

# Determination of Arsenic Species Traces from Surface and Drinking Water Using Stripping Voltammetry

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*A quick and sensitive determination method was developed for arsenic species traces in surface and drinking water via stripping voltammetry techniques. A hanging mercury drop electrode (HMDE) was used as working electrode. As (III) is determined directly and As (V) is calculated by subtraction between total As and As (III). In order to determine total As, the entire quantity of arsenic is reduced to As (III), which represents the electrochemical active specie. A large number of tests were performed in order to achieve the optimum setup of equipment's parameters, studies on a large range of interferences were done and at the end the method was in house validated.*

*Keywords: stripping voltammetry, arsenic speciation, HMDE.*

Various techniques may be used for the determination of metals in water samples [1-4]. Given their toxicity and ability to bioaccumulate [5], the legislation establish lower maximum concentration limits in environmental factors thus imposing the need for analytical techniques with higher sensitivity and selectivity [6-8].

In order to determinate the toxicity and the hazardousness of arsenic compounds new validated methods have been used for types of arsenic traces in water [9]

An important role in solving these problems belongs to the methods using high sensitivity to determine the concentrations of trace compounds, out of which it can be mentioned: electrochemical techniques (polarography, anodic and cathodic stripping voltammetry); atomic absorption spectrometry; inductively coupled plasma techniques with detection through mass spectroscopy or emission spectroscopy (ICP-MS, ICP-OES) [10].

Electrochemical methods present high sensitivities and it can be used with good results for determination of heavy metals traces from surface and drinking water. Beside high sensitivity and selectivity, stripping voltammetry techniques has relatively low cost and the procedures used for determinations are simple [11]. Due to their high selectivity, these techniques can be used for determination of arsenic species traces with good results [12].

## Experimental part

The method selected for determination of arsenic species from surface and drinking water uses the technique of differential pulse cathodic stripping voltammetry. Electroactive specie is As (III) and As (V) was calculated by subtraction between total As and As (III). As (V) reduction to As (III) was realised through addition of 0.02M L-cysteine and 0.03M HCl within the water sample. The sample was heated for about 6 min at 70°C. Accumulation on mercury drop followed by stripping process is performed in a hydrochloric acid solution that contains Cu (II) and Se (IV) ions [1]. A  $Cu_xAs_ySe_z$  type intermetallic complex is formed on mercury electrode during the deposition period. The

complex enhances method's sensitivity and improves peak's shape.

A series of tests for setting up the equipment's optimum working parameters were needed in the first stage of experiments. The parameters optimised in order to obtain maximum performances were: deposition potential; drop size; deposition time; HCl concentration within the support electrolyte, Cu concentration within the support electrolyte, Se concentration within the support electrolyte; linearity domain of calibration curve (optimum working domain), performance characteristics of the developed method, which are obtained from calibration data. All the other used parameters are the ones recommended by the equipment's producer.

## Reagents and materials:

- Ultrapure water was used for all solutions
- As (III) 1000mg/L solution was prepared through solubilisation of 0.132g  $As_2O_3$  (Merck) (previously dried at 110°C for 2h) in 2mL ultrapure NaOH 20% concentration. Solubilised compound was adjusted to pH 2 with ultrapure HCl 30% and diluted with water at 100ml, resulting a 1g/L solution.
- Cu( $NO_3$ )<sub>2</sub> 1g/L solution (Merck);
- SeO<sub>2</sub> Merck 1g/L solution diluted to 1mg/L;
- L-cysteine 1M solution (Merck).
- Sodium dodecyl sulphate (SDS) anionic surfactant (Merck);
- Fe( $NO_3$ )<sub>3</sub> 1g/L solution (Merck);
- Zn( $NO_3$ )<sub>2</sub> 1g/l solution (Merck);
- Cd( $NO_3$ )<sub>2</sub> 1g/L solution (Merck);
- Mn( $NO_3$ )<sub>2</sub> 1g/L solution (Merck);

## Results and discussions

Experiments within the 0.4-0.6 V domain were performed in order to determine *optimum deposition potential*, and implicitly the maximum signal (measured in nano Coulombs). It was observed that signal's maximum value is obtained at a deposition potential of 0.44V. The obtained results are presented in the figure 1.

