



Determination of nickel(II) by ion-transfer to hydroxide medium using sequential injection-electrochemical analysis (SIECA)

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ABSTRACT

A method for the determination of Ni(II) using ion-transfer to a hydroxide medium has been developed by the sequential injection-electrochemical analysis (SIECA), a combination between an automated flow-based analysis and electrochemical techniques with a homemade screen-printed carbon electrode (SPCE). A sample/standard solution was introduced into an electrochemical flow cell where the Ni(II) in the solution was electrochemically reduced and accumulated on the SPCE. The accumulated Ni was then oxidized to Ni(II) in a hydroxide medium, which led to the formation of nickel hydroxide (Ni(OH)₂) and nickel oxyhydroxide (NiOOH) on the SPCE. The electrochemical response associated with Ni(OH)₂ and NiOOH was subsequently determined by square-wave voltammetry to account for Ni(II). Under optimal conditions, the proposed method provides a low detection limit of 0.02 mg mL⁻¹. This method was further applied to determine the Ni(II) content of standard-spiked mineral water samples with satisfactory results.

1. Introduction

Nickel (Ni) is a silvery-white metallic element found in the Earth's crust. This element is one of the metals that humans have exploited for daily life since its discovery in 1751 [1]. Because of its properties, which include good corrosion resistance and strength, nickel is commonly used to make coins, stainless steels, magnets, jewelry, electronic devices, and even catalyst [2]. Consequently, these industries are common sources of nickel pollution, which can be released into the environment at ppm-level concentration [3]. A large amount of nickel in any environmental compartment must be considered life threatening if it exposes living organisms to the metal. To be more precise, prolonged contact with nickel can cause dermatitis and nasopharyngeal carcinoma [4]. On the basis of the hazards of nickel, the World Health Organization (WHO) has set the Ni concentration limit in drinking water to not exceed 0.07 mg L⁻¹ [5]. Hence, a rapid, sensitive, selective, inexpensive and simple method for determining of Ni needs to be developed to monitor and control the amount of Ni in the environment.

Atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) techniques are well-known standard methods for the determination of Ni in water sample [6,7]. Other methods, including UV–visible absorption spectroscopy [8] and capillary electrophoresis [9,10], have also been extensively used for Ni detection. However, these techniques are time-consuming, expensive in terms of instrumenta-

tions and maintenance costs, and non-portable, which makes them inconvenient for fieldwork monitoring. An electrochemical method is a viable alternative for fieldwork monitoring and on-line analysis because it can be miniaturized using relatively low-cost devices; it also features high sensitivity, good selectivity, simplicity, and a short analysis time.

Stripping voltammetry is one of the most powerful electrochemical method for the determination of trace metal ions, including Ni(II), in environmental and biological samples because of its excellent limits of detection, high selectivity and suitability for automated analysis [11,12]. However, the conventional stripping voltammetry provides a low electrochemical signal for Ni because the electrochemical reaction of the Ni(s)/Ni(II) redox couple is an irreversible reduction at a highly negative potential of more than -1.1 V vs SCE [13]. The adsorptive mode of stripping voltammetry overcomes these problems by incorporating dimethylglyoxime (DMG), a chelating agent, into the solution to improve the sensitivity, as reported in several publications [14–16]. However, the chelating agent and its Ni complex are toxic. To avoid any chelating agents, this work therefore proposes an alternative stripping voltammetric method using ion-transfer to a hydroxide medium. Instead of the measuring the Ni(s)/Ni(II) redox couple, Ni(s) is oxidized in a hydroxide solution at a highly positive potential to form nickel oxyhydroxide (NiOOH) and then the electrochemical response of the Ni(II)/Ni(III) redox couple is subsequently recorded by voltammetry. To achieve a convenient and low-cost method, a disposable

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electrode specifically, a screen-printed carbon electrode (SPCE) was selected because it is easily mass produced at the laboratory scale and because its surface can be easily modified to fit the aim of the analysis related to a specific analyte.

To automatically replace a sample solution with hydroxide solution in the stripping step, sequential injection analysis (SIA) is used as an automated approach because of its high-throughput, precision and accuracy compared to batch analysis. This system requires a small volume of sample and reagents, and the solution zones can be manipulated in narrow-bore tubing. Moreover, SIA can reduce human and glassware errors and mitigate health risks associated with direct contact with toxic chemicals.

Hence, the aim of this work is to develop a chelating-agent-free method for the automated determination of Ni(II) ion content through the electrochemical response of a Ni(II)/Ni(III) redox couple by ion-transfer to a hydroxide medium using sequential injection-electrochemical analysis (SIECA).

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used without further purification. Ni(II) standard solution (999 mg L^{-1} , standard solution for AAS) was obtained from Fluka Analytical, New York, USA. Sodium hydroxide (NaOH) and hydrochloric acid (fuming 37% HCl) were purchased from Merck, Germany. Sodium chloride (NaCl) was acquired from Carlo Erba, France. All aqueous solutions were prepared with ultrapure water (resistivity of $18 \text{ M}\Omega \text{ cm}$) from a Milli-Q® water purification system (Merck-Millipore, Singapore). For the interference study, several solutions of heavy-metal ions Pb(II), Cd(II), Zn(II), Cu(II) and Au(III) were prepared from their respective standard solution (1000 mg L^{-1} , analytical grade for AAS, VWR International, Belgium).

