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Research Article

Investigation of Adsorption Studies of Different Arsenic Species Using the Diffusive Gradients in Thin Film (DGT) Technique

Türkan BÖRKLÜ BUDAK [a,*]

[a] *Chemistry Department, Faculty of Science and Art, Yildiz Technical University, Istanbul, TURKEY*
** Corresponding author's e-mail address: turkanborklu@yahoo.com*
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ABSTRACT

The amount of arsenic (As) in the earth increases every day and adversely affects the life of all living beings, including human health. Therefore, studies on the development of As determination methods are gradually gaining importance. The foundation of the Diffusive Gradients in Thin Film (DGT) technique addressed in this study is based on the diffusion process. The analyte to be determined passes through different layers in the DGT unit and reaches the adsorber gel layer. In the study presented, the gel obtained from iron (III) oxide (Fe_2O_3) was used as the adsorber layer. The use of the DGT technique in the amount determination of As(III) and As(V) species in the aqueous medium was examined and all the measurements performed during the experimental studies were observed to be made with an ICP-MS device. Different parameters were evaluated in terms of different pH values, ionic strength effects, gel layer thickness and the effects of the eluent materials and the most suitable working conditions were determined.

Keywords: *Arsenic, DGT, Iron(III) Oxide*

Difüzyon Yöntemi (Diffusive Gradients in Thin Film; DGT) Kullanılarak Farklı Arsenik Türlerinin Adsorpsiyon Çalışmalarının Araştırılması

ÖZET

Yeryüzünde bulunan arsenik (As) miktarı günden güne artış göstererek insan sağlığı da dahil olmak üzere tüm canlı hayatını olumsuz yönde etkilemektedir. Bu nedenle As tayin yöntemlerinin geliştirilmesine yönelik çalışmalar her geçen gün önem kazanarak artmaktadır. Bu çalışmada yer alan Diffusive Gradients in Thin Film (DGT) yönteminin temeli difüzyon işlemine dayanmaktadır. Tayin edilmek istenilen analit, DGT ünitesinin içerisinde bulunan farklı katmanlardan geçerek adsorplayıcı jel tabakasına ulaşmaktadır. Sunulan çalışmada adsorplayıcı tabaka olarak demir (III) oksit (Fe_2O_3)'den elde edilen jel kullanılmıştır. DGT yönteminin sulu ortamda As(III) ve As(V) türlerinin miktar tayininde kullanımı incelenmiş deneysel çalışmalar sırasında gerçekleştirilen tüm ölçüm işlemleri, ICP-MS cihazı ile gerçekleştirilmiştir. Farklı pH değerleri, farklı derişimde iyonik şiddet etkileri, jel tabakası kalınlığı ve kullanılan eluent maddelerin etkileri bakımından farklı parametreler değerlendirilmiş, en uygun çalışma koşulları belirlendi.

Anahtar Kelimeler: *Arsenik, DGT, Demir (III) Oksit*

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I. INTRODUCTION

Arsenic (As) is an element that is present in a large amount on the earth and can exhibit a carcinogenic effect by reducing water quality [1-3]. It is especially found in ground waters at high concentrations. Therefore, the maximum concentration of As that can be found in the drinking water is tried to be controlled by some limit values. For example, the WHO determined this value to be at most 10 μgL^{-1} [4,5]. A group of elements (As, Sb, Se), including As, are listed by US-EPA as the major water pollutants, while As and Cr are qualified as the number one carcinogenic substances by IARC [6].

In recent years, more than 60 million people have been exposed to high amounts of As since they have to consume dirty drinking water [7]. If the main reasons for the increase in the amount of As worldwide are examined, man-made reasons such as the paint industry, mining, copper smelting industry, glass production, electronic waste disposal, the use of some pesticides and herbicides, and the consumption of fossil fuels, can be listed [8].

Toxic effects of As change according to the solubility of the compounds it forms, the stability of the formed complexes, and the oxidation step it has [9-11]. As, which concentrates in nature, in waters, and sediments, is found in the forms of As(V) and As(III) [12-14].

