



Electrochemical Behaviour of Gold Thin Film Glassy Carbon Electrode for Determination of Chromium(VI)

N. BROLI^{*✉}, L. VALLJA[✉], M. VASJARI[✉], A. SHEHU[✉] and S. DUKA[✉]

Department of Chemistry, Faculty of Natural Science, University of Tirana, Bulevardi 'Zogu I', No. 2, Postal Code 1001, Tirana, Albania

*Corresponding author: Tel: +355 68 2092552; E-mail: nevilabroli@yahoo.com; nevila.broli@fshn.edu.al

Received: 7 January 2021;

Accepted: 13 February 2021;

Published online: 16 April 2021;

AJC-20317

A modified glassy carbon electrode (Au_{film}/GCE) using a gold film was constructed for determination of chromium(VI) in real water samples. A GCE was immersed in HAuCl₄ solution (10⁻³ M) and the thin layer of gold was electrodeposited for 10 min at -0.4 V (vs. Ag/AgCl). Compared with only GCE, a strong affinity between chromium and gold species was observed with an increase in Cr(VI) signal. The type of supporting electrolytes, electrodeposition time, scan rate, pH, modulation time and the modulation amplitude were optimized through differential pulse-anodic stripping voltammetry (DP-ASV). A calibration graph acquired using the accumulation time of 120 s with a sensitivity of 1.3 × 10⁻² μA/μg L⁻¹ was linear in the range of 10-120 μg L⁻¹. A low detection limit of 5.5 μg/L Cr(VI) and a strong correlation coefficient R² = 0.9971 were obtained under the optimal experimental conditions. Signals were reproducible and exhibited a relative standard deviation of ±4.5%. A modified sensor was employed to determine the Cr(VI) content in the sewage water samples.

Keywords: Glassy carbon electrode, Chromium(VI), Thin gold film, Differential pulse anodic stripping voltammetry.

INTRODUCTION

Chromium metal is commonly found in two oxidation states, Cr(III) and Cr(VI) in aquatic systems. These two oxidation states of chromium exhibit differently in natures. At trace levels, chromium(III) is a supplement essential to the human body and when combines with different enzymes to transform proteins, sugars and fats. Depending on pH, chromium(VI) is available as HCrO₄⁻, CrO₄²⁻, Cr₂O₇²⁻ or H₂CrO₄ and is toxic, mutagenic as well as carcinogenic. The various oxidation states of chromium considerably influence the bioavailability and toxicity of chromium [1]. The determination of Cr(VI) is more essential than Cr(III) since Cr(VI) has higher solubility and thus bio-availability is more toxic at lower concentrations than Cr(III), which appears to form stable complexes in the soil [2]. Thus, the design of an analytical method which is capable of selective measurement of chromium(VI) is of great importance. According to El-Shahawi *et al.* [3,4], the chemical speciation of chromium in environmental samples is necessary for the accurate determination of the pollution source and levels. Chromium(VI) is usually determined by UV-VIS spectrophotometry by means of diphenylcarbazide in acidic solutions [5].

The voltammetric methods are advantageous in speciation of chromium because they offer a low detection limit and the determinations can be carried out without any additional separation step. In particular, adsorptive stripping voltammetry (AdSV) is of interest due to its high sensitivity and selectivity [6]. Welch *et al.* [7] studied the reduction mechanism of Cr(VI) at solid electrodes in acidic media and its analytical application. Dai *et al.* [8] reported that the metal nanoparticles have shown superior or advantageous properties for a wide range of technological applications and provide three important functions for electroanalysis: like improved mass transport, high effective surface area and catalytic properties. In this work, a gold thin film modified glassy carbon electrode Au_{film}/GCE was prepared by electrochemical method, in order to improve analytical performance of glassy carbon electrode (GCE) for quantitative determination of chromium(VI) in water. The influence of several physico-chemical parameters such as pH, type of supporting electrolyte) and instrumental parameters like deposition time, scan rate, modulation amplitude on the DP-ASV response has been evaluated. From the estimated results, this sensor could be an alternative method for a sensitive detection of Cr(VI) in water sample with differential pulse anodic stripping voltammetry.

