Mine Water Environ (2016) 35:547–552
DOI 10.1007/s10230-015-0357-1

TECHNICAL COMMUNICATION

Electrochemical Monitoring of Nickel(II) in Mine Water

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Received: 9 March 2015 / Accepted: 19 July 2015 / Published online: 31 July 2015

Abstract This paper presents preliminary results in the development of a method for rapid real-time monitoring of Ni(II) in mine water. A simple electrochemical approach using a differential pulse voltammetry was developed and demonstrated by analysis of real samples.

Keywords Sensor · Dimethylglyoxime · Mining water · Environmental waters

Introduction

In general, mining adversely affects water quality in four ways: metal contaminants, processing chemicals, acid main drainage, and erosion/sediment (Gambhir et al. 2012). Metals can be a persistent problem, for although they can be transformed to a different oxidation state, precipitated, dissolved, or complexed, they are not biodegradable. Metals can be bioaccumulated in living organisms and thus must be strictly monitored. As mine site discharge waters are often contaminated by number of organic and inorganic compounds, development of methods and tools for rapid real-time selective monitoring of potentially toxic metals is of great interest.

Nickel naturally appears in the environment; however, its amount in nature is increased by anthropogenic activities, such as coal and oil combustion, metal production, and mining. Ni is a moderately toxic metal that can cause skin allergies, asthma, and in some cases, cancer (Foxall 2009). Its concentrations in environmental waters should not exceed 0.1 mg/L; the metal and its compounds appear on the list of priority substances within the EU Water framework directive 2008 (Annex II of EU Directive 2008/105/EC).

Current standard methods for determination of Ni in waters include atomic absorption spectroscopy (AAS) and ion-coupling plasma (ICP) technique. These methods show appropriate sensitivity and selectivity; however, non-portability of instrumentation and time-consuming analyses make them unsuitable for "on-site" measurements. Transportation of samples to the laboratory and sample pretreatment using additional chemicals and filtration can significantly increase the overall time of analysis and cause analyte loss. In contrast to current standard techniques, electrochemical methods offer the possibility for miniaturization and construction of portable analyzers that can be used for real-time analysis in the field. These methods are also rapid and highly sensitive and offer the possibility for increased selectivity by modification of the working electrode by a suitable chemical modifier.

However, in contrast to some other metals (e.g. Cu, Pb, Fe), electrochemical determination of Ni(II) is complicated and usually suffers from low electrochemical signals and irreversible reduction at very negative potential (Baldwin et al. 1986). Ni(II) is often remediated from mine waters by complexation with organic ligands (Verma and Singh 2005) or bioorganisms (Fomina and Gadd 2014); a similar principle is used in electrochemical determination in order to increase sensitivity and selectivity, and to shift reduction of Ni(II) to more positive values. Sensitivity of Ni(II) determination has been increased using, for example, a cation exchanger Dowex 50 W (Gonzales et al. 2002), 2-aminothiazole (Takeuchi et al. 2007), and dsDNA

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(Ferancova et al. 2010), providing nanomolar level detection limits. However, as these modifiers are known to interact with many metal cations, selectivity was not improved significantly and measurement protocol required additional preconcentration or purification steps to eliminate interference. In order to improve selectivity of Ni(II) determination significantly, dimethylglyoxime (DMG) was incorporated as a selective Ni(II) chelating agent in the electrode material. DMG powder can be mixed with graphite powder and liquid binder (Zhang et al. 1996) or, in order to get better coverage of graphite particles with DMG, ethanolic DMG solution can be mixed with the graphite powder and, after ethanol evaporation, the liquid binder can be used to prepare a modified paste (Baldwin et al. 1986; Tartarotti et al. 2006; Thomsen et al. 1988). Detection limits comparable or less than those obtained for carbon paste electrodes (CPEs) using other modifiers were obtained and the selectivity with respect to interfering metal cations was increased up to 100 times.

