We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Carbon-Based Electrode Application for Determination and Differentiation of Chromium Ion Species Using Voltammetric Method

Santhy Wyantuti, Safri Ishmayana, Diana Rakhmawaty Eddy and Yeni Wahyuni Hartati

Abstract

Cr(III) and Cr(VI) have significantly different toxicological properties, with the latter being toxic for human health. The anodic stripping voltammetry using pencil graphite electrode (PGE) was developed to determine Cr(III), and it can measure the ion within linear range 12.5–75 ppm with 0.31 ppm detection limit, while adsorptive striping voltammetry was used to determine very low level of Cr(VI) using PGE with the addition of diethylenetriaminepentaacetic acid (DTPA). The results indicate that Cr(VI) can give electrochemical response when adsorptive stripping voltammetry was used, and addition of DTPA gives a specific Cr(VI) peak at –0.65 V. A more advanced method was developed for the differentiation of Cr(VI) and Cr(III) using gold nanoparticle-modified glassy carbon electrode (AuNP-GCE). The AuNP-GCE was applied as electrochemical sensor for Cr(VI) and Cr(III) analysis. The electrode can differentiate Cr(VI) from Cr(III) using different conditions. Linear range for Cr(VI) determination using the method was between 0.050 and 0.250 μg/L, with detection limit of 2.38 ng/L, while for Cr(III), the linear range was between 0.500 and 75.000 ng/L, with detection limit of 0.010 ng/L. The study of other ions' effects on the method showed that copper(II), cadmium(II), nickel(II), and iron(III) do not interfere the measurement.

Keywords: Cr(III), Cr(IV), glassy carbon electrode, gold nanoparticle, pencil graphite electrode, voltammetry

1. Introduction

Chromium occurs in nature in two valencies, Cr(III) and Cr(VI). The two ionic species have distinct toxicity and reactivity [1]. Cr(VI) has high toxicity, while Cr(III) is less toxic, and the latter is also known to be one of the essential ions for humans, which is required in particular amount in the diet [2]. Due to

their opposite nature in toxicity, it is important to distinguish between Cr(III) and Cr(VI). Therefore, specific and sensitive determination methods to distinguish both of the species are required.

Since Cr(III) belongs to essential nutrition ion required for maintaining normal physiological function, thus trace amount determination of Cr(VI) becomes very important to avoid toxic intake in the diets [3]. There have been several sensitive methods used for Cr(III) and Cr(VI) determination including atomic absorption spectrophotometry (AAS) [4, 5], plasma mass spectroscopy [6], spectrofluorimetry [7], chemiluminescence [8], spectrophotometry [9], and electrochemical methods [10–12]. Determination of chromium ions using voltammetric method is evolving along with the requirements to accurately measure the ionic species [13–18].

The material of working electrode influences the performance of voltammetric method. Application of carbon-based electrode utilization is currently growing in electroanalytical field because it has some advantages including wide electrical potential range, low background current, inexpensive, inert, and suitable for a wide variety of sensors [19]. Modification of the electrode is being explored to enhance the electrode performance [20, 21]. The modified electrode needs to be evaluated for their performance. In the present chapter, investigation of carbon-based electrode without and with modification was evaluated for their performance to determine Cr(VI) and Cr(III).

2. Anodic stripping voltammetry with pencil graphite electrode for determination of Cr(III)

For determination of Cr(III) using graphite pencil electrode (GPE), three solvents were trialed [21], i.e., 0.01 M hydrochloric acid, acetate buffer pH 5.0, and double distilled water. Potential range from -800 to 1000 mV with 90 s deposition time, 10 s cleaning time, and 20 mV/s scan rate was used for the measurement using anodic stripping voltammetry. This experiment was performed to measure the background signal in order to get a correction factor which can avoid the presence of undesired peak current from the solvent. No peak was detected when 0.01 M hydrochloric acid was used at the condition applied, while acetate buffer pH 5.0 and double distilled water gave relatively high peak current which can interfere the measurement (data not shown). Therefore, hydrochloric acid was chosen as solvent for the method. For further experiment, Cr(III) solution was made by dissolving Cr(III) chloride in 0.01 M hydrochloric acid as solvent.

An experiment for investigating the linearity of the method was performed by measuring Cr(III) within 1–500 ppm range. The experiment was performed using a potential range of -1.5 to $+1.0$ V with 60 s of deposition time, 10 s of cleaning time, and 50 mV/s of scan rate. The electrode used in the experiment was pencil graphite electrode, and the linear concentration range was determined by correlating height of peak current and concentration of Cr(III). The linear concentration range was found in 12.5–75 ppm range, and the result is presented in **Figure 1**.

The range of linear concentration at 12.5–75 ppm gave correlation coefficient of 0.9936, which indicate good relationship with correlation equation of $y = 0.1778x + 0.747$. PGE can be used as working electrode for determination of Cr(III) with optimum condition achieved at 60 s of deposition time and 50 mV/s of scan rate. Linear range of Cr(III) measurement with the proposed condition was 12.5–75 ppm with 0.31 ppm limit of detection.
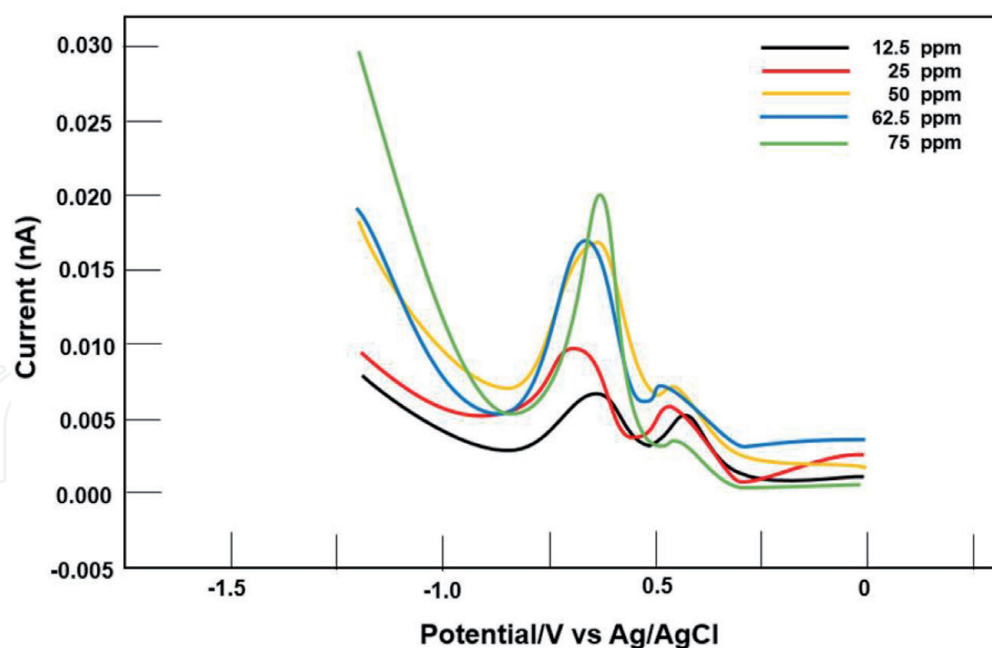
Figure 1.
Typical peak response of chromium(III) voltammogram using PGE. Experiment condition: solvent = 0.01 M hydrochloric acid, chromium(III) concentration = 12.5, 25, 50, 62.5, and 75 ppm was performed sequentially with 60 s of deposition time, 50 mV/s of scan rate, and deposition potential at −1260 mV [21].

