



# Low-cost reusable sensor for cobalt and nickel detection in aerosols using adsorptive cathodic square-wave stripping voltammetry



Jaruwan Mettakoonpitak<sup>a</sup>, Dan Miller-Lionberg<sup>b</sup>, Thomas Reilly<sup>b</sup>, John Volckens<sup>c</sup>, Charles S. Henry<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Colorado State University, Fort Collins, CO 80523, USA

<sup>b</sup> Access Sensor Technologies LLC, 430 N College Ave St. 410, Fort Collins, CO 80524, USA

<sup>c</sup> Department of Mechanical Engineering, Colorado State University, Fort Collins, CO 80523, USA

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## ABSTRACT

A low-cost electrochemical sensor with Nafion/Bi modification using adsorptive stripping voltammetry for Co and Ni determination in airborne particulate matter and welding fume samples is described. Carbon stencil-printed electrodes (CSPEs) manufactured on low-cost PET films were utilized. Dimethylglyoxime (DMG) was used as a Co(II) and Ni(II) chelator with selective chemical precipitation for trace electrochemical analysis. Electrochemical studies of the Nafion/Bi-modified CSPE indicated a diffusion-controlled redox reaction for Co and Ni measurements. The Nafion coating decreased the background current and enhanced the measured peak current. Repeatability tests based on changes in percent relative standard deviation (RSD) of peak current showed the electrode could be used at least 15 times before the RSD exceeded 15% (the reported value of acceptable repeatability from Association of Official Analytical Chemists (AOAC)) due to deterioration of electrode surface. Limits of detection were  $1 \mu\text{g L}^{-1}$  and  $5 \mu\text{g L}^{-1}$  for Co and Ni, respectively, which were comparable to electrochemical sensors requiring more complicated modification procedures. The sensor produced a working range of 1–250 and 5–175  $\mu\text{g L}^{-1}$  for Co and Ni, respectively. Interference studies showed no other metal species interfered with Co and Ni measurements using the optimized conditions. Finally, the developed sensors were applied for Co and Ni determination in aerosol samples generated from Co rods and a certified welding-fume reference material, respectively. Validation with ICP-MS showed no statistically different results with 95% confidence between sensor and the ICP methods.

## 1. Introduction

Co and Ni exposure are detrimental to human health depending on the magnitude and duration of exposure [1–7]. Occupational exposure to Co has been linked to a variety of respiratory tract and skin disorders such as skin lesions from allergy, inflammation of nasopharynx, and bronchial asthma [4]. Mortality from Co exposure can also occur when individuals reach to the final stage at which *cor pulmonale* and cardiorespiratory failure take place [4]. Long-term exposure to Ni has been associated with incidence of nasal cancer [8]. High occupational exposure of Co and Ni occurs primarily in industrial settings [9]. The amount of Co found in industrial areas can exceed  $10 \text{ ng m}^{-3}$ , which is substantially higher than in remote areas ( $1 \times 10^{-4} \text{ ng m}^{-3}$ ) [10]. Similarly, Ni can be released from a variety of industrial processes such as welding (e.g., from stainless steel), leading to high occupational exposures [3,11]. Therefore, measurement of Co and Ni in aerosols is important for understanding Co and Ni exposure.

Conventional measurements of Co and Ni measurements are performed using spectrophotometry coupled with flow injection analysis [12], atomic absorption spectrometry [13], X-ray fluorescence spectrometry [14], and inductively coupled plasma spectroscopy [15]. These traditional methods require expensive and/or complicated equipment and long, laboratory-based analysis. Several fast, low-cost sensors have been proposed for metal detection [16–21]. Recently, we have achieved colorimetric detection for Ni in particulate matter (PM) with microfluidic paper-based analytical devices ( $\mu\text{PADs}$ ) [18,22,23]. Here, we describe a low-cost electrochemical sensor (less than \$0.1) for Co and Ni with improved sensitivity and selectivity [16,17,24,25]. Several other reports utilized Hg thin film electrodes [26,27] or cation exchanger-modified electrodes [28] for detecting Co and Ni, but these electrodes require relatively complicated preparation procedures. Bi was also introduced to avoid the use of Hg while providing analogous analytical capability of forming metal amalgams to generate well-defined peaks and reproducible stripping signals [29–31]. For trace Co(II)

\* Corresponding author.