Each point of the graph represents an average value. Up to nine tests were performed for each point. Another

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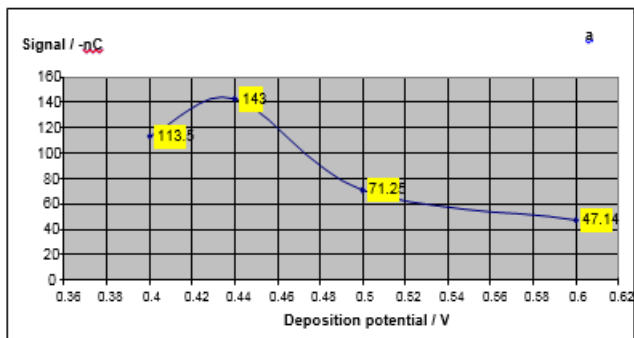


Fig.1. Signal variation vs. deposition potential for Arsenic (III) solutions with de 3 µg/L concentration

parameter that was optimised in order to maximise the signal intensity was the *dimension of mercury electrode drop*. The drop's size can vary from 1 to 9 units corresponding to a surface between 15 and 60 mm<sup>2</sup>. Experimental results led to the conclusion that maximum signal for determination of As (III) is obtained for a drop dimension of 8 units. Figure 2 presents the signal variation vs. dimension of mercury drop on which analyte pre-concentration is realised. Each point represents an average value, for each point up to nine tests were performed.

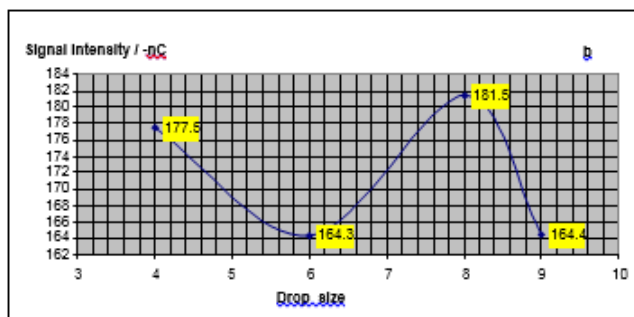


Fig. 2 Signal variation vs. mercury drop size for Arsenic (III) solutions with 3 µg/L concentration

*Deposition time* is also an important parameter for stripping voltammetry. Tests as various deposition times were performed in order to optimise this parameter. Tests showed that the signal value increases with longer deposition periods. Yet, two types of peaks can be observed following the increase of deposition time. For deposition times up to 60s the peak is sharp and symmetric, and the signal value shows a varying linear variation. For deposition periods longer than 60 s the peak widens and flattens and peak's position is gradually modifying within the  $\approx -0.68 - 0.8V$  range. Produced modifications (peak's shape and potential) along with the significant increase of deposition time are suggesting the formation on the electrode of Cu<sub>x</sub>Se<sub>y</sub>As<sub>z</sub> type intermetallic compounds with various stoichiometric ratios. Taking into account these findings, the optimum deposition time was set at 60s.

A significant role in performing the analyses based on electrochemical methods is played by the support electrolyte. A solution of Cu (II) and Se (IV) ions in HCl was used as support electrolyte for As (III) determination. Obviously the signal is depending on the support electrolyte concentrations' variation. In order to obtain a maximum signal, experiments were performed at various concentrations of these components within the analysed sample. A sample volume of 10 mL were used in all performed experiments. Highest signal is obtained for a concentration of about 1M/L HCl (about 1.1mL HCl 30% Merck in 10 mL sample) (fig. 3).