3. The development of graphite pencil electrode for Cr(VI) determination using adsorptive stripping voltammetry

The addition of a chelating agent in the form of ligands to the Cr(VI) signal measurements has been done in several previous studies such as addition of rubeanic acid ligand [22] and addition of diethylenetriaminepentaacetic acid (DTPA) as ligand with electrolyte support of morpholinoethanesulfonate acid buffer (MES) [23]. From previous studies it can be concluded that the addition of a ligand for the measurement of Cr(VI) signal by voltammetry can increase the measurement sensitivity [24]. **Figure 2** shows that after the addition of the DTPA, the peak generated on the voltammogram becomes specific, and no further undesirable impurity peaks occur (black line designated as d). After background correction, it can be concluded that with the addition of DTPA, the impurity peaks were reduced, a specific peak on the voltammogram was produced, and the peak current height of chromium increases so that the measurement sensitivity also increases.

Calibration curve was prepared by measuring differential pulse adsorptive stripping voltammetry of Cr(VI) with the following concentrations: 1, 10, 20, and 30 ppm. The voltammetric measurement was carried out at a potential deposition condition of +810 mV, a scan rate of 50 mV/s, and a deposition time of 60 s with stirring using a magnetic stirrer.

From **Figure 3** it can be seen that the peak current height increases with increasing analyte concentration in the voltammetric cell. This may be due to the increasing number of Cr species deposited on the working electrode when the analytical concentration is added, thereby increasing the peak current in the voltammogram. The linear regression of the standard curve is y = 0.6319x + 8.5796 with correlation coefficient of 0.957.

The measurement of Cr(VI) peak current was performed triplicate to calculate precision value. For 1 ppm, a fairly low standard deviation was obtained which is 0.3466. This indicates that the measurement results have a fairly good accuracy or precision, and from the calculation, the coefficient of variation of
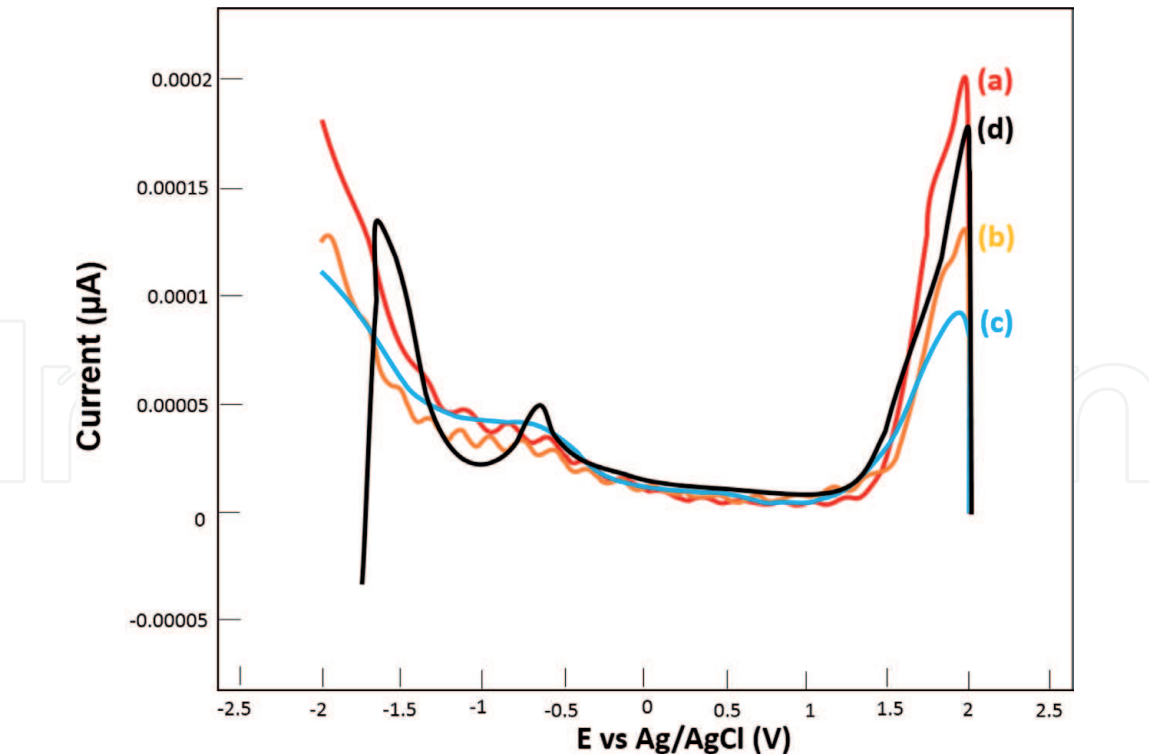
Figure 2.
Voltammogram of (a) 0.2 M acetate buffer pH 6.0, (b) DTPA 868 ppm, (c) 30 ppm Cr(VI), and (d) 30 ppm Cr(VI) with addition of DTPA. Measurement conditions: potential deposition, +810 mV; deposition time, 60 s; scan speed, 50 mV/s; potential range, +2000 V to −2000 mV.
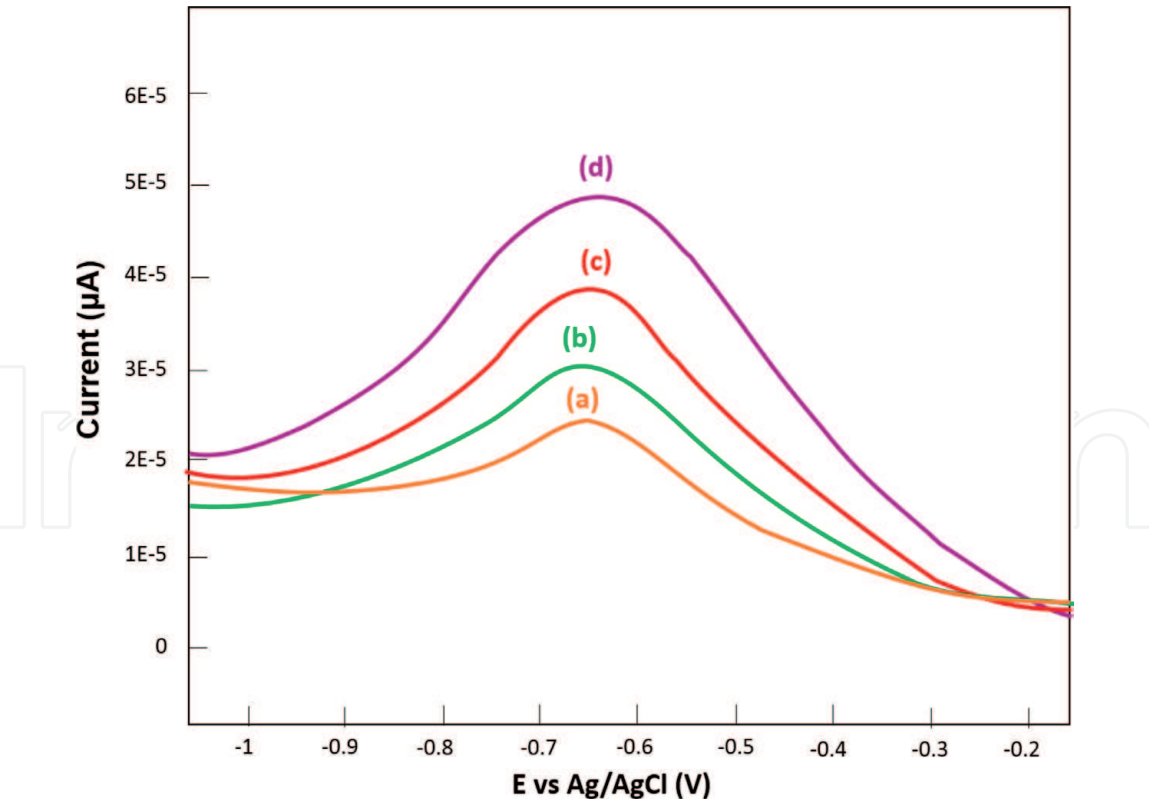

