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Contributed Paper

Preparation of an Economic Home-Made Ag/AgCl Electrode from Silver Recovered from Laboratory Wastes

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ABSTRACT

In this work, a Ag/AgCl electrode was prepared from silver obtained from recovery of laboratory waste via the cementation technique. The extracted silver metal has purity of 89.4-97.0%, as examined by the Volhard's titration. Silver was melted, poured into a cast, and elongated to be a silver wire with the size of 1 mm o.d. and length of 1.33 m. The wire was then used to prepare Ag/AgCl electrode by immersing it into a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to form a AgCl film on the silver wire. This electrode was used as a working electrode for chloride determination or further fabricated as a reference electrode. For reference electrode preparation, the Ag/AgCl electrode was immersed in a saturated solution of KNO_3 contained in a glass tube plugging with agar at one end to act as a salt bridge. The working and reference electrodes were tested for potentiometric determination of chloride. Electrical potential was plotted versus logarithm of chloride concentration to obtain two linear calibration graphs, 5-20 ppm and 20-60 ppm, with the linear equation of $y = 0.0018x - 0.0347$ and $y = 0.0006x - 0.0121$, respectively. Moreover, the precision (%RSD) examined with 1 and 20 ppm of chloride solution was 0.9% and 2.7% ($n=11$), respectively. The prepared electrodes were used for determination of chloride in real samples comparing the results by t-test to those determined by the precipitation titration method. It was found that both methods have no significant difference at 95% confidence level.

Keywords: Ag/AgCl electrode, recovery of silver, laboratory waste, chloride determination

1. INTRODUCTION

Laboratory waste refers to waste generated in experiments for education, research and examination purposes. Treatment of laboratory wastes is more difficult than treating either industrial

waste or wastewater due to various sources, causing inability to identify their constituents [1]. Heavy metal is one of the toxic components that contaminates in laboratory waste and frequently be discharged into

environment without an appropriate treatment. Conventional methodology for treating heavy metals such chemical precipitation [2-3], stabilization and solidification [4-6] could restrain the metal toxicity by immobilization its movement. However, due to the high value of some metals, the recycling method seems to be a better way for waste treatment of these metals than fixing them in a solid form.

Silver is classified as heavy metal and precious metal that mostly found in chemical laboratory waste because of its various employable, especially as the reagents for some analytical work; such as AgNO_3 for the precipitation titration [7], AgSO_4 as the catalyst for COD determination [7], as well as the Tollen's reagent for aldehyde/ketone analysis [8]. Therefore, silver is often unfortunately effused with laboratory waste and threat to the environment and public health.

Apart from the problem of the contamination of heavy metal from laboratory waste, one of important problems that usually found in the scientific education of the academic institute, especially in the remoted area of the developing country, is the lack of experimental apparatuses due to their high cost and inadequate of budget [9]. Therefore, self-producing of uncomplicated apparatus using raw materials that easily found locally, in order to provide economic and effective devices might be an alternative approach to solve the mentioned problem. In addition, some valuable materials such as precious metals can be acquired from recycling of laboratory waste. This should also decrease contamination of toxic waste to the environment.

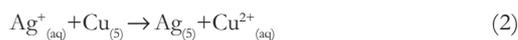
In this work, we propose the idea to recover silver metal from laboratory waste and employ it to prepare Ag/AgCl electrode. This electrode is usually used in

electrochemistry experiment as both reference and working electrodes due to its advantages such as electrochemically reversibility, high exchange current and high reproducible potential [10]. Although there are some reports on the self-preparation of Ag/AgCl electrode, but a silver wire obtained from a jewelry shop [11-12] or a silver synthesized from a commercial AgNO_3 [10] was used.

From the survey of wastes which contained silver in our laboratory, we found that they included (i) the excess of AgNO_3 solution left over from the experiment, and (ii) AgCl precipitate produced from the Argentometric titration. The cementation process was applied to the recovery of metallic silver because of its high process efficiency to remove or detoxify heavy metal to gain pure metallic form while require a simple treatment facility [13]. First, the collected solid waste had been converted to liquid form. The precipitate of AgCl was dissolved in concentrated ammonia solution to leach the silver as the complex ion of $[\text{Ag}(\text{NH}_3)_2]^+$ as the following reaction [14-15].



A copper wire was served as the reductant to reduce Ag^+ (in AgNO_3 solution) and $[\text{Ag}(\text{NH}_3)_2]^+$ (product from the reaction (1)) to be elemental form according to the reactions (2) and (3), respectively.



The metallic silver product in crystalline powder form was melted and elongated at a local silverware shop to provide a silver wire that ready for the electrode preparation. The home-made Ag/AgCl working and

reference electrodes were assembled to a multimeter for a potentiometric detection set-up, and demonstrated to the analysis of chloride ion in real samples. There are two advantages from this work, firstly the expense for fabrication of the proposed electrodes was lower than the commercially available electrode and secondly it helps to diminish the discharge of some heavy metals into the environment.

