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Application of Gold Nanoparticles with 1,6-Hexanedithiol Modified Screen-Printed Carbon Electrode as a Sensor for Determination of Arsenic in Tea and Coffee Samples

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Abstract

The development of electrochemical nano sensor for the detection of total arsenic in tea and coffee samples was described based on the formation of gold nanoparticles (Au NPs). Screen printed carbon electrodes were modified with gold nanoparticles and linked with 1,6-hexanedithiol self-assembled monolayers. The electrode position of Au nanoparticles was performed in 10 mL of the solution that totally cover the screen-printed carbon electrode (SPCE) while applying a constant potential of -0.4 V (vs Ag within SPCE) for 600 sec. Cyclic voltammetry was used to characterize the gold nanoparticles before and after modification with 1,6-hexanedithiol self-assembled monolayers on SPCE. Square wave anodic stripping voltammetry with multi point standard addition method was used for the detection of As (III) and As(V) on Au NPs-1,6-hexanedithiol modified SPCE under optimized conditions. As (III) and As(V) were deposited for 60 seconds by the reduction of arsenic in buffer solution. It was found that Au- NPs with 1,6-hexanedithiol modified SPCE had the highest anodic stripping peak current at 0.201V. The limit of detection for arsenic was found to be 1.7 ng ml^{-1}. The limits of detections determined were below the corresponding guideline value from the World Health Organization (WHO). The developed method was successfully applied to determine arsenic in tea and coffee samples. In addition, seventeen different tea samples come from different countries of east Asia (China, India and Sri Lanka) and Egypt and eleven samples of coffee, which is the best-selling in the Libyan markets were also collected. The highest arsenic value detected was (0.167±0.015 mg/kg). According to the present safety limits for As residues in tea and coffee; all the tested tea and coffee brands are safe for human consumption. The maximum limit for arsenic residue was exceeded by (1.67%) only in one sample of dried black tea from Egypt (Aluorsa). The modified nano electrode exhibited excellent reproducibility and high stability.

Keywords: Au nanoparticles, self-assembled monolayers, electrochemical Nano sensor, arsenic, food safety, striping voltammetry.

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Introduction

Arsenic exists in natural water in inorganic and organic forms. The inorganic form of arsenic is more toxic compared to its organic form. Inorganic arsenic is the predominant form in contaminated ground water. Arsenic exists in -3, 0,+3, and +5 oxidation states. Two forms are common in natural waters: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), referred to as As (III) and As (V) (Chang et al., 2016). It has been analyzed that arsenate [As(III)] (H_3AsO_3,$H_2AsO_1^{-3}$,$HAsO_2^{-3}$ is 60 times more poisonous and mobile than arsenate [As(V)] (H_2AsO_4 , $HAsO_4^{-2}$] and 70 times more toxic than the methylated species. So, for domestic uses, it is highly essential to remove As(III) from the groundwater (DE et al., 2009). Long term exposure to arsenic levels can result in permanent and severe damage to human health. Arsenic and its compounds are reported to be carcinogenic, mutagenic, and tetragenic in nature. People with arsenical skin manifestations, and drinking contaminated water, have high levels of arsenic in hair, nail, urine, and skin scales causing melanosis leucomelanosis, keratosis, nonpitting swelling and gangrene, etc. Chronic arsenic contamination also leads to skin, lung, bladder, and kidney cancer as well as pigmentation changes, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite and nausea (Cullen, 2015; Yogarajah and Tasi, 2015). The contamination of groundwater by inorganic arsenic is a serious problem all over the world. The World Health Organization recommends that the maximum concentration of arsenic in drinking water is 10 ppb, though for some countries, such as Bangladesh, 50 ppb is still the action limit. To accurately determine the arsenic concentration in water samples, many methods that include atomic spectrometry techniques, such as AFS, ICP-MS, ICP-AES, and HG-AAS have been developed (Dhillon et al., 2015; Radke et al., 2012; Luong et al., 2014). All these techniques have detection limits low enough to allow reliable measurement of concentrations at 10 ppb and can tolerate the matrix effects from a variety of water samples. These instruments are very expensive, large and they need more time, supplies of stable power and gases to work with it. As a portable instrument, electrochemistry instrumentation, which can perform anodic stripping voltammetry (ASV) and Cathodic Stripping Voltammetry (CSV) has some advantages over the various "naked-eye" arsenic test kits. These electrochemical techniques are able to determine arsenic at trace levels within few minutes. In addition, these techniques can also distinguish between different oxidation states, are easy to operate and, compared with other instrumental techniques, are comparatively cheap. However, these methods also suffer from interferences and matrix effects, which means that voltammetric methods are rarely used for arsenic determination in complex matrixes, such as food samples (Costa et al., 2016; Liao et al., 2018). Therefore, it is necessary to develop highly sensitive, time-saving, and capable of on-site and cost-effective methods (Meline et al., 2019). In this study, an electrochemical nanosensor based on gold nanoparticles with 1,6-hexanedithiol modified screen-printed carbon electrode (40 -70 nm) has been applied for the determination and analysis of traces of arsenic with high sensitivity and selectivity in environmental samples.

