Vol.7, No.2, 2022
e-ISSN 2502-4787

ELECTROCHEMICAL DETECTION OF Pb(II) USING A PENCIL ELECTRODE WITH SQUARE WAVE ANODIC STRIPPING VOLTAMMETRY METHOD

Muhammad Zamhari[1*], Muhamad Aditya Hidayah[1], Gerda Pintoko Tunjungsari[1], Endaruji Sedyadi[2]

[1]*Chemistry Education, Faculty of Teacher Training and Education, Universitas Islam Negeri Sunan Kalijaga, Sleman, Yogyakarta, Indonesia*
[2]*Chemistry, Faculty of Science and Technology, Universitas Islam Negeri Sunan Kalijaga, Sleman, Yogyakarta, Indonesia*

E-mail: *muhammad.zamhari@uin-suka.ac.id

Received: 06 April 2022. Accepted: 19 November 2022. Published: 31 Desember 2022

DOI: 10.30870/educhemia.v7i2.14756

Abstract: This work describes a simple and inexpensive Pb(II) determination by a pencil electrode using the square wave anodic stripping voltammetry (SWASV) method. This research was applied using a batch cell system on 10 mL of 0.1 M acetate buffer pH 4.5. The precision was performed with repeatability and reproducibility in Pb(II) concentrations of 0.2, 0.4, 0.6, and 0.8 µg mL^{-1}. Two linear ranges were obtained in the concentration of 0.1–1.0 and 2.0–8.0 µg mL^{-1}. This method offers a detection limit of 0.07 µg mL^{-1} and a quantification limit of 0.24 µg mL^{-1}. The technique performed good repeatability (RSD= 7.28–9.53%) and good reproducibility (RSD=7.07–15.10%). The precisions are accepted according to the Association of Official Analytical Chemists (AOAC) standard (RSD repeatability <11% and RSD reproducibility <16% at a concentration of 1 µg mL^{-1}). The method offered high operational stability up to 18 measurements (RSD=4.6%). The technique performs acceptable results with low random error in determining Pb(II).

Keywords: pencil electrode; square wave anodic stripping voltammetry; lead

Abstrak: Artikel ini memaparkan penentuan Pb(II) yang sederhana dan murah dengan elektroda pensil menggunakan metode square wave anodic stripping voltametry (SWASV). Pengujian ini dilakukan dengan sistem *batch cell* pada 10 mL buffer asetat 0,1 M pH 4,5. Uji presisi dilakukan dengan uji repeatibilitas dan reprodusibilitas pada konsentrasi Pb(II) 0,2, 0,4, 0,6, dan 0,8 µg mL^{-1}. Penentuan Pb(II) menghasilkan dua kurva kalibarasi, yaitu pada rentang 0,1–1,0 dan 2,0–8,0 µg mL^{-1}. Metode ini menawarkan batas deteksi dan batas kuantifikasi yang baik secara berturut-turut 0,07 µg mL^{-1} dan 0,23 µg mL^{-1}. Metode ini menghasilkan repeatibilitas yang baik (RSD= 7.28–9.53%) dan reprodusibilitas yang baik (RSD=7,07–15,10%). Hasil ini diterima sesuai dengan standar AOAC (RSD repeatibilitas <11% dan RSD reprodusibilitas <16% pada konsentrasi 1 µg mL^{-1}). Metode ini menawarkan stabilitas operasional yang tinggi untuk penentuan simultan hingga 18 pengukuran (RSD=4.6%). Kemudian, metode tersebut melakukan hasil yang dapat diterima dengan kesalahan acak yang rendah dalam penentuan Pb(II).

Kata kunci: elektroda pencil; square wave anodic stripping voltammetry; timbal

INTRODUCTION

Lead is a dangerous heavy metal that threatens the human body (Oleko et al., 2022). Exposure to this metal of more than 0.015 μg mL^{-1} will lead to kidney and liver problems, cancer, and high blood pressure (Teerasarntipan et al., 2020, Abd-AlGhafar et al., 2022). More hurtful things will occur to children because they can interfere with the child's physical and mental growth (O'Connor et al., 2020). In addition, this will impact the decline in children's ability to focus and learning abilities (USEPA, 2009).

