

Research Article

Solar UV Photooxidation as Pretreatment for Stripping Voltammetric Trace Metal Analysis in River Water

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The application of solar ultraviolet radiation as sample pretreatment or preparation step in stripping voltammetric analysis of trace metals in presence of low levels of dissolved organic carbon (DOC) natural water samples (river water) was studied. River water samples were collected from downstream of Warnow river (Germany) and acidified to pH of 2 ± 0.2 (by addition of 1 mL of ultrapure 65% HNO₃ per liter sample). Furthermore, 100 μ L/L of hydrogen peroxide solution (ultrapure, 30% H₂O₂) was added to the samples as photochemical reaction initiator. The samples were transferred to polyethylene terephthalate (PET) bottles and irradiated with solar radiation of UV-A intensity of 3.6 mW/m² for six hours, and the concentrations of Zn, Cd, Pb, and Cu were determined by differential pulse anodic stripping voltammetry (DPASV). The comparison of the values with the results obtained for the original untreated sample and artificial UV-treated one proved that solar UV radiation can be applied to the digestion of dissolved organic carbon in trace metal analysis in natural waters like river water, lake waters, well waters, and so forth.

1. Introduction

The determination of the concentration of trace elements requires homogeneous samples which are free of organic matter that might interact with the electrode materials by adsorbing to the electrode and reducing the active surface area of the electrode. It also complexes with the metals ions, can increase background current or shift the peak potential disturbing the signal and making the determination impossible [1]. The determination of the metal ions by adsorptive stripping voltammetric (AdSV) method is applied for metal ions that do not form amalgams with mercury and in the absence of dissolved organic matter (DOM) that interacts with the electrodes or the metal ions. Methods like wet digestion and dry ashing have been introduced long ago in the mineralization of organic matter for both liquid and solid samples. Application of these methods is associated with high risk of contamination of the sample due to the addition of different acidic agents like mineral acid, bisulfate ions, and others. To avoid the problem of contamination

of the samples, an alternative clean and efficient method of sample treatment by UV irradiation has been developed long ago [2, 3]. The method is considered environmentally friendly, effective and minimizes the risks of contamination or loss of sample through evaporation [3]. Commercially, there are several UV sources designed for general and specific purposes to be used in science laboratories, industries water and wastewater treatment plants, and so forth. Nowadays, heavy metals in liquid samples are determined by the use of sample preparation methods of these commercially available UV digesters. The most common ones contain mercury lamps and electrodeless cadmium lamps. Numerous publications deal with determination of metals in UV-digested natural water samples such as copper, lead, cadmium and zinc [4, 5], copper and mercury [6], chromium, iron [7], arsenic [8], and antimony and bismuth [9]. Until now, irradiation with powerful UV lamps is considered essential to ensure complete digestion of the organic sample matrix. However, this prevents mobile or remote application in the environment.

The main natural source of UV is the sun. Extreme UV, UVC, and UVB constitute 99% of the total UV radiation reaching the planet Earth and are absorbed in the upper atmosphere by ozone, oxygen, and nitrogen. The atmosphere is transparent to UVA (315–400 nm), and 99% of the total UV-radiation reaching the earth's crust is UVA. This radiation may reach the ground scattered, diffused, or reflected. Its intensity is also dependent on the cloudiness, latitude, season, altitude, elevation of the sun, and so forth. Transmittance is also dependent on the optical property of the transparent object, or it is a function of the type, thickness, angle of incidence, and specific wavelength [10]. Identification and optimization of the transmittance of large number of materials has been investigated. Pyrex glass (borosilicate type) has maximum transmission level at 340 nm and beyond [11]. Transparent plastic materials include Lucite and Plexiglass [12], polyethylene [13], and polyethylene terephthalate (PET) [14]. In case of water, transmittance depends on the water depth and turbidity, which internally depends on the presence or absence of light-absorbing and coloring materials, and mineral salts, humates, as well as wavelength of the radiation [15–18]. Solar UV is increasingly investigated in the areas of photochemistry and biophotochemistry because of its prominent ecological and environmental roles. In addition to biological activities, solar UV is the most important element in natural disintegration of most organic compounds in soil, water, and air [19]. Surface waters such as river waters contain complex organic substances like humic acids, fulvic acids, glycolic acid, peptides, proteins, aminoacids, lipids, and polysaccharides [20]. Humic acids contain negatively charged ions due to the dissociation of carboxylic acid and hydroxyl functional groups and also possess amphipathic character owing to the presence of both hydrophobic and hydrophilic moieties [21]. They are the most important sunlight absorbers in natural waters that can photosensitize the oxidation of certain aquatic pollutants and biologically important substances [22]. The UV irradiation of such samples produces reactive intermediates like excited states of DOM, hydrogen peroxide [23], singlet oxygen [24], hydrated electrons, superoxide ions [25], organoperoxy radicals, hydroxyl radicals, and halogen radicals [23]. These intermediates react with dissolved organic matters, and some of them are nonselectively decomposing organic compounds to carbon dioxide, N_2 , and phosphate. The use of certain inorganic peroxides (hydrogen peroxide and sodium persulphate) remarkably enhances the rate of degradation of organic contaminants because they trap the photogenerated electrons more efficiently than O_2 [26].

