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Research Article

Determination of Uric Acid Using 2D-MoS_2 Modified GCE

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Abstract

Uric acid (UA) is the end product of purine metabolism in the human body. The determination of the amount of uric acid in biological samples is made by many analytical methods. However, due to the high cost and time consumption of these methods, many sensors have been developed for the determination of uric acid by electrochemical methods. Analysis of biological samples using electrochemical methods is possible in a shorter time and with cheaper devices. In this study, electrochemical determination of uric acid was performed by modifying the glassy carbon electrode with two-dimensional molybdenum disulfide using two different methods (drop-coating and electrochemical coating). From the uric acid determination with the MoS2(1)/GCE numbered electrode, the sensitivity was found to be 11.4 µA.mM^{-1}, the linear operating range from 4 µM to 520 µM, and the detection limit was 0.8 µM. With MoS2(2)/GCE, the 1st linear working range against Uric acid was found to be 0.1 µM – 20 µM, the sensitivity was 331 µA.mM^{-1} and the detection limit was 6.7x10^{-8} M. The 2nd linear operating range was 20 µM - 687 µM, and the sensitivity was determined as 62.4 µA.mM^{-1}. In order to determine the efficiency of uric acid determination with MoS2(2)/GCE, Uric acid determination in blood serum samples obtained from the hospital was successfully performed with MoS2(2)/GCE with a relative error of 3.7%.

Keywords: Uric acid, Two-Dimensional Molybdenum disulfide, Electrochemical Determination

2D-MoS_2 ile Modifiye Edilen GCE Kullanılarak Ürik Asit Tayini

Öz

Ürik asit (UA) insan vücudundaki pürin metabolizmasının son ürünüdür. Biyolojik örneklerde ürik asit miktarının belirlenmesi birçok analitik yöntemle yapılmaktadır. Ancak bu yöntemlerin yüksek maliyet ve zaman tüketimi nedeniyle elektrokimyasal yöntemlerle ürik asit tayini için birçok sensör geliştirilmiştir. Biyolojik numunelerin elektrokimyasal yöntemlerle analizi daha kısa sürede ve ucuz cihazlarla mümkün olmaktadır. Bu çalışmada, camsı karbon elektrotun iki farklı yöntem (damlatarak kaplama ve elektrokimyasal kaplama) kullanılarak iki boyutlu molibden disülfür ile modifiye edilmesiyle ürik asidin elektrokimyasal tayini yapıldı. MoS2(1)/GCE numaralı elektrot ile yapılan ürik asit tayininde duyarlılığın 11,4 µA.mM^{-1}, doğrusal çalışma aralığının 4 µM ile 520 µM arasında olduğu ve tespit limitinin 0,8 µM olduğu belirlendi. MoS2(2)/GCE ile ürik aside karşı 1. doğrusal çalışma aralığı 0,1 µM – 20 µM, hassasiyet 331 µA.mM^{-1} ve tespit limiti 6,7x10-8 M olarak bulunmuştur. 2. doğrusal çalışma aralığı 20 µM - 687 µM, duyarlılığı ise 62,4 µA.mM^{-1} olarak belirlendi. MoS2(2)/GCE ile ürik asit tayininin etkinliğini belirlemek amacıyla hastaneden alınan kan serum örneklerinde Ürik asit tayini MoS2(2)/GCE ile %3,7 bağıl hata ile başarılı bir şekilde gerçekleştirildi.

Anahtar Kelimeler: Ürik asit, İki Boyutlu Molibden disülfür, Elektrokimyasal Tayin.

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1. Introduction

Molybdenum disulfide (MoS_2): It is one of the important two-dimensional (2D) transition metal dichalcogenides from graphene analogues. MoS_2 is the most interesting material of this group with its graphite-like structure [1]. Transition metal dichalcogenides (TMD) are denoted by the general formula MX_2 (M = Mo, W, V, Nb, Ta, Ti, Zr, Hf and X = S, Se, Te). They have found a very wide application area by forming an interesting group of materials with unique electronic, optical, thermal, mechanical and electrical properties and structures similar to graphene [2]. For example; such as in lubricants, hydrogen storage, catalysts, transistors, optics, nanoelectronics. TMDs contain aggregates in planar structure with weak van-der-waals-force. In recent years, the most studied of the transition metal dichalcogenides are MoS_2 and WS_2. The layered structure of MoS_2 is shown in Figure 1 [3].