EXPERIMENTAL

Differential pulse anodic stripping voltammetric mode (DP-ASV) were conducted using electrochemical analyzer (MEC-12B). The glassy carbon electrode modified with Au-nanofilm was used as working electrode. Ag/AgCl electrode (saturated KCl) was used as reference electrode and a platinum wire as auxiliary electrode. A gold nanofilm onto the surface of the working GCE was prepared by electrodeposition before each electrochemical measurement.

Standard solutions of Cr(VI) (100 mg/L), 0.1 M HCl, 0.1 M HNO₃, 0.1 M H₂SO₄ and all other solutions were prepared from the respective AR grade chemicals purchased from Sigma Group Chemical Reagents Co. Ltd. and used without any further purification. A solution of chloroauric acid (HAuCl₄) (0.108 g Au in 100 mL HAuCl₄) in 0.1 M HCl was used in electrochemical cell to deposit Au nanofilm at the GCE surface.

Preparation of Au_{film}/GCE: The Au_{film}/GCE sensor was prepared by electrodeposition. Initially, the glassy carbon electrode was rinsed with water to remove any residual polishing material. Then, the surface of the electrode was polished gently with the Al₂O₃ powder with particle sizes 0.01; 0.5; 1.0 μm, purified with distilled water and ethanol (98%). The procedure for the electrodeposition of gold nanofilm at GCE was adapted from published method [6]. The GCE was immersed into solution containing 15 mL of 0.1 M HCl and 140 μL of HAuCl₄ (0.108 g of Au in 100 mL of HAuCl₄ solution) and deposition was conducted at the potential of -0.4 V (vs. Ag/AgCl) for 10 min. Thereafter, the stripping step was performed till +0.6 V in stirring condition for 25 s.

Electrochemical measurements: The electrochemical measurements were performed using modified Au_{film}/GCE and unmodified GCE electrode applying differential pulse anodic stripping voltammetry (DP-ASV) technique. In the electrochemical cell containing 15 mL of 0.1 M HCl (pH = 1) as a supporting electrolyte anodic stripping voltammograms were recorded between -0.2 to +0.8 V, by applying differential pulse mode with the deposition time 120 s, scan rate 100 mV/s, step potential 4 mV, amplitude 20 mV and modulation time 5 m/s. During the deposition step, the potential was kept at -0.2 V for 120 s. After recording background voltammogram successive standard solution of chromium(VI) was added into the electrochemical cell and the voltammograms were recorded after each addition. The same electrochemical conditions were used to determine Cr(VI) in the sewage water samples.

Sewage water analysis and recovery: The sewage water samples were collected from a nearby an industrial factory of leather processing and cleaning. The water sample taken was purified by a vacuum filtration process as the sample contained numerous solid suspensions. Filtered sewage water (2 mL) were introduced into electrochemical cell containing 15 mL HCl (0.1 M). Recovery experiments were performed by spiking standard Cr(VI) stock solution to the water sample following by the determining the analyte using DP-ASV experiments.

RESULTS AND DISCUSSION

Electrochemical response of Cr(VI) on Au_{film}/GCE sensor: The effect of gold film in the electrochemical detection

of chromium(VI) was studied using the differential pulse anodic stripping voltammetry in a solution 0.1 M HCl (pH = 1) containing Cr(VI). The successive voltammograms were recorded between -0.2 to +0.8 V using a scan rate 100 mV/s, step potential 4 mV, amplitude 20 mV and modulation time 5 ms. Although the anodic peaks of Cr(VI) using modified and bare electrode in the electrochemical cell contained 100 μg L⁻¹ of Cr(VI) appeared at potential +0.3 V, the highest peak was obtained with modified electrode. This can be attributed to the strong affinity between gold and chromium(IV).

