



UMCS

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**Nowe zastosowania elektrod
sitodrukowanych w analizie śladowej jonów
metali w próbkach wód**

Praca doktorska
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Lista publikacji będących przedmiotem rozprawy doktorskiej

Publikacja 1

K. Tyszczyk-Rotko, **Katarzyna Domańska**, *Simple and sensitive voltammetric procedure for determination of Cd(II) and Pb(II) using bismuth-coated screen-printed carbon electrode prepared with mediator*, Journal of The Electrochemical Society, 164 (2017) H537-H544.

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Publikacja 2

Katarzyna Domańska, K. Tyszczyk-Rotko, *Integrated three-electrode screen-printed sensor modified with bismuth film for voltammetric determination of thallium(I) at the ultratrace level*, Analytica Chimica Acta, 1036 (2018) 16-25.

(IF₂₀₁₈ = 5,256; MNiSW = 45)

Publikacja 3

K. Tyszczyk-Rotko, **Katarzyna Jędruchniewicz**, *Ultrasensitive sensor for uranium monitoring in water ecosystems*, Journal of The Electrochemical Society 166 (2019) B837-B844.

(IF₂₀₁₈ = 3,120; MNiSW = 40)

Publikacja 4

Katarzyna Jędruchniewicz, K. Tyszczyk-Rotko, *A new modified screen-printed sensor for monitoring of ultratrace concentrations of Mo(VI)*, Journal of Electroanalytical Chemistry, 847 (2019) 113228-113236.

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Wstęp i cel badań

Problem zanieczyszczenia środowiska naturalnego metalami ciężkimi stale przybiera na sile. Przemysł energetyczny, wydobywczy, hutniczy, rolnictwo oraz transport stanowią główne źródła emisji jonów metali ciężkich do wód, gleby oraz powietrza. Stanowią one poważne zagrożenie dla organizmów żywych ze względu na to, że są niemalże niebiodegradowalne, z łatwością migrują w środowisku oraz zdolne są do bioakumulacji zarówno w tkankach roślinnych, jak i zwierzęcych [1-2]. Prowadzi to do przedostawania się metali ciężkich do łańcucha pokarmowego, co szkodliwie oddziałuje na zdrowie organizmów żywych, w tym także na organizm człowieka [3-4].

Spożywanie zanieczyszczonej wody oraz pożywienia skutkuje zaburzeniami funkcjonowania organizmu oraz występowaniem poważnych schorzeń, w tym także chorób nowotworowych. Kumulacja metali ciężkich w organizmie zachodzi w określonych organach, zwłaszcza uczestniczących w procesie detoksykacji organizmu (wątrobie, nerkach). Ponadto, metale mogą nagromadzać się w mózgu, kościach i mięśniach. Skutki działania toksycznych związków metali ciężkich nie zawsze są natychmiastowe. Mogą ujawniać się po latach, a nawet dopiero w kolejnych pokoleniach [5].

Nie tylko metale o toksycznych właściwościach stanowią zagrożenie dla zdrowia człowieka. Nadmierne spożywanie mikroelementów niezbędnych do prawidłowego funkcjonowania organizmu może prowadzić do zaburzeń równowagi dynamicznej pierwiastków w organizmie. Stałe przyjmowanie pożywienia, bądź wody o podwyższonej ich zawartości prowadzi do występowania niepożądanych objawów, a nawet może ujawniać działanie toksyczne [6-7].

Postępujący proces degradacji środowiska stwarza konieczność prowadzenia ciągłej kontroli poziomu zanieczyszczeń. Stały monitoring jakości wód daje możliwość szybkiego wykrywania skażenia wody i zapobiegania rozprzestrzenianiu zanieczyszczeń poprzez wdrożenie odpowiednich technologii uzdatniania wody. Doskonałym narzędziem pozwalającym na prowadzenie analiz poza laboratorium, w miejscu pobrania próbki (analiza polowa) jest przenośna aparatura [8].

Stosowanie aparatury przenośnej do zadań analitycznych ujawnia szerokie spektrum zalet. Przede wszystkim analiza w terenie pozwala na uzyskanie wyników w krótkim czasie i w związku z tym umożliwia wczesne wykrycie zanieczyszczenia wód. Ponadto, umożliwia prowadzenie kontroli parametrów wody ulegających szybkim

zmianom. Analiza próbek wód w terenie dodatkowo eliminuje koszty transportu oraz przechowywania próbek, a także błędy pomiarowe (w czasie transportu i przechowywania może dochodzić do zmiany składu próbki w czasie) [8-10].

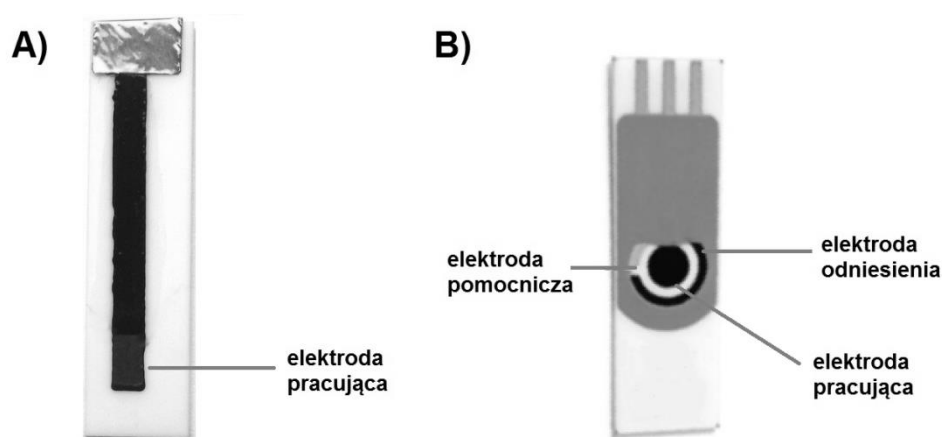
Woltamperometria może być wykorzystywana do analizy ilościowej i jakościowej w terenie. Przenośna aparatura z wbudowanym analizatorem elektrochemicznym jest prostym w obsłudze narzędziem, pozwalającym na uzyskanie wiarygodnych wyników nawet w kilka minut [11, 12].

Celem badań prowadzonych w trakcie realizacji niniejszej rozprawy doktorskiej było opracowanie woltamperometrycznych procedur oznaczania wybranych jonów metali w próbkach wód naturalnych z wykorzystaniem elektrod sitodrukowanych, które mogą być stosowane w analizatorach przenośnych. W badaniach zastosowano woltamperometrię strippingową z uwagi na dodatkowy etap zateżniania analitu na powierzchni elektrody, co umożliwia prowadzenie oznaczeń jonów metali na niskich poziomach stężeń. W celu poprawy właściwości elektrochemicznych elektrod pracujących zastosowano modyfikacje ich powierzchni błonką metalu (bizmutu i ołowiu) bez i z zastosowaniem odtwarzalnie osadzanego mediatora. W badaniach skupiono się ponadto na opracowaniu procedur minimalizacji interferencji pochodzących od matrycy próbek wód naturalnych. Opracowane procedury oznaczania wybranych jonów metali sprawdzono z wykorzystaniem certyfikowanych materiałów odniesienia oraz zastosowano w analizach próbek wód środowiskowych.

1. Aktualny stan wiedzy

1.1. Elektrody sitodrukowane

Odpowiednim narzędziem do zastosowań w przenośnych urządzeniach kontrolno-pomiarowych okazały się elektrody otrzymywane technologią sitodruku. Po raz pierwszy technologię tę zastosowano do produkcji elektrod w latach 90-tych XX w. Umożliwia ona wytwarzanie między innymi sitodrukowanych elektrod pracujących, bądź zespolonego układu pomiarowego, gdzie na powierzchni nośnika umieszczona jest elektroda pracująca, odniesienia oraz pomocnicza. Na **rysunku 1** przedstawiono oba rodzaje elektrod. Te, obecnie dostępne w handlu elektrody sitodrukowane (**Rys. 1B**), charakteryzują się niewielkim rozmiarem i niskim kosztem produkcji. Ponadto, wyniki otrzymywane przy ich użyciu charakteryzują się satysfakcjonującą powtarzalnością. Dane literaturowe wskazują na to, że mogą być stosowane w woltamperometrycznych oznaczeniach zarówno jonów metali, jak i substancji biologicznie aktywnych na niskich poziomach stężeń [11, 13].



Rys. 1. A) Sitodrukowana elektroda węglowa i B) zespolony układ pomiarowy z sitodrukowaną elektrodą pracującą, pomocniczą oraz odniesienia.

Produkcja elektrod sitodrukowanych polega na przetłoczeniu tuszu przez uprzednio przygotowaną formę na ceramiczne lub plastikowe podłoże. Dodatkową zaletą tych elektrod jest fakt, iż skład tuszu może być dowolnie modyfikowany, w zależności od stawianych wymagań aplikacyjnych danej elektrody. Kompozycja tuszu wpływa na przewodność czy rezystancję otrzymanego materiału [14]. Od składu tuszu zależy także czułość, jak i selektywność danej analizy. Stosuje się w tym celu dodatki różnorodnych

substancji (modyfikatorów), takich jak: metale, enzymy, polimery, czy czynniki kompleksujące [15]. Dodatkowo, właściwości elektrod można zmieniać przez modyfikację ich powierzchni np. błonką metalu, polimerem, czy enzymem. Cechy elektrod sitodrukowanych, takie jak rozmiar, grubość, czy kształt dopasowuje się do wymagań użytkownika. Szereg zalet charakteryzujących elektrody sitodrukowane sprawia, że są one coraz chętniej stosowane, a producenci oferują coraz bardziej udoskonalone konstrukcje [16, 17].

1.2. Modyfikacja powierzchni elektrod sitodrukowanych

W literaturze można odnaleźć szereg prac opisujących różne sposoby modyfikacji powierzchni elektrod pracujących oraz przykłady ich zastosowań [18-37]. Przyczyną wprowadzenia etapu modyfikacji powierzchni elektrod jest między innymi dążenie do zwiększenia ich powierzchni aktywnej, na której nagromadzane są oznaczane substancje i/lub poprawa szybkości przeniesienia elektronów. Oba te efekty skutkują wzmocnieniem sygnału analitycznego oznaczanej substancji/ionu metalu i obniżeniem granic wykrywalności analitu. Inną, częstą przyczyną prowadzenia modyfikacji powierzchni elektrod jest dążenie do minimalizacji interferencji pochodzących od innych składników próbki (zwiększenie selektywności pomiarów), a w przypadku analizy więcej niż jednej substancji również poprawa rozdzielania ich sygnałów analitycznych.

Obecnie, elektrody sitodrukowane z modyfikowaną powierzchnią są coraz częściej wykorzystywane w oznaczeniach jonów metali. Dzięki nim możliwe jest prowadzenie analiz na śladowym poziomie stężeń, także w warunkach polowych [11]. W **tabeli 1** zestawiono przykłady zastosowań elektrod sitodrukowanych z modyfikowaną powierzchnią do analizy Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI).

Tabela 1. Zestawienie parametrów analitycznych procedur oznaczania Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI) na elektrodach sitodrukowanych.

Oznaczany jon	Stosowana elektroda	Granica wykrywalności (mol L ⁻¹)	Granica oznaczalności (mol L ⁻¹)	Zakres liniowy krzywej kalibracyjnej (mol L ⁻¹)	Czas załączenia analitu (s)	Technika	Publikacja
Cd(II)	ex-situ BiSPCE	-	-	$1,0 \times 10^{-8} - 2,5 \times 10^{-6}$	60	DPASV	[18]
Pb(II)		-	-	$1,0 \times 10^{-8} - 1,3 \times 10^{-6}$			
Zn(II)		-	-	$1 \times 10^{-7} - 8 \times 10^{-6}$			
Cd(II)	CBMFE	$2,2 \times 10^{-9}$	-	$2,7 \times 10^{-9} - 4,5 \times 10^{-7}$	60	DPASV	[19]
Pb(II)		$3,9 \times 10^{-10}$	-	$7,2 \times 10^{-10} - 2,9 \times 10^{-7}$			
Zn(II)		$8,4 \times 10^{-8}$	-	$1,2 \times 10^{-7} - 3,4 \times 10^{-6}$			
Cd(II)	elektroda sitodrukowana modyfikowana 6% cytrynianem bizmutu	$9,8 \times 10^{-9}$	-	$8,9 \times 10^{-8} - 7,1 \times 10^{-7}$	120	DPASV	[20]
Pb(II)		$4,3 \times 10^{-9}$	-	$2,4 \times 10^{-8} - 1,9 \times 10^{-7}$			
Cd(II)	SPCE GS-Nafion/Au	$3,1 \times 10^{-9}$	-	$7,1 \times 10^{-9} - 4,4 \times 10^{-7}$	240	DPASV	[21]
Pb(II)		$1,1 \times 10^{-9}$	-	$2,4 \times 10^{-9} - 2,9 \times 10^{-7}$			
Cd(II)	Bi _{sp} SPE	$8,9 \times 10^{-10}$	$2,9 \times 10^{-9}$	$2,9 \times 10^{-9} - 1,1 \times 10^{-7}$	360	DPASV	[22]
Pb(II)		$7,7 \times 10^{-10}$	$2,6 \times 10^{-9}$	$2,6 \times 10^{-9} - 9,6 \times 10^{-8}$			
Cd(II)	Bi _{sp} SPE	$8,9 \times 10^{-10}$	$3,1 \times 10^{-9}$	$3,1 \times 10^{-9} - 9,4 \times 10^{-8}$	360	DPASV	[23]
Pb(II)		$8,7 \times 10^{-10}$	$2,8 \times 10^{-9}$	$2,8 \times 10^{-9} - 8,2 \times 10^{-8}$			

Cd(II)	in-situ SbSPCE	$3,0 \times 10^{-8}$	$9,8 \times 10^{-8}$	$9,8 \times 10^{-8} - 6,4 \times 10^{-7}$	120	DPASV	[24]
Pb(II)		$2,4 \times 10^{-8}$	$8,1 \times 10^{-8}$	$8,1 \times 10^{-8} - 3,0 \times 10^{-7}$			
Cu(II)		$2,5 \times 10^{-8}$	$8,3 \times 10^{-8}$	$8,3 \times 10^{-8} - 1,6 \times 10^{-6}$			
Cd(II)	Bi/SPE	$1,8 \times 10^{-9}$	-	$4,5 \times 10^{-9} - 1,1 \times 10^{-7}$	120	SWASV	[25]
Pb(II)		$9,7 \times 10^{-10}$	-	$2,4 \times 10^{-9} - 5,8 \times 10^{-8}$			
Cd(II)	N/IL/G/SPCE	$5,3 \times 10^{-10}$	-	$8,9 \times 10^{-10} - 8,9 \times 10^{-7}$	120	SWASV	[26]
Pb(II)		$3,9 \times 10^{-10}$	-	$4,8 \times 10^{-10} - 4,8 \times 10^{-7}$			
Zn(II)		$1,4 \times 10^{-9}$	-	$1,5 \times 10^{-9} - 1,5 \times 10^{-6}$			
Cd(II)	MHCS-Nafion/SPCE	$1,5 \times 10^{-8}$	-	$1,8 \times 10^{-8} - 1,8 \times 10^{-6}$	240	SWASV	[27]
Pb(II)		$6,6 \times 10^{-9}$	-	$9,7 \times 10^{-9} - 9,7 \times 10^{-7}$			
Cd(II)	SPG	$8,9 \times 10^{-10}$	-	$8,9 \times 10^{-9} - 2,7 \times 10^{-6}$	190	SWASV	[28]
Pb(II)		$4,8 \times 10^{-10}$	-	$4,8 \times 10^{-9} - 1,5 \times 10^{-6}$			
Cd(II)	Bi/MWNT-IL/SPCE	$4,5 \times 10^{-9}$	-	$8,9 \times 10^{-9} - 5,3 \times 10^{-7}$	400	SWASV	[29]
Pb(II)		$5,8 \times 10^{-10}$	-	$4,8 \times 10^{-9} - 2,9 \times 10^{-7}$			
Cd(II)	BiF/SPCE	$1,4 \times 10^{-9}$	$4,5 \times 10^{-9}$	$5 \times 10^{-9} - 1 \times 10^{-6}$	190	SWASV	Publikacja 1
Pb(II)	przygotowana z zastosowaniem mediatora	$1,4 \times 10^{-10}$	$4,7 \times 10^{-10}$	$5 \times 10^{-10} - 5 \times 10^{-7}$			

Cd(II)	SPE/SWCNHs/BiF	$1,8 \times 10^{-9}$	-	$8,9 \times 10^{-9} - 5,3 \times 10^{-7}$	150	SWASV	[30]
Pb(II)		$1,9 \times 10^{-9}$	-	$4,8 \times 10^{-9} - 2,9 \times 10^{-7}$			
Cd(II)	P-g-C ₃ N ₄ /O-MWCNTs/SPE	$2,7 \times 10^{-10}$	-	$3,8 \times 10^{-8} - 7,0 \times 10^{-7}$ $7,0 \times 10^{-7} - 2,2 \times 10^{-6}$	240	DPASV	[31]
Pb(II)		$3,9 \times 10^{-11}$	-	$1,7 \times 10^{-9} - 3,1 \times 10^{-8}$ $3,1 \times 10^{-8} - 5,3 \times 10^{-7}$			
Hg(II)		$2,0 \times 10^{-10}$	-	$2,4 \times 10^{-8} - 4,6 \times 10^{-7}$			
Zn(II)		$9,2 \times 10^{-10}$	-	$6,4 \times 10^{-8} - 3,1 \times 10^{-6}$			
Cd(II)	Bi _{sp} SPE	$3,2 \times 10^{-8}$	-	$2,7 \times 10^{-7} - 8,0 \times 10^{-7}$	120	SWASV	[32]
Pb(II)		$1,9 \times 10^{-8}$	-	$1,5 \times 10^{-7} - 4,3 \times 10^{-7}$			
Tl(I)	SPCE modyfikowana prekursorem bizmutu: tlenkiem bizmutu	$4,9 \times 10^{-9}$	-	$2,4 \times 10^{-8} - 2,2 \times 10^{-7}$	120	DPASV	[33]
	glinianem bizmutu	$4,4 \times 10^{-9}$	-	$2,4 \times 10^{-8} - 2,0 \times 10^{-7}$			
	cyrkonianem bizmutu	$5,4 \times 10^{-9}$	-	$2,4 \times 10^{-8} - 2,0 \times 10^{-7}$			
	in situ-BiFSPCE	$7,8 \times 10^{-9}$	-	$2,4 \times 10^{-8} - 2,0 \times 10^{-7}$			
Tl(I)	crown-6-SPCNFE	$5,3 \times 10^{-8}$	-	$5,8 \times 10^{-9} - 1,3 \times 10^{-6}$	120	DPASV	[34]
In(III)		$1,2 \times 10^{-7}$	-	$1,6 \times 10^{-8} - 2,6 \times 10^{-6}$			

Tl(I)	BiF/SPCE	$8,47 \times 10^{-10}$	$2,9 \times 10^{-9}$	$5 \times 10^{-9} - 1 \times 10^{-6}$	60	SWASV	Publikacja 2
		$6,71 \times 10^{-12}$	$2,2 \times 10^{-11}$	$5 \times 10^{-11} - 1 \times 10^{-9}$	300		
U(VI)	4-CP-SPE	$7,0 \times 10^{-10}$	2×10^{-9}	$8,5 \times 10^{-10} - 5,0 \times 10^{-8}$	900	SWAdSV	[35]
U(VI)	GRA-SPE	$4,5 \times 10^{-9}$	-	$5,0 \times 10^{-9} - 1,0 \times 10^{-7}$	1800	DPAdSV	[36]
U(VI)	PbF/SPCE	$1,90 \times 10^{-11}$	$6,3 \times 10^{-11}$	$1 \times 10^{-10} - 1 \times 10^{-8}$	60	DPAdSV	Publikacja 3
Mo(VI)	Cup-SPCE	$2,6 \times 10^{-8}$	-	$5,2 \times 10^{-8} - 2,1 \times 10^{-6}$ $2,1 \times 10^{-6} - 2,1 \times 10^{-5}$	720	DPAdSV	[37]
Mo(VI)	PbF/SPCE	$2,12 \times 10^{-10}$	$7,1 \times 10^{-10}$	$1 \times 10^{-9} - 5 \times 10^{-8}$	60	DPAdSV	Publikacja 4

ex-situ BiSPCE - sitodrukowana elektroda węglowa *ex situ* modyfikowana bizmutem; **CBMFE** – elektroda węglowa modyfikowana błoną rtęci; **SPCE|GS-Nafion/Au** - sitodrukowana elektroda węglowa modyfikowana grafenem, Nafionem i złotem; **Bi_{sp}SPE** - elektroda sitodrukowana napyłana warstwą bizmutu; **in-situ SbSPCE** - sitodrukowana elektroda węglowa modyfikowana *in situ* antymonem; **Bi/SPE** - sitodrukowana elektroda grafitowa modyfikowana tlenkiem bizmutu; **N/IL/G/SPCE** - sitodrukowana elektroda węglowa modyfikowana nanokompozytem: Nafion/ciecz jonowa/grafen; **MHCS-Nafion/SPCE** - sitodrukowana elektroda węglowa modyfikowana kompozytem Nafionu i mikroporowatych pustych kul węglowych; **SPG** - sitodrukowana elektroda grafenowa; **Bi/MWNT-IL/SPCE** - sitodrukowana elektroda węglowa modyfikowana wielościennymi nanorurkami węglowymi, cieczą jonową i błoną bizmutu; **SPE/SWCNHs/BiF** - sitodrukowana elektroda pokryta jednościennymi nanorogami węglowymi i błoną bizmutu; **P-g-C₃N₄/O-MWCNTs/SPE** - elektroda sitodrukowana modyfikowana nanokompozytem utlenionych wielowarstwowych nanorurek węglowych i porowatych nanocząstek grafitowego azotku węgla; **crown-6-SPCNFE** - sitodrukowana elektroda węglowa modyfikowana nanorurkami węglowymi i 4-karboksybenzo-18-korona-6; **4-CP-SPE** - elektroda sitodrukowana modyfikowana grupami 4-karboksyfenylowymi; **GRA-SPE** - sitodrukowana elektroda grafitowa; **Cup-SPCE** - sitodrukowana elektroda węglowa modyfikowana błoną kupferronu i tetrafenyloboranu; **SWASV** - anodowa woltamperometria stripingowa fali prostokątnej; **SWAdSV** - adsorpcyjna woltamperometria stripingowa fali prostokątnej; **DPASV** - impulsowo-różnicowa anodowa woltamperometria stripingowa; **DPAdSV** - impulsowo-różnicowa adsorpcyjna woltamperometria stripingowa

2. Badania własne

Przeprowadzone badania miały na celu opracowanie woltamperometrycznych procedur oznaczania wybranych jonów metali (Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI)) z wykorzystaniem modyfikowanych błonką bizmutu lub ołowiu sitodrukowanych elektrod węglowych, które mogą być stosowane w analizie polowej próbek wód. W trakcie prowadzonych badań między innymi:

- zoptymalizowano procedury modyfikacji elektrod sitodrukowanych,
- scharakteryzowano powierzchnie elektrod modyfikowanych stosując szereg nowoczesnych technik,
- zoptymalizowano procedury oznaczania wybranych jonów metali,
- zoptymalizowano procedury minimalizacji interferencji pochodzących od składników próbek wód środowiskowych,
- wyznaczono parametry analityczne opracowanych procedur,
- sprawdzono opracowane procedury wykorzystując do tego celu certyfikowane materiały odniesienia oraz zastosowano je do analizy próbek wód środowiskowych.

2.1. Procedury modyfikacji powierzchni elektrod błonką metalu i ich charakterystyka

Mimo swoich zalet, stosowane często w oznaczeniach woltamperometrycznych elektrody rtęciowe, ze względu na toksyczny charakter rtęci i soli rtęci zaczęły być zastępowane przez inne elektrody. W 2000 roku po raz pierwszy Wang i współpracownicy zaproponowali zastosowanie w oznaczeniach woltamperometrycznych błonkowej elektrody bizmutowej (BiFE) [38]. Jedną z zalet błonkowych elektrod bizmutowych jest fakt, iż uznawane są za elektrody przyjazne dla środowiska naturalnego. W 2005 roku po raz pierwszy do modyfikacji powierzchni elektrody węglowej zastosowano błonkę ołowiu (PbFE) [39]. Elektrody modyfikowane błonką ołowiu, podobnie jak bizmutu, stanowią dobrą alternatywę dla elektrod rtęciowych, a praca z PbFE jest bezpieczniejsza w porównaniu do elektrod rtęciowych ze względu na zdecydowanie mniejszą lotność związków ołowiu stosowanych do przygotowania elektrody. Zarówno błonkowe elektrody bizmutowe, jak i ołowiowe znalazły szereg zastosowań w analizie jonów metali i związków biologicznie aktywnych [40-50].

Jednym ze sposobów na poprawę właściwości elektrochemicznych elektrod modyfikowanych błonką metalu jest zastosowanie odtwarzalnie osadzanego mediatora w etapie przygotowywania elektrod [51-55]. Wówczas, do roztworu elektrolitu, oprócz jonów metalu służących do osadzania błonki (jony modyfikatora, np. Pb(II), Bi(III), Sb(III)) wprowadza się także jony mediatora (np. Zn(II), Cd(II)). Pierwszy etap osadzania błonki polega na przyłożeniu odpowiednio dobranego potencjału tak, aby na powierzchni elektrody redukcji ulegały jony modyfikatora i mediatora. W kolejnym etapie należy zastosować potencjał bardziej dodatni, powodujący usunięcie mediatora (poprzez jego utlenienie) przy dalszym osadzaniu błonki metalu. Tak przeprowadzony proces osadzania błonki metalu przyczynia się do zwiększenia powierzchni aktywnej elektrody, co przekłada się na wzmocnienie sygnału analitycznego oznaczanej substancji i obniżenie granicy wykrywalności.

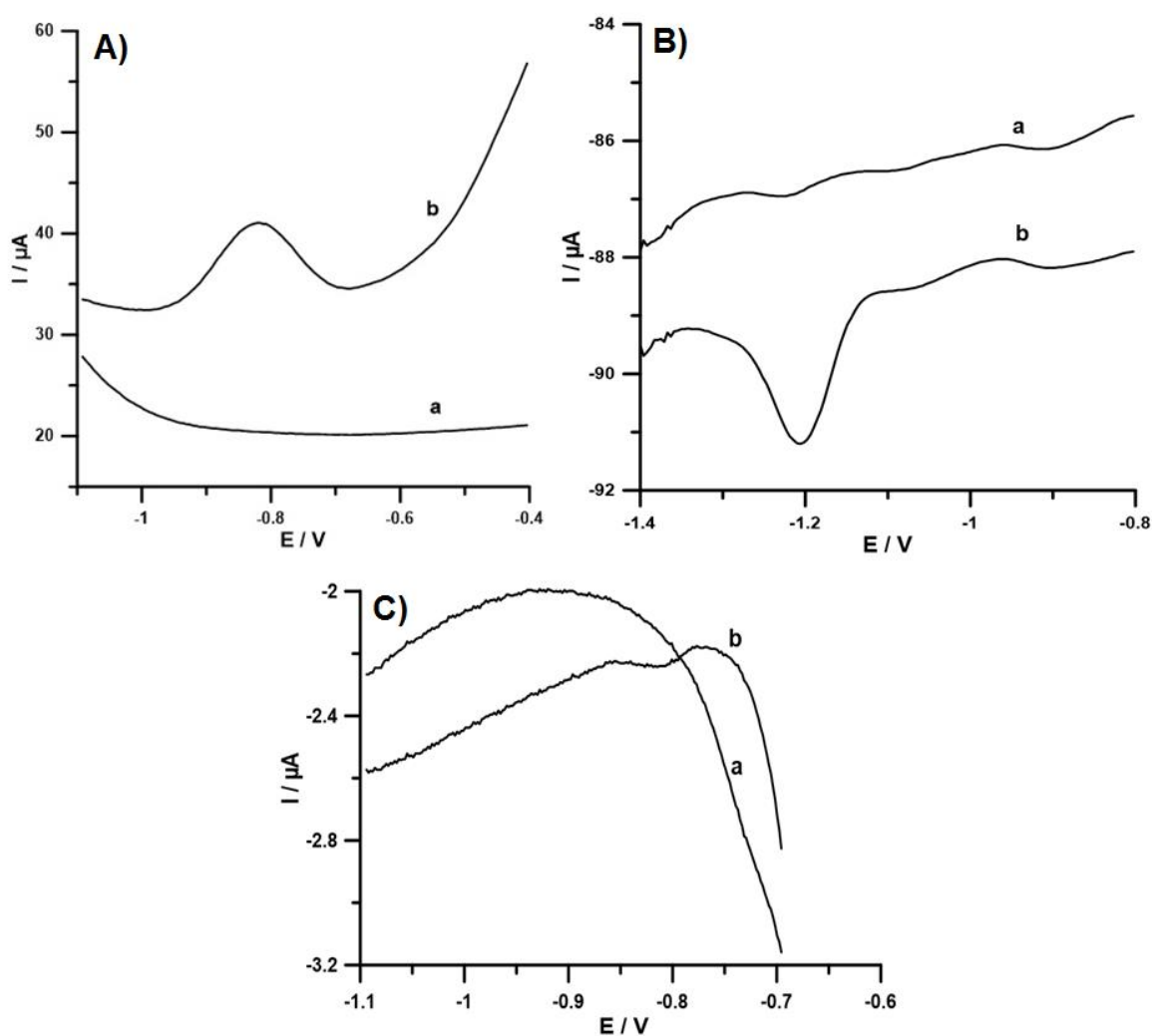
W niniejszej pracy do modyfikacji powierzchni elektrod sitodrukowanych zastosowano błonkę bizmutu w oznaczeniach Cd(II), Pb(II) i Tl(I) (**Publikacja 1 i 2**) oraz błonkę ołowiu w oznaczeniach U(VI) oraz Mo(VI) (**Publikacja 3 i 4**). Dodatkowo, w **Publikacji 1** w etapie osadzania błonki bizmutu zastosowano odtwarzalnie osadzany mediator (Zn).

Optymalizacja procedur modyfikacji powierzchni elektrod błonką metalu polegała na doborze rodzaju i stężenia jonu modyfikatora, potencjału oraz czasu osadzania błonki. W przypadku błonkowej elektrody bizmutowej osadzonej z zastosowaniem odtwarzalnie osadzanego mediatora, dodatkowo dobrano jego stężenie oraz potencjał i czas usuwania (utleniania) z powierzchni elektrody. Przeprowadzono również optymalizację etapu elektrochemicznego oczyszczania powierzchni elektrody. W **tabeli 2** zebrano zoptymalizowane parametry procedur modyfikacji powierzchni elektrod sitodrukowanych.

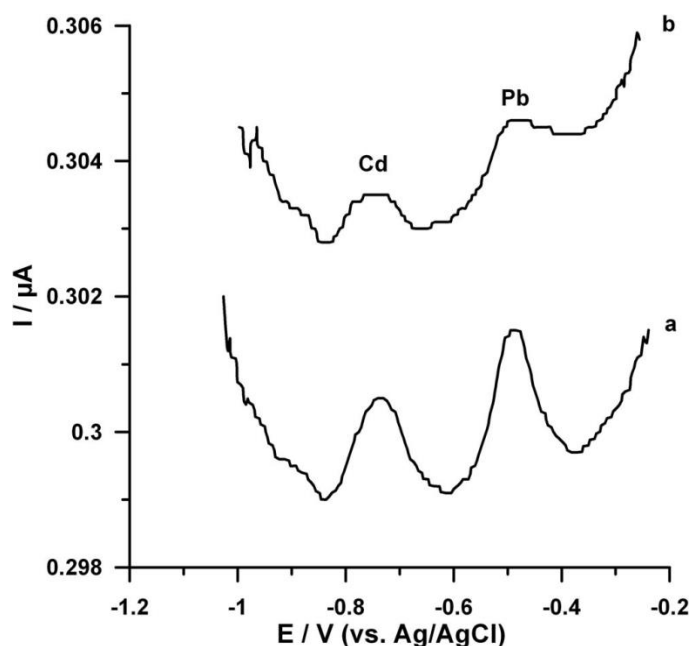
Tabela 2. Parametry procedur modyfikacji powierzchni sitodrukowanych elektrod węglowych błonką metalu w oznaczeniach Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI) (Publikacje 1-4).

Parametr	Oznaczany jon			
	Cd(II) Pb(II)	Tl(I)	U(VI)	Mo(VI)
Rodzaj elektrody	SPCE*	SPCE**	SPCE**	SPCE**
Modyfikator powierzchni elektrody	Bi	Bi	Pb	Pb
Stężenie jonu-modyfikatora (mol L ⁻¹)	2×10^{-5}	1×10^{-5}	$2,5 \times 10^{-5}$	2×10^{-3}
Mediator	Zn	-	-	-
Stężenie mediatora (mol L ⁻¹)	2×10^{-5}	-	-	-
Potencjał (V) / czas elektrochemicznego oczyszczania elektrody (s)	-	0,5 / 10	0,2 / 10	0,5 / 30
Potencjał (V) / czas osadzania błonki metalu (s)	-1,65 / 180	-1,1 / 60	-1,1 / 60	-0,9 / 45
Potencjał (V) / czas utleniania mediatora (s)	-0,95 / 10	-	-	-
Publikacja	1	2	3	4
SPCE* - sitodrukowana elektroda węglowa; SPCE** - zespolony układ pomiarowy z sitodrukowaną węglową elektrodą pracującą				

Modyfikacja powierzchni sitodrukowanych elektrod węglowych błonką metalu (ołowiu, bizmutu) przyczyniła się do znaczącego wzmocnienia sygnałów analitycznych oznaczanych jonów metali (**Rys. 2**). Dodatkowe wzmocnienie sygnałów Cd(II) i Pb(II) uzyskano dzięki zastosowaniu odtwarzalnie osadzanego mediatora w etapie osadzania błonki bizmutu (**Rys. 3**).



Rys. 2. Woltamperogramy uzyskane podczas oznaczania: A) Tl(I) o stężeniu $2 \times 10^{-7} \text{ mol L}^{-1}$, B) U(VI) o stężeniu $1 \times 10^{-7} \text{ mol L}^{-1}$ oraz C) Mo(VI) o stężeniu $5 \times 10^{-7} \text{ mol L}^{-1}$ na sitodrukowanej elektrodzie węglowej niemodyfikowanej (a) oraz modyfikowanej błonką Bi (A(b)) lub Pb (B(b) i C(b)) (**Publikacje 2-4**).



Rys. 3. Woltamperogramy otrzymane przy oznaczaniu 2×10^{-7} mol L⁻¹ Cd(II) i 2×10^{-7} mol L⁻¹ Pb(II) na sitodrukowanej elektrodzie węglowej modyfikowanej błonką bizmutu a) z i b) bez zastosowania odtwarzalnie osadzanego (**Publikacja 1**).