Experiments for determination of Cu (II) and Se (IV) concentrations in sample were performed in the same way in order to obtain a maximum signal. It was found that for

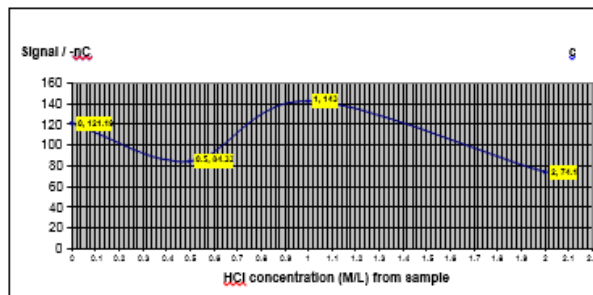


Fig.3. Signal intensity vs. HCl concentration in sample for As (III) solutions with 3µg/L concentration

a concentration of 4.6 mg/L Cu (II) (corresponding to the addition of 50 µL Cu (II) solution 1g/L in 10mL sample) and 3.7µg/L Se (IV) (corresponding to the addition of 40µL Se (IV) solution 1g/L in 10 mL sample) the signal obtained on the electrode is maximum.

Following the performed experiments, optimum parameters for determination of As (III) from aqueous solutions were set up. The optimised parameters as well as those recommended by the equipment's producer are presented within table 1.

Table 1

OPTIMUM PARAMETERS USED FOR As(III) DETERMINATION

Start potential	-1.2V
End final	-0.1V
Pulse amplitude	0.05V
Pulse time	0.05s
Voltage step	0.003967V
Voltage step time	1s
Sweep rate	0.0040V/s
Deposition potential	0.44V
Deposition time	60s
Equilibration time	15s
Initial purging time	300s

The performance characteristics of the developed method are obtained from calibration data. In accordance with SR ISO 8466/1;2 [5] for evaluation of analytical methods and estimation of performance characteristics, a statistical assessment of calibration linear function is required.

The following statistical performance characteristics of the method resulted from the statistical assessment (in accordance with SR ISO 8466-1:1999 standard):

- working domain, experimentally established and statistically verified, between the lowest and the highest concentration that can be determined, is between 1 µg/L and 7 µg/L;
- calibration line equation:  $y = -1.32E-08 + 0.051x$ ;
- analytical calculation equation:  $x = 19.625y + 2.60E-07$ ;
- variation coefficient: 0.72%;
- standard deviation,  $S_{x_0}$ : 2.88E-08;
- residual standard deviation,  $S_y$ : 1.47E-09;
- the intercept of calibration line ( $a = -1.32E-08$ );
- sensitivity,  $b$ , (calibration function slope, regression coefficient  $b = 0.051$ );

Tests were performed on synthetic solutions of 1µg/L, 3 µg/L and 7 µg/L As (V). The results are presented within the table 2.

A study on the assessment of effects of the interferences that usually are met in surface and drinking water was performed, after setting up of the optimum parameters.

Analysed solution	Reduction efficiency (%)	Obtained result ( $\mu\text{g/l}$ )	Standard deviation for concentration (%)
Synthetic solution 1 $\mu\text{g/l}$	84.7	0.847	2.634
Synthetic solution 3 $\mu\text{g/l}$	91.73	2.752	4.53
Synthetic solution 7 $\mu\text{g/l}$	96.63	6.764	4.58

**Table 2**  
RESULTS OF REDUCTION TESTS ON  
SYNTHETIC SOLUTIONS OF  
1, 3 AND 7  $\mu\text{g/L}$  As (V)

Three significant categories of interferences are emphasized by the literature studies [2-4].

Thus, a first category are metallic ions that can be reduced and deposited on dropping mercury electrode, where some metals can form inter-metallic compounds with As or Cu.

A second category of interferences are consisting of the compounds with tensioactive properties that can be adsorbed on electrode surface or can adsorb As on their surface (such as iron based adsorbents), influencing arsenic activity.

