

Measurement of Urinary Nickel and Cobalt Using Square Wave Adsorptive Cathodic Stripping Voltammetry and UV Sample Digestion

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Abstract: This work presents a method for the simultaneous measurement of nickel (Ni) and cobalt (Co) by square wave adsorptive cathodic stripping voltammetry on a Bi film electrode with dimethylglyoxime as the ligand. Electrolyte concentrations and voltammetric run parameters were optimized for the simultaneous measurement of Ni and Co at concentrations relevant for the routine monitoring of Ni and Co excreted by Ni/Co mine and refinery workers in their urine. To assess the optimized procedure's viability it was applied to spiked urine samples and a certified urine standard. Urine samples were digested using UV photolytic digestion with hydrogen peroxide.

Key words: bismuth film electrode, dimethylglyoxime, nickel, cobalt, square-wave adsorptive cathodic stripping voltammetry, urine analysis, ultraviolet photolysis

1. Introduction

Inhalation of Ni and/or Co containing dusts and compounds has been linked with an increased risk of developing nose, throat, and lung cancers [1, 2]. Ni/Co mine and refinery workers are frequently at risk of exposure to Ni and Co from ore baring dusts. Monitoring occupational exposure to Ni and Co can be used to manage staff exposure [1, 2]. This can be achieved by monitoring Ni and Co excreted in a staff member's urine [1-4]. At an undisclosed Ni/Co mine and refinery workers are removed from the workplace if their urine exceeds 75 μ gL⁻¹ Ni or 15 μ gL⁻¹ Co [3].

The instrument most commonly used for the detection of metal ions in urine is inductively coupled plasma mass spectroscopy (ICP-MS) [4]. However, as

is the case here, ICP-MS is often not available on remote mine sites and samples need to be shipped to a chemical laboratory for analysis, which can result in long analytical turnaround times, one to four weeks.

Modern voltametric instruments offer an inexpensive and portable alternative to ICP-MS [5]. Simultaneous measurement of Ni and Co using square-wave adsorptive cathodic stripping voltammetry (SW-AdCSV) with a bismuth film (BiF) electrode and dimethylglyoxime (DMG) as the ligand is well documented in literature [6-10]. However voltammetric analysis of urine for Ni and Co is difficult due to the presence of interfering organic compounds [11]. Ultraviolet (UV) sample digestion has been coupled with voltammetry for the mineralisation of urine samples [11-13]. Here the aim was to develop an on-site SW-AdCSV procedure using UV sample digestion for the rapid simultaneous measurement of Ni and Co in urine at concentrations up to 100 µgL⁻¹ Ni and 20 µgL⁻¹ Co. An onsite

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analytical procedure for urinary Ni and Co would reduce analytical turnaround times and improve monitoring of Ni and Co in exposed personnel.

2. Experimental

2.1 Equipment

2.1.1 Reagents and Materials

1000 mgL⁻¹ standard solutions of Bi³⁺, Ni²⁺ and Co²⁺ from Australian Chemical Reagents were diluted with 0.10 molL⁻¹ HNO₃ as required. 0.20 molL⁻¹ NH₄⁺ buffer (pH 9.35) was prepared from analytical grade NH₄OH and NH₄Cl, Rowe Scientific. 0.10 molL⁻¹ DMG solution was prepared from analytical grade Na₂DMG, Rowe Scientific. 1.0 molL⁻¹ NaOH and HCl were prepare form analytical grade reagents, Rowe Scientific. Analytical grade 30% H₂O₂, Rowe Scientific was used as supplied. A certified urine standard, ClinCheck (Munich) was reconstituted as per the manufacturer's instructions.

10 W Atlantic Ultraviolet Corporation ster-l-ray germicidal lamps, a GSL Electronics 12 V 20 W power supply and 8 mL Hubei Yunsheng Quartz Products quartz glass test tubes were used to construct a UV digester.

2.1.2 Apparatus

The voltammetric instrument used was a Modern Water PDV6000ultra fitted with an Ag/AgCl reference electrode, glassy carbon working electrode and Pt wire auxiliary electrode. The glassy carbon working electrode (surface area 3.0 mm^2) was polished using 0.1 µm alumina slurry on a Buehler polishing pad daily, and modified with a BiF by plating 20 mgL⁻¹ Bi solution for 300 s at -1100 mV.

A UV digester was constructed by encasing 12, 10 W UV lamps inside an opaque plastic container in three vertical banks of four UV lamps. 12, 8 mL quartz glass test tubes were arranged on each side of the central bank of UV lamps.