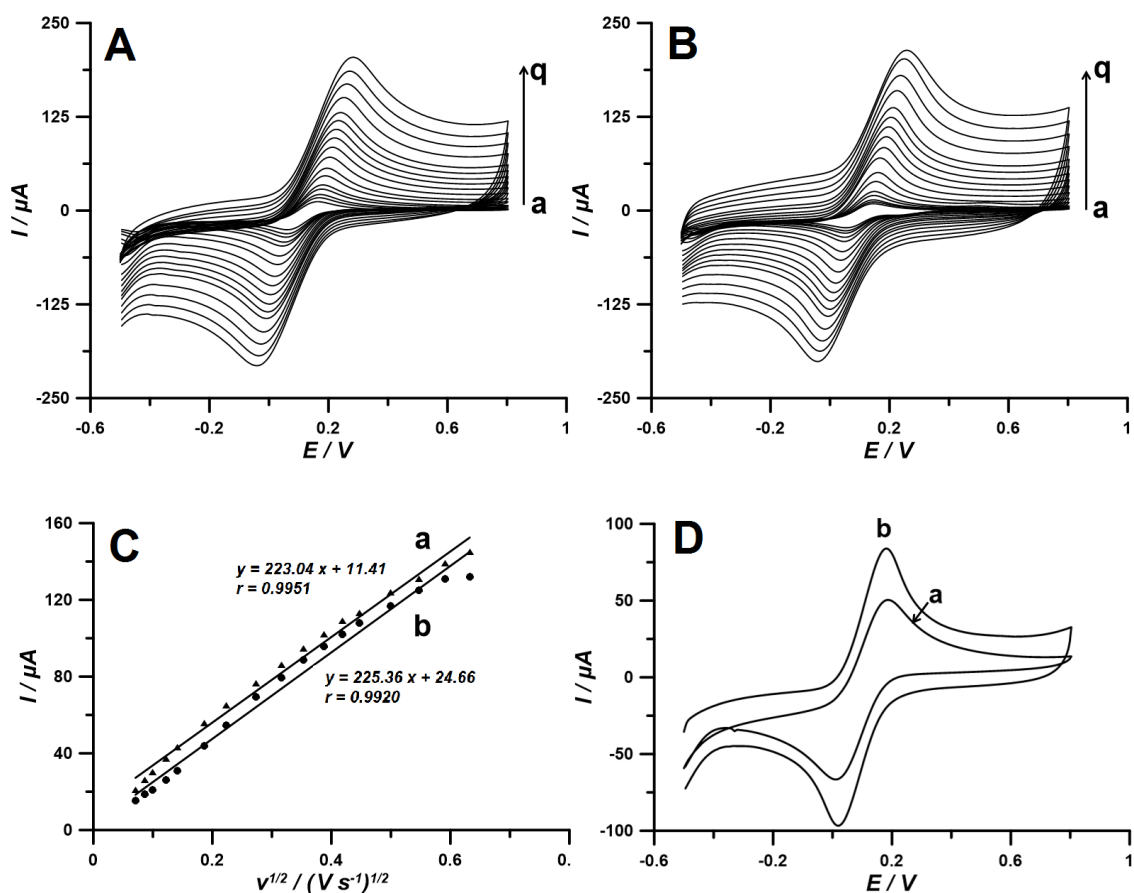
Morfologia powierzchni elektrod niemodyfikowanych oraz modyfikowanych błonką metalu została zbadana z wykorzystaniem:

- mikroskopu optycznego (**Publikacja 1 i 2**),
- profilometru optycznego (**Publikacja 1**),
- mikroskopu sił atomowych (AFM) (**Publikacja 1**),
- skaningowego mikroskopu elektronowego (SEM) (**Publikacja 2 i 3**),
- transmisyjnego mikroskopu elektronowego (TEM) (**Publikacja 3 i 4**).

Skład powierzchni elektrod niemodyfikowanych i modyfikowanych zbadano z wykorzystaniem rentgenowskiej spektroskopii fotoelektronów (XPS) (**Publikacja 1 i 2**) i spektroskopii dyspersji energii promieniowania rentgenowskiego (EDX) (**Publikacja 3 i 4**). Otrzymane wyniki potwierdziły między innymi istotne różnice w strukturze, morfologii i składzie powierzchni elektrod niemodyfikowanych i modyfikowanych błonką metalu oraz zależność mikroskopowej struktury powierzchni od parametrów procedury osadzania błonki metalu.

W celu dodatkowej charakterystyki powierzchni elektrody pracującej, w pracy dotyczącej oznaczania Mo(VI) (**Publikacja 4**), obliczono i porównano wielkość powierzchni aktywnej elektrody niemodyfikowanej względem modyfikowanej błonką ołowiu. Na podstawie otrzymanych wyników stwierdzono, że modyfikacja powierzchni

elektrody jedynie w nieznacznym stopniu zwiększyła powierzchnię aktywną elektrody SPCE ($0,06178 \pm 0,0003 \text{ cm}^2$ ($n = 3$) vs. $0,06225 \pm 0,0001 \text{ cm}^2$ ($n = 3$)). W związku z tym, że etap modyfikacji powierzchni elektrody znacząco wpłynął na wzmocnienie sygnału analitycznego Mo(VI), wykonano obliczenia szybkości przenoszenia elektronów na elektrodzie modyfikowanej względem elektrody niepokrytej błonką ołowiu. Obliczona wartość względnego rozdzielania pików, $\chi^\circ_{\text{PbF/SPCE}} = 2,104 \pm 0,095$ ($n = 3$), jest bliższa wartości teoretycznej niż w przypadku niemodyfikowanej SPCE, gdzie $\chi^\circ_{\text{SPCE}} = 2,829 \pm 0,035$ ($n = 3$). Oznacza to, że modyfikacja powierzchni błonką ołowiu przyczyniła się do poprawy szybkości przenoszenia elektronów. Na **rysunku 4** przedstawiono otrzymane woltamperogramy cykliczne oraz zależności natężenia prądu pikowego od pierwiastka kwadratowego z szybkości skanowania.



Rys. 4. Woltamperogramy cykliczne uzyskane w roztworze zawierającym $5 \times 10^{-3} \text{ mol L}^{-1}$ $K_3[Fe(CN)_6]$ i $0,1 \text{ mol L}^{-1}$ KCl z zastosowaniem: A) niemodyfikowanej SPCE i B) SPCE modyfikowanej błonką ołowiu w zakresie szybkości skanowania od 5 do 400 mV s^{-1} (a-q); C) zależność natężenia prądu pikowego utleniania od pierwiastka kwadratowego z szybkości skanowania (w zakresie szybkości skanowania od 5 do 400 mV s^{-1}) oraz D) woltamperogramy cykliczne uzyskane na: a) niemodyfikowanej SPCE oraz b) PbF/SPCE dla szybkości skanowania 50 mV s^{-1} (**Publikacja 4**).

2.2. Woltamperometryczne procedury oznaczania wybranych jonów metali

Woltamperometryczne procedury oznaczania wybranych jonów metali (Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI)) zostały zoptymalizowane. Oznacza to, że przeprowadzono badania mające na celu dobór składu roztworu podstawowego, tj.: rodzaju elektrolitu, jego stężenia i pH oraz typu i stężenia czynnika kompleksującego (w przypadku zastosowania adsorpcyjnej woltamperometrii strippingowej, **Publikacja 3 i 4**). Ponadto, zoptymalizowano potencjał i czas zatężania analitu na powierzchni elektrody. Dobrano także technikę rejestracji sygnału analitycznego oraz jej parametry, takie jak amplituda, częstotliwość, szybkość skanowania. Zoptymalizowane parametry oznaczeń Cd(II) i Pb(II), Tl(I), U(VI) oraz Mo(VI) z zastosowaniem modyfikowanych błonką bizmutu lub ołowiu sitodrukowanych elektrod węglowych zestawiono w **tabeli 3**.

W zoptymalizowanych warunkach przeprowadzono pomiary dla wzrastających stężeń badanych jonów, wyznaczono liniowe zakresy krzywych kalibracyjnych, obliczono granice wykrywalności i oznaczalności (**Tabela 4**). Woltamperometryczne procedury oznaczania wybranych jonów metali opisane w pracach zawartych w niniejszej rozprawie doktorskiej charakteryzują się jednymi z najniższych (w przypadku Cd(II) i Pb(II)) lub najniższymi (w przypadku Tl(I), U(VI), Mo(VI)) granicami wykrywalności spośród dostępnych w literaturze prac, w których do oznaczeń tych jonów wykorzystywano elektrody sitodrukowane (**Tabela 1**). Dodatkową zaletą zaproponowanych elektrod jest prosty i szybki proces modyfikacji ich powierzchni.

Tabela 3. Zestawienie parametrów procedur oznaczania Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI) z wykorzystaniem sitodrukowanych elektrod węglowych modyfikowanych błonką bizmutu lub ołowiu (**Publikacje 1-4**).

Parametr	Oznaczany jon			
	Cd(II) Pb(II)	Tl(I)	U(VI)	Mo(VI)
Typ i stężenie elektrolitu podstawowego (mol L ⁻¹)	bufor octanowy (CH ₃ COOH + CH ₃ COONa, pH = 3,8); 0,05	0,0265 CH ₃ COONH ₄ + 0,0235 CH ₃ COOH + 0,0235 NH ₄ Cl (pH = 4,6)	0,092 CH ₃ COONH ₄ + 0,008 CH ₃ COOH + 0,008 NH ₄ Cl (pH = 5,9)	0,0385 CH ₃ COONH ₄ + 0,0615 CH ₃ COOH + 0,0615 NH ₄ Cl (pH = 4,2)
Jon modyfikatora; stężenie (mol L ⁻¹)	Bi(III); 2 × 10 ⁻⁵	Bi(III); 1 × 10 ⁻⁵	Pb(II); 2,5 × 10 ⁻⁵	Pb(II); 2 × 10 ⁻³
Dodatkowy składnik roztworu; stężenie (mol L ⁻¹)	Zn(II) ^a ; 2 × 10 ⁻⁵	EDTA ^b ; 1 × 10 ⁻⁵	kupferron ^c ; 1 × 10 ⁻⁴	czerwień alizarynowa S ^c ; 2 × 10 ⁻⁷
Potencjał (V) / czas elektrochemicznego oczyszczania elektrody (s)	-	0,5 / 10	0,2 / 10	0,5 / 30
Potencjał (V) / czas osadzania błonki metalu (s)	-1,65 / 180	-1,1 / 60	-1,1 / 60	-0,9 / 45
Potencjał (V) / czas zatężania analitu/nagromadzania kompleksów analitu (s)	-1,65 / 180 i -0,95 / 10	-1,1 / 60	-0,75 / 60	-0,6 / 60
Technika rejestracji sygnału	SWASV	SWASV	DPAdSV	DPAdSV
Zakres rejestracji sygnału analitycznego (V)	-1,0 do -0,25	-1,1 do 0,5	-0,65 do -1,75	-0,65 do -1,1
Amplituda (mV)	75	75	150	25
Częstotliwość (Hz)	40	40	-	-
Szybkość skanowania (mV s ⁻¹)	400	150	100	50
Publikacja	1	2	3	4

^a - jonu mediatora; ^b - sól dwusodowa kwasu etylenodiaminotetraoctowego, czynnik kompleksujący stosowany do minimalizacji interferencji; ^c - czynnik kompleksujący oznaczany jon metalu; **SWASV** - anodowa woltamperometria strippingowa fali prostokątnej; **DPAdSV** - impulsowo-różnicowa adsorpcyjna woltamperometria strippingowa

Tabela 4. Zestawienie parametrów analitycznych opracowanych procedur oznaczania Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI) na sitodrukowanych elektrodach węglowych modyfikowanych błonką bizmutu lub ołowiu (**Publikacje 1-4**).

Oznaczany jon	Stosowana elektroda	Granica wykrywalności (mol L ⁻¹)	Granica oznaczalności (mol L ⁻¹)	Zakres liniowy krzywej kalibracyjnej (mol L ⁻¹)	Współczynnik korelacji (r)	Czas zateżania (s)	Technika	Publikacja
Cd(II) ¹	BiF/SPCE	$2,85 \times 10^{-9}$	$9,50 \times 10^{-9}$	$1 \times 10^{-8} - 2 \times 10^{-6}$	0,9988	190	SWASV	1
Pb(II) ²	osadzana z	$5,95 \times 10^{-10}$	$1,98 \times 10^{-9}$	$2 \times 10^{-9} - 2 \times 10^{-7}$	0,9991			
Cd(II) ³	zastosowaniem	$1,35 \times 10^{-9}$	$4,50 \times 10^{-9}$	$5 \times 10^{-9} - 1 \times 10^{-6}$	0,9996			
Pb(II) ³	mediatora	$1,41 \times 10^{-10}$	$4,70 \times 10^{-10}$	$5 \times 10^{-10} - 5 \times 10^{-7}$	0,9987			
Cd(II) ⁴	BiF/SPCE	$2,95 \times 10^{-8}$	$9,83 \times 10^{-8}$	$1 \times 10^{-7} - 2 \times 10^{-5}$	0,9977	190	SWASV	1
Pb(II) ⁵	osadzana z	$1,32 \times 10^{-8}$	$4,39 \times 10^{-8}$	$5 \times 10^{-8} - 2 \times 10^{-6}$	0,9994			
Cd(II) ³	zastosowaniem	$5,84 \times 10^{-8}$	$1,95 \times 10^{-7}$	$2 \times 10^{-7} - 2 \times 10^{-5}$	0,9997			
Pb(II) ³	mediatora	$5,59 \times 10^{-9}$	$1,86 \times 10^{-8}$	$2 \times 10^{-8} - 1 \times 10^{-6}$	0,9981			
Tl(I)	BiF/SPCE	$8,47 \times 10^{-10}$	$2,9 \times 10^{-9}$	$5 \times 10^{-9} - 1 \times 10^{-6}$	0,9996	60	SWASV	2
		$6,71 \times 10^{-12}$	$2,2 \times 10^{-11}$	$5 \times 10^{-11} - 1 \times 10^{-9}$	0,9990	300		
U(VI)	PbF/SPCE	$1,90 \times 10^{-11}$	$6,3 \times 10^{-11}$	$1 \times 10^{-10} - 1 \times 10^{-8}$	0,9988	60	DPAdSV	3
Mo(VI)	PbF/SPCE	$2,12 \times 10^{-10}$	$7,1 \times 10^{-10}$	$1 \times 10^{-9} - 5 \times 10^{-8}$	0,9995	60	DPAdSV	4

¹ - w obecności stałego stężenia Pb(II) równego 5×10^{-8} mol L⁻¹; ² - w obecności stałego stężenia Cd(II) równego 2×10^{-7} mol L⁻¹; ³ - dla jednoczesnego wzrastającego stężenia Cd(II) i Pb(II); ⁴ - w obecności stałego stężenia Pb(II) równego 5×10^{-7} mol L⁻¹; ⁵ - w obecności stałego stężenia Cd(II) równego 2×10^{-6} mol L⁻¹; **BiF/SPCE** - sitodrukowana elektroda węglowa modyfikowana błonką bizmutu; **PbF/SPCE** - sitodrukowana elektroda węglowa modyfikowana błonką ołowiu; **SWASV** - anodowa woltamperometria strippingowa fali prostokątnej; **DPAdSV** - impulsowo-różnicowa adsorpcyjna woltamperometria strippingowa

Dla każdej z opracowanych procedur oznaczania Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI) na sitodrukowanych elektrodach węglowych modyfikowanych błonką bizmutu lub ołowiu zbadana została powtarzalność sygnału analitycznego. Wartości względnych odchyłeń standardowych (RSD, $n = 10$) dla wybranych stężeń oznaczanych jonów metali przedstawiono w **tabeli 5**.

Tabela. 5. Zestawienie wartości RSD otrzymanych dla wybranych stężeń oznaczanych jonów na sitodrukowanych elektrodach węglowych modyfikowanych błonką bizmutu lub ołowiu.

Jon metalu	Typ elektrody	Stężenie (mol L ⁻¹)	RSD (n = 10) (%)	Publikacja
Cd(II)	BiF/SPCE*	5×10^{-8}	2,35	1
Pb(II)		2×10^{-8}	3,18	
Tl(I)	BiF/SPCE	5×10^{-8}	2,14	2
		2×10^{-7}	1,23	
U(VI)	PbF/SPCE	5×10^{-8}	3,90	3
Mo(VI)	PbF/SPCE	1×10^{-8}	2,93	4
		5×10^{-8}	3,19	

RSD - względne odchylenie standardowe; **BiF/SPCE** - sitodrukowana elektroda węglowa modyfikowana błonką bizmutu; * - elektroda przygotowywana z zastosowaniem odtwarzalnie osadzanego mediatora; **PbF/SPCE** - sitodrukowana elektroda węglowa modyfikowana błonką ołowiu

Wartości RSD w zakresie od 1,23 do 3,90% potwierdzają, że zastosowanie sitodrukowanych elektrod węglowych modyfikowanych błonką bizmutu lub ołowiu w oznaczeniach Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI) pozwala na otrzymywanie powtarzalnych sygnałów analitycznych.

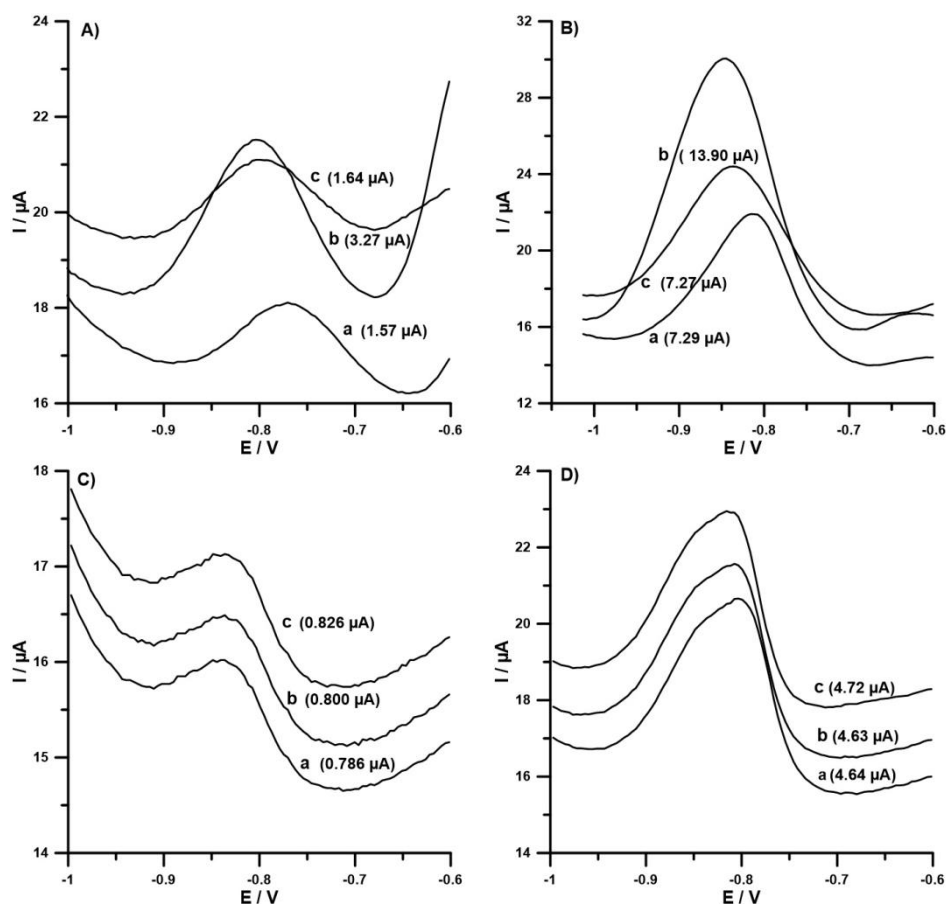
Kolejnym wyznaczonym parametrem była odtwarzalność elektrody do elektrody. Jej wyznaczenie polegało na zarejestrowaniu pomiarów na trzech różnych elektrodach przygotowywanych według tej samej procedury. Wartości RSD ($n = 9$) uzyskane na elektrodzie BiF/SPCE (**Publikacja 2**) i PbF/SPCE (**Publikacja 3**) (dla stężenia odpowiednio 1×10^{-7} mol L⁻¹ Tl(I) i 5×10^{-8} mol L⁻¹ U(VI)) wynosiły 2,5 i 5,4%. Niskie wartości RSD świadczą o dobrej odtwarzalności przygotowywanych elektrod.

Zbadano również odtwarzalność sygnału w funkcji czasu dla elektrody PbF/SPCE (**Publikacja 3**) poprzez rejestrację 10 woltamperogramów dla stężenia 5×10^{-8} mol L⁻¹ U(VI) w pięciu kolejnych dniach. Na podstawie otrzymanych wyników obliczono wartość RSD. Niska wartość względnego odchylenia standardowego (4,5%) świadczy o braku

zmienności właściwości elektrody, skutecznym sposobie elektrochemicznego oczyszczania elektrody i braku występowania efektu pamięci [56].

2.3. Interferencje oraz sposoby ich minimalizacji

W trakcie prowadzonych badań sprawdzono selektywność opracowanych procedur oraz zaproponowano sposoby minimalizacji występujących interferencji. Podczas badania wpływu jonów metali, które mogą występować w próbkach wód środowiskowych na sygnał analityczny oznaczanych jonów Cd(II), Pb(II), U(VI) i Mo(VI) nie stwierdzono negatywnego ich wpływu (sygnał analityczny po dodaniu interferenta nie zmienił się o więcej niż $\pm 5-10\%$ w porównaniu do oryginalnej wartości, **Publikacja 1, 3 i 4**). W przypadku Tl(I) istotnym źródłem interferencji okazała się obecność w analizowanym roztworze jonów Cd(II) i Pb(II). Zaobserwowano nakładanie się sygnałów Tl(I) i Cd(II) oraz znaczący spadek sygnału Tl(I) w obecności jonów Pb(II). W prowadzonych badaniach do minimalizacji interferencji zastosowano dodatek roztworu EDTA (sól dwusodowa kwasu etylenodiaminotetraoctowego) [57-61]. EDTA tworzy trwałe kompleksy z jonami Cd(II) i Pb(II), dzięki czemu negatywny wpływ tych jonów na sygnał Tl(I) został zminimalizowany (**Rys. 5**) (**Publikacja 2**).



Rys. 5. Woltamperogramy zarejestrowane w roztworze buforowym ($0,0265 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4 + 0,0235 \text{ mol L}^{-1} \text{ CH}_3\text{COOH} + 0,0235 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$) o $\text{pH} = 4,6 \pm 0,1$ zawierającym $2 \times 10^{-6} \text{ mol L}^{-1} \text{ Bi(III)}$ i: A) a) $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Tl(I)}$; b) jak (a) + $1 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ i c) jak (b) + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; B) a) $2 \times 10^{-7} \text{ mol L}^{-1} \text{ Tl(I)}$; b) jak (a) + $4 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ i c) jak (b) + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; C) a) $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Tl(I)}$ + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; b) jak (a) + $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Pb(II)}$ i c) jak (a) + $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb(II)}$; D) a) $2 \times 10^{-7} \text{ mol L}^{-1} \text{ Tl(I)}$ + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; b) jak (a) + $2 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb(II)}$ i c) jak (a) + $2 \times 10^{-6} \text{ mol L}^{-1} \text{ Pb(II)}$ (**Publikacja 2**).

W przypadku każdej z opracowywanych procedur, badano wpływ substancji powierzchniowo czynnych: niejonowego Tritonu X-100, anionowego siarczanu dodecyłu sodu (SDS) i kationowego bromku cetylotrimetyloamoniowego (CTAB) na sygnał analityczny oznaczanego jonu metalu. Wpływ obecności substancji powierzchniowo czynnych na sygnał Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI) przedstawiono w **tabeli 6**.

Tabela 6. Wpływ substancji powierzchniowo czynnych na sygnał oznaczanych jonów Cd(II), Pb(II), Tl(I), U(VI) oraz Mo(VI) (**Publikacje 1-4**).

Oznaczany jon / stężenie (mol L ⁻¹)	Stężenie (mg L ⁻¹)	Sygnał względny (%)		
		Triton X-100	CTAB	SDS
Cd(II) / 5×10^{-7}	0,2	87,1	80,7	56,6
	0,5	57,1	54,8	35,8
	1	35,4	32,4	36,5
	2	23,0	21,3	33,0
	5	13,1	17,4	20,1
Pb(II) / 5×10^{-8}	0,2	105,8	92,0	96,6
	0,5	84,0	87,6	86,0
	1	73,2	83,9	84,3
	2	57,7	67,2	76,4
	5	47,5	57,9	79,2
Tl(I) / 1×10^{-7}	0,2	105,7	102,1	101,6
	0,5	103,4	73,3	98,9
	1	101,4	36,5	96,2
	2	105,7	20,3	92,2
	5	106,7	12,7	82,2
	10	56,2	0	70,5
	20	31,1	0	56,5
	50	8,4	0	50,2
U(VI) / 5×10^{-8}	0,25	34,4	18,0	84,2
	0,5	14,6	0,08	80,3
	1	0	0	71,6
	2	0	0	61,6
	5	0	0	31,6
	10	0	0	18,8
	20	0	0	0
	50	0	0	0
Mo(VI) / 5×10^{-8}	0,2	101,4	102,0	102,3
	0,5	101,4	80,3	102,7
	1	75,7	57,9	101,0
	2	58,6	38,9	97,8
	5	41,3	20,8	96,7
	10	26,1	11,6	89,6
	20	0	0	54,9
	50	0	0	0

Sygnał względny (%) - stosunek wysokości piku analitu po dodatku substancji powierzchniowo czynnej do wysokości początkowej sygnału wyrażony w procentach

Ze względu na to, że opracowane procedury mają mieć zastosowanie w analizie polowej, do minimalizacji negatywnego wpływu spowodowanego obecnością substancji powierzchniowo czynnych w przypadku oznaczeń Tl(I), U(VI) i Mo(VI) w próbkach wód środowiskowych zastosowano żywice adsorpcyjne (Amberlite XAD-7, Amberlite XAD-16) [62-66]. W trakcie prowadzonych badań zoptymalizowano procedurę minimalizacji interferencji poprzez dobór masy i czasu wytrząsania żywicy z próbką (**Tabela 7**). Zoptymalizowane procedury minimalizacji występujących interferencji są proste w wykonaniu, niewymagające długiego nakładu czasu, a także są możliwe do zastosowania w warunkach laboratoryjnych oraz w terenie.

Tabela 7. Zoptymalizowane warunki procedury minimalizacji interferencji pochodzących od substancji powierzchniowo czynnych oraz dopuszczalne stężenie substancji powierzchniowo czynnej (nie powodujące zmiany wielkości sygnału oznaczanego jonu metalu o więcej niż $\pm 10\%$) (**Publikacje 2-4**).

Oznaczany jon	Typ żywicy	Masa żywicy (g)	Czas wytrząsania żywicy z próbką (s)	Dopuszczalne stężenie substancji powierzchniowo czynnej (mg L^{-1})	Publikacja
Tl(I)	Amberlite XAD-7	0,5	30*	2 ^{a, b, c}	2
U(VI)	Amberlite XAD-16	0,5	30**	20 ^{a, b} 3 ^c	3
Mo(VI)	Amberlite XAD-16	0,025	30**	2 ^{a, b, c}	4

* - żywica dodawana bezpośrednio do naczynka woltamperometrycznego; ** - żywica dodawana do osobnego naczynka; ^a - Triton X-100; ^b - CTAB; ^c - SDS

2.4. Zastosowanie opracowanych procedur do analizy próbek wód

W celu sprawdzenia opracowanych woltamperometrycznych procedur przeprowadzono analizę ilościową Cd(II), Pb(II), Tl(I) i Mo(VI) w certyfikowanych materiałach odniesienia (TMRAIN-04 (woda deszczowa), SRM 1640a (woda naturalna) oraz SPS SW2 (woda powierzchniowa)). Oznaczenia prowadzono metodą dodatku wzorca, a otrzymane wyniki zestawiono w **tabeli 8**. Próbkę przed pomiarem zostały przygotowane zgodnie z procedurą opisaną w podrozdziale 2.3 (**Publikacja 2-4**) lub zostały poddane bezpośredniej analizie, bez etapu przygotowywania (**Publikacja 1**).

Tabela 8. Zestawienie wyników otrzymanych podczas oznaczania Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI) w certyfikowanych materiałach odniesienia (**Publikacje 1-4**).

Certyfikowany materiał odniesienia	Oznaczany jon	Stężenie oznaczone $\pm$ SD (n = 3)	Stężenie certyfikowane $\pm$ SD (n = 3)	Błąd względny (%)	Δm / U_A	Publikacja
TMRAIN-04	Cd(II)	$0,57 \pm 0,033^a$	$0,52 \pm 0,030^a$	9,6	0,041/ 0,048	1
	Pb(II)	$0,39 \pm 0,041^a$	$0,35 \pm 0,035^a$	11,4	0,045/ 0,059	1
	Tl(I)	$1,91 \pm 0,095^b$	$1,84 \pm 0,29^b$	3,7	-	2
SRM 1640a	Tl(I)	$7,86 \pm 0,27^b$	$7,86 \pm 0,073^b$	0	-	2
	U(VI)	$0,11 \pm 0,0066^c$	$0,11 \pm 0,0011^c$	0	-	3
	Mo(VI)	$0,45 \pm 0,014^c$	$0,47 \pm 0,006^c$	4,3	-	4
SPS SW-2	Tl(I)	$0,128 \pm 0,013^b$	$0,122 \pm 0,00098^b$	4,9	-	2
	Mo(VI)	$0,54 \pm 0,025^c$	$0,52 \pm 0,003^c$	3,8	-	4

SD - odchylenie standardowe; ^a - stężenie wyrażone w $\mu\text{g L}^{-1}$; ^b - stężenie wyrażone w nmol L^{-1} ; ^c - stężenie wyrażone w $\mu\text{mol L}^{-1}$; Δm - bezwzględna różnica między średnią wartością zmierzoną a wartością certyfikowaną; U_A - łączona niepewność wyniku i wartości certyfikowanej; **błąd względny** - $(\text{stężenie oznaczone} - \text{stężenie certyfikowane}) / \text{stężenie certyfikowane} \times 100\%$

Na podstawie otrzymanych wyników stwierdzono, że opracowane woltamperometryczne procedury oznaczania Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI) z wykorzystaniem sitodrukowanych elektrod węglowych modyfikowanych błonką bizmutu lub ołowiu mogą być stosowane w analizie próbek wód.

W przypadku metody jednoczesnego oznaczania Cd(II) i Pb(II) wykonano również pomiary dla próbek wód z rzeki Krzny oraz Morza Bałtyckiego. Oznaczenia wykonano jednocześnie dla próbek wód niezmineralizowanych (brak etapu przygotowania próbki) oraz dla porównania dla próbek zmineralizowanych (mineralizacja UV przez 3 godziny) (**Publikacja 1**), natomiast procedurę oznaczania U(VI) zastosowano do analizy próbek pobranych z rzeki Bystrzycy (**Publikacja 4**). Otrzymane wyniki zestawiono w **tabeli 9**. Wartości odzysków bliskie 100% potwierdzają niewielki wpływ matrycy analizowanych próbek wód na sygnał analityczny oznaczanych jonów metali.

Tabela 9. Wyniki otrzymane podczas oznaczania Cd(II) i Pb(II) z wykorzystaniem BiF/SPCE oraz U(VI) z użyciem PbF/SPCE w próbkach wód środowiskowych.

Próbka	Oznaczany jon	Stężenie dodane (nmol L ⁻¹)	Stężenie oznaczone (nmol L ⁻¹)	Odzysk (%)	RSD (n = 5) (%)
Rzeka Krzna	Cd(II)	20	19,04	95,2	3,5
		80	81,28	101,6	3,3
	Pb(II)	2	2,10	105,0	2,9
		8	7,65	95,6	4,2
	Cd(II)*	20	20,67	103,4	4,8
		80	76,40	95,5	5,1
	Pb(II)*	2	1,90	95,0	3,5
		8	7,66	95,8	4,3
Morze Bałtyckie	Cd(II)	20	19,90	99,5	4,5
		80	78,16	97,7	4,8
	Pb(II)	2	2,11	105,5	5,0
		8	8,34	104,3	3,3
	Cd(II)*	20	20,98	104,9	5,3
		80	82,32	102,9	3,7
	Pb(II)*	2	2,08	104,0	4,5
		8	8,38	104,8	4,3
Rzeka Bystrzyca	U(VI)	5	5,02	100,4	4,4
		20	19,7	98,5	1,8

* - próbkę poddano procesowi mineralizacji przed oznaczeniem

3. Podsumowanie

W niniejszej rozprawie doktorskiej zaproponowano zastosowanie sitodrukowanych elektrod węglowych modyfikowanych błonką bizmutu lub ołowiu bez i z wykorzystaniem odtwarzalnie osadzanego mediatora do analizy śladowej jonów Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI). Otrzymane elektrody stanowią alternatywę dla elektrod rtęciowych i innych elektrod opisanych w literaturze.

Modyfikacja powierzchni elektrody SPCE błonką bizmutu lub ołowiu pozwoliła na znaczące wzmocnienie sygnałów analitycznych oznaczanych jonów Cd(II), Pb(II), Tl(I) i U(VI) (**Publikacje 1-3**). Efekt ten spowodowany był zmianą struktury, morfologii i składu chemicznego powierzchni, co potwierdziły wykonane badania z wykorzystaniem nowoczesnych technik instrumentalnych: SEM, TEM-EDX, mikroskopii i profilometrii optycznej, AFM i XPS. Innym efektem, który przyczynił się do wzmocnienia sygnału analitycznego Mo(VI) na SPCE modyfikowanej błonką ołowiu była poprawa szybkości przenoszenia elektronów (**Publikacja 4**).

Dodatkowe wzmocnienie sygnałów analitycznych Cd(II) i Pb(II) uzyskano poprzez zastosowanie odtwarzalnie osadzanego mediatora (Zn) w etapie osadzania błonki bizmutu na powierzchni elektrody pracującej (**Publikacja 1**). Zastosowanie mediatora przyczyniło się do zmiany mikroskopowej struktury osadzonej błonki, co z kolei skutkowało zwiększeniem powierzchni aktywnej elektrody.

Woltamperometryczne procedury oznaczania wybranych jonów metali opisane w pracach zawartych w niniejszej rozprawie doktorskiej charakteryzują się jednymi z najniższych (w przypadku Cd(II) i Pb(II)) lub najniższymi (w przypadku Tl(I), U(VI), Mo(VI)) granicami wykrywalności spośród dostępnych w literaturze prac, w których do oznaczeń tych jonów wykorzystywano elektrody sitodrukowane. Dodatkową zaletą zaproponowanych elektrod jest prosty i szybki proces modyfikacji ich powierzchni.

Opracowane metody oznaczeń z wykorzystaniem modyfikowanych błonką bizmutu lub ołowiu sitodrukowanych elektrod węglowych mogą być z powodzeniem stosowane do analizy próbek wód naturalnych. Cel ten osiągnięto między innymi dzięki optymalizacji procedur minimalizacji interferencji pochodzących od matrycy próbek wód środowiskowych (wpływ obcych jonów metali oraz substancji powierzchniowo czynnych został wnikliwie zbadany, a w przypadku występowania negatywnego wpływu podjęto kroki w celu jego minimalizacji). Zaproponowane procedury minimalizacji występujących

interferencji są proste w wykonaniu, niewymagające długiego nakładu czasu, a także są możliwe do zastosowania w warunkach laboratoryjnych oraz w terenie.

Opracowane procedury oznaczania jonów Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI) oraz minimalizacji interferencji zostały sprawdzone poprzez analizę certyfikowanych materiałów odniesienia. Stężenia oznaczonych jonów metali zgodne z wartościami certyfikowanymi świadczą o tym, że opracowane procedury mogą być z powodzeniem stosowane do ilościowej analizy próbek wód naturalnych. Warto zauważyć, że zaproponowane elektrody mogą być w przyszłości zastosowane w analizie polowej, co dodatkowo eliminuje problem transportu, przechowywania próbki oraz zmiany jej parametrów w czasie.

Badania realizowane w ramach niniejszej pracy doktorskiej pozwoliły na poszerzenie wiedzy dotyczącej przygotowania, charakterystyki i zastosowania modyfikowanych błonką metalu elektrod sitodrukowanych. Przeprowadzone eksperymenty pozwoliły na otrzymanie woltamperometrycznych procedur oznaczania śladowych stężeń jonów Cd(II) i Pb(II), Tl(I), U(VI) i Mo(VI) w próbkach wód środowiskowych w warunkach laboratoryjnych, jak również w terenie.

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5. Streszczenie w języku polskim

Niniejsza rozprawa doktorska obejmuje prace dotyczące przygotowania, charakterystyki i zastosowania sitodrukowanych elektrod węglowych modyfikowanych błonką bizmutu lub ołowiu bez i z wykorzystaniem mediatora w oznaczeniach śladowych stężeń jonów metali (Cd(II) , Pb(II) , Tl(I) , U(VI) i Mo(VI)) w próbkach wód środowiskowych.

Badania realizowane w ramach niniejszej pracy obejmowały optymalizację procedury modyfikacji powierzchni sitodrukowanych elektrod węglowych błonką bizmutu lub ołowiu, tj. dobór rodzaju i stężenia jonów modyfikatora, potencjału oraz czasu osadzania błonki, stężenia oraz potencjału i czasu usuwania mediatora z powierzchni elektrody. Modyfikacja powierzchni sitodrukowanych elektrod węglowych błonką ołowiu i bizmutu przyczyniła się do znaczącego wzmocnienia sygnałów analitycznych oznaczanych jonów Cd(II) , Pb(II) , Tl(I) , U(VI) i Mo(VI) . Dodatkowe wzmocnienie sygnałów Cd(II) i Pb(II) uzyskano dzięki zastosowaniu odtwarzalnie osadzanego mediatora w etapie osadzania błonki bizmutu.