The As(V) oxidation step of the element As, which is found in the periodic table as a transition element, is more prominent in aerobic waters. When the literature data are examined, it is observed that elements such as As, Sb, and Mo, can be detected by atomic absorption/fluorescence spectrometry [15], inductively coupled plasma mass spectrometry (ICP-MS) [16], enzymatic assays [17], monoclonal antibodies tests [18] and biosensor platforms [19]. The analysis conducted with these methods, which are highly sensitive and have low detection limits, has limited possibilities in terms of monitoring the analysis at the site, where sampling is performed. The point of criticism targets the adverse effects that may occur in the sample collection step rather than the related methods [20]. When the studies in the literature are examined, the DGT technique can be explained as follows:

There are polyacrylamide hydrogel, a protective membrane filter, and a binder layer in the DGT unit. The membrane filter layer is exposed to the environment to be analyzed by means of an "open part" found in the structure. The analyte passing through the membrane filter comes to the hydrogel, and substances of which pores are smaller than the hydrogel reach the binding gel layer. In this way, it allows the diffusion of the desired analyte species and is collected by adsorption. The analyte collected by the adsorption process is taken up into the solution with the aid of an appropriate eluent solution and determined in the laboratory.

A Chelex 100 cation exchanger is used as the adsorbent in DGT units. Recently, however, it is observed in the literature that adsorbents containing the ferrihydrite structure have been used for the purpose of anion measurements. They are mainly used in phosphate and inorganic arsenic determinations [21].

This study aimed to determine the amount of As species in freshwater by using the DGT technique. In this way, the performance of the DGT technique in the evaluation of the hazards caused by As in freshwaters will be assessed. Fe_2O_3 resin was used as the ion exchanger in the DGT technique, and analyte measurements were performed by an ICP-MS device.

II. MATERIALS AND METHOD

In this part of the article, information is given about the materials used during the experimental studies and the experimental methods followed.

A. MATERIALS

The gel sheets in the DGT technique to be used were prepared according to the method given in the prescription [22]. The gel sheets; binding layer (Fe_2O_3 gel layer), diffusion layer and protective layer (by filter paper) were correctly inserted into the disc and closed, as shown in Figure 1. The As solutions used were prepared as 500 mgL^{-1} from $Na_2HAsO_4.7H_2O$ (Sigma–Aldrich) for As(V) and 500 mgL^{-1} from As_2O_3 (Sigma–Aldrich) for As(III) were dissolved in purified water (18.2 MΩ cm, Milli-Q Millipore). To avoid possible oxidation changes, solutions were used within 1 day of preparation.

B. METHOD

B. 1. DGT Preparation And Application

The aperture of DGT units that are exposed to the solution medium is 3.12 cm^2. The thickness of the diffusion layer used is 0.4 mm. The gel layer obtained from Fe_2O_3 was used as the resin layer. The filter used for protective purposes is of cellulosic nitrate filter structure and has a thickness of 0.14 mm. With the diffusion layer, it is used to separate the exposed solution from each other like in Figure 1.

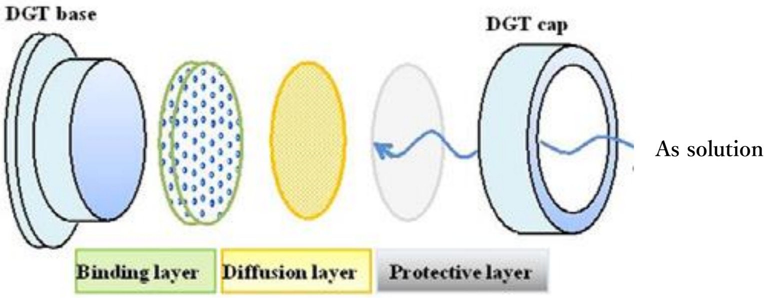

Figure 1. *Schematic representation of DGT layers [23]*

In order to be able to apply DGT devices, 2 liters of the solution containing 500 mgL^{-1} As was added to the working vessel in which the synthetic working medium was created. DGT devices were placed inside it in a sensitive way. It was stirred by a magnetic stirrer and kept at room temperature (25°C) for the required time. DGT devices were then taken from the medium, washed with Milli-Q water (Millipore), and the adsorbent gel layer, which was carefully removed from the disc, was placed inside 1 mL of the concentrated HNO_3 solution; thus, it was taken into the adsorbed As solution. Finally, it was analyzed in the ICP-MS device by diluting at appropriate ratios.