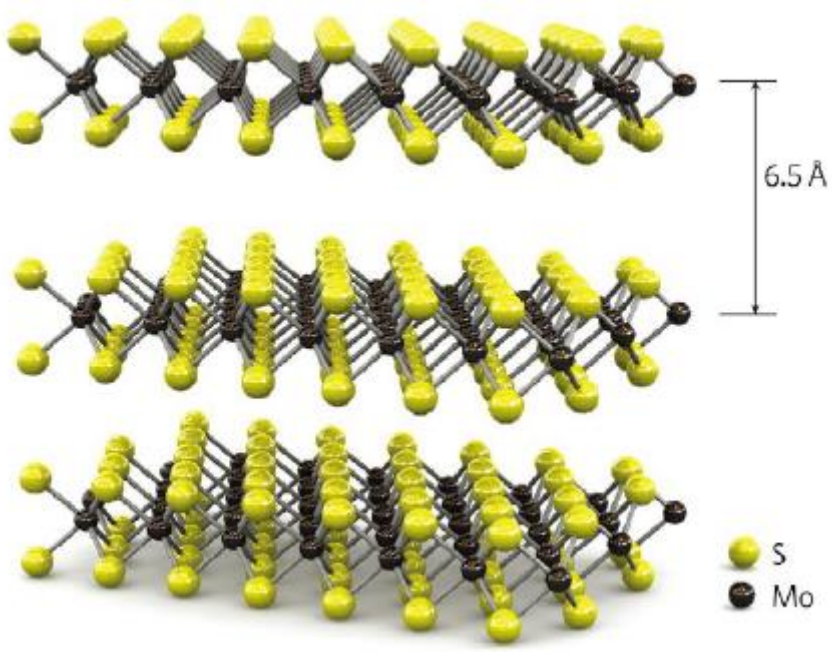

Figure 1. Layered structure of MoS_2, monolayer thickness 6.5 Å

MoS_2 has a hexagonal layer configuration. Atoms in the layer are connected by strong covalent bonds, the layers are connected to each other by weak forces, as in graphite, and each molybdenum layer is sandwiched between two sulfur layers [4]. In this study, glassy carbon electrode was modified using two-dimensional MoS_2 and used for uric acid determination. The amount of uric acid in the blood, which is the end product of purine metabolism in the human body [5]; It indicates the balance between the production of uric acid in the liver and intestine and its excretion through the kidneys. Most of the uric acid is excreted by the kidneys, and a small amount is excreted through the intestines. Depending on the foods and their uric acid content, the amount of uric acid in the blood constantly changes. In a healthy adult, blood uric acid levels range between 4-7 mg/100 mL in men and 3-6 mg/100 mL in women [6]. An increase in uric acid can be an indicator of many diseases. Determination of uric acid level is an important examination in the treatment of gout, but it also provides information about many other diseases. An increase in uric acid is seen in many diseases such as leukemia (blood

cancer), some anemia, lymphatic system cancers, and some hormonal disorders such as hyperthyroidism (overwork of the thyroid gland). In such cases, detecting the uric acid concentration in the urine is useful for early diagnosis of the disease. Electrochemical determination of uric acid is possible. Figure 2 shows the electrochemical oxidation of uric acid [7].

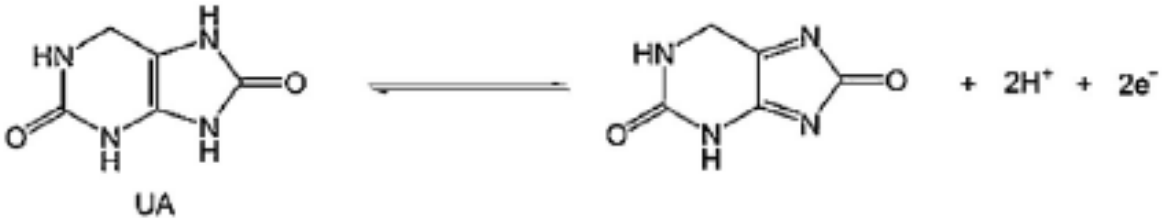

Figure 2. Electrochemical oxidation of uric acid

Electro-analytical techniques allow the qualitative and quantitative determination of a large number of inorganic and organic substances. These techniques have been developing more rapidly in recent years due to some of their superiorities over other analytical techniques (spectroscopy, chromatography, etc.) and find application areas. These superiorities are sensitivity, speed, ease of sample preparation, selectivity, low detection limit and low cost. Uric acid determination can be determined by different methods such as chromatographic [8,9] and spectrophotometric [10,11]. However, due to the superiorities mentioned above, an increase in the determination of uric acid by electrochemical method [12-16] has been observed in recent articles.

In this study, MoS_2 modified electrodes were prepared by drop coating and electrochemical coating techniques and exploited for uric acid determination in blood sample.

2. Materials and Methods

Electrochemical measurements were done in a three-electrode system with a computer-controlled CHI 660E potentiostat. Glassy carbon electrode (GCE) and modified glassy carbon electrodes (MoS2(1)/GCE electrode and MoS2(2)/GCE electrode) were used as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. MoS_2 in powder form was obtained from Özdogu Madencilik Ltd.Şti. and uric acid was obtained from Sigma Aldrich. Standard solutions of uric acid were prepared in phosphate buffer pH=7. Phosphate buffer solution (pH=7) was used as the supporting electrolyte. For the preparation of MoS2(1)/GCE electrode and MoS2(2)/GCE electrode, drop coating method and electrochemical coating method were applied. Uric acid was determined using the MoS2(1)/GCE electrode prepared by taking 5 µL of the coating suspension. Since the preparation of the MoS2(1)/GCE electrode prepared by the drop coating method was given in detail in our previous publication [17]. Electrochemical coating method was used for the preparation of the MoS2(2)/GCE electrode. In another study, the cleaned surface of GCE electrodes was coated in three different times and the optimum time determination was determined as 3600 seconds (18). For this reason, 3600 seconds was preferred as the duration

in this study. The coating was carried out by keeping the GCE in 0.5 M NaOH containing the coating suspension (10% v/v) at constant potential (1.0 V) for 60 minutes. Detailed information on how the MoS2(2)/GCE electrode is prepared can be found in doctoral thesis [18]. The differential pulse voltammetry (DPV) method was used for uric acid determination.

