

INTERFERING EFFECTS OF DIFFERENT SUBSTANCES EXISTING IN ENVIRONMENTAL MATRIX ON As DETERMINATION BY STRIPPING VOLTAMMETRY

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ABSTRACT

This paper evaluates the effects of the interferences on the method of determination of the As species through stripping voltammetry, using as a working electrode the dropping Mercury electrode.

The interferences found in the determination of As through the voltammetric methods can be classified in three categories:

- **The metallic ions** which can form intermetallic compounds with As (Cd) that are accumulated on the hanging Mercury electrode;
- **Compounds with tensioactive properties** which can be absorbed on the surface of the electrode or which can absorb As on their surface;
- **Compounds which can determine complexes or precipitates** with As (Fe, Zn, Mn).

The effected studies led to the following results:

- **Iron** interferes in the correct evaluation of the result at concentrations higher than 13000µg/l, concentration corresponding to a As(III):Fe 1:4200 ratio;
- **Zinc** presents interferences over 5000 µg/l values corresponding to a As(III):Zn ratio of 1:1700;
- The interference of **Cadmium** is very strong over 150 µg/l values;
- **The tensioactive compounds** over 500 µg/l concentrations, corresponding to a As(III) ratio: the tensioactive compounds of 1:167 completely block the determination of arsenic species. The samples were submitted to the UV digestion and then cysteine was added in order to determine the total arsenic, but the results were totally unsatisfactory;
- **Mangan** proved not to have interference effects even over concentrations of 30mg/l.
- Following these results, as well as the previous studies, we came to the conclusion that the method can be successfully applied on surface and drinking waters or on waters with low metal concentrations, as well as on waters with a reduced organic charge.

Keywords: stripping voltammetry, interfering effects, Arsenic speciation, HMDE.

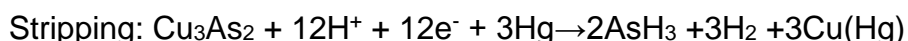
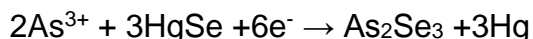
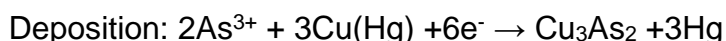
INTRODUCTION

Due to the different degrees of toxicity and, implicitly, of the danger presented by the arsenic compounds, precise and credible determination methods are needed for determining the traces of these arsenic species in water. Thus, not only the identification of metal's role in these processes becomes possible, but also the prevention and diagnosis of the diseases caused by their presence.

In solving these problems, a special role is detained by the methods with a high sensibility in determining the concentration of substances at traces level, among which the electrochemical techniques (polarographical, the anodic and cathodic stripping voltammetry) [1,2].

The electrochemical methods are highly sensitive and can be successfully used in determining the traces of heavy metals from the natural resources of water and from the waste water. The techniques of stripping voltammetry are noticeable by the very high sensitivity and selectivity, as well as by relatively low costs. Also, the procedures necessary for the analysis are simple. Due to the high selectivity of these techniques, its can be used in determining the species of arsenic, with excellent results.

The method selected for the determination of the arsenic species from the surface and waste water uses the technique of stripping voltammetry by cathodic differential pulse [3-7]. The electroactive specie is As (III), As (V) being determined by the difference between total As and As (III), after reduction. The As (V) reduction to As (III) is obtained by adding in the water sample 20mM of L-cysteine and 0,03M HCl. The sample is warmed for approximately 6 minutes at 70°C. The accumulation on mercury drop, followed by the stripping process, was made in a solution of chlorhydric acid, solution containing ions of Cu (II) and Se (IV). By combining Cu (II) and Se (IV) with As (III), an intermetallic complex is formed on the mercury electrode, during the depositing phase, of the $Cu_xAs_ySe_z$ type – complex that increases the sensitivity of the method and improves the form of the peak. The total arsenic is determined by the reduction of the entire quantity of arsenic to arsenic (III). This process is described by the following process:



EXPERIMENTAL PART

Reagents and materials:

- For the solutions used in all experiments only ultrapure water was used;
- The As (III) 1000mg/l solution was prepared by rendering soluble 0,132g of As_2O_3 (Merck) (previously dried at 110°C for 2h) in 2mL ultrapure NaOH of 20% concentration. The solution thus rendered soluble is brought to pH 2

with ultrapure HCl and is diluted with water in a 100ml volumetric flask, obtaining a solution of 1g/l.

- Solution of suprapure[®] HCl 30% Merck;
- Solution of Cu(NO₃)₂ Merck 1g/l in HNO₃;
- Solution of SeO₂ Merck in HNO₃ 1g/l brought to 1mg/L;
- L-cystein 1M Merck. For a 10ml sample 0.2 ml L- cystein 1M will be used, to which approximately 35µl HCl 30% will be added;
- Solution of ultrapure oxygenated water 30% Merck;
- Working solutions of: As (III) 1mg/l, Cu (II) 1g/l, Se (IV) 1mg/l. Are obtained from the above solutions through water dilution;
- Inert gas for - Ar of 5.3 (99.9993%) Linde purity
- Stripping voltammeter Metrohm 797 VA Computrace;
- Digester UV Metrohm 705 UV

The optimized parameters, as well as the ones recommended by the producer are presented in table 1.

