

Optimization of The Cathodic Stripping Voltammetry for The Determination of Metal Ni (II) in The River Water

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Abstract: The study was carried out to determine the metal Ni(II) concentration in river water samples using cathodic stripping voltammetry (CSV) method. In order to achieve optimum conditions for the determination of metal Ni(II), the accumulation potential and accumulation time conditions of the CSV method have been achieved. The results of this research obtained under the optimum conditions for Ni(II) measurement using an electrolyte solution of ammonium chloride with a potential accumulation (acc_v) of -0.7 V and a time accumulation (acc_t) of 60 s. The relative standard deviation of the 10 $\mu\text{g/L}$ Ni(II) standard solution ($n=8$) is 0.53%, the recovery value is 98.82%. The CSV method for the determination of Ni(II) metal has been successfully applied to river water samples.

Keywords: cathodic stripping voltammetry, Ni(II), deposition, river water.

INTRODUCTION

Nickel is a hard silver-white metal. Tough, malleable, and very strong. Nickel has several oxidation numbers, namely 0, I, II, III, and VI but in its compounds, nickel is generally more stable at oxidation number II both in solution and rust. Nickel is toxic and can cause acute pneumonitis, asthma, nervous system disorders, skin infections, nasal cavity cancer, and lung cancer (Ismail et al. 2018). Nickel in drinking water has a maximum concentration of 0.1 mg/L. The toxic nature of nickel and its salts has been discovered in several experimental animals over the years (Vongdala et al. 2019). Therefore, the presence of this metal in nature should always be monitored.

There have been many methods for determining nickel metal, such as spectrophotometry, Atomic Absorption Spectrophotometer-flame (AAS-flame) after the pre-concentration process, Inductive Coupled Plasma (ICP) followed by a pre-concentration step, potentiometer using nickel selective electrodes, and the stripping voltammetry method (Koropitan and Cordova 2017; Nindyapuspa and Ni'Am 2018). The stripping voltammetry method is the best method for determining metals compared to AAS, ICP, and potentiometry because it has a low detection limit, namely, on the $\mu\text{g/L}$ (ppb) scale, the pre-concentration process is very fast, less than 1 minute, optimum in measuring at high salt content (Ensafi, Khayamian, and Khaloo 2004; Esteban, Ariño, and Díaz-cruz 2003; Guzsavány et al. 2014; Morsi et al. 2011; Raj, Raina, and Dogra 2013).

The stripping voltammetric method requires a ligand to form a complex with the analyte to be analyzed. Determination of Ni(II) of the CSV method, ligands such as oxen derivatives, 8-hydroxyquinoline, hydroxy naphthol blue, and dithiocarbamate derivatives have been studied (Afkhami et al. 2013; Campisi et al. 2016; Pardi et al. 2019). The optimization of the stripping photometric method of accumulated time and accumulation

potential is an important factor in the measurement. Therefore, research was conducted to determine the optimum condition of Ni (II) metal using anodic stripping voltammetry, namely based on the parameters of the acc_v , and the acc_t on the optimum measurement conditions.

RESEARCH METHODS

Materials and Tools

The material is used Ni(II) metal 1000 mg/L, NH_4Cl , HNO_3 , HCl , NH_4OH , ethanol-water, aquadest and samples. The tools applied are voltammeter (Metrohm 797), WE: Hanging Mercury Drop Electrode (HMDE), RE: $Ag/AgCl/KCl$, 3 M, AE: Pt electrode, pH meter (913 pH meter, Metrohm), and Mettler AE 200 analytical balance (Toledo OH-USA).

Procedures

Determination of Optimum Conditions

Accumulation Potential (acc_v)

10 mL standard solutions of Ni(II) 10 $\mu g/L$, 0.2 mL NH_4Cl , 0.1 M, 0.3 mL complexion 1 mM, adjust pH 11, acc_t 60 s, measurement of solution with an acc_v variation of -0.1V to -1V.

Accumulation Time (acc_t)

10 mL standard solutions of Ni(II) 10 $\mu g/L$, 0.2 mL NH_4Cl , 0.1 M, 0.3 mL complexion 1 mM, adjust pH 11, accumulation potential -0.7 V, measure the solution with variations in acc_t 20 seconds to 100 seconds.

Sample Preparation

The sample used to apply the optimum conditions for the determination of Ni(II) is the water from the Lubuk Minturun River, Padang City, West Sumatra, Indonesia. The samples taken were added with HNO_3 65% with a ratio of 1:1000 so that the Ni(II) metal in the sample was not oxidized.