Through the Food and Drug Supervisory Agency (BPOM), the government has issued regulation number 23 of 2007 concerning the maximum limit of heavy metal contamination in processed food. According to the regulation, the maximum limit for lead in coffee, tea, grain drinks, and hot cereal is 2 μg mL^{-1} (BPOM, 2017). However, this amount of lead can be exacerbated by the lead entry from outside the drink, such as motor vehicle fumes (Kahar et al., 2020, O'Shea et al., 2020, Budiman et al., 2021). The number of stalls located on the side of the main road has the potential to an entry for lead pollutants in food and beverages (Awad et al., 2018). Leaded gasoline can cause lead pollution and undoubtedly affect health (BPOM, 2017). Therefore, it is necessary to detect lead as early as possible to prevent exposure to this heavy metal in the human body.

Several instruments can be used to detect these hazardous metals, including atomic absorption spectroscopy (AAS) (Li et al., 2021b, Jamali et al., 2021), inductively coupled plasma with optical emission spectroscopy (ICP-OES) (Sereshti et al., 2012), and inductively coupled plasma by mass spectroscopy (ICP-MS) (Nakata et al., 2021, Baalousha et al., 2021). The three sophisticated instruments can detect and know the amount of lead very well. However, these instruments are costly and require a reliable operator (Rawat et al., 2022). A simple way that can be done is by colorimetry (Yan et al., 2020, Chen et al., 2022). However, this method is not effective enough to use if the solution already has a different color, such as coffee.

An alternative method that can be used to determine heavy metals in beverages is electrochemistry (Wang et al., 2020). This method provides high sensitivity, inexpensive, and easy to

implement for detecting heavy metals (Zamhari et al., 2017). One technique that can be used to detect lead in beverages is square wave anodic voltammetry (Mohammed et al., 2022)). Many electrodes can be used in this technique, including diamond, gold, mercury (mercury), platinum, and glassy carbon electrode (GCE) electrodes (Zamhari et al., 2017, Sawan et al., 2020). However, these electrodes are very expensive.

Using a pencil as a working electrode in this technique allows this method to be very affordable and applicable in everyday life (Congur and GÜL, 2021). Pencils contain graphite in varying degrees. Due to the mobility of electrons in orbitals, graphite is a good conductor of electricity (Li et al., 2021a). Graphite is often used as a dry lubricant in locks because the layer structure, held together only by van der Waals forces, can shift quickly (Zhang et al., 2021). Diamonds also contain carbon atoms bonded to four other carbon atoms, so all electrons are used in local bonds (Sundqvist, 2021). Therefore, this study aims to determine the level of precision and stability test for pencil electrodes in determining lead levels using pencil electrodes using the square wave anodic stripping voltammetry (SWASV) method.

METHOD

Materials and Apparatus

The materials to be used in this research are Lead (II) nitrate ($Pb(NO_3)_2$), potassium chloride (KCl), glacial acetic acid (CH_3COOH), and sodium acetate (CH_3COONa) from Merck, Germany. Potassium ferricyanide ($K_3[FeCN)_6]$) from Pudak Scientific, Indonesia. Distilled water used from CV Progo Mulyo, Indonesia. All chemicals used are analytical grade. Alumina powder measuring 0.1 µm was obtained from Kimyong Online Store, Indonesia. The equipment used in this study is a potentiostat from IO Rodeo, USA. A batch system was carried out using three electrodes, i.e., a Ag/AgCl reference electrode, a Pt wire counter electrode, and a pencil electrode with a diameter of 5 mm were obtained from the Kimyong Online Store, Indonesia.