Materials and methods

Reagents

1,6-hexanedithiol 99% was obtained from Sigma-Aldrich, Hydrogen teterachloro aurate (III) 99.9% trace metal basis was purchased from Sigma-Aldrich, Nitic acid, Hydrochloric acid and Sulphuric acid were obtained from Fluka and all were environmental grade plus (<10 ppt arsenite),99.98% (Sigma) $K_3Fe(CN)_6$ trace metals basis, 70% $HClO_4$ (Aldrich) ,99.99% trace metals basis and for metal ion binding/assay using ultra-pure water (Millipore Milli-Q). All other chemicals were of analytical grade and used as received without any purification.

Preparation of 1000ppm of arsenic

1000 ppm of As (III) (Fluka) stock solution was used immediately. From stock solution, it can prepare a range of concentrations of target metal ions (1.0 to 500 ppb). The effect of ligand protonation state was explored separately by adjusting the solution pH (with 0.01 M KOH or 0.01 M HNO_3). The pH was measured with a pH meter (WTW, Germany).

Apparatus

Electrochemical experiments were carried out on µStat 400 Bipotentiostat / Galvanostat from DropSens and CHI660E power Potentiostat from CH Instruments. A combined three electrode system (SPE) was employed with an Ag electrode as a reference electrode, Pt electrode as counter electrode and carbon electrode as working electrode. High purity argon gas was used to displace oxygen from the electrochemical cell before results were collected.

Analysis of tea and coffee samples

The samples were collected from different markets and mills in Tripoli City. Two types of samples tea and coffee were collected, eleven samples of coffee, which is the best-selling in the Libyan markets and the most among of the people (Brazil, India, Syria, Yemen). Seventeen different tea samples come from different countries of east Asia (China, India, SriLanka) and Egypt. Collected samples were shown in tables 1 and 2.

The samples were firstly dried in oven for 2 h at 80^{o}C.The samples of dried tea were homogenized in a ceramic mortar, the samples (1.0 gram) were digested in close system Microwave digestion system in a mixture of 5ml pure nitric acid and 5ml deionized water. The samples were submitted to microwave digester using five steps program. Blank sample was carried out in the same way. The digests ware secondly filtered through a quantitative filter paper (Whatman 42). The resulting solution was transferred to polypropylene volumetric flask and the volume was completed to 50ml with deionized water. Every sample was repeated three times (N=3).