The third category of compounds that can interfere in As determination is represented by the compounds that can form complexes or precipitates with As or Cu (Fe).

Tests were performed using representative matrix: a surface water sample from Aries River was used. The sample was previously filtered.

The tests were carried on the same working domain as for the calibration curve. Same working methodology and same reagents used for calibration curve were used during the tests but instead of ultrapure water the real water samples were used near calibration solutions from the same concentration domain with the one used for calibration curve (set up during previous researches as linearity domain of the calibration curve).

In order to emphasize the effects of the possible interferences, a known concentration of analyte was added. Then, after adding the interference compound at various concentrations the recovery efficiencies were calculated. The interference effect of Zn, Mn, Cd, Fe and tensioactive compounds was studied.

The real surface water matrix is presented within table 3.

From the analyse of main performance parameters of calibration curves for ultrapure water and studied water sample it was observed that there are no significant variations, both curves can be used on the selected working domain. The calibration curve for the studied matrix is presented in figure 4.

The next step was to add various compounds, susceptible to interfere with the determination process of As (III) (active electrochemical) and recovery efficiencies were calculated. From the literature [6-11] it was found that the main interferences are caused by iron, zinc, manganese, cadmium, as well as tensioactive compounds [12,13]. The interference causes were explained earlier.

The calibration curve for the studied matrix was developed, and then a known quantity of analyte was added (due to the fact that the arsenic was found below the detection limit within the surface water matrix). 3  $\mu\text{g/L}$  of As (III) was added and the obtained result was of 3.09  $\mu\text{g/L}$ .

Known quantities of interference compounds were then added at various concentrations and their effect upon the determination was monitored by calculation of recovery efficiencies. This procedure was applied for all studied interferences.

The obtained results are presented in tables 4 ÷ 8.

**Table 3**  
SURFACE WATER SAMPLE MATRIX

No	Indicators	M.U	Aries River
1	Phosphates	mg/L	0.052
2	Nitrates	mg/L	1.04
3	Nitrites	mg/L	0.03
4	Chlorides	mg/L	14.05
5	Sulphates	mg/L	52
6	Filtered residue	mg/L	178
7	COD Cr	mg O <sub>2</sub> /L	11.16
8	Ammonia	mg/L	0.296
9	Copper	mg/L	<0.003
10	Manganese	mg/L	<0.003
11	Zinc	mg/L	0.011
13	Anionic surfactants	mg/L	<0.05
14	Non-ionic surfactants	mg/L	<0.05
15	Iron	mg/L	0.07
16	Nickel	mg/L	<0.004
17	Cobalt	mg/L	<0.01
18	Lead	mg/L	<0.01
19	Cadmium	mg/L	<0.001
20	Total Chromium	mg/L	<0.005
21	Arsenic	mg/L	< 0.026 x 10 <sup>-3</sup>

The experiments showed that:

-Iron is interfering strongly for concentrations exceeding 13000 ( $\mu\text{g/L}$ ), corresponding to an As (III)/Fe ratio of 1:4200

-Zinc influence upon the As (III) specie determination started to be visible at concentration exceeding 5mg/L, corresponding to an As (III)/ Zn ratio of about 1:1700.

-Even if the literature is mentioning that manganese interfere in determination of As (III), the fact was not confirmed for the studied case. The manganese concentration within the electrolytic cell was raised up to 30 mg/L

-Strong interferences occur for Cd concentrations above 150 $\mu\text{g/L}$ , corresponding to an As (III)/Cd ratio of 1:48.

Tensioactive compounds can strongly influence the results obtained for arsenic determination via stripping voltammetry. This is due to their adsorption on the mercury drop, practically blocking analyte deposition and pre-concentration on the drop.

As it can be observed, for concentration of 0.5mg/L tensioactive compounds present strong interferences, recovery efficiencies being very small. To better see the effect upon the determination, the voltammetry graphs at various concentrations of added tensioactive compounds within the electrolytic cell are presented in figure 5.

