Notes

Simultaneous Determination of Nickel and Cobalt in Natural Water and Sediment Samples on an *in-situ* Plated Mercury Film Electrode by Adsorptive Cathodic Stripping Voltammetry

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Several voltammetric methods have been reported for the reliable determination of trace and ultra-trace concentrations of nickel and cobalt.[1-10] In particular, adsorptive cathodic stripping voltammetry, which utilizes a suitable complexing agent to enhance the electrode behavior of both metals, is considered to be one of the most sensitive methods for their determination. The range of complexing agents that has been employed for this purpose includes 2,2′-bipyridine, dimethylglyoxime, 1-(2-pyridylazo)-2,7-dihydroxy-naphthalene and noxime. Of these, the use of dimethylglyoxime (DMG) has gained wider use for the adsorptive voltammetric determination of ultra-trace concentrations of nickel and cobalt in various sample materials.

Most of the determinations of nickel and cobalt by adsorptive cathodic stripping voltammetry (AdCSV) to date has been based on the use of a hanging mercury drop electrode.[3-10] In recent years, the use of a mercury film electrode[11-14] has been reported for either individual or simultaneous determinations of nickel and cobalt. The simultaneous determination of both metals by AdCSV on a mercury film electrode was reported by Economou *et al*.[11] This method involves the use of an *ex-situ* plated mercury film for simultaneous determination of Ni and Co by square-wave adsorptive stripping voltammetry. The extra step created by the *ex-situ* plating of mercury film and other associated limitations reported in that paper has not attracted much interest in this method. However, it may be possible to attract more interest in this approach if a simpler method involving *in-situ* plating of mercury is available, as has been demonstrated by the current wide use of anodic stripping voltammetry on *in-situ* plated mercury film electrodes. Furthermore, the use of an *in-situ* plated mercury film electrode will enable simpler operation and will provide greater opportunity for automation of the technique.

In this paper, we discuss the suitability of an *in-situ*

plated mercury film on a glassy carbon electrode for the simultaneous determination of trace and ultra-trace concentrations of nickel and cobalt, investigated by AdCSV. Also, the use of a mercury-plated electrode for a reliable AdCSV determination of these metals in water and sediment samples is considered.

Experimental

Apparatus

All voltammetric measurements were performed with a MacLab potentiostat (AD Instruments Pty Ltd, NSW, Australia) connected to a two channel MacLab/2e interface and a Macintosh LC 475 computer. The MacLab EChem software (version 1.3.1) was used to record and save all voltammetric measurements. The Igor Pro spreadsheet software package was used to edit and present the collected data.

The working electrode was a 1 mm diameter glassy carbon (Cypress Systems, Inc., Lawrence, Kansas, USA) embedded in polyether ether ketone. A miniature silver–silver chloride reference electrode (Cypress Systems, Inc.) with an internal filling solution of 3 M KCl, saturated with silver chloride, was used. A platinum wire served as the auxiliary electrode and a magnetic stirrer was used for the mixing/stirring of solutions.

Reagents and samples

All reagents were of ultrapure or analytical reagent grade. All solutions were prepared with Milli-Q water. An ammonia/ammonium chloride buffer (NH_3/NH_4Cl) was prepared by mixing equal amounts of 8 M NH_3 (Fluka Chemical ultrapure) and 4 M HCl (BDH Aristar). The pH was adjusted by the addition of either NH_3 or HCl. A dimethylglyoxime (Ajax Chemicals) stock solution (0.1 M) was prepared by dissolving an appropriate amount in 100% ethanol (Ajax Chemicals). Stock solutions of 1 g/l of cobalt (May & Baker), nickel (Ajax Chemicals), zinc (Ajax Chemicals) and

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mercury (Mallinckrodt) were prepared by dissolving appropriate amounts of the chloride salts in 0.1 M HCl. The required standards were prepared daily by dilution of the stock solution with Milli-Q water.

Standard reference water (1643c) and sediment reference (Buffalo) samples were obtained from the National Institute of Standards and Technology (USA). All glassware and polyethylene bottles were soaked in a mixture of 1 M HCl and 1 M HNO$_3$. The voltammetric cell, magnetic stirrer, cell lid and cap were cleaned with Milli-Q water after use and stored in a 1 M HCl bath.