2.2 Methodology

2.2.1 Optimisation of Voltammetric Parameters

Deposition voltage, deposition time, sweep rate and pulse amplitude were investigated between -500 to -1100 mV, 15 to 120s, 25 to 500 mVs⁻¹ and 10 to 150 mV, respectively. Electrolyte pH, NH₄⁺ and DMG concentrations were investigated from 8.0 to 10.0, 0.0 to 0.5 molL⁻¹ and 0.0 to 7.5 mmolL⁻¹, respectively. Conditions optimal for the measurement of Ni and Co concentrations up to 100 μ gL⁻¹ Ni and 20 μ gL⁻¹ Co were selected. Limit of detection, %RSD over 10 measurements and linear working range were determined using the chosen parameters.

2.2.2 Digestion and Analysis of Urine

Urine samples were all mineralised by dispensing 2.00 mL urine into a quartz tube with 200 μ L 30% H₂O₂and approximately 3 mL H₂O. Samples were irradiated for 60 minutes. After digestion, 2.00 mL 1.0 molL⁻¹ NH₄⁺ buffer and 150 μ L 0.10 molL⁻¹ DMG were added and the samples diluted to 20.00 mL.

To analyse, Ni-DMG and Co-DMG were accumulated at -700 mV for 60 s, after a 10 s equilibration period at -700 mV a square-wave scan was recorded from -700 mV to -1250 mV at 100 mVs⁻¹, pulse amplitude 50 mV and frequency 50 Hz. Peaks were quantified by 2 standard additions, $R^2 > 0.990$.

3. Results and Discussion

3.1 Optimization of Voltammetric Parameters

Investigation of the voltammetric parameters revealed that altering deposition potential from -500 to -800 mV showed a slight increase in the response for Ni, after which response decreased due to reduction of Ni-DMG (Fig. 1). The response for Co increased slightly between -500 and -700 mV, after which it decreased slightly (Fig. 1). Increasing sweep rate from 25 to 500 mV/s revealed response for both Ni and Co increased, however sweep rates above 100 mVs⁻¹ produced poorly defined voltammetric waves. This

was due to decreased data points gathered as a result of increased sweep rate (Fig. 2). Increasing square wave pulse amplitude from 10 to 50 mV increased response for both Ni and Co, after which response was stable (Fig. 3). It was also noted that increasing pulse amplitude resulted in increased baseline current. Therefore, in order to achieve the required limits of detection and linear working range for Ni and Co whilst minimising background current and maintaining well defined voltammetric waves a deposition voltage of -700 mV, sweep rate of 100 mVs⁻¹ and pulse amplitude of 50 mV were selected.



Fig. 1 Response for 20 μ gL⁻¹ Ni (circle) and Co (dot) solution in 0.20 molL⁻¹ NH₄⁺, 50 μ molL⁻¹ DMG (pH 9.35) at various deposit potentials. Deposition time = 15 s, pulse amplitude = 50 mV and sweep rate = 50 mVs⁻¹.



Sweep Rate / mVs⁻¹

Fig. 2 Response for 20 μ gL⁻¹ Ni (circle) and Co (dot) in 0.20 molL⁻¹ NH₄⁺, 250 μ molL⁻¹ DMG (pH 9.35) at various sweep rates. Deposition time 15 s, Pulse amplitude 50 mV and deposition voltage -700 mV.



Fig. 3 Response for 20 μ gL⁻¹ Ni (circle) and Co (dot) in 0.20 molL⁻¹ NH₄⁺, 250 μ molL⁻¹ DMG (pH 9.35) at various pulse amplitudes. Deposition time 15s, sweep rate 50 mVs⁻¹ and deposition voltage -700 mV.

3.2 Optimization of Electrolyte Concentrations

Varying electrolyte pH revealed response for Ni increased from 8.0 to 9.35, whilst Co increased from 8.0 to 9.5; after which the response for both Ni and Co decreased slightly. Due to greater response and reproducibility an electrolyte pH of 9.35 was used for further experiments (Fig. 4). Varying electrolyte NH_4^+ concentration revealed response for Ni was greatest at 0.30 molL^{-1} and Co at $0.20 \text{ molL}^{-1} \text{ NH}_{4}^{+}$. Higher NH_{4}^{+} concentrations decreased response for both Ni and Co (Fig. 5). Due to the response for Co being greatest, 0.20 molL⁻¹ was selected for further experiments. Altering electrolyte DMG concentration between 0 and 7.5 mmolL⁻¹ revealed response for Ni increased rapidly, but stabilized by 0.050 mmolL⁻¹. Whilst response for Co continues to increase with increasing DMG concentration, until it too stabilized at 1.00 mmolL⁻¹. At 0.25 mmolL⁻¹ response for Ni and Co were equal (Fig. 6). However, due to the need to detect Co at concentration five times lower than Ni, 0.75 mmolL⁻¹ DMG was selected for further analysis, as this resulted in Co response five times greater than that of Ni.

