Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2023.29325

286 (2023) 248–256
February

Anodic stripping voltammetric determination of Se(IV) by means of a novel reusable gold microelectrodes array

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Received 16 September 2022; Accepted 21 January 2023

ABSTRACT

A novel type of voltammetric sensor – reusable, durable, long-term use gold microelectrodes array was presented, characterized and used for developing the procedure of Se(IV) determination by anodic stripping voltammetry. There was a double activation of working microelectrode carried out during the measurements that was ran at the potential of –1.5 V within 2 s at the start of the measurement and then after deposition step at –1.2 V within 1 s. Thanks to such a procedure an increase of Se(IV) peak current and a slight lowering of the background current was observed. The optimization of analytical procedure was performed. A calibration graph was linear in the range from 3×10^{-9} to 3×10^{-8} mol·L^{-1} (deposition time 180 s). The obtained detection limit for selenium ions determination following deposition time of 180 s was 8.3×10^{-10} mol·L^{-1}. Repeatability of the method calculated as RSD for Se(IV) concentration of 3×10^{-8} mol·L^{-1} was 3.5% ($n = 7$). The proposed procedure was successfully applied for Se(IV) ions determination in water certified reference materials. Good recovery of Se(IV) from river water sample was also obtained.

Keywords: Selenium; Stripping analysis; Double activation; Determination; Gold microelectrodes array

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1. Introduction

Selenium is an important micronutrient, needful for the proper functioning of organisms and for a protection from diseases. Selenium deficiency can be the reason of disorders of the immune system, increased risk of cancer occurrence, damage to the myocardium, symptoms of hypothyroidism and Keshan disease [1,2]. Selenium occurs in compounds at various oxidation states from –II to +VI. These forms differ in toxicity, reactivity, and bioavailability. The most widespread forms of this element occurring in the environment are compounds with selenium at +IV and +VI oxidation states. Among them Se(IV) is the form characterized by the highest toxicity. Maximum selenium concentration that can occur in drinking water (10 μg·L^{-1}) is restricted by European Union regulations [3]. Due to these facts there is a necessity for monitoring content of this element in various environmental samples at trace level concentrations, however, it is more important to analyze selenium speciation than to determine the total concentration of inorganic selenium.

Se(IV) have been determined by many analytical methods like: inductively coupled plasma atomic emission

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spectroscopy (ICP-AES) [4,5], hydride generation atomic absorption spectrometry (HG AAS) [6], hydride generation atomic fluorescence spectrometry (HG AFS) [7], inductively coupled plasma mass spectrometry (ICP-MS) [8], neutron activation analysis (NAA) [9] and others [10–12].

Electrochemical methods (especially stripping voltammetry) are competitive analytical methods to mentioned above because of low cost of instrumentation and possibility of performing field analysis. As a consequence of an application of the preconcentration step of an analyte on the surface of working electrodes during the measurement procedure, high sensitivity of voltammetric analysis is obtained. Variety of working electrodes were used in the course of selenium determination, such as: mercury drop and film electrodes [13–17], hanging copper amalgam drop [18], gold macroelectrode [19,20], gold microelectrode [21,22], arrays of gold microelectrodes [23], rotating gold disk [24], electrodes modified with gold nanoparticles [25–28], a set of two gold working electrodes [29], bismuth film [30], bismuth/mercury film [31], electrodes made from Ag [32,33], electrodes made from Cu [34,35], and many others [36–39]. Furthermore cathodic and anodic stripping voltammetry was utilized to analyze selenium speciation, mainly Se(IV) and Se(VI) (after its reduction to Se(IV)) [40,41].

Among variety of electrochemical sensors, utilization of microelectrodes results in many benefits. Firstly, microelectrodes provide the opportunity to analyze samples with very small volumes, from diluted solutions and solutions with organic solvent. In the course of microelectrodes utilization, the preconcentration of analytes can be performed from unmixed solutions due to the presence of spherical diffusion at the surface of the microelectrode and, consequently, in-field analyzes can be provided. Next, microelectrodes utilization gives a possibility of miniaturization of measurements arrangement. Furthermore, using microelectrodes leads in many cases to obtain favorable signal to noise ratio [42,43]. There is also a possibility of microelectrodes arrays or ensembles construction. Thanks to such a solution the recorded current is the sum of the currents recorded on individual microelectrodes, and therefore it is strengthened and less sensitive to disturbances. For the construction of microelectrodes metallic electrode materials [21,23,44–48] as well as various carbon materials and composites were utilized [49–53].