3. Results and Discussions

3.1. Determination of Uric Acid with MoS2(1)/GCE

Uric acid determination was made with MoS2(1)/GCE electrode prepared. The differential pulse (DP) voltammograms versus increasing uric acid concentrations with MoS2(1)/GCE (in pH=7 phosphate buffer) are given in Figure 3 and the calibration curve produced from the peak currents of DP voltammograms is given in Figure 4.

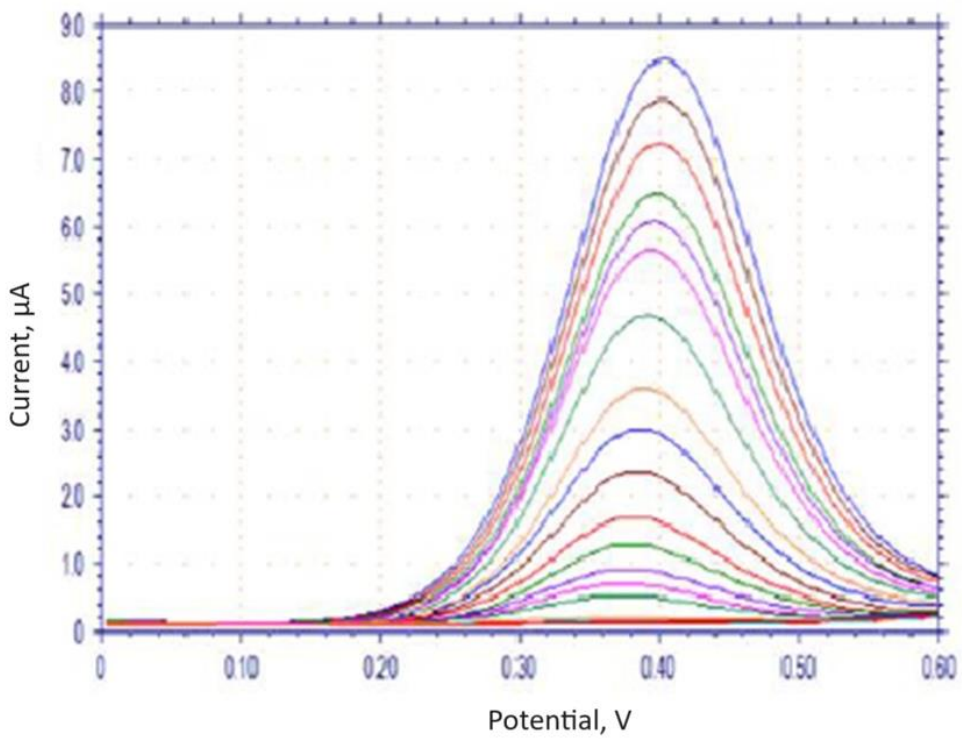

Figure 3. DP voltammograms at different concentrations for Uric Acid determination with MoS2(1)/GCE

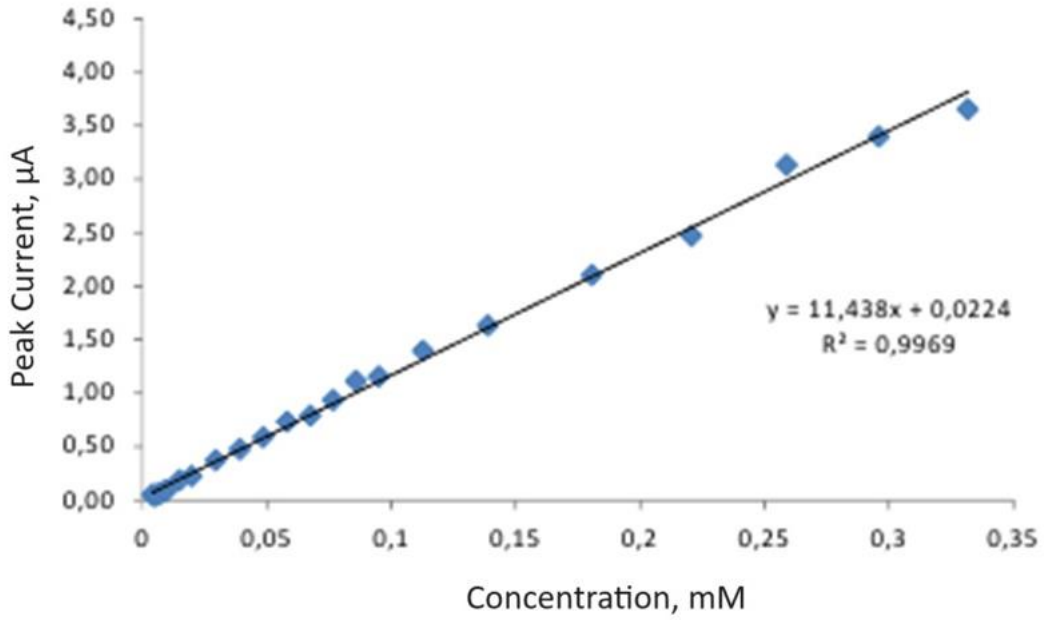

Figure 4. The plot of peak currents versus UA concentration measured by MoS2(1)/GCE

For comparison, differential pulse voltammograms against increasing uric acid concentrations in pH=7 phosphate buffer with GCE were given in Figure5 and concentration versus peak currents plot is given in Figure 6.