Table (1). Brands and origin of tea samples

No.	Product Name	Origin	Product Type	Packaging
1	Ferdouse Tea	India	Red	Normal
2	Aluorsa Tea	Egypt	Red	Normal
3	Nabeit Tea	China	Green	Normal
4	Lipton Tea	Indonesia	Green	Bags
5	Elzdehar Tea	SriLanka	Red	Normal

6	Asam Tea	India	Red	Normal
7	Alrabih Tea	Egypt	Green	Bags
8	Elzhara Tea	SriLanka	Red	Bags
9	Algafihal Tea	China	Green	Normal
10	Ahamad Geen Tea	China	Green	Bags
11	Elkozii Red Tea	SriLanka	Red	Bags
12	Kozzi coffee	SriLanka	Green	Bags
13	Azwaad Tea	China	Green	Normal
14	Alrahla Tea	China	Green	Normal
15	Ahmad Tea	China	Red	Bags
16	Etwminia Tea	SriLanka	Red	Normal
17	Answer Ali Tea	SriLanka	Green	Normal

Table (2). Brands and origin of coffee samples

No.	**Product Name**	**Origin**	**Product Form**	**Product type**
1	Indian Coffee	India	Powder	Mixed Cardamom
2	Brazilian coffee	Brazil	Powder	Pure
3	Brazilian coffee (Han)	Brazil	Powder	Mixed Cardamom
4	Mixed Coffee	India	Powder	Mixed Cardamom
5	Mixed coffee	Vietnam	Powder	Mixed Cardamom
6	Saurian coffee	Brazil	Powder	Pure
7	Alsalla Coffee	Vietnam	Powder	Pure
8	Dubai coffee	Brazil	Powder	Mixed Cardamom
9	Surian Coffee Han	Brazil	Powder	Mixed Cardamom
10	Indian Pure coffee	India	Grain	Pure
11	Yemen Coffee	Yemen	Powder	Pure

Preparation of Screen-printed carbon electrode modified with gold nanoparticles

Gold solution, 6.0 mM $HAuCl_4.3H_2O$ was prepared in 0.1 M HNO_3. The electrode position of Au was performed in 10 mL of the solution that totally cover the screen-printed carbon electrode while applying a constant potential of -0.4 V (vs Ag within SPCE) for 600 sec. The gold nanoparticle modified SPCE was rinsed using ultra-pure water and blot dried. Cyclic voltammograms of gold nanoparticles modified screen printed carbon electrode and gold electrode nanoparticles modified screen printed carbon electrode covered with self-assembled monolayer of 1,6-hexanedithiol are shown in Figure 1. In the case of $[Fe(CN)_6]^{3-/4-}$ solution, the I-E curves corresponding to the oxidation and reduction reactions was decreased by covering the screen-printed carbon modified gold nanoparticles with self-assembled monolayer of 1,6-hexanedithiol. These findings agree with earlier reports, claiming that 18-24 hours of immersion of the screen-printed carbon modified gold nanoparticles electrode in 1,6-hexanedithiol solution is enough to form a monolayer with almost 100% coverage (Feng et al., 2005).

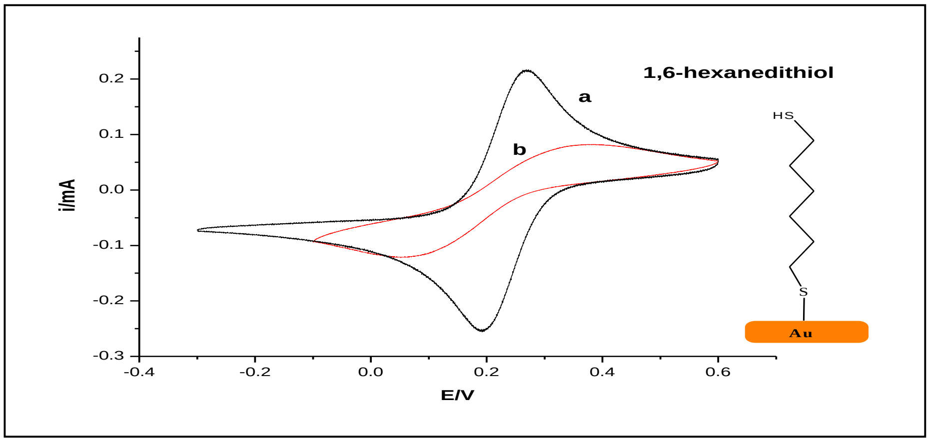

Figure (1): Cyclic voltammograms of gold nanoparticles modified screen printed carbon electrode (a) and (b) modified with 1,6-hexanedithiol in 5 mM $K_3Fe(CN)_6$ + 1M KCl. SAM formed in 10 mM thiol ethanol solution, 48 h immersion. Scan rate 0.1V s^{-1}.