The present article demonstrates a novel procedure of selenium(IV) determination which combines the advantages of anodic stripping voltammetry with those ensured by the utilization of a high stability and long-term use array of gold microelectrodes of a new way of design. The presented sensor was activated with two negative potential steps during standard procedure of measurements. Such a way of an electrode activation has led to an increase of measurements sensitivity as compared to results obtained without applying microelectrode activation. Furthermore, a slight decrease of background current was observed after applying two short-lived activation steps, first one at –1.5 V at the beginning of measurements and second one after deposition of selenium at –1.2 V. A way of construction of voltammetric sensor was described. The satisfactory results obtained with the use of an array of gold microelectrodes in the course of Se(IV) ions determination are presented below.

2. Experimental setup

2.1. Instrumentation

The measurements were performed using EA 9 analyzer made by MTM – ANKO, Cracow, Poland. A three-electrode cell of a volume of 10 mL was used. In order to assess a resistance of gold microelectrodes array electrochemical impedance spectroscopy spectrum was recorded using the electrochemical analyzer μAutolab/FRA2 (Eco Chemie, Netherlands) with GPES software. As a working electrode an array of gold microelectrodes was used. For fabrication of an array of gold microelectrodes a homemade silica preform with 792 holes was used. The holes were filled with melted gold using the procedure similar to that reported by Lee et al. [54], Kacanovska et al. [55] and Schmidt et al. [56]. For this purpose gold was melted at temperature of about 1,140°C and then pressure was increased to 20 bars to fill the holes in the preform with melted gold. Next about 5 mm of a preform filled with gold shown in Fig. 1A was polished at both ends and pressed into PEEK casing. Electrical contact from gold microelectrodes in the array was made using graphitized carbon black powder and a copper wire. A real view of a fragment of the surface of a working microelectrodes array is shown in Fig. 1B. Such a way of construction of gold microelectrodes array is much more simplified as compared to several-step preparation of a gold microelectrode ensemble based on carbon black–polyethylene composite [57], self-assembled gold microelectrode arrays [58] or lithographically fabricated microelectrodes array [59,60]. Furthermore, an approach of microelectrodes array design presented in this article has led to obtaining a high-stability, long-term use sensor that can be utilized at least for a period of 24 months and no significant changes in obtained analytical signals were observed in contrast to previously published research [57] where changes in sensitivity of determinations were observed after 10 days of an electrode operation. Two-year stability and reusability of the proposed gold microelectrodes array was successfully tested during student practical laboratory classes within indicated period of time. An array

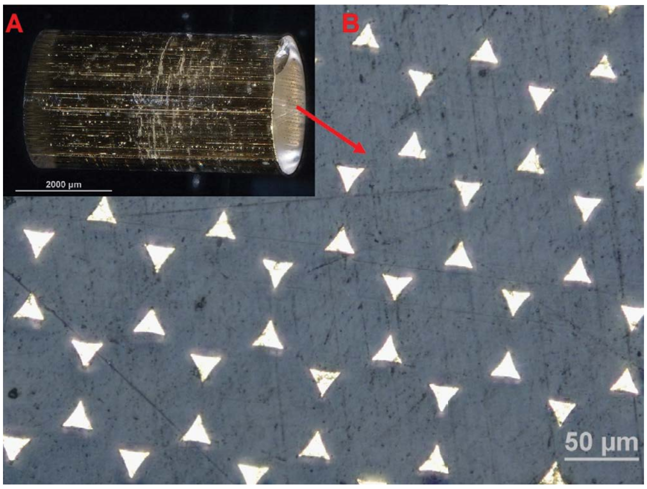

Fig. 1. (A) A real view of the preform filled with gold according to a procedure described in Instrumentation section. (B) A real view of a fragment of a surface of a gold microelectrodes array.

of working microelectrodes was polished daily using an abrasive paper of 2500 grit and then sonicated in water for 30 s using an ultrasonic cleaner (Sonic-3, Polsonic, Poland). Platinum wire and an Ag/AgCl electrode filled with saturated NaCl were used as the auxiliary and reference electrodes, respectively.