Electrode Preparation and Characterization

A 5.0 mm pencil electrode was prepared and polished using 0.1 µm alumina slurries, rinsed by distilled water, and electrochemically cleaned by amperometry in 0.1 M HNO_3 by applying 0.5 V for 6 minutes. The prepared electrode was electrochemically characterized in 1 mM $K_3[Fe(CN)_6)]$ in

0.10 M KCl by applying cyclic voltammetry in the range of -0.7 to 0.7 V, sample rate of 100 Hz and scan rate of 0.5 V/s.

Procedure and Analytical Performance

Pb(II) determination was performed by square wave anodic stripping voltammetry (SWASV) in a batch system containing 10 mL of 0.1 M acetate buffer pH 4.5. The test was conducted by immersing three electrodes into a batch system. In the measuring process, accumulation potential (Ea) of -1.4 V was applied for 180 s under stirring. This process was stopped for 10 s for equilibrium. The SWASV was recorded at -1.4 to 0.3 V. Prior to sequence determination, the electrode was cleaned by performing 0.3 V for 60 s.

Validation Parameters tested were determination of linearity (linear range), repeatability, reproducibility, stability and determination of limit of detection (LOD) and quantification (LOQ).

a. Linearity

To quantitatively determine Pb(II), it is necessary to investigate the linear range of Pb(II) concentration. The linearity between the analyte and the signal is determined by the correlation coefficient (*r*). A positive correlation coefficient indicates a positive relationship and vice versa. The linear range is the interval between the lowest lead (II) concentration to the highest concentration.

b. Limit of Detection (LOD) and Limit of Quantification (LOQ)

The detection limit is the lowest concentration of the sample that can be detected but cannot be accurately measured. While LOQ is the lowest concentration that can be measured accurately. The method of determining LOD and LOQ in this study will use the following formula,

$$LOD = \frac{3SD}{m} \qquad LOQ = \frac{10SD}{m}$$

with *SD* as deviation standard of intercept and *m* as the slope of linear range.

c. Repeatability and reproducibility

This step was done by testing Pb(II) in the concentration of 0.2, 0.4, 0.6, and 0.8 µg mL^{-1}. Repeatability was applied by testing in six repetitions. The reproducibility of this research was conducted by comparing the sensitivity of six electrodes prepared on different days. The RSD obtained was compared to the Association of Official Analytical Chemists (AOAC) standard.

d. Operational Stability

Operational stability performance was conducted by adding 0.4 µg mL^{-1} of Pb(II) into the system and repeatedly running the

SWASV. The response of first cycle was set of 100% response. The operational stability was determined by the number of cycles before the sensitivity change more than 10%.

RESULTS AND DISCUSSION

Electrode Preparation and Characterization

The pencil working electrode used in this study contains graphite. The most abundant carbon compounds are organic materials commonly found in coal, petroleum, natural gas, and living plants and animals (Abdel-Shafy and Mansour, 2016). The amount of carbon found as graphite and diamond is relatively small compared to organic compounds, but carbon is an important material (Bewilogua and Hofmann, 2014). The SPU clearly shows an increasing trend of metallic character in one group. Carbon is a nonmetal. Silicon and germanium are metalloids, while tin and lead are elements with a metallic nature. Graphite is often used as a dry lubricant in locks because the layer structure, held together only by van der Waals forces, can shift easily (Németh et al., 2020).

Prior to use, the working electrode was polished in the 0.1 µm alumina slurries repeatedly with the number 8 pattern until it provided a homogeneous surface. The process was executed to have the best possible precision in the next stage. Each process carried out was continued by rinsing the electrodes using distilled water.

Furthermore, the pencil electrode was immersed in 0.1 M HNO_3 for 5 minutes. It helped release the impurities on the surface of the electrode and dissolved them into the acid solution. This step is essential to perform zero interference when conducting the Pb(II) determination. Then, the electrode was electrochemically cleaned using the amperometric method. The parameter used in this step is to apply a potential of 0.5 V for 6 minutes. The flat results obtained indicate no peak produced after the cleaning process (Figure 1). It stated the absence of impurities on the electrode surface. The electrodes received had shown promising results, and this preparation was carried out before Pb(II) determination. The entire electrode preparation was ended by rinsing distilled water on the electrodes to ensure that no impurities were left behind.