Start potential	-1,2V
End potential	-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
Depositiontime	60s
Equilibration time	15s
Initial purging time	300s

Table 1. The optimal parameters used in determining As (III)

The reduction of arsenic (V) to As (III) is very effective. Tests on synthetic solutions of 1µg/l, 3 µg/l and, respectively, 7 µg/l As (V) have been performed mean recovery efficiency being around 96%.

The interferences found in the determination of As through voltammetric methods can be classified in three categories:

-The metallic ions which can form intermetallic compounds with As (Cd) that are accumulated on the hanging Mercury electrode;

-Compounds with tensioactive properties which can be absorbed on the surface of the electrode or which can absorb As on their surface;

-Compounds which can determine complexes or precipitates with As (Fe, Zn, Mn).

Interfering studies

We performed a large number of tests on representative types of matrix samples. Thus, we used a surface water matrix from Aries river on the same concentration range on which the calibration curve has been performed. The

sample was previously filtrated. In order to establish the matrix influence on arsenic species determinations we need to evaluate statistic performance parameters according to SR ISO 8466/1;2 [8] for the surface and ultrapure water.

Another criterion taken into account in studying of matrices was represented by the effects of the possible interferents. In order to accomplish this, we need to add the analyte in known concentration, and then, after adding the interferent at different concentrations, we calculate the recovery efficiency.

From the analysis of key performance parameters of calibration curves for the studied surface water and ultrapure water could be easily notice that they do not vary significantly, as both curves can be used on the chosen domain (1-7 μ g/l).

Based on these findings, the addition of different compounds has been performed, compounds able to interfere in the determination of As (III), an electrochemically active species, the recovery efficiency being calculated afterwards. The performed tests have shown that the studied surface water sample does not contain traces of arsenic.

Thus, in the case of surface water, the literature has shown that in the determination of arsenic species by stripping voltammetry techniques Iron, Zinc, Manganese, Cadmium, and surfactant compounds can interfere [9].

RESULT AND DISCUSSION

The influence of Iron on the determination of As (III) species

In order to establish the influence of Iron on the determination of arsenic (III) of the analyzed samples, we drew the calibration curve on the studied surface water sample and then a solution of known concentration of analyze was made. After this stage we added the interfering ions in different concentrations and studied its effect on determinations by calculating the recovery efficiency.

This procedure was applied to all studied interferents. In the case of the studied matrix, we added As (III) at a concentration of 3 μ g/l in the electrochemical cell. The obtained result was 3.09 μ g/l. Following these determinations, we switched to the addition of Iron in different concentrations and we monitored its interference. Thus Iron was added, in concentrations corresponding to 9 mg/l, 13 mg/l, 17 mg/l and 30 mg/l. The results of these determinations and the recovery efficiency are presented in Table 2.

Iron concentration (μ g/l)	Concentration of As (III) added (μ g/l)	Concentration of As (III) recovered (μ g/l)	Recovery efficiency (%)
9000	3.09	2.959	95.76
13000	3.09	2.717	87.93
17000	3.09	2.498	80.84
30000	3.09	2.329	75.37

Table 2. Recovery efficiency values of As (III) after adding different concentrations of Iron

As seen from the table above, the Iron begins to show strong interference at a concentration greater than 13000 µg/l, corresponding to a concentration ratio As (III)/Fe equal to 1:4200.

The influence of Zinc on determining the species of As (III) by stripping voltammetry

Following the same procedure as in studying the influence of Iron on the determinations of As (III), Zinc was added in different concentrations and implicitly to concentration ratios that were different from the analyte concentration.

Initially As (III) was added, in the same electrolytic cell concentration as in the case of As with Iron, namely 3µg/l. The results of these determinations and the recovery efficiency are presented in Table 3.

Zinc concentration (µg/l)	Concentration of As (III) added (µg/l)	Concentration of As (III) recovered (µg/l)	Recovery efficiency (%)
2600	3.09	2.905	94
5000	3.09	2.658	86
9000	3.09	2.55	82.5
13000	3.09	2.45	79.3
17000	3.09	2.38	77

Table 3. Recovery efficiency values of As (III) after adding different concentrations of Zinc

As shown, the influence of Zinc in the determination of As(III) species becomes visible at a concentrations above 5 mg/l, which corresponds to an As (III) / Zn ratio of approximately 1:1700.

The influence of Manganese on the determination of As (III) species by stripping voltammetry

In the case of Manganese we followed the same procedure as in case of Iron and Zinc. Although the literature mentions that Manganese has an interfering effect in the determination of As (III), in our case this was not confirmed, tests ranging up to a concentration of Manganese of 30 mg/l in the electrolytic cell.

The results of these determinations and the recovery efficiency are presented in Table 4.