Figure 3.
Voltammogram of Cr(VI) using PGE with concentration of (a) 1, (b) 10, (c) 20, and (d) 30 ppm with DTPA addition. Measurement conditions: potential deposition, +810 mV; deposition time, 60 s; scan rate, 50 mV/s; potential range, +2000 V to −2000 mV.

4.56% was also obtained. The addition of DTPA as ligand can be used to detect Cr(VI) and can produce a specific peak for Cr(VI) at a potential region of −0.6474 V.

4. Voltammetric determination of Cr(VI) using gold nanoparticle-modified glassy carbon electrode

AuNP was synthesized using citric ion as capping agent. After reduction using NaBH$_4$ solution, the gold solution color was changed from yellow to red ruby (λ_{max} = 518 nm), which indicate that AuNP colloid was formed with average dimension of 2–5 nm [25]. Characterization using TEM indicates that the average diameter of the colloid was ~2.2 nm (**Figure 4**). This gold nanoparticle was then used to modify the GCE.

GCE was modified by attaching AuNP onto the electrode surface. Modification of GCE was initiated by polishing the electrode followed by activation. This step was performed so that the electrode can be covered evenly and maximally by the AuNP, which eventually can increase sensitivity when used to determine the analyte. Photochemical reaction is one of the many methods to activate the GCE surface. The photochemical reaction was performed by immersing the electrode into concentrated ammonium hydroxide and followed by irradiation under UV light for 6 hours at 254 nm [26]. This process is known as self-assembly which can substitute hydrogen group (–H) with amine group (–NH$_2$) of the electrode. Due to the nature of the amine group, more AuNP can be attached to the electrode and improve binding to the electrode [27], as indicated by SEM-EDS data. SEM-EDS data demonstrated that the self-assembly process was better than the adsorption process. Modification of GCE by self-assembly process reached 11.55% of AuNP covering the electrode (**Figure 5**), while the adsorption process (direct immersion of the electrode) only reached 2.05% covering according to SEM-EDS data.

From the present study, it was found that optimum deposition potential and deposition time for determination of 0.5 µg/L Cr(VI) in 0.01 M hydrochloric acid as