The optimum conditions for determination of As(III) and As(V) using square wave anodic stripping voltammetry on gold nanoparticles-1,6-hexanedithiol modified screen printed carbon electrodes is shown in Table 3.

Table (3). Summary of optimum conditions for As (III) and As(V) determination in aqueous samples using gold nanoparticles modified screen printed carbon electrode constructed in this study

σ Min	**1 nA**	**σ Max**	**1mA**
E begain	-0.20V	E end	0.35V
Estep	0.005V	Eamp	0.05V
Econd	0.60V	Edep	-1.0 V
Frequency	50Hz	Tcond	20 seconds
Tdep	60 seconds	Teq	15 seconds

Determination of Total Arsenic

- Add 20 ml of sample water to the sample beaker.
- Add 3ml of 12M Hydrochloric Acid to the sample. The acid functions as the buffer, and oxidizing. There is no need to use Buffer solution here.

Determination of Arsenic (III)

- Add 5ml of buffer solution (citric acid /sodium chloride and ascorbic acid pH=2.50) to the sample beaker.
- Add 30 ml of sample water to the sample beaker.

Square wave anodic stripping voltammetry was used for the detection of As(III) and As(V) under optimized conditions. Total arsenic was deposited for 60 seconds by the reduction of Arsenic in buffer solution: (citric acid and sodium chloride/ascorbic acid pH 2.50 for As (III) and 12M HCl for total arsenic, followed by As stripping between -0.20 and 0.35 V at the following parameters: E_{step}=5mV, frequency: 60 Hz, amplitude: 0.05V and E_{cond}=0.60 V. The characteristic peak for As (III) on gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode was observed at 0.201V as shown in Figure 2. The As (III) sample (5.0 ppm= 5000 ppb) was prepared fresh daily from a 1000 mg/L standard solution (Fluka).

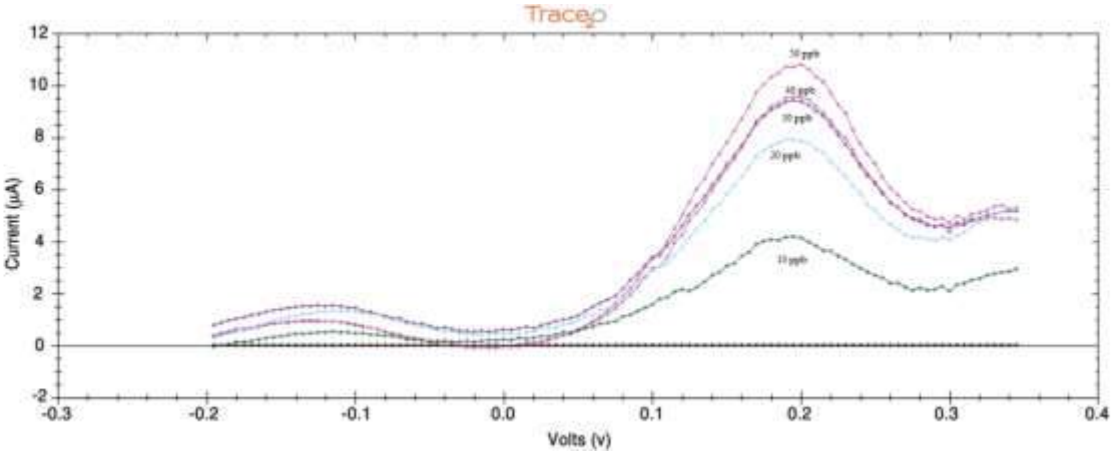

Figure (2): Square wave anodic stripping voltammograms of gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode in solution 10,20,30,40 and 50 ppb As(III) at pH 2.0, deposition Time 60 seconds, accumulation time 60s, accumulation potential 0.21V,scan rate $0.1Vs^{-1}$, frequency 100Hz, amplitude 0.025V and increment 0.005V