Morfologia powierzchni elektrod niemodyfikowanych oraz modyfikowanych błonką metalu została zbadana z wykorzystaniem: mikroskopii i profilometrii optycznej, mikroskopii sił atomowych, elektronowej mikroskopii skaningowej i transmisyjnej. Skład chemiczny powierzchni elektrod niemodyfikowanych i modyfikowanych zbadano z wykorzystaniem rentgenowskiej spektroskopii fotoelektronów i spektroskopii dyspersji energii promieniowania rentgenowskiego. Otrzymane wyniki potwierdziły między innymi istotne różnice w strukturze, morfologii i składzie powierzchni elektrod niemodyfikowanych i modyfikowanych błonką metalu oraz zależność mikroskopowej struktury powierzchni od parametrów procedury osadzania błonki metalu. W celu dodatkowej charakterystyki powierzchni elektrody pracującej w pracy dotyczącej oznaczania Mo(VI) obliczono i porównano wielkość powierzchni aktywnej elektrody niemodyfikowanej względem modyfikowanej błonką ołowiu oraz szybkość przenoszenia elektronów. Na podstawie przeprowadzonych obliczeń stwierdzono, że modyfikacja powierzchni elektrody jedynie w nieznacznym stopniu zwiększyła powierzchnię aktywną elektrody, ale przyczyniła się do poprawy szybkości przenoszenia elektronów.

W trakcie realizacji badań do niniejszej rozprawy doktorskiej wykonano również optymalizację woltamperometrycznych procedur oznaczeń jonów Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI), tj. rodzaju elektrolitu, jego stężenia i pH oraz typu i stężenia czynnika kompleksującego (w przypadku zastosowania adsorpcyjnej woltamperometrii strippingowej). Ponadto, zoptymalizowano potencjał i czas zatężania analitu na powierzchni elektrody. Dobrano także technikę rejestracji sygnału analitycznego oraz jej parametry, takie jak amplituda, częstotliwość, szybkość skanowania.

Woltamperometryczne procedury oznaczania wybranych jonów metali opisane w pracach zawartych w niniejszej rozprawie doktorskiej charakteryzują się jednymi z najniższych (w przypadku Cd(II) i Pb(II)) lub najniższymi (w przypadku Tl(I), U(VI), Mo(VI)) granicami wykrywalności spośród dostępnych w literaturze prac, w których do oznaczeń tych jonów wykorzystywano elektrody sitodrukowane. Dodatkową zaletą zaproponowanych elektrod jest prosty i szybki proces modyfikacji ich powierzchni.

W ramach badań objętych niniejszą rozprawą doktorską przeprowadzono również eksperymenty mające na celu sprawdzenie wpływu matrycy próbek wód środowiskowych (jonów metali i substancji powierzchniowo czynnych) na sygnał oznaczanych jonów. W przypadku występowania interferencji zaproponowano i zoptymalizowano procedury ich minimalizacji. Etap ten umożliwił zastosowanie opracowanych procedur do analizy wybranych jonów metali w próbkach wód bez konieczności ich mineralizacji. Negatywny wpływ jonów Cd(II) i Pb(II) na sygnał Tl(I) został zminimalizowany poprzez zastosowanie roztworu soli dwusodowej kwasu etylenodiaminotetraoctowego (EDTA) jako czynnika kompleksującego przeszkadzające jony. Natomiast efekt tłumienia sygnału analitycznego Tl(I), U(VI) oraz Mo(VI) przez substancje powierzchniowo czynne został zminimalizowany dzięki zastosowaniu żywicy adsorpcyjnej (Amberlite XAD-7 lub Amberlite XAD-16). Sposób ten jest korzystniejszy od stosowanej w warunkach laboratoryjnych mineralizacji próbki ze względu na krótszy czas usuwania matrycy organicznej z próbek wód oraz możliwość wykonania tego etapu w warunkach polowych. Stężenie EDTA, masa żywicy i czas jej wytrząsania z próbką zostały odpowiednio dobrane na podstawie przeprowadzonych badań eksperymentalnych.

Potwierdzenie możliwości zastosowania zaproponowanych elektrod sitodrukowanych w oznaczeniach śladowych stężeń jonów Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI) osiągnięto wykonując analizę certyfikowanych materiałów odniesienia: TMRAIN-04 (woda deszczowa), SRM 1640a (woda naturalna) oraz SPS SW2 (woda powierzchniowa). W przypadku metody jednoczesnego oznaczania Cd(II) i Pb(II)

wykonano również pomiary dla próbek wód z rzeki Krzny oraz Morza Bałtyckiego, natomiast procedurę oznaczania U(VI) zastosowano do analizy próbek pobranych z rzeki Bystrzycy. Wartości odzysków bliskie 100% potwierdzają niewielki wpływ matrycy analizowanych próbek wód na sygnał analityczny oznaczanych jonów metali.

Na podstawie otrzymanych wyników stwierdzono, że opracowane woltamperometryczne procedury oznaczania Cd(II), Pb(II), Tl(I), U(VI) i Mo(VI) z wykorzystaniem sitodrukowanych elektrod węglowych modyfikowanych błonką bizmutu lub ołowiu mogą być stosowane w analizie próbek wód środowiskowych. Opracowane procedury z zastosowaniem sitodrukowanych elektrod węglowych modyfikowanych błonką bizmutu lub ołowiu mogą być stosowane nie tylko w warunkach laboratoryjnych, ale także w przenośnych analizatorach elektrochemicznych, umożliwiającym prowadzenie pomiarów w terenie.

4. Streszczenie w języku angielskim

The following doctoral dissertation is devoted to the preparation, characterization and application of screen-printed carbon electrodes modified with bismuth or lead film prepared with or without the use of mediator in trace analysis of metal ions (Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI)) in environmental water samples.

The research carried out within this study included optimization of the procedure of surface modification of screen-printed carbon electrodes with bismuth or lead film, i.e. selection of the type and concentration of modifier ions, potential and time of film plating, concentration of the mediator, potential and the time of its removal from the electrode surface. Modification of screen-printed carbon electrodes surfaces with bismuth or lead film contributed to significant enhancement of analytical signals of the determined ions Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI). Additional amplification of Cd(II) and Pb(II) signals was obtained by using a reversibly deposited mediator at the stage of bismuth film plating. The morphology of unmodified electrodes surface and electrodes modified with the metal film was examined with the use of optical microscopy and profilometry, atomic force microscopy, scanning and transmission electron microscopy. The surface composition of unmodified and modified electrodes was studied using X-ray photoelectron spectroscopy and X-ray energy-dispersive spectroscopy. The obtained results confirmed, among others, significant differences in the structure, morphology and surface composition of unmodified and modified electrodes, and the dependence of microscopic surface structure on the parameters of the metal film plating procedure. In order to obtain additional characteristics of working electrode surface in the research on Mo(VI) determination, the size of the unmodified electrode's active surface in relation to that of the electrode modified with lead film, and the rate of electron kinetics were calculated and compared. On the basis of the conducted calculations, it was found that the modification of the electrode surface only slightly increased the active surface area but contributed to the increase the speed of electron transfer kinetics.

In the course of the research for this dissertation, optimization of voltammetric procedures for determination of Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI) ions, i.e. the type of electrolyte, its concentration and pH, as well as the type and concentration of the complexing agent (in case of adsorptive stripping voltammetry) was performed. In addition, the potential and time of the analyte deposition on the electrode surface were optimized.

The technique of voltammograms registration and its parameters, such as amplitude, frequency, scan rate, were also selected.

Voltammetric procedures for determination of selected metal ions described in this dissertation are characterized by one of the lowest (in the case of Cd(II) and Pb(II)) or the lowest (in the case of Tl(I), U(VI), Mo(VI)) detection limits among the works available in the literature in which screen-printed electrodes were used for the determination of these ions. The additional advantage of these electrodes is a simple and fast surface modification process.

Within the framework of the research covered by this PhD dissertation, experiments were also conducted to examine the influence of the matrix of environmental waters samples (metal ions and surface active substances) on the signal of the determined ions. In the case of the occurrence of interferences, procedures for their minimization have been proposed and optimised. This stage enabled the application of the developed procedures for the analysis of selected metal ions in water samples without the need of their mineralization. Negative effects of Cd(II) and Pb(II) ions on the Tl(I) signal were minimized by using a solution of ethylenediaminetetraacetic acid disodium salt (EDTA) as an agent complexing the disturbing ions. The effect of suppression of the analytical signal Tl(I), U(VI) and Mo(VI) by surface active substances was minimized by the use of adsorptive resin (Amberlite XAD-7 or Amberlite XAD-16). This method is more advantageous than laboratory mineralization of the sample due to the shorter time of removing the organic matrix from water samples and the possibility to perform this stage in field conditions. The EDTA concentration, the mass of the resin and the time of shaking with the sample were properly selected based on the experimental tests carried out.

Confirmation of the applicability of the proposed screen-printed electrodes in the determination of Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI) ions concentrations was achieved by analysis of certified reference materials: TMRain-04 (rainwater), SRM 1640a (natural water) and SPS SW2 (surface water). In the case of simultaneous Cd(II) and Pb(II) determination method, measurements were also performed for samples of the waters from the Krzna River and the Baltic Sea, while the U(VI) procedure was used for the analysis of samples collected from the Bystrzyca River. The recovery values close to 100% confirm the small influence of analyzed water samples matrix on the analytical signal of the determined metal ions.

On the basis of the obtained results it was found that the developed voltammetric procedures for the determination of Cd(II), Pb(II), Tl(I), U(VI) and Mo(VI) using screen-

printed carbon electrodes modified with bismuth or lead film can be used in the analysis of environmental waters samples. The procedures developed with the use of screen-printed carbon electrodes modified with bismuth or lead film can be used not only in laboratory conditions but also in portable electrochemical analyzers, enabling the field analysis.

5. Omówienie pozostałych osiągnięć naukowych

Spis publikacji nie wchodzących w skład rozprawy doktorskiej

1. K. Tyszczyk-Rotko, **K. Domańska**, I. Sadok, M. Wójciak-Kosior, I. Sowa, *Voltammetric procedure for the determination of oleanolic and ursolic acids in plant extracts*, Analytical Methods 7 (2015) 9435-9441.

(IF₂₀₁₅ = 1,915; MNiSW = 25)

2. K. Tyszczyk-Rotko, **K. Domańska**, K. Vytřas, R. Metelka, A. Nosal-Wiercińska, M. Sýs, *Application of screen-printed carbon electrode modified with lead in stripping analysis of Cd(II)*, Open Chemistry 15 (2017) 28-33.

(IF₂₀₁₇ = 1,425; MNiSW = 14)

3. K. Tyszczyk-Rotko, **K. Domańska**, B. Czech, M. Rotko, *Development simple and sensitive voltammetric procedure for ultra-trace determination of U(VI)*, Talanta 165 (2017) 474-481.

(IF₂₀₁₇ = 4,244; MNiSW = 40)

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Łączny IF prac nie wchodzących w skład rozprawy doktorskiej: 15,706

Łączna liczba punktów MNiSW prac nie wchodzących w skład rozprawy doktorskiej: 154

Łączny IF wszystkich prac: 30,962

Łączna liczba punktów MNiSW: 314

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domieszkowanej borem modyfikowanej błonką Nafionu i bizmutu, IX edycja Konferencji Młodych Naukowców „Wpływ Młodych Naukowców na Osiągnięcia Polskiej Nauki”, Kraków, 05.12.2015 r. (poster)

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Wyróżnienia

1. Współautor wyróżnionego posteru pt. „*Analiza płynów fizjologicznych i preparatów farmaceutycznych z wykorzystaniem elektrod modyfikowanych polimerem i metalem*” zaprezentowanego przez Ilonę Sadok podczas VI edycji Ogólnopolskiej Konferencji Studenckiej Nowoczesne Metody Doświadczalne w Fizyce, Chemii i Inżynierii, która odbyła się w dniach 27-29.11.2015 r. w Lublinie.
2. Wyróżnienie za komunikat ustny pt. „*Chrom(VI) – występowanie, właściwości i zastosowanie, oraz woltamperometryczne procedury oznaczania Cr(VI) z wykorzystaniem elektrod węglowych modyfikowanych bizmutem*” wygłoszony podczas Konferencji Młodych Naukowców NOWE WYZWANIA DLA POLSKIEJ NAUKI „Spojrzenie Młodych Naukowców”, która odbyła się 17.04.2016 r. w Poznaniu.

3. Współautor wyróżnionego posteru pt. *„Poprawa czułości i selektywności oznaczeń związków biologicznie aktywnych na elektrodach modyfikowanych błonką metalu i polimeru”*, zaprezentowanego przez Ilonę Sadok podczas Konferencji Młodych Naukowców NOWE WYZWANIA DLA POLSKIEJ NAUKI „Spojrzenie Młodych Naukowców”, która odbyła się 17.04.2016 r. w Poznaniu.
4. Nagroda za zajęcie III miejsca w konkursie na najlepszą prezentację ustną I sesji pt. *„Woltamperometria – skuteczna metoda oznaczania śladowych stężeń kwasu oleanolowego i ursolowego”* wygłoszoną podczas VII Lubelskiego Symposium Doktorantów Nauk Farmaceutycznych wraz z Otwartym Seminarium Nauk o Życiu, które odbyło się 19.04.2016 r. w Lublinie.
5. Współautor wyróżnionego komunikatu ustnego pt. *„Nowe woltamperometryczne procedury oznaczania Hg(II) na elektrodach modyfikowanych funkcjonalizowanym polisiloksanem i metalem”* wygłoszonego przez Ilonę Sadok podczas Konferencji Młodych Naukowców „Nauki Biologiczne i Chemiczne. Spojrzenia Młodych Naukowców”, która odbyła się 22.10.2016 r. w Krakowie.
6. Wyróżnienie za zaprezentowany poster pt. *„Wpływ mediatora (Zn) na sygnał analityczny Cd i Pb otrzymany na sitodrukowanej elektrodzie węglowej modyfikowanej bizmutem”* podczas Konferencji Młodych Naukowców nt. „Zagrożenia dla Środowiska. Spojrzenie Młodych Naukowców”, która odbyła się 23.10.2016 r. w Krakowie.
7. Wyróżnienie za komunikat ustny pt. *„Zagrożenia wynikające z obecności Cd i Pb w środowisku oraz woltamperometryczna procedura ich oznaczania na sitodrukowanej elektrodzie węglowej modyfikowanej błonką bizmutu”* podczas IV Ogólnokrajowej Konferencji „Młodzi Naukowcy w Polsce – Badania i Rozwój” (Lublin 25.11.2016 r.).
8. Nagroda na zajęcie II miejsca na najlepszą prezentację ustną pt. *„The application of modified integrated screen-printed sensor for the voltammetric determination of U(VI)”* zaprezentowaną podczas XII edycji konferencji „Copernican International Young Scientists Conference”, która odbyła się w dniach 28-29.06.2018 r. w Toruniu.

9. Nagroda za zajęcie III miejsca w konkursie posterów za plakat pt. *„Analiza śladowa jonów Mo(VI) w próbkach wód z zastosowaniem miniaturowego czujnika PbF/SPCE”* zaprezentowany podczas II Ogólnopolskiego Symposium Młodych Naukowców „ProDoc”, które odbyło się 12.06.2019 r. w Lublinie.
10. Nagroda za zajęcie II miejsca w konkursie na najlepszy poster za plakat pt. *„Nowe zastosowanie PbF/SPCE w voltamperometrycznych oznaczeniach molibdenu(VI)”* zaprezentowany podczas VI Forum Młodych Przyrodników, które odbyło się 25.05.2019 r. w Lublinie.
11. Współautor nagrodzonego I miejscem w konkursie na najlepszy poster plakatu pt. *„Oznaczanie cytrynianu sildenafilu na miniaturowej zespolonej elektrodzie węglowej”* zaprezentowanego przez Agnieszkę Sasal podczas VI Forum Młodych Przyrodników, które odbyło się 25.05.2019 r. w Lublinie.

Projekty badawcze

1. Kierownik zadania badawczego pt. *„Sitodrukowane elektrody węglowe modyfikowane metalem: przygotowanie, charakterystyka i nowe zastosowania”* finansowanego z konkursu wydziałowego dotyczącego podziału dotacji celowej na prowadzenie badań naukowych lub prac rozwojowych oraz zadań z nimi związanych, służących rozwojowi młodych naukowców oraz uczestników studiów doktoranckich na Wydziale Chemii UMCS, 2017 rok.
2. Kierownik zadania badawczego pt. *„Nowe, miniaturowe czujniki voltamperometryczne do monitoringu jonów metali ciężkich w próbkach wód”* finansowanego z konkursu wydziałowego dotyczącego podziału dotacji celowej na prowadzenie badań naukowych lub prac rozwojowych oraz zadań z nimi związanych, służących rozwojowi młodych naukowców oraz uczestników studiów doktoranckich na Wydziale Chemii UMCS, 2018 rok.

Stypendia naukowe

1. Stypendium dla Najlepszych Doktorantów przyznane przez JM Rektora UMCS w roku akademickim 2017/2018.
2. Stypendystka zwiększonego stypendium doktoranckiego z dotacji podmiotowej na dofinansowanie zadań projakościowych przyznanego przez Uniwersytet Marii Curie-Skłodowskiej w Lublinie na rok akademicki 2018/2019.
3. Stypendystka „Miejskiego programu stypendialnego dla studentów i doktorantów” na rok akademicki 2018/2019 przyznanego przez Prezydenta Miasta Lublin, Krzysztofa Żuka w dniu 12 marca 2019 r.

Dodatkowa działalność

1. Członek Koła Naukowego Alkahest działającego przy Wydziale Chemii Marii Curie-Skłodowskiej w Lublinie (październik 2015 r. - październik 2018 r.).
2. Członek Sekcji Studenckiej Polskiego Towarzystwa Chemicznego od października 2015 r. do chwili obecnej.
3. Członek Rady Wydziału Chemii w roku akademickim 2015/2016.
4. Przewodnicząca Komitetu Organizacyjnego IV Ogólnopolskiego Turnieju All-Chemicznego, który odbył się w dniach 10 marca 2018 r. oraz 8 czerwca 2018 r. na Wydziale Chemii UMCS.
5. Członek Komisji Plakatowej podczas V Ogólnopolskiego Turnieju All-Chemicznego, który odbył się 9 marca 2019 r. na Wydziale Chemii UMCS.

**ANEKS - TEKSTY PUBLIKACJI BĘDĄCYCH
PRZEDMIOTEM ROZPRAWY DOKTORSKIEJ**

Publikacja 1

K. Tyszczuk-Rotko, **Katarzyna Domańska**, *Simple and sensitive voltammetric procedure for determination of Cd(II) and Pb(II) using bismuth-coated screen-printed carbon electrode prepared with mediator*, Journal of The Electrochemical Society, 164 (2017) H537-H544.



Simple and Sensitive Voltammetric Procedure for Determination of Cd(II) and Pb(II) Using Bismuth-Coated Screen-Printed Carbon Electrode Prepared with Mediator

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In this paper, in-situ deposited bismuth films that have been plated with the use of a zinc mediator on either self-produced or commercially available screen-printed carbon electrodes (BiF/SPCEs) are assessed for their potential as Cd(II) and Pb(II) determinates, and as for being cheap and environmentally friendly alternatives to mercury and other bismuth-coated electrodes. Herein, the composition of the supporting electrolytes and the influence of procedure parameters on the sensitivity of Cd and Pb responses are discussed. The voltammetric studies were also complemented by optical and atomic force microscopic, and optical profilometry observations, as well as by X-ray photoelectron spectroscopic analysis. The obtained detection limits for Cd(II) and Pb(II) were 1.35×10^{-9} and 1.41×10^{-10} mol L⁻¹ (the deposition time of 190 s), respectively. The proposed voltammetric procedure was then applied for the simultaneous determination without a preliminary mineralization step of Cd(II) and Pb(II) in certified reference material, as well as in sea and river water samples. The obtained results were found to be satisfactory. © 2017 The Electrochemical Society. [DOI: 10.1149/2.1641707jes] All rights reserved.

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Heavy metals are characterized by their high densities, high atomic weights and potential environmental toxicity.¹ Despite the fact that heavy metals naturally occur in the Earth's crust, the majority of environmental pollution is brought about by anthropogenic activities such as industrial production and utilization, mining, metallurgy and the formulation of metals and metal-containing compounds.²⁻⁴ Increasing heavy metals environmental contamination is also a result of coal burning, petroleum combustion and refining.¹ Heavy metals pollution has a hazardous short and long term influence on human health, and it significantly enhances the negative environmental effects of such natural phenomena as volcano eruptions and weathering processes.^{5,6}

Cadmium and lead are heavy metals which are very toxic for animals, and these particularly induce many ill-health effects - both in the short and long term. These hazardous elements can accumulate in both water and soil, and as a consequence, contaminate crops, thus, the food supply chain.⁷ Cadmium ions are quite soluble in water and are readily absorbed in plant tissues and in animal organs such as the liver and kidneys. Indeed, cadmium contamination has been found in wheat and rice, as well as in sea foods such as mussels. Lead is also known to accumulate in plant tissues, particularly in crops of large leaf area e.g. cabbage and spinach.⁸

The afore-mentioned toxic elements are introduced into animals (particularly the higher animals such as human-beings) by two routes: inhalation and ingestion.⁹ Cadmium has a severe influence on the respiratory and digestive system. Due to its chronic inhalation, adenocarcinoma of the lung is formed,¹⁰ while, after direct ingestion, immediate symptoms include excessive salivation, vomiting, abdominal pain, loss of consciousness and vertigo.¹¹ Lead, too, is easily accumulated in the organs of higher animals, especially in the liver, kidneys, heart and brain, however, the vast majority of lead in the body is located within the skeleton.¹² Lead has a negative influence on the nervous system and can induce headache, irritability and memory loss.^{13,14} Still, the most dangerous effects are seen in pregnant women. Herein, the lead absorbed by the mother is transfer to the developing fetus.¹⁵ On account of the presence of hazardous heavy metals in food chain, their contamination should be constantly controlled.⁹

The most common methods to determine and then quantitatively analyze Cd(II) and Pb(II) content include electrothermal and flame atomic absorption spectrometry, inductively coupled plasma atomic emission and mass spectrometry.¹⁶⁻¹⁸ However, spectrometric methods are unsuitable for in-situ measurements owing to the complex instrumentation required. Additionally, the stated spectrometric methods are expensive, cumbersome and time consuming. Moreover, they

require the analysis to be performed by skilled personal in a specialized manner.¹⁹ In contrast, voltammetry makes it possible to simple and easy trace the presence of Cd(II) and Pb(II) in environmental samples, doing so with good sensitivity, selectivity and low cost.²⁰

It is possible to place influence via electrode choice or modification, on Cd(II) and Pb(II) determination procedure parameters, and, hence, to decrease the detection limitations. Such alterations include employing hanging mercury drop electrode (HMDE),²¹ bismuth film electrode modified with mesoporous silica nanoparticles,²² bismuth film/1-nitroso-2-naphthol/naftion modified glassy carbon electrode,²³ PEDOT/PSS modified glassy carbon electrode²⁴ and many others.

In recent years, for the purposes of performing rapid 'in situ' analysis, analytical chemists have taken into their arsenal, sensitive yet, reliable, extremely inexpensive and portable, reproducible screen-printed sensors.^{25,26} Following this interesting trend, the purpose of this work was to optimize a novel voltammetry procedure for the simultaneous determination of cadmium(II) and lead(II) in non-pretreated water samples, using an environmental friendly bismuth film screen-printed carbon electrode (BiF/SPCE). The current literature has revealed that bismuth modified screen-printed electrodes (SPEs) can be applied for the simultaneous determination of Cd(II) and Pb(II).²⁷⁻³⁵ However, in this paper, for the first time the screen-printed carbon electrode was in-situ modified with bismuth film using a reversibly deposited mediator metal (Zn) in order to improve the sensitivity of Cd(II) and Pb(II) determination.^{36,37} Then, the proposed sensor was employed for the simultaneous assay of Cd(II) and Pb(II) without the sample pretreatment step in certified reference material as well as in sea and river water samples.

Experimental

Reagents and water samples.—A 1 mol L⁻¹ acetate buffer solution, used as a supporting electrolyte, was prepared from CH₃COONH₄ and HCl (30%, Suprapur) obtained from Sigma-Aldrich. The stock standard solutions of Pb(II), Cd(II) and Bi(III) (1 g L⁻¹) were purchased from Merck. The working solutions of Cd(II), Pb(II) and Bi(III) were then prepared by way of the appropriate dilution of the stock standard solutions in 0.1 mol L⁻¹ HNO₃ (Merck). To study the interference effect, standard solutions of Mo(VI), Ni(II), Fe(III), Cu(II), Sb(III) and V(V) (1 g L⁻¹, Merck) were used. Beyond this, Triton X-100, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were purchased from Fluka. All solutions were prepared using ultra-purified water (> 18 MΩ cm) supplied by a Milli-Q system (Millipore, UK).

Certified reference material, rain water TMRain-04, was obtained from the National Research Council, Canada. The natural water

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samples were collected from the Baltic Sea (Władysławowo, Poland) and Krzna River (Jelnica, Poland), and the sea and river water samples were first filtered using a 0.45 μm Millipore filter. All materials were analyzed directly in the form in which they had been purchased or collected, as well as in (regarding the sea and river samples) after a 3 hour mineralization using a UV-digester made by Mineral, Poland. Before the UV-mineralization, the sea and river water samples were acidified to pH = 2 using concentrated HNO_3 .

Apparatus.—The electrochemical experiments were carried out by way of an $\mu\text{Autolab}$ analyzer equipped with USB electrochemical interface and driven via a GPES 4.9 software package (Eco Chemie, Netherlands), in conjunction with a three electrode system and a personal computer for data storage and processing. For research purposes, a conventional three electrode quartz cell with a volume of 5 mL was used with (*) an Ag/AgCl as a reference electrode, a platinum wire (as a counter electrode) and as a working electrode, a bismuth film modified in-lab fabricated screen-printed carbon electrode. This was competitively assessed with a (**) three electrode screen-printed sensor with a graphite working electrode (1 mm diameter) coated during analysis with bismuth film, as well as a platinum counter electrode and a Ag/AgCl reference electrode (BVT, AC1.W4.R1, Czech Republic).

Atomic force microscopy (AFM) measurements were performed using a Digital Instruments NanoScope III (USA, 2001). The electrodes surface was also imaged through employing a confocal Nikon Eclipse MA 200 microscope. In addition, the electrode surface profile measurements were carried out by way of a Veeco's Contour GT-K1 optical profilometer, while the X-ray photoelectron spectroscopy (XPS) spectra were obtained using a Multi-Chamber Analytical System (Prevac, Poland).

Preparation of the screen-printed carbon electrodes.—The screen-printed carbon electrodes were prepared using a commercial carbon ink (C10903D14, Gwent Electronic Materials Ltd., Pontypool, UK), by way of the screen-printing of the ink onto the ceramic supports (each $40 \times 10 \text{ mm}$). Regarding the ceramic substrates, thickened carbon ink layers were formed on these through utilizing an etched stencil (thickness 100 μm , electrode printing area 105 mm^2) and a screen-printing device kit (UL 1505 A, Tesla, Czech Republic). The printed electrodes were dried at 60°C for 30 min and then were covered with a layer of PVC insulation, leaving a defined rectangular shaped ($5 \times 3 \text{ mm}$) as working area and a similar area on the other side for electrical contact.

Procedure of bismuth film coating and Cd(II) and Pb(II) voltammetric determination.—The screen-printed working electrode was modified with a bismuth film using an in-situ plating method and a reversibly deposited zinc mediator. The bismuth film coating and the voltammetric determinations of cadmium and lead under optimized conditions were carried out in a solution containing 0.05 mol L^{-1} acetate buffer (pH 3.8 ± 0.1), $2 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III), $2 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) and variable concentrations of Cd(II) and Pb(II). The potential of the electrode was changed in the following sequence: -1.65 V for 180 s and -0.95 V for 10 s. In the first step, Bi, Zn, Pb and Cd were deposited simultaneously onto a screen-printed carbon surface. During the second step, zinc was stripped from the surface, while bismuth, lead and cadmium continued to be deposited. During both steps, the solution was stirred using a magnetic stirring bar. Afterwards, the stirring was stopped, and following 5 s of equilibration time, anodic square wave voltammograms were recorded between -1.65 and 0.5 V with a frequency of 40 Hz, an amplitude of 75 mV and a scan rate of 400 mV s^{-1} . The recorded voltammograms were cut in the potential range from -1.0 to -0.25 V .

It should be noted that the measurements were carried out utilizing an non-deaerated solution. Moreover, the background current measurements were subtracted from the voltammetric curves registered during the determination of Cd(II) and Pb(II).

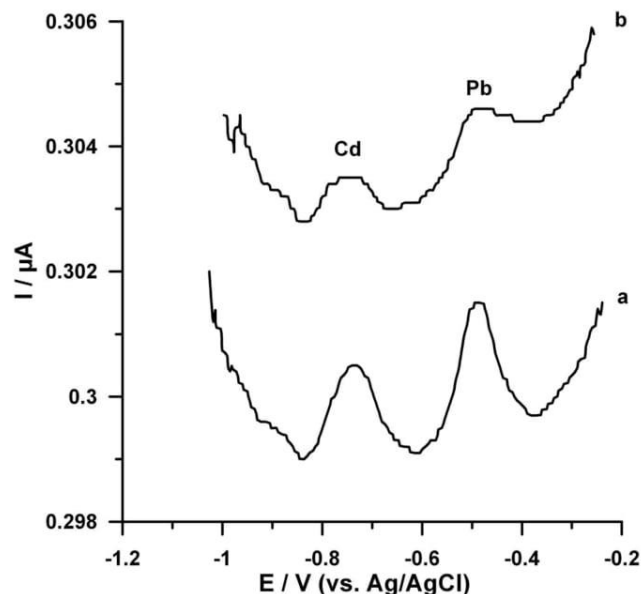


Figure 1. Square wave voltammograms obtained at the in situ BiF/SPCE prepared without (a) and with (b) the use of a zinc mediator. The measurements were carried out in solutions containing 0.1 mol L^{-1} acetate buffer (pH 4.6 ± 0.1), $2 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III), 0 (a) or $2 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) (b), $2 \times 10^{-7} \text{ mol L}^{-1}$ Cd(II) and $2 \times 10^{-7} \text{ mol L}^{-1}$ Pb(II). The Zn, Cd, Pb and Bi were deposited simultaneously at a potential of -1.6 V for 120 s. The potential and time of the Zn oxidation and further deposition of Cd, Pb and Bi were -0.95 V and 5 s, respectively. Stripping parameters: frequency of 10 Hz, amplitude of 50 mV and scan rate of 10 mV s^{-1} .

Results and Discussion

Preliminary measurements.—In order to identify the oxidation potentials of zinc, cadmium, lead and bismuth, the square wave voltammogram was registered. This was generated within the acetate buffer solution of pH 4.5 after the electrodeposition of these metals (-1.6 V for 120 s) onto a screen-printed carbon electrode surface in the potential range of -1.6 to 0.5 V . At a potential in the range from -0.875 to -0.95 V , it was noted that zinc will be stripped from the surface, while cadmium, lead and bismuth will continue the deposition. Additionally, zinc, cadmium, lead and bismuth can be deposited simultaneously at potentials more negative than -1.25 V . In further measurements, a potential of -1.6 V and time of 120 s were used for simultaneously plating zinc, cadmium, lead and bismuth; and a potential of -0.95 V and time of 5 s were used for stripping zinc and bringing about further deposition of cadmium, lead and bismuth.

A comparative study of the in-situ BiF/SPCE, prepared with and without the use of a zinc mediator for measuring $2 \times 10^{-7} \text{ mol L}^{-1}$ Cd(II) and Pb(II) as model analyte ions, is presented in Fig. 1. As can be seen, well-defined, sharp and well-separated signals of Cd and Pb were obtained using both electrodes. However, the use of a zinc mediator brought about a 2-fold increase in the Cd(II) and Pb(II) signals, as well as a decrease in the background current at the in-situ prepared BiF/SPCE, respectively. Therefore, further study focused on the characterization of the BiF/SPC electrode surface, the optimization procedure of electrode preparation with the use of a zinc mediator and the simultaneous detection of Cd(II) and Pb(II), as well as a refinement of application of the proposed procedure for determining these metal ions in water samples without sample pretreatment.

Characterization of the electrode surface.—Changes in the surface morphology of the bismuth deposit prepared without and with the use of mediator onto a screen-printed carbon electrode surface were noted after optical and atomic force microscopic, and optical profilometry observations (Fig. 2A). In this figure, on the optical microscope images, the bismuth particles can be clearly seen as bright

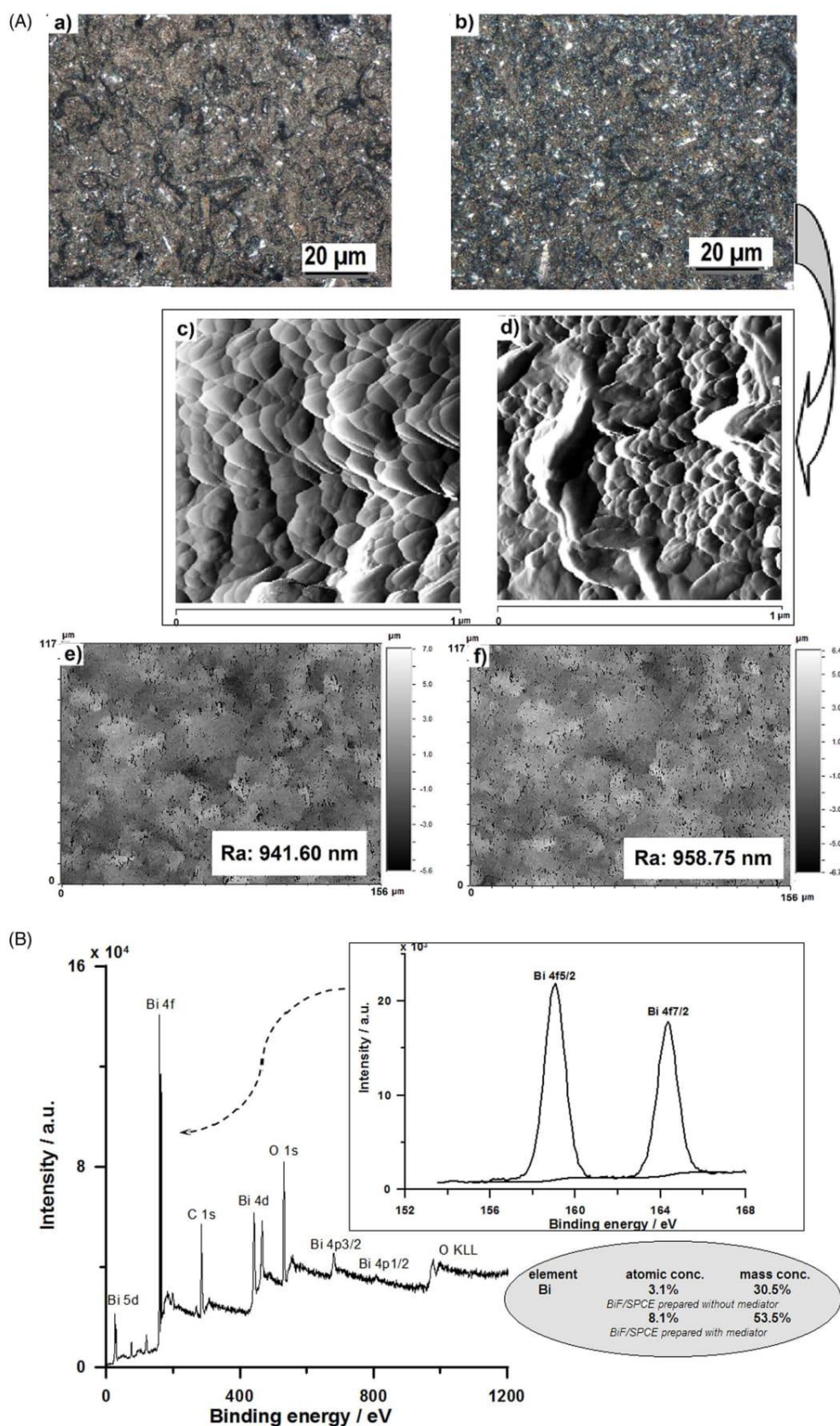


Figure 2. A) Optical microscope (a and b) and profilometer (e and f) images of the BiF/SPCE surface prepared without (a and e) and with (b and f) the use of a zinc mediator. AFM images of a bare SPCE (c) and the BiF/SPCE prepared with mediator (d). Fig. 2B) XPS spectrum of the BiF/SPCE prepared with the use of a zinc mediator with deconvoluted Bi 4f region. In this work, the solutions for the electrode preparation containing 0.05 mol L^{-1} acetate buffer ($\text{pH } 3.8 \pm 0.1$), $2 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III), and 0 (a and e) or $2 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) (b, d and f). Other parameters were as in Fig. 1.