Most of these approaches were only tested in a buffer solution or in model samples spiked with Ni(II). Only a few of the developed sensors have been applied to determine Ni(II) in real samples, such as certified reference materials (Baldwin et al. 1986; Thomsen et al. 1988) and fuel ethanol (Tartarotti et al. 2006). However, natural and waste waters contain high percentages of dissolved organic carbon which originates mostly from humic substances (Morel and Hering 1993). These compounds form complexes with metals and change their kinetics (Chakraborty et al. 2006). Thus, behavior of Ni(II) in real mine waters can be very different from that observed in buffer solution or model samples, and developed sensors and methods must be optimized for this specific application.

A simple electrochemical approach to rapid real-time monitoring of Ni(II) concentration in mine site discharge water is presented. A DMG-modified CPE was developed and characterized by cyclic voltammetry and optimized by a differential pulse voltammetric procedure for determination of Ni(II) in mine water. Finally, the optimized procedure was successfully used for Ni(II) determination in real mine water.

Experimental Methods

Chemicals

Carbon powder and white Vaseline (both from Sigma-Aldrich) were used to prepare the carbon paste. A stock solution of DMG (Sigma-Aldrich) was prepared in ethanol (99 %). Electrochemical measurements were done in a pH 8.0 ammonium buffer solution consisting of ammonium chloride (Sigma) and ammonia solution (Sigma). Standard solutions of Ni(II) and potential interfering metals (Fluka) were prepared in an ammonium buffer solution. Mine site discharge water samples with high and low Ni(II) concentrations were diluted with ammonium buffer in a 1:1 ratio and used without further pretreatment.

Instrumentation

Cyclic voltammetric and differential pulse voltammetric measurements were performed using a PalmSens potentiostat (PalmSens, the Netherlands) connected to a personal computer. A three-electrode system was used, consisting of a DMG/CPE working electrode (with a geometric surface area of 3.1 mm^2), a Pt/Ti counter electrode (Edaq), and a silver/silver chloride reference electrode (Edaq).

Preparation of DMG/CPE

The method for DMG/CPE preparation was adopted from Baldwin et al. (1986) and optimized for this application. Briefly, a 2 % DMG solution in ethanol was prepared (limited by low DMG solubility). Ten mL of this solution was thoroughly mixed with 500 mg of carbon powder in a mortar and then the ethanol was allowed to evaporate overnight. The optimum DMG content in the electrode material was 28 % with respect to the carbon powder (w/w). Dry modified carbon powder was mixed with the appropriate amount of Vaseline to form a homogeneous paste. A Teflon® electrode body was then filled with the DMG-modified paste; contact was provided by a copper screw.

Characterization of DMG/CPE by Cyclic Voltammetry

Cyclic voltammetry (CV) was used to electrochemically characterize the DMG/CPE. To do this, we selected an appropriate Ni(II) concentration that would saturate the electrode surface (as discussed below). Prior to the measurement, Ni (II) was accumulated on the DMG/CPE surface in stirred open circuit conditions (i.e. no potential was applied) for 120 s. CV was measured over the potential range of −0.5 to −1.25 V at different scan rates (5–1000 mV/s). The peak current of Ni(II) reduction depends linearly on the scan rate. This result is characteristic for the surface attached analyte, which confirms Ni(II) complexation by the DMG. Surface coverage with Ni(II) was obtained from the dependence of the Ni(II) cathodic peak current (*Ipc*) on the scan rate (v), according to Eq. (1) (Eckermann et al. 2010):

$$Ipc = \left(n^2F^2/RT\right)A\Gamma v \qquad (1)$$

where n is the number of electrons exchanged, F is Faraday's constant, R is the gas constant, T is the absolute temperature, A is the electrode surface area, and Γ is the surface coverage with electroactive molecules. The surface coverage of DMG/

CPE with Ni(II) was calculated as 3.48×10^{-12} mol from the slope of linear dependence, which was converted to 2.10×10^{12} ions of Ni(II), using the Avogadro constant. By assuming that complexation preferably leads to formation of a Ni:DMG ratio of 1:2 (complex $Ni(DMG)_2$), we estimated the number of DMG molecules involved in the Ni(II) complexation as 4.2×10^{12}. By considering the geometric electrode area, the amount of DMG used for the DMG/CPE preparation, and assuming that DMG is homogeneously distributed in the modified paste, we estimated the thickness of the DMG-modified paste layer saturated with Ni(II) as 0.57 nm.

