Low-Cost Reusable Sensor for Cobalt and Nickel Detection in Aerosols Using Adsorptive Cathodic Square-Wave Stripping Voltammetry

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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 μg L^{-1} and 5 μg 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 μg 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.

Highlights

Carbon stencil-printed electrode; Bi modified electrode; Co and Ni detection; Aerosol analysis; Adsorptive cathodic square-wave stripping voltammetry

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 ng m^{-3}, which is substantially higher than in remote areas (1×10^{-4} 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 (µPADs) [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) 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 18.2 MΩ 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 μm, 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 (Figure S1a). A photograph of a representative CSPE is shown in Figure S1b.

2.3 Electrode Modification

Electrode modification of Nafion/Bi CSPE was accomplished by dropcasting 1 μL of 0.5% Nafion dissolved in 50% v/v isopropanol/water onto the CSPE working electrode and allowing it to dry. 50 μL of 10 mg mL^{-1} Bi_2O_3 in 0.1 M acetate buffer pH 4.5 was electroplated on the CSPE surface using an optimum deposition potential of −1.4 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 µg L^{-1} Co(II) and Ni(II) in 0.01 M ammonium buffer pH 9.0 (used as supporting electrolyte) containing 2×10^{-4} M DMG was performed using Nafion-modified BiCSPE (Nafion/BiCSPE). The potential was swept from −0.85 to −1.30 V versus a carbon pseudo-reference electrode with scan rates of 40–90 mV s^{-1}. Square-wave cathodic stripping voltammetry (SWCSV) was carried out by pipetting 50.0 µL of standard Co(II) and Ni(II) in 0.01 M ammonium buffer pH 9.0 containing 2×10^{-4} M DMG onto the electrode. An optimum deposition potential was −0.85 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 V, and with an optimized step potential of 2 mV, amplitude of 25 mV, and frequency of 60 Hz.

2.4 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 ±5% [39].

2.5 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 µL of 5% w/v SDS in Milli-Q water to aid in filter wetting and 2 µL 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 µL aliquot of 5% SDS was added to the punch between each heating step. Each punch was then neutralized with 2 M Na$_2$CO$_3$ after the last digestion step. Verification that the punch was neutralized was performed with pH paper. A 50 µL of 0.01 M ammonium buffer pH 9.0 containing 2×10^{-4} M DMG was used to elute metals from the digested filter and the digestion container. 50 µL 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.

3. Results and Discussion

3.1 Co and Ni determinations using unmodified and Bi modified CSPEs

The analytical behavior of BiCSPEs for measuring Ni(II) and Co(II) DMG complexes was compared to that of the unmodified CSPEs. Ammonium buffer at pH 9.0 was used in this work because it was previously reported to provide a wide potential window for Bi thin-film electrodes generated by electroplating [31]. Figure 1a shows a cathodic peak current (23.0 ± 1.1 μA) at −1.16 ± 0.05 V (vs C pseudo-reference) by reducing Co(II)DMG with a BiCSPE; alternatively, no measurable peak is produced under these conditions with an unmodified CSPE. For detecting Ni(II)DMG with a BiCSPE (Figure 1b), the cathodic peak current (12.7 ± 0.8 μA) occurs at −1.07 ± 0.04 V and the peak is not present when using unmodified CSPE. These results demonstrate that BiCSPE can detect Co(II) and Ni(II) when these metals are complexed with DMG.

3.2 Electrochemical Characterization

The mass transfer process of Co(II) and Ni(II) to BiCSPEs was studied as shown in Figure 2. In a diffusion-controlled electrochemical redox reaction, the peak current (i_p) shows a linear relationship with the square root of the scan rate as described by the Randles-Sevcik equation [41]:

