

Research Article

Solar UV-Assisted Pretreatment of River Water Samples for the Voltammetric Monitoring of Nickel and Cobalt Ultratracess

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The application of solar UV radiation as sample digestion method is reported. The method is employed in adsorptive stripping voltammetric determination of nickel and cobalt in river water samples. The river water samples were collected from downstream of Warnow River (Germany) and acidified to pH of 2 ± 0.2 by addition of ultrapure 65% HNO₃. Furthermore, 3.4 mgL⁻¹ ultrapure hydrogen peroxide solution was added to the samples as photochemical reaction initiator. The samples were transferred to UV-A transparent polyethylene terephthalate bottles and put in the sunshine for UV irradiation for six and 12 hours at a UV-A intensity of 3.90 mW/m². The comparison of the concentration values showed that, 6 hours of solar UV irradiation at 3.90 mW/m² UV-A intensity is not sufficient to complete the digestion process though it yields much better results than the undigested original sample. However, 12 hours of solar UV-A irradiation under similar conditions is almost as effective as a 30 W artificial UV lamp (254 nm) and can be applied to the digestion of dissolved organic carbon in trace nickel (II) and cobalt (II) analysis in natural waters such as river water, lake waters, and well waters.

1. Introduction

The determination of trace metals in natural waters like river water is crucial especially for those metals causing health hazards and environmental effects. Metal pollutants exist bounded by organic and/or inorganic matrices in the environment and thus the determination of these metals in natural waters becomes complicated unless they are separated from the matrices by application of proper sample pretreatment methods [1]. Electrochemical methods and especially the voltammetric determination of metal ions require homogenous samples, free of organic matter which interacts with the metal ions and with the electrode material. Dissolved organic matter (DOM) may form complexes with metal ions preventing them from reduction at the working electrode or shifting the electrochemical redox potential towards negative direction. Such compounds can also affect the determination

by interacting with the electrode material forming adsorbed films or changing surface tension. Furthermore, DOM can undergo electrochemical redox reactions at the electrodes leading to increased background currents. Thus, DOM can make the voltammetric determination of trace metals impossible [2].

Methods like wet digestion and dry ashing have been employed for many decades. However, these methods involve high risk of contamination [3] that comes from impurities of the oxidizing agents like mineral acids, bisulfates, or others. These methods also require ultrapure reagents, which is relatively unaffordable by many laboratories especially in developing countries. Clean, efficient, and environmentally friendly methods like UV digestions are also in use since their introduction by Armstrong et al. in 1966 [4]. UV radiation decomposition has been described for DDT (1,1(4,4'-dichlorodiphenyl)-2,2,2-trichloroethane),

HCB (hexachlorobenzene), PCP (pentachlorophenol), TNT (1,3,5-trinitrotoluene) [5], and atrazine (a herbicide) [6] following absorption of 180–250 nm radiation.

Under the influence of UV radiation, different oxidants like singlet oxygen [7], superoxide radicals and alkylperoxy radicals [8], and hydroxyl radical and hydrogen peroxide [9] are formed. The subsequent reaction of these radicals with organic matter is one of the natural ways of biodegradation in aquatic systems [9–12]. Microwave-assisted, high-temperature UV digestion procedure was developed for the accelerated decomposition of interfering dissolved organic carbon (DOC) prior to trace element analysis of liquid samples such as industrial/municipal wastewater, groundwater, surface water, body fluids, infusions, beverages, and sewage [13]. UV digestion instruments for the UV photolysis of water samples with a low to moderate amount of organic matter were developed and commercially available for use. However, these instruments are relatively expensive which makes them difficult to be used in some laboratories.

Solar UV radiation was used in the presence of semiconductors as catalysts in photodegradation of phenol [14, 15]. We recently reported on a direct solar UV digestion method for stripping-voltammetric determination of zinc, cadmium, lead, and copper. Only small amounts of oxidant (H_2O_2) were necessary for the pre-treatment of natural water samples (river water) that contained low DOC concentrations [16]. The addition of H_2O_2 to the samples before irradiation increased the mineralization efficiency of the H_2O_2 /UV system (88% of total organic carbon (TOC) reduction) compared with a UV-Only system (28% TOC reduction) at 4 hours of irradiation [16]. Also uranium ultratracés could be detected this way [17]. Therefore, the application of solar radiation as a UV source for sample preparation helps the application to be effective in many laboratories because of its nature. The method is cheap, clean, mobile, and environmentally friendly.

