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Rapid and direct electrochemical determination of Ni(II) in industrial discharge water

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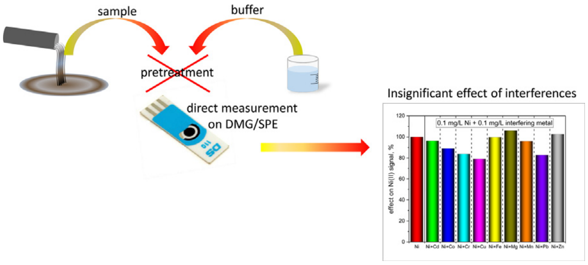
HIGHLIGHTS

- Direct on-site determination of Ni(II) in mine water.
- No need of sample pretreatment.
- Analytical performance suitable for analysis of industrial and environmental waters.
- Insignificant effect of interferences including dissolved oxygen.
- Simple correlation of electrochemical signal to a wide range of common outdoor temperature is possible.

GRAPHICAL ABSTRACT



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ABSTRACT

Industrial water contains a number of contaminants, such as organic pollutants and heavy metals, which can significantly affect the quality of soil, ground and environmental waters. We have successfully optimized and tested an electrochemical method and sensor modified with dimethylglyoxime for monitoring of nickel(II). The detection limit was 0.03 mg/L and determination limit was 0.09 mg/L. Linear concentration range was observed from 0.06 to 0.5 mg/L Ni(II) and it is suitable for the analysis of environmental waters. The effect of all parameters important for on-site measurements (such as interferences, presence of dissolved oxygen, temperature) was investigated and considered in the analysis of mine discharge water. Water samples were analyzed without any pretreatment or filtration. A low level of error (5.6%) was observed for analysis demonstrating the usability of the optimized sensor and method for on-site measurements.

1. Introduction

Water is used in many industrial and mining operations and during processing it is contaminated with various pollutants. Metals are often dissolved at high concentrations in these waters and their discharge can cause serious environmental problems and strongly contaminate surrounding environmental waters (streams, rivers, lakes, wetlands, ground water), soils, affect the health of plants and animals [1] and finally contaminate the food chain. Common contaminant in wastewaters from a range of industries (mining, metal plating, metal production) is nickel [2,3]. Due to negative health effects, such as allergic skin reaction [3] or carcinogenic effect [4], as well as the increasing presence of nickel and its salts in the environment, these compounds are put on the list of priority substances of EU Water framework directive (EU WFD) since 2008. Therefore, the presence of nickel in industrial and mining discharge waters must

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be strictly monitored. As these waters usually contain a number of dissolved metals and other organic and inorganic compounds, development of selective methods and tools for rapid real-time monitoring of nickel is very challenging.

Presently, standard methods for the determination of Ni in waters include atomic absorption spectrometry (AAS) and ion-coupling plasma (ICP) techniques. Non-portability and time-consuming analyses make these methods unsuitable for "on-site" measurements. Sample handling requires sample pretreatment and transportation of samples into the laboratory. Electrochemical methods utilizing various sensors start to be recognized as a promising solution for on-site /on-line analyses mainly due to the possibility of miniaturization and construction of small size portable analyzers, moreover they are rapid and highly sensitive. Methods, such as polarography, voltammetry as well as stripping voltammetric methods have already been proposed for the determination of Ni. However, low electrochemical signals and irreversible reduction at very negative potential (more than −1100 mV vs. SCE) [5] can cause problems in the determination of low concentrations of Ni(II). Mercury based working electrodes can overcome these problems but the toxicity of mercury to living organisms as well as diverse effect on the environment limits the application of these electrodes.

To increase the sensitivity as well as selectivity of Ni(II) determination on mercury-free electrodes and eliminate the effect of interfering metals in real water samples Ni(II) is often determined after its interaction with a suitable complexing (chelating) agent. Selection of complexing agent depends on the application of the sensor. For example, dsDNA modified carbon nanofiber paste electrode showed excellent sensitivity and detection limit down to 7 nmol/L due to electrostatic interaction of Ni(II) with DNA [6], however, lack of selectivity and applicability in more toxic environments, such as industrial waters, is problem. On the other hand, dimethylglyoxime (DMG) offers sufficient selectivity for the determination of Ni(II) in the presence of other metal cations [5]. Mercury-free sensors for determination of Ni(II) with DMG as a ligand are based on different types of electrodes, such as glassy carbon, carbon paste, sol–gel [7–9]. However, screen-printed electrodes (SPE) seem to be the most suitable for real applications. Only one reference can be found on this topic. DMG was incorporated in the ink for the construction of screen-printed electrodes [10] and showed excellent sensitivity for the determination of trace concentrations of Ni(II). Electrodes were tested in river water samples, but effect of interferences was not considered.