Optimization of experimental parameters: The optimization of DP-ASV instrumental parameters influencing in the current response of analyte is very important step in the development of electroanalytical methodology. The effect of different parameters such as pH, type of supporting electrolyte and the accumulation time was investigated in order to optimize analytical performance of Au_{film}/GCE sensor for the determination Cr(VI) in water solution. All experiments were performed at 50 μg L⁻¹ Cr(VI) and step potential of 4 mV.

Response time: The response obtained using modified sensor, Au_{film}/GCE in Cr(VI) solution applying the different accumulation time (30, 60, 120 and 180 s) is shown in Fig. 1. It can be seen that the response increases linearly up to 120 s accumulated time and thereafter decreases, reflecting the electrode surface saturation. Therefore, an accumulation time of 120 s was used for all further measurements.

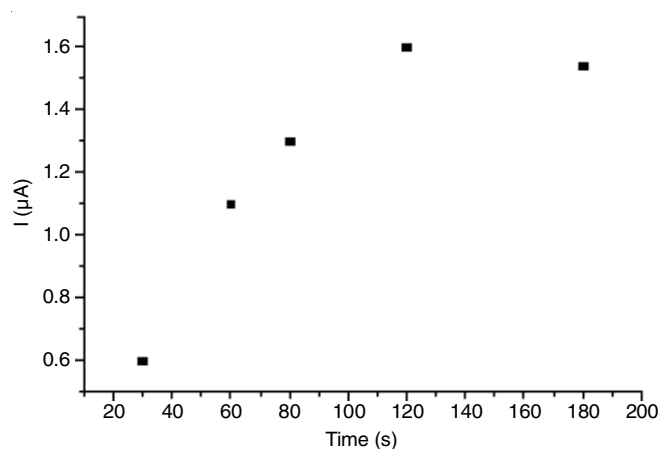


Fig. 1. Effect of the accumulation time (30 s; 60 s; 120 s; 180 s) at Au_{film}/GCE, in 0.1 M HCl for concentration 50 μg L⁻¹ Cr(VI)

Selection of electrolyte: Selection of suitable supporting electrolyte is important on sensor response since it has effect on the kinetics of the charge transfer processes. The effect of supporting electrolyte type and the pH on the electrochemical signal of Cr(VI) on Au_{film}-GCE was investigated also in a solution containing 50 μg L⁻¹ Cr(VI).

Various inorganic acids *viz.* hydrochloric acid, nitric acid and sulfuric acid (0.1 M) were applied to investigate their impact on the electroanalytical signal of Cr(VI). The best (position shift to negative potential, height and width) anodic peak for Cr(VI) using Au_{film}/GCE was obtained when HCl used as the supporting electrolyte (Fig. 2a). The difference between the sensitivity of Cr(VI) in different media *viz.* HNO₃, HCl and