Tap water samples were collected from a laboratory tap, which was left running for more than 5 min. Swamp water samples were collected at the Penrith Campus of the University of Western Sydney Nepean and creek water samples were collected at Kingsgrove (NSW, Australia). One of the two samples collected at each site was acidified on site with 0.1 M HCl. All of the samples (filtered/unfiltered) were stored in a refrigerator until required for analysis.

Sediment samples were collected around the Mount Pipper Power Station (Cullent Bullen, NSW, Australia).

Sample digestion

The sediment samples were digested as follows. The samples were oven dried overnight at 100˚C. After cooling to room temperature, 1 g of each sample was placed in a precleaned silica crucible. The crucibles were transferred to a cool muffle furnace and a temperature ramp of 50˚C/min was applied. Heating was continued until a temperature of 250˚C was reached, which was held for 2 h. Then, the temperature was increased at the same rate to 500˚C and held at this temperature for 6 h. After this period, the sample crucibles were removed and allowed to cool. The residues in the crucibles were acidified with 5 ml 1 M HCl and then heated on a hotplate at 100˚C for 30 min to extract and dissolve the metals. The resulting sample solution was transfered to a 25 ml volumetric flask and made up to volume with 0.1 M HCl. The sample solutions were either allowed to stand overnight, to enable the residue to settle out, or filtered with a precleaned 0.45 μm membrane filter. An aliquot of each sample was taken for Ni and Co determination by AdCSV.

Adsorptive voltammetric determination

The glassy carbon electrode was cleaned and polished to a mirror-like finish with 0.05 μm alumina slurry and then inserted into a cell containing 40 μl of 1 g/l mercury solution, 10 μl of 0.1 M DMG solution, 160 μl of a 4 M ammonia buffer (pH 9.7) and 1800 μl of Milli-Q water. After the solution was deoxygenated with nitrogen for 5 min, a blanket of nitrogen was maintained over the solution. An initial *in-situ* plating of the mercury film was achieved by holding the potential at –1000 mV for 240 s. The adsorptive stripping of nickel and cobalt complexes was accomplished under the following conditions: mode, differential pulse; adsorption

potential, –700 mV *versus* Ag/AgCl (3 M KCl); adsorption time, 60 s; rest period, 15 s; scan rate, 6 mV/s; step height, 4 mV; pulse height, 50 mV. The nickel and cobalt peaks appeared at –960 mV and –1050 mV, respectively. After each measurement, the mercury film was cleaned by applying a cleaning potential of –1500 mV for 20 s to reduce or eliminate zinc interference.[11] The concentrations of both metals in each sample were quantified by use of a standard additions method. At the end of each sample analysis the mercury film was wiped off with a clean tissue.

Results and Discussion

in-situ plating of mercury

Figure 1 shows the influence of repeated measurements on the sensitivity and reproducibility of the Ni and Co peaks obtained with an *in-situ* plated Hg film. Apart from the first measurement, the peak currents remained essentially the same for the other 10 repeated measurements. The relative standard deviation for the repeat measurement was 0.13% and 0.16% for nickel and cobalt, respectively. These results demonstrate that the *in-situ* plated film can be reliably used for Ni and Co determinations by AdCSV. Although it was not necessary to apply a cleaning potential in standard solutions, this was retained to help overcome a problem that may be encountered with high Zn concentrations in sediment samples.