$$i_p = (2.69 \times 10^5)\, n^{3/2} A D_0^{1/2} C \upsilon^{1/2},$$

where n is the number of electrons transferred in the redox reaction, A is the effective electrode area in cm^2, D is the diffusion coefficient in $cm^2\ s^{-1}$, C is theconcentration in mol cm^{-3} and υ is the scan rate of the cyclic voltammogram in $V\ s^{-1}$. Figure 2 shows cyclic voltammograms at various scan rates of Co(II)DMG complex (Figure 2a) and Ni(II)DMG complex (Figure 2c). The peak currents (i_p) at various square roots of scan rate of Co(II)DMG and Ni(II)DMG complexes detection are shown in Figures 2b and 2d, respectively. The peak current increases linearly with the square root of the scan rate for both complexes, suggesting that the mass transfer process is diffusion-controlled. Moreover, the adsorption of Co(II)DMG and Ni(II)DMG existed on BiCSPE that was observed from the linear relationship between peak currents and scan rates as shown in Figure S2a and S2b. However, the correlation coefficients (R^2) of the linear fit from diffusion controlled process ($R^2 = 0.994$ for Co and 0.965 for Ni) were better than those from the adsorption process ($R^2 = 0.982$ for Co and 0.943 for Ni). Therefore, the mass transfer process for Co and Ni was predominantly controlled by the diffusion process. Additionally, cyclic voltammograms of both Co(II)DMG (Figure 2a) and Ni(II)DMG (Figure 2c) show one peak during cathodic scan and no peak during anodic scan, indicating the reduction of the complexes is irreversible. The peak potential appears to shift with increasing scan rate caused by the decrease of electron transfer rate constant [42]. In addition, a CV was recorded in 0.1 M ammonium buffer pH 9.0 containing 2×10^{-4} M DMG (Figure S3) demonstrated that the appearance of the slopped background in the cyclic voltammograms of Co(II)DMG and Ni(II)DMG was due to the onset of oxygen reduction at −1.25 V [43].

3.3 Effect of Nafion coating and Bi electroplating time

Nafion was utilized to enhance detection current. Nafion, as a cation exchange polymer, is insoluble in water, electrochemically inert, and non-electroactive making it suitable for electrode modification [44]. The sulfonate group in Nafion allows selective preconcentration of cations resulting in improved detection performance [45]. Figure 3 shows coating Nafion onto CSPE before Bi-electroplating increased the peak current of Co(II)DMG to 12.2 μA from 4.8 μA without Nafion coating.

We also investigated the influence of electrochemical deposition time for electroplating Bi on CSPEs for Co(II) and Ni(II) detection (Figure 3b). As expected, when increasing the deposition time, the current density (defined as the ratio of peak current [μA] to area of the working electrode [28.3 mm^2]) for both Co(II)DMG and Ni(II)DMG increases until reaching a plateau at 20 min. Therefore, 20 min was chosen as an optimum time for electroplating Bi on CSPEs.

3.4 Repeatability of Nafion/BiCSPE for Co(II) and Ni(II) detections

After optimizing the detection conditions of Nafion/BiCSPE, the electrode lifetime was tested by determining how many runs could be performed with a single low-cost electrode system. Repeated runs using the same electrode for standard Co and Ni measurements were performed as shown in Figure 4. Three separate Nafion/BiCSPE electrodes were used to determine repeatability for each metal (labelled in different colors in Figure 4). The peak currents were stable for 15 runs as shown in Figure 4a (Co(II)) and Figure 4b (Ni(II)). The %RSDs (7.3 ± 0.5 % for Co(II) and 9.1 ± 0.6 % for Ni(II)) of 15 runs for Co(II) are less than the reported value from AOAC (for the detection in μg L^{-1} level) (15%) on three separated Nafion/BiCSPEs [35]. The results indicate that Nafion/BiCSPEs can be used for up to 15 times. No attempt was made to extend the system beyond 15 runs given the low-cost of the electrodes. For Ni(II) detection (Figure 4b), the modified electrodes also provided acceptable repeatability with %RSDs of 15 runs <15%. However, %RSDs of Nafion/BiCSPEs at run 12 to 15 for Ni(II) detection increased slightly, which is different from Co(II) detection where %RSDs maintained stable for 15 runs. We hypothesized that the deposition time of each metal caused a change in the surface morphology leading to smaller peak currents. This assumption was verified by imaging the surface of the Nafion/BiCSPE with scanning electron microscopy (Figure 5). When comparing the surface after measuring Co(II) (Figure 5c) and Ni(II) (Figure 5d), Nafion (represented as the bright flat sheets) and Bi (represented as the small crystals) were more deteriorated relative to those on the surface of the unused CSPE (Figure 5b). Moreover, as hypothesized, the electrode morphology when detecting Ni(II) with 45 s deposition time (Figure 5d) changed more than that for the Co(II) measurement that required a 15 s deposition time (Figure 5c).