Figure 4.
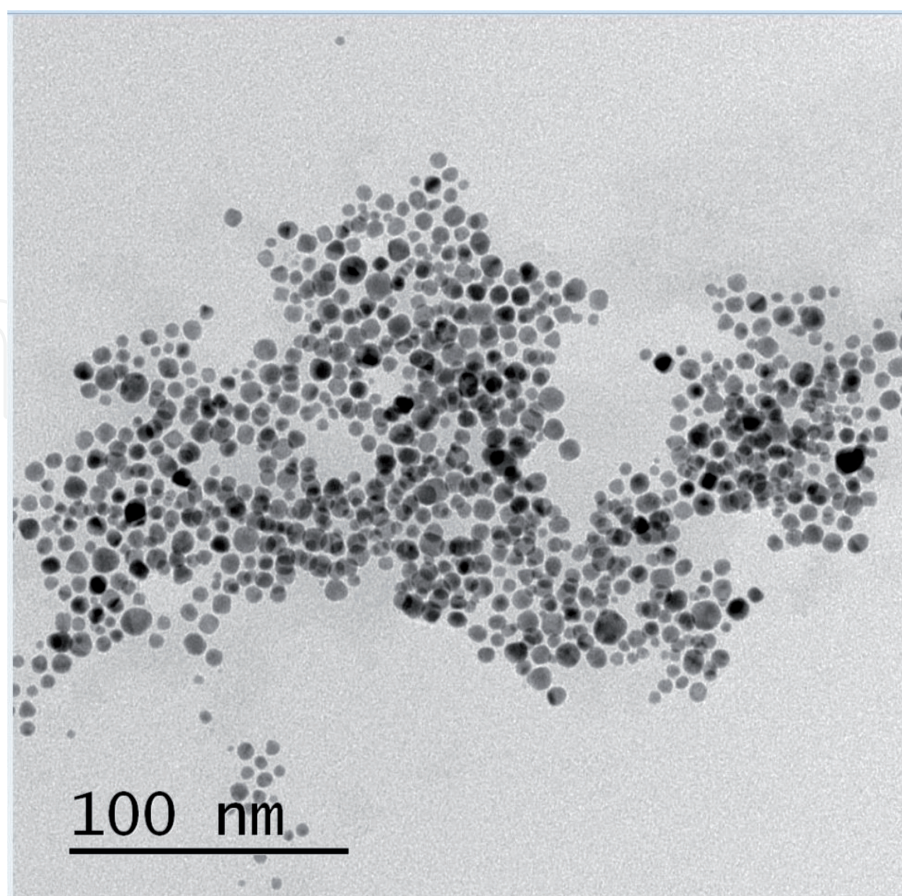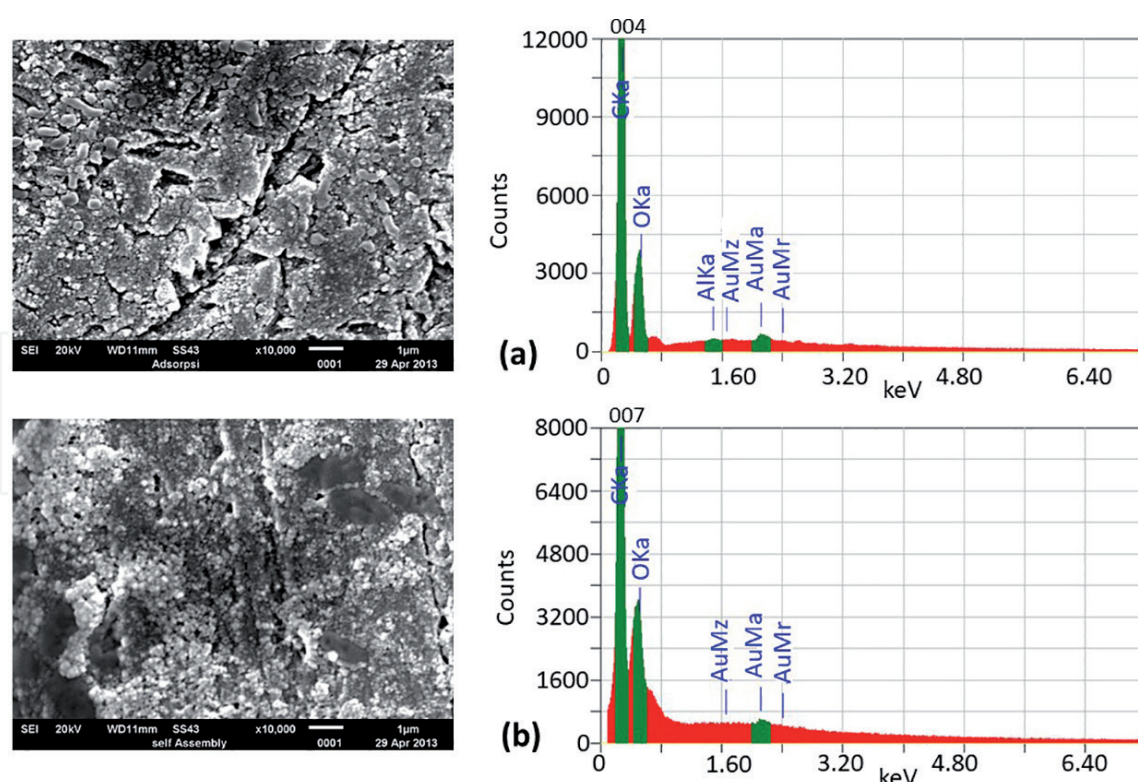*TEM image of gold nanoparticles.*

Figure 5.
SEM image of gold nanoparticle-modified glassy carbon electrode surface. Modification was conducted using (a) adsorption and (b) self-assembly process.
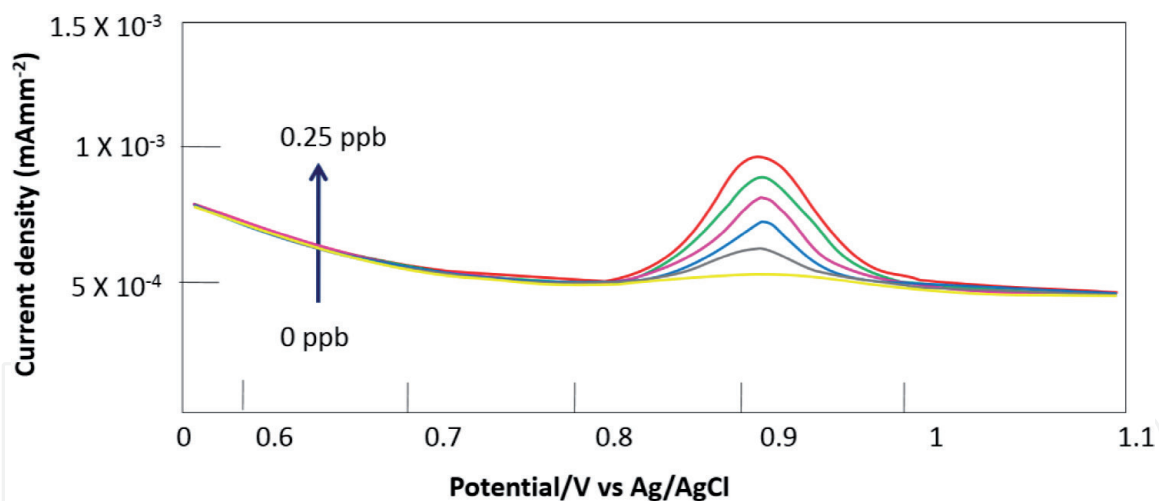

Figure 6.
Voltammogram of various chromium(VI) concentrations (0–0.25 μg/L) with AuNP-GCE. The condition of measurement is as follows: deposition potential, deposition time, scan rate, and amplitude modulation at 800 mV, 120 s, 50 mV/s, and 500 mV, respectively.

supporting electrolyte solution were 800 mV and 120 s, respectively. The optimum condition was then applied to develop a calibration curve with concentration ranging from 0 to 25 μg/L, and the current density to potential data of the concentrations is presented in **Figure 6**. From the data, a linear calibration curve ($r^2 = 0.9896$) was developed and is presented on **Figure 7** with correlation coefficient and linear regression equation of 0.9911 and $I = 2.25 \times 10^{-3} C + 5.89 \times 10^{-4}$, respectively. Through calculation, it was obtained that limit of detection and precision of the method are 2.38 ng/L and 99.14%, respectively.