Being essential elements, cobalt and nickel become toxic at higher concentration because of their interaction with biological systems [18]. Nickel, for instance, needs exhaustive ecochemical and ecotoxicological investigations on its fate and behavior in ecosystem of terrestrial and aquatic environment. It is among the toxic metals, a significant topic of environmental surveillance, food control, occupational medicine, toxicology, and hygiene [19]. Adsorptive stripping voltammetry (AdSV) for cobalt and nickel elements was an important advancement, permitting lower detection limits [20]. This involves a nonelectrolytic preconcentration step [21]. In this case [20], the accumulation of Co and Ni as dimethylglyoxime (DMG) complexes in ammoniacal buffer at the hanging mercury drop electrode (HMDE) is followed by reduction of the adsorbed complex to the zero oxidation state.

In this paper, both nickel (II) and cobalt (II) are determined in river water samples by differential pulse adsorptive stripping voltammetric (DP-AdSV) method after the samples were digested by means of solar UV (UV-A) radiation in presence of hydrogen peroxide. The effects of different UV treatment protocols are also investigated by means of pseudopolarography.

TABLE 1: Instrumental parameters for AdSV experiments.

Working electrode	SMDE
Measurement mode	DP
Purging time	600 s
Pulse amplitude	0.05 V
Deposition potential	-0.7 V
Deposition time	120 s
Equilibration time	5 s
Start potential	-0.8 V
End potential	-1.2 V
Voltage step	0.005 V
Voltage step time	0.3 s
Sweep rate	0.013 V/s

2. Experimental

2.1. Instrumentation. A μ Autolab potentiostat (Ecochemie) with General Purpose Electrochemical System (GPES) 4.9 software package was connected to a Metrohm 663 VA Stand with an electrolysis cell equipped with a three-electrode system. The latter consisted of a HMDE as working electrode, a glassy carbon counter electrode, and a Ag/AgCl (3 M KCl) reference electrode and was used for both the calibration studies and the pseudopolarographic experiments. Differential Pulse Adsorptive Stripping Voltammetric (DP-AdSV) method was used in both cases with the parameters given in Table 1.

2.2. Reagents. Ultrapure water ($>18.2\text{M}\Omega\text{cm}^{-1}$, TOC $< 2\ \mu\text{g}\text{L}^{-1}$) was produced using an Ultra Clear system by SG Water GmbH, Germany (now Evoqua Water Technologies LLC, <http://www.water.siemens.com/>), in order to prepare all solutions. All reagents were obtained from certified manufacturers (Fluka, Merck) and were delivered as analytical grade or ultrapure grade reagents (TraceSelect or Suprapur), where possible. $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer (pH = 9.5) was prepared as supporting electrolyte from ammonia solution ($w_{\text{NH}_3} = 25\%$) and hydrochloric acid ($w_{\text{HCl}} = 30\%$). $0.1\text{mol}\text{L}^{-1}$ of dimethylglyoxime (DMG) in ethanol and triethanolamine (TEA) in water (1:1) were prepared as complexing agents in AdSV measurements. Commercial $1000\text{mg}\text{L}^{-1}$ stock solutions of the metals (Ni^{2+} and Co^{2+}) were diluted as required for standard additions. 65% HNO_3 was used to acidify the water samples to $\text{pH } 2 \pm 0.2$ ($1\text{m}\text{L}\text{L}^{-1}$) and 30% H_2O_2 was added to speed up the UV photocatalytic degradation process. After the UV irradiation periods, $10\ \mu\text{L}$ of $0.1\text{mol}\text{L}^{-1}$ hydroxylammonium sulfate was added to 20 mL of each sample to remove newly formed nitrite and hypochlorite as well as any remaining H_2O_2 .

2.3. Sample Collection, Preparation, and Preservation. River water samples were collected in July 2011 based on the river water sampling protocols (EPA guidelines for regulatory monitoring and testing water and waste water). The sampling

TABLE 2: Experimental result for nickel (II) in 0 hours irradiated (*Original Sample*), 6 and 12 hours solar UV irradiated (*SoUV Sample*), and 6 hours artificial UV irradiated (*UV Sample*).