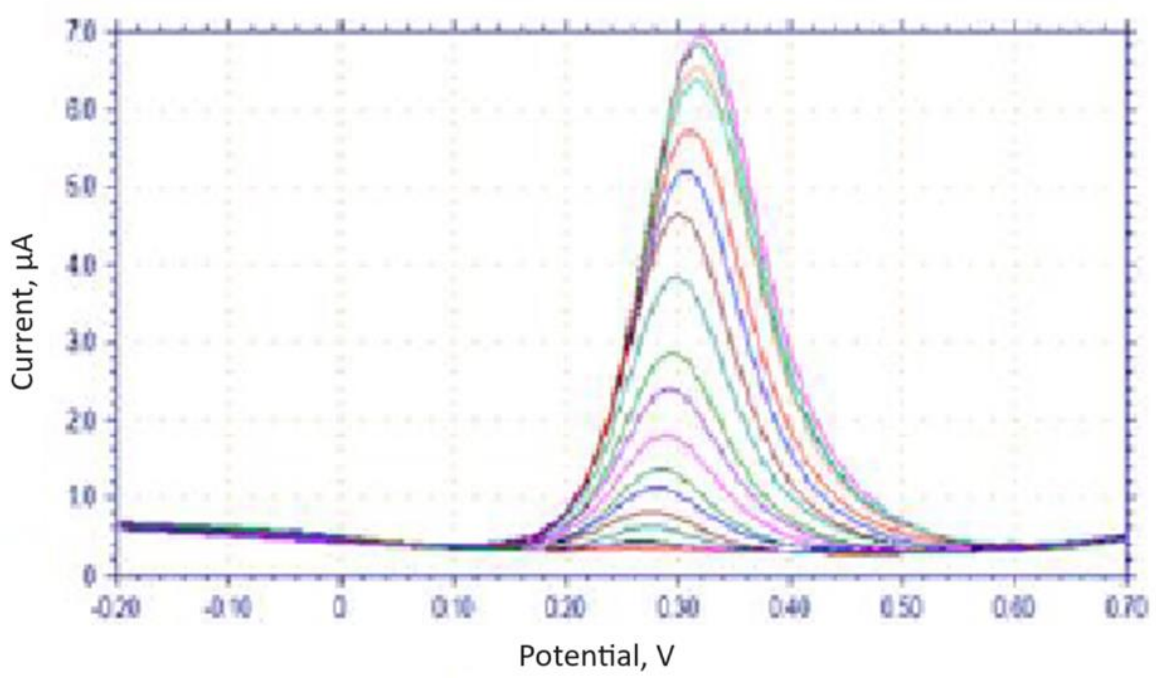

Figure 5. DP voltammograms at different concentrations for UA determination by GCE