2. MATERIALS AND METHODS

2.1 Chemicals

Deionized water (obtained by a system of Mili-Q, Millipore, Sweden) was used throughout. All chemicals used were of analytical reagent grade. A chloride standard stock solution (0.0282 M) was prepared by dissolving 1.6657 g of sodium chloride (LABSCAN, Australia) in water and adjusting a volume to 1,000 mL in a volumetric flask. Working standardsolutions of desired concentrations were prepared by diluting the stock solution with water. A working electrolyte solution (0.5 M) of potassium nitrate was prepared by dissolving 5.107 g of potassium nitrate (QREC, New Zealand) in 100 mL of water. A ferric chloride solution (0.5 M) in 1 M hydrochloric acid (LABSCAN, Australia) was prepared by weighing 14.078 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (UNILAB, Australia) and dissolving in 100 mL of 1 M HCl. Agar used as salt bridge was weighed 0.2545 g and dissolved with 0.5 M KNO_3 50 mL.

2.2 Treatment of Silver-contained Wastes

An excess AgNO_3 solution from laboratory was collected for a semester (4 months) and filtered through a filter paper No.1 (Whatman, England). Waste of silver chloride precipitate from practical laboratory on the precipitation titration experiment was also filtered from waste

solution. The filtrate was tested by adding a few drops of chloride solution to assure complete precipitation of silver ion as silver chloride. The precipitate was left at the ambient temperature for drying and further dissolved with a concentrated NH_3 solution (JT Baker, USA) at the $\text{AgCl}:\text{NH}_3$ ratio of 1:10 to obtain a solution of $[\text{Ag}(\text{NH}_3)_2]^+$. Both solutions were then treated by cementation process as described below.

2.3 Silver Cementation Process

Cementation process was performed in a glass beaker with a volume of 400 mL equipped with a mechanical stirrer. Each waste solution of 250 mL was placed in a beaker. A copper wire was immersed into the solutions while the beaker contents began to be agitated with a speed of 1,000 rpm. The metallic product from cementation reaction has been observed since the beginning of the experiment. Because silver deposited on a Cu wire surface affected to the cementation efficiency, the wire was manually shaken every 1 minute to remove the silver metal. The cementation process was carried out until no silver occurred as judge by visual observing. The solution was immediately filtered through a filter paper. The filtrate was added with chloride solution to ensure the complete cementation reaction and then treated with NaOH to precipitate copper(II) ion. The metallic silver in powder form as shown in Figure 1 was dried at room temperature. The purity of the obtained silver was estimated based on Argentometric titration [16]. A silver of 0.500 g was dissolved in 1 M HNO_3 30 mL, heated at 80°C and stirred for 1 h. A solution was adjusted the volume to be 50 mL and used as the reagent for the titrimetric process.

2.4 Silver Wire Casting Process

A silver casting process was carried out



Figure 1. The obtained metallic silver in powder form.

at a silverware shop in Chiang Mai city based on a Thai local wisdom. A portion of silver powder (12.431 g) was placed into a crucible with the addition of popped rice (*Thai name: Kao-tork*) to aid the faster melting of silver and removing of some impurities to provide the higher purity of silver. Silver was burned by torch with the temperature over 1,000°C. Molten silver was then poured into a stationary mold which also heated in order to prevent the breakout of molten metal while pouring. A mold held this material as it solidified to form a silver ingot. To make a wire, a manual swaging machine was employed for radial reduction of an ingot by replicatedly drawing it through a reducing die as the desired diameter. The purity of a silver wire was also determined based on Argentometric titration prior to prepare an electrode.

2.5 Preparation of an Ag/AgCl Electrode

A silver wire (1.0 mm in diameter) was used to prepare an Ag/AgCl electrode. The wire was cut to 10 cm long, polished and cleaned before immersing it about 6.5-7.0 cm into a solution of 0.5M FeCl₃ for 12 h, to form a AgCl film on the silver wire. The electrode was then washed with water and used as a working electrode. For reference electrode preparation, a Ag/AgCl electrode

was immersed in a 0.5 M KNO₃ contained in a glass tube (length 15 cm, diameter 0.5 cm) which was plugged the end of tube (2.0 cm) with agar to serve as a salt bridge [11]. Both working and reference electrodes were assembled with a digital multimeter (Mastech, China), operating as a voltmeter to set-up for potentiometric detection of chloride ion. The efficiency of the proposed electrodes was tested with the standard chloride solution and also applied to real sample analysis.