Solar UV radiation in combination with TiO_2 photocatalysts was tested for its application to the disinfection of water and destruction of pathogens and mineralization of organic compounds [26, 27]. In the above investigations, several parameters such as the intensity of UV radiation, the water depth, latitude, water temperature, and angle of incidence were also tested. The result of this experiment showed that almost all human pathogens were killed or deactivated. Following this investigation, the idea of solar water disinfection (SODIS) is promoted as one of the remedies to provide safe water to people living in developing nations.

In the present investigation, the application of solar UV radiation as a sample preparation step in voltammetric determination of trace metals (Zn, Cd, Pb, and Cu) in low DOC surface waters (river water) is tested. The solar UV irradiation took place in the mid summer at mid latitude ($54^{\circ}05'N$, $12^{\circ}07'E$, Rostock, Germany). The results are compared with the results obtained from the undigested original sample and artificial UV irradiated sample. The nature of labile metal ions in the original, solar UV-irradiated and artificial UV-irradiated sample is studied by applying the pseudopolarographic method.

Pseudopolarography had been introduced some decades ago to allow for speciation of complexed metal ions at the trace level [28–31].

2. Experimental

2.1. Instrumentation and Operating Conditions. A μ Autolab potentiostat (Ecochemie) with General Purpose Electrochemical System (GPES) 4.9 software package connected to a Metrohm 663 VA Stand electrolysis cell with a three-electrode system consisting of a HMDE as working electrode, a glassy carbon counter electrode, and Ag/AgCl (3 M KCl) reference electrode was used for the determination of the concentration and pseudopolarographic analysis of the metals. Differential pulse anodic stripping voltammetric (DPASV) method is used for the measurement of both the concentration and pseudopolarography (Table 1).

2.2. Reagents. All reagents used for this experiment were obtained from certified manufacturers (Merck, Fluka) and were ultrapure grades. The stock solutions of Zn^{2+} , Cd^{2+} , Pb^{2+} , and Cu^{2+} (1000 mg/L) were diluted with water as needed. All stock solutions were acidified containing 0.5% HNO_3 . Sodium acetate buffer containing 0.1 M KCl (pH = 4.6) was used as supporting electrolyte. All dilutions were made using ultrapure water ($>18.2 M\Omega$, TOC < 2 ppb). Ultrapure nitric acid (65%) was used to acidify the water sample at the spot of sampling to avoid adsorption of the metal ions to the walls of the containers and to hinder biological activities. H_2O_2 (30%) was added as supporting oxidizing agent while amidosulfonic acid and hydroxysulfonic acids were used to remove excess hydrogen peroxide prior to the determination. Humic acid (20% ash) was used for preparation of “artificial river water” containing approximate concentration of the acid as in natural river water.

2.3. Sample Collection, Preparation, and Preservation. River water samples were collected based on the river water sampling protocols (EPA guidelines for regulatory monitoring and testing water and waste water) from the downstream of Warnow river (Rostock, Germany). Plastic bottles were used as sample containers, and the samples were acidified with ultra pure HNO_3 , to pH of 2 ± 0.2 (1 mL of 65% HNO_3 per liter of sample water). After taking the samples to the laboratory, they were filtered through a $0.45 \mu m$ pore size cellulose acetate membrane filter inserted in a Millipore filtration glass assembly and, then, $100 \mu mol/L$ of ultrapure

TABLE 1: Instrument operating parameters for simultaneous analysis of Zn(II), Cd(II), Pb(II), and Cu(II) in river water by differential pulse voltammetry.