3.5 Electrochemical measurement of Co(II) and Ni(II)

The linear working ranges for measuring Co(II) and Ni(II) at Nafion/BiCSPE are shown in Figure 6. The decrease of current density at high concentration of Ni(II)DMG (200 μg L^{-1}) in Figure 6d was caused by electrode fouling bringing about incomplete reduction of Ni(II)DMG [46]. The Bi deposition time significantly influenced the linear ranges of Co(II) and Ni(II) as shown in Table 1. The widest linear range was observed when using the

deposition time of 15 s and 45 s for Co(II) (20–250 μg L^{-1}) and Ni(II) (50–175 μg L^{-1}), respectively. Longer Bi deposition time allowed detection at lower concentration ranges for Co(II) and Ni(II) (1–50 μg L^{-1} for Co(II)) and 5–50 μg L^{-1} for Ni(II)) at 240 s deposition time). Likewise, a longer deposition time provided lower LODs than a shorter deposition time. LODs for Co(II) and Ni(II) using 240 s deposition time were 1 μg L^{-1} and 5 μg L^{-1}, respectively, where LOD was defined as the concentration giving a peak height of three times the root-mean-square of the baseline noise. The LODs of Co(II) and Ni(II) detection at each deposition time are summarized in Table 1. The voltammograms and calibration curves for Co and Ni using 120 s and 240 s deposition time are shown in Figures S4 and S5, respectively.

3.6 Interference Study

As the goal of this work is to detect Ni and Co in sample matrices such as welding fume, the tolerance ratio for key interferences was determined. The tolerance ratio is defined as the mass ratio of an interfering species relative to the target metal that gives a change in peak current of ±5% [39]. The tolerance ratios between interfering species and Co(II) and Ni(II) are shown in Table 2. The results indicated that none of the tested interfering elements affected Co(II) and Ni(II) detection at a significant level except Cu(II). The tolerance ratio between Cu(II) and Ni(II) was low because DMG can also chelate with Cu(II) [47]. While there are known strategies to address Cu interferences, Cu(II) is present at very low levels in welding fume and related samples making removal of the interference unnecessary. As a result, the proposed method showed selectivity and sensitivity toward Co(II) and Ni(II) to enable analysis of aerosol samples and welding fume samples.

3.7 Co(II) and Ni(II) detections in environmental samples

Adsorptive cathodic stripping square-wave voltammetry was applied for detecting Co(II) and Ni(II) through complexing with DMG in Cobalt-generated aerosol and welding fume samples. The voltammograms for Co(II) determination are shown in Figure S6a. The amount of Co(II) measured by Nafion/BiCSPE and the validation method (ICP-MS) was summarized in Table 3. In the case of Ni(II) determination, the signal of Ni(II)DMG in welding fume reference materials (SSWF-1 and MSWF-1) is shown in Figure S6b. The amount of Ni(II) detected in SSWF-1 was 3.3 ± 0.2 %, close to the certified value (3.7%) as shown in Table 4. For MSWF-1, the amount of Ni(II) was under detection limit and corresponded to the reference data showing that the sample did not contain Ni(II). Quantitation of Co(II) and Ni(II) in different samples is summarized in Table 3 and 4, respectively. A paired Student's *t*-test was used to compare measured Co(II) values between Nafion/BiCSPE and ICP-MS. For Co, the t value (−9.00) is less than the critical t value (3.182, P=0.05) for n-1=3 degrees freedom when n = 4 implying that the null hypothesis is not rejected. Therefore, the proposed method does not provide significantly different results with 95% confidence for Co detection.