Analytical Procedure for Ni(II) Determination

Electrochemical determination of Ni(II) was performed by differential pulse voltammetry (DPV) in the potential range of 0 to −1.5 V using a scan rate of 0.05 V/s. After every measurement, the surface of the DMG/CPE was regenerated by polishing on a wet filter paper.

Results and Discussion

Optimization of Conditions for Ni(II) Determination

Differential pulse voltammetric determination of Ni(II) usually suffers from low electrochemical signals and irreversible reduction at very negative potential (i.e. more than −1100 mV versus a saturated calomel electrode (Baldwin et al. 1986)). To prove the pre-concentration effect of DMG, we compared the voltammetric signals of Ni(II) obtained on DMG/CPE to those obtained on bare CPE (Fig. 1).

Ni(II) shows a well-developed reduction signal at a potential of −1.1 V at DMG/CPE (Fig. 1 red curves), but only very small signals were observed on bare CPE (Fig. 1a, black curves). Due to oxygen reduction observed at a potential of −0.8 V, oxygen has to be considered as a major source of interference. Therefore, all solutions were bubbled with N_2 prior to measurement. Several authors have reported the accumulation of Ni(II) in DMG at an applied negative potential, for example −420 mV versus SCE at DMG/CPE (Thomsen et al. 1988) or −800 mV versus Ag/AgCl at screen-printed DMG modified carbon ink electrode (Wang et al. 1996). Others used open circuit conditions during the accumulation step (Tartarotti et al. 2006). However, the comparison of potentiostatic and open circuit accumulation on electrochemical signal of Ni(II) has not yet been discussed. Therefore, we investigated the effect of accumulation conditions using DMG/CPE.

Well-developed signals of Ni(II) were observed at both, high and low tested concentrations (Fig. 1, red lines) at DMG/CPE. Signals obtained after accumulation at open circuit conditions were smaller than those obtained after accumulation at −0.8 V. In contrast, at unmodified CPE (Fig. 1, black lines) no signal of Ni(II) can be seen after