The signal is drastically decreasing with the quantity of added tensioactive compound, and totally disappears at a concentration of 5000 $\mu\text{g/L}$ . Samples were UV digested in order to determine the total arsenic but the results also showed strong interferences.

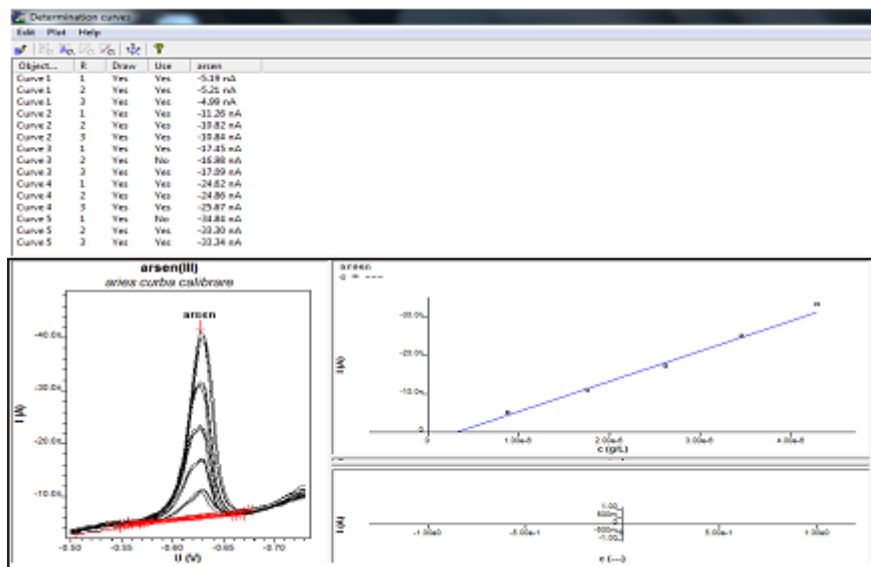


Fig.4 Calibration curve of studied matrix

Fe (µg/L)	Added As (III) (µg/L)	Recovered As (III) (µg/L)	Recovery efficiencies (%)
9000	3.09	2.959	95.76
13000		2.717	87.93
17000		2.498	80.84
30000		2.329	75.37

**Table 4**  
RECOVERY EFFICIENCIES FOR As(III) FOLLOWING THE ADDITION OF Fe IN VARIOUS CONCENTRATIONS

Zn (µg/L)	Added As (III) (µg/L)	Recovered As (III) (µg/L)	Recovery efficiencies (%)
2600	3.09	2.905	94
5000		2.658	86
9000		2.55	82.5
13000		2.45	79.3
17000		2.38	77

**Table 5**  
RECOVERY EFFICIENCIES FOR As(III) FOLLOWING THE ADDITION OF Zn IN VARIOUS CONCENTRATIONS

Mn (µg/L)	Added As (III) (µg/L)	Recovered As (III) (µg/L)	Recovery efficiencies (%)
5000	3.09	2.905	94
17000		2.99	96.76
30000		2.941	95.17

**Table 6**  
RECOVERY EFFICIENCIES FOR As(III) FOLLOWING THE ADDITION OF Mn IN VARIOUS CONCENTRATIONS

Cd (µg/L)	Added As (III) (µg/L)	Recovered As (III) (µg/L)	Recovery efficiencies (%)
75	3.107	3.074	98.94
150		3.468	111.6
300		4.407	141.8
2600		23.94	770.52
9000		79.7	2565

**Table 7**  
RECOVERY EFFICIENCIES FOR As(III) FOLLOWING THE ADDITION OF Cd IN VARIOUS CONCENTRATIONS

Tensioactive compounds (µg/L)	Added As (III) (µg/L)	Recovered As (III) (µg/L)	Recovery efficiencies (%)
500	3.09	1.866	60.38
1000		1.12	36.25
2500		Below the detection limit	Below the detection limit
5000		Below the detection limit	Below the detection limit

**Table 8**  
RECOVERY EFFICIENCIES FOR As(III) FOLLOWING THE ADDITION OF TENSIOACTIVE COMPOUNDS IN VARIOUS CONCENTRATIONS

Performance parameters of the method were calculated in order to determine if the method can be used for analyse on surface, underground and drinking water.

