armalis S., Pockevičiūtė D., Tatolytė O. (1996). *Influence of hydrodynamic conditions of the solution on the sensitivity of stripping analysis of trace metals*. Fresenius J. Anal. Chem., 354, 696 – 698.
3. Bodewig G., Valenta P., and Nurnberg H. W. (1982). *Trace Determination of As(III) and As(V) in Natural Water by Differential Pulse Anodic Stripping Voltammetry*. Fresenius Z. Anal. Chem., 311, 187 - 191.
4. Feeney R. and Kounaves S. P. (2000). *On-Site Analysis of Arsenic in Groundwater Using a Microfabricated Gold Ultramicroelectrode Array*. Anal. Chem., 72, 2222 - 2228.
5. Forsberg G., O'Laughlin J.W., Megargle R.G. & Koirtz Johann S.R. (1975). *Determination of Arsenic by Anodic Stripping Voltammetry and Differential Pulse Anodic Stripping Voltammetry*. Analytical Chemistry, Vol.47, No.9, 1586-1591.
6. Fresenius W., Quentin K.E., Schneider W. (1988). *Water Analysis*, Springer-Verlag Berlin Heidelberg, Germany, pp. 333-340.
7. Goñmez -Ariza J. L., Sañchez-Rodas D., Girañdez I., Morales E. (2000). *A comparison between ICP-MS and AFS detection for arsenic speciation in environmental samples*. Talanta, 51, 257 - 268.
8. Greulach U., Henze G. (1995). *Analysis of arsenic(V) by cathodic stripping voltammetry*. Analytica Chimica Acta, 306, 217-223.

9. Gründler P. and Flechsig G.U. (1998). *Deposition and stripping at heated microelectrodes. Arsenic(V) at a gold electrode*. Electrochimica Acta, Vol. 43, No. 23, 3451 - 3458.
10. Huang H., Dasgupta P. K. (1999). *A field-deployable instrument for the measurement and speciation of arsenic in potable water*. Analytica Chimica Acta, 380, 27 - 37.
11. Kopanica M., Novotný L. (1988). *Determination of traces arsenic by anodic stripping voltammetry in solutions, natural waters and biological material*. Analytica Chimica Acta, 368, 211-218.
12. Li H., Smart R. B. (1996). *Determination of sub-nanomolar concentration of arsenic(III) in natural water by square wave cathodic stripping voltammetry*. Analytica Chimica Acta, 325, 25 - 32.
13. Locatelli C., G. Torsi (2000). *Determination of Se, As, Cu, Pb, Cd, Zn, and Mn by anodic and cathodic stripping voltammetry in marine environment matrices in the presence of reciprocal interference. Proposal of a new analytical procedure*. Microchemical Journal, 65, 293 - 303.
14. Skoog D.A., D.M. West, and F.J. Holler (1994). *Analytical Chemistry*, 6th Ed., Saunders College Publishing, USA, pp. 32-33.
15. Smith A. H., Lingas E. O., & Rahman M. (2000). *Contamination of drinking-water by arsenic in Bangladesh: a public health emergency*, Bulletin of the WHO, 78(9), 1093 – 1103.
16. Sun Y-C., Mierzwa J., Yang M-H. (1997). *New method of gold-film electrode preparation for anodic stripping voltammetry determination of arsenic (III and V) in seawater*. Talanta, 44, 1379-1387.
17. Thomps M., Lowthian P. J. (1995). *A Horwits - like Function Describes Precision in a Proficiency Test*, Analyst, Vol. 120, 271 - 272.
18. Yan X. P., Kerrich R., and Hendry M. J. (1998). *Determination of (Ultra) trace Amount of Arsenic(III) and Arsenic(V) in Water by Inductively Coupled Plasma - Mass Spectrometry Coupled with Flow Injection On - Line Sorption Preconcentration and Separation in a Knotted Reactor*. Anal. Chem., 70, 4736 - 4742.