	<i>Original Sample</i> 0 hrs	Nickel <i>SoUV Sample</i>		<i>UV Sample</i> 6 hrs
		6 hrs	12 hrs	
Concentration (μgL^{-1})	1.66 ± 0.06	2.12 ± 0.10	2.62 ± 0.06	2.71 ± 0.02
Recovery rate (%)	87.80 ± 0.95	90.80 ± 0.55	95.20 ± 0.43	99.00 ± 0.42
Blank recovery rate (%)		100.48 ± 0.20		

site was located at the south bank of Unterwarnow (the estuary of Warnow River in Rostock, Germany, at $54^{\circ}05'38.12''\text{N}$, $12^{\circ}09'06.33''\text{E}$). Laboratory grade PE plastic bottles were used as sample containers after careful cleaning. The samples were acidified with ultrapure HNO_3 to adjust the pH to 2 ± 0.2 . After taking the sample to the laboratory, it was filtered through a $0.45 \mu\text{m}$ pore size cellulose acetate membrane filter inserted in a Millipore filtration glass assembly and then 3.4 mgL^{-1} H_2O_2 was added. Then, the same sample was divided into three aliquots in containers labeled as *Original Sample*, 6-hour *SoUV Sample*, 12-hour *SoUV Sample*, and *UV Sample*. We stored the *Original Sample* in a refrigerator at 4°C until determination. The two *SoUV Samples* were transferred to a carefully cleaned UV-A transparent (330–450 nm) polyethylene terephthalate (PET) bottle and exposed to solar radiation of UV-A intensity of ca. 3.6 mWcm^{-2} for 6 and 12 hours, respectively. We transferred the third aliquot designated as *UV Sample* to a UV-transparent (200–450 nm) quartz glass tube and irradiated for 6 hours by means of a 30 W artificial UV source generating a 254 nm UV radiation (low-pressure mercury-vapor lamp). The blank samples were obtained by performing the same sample pretreatment procedures from acidification with nitric acid to irradiation, though using ultrapure water instead of river water.

The solar irradiation period was chosen to be in midsummer (July 2011) between 10:00 a.m. and 4:00 p.m. to obtain maximum efficiency of solar radiation as a result of increase of latitude and the incident angle of the radiation from the sun. In addition to this, an aluminum solar collector was used to increase the solar radiation intensity. This also increased the infrared intensity of the incident radiation enhancing the synergetic effect of elevated water temperature and UV radiation [18]. All the three samples were stored in a refrigerator at 4°C until determination. Artificial river water containing 10.00 mgL^{-1} humic acid was prepared to compare and estimate the concentration of humic acid in the original Warnow River water by means of UV/Vis spectrophotometry. Humic acid is the most abundant component of dissolved organic water in natural waters such as river water.

2.4. Procedure. For each analysis, 20 mL of the river water samples was taken into the voltammetric cell. To this cell, 1 mL of ammonia buffer was added as a supporting electrolyte and to adjust the pH of the solution to 9.5. Similarly, $150 \mu\text{L}$ of 0.10 molL^{-1} of DMG in ethanol and $150.00 \mu\text{L}$ of triethanolamine (TEA) in a 1 : 1 water solution were added as a complexing agent. After deaeration by purging with nitrogen

for 600 s, the two heavy metals were analyzed simultaneously under the given operating conditions and three replicate measurements were taken for each of the four categories of sample specified in sample preparation procedure. Standard addition method was used to determine the concentrations of the metal ions in the samples. Pseudopolarographic data for nickel were taken by DP-AdSV with a HMDE as working electrode and a supporting electrolyte of $\text{NH}_3/\text{NH}_4\text{Cl}$ (pH of 9.5).

Also here three replicate measurements were performed for each metal of the four sample categories. To estimate the concentration of humic acid in the original river water sample, UV/Vis spectra were recorded for *Original Sample*, twofold diluted *Original Sample*, 6-hour and 12-hour *SoUV Samples*, and *UV Samples*. Afterwards, these spectra were compared with those of an artificial river water sample containing 10.00 mgL^{-1} humic acid.