The method was validated by series of tests for estimation of its performance parameters. Obtained results are presented in table 9.



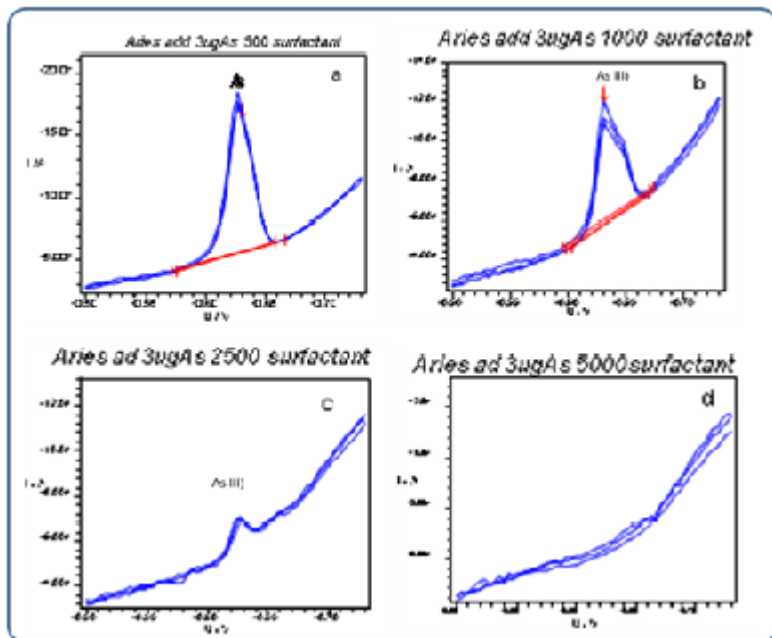


Fig. 5 Voltammetry graphs obtained after addition of 500, 1000, 2500, 5000 µg/L tensioactive compounds

No.	Parameter	As (III) via stripping voltammetry
1	Accuracy	99.48 %
2	Fidelity	CV= 4.799109%
3	Repeatability	$r = 0.404050877 \mu\text{g/L}$
4	Reproducibility	$R_L = 0.648478 \mu\text{g/L}$
5	Sensitivity	$b = 0.051$
6	Detection limit	$LoD = 0.08362117 \mu\text{g/L}$
7	Quantification limit	$LoQ = 0.278737232 \mu\text{g/L}$
8	Working domain	1 µg/L – 7 µg/L Calibration curve is linear on the studied concentration range
9	Selectivity	-Fe is interfering for concentrations exceeding 13000 µg/L -Zn presents interferences for values above 5000 µg/L -Cd interference is very strong for values above 150 µg/L, -Mn proved to have no interferences even for concentration of 30 mg/L. - Tensioactive compounds in concentrations above 500 µg/L corresponding to an As(III):tensioactive compounds ratio of 1:167 are completely blocking the determination of arsenic species. Remark: The method can be successfully applied for surface and drinking water as well for water with low concentration of metals and organic load
10	Recovery	96.56%

**Table 9**  
PERFORMANCE PARAMETERS  
FOR THE METHOD OF  
DETERMINATION OF ARSENIC  
SPECIES VIA STRIPPING  
VOLTAMMETRY

## Conclusions

Experiments on synthetic and real samples showed that the method is linear on the selected domain (1-7 µg/L). The method's performance parameters confirmed that the method can be used for analyses on surface, underground, drinking water and can be applied for the determination of arsenic traces in water. The method is not suitable for samples with high content of heavy metals or high organic load.

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