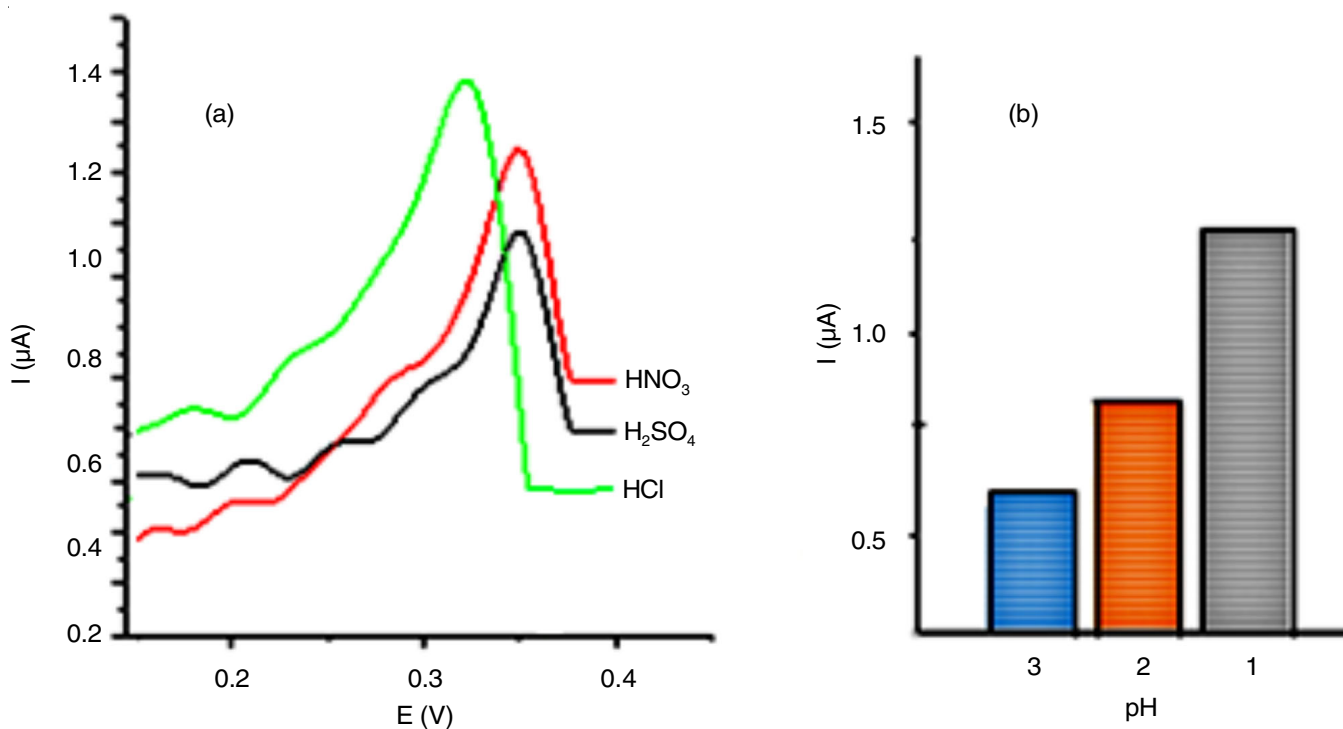


Fig. 2. (a) Anodic stripping voltammograms of 50 µg L⁻¹ Cr(VI) at various electrolyte. (b) Effect of pH on the peak current for the determination of Cr(VI) on Au_{film}-GCE

H₂SO₄ was probably due to the difference in the diffusion rate of species to the electrode surface [9]. It may also reflect that adsorption on the electrode and the variation between acids suggests that the adsorption of anions plays a significant role in the reduction.

Effect of pH: The effect of pH on peak current using modified sensor is shown in Fig. 2b by varying the concentration of HCl from 0.001 to 0.1 M, which correspond pH 3 to 1, respectively. The highest signal in solution of Cr(VI) 50 µg L⁻¹ using Au_{film}/GCE sensor was obtained at 0.1 M HCl (pH = 1). A lower signal of anodic peak current indicated proton dependent process [10]. For this reason, lower analytical signal was obtained in the case of lower concentration of electrolyte (0.001 M HCl), possibly because of the low availability of protons. Therefore, 0.1 M hydrochloric acid solution was used as the optimum concentration of supporting electrolyte for the rest of this study.

Scan rate: The scan rate and modulation magnitude were optimized in order to obtain the best signal with high sensitivity toward analyte Cr(VI). With increasing of modulation amplitude was observed that the peak current increases gradually up to 50 mV and then remained constant but the peak becomes wider. The most suitable amplitude was chosen at 20 mV to get the highest and sharper peak. Also by increasing the scan rate from 50 to 150 mV/s, peak current increased proportionally up to 100 mV/s. However, increasing the scan rate more than 100 mV/s, no effect to the peak was observed. To obtain the highest signal of Cr(VI) scan rate at 100 mV/s was chosen in further experiments. Table-1 summarizes the operating conditions optimized for the DP-ASV analysis of Cr(VI) using a Au_{film}-GCE.