2.2. Reagents

1 mol·L^{-1} $HClO_4$ was prepared from 70% reagent (99.999% trace metals basis) purchased from Sigma-Aldrich. Standard stock solution of Se(IV) at a concentration of 1,000 ± 4 mg·L^{-1} was purchased from Sigma-Aldrich. Other reagents were obtained from POCh (Poland) and were used as received. For evaluation of the correctness of measurements, the certified reference materials SPS-SW1 (surface water) supplied by Spectrapur Standards AS (Oslo, Norway) and TM-25.5 (water of Lake Ontario) purchased from Environment and Climate Change (Canada) were used. Water used to prepare all solutions was purified in the Millipore system.

2.3. River water sample analysis

Real water sample collected from Bystrzyca river (eastern areas of Poland) and stored in a refrigerator until use was filtered using a membrane filter (0.45 µm). 5 mL of such a prepared sample was transferred to an electrochemical cell. Then 200 µL 1 mol·L^{-1} $HClO_4$ and 4.8 mL deionized water were added for dilution the sample by the factor of 2. Taking into account the fact that river water contains humic substances that cause partial suppression of selenium oxidation peak, 0.5 g XAD-7 resin was added to an electrochemical cell. Sample was mixed within 5 min using a magnetic stirring bar. Such a procedure of removing humic substances before voltammetric determinations was described previously in the literature [61]. Then determinations of Se(IV) were performed using a standard procedure of measurements by means of standard addition method.

2.4. Standard procedure of measurements

A given volume of the sample was transferred into the voltammetric cell and then 200 µL of 1 mol·L^{-1} $HClO_4$ was added and adjusted to the volume of 10 mL with deionized water. At the beginning the first activation step was performed at potential of –1.5 V within 2 s. Then deposition step was performed using an array of gold microelectrodes at a potential of –0.2 V for 180 s from stirred solution. Upon completion of this stage the second activation step was performed at the potential of –1.2 V for 1 s. After equilibration time of 2 s at a potential of +0.3 V a differential pulse voltammogram was recorded while the potential was changed in the range from +0.3 to +1.0 V. The step potential, pulse height and pulse period were 4 mV, 50 mV and 40 ms, respectively. After each measurement the potential of +1.0 V was applied within 10 s to working gold microelectrodes array in order to clean electrode's surface from target metals remaining after measurement. After each measurement a new sample solution was prepared. The measurements were performed without solution deoxygenation.

3. Result and discussion

During preliminary experiments it was observed that application of standard procedure of measurement with two activation steps of an array of microelectrodes at potential of –1.5 V and –1.2 V within 2 and 1 s, respectively, has led to an increase of Se(IV) signal and a slight lowering of the background current as compared with results obtained without activation. Such a polarization of working electrode at high negative potentials during measurements procedure was presented previously in the literature [62,63]. Anodic stripping voltammograms obtained after measurements without activation or with single or double activation of working gold microelectrodes array are presented in Fig. 2. On the basis of these results it can be concluded that the application of two steps of electrode activation leads to the most favorable results in terms of selenium peak current and background current. Optimization of analytical procedure of voltammetric Se(IV) determination is presented below.

3.1. Characteristic of gold microelectrode arrays

In order to get more insights to the electrochemical characteristic of the proposed gold microelectrodes array its response from a solution containing 1 mol·L^{-1} KCl and 2 × 10^{-3} mol·L^{-1} $K_3Fe(CN)_6$ by means of cyclic voltammetry was studied at scan rate equal to 1 V·s^{-1}. The scan rate of 1 V·s^{-1} was chosen in order to substantially decrease the current corresponding to spherical diffusion. On the basis