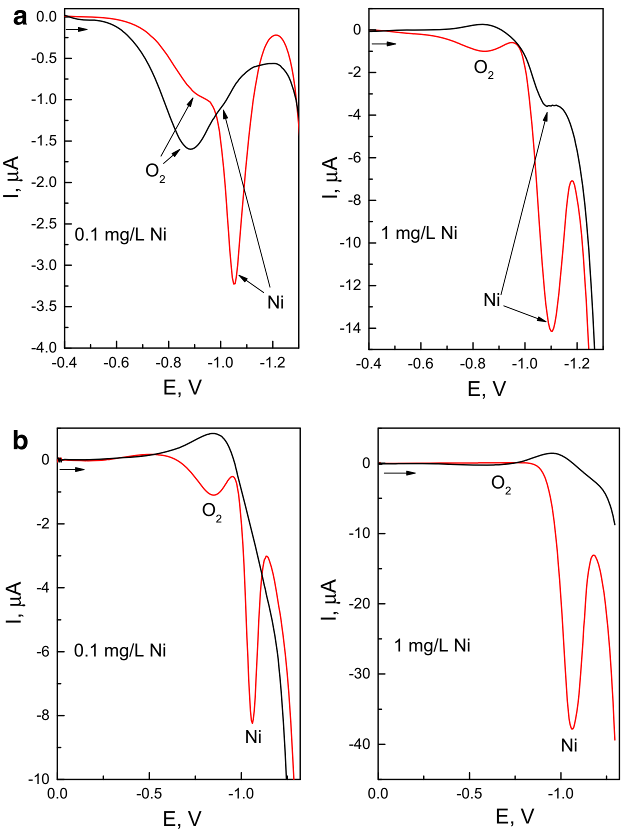

Fig. 1 DP voltammograms of Ni(II) obtained on CPE (*black*) and DMG/CPE (*red*) after 120 s accumulation at potential of −0.8 V (**a**); and at open circuit conditions (**b**) after subtraction of measurement in blank solution

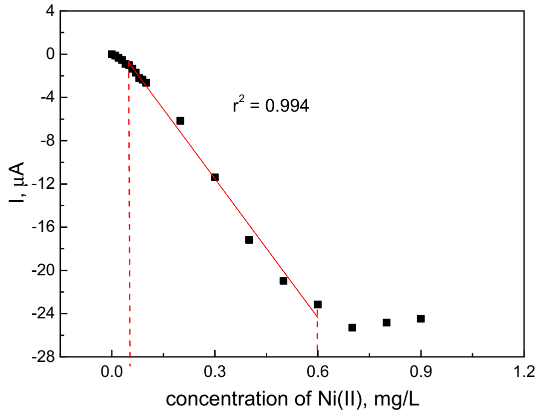

Fig. 2 Calibration curve for Ni(II) at DMG/CPE obtained at optimized determination conditions: accumulation 120 s at open circuit conditions, ammonium buffer of pH 8.0, DPV from 0 to −1.2 V, scan rate of 10 mV/s

Table 1 Stability constants of Ni(II) and interfering metals with DMG

Metal	Stability constant	References
Ni(II)	14.60	Furia (1972)
Cu(II)	11.94	Furia (1972)
Cd(II)	11.50	Saito and Moffett (2001)
Zn(II)	7.70	Furia (1972)

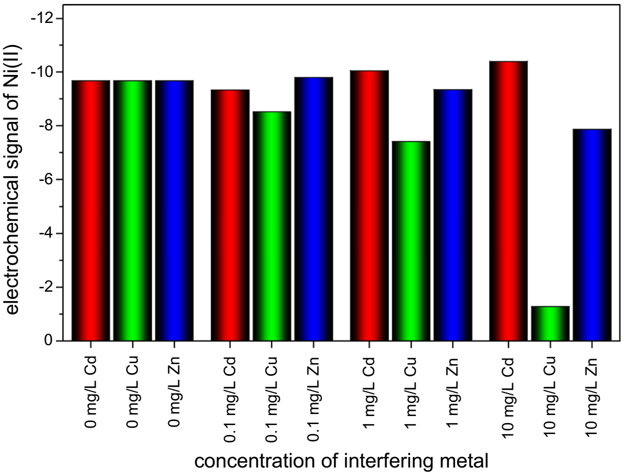

Fig. 3 Effect of interfering metals on signal of 0.1 mg/L Ni(II)

accumulation at open circuit conditions. However, when potential of −0.8 V was applied during accumulation step small signal of Ni(II) was observed. This confirms that Ni(II) can electrostatically interact with carbon particles of the electrode material. Even we expect the homogenous mixture of DMG and carbon in the electrode material of DMG/CPE uncovered carbon particles are here also present and their amount cannot be defined. Therefore, electrochemical interaction of Ni(II) with these particles can lead to non-specific interactions and errors when potential is applied during accumulation step. To avoid it and specify the determination mechanism only to DMG—Ni(II) interaction we used open circuit conditions in further experiments.