Figure 2 shows the influence of increasing the mercury *in-situ* plating time on the nickel and cobalt peaks. In this case, the mercury film was initially plated by applying a constant potential of –1000 mV for a specified time prior to adsorption of the complexes. The results showed that the cobalt peak increased substantially with increasing plating time, while the nickel response remained essentially the same. The observed increase in the cobalt peak current is indicative of its greater extent of adsorption on the *in-situ* plated mer-
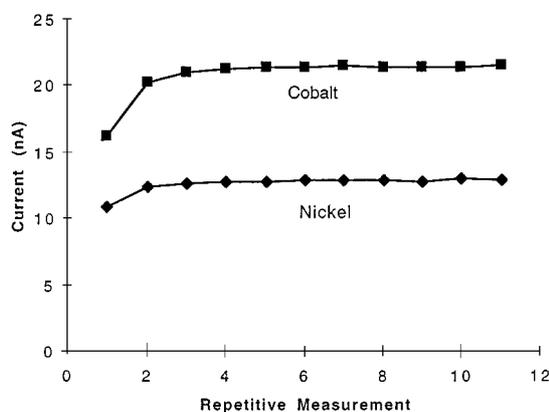
Fig. 1   Repeated measurement of nickel and cobalt by AdCSV on an *in-situ* plated Hg film electrode: 20 mg/l Hg; 5×10^{-4} M DMG; 1 μg/l Ni; 1 μg/l Co; E_{ads}, –700 mV, t_{ads}, 60 s.
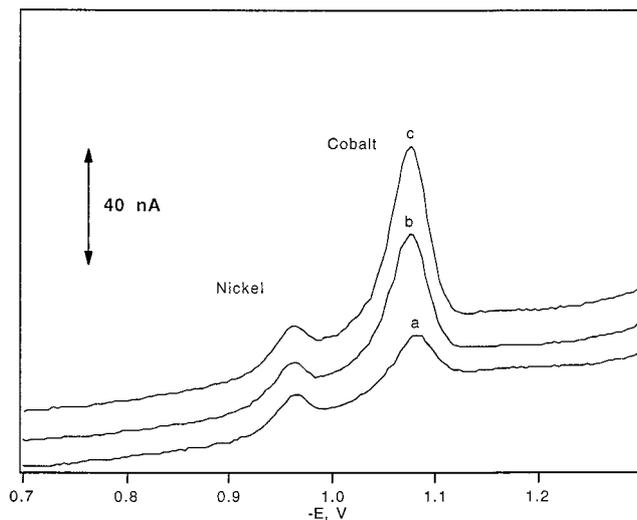
Fig. 2   Influence of the *in-situ* mercury plating time on the nickel and cobalt peaks. (a) 60 s, (b) 120 s and (c) 240 s. Other conditions are as in Fig. 1.
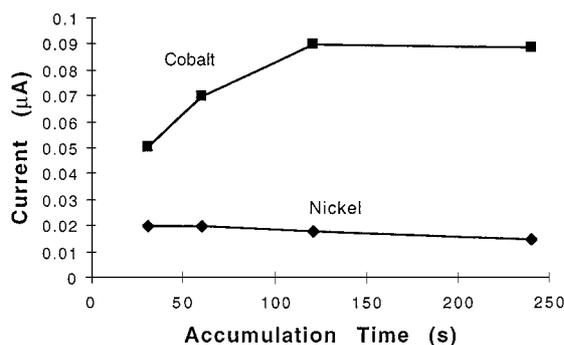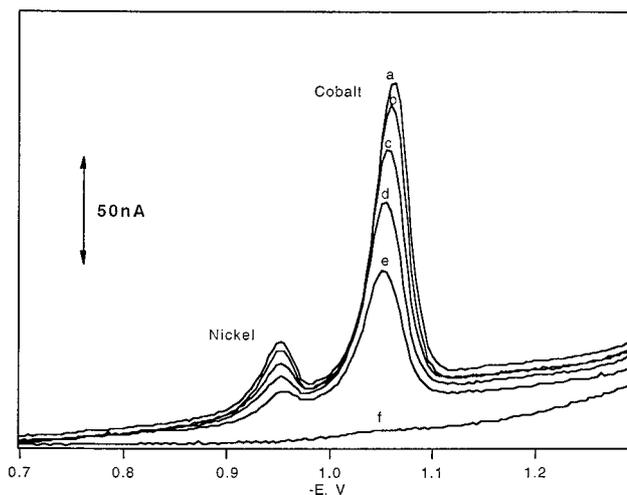

Fig. 4   Influence of Triton X-100 on the nickel and cobalt peaks. (a) 0, (b) 0.1, (c) 0.3, (d) 0.5, (e) 0.9 and (f) 2 mg/l. The other conditions are as in Fig. 1.

Fig. 3   Influence of the adsorption time on the nickel and cobalt peaks. The other conditions are as in Fig. 1.

cury film. The optimum response for cobalt was obtained with a plating time of 240 s.