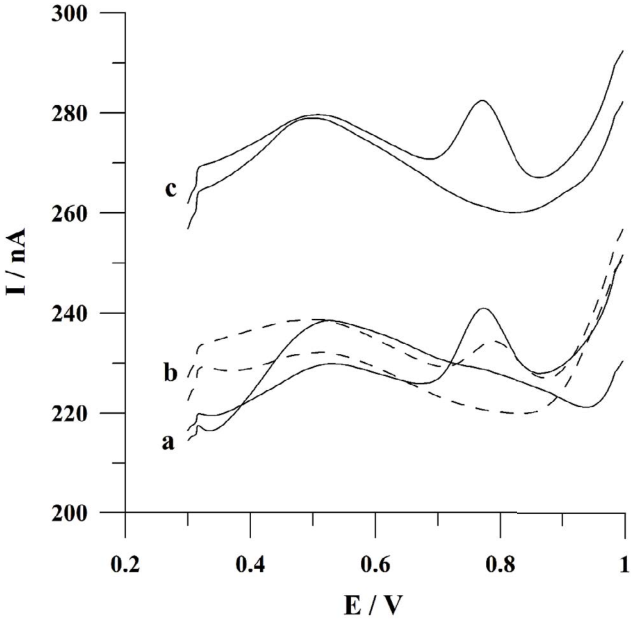

Fig. 2. Anodic stripping DP voltammograms obtained for blank and 2 × 10^{-8} mol·L^{-1} Se(IV) after measurements carried out: with two activation steps at potential of –1.5 V within 2 s and –1.2 V within 1 s (solid lines a); without microelectrode activation (dashed lines b); with one activation step at potential of –1.5 V within 2 s (solid lines c). Potential and time of deposition: –0.2 V, 180 s. The step potential, pulse height and pulse period were 4 mV, 50 mV and 40 ms, respectively.

of the peaks current value of the obtained cyclic voltammogram electrochemically active surface area of the working microelectrodes array was calculated using abbreviated Randles–Sevcik equation. The calculated active surface area of the proposed gold microelectrodes array is equal to about 0.00076 cm^{-2}. In addition the above result was compared with theoretically calculated total surface area of the presented sensor equal to about 0.00151 cm^{-2}. The obtained results pointed to the fact that approximately 50% of a total surface area of the proposed gold microelectrodes array is electrochemically active.

Intending to investigate microelectrodes properties of the presented gold microelectrodes array cyclic voltammogram was recorded from a solution containing 1 mol·L^{-1} KCl and 1 × 10^{-3} mol·L^{-1} $K_3Fe(CN)_6$ at scan rate of 10 mV·s^{-1}. The obtained results are shown in Fig. 3. On the basis of the nearly sigmoidal shape of cyclic voltammogram it can be concluded that the proposed sensor is characterized by microelectrode properties.

The proposed microelectrode's resistance value was experimentally determined from the electrochemical impedance spectroscopy spectrum and measured with the use of ohmmeter. The designated resistance value was equal to 5.5 ± 0.5 Ω. More details of the resistance value determination are provided in Supplemental file.

3.2. Deposition conditions

The influence of deposition potential of a microelectrodes array was investigated from –0.4 to +0.2 V. Concentration of Se(IV) was 5 × 10^{-8} mol·L^{-1}. Deposition time was 180 s. The obtained results are presented in Fig. 4. It was observed that Se(IV) peak current increases from a potential of +0.2 V up to potential of –0.4 V. For further studies the potential of –0.2 V was chosen because at more negative potential values interferences from foreign ions potentially present in the sample solution may increase.

Deposition time of selenium was studied in the range from 60 to 600 s. The obtained results are shown in Fig. 5. The concentration of Se(IV) was 2 × 10^{-8} mol·L^{-1}. It was found that Se(IV) signal increased to 180 s and then increased more slowly. Further studies were performed using deposition time of 180 s in order to decrease the time of measurements.

3.3. Calibration data

The calibration graph for Se(IV) for deposition time of 180 s was linear in the range from 3 × 10^{-9} to 3 × 10^{-8} mol·L^{-1} and obeyed the equation $y = 0.9604x + 0.288$, where y and x are the peak current (nA) and Se(IV) concentration (nmol·L^{-1}), respectively. The linear correlation coefficient r was 0.9996. The relative standard deviation (RSD) from seven determinations of selenium at a concentration of 3 × 10^{-8} mol·L^{-1} was 3.5%. The detection limit estimated from three times the standard deviation at a low Se(IV) concentration and deposition time of 180 s was about 8.3 × 10^{-10} mol·L^{-1}. The obtained detection limit is comparable to that reported by Andrews and Johnson [24] for selenium(IV) determination at a rotating gold disc electrode, however, at longer deposition time of 10 min. Furthermore, Andrews and Johnson [24] determinations were performed after oxygen removing from the solutions and pretreatment time of rotating gold disc electrode was longer as compared to the short-lived activation step of the proposed gold microelectrode array. Voltammograms obtained for increasing concentrations of