Table 2 Results from Ni(II) analysis of real samples in mg/L

Sample	ICP reference analysis	DPV	Error (%)
S1	0.014	0.018	28
S2	0.180	0.188	4

Complexation of Ni(II) with DMG is quantitative in solutions of pH 7.5–9 (Salesin and Gordon 1960). The voltammetric response of Ni(II) increased significantly with increasing pH, and peaked at pH 8.0. The effect of accumulation time was studied in open circuit conditions in the pH 8.0 ammonium buffer and at a Ni(II) concentration of 0.1 mg/L. At these conditions, the adsorption isotherm reached saturation at 120 s.

A calibration curve measured at optimum conditions in the concentration range of 0.01–0.9 mg/L Ni(II) showed linearity from 0.08 to 0.6 mg/L, with a correlation coefficient of 0.998 (Fig. 2). The detection limit, calculated according to Mocák et al. (2009), was 0.027 mg/L and the quantification limit was 0.081 mg/L.

Fig. 4 Analysis of real samples using standard addition method

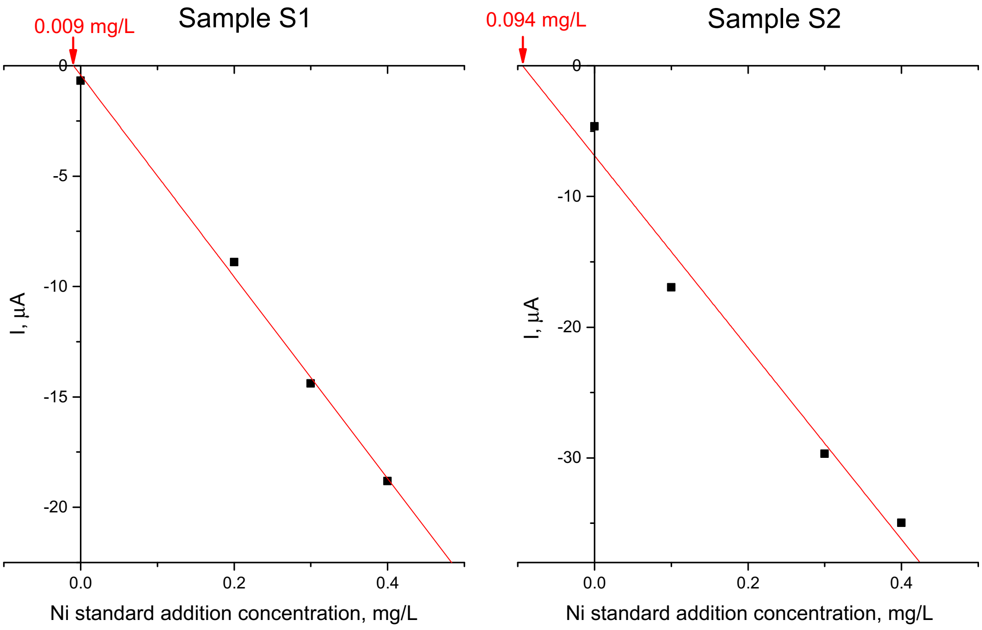

Table 3 Cation analysis using standard ICP methods at an external laboratory; concentrations in mg/L

	pH	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Na	Ni	Pb	Se	U	V	Zn
S1	7.0	–	0.53×10^{-3}	–	0.05×10^{-3}	7.6×10^{-3}	1.1×10^{-3}	0.29	–	–	–	–	0.014	0.0028	$<0.2 \times 10^{-3}$	0.12×10^{-3}	0.9×10^{-3}	0.510
S2	6.6	0.540	$<1 \times 10^{-3}$	488	1×10^{-3}	12×10^{-3}	–	5.7×10^{-3}	3.1	81	3.1	457	0.18	–	–	$<1 \times 10^{-3}$	–	0.35

Interference Study and Analysis of Mine Discharge Water

Real mine discharge waters usually contain different concentrations of a high number of metal cations. Therefore, the effect of potential interferences had to be considered and investigated. Cu(II), Zn(II), and Cd(II), which form stable complexes with DMG like Ni(II) does, were chosen as potential interferences (Table 1). Moreover, Cu(II) and Zn(II) were also expected to be the main interfering metals in our real water samples.