The use of increasing adsorption time also had different influences on the nickel and cobalt peaks. Figure 3 shows that the cobalt response increased rapidly with increasing adsorption time up to 120 s, while the nickel peak remained unchanged. These observations again support the view that the Co-DMG complex(es) is more readily adsorb to the *in-situ* plated Hg film. It has been suggested in previous studies that the presence of a positively charged cobalt complex[15] and of a neutral nickel complex[16] may be responsible for the observed differences in the adsorption of the complexes. As expected, the use of a longer adsorption time enhances the adsorption of the positively charged DMG complex beyond that of the neutral Ni-DMG complex at the chosen negative adsorption potential. An adsorption time of 60 s was chosen for a more rapid measurement of both metals. However, longer adsorption times may be considered for natural water samples where ultra-trace concentrations of nickel and cobalt are encountered.

The other optimum conditions obtained in this study

with the *in-situ* plated mercury film for the simultaneous determination of nickel and cobalt, such as pH 9.6, 0.15 M ammonia buffer and 5×10^{-4} M DMG, were identical to those obtained previously with a HMDE.[10]

Organic and inorganic interferences

Although it has been demonstrated previously[10,14] that organic substances such as surfactants could interfere with the AdCSV responses for nickel and cobalt by competing for electrode sites on a HMDE, it was still useful to examine the extent of interference experienced with an *in-situ* plated mercury film. Figure 4 shows that as little as 100 µg/l of Triton X-100 was sufficient to cause a slight suppression of the cobalt peak obtained with the *in-situ* plated film. Complete suppression of both peaks was observed in the presence of 2 mg/l of the surface active agent. The attainment of both responses in the presence of <2 mg/l of Triton X-100 suggests that the method is only tolerant to low concentrations of dissoved organics in real samples; however, this problem can be readily overcome by ultraviolet irradiation prior to AdCSV measurements. The suppressive effect caused by the presence of residual organic substances can also, in some cases, be overcome by use of the standard additions method for quantification.

Owing to the relatively high selectivity of DMG for nickel and cobalt, little or no interference is experienced on the *in-situ* plated Hg film from inorganic substances, unless an excessively large quantity of a particular element is present. The only inorganic substance that can interfere with the cobalt response is zinc. Samples with considerably higher amounts of zinc(II) ions gave an additional peak close to that of cobalt and may, in some cases, interfere by overlapping with the cobalt peak. Figure 5 shows that the presence of 100 µg/l of zinc can be tolerated for a reliable measurement
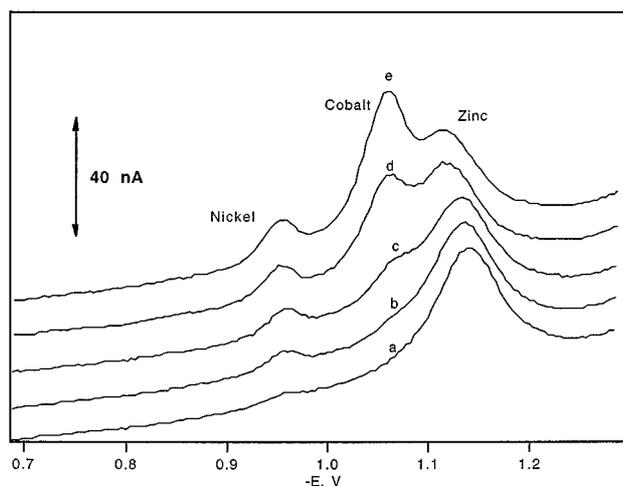
Fig. 5 Influence of zinc on nickel and cobalt peaks. The concentrations of nickel and cobalt; (a) 0.0, (b) 0.2, (c) 0.6, (d) 1.0 and (e) 1.4 μg/l. The zinc concentration in all solutions is 100 μg/l. The other conditions are as in Fig. 1.

of ⩾1 μg/l nickel and cobalt on the *in-situ* plated film. Even though the zinc peak was still evident at this concentration, the cobalt peak was well resolved from it, and could be reliably measured.

Analytical applications

The nickel and cobalt peaks obtained with an adsorption time of 60 s increased with increasing concentration from 0.1 μg/l to 13 μg/l and 0.03 μg/l to 15 μg/l, repetively. The sensitivities of nickel and cobalt peaks within these ranges were 15.5 nA/μg l^{-1} and 90.6 nA/μg l^{-1}, respectively. The sensitivities of these peaks can be improved by using a longer adsorption time. However, it was considered that the use of an adsorption time of 60 s is sufficient for reliable simultaneous determinations of nickel and cobalt in natural water and sediment samples.