To see whether we can distinguish Cr(VI) from Cr(III) using condition described earlier, we measure individual and mixture of the ionic species. The result
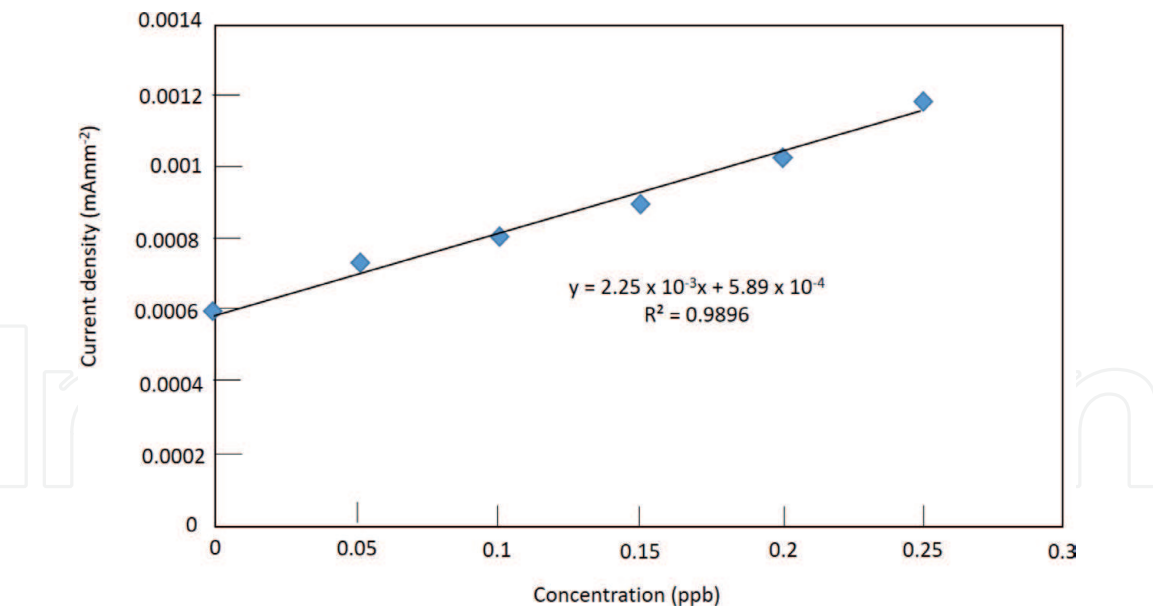
Figure 7.
Calibration curve of various chromium(VI) concentrations with deposition potential, deposition time, scan rate, and amplitude modulation at 800 mV, 120 s, 50 mV/s, and 500 mV, respectively.
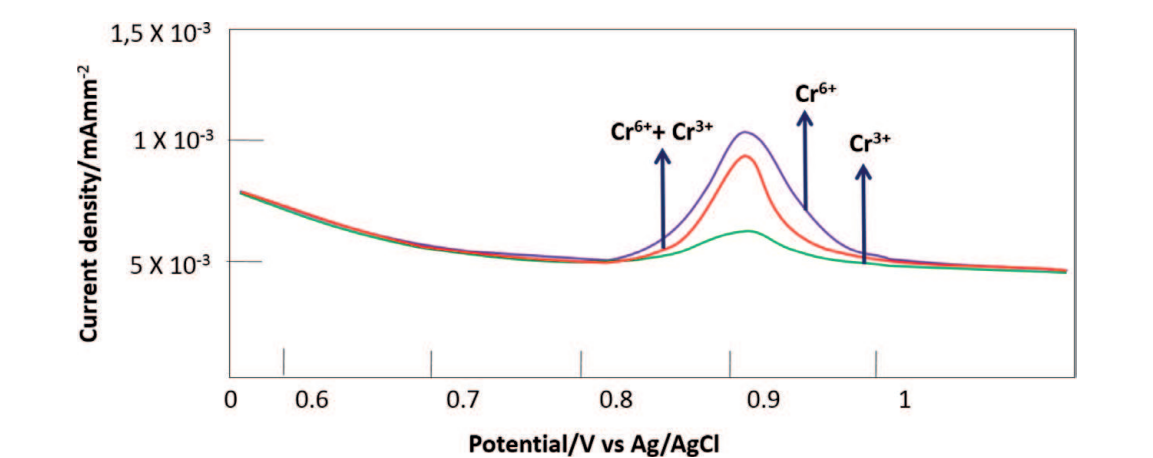

Figure 8.
Voltammogram of Cr(III) and Cr(VI) and mixture of Cr(III) and Cr(VI) in 0.01 M hydrochloric acid using AuNP-GCE against Ag/AgCl with deposition potential of 800 mV, deposition time of 120 s, and amplitude modulation of 0.05 V.

is presented in **Figure 8**. In contrast with Cr(VI), it was found that in this condition Cr(III) does not give a sharp peak. However, it seems that the peak of the mixture was slightly reduced compared to Cr(VI) peak. Therefore, we can measure Cr(VI) in this condition with a neglected effect from Cr(III).

5. Voltammetric detection of Cr(III) using gold nanoparticle-modified glassy carbon electrode

To determine the optimum condition for determination of Cr(III) using AuNP-GCE, a preliminary experiment was conducted by varying deposition potential. The potential used were ranging from −2.0 to −1.0 V with scan rate and amplitude modulation of 0.05 V/s and 0.05 V, respectively. The highest efficiency for Cr(III) 500 ppb in 0.2 M acetate buffer was found at −1.5 V, while optimization of deposition time leads us to conclude that the best result was obtained at 90 s [17]. The optimized parameters are very crucial in stripping step that have

pronounced effect on both sensitivity and linear range. Therefore, from the preliminary experiment, we conclude that the optimum condition for determination of Cr(III) using AuNP-GCE is using −1.5 V of deposition potential and 90 s of deposition time.