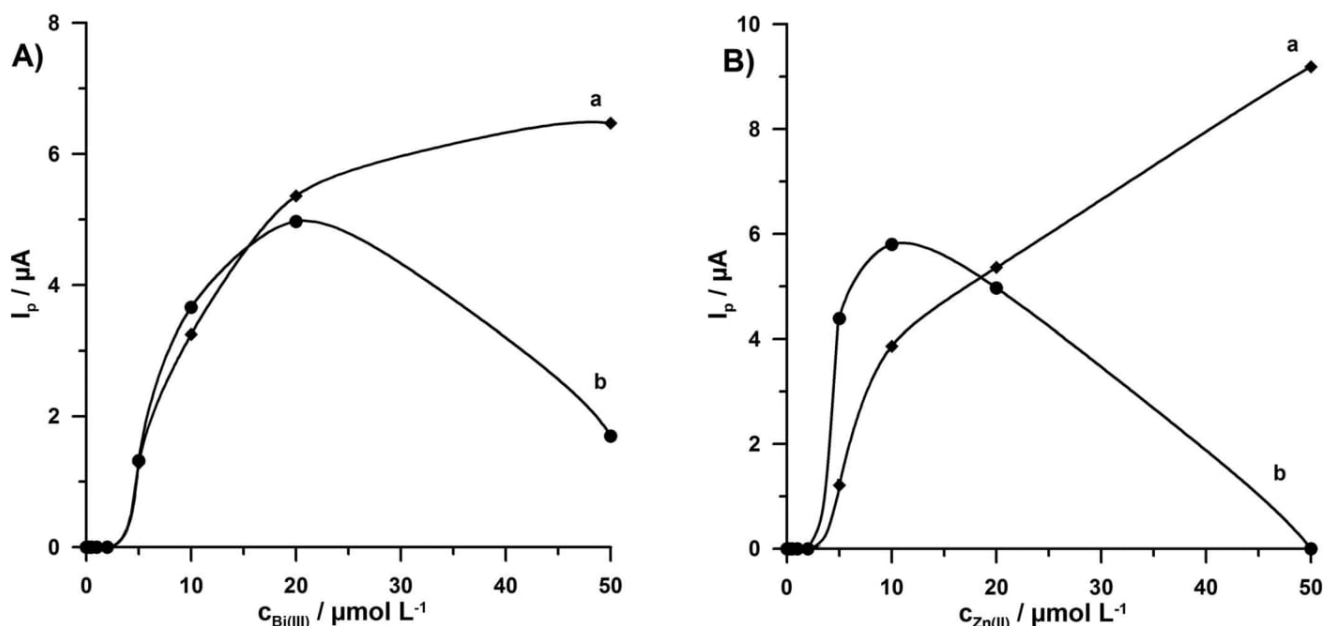


Figure 3. Influence of: A) Bi(III) and B) Zn(II) concentration on the voltammetric signals of Cd(II) (a) and Pb(II) (b). The measurements were carried out in solution containing 0.05 mol L^{-1} acetate buffer ($\text{pH } 3.8 \pm 0.1$), from 0 to $5 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III) (A) or $2 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III) (B), $2 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) (A) or from 0 to $5 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) (B), $5 \times 10^{-8} \text{ mol L}^{-1}$ Cd(II) and $2 \times 10^{-8} \text{ mol L}^{-1}$ Pb(II). Other parameters were as in Fig. 1.

structures (Figs. 2Aa and 2Ab). On the surface of the electrode prepared with a mediator, the amount of these structures is much higher. This leads to the conclusion that the zinc mediator induced an increase in the bismuth particle surface coverage. This result is consistent with the literature data.³⁷

The AFM images presented in Figs. 2Ac and 2Ad reveal the structure of the deposited film at higher magnification than that obtained by optical microscope. Herein, a pattern that is typically characteristic of a heterogeneous screen-printed carbon surface can be seen in the case of the bismuth-free and bismuth modified samples. However, in the second case, on the AFM images, the agglomerates of bismuth particles can be clearly seen as patchy structures.

The heterogeneous bismuth film screen-printed carbon electrode surfaces modified without and with the use of mediator are also seen in the optical profiles (Figs. 2Ae and 2Af). These reveal that the zinc mediator, to a negligible extent, increases the roughness (R_a) of the bismuth deposit.

The XPS analysis undoubtedly confirms the presence of bismuth on the electrode surface (Fig. 2B). The XPS atomic Bi composition of the deposited films prepared without and with mediator is 3.1% and 8.1%, respectively. The latter higher content of bismuth at the electrode surface is related to the use of a zinc mediator in the electrode modification step. This effect was also confirmed using microscopic study.

Composition of the solution.—The influence of the following supporting electrolytes on the cadmium and lead peak currents was assessed: sulfuric acid, hydrochloric acid, acetate buffer ($\text{pH } 3.8, 4.6$ and 6.0 ± 0.1) at 0.1 mol L^{-1} concentration. These measurements were carried out in solutions containing $2 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III), $1 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II), $5 \times 10^{-8} \text{ mol L}^{-1}$ Cd(II) and $2 \times 10^{-8} \text{ mol L}^{-1}$ Pb(II). In the acid solutions, no Cd and Pb peaks were received, while well-defined voltammetric signals were obtained in the acetic buffer solutions. Indeed, the highest peak currents of Cd(II) and Pb(II) were obtained in the acetic buffer solution of $\text{pH } 3.8$. On the basis of these results, further measurements were carried out in this solution, and its concentration was evaluated from 0.025 to 0.15 mol L^{-1} . As a result of such work, the highest values of Cd(II) and Pb(II) peak

currents were obtained at 0.05 mol L^{-1} concentration, hence this was adopted for all subsequent experiments.

As stated within published work,³⁷ concentrations of Bi(III) and Zn(II) in the solution are the main chemical factors that determine the morphology of the in-situ plated bismuth film, and consequently, the analytical results. Therefore, the influence of Bi(III) concentration in the supporting electrolyte was investigated within the range of 0 to $5 \times 10^{-5} \text{ mol L}^{-1}$. For this purpose, the screen-printed carbon electrode was immersed in 0.05 mol L^{-1} acetate buffer solution ($\text{pH } 3.8 \pm 0.1$) containing $2 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II), $5 \times 10^{-8} \text{ mol L}^{-1}$ Cd(II), $2 \times 10^{-8} \text{ mol L}^{-1}$ Pb(II) and increasing Bi(III) concentrations. The bismuth film was deposited under stirring on the electrode surface at the potential of -1.6 V for 60 s, and then at -0.95 V for 5 s. As shown in Fig. 3A, the Cd (curve a) and Pb (curve b) voltammetric signals reach the maximum values at Bi(III) concentrations of 5×10^{-5} and $2 \times 10^{-5} \text{ mol L}^{-1}$, respectively. Since the peak current of Pb(II) drastically decreased at $5 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III), the Bi(III) concentration of $2 \times 10^{-5} \text{ mol L}^{-1}$ was chosen for further experiments. Next, the influence of Zn(II) concentration was studied using a 0.05 mol L^{-1} acetate buffer solution ($\text{pH } 3.8 \pm 0.1$) containing $2 \times 10^{-5} \text{ mol L}^{-1}$ Bi(III), $5 \times 10^{-8} \text{ mol L}^{-1}$ Cd(II), $2 \times 10^{-8} \text{ mol L}^{-1}$ Pb(II) and increasing Zn(II) concentrations (from 0 to $5 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II)). The obtained results are presented in Fig. 3B. Herein, it can be observed that the peak current of Cd(II) increases in all studied range of Zn(II) concentrations, while the peak current of Pb(II) increases to $1 \times 10^{-5} \text{ mol L}^{-1}$ Zn(II) concentration and then decreases. The Zn(II) concentration of $2 \times 10^{-5} \text{ mol L}^{-1}$ was, hence, chosen for further study, as this is a compromise between the increase of Cd signals and the decrease of Pb signals.

Optimization of the bismuth film plating and metal ions determination procedure parameters.—The potential of the zinc mediator, bismuth film, cadmium and lead deposition was investigated in the range of -1.7 to -1.2 V for the Cd(II) and Pb(II) concentrations of 5×10^{-8} and $2 \times 10^{-8} \text{ mol L}^{-1}$, respectively. The potential and time of the zinc oxidation and further deposition of bismuth, cadmium and lead were -0.95 V and 5 s, respectively. The obtained results are presented in Fig. 4A. The results indicate that the mediator, bismuth film and detected metal ions can be electro-deposited most effectively

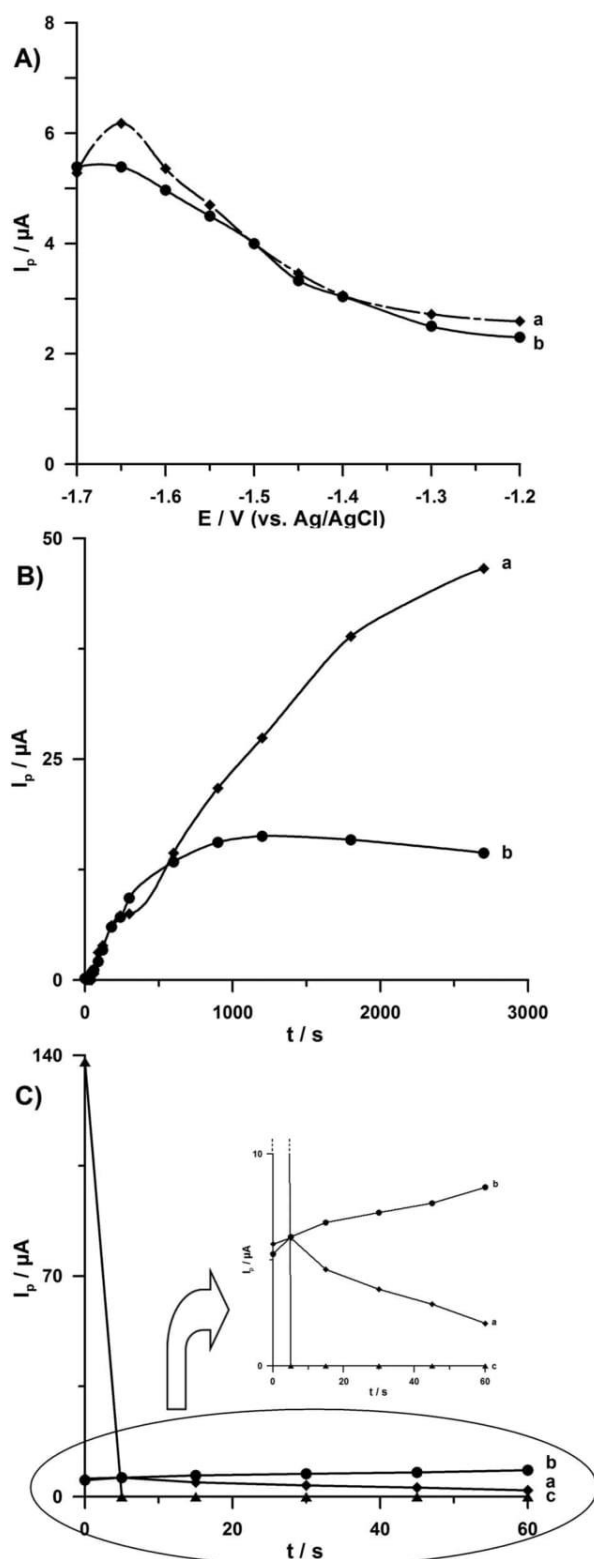


Figure 4. Influence of: A) the potential and B) the time of simultaneous Zn, Bi, Cd and Pb deposition, and C) the time of oxidation of zinc and further deposition of Bi, Cd and Pb on the voltammetric signals of Cd(II) (a), Pb(II) (b) and Zn(II) (c). The solution containing 0.05 mol L⁻¹ acetate buffer (pH 3.8 $\pm$ 0.1), 2 $\times$ 10⁻⁵ mol L⁻¹ Bi(III), 2 $\times$ 10⁻⁵ mol L⁻¹ Zn(II), 5 $\times$ 10⁻⁸ mol L⁻¹ Cd(II) and 2 $\times$ 10⁻⁸ mol L⁻¹ Pb(II). The Zn, Cd, Pb and Bi were deposited simultaneously at potential of -1.65 V (A and B) for 180 s (A and C). The potential and time of the Zn oxidation and further deposition of Cd, Pb and Bi were -0.95 V (A, B and C) and 5 s (A and B), respectively.

on the electrode surface at a potential of -1.65 V, so this value was chosen for further study. The time of simultaneous Zn, Bi, Cd and Pb deposition onto the electrode surface was also studied. In doing so, the deposition time was changed within the range of 0 to 2700 s, and its influence on the oxidation peaks of cadmium and lead was studied. The obtained results are presented in Fig. 4B. In this part of the study, the maximum currents were reached within 2700 and 1200 s for Cd(II) and Pb(II) ions, respectively. However, for further measurements, a time of 180 s was chosen in order to decrease the total time of analysis.

In accordance with the results described in Preliminary measurements section a potential and time of -0.95 V and 5 s were chosen for stripping zinc and to bring about further deposition of bismuth, cadmium and lead, respectively, and in this part of experiment, the time of the oxidation of the zinc and the further deposition of Bi, Cd and Pb was examined in detail. So as to achieve this, the time was modified within the range of 0 to 60 s, and the effect of its influence on the Zn, Cd and Pb peaks was studied (Fig. 4C). As a result of such work, it was observed that the Cd peak increases up to the time of 5 s, and then decreases. In the case of the Pb peak current, this increases with the prolongation time up to 60 s. As can be seen in Fig. 4C, all the zinc is stripped from the surface of the electrode within an oxidation time of 5 s. As a compromise between the value of the peak currents of Cd and Pb, and the complete oxidation of zinc, the time of 10 s was chosen for further study.

The influence of diverse levels of the instrumental parameters (frequency, amplitude and scan rate) of square-wave scan mode on the Cd(II) (5 $\times$ 10⁻⁸ mol L⁻¹) and Pb(II) (2 $\times$ 10⁻⁸ mol L⁻¹) peak currents was subsequently investigated. In doing so, the frequency was modified within a range of 10–100 Hz. As a result of such work, it was observed that Cd and Pb peaks attained maximum values at a frequency of 40 Hz, hence, this value was chosen for further study. In assessing the influence of the amplitude on the Cd and Pb oxidation, peak currents were investigated within the range of 10 to 100 mV. Such work revealed that the Cd peak attained maximal and nearly stable value within amplitudes ranging from 75 to 100 mV. In the case of Pb(II) determination, the signal increases along with increases of amplitude up to 75 mV. Thus, an amplitude of 75 mV was chosen for further study. In investigating the dependence of the Cd and Pb signals on scan rate (10–800 mV s⁻¹), an increase of Cd and Pb signals and background current was observed with the increase of scan rate. Furthermore, a distorted Cd peak shape was observed at any scan rate higher than 400 mV s⁻¹. On the basis of the obtained results, a scan rate of 400 mV s⁻¹ was chosen for further measurements.

Finally, the need for cleaning working electrode surface after each measurement was verified. In this case, 10 successive measurements of 5 $\times$ 10⁻⁸ mol L⁻¹ Cd(II) and 2 $\times$ 10⁻⁸ mol L⁻¹ Pb(II) analytical signals using both purification at 0.5 V for 30 s and no purification, were performed. In so-doing, relative standard deviations of the Cd peak current of 5.39% and 2.35%, and the Pb peak current of 1.92% and 3.18% with and without purification of the electrode surface were obtained, respectively. On the basis of these results, further study was conducted without an incorporated cleaning step.

Calibration graphs.—The proposed voltammetric procedure involving the BiF/SPCE prepared by way of a mediator was employed for both individual and simultaneous determination of Cd(II) and Pb(II). For this purpose, measurements were taken in solutions containing: constant concentration of one determined ion and increasing concentrations of the second, and simultaneous increases of both determined metal ions. All measurements were performed utilizing a bismuth film modified in-lab fabricated screen-printed carbon electrode (BiF/SPCE) device, and a commercially available BVT three-electrode screen-printed sensor (BVT BiF/SPCE), for a total cadmium and lead deposition time of 190 s (-1.65 V for 180 s and -0.95 V for 10 s). For this case, Pb(II) concentration was modified with a range of 2 $\times$ 10⁻¹⁰ to 5 $\times$ 10⁻⁷ mol L⁻¹ (for BiF/SPCE) or 5 $\times$ 10⁻⁹ to 5 $\times$ 10⁻⁶ mol L⁻¹ (for BVT BiF/SPCE), while the Cd(II) concentration was made equal to 2 $\times$ 10⁻⁷ mol L⁻¹ (for BiF/SPCE) or 2 $\times$ 10⁻⁶ mol

Table I. The data obtained at the BiFE/SPCE (1-3) and the BVT BiF/SPCE (4-6) during: (1, 4) Pb(II) determination in the presence of constant concentration of Cd(II), (2, 5) Cd(II) determination in the presence of constant concentration of Pb(II), (3, 6) simultaneous determination of increasing concentrations of Cd(II) and Pb(II).

No.	LR [mol L ⁻¹]	LRE	r	LOD [mol L ⁻¹]	LOQ [mol L ⁻¹]
1	$2 \times 10^{-9} - 2 \times 10^{-7}$	$I_p (\mu A) = 0.58 \times C (\text{nmol L}^{-1}) - 1.64$	0.9991	5.95×10^{-10}	1.98×10^{-9}
2	$1 \times 10^{-8} - 2 \times 10^{-6}$	$I_p (\mu A) = 0.13 \times C (\text{nmol L}^{-1}) - 1.88$	0.9988	2.85×10^{-9}	9.50×10^{-9}
3	Cd(II) $5 \times 10^{-9} - 1 \times 10^{-6}$ Pb(II) $5 \times 10^{-10} - 5 \times 10^{-7}$	$I_p (\mu A) = 0.20 \times C (\text{nmol L}^{-1}) - 0.95$	0.9996	1.35×10^{-9}	4.50×10^{-9}
4	$5 \times 10^{-8} - 2 \times 10^{-6}$	$I_p (\mu A) = 0.57 \times C (\text{nmol L}^{-1}) + 0.23$	0.9987	1.41×10^{-10}	4.70×10^{-10}
5	$1 \times 10^{-7} - 2 \times 10^{-5}$	$I_p (\mu A) = 16.48 \times C (\mu\text{mol L}^{-1}) - 0.26$	0.9994	1.32×10^{-8}	4.39×10^{-8}
6	Cd(II) $2 \times 10^{-7} - 2 \times 10^{-5}$ Pb(II) $2 \times 10^{-8} - 1 \times 10^{-6}$	$I_p (\mu A) = 2.87 \times C (\mu\text{mol L}^{-1}) + 0.60$ $I_p (\mu A) = 17.18 \times C (\mu\text{mol L}^{-1}) - 0.040$ $I_p (\mu A) = 1.60 \times C (\mu\text{mol L}^{-1}) + 0.23$	0.9977 0.9997 0.9981	2.95×10^{-8} 5.84×10^{-8} 5.59×10^{-9}	9.83×10^{-8} 1.95×10^{-7} 1.86×10^{-8}

LR: linear range; LRE: linear regression equation, r: correlation coefficient, LOD: limit of detection, LOQ: limit of quantification.

L⁻¹ (for BVT BiF/SPCE). Additionally, similar measurements were carried out utilizing a solution containing a constant concentration of Pb(II) made equal to 5×10^{-8} mol L⁻¹ (for BiF/SPCE) or 5×10^{-7} mol L⁻¹ (for BVT BiF/SPCE) and increasing concentrations of Cd(II) in the range of 1×10^{-9} to 5×10^{-6} mol L⁻¹ (for BiF/SPCE) or 5×10^{-8} to 5×10^{-5} mol L⁻¹ (for BVT BiF/SPCE). Finally, Cd(II) and Pb(II) were determined while simultaneously increasing their concentrations from 5×10^{-10} to 5×10^{-6} mol L⁻¹ (for BiF/SPCE) or 5×10^{-9} to 5×10^{-5} mol L⁻¹ (for BVT BiF/SPCE). In all cases, optimized conditions were applied for finding the linear range (LR), the linear regression equation (LRE), the correlation coefficient (r), the limit of detection (LOD) and the limit of quantification (LOQ). In such work, the detection and quantification limits of Cd(II) and Pb(II) were estimated at 3 or 10 times the standard deviation ($n = 5$) for the lowest determined concentration of Cd(II) and Pb(II) divided by the slope of the linear regression equation, respectively. The obtained results are collected in Table I. As can be seen, the detection and quantification limits are higher when the commercially available electrodes and three-electrode screen-printed sensor (BVT BiF/SPCE) was utilized, rather than the in-lab fabricated screen-printed carbon electrodes and

device. This effect is connected with the lowered surface area of the working electrode (0.79 vs. 15.0 mm²). Table II reveals a comparison of the analytical parameters obtained by the proposed method at the BiF/SPCE, with those obtained by way of utilizing similar electrochemical techniques and metal modified screen-printed electrodes for simultaneous Cd(II) and Pb(II) determination. The comparison shows that bismuth film modified screen-printed carbon electrode provide lower detection limit.^{28-33,35,38-45} Indeed, it is in one case alone³⁴ that the Cd(II) detection limit is lower (8.90×10^{-10} mol L⁻¹ for the deposition time of 340 s) than that obtained by the procedure presented in this work (1.35×10^{-9} for the deposition time 190 s). However, in the latter case, the detection limit can be easily lowered by prolonging the deposition time.

Effect of interferences.—The effects of co-existing ions in the sample solution were tested using a fixed concentration of 2×10^{-7} mol L⁻¹ Cd(II) and 2×10^{-8} mol L⁻¹ Pb(II). As a result, the tolerance levels of foreign ions were discovered to be 2×10^{-8} mol L⁻¹ of Mo(VI), Ni(II), Fe(III), Cu(II), Sb(III), V(V) for Cd(II), and 2×10^{-7} mol L⁻¹ of Mo(VI), Ni(II), Fe(III) and 2×10^{-6} mol L⁻¹ of Cu(II),

Table II. Comparison of different working metal modified screen-printed electrodes for the simultaneous determination of Cd(II) and Pb(II).

Modifier of SPE surface	Electrochemical technique	Deposition time [s]	Detection limit [mol L ⁻¹]		Reference
			Cd(II)	Pb(II)	
In situ plated BiF	SWASV	120	3.20×10^{-8}	1.21×10^{-8}	28
Ex situ plated BiF	DPASV	60	-	-	29
Bismuth from Bi ₂ O ₃	CCSCP	120	1.42×10^{-7}	3.86×10^{-8}	30
Bismuth from Bi ₂ O ₃	SWASV	120	2.22×10^{-8}	2.41×10^{-8}	31
Bismuth from Bi ₂ O ₃	SWASV	300	1.33×10^{-8}	1.11×10^{-8}	32
Bi nanoparticles	SWASV	120	1.16×10^{-8}	4.34×10^{-9}	33
Sputtered Bi	DPASV	360	8.90×10^{-10}	8.69×10^{-10}	34
In situ plated BiF	SIA-SWASV	180	6.14×10^{-9}	4.30×10^{-9}	35
Ex situ plated MF	SWASV or PSA	180	8.90×10^{-9}	1.93×10^{-9}	38
In situ plated MF	SWASV	120	1.78×10^{-8}	4.83×10^{-9}	39
Cellulose-derivative mercury coating	SWASV	240	8.90×10^{-9}	1.45×10^{-9}	40
Cellulose-derivative mercury coating	SWASV with SIA	240	5.34×10^{-9}	6.76×10^{-9}	41
MF coated by a crown-ether based membrane	LSASV	120	5.96×10^{-9}	4.01×10^{-9}	42
Mercury nano-droplets	SWASV	300	1.20×10^{-8}	2.30×10^{-8}	43
Gold	SWASV	120	1.25×10^{-8}	2.41×10^{-9}	44
Graphene-Nafion-gold nanocomposite film	DPASV	240	3.11×10^{-9}	1.11×10^{-9}	45
In situ plated BiF with mediator	SWASV	190	1.35×10^{-9}	1.41×10^{-10}	This work

BiF: bismuth film; MF: mercury film; SWASV: square wave anodic stripping voltammetry; DPASV: differential pulse anodic stripping voltammetry; CCSCP: constant current stripping chronopotentiometry; PSA: potentiometric stripping analysis; SIA: sequential injection analysis; LSASV: linear sweep anodic stripping voltammetry.

Table III. Results of Cd(II) and Pb(II) determination in certified reference material.

Analytical parameters	Certified reference material (TMRAIN-04)	
	Cd(II)	Pb(II)
Measured value $\pm$ SD ^a ($\mu\text{g L}^{-1}$)	0.57 ± 0.033	0.39 ± 0.041
Certified value $\pm$ SD ($\mu\text{g L}^{-1}$)	0.52 ± 0.030	0.35 ± 0.035
Δm^b	0.041	0.045
U_{Δ}^c	0.048	0.059

^aStandard deviation (SD) for $n = 3$.^bAbsolute difference between mean measured value and certified value.^cExpanded uncertainty of difference between results and certified value. $\Delta m \leq U_{\Delta}$, no significant difference between measured results and certified value at 95% confidence level (coverage factor, $k = 2$).

Sb(III), V(V) for Pb(II). In such work, the tolerable limit was defined as the amount of foreign ions that produced an error not exceeding 5.0% in the peak currents of the determined cadmium and lead.

The influence of surfactants on the peak current of 5×10^{-7} mol L^{-1} Cd(II) and 5×10^{-8} mol L^{-1} Pb(II) was investigated by the addition of Triton X-100, CTAB and SDS (in a range from 0 to 2.0 mg L^{-1}) to the studied solution. As a result, it was seen that the addition of 2.0 mg L^{-1} Triton X-100 decreased the height of Cd(II) and Pb(II) stripping signals to 23.0% and 57.7% of their original values (respectively), while, 2.0 mg L^{-1} SDS decreased the cadmium and lead peaks to 33.0% and 76.4% of their original values (respectively), and the addition of 2.0 mg L^{-1} of CTAB decreased the height of Cd(II) and Pb(II) stripping signals to 21.3% and 67.2% of their original values (respectively). Because the cadmium and lead signals, after the addition of all surfactants at concentration of 2.0 mg L^{-1} , were still clearly visible and easy to measure, it was realized that Cd(II) and Pb(II) could be accurately ascertained in water samples without a preliminary mineralization step.

Application of the voltammetric procedure.—The proposed voltammetric procedure using the BiF/SPCE prepared with a mediator was applied for determining the presence of Cd(II) and Pb(II) in certified reference material (rain water, TMRAIN-04) and in water samples that were collected from the Baltic Sea and from the Krzna River. A comparison of the measurement result with the certified value indicates that there is no significant difference between the former and the latter at a confidence level of about 95% (Table III).⁴⁶ It has to be noted that the certified material was used without pretreatment.

Preliminary investigation revealed that the Cd(II) and Pb(II) concentrations in the Baltic Sea and Krzna River samples were below the detection limit of the proposed procedure. Therefore, the analyzed samples were spiked with Cd(II) and Pb(II) at different concentration levels, and the cadmium and lead contents were assessed using the standard additional method. In such work, the samples were analyzed without and with the use of UV-mineralization. The results are summarized in Table IV. The recovery values are between 95.2 and 105.3% for the determined metal ions, with a relative standard deviation between 2.9 and 5.1%. As can be seen in Table IV, there is no significant difference between the results obtained without and with prior UV-mineralization of the water sample.

In summary, it can be stated that the obtained results show the analytical usefulness of the proposed voltammetric procedure for the determination, without sample pretreatment, of trace Cd(II) and Pb(II) in natural water samples.

Conclusions

In this paper, significant progress has been made in the development of suitable electrochemical procedure for a simple, sensitive

Table IV. Results of Cd(II) and Pb(II) determination at the BiF/SPCE prepared in natural water samples without and with the use of UV-mineralization.

Sample		Cd(II) and Pb(II)		Recovery (%)	RSD (n = 5) (%)
		added (nmol L^{-1})	found (nmol L^{-1})		
Krzna River	Cd(II)	20.0	19.04	95.2	3.5
		80.0	81.28	101.6	3.3
	Pb(II)	2.0	2.10	105.0	2.9
		8.0	7.65	95.6	4.2
Without ^a	Cd(II)	20.0	20.67	103.4	4.8
		80.0	76.40	95.5	5.1
	Pb(II)	2.0	1.90	95.0	3.5
		8.0	7.66	95.8	4.3
Baltic Sea	Cd(II)	20.0	19.90	99.5	4.5
		80.0	78.16	97.7	4.8
	Pb(II)	2.0	2.11	105.5	5.0
		8.0	8.34	104.3	3.3
Without ^a	Cd(II)	20.0	20.98	104.9	5.3
		80.0	82.32	102.9	3.7
	Pb(II)	2.0	2.08	104.0	4.5
		8.0	8.38	104.8	4.3

^aWithout of UV-mineralization of the samples.^bWith 3 h UV-mineralization of the samples.

and selective Cd(II) and Pb(II) determination in natural water samples without pretreatment step, due to the application of bismuth film coated screen-printed electrode prepared with a reversibly deposited zinc mediator. According to our knowledge, this is the first application in situ plated bismuth film screen-printed carbon electrode prepared with mediator for the determination of Cd(II) and Pb(II) in environmental water samples. Herein, the bismuth film plated in situ with the use of mediator onto the self-produced or commercially available SPCE surface induced an increase in the peak currents of both determined metal ions, and a decrease of background current. It has to be mentioned, that the proposed procedure can be used in laboratory analysis as well as in rapid 'in situ' analysis (in the place of sampling) mainly due to facts that: 1) it is simple, sensitive and selective, 2) the water samples need no preparation step, 3) the working electrode (in situ plated bismuth film electrode screen-printed electrode) can be applied in portable analyzers.

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Publikacja 2

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Integrated three-electrode screen-printed sensor modified with bismuth film for voltammetric determination of thallium(I) at the ultratrace level

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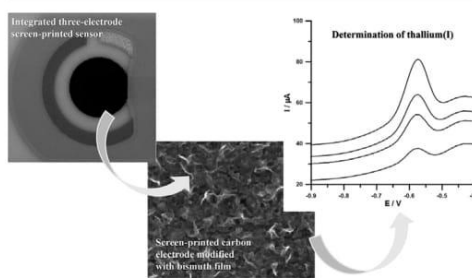
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HIGHLIGHTS

- Integrated three-electrode screen-printed sensor was used for Tl(I) determination.
- In situ plating of bismuth film increases sensor sensitivity.
- The method allows Tl(I) quantification at picomolar concentrations.
- The sensor was successfully applied for analysis of Tl(I) in water samples.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present paper, for the first time, the integrated three-electrode screen-printed sensor with in situ plated bismuth film carbon working electrode was applied for the ultratrace determination of thallium(I) (Tl(I)). Under optimized conditions extremely low limits of detection were reached, 8.47×10^{-10} and $6.71 \times 10^{-12} \text{ mol L}^{-1}$ for the deposition times of 60 s and 300 s, respectively. The influences of foreign metal ions and surfactants on the voltammetric signal of thallium in natural samples were minimized using $1 \times 10^{-5} \text{ mol L}^{-1}$ EDTA and Amberlite XAD-7 resin added to the buffer solution ($\text{CH}_3\text{COONH}_4$, CH_3COOH and NH_4Cl) of $\text{pH} = 4.6 \pm 0.1$. The developed voltammetric method with integrated three-electrode screen-printed sensor was validated with use of certified reference materials (surface, rain and natural water) and can be in future applied to field analyses of Tl(I).

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1. Introduction

Thallium is a heavy metal, which naturally occurs in the environment in low concentrations [1] (e.g. the contents of thallium dissolved in groundwater samples collected near Poznan city

(Poland) ranged from 0.0051 to 0.47 ppb [2]). Increasing level of thallium may be caused by natural phenomena and human activities (e.g. the concentration of thallium in water samples collected from water reservoirs in the vicinity of 3 big Polish Pb-Zn smelters ranged from 0.02 to 9.69 ppb [3]). Thallium is utilized in the industry for the production of catalysts, pigments, low temperature thermometers and optical lenses. It can be also used in agriculture as insecticide [4]. Thallium and thallium - based compounds exhibit higher water solubility compared to other heavy metals. They are

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therefore also more mobile (e.g. in soil), generally more bioavailable and tend to bioaccumulate in living organisms [2]. Thallium accumulates in the nervous system, bones and the kidneys. Major syndromes of poisoning are intestinal and stomach ulcers, polyneuropathy and alopecia. Besides, thallium causes insomnia, weight loss, headaches, muscle pain and internal bleeding [5,6]. The threat posed by thallium is the main reason for the monitoring of environmental contamination therewith.

As the concentrations of Tl(I) in environmental samples are low [2], an analytical technique, which enables its determination has to be very sensitive. The most novel techniques for trace analysis of Tl(I) characterized by their selectivity and high sensitivity are inductively coupled plasma mass spectrometry (ICP-MS) [7,8], and atomic absorption spectrometry-based techniques: FAAS [9], GFAAS [10] and ETAAS [11]. The good alternative for these methods is stripping voltammetry (e.g. for validation of ICP-MS measurement while the certified reference materials are missed). Numerous advantages of this method, such as low detection limits, good selectivity and accuracy, cheap and fast analysis make it adequate for performing routine analyses of environmental samples. One of the most important advantages is the easy equipment miniaturization, which makes it possible to perform sample analysis in field (on site, where the sample is collected) [12]. The aforesaid qualities of the voltammetric techniques make them attractive for use in routine analyses.

Mercury electrodes, such as the hanging mercury electrode and mercury film electrodes are traditionally used for determination of thallium by anodic stripping voltammetry [13–16]. For more than three decades, mercury-free electrodes have come into use with the view to replace mercury in voltammetric determination of Tl(I) [17–34]. It should be noted that from mercury-free electrodes bismuth based electrodes became growingly popular [23–34]. This type of electrode modification was chosen in this paper due to simplicity of performance and the eco-friendly character of the modifier.

In the 1990 the screen-printed technology was used, for the first time, for manufacture of electrochemical sensors. It offered making sensitive, selective and low-cost analytical tools for rapid analysis. Technology of their production allows the introduction of various modifications in both the printing ink and the surface of the electrode. Change in the ink composition and surface treatment of the electrode surface influences the properties of the electrodes. It may improve their sensitivity and selectivity [35,36]. Furthermore, since they can readily be used in portable devices, on-site analyses can be carried out.

In this work the commercially available integrated three-electrode screen-printed sensor with carbon electrode modified in situ during measurement with bismuth film was used for the determination of Tl(I) in natural water samples without long and complicated pretreatment. It should be mentioned that this sensor configuration was used the first time for Tl(I) determination. The objective of performed experiments was to optimize the novel, simple, sensitive, rapid and low cost voltammetric method with the use of commercially available miniaturized integrated three-electrode screen printed sensor with bismuth film electrode for the determination of ultratrace concentrations of Tl(I) for its future use not only in laboratory but in field analyses as well.

2. Materials and methods

2.1. Apparatus

All experiments were performed using a μ Autolab analyzer (Eco Chemie, The Netherlands), which was combined with a computer equipped with an electrochemical USB interface and driven with

use of the GPES 4.9 software package (Eco Chemie, The Netherlands). Commercially available integrated three-electrode screen-printed sensor (DropSens) with a carbon working electrode (4 mm diameter), a platinum auxiliary electrode and silver reference electrode was used to carry out the experiments. It should be mentioned that silver reference electrode in the presence of chloride ions from supporting electrolyte acts as Ag/AgCl/Cl-electrode. The carbon electrode was plated with bismuth film in situ, during measurements. Besides, the classical quartz cell with the volume of 10 mL was used.

Optical microscopes: multizoom AZ 100 M microscope (Nikon) and confocal Eclipse MA 200 microscope (Nikon) were applied for imaging the electrode surface. Additionally, for the purpose of accurate recognition of the surface morphology, the FEI Quanta 3D scanning electron microscope (SEM) was employed. X-ray photoelectron spectroscopy (XPS) spectra were received using a Multi-Chamber Analytical System (Prevac, Poland).

2.2. Reagents

The supporting electrolyte was prepared by mixing 40 mL of 5 mol L⁻¹ of CH₃COONH₄ (Sigma-Aldrich) and 94 mL of 1 mol L⁻¹ HCl (Fluka). Then, the flask was filled with distilled water to a volume of 200 mL. The concentration of CH₃COONH₄ was 1 mol L⁻¹ and HCl was 0.47 mol L⁻¹. Due to the reaction between these reagents buffer solution (0.53 mol L⁻¹ CH₃COONH₄, 0.47 mol L⁻¹ CH₃COOH and 0.47 mol L⁻¹ NH₄Cl) of pH = 4.6 ± 0.1 was obtained. Solution of disodium salt of ethylenediaminetetraacetic acid (EDTA) (Sigma-Aldrich) was prepared by dissolving appropriate amount of reagent in distilled water. The solution of Tl(I) and Bi(III) was prepared from the stock standard solution (1 g L⁻¹, Merck) in 0.1 mol L⁻¹ HNO₃. The interference effect was checked using standard solutions of 1 g L⁻¹ Fe(III), Cu(II), V(V), Zn(II), Mn(II), Ni(II), Sn(IV), Se(IV), Mo(VI), Sb(III), Cd(II) and Pb(II) (Merck). The influence of organic substances was investigated based on the following surfactants: Triton X-100, sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB), which were all purchased from Fluka. Solutions were prepared using ultra-purified water (>18 M Ω cm) supplied by a Milli-Q system (Millipore, UK). Amberlite XAD-7 resin (Sigma) was prepared by rinsing four times with distilled water and dried at 50 °C before use.