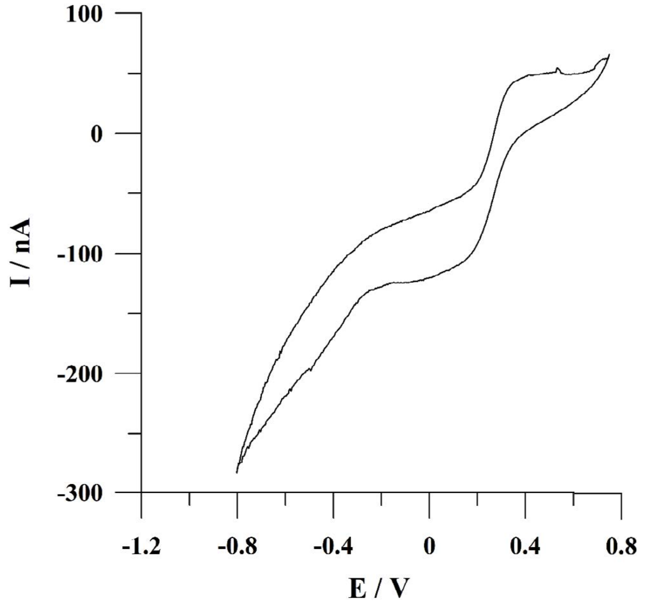

Fig. 3. Cyclic voltammogram recorded from a solution containing 1 × 10^{-3} mol·L^{-1} $K_3Fe(CN)_6$ + 1 mol·L^{-1} KCl obtained at gold microelectrodes array. Scan rate: 10 mV·s^{-1}. Start potential: 0.75 V; first vertex potential: –0.8 V; second vertex potential: 0.75 V.

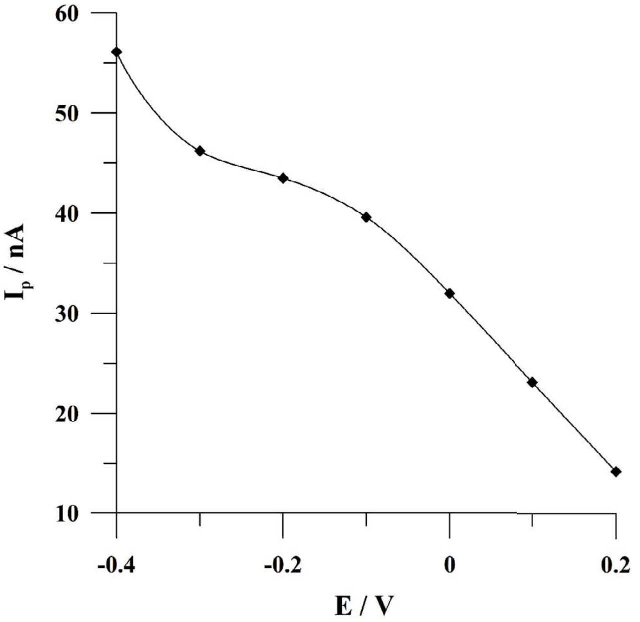

Fig. 4. Influence of deposition potential on Se(IV) peak current. Concentration of Se(IV): 5 × 10^{-8} mol·L^{-1}; $HClO_4$: 0.02 mol·L^{-1}. Deposition time: 180 s. DPV parameters: the step potential, pulse height and pulse period were 4 mV, 50 mV and 40 ms, respectively.

Se(IV) are presented in Fig. 6. The linear calibration graph is presented in an inset to Fig. 6. The analytical features of the presented procedure and previously published voltammetric procedures for selenium(IV) determination using a gold microelectrodes array are summarized in Table 1. On the basis of data presented in Table 1 it can be concluded that the procedure of selenium(IV) determination with the use of a reusable gold microelectrodes array proposed in this article ensures obtaining the lowest detection limit as compared to other procedures utilizing such a kind of electrodes.

3.4. Interferences

The interference of foreign ions was studied for a solution containing Se(IV) ions at a concentration of 3 × 10^{-8} mol·L^{-1} and deposition time of 180 s. The influence of the added foreign ions on the Se(IV) peak current is presented in Table 2. The obtained results indicate that the presence of a 500-fold excess of Mo(VI), As(V), Zn(II), Co(II), Fe(III), Se(VI) and 200-fold excess of Ni(II) does not influence the Se(IV) signal. In the course of Cu(II), Cd(II) and Hg(II) the developed procedure is characterized by less tolerable range of excess concentrations of mentioned ions, however, such high concentrations of foreign ions are rarely present in natural water samples. Interferences occurring in the presence of Pb(II) and As(III) excess can be easily minimized by omitting the second step of microelectrode activation conducted at potential of –1.2 V within 1 s. Our observations can be explained in the following manner: during the second activation step at –1.2 V Pb(II) and As(III) underwent reduction process and in reduced form may react with Se(0) obtained during preconcentration step forming intermetallic compounds. As a consequence selenium oxidation peak current was observed to be decreased. Results obtained after performing experiment without the second step of electrode activation indicate that 20-fold excess of As(III) and 10-fold excess of Pb(II) did not influence Se(IV) peak current.