E-mail address: [chuck.henry@colostate.edu](mailto:chuck.henry@colostate.edu) (C.S. Henry).

and Ni(II) analysis, dimethylglyoxime (DMG) has been used as a chelator to selectively complex Co(II) and Ni(II) before detecting these complexes with adsorptive stripping voltammetry that could adsorptively accumulate sub-ppb level of complexes on the working electrode [32–34].

Here, carbon stencil-printed electrodes (CSPEs) were modified with bismuth, fabricated on polyethylene transparency (PET) sheets, and used to detect Co and Ni in particulate matter and welding fume. In the proposed method, DMG was employed as a chelating agent for complexing with Co and Ni and the complexes were detected by adsorptive cathodic stripping voltammetry. The ability of Bi-modified CSPE (BiCSPEs) to analyze Co(II)DMG and Ni(II)DMG was compared with that of unmodified CSPEs. Electrochemical characterization indicated a diffusion-controlled redox reaction for Co and Ni complexes. Nafion coating of the electrode surface enhanced peak current and lowered background current, improving the detection limit. Sensor precision was within the Association of Official Analytical Chemists (AOAC) relative standard deviation (RSD) limit of 15% [35]. Common metals that might interfere with Co and Ni measurements were analyzed and none of them showed significant interference. Finally, Nafion/BiCSPEs were applied for Co and Ni detection in aerosols and welding fume samples. Samples were validated with inductively coupled plasma mass spectrometry (ICP-MS) and the techniques provided statistically similar results. This work demonstrates the development of a low-cost, portable, and disposable sensor for Co and Ni with detection limits at ppb levels.

## 2. Experimental

### 2.1. Materials and methods

Zinc(II) nitrate, chromium(III) chloride, cobalt(II) chloride, aluminum sulfate, bismuth(III) oxide, sodium dodecyl sulfate (SDS), sodium acetate trihydrate, and trimethylsilylated Nafion® were purchased from Sigma–Aldrich (St. Louis, MO). Potassium dichromate, iron(II) sulfate, iron(III) nitrate, manganese(II) chloride tetrahydrate, sodium nitrate, potassium nitrate, calcium nitrate tetrahydrate, hydrochloric acid, and ammonium chloride were purchased from Fisher Scientific (Waltham, MA). Copper(II) nitrate, ammonium hydroxide, sodium bicarbonate, and nitric acid were purchased from Mallinckrodt (St. Louis, MO). Nickel(II) sulfate hexahydrate was purchased from Acros (Morris, NJ). Dimethylglyoxime was purchased from Fluka (St. Louis, MO). Glacial acetic acid was purchased from EMD Millipore (Billerica, MA). Certified welding fume reference materials (SSWF-1 and MSWF-1) were obtained from Health & Safety Laboratory (Buxton, Derbyshire, UK). Milli-Q water from Millipore ( $R \geq 18.2 \text{ M}\Omega \text{ cm}$ ) was used for all experiments. All chemicals were used as received without further purification. Carbon Ink purchased from Ercon (Wareham, MA), graphite powder (diameter  $< 20 \mu\text{m}$ , Sigma–Aldrich, St. Louis, MO), and transparency film PP2200 (3M, St. Paul, MN) were used for electrode fabrication. A 30 W Epilog Zing Laser Cutter and Engraver (Golden, CO) was used to create electrode patterns on a transparency sheet using Corel Draw X4 program for stencil printing. A CHI1242B potentiostat (CH Instruments) was used for all electrochemical measurements. Electrodes were imaged using a JSM-6500F scanning electron microscope (JEOL USA Inc., Peabody, MA).

### 2.2. Fabrication of CSPEs

CSPEs were prepared as previously described [36–38]. Home-made electrode inks were created by adding 0.43 g graphite to 1.00 g of the commercial carbon ink followed by hand mixing until homogeneous. All of the working, counter, and reference electrodes were stencil printed on a PET sheet through a laser-cut stencil. The circle-shape working electrode had 3 mm diameter. After printing, the electrodes were dried at 65 °C for 1 h. A laser-cut, ring-shaped piece of adhesive

tape was used for confining the solution droplet to the electrodes (Fig. S1a). A photograph of a representative CSPE is shown in Fig. S1b.