For the analysis following certified reference materials were used: TMRAIN-04 (rain water, the National Research Council, Canada), SRM 1640a (natural water, National Institute of Standards and Technology, USA) and SPS-SW2 (surface water, Spectrapure Standards AS, Norway). All water samples were added to the supporting electrolyte and analyzed after 30 s shaking with 0.5 g Amberlite XAD-7 resin.

2.3. Voltammetric procedure

The measurements were performed under optimized conditions from buffer solution (0.0265 mol L⁻¹ CH₃COONH₄, 0.0235 mol L⁻¹ CH₃COOH and 0.0235 mol L⁻¹ NH₄Cl) of pH = 4.6 ± 0.1 containing 1 × 10⁻⁵ mol L⁻¹ EDTA, 1 × 10⁻⁵ mol L⁻¹ Bi(III) and Tl(I). The following sequence of potentials was applied to the electrode: 0.5 V for 10 s and -1.1 V for 60 s. First step was performed for electrochemical cleaning of the working electrode surface. Then, during the second step the bismuth film was plated and thallium was deposited onto the surface of the electrode simultaneously. During both steps the solution was stirred with the use of magnetic stirring bar. After the equilibrium period of 5 s, square wave voltammograms were recorded from -1.1 to 0.5 V. The frequency of the measurements was

40 Hz, the amplitude 75 mV and the scan rate 150 mV s^{-1} . Measurements were recorded from non-deaerated solutions. The background current was subtracted from each registered voltammograms and then they were cut from -0.9 to -0.45 V .

3. Results and discussion

3.1. The working electrode surface selection and characteristics

The electrode surface modification can influence both the height and the shape of the signal obtained for analyzed substance. Furthermore, in order to show possibility of application of developed sensor in field analysis of Tl(I) four types of commercially available, integrated screen-printed electrodes were applied: (1) screen-printed carbon electrode with platinum auxiliary electrode and silver reference electrode, (2) screen-printed carbon electrode modified in situ with bismuth film, with platinum auxiliary electrode and silver reference electrode, (3) screen-printed carbon electrode modified with bismuth (III) oxide (Bi_2O_3), with carbon auxiliary electrode and silver reference electrode, and (4) thick-film bismuth electrode with carbon auxiliary electrode and silver reference electrode. The electrode 2 was modified during measurement of Tl(I) with a bismuth film. Measurements were performed from buffer solution ($0.053 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.047 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.047 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$) of $\text{pH} = 4.6 \pm 0.1$ containing $5 \times 10^{-3} \text{ mol L}^{-1} \text{ EDTA}$, $2 \times 10^{-6} \text{ mol L}^{-1} \text{ Bi(III)}$ (only in the case of the electrode 2) and 5×10^{-9} or $1 \times 10^{-8} \text{ mol L}^{-1} \text{ Tl(I)}$. It was found that the signal obtained with the use of in situ modified bismuth-film carbon electrode is the highest, best shaped and easiest to measure in comparison to the other working electrodes. Additionally, modification of the electrode surface with bismuth film results in benefits of increased sensitivity. The in situ plating is simple and rapid in principle (electrode surface is plated during deposition of Tl). Therefore, this type of the electrode was recognized as the most appropriate for Tl(I) analysis and was used for the further studies.

The effect of covering the working electrode surface with bismuth was confirmed after comparison of the images of bare and in situ modified electrode surface obtained through optical and scanning electron microscopes (Fig. 1A). In the optical microscope image, the presence of bismuth particles is marginally visible in form of shining bright points (Fig. 1Ab), which did not appear on the bare electrode surface (Fig. 1Aa). The images obtained by scanning electron microscope show homogenous structure of the unmodified carbon working electrode (Fig. 1Ac). After the in situ deposition of bismuth bright wavy lines appeared on the electrode surface, which are clusters of bismuth particles (Fig. 1Ad). It was further confirmed by XPS spectra (Fig. 1B), which revealed significant amounts of Bi. Based on the results obtained we concluded that modification of the electrode surface with bismuth film leads to increase of the working electrode surface area and in consequence enhances Tl(I) peak current.

3.2. Effect of the type, pH and concentration of the supporting electrolyte

In search for the appropriate type of the supporting electrolyte for the determination of Tl(I) the solutions prepared by mixing $1 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$ with appropriate volume of $1 \text{ mol L}^{-1} \text{ HCl}$ to achieve pH values of 3.8, 4.6 and 5.9, $1 \text{ mol L}^{-1} \text{ HCl}$, $1 \text{ mol L}^{-1} \text{ PIPES}$ buffer ($\text{pH} = 7.0$) and $1 \text{ mol L}^{-1} \text{ PIPES}$ buffer ($\text{pH} = 7.0$) with addition of 0.1 mol L^{-1} sodium-potassium tartrate (applied in order to prevent precipitation of bismuth hydroxide) were investigated. 1.0 mL these solutions were added to voltammetric cell. The square wave voltammograms were recorded from solution containing also

$5 \times 10^{-3} \text{ mol L}^{-1} \text{ EDTA}$, $2 \times 10^{-6} \text{ mol L}^{-1} \text{ Bi(III)}$ and increasing concentrations of Tl(I), ranging from 5×10^{-9} to $5 \times 10^{-7} \text{ mol L}^{-1}$.

The best analytical signals of Tl(I) were received for the solution prepared by mixing $1 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$ with appropriate volume of $1 \text{ mol L}^{-1} \text{ HCl}$ to achieve pH value of 3.8, 4.6 and 5.9. The peak currents were similar when the pH was between 3.8 and 4.6. Use of a solution with a higher pH (4.6) caused a decrease in Pb(II) peak current. This effect is desirable due to occurrence of Pb(II) ions in real water samples. Low pH values favor deposition of lead on the working electrode surface. When the solution with pH of 5.9 was used no signal of Pb(II) was obtained. However, the peak current of Tl(I) decreased about 10 times relative to previous ones. No signals of Tl(I) were obtained using PIPES buffer with and without addition of the sodium-potassium tartrate solution in the tested concentration range. Based on conducted research the buffer solution containing $0.053 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.047 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.047 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ of $\text{pH} = 4.6 \pm 0.1$ was selected.

The influence of the concentration of $\text{CH}_3\text{COONH}_4$ used for preparation of the supporting electrolyte on Tl(I) signal was examined in the range from 0.0125 to 0.125 mol L^{-1} . This influence was checked on the signal of Tl(I) obtained for the concentration of 5×10^{-8} and $2 \times 10^{-7} \text{ mol L}^{-1}$. The highest signals were obtained for the concentration of $\text{CH}_3\text{COONH}_4$ used for preparation of the supporting electrolyte equal to 0.05 mol L^{-1} .

3.3. Influence of EDTA and Bi(III) concentration

Authors of works that involved stripping voltammetry for Tl(I) determination frequently use EDTA to minimize the influence of Cd(II) and Pb(II) ions [27,29,30,33,34]. These common pollutants are electrochemically active and their peaks appear close to the Tl(I) peak, which renders the performance of quantitative analysis difficult. Addition of EDTA to the solution creates permanent complexes with interfering ions and in consequence they no longer influence the Tl(I) signal. It should be noted that in the published paper the influence of supporting electrolyte pH on masking effect of EDTA was studied. It was confirmed that bivalent ions (Pb(II), Cd(II) and Cu(II)) can be masking using EDTA not only at pH 4–5 but also in highly acidic media [37]. It should be mentioned, that DTPA forms more stable complexes with interfering on the Tl(I) signal ions than EDTA, but at pH in the range of 5.5–6.2 [38,39].

In order to minimize influence of Cd(II) and Pb(II) on the peak current of Tl(I) (5×10^{-8} and $2 \times 10^{-7} \text{ mol L}^{-1}$) EDTA at concentration in the range from 5×10^{-7} to $5 \times 10^{-5} \text{ mol L}^{-1}$ was added to the supporting electrolyte. Based on amounts of Cd(II) and Pb(II) present in the real water samples at most 2-fold molar excess of Cd(II) and 10-fold molar excess of Pb(II) relative to Tl(I) concentration were added to the solution. The first stage included adding $1 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ (in the case of Tl(I) concentration of $5 \times 10^{-8} \text{ mol L}^{-1}$) and $4 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ (in the case of Tl(I) concentration of $2 \times 10^{-7} \text{ mol L}^{-1}$). Then portions of EDTA were added to the solution. As it seen in Fig. 2A and B the Tl(I) signal increased after addition of Cd(II) to the solution and then returned to its original value when the concentration of EDTA was equal to $1 \times 10^{-5} \text{ mol L}^{-1}$. It should be added that higher concentrations of EDTA caused slight decrease of the Tl(I) signal.

Then, two series of experiments were conducted. In the first one, to the solution containing Tl(I) ($5 \times 10^{-8} \text{ mol L}^{-1}$) and EDTA ($1 \times 10^{-5} \text{ mol L}^{-1}$) $5 \times 10^{-8} \text{ mol L}^{-1}$ and then $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb(II)}$ were added. In the second case to the solution containing Tl(I) ($2 \times 10^{-7} \text{ mol L}^{-1}$) and EDTA ($1 \times 10^{-5} \text{ mol L}^{-1}$) $2 \times 10^{-7} \text{ mol L}^{-1}$ and then $2 \times 10^{-6} \text{ mol L}^{-1} \text{ Pb(II)}$ were added and analytical signals of Tl(I) were observed. Based on obtained results (Fig. 2C and D) it was found that even a 10-fold excess of Pb(II) did not influence the Tl(I) signal, provided that $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$ is added to the

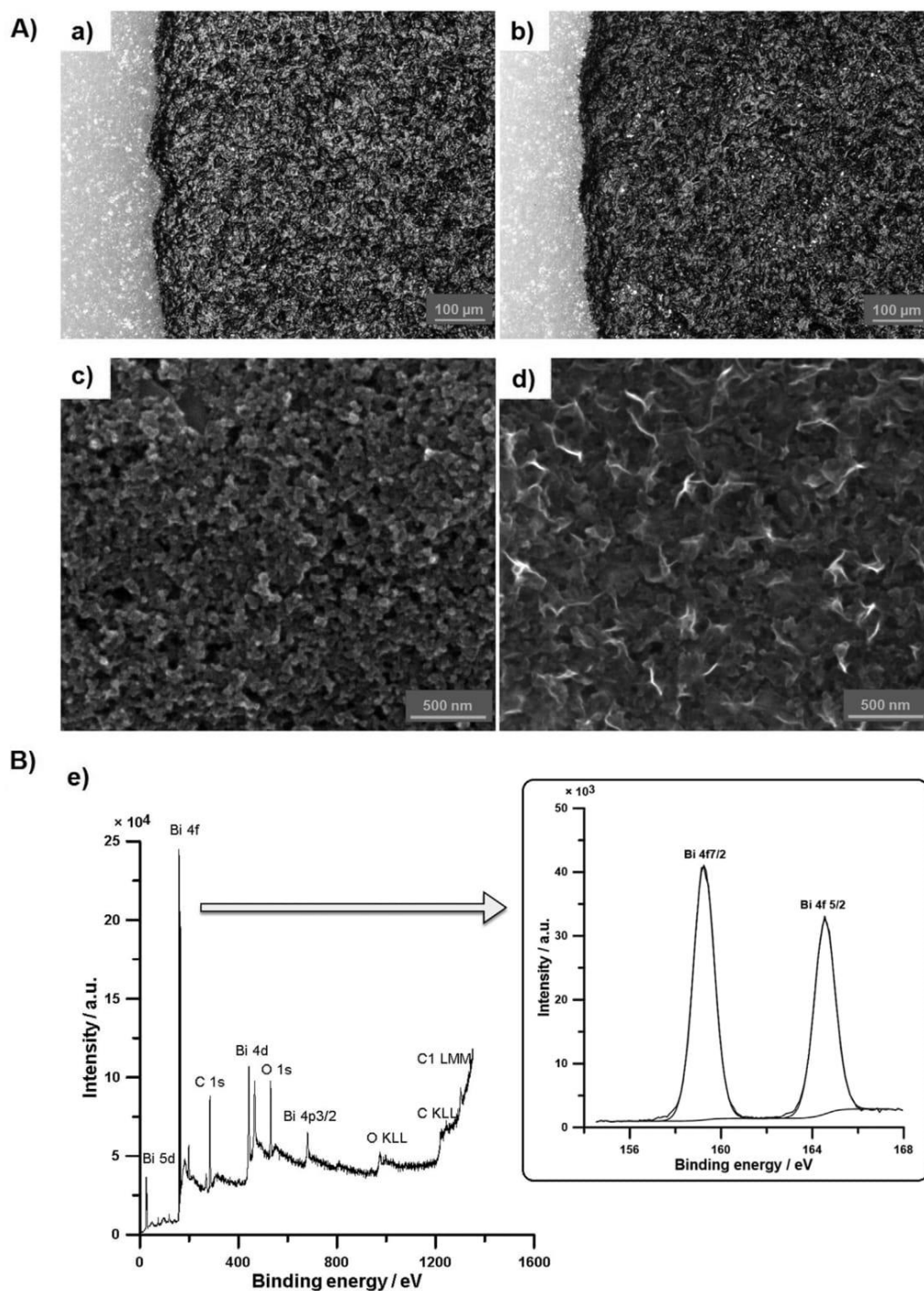


Fig. 1. A) Images obtained through optical microscope (a and b) and scanning electron microscope (c and d) for the bare (a and c) and modified with bismuth film (b and d) working carbon electrode. B) XPS spectrum of the working carbon electrode modified with bismuth with deconvoluted Bi 4f region. Bismuth film modified electrode (b and d) was prepared in situ from the buffer solution ($0.0265 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.0235 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.0235 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$) of $\text{pH} = 4.6 \pm 0.1$ containing $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$ and $1 \times 10^{-5} \text{ mol L}^{-1} \text{ Bi(III)}$.

analyzed solution. It means that the analytical signal does not change more than in the range of $\pm 5\%$ after addition of the aforementioned amounts of Pb(II) .

Preliminary studies have shown that bismuth coating of the screen-printed carbon electrode significantly enhances its analytical signal. On this account, the influence of Bi(III) concentration on

Tl(I) signal was tested. Examined concentrations of Bi(III) were from 0 to $2 \times 10^{-5} \text{ mol L}^{-1}$ and the influence on analytical signal of Tl(I) for concentrations of 5×10^{-8} and $2 \times 10^{-7} \text{ mol L}^{-1}$ investigated. The results obtained demonstrate that the determination of Tl(I) from the solution containing $1 \times 10^{-5} \text{ mol L}^{-1} \text{ Bi(III)}$ results in the highest peak current.

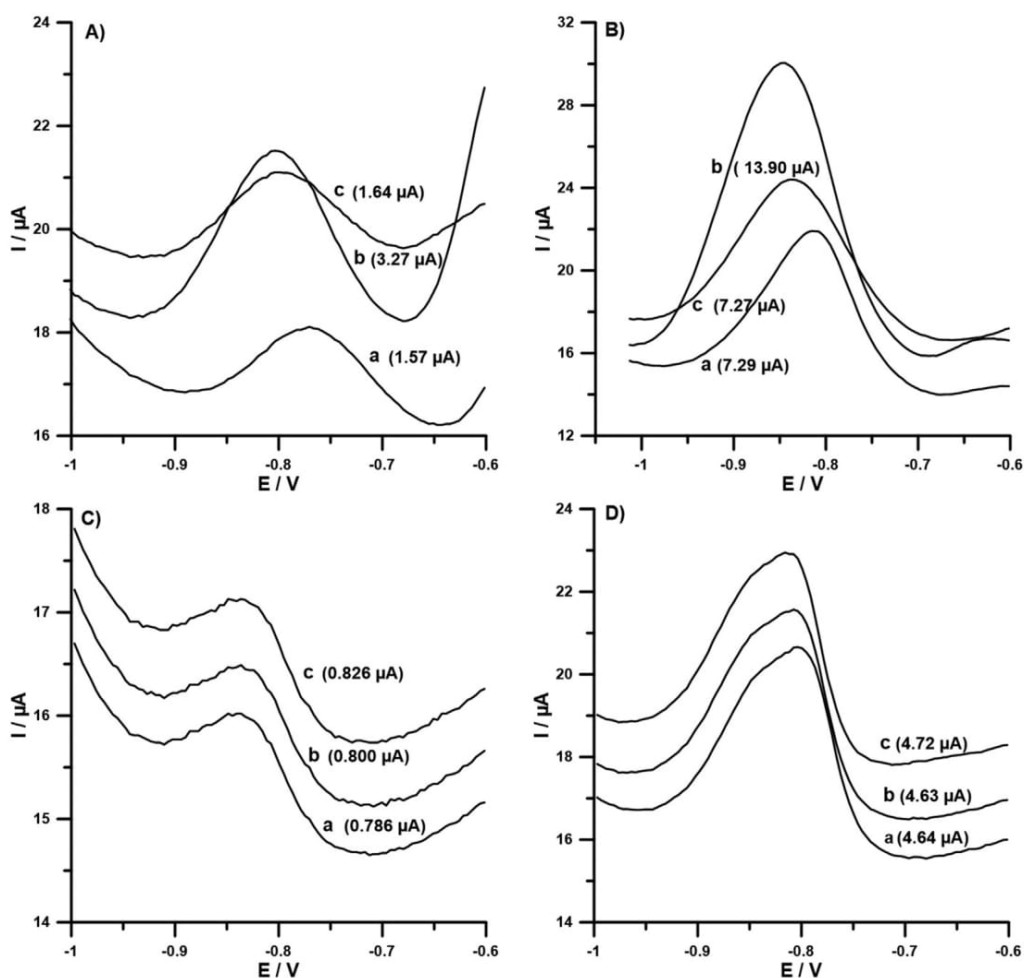


Fig. 2. Square wave voltammograms obtained for the buffer solution ($0.0265 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.0235 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.0235 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$) of $\text{pH} = 4.6 \pm 0.1$, containing $2 \times 10^{-6} \text{ mol L}^{-1} \text{ Bi(III)}$ and: A) a) $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Tl(I)}$; b) as (a) + $1 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ and c) as (b) + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; B) a) $2 \times 10^{-7} \text{ mol L}^{-1} \text{ Tl(I)}$; b) as (a) + $4 \times 10^{-7} \text{ mol L}^{-1} \text{ Cd(II)}$ and c) as (b) + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; C) a) $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Tl(I)}$ + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; b) as (a) + $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Pb(II)}$ and c) as (a) + $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb(II)}$; D) a) $2 \times 10^{-7} \text{ mol L}^{-1} \text{ Tl(I)}$ + $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$; b) as (a) + $2 \times 10^{-7} \text{ mol L}^{-1} \text{ Pb(II)}$ and c) as (a) + $2 \times 10^{-6} \text{ mol L}^{-1} \text{ Pb(II)}$. Electrochemical cleaning of the electrode surface was performed at the potential of 0.3 V for 10 s , simultaneous Bi film plating and Tl depositing at -1.1 V for 60 s .

3.4. Optimization of the procedure parameters

The influence of potential and time for simultaneous Bi plating and Tl deposition on Tl(I) peak current were investigated for the Tl(I) concentrations of 5×10^{-8} and $2 \times 10^{-7} \text{ mol L}^{-1}$. The potential ranged from -0.9 to -1.4 V for time of 60 s . As can be seen in Fig. 3A, the maximum Tl(I) peak currents were obtained for the potential of -1.1 V , so for further measurements this value of potential was adopted. Subsequently the influence of time of simultaneous plating Bi and deposition of Tl was checked for the selected potential in the range from 0 to 2700 s . The dependence of time on the voltammetric signal is presented in Fig. 3B. Prolonging this time caused enhancement of peak current. In order to reduce total analysis time, the time for simultaneous Bi plating and deposition of Tl of 60 s was selected for the further studies. Furthermore, measurements to the calibration curve were carried out also for the time of 300 s in order to demonstrate an easy way to lower detection limit of Tl(I).

The remaining procedure parameters such as frequency, amplitude and scan rate were optimized for 5×10^{-8} and $2 \times 10^{-7} \text{ mol L}^{-1}$ concentrations of Tl(I). The frequency was changed in the range from 10 to 80 Hz . For the concentration of

$5 \times 10^{-8} \text{ mol L}^{-1} \text{ Tl(I)}$, the best results were obtained for frequency of 40 Hz . For higher concentration of Tl(I) ($2 \times 10^{-7} \text{ mol L}^{-1}$) the peak current increased proportionally to frequency, but it became wider and thus more difficult to measure. For this reason 40 Hz was chosen as an optimal value. Amplitude was modified in the range of 10 – 100 mV . For the lower concentration of Tl(I), the highest peak was obtained for 50 mV and those obtained for 75 mV were slightly lower. In the case of higher concentration of Tl(I) the highest signal was obtained for 75 mV , so this value was selected for further work. The examination of optimal scan rate was performed in the range of 10 – 500 mV s^{-1} . With the increase of scan rate value analytical signal was enhancing and becoming wider. Scan rate of 150 mV s^{-1} was found to be optimal.

3.5. Electrochemical cleaning, repeatability, reproducibility

During measurements both metals (Bi and Tl) are deposited onto the electrode surface and might not be completely removed after analysis. The residues may remain and influence the subsequent signals of Tl(I). The electrode design makes it impossible to perform mechanical cleaning of the working electrode surface. Due to this fact, the necessity of electrochemical cleaning of the working

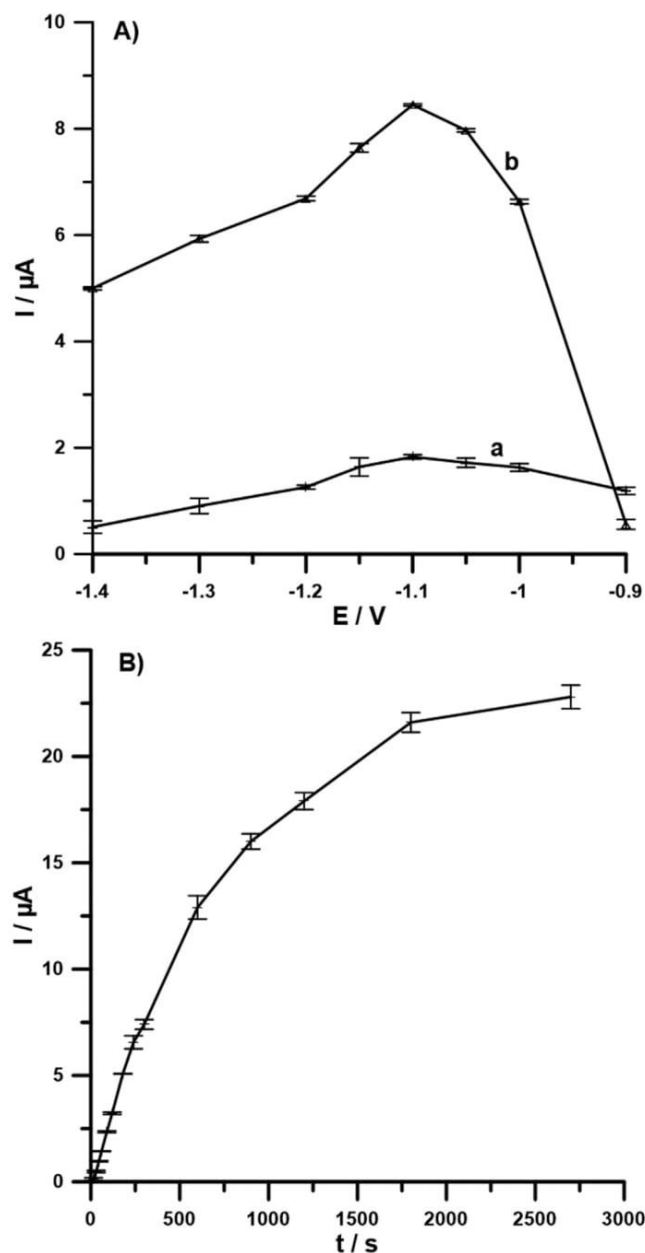


Fig. 3. Influence of simultaneous Bi plating and Tl deposition potential (A) and time (B) on the voltammetric signal of Tl(I). The buffer solution ($0.0265 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.0235 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.0235 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$) of $\text{pH} = 4.6 \pm 0.1$ containing $1 \times 10^{-5} \text{ mol L}^{-1} \text{ Bi(III)}$, $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$ and $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Tl(I)}$ (A (a) and B) or $2 \times 10^{-7} \text{ mol L}^{-1} \text{ Tl(I)}$ (A (b)). Bi was plated and Tl was deposited simultaneously for 60 s (A) at potential of -1.1 V (B). The obtained, average values are shown with standard deviation for $n = 3$.

electrode was verified. For this purpose the cleaning potentials of 0.3 and 0.5 V were applied for the times of 10 and 60 s. Afterwards, measurements were performed without the cleaning step. Voltammograms were recorded 10 times for the concentrations of Tl(I) equal to 5×10^{-8} and $2 \times 10^{-7} \text{ mol L}^{-1}$. Table 1 contains the calculated relative standard deviations for each of the investigated cases. In the light of lower RSD values obtained for measurements performed with cleaning potential of 0.5 V, this value was selected for the further studies. Significant differences between relative standard deviations obtained for time 10 and 60 s were not recorded,

Table 1

Relative standard deviation (RSD) values obtained for determination of Tl(I) without and with electrochemical cleaning step.

Cleaning potential [V]	Time [s]	RSD ^a ($n = 10$) [%]	RSD ^b ($n = 10$) [%]
—	0	5.02	4.12
0.3	10	3.64	2.45
	60	4.31	1.97
0.5	10	2.14	1.23
	60	3.77	0.83

RSD – relative standard deviation.

^a $C_{\text{Tl(I)}} = 5 \times 10^{-8} \text{ mol L}^{-1}$.

^b $C_{\text{Tl(I)}} = 2 \times 10^{-7} \text{ mol L}^{-1}$.

albeit since the procedure should be suitable for rapid field analysis, it was decided to cut the total analysis time and electrochemical cleaning time of 10 s was approved.

Additionally, values of relative standard deviation (2.14% for $5 \times 10^{-8} \text{ mol L}^{-1}$ of Tl(I) and 1.23% for $2 \times 10^{-7} \text{ mol L}^{-1}$ of Tl(I), $n = 10$) confirm the satisfactory repeatability of measurements carried out with use of the integrated three-electrode screen-printed sensor with in situ plated bismuth film carbon working electrode. In order to test electrode-to-electrode reproducibility of the proposed electrode measurements were performed for the concentration of Tl(I) $1 \times 10^{-7} \text{ mol L}^{-1}$ with the use of three independently prepared electrodes. Based on obtained findings relative standard deviation was calculated and its value is 2.45% ($n = 9$). This proves that the reproducibility of the proposed sensor is satisfactory.

3.6. Calibration graphs

The optimized voltammetric procedure with the use of integrated screen-printed sensor consisting of an in situ plated bismuth film carbon working electrode was adapted for the determination of Tl(I). Measurements for calibration graphs were carried out for the deposition time of 60 and 300 s. The wide ranges of linearity were obtained, from 5×10^{-9} to $1 \times 10^{-6} \text{ mol L}^{-1}$ and from 5×10^{-11} to $1 \times 10^{-9} \text{ mol L}^{-1}$ for deposition times of 60 and 300 s, respectively. The equation of calibration graph was $y = (56.38 \pm 0.17)x - (0.90 \pm 0.016)$ for deposition time of 60 s, where x – Tl(I) concentration [$\mu\text{mol L}^{-1}$] and y – peak current [μA]. The linearity of the calibration curve is confirmed by correlation coefficient ($r = 0.9996$). For deposition time of 300 s the equation for calibration graph was $y = (18.73 \pm 0.09)x - (0.81 \pm 0.042)$, where x – Tl(I) concentration [nmol L^{-1}] and y – peak current [μA]. The correlation coefficient (r) was 0.9990. The standard deviations for the slope and y-intercept of calibration graphs were calculated for three repetitions. The calibration graphs for deposition time of 60 and 300 s as well as voltammograms obtained for the determination of Tl(I) at deposition time of 300 s are presented in Fig. 4. Limits of detection (LOD) and quantification (LOQ) were calculated as 3 or 10 times the standard deviation ($n = 5$) for the blank divided by the slope of the calibration curve. Obtained LODs were $8.47 \times 10^{-10} \text{ mol L}^{-1}$ and $6.71 \times 10^{-12} \text{ mol L}^{-1}$ and LOQs were $2.87 \times 10^{-9} \text{ mol L}^{-1}$ and $2.24 \times 10^{-11} \text{ mol L}^{-1}$ for deposition times of 60 and 300 s, respectively. The obtained results (linear range, detection limit and deposition time) were compared with those of other voltammetric methods for Tl(I) determination at Bi based electrodes (Table 2) [23–34]. When compared with other voltammetric methods, the obtained LODs are generally lower. The similar limit of detection was obtained in paper [34], but the distinguishing quality of the present procedure is the application of commercially available, miniaturized, and integrated three-electrode sensor, which is easily modified during rapid analysis and suitable for use

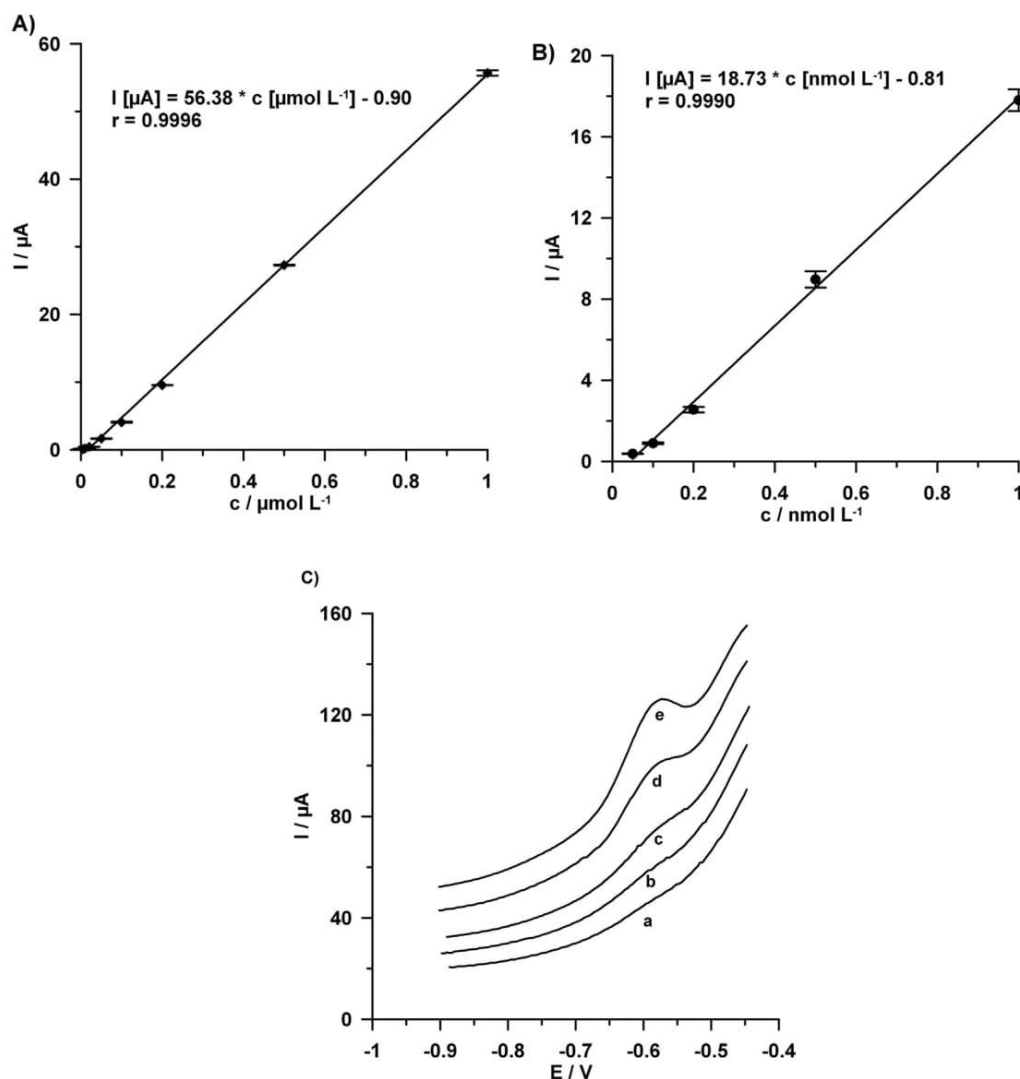


Fig. 4. The calibration graphs of Tl(I) in the linear range for the deposition time of: A) 60 and B) 300 s. C) Square wave voltammograms for additions of increasing concentrations of Tl(I): a) 5.0×10^{-11} , b) 1.0×10^{-10} , c) 2.0×10^{-10} , d) 5.0×10^{-10} , e) $1.0 \times 10^{-9} mol L^{-1}$ in buffer solution ($0.0265 mol L^{-1} CH_3COONH_4$, $0.0235 mol L^{-1} CH_3COOH$ and $0.0235 mol L^{-1} NH_4Cl$) of $pH = 4.6 \pm 0.1$, solution containing $1 \times 10^{-5} mol L^{-1}$ EDTA, $1 \times 10^{-5} mol L^{-1}$ Bi(III). Electrochemical cleaning of the electrode surface was performed at the potential of 0.5 V for 10 s, simultaneous Bi film plating and Tl depositing at -1.1 V for 60 (A) and 300 s (B and C).

in a portable analyzer. It should be mentioned that there are other methods that allow the determination of thallium on a higher or similar level of concentration. In the case of ICP-MS limits of detection amount to $1.95 \times 10^{-12} mol L^{-1}$ [7] and $4.89 \times 10^{-11} mol L^{-1}$ [8], in case of FAAS $6.12 \times 10^{-9} mol L^{-1}$ [9], GFAAS $2.45 \times 10^{-9} mol L^{-1}$ [10] and ETAAS $9.78 \times 10^{-11} mol L^{-1}$ [11]. The main disadvantage of these methods is lack of possibility of performing the analysis outside the laboratory. The proposed procedure enables application of the miniaturized sensor in a portable apparatus and the conduction of sensitive and rapid analysis at the sampling site (field analysis).

3.7. Study of interferences

The influence of various metal ions occurrence in water samples was checked for the constant concentration of Tl(I) equal to $1 \times 10^{-7} mol L^{-1}$. No influence on thallium peak was observed after addition of $5 \times 10^{-7} mol L^{-1}$ Cu(II), Sb(III), Mo(VI), V(V) and Sn(IV), $1 \times 10^{-6} mol L^{-1}$ of Zn(II), Ni(II) and Se(IV), $2 \times 10^{-7} mol L^{-1}$ of

Mn(II) and $5 \times 10^{-6} mol L^{-1}$ of Fe(III). It means that presence of the aforesaid amounts of metal ions does not trigger a thallium peak current error in excess of $\pm 5\%$. The influence of Cd(II) and Pb(II) on Tl(I) signal was checked and is presented in section 3.3.

The presence of organic substances in natural water samples negatively influences the voltammetric signals. Therefore the effect of surfactants on Tl(I) signal was also investigated. CTAB, SDS and Triton X-100 were added in concentrations ranging from 0 to $50 mg L^{-1}$ to the solution containing $1 \times 10^{-7} mol L^{-1}$ of Tl(I). It was found that the addition of $1 mg L^{-1}$ SDS and $5 mg L^{-1}$ Triton X-100 does not lead to decrease of Tl(I) peak by more than $\pm 5\%$. However, SDS and Triton X-100 concentrations of $10 mg L^{-1}$ decreased the Tl(I) peak height to 71 and 56% of its original value, respectively. The most significant influence on Tl(I) peak current was observed during addition of CTAB. The Tl(I) peak completely disappeared at CTAB concentration of $10 mg L^{-1}$. According to the literature data, natural waters contain surfactants with the surface active effect similar to the influence induced by 0.2–2.0 ppm of Triton X-100 [40]. The obtained results and the literature data demonstrate that

Table 2

The comparison of the voltammetric method enabled Tl(I) determination with the use of bismuth based working electrodes.