3. Results and Discussion

3.1. Standard Addition Experiments and Recovery Rates. Figure 1 displays DP-AdSV responses of river water samples pretreated in different ways. All the data are based upon standard addition experiments. The analytical results obtained by extrapolation of the standard addition calibration curves (Figures 2 and 3) are given in Table 2.

Nickel concentrations determined in the river water increased by 28% and 58% upon irradiation with solar UV for 6 and 12 hours, respectively. Irradiation with artificial UV light for 6 hours led to a 63% increase in the detected nickel concentration.

The *Original Sample* would not show any significant increase of cobalt (II) peak current even after the addition of $3 \mu\text{gL}^{-1}$ of cobalt (II) standard solution. This reveals that DOM in the river water complexed all of the added cobalt (II) ions. For the 6- and 12-hour *SoUV Samples*, there were no significant increases in the cobalt (II) peak current after the addition of $2 \mu\text{gL}^{-1}$ of cobalt (II). This indicates that complexing organic matter was still present in the water consuming up to $2 \mu\text{gL}^{-1}$ cobalt (II); thus, the digestion process was incomplete. For the *UV Sample*, the peak current increase was significantly improved suggesting the completion of the digestion process. Here a standard addition calculation was conducted using quadratic fit. In general, 12 hours of solar UV irradiation was not enough to complete the digestion at the given solar UV intensity. This is why we observed deviation of the cobalt (II) calibration

TABLE 3: Experimental results for cobalt (II) in the 0 hours irradiated (*Original Sample*), 6 and 12 hours solar UV irradiated (*SoUV Sample*), and 6 hours artificial UV irradiated (*UV Sample*).

	Cobalt			
	Control 0 hrs	6 hrs	SoUV 12 hrs	UV 6 hrs
Concentration (μgL^{-1})	0.00	0.00	0.00	0.33 ± 0.02
Recovery rate (%)	45.00 ± 0.24	65.00 ± 0.14	72.00 ± 0.08	86.50 ± 17
Blank recovery rate (%)			102.34 ± 0.43	

TABLE 4: Determination of the recovery rate for nickel (II) in 0 hours irradiated (*Original Sample*), 6 and 12 hours solar UV irradiated (*SoUV Sample*), and 6 hours artificial UV irradiated (*UV Sample*).

Nickel	Concentration before spiking (μgL^{-1})	Spiked concentration (μgL^{-1})	Concentration after spiking (μgL^{-1})	Recovered concentration (μgL^{-1})	Recovery rate (%)
<i>Original Sample</i>	1.66	5.00	6.05	4.39	87.80
6 h <i>SoUV Sample</i>	2.12	5.00	6.66	4.54	90.80
12 h <i>SoUV Sample</i>	2.62	5.00	7.38	4.76	95.20
<i>UV Sample</i>	2.71	5.00	7.66	4.95	99.00
Blank	0.00	5.00	5.02	5.02	100.48

curve from linearity. The results also indicate that cobalt (II) could be used for titration of complexing compounds in river water. We used square functions for regression fits and to calculate the concentration of cobalt (II) for the *UV Sample*. The calculated cobalt (II) concentration in the *UV Sample* was $0.33 \mu\text{gL}^{-1}$ (Table 3). These findings indicate that more than 12 hours of solar UV irradiation is needed to complete the digestion in Central Europe, or, otherwise, more intense solar UV radiation (such as equatorial or tropical sun) would be needed for cobalt determination. Furthermore, the effects of UV irradiation were confirmed by improvements of the recovery rate (Tables 4 and 5).

We did not calculate the concentration of cobalt (II) in the *Original Samples* and the 6- and 12-hour *SoUV Samples* using calibration curves because of the substantial deviation from linearity. Instead, we calculated the percentage of DOM that had been decomposed by solar and artificial UV irradiation from the recovery experiments. The determination of recovery values for nickel was conducted using standard addition method by spiking concentrations of 5, 10, and $15 \mu\text{gL}^{-1}$ of nickel (II) following an addition of $5 \mu\text{gL}^{-1}$ nickel (II) in the very beginning right before sample pretreatment to be recovered as a known concentration value in all types of samples.