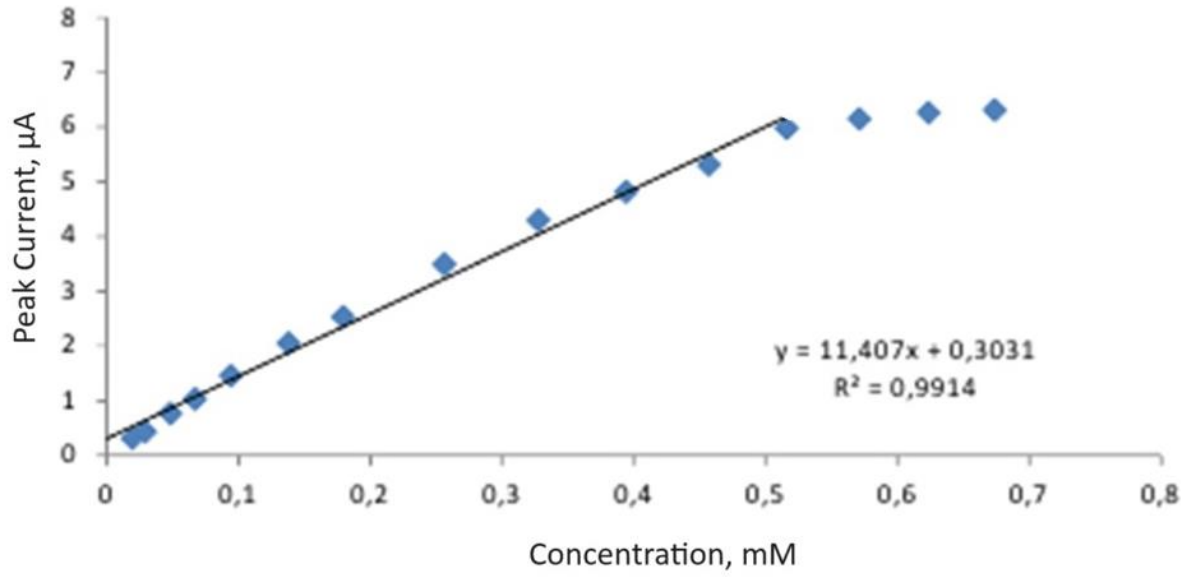

Figure 6. The plot of peak currents versus UA concentration measured by GCE

When Table 1 is examined, the sensitivity value for MoS2(1)/GCE and uric acid was found to be 11.44 µA/mM, and the sensitivity value for GCE for uric acid was 11.41 µA/mM. It showed almost the same catalytic efficiency for uric acid with MoS2(1)/GCE compared to GCE.

Table 1. Comparison of the values obtained in the determination of UA with MoS2(1)/GCE and GCE

	Electrode Name	
	GCE	MoS2(1)/GCE
Linear Operating Range (µM)	4-520	4-520
Line Equation (µA/ mM)	y=11.407x +0.3031	y=11.438x +0.0224
R^2	0.9914	0.9969
Sensitivity (µA/ mM)	11.41	11.44

Analytical performance values for uric acid with MoS2(1)/GCE were given in Table 2.

Table 2. Analytical performance values for uric acid with MoS2(1)/GCE

Linear Working Range (µM)	4 - 520
Sensitivity ($\mu A.mM^{-1}$)	11.4
LOD (µM)	0.84
LOQ (µM)	2.81

After taking the differential pulse voltammograms at varying uric acid amounts with MoS2(2)/GCE, they were superimposed and the resulting graph is given in Figure 7, and the peak currents against concentration are plotted in Figure 8. As seen in Figure 8, first a linear

interval with a higher slope and then a second linear interval with a lower slope were found for the concentration range studied. The 1st linear operating range is presented in Figure 9 and the 2nd linear operating range is presented in Figure 10.

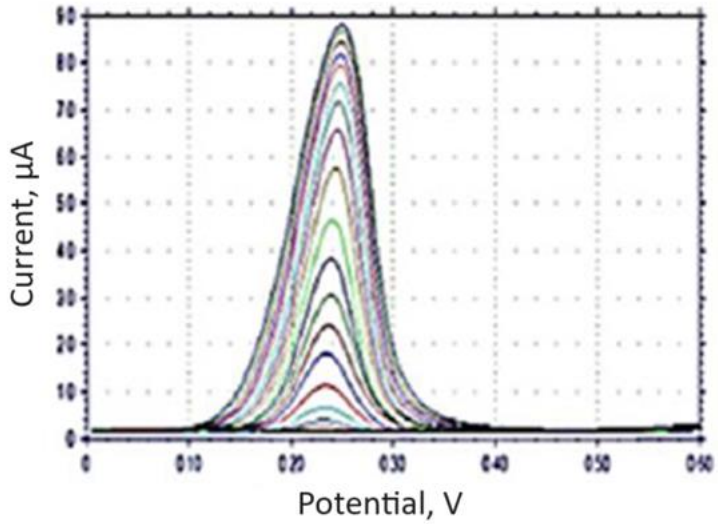

Figure 7. DP voltammograms at different concentrations for UA determination with MoS2(2)/GCE

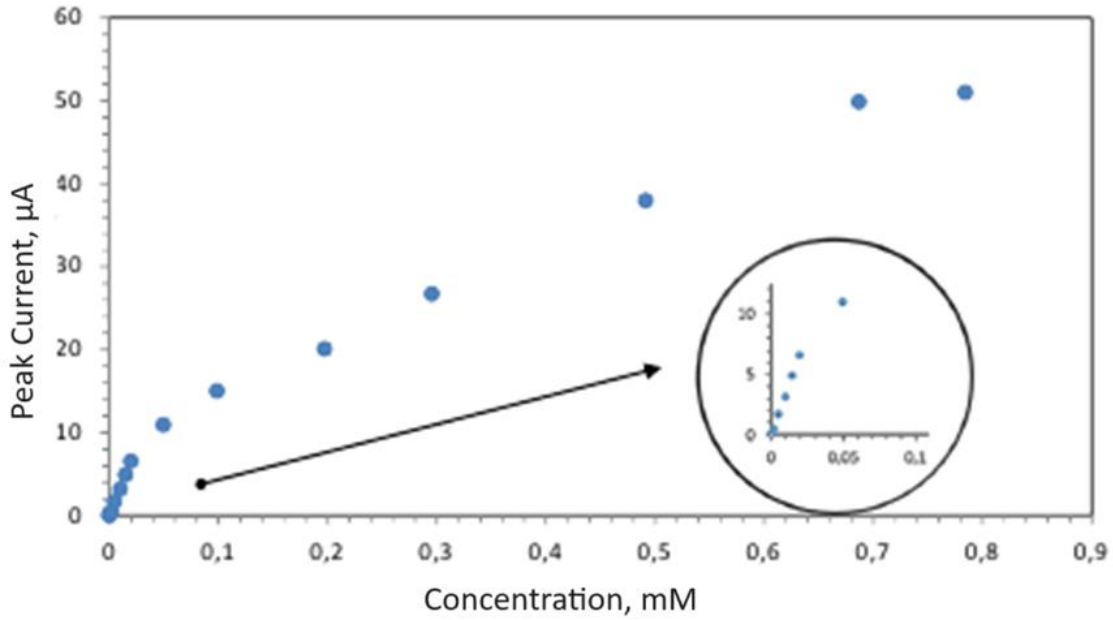

Figure 8. The plot of peak currents versus UA concentration measured by MoS2(2)/GCE