4. Conclusion

A home-made Nafion/BiCSPE was fabricated for trace Co(II) and Ni(II) determination by chelating with DMG. The proposed sensors provided LODs of 1 μg L^{-1} and 5 μg L^{-1} for

Co(II) and Ni(II), respectively. The key factor leading to improved performance was the electroplating of a thin film of Bi onto the electrode surface. Nafion coating also enhanced peak current and decreased background current. The resulting electrodes and chemistry allowed for repeated Co(II) and Ni(II) measurements up to 15 times based on changes in %RSD. Furthermore, the Nafion/BiCSPE was selective for Co(II) and Ni(II) against other possible metal interferences. Cu(II) was the only element that caused a significant change in signal but was not a problem with the target samples because of its low concentration. The resulting system was used to measure Co(II) and Ni(II) in aerosol samples and welding fume, respectively. Results from the electroanalytical system were statistically similar with the results from ICP-MS (for Co) and close to certified values (for Ni). The results show that the Nafion/BiCSPEs using adsorptive stripping voltammetry have great potential for selective and sensitive determination of Co(II) and Ni(II) in environmental applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- Low-cost, simple, and portable electrochemical sensors were proposed.

- Adsorptive cathodic stripping voltammetry of Co and Ni was carried out using Bi modified carbon stencil-printed electrodes.

- Low detection limits (1 ppb for Co and 5 ppb for Ni) were achieved with the low-cost sensors.

- High repeatable use of the electrodes (up to 15 times with no problem (%RSD < 15%)) was obtained when compared with the reported value of acceptable repeatability from Association of Official Analytical Chemists.