The concentration of labile trace elements, C_{DGT}, in the sample is then derived using Eq. (1) based on Fick's first law [16]:

$$C_{DGT} = M\Delta g/(DAt) \qquad (1)$$

In this equation, M represents the adsorbed As amount, Δg represents the total thickness of the diffusion gel filter membrane, D represents the diffusion coefficient at 25 °C required for As and taken from the tables, A represents the open surface area of the DGT unit that is in contact with the medium (3.14 cm^2), and t represents the exposure time.

B. 2. Experimental Procedure

In the experimental studies, firstly, by studying at different pH values in the range of pH 3-9, the adsorption of As(V) by the DGT unit was investigated. For this purpose, DGT units were immersed in an aqueous solution containing 500 mgL^{-1} As(V). The units were taken at certain times. In order to determine the As(V) retained by the Fe_2O_3 layer, which is the diffusion gel, the removed gel layer was taken up in the concentrated HNO_3 solution and determined in the ICP-MS device by diluting at specific ratios. All of these procedures were repeated for different pH values. The same trials were performed for As(III). The obtained results are shown in Figure 2.

In the continuation of the experimental studies, the effects of different ionic strengths on the determination of As(III) and As(V) were examined. For this purpose, $NaNO_3$ solutions, including 0.0 M, 0.1 M, 0.2 M, 0.3 M, 0.4 M, and 0.5 M, were added to the solution containing 500 mgL^{-1} As(III) and As(V). After that the experimental studies were repeated. The obtained results are shown in Figure 3.

During the determination of As species by the DGT technique, the effects of Fe_2O_3 gel layers of different thicknesses on experimental results were investigated. For this purpose, 0.4 mm, 0.8 mm, 1.2 mm, and 1.6 mm thick Fe_2O_3 gels were prepared and applied to DGT units. Experimental studies were applied separately to As(III) and As(V) solutions prepared as 500 mgL^{-1}. The obtained results are shown in Figure 4.

The maximum capacity of the As(III) and As(V) mixture sample that may be determined was then tried to be determined. Therefore, solutions containing 500 mgL^{-1} As(III) and As(V) were prepared. The total amount of As adsorbed in Fe_2O_3 gel layers at different time periods was determined on the ICP-MS device. The results are shown in Figure 5.

Finally, the effects of different eluent solutions on the results were examined. DGT units were placed in the As(V) solution prepared as 500 mgL^{-1}, and Fe_2O_3 gel sheets were taken after certain times and eluted with different solutions, and the amount of the adsorbed As(V) was determined. The same trials were also performed for As(III). The obtained results are shown in Figure 6.

III. RESULTS AND DISCUSSION

The determination of As(III) and As(V) in the aqueous medium was performed by using the DGT technique based on the diffusion technique. The effects of different parameters on the results obtained during the experimental studies were examined. The parameters investigated can be listed as pH, different ionic strengths, the adsorbent gel layer thickness used, and different eluent effects. Furthermore, the maximum As(III) and As(V) mixture amount, which could be adsorbed by DGT units formed by using Fe_2O_3 gel sheets was also investigated.

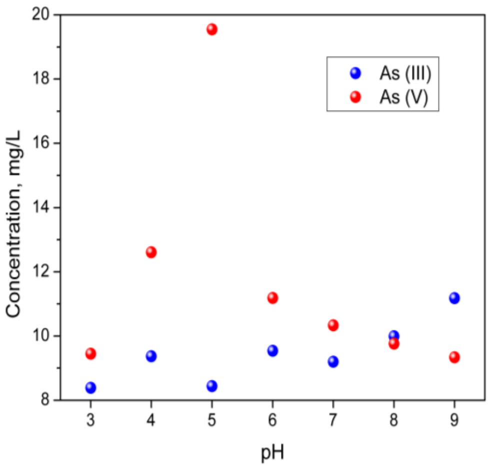

Figure 2. *Evaluation of different pH effects*

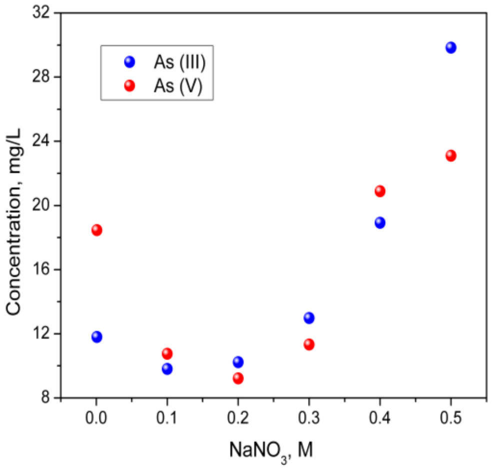

Figure 3. *Experimental data of different ionic strength studies*

When the obtained data were analyzed, as shown in Figure 2 the most suitable working pH value was determined to be pH=9 for As(V) and pH=5 for As(III). Similarly, the data in Figure 3 were examined and the optimum ionic strength concentration was determined to be 0.5 M $NaNO_3$.