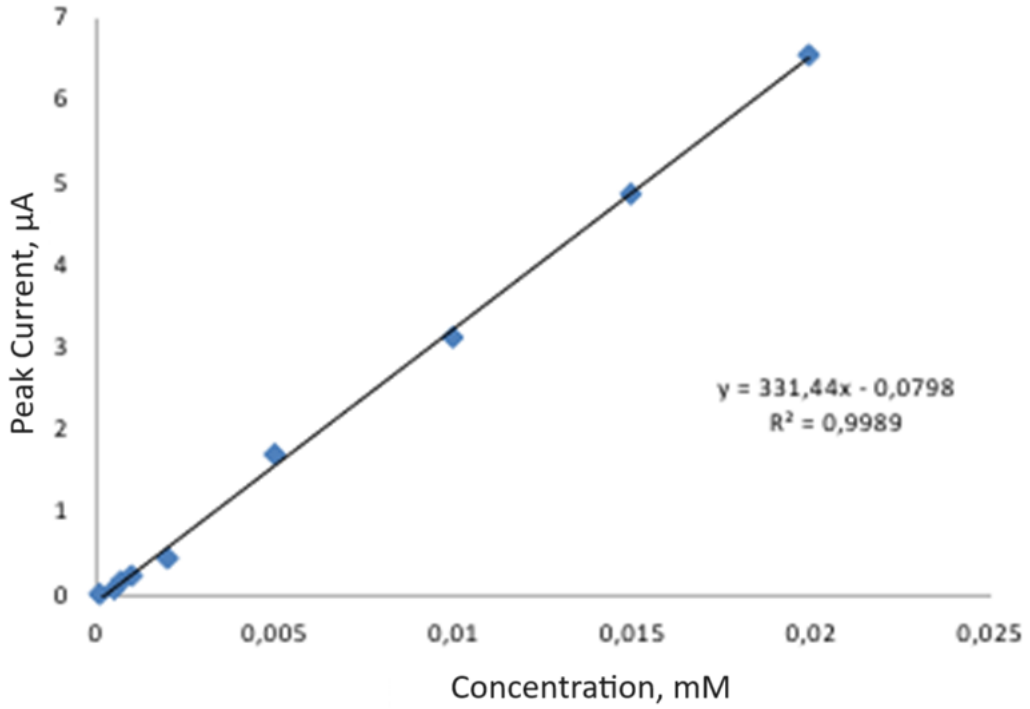

Figure 9. 1st linear operating range for UA determination with MoS2(2)/GCE

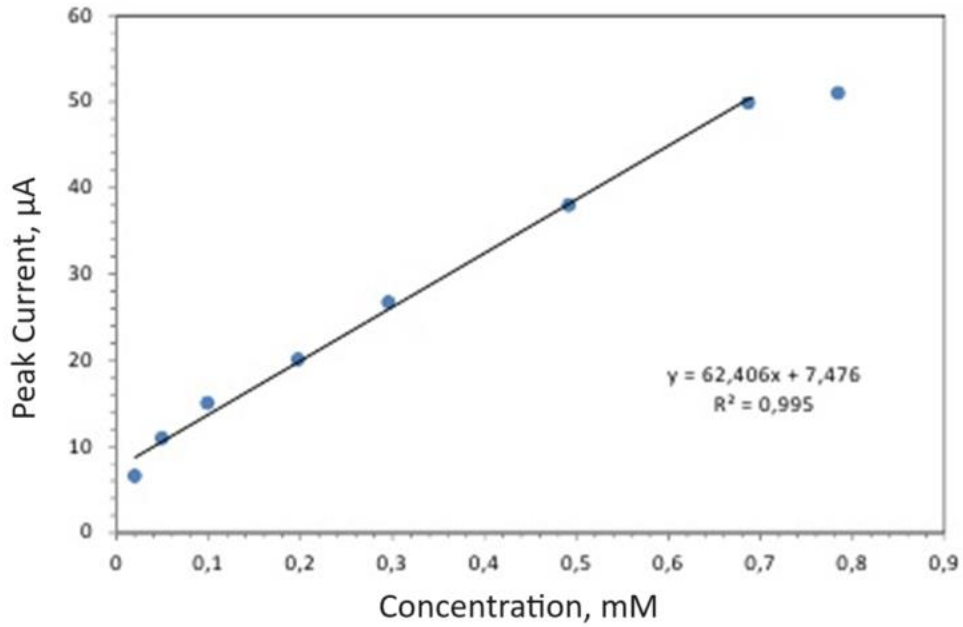

Figure 10. 2nd linear operating range for UA determination with MoS2(2)/GCE

Table 3 has been prepared to compare electrode sensitivity with GCE and MoS2(2)/GCE.