TABLE-1
SUMMARIZES THE OPERATING CONDITIONS
OPTIMIZED FOR Cr(VI) DETERMINATION WITH
DP-ASV USING A Au_{film}-GCE SENSOR

Experimental conditions: (DP-ASV)	Optimized value
Supporting electrolyte	HCl 0.1 M
pH	1.0
Deposition time	120 s
Deposition potential	-0.2 V
Detection potential ^a	+0.3 V
Scan rate	100 mV/s
Potential scan	-0.2 to 0.8 V
Modulation amplitude	20 mV
Modulation time	5 ms

^avs. Ag/AgCl, saturated KCl

Analytical parameters: The analytical performance of modified sensor Au_{film}/GCE for the determination of Cr(VI) were estimated by DP-ASV technique under optimal conditions. The differential pulse anodic stripping voltammograms for different concentrations of Cr(VI) are illustrated in Fig. 3a. The calibration plot is linear over the range from 10 to 120 µg L⁻¹. Limits of detection calculated based on three times the standard deviation was averaged to 5.5 µg L⁻¹. The relative standard deviation for Cr(VI) determination at the concentration 120 µg L⁻¹ was 4.7% (n = 4). The results obtained in this work demonstrate the improvement of the reproducibility and sensitivity for determination of Cr(VI) using Au_{film}/GCE sensor and DP-ASV.

The sensitivity of the present method studied in this work shows advantages in terms of sensitivity and low detection limit when compared with reported electroanalytical methods (Table-2).

TABLE-2
PERFORMANCE OF DIFFERENT MODIFIED ELECTRODES FOR Cr(VI) DETERMINATION

Modified electrode	Method	LOD ($\mu\text{g/L}$)	LDR ($\mu\text{g/L}$)	Reference
Electrochemically activated GCE	DPV	6.25	20.8-13000	[11]
Gold screen printed macro electrode	LSV	228	520-84240	[12]
AuNP-ITO electrode ^d	CV ^c	104	260-5200	[13]
	Amperometry	5.2	26-2600	
Ag NPs ^a - carbon SPE ^c	DPV	44.2	26-1976	[14]
Au NPs - carbon SPE	DPV	20.8	20.8-1664	
Ag _{plated} -GCE	DP-ASV	5.2	18.2-2080	[15]
Graphite screen printed electrode	LSV	18.7	99.8-998.4	[16]
Au _{film} -GCE	DP-ASV	5.5	10-120	This work

^aNPs = nanoparticles, ^bLSV = Linear sweep voltammetry, ^cCV = Cyclic voltammetry, ^dAuNP-ITO electrode = Gold nanoparticle-electrodeposited indium-tin oxide electrode, ^eSPE = screen printed electrode

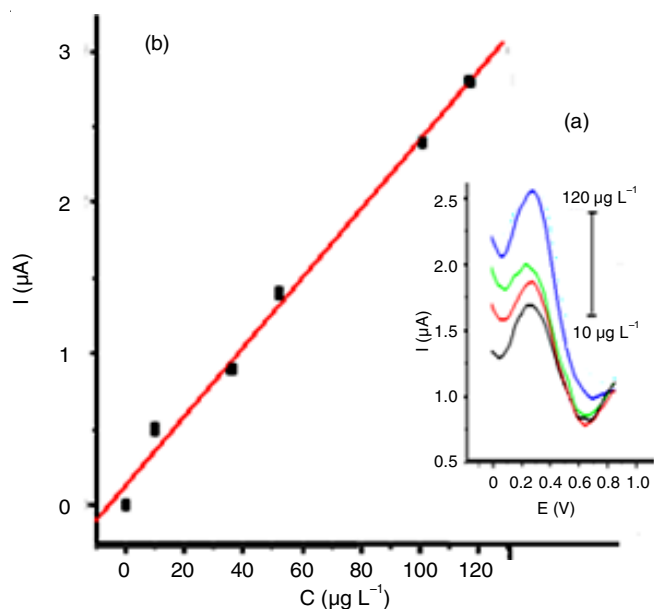


Fig. 3. (a) DP-AS voltammograms registered with Au_{film}/GCE electrode in HCl 0.1 M, $t_{\text{dep}} = 120$ s, potentiostatic from -0.2 to 0.8 V in different concentration of Cr(VI). (b) Calibration curve of various Cr(VI) concentrations