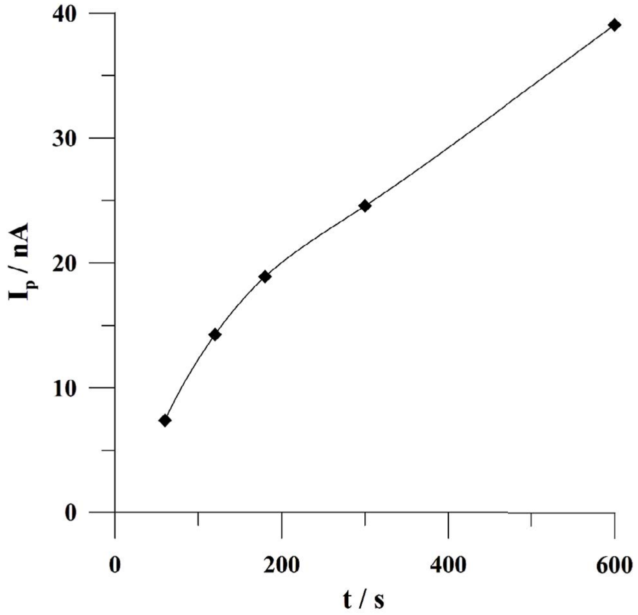

Fig. 5. Influence of deposition time on Se(IV) peak current. Concentration of Se(IV): 2 × 10^{-8} mol·L^{-1}. Deposition potential: –0.2 V. DPV parameters: the step potential, pulse height and pulse period were 4 mV, 50 mV and 40 ms, respectively.

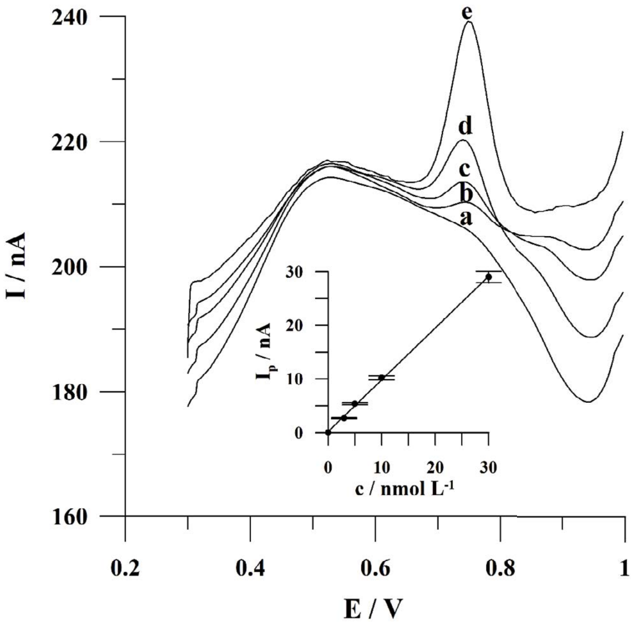

Fig. 6. Anodic stripping voltammograms obtained for increasing concentrations of Se(IV): (a) blank, (b) 3 × 10^{-9} mol·L^{-1}, (c) 5 × 10^{-9} mol·L^{-1}, (d) 1 × 10^{-8} mol·L^{-1}, and (e) 3 × 10^{-8} mol·L^{-1}. Deposition time: 180 s. Inset: a linear range of Se(IV) concentrations. DPV parameters: the step potential, pulse height and pulse period were 4 mV, 50 mV and 40 ms, respectively.

Table 1
The analytical features of the presented procedure and previously published voltammetric procedures for selenium(IV) determination using a gold microelectrodes array

Working electrode	Stripping technique	Accumulation time (s)	Linear dynamic range (mol·L^{-1})	Detection limit (mol·L^{-1})	References
AuμEA	SWASV	60	1 × 10^{-7} – 1 × 10^{-5}	2.5 × 10^{-8}	[19]
AuμA	SWASV	10–200	0–1.2 × 10^{-6}	5.4 × 10^{-9}	[23]
mAuμA	SWASV	–	–	≈10^{-9}	[64]
AuμA	DPASV	180	3×10^{-9} – 3 × 10^{-8}	8.3 × 10^{-10}	This work

AuμEA – gold microband electrode array; AuμA – gold ultramicroelectrode arrays; mAuμA – modified gold microelectrode array.