The data given in Table 1 show that there is a good

agreement between the results obtained by AdCSV on the *in-situ* plated Hg film for nickel and cobalt in the reference water sample and the certified values. The reproducibility of the measurement in the water sample was also very good with 1% rsd for nickel and 0.5% rsd for cobalt. The established detection limits (based on 3 times standard deviation) obtained by this method in the reference water sample were 0.1 and 0.03 μg/l for nickel and cobalt, respectively. If required, it is possible to lower the detection limits further by use of longer adsorption times and higher purity reagents.

The results given in Table 1 also demonstrate that nickel and cobalt can be reliably determined in sediment samples by AdCSV on the *in-situ* plated film, even in the presence of a high concentration of zinc. However, it is interesting to note that the nickel concentrations found in the sediment samples were not significantly influenced by the sample dilution factor. In fact, all of the nickel concentrations obtained with the various dilution factors were within the certified value. In contrast, the cobalt concentrations found in the sediment samples were significantly affected by the dilution factor. Generally, the concentrations of cobalt found decreased with increasing dilution factor. It appears that the cobalt determination is more affected by zinc interference as its concentration in the sample is lowered. However, the concentration of cobalt found by use of a dilution factor of 100 is close to the certified value.

The data in Table 2 indicate that the nickel and cobalt concentrations found in natural water samples were significantly influenced by the extent of sample pretreatment, prior to the AdCSV measurement. The higher concentrations of these metals obtained in swamp water with acidification and ultraviolet irradiation suggests that high proportions of nickel and cobalt in the sample were present in the bound form. Evidently, the concentrations of these metals in the non-acidified swamp water represent the free forms of the metals, while those found after acidification are indicative of the sum

Table 1 Nickel and cobalt concentrations found in reference water and sediment samples

Sample	Metal	Dilution factor	Found (μg/g±s.d.)	Certified value (μg/g±s.d.)	r^2
Ref.	nickel	—	63.0±0.7	60.6±7.3	0.9878
Water[a]	cobalt		23.5±0.2	23.5±0.8	0.9961
Buffalo	nickel	100	42.6±0.9	44.1±3.0	0.9800
Sed.[b]	cobalt		15.3±0.6	14.0±0.6	1.0000
Buffalo	nickel	240	43.7±0.7	44.1±3.0	0.9911
Sed.[b]	cobalt		12.1±0.6	14.0±0.6	0.9941
Buffalo	nickel	400	45.6±0.5	44.1±3.0	0.9964
Sed.[b]	cobalt		7.0±0.3	14.0±0.6	0.9910

a. $n=4$; μg/l ± s.d.
b. $n=3$; total zinc concentration in the Buffalo sediment is 438±12 μg/g.

Table 2 Nickel and cobalt concentrations found in water samples

| Water sample	Metal	Found±s.d. (μg/l)	r^2
Tap	nickel	0.23±0.01	0.9942
(not acidified)	cobalt	Undetected	0.9942
Swamp	nickel	0.45±0.02	0.9924
(not acidified)	cobalt	0.031±0.002	0.9922
Swamp	nickel	1.10±0.05	0.9928
(acidified)	cobalt	0.19±0.01	0.9979
Swamp	nickel	3.42±0.09	0.9989
(UV treated)	cobalt	0.82±0.04	0.9904
Wolli Creek	nickel	1.67±0.03	0.9978
(acidified)	cobalt	0.098±0.004	0.9967
Wolli Creek	nickel	1.89±0.04	0.9905
(UV treated)	cobalt	0.67±0.01	0.9902