The multi-point standard addition method for determination of total arsenic in water sample was shown in Figure 3. The multi-point standard addition method was prepared under the optimum conditions using square wave voltammetry at different As (III) concentrations. The calibration plot was linear over the range of 0.1-50 µg ml^{-1} As (III) with regression equation of I_p (µA) = 0.138 C(ng ml^{-1}) + 5.235 (R= 0.987). The limit of detection ($3S_b$/m) was calculated as 1.7 ng ml^{-1}. The relative standard deviation (RSD) for 10 ng ml^{-1} As (III) was 2.66 (n=8) showing good reproducibility of the fabricated sensor based on gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode. It was found from the Figures 2 and 3, that the oxidation peak (stripping) is board peak and more significant than the corresponding reduction peak; hence, the oxidation peak was systematically studied using SWASV to achieve the desired detection limit. The stripping voltammetric determination of arsenic proceeds through the following two steps:

Step 1: Pre-concentration of As (III) from the bulk of the electrolytic solution onto the modified electrode surface under the applied potential of –0.35 V for preselected time of 60 seconds under constant stirring.

Step 2: Stripping (oxidation) of As (0) from the electrode surface into the bulk of the electrolytic solution as As (III). This anodic stripping step generates quantifiable analytical signal, and the signal current has been correlated to the arsenic concentration in the sample.

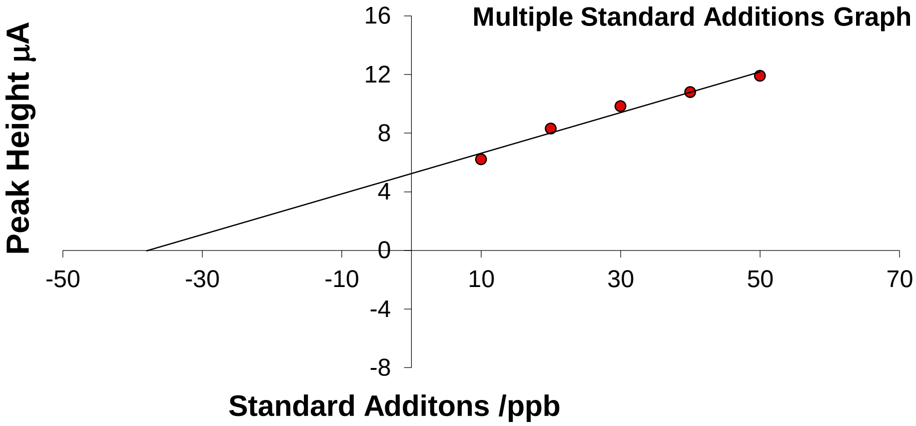

Figure (3): Multi point standard addition method gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode in solution 10,20,30,40 and 50 ppb As(III) at pH 2.0, deposition Time 60 seconds

Results and discussion

Effect of pH of pre-concentration solution

To test whether the pH would have any effect on the determination of arsenic species during the pre-concentration processes, the gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode was immersed in a (50 ppb As III) solution at different pH (2, 3, 5 and 8). Solutions of different pH were adjusted to the appropriate pH with 0.1M HCl and 0.1M KOH. Figure 4, shown the influence of electrolyte solution pH on the electrochemistry of complex arsenic. Clearly, at pH 2 has a good response, which was obtained, as seen by low currents and a large separation in peak potential and the peaks exhibited irregular shape indicating that the pH had a strong effect on the pre-concentration processes.