Table 2
Relative Se(IV) signal in the presence and absence of foreign ions. Solution composition: 3×10^{-8} mol·L^{-1} Se(IV) and 0.02 mol·L^{-1} $HClO_4$. Deposition conditions: –0.2 V, 180 s. DPV parameters: the step potential, pulse height and pulse period were 4 mV, 50 mV and 40 ms, respectively

Foreign ions	Molar excess of foreign ion	Relative signal of Se(IV)
	5	1.37
Cu(II)	25	1.68
	50	1.65
Fe(III)	500	1.05
Zn(II)	500	1.01
Mo(VI)	500	0.94
	30	1.34
Cd(II)	200	1.54
	500	1.92
Co(II)	500	1.19
Ni(II)	200	1.01
	1	0.77
Pb(II)	10	0.17
	10***	0.98***
As(V)	500	0.85
	2	0.40
As(III)	20	0.08
	20***	1.03***
Se(VI)	500	0.91
	1	1.71
Hg(II)	2	1.78
	5	0.50

*Molar excess of foreign ion was calculated as a ratio of an interfering ion's concentration to Se(IV) concentration. Ions concentration were given in mol·L^{-1}.

**Relative signal was calculated as ratio of Se(IV) peak currents obtained after and before the addition of the excess concentration of interfering ion.

***The studies were provided with omitting the second step of working microelectrodes array activation at –1.2 V for 1 s in the standard procedure of measurement.

3.5. Analytical applications

The described ASV procedure was applied for determination of Se(IV) in certified water reference materials SPS-SW1 (surface water) and TM 25.5 (Lake Ontario water). The determinations were carried out using the standard additions method following deposition time of 180 s. The result obtained after analysis of SPS-SW1 (diluted by the factor of 2.5) equal to 2.21 µg·L^{-1} with a standard deviation of 4.2% ($n = 5$) agrees well with the certified value of 2.00 µg·L^{-1} (±) 0.02. Satisfactory results were also obtained in the course of Se(IV) determination in TM 25.5. The result of 27.6 µg·L^{-1} (standard deviation of 4.7%; $n = 5$) is consistent with the certified value of 29.2 µg·L^{-1} ± 3.4. Anodic stripping voltammograms obtained in the course of Se(IV) determination in a sample of certified water reference material TM 25.5 are presented in Fig. 7.

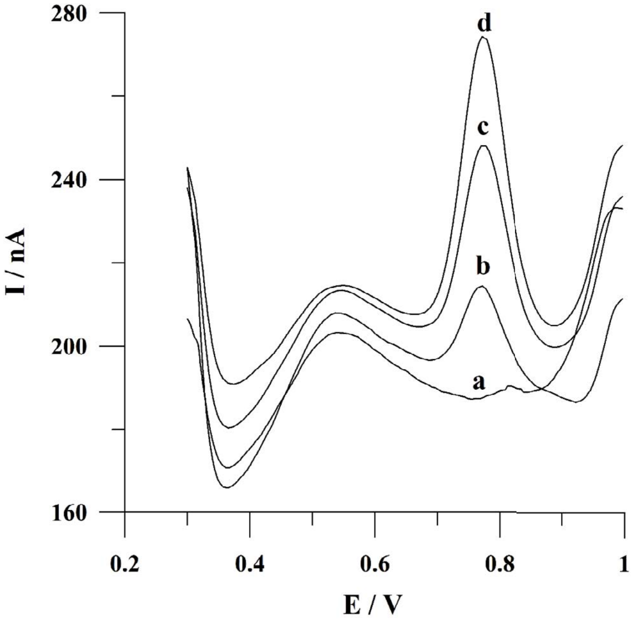

Fig. 7. Anodic stripping voltammograms obtained in the course of Se(IV) determination in a sample of certified water reference material TM 25.5 (factor of dilution 37): (a) blank, (b) as (a) + 0.27 mL TM 25.5, (c) as (b) + 1×10^{-8} mol·L^{-1} Se(IV) and (d) as (b) + 2×10^{-8} mol·L^{-1} Se(IV). Deposition time: 180 s. DPV parameters were the same as in caption to Fig. 6.