The optimum condition was then applied to prepare a calibration curve of Cr(III) using AuNP-GCE differential pulse stripping voltammetry. The calibration curve was obtained by varying concentration of Cr(III) and measuring it at −1.5 V of deposition potential, 90 s of deposition time, 0.05 V/s of scan rate, and 0.05 V of amplitude modulation. The voltammetric measurement and calibration curve are presented in **Figure 9**. By calculation, a linear regression equation and correlation coefficient of y = 0.142 + 0.004x and r = 0.9955, respectively, were obtained. The result showed that the linear range was obtained at 0.5–75 ppb range. The reproducibility of the method was then determined from the replicate measurement of 1 ppb Cr(III). The calculation results in a mean of current response of 0.14 µA ppb^{-1}, which is referred to as sensitivity of the method. It corresponds to the value of relative standard deviation (RSD) of 2.4%. Based on calculation suggested by Miller and Miller [28], limit of detection of the method is 0.01 ppb, which is three times of the value of standard deviation baseline. Utilization of AuNP-modified electrode improves at least one order of magnitude detection limit compared to voltammetric method using film electrode. Limited publication of voltammetric detection of Cr(III) compared to Cr(VI) and poor sensitivity of non-gold electrode lead us to infer that gold or gold-modified electrodes are required to get high-quality Cr(III) voltammetric profiles. It is previously reported that high-quality voltammetric profiles for Cr(III) appear when gold electrode is used [29].

Optimum condition was then applied for determination of Cr(III) in electroplating wastewater, which is a more complex matrix than the standard solution. Based on standard addition method, we found that the concentration of Cr(III) in the sample was 0.146 ppm, corresponding to 97% recovery and in good agreement with the result from AAS method (AAnalyst 400, PerkinElmer) after appropriate
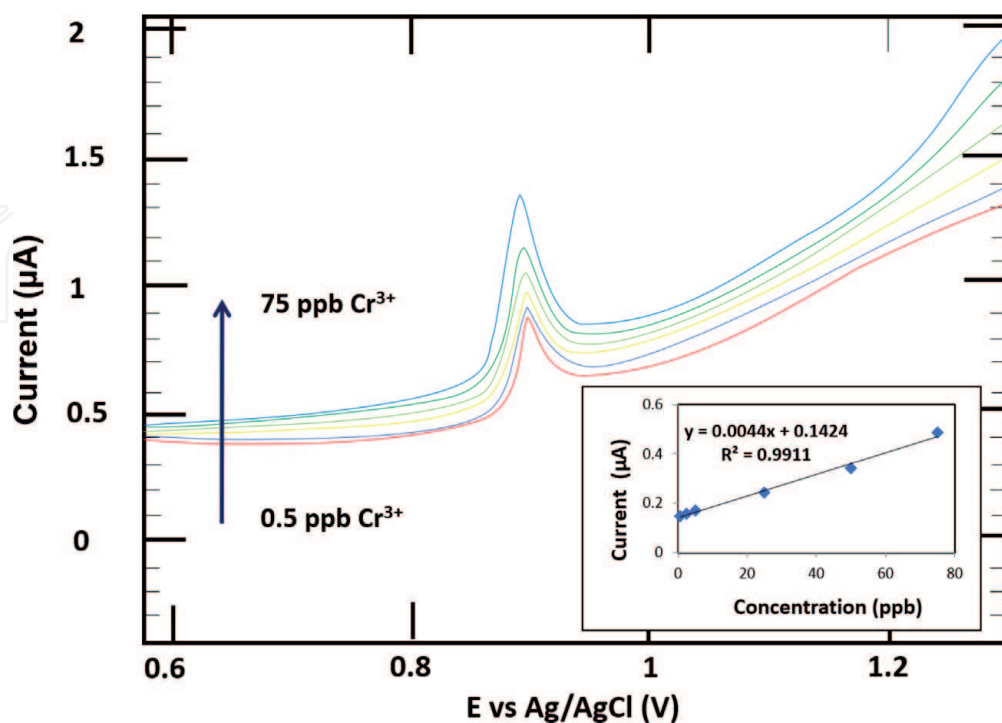

Figure 9.
Voltammetric performance for Cr(III) concentration variation. Inset shows corresponding calibration curve at an optimum condition.
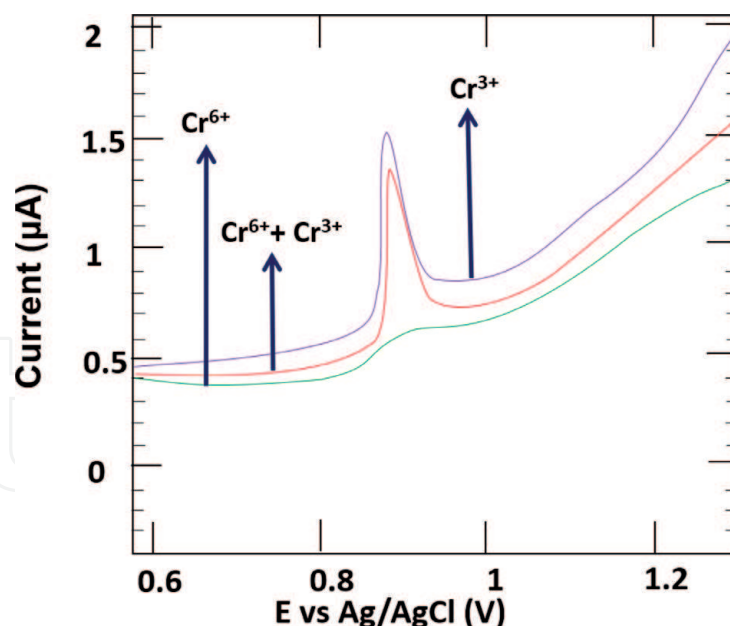
Figure 10.
Voltammogram Cr(III) and Cr(VI) and mixture of Cr(III) and Cr(VI) in acetate buffer pH 5 using AuNP-GCE electrode against Ag/AgCl electrode with deposition potential of −1500 mV, deposition time of 90 s, and amplitude modulation of 50 mV.

extraction. Therefore, the proposed voltammetric method using the fabricated electrochemical AuNP-GCE sensor gives satisfactory result and is applicable for determination of Cr(III) in complex matrix, such as wastewater.

There is a possibility that Cr(VI) interferes the Cr(III) measurement in the proposed condition. Therefore, we measure the voltammogram of individual and mixture of the ionic species. The results are presented in **Figure 10**. From the figure, it is clear that by using the proposed condition, clear peak was only detected for Cr(III) species, while Cr(VI) did not show any significant peak at the corresponding potential. Mixture of Cr(III) and Cr(VI) also gives similar peak which corresponds to the individual Cr(VI) peak.