Working electrode/technique	Linear range [mol L ⁻¹]	Detection limit [mol L ⁻¹]	Deposition time [s]	Reference
BiFE/SWASV	—	—	120	[23]
BiFE/SWASV	9.80×10^{-8} – 9.80×10^{-7}	1.96×10^{-8}	120	[24]
Bi-graphite electrode/ ASV	4.89×10^{-8} – 4.89×10^{-6a}	4.89×10^{-9}	600	[25]
BiFE/DPASV	0 – 9.78×10^{-7}	4.42×10^{-9}	60	[26]
BiFE/SWASV	2.00×10^{-9} – 3.00×10^{-8}	6.00×10^{-10}	300	[27]
BiFE ^b /SWASV	1.20×10^{-8} – 1.50×10^{-7}	1.08×10^{-8}	120	[28]
Bi nanopowder electrode/SWASV	4.89×10^{-9} – 4.89×10^{-8}	1.46×10^{-10}	600	[29]
Microfabricated BiFEs/ SWASV	4.89×10^{-8} – 4.89×10^{-7}	2.93×10^{-9}	240	[30]
BiF/GCE/SWASV	4.89×10^{-8} – 3.91×10^{-7}	—	—	—
BiF/GCE/SWASV	5.00×10^{-9} – 2.00×10^{-7}	1.91×10^{-9}	120	[31]
BiF/CFE/SWASV	5.00×10^{-9} – 4.50×10^{-7}	2.04×10^{-9}	120	[31]
SPEs modified with Bi	2.45×10^{-8} – 2.20×10^{-7c}	4.89×10^{-9}	120	[32]
precursor compounds/ DPASV	2.45×10^{-8} – 1.96×10^{-7d}	5.38×10^{-9}	120	[32]
	2.45×10^{-8} – 1.96×10^{-7e}	4.40×10^{-9}	120	[32]
BiF/SPE/DPASV	2.45×10^{-8} – 1.96×10^{-7}	7.83×10^{-9}	120	[32]
BiFE/SWASV	5.00×10^{-11} – 5.00×10^{-9}	2.10×10^{-11}	600 ^f	[33]
BiABE/DPASV	5.00×10^{-11} – 1.40×10^{-9}	5.00×10^{-12}	300	[34]
BiFE/SPCE/SWASV	5.00×10^{-9} – 1.00×10^{-6}	8.47×10^{-10}	60	This work
	5.00×10^{-11} – 1.00×10^{-9}	6.71×10^{-12}	300	

BiFE - bismuth film electrode; SWASV - square wave anodic stripping voltammetry; DPASV - differential pulse anodic stripping voltammetry; GCE - glassy carbon electrode; CFE - carbon film electrode; SPE - screen-printed electrode; BiABE - bismuth bulk annular band electrode; BiFE/SPCE - bismuth film screen-printed carbon electrode.

^a Accumulation time of 2–3 min.

^b Rotating-disc bismuth film electrode.

^c Modifier - bismuth oxide.

^d Modifier - bismuth zirconate.

^e Modifier - bismuth aluminate.

^f Double deposition.

the determination of Tl(I) by the proposed method in water samples can be performed without sample preparation. However, in environmental water samples containing high concentrations of organic compounds the results show the necessity to minimize the negative effect of surfactants on Tl(I) peak. One of the methods commonly used for decomposition of the interfering organic matrix is the mineralization of sample. This method is effective but not adequate in case of field analysis. In order to resolve this problem, the application of Amberlite XAD-7 resin was proposed [40–42]. This method of sample preparation is easy to perform outside the laboratory. Volumes of the resin and sample shaking time were optimized. Optimization of the mass of resin (0.15, 0.3, 0.5 or 1.0 g) for time of shaking equal to 4 min was carried out for concentration of Tl(I) equal to 1×10^{-7} mol L⁻¹. 1×10^{-5} mol L⁻¹ EDTA and increasing concentrations of CTAB (0–50 mg L⁻¹) were added to the solution containing 0.0265 mol L⁻¹ CH₃COONH₄, 0.0235 mol L⁻¹ CH₃COOH and 0.0235 mol L⁻¹ NH₄Cl (pH = 4.6 ± 0.1). CTAB was selected as a representative surfactant due to its greatest negative impact on Tl(I) peaks. After each addition of surfactant, the solution was shaken for 4 min in the presence of resin. During this stage surfactants were adsorbed on the resin surface but Tl(I) remained in the solution. Fig. 5 presents the influence of CTAB on the relative signal of Tl(I). As we see in the case of CTAB concentrations that were lower and higher than 5.0 mg L⁻¹ the best results were obtained for 0.5 and 1.0 g of Amberlite XAD-7 resin, respectively. To reduce the amount of used reagent, 0.5 g of resin was recognized as sufficient for the removal of surfactants.

For 0.5 g of Amberlite XAD-7 the sample shaking time was optimized. For this purpose we first recorded the voltammograms for the solution containing 0.0265 mol L⁻¹ CH₃COONH₄, 0.0235 mol L⁻¹ CH₃COOH and 0.0235 mol L⁻¹ NH₄Cl (pH = 4.6 ± 0.1), 1×10^{-5} mol L⁻¹ EDTA, 1×10^{-5} mol L⁻¹ Bi(III) and 1×10^{-7} mol L⁻¹ Tl(I). Then we added 2 mg L⁻¹ of CTAB and 0.5 g of resin to the electrochemical cell and the solution was shaken for various periods of time, ranging from 15 to 240 s. The studies

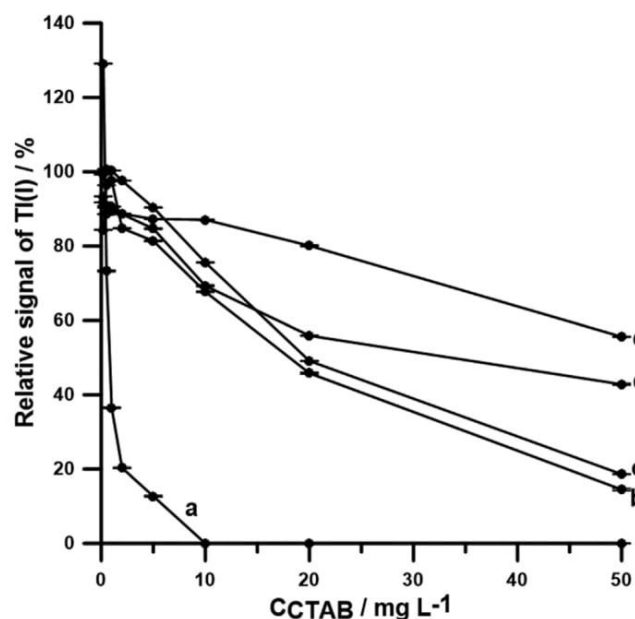


Fig. 5. The influence of CTAB on relative signal of 1×10^{-7} mol L⁻¹ Tl(I) without (a) and with mixing of the solution with 0.15 g (b), 0.3 g (c), 0.5 g (d) and 1.0 g (e) of Amberlite XAD-7 resin. Time of mixing 4 min. Electrochemical cleaning of the electrode surface was performed at the potential of 0.5 V for 10 s, simultaneous Bi film plating and Tl depositing at -1.1 V for 60 s. The obtained, average values are shown with standard deviation for $n = 3$.

demonstrated that after 30 s the Tl(I) peak current returned to $92.0 \pm 0.9\%$ of its original value (i.e. before the addition of CTAB to solution). Therefore, the 30 s time was chosen for further measurements.

3.8. Application

The newly developed procedure was applied for the determination of Tl(I) in certified reference materials: SPS SW-2 (surface water), SRM 1640a (natural water) and TMRain-04 (rain water). Before the determination of Tl(I), and in order to eliminate influence of organic substances on the analytical signal of Tl(I), 0.5 g of Amberlite XAD-7 resin was added to the electrochemical cell containing buffer solution ($0.0265 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.0235 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.0235 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$) of $\text{pH} = 4.6 \pm 0.1$, $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$, $1 \times 10^{-5} \text{ mol L}^{-1} \text{ Bi(III)}$, and an appropriate volume of sample and it was shaken for 30 s. Then measurements were performed under optimized conditions for the same cell, without removal of resin. Quantification was carried out with the use of standard additional method. Examples of voltammograms registered during determination of Tl(I) in certified reference material (SPS SW-2) are shown in Fig. 6. Results obtained during water samples analyses are presented in Table 3. As can be seen, the relative error between result obtained by the proposed method and certified value is lower than 5%. Additionally, according to the t-Student test there are no significant differences between the recoveries obtained by both methods, suggesting 95% confidence level. The calculated t values ($t_{\text{exp.}}$) are in the range of 0–0.65, which is below the critical value equal to 1.81 (for degrees

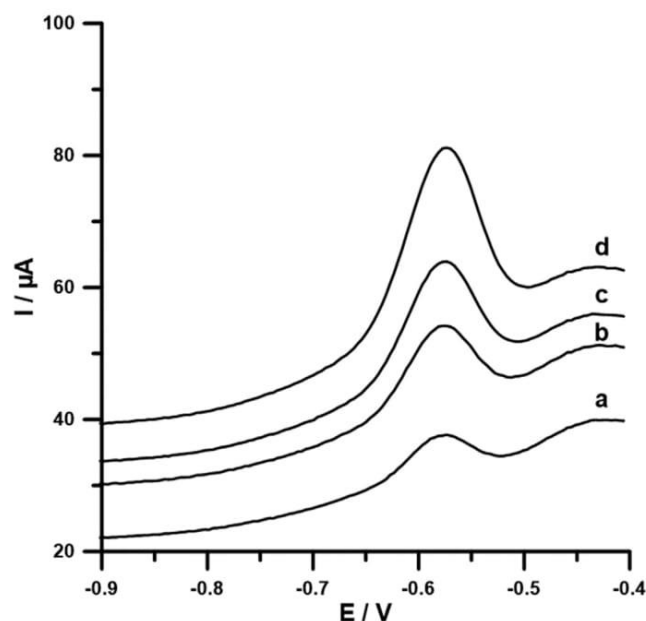


Fig. 6. Square wave voltammograms registered from the buffer solution ($0.0265 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.0235 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.0235 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$) of $\text{pH} = 4.6 \pm 0.1$, containing: a) $1 \times 10^{-5} \text{ mol L}^{-1} \text{ EDTA}$, $1 \times 10^{-5} \text{ mol L}^{-1} \text{ Bi(III)}$ and $164 \mu\text{L}$ sample, b) as (a) + $2 \times 10^{-10} \text{ mol L}^{-1} \text{ Tl(I)}$, c) as (a) + $4 \times 10^{-10} \text{ mol L}^{-1} \text{ Tl(I)}$ and d) as (a) + $6 \times 10^{-10} \text{ mol L}^{-1} \text{ Tl(I)}$. Electrochemical cleaning of the electrode surface was performed at the potential of 0.5 V for 10 s , simultaneous Bi film plating and Tl depositing at -1.1 V for 300 s .

Table 3

Results received during determination of Tl(I) in certified reference materials.

Certified reference material	Measured value $\pm \text{SD}$ ($n = 3$) [nmol L^{-1}]	Certified value $\pm \text{SD}$ ($n = 3$) [nmol L^{-1}]	Relative error [%]	$t_{\text{exp.}}$
SRM 1640a	7.86 ± 0.27	7.86 ± 0.073	0	0
SPS SW-2	0.128 ± 0.013	0.122 ± 0.00098	4.92	0.65
TMRain-04	1.91 ± 0.095	1.84 ± 0.29	3.66	0.34

of freedom, f , equal to 4, $f = n_1 + n_2 - 2$). The obtained results prove that the use of integrated screen-printed carbon sensor with in situ plated bismuth film carbon working electrode allowed to obtain precise, and accurate results in water samples.

4. Conclusions

Commercially available integrated three-electrode screen-printed sensor with carbon electrode modified in situ with bismuth film turned out to be an excellent device for voltammetric determination and quantification of Tl(I) in natural water samples. The proposed sensor is environmentally friendly. Simplicity and very short time of the electrode preparation enable fast, sensitive (limits of detection are 8.47×10^{-10} and 6.71×10^{-12} for the deposition times of 60 and 300 s, respectively) and selective analysis. Thanks to the addition of EDTA and 30 s of sample shaking with Amberlite XAD-7 resin the influence of foreign metal ions and organic matter in water samples were minimized. It should be noted that voltammetric measurements were performed without removal of resin from the electrochemical cell. Furthermore, the proposed sensor and simple procedure for Tl(I) determination are potentially applicable for field analysis.

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Publikacja 3

K. Tyszczyk-Rotko, **Katarzyna Jędruchniewicz**, *Ultrasensitive sensor for uranium monitoring in water ecosystems*, Journal of The Electrochemical Society 166 **(2019)** B837-B844.



Ultrasensitive Sensor for Uranium Monitoring in Water Ecosystems

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In the present paper, sensor based on the integrated three-electrode screen-printed system with in situ plated lead film working electrode (SPCE/PbF) was fabricated, and its microscopic and electrochemical characteristics were investigated. For the first time, a new supporting electrolyte composition ($\text{CH}_3\text{COONH}_4$, CH_3COOH and NH_4Cl of $\text{pH} = 5.9 \pm 0.1$) has been proposed in order to improve electrochemical response of SPCE/PbF toward U(VI) determination. The differential pulse adsorptive stripping voltammetric (DPAdSV) signal of U(VI) increased linearly from 0.1 to 10 nmol L^{-1} with limit of detection of 0.019 nmol L^{-1} and sensitivity of $0.97 \pm 0.00015 \mu\text{A/nmol L}^{-1}$. The applicability of the SPCE/PbF for trace concentrations of U(VI) in water samples with the use of resin in order to minimize the influence of organic matrix was successfully demonstrated.

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Uranium is an element that naturally occurs in the three isotopic forms of ^{238}U (99.27%), ^{235}U (0.72%) and ^{234}U (0.0054%).¹ In the environment uranium occurs in oxocationic form UO_2^{2+} , where uranium oxidation state is +VI (the most stable form).² Uranium is a comparatively mobile element and it is harmful to health due to its radioactivity and chemical toxicity.^{3–5} Concentrations of uranium in environmental samples are generally very low (e.g. in the Kalikratia area in Northern Greece uranium concentration in groundwater were in the 0.01–10 $\mu\text{g L}^{-1}$ range), but due to the usage of uranium in production of nuclear energy and its acquisition stages: uranium mining, milling, conversion and enrichment, the contamination levels can significantly increase.^{6–8}

People who working with uranium products and processes or living in contaminated areas (e.g. military zones) are the most exposed to toxic effects of uranium.⁹ Uranium's most likely pathway the human body is through contaminated water and food.¹⁰ The organs exposed directly to the toxic activity of uranium are the kidneys and the skeleton, where it tends to accumulate.^{9,11} It was also demonstrated that uranium is toxic to the lungs, the liver and the brain.⁷ Therefore, it is necessary to control uranium contamination levels in environmental samples such as water, soil and air.

Different instrumental techniques enable uranium determination in environmental samples. Suitable techniques for this purpose are, for example inductively coupled plasma optical emission spectrometry (ICP-OES),^{12,13} inductively coupled plasma optical emission spectrometry (ICP-MS),^{14–16} spectrophotometry,^{17,18} fluorometry,¹⁹ gamma-ray spectroscopy²⁰ or accelerator mass spectrometry.²¹ However, each of them has limitations which hamper their use, e.g. strong spectral interferences of other elements (Ca, Fe, V, Zr) during the determination of uranium by ICP-OES or constricted quantification in high saline samples due to suppression of the analyte ionization.²² Furthermore, the mentioned methods are not suitable for field analysis (large size of apparatus) and their use generates high costs (purchase and maintenance of expensive equipment, consumption of large amount of high quality of reagents).

Electrochemical techniques, especially voltammetry, offer performance of sensitive, precise and fast analyses.²³ One of the most popular sensors involved for uranium determination is the hanging mercury drop electrode (HMDE), which has a lot of advantages, but it is rarely applied because of volatility and toxicity of mercury.^{24–30} Examples of alternative electrodes used for uranium quantification were: double electrode system, where the first electrode was modified with lead glassy carbon electrode (GCE) with a large surface area and the second was an ensemble of five carbon composite microelectrodes also modified with lead, glassy carbon electrodes modified in situ with various metals: bismuth, mercury and lead or ex situ bismuth-coated GCE.^{31–36} Moreover, other modified sensors were also applied: polymer coated glassy carbon electrode obtained by electropolymerization

of N-phenylanthranilic acid and carbon nanotube-modified GCE.^{37,23} For the same purpose application of rotating-disk bismuth-film electrode also was possible.³⁸ All of the proposed sensors ensure low detection limits, but they allow the analyses to be carried out only in the laboratories. They cannot be applied in a portable analyzer, thus rendering a field analysis impossible.

Due to increasing environmental pollution especially heavy metal pollution it is necessary to develop proper tools for carrying out rapid analysis at the place where the sample is collected.³⁹ This enables us to control of metal ions and organic pollutants concentrations and prevent long-scale environmental contamination.⁴⁰ Screen-printing is a promising technology used for the production of inexpensive and miniaturized sensors for rapid routine analyses.^{41,42} Integrated screen-printed electrodes (SPE) are the type of miniaturized sensor, where a three-electrode system is placed on a support and they can be incorporated in portable analyzers and applied in field analyses.⁴³ Due to the miniaturized size of SPEs, they enable the analysis of small sample volumes and reduce reagents consumption. Other advantages of this devices are commercial availability, low cost, high reproducibility and possibility to application in fast and simple quantification of wide range of substances at very low concentrations.^{44,45}

To the best of our knowledge, there is only one work in the subject literature, where screen-printed sensor (graphite screen-printed electrode) was applied as a working electrode for uranium determination.⁴⁶ However, application of this sensor does not provide a sufficiently low detection limit, as well a short time of analysis of U(VI) in the environmental water samples. The limit of detection at a preconcentration time of 30 min. was 4.5 nmol L^{-1} . Therefore, there is still a need to develop sensor that will allow to determine very low U(VI) concentrations (the order of 10^{-11} – $10^{-10} \text{ mol L}^{-1}$) not only in the laboratory but also in the place where the sample was collected. Therefore the aim of our research was to fabricate screen-printed sensor for the selective and sensitive determination of U(VI) in environmental water samples.

Experimental

Materials.—5 mol L^{-1} $\text{CH}_3\text{COONH}_4$ (Sigma-Aldrich) and 1 mol L^{-1} HCl (Fluka) were used for the preparation of supporting electrolyte. After mixing the appropriate volumes of these reagents and after allowing for the reaction between them the buffer solution (0.92 mol L^{-1} $\text{CH}_3\text{COONH}_4$, 0.08 mol L^{-1} CH_3COOH and 0.08 mol L^{-1} NH_4Cl) of $\text{pH} = 5.9 \pm 0.1$ was obtained. The standard solutions of U(VI) (0.01 mol L^{-1}) was prepared from $(\text{CH}_3\text{COO})_2\text{UO}_2 \cdot 2\text{H}_2\text{O}$ by dissolution of reagent in 0.1 mol L^{-1} HNO_3 . A 0.01 mol L^{-1} solution of $\text{Pb}(\text{NO}_3)_2$ was prepared from reagent acquired from Sigma-Aldrich. The interference effect was checked using standard solutions of Zn(II), Co(II), Cu(II), Cd(II), Mn(II), Fe(III), Al(III), V(V), Mo(VI) and Ni(II) (Merck). Triton X-100, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were purchased from Fluka. 0.02 mol L^{-1} cupferron (N-nitrosophenylhydroxylamine ammonium salt, Merck) solution was subsequently prepared every day

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by dissolving the reagent in water. Amberlite XAD-7 and XAD-16 resins (Sigma) were prepared by rinsing four times with distilled water and dried at 50°C before use. The certified reference material, SRM 1640a (trace element in natural water, National Institute of Standards and Technology, USA) was obtained from Sigma-Aldrich. The environmental water samples were collected from Bystrzyca river (Lublin, Poland). All water samples were added to the supporting electrolyte and analyzed after 30 s by shaking with 0.5 g Amberlite XAD-16 resin. Additionally, the analysis of samples of certified reference material after UV mineralization (3 hours) was also performed.

Instrumentation.—The voltammetric measurements were performed in a potentiostat μ Autolab integrated with GPES 4.9 software (Eco Chemie, Utrecht, The Netherlands) and electrode stand (M164D, MTM Anko, Krakow, Poland). The measurements were carried out using sensor based on the integrated three-electrode screen-printed system with in situ plated lead film carbon working electrode (SPCE/PbF) in a 10 mL one-compartment electrochemical cell. The lead film was electrochemically plated at the carbon working electrode surface (4 mm diameter) of commercially available integrated three-electrode screen-printed sensor (DropSens, ref. 150) with a platinum auxiliary electrode and silver reference electrode.

In order to acquire images of the surface morphology and the destitution of lead particles, high-resolution microscopes, FEI Dual-Beam Quanta 3D FEG scanning electron microscope (SEM) and Tecnai G2 T20 X-TWIN (FEI) transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectrometer (EDS) were employed.

The water samples were mineralized using a UV-digester made by Mineral, Poland. The conductivity of supporting electrolytes was measured with use of conductivity meter, (CDM 83, Radiometer).

Electrochemical assays.—The differential pulse adsorptive stripping voltammetry (DPAdSV) was employed as a sensitive voltammetric technique for the quantification of U(VI). Under optimized conditions the voltammetric measurements of U(VI) were performed in buffer solution (0.092 mol L⁻¹ CH₃COONH₄, 0.008 mol L⁻¹ CH₃COOH and 0.008 mol L⁻¹ NH₄Cl) of pH = 5.9 ± 0.1, containing 2.5 × 10⁻⁵ mol L⁻¹ Pb(II) and 1 × 10⁻⁴ mol L⁻¹ cupferron. Electrochemical cleaning of the electrode surface was performed at the potential of 0.2 V for a period of 10 s. Then, at the potential of -1.1 V for 60 s the lead film was plated in situ at the carbon screen-printed working electrode surface, and at -0.75 V for 60 s the simultaneous further deposition of lead and U(VI)-cupferron complexes accumulation were performed. After the equilibrium period of 5 s, the differential pulse voltammograms were recorded in the potential range from -0.65 to -1.75 V. The experimental conditions for the differential pulse voltammetry (DPV) were: pulse amplitude of 150 mV and scan rate of 100 mV s⁻¹. The background current was subtracted from each registered voltammograms and then they were cut from -0.65 to -1.3 V.

Results and Discussion

Selection of support and surface modifier.—One the most sensitive methods of U(VI) determination is based on the adsorption of a U(VI)-cupferron complexes at the lead film electrode surface.^{31,34,35} However, the proposed sensor and procedures of measurement are not adapted for field analysis, at the sample collection site. These limitations were overcome, in the present paper, by applying sensor based on the integrated three-electrode screen-printed system with lead film working electrode, and a simple method of sample preparation.

In the first stage of experiments, the lead film electrodes plated at the different, commercially available screen-printed supports were checked. No analytical signal of U(VI) was obtained in the tested range of concentrations (1 × 10⁻⁸ – 1 × 10⁻⁷ mol L⁻¹) with the use of following supports: carbon nanofibers modified screen printed carbon electrode (DropSens, ref. CNF110), multi-walled carbon nanotubes modified screen printed carbon electrode (DropSens, ref. CNT110),

graphene modified screen printed carbon electrode (DropSens, ref. GPH110), as well as commercially available lead film screen printed electrode (DropSens, ref. PB10). The well-shaped and symmetrical reduction peaks of U(VI)-cupferron complexes were obtained only at three-electrode screen-printed sensor carbon working electrode (DropSens, ref. 150) modified in situ with lead film in the solution containing 0.2 mol L⁻¹ acetate buffer of pH equal to 4.2 ± 0.1, 2.5 × 10⁻⁵ mol L⁻¹ Pb(II) and 6 × 10⁻⁵ mol L⁻¹ cupferron. The U(VI)-cupferron complexes were accumulated at potential of -0.75 V for 60 s. These conditions were derived from the previously published work.³⁵ The influence of other screen printed carbon electrode surface metal film modifiers (bismuth, antimony, gold) on the U(VI) signals (1 × 10⁻⁸ – 1 × 10⁻⁷ mol L⁻¹) was also investigated. No analytical signal of U(VI) was obtained with the use tested metal film modifiers. In the further part of the experimental work, the research was conducted using the integrated three-electrode screen-printed sensors with in situ plated lead film carbon working electrode.

Selection of supporting electrolyte, the effects of its pH and concentration.—In this paper, for the first time, a new supporting electrolyte composition (CH₃COONH₄, CH₃COOH and NH₄Cl) has been proposed in order to improve the electrochemical response of SPCE/PbF toward U(VI) determination. As it can be seen in Fig. 1A, the application of buffer solution (0.077 mol L⁻¹ CH₃COONH₄, 0.123 mol L⁻¹ CH₃COOH and 0.123 mol L⁻¹ NH₄Cl) of pH 4.2 obtained after mixing 0.2 mol L⁻¹ CH₃COONH₄ with 0.123 mol L⁻¹ HCl instead of 0.2 mol L⁻¹ acetate buffer solution (CH₃COONa and CH₃COOH) of pH 4.2, as recommended in previous works,^{31,34,35} contributes to the amplification of the U(VI) signals (1.08 vs. 0.36 μ A for 5 nmol L⁻¹ of U(VI) and 2.03 vs. 0.69 μ A for 10 nmol L⁻¹ of U(VI), respectively), improving the shape of the peak and shifting the potential of the peak toward less-negative potentials (-0.96 vs. -1.12 V, respectively). It is connected with improvement of conductivity of the supporting electrolyte, which was confirmed by conductivity measurements (3.63 vs. 1.09 mS cm⁻¹, respectively). It should be mentioned that the reduction mechanism of U(VI)-cupferron complexes was investigated and is well described in literature.^{32,47} Thus, it can be concluded that the obtained peaks in buffer solution (0.077 mol L⁻¹ CH₃COONH₄, 0.123 mol L⁻¹ CH₃COOH and 0.123 mol L⁻¹ NH₄Cl) of pH 4.2 at potential of -0.96 V are connected with the U(VI) to U(V) reduction process ([U(VI)-cupferron]_{ads} + e → [U(V)-cupferron]_{ads}) and lower peaks at potential of -1.18 V are connected with U(V) to U(III) reduction process ([U(V)-cupferron]_{ads} + 2e → [U(III)-cupferron]_{ads}). For analytical purposes, the higher peaks at the potential of -0.96 V were used.

In the next stages of work, the influence of pH and concentration of supporting electrolyte on the peak current of U(VI) was examined. The influence of pH of the buffer solution (CH₃COONH₄, CH₃COOH and NH₄Cl) on the stripping response was studied in the range of 3.8 to 6.5. As it can be seen in Fig. 1B, the responses for the U(VI) at concentrations of 5 and 10 nmol L⁻¹ increase rapidly with the pH and then drop rapidly above pH of 5.9. This profile indicates that pH of 5.9 offers the most favorable performance. The increase and then drop of the analytical signal might have been caused by different form of cupferron in different pH values.³⁷ The amino oxide form of cupferron (varying from neutral to slightly acidic) favors the catalytic mechanism. Next, the influence of the concentration of the supporting electrolyte of pH = 5.9 ± 0.1 on the peak current in solution containing 5 and 10 nmol L⁻¹ U(VI) was studied in the range from 0.046 to 0.23 mol L⁻¹ with reference to CH₃COONH₄. As can be seen in Fig. 1C, the highest signal levels were obtained for the pH 5.9 buffer containing 0.092 mol L⁻¹ CH₃COONH₄, 0.008 mol L⁻¹ CH₃COOH and 0.008 mol L⁻¹ NH₄Cl, therefore such concentrations of buffer components were selected for the subsequent experiments.

Effect of Pb(II) and cupferron concentrations.—The influence of the concentration of Pb(II) in the range of 0–2.5 × 10⁻⁴ mol L⁻¹ on the peak current of U(VI) (0.5 and 5 nmol L⁻¹) was studied (Fig. 2A). The obtained results demonstrated that well-defined U(VI) peaks were

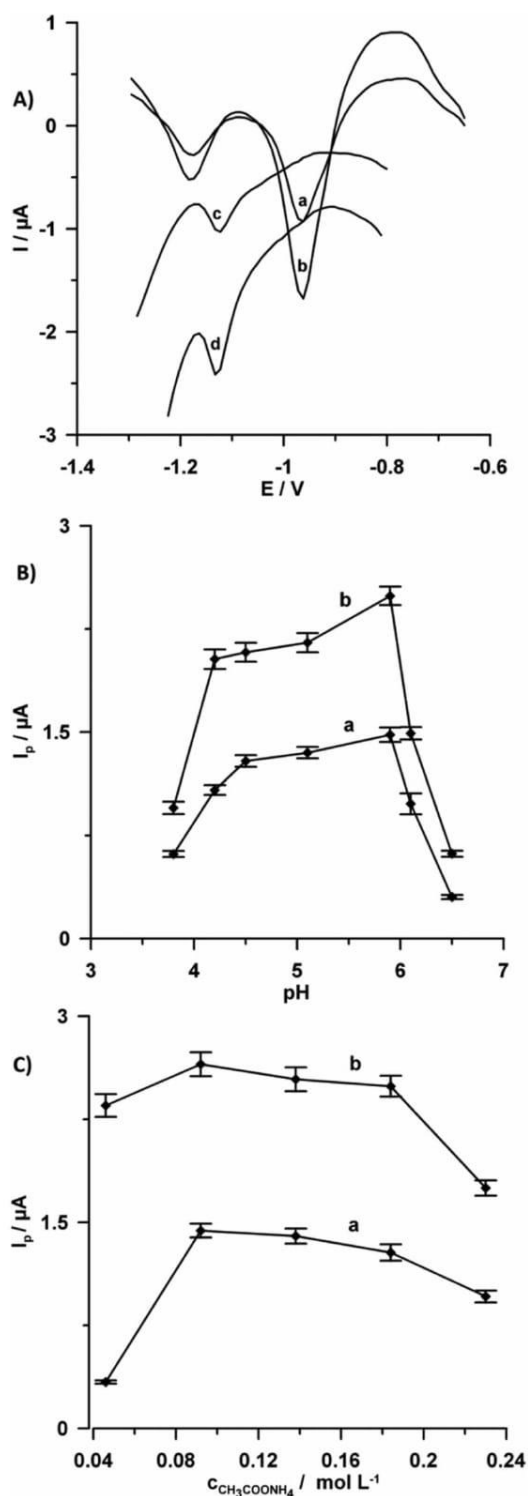


Figure 1. (A) Comparison of the DPAdSV voltammograms obtained at the SPCE/PbF for 5 (a and c) and 10 nmol L^{-1} (b and d) of U(VI) in buffer solution ($\text{CH}_3\text{COONH}_4$, CH_3COOH and NH_4Cl) of pH 4.2 obtained after mixing 0.2 mol L^{-1} $\text{CH}_3\text{COONH}_4$ with 0.123 mol L^{-1} HCl (c and d) and in 0.2 mol L^{-1} acetate buffer solution (CH_3COONa and CH_3COOH) of pH 4.2 (a and b). The influence of pH (B) and concentration (C) of the buffer solution ($\text{CH}_3\text{COONH}_4$, CH_3COOH and NH_4Cl) on the stripping response of 5 (a) and 10 nmol L^{-1} (b) of U(VI). The lead film was deposited at -1.1 V for 60 s, the U(VI)-cupferron complexes were accumulated for 60 s at the potential of -0.75 V.

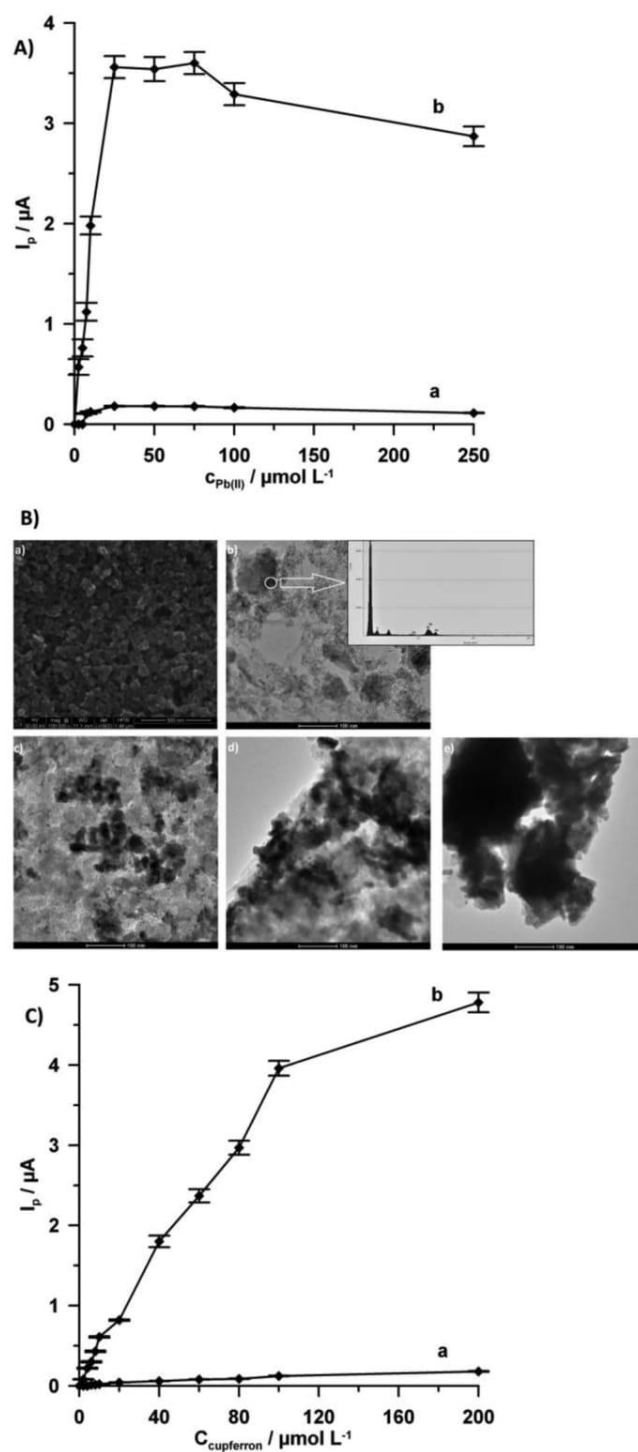


Figure 2. (A) The influence of the Pb(II) concentration on the peak current of U(VI) (0.5 and 5 nmol L^{-1} , a and b, respectively). (B) SEM (a) and TEM (b-e) images of SPCE/PbF obtained from solution containing different concentrations of Pb(II) : $2.5 \times 10^{-5} \text{ mol L}^{-1}$ (a and b), $1 \times 10^{-4} \text{ mol L}^{-1}$ (c), $2.5 \times 10^{-4} \text{ mol L}^{-1}$ (d), $2.5 \times 10^{-3} \text{ mol L}^{-1}$ (e). EDS spectrum of highlighted part of TEM image (inset of Fig. 2Bb). (C) The influence of cupferron concentration on the peak current of U(VI) (0.5 and 5 nmol L^{-1} , a and b, respectively). Other conditions as in Fig. 1.

observed only at the screen printed carbon electrode modified with lead, thus confirming earlier studies, which indicated that lead film modified electrode significantly influences on the electrochemical response toward U(VI) reduction in comparison with the unmodified electrode.^{31,34,35} Additionally, it was found that the U(VI) peaks reach maximum values in the concentration range of Pb(II) $2.5 \times 10^{-5} - 7.5 \times 10^{-5} \text{ mol L}^{-1}$, and then the peak currents slightly decreased. Therefore we selected the concentration of $2.5 \times 10^{-5} \text{ mol L}^{-1}$ of Pb(II) for further experiments. Furthermore, the morphology of screen printed carbon layer modified with lead film was characterized by SEM and TEM techniques (Fig. 2B). The SEM image for the SPCE/PbF obtained from solution containing $2.5 \times 10^{-5} \text{ mol L}^{-1}$ Pb(II), indicated that the screen printed carbon surface is homogeneous, yet the lead particles were not visible. However, higher magnifications screen printed structure with agglomerates of lead nanoparticles can be seen in TEM image. The presence of lead is manifested by a series of signals on the EDS spectrum. The reduction of the U(VI) signal for the Pb(II) concentrations above $7.5 \times 10^{-5} \text{ mol L}^{-1}$ can be explained by the active surface electrode being blocked by the forming lead film. The TEM images (Fig. 2B) show the lead film deposition as the concentration of Pb(II) increases.