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Fig. 4 Response for 20 μ gL⁻¹ Ni (circle) and Co (dot) in 0.20 molL⁻¹ NH₄⁺, 250 μ molL⁻¹ DMG at various pH values. Deposition time 15 s, sweep rate 100 mVs⁻¹, pulse amplitude 50 mV and deposition voltage -700 mV.



Fig. 5 Response for 20 μ gL⁻¹ Ni (circle) and Co (dot) in 0.05 to 0.50 molL⁻¹ NH₄⁺, 250 μ molL⁻¹ DMG (pH 9.35). Deposition time = 15 s, sweep rate = 100 mVs⁻¹, pulse amplitude = 50 mV and deposition voltage = -700 mV.

3.3 Deposition Time Optimization

Using the chosen electrolyte and voltammetric parameters a solution containing $1.0 \ \mu g L^{-1}$ Co and $5.0 \ \mu g L^{-1}$ Ni was examined at different deposition times.

Response for both Ni ad Co increased linearly with up to 60s deposition time, after which the increase in response for Ni and Co diminished (Fig. 7). To achieve the required sensitivity and linear working range for this application a deposition time of 60 s was chosen.



Fig. 6 Response for 20 μ gL⁻¹ Ni (circle) and Co (dot) in 0.20 molL⁻¹ NH₄⁺ with 0.025 to 1.0 mmolL⁻¹ DMG (pH 9.35). Deposition time = 15 s, sweep rate = 100 mVs⁻¹, pulse amplitude = 50 mV and deposition voltage = -700 mV.



Fig. 7 Response for 5.0 μ gL⁻¹ Ni (circle) and 1.0 μ gL⁻¹Co (dot) in 0.20 molL⁻¹ NH₄⁺ with 0.75 mmolL⁻¹ DMG (pH 9.35). Sweep rate = 100 mVs⁻¹, pulse amplitude = 50 mV and deposition voltage = -700 mV.

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3.4 Linear Working Range, Limit of Detection and Reproducibility

Using the chosen electrolyte, voltammetric parameters and deposition time, the response for Ni was linear up to 9.0 μ gL⁻¹, R² = 0.9941; whilst Co was linear up to 5.0 μ gL⁻¹, R² = 0.9955 (Fig. 8 & Fig. 9). Ten measurements of a solution containing $1.0 \ \mu g L^{-1}$ Ni and 0.5 μ gL⁻¹ Co (Fig. 8) produced a mean response and standard deviation of 4.84 (0.134) µA and 5.50 (0.060) µA, for Ni and Co respectively. Which gave percentage residual standard deviations of 5.28% for Ni and 4.47% for Co, indicating the reproducibility of the Ni and Co peaks were acceptable. The instrument detection limit (DL) was defied as three times the baseline noise, whilst the practical quantification limit (PQL) was defined as 10 times the standard deviation. The baseline noise was found to be 0.65 μ A, giving a DL of 0.13 μ gL⁻¹Ni and 0.06 μ gL⁻¹Co, and a PQL of 0.53 μ gL⁻¹Ni and 0.22 μ gL⁻¹ Co (Fig. 10). These PQL's and linear working ranges are of practical significance for this application, since using a one in ten sample dilution would allow



Fig. 8 Linear working ranges for Ni (circle) and Co (dot) in 0.20 molL⁻¹ NH₄⁺ with 0.75 mmolL⁻¹ DMG (pH 9.35). Deposition time = 60 s, sweep rate = 100 mVs⁻¹, pulse amplitude = 50 mV and deposition voltage = -700 mV.Co(μ A) = 4.511[Co]+1.7217 and Ni(μ A) = 1.5645[Ni]+0.9711.



Fig. 9 Voltammetric waves of the linear working ranges for Ni (-1.05 V) and Co (-1.15 V) in 0.20 molL⁻¹ NH_4^+ with 0.75 mmolL⁻¹ DMG (pH 9.35). Deposition time = 60 s, sweep rate = 100 mVs⁻¹, pulse amplitude = 50 mV and deposition voltage = -700 mV.