Sample Measurement

10 mL river water sample, 0.2 mL NH_4Cl , 0.1M, 0.3 mL 1 mM complexion, adjust pH 11, acc_v -0.7V, acc_t 60 sec (optimal conditions). Measurements were carried out using the standard addition method to obtain the concentration of Ni(II) in the sample with the equipment set conditions, namely, the HMDE, droplet size 7, the method used differential pulse (DP), Sweep Rate 0.0132 V/s, stirring time 240 seconds, equilibration time 10 seconds, amplitude 0.05 V, initial potential -0.45 V, final potential 0.98V, 1/2 peak potential for Ni(II) 0.82V.

Determination of Relative Standard Deviation and Recovery

The relative standard deviation (SDR) was determined by measuring 10 mL of 10 $\mu g/L$ Ni(II) standard solution, 0.2 mL of 0.1 M NH_4Cl , 0.3 mL of 1 mM complexion, adjust pH 11, acc_v -0.7 V, acc_t 60 s (optimum condition) with 8 repetitions. Determination of recovery was carried out using a spike sample (10 mL sample), 0.2 mL NH_4Cl , 0.1 M, 0.3 mL complexion 1 mM, set pH 11, acc_v , and acc_t (optimum conditions).

RESULTS AND DISCUSSION

Accumulated Potential Variation

The acc_v is a potential that is useful for increasing the reduced analyt (adherence) to the HMDE. In this study, Acc_v was measured between -0.1 V and -1.0 V (Figure 1).

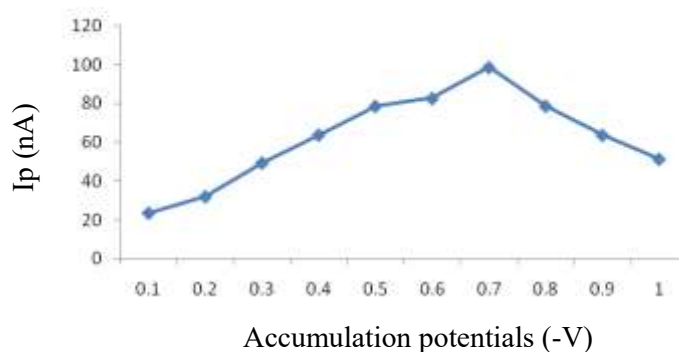


Figure 1. Acc_v curve Vs peak current (IP) of Ni(II) metal

Figure 1 shows The acc_v of Ni(II) metal, at a potential of -0.1 V to -0.7 V, there is an increase in the peak current of Ni(II) metal, this reveals that at this potential more and more Ni(II) metal is deposited on the metal-HMDE. Then at The acc_v of -0.8V to -1.0 V the peak current produced decreases, this shows that less Ni(II) metal is deposited at that potential. Therefore, the potential -0.7 V is the optimum potential for the measurement of Ni(II) (Batchelor-Mcauley et al. 2015; Lee, Kim, and Shin 2021; Mohadesi et al. 2011).

Accumulated Time (acc_t) Variation

The acc_t is the time required for the analyt to be deposited on the HMDE. Optimization of the determination of Ni(II) used the acc_t range of 20, 30, 40, 50, 60,70, 80, 90, 100 seconds (Figure 2).

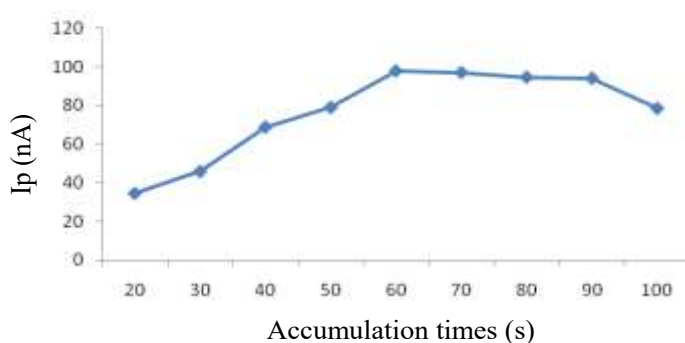


Figure 2. Acc_t curve Vs. peak current (IP) for Ni(II).