According to Panelli et al. cupferron plays the double role of complexing and oxidizing agent, leading to a parallel chemical re-oxidation of U(III) to U(V) and hence to an enhanced signal.⁴⁷ Therefore, investigation of the impact of cupferron concentrations on the analytical signal of U(VI) is an important stage in the optimization of the procedure. Therefore, the influence of cupferron concentration was investigated in the range from $0-2 \times 10^{-4} \text{ mol L}^{-1}$ for the U(VI) concentrations of 0.5 and 5 nmol L^{-1} (Fig. 2C). The responses increase rapidly with the ligand concentration in the entire examined range. However, for the cupferron concentrations above $1 \times 10^{-4} \text{ mol L}^{-1}$ the U(VI) peaks (for 0.5 nmol L^{-1}) are distorted. That's why further studies were conducted using the cupferron concentration of $1 \times 10^{-4} \text{ mol L}^{-1}$.

Optimization of lead film plating and U(VI) determination procedure.—The results obtained during optimization of the potential and deposition time of lead film are shown in Fig. 3A. The influence of deposition potential ($E_{\text{dep.}}$, from -1.3 to -0.75 V) and deposition time ($t_{\text{dep.}}$, from 0 to 180 s) on the peak current height for 0.5 and 5 nmol L^{-1} of U(VI) were studied. The results indicate that lead film can be deposited most effectively on the electrode surface at the potential of -1.1 V , so this value was chosen for further study. Furthermore, the deposition time of 60 s was selected, even though the peak current increases with increase of time in the whole studied range. Such a choice was dictated by distortion of the U(VI) peak at times that were higher than 60 s, and the fact that the analyses are to be conducted in field conditions, so the analysis time must be short.

The accumulation conditions strongly influence the sensitivity and limit of detection of the stripping voltammetry techniques. Therefore, the influence of accumulation potential ($E_{\text{acc.}}$, from -1.1 to -0.6 V) and time ($t_{\text{acc.}}$, from 0 to 600 s) of U(VI)-cupferron complexes on the peak current height of 0.5 and 5 nmol L^{-1} U(VI) were studied (Fig. 3B). As can be seen, the highest peak currents for both studied concentrations of U(VI) were obtained at the potential in the range of -0.7 – $(-0.8) \text{ V}$, so for further study we selected the potential of -0.75 V for U(VI)-cupferron complexes accumulation. It should be mentioned that at this value of the potential the further deposition of lead film is also performed. In the case of accumulation time, the peak current of U(VI) for both studied concentrations increased almost linearly up to the value of 300 s. Further increase of $t_{\text{acc.}}$ caused decrease of voltammetric signals of U(VI). For the subsequent studies the accumulation time of 60 s was chosen, due to fact of future application of the sensor for the field analyses of U(VI). However, in order to improve the detection and quantification limits of method the prolongation of the accumulation time up to 300 s is recommended.

To optimize the conditions of the differential pulse adsorptive stripping voltammetric determination of U(VI), the following instrumental parameters were varied: pulse amplitude (dE, from 25 to 200 mV) and

Table I. Analytical parameters obtained during differential pulse adsorptive stripping voltammetric determination of U(VI) at the SPCE/PbF in buffer solution ($\text{CH}_3\text{COONH}_4$, CH_3COOH and NH_4Cl) of pH = 5.9 ± 0.1 .

Parameter	
Linear range [nmol L^{-1}]	0.1–10
Accumulation time [s]	60
Slope (b) $\pm$ SD [$\mu\text{A/nmol L}^{-1}$]	0.97 ± 0.00015
Intercept (a) $\pm$ SD [μA]	0.029 ± 0.0062
Correlation coefficient (r)	0.9988
LOD [nmol L^{-1}]	0.019
LOQ [nmol L^{-1}]	0.063
Intra-day precision (RSD) [%]	2.2
Inter-day precision (RSD) [%]	4.5
Reproducibility (RSD) [%]	5.4

SD – standard deviation for $n = 3$; RSD – relative standard deviation for $n = 10$ and U(VI) concentration of 0.5 nmol L^{-1} .

scan rate (v , from 25 to 125 mV s^{-1}) (Fig. 3C). It was found, that for both studied concentrations of U(VI) (0.5 and 5 nmol L^{-1}) the peak current increased with increases of dE up to 150 mV and v up to 100 mV s^{-1} . In view of these results, the pulse amplitude of 150 mV and scan rate of 100 mV s^{-1} were selected for further experiments.

Analytical performance.—Quantitative evaluations were carried out using DPAdSV technique from the linear relationships between the peak currents and increasing concentrations of U(VI) under optimized conditions. The obtained voltammograms were background-subtracted using application included in the GPES software suite (Fig. 4). The corresponding plot was created from the mean value of three replicated measurements for each concentration of U(VI) (inset of Fig. 4), and it was linear in the range from 0.1 to 10 nmol L^{-1} . The sensitivity of U(VI) determination was evaluated from the slope of calibration plot and it was $0.97 \pm 0.00015 \mu\text{A/nmol L}^{-1}$. The limits of detection (LOD) and quantification (LOQ) were calculated from the calibration plot according to the IUPAC recommendations: $k \text{ SD}_a/b$, where $k = 3$ for LOD and $k = 10$ for LOQ, SD_a is the standard deviation of the intercept ($n = 3$), and b is a slope of the calibration plot.⁴⁸ The estimated LOD and LOQ values for U(VI) on the SPCE/PbF were 0.019 and $0.063 \text{ nmol L}^{-1}$, respectively. The parameters obtained with use of the SPCE/PbF were summarized in Table I. It should be clearly indicated that for the shortest analysis time the proposed sensor allows to obtain the lowest limits of detection and quantification compared to all other sensors.^{23–38,46} Additionally, for the first time, the proposed sensor can be applied in portable analyzer, which enables us to perform field analysis of U(VI) in concentrations that actually occur in environmental water samples. Furthermore, the obtained limit of detection is significantly lower than obtained for another techniques applied for uranium determination in environmental samples: 2.4 nmol L^{-1} and 1.8 nmol L^{-1} for ICP-OES,^{12,13} 210 nmol L^{-1} for ICP-MS,¹⁴ 2.5 nmol L^{-1} for spectrophotometry¹⁷ and 0.13 nmol L^{-1} for fluorometric determination of uranium.¹⁹

In addition, the precision of the proposed DPAdSV technique using the SPCE/PbF as an intra-day and inter-day precision was tested by recording ten voltammograms at the concentration of U(VI) of 0.5 nmol L^{-1} . Intra-day precision expressed as within-laboratory within-day variations was estimated at 3.9%, while the inter-day value expressed as within-laboratory across-day (5 days) variations was 4.5%. Such repeatability of the signal reflects the efficient cleaning step (0.2 V for 10 s), i.e. removal of the lead film and U(VI)-cupferron complexes from the previous measurement and absence of memory effect.³² The reproducibility of the SPCE/PbF was evaluated by recording differential pulse voltammograms in the same solution containing 0.5 nmol L^{-1} U(VI) using three different SPCEs modified with PbF.

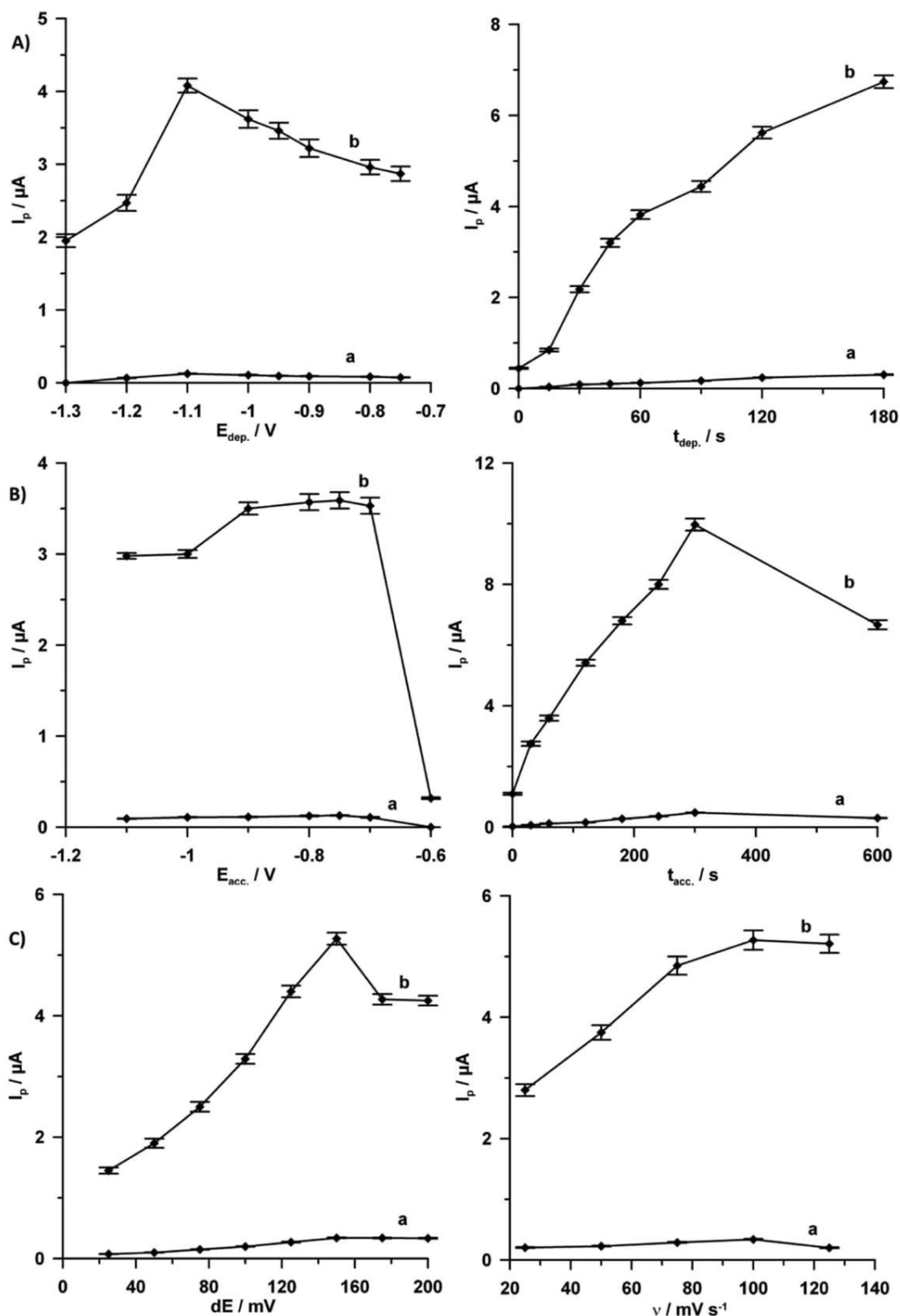


Figure 3. The influence of optimized parameters on the stripping signal of 0.5 (a) and 5 nmol L⁻¹ (b) U(VI): (A) the potential ($E_{dep.}$, from -1.3 to -0.75 V, left figure) and time ($t_{dep.}$, from 0 to 180 s, right figure) deposition of lead film, (B) the accumulation potential ($E_{acc.}$, from -1.1 to -0.6 V, left figure) and time ($t_{acc.}$, from 0 to 600 s, right figure) of U(VI)-cupferron complexes, (C) pulse amplitude (dE , from 25 to 200 mV, left figure) and scan rate (v , from 25 to 125 mV s⁻¹, right figure). The obtained, average values of peak current are shown with standard deviation for $n = 3$. Other conditions as in Electrochemical assays section.

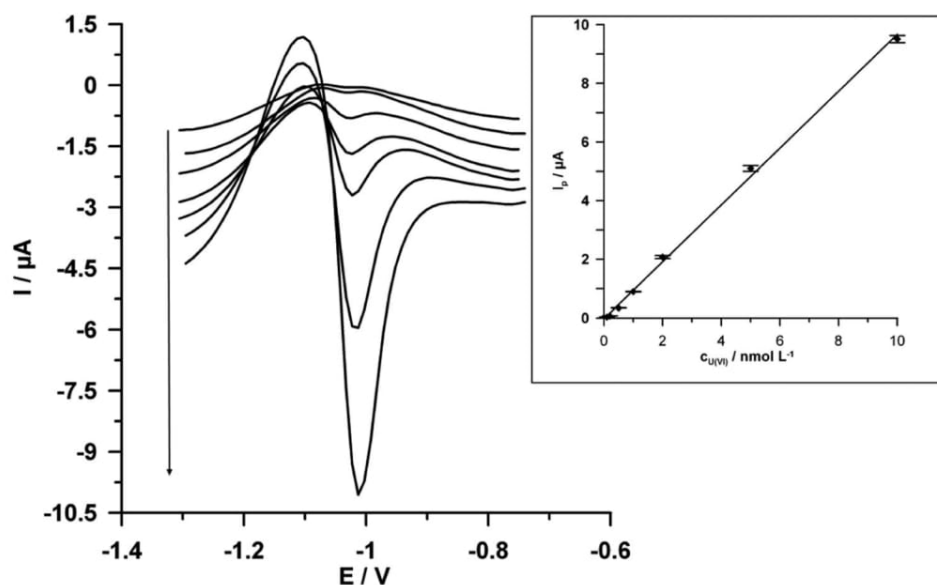


Figure 4. DPAdSV voltammograms recorded at the SPCE/PbF in the supporting electrolyte containing increasing concentrations of U(VI) (from the top to the bottom): 0.1, 0.2, 0.5, 1, 2, 5, to 10 nmol L⁻¹, respectively. Inset: the corresponding calibration graph. The obtained, average values of peak current are shown with standard deviation for $n = 3$. Other conditions as in Electrochemical assays section.

The RSD was calculated as 5.4% ($n = 9$) confirming the satisfactory reproducibility of the proposed sensor.

Study of selectivity.—The selectivity of the developed DPAdSV procedure for the determination of U(VI) with the use of SPCE/PbF was studied. The major sources of interferences in voltammetric measurements based on adsorption of analyte are surfactants that can block the electrode surface and other metal ions that form complexes with the complexing agent for analyte. The effect of several metal ions as well as surfactants on the U(VI) (5.0 nmol L⁻¹) was studied. The experimental results are presented in Table II. The tolerance limit was defined as the concentration of the interferent, which resulted in and error in excess of $\pm 10\%$ in the determination of U(VI). The obtained results suggested that: *) no significant changes in reduction peak of U(VI)-cupferron complex were observed with the concentrations of the tested metal ions, which can be found in environmental water samples, **) surfactant have a significant impact on the analytical signals, therefore their impact must be minimized. Because the sensor is to be used for work outside the laboratory, application of Amberlite XAD-7

and Amberlite XAD-16 resins was proposed. In the first step of experiments, the predicted adsorption of U(VI)-cupferron complexes on the resins surface was confirmed by decreasing voltammetric signal of U(VI) from measurement to measurement. Therefore, the measurements were performed in two-steps. In the first step, the 10 mL of appropriate concentration of standard solution of surfactant and/or U(VI) was shaken for 30 s with 0.5 g of resin (the mass and time of shaking were taken from previous work).⁴⁹ In the second step, the appropriate volume of the solution was transferred to the voltammetric cell and measurements were performed according procedure described in Electrochemical assays section. On the basis of the obtained results (see Table II) it can be concluded that this simple method forms a very effective way for minimizing influence of an organic matrix of water samples on the analytical signal. The studies also demonstrated that the use of Amberlite XAD-16 resin allows to determine U(VI) in the presence of higher concentrations of surfactants in comparison to Amberlite XAD-7 resin, so the Amberlite XAD-16 resin was selected for further studies.

Analytical application.—The applicability of the developed procedure utilizing an integrated three-electrode screen-printed sensor with in situ plated lead film carbon working electrode was tested by means of certified reference material (SRM 1640a, natural water) and Bystrzyca river water samples. It was found that U(VI) was not detectable in the river water samples, thus the samples were spiked with appropriated concentrations of standard solution of uranium. In both cases 10 mL of the samples were shaken with 0.5 g of Amberlite XAD-16 resin for 30 s before analysis and then the appropriate volume of the sample was transferred to the voltammetric cell and quantifications were performed using the standard additional method. Additionally, in order to confirm the correctness of the procedure of minimizing interference, analysis of samples of certified reference material after UV mineralization was also performed. Examples of voltammograms registered during determination of U(VI) in analyzed river water samples are shown in Fig. 5. As can be seen in Table III the relative error between result obtained by the proposed method and certified value is equal to 0, which proves the high degree of accuracy of the method. It was also confirmed by the t-Student test. The calculated t value (t_{exp} , 0) does not exceed the critical value t_{crit} (4.303, level of significance of 0.05, number of degrees of freedom (f) of 2, $f = n - 1$), and therefore it must be concluded that the measured value is not different from the certified value in a statistically significant manner. Furthermore, there

Table II. Maximum tolerance concentration of interfering species with 5.0 nmol L⁻¹ U(VI) under optimum conditions.

Meal ions	Tolerance concentration [nmol L ⁻¹]		
Zn(II), Co(II)	50000		
Cu(II)	10000		
Cd(II), Mn(II), Fe(III)	5000		
Al(III)	1000		
V(V), Mo(VI), Ni(II)	100		
Surfactants	Tolerance concentration [ppm]		
	without resin	Amberlite XAD-7 ^a	Amberlite XAD-16 ^a
CTAB	0.01	20	20
Triton X-100	0.01	1	20
SDS	0.1	1	3

^athe sample shaking with 0.5 g of resin for 30 s.

Table III. Analytical application of DPAdSV technique with the use of SPCE/PbF for the U(VI) determination.

Certified reference material	Measured value $\pm$ SD (n = 3) [$\mu\text{mol L}^{-1}$] ^a	Measured value $\pm$ SD (n = 3) [$\mu\text{mol L}^{-1}$] ^b	Certified value $\pm$ SD [$\mu\text{mol L}^{-1}$]	Relative error [%] ^c	t _{exp.}
SRM 1640a	0.11 $\pm$ 0.0066	0.10 $\pm$ 0.0092	0.11 $\pm$ 0.0011	0	0 ^d ; 1.53 ^e
Sample	Added [nmol L ⁻¹]	Found [nmol L ⁻¹]	Recovery $\pm$ RSD (n = 3) [%]		
Bystrzyca river	0	-	-		
	5.0	5.02	100.4 $\pm$ 4.4		
	20.0	19.7	98.5 $\pm$ 1.8		

^athe sample shaking with 0.5 g of Amberlite XAD-16 resin for 30 s.^bUV- mineralization of the sample for 3 hours.^crelative error [%] = (certified value – measured value^a)/certified value $\times$ 100%.^dcompare the certified and measured^a values.^ecompare two sets of measured values^{a,b}.

are no significant differences between two sets of measured values (first set – the sample shaken with 0.5 g of Amberlite XAD-16 resin for 30 s, second set – UV- mineralization of the sample for 3 hours) for the level of significance of 0.05. The calculated *t* value (t_{exp.}) is 1.53, which is below the critical value equal to 2.776 (number of degrees of freedom (*f*) of 4, *f* = *n*₁ + *n*₂ – 2).⁵⁰ Moreover, the recovery values employing the proposed procedure are 98.5 and 100.4 % with the relative standard deviations (RSDs) of 1.8 and 4.4% for the determined U(VI) in Bystrzyca river samples. These results further demonstrate the satisfactory degree of accuracy of the proposed method, as well as its precision.

Conclusions

In the present article, a new type of electrochemical sensor – the integrated three-electrode screen-printed sensor with in situ plated lead film carbon working electrode (SPCE/PbF) – was applied for the first time for the determination of U(VI) by means of differential pulse adsorptive stripping voltammetry (DPAdSV). Furthermore, for the first time, a new supporting electrolyte composition (CH₃COONH₄, CH₃COOH and NH₄Cl of pH = 5.9 $\pm$ 0.1) has been proposed in order to improve electrochemical response of SPCE/PbF toward U(VI) determination. It was shown that under optimized conditions it is possible

to determine ultratrace concentrations of U(VI) with a low detection limit of 0.019 nmol L⁻¹ for the accumulation time of U(VI)-cupferron complexes of 60 s. Negligible influence of metal ions as well as surfactants after application of simple method of sample preparation (shaking the sample within 30 s with 0.5 g of resin) were observed. By analyzing the certified reference material and Bystrzyca river water samples, the usefulness of the SPCE/PbF in environmental analysis of water samples was demonstrated. To the best of our knowledge, for the first time ever, the proposed sensor can be applied in portable analyzer, thus enabling the performance of field analyses of U(VI) in concentrations that actually occur in environmental water samples.

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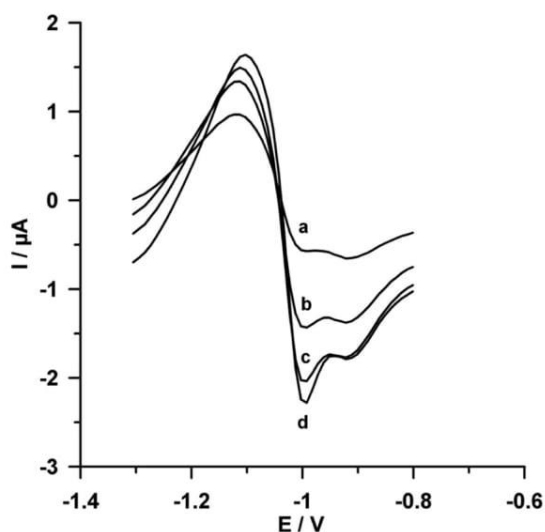


Figure 5. DPAdSV voltammograms recorded at the SPCE/PbF in the course of U(VI) determination in Bystrzyca river water sample: a) 1000 μL of sample, b) as (a) + 0.5 nmol L⁻¹, c) as (a) + 1 nmol L⁻¹, d) as (a) + 1.5 nmol L⁻¹ of U(VI). The sample was shaken with 0.5 g of Amberlite XAD-16 resin for 30 s. Other conditions as in Electrochemical assays section.

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Publikacja 4

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A new modified screen-printed sensor for monitoring of ultratrace concentrations of Mo(VI)

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ABSTRACT

A screen-printed sensor with carbon working electrode *in situ* modified with lead film (PbF/SPCE) was proposed for the adsorptive stripping voltammetric determination of Mo(VI) in natural water samples. For this purpose, Alizarin Red S was applied as a complexing agent. Application of the PbF/SPCE allows to obtain low limit of molybdenum detection ($2.1 \times 10^{-10} \text{ mol L}^{-1}$) and wide linear range of calibration graph (from 1×10^{-9} to $5 \times 10^{-8} \text{ mol L}^{-1}$) for accumulation time of 60 s. Additionally, the developed method was employed to quantify Mo(VI) concentration in two certified reference materials. It was made possible due to introduction of fast and simple sample preparation step for minimizing negative impact of surfactants through shaking water sample (10 mL) with 0.5025 g of Amberlite XAD-16 resin for 30 s. The proposed method with the use of screen-printed sensor is suitable for field analysis.

1. Introduction

Naturally molybdenum does not occur in environment in the metallic form. Predominantly it exists in the Mo(IV) and Mo(VI) species [1]. The concentration of molybdenum in the urban air is about $0.01\text{--}0.03 \mu\text{g L}^{-1}$ in nonurban areas it varies between 0.001 and $0.0032 \mu\text{g L}^{-1}$ and it is not considered as a pathway of molybdenum exposure for humans [2]. Molybdenum compounds may get into the human body through the alimentary pathway. Natural waters contamination with molybdenum is diverse and depends on the water type: in the oceans the concentration of molybdenum is estimated at $0.01 \mu\text{g L}^{-1}$, in drinking water it ranges from 0.11 to $6.21 \mu\text{g L}^{-1}$ and in mineral water it is approximately between 2.3 and $3.3 \mu\text{g L}^{-1}$ [3]. In some places the concentration of Mo can increase (mining areas), for example in Colorado the content of Mo has increased to $400 \mu\text{g L}^{-1}$ (a dose of $150\text{--}500 \mu\text{g day}^{-1}$ is considered safe for adults) [4]. Food can be also significant source of molybdenum, as found e.g. in organ meats, legumes or grains [5]. This element is necessary to maintain good body condition but intake of its large doses can be detrimental [6]. Referring to literature data, in some areas of Armenia the soil contamination of Mo was higher compared to other regions (daily intake of Mo in this area was about 10-times higher). The survey of inhabitants reveals the occurrence of symptoms similar to gout (arthralgia in the knee joints, hands, and feet) [3]. Consequently, it is important to control the molybdenum pollution level in environmental samples (water, soil).

Molybdenum quantification can be performed using different analytical methods [7]. The most widespread and most often applied ones are spectrophotometry [8–10], electrothermal atomic absorption spectrometry (ETAAS) coupled with dispersive liquid-liquid extraction (DLLME) [11,12], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [13,14], inductively coupled plasma mass spectrometry (ICP-MS) [14,15] and ion chromatography [16]. Stripping voltammetry forms a good alternative for the aforesaid methods due to its low cost, simplicity and great possibilities of conducting determinations of metal ions.

A lot of literature data concerning voltammetric determination of Mo(VI) applies to hanging mercury drop electrode [17–24]. In the last decades this type of electrode was one of the most frequently used ones, due to high reproducibility, and it was also considered extremely attractive due to its wide scope of application [25]. In order to reduce work with toxic and simultaneously volatile mercury compounds, different types of sensors for Mo(VI) were developed: bismuth film electrode (BiFE) [26], lead film electrode (PbFE) [27], acetylene black paste electrode (ABPE) [28], multi-walled carbon nanotubes modified carbon paste electrode (MWCNT/CPE) [29] or PVC based sensors [30]. The screen-printing technology was first employed for electrochemical sensors construction in the 1990s [31]. It gives possibility to create environment-friendly, disposable and miniaturized sensors for trace analysis. Additionally, this type of sensors is miniaturized and suitable for portable analyzers for field analysis [32]. It brings many benefits,

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e.g. the possibility to perform preliminary measurements at the place of sampling (eliminating sample transport and storing) and fast detection of water contamination [33]. Literature data reports one work on Mo(VI) determination with use of screen-printed sensor modified with cupferron-tetraphenylborate ion-pair drop coated (Cup-SPCE) [34]. This work presents novel voltammetric method for molybdenum(VI) determination at very low concentration levels with the use of simple prepared screen-printed sensor, modified with lead film.

2. Experimental

2.1. Apparatus

A μ Autolab analyzer (Eco Chemie, Netherlands) was used to conduct all voltammetric experiments. The analyzer and computer were connected with USB electrochemical interface. The three-electrode electrode system used for voltammetric measurements was a commercially available screen-printed electrode consisting of a carbon electrode (4 mm diameter) as a working electrode, a platinum auxiliary electrode and a silver reference electrode (DropSens). The working electrode surface was modified *in situ* with lead during each measurement. The sensor was immersed in the supporting electrolyte placed in a quartz cell (volume 10 mL). The surface of unmodified sensors and those modified with lead was imaged with the use of high resolution scanning transmission electron microscope (Tecnai G2 T20 X-TWIN (FEI)) equipped with an energy dispersive X-ray spectrometer (EDS).

2.2. Reagents

The supporting electrolyte was prepared from solution of $\text{CH}_3\text{COONH}_4$ (Sigma-Aldrich) and HCl (30%, Suprapur) with concentration of 1 mol L^{-1} $\text{CH}_3\text{COONH}_4$ and 0.615 mol L^{-1} HCl to obtain a buffer solution of $\text{pH } 4.2 \pm 0.1$ (after reaction between substrates the solution contained 0.385 mol L^{-1} $\text{CH}_3\text{COONH}_4$, 0.615 mol L^{-1} CH_3COOH and 0.615 mol L^{-1} NH_4Cl). Working solutions of Mo(VI) (consisting of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) were prepared from the stock standard solution (1 g L^{-1} , Merck) in deionized water. 0.1 mol L^{-1} solution of $\text{Pb}(\text{NO}_3)_2$ was prepared by dissolving appropriate amount of reagent (Sigma-Aldrich) in water. Alizarin Red S (Sigma-Aldrich) used as a complexing agent of concentration $1 \times 10^{-2} \text{ mol L}^{-1}$ was prepared by dissolving its appropriate amount in deionized water and from this solution, the working solution with concentration of $1 \times 10^{-4} \text{ mol L}^{-1}$ was prepared by dilution every day. The influence of foreign ions was examined for the following metal ions: Zn(II), Co(II), Cu(II), Ni(II), Fe(III), Mn(II), Cd(II), V(V), Al(III), Cr(VI), Sn(IV), W(VI) and Mg(II). Their working solutions were prepared from the stock standard solutions (1 g L^{-1} , Merck). Surfactants used to test the influence of organic substances on Mo(VI) peak were: Triton X-100, sodium dodecyl sulphate (SDS) and cetyltrimethylammonium bromide (CTAB), all purchased from Fluka. Ultra-purified water ($\gg 18 \text{ M}\Omega \text{ cm}$) used for solutions preparing was supplied by a Milli-Q system (Millipore, UK). The Amberlite XAD-16 (Sigma) resin used for preliminary preparation of water samples before voltammetric analysis, was prepared by rinsing it four times and drying at 50°C . The following certified reference materials were applied for the quantification of Mo(VI): SPS-SW2 (surface water, Spectrapure Standards As, Norway) and SRM 1640a (natural water, National Institute of Standards and Technology, USA).

2.3. Electrochemical measurements

Base solution used for Mo(VI) determination contained: buffer solution ($0.0385 \text{ mol L}^{-1}$ $\text{CH}_3\text{COONH}_4$, $0.0615 \text{ mol L}^{-1}$ CH_3COOH and $0.0615 \text{ mol L}^{-1}$ NH_4Cl) of $\text{pH} = 4.2 \pm 0.1$ as a supporting electrolyte,

$2 \times 10^{-3} \text{ mol L}^{-1}$ $\text{Pb}(\text{NO}_3)_2$ added to modify the WE surface with lead film, $2 \times 10^{-7} \text{ mol L}^{-1}$ of Alizarin Red S used for Mo(VI) complexing.

Before each measurement the potential of 0.5 V for 30 s was applied in order to clean of working electrode surface ($\text{Pb} - 2\text{e} \rightarrow \text{Pb}^{2+}$). After that, modification of the working electrode was performed using *in situ* method at the potential of -0.9 V for 45 s ($\text{Pb}^{2+} + 2\text{e} \rightarrow \text{Pb}$). Subsequently, at potential of -0.6 V applied for 60 s the complexes Mo(VI)-Alizarin Red S were accumulated on the WE surface and analytical signal of molybdenum was received as a result of complexes reduction during potential sweep from -0.65 to -1.1 V using differential pulse voltammetry technique. Other parameters of the applied technique were amplitude of 25 mV , scan rate of 50 mV s^{-1} and step potential of 0.3 V . The signal of Mo(VI) was measured after subtracting the background. The analyses of real water samples were performed at room temperature, using standard addition method in order to minimize the effect of the sample matrix.

3. Results and discussion

3.1. Selection of the electrode

To maximally simplify the whole method of molybdenum(VI) quantification, cheap and miniaturized screen-printed electrodes were purchased. This approach eliminates the often complicated electrode preparation processes and allows to apply reproducible sensors in portable analyzers for field analysis. Literature data [27] proves that lead is a suitable metal modifier of the carbon electrode dedicated for voltammetric determination of molybdenum(VI). Therefore, each type of screen-printed carbon sensors surfaces used in examination was *in situ* modified with lead. $6 \times 10^{-7} \text{ mol L}^{-1}$ of Alizarin Red S and $3.75 \times 10^{-4} \text{ mol L}^{-1}$ $\text{Pb}(\text{NO}_3)_2$ were added to the buffer solution (0.053 mol L^{-1} $\text{CH}_3\text{COONH}_4$, 0.047 mol L^{-1} CH_3COOH and 0.047 mol L^{-1} NH_4Cl) with of $\text{pH} = 4.6 \pm 0.1$. Voltammograms were recorded for $5 \times 10^{-7} \text{ mol L}^{-1}$ of Mo(VI). The best electrode for Mo(VI) determination was selected from the following types of screen-printed electrodes: carbon electrode modified with nanotubes and lead (with carbon auxiliary electrode and silver reference electrode); carbon electrode modified with nanofibers and lead (with carbon auxiliary electrode and silver reference electrode); carbon electrode modified with graphene and lead (with carbon auxiliary electrode and silver reference electrode); carbon electrode modified with lead (with platinum auxiliary electrode and silver reference electrode); carbon electrode modified with lead (with carbon auxiliary electrode and silver reference electrode) and thick-film lead electrode with carbon auxiliary electrode and silver reference electrode. Diameter of each working electrodes was 4 mm . Signals of Mo(VI) obtained with the use of proposed electrodes are shown in Fig. 1. The highest and best-shaped peak was observed using screen-printed carbon electrode modified *in situ* with lead and also consisting of platinum auxiliary electrode and silver reference electrode. To prove that modification of the WE with lead film has significant influence on sensitivity of the method, voltammograms for $5 \times 10^{-8} \text{ mol L}^{-1}$ of Mo(VI) were recorded for both unmodified screen printed carbon electrodes and lead-modified ones (Fig. 2).

3.2. Optimization of the type, pH and concentration of the supporting electrolyte

Based on the developed method the most favorable value of pH of the supporting electrolyte for Mo(VI) determination is 4.6 [27]. So the following types of supporting electrolytes ($\text{pH} = 4.6 \pm 0.1$) were checked: (1) 0.1 mol L^{-1} acetic buffer ($\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$), (2) buffer solution (0.053 mol L^{-1} $\text{CH}_3\text{COONH}_4$, 0.047 mol L^{-1} CH_3COOH and 0.047 mol L^{-1} NH_4Cl) and (3) buffer solution (0.052 mol L^{-1} $\text{CH}_3\text{COONH}_4$, 0.048 mol L^{-1} CH_3COOH and 0.047 mol L^{-1} NH_4NO_3). To the solution of the one of proposed type of electrolyte, $3.75 \times 10^{-4} \text{ mol L}^{-1}$ $\text{Pb}(\text{NO}_3)_2$, $6 \times 10^{-7} \text{ mol L}^{-1}$ Alizarin Red S and two doses of Mo(VI): 1×10^{-8} and $5 \times 10^{-8} \text{ mol L}^{-1}$, were added. In case of acetic buffer, any peaks on voltammograms were observed. For

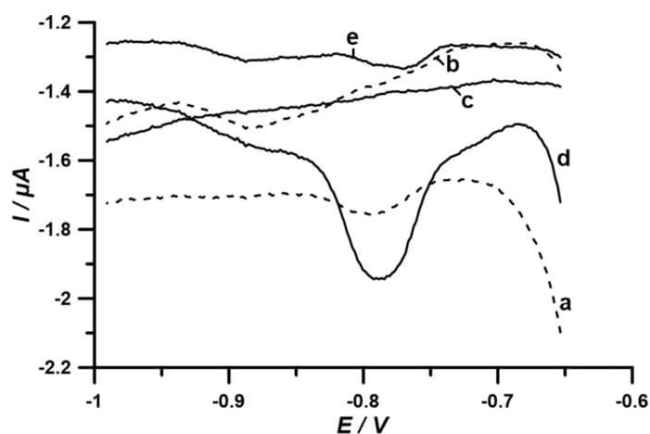


Fig. 1. Voltammograms obtained for 5×10^{-7} mol L $^{-1}$ of Mo(VI) with the use of different screen-printed carbon sensors modified with: a) nanotubes and lead, b) nanofibers and lead, c) graphene and lead or only with lead film (d and e). Auxiliary electrode was carbon (a, b, c and e) or platinum (d) and the reference electrode was silver.

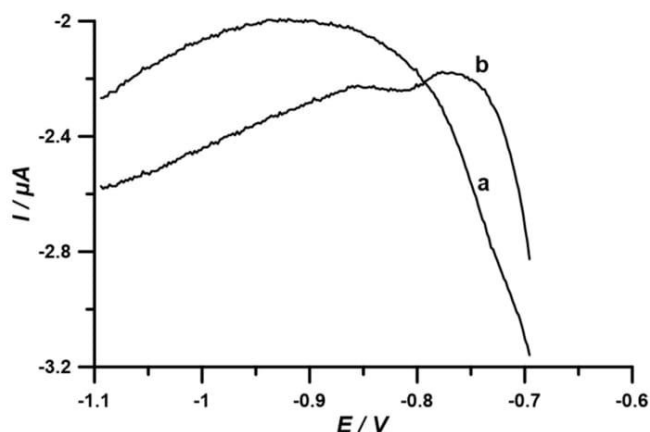


Fig. 2. Differential pulse voltammograms obtained for 5×10^{-7} mol L $^{-1}$ Mo(VI) with the use of screen-printed carbon electrodes that were a) unmodified and b) modified with lead film ($C_{Pb(II)} = 2 \times 10^{-3}$ mol L $^{-1}$).

the solution of CH_3COONH_4 , CH_3COOH and NH_4NO_3 , molybdenum signal was visible only for higher concentration and when the mixture of CH_3COONH_4 and HCl was used, well-shaped signals were obtained for both concentrations of Mo(VI). Therefore, for the subsequent part of our experiment, the influence of supporting electrolyte pH based on mixture of CH_3COONH_4 , CH_3COOH and NH_4Cl was checked.