Electrode characterization was carried out to ensure that the electrodes could give a good signal. This step was performed with a batch system using a rodeo IO potentiostat. A three-electrode system consisting of graphite as a working electrode, Ag/AgCl as a reference

electrode and platinum as a counter electrode. This step was carried out in a solution of 1 mM mM $K_3[Fe(CN)_6]$ in 0.10 M KCl using the cyclic voltammetry method with a voltage range of -0.7 V to 0.7 V with a sample rate of 100 Hz and a scan rate of 0.5 V. /s.

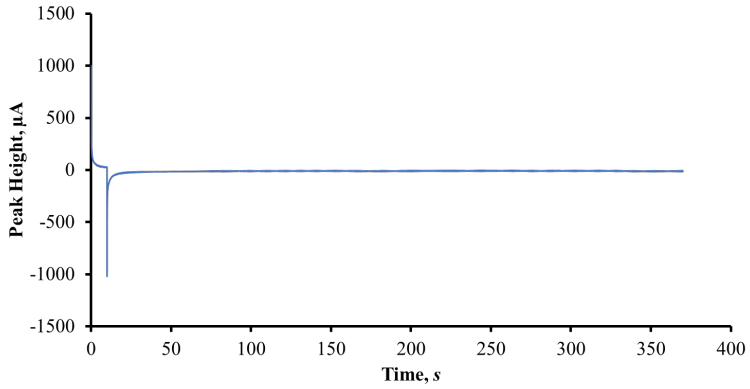

Figure 1. Amperogram cleaning of the pencil working electrode in 0.1 M HNO_3 solution using the amperometry method by applying 0.5 V for 6 minutes

The cyclic voltammogram in Figure 2 shows the anode and cathode peaks. The high and wide peaks of $Fe(CN)_6^{3-/4-}$ at the anode and cathode peaks confirmed that the pencil electrode performed excellent performance. The electrode that had been prepared provided good conductivity and was ready to be used.

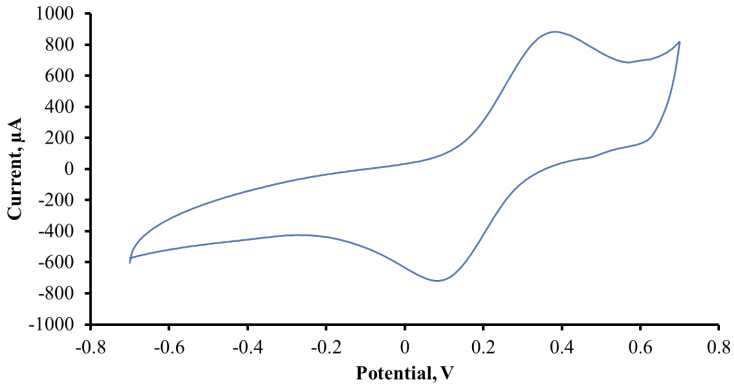

Figure 2. Cyclic Voltammogram of pencil electrodes in a solution of 1 mM $K_3[Fe(CN)_6]$ in 0.10 M KCl by cyclic voltammetry method with a voltage range of -0.7 to 0.7 V with a sample rate of 100 Hz and a scan rate of 0.5 V /s using pencil electrode

Analytical Performance

a. Linear Range, Limit of Detection (LOD), and Limit of Quantification (LOQ)

A linear range or calibration curve is tested to determine the range of Pb(II) concentration that can be tested by the developed method. This linear range was carried out with Pb(II) concentration of 0.00 ppb to 1000 ppb. Figure 3a shows the voltammogram of the Pb(II) test using 0.1 M acetate buffer with a pH of 4.5. The method used was Square Wave Anodic Stripping Voltammetry with a sample rate of 25 Hz, accumulation potential (Ea) -1.4 V for 180 seconds, and voltammetry ranges from -1.4 V to 0.3 V. The voltammogram shows a peak of Pb(II) at -0.49 V. This indicates that Pb(II) is released from the electrode surface and returns to the solution at a potential of -0.49 V. Figure 3b shows that the developed method has two linear ranges in the range of 0.1–1.0 µg mL^{-1} (r = 0.993) and 2.0–8.0 µg mL^{-1} (r = 0.991). The limit of detection (LOD) and limit of quantification (LOQ) of Pb(II) were 0.07 ppb and 0.24 µg mL^{-1}, respectively. The LOD value covers the maximum Pb(II) level in the drinking water, 2.0 µg mL^{-1}.

b. Repeatability and Reproducibility

The precision test was carried out using repeatability and reproducibility. The repeatability investigation was carried out by testing Pb(II) in the solution six times in a concentration range of 0.2–0.8 µg mL^{-1}. The results of repeatability performed the RSD are in the range of 7.28–9.53% which are still below the 11% set by the AOAC in that concentration range (AOAC, 2012) (Figure 4).