Furthermore described procedure was applied for Se(IV) determination in natural water samples collected from Bystrzyca river water. Se(IV) concentration in these samples was below the detection limit of described procedure, so recoveries of selenium from the sample spiked with Se(IV) at concentrations of 1×10^{-8}, 2×10^{-8} and 3×10^{-8} mol·L^{-1} were studied. The obtained recoveries of Se(IV) were in the range from 99% to 106% with a relative standard deviation not exceeding 4.1% that led to the conclusion that selenium(IV) potentially present in water samples can be determined by means of the proposed procedure.

The obtained results indicate that the proposed procedure can be applied to Se(IV) determination in environmental water samples.

4. Conclusions

On the basis of presented results it can be concluded that a reusable, durable, long-term use gold microelectrodes array can be successfully used for the determination of Se(IV) by differential pulse anodic stripping voltammetry. Thanks to the application of two steps of activation of microelectrodes array an increase of analytical signal of selenium and a slight decrease of background current were obtained as compared to results observed after measurements without two activation steps. The method offers a linear dynamic range from 3×10^{-9} to 3×10^{-8} mol·L^{-1} at deposition time of 180 s. The detection limit for Se(IV) using deposition time of 180 s was 8.3×10^{-10} mol·L^{-1} and may be lowered by deposition time prolongation. The reported detection limit for selenium determination is the lowest value obtained so far with the use of a gold microelectrodes array. The proposed method is simple, sensitive and allows for Se(IV) determination in natural waters without complicated sample pretreatment that was confirmed by analysis of water certified reference materials and real water samples.

A novelty of this work is the usage of a reusable solid gold microelectrodes array as a new voltammetric sensor. Utilization of the proposed gold microelectrodes array of a new way of design results in following advantages. Such a kind of working electrode is characterized by its durability, high stability, reusability and environmentally friendly character. Thanks to the latter properties the proposed gold microelectrodes array become an alternative to surface modified and lithographically patterned microelectrodes array [57–60].

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Supplementary information

S1.1. Determination of resistance of gold microelectrodes array

The proposed microelectrode's resistance value was checked in two ways. Firstly, the microelectrode's resistance was determined from the electrochemical impedance spectroscopy spectrum recorded using a gold microelectrodes array as a working electrode. The impedance data were collected at 39 frequencies in the range from 10 to 3,000 Hz and analyzed by expressions valid for Randles equivalent circuit R1 (C1R2) recorded at potential of –0.2 V. The impedance spectrum recorded during this experiment from a solution containing 0.1 mol·L^{-1} $HClO_4$ and 1 × 10^{-3} mol·L^{-1} Se(IV) is presented in Fig. S1. On the basis of this result the determined resistance of the gold microelectrodes array was equal to 5.5 ± 0.5 Ω. This value was obtained by the approximation from the EIS spectrum graph achieved from measurements controlled by FRA software, version 4.9 (Eco Chemie, The Netherlands).

Secondly, the resistance was measured by placing gold microelectrodes array on a metallic copper plate covered with carbon nanotubes using ohmmeter. The results of such measurements were equal to 5.2 ± 0.2 Ω and confirms the results of EIS measurements.

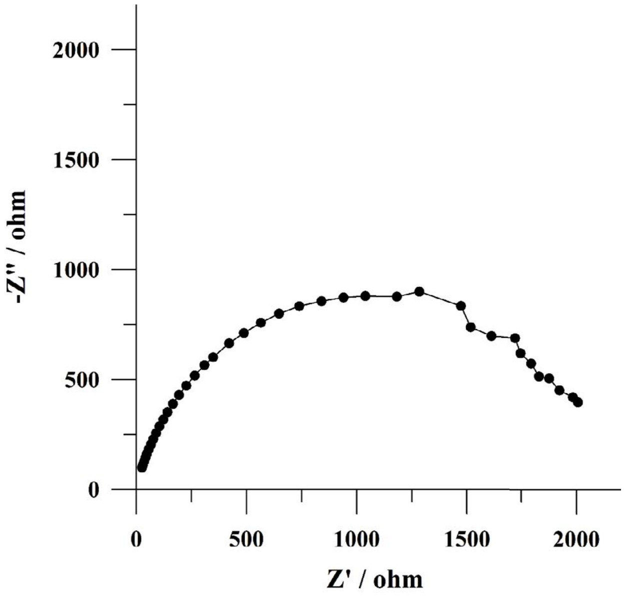

Fig. S1. EIS spectrum for gold microelectrodes array recorded from a solution containing 0.1 mol·L^{-1} $HClO_4$ and 1 × 10^{-3} mol·L^{-1} Se(IV) at potential of –0.2 V.