Figure 2 shows the acc_t on the peak current of Ni(II). Theoretically the longer the time used, the more analyte will be deposited on the HMDE which is indicated by an increase in peak current from 20 s to 60 s, but at 70 s up to 90 s the peak current does not increase (constant) and decreases at 100 s. This occurs because of the saturation of the HMDE if the deposition process is too long. So that the acc_t 60 s was used as the optimum time for the determination

of Ni(II) metal (Afkhani et al. 2013; Deswati et al. 2017; Khaled et al. 2014; Rahmi et al. 2021).

Relative Standard Deviation (RSD)

The accuracy of a method can be seen from the determination of the RSDS value. Seeing the SDR value can be conducted by measuring the standard metal Ni(II) 8 times (Table 1).

Table 1. Measurement of Ni(II) Metal Standard Solution 10 µg/L

Repetition	Peak Current (nA)
1	98.6
2	98.2
3	97.4
4	98.3
5	97.7
6	99.1
7	98.3
8	98.4
Average	98.25
Standard Deviation	0.52
SDR	0.53%

Table 1 reveals the measurement of the standard solution of Ni (II) metal with 8 repetitions which obtained an average peak current of 98.25 nA, a standard deviation of 0.52, and an SDR of 0.53%. Based on the SDR results obtained, it shows good accuracy of the CSV method (Deswati et al. 2018).

Recovery

The level of accuracy of the method can be determined by determining the recovery from the sample solution which is carried out by comparing the spike sample concentration obtained with the analyte concentration in the sample which has been added to a number of 5, 10, and 15 µg/L Ni(II) metal standard solutions (Table 2).

Table 2. The results of recovery of metal Ni (II)

No.	Added standard concentration (µg/L)	Sample concentration before spike (µg/L)	Spike concentration (µg/L)	sample Recovery (%)
1	5	89.846	93.193	98.25
2	10	89.846	97.775	98.04
3	15	89.846	105.035	100.18
Amount				296.47
Average				98.82

Table 2 reveals the recovery value, which is 98.82%. The recovery value in this study is quite good because the recovery value obtained is close to 100% (Cai et al. 2012; Deswati et al. 2017).

Application of Sample

10 mL river water sample, 0.2 mL NH_4Cl 0.1 M, 0.3 mL complexing 1 mM, adjust pH 11, acc_v -0.7 V, acc_t 60 s (optimum conditions). Measurements were carried out using the standard addition method to obtain the concentration of Ni(II) in the sample with the equipment set conditions, namely, the HMDE, droplet size 7, the method used differential pulse (DP), Sweep Rate 0.0132 V/s, stirring time 240 seconds, equilibration time 10 seconds, amplitude 0.05 V, initial potential -0.45 V, final potential 0.98V, 1/2 peak potential for Ni(II) 0.82V.

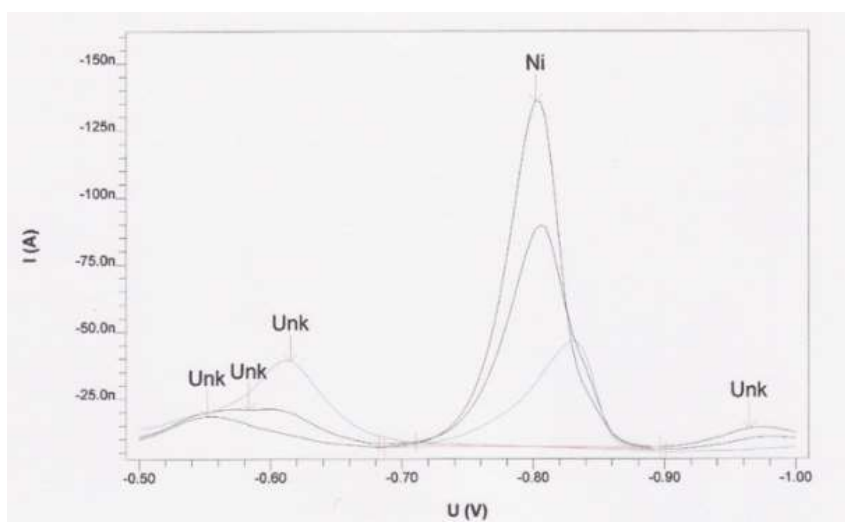


Figure 3. Voltammogram of Lubuk Minturun water sample using standard addition method.