The reproducibility was investigated for the Pb(II) test by using six electrodes on different days. The test was carried out in the concentration of 0.2–0.8 µg mL^{-1} Pb(II). The result shows good reproducibility with the RSD in the range of 7.07 to 15.10% which are still below the 16% set by AOAC (Figure 5). Those revealed that the repetitions to detect Pb(II) have good precision.

c. Operational Stability

This study was conducted to determine the performance of the developed method by repeatedly testing the analyte. The stability test was carried out at Pb(II) concentration of 0.4 µg mL^{-1}. This investigation showed that the 5 mm pencil electrode could be used simultaneously for 18 times Pb(II) testing (Figure 6). The 19^{th} test resulted in a 10% change in response. The average percentage obtained was 102.2±4.7% with the RSD of 4.6%. It revealed the method

performs acceptable results with low random error in determining Pb(II).

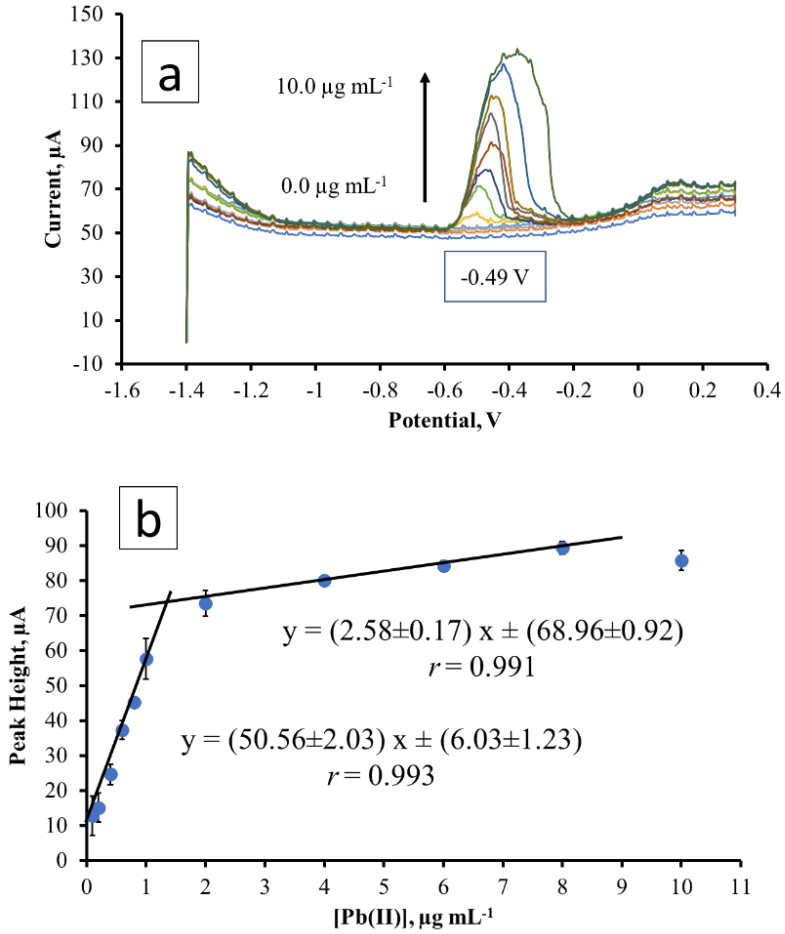

Figure 3. (a) voltammogram and (b) calibration curve of Pb(II) determination in 10 mL of 0.1 M acetate buffer pH 4.5 with a concentration range of 0 – 10.0 µg mL^{-1}