3. RESULTS AND DISCUSSION

3.1 Quantity and Purity of Silver

Wastes of AgNO₃ solution and AgCl precipitate were 1,500 mL and 70.06 g, respectively. They were treated based on the cementation process as the previous mention. The metallic silver obtained were 24.58 g and 33.69 g, respectively. A percentage yield of silver from AgCl precipitate was found at 63.9%. The purities of silver from both types of waste were estimated in the range of 89.4-97.0%.

3.2 Preparation of Silver Wire

Silver powder 12.43 g was melted and poured into a mold to gain the silver ingot. An ingot was reduced the size with a die to obtain a silver wire with the diameter of 1.0 mm, length 1.33 m and weight 11.27 g. The decrease of weight of silver might be caused from the removal of impurity during the melting process. Silver wire purity was found to be 99.1%. With this obtained silver wire, it could be used to make a Ag/AgCl electrode at least 13 pieces.

3.3 Analytical Characteristics of the Prepared Electrodes

The Ag/AgCl electrode was prepared as described in section 2.5 and set up as a potentiometric detection apparatus. The home-made set up was investigated for its

analytical characteristics to ensure that it gave the comparable efficiency to the commercially available Ag/AgCl electrode. Relative standard deviation for 11 replicate determinations of 0.028 and 0.56 mM chloride standard solutions were 0.91 and 2.7%, respectively. Two linear calibration ranges, 0.028-0.56 mM ($y = 0.0018x - 0.0347$, $R^2 = 0.9987$) and 0.56-1.97 mM ($y = 0.0006x - 0.0121$, $R^2 = 0.9932$) were obtained. The stability of the electrode was investigated by detection of concentration of chloride standard solutions (0.028, 0.56 and 1.13 mM) for a 24 h period of time. The voltages of these solutions were quite constant (%RSD = 0.53, 1.0 and 0.82, respectively) that indicated the stability of the electrode at least 24 h.

3.4 Interference Study

Effects of foreign ions including: F^- , I^- , Br^- , NO_3^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} , Ca^{2+} , Fe^{3+} and Al^{3+} of known concentration were added to a solution containing fixed concentration (0.28 mM) of Cl^- . The tolerance limits, defined as the maximum concentrations of a foreign ion that causing a deviation of voltage of less than $\pm 5\%$ of the mean value of the voltage due to standard solutions without foreign ion [17], are concluded in Table 1. The results showed that some ions, i.e., Fe^{3+} , CO_3^{2-} , I^- and Br^- , would interfere with the determination of chloride. Therefore, if applying the proposed electrodes to the analysis of some samples that contain high concentration of these ions, sample pretreatment procedures are needed.

Table 1. Maximum tolerance concentration ratios of diverse ions on the determination of chloride.

Foreign ions	Tolerance limit (C_{ion}/C_{Cl})
Ca^{2+} , F^- , NO_3^- , SO_4^{2-}	25
PO_4^{3-} , Al^{3+}	10
Fe^{3+}	5
CO_3^{2-} , I^- , Br^-	0.5

3.5 Application to Water and Salt Sample Analysis

Water and salt samples were analyzed for the chloride content by the proposed set-up and also by a titrimetric method [7]. Two brands of mineral water were taken from a local supermarket. Wastewaters were collected from drain around Chiang Mai Rajabhat University. They were filtered through a filter paper No.5 and analyzed within 24 h. Sea salts which also obtained from a supermarket were weighed at 0.170-0.180 g before dissolved with DI water to be the volume of 100 mL. The results are summarized in Table 2. According to the t-test at 95% confidence level, there is no significant difference between both methods.

Table 2. Chloride contents in water and salt samples.

Sample	Chloride concentration/mM	
	Potentiometry*	Titration*
Mineral water 1	0.48 \pm 0.01	0.56 \pm 0.02
Mineral water 2	0.60 \pm 0.02	0.62 \pm 0.04
Wastewater 1	1.16 \pm 0.01	1.1 \pm 0.1
Wastewater 2	1.85 \pm 0.01	1.3 \pm 0.1
Salt 1	25.4 \pm 0.1	29 \pm 2
Salt 2	23.6 \pm 0.3	32.0 \pm 0.1

* Mean of triplicate results.

4. CONCLUSIONS

We propose the idea of recovery silver metal from laboratory waste and employ it for fabrication of Ag/AgCl electrode to be used in the electrochemical experiment for potentiometric determination of chloride. The procedure for recovery of silver is simple and low cost. With integration of local wisdom of Chiang Mai long history silversmith craft, the high purity silver wire appropriate for preparation of Ag/AgCl electrode was obtained. The electrodes were satisfactory demonstrated for potentiometric determination of chloride in various real samples, giving good precision and accuracy

as compared to the titrimetric standard method. The work shows good laboratory management for recycle of laboratory waste and initiates the fabrication of cost effective apparatus in the laboratory under limited budget.

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