Figure 3 reveals the voltammogram for measuring river water samples using the standard addition method

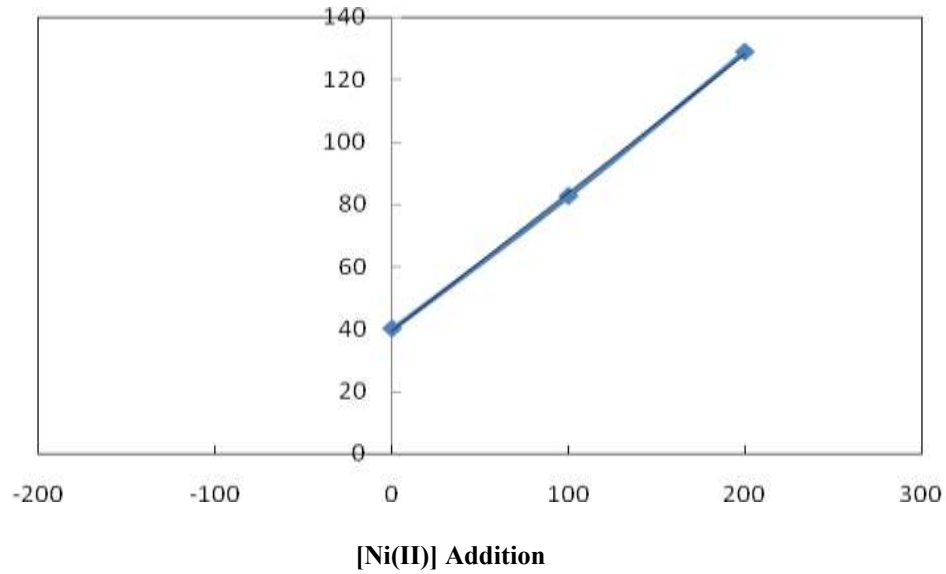


Figure 4. The Measuring curve of upstream water samples with standard addition method

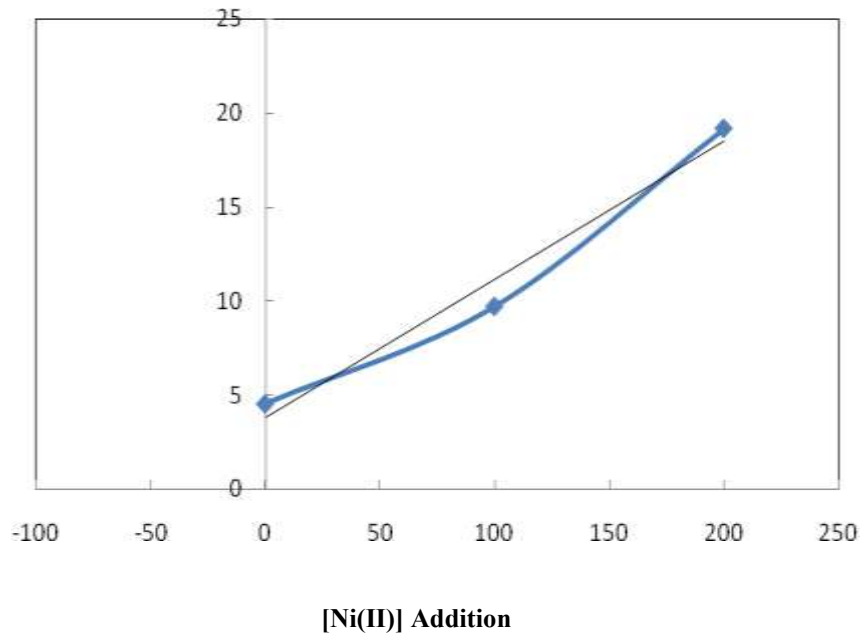


Figure 5. Estuary water sample measurement curve with standard addition method

The concentration of the sample obtained is shown on the addition curve, namely upstream 89.846 $\mu\text{g/L}$ and estuary 53.842 $\mu\text{g/L}$.

CONCLUSIONS

The determination of metal Ni(II) in river water samples using the CSV method, the optimum conditions for the measurement of Ni(II) were obtained using an ammonium chloride electrolyte solution with an acc_v of -0.7 V, and acc_t of 60 s. The SDR of 10 $\mu\text{g/L}$ ($n=8$): 0.53%, the recovery: 98.82 %, and the concentration of the water sample of the Lubuk Minturun river, Indonesia is 89.846 $\mu\text{g/L}$ and the estuary is 53.842 $\mu\text{g/L}$.

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