- The sensors were applied for Co and Ni detection in aerosols.
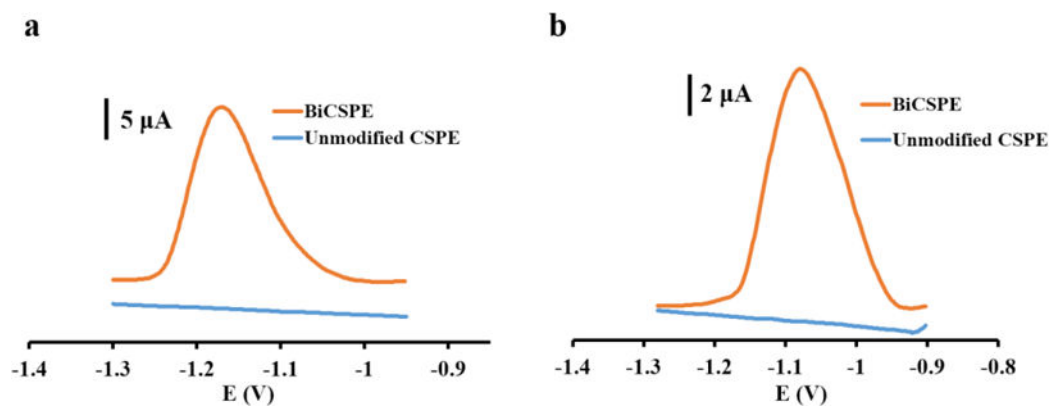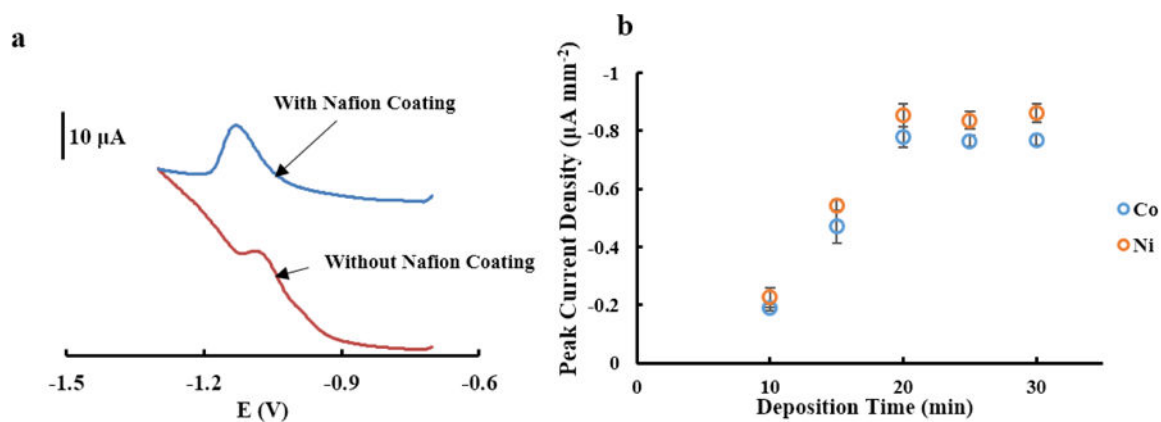
Figure 1.
(a) Square wave voltammograms of 100 μg L^{-1} Co(II)DMG complex using unmodified CSPE and Bi modified CSPE with 120 s deposition time. (b) Square wave voltammograms of 100 μg L^{-1} Ni(II)DMG complex using unmodified CSPE and Bi modified CSPE with 120 s deposition time.
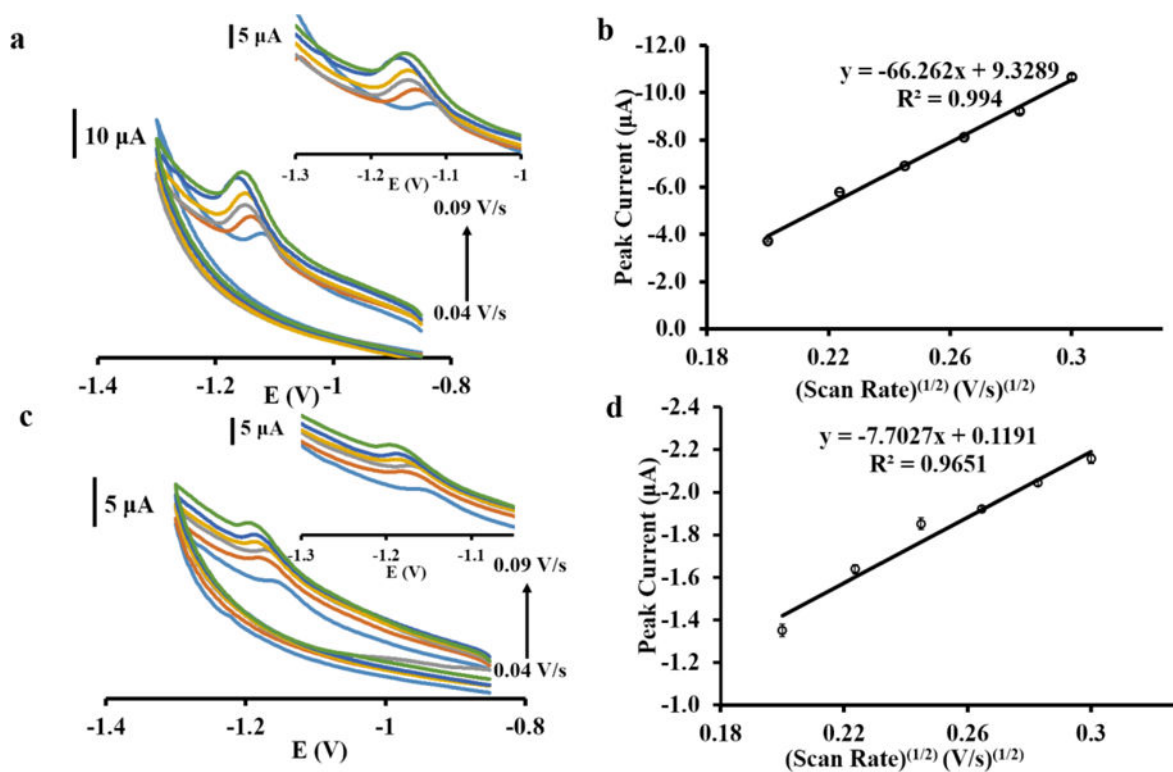
Figure 2.