The influence of buffer solution pH containing 0.1 mol L $^{-1}$ CH_3COONH_4 and appropriate amount of HCl to achieve pH of: 3.8 ± 0.1 , 4.2 ± 0.1 , 4.6 ± 0.1 , 5.1 ± 0.1 and also solution of 0.1 mol L $^{-1}$ HCl (pH = 1) and 0.1 mol L $^{-1}$ CH_3COONH_4 (pH $\sim$ 7) on peak current of 1×10^{-8} and 5×10^{-8} mol L $^{-1}$ of Mo(VI) were tested. 6×10^{-7} mol L $^{-1}$ of Alizarin Red S was also added to the base solutions. Obtained results are shown in Fig. 3A. Based on the results, pH = 4.2 ± 0.1 was selected (due to its best intensity of signals for both concentrations) for the subsequent step of method optimization. Then, the proper concentration of supporting electrolyte was selected. The CH_3COONH_4 concentration was varied from 0.01 (with addition of 0.00615 mol L $^{-1}$ HCl) to 0.2 mol L $^{-1}$ (with addition of 0.123 mol L $^{-1}$ HCl) and measurements were performed for Mo(VI) concentrations of 1×10^{-8} and 5×10^{-8} mol L $^{-1}$. The highest peak currents were obtained for the solution containing 0.1 mol L $^{-1}$ of CH_3COONH_4 with the addition of 0.0615 mol L $^{-1}$ HCl (Fig. 3B).

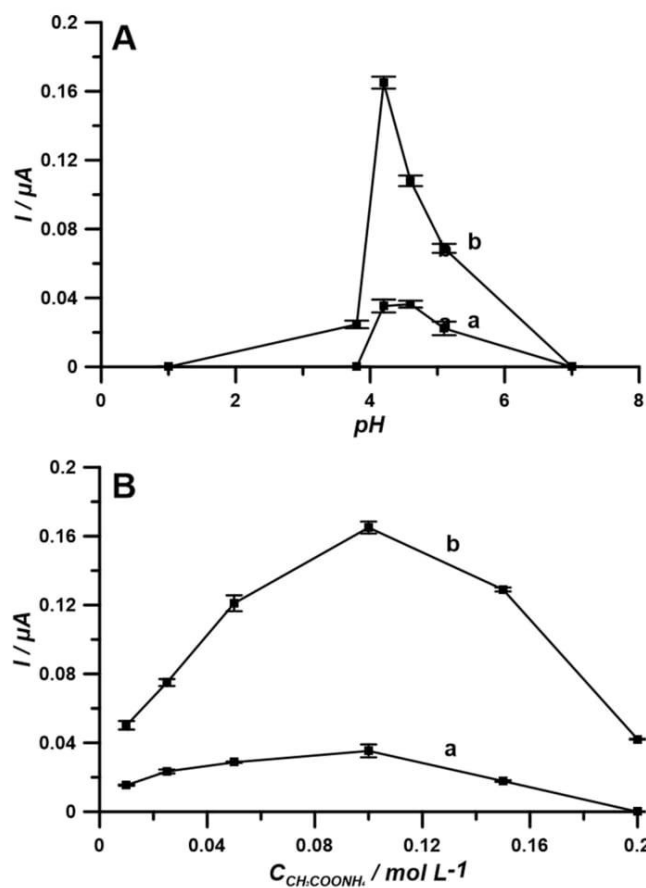


Fig. 3. The influence of A) pH and B) concentration of supporting electrolyte on Mo(VI) peak current obtained for the following concentrations of Mo(VI): a) 1×10^{-8} and b) 5×10^{-8} mol L $^{-1}$.

3.3. Selection of appropriate complexing agent and its concentration

In the next part of experiment, the different types of complexing agents were tested to find the one suitable for Mo(VI) determination. Three substances were used: Alizarin Red S, cupferron and chloranilic acid in concentrations equal to 6×10^{-7} mol L $^{-1}$. Measurements were performed for 1×10^{-8} and 5×10^{-8} mol L $^{-1}$ Mo(VI). Results proved that Alizarin Red S is the most appropriate complexing agent for Mo(VI) determination because only in the presence of this substance, the analytical signal of molybdenum was visible and measurable. So afterwards its concentration was optimized. The tested range of Alizarin Red S concentrations was from 2×10^{-8} to 8×10^{-7} mol L $^{-1}$ and measurements were carried out also without the complexing agent. Voltammograms were recorded for 1×10^{-8} and 5×10^{-8} mol L $^{-1}$ of Mo(VI). 2×10^{-7} mol L $^{-1}$ was selected as the optimal value of Alizarin Red S concentration due to the highest peak currents obtained for both concentration levels of Mo(VI).

3.4. Optimization of Pb(II) concentration and characteristics of electrodes surface

Modification of the working electrode surface may lead to the transformation of the electrode surface and allow to determine lower concentration of the analyte. In this work lead was applied as a great metal-modifier of the carbon electrode surface for Mo(VI) determination, which causes lowering the detection limit. Lead film was *in situ* deposited during each measurement at potential -1.45 V for 30 s. At

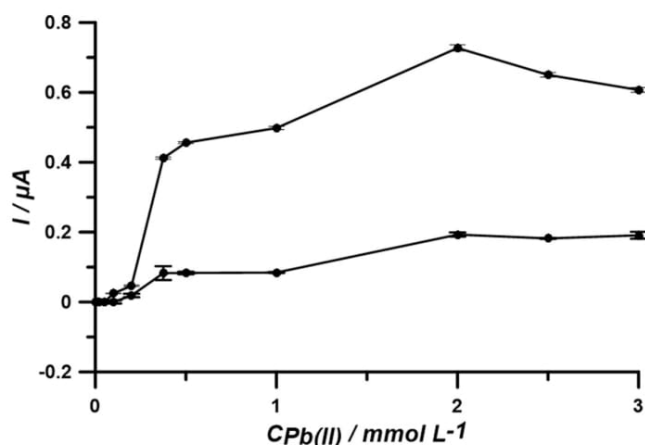


Fig. 4. The dependence of Pb(II) concentration on analytical signals of a) $1 \times 10^{-8} \text{ mol L}^{-1}$ and b) $5 \times 10^{-8} \text{ mol L}^{-1}$ Mo(VI).

this potential ionic form of lead was reducing to metallic form. Optimal concentration of $\text{Pb}(\text{NO}_3)_2$, as a source of lead(II) ions in the solution, was experimentally selected. The influence of Pb(II) concentration on Mo(VI) peak was checked in the range from $1 \times 10^{-6} \text{ mol L}^{-1}$ to $3 \times 10^{-3} \text{ mol L}^{-1}$. The peak current obtained for 1×10^{-8} and $5 \times 10^{-8} \text{ mol L}^{-1}$ Mo(VI) was found to be maximum when the lead film was created from solution containing $2 \times 10^{-3} \text{ mol L}^{-1}$ of Pb(II) (Fig. 4). When the concentration of Pb(II) was higher, metallic lead fragments were detached from the surface during the deposition step.

The surface images of unmodified carbon working electrodes and those modified with lead film were acquired with the use of high resolution transmission electron microscope (S/TEM) and the presence of Pb on modified electrodes were confirmed by energy-dispersive X-ray spectroscopy (EDS). The images of unmodified electrodes and those modified with various amount of Pb (different concentrations of Pb(II) added to the electrolyte solution) are presented in Fig. 5.

Electrochemical characteristics of unmodified carbon working electrodes and those modified with lead were tested in a solution of $0.1 \text{ mol L}^{-1} \text{ KCl}$ and $5 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$. At the beginning a potential -0.95 V was applied for 45 s (the stage of lead deposition) and voltammograms were recorded in the range from -0.5 to 0.8 V (step potential 0.5 V). Cyclic voltammograms were recorded, at different scan rates ranging from 5 to 400 mV s^{-1} , for unmodified screen-printed carbon electrode (Fig. 6A) and the one modified with lead (Fig. 6B) and the dependence of anodic peak current (I_{an}) and square root of the scan rates ($\nu^{1/2}$) were determined. Based on the Randles-Sevcik equation [35], the active surface areas of the working electrode surfaces were calculated. For the bare SPCE the active surface area equals to $0.06178 \pm 0.0003 \text{ cm}^2$ ($n = 3$), while the area of PbF/SPCE was calculated to be $0.06225 \pm 0.0001 \text{ cm}^2$ ($n = 3$) so no significant differences between examined electrodes were recorded.

For different scan rates well-defined anodic and cathodic peaks were noted. The separation of both peaks for unmodified SPCE for the selected scan rate (50 mV s^{-1}) was estimated to be $166.05 \pm 0.03 \text{ mV}$ ($n = 3$), while for PbF/SPCE this value was $122.05 \pm 0.10 \text{ mV}$ ($n = 3$). These results prove the improvement of reversibility of the redox reaction on the PbF/SPCE relative to bare SPCE. Subsequently, the rate of the electrons transport was evaluated, based on relative peak separations (χ°). It was calculated for the reaction of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ for equation: $\chi^\circ = (E_{an} - E_{cath}) / 0.058$, where E_{an} - potential of anodic peak and E_{cath} - potential of cathodic peak (mV) [36]. Theoretical value of mentioned reaction equals 1. For the PbF/SPCE calculated value of relative peak separation was 2.104 ± 0.095 ($n = 3$) and it proves to be closer to the theoretical value than this obtained on bare SPCE (2.829 ± 0.035 , $n = 3$). Therefore it can be concluded that

modification of the electrode causes an acceleration of electron transfer kinetics.

3.5. Electrochemical cleaning of WE surface

The first step of parameters optimization for the technique was the verification if the electrochemical cleaning of WE surface is necessary. For this purpose the voltammograms were recorded for concentrations of Mo(VI) of 1×10^{-8} and $5 \times 10^{-8} \text{ mol L}^{-1}$ without the cleaning step. In this case, peak current was constantly increasing along with subsequent measurements, thus proving that electrochemical cleaning has to be conducted before each measurement. In the next step four modes of cleaning were proposed: (1) -1.45 V for 10 s and 0.5 V for 10 s, (2) -0.9 V for 10 s and 0.5 V for 10 s, (3) 0.5 V for 10 s and (4) 0.5 V for 30 s. Based on 10 performed measurements, relative standard deviations (RSD) were calculated. The lowest values of RSD were obtained when the potential of 0.5 V was applied for 30 s and they equal 2.93% and 3.19% for 1×10^{-8} and $5 \times 10^{-8} \text{ mol L}^{-1}$ of Mo(VI), respectively. These values of RSD are low enough for quantification process, so the potential of 0.5 V and time 30 s was selected as optimal for this method.

3.6. Optimization of potential and time of lead film depositing and Mo(VI)-Alizarin Red S complexes accumulation on Mo(VI) peak current

The second stage of Mo(VI) determination was the deposition of lead film on the WE surface. So potential and time of the modification process were optimized. Lead film was deposited at potentials ranging from -0.6 to -1.5 V for 30 s and voltammograms recorded for Mo(VI) concentrations of 1×10^{-8} and $5 \times 10^{-8} \text{ mol L}^{-1}$. The highest peak registered for Mo(VI)-Alizarin Red S reduction complexes was reached at -0.9 V . This potential was recognized as the best for electrochemical modification of the electrode. The time of Pb deposition varied from 0 to 120 s. The peak high of molybdenum was increasing with the elongation of Pb deposition process. For the time equal to or longer than 60 s the amount of metallic lead was so large that it caused its separation from the WE surface and in consequence lack of repeatability of measurements. 45 s of Pb deposition was considered as the best for film formation.

Before recording of voltammograms Mo(VI)-Alizarin Red S complexes were accumulated onto working electrode surface. To choose the most suitable potential, the range from -0.9 to -0.6 V was tested. From the potential value of -0.9 to -0.6 V the molybdenum peak was increasing and for potential -0.5 V it significantly decreased. This effect might be caused by lead film oxidation and its stripping from the surface. For the selected potential of -0.6 V , the time of complexes accumulation was tested in the range from 0 to 300 s. The intensity of Mo(VI) peak was increased from 0 to 180 s and then for time of 240 and 300 s a drop in its height was observed. In order to shorten the whole analysis, the time of 60 s was selected. In Fig. 7. the dependence of potential and time of complexes accumulation on the analytical signal of Mo(VI) are shown.

3.7. Optimization of amplitude, scan rate and step potential

Voltammetric technique parameters such as amplitude, scan rate and step potential were optimized for solution containing $0.385 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.615 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.615 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ ($\text{pH} = 4.2 \pm 0.1$), $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$, $2 \times 10^{-7} \text{ mol L}^{-1}$ Alizarin Red S and $2 \times 10^{-7} \text{ mol L}^{-1}$ Mo(VI). Electrochemical cleaning of WE surface was performed at 0.5 V for 30 s, deposition of lead film at -0.9 V for 45 s and accumulation of complexes Mo(VI) with Alizarin Red S at potential of -0.6 V for 60 s. Differential pulse voltammograms were recorded from -0.65 to -1.1 V . The selection of amplitude was performed in the range from 10 to 125 mV. The best shaped and the highest signal of Mo(VI) was recorded for the amplitude of 25 mV. Scan rate was modified in the range from 20 to 125 mV s^{-1} . Based on the obtained results the 50 mV s^{-1} was selected due to its highest analytical signal of Mo(VI). During the

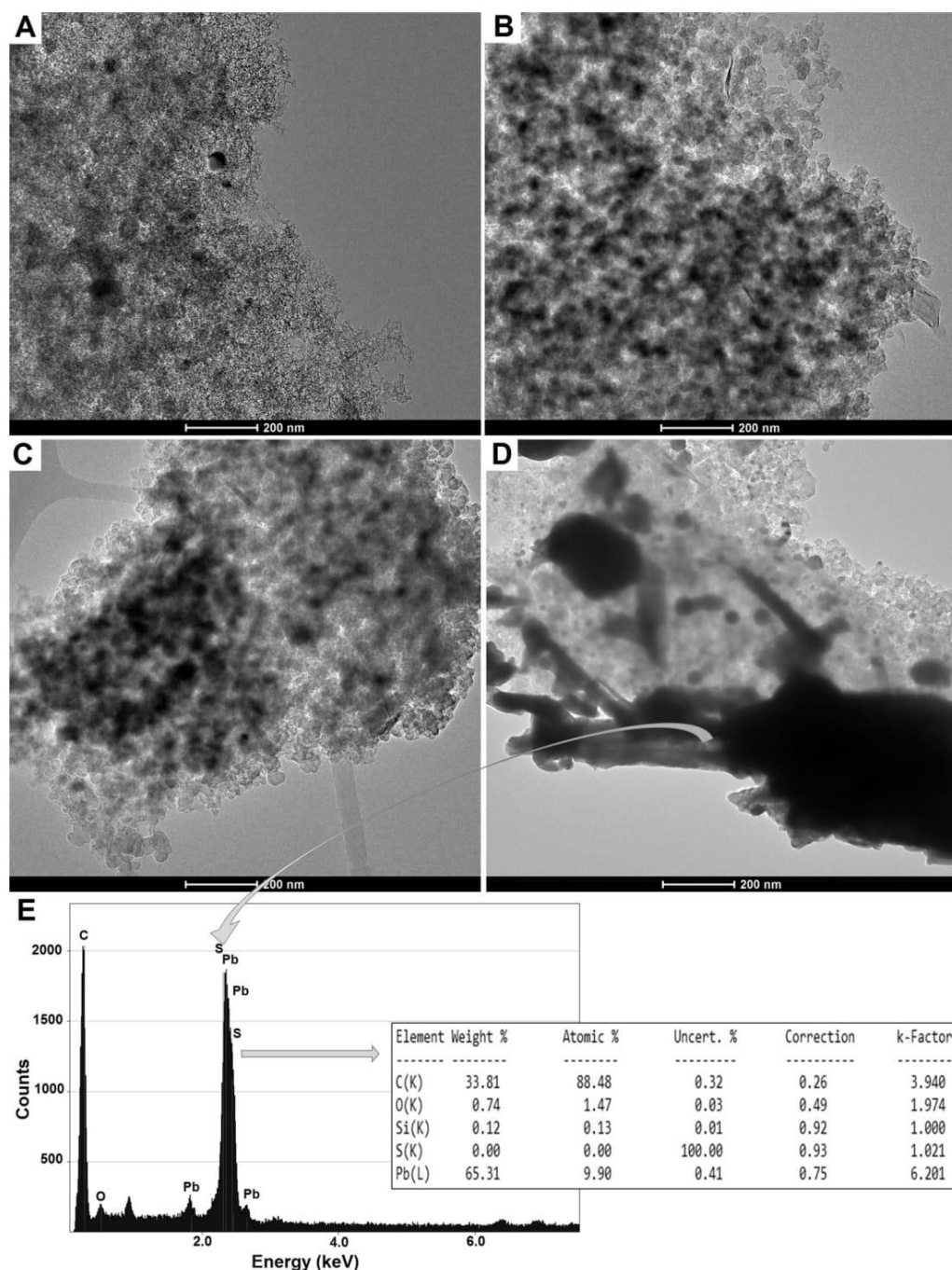


Fig. 5. The images of the working electrode surfaces of unmodified carbon electrode (A) and one modified with lead for Pb(II) concentrations of: $2 \times 10^{-5} \text{ mol L}^{-1}$ (B), $2 \times 10^{-4} \text{ mol L}^{-1}$ (C) and $2 \times 10^{-3} \text{ mol L}^{-1}$ (D) and EDS spectra obtained for electrode modified with lead from the solution of $2 \times 10^{-3} \text{ mol L}^{-1}$ Pb(II) (E).

change of step potential there was not significant changes of peak high, but in comparison to signals obtained for the other values of step potential, 0.3 V was recognized as the optimal value for Mo(VI) determination (slightly higher and well-shaped peak).

3.8. Calibration graph

To know the working concentration ranges of the proposed method for molybdenum(VI) quantification, in optimized conditions, the measurements for calibration graph were performed with the use of screen-printed electrode with carbon working electrode modified *in situ* with lead. Mo(VI) was added to the base solution starting with the

concentration of 1×10^{-10} to $1 \times 10^{-7} \text{ mol L}^{-1}$, but linear increase of molybdenum peak started from 1×10^{-9} to $5 \times 10^{-8} \text{ mol L}^{-1}$ (time of accumulation: 60 s). Fig. 8. shows differential pulse voltammograms obtained in linear range and the determined calibration curve. The equation of the signed curve is $y = (0.012 \pm 0.0003) x + (0.017 \pm 0.0007)$, where y is the mean peak current (μA) and x is a Mo(VI) concentration (nmol L^{-1}). Correlation coefficient (r) calculated for the curve equals 0.9995, which proves its perfect linearity. The detection limit (LOD) and quantification limit (LOQ) were deduced from the slope of the calibration curve. The limit of detection and quantification were calculated as 3 and 10-times of the SD ($n = 3$) for the blank divided by the calibration curve slope

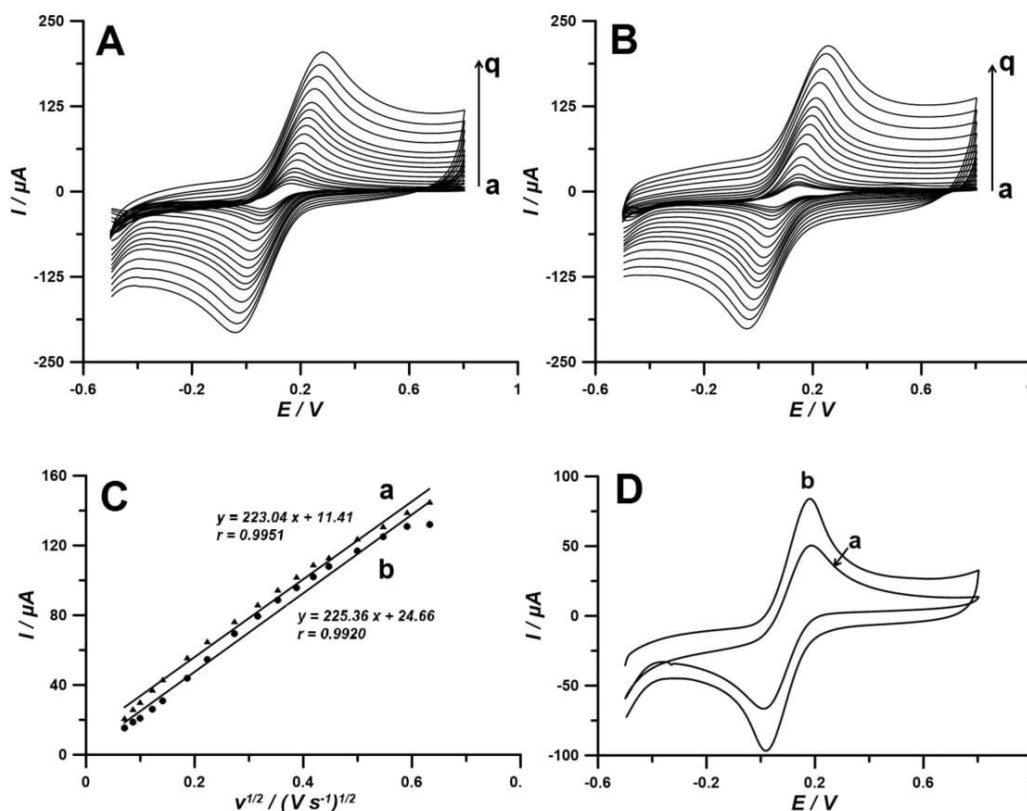


Fig. 6. Cyclic voltammograms obtained in solution containing $5 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ and $0.1 \text{ mol L}^{-1} \text{ KCl}$ with the use of: A) unmodified screen-printed carbon electrode and B) one modified with lead, for the scan rate range from 5 to 400 mV s^{-1} (a-q); C) dependence between anodic peak current and scan rates square roots (in the range of square root from 5 to 400 mV s^{-1}) and D) cyclic voltammograms obtained for: a) unmodified screen-printed carbon electrode, and b) one modified with lead, for scan rate of 50 mV s^{-1} .

($\text{LOD} = 3\text{SD}/a$; $\text{LOQ} = 10\text{SD}/a$) and they equal 2.1×10^{-10} and $7.1 \times 10^{-10} \text{ mol L}^{-1}$, respectively. In literature data lead film electrode has been already used for the determination of Mo(VI) [27]. However, the LOD of that method is higher than LOD obtained in this work (LODs: 9.0×10^{-10} vs. $2.1 \times 10^{-10} \text{ mol L}^{-1}$). In addition, screen-printed electrodes are appropriate for using in portable analyzers. Screen-printed sensor for the determination of Mo(VI) was also applied in the reference [34]. There, LOD is 2.5 ng mL^{-1} ($\sim 2.6 \times 10^{-8} \text{ mol L}^{-1}$), so two order of magnitude higher than in this work ($2.1 \times 10^{-10} \text{ mol L}^{-1}$). Additionally, the electrode preparation process in reference [34] is much more complicated. So, the developed method of Mo(VI) determination with the use of PbF/SPCE is a new, simple and sensitive alternative which enables performing measurements in and outside the laboratory.

3.9. Interferences (foreign metal ions and surfactants)

The aim of the proposed method is its application for quantification of Mo(VI) in natural water. Therefore, the influence of substances present in this type of samples was tested, namely of foreign metal ions and surfactants. The influence of foreign metal ions present in natural water samples on molybdenum peak was checked based on the addition of following metal ions: Zn(II), Co(II), Cu(II), Ni(II), Fe(III), Mn(II), Cd(II), V(V), Al(III), Cr(VI), Sn(IV), W(VI) and Mg(II). To the solution containing $0.0385 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$, $0.0615 \text{ mol L}^{-1} \text{ CH}_3\text{COOH}$ and $0.0615 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ ($\text{pH} = 4.2 \pm 0.1$), $2 \times 10^{-4} \text{ mol L}^{-1} \text{ Pb}(\text{NO}_3)_2$, $2 \times 10^{-7} \text{ mol L}^{-1}$ Alizarin Red S and $5 \times 10^{-7} \text{ mol L}^{-1} \text{ Mo(VI)}$ further portions of foreign metal ions were added in the range from 0.1 to 1000-fold excess. During measurements peak current of Mo(VI) was observed and in the case of $\ll 10\%$ increase/decrease of peak

height, any negative influence was considered. Table 1 shows the tolerable excess of foreign metal ions relative to molybdenum concentration.

All of tested ions have no significant influence on analytical signal of Mo(VI). Based on data of certified reference materials of natural water samples (SPS-SW2 and SRM 1640a) the ratio of each ions concentration in every case is lower than tolerable value for proposed method. Therefore no procedure for minimizing or eliminating the influence of foreign metal ions has to be applied and quantification of Mo(VI) can be performed without further steps.

Based on each type of surface active substances: cationic (CTAB), anionic (SDS) and non-ionic (Triton X-100) the effect of surfactants on Mo(VI) peaks was tested. Measurements were performed analogously as in the tests discussed above. Each surfactant was added to the solution in concentrations ranging from 0.2 to 50 mg L^{-1} . Any significant influence was observed in the presence of SDS in the sample. It was not until its concentration reached 10 mg L^{-1} that SDS caused decrease of Mo(VI) signal to 89.6% of its original value. Clearly more significant impact on Mo(VI) signal was noted in the presence of Triton X-100 and CTAB. Already at 1 mg L^{-1} Triton X-100 and at 0.5 mg L^{-1} of CTAB the analytical signal was suppressed to 75.7% and 80.3%, respectively. Because of the significant negative effect of surfactants on voltammetric signals in natural water samples, the preparatory procedure for eliminating or minimizing the impact of surfactants was deemed necessary.

3.10. Minimizing of the negative effect of surfactants (mass of resin and time of mixing optimization)

In order to minimize the negative influence of surfactants occurring in natural water samples we applied the adsorptive resin Amberlite

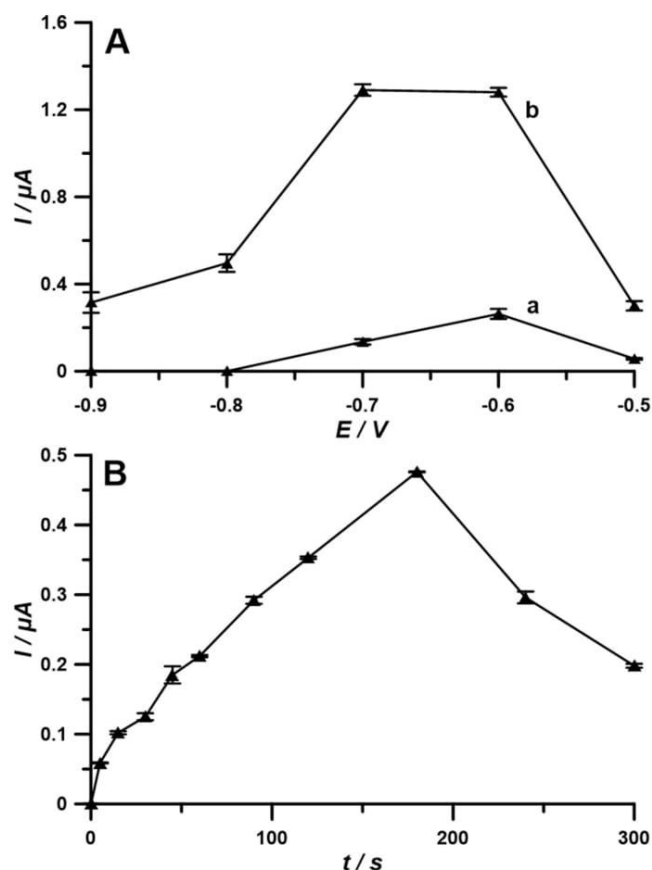


Fig. 7. The influence of: A) potential and B) time of Mo(VI)-Alizarin Red S complexes accumulation on analytical signal of: 1×10^{-8} (A(a)), 5×10^{-8} mol L⁻¹ (A(b)) and 2×10^{-8} mol L⁻¹ (B). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

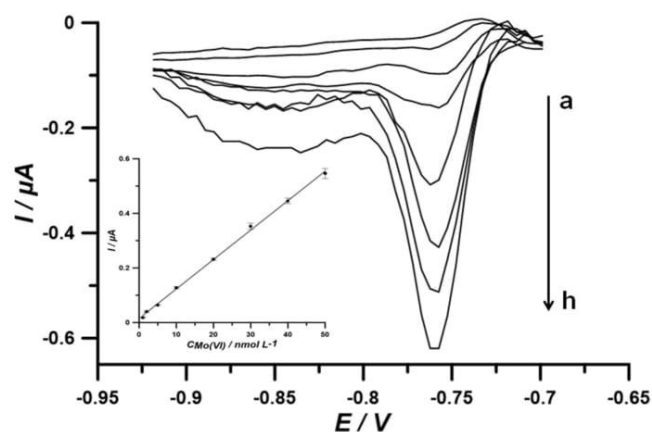


Fig. 8. Differential pulse voltammograms obtained for linear range of the calibration curve for concentrations of Mo(VI) ranging from 1×10^{-9} to 5×10^{-8} mol L⁻¹ (a-h) and the calibration graph for Mo(VI) determination.

XAD-16. This method was proposed for organic matrix removal in voltammetric method for U(VI) [37] and Bi(III) and Cd(II) determination [38]. At the beginning, the adsorption of complexes Mo(VI)-Alizarin Red S on the resin surface was tested. Voltammograms for the solution of acetic buffer solution ($\text{pH} = 4.2 \pm 0.1$), 2×10^{-3} mol L⁻¹ of $\text{Pb}(\text{NO}_3)_2$, 2×10^{-7} mol L⁻¹ of Alizarin Red S and 2×10^{-8} mol L⁻¹ of Mo(VI) were recorded. Next, 0.5 g of Amberlite

Table 1

Tolerable excess of foreign metal ions in determination of Mo(VI) at concentration level of 5×10^{-7} mol L⁻¹.

Metal ion	Tolerable excess ^a
Zn(II), Mn(II), Al(III), Mg(II)	1000
Co(II), Cu(II), Fe(III)	100
Sn(IV)	20
Ni(II), Cd(II), V(V)	10
Cr(VI), W(VI)	2

^a caused change of Mo(VI) peak current $\ll 10\%$.

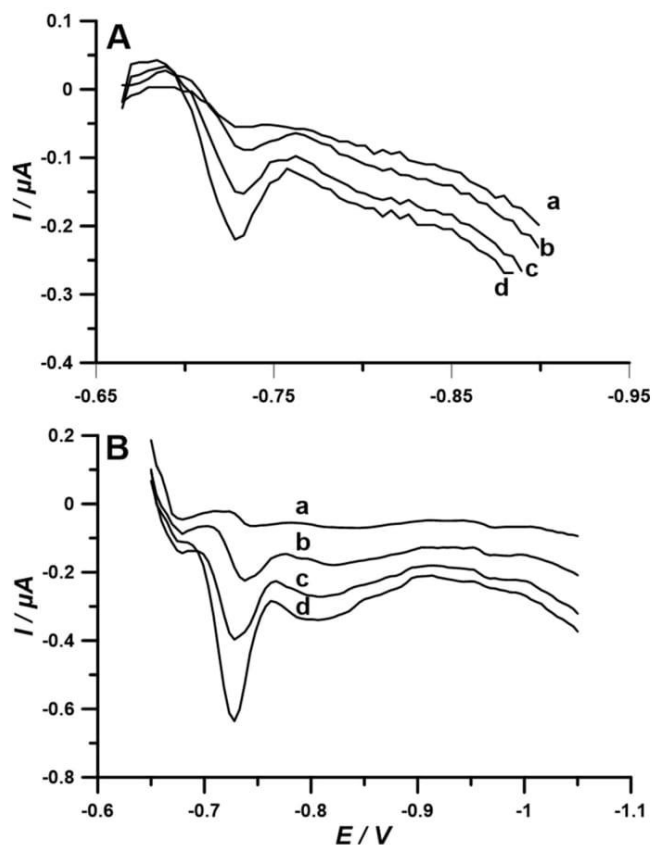


Fig. 9. Differential pulse voltammograms registered during analysis of certified reference materials SRM 1640a (A) and SPS SW-2 (B): a) 100 μL of the sample; b) as (a) + 1×10^{-8} mol L⁻¹; c) as (a) + 2×10^{-8} mol L⁻¹; d) as (a) + 3×10^{-8} mol L⁻¹ Mo(VI).

XAD-16 was added to the voltammetric cell and after 30 s of mixing the content thereof with resin, voltammograms were recorded. The molybdenum peak became invisible. This indicates that complexes of Mo(VI) with Alizarin Red S were adsorbed on the resin. Therefore, mixing of the sample with the resin has to be performed in a separate vessel.

Subsequently we checked the effectiveness of surfactants removal with the use of 0.5 g of Amberlite XAD-16 for time of mixing/shaking of 30 s. The range of the surfactants (SDS, CTAB and Triton X-100) concentrations was from 0.2 to 50 mg L⁻¹. In all cases, 0.5 g of the resin and 30 s of mixing it with solution was sufficient for eliminating the signal attenuation effect in the studied range. It was concluded that used mass of resin can be reduced and in the subsequent step of examination, the mass of resin was selected.

Optimization of the resin mass was performed in the range from 0.01 to 0.5 g. At the beginning the analytical signal of 2×10^{-8} mol L⁻¹ Mo(VI) was registered. Subsequently different amounts of the resin (0.01, 0.025, 0.05, 0.1, 0.25, 0.5 g or 0.75 g) were

Table 2

Results obtained during quantification of Mo(VI) in certified reference materials.

Certified reference material	Determined concentration of Mo(VI) $\pm$ SD ($n = 3$) [$\mu\text{mol L}^{-1}$]	Certified concentration $\pm$ SD [$\mu\text{mol L}^{-1}$]	Relative error [%]
SRM 1640a	0.45 $\pm$ 0.014	0.47 $\pm$ 0.006	4.3
SPS SW-2	0.54 $\pm$ 0.025	0.52 $\pm$ 0.003	3.8

added to the solution containing $1 \times 10^{-5} \text{ mol L}^{-1}$ of Mo(VI) and the surfactants mixture (2 mg L^{-1} SDS, 2 mg L^{-1} CTAB and 2 mg L^{-1} Triton X-100) and placed in a separate vessel, and the solution was shaken for 30 s. After this time, $20 \mu\text{L}$ of the resulting solution was added to the voltammetric cell and measurements were recorded. Measurements were repeated minimum seven times and relative standard deviation was calculated. Based on the calculated recovery values ($\sim 100\%$) and RSD values ($\leq 5\%$) the effectiveness of surfactants removal was estimated. Satisfactory results have already been obtained for 0.025 g of the resin (RSD = 2.63% for $n = 7$; recovery value 108.5%). For smaller mass of resin, the recovery was $\sim 100\%$, but relative standard deviation equaled to 6.40% . So 0.01 g of the resin was considered to be inadequate for complete removal of surfactants from the solution.

The time of resin and the sample mixing was similarly selected. The sample containing $1 \times 10^{-5} \text{ mol L}^{-1}$ of Mo(VI), 2 mg L^{-1} SDS, 2 mg L^{-1} CTAB and 2 mg L^{-1} Triton X-100 was shaken with 0.025 g of Amberlite XAD-16 for 15, 30, 45 and 60 s. Satisfactory results (i.e. recovery value and RSD) were obtained for 30 s of the resin and sample mixing. The shorter time was considered too short in view of RSD value (4.63% vs. 2.63% for 15 and 30 s, respectively).

3.11. Application

The developed method of voltammetric determination of Mo(VI) with the use of screen-printed electrode with carbon working electrode modified *in situ* with lead was applied for quantification of Mo(VI) in certified reference materials: SRM 1640a (natural water) and SPS SW-2 (surface water). Water samples were initially prepared before quantitative analysis through shaking 10 mL of the sample with 0.025 g of Amberlite XAD-16 for 30 s was performed. Concentrations of Mo(VI) were estimated using the standard additional method. Registered voltammograms are presented in Fig. 9. and calculated concentrations of Mo(VI) in analyzed samples are summarized in Table 2.

4. Conclusions

A commercially available screen-printed three-electrode sensor was successfully adopted for voltammetric determination of Mo(VI). The surface of carbon working electrode was modified during analysis through electrochemical reducing of lead ions to metallic form. That fast and simple modification significantly reduced limit of molybdenum detection. To enable voltammetric quantification of Mo(VI) in real water samples, the negative influence of surfactants was minimized through application of adsorptive resin: 0.025 g of Amberlite XAD-16 and shaking 10 mL of sample with the resin for 30 s. Applicability of the developed method was checked through analysis of certified reference materials with satisfactory results.

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