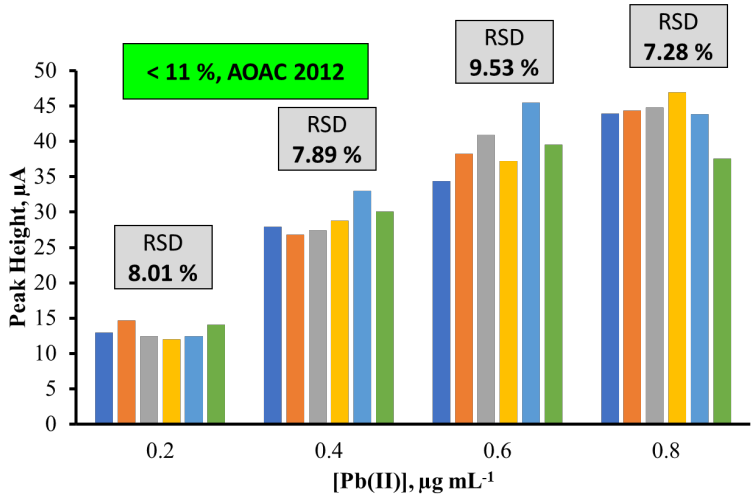

Figure 4. Repeatability study on Pb(II) using pencil electrodes in a concentration range of 0.2–0.8 µg mL^{-1}

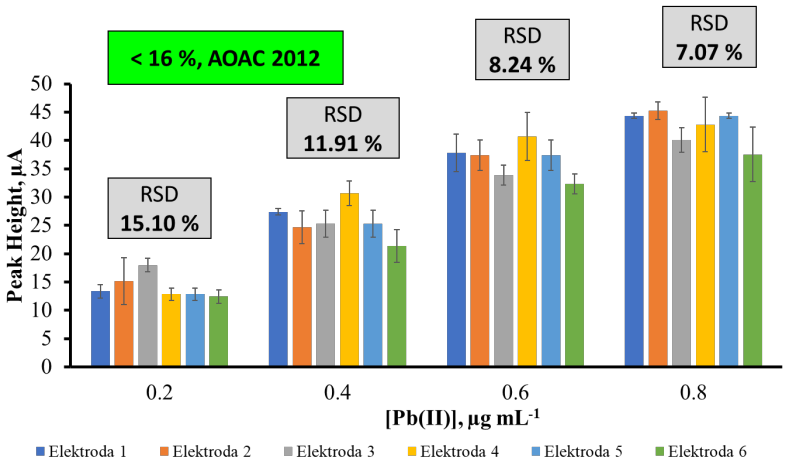

Figure 5. Reproducibility study on Pb(II) using pencil electrodes in a concentration range of 0.2–0.8 µg mL^{-1}

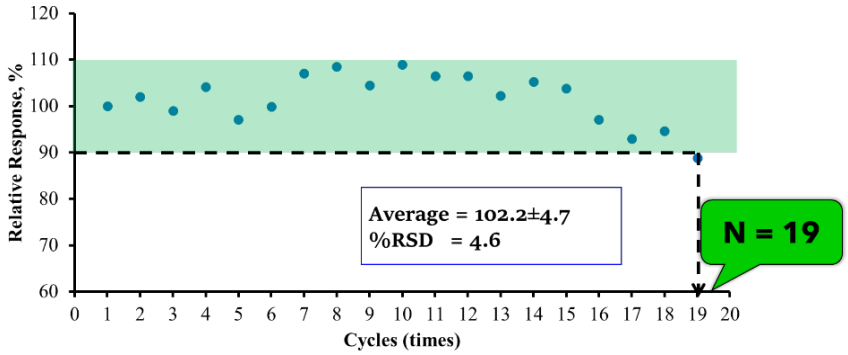

Figure 6. Stability investigation of 5 mm pencil electrode to detect Pb(II) at a concentration of 0.4 µg mL^{-1}

CONCLUSION

The Pb(II) determination study using a pencil electrode with the square wave anodic voltammetry method showed promising results. The working electrode used in this study was a pencil with a diameter of 5 mm. The validation results show that this method has two linear ranges, good repeatability and reproducibility which accepted by AOAC. The working electrode can also be used simultaneously up to 18 times. This research shows the good performance of an inexpensive electrode and method in Pb(II) detection.