Manganese concentration (µg/l)	Concentration of As (III) added (µg/l)	Concentration of As (III) recovered (µg/l)	Recovery efficiency (%)
5000	3.09	2.905	94
17000	3.09	2.99	96.76
30000	3.09	2.941	95.17

Table 4. Recovery efficiency values of As (III) after adding different concentrations of Manganese

The influence of Cadmium on the determination of As (III) species by stripping voltammetry

In order to determinate if the presence of Cadmium influences the determination of As (III) species, we worked as in the case of the previous cases.

The results demonstrated a strong interference even at low concentrations of Cadmium. The obtained results and the recovery efficiency are presented in Table 5.

Cadmium concentration (µg/l)	Concentration of As (III) added (µg/l)	Concentration of As (III) recovered (µg/l)	Recovery efficiency (%)
75	3,107	3.074	98.94
150	3,107	3.468	111.6
300	3,107	4.407	141.8
2600	3,107	23.94	770.52
9000	3,107	79.7	2565

Table 5. Recovery efficiency values of As (III) after adding different concentrations of Cadmium

As is seen from the table above, concentrations higher than 150µg/l Cd, corresponding to a ratio As (III)/Cd 1:50, lead to strong interference effects and the result is incorrect.

The influence of surfactant compounds on the determination of As (III) species by stripping voltammetry

Surfactant compounds can have powerful effects in influencing the results. This happens because they are adsorbed on the mercury drop, thus blocking the accumulation and preconcentration of the analyte [10-14]. Experiments fully demonstrate it. The obtained results and the recovery efficiency are presented in Table 6.

Surfactant concentration (µg/l)	Concentration of As (III) added (µg/l)	Concentration of As (III) recovered (µg/l)	Recovery efficiency (%)
500	3.09	1.866	60.38
1000	3.09	1.12	36.25
2500	3.09	0	0
5000	3.09	0	0

Table 6. Recovery efficiency values of As (III) after adding different concentrations of surfactants

As we can see, at concentrations of 0.5 mg/l, surfactant compounds (Sodium dodecyl sulfate) have strong interference effects, the recovery efficiency being very low.

The effect of the interference is comparatively illustrated in Figure 1. The shape of the voltammogram became very deformed by the increasing concentrations of surfactant in the electrolytic cell.

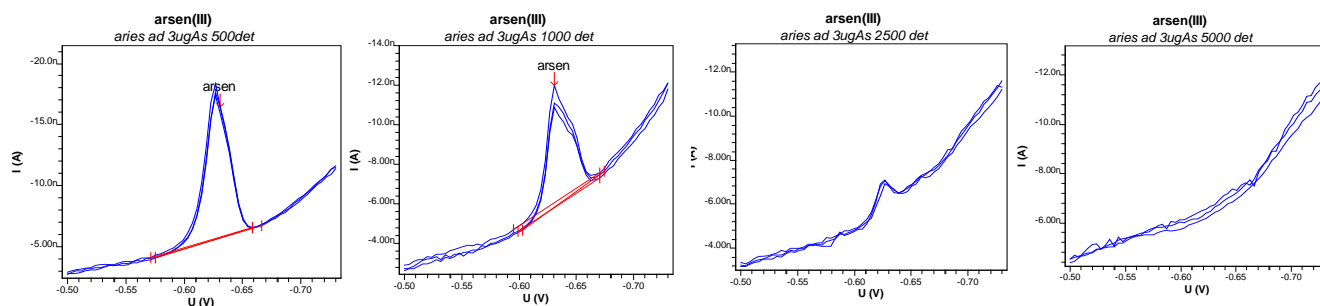


Fig. 1 The shape of the voltammogram obtained after adding 500, 1000, 2500 and 5000µg/l surfactant compounds

As we can see, the signal drops drastically, reaching a concentration of 5000 µg/l, only to disappear completely afterwards. Samples were exposed to UV digestion in order to determine the total arsenic, but the results also showed a strong interference.

CONCLUSIONS

- Calibration curves were drawn for ultrapure water and the studied matrix;
- The analysis of key performance parameters of calibration curves for the studied surface and ultrapure waters can be easily seen as they do not vary significantly, both curves being usable on the chosen domain;
- The commonly encountered effects of the interference in surface water and wastewater were verified;
- Iron interferes in the accurate arsenic determination at concentrations higher than 13000µg/l, concentration corresponding to a ratio of 1:4200;
- Zinc interferences at concentration values over 5000 µg/l, corresponding to a ratio As (III): Zn of 1:1700;
- The interference of Cadmium is very powerful over values of 150 µg/l;
- The tensioactive compounds (anionic surfactant) at concentrations greater than 500 µg/l corresponding to an As(III) raport – tensioactive compounds of 1:167 – completely block the determination of the arsenic species. The samples were submitted to the UV digestion and then cysteine was added in order to determine the total arsenic, but the results were unsatisfactory.
- Manganese proved to have no interferent effects, not even in concentrations of over 30mg/l.

In conclusion, the method can be successfully applied in the case of surface and drinking water, or for water with low levels of metal, as well as for waters with low organic charge.

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