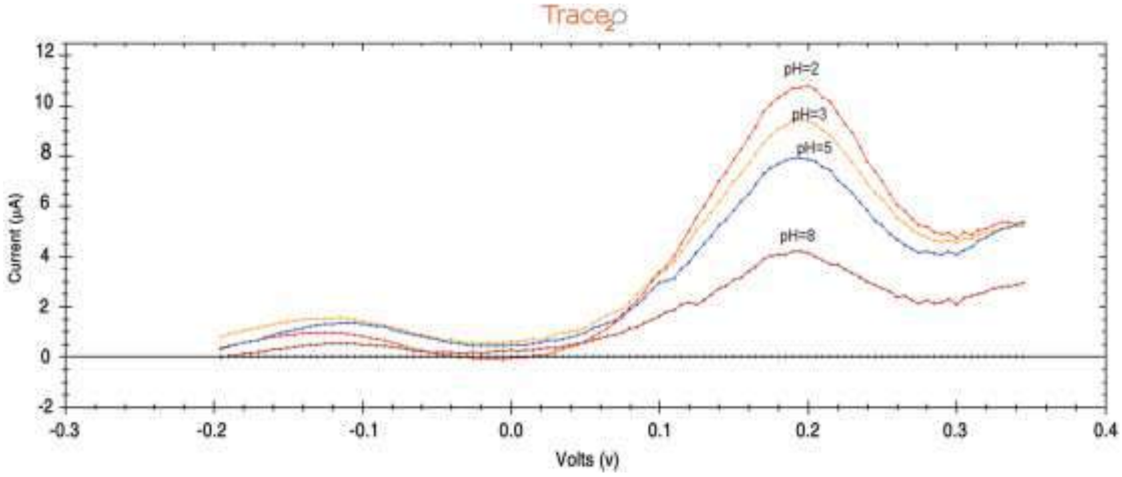

Figure (4): Square wave anodic stripping voltammograms with gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode in solution containing 50 ppb As(III) at different pH values (pH=2,pH=3,pH=5 and pH=8), deposition Time 60 seconds.

The effect of interfering metal ions

The effect of commonly interfering ions like Hg (II),Cd (II),Zn (II) and Pb (II), was investigated using for gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode. It was found that in a 50ppb As (III) containing solution 100 folds of interfering metal ions did not influence the current peak response of As (III) as shown in Figure 5.

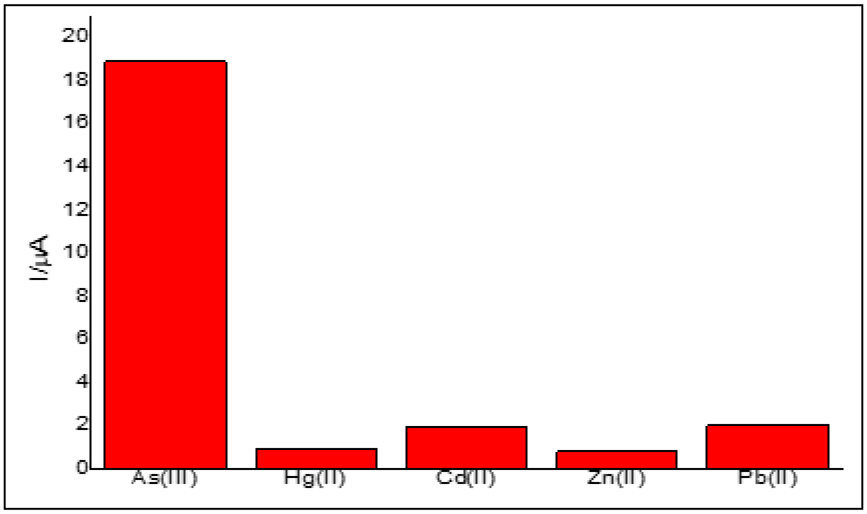

Figure (5) Effect of interference metal ions on As(III) 50ppb determination in aqueous solutions pH=2.0,accumulation time 60s, accumulation potential 0.21V,scan rate 0.1Vs^{-1}, frequency 100Hz, amplitude 0.025V and increment 0.005V

Analysis at low As (III) concentrations, taking into account that the World Health Organization (WHO) specifies 10 ppb as the most As (III) in drinking water will be more stable and exact on nano Au (111) surfaces, or surfaces deposited with effective growth directing ligands such as thiols, which will perform better than general polycrystalline Au materials (Etorki et al., 2017; Zhang et al., 2016).