### 2.3. Electrode modification

Electrode modification of Nafion/Bi CSPE was accomplished by dropcasting 1  $\mu\text{L}$  of 0.5% Nafion dissolved in 50% v/v isopropanol/water onto the CSPE working electrode and allowing it to dry. 50  $\mu\text{L}$  of 10  $\text{mg mL}^{-1}$   $\text{Bi}_2\text{O}_3$  in 0.1 M acetate buffer pH 4.5 was electroplated on the CSPE surface using an optimum deposition potential of  $-1.4 \text{ V}$  vs. carbon pseudo-reference electrode and deposition time of 20 min. After Bi modification, the CSPE was rinsed with 0.01 M ammonium buffer pH 9.0 prior to use.

### 2.4. Electrochemical measurements

Cyclic voltammetry (CV) of 50  $\mu\text{g L}^{-1}$  Co(II) and Ni(II) in 0.01 M ammonium buffer pH 9.0 (used as supporting electrolyte) containing  $2 \times 10^{-4} \text{ M}$  DMG was performed using Nafion-modified BiCSPE (Nafion/BiCSPE). The potential was swept from  $-0.85$  to  $-1.30 \text{ V}$  versus a carbon pseudo-reference electrode with scan rates of 40–90  $\text{mV s}^{-1}$ . Square-wave cathodic stripping voltammetry (SWCSV) was carried out by pipetting 50.0  $\mu\text{L}$  of standard Co(II) and Ni(II) in 0.01 M ammonium buffer pH 9.0 containing  $2 \times 10^{-4} \text{ M}$  DMG onto the electrode. An optimum deposition potential was  $-0.85 \text{ V}$  and the deposition time was varied from 15 s to 240 s as indicated in experimental details below. SWCSV was performed after a 10-s equilibration time from  $-0.9$  to  $-1.5 \text{ V}$ , and with an optimized step potential of 2 mV, amplitude of 25 mV, and frequency of 60 Hz.

### 2.5. Interference study

An interference study was performed using Cr(III), Cr(VI), Fe(II), Fe(III), Mn(II), Zn(II), Cu(II), Na(I), K(I), Ca(II), and Al(III) and the target metals, Co(II) and Ni(II). The mass ratios between the interfering metals and the target analytes were varied to determine tolerance ratios for potential interfering species. The tolerance ratio is defined as the mass ratio that creates a change in peak current of  $\pm 5\%$  [39].

### 2.6. Sample collection and sample preparation

Cobalt aerosol was generated from a cobalt rod (ESPI Metals, Ashland, OR) using an arc-discharge generator with ultra-pure nitrogen as the flow. Aerosol was collected on 37-mm MCE filters (SKC Limited, Dorset, UK). The mass of the Co aerosol samples is shown in Table S1. A 5-mm diameter punch was removed from the 37-mm diameter filter for CSPE analysis. Before quantifying Co(II), punches were digested using a modification to a previously published procedure [22]. The digestion was performed by adding 8  $\mu\text{L}$  of 5% w/v SDS in Milli-Q water to aid in filter wetting and 2  $\mu\text{L}$  of concentrated nitric acid onto the 5-mm diameter punch. The punch was then placed in a microwave on high power for 15 s and repeated twice (i.e., a total of three heated digestions for 45 s total). A 15  $\mu\text{L}$  aliquot of 5% SDS was added to the punch between each heating step. Each punch was then neutralized with 2 M  $\text{Na}_2\text{CO}_3$  after the last digestion step. Verification that the punch was neutralized was performed with pH paper. A 50  $\mu\text{L}$  of 0.01 M ammonium buffer pH 9.0 containing  $2 \times 10^{-4} \text{ M}$  DMG was used to elute metals from the digested filter and the digestion container. 50  $\mu\text{L}$  of the eluent was analyzed for Co(II) using the optimal settings described above from three punches of each sample filter to create replicate measurements.

Welding fume reference materials (SSWF-1 and MSWF-1) (the preparation was described in HSL report AS/2012/12 [40]) were digested using aqua regia (3:1 of hydrochloric acid: nitric acid). The sample masses and volumes of aqua regia solution, water, and 2 M sodium bicarbonate (for neutralization) used are shown in Table S2.

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