(a) Cyclic voltammograms of 50 μg L^{-1} Co(II)DMG complex using Bi modified CSPE with different scan rates (40–90 mV s^{-1}). The expansion of reduction peaks of Co(II)DMG is shown in inset. (b) Relationship between peak current and square root of scan rate from (a) (n=3). (c) Cyclic voltammograms of 50 μg L^{-1} Ni(II)DMG complex using Bi modified CSPE with different scan rates (40–90 mV s^{-1}). The expansion of reduction peaks of Ni(II)DMG is shown in inset. (d) Relationship between peak current and square root of scan rate from (c) (n=3).
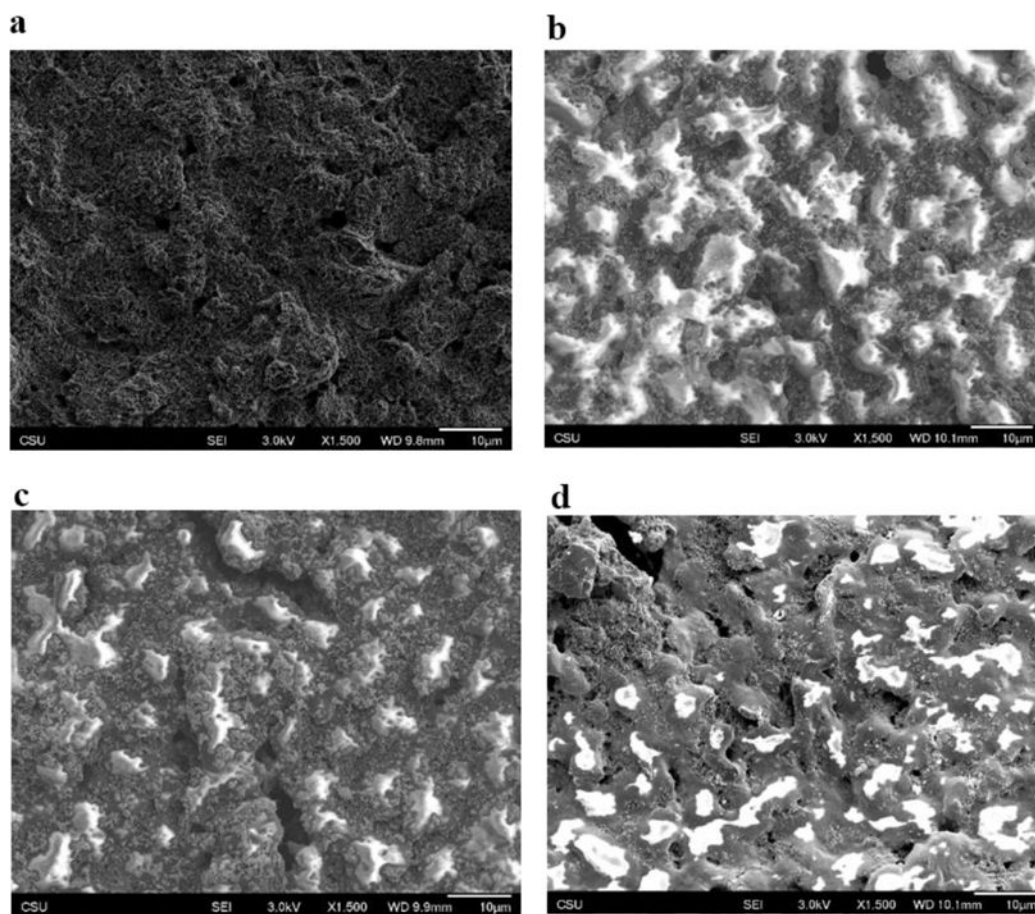
Figure 3.