Fig. 10 Voltammetric wave for 1.0 μ gL⁻¹ Ni (-1.05 V) and 0.5 μ gL⁻¹ Co (-1.15 V) in 0.20 molL⁻¹ NH₄⁺ with 0.75 mmolL⁻¹ DMG (pH 9.35). Deposition time = 60s, sweep rate = 100 mVs⁻¹, pulse amplitude = 50 mV and deposition voltage = -700 mV.

samples with 5.3 to 90 μ gL⁻¹ Ni and 2.2 to 50 μ gL⁻¹ Co to be quantified simultaneously. Both these ranges are acceptable, compared to the 100 μ gL⁻¹ Ni and 20 μ gL⁻¹ Co ranges proposed in the Introduction.

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3.5 Analysis of Urine Samples

To demonstrate that the Ni/Co methods developed here were suitable for the analysis of urine samples, the procedures were applied to a Ni/Co standard, certified urine standard and spiked urine sample. Analysis of the standards and spiked sample returned acceptable percentage recoveries for both Ni and Co, 94.9 to 102% (Table 1). Whilst 99% confidence intervals calculated from triplicate analysis revealed that the precision of these measurements ranged between $\pm 2.00\%$ to 25.1% (Table 1). Although the precision of the measurements is not as high as could be desired, these results are promising and indicate the voltametric and sample digestion procedures developed here are capable of measuring Ni and Co in urine and may be appropriate for the monitoring of on-site exposer to Ni and Co in mine/refinery employees.

The procedures developed here will now be trialled at an undisclosed Ni Co mine and refinery. If these trials prove successful then the onsite voltametric analysis of urine samples for Ni and Co will offer a substantial improvement in analytical turnaround time; approximately 2 hours compared to up to several weeks.

This paper also demonstrates that the sensitivity of Ni and Co using the BiFESW-AdCSV procedure with DMG as the ligand can be altered by adjusting DMG concentration. This can be used to tailor sensitivity of Ni and Co to suit individual applications.

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References

D. G. Barceloux, Nickel, *Clinical Toxicology* 37 (1999)
 (2) 239-258.

- [2] D. G. Barceloux, Cobalt, *Clinical Toxicology* 37 (1999)
 (2) 201-216.
- [3] BHP Billiton, BHP billiton sustain-ability report full report 2006, BHP Billiton, Perth, 2006.
- [4] K. Kozlowska, Z. Polkowska, A. Przyjazny and J. Namiesnik, Analytical procedures used in examining human urine samples, *J. Polish Journal of Environmental Studies* 12 (2003) (5) 503-521.
- [5] M. Wajrak and P. McCafferty, Utilisation and validation of a rapid, on-site capability for metal analysis, *Proceedings from Ozwater'09, Australia's National Water Conference and Exhibition*, Ar-tarmon, NSW, 2009.
- [6] G. M. S. Alves, J. M. C. S. Magalhaes and H. M. V. M. Soares, Simultaneous determination of nickel and cobalt using a solid bismuth vibrating electrode by adsorptive cathodic stripping voltammetry, *Electronalysis* 25 (2013) (5) 1247-1255.
- [7] E. A. Hutton, B. Ogorevc, S. B. Hoevar and M. R. Smyth, Bismuth film micro electrode for direct voltammetric measurement of trace cobalt and nickel in some simulated and real body fluid samples, *Analytica Chimica Acta* 557 (2006) (1-2) 57-63.
- [8] M. Morfobos, A. Economou and A. Voulgaropoulos, Simultaneous determination of nickel(II) and cobalt(II) by square wave adsorptive stripping voltammetry on a rotating-dics bismuth-film electrode, *Analytica Chimica Acta* 519 (2004) (1) 57-64.
- [9] A. Mardegan, S. Dal Borgo, P. Scopece, L. M. Moretto, S. B. Hocevar and P. Ugo, Simultaneous adsorptive cathodic stripping voltammetric determination of nickel(II) and cobalt(II) at an in situ bismuth-modified gold electrode., *Electroanalysis* 25 (2013) (11) 2471-2479.
- [10] C. Horng, P. Horng, J. Hsu and J. Tsai, Simultaneous determination of urinary cadmium, cobalt, lead and nickel concentrations in steel reduction workers by differential pulse stripping voltammetry, *Archives of Environmental Health: An International Journal* 8 (2003) (2) 104-110.
- [11] Z. Yang, X. Hou and B. T. Jones, Determination of platinum in clinical samples, *Applied Spectroscopy Reviews* 37 (2002) (1) 57-88.
- [12] N. B. Ivanenko, A. A. Ganeev, N. D. Solovyev and L. N. Moskvin, Determination of trace elements in biological fluids, *Journal of Analytical Chemistry* 66 (2011) (9) 900-915.
- [13] R. Schierl, H. G. Fries, C. van de Weyer and G. Fruhmann, Urinary excretion of platinum from platinum industry workers, *Occupational & Environmental Medicine* 55 (1998) (2) 138-140.