REFERENCES

Abd-Alghafar, W. N., Aly, F. A., Sheribah, Z. A. & Saad, S. 2022. Green HPLC method with time programming for the determination of the co-formulated eye drops of tafluprost and timolol in their challengeable ratio. *BMC chemistry,* 16**,** 1-11.

Abdel-Shafy, H. I. & Mansour, M. S. 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian journal of petroleum,* 25**,** 107-123.

AOAC 2012. Guidelines for Standard Method Performance Requirements. *In:* ANALYSIS, A. O. M. O. (ed.). Association of Official Analytical Chemists.

Awad, O. I., Mamat, R., Ali, O. M., Sidik, N. C., Yusaf, T., Kadirgama, K. & Kettner, M. 2018. Alcohol and ether as alternative fuels in spark ignition engine: A review. *Renewable and Sustainable Energy Reviews,* 82**,** 2586-2605.

Baalousha, M., Wang, J., Erfani, M. & Goharian, E. 2021. Elemental fingerprints in natural nanomaterials determined using SP-ICP-TOF-MS and clustering analysis. *Science of The Total Environment,* 792**,** https://www.sciencedirect.com/science/article/abs/pii/S0048969721034975.

Bewilogua, K. & Hofmann, D. 2014. History of diamond-like carbon films—from first experiments to worldwide applications. *Surface and Coatings Technology,* 24**,** 214-225.

BPOM 2017. Batas maksimum cemaran logam berat dalam pangan olahan. *In:* Makanan, B. P. O. D. (ed.) *nomor 23 tahun 2017.* Jakarta.

Budiman, H., Wibowo, R., Zuas, O. & Gunlazuardi, J. 2021. Preparation of TiO_2 Nanotube Using Anodization Method: Charactherization and Its Application for CO Sensor. *EduChemia,* 6**,** 159-171.

Chen, Z., Zhang, Z., Qi, J., You, J., Ma, J. & Chen, L. 2022. Colorimetric detection of heavy metal ions with various chromogenic materials: strategies and applications. *Journal of Hazardous Materials* 441**,** 129889.

Congur, G. & Gül, Ü. D. 2021. Phenol monitoring in water samples using an inexpensive electrochemical sensor based on pencil electrodes modified with DTAB surfactant. *Journal of*

Environmental Chemical Engineering, 9**,** 105804.

Jamali, S., Khoso, M. A., Zaman, M. H., Jamil, Y., Bhutto, W. A., Abbas, A., Mari, R. H., Kalhoro, M. S. & Shaikh, N. M. 2021. Elemental analysis of Kohl using laser ablation and atomic absorption spectroscopy (AAS) techniques. *Physica B: Condensed Matter* 620**,** 413278.

Kahar, A., Bella, N. F. K. & Rappe, E. 2020. Analisis Kandungan Logam Berat Timbal (Pb) pada Jajanan Gorengan di Kota Makassar. *Sulolipu: Media Komunikasi Sivitas Akademika dan Masyarakat,* 20**,** 135-143.

Li, C., Ge, H. S., Daquan & Zhou, X. 2021a. Novel conductive wearing course using a graphite, carbon fiber, and epoxy resin mixture for active de-icing of asphalt concrete pavement. *Materials and Structures,* 54**,** 1-17.

Li, K., Yang, H., Yuan, X. & Zhang, M. 2021b. Recent developments of heavy metals detection in traditional Chinese medicine by atomic spectrometry. *Microchemical Journal,* 160**,** 105726.

Mohammed, M. Q., Ismail, H. K., Alesary, H. F. & Barton, S. 2022. Use Of A Schiff Base-Modified conducting polymer electrode for electrochemical assay of Cd(II) and Pb(II) ions by square wave voltammetry. *Chemical Papers,* 76**,** 715-729.