$n=4$.
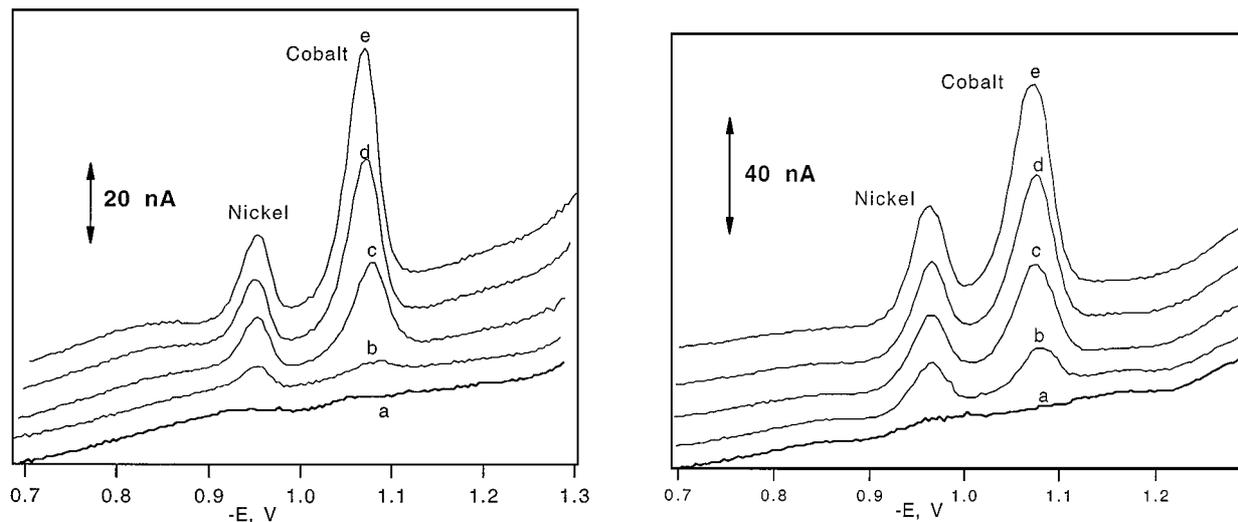
Fig. 6   Determination of nickel and cobalt in (a) non-acidified swamp water and (b) sediment sample 20F. The concentrations of Ni and Co added for water sample: (a) background response, (b) sample, (c) +100, (d) +300 and (e) +500 ng/l; concentrations of Ni and Co added for sediment: (a) background response, (b) sample, (c) +200, (d) +400 and (e) +600 ng/l. Other conditions are as in Fig. 1.

of the free and inorganic bound forms; also those obtained after ultraviolet irradiation are the total concentrations, which include the organic bound form. The relatively high concentrations found in the ultraviolet irradiated samples suggest that most of the nickel and cobalt in creek and swamp water samples were present as an organic bound form(s). Figure 6a shows typical stripping voltammograms for the quantification of both metals in a swamp water sample. Evidently, the nickel and cobalt concentrations in the water sample were readily quantified by use of the standard additions method with AdCSV on the mercury film electrode.

The nickel and cobalt concentrations in two sediment samples containing low and relatively high zinc concentrations were also successfully determined by AdCSV on the *in-situ* plated film. Figure 6b shows typical stripping voltammograms for the quantification of both metals in a sediment sample. Again, the use of standard additions method proved to be useful for the quantification of the nickel and cobalt concentrations in sediment samples by AdCSV on a mercury film electrode. The data given in Table 3 show that the results obtained for nickel and cobalt in the sediment samples by this method agreed reasonably well with those obtained by atomic absorption spectroscopy (AAS).

In conclusion, the use of an *in-situ* plated mercury film electrode enabled rapid and reliable simultaneous determinations of nickel and cobalt in natural water and sediment samples by AdCSV. The detection limits obtained by this method in water samples with an adsorption time of 60 s were 0.1 μg/l and 0.03 μg/l for nickel and cobalt, respectively. The nickel and cobalt responses increased linearly with increasing concentra-

Table 3   Comparison of nickel and cobalt concentrations found in sediment samples by AAS and AdCSV

Sediment sample	Metal	Found±s.d. (μg/g)		r_2
		AAS	AdCSV	
20F	nickel	17.7±0.7	17.6±0.4	0.9928
	cobalt	2.9±0.5	2.7±0.7	0.9901
	zinc	34±3	—	—
28F	nickel	157±2	156.0±0.8	0.9941
	cobalt	95.9±0.3	80.0±0.9	0.9958
	zinc	1033±6	—	—

n=3.

tion from 0.1 – 13 μg/l and 0.03 – 15 μg/l, respectively. The ultraviolet irradiation of water samples prior to AdCSV revealed that most of the nickel and cobalt in the creek and swamp water samples were present in the organic bound form(s). The reliability of the method for the determination of nickel and cobalt in sediment samples was not affected by the presence of high zinc concentrations. Excellent agreement was obtained for the concentrations of both metals found in the sediment samples by AdCSV and AAS.

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