6. Study on interfering ions

In order to evaluate the effect of foreign metal ions dissolved in the media, solutions containing 50 ppb of Cr(III) and each of the following metals Cd(II), Cu(II), Zn(II), Cr(VI), Ni(II), and Fe(III) all at the same concentration of 50 ppb were prepared. Measurement was conducted at an optimum condition described in Subchapter 4, and the result is presented in **Table 1**. The effect of interfering metal ion on Cr(III) was indicated by the change in peak current signal during measurement. The addition of foreign ions does not influence the peak current corresponding to Cr(III). The percentage variations of the peak current induced by the presence of interfering ions with respect to Cr(III) alone are 1.02% for Cd(II), 0.88% for Cu(II), 0.29% for Zn(II), 3.70% for Cr(VI), 0.07% for Ni(II), and 0.40% for Fe(III). These deviations from Cr(III) measurement at 0.9470 V and 1.360 μA remain acceptable, and, therefore, the accurate detection of Cr(III) is still possible under these conditions.

Cd(II) and Zn(II) ions have a standard reduction potential similar to Cr(III) ion. During the current measurement of Cr(III) with the presence of interfering ions, they also deposited on the electrode surface, reducing the amount of Cr(III) on the electrode surface. At the deposition stage, when −1.5 V electric potential was

Interfering metal ion	Potential (V)	Current (μA)	Change (%)
None	0.9470	1.360	–
Cd(II)	0.8857	1.374	1.02
Cu(II)	0.8357	1.348	0.88
Zn(II)	0.8507	1.356	0.29
Cr(VI)	0.9359	1.323	3.7
Ni(II)	0.9100	1.361	0.07
Fe(III)	0.8507	1.356	0.4

Table 1.
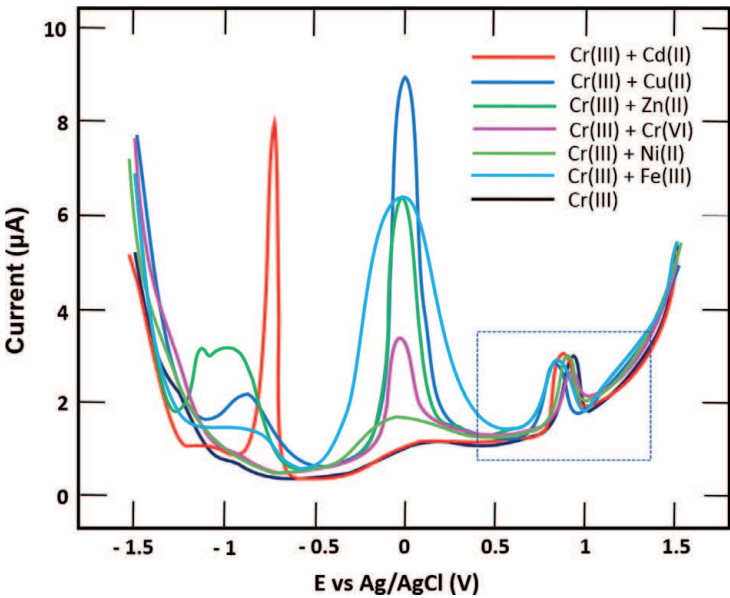*Result of measurement of 50 ng/L Cr(III) in the presence of 50 ng/L interfering metal ions.*

Figure 11.
Differential pulse voltammogram of Cr(III) using AuNP-GCE with −1.5 V of deposition potential, 90 s of deposition time, 0.05 V/s of scan rate, and 0.05 V of amplitude modulation against Ag/AgCl. Concentration of Cr(III) was 50 ppb in acetate buffer pH 5 without and with the presence of Cd(II), Cu(II), Zn(II), Cr(VI), Ni(II), or Fe(III) as interfering ions with concentration of 50 ppb.

applied, the ions will be reduced too because their standard reduction potential are more positive than the deposition potential applied. The effect of interfering metal ion is presented in **Figure 11**.

Fe(III), Cr(VI), Cu(II), and Ni(II) ions have more positive standard reduction potential than Cr(III), and therefore when −1.5 V potential was applied, the interfering ions were also reduced and causing less Cr(III) reduced than it should be. Therefore, the peak of Cr(III) is reduced, while Zn(II) and Cd(II) have more negative standard reduction potential than Cr(III), and therefore when reduction potential was applied, Cr(III) will be reduced followed, in order, by Zn(II) and Cd(II).

7. Conclusions

Carbon-based electrode can be applied as working electrode for the determination of Cr(III) and Cr(VI). PGE can detect the presence of Cr(III) in solution, while for Cr(VI) addition of DTPA is needed to get a specific peak current of Cr(VI). The

two methods utilizing PGE can detect Cr(III) and Cr(VI) in ppm scale. To enhance the analytical performance, AuNP-GCE was used as working electrode, and it showed better results. The modified electrode can measure both Cr(III) and Cr(VI) in ppb scale. By using a different condition, we succeeded to measure Cr(III) and Cr(VI) with the same working electrode.

Acknowledgements

Author details

Santhy Wyantuti*, Safri Ishmayana, Diana Rakhmawaty Eddy
and Yeni Wahyuni Hartati
Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Universitas Padjadjaran, Sumedang, West Java, Indonesia

*Address all correspondence to: santhy.wyantuti@unpad.ac.id

IntechOpen

References

[1] Cespón-Romero RM, Yebra-Biurrun MC, Bermejo-Barrera MP. Preconcentration and speciation of chromium by the determination of total chromium and chromium(III) in natural waters by flame atomic absorption spectrometry with a chelating ion-exchange flow injection system. Analytica Chimica Acta. 1996;**327**(1):37-45. DOI: 10.1016/0003-2670(96)00062-1

[2] Costa M, Klein CB. Toxicity and carcinogenicity of chromium compounds in humans. Critical Reviews in Toxicology. 2006;**36**(2):155-163. DOI: 10.1080/10408440500534032

[3] Domínguez-Renedo O, Alonso-Lomillo MA, Arcos-Martinez MJ. Optimisation procedure for the inhibitive determination of chromium(III) using an amperometric tyrosinase biosensor. Analytica Chimica Acta. 2004;**521**(2):215-221. DOI: 10.1016/j.aca.2004.06.026

[4] Bağ H, Türker AR, Lale M, Tunçeli A. Separation and speciation of Cr(III) and Cr(VI) with *Saccharomyces cerevisiae* immobilized on sepiolite and determination of both species in water by FAAS. Talanta. 2000;**51**(5):895-902. DOI: 10.1016/S0039-9140(99)00354-9

[5] Kiran K, Kumar KS, Prasad B, Suvardhan K, Lekkala RB, Janardhanam K. Speciation determination of chromium(III) and (VI) using preconcentration cloud point extraction with flame atomic absorption spectrometry (FAAS). Journal of Hazardous Materials. 2008;**150**(3):582-586. DOI: 10.1016/j.jhazmat.2007.05.007