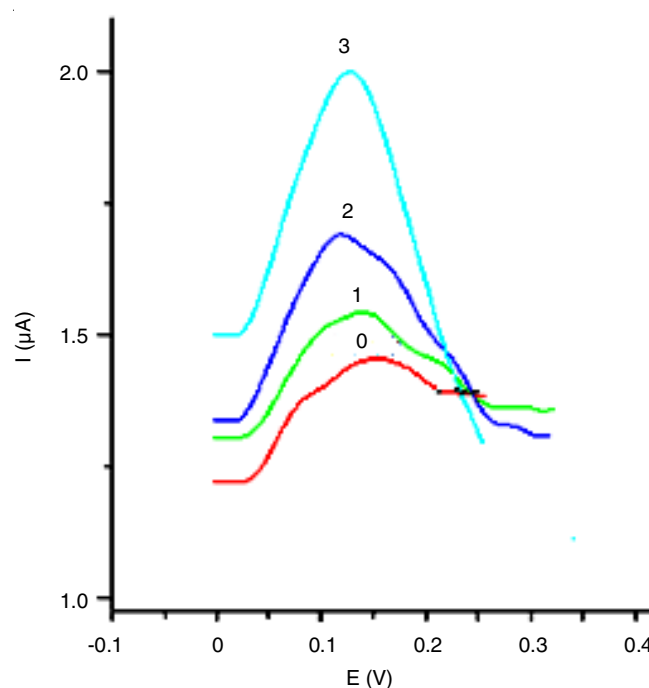


Fig. 4. DP-AS Voltammograms for standard additions of Cr(VI) in a sewage water sample, (0) sample signal before spiking and in concentrations (1) 30, (2) 60, (3) 88 $\mu\text{g/L}$ Cr(VI)

Real sample analysis: The modified glassy carbon electrode was successfully applied for the Cr(VI) determination in the sewage water sample. A sample solution was acidified with nitric acid and then 2 mL portion was pipetted out was diluted in 15 mL of 0.1 M HCl for the analysis. The content of chromium was determined using standard addition methods and the recoveries of added Cr(VI) were studied. The recoveries results were used as the quality control for the analytical determination of Cr(VI) in real samples taken from the nearby industrial leather processing and cleaning factory. The signal of the sample solution before spiking Cr(VI) was recorded (Fig. 4) and then addition of Cr(VI) were done to the solution and the voltammograms are recorded.

The voltammetric signals after the additions of Cr(VI), from 30 to 88 $\mu\text{g L}^{-1}$ are shown in Fig. 4. An increase in the anodic signals was obtained with increasing the concentration of Cr(VI). The recovery results of analyses are given in Table-3, together with the total chromium found by Au_{film}/GCE in sewage samples. The concentration of chromium(VI) in the analyzed samples was found to be $150 \pm 0.6 \mu\text{g L}^{-1}$, which is

much higher than the allowance level of Cr(VI) in surface water [17]. Cr(VI) recovered from the concentrations of 176 and 88 $\mu\text{g L}^{-1}$ was 100.3% and 97.3%, respectively, with an RSD of 4.8-5.4%. The results indicated that the proposed method can be easily employed for the regular analysis of chromium(VI) and be used for the Cr(VI) determination even in the presence of an excess Cr(III) ions.

TABLE-3
RECOVERY TEST WITH SEWAGE WATER SAMPLES

Sample (sewage water) ($\mu\text{g L}^{-1}$)	Cr(VI) ($\mu\text{g L}^{-1}$)		Spike recovery (%)
	Added	Found	
Chromium conc.	88	86.1 ± 0.8	97.8
	150 ± 0.6	176.5 ± 0.5	100.3