In the case of cobalt (II), we spiked $8 \mu\text{gL}^{-1}$ of the metal ions to the *Original Sample* in which only $3.60 \mu\text{gL}^{-1}$ (45.00%) was recovered, and, thus, $4.40 \mu\text{gL}^{-1}$ (55%) was complexed by natural matrix components. The standard additions in this case were 8 and $16 \mu\text{gL}^{-1}$ of cobalt (II) standard solution. The known concentration of cobalt (II) spiked to the other samples was $2 \mu\text{gL}^{-1}$. Therefore, the added standard concentrations were 2 and $4 \mu\text{gL}^{-1}$ of cobalt (II) standard solution. We used linear calibration plots in these standard additions to calculate the recovered amount of cobalt (II). The results of the recovery tests clearly showed the presence of too much DOM in the *Original Sample* (enough to complex $4.40 \mu\text{gL}^{-1}$

of added cobalt (II)) in the river water sample. In the case of the 6- and 12-hour *SoUV Samples* and the *UV Samples*, only 0.59, 0.48, and $0.27 \mu\text{gL}^{-1}$ were absorbed indicating the equivalent concentration of undigested complexing ligands. Thus, we observed that only 13.41, 10.90, and 6.14 percent of the original DOM were remaining after 6- and 12-hour solar and artificial UV irradiation, respectively. In other words, 86.59, 89.10, and 93.86 percent of the original complexing ligands were destroyed after 6-hour solar UV, 12-hour solar UV, and artificial UV irradiation, respectively.

Both metals can be complexed with either ligands from the river water (e.g., humic acids) or the DMG used as the AdSV agent in our stripping voltammetric experiments. Both sorts of ligands are competing for the metal ions in the sample and a major fraction is usually bound by the natural matrix ligands making it unavailable for stripping analysis. Therefore, the natural matrix ligands have to be destroyed first and this can be done by UV digestion. Our results demonstrate that even irradiation with UV-A from sunlight can remove major parts of the natural matrix ligands. Of course, longer irradiation time is expected to complete UV digestion. However, this is not easy to achieve in Central Europe. Therefore, we recommend this sample pretreatment procedure for regions of low geographic latitude, which we have already tested at low latitude equatorial region.

3.2. Pseudopolarography. Figure 4 depicts pseudopolarograms of nickel (II) recorded in Warnow River water samples without any pretreatment (*Original Sample*) and after the various irradiation procedures (*SoUV Sample* and *UV Sample*). The cobalt (II) level in these samples was too low to be detected in all irradiation experiments. The results demonstrate a dramatic effect of the UV irradiation upon the stripping response of nickel (II) in the range between 1.05 and 0 V potential depositions. Whereas the maximal achievable voltammetric signals increased 10-fold for artificial UV

TABLE 5: Determination of the recovery rate for cobalt (II) in 0 hours irradiated (*Original Sample*), 6 and 12 hours solar UV irradiated (*SoUV Sample*), and 6 hours artificial UV irradiated (*UV Sample*).

Cobalt	Concentration before spiking (ppb)	Spiked concentration (ppb)	Concentration after spiking (ppb)	Recovered concentration (ppb)	Recovery rate (%)
Original	0.00	8.00	3.60	3.60	45.00
6 hrs SoUV	0.00	2.00	1.30	1.30	65.00
12 hrs SoUV	0.00	2.00	1.45	1.45	72.50
UV	0.33	2.00	2.06	1.73	86.50
Blank	0.00	2.00	2.05	2.05	102.34