Application of gold nanoparticles with 1,6-hexanedithiol modified screen printed carbon electrode to water reference material sample

With the purpose to evaluate the potential application of the developed method, reference material water sample (NIST-SRM-1643F As concentration =56.85 ± 0.37) was used for analytical assay. Multi point standard addition protocol has been used for detection, and satisfactory data of recoveries were obtained (present in Table 4).

Table (4): Certified As concentrations and the % recoveries for the amount of As. % recovery is the experimental concentration of arsenic in the sample divided by the certified arsenic concentration in the reference material (NIST-SRM-1643F).

	(NIST-SRM-1643F)
Certified As Conc. (ppb)	56.85 ± 0.37
Experimental % recovery :	50.09
Experimental % recovery	46.33
Experimental % recovery	51.98
Experimental % recovery	44.07
Experimental % recovery	58.77
Average % recovery	50.25
Standard Deviation	5.68

The validation of the gold Au-NPs- 1,6-hexanedithiol modified screen printed carbon electrode toward As (III) measurements has been examined by applying the method to real tea and coffee samples . The recovery of this method is reported by Etorki et al., (2019). The results of As (III) concentrations are shown in Tables 5 and 6. Concentrations of As(III) species found in tea samples were in the range of 0.02±0.001 to 0.167±0.015 (mg/kg) and the Coffee samples were in the range of 0.038±0.001 to 0.150±0.005 (mg/kg). These concentrations were not significantly different to those reported by Shi et al., (2008) and Grijalba et al., (2015) for similar samples and all results are below the WHO, (2006) standards.

Table (5): Arsenic concentration in tea and coffee samples, N=3

Name of Sample	Mean mg\kg	S.D	Minimum	Maximum
Ferdouse Tea	0.037	0.006	0.03	0.04
Aluorsa Tea	0.167	0.015	0.15	0.18
Nabeit Tea	0.110	0.010	0.1	0.12
Lipton Tea	0.144	0.014	0.13	0.16
Elzdehar Tea	0.120	0.010	0.11	0.13
Asam Tea	0.157	0.012	0.15	0.17
Alrabih Tea	0.105	0.030	0.085	0.14
Elzhara Tea	0.037	0.006	0.03	0.04
Indian Coffee	0.022	0.001	0.021	0.023
Brazilian coffee	0.051	0.002	0.05	0.053
Brazilian coffee (Han)	0.055	0.002	0.054	0.057
Mixed Coffee	0.047	0.002	0.045	0.048
Algafihal Tea	0.157	0.003	0.155	0.16

Table (6): Arsenic concentration in tea and coffee samples, N=3

Name of Sample	Mean mg\kg	S.D	Minimum	Maximum
Ahamad Geen Tea	0.122	0.001	0.121	0.123
Elkozii Red Tea	0.150	0.005	0.145	0.154
Mixed coffee	0.054	0.002	0.052	0.055
Saurian coffee	0.064	0.002	0.062	0.065
Alsalla Coffee	0.056	0.002	0.055	0.058
Kozzi coffee	0.129	0.004	0.125	0.133
Azwaad Tea	0.079	0.002	0.077	0.081
Alrahla Tea	0.129	0.003	0.125	0.131
Dubai coffee	0.063	0.001	0.062	0.064

Ahmad Tea	0.057	0.001	0.056	0.058
Etwminia Tea	0.092	0.002	0.09	0.093
Yemen Coffee	0.064	0.002	0.062	0.066
Surian Coffee Han	0.038	0.001	0.037	0.039
Answer Tea	0.123	0.003	0.12	0.126
Indian Pure coffee	0.052	0.008	0.0511	0.053

The reproducibility has been investigated by using the same gold Au-NPs- 1,6-hexanedithiol modified screen-printed carbon electrode ten repetitive measurements in 1M HCl as a supporting electrolyte solution containing 5ppb As under identical conditions for all these experiments was found to be ±4.7%.