Nakata, H., Mm Nakayama, S., Yabe, J., Muzandu, K., Toyomaki, H., Yohannes, Y. B., Kataba, A., Zyambo, G., Ikenaka, Y., Choongo, K. & Ishizuka, M. 2021. Assessment of LeadCare® II analysis for testing of a wide range of blood lead levels in comparison with ICP–MS analysis. *Chemosphere,* 271**,** 129832.

Németh, P., Mccoll, K., Garvie, L. A., Salzmann, C. G., Murri, M. & Mcmillan, P. F. 2020. Complex nanostructures in diamond. *Nature materials,* 19**,** 1126-1131.

O'connor, D., Hou, D., Ok, Y. S. & Lanphear, B. P. 2020. The Effects Of Iniquitous Lead Exposure On Health. *Nature Sustainability,* 3**,** 77-79.

O'shea, M. J., Vann, D. R., Hwang, W.-T. & GIERÉ, R. 2020. A mineralogical and chemical investigation of road dust in Philadelphia, PA, USA. *Environmental Science and Pollution Research,* 27**,** 14883-14902.

Oleko, A., Pecheux, M., Saoudi, A., Zeghnoun, A., Hulin, M., Le Barbier, M., Menard, C., Denys, S. & Fillol, C. 2022. Estimation of blood lead levels in the French population using two

complementary approaches: Esteban (2014–2016) as part of the human biomonitoring program and the national surveillance system for childhood lead poisoning (2015–2018). *Environmental Research,* 213**,** 113630.

Rawat, K., Sharma, N. & Singh, V. K. 2022. X-Ray Fluorescence and Comparison with Other Analytical Methods (AAS, ICP-AES, LA-ICP-MS, IC, LIBS, SEM-EDS, and XRD). *X-Ray Fluorescence in Biological Sciences: Principles, Instrumentation, and Applications***,** 1-20.

Sawan, S., Maalouf, R., Errachid, A. & Jaffrezic-Renault, N. 2020. Metal and metal oxide nanoparticles in the voltammetric detection of heavy metals: A review. *TrAC Trends in Analytical Chemistry,* 131**,** 116014.

Sereshti, H., Heravi, Y. E. & Samadi, S. 2012. Optimized ultrasound-assisted emulsification microextraction for simultaneous trace multielement determination of heavy metals in real water samples by ICP-OES. *Talanta,* 97**,** 235-241.

Sundqvist, B. 2021. Carbon under pressure. *Physics Reports,* 909**,** 1-73.

Teerasarntipan, T., Chaiteerakij, R., Prueksapanich, P. & Werawatganon, D. 2020. Changes in inflammatory cytokines, antioxidants and liver stiffness after chelation therapy in individuals with chronic lead poisoning. *BMC gastroenterology,* 20**,** 1-9.

USEPA 2009. Drinking Water Contaminants–Standards and Regulations. *In:* United States Environmental Protection Agency (Ed.). Washington Dc.

Wang, L., Peng, X., Fu, H., Huang, C., Li, Y. & Liu, Z. 2020. Recent advances in the development of electrochemical aptasensors for detection of heavy metals in food. *Biosensors and Bioelectronics,* 147**,** 111777.

Yan, Z., Yuan, H., Zhao, Q., Xing, L., Zheng, X., Wang, W., Zhao, Y., Yu, Y., Hu, L. & Yao, W. 2020. Recent developments of nanoenzyme-based colorimetric sensors for heavy metal detection and the interaction mechanism. *Analyst* 145**,** 3173-3187.

Zamhari, M., Numnuam, A., Limbut, W., Kanatharana, P. & Thavarungkul, P. 2017. Simultaneous Electrochemical Detection of Co (II) and Cu (II) by 1-Diazo-2-Naphthol-4-Sulfonic Acid/MWCNTs Modified Electrode. *Electroanalysis,* 29**,** 2348-2357.

Zhang, H., Yang, Y., Ren, D., Wang, L. & HE, X. 2021. Graphite as anode

materials: Fundamental mechanism, recent progress and advances. *Energy Storage Materials,* 36**,** 147-170.