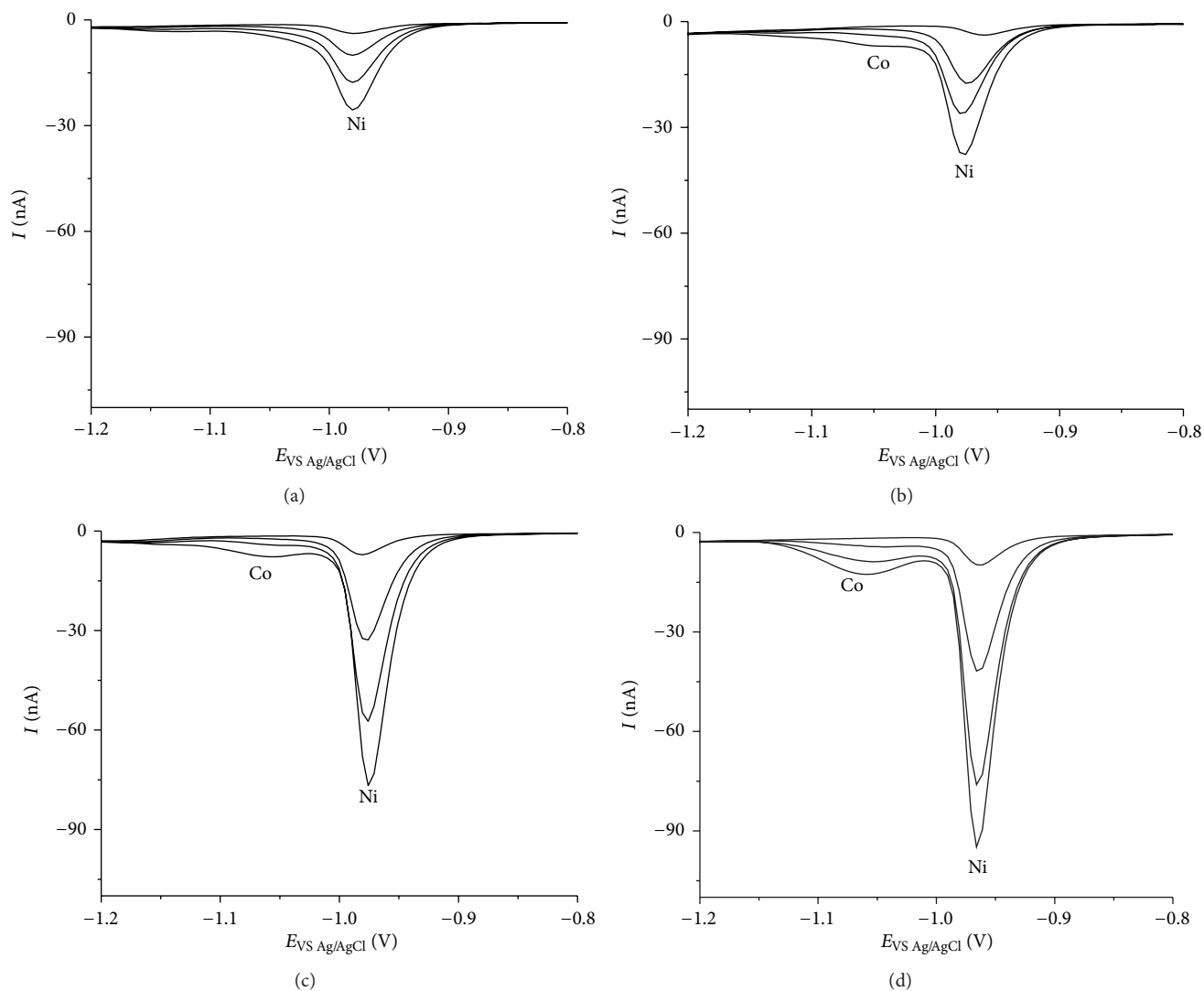


FIGURE 1: Voltammograms of nickel (II) and cobalt (II) for (a) *Original Sample*, (b) 6-hour *SoUV Sample*, (c) 12-hour *SoUV Sample*, and (d) *UV Sample* measured in the presence of ammonia buffer ($\text{NH}_3/\text{NH}_4\text{Cl}$, pH = 9.5) as a supporting electrolyte and DMG-TEA as complexing agents. The standard concentrations were $5, 10,$ and $15 \mu\text{gL}^{-1}$ for nickel (II) and $1, 2,$ and $3 \mu\text{gL}^{-1}$ for cobalt (II).

and 7-fold for solar UV irradiation, also the potentials shifted towards positive direction. Both the pseudopolarographic “half wave” potential and the current maximum potential were shifted by max. 300 mV. This means that, with increasing UV irradiation dose, it becomes easier to form and adsorb

the $[\text{Ni}(\text{dmgH})_2]$ complex during the accumulation step in AdSV measurements.