[6] Hirata S, Honda K, Shikino O, Maekawa N, Aihara M. Determination of chromium(III) and total chromium in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry. Spectrochimica Acta Part B: Atomic Spectroscopy. 2000;**55**(7):1089-1099. DOI: 10.1016/S0584-8547(00)00169-5

[7] Tang B, Yue T, Wu J, Dong Y, Ding Y, Wang H. Rapid and sensitive spectrofluorimetric determination of trace amount of Cr(III) with o-vanillin-8-aminoquinoline. Talanta. 2004;**64**(4):955-960. DOI: 10.1016/j.talanta.2004.04.016

[8] Gammelgaard B, Y-p L, Jøns O. Improvement on simultaneous determination of chromium species in aqueous solution by ion chromatography and chemiluminescence detection. Analytica Chimica Acta. 1997;**354**(1-3):107-113. DOI: 10.1016/S0003-2670(97)00421-2

[9] Kaneko M, Kurihara M, Nakano S, Kawashima T. Flow-injection determination of chromium(III) by its catalysis on the oxidative coupling of 3-methyl-2-benzothiazolinone hydrazone with *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3-methoxyaniline. Analytica Chimica Acta. 2002;**474**(1-2):167-176. DOI: 10.1016/S0003-2670(02)01005-X

[10] Chatzitheodorou E, Economou A, Voulgaropoulos A. Trace determination of chromium by square-wave adsorptive stripping voltammetry on bismuth film electrodes. Electroanalysis. 2004;**16**(21):1745-1754. DOI: 10.1002/elan.200403051

[11] Husáková L, Bobrowski A, Šrámková J, Królicka A, Vytřas K. Catalytic adsorptive stripping voltammetry versus electrothermal atomic absorption spectrometry in the determination of trace cobalt and chromium in human urine. Talanta. 2005;**66**(4):999-1004. DOI: 10.1016/j.talanta.2005.01.003

[12] Safavi A, Maleki N, Shahbaazi HR. Indirect determination of hexavalent chromium ion in complex matrices by adsorptive stripping voltammetry at a mercury electrode. Talanta. 2006;**68**(4):1113-1119. DOI: 10.1016/j.talanta.2005.07.015

[13] Campbell FW, Compton RG. The use of nanoparticles in electroanalysis: An updated review. Analytical and Bioanalytical Chemistry. 2010;**396**(1):241-259. DOI: 10.1007/s00216-009-3063-7

[14] Hong J, Wang W, Huang K, Yang W-Y, Zhao Y-X, Xiao B-L, et al. A highly efficient nano-cluster artificial peroxidase and its direct electrochemistry on a nano complex modified glassy carbon electrode. Analytical Sciences. 2012;**28**(7):711-716. DOI: 10.2116/analsci.28.711

[15] Jin W, Wu G, Chen A. Sensitive and selective electrochemical detection of chromium(VI) based on gold nanoparticle-decorated titania nanotube arrays. Analyst. 2014;**139**(1):235-241. DOI: 10.1039/C3AN01614E

[16] Saha K, Agasti SS, Kim C, Li X, Rotello VM. Gold nanoparticles in chemical and biological sensing. Chemical Reviews. 2012;**112**(5):2739-2779. DOI: 10.1021/cr2001178

[17] Wyantuti S, Hartati YW, Firdaus ML, Panatarani C, Tjokronegoro R. Fabrication of gold nanoparticles-modified glassy carbon electrode and its application for voltammetric detection of Cr(III). International Journal of Scientific & Technology Research. 2015;**4**(1):135-139

[18] Wyantuti S, Tjokronegoro R, Hartati YW, Panatarani C. Cyclic voltammetry study of chromium(VI) and chromium(III) at a gold nanoparticles-modified glassy carbon electrode. Procedia Chemistry.

2015;**17**:170-176. DOI: 10.1016/j.proche.2015.12.109

[19] Wang J. Analytical Electrochemistry. 3rd ed. New Jersey: John Wiley & Sons; 2006

[20] Bui M-PN, Li CA, Han KN, Pham X-H, Seong GH. Simultaneous detection of ultratrace lead and copper with gold nanoparticles patterned on carbon nanotube thin film. Analyst. 2012;**137**(8):1888-1894. DOI: 10.1039/C2AN16020J

[21] Wyantuti S, Hafidza RA, Ishmayana S, Hartati YW. Anodic stripping voltammetry with pencil graphite electrode for determination of chromium(III). Journal of Physics: Conference Series. 2017;**812**:012006. DOI: 10.1088/1742-6596/812/1/012006

[22] Abbasi S, Bahiraei A. Ultra trace quantification of chromium(VI) in food and water samples by highly sensitive catalytic adsorptive stripping voltammetry with rubeanic acid. Food Chemistry. 2012;**133**(3):1075-1080

[23] Korolczuk M, Stępniowska A. Determination of Cr(VI) in the presence of high excess of a Cr(III) by adsorptive stripping voltammetry. Talanta. 2012;**88**:427-431. DOI: 10.1016/j.talanta.2011.11.012

[24] Wyantuti S, Anjani R, Hartati YW. The development of graphite pencil electrode for chromium(VI) determination using adsorptive stripping voltammetry. In: Poceeding of the Bengkulu International Conference on Science and Education. Bengkulu: Universitas Bengkulu; 14-15 December 2017. p. 310-313

[25] Frens G. Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. Nature Physical Science. 1973;**241**(105):20-22

[26] Wyantuti S, Ishmayana S, Hartati YW. Voltammetric determination of Cr(VI) using gold nanoparticles-modified glassy carbon electrode. Procedia Chemistry. 2015;**16**:15-23. DOI: 10.1016/j. proche.2015.12.010

[27] Tian R-H, Rao TN, Einaga Y, Zhi J-F. Construction of two-dimensional arrays gold nanoparticles monolayer onto boron-doped diamond electrode surfaces. Chemistry of Materials. 2006;**18**(4):939-945. DOI: 10.1021/ cm0519481

[28] Miller J, Miller JC. Statistics and Chemometrics for Analytical Chemistry. 6th ed. Canada: Pearson Education; 2010. p. 296

[29] Welch CM, Hyde ME, Nekrassova O, Compton RG. The oxidation of trivalent chromium at polycrystalline gold electrodes. Physical Chemistry Chemical Physics. 2004;**6**(12):3153-3159. DOI: 10.1039/B404243C