Conclusion

A gold thin film glassy carbon electrode (Au_{film}/GCE) was studied using DP-ASV for the determination of chromium(VI)

in liquid discharges of the leather processing industry. This method has advantages regarding the low cost for the fabrication of modified sensor, simple preparation, wide linear calibration zone, sensitivity and lowest limit of detection. It has been shown that after proper optimization of the experimental conditions, the electrode prepared was suitable for the determination of Cr(VI) with high sensitivity and good reproducibility. The method developed gave satisfactory results and recovery of 97.8% obtained for a concentration of 88 $\mu\text{g L}^{-1}$, when applied to real samples. Thus, the proposed sensor can be easily applied for analysis of chromium(VI) in industrial and environmental polluted water samples.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- H. Oliveira, *J. Botany*, **2012**, 375843 (2012); <https://doi.org/10.1155/2012/375843>
- A. Sharma, D. Kapoor, J. Wang, B. Shahzad, V. Kumar, A.S. Bali, S. Jasrotia, B. Zheng, H. Yuan and D. Yan, *Plants*, **9**, 100 (2020); <https://doi.org/10.3390/plants9010100>
- M.S. El-Shahawi, S.S.M. Hassan, A.M. Othman, M.A. Zyada and M.A. El-Sonbati, *Anal. Chim. Acta*, **534**, 319 (2005); <https://doi.org/10.1016/j.aca.2004.11.085>
- M.S. El-Shahawi, S.S.M. Hassan, A.M. Othman and M.A. El-Sonbati, *J. Microchem.*, **89**, 13 (2008); <https://doi.org/10.1016/j.microc.2007.10.006>
- R. Rudel and K. Terytze, *Chemosphere*, **39**, 697 (1999); [https://doi.org/10.1016/S0045-6535\(99\)00134-4](https://doi.org/10.1016/S0045-6535(99)00134-4)
- G. Liu, J.Y.-Y. Lin, Y.H. Wu and Y. Lin, *Environ. Sci. Technol.*, **41**, 8129 (2007); <https://doi.org/10.1021/es071726z>
- C.M. Welch, C.E. Banks, A.O. Simm and R.G. Compton, *Anal. Bioanal. Chem.*, **382**, 12 (2005); <https://doi.org/10.1007/s00216-005-3205-5>
- X. Dai, G.G. Wildgoose, C. Salter, A. Crossley and R.G. Compton, *Anal. Chem.*, **78**, 6102 (2006); <https://doi.org/10.1021/ac060582o>
- R.T. Kachoosang and R.G. Compton, *Sens. Actuators B: Chem.*, **178**, 555 (2013); <https://doi.org/10.1016/j.snb.2012.12.122>
- D. Yamada, T.A. Ivandini, M. Komatsu, A. Fujishima and Y. Einaga, *J. Electroanal. Chem.*, **615**, 145 (2008); <https://doi.org/10.1016/j.jelechem.2007.12.004>
- L. Richtera, H.V. Nguyen, D. Hynek, J. Kudr and V. Adam, *Analyst*, **141**, 5577 (2016); <https://doi.org/10.1039/C6AN00983B>
- J.P. Metters, R.O. Kadara and C.E. Banks, *Analyst*, **137**, 896 (2012); <https://doi.org/10.1039/c2an16054d>
- M.-C. Tsai and P.-Y. Chen, *Talanta*, **76**, 533 (2008); <https://doi.org/10.1016/j.talanta.2008.03.043>
- O. Domínguez-Renedo, L. Ruiz-Espelt, N. García-Astorgano and M.J. Arcos-Martínez, *Talanta*, **76**, 854 (2008); <https://doi.org/10.1016/j.talanta.2008.04.036>
- Z. Stojanovic, Z. Koudelkova, E. Sedlackova, D. Hynek, L. Richtera and V. Adam, *Anal. Methods*, **10**, 2917 (2018); <https://doi.org/10.1039/C8AY01047A>
- P.M. Hallam, D.K. Kampouris, R.O. Kadara and C.E. Banks, *Analyst*, **135**, 1947 (2010); <https://doi.org/10.1039/c0an00228c>
- U.S. Environmental Protection Agency, Toxicological, Review of Hexavalent Chromium, National Center for Environmental Assessment, Office of Research and Development, Washington, DC (1998).