Table 3. Comparison of MoS2(2)/GCE values obtained in uric acid determination with GCE

	Electrode Name		
	GCE	MoS2(2)/GCE	MoS2(2)/GCE
Linear Operating Range (µM)	20 - 520	0.1 – 20	20 – 687
Line Equation (µA/mM)	y=11.407x+0.3031	y = 331.44x–0.798	y = 62.406x+7.4757
R^2	0.9914	0.9989	0.9948
Sensitivity (µA/ mM)	11.41	331.4	62.4

When Table 3 is examined, it was observed that the sensitivity of MoS2(2)/GCE and uric acid determination increased 29 times in the 1st linear operating range compared to GCE. In addition, it was found that the sensitivity value in the 2nd linear operating range with MoS2(2)/GCE increased by 5.5 times compared to GCE. As can be seen, it has been possible to determine uric acid in a wide range from very low to very high concentrations with MoS2(2)/GCE and with high sensitivity. Analytical performance values of MoS2(2)/GCE for uric acid are presented in Table 4.

Table 4. Analytical performance values for uric acid with MoS2(2)/GCE

1.Linear Working Range(LWR) (µM)	0.1 – 20
(1. LWR) Sensitivity (µA.mM^{-1})	331.4
2.Linear Working Range(LWR) (µM)	20 – 687
(2. LWR) Sensitivity (µA.mM^{-1})	62.4
LOD (nM)	67
LOQ (nM)	224

3.2. Determination of Uric Acid in Blood Samples with MoS2(2)/GCE

For the determination of uric acid in blood serum with MoS2(2)/GCE, DP voltammograms were produced from 1 mL of sample by adding 9 mL of pH=7 phosphate buffer. This process was repeated three times. Then, uric acid solutions were prepared at known concentrations in pH=7 buffer solution. Concentrations were calculated for three samples by taking the DP voltammograms by the standard addition method. The received DP voltammograms are superimposed and presented in the concentration-peak current graphs. Concentration-peak current graphs for sample1, sample 2 and sample 3 are given in Figure 11, Figure 12 and Figure 13, respectively.

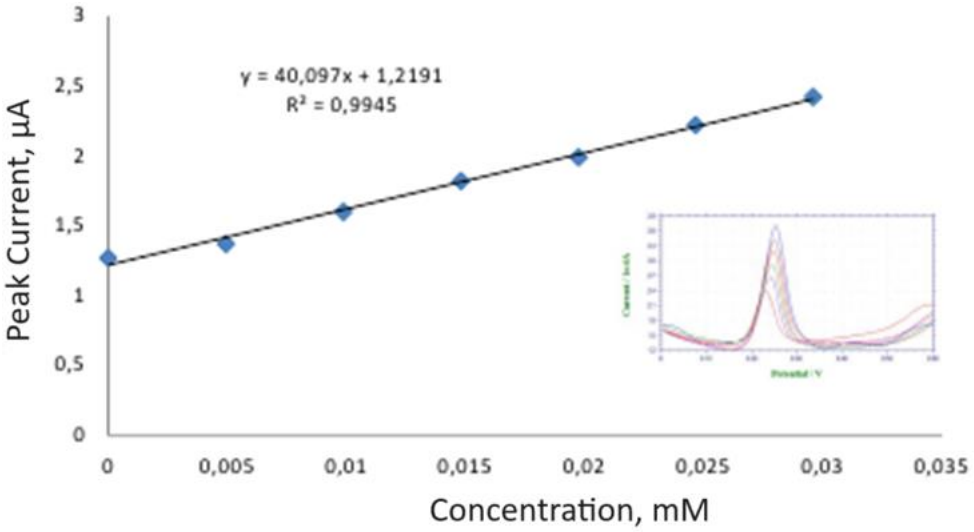

Figure 11. By standard addition method in the blood serum sample 1 with MoS2(2)/GCE uric acid determination