(a) Square-wave voltammograms of 100 μg L^{-1} Co(II)DMG complex using Bi modified CSPE with/without Nafion coating using 120 s deposition time. (b) Representative graph for 100 μg L^{-1} Co(II)DMG and 100 μg L^{-1} Ni(II)DMG at various electrodeposition times of Bi (n=3).
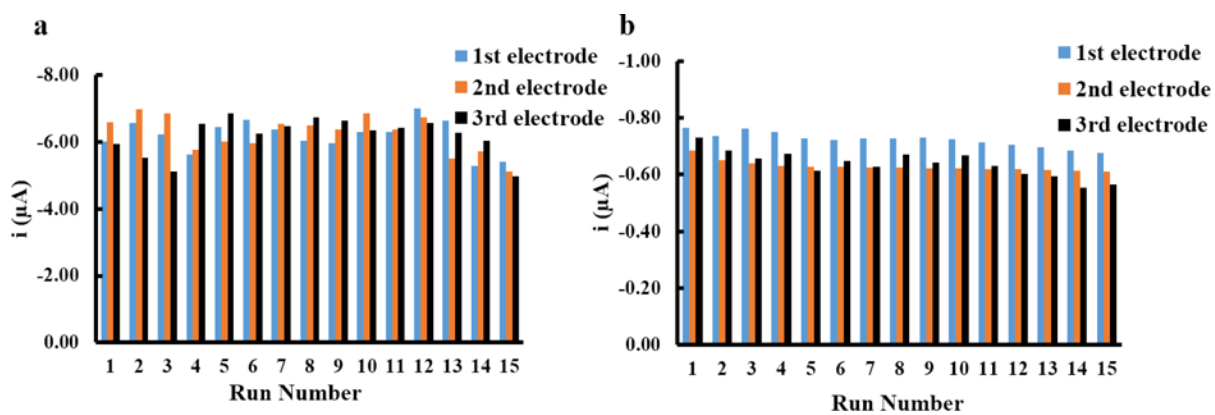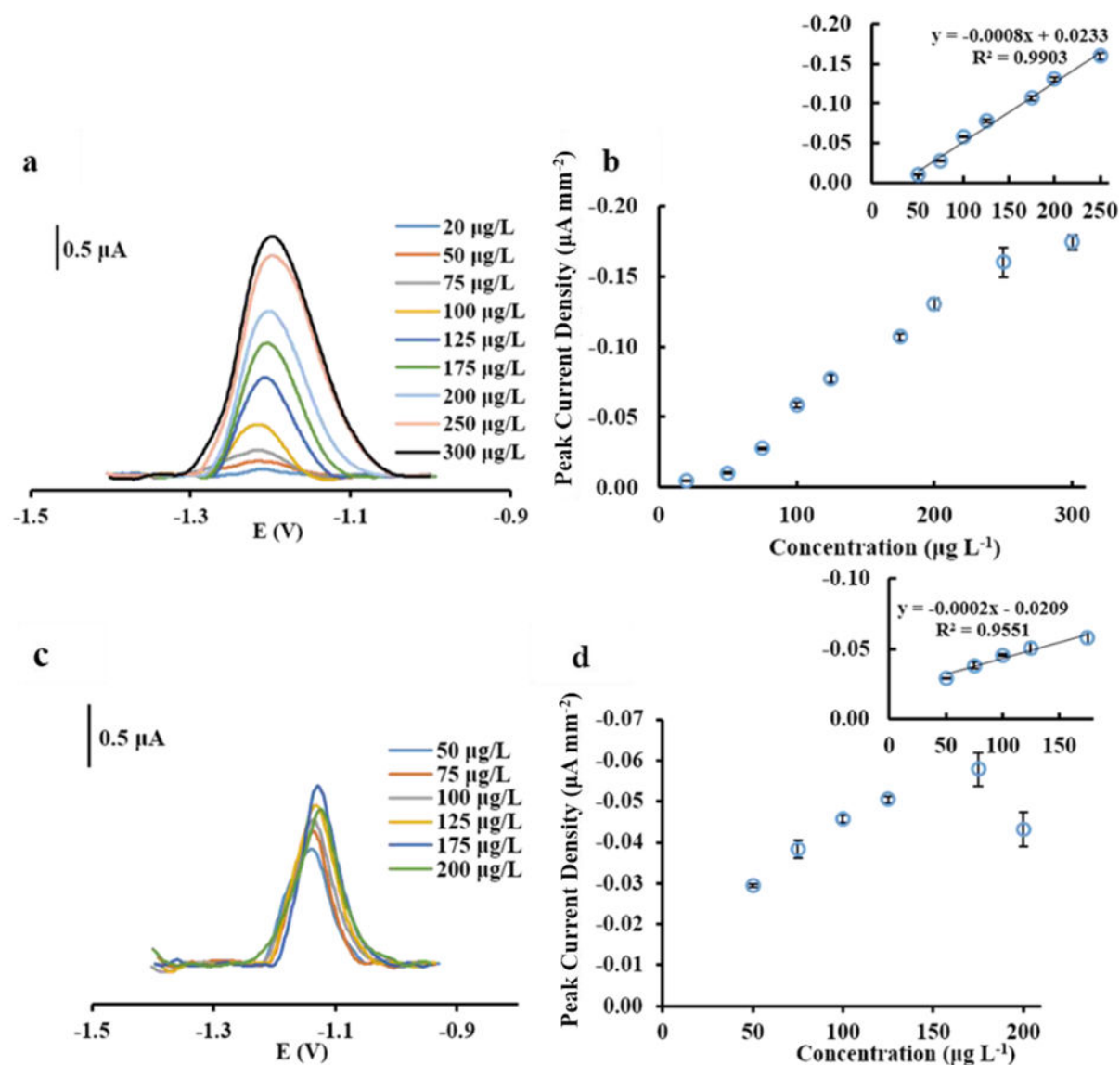
Figure 4.
(a) Repeatability of three Nafion/BiCSPEs to measure current of 50 μg L^{-1} Co(II)DMG complex using 15 s deposition time. (b) Repeatability of three electrodes to measure current of 50 μg L^{-1} Ni(II)DMG complex using 45 s deposition time.