Industrial waste waters usually contain high amount of organic and inorganic contaminants [11]. These substances can form complexes with metals and change their kinetics [12]. Thus the behavior of Ni(II) in real industrial and mine waters can be very different from that observed in buffer solution or natural samples. Developed sensor and methods must, therefore, be optimized for this specific sample and application. Recently we submitted preliminary results for the application of DMG based electrochemical sensor for the determination of Ni(II) in mine site discharge waters [13]. The aim was to obtain the sensitivity suitable for environmental water limits for Ni(II) (0.1 mg/L). Our sensor showed significantly lower detection limit 27 μg/L, but due to properties of electrode material (carbon paste), such as high porosity, softness, requirement of mechanical regeneration, and due to interference of dissolved oxygen, the sensor was not suitable for on-line/on-site application.

In the present work, commercial screen-printed electrodes were modified with DMG in Nafion (DMG-N/SPE) and with respect to real on-site application in industrial discharge water, we considered effect of dissolved oxygen, metal cation interferences, and temperature. Sensor and method were developed in order to fulfill requirements of mining companies for reliable detection of Ni(II) within the environmental concentration limit of 0.1 mg/L. Long-term stability studies showed that DMG-N/SPE sensors stored at 4 °C was stable for at least one month. Results from on-site measurements showed 5.6% error compared to ICP analysis.

2. Materials and methods

2.1. Materials and instruments

Stock solution of DMG (Sigma–Aldrich) was prepared in ethanol (99%). Nafion was purchased from Sigma in the form of 5% ethanolic solution. Electrochemical measurements were done in ammonium buffer solution of pH 8.0 consisting of ammonium chloride (Sigma) and ammonia solution (Sigma) prepared in deionized water (18.2 MΩ). Standard solutions of Ni(II) and selected interfering metals (Fluka) were prepared in proper concentration in ammonium buffer solution. All chemicals were of analytical-reagent grade purity. Real mining site discharge water samples (pH 6.6) with high and low content of Ni(II) were diluted with ammonium buffer of pH 8.0 in the ratio of 1:1 and used without further pretreatment.

Manually operated measurements were performed using PalmSens potentiostat (PalmSens, Netherland) connected to personal computer. Electrodes used in measurements were commercial screen-printed carbon electrodes (DropSens, Spain) consisting of 4 mm diameter carbon working electrode (WE), carbon counter electrode (CE) and silver reference electrode (RE).

2.2. Modification of working electrode

Surface of WE was modified by drop-casting with 1 μL of solution of 0.7% DMG in Nafion always one day prior to measurement and let to evaporate to dryness at room temperature. Modified electrodes (DMG-N/SPE) were not regenerated after measurement but used as a disposable sensors.

2.3. Standard Ni solution and real water sample preparation

For optimization of measurement conditions and analysis of samples using standard addition method, standard Ni solution was diluted into 0.1 M ammonium buffer solution. Real water samples were diluted with ammonium buffer at the ratio of 1:1.

2.4. Measuring protocol

Prior to the measurement, DMG-N/SPE was incubated in ammonium buffer for 6 min in order to hydrate modifier layer. After the incubation step DMG-N/SPE was transferred into the Ni solution (or sample solution) in ammonium buffer. Ni was accumulated at the surface of DMG-N/SPE at open circuit conditions (i.e., no potential was applied) for 120 s under stirring. Electrochemical measurements were performed by differential pulse voltammetry (DPV) in the potential range from 0 to −1.5 V using scan rate of 50 mV/s.

3. Results and discussion

3.1. Optimization of determination conditions

Several ratios of DMG:Nafion solution (1:1, 1:1.4, 1:1.7, and 1:2) were tested for the optimum modification of SPE with respect to the highest sensitivity and stability. Tests did not show any significant differences in Ni(II) responses among tested ratios. However, sensors modified with DMG:Nafion ratio of 1:1.7 showed the lowest variation of current responses among individual modified electrodes and therefore was selected for further experiments.