2.2. Electrodes and electrochemical flow cell

In-house SPCEs used as a working electrode were fabricated by screen-printing carbon sensor paste (C2030519P4, Gwent Group, Singapore) onto a PVC substrate (0.3 mm thick). The printed PVC plate were baked in an oven for 1 h at $55 \text{ }^\circ\text{C}$ to dry the carbon paste. The carbon paste was printed onto the PVC plate and baked under the same conditions again to obtain SPCEs. The SPCEs were stored in a desiccator at room temperature.

A cross-flow cell, model MF-1093, was purchased from Bioanalytical Systems Inc. (USA). The flow cell consisted of a 1.0-mm-thick silicone gasket as a spacer and a three-electrode system in which a SPCE was used as the working electrode instead of a commercial glassy carbon electrode. An Ag/AgCl electrode (RE-3V, ALS, Japan) and a stainless steel outlet tube of the flow cell were used as the reference electrode and the auxiliary electrode, respectively.

2.3. Instrumentations

A schematic of SIECA for the determination of Ni(II) ion by ion-transfer to a hydroxide medium is shown in Fig. 1. All electrochemical techniques were carried out using a portable potentiostat, PalmSens3 (PalmSens BV, The Netherlands) that was controlled via a laptop with PSTrace 4.4 software. The sequential injection system used in this work was an MGC Auto-Pret MP-014S (MGC Japan) which consisted of a 5.0 mL syringe pump with a syringe valve (PSD/4, Hamilton, USA), a 5.3 mL PTFE holding coil (0.8 mm i.d.), an 8-port selection valve (HVXM 8-5, Hamilton, USA), and a 0.5 mm i.d. PTFE tubing with PEEK connectors. This system was controlled via SIA MPV Ver. 5.0 software (MGC Japan) which included a special command to start the PSTrace 4.4 software. Therefore, the sequential injection system and

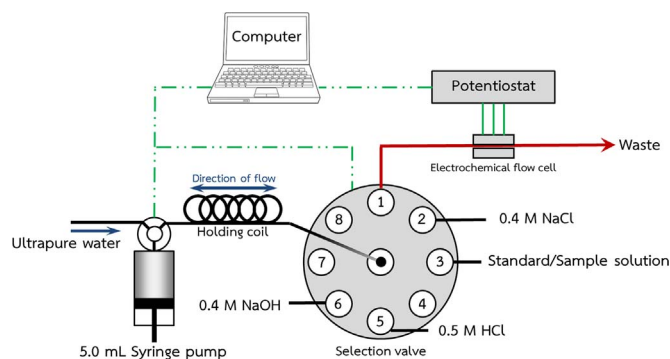
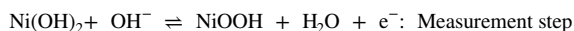
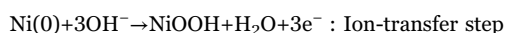
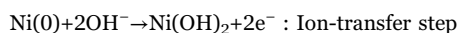
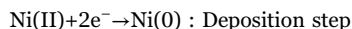


Fig. 1. Schematic of the sequential injection-electrochemical analysis (SIECA) for the determination of Ni(II) concentration by ion-transfer to hydroxide medium.

the potentiostat were completely synchronized for the flow analysis using electrochemical techniques.

2.4. Analytical procedure

To determine Ni(II) concentration by ion-transfer to hydroxide medium using SIECA, the step sequence including important parameters shown in Table 1 was followed. The method can be divided into 5 steps: the initial, deposition, oxidation, measurement, and cleaning steps. Five hundred microliters of a 0.6 M NaOH solution and 1800 μL of sample solution were sequentially aspirated into the holding coil in the initial step. In the deposition step, the aspirated solutions were injected in the reverse direction into the flow cell in which the deposition potential (E_{dep}) was applied at $-2.0 \text{ V vs Ag/AgCl}$. The Ni(II) in the sample solution was reduced to Ni(0), which accumulated on the electrode surface. Then, the NaOH solution was injected to push the remaining sample solution out of the flow cell. In the oxidation step, 900 μL of a NaOH solution was injected into the flow cell while the oxidation potential (E_{ox}) of $+1.0 \text{ V vs Ag/AgCl}$ was simultaneously applied to oxidize the accumulated Ni in the hydroxide medium to form nickel oxyhydroxide (NiOOH) and nickel hydroxide (Ni(OH)₂) which was oxidized again to NiOOH because of the highly positive potential; this step is called the ion-transfer step. Next, square-wave voltammetry (SWV) was carried out to record the electrochemical response of the Ni(II)/Ni(III) redox couple by scanning the potential from $+0.0$ to $+0.8 \text{ V vs Ag/AgCl}$ with square wave parameters of 50 Hz frequency, 50 mV amplitude and 6 mV potential step. Finally, the electrode was cleaned with 0.5 M HCl solution that flowed through the flow cell at a high flow rate of $50 \mu\text{L s}^{-1}$ while the cleaning potential was applied at $+1.0 \text{ V vs Ag/AgCl}$. The end of the flow stream was a blank solution of 0.4 M NaCl for conditioning the flow cell for the next measurement. All experiments were performed at room temperature ($\sim 25 \text{ }^\circ\text{C}$). The overall mechanisms are as follows:



3. Results and discussion

3.1. Electrochemical behavior of Ni(II)/Ni(III) redox couple in hydroxide medium

According to the step sequence in Table 1, a solution containing 1.00 mg L^{-1} Ni(II) in 0.4 M NaCl was determined by ion-transfer to a hydroxide medium (0.4 M NaOH); hydroxyl compounds of Ni(II) and

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