The effects of solar UV irradiation treatment were larger in case of nickel (II) and cobalt (II) compared with our earlier studies of zinc, cadmium, lead, and copper [15]. The main

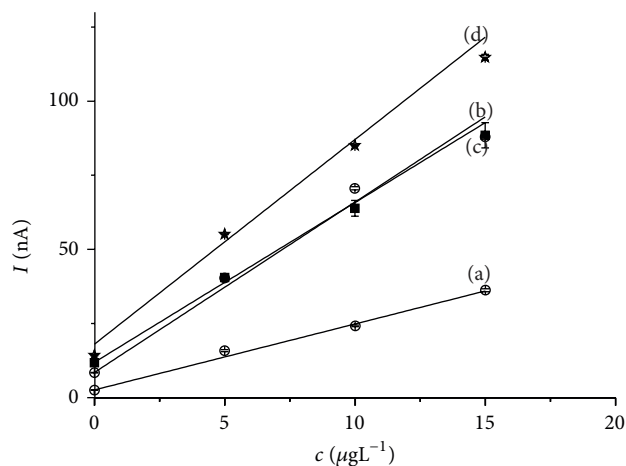


FIGURE 2: Standard addition calibration curves for nickel (II) in (a) *Original Sample*, (b) 6-hour *SoUV Sample*, (c) 12-hour *SoUV Sample*, and (d) 6-hour *UV Sample*. Added standard concentrations of nickel were 5, 10, and 15 μgL^{-1} .

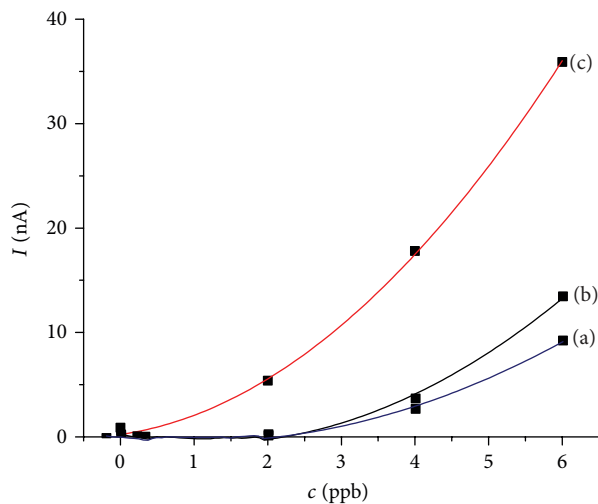


FIGURE 3: Standard addition calibration curves for Co (II) in (a) 6-hour *SoUV*, (b) 12-hour *SoUV Sample*, and (c) 6-hour *UV Sample*. Added concentrations of Co were 2, 4, and 6 ppb.

reason can be found in complexation of the analyte cations, which is on one hand needed for adsorptive accumulation. On the other hand, this desired process competes with complexation of the metal ions and humic substance ligands. The latter interactions seem to be strong as well. Another reason can be found in interfacial activity of the dissolved organic compounds in river water samples as they disturb the adsorptive accumulation of the analyte ion complexes with DMG.

3.3. UV-Vis Spectrophotometry. UV-Vis spectral absorption of the samples was observed at 300 nm, which is a characteristic band of excitation of π -electrons in the benzene ring, which is also the major structural constituent of humic substances like humic acid and fulvic acid. The peak heights

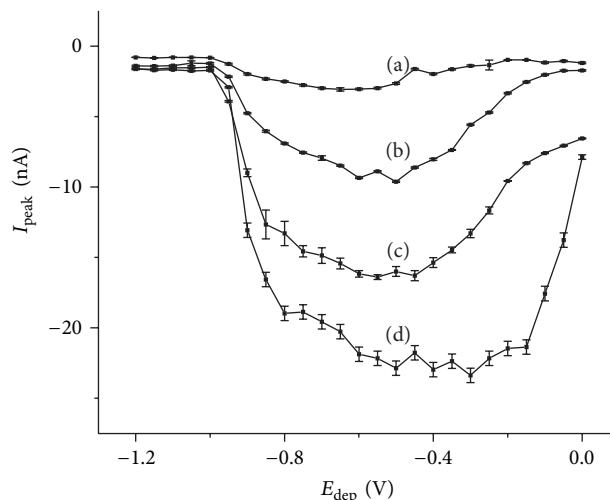


FIGURE 4: AdSV pseudopolarograms of nickel for *Original Sample* (a), 6-hour *SoUV Sample* (b), 12-hour *SoUV Sample* (c), and 6-hour *UV Sample* (d). The single stripping voltammograms were recorded within a potential range from -0.2 V to -1.2 V in the presence of $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer at pH 9.5 as supporting electrolyte and DMG-TEA as complexing agents while other instrumental operating parameters were kept constant as given in Table 1.