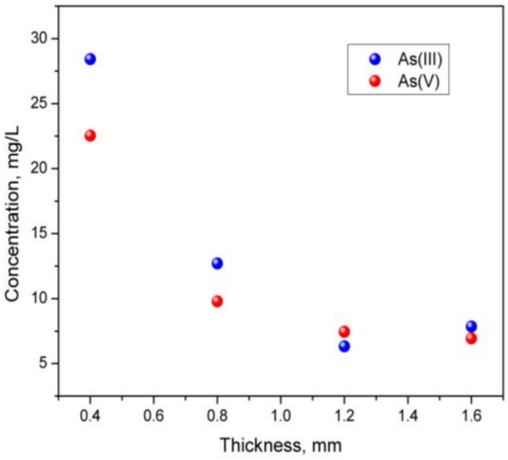

Figure 4. *The effect of different gel layer thicknesses on experimental results*

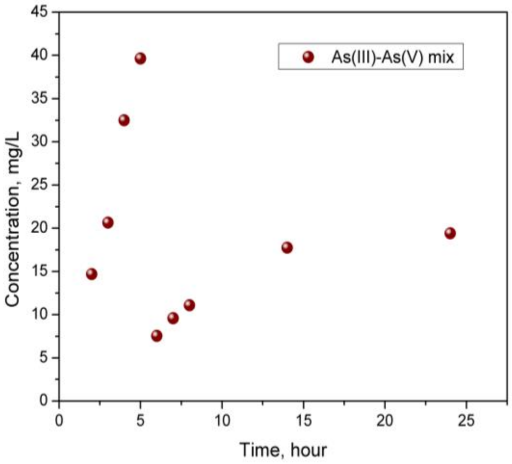

Figure 5. *Determination of the maximum amount of As that can be adsorbed*

When Figure 4 was examinated the most suitable gel layer thickness was found as 0.4 mm. In the studies, the maximum amount of As(III) and As(V) that could be adsorbed was determined to be 41.63 mgL^{-1} as shown in Figure 5.

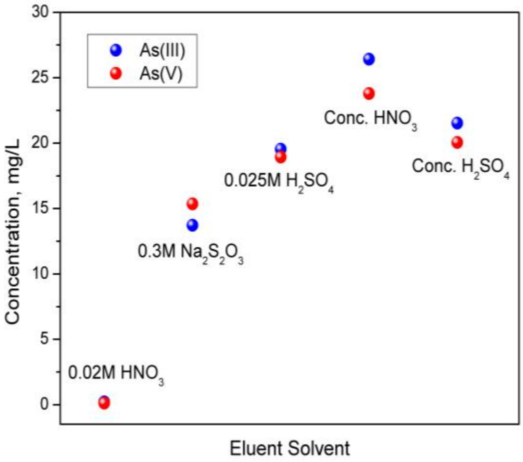

Figure 6. *Results of different eluent solution experiments*

The concentrated HNO_3 used in the experiments as the eluent provided the best results, as shown in Figure 6.

IV. CONCLUSION

In this study, the analysis of As element, which has many harmful effects on human health and nature, in the aqueous medium was carried out successfully by using the DGT technique in parallel with the literature data. The most suitable working parameters were tried to be determined. The DGT technique, which is observed to have a wide usage area when worldwide applications are examined, can minimize the adverse effects that may occur at the sample collection step, which constitutes one of the most important steps of experimental studies, by making in situ monitoring of this stage possible in its natural environment. Furthermore, it is a quick and easily applicable technique.

Despite its mentioned advantages, when the DGT practices performed in Turkey are examined, not much data can be obtained. The present study is thought to be valuable in terms of its leading the applicability of the DGT technique in Turkey. The results, which are parallel to the literature data, are important since they demonstrate that this technique can also be successfully applied in Turkey.

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