Conclusions

The developed novel electrochemical nanosensor based on screen printed carbon electrode modified with gold nanoparticles and linked with 1,6-hexanedithiol self-assembled monolayers have successfully applied to determine As (III) in tea and coffee samples traded in Libyan markets. The electrochemical nanosensor gave nice sensitivity, selectivity and reproducibility. The limit of detection value for arsenic was calculated to be 1.7 ng ml^{-1}.

Acknowledgements

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تطبيق جسيمات الذهب النانومترية المرتبطة مع 6,1–هكسان ثنائي ثايول المعدلة فوق شاشة قطب الكربون المطبوع كمستشعر نانومتري للكشف عن الزرنيخ في عينات الشاي والقهوة

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[4] قسم علوم وتقنية الأغذية، كلية الزراعة، جامعة طرابلس

المستخلص

تم وصف تطوير مستشعر النانو الكهروكيميائي للكشف عن الزرنيخ الكلي في عينات الشاي والقهوة بناءً على تكوين جسيمات الذهب النانومترية (Au NPs). تم تعديل أقطاب الكربون المطبوعة بجسيمات الذهب النانومترية وربطها بـ 1.6–هكسان ثنائي ثايول عن طريق الرابطة التساهمية Au–S. تم في البداية إجراء الترسيب الوزني الكهربائي لجسيمات الذهب النانومترية في 10مل من المحلول الذي يغطي قطب الكربون المطبوع بالكامل أثناء تطبيق جهد ثابت قدره –0.4 فولت (مقابل Ag داخل SPCE) لمدة 600 ثانية. تم توصيف جزئيات الذهب النانومترية باستخدام التقنية الفولتامترية الحلقية قبل وبعد ارتباطها بالمتصلة. استخدمت تقنية الفولتامتري النزعي ذو الموجات المربعة في الكشف على أيونات الزرنيخ الثلاثية والخماسية في المحاليل المائية وذلك بعد ادمصاصها على سطح 1.6–هكسان ثنائي ثايول المرتبطة بجسيمات الذهب النانومترية. لقد أعطى مستشعر النانو الكهروكيميائي الذي تم تحضيره قيمة عالية للتيار النزعي الأنودي عند 0.201 فولت. تم تعيين الحد الأدنى لقيمة الكشف عن الزرنيخ والتي كانت 1.7 نانوغرام لكل مل وهي أقل من الحد الأقصى لتركيز أيون الزرنيخ في المياه الصالحة للشرب الذي حددته منظمة الصحة العالمية (WHO). تم تطبيق الطريقة المطورة بنجاح للكشف عن الزرنيخ في عينات الشاي والقهوة حيث تم تجميع 17 عينة شاي مختلفة من دول مصنعة من شرق آسيا ومصر، وتم جمع 11 عينة من القهوة الأكثر تداولاً في الأسواق الليبية. تم الكشف عن الحد الأقصى لتركيز الزرنيخ الذي بلغ 0.167 ± 0.015 ملغم/كغم. تم تحديد معظم عينات الشاي والقهوة المختارة في هذه الدراسة على أنها آمنة للاستهلاك البشري من حيث تراكيز الزرنيخ فيها باستثناء عينة واحدة حيث زادت نسبة الزرنيخ فيها وبلغت حوالي 1.7% وهي عينة الشاي الأسود المجفف من مصر والمعروف باسم شاي العروسة. أظهر قطب النانو المعدل قابلية عالية لإعادة نفس النتائج لكل عينة مع ثباتية عالية.

الكلمات المفتاحية: الجسيمات النانوية Au، Self–assembled monolayers ، مستشعر النانو الكهروكيميائي، الزرنيخ، سلامة الغذاء، تجريد الفولتميتر.

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