Figure 5.
(a) SEM images of CSPE. (b) Nafion/BiCSPE. (c) Nafion/BiCSPE after 20 runs of 50 μg L^{-1} Co(II)DMG complex. (d) Nafion/BiCSPE after 20 runs of 50 μg L^{-1} Ni(II)DMG complex.

Figure 6.

(a) Square-wave voltammograms of Co(II)DMG complex from 1–100 μg L^{-1} using 15 s deposition time. (b) Representative calibration graph for Co(II)DMG complex. Linear fit of calibration graph for Co(II)DMG complex (b inset) (n=3). (c) Square-wave voltammograms of Ni(II)DMG complex from 5–100 μg L^{-1} using 45 s deposition time. (d) Representative calibration graph for Ni(II)DMG complex. Linear fit of calibration graph for Co(II)DMG complex (d inset) (n=3).

Table 1

Linearity range with various deposition times

Deposition Time (s)	Co(II) (µg L^{-1})		Ni(II) (µg L^{-1})	
	Linearity range	**LOD**	**Linearity range**	**LOD**
15	20–250	20	–	–
45	–	–	50–175	50
120	20–100	20	20–75	20
240	1–50	1	5–50	5

Table 2

Tolerance ratio of interfering ions in the electrochemical determination of 100 μg L^{-1} of Co(II)DMG complex and Ni(II)DMG complex

Interference	Tolerance Ratio for Co(II)DMG Complex	Tolerance Ratio for Ni(II)DMG Complex
Cr^{3+}	500	500
Cr^{6+}	100	100
Fe^{2+}/Fe^{3+}	500	50
Mn^{2+}	>500	50
Zn^{2+}	100	>500
Cu^{2+}	100	10
Na^+	100	500
K^+	100	100
Ca^{2+}	100	500
Al^{3+}	>500	>500

Table 3

Co(II) Determination in aerosol samples (n=3)

Sample	Concentration of Co (µg)	
	BiCSPE	**ICP-MS**
1	36 ± 1.4	41 ± 0.9
2	40 ± 1.2	43 ± 1.0
3	37 ± 1.1	42 ± 0.8
4	59 ± 1.9	64 ± 1.3

Table 4

Ni(II) Determination in welding fume samples (n=3)

Sample (Certified Reference Material)	%Ni (Experimental value)	%Ni (theoretical value)
SSWF-1	3.3±0.2	3.7
MSWF-1	below LOD	0