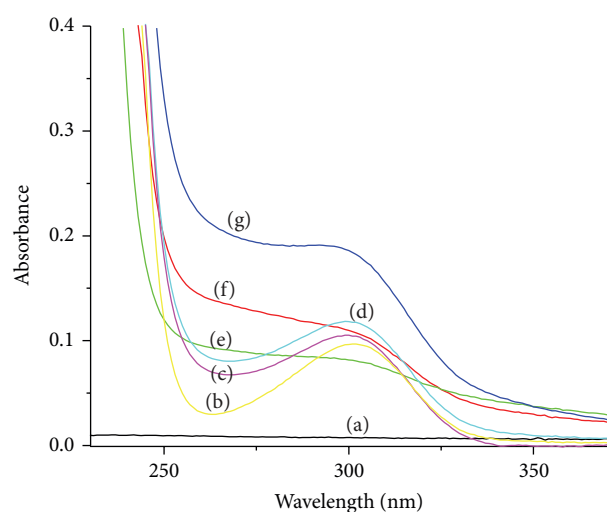


FIGURE 5: UV-Vis spectra for (a) blank, (b) 6-hour *UV Sample*, (c) 12-hour *SoUV Sample*, (d) 6-hour *SoUV Sample*, (e) 10 ppm humic acid, (f) 2-fold diluted *Original Sample*, and (g) *Original Sample*.

suggest that the concentration of this humic substance in the artificial UV irradiated sample is less than 10.0 mgL^{-1} while that of 6-hour solar UV irradiated sample is nearly 10.0 mgL^{-1} . The spectral pattern suggests that the amount of dissolved organic matter (DOM) decreased with intensified UV irradiation (Figure 5). That means an increasing radiation dose results in the decomposition and removal of the dissolved UV-absorbing organic matter. In a similar manner, we have estimated the concentration of humic substance in the original river water sample to be 10-fold of 10.0 mgL^{-1} humic acid, that is, about 100 mgL^{-1} . Humic substances are

also the most important component of DOM in the river water at that concentration.

4. Conclusions

We found that hydrogen peroxide-assisted irradiation of river water samples with solar UV provides effective means for sample preparation as needed for AdSV determination of nickel and cobalt on hanging mercury drop electrodes. The effect of UV irradiation treatment was even larger compared to anodic stripping voltammetry of 4 other heavy metals (Zn, Cd, Pb, and Cu) in the same river, as reported earlier.

The approach reported here should be very useful for mobile electrochemical heavy metal analysis in regions where intense sunlight is available.

Conflict of Interests

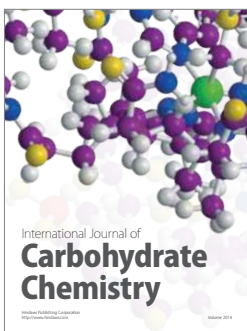
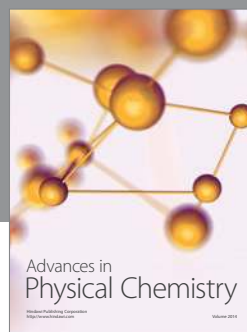
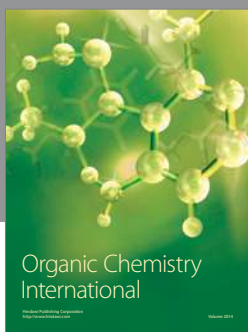
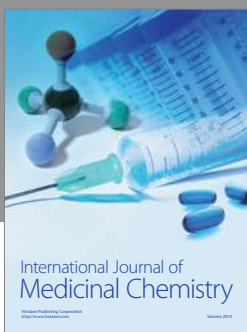
The authors declare that there is no conflict of interests regarding the publication of this paper.

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