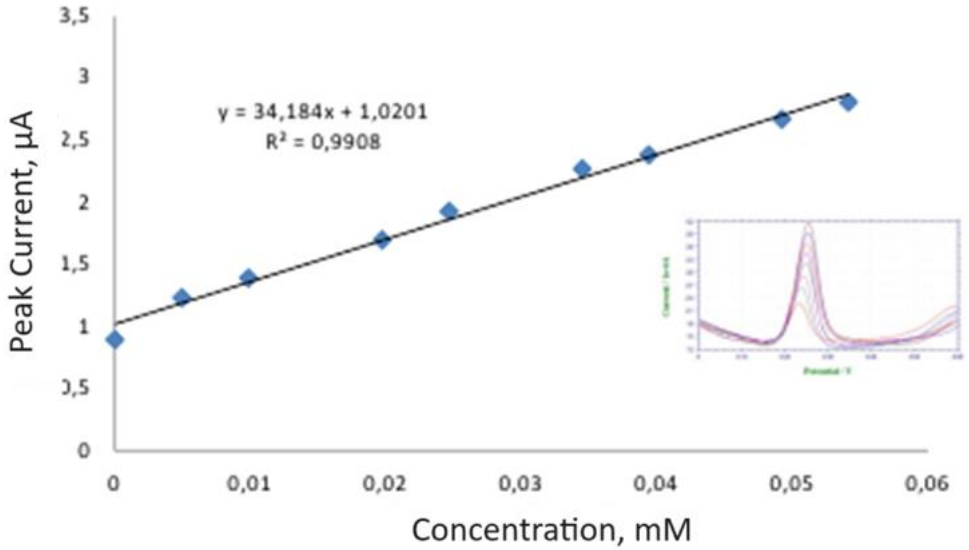

Figure 12. By standard addition method in the blood serum sample 2 with MoS2(2)/GCE uric acid determination

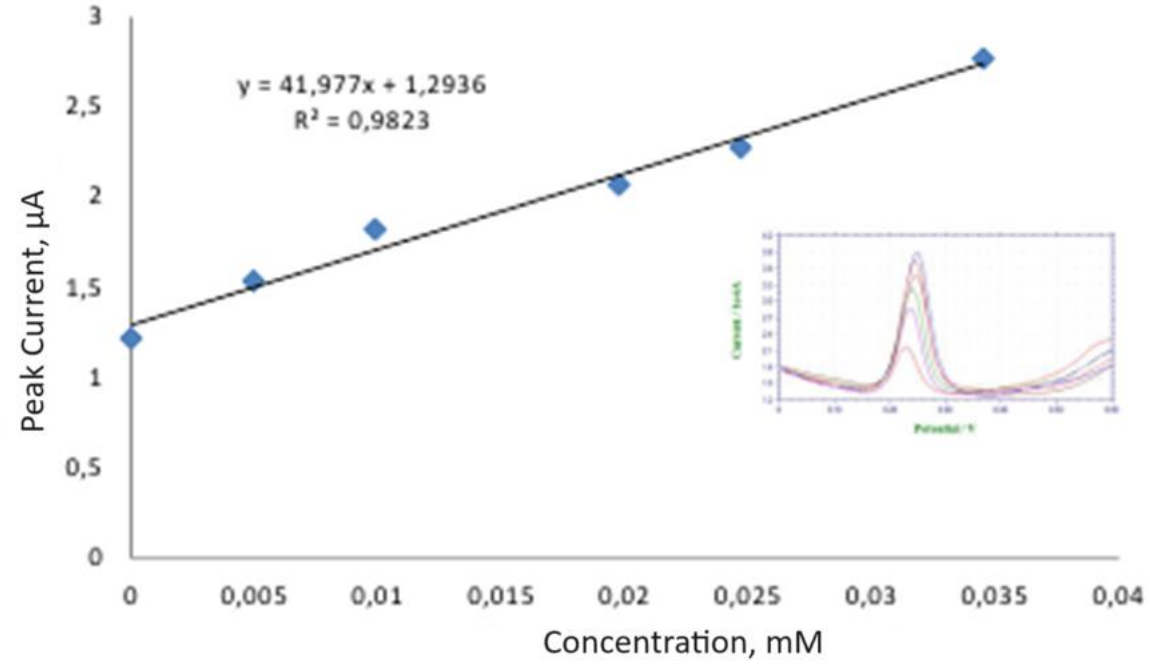

Figure 13. By standard addition method in the blood serum sample 3 with MoS2(2)/GCE uric acid determination

In Table 5, uric acid values obtained from real samples are presented with their relative errors.

Table 5. Uric acid concentrations obtained from real samples with MoS2(2)/GCE, with their relative errors

Sample	Calculated UA Concentration (mM)	UA Values in Blood (mg/100mL)	Real Value (mg/100 mL)	% Relative Error
1	0.03040	5.11	5.3	3.6
2	0.02984	5.02	5.3	5.3
3	0.03082	5.18	5.3	2.3

(X) average = 5.10 mg, t = 4.30 (at 95% Confidence level)

95% Confidence Level = 5.10 ± 0.20 mg

The real value is 5.3 mg/100 mL which is in between the range of given confidence level. Results can be given at 95% confidence intervals.

4. CONCLUSIONS

In the determination of uric acid with the modified electrode (MoS2(1)/GCE) obtained by the drop-coating method; sensitivity was found to be 11.4 μA.mM^{-1}, linear operating range from 4 μM to 520 μM, and the detection limit was 0.8 μM. In the determination of uric acid with the electrode (MoS2(2)/GCE) obtained by electrochemical coating method, the 1st linear working range was found to be 0.1 μM – 20 μM, the sensitivity was 331 μA.mM^{-1}, and the detection limit was $6.7x10^{-8}$ M. The 2nd linear operating range was 20 μM - 687 μM, the sensitivity was determined as 62.4 μA.mM^{-1}. In order to determine the effectiveness of uric acid determination with MoS2(2)/GCE, uric acid determination in blood serum samples obtained from the hospital was successfully performed with MoS2(2)/GCE with a relative error of 3.7%.

Ethics in Publishing

There are no ethical issues regarding the publication of this study

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