We investigated the effect of interfering metal cations at the same concentration, a 10-fold, and a 100-fold excess, for a signal of 0.1 mg/L Ni(II) (Fig. 3). We observed that at equal and tenfold concentrations, Cd and Zn did not significantly change the Ni(II) electrochemical signal. However, 10 mg/L of Zn decreased the Ni(II) signal by 18 % and 10 mg/L of Cd increased the Ni(II) signal by 18 %. Cu(II) had a minor effect on the Ni(II) signal in the same concentration range, but caused a 23 % decrease of Ni(II) signal at 1 mg/L, and an 87 % decreased signal of Ni(II) at 10 mg/L Cu(II).

Real mine site discharge water samples with low (S1) and high (S2) concentration of Ni(II) were obtained from two different mining areas in Finland. Samples were diluted with the pH 8.0 buffer solution at a 1:1 ratio and used without further pretreatment. Samples were analyzed using the standard addition method (Fig. 4).

Samples were also analyzed by standard ICP method at an external laboratory. A comparison of the results from the ICP and the DPV method optimized in our work (Table 2) shows that since the Ni(II) content in sample S1 was below the linear concentration range, the electrochemical determination showed a high error (28 %), as expected. In contrast, the content of Ni(II) in sample S2 was in the linear concentration range, which allowed the determination of Ni(II) with a low level of error (4 %).

The actual samples contained a high number of interfering metals (Table 3). Concentrations of some metals in sample S2 (Zn, Mn, Fe, and Al) were significantly higher than the Ni(II) concentration. However, these metals did not significantly affect Ni(II) determination by DMG/CPE.

Conclusions

In order to develop a method that could be used in the field to analyze Ni(II), a DMG/CPE electrode was prepared and characterized by cyclic voltammetry. The surface coverage of DMG/CPE by Ni(II) reached 3.48×10^{-12} mol and, by assuming the content of DMG in paste and formation of $Ni(DMG)_2$ complex, we estimated that the thickness of the DMG-modified paste layer that was saturated with Ni(II) was 0.57 nm. This confirmed the partially porous structure of the DMG/CPE (Švancara et al. 2012).

We demonstrated the reliable determination of Ni(II) in mine water. Conditions for differential pulse voltammetric determination were optimized and the DMG/CPE exhibited a linear concentration range from 0.08 to 0.6 mg/L, with a detection limit of 0.027 mg/L, which is suitable for Ni(II) determination in environmental waters. In order to confirm this result, samples obtained from two mine sites in Finland were analyzed using our optimized method and compared to results with the standard ICP method, performed in an external laboratory. Our results showed a low level of error (4 %) for voltammetric analysis. Due to the specific reaction between Ni(II) and DMG, the effect of interfering ions was generally limited.

However, it was also shown that Cu(II), which has, among interferences, the highest stability constant with DMG, but was not present at high concentrations in the mine water samples, had the most significant effect on the Ni(II) signal, and could potentially interfere with the determination of Ni(II) in mine water if it is present at concentrations above those of Ni(II). Also, dissolved oxygen has to be considered as a major potential source of interference and should be removed from solution.

This work was performed to confirm that it is possible to electrochemically analyze mine water directly without any pretreatment. The tested electrochemical sensor showed the required sensitivity, specificity, and robustness. Based on these results, future tests will employ the use of screen-printed electrodes to obtain higher sensitivity and to develop a field method and instrument for real-time nickel concentration determination in mine water.

Acknowledgments This research was financially supported by the Finnish Funding Agency for Technology and Innovation (TEKES) through the Green Mining Program and industrial partners Metso Automation Oy, Outotec Oyj, Talvivaara Mining Company Plc, and Ima Engineering Ltd.

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