1	Working electrode	HMDE
2	Calibration	Standard addition
3	Mode	DP
4	Purging time (s)	10 to 600 as stated in the text
5	Deposition potential (V)	-1.15
6	Deposition time (s)	120
7	Equilibration time (s)	10
8	Modulation time (s)	0.05
9	Interval time (s)	0.5
10	Start potential (V)	-1.15
11	End potential (V)	0.05
12	Scan rate (V/s)	0.01

30% H₂O₂, was added. The samples were then divided into three aliquots designated as *Original Sample*, *SoUV Sample*, and *UV Sample*. The *Original Sample* was stored in refrigerator at 4°C until determination took place and was used as control sample. The *SoUV Sample* was transferred to a UVA-transparent (330–450 nm) polyethylene terephthalate (PET) bottles and exposed to solar radiation of UVA intensity of 3.6 mW/cm² for 6 hours. The *UV Sample* was transferred to a UV-transparent (at 254 nm) quartz glass tube and irradiated by artificial UV lamp of 30 W and 254 nm for similar hours. The solar irradiation time was chosen between 10:00 AM. and 4:00 PM. to obtain maximum efficiency of solar radiation as a result of increase of the incident angle of the radiation. In addition to this, using an aluminum solar collector increased 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 [32]. All the three samples were stored in a refrigerator at 4°C until determination. Artificial water containing 1.0 mg/L and 0.1 mg/L of humic acid was prepared to compare and estimate the concentration of humic acid in the original Warnow river water by UV-VIS spectrophotometer.

2.4. Procedure. For the determinations of the concentrations of Zn, Cd, Pb, and Cu, 20 mL of the river water samples (Warnow river), 2 mL of 0.1 M KCl and 2 mL of sodium acetate buffer (pH = 4.6) were taken into the voltammetric cell. After the deaeration by purging with nitrogen for 10 minutes, all 4 heavy metals were analyzed simultaneously under the given operating conditions and three replicate measurements were taken for all the three samples of the specified procedures. Standard addition method was used to determine the concentrations of the metal ions in the samples.

Pseudopolarographic data was measured by differential pulse anodic stripping voltammetry (DPASV) with HMDE as working electrode and a supporting electrolyte of acetate buffer containing 0.1 M KCl at pH of 4.5. Accumulation potential (E_{acc}) was scanned between -1.20 V and -0.60 V for Zn and -1.2 V and 0.10 V for Cu with scan increment

($E_{sc,inc}$) of 0.05 V. The time interval (t_{int}) was 0.5 s at scan rate ($E_{sc,rate}$) of 0.01 V/s. Three replicate measurements were taken for each metal of the three sample types.

To estimate the concentration of humic acid in the original river water sample, UV-VIS spectra was taken for 1000 and 100 times diluted original Warnow river water sample and compared with 1 mg/L and 0.1 mg/L of artificially prepared humic acid solution.

3. Results and Discussions

In this study, the concentrations of the zinc, cadmium, lead, and copper metal ions in the river water of all the sample's categories have been successfully determined by DPASV technique. Voltammograms are presented in Figures 1(a), 1(b), and 1(c). The concentrations of the metal ions Zn, Cd, Pb, and Cu in the *Original Sample*, the *SoUV Sample* and the *UV Sample* were determined by standard addition (i.e., extrapolation of the calibration curve). The standard additions are depicted in Figures 2–5, and the according numbers are given in Table 2.

According to these measurements, the concentration of zinc was found to be 17 ± 0.43 , 22.86 ± 0.41 , and 26 ± 0.40 ppb, for *Original Sample*, *SoUV Sample*, and *UV Sample*, respectively. In similar procedures, the concentrations of cadmium in the three sample types were obtained as 0.03 ± 0.001 , 0.05 ± 0.003 , and 0.05 ± 0.005 ppb. In the case of lead, the *Original Sample*, *SoUV Sample*, and *UV Sample* contained 4.36 ± 0.05 , 7.07 ± 0.02 , and 7.50 ± 0.01 ppb, respectively. Copper concentration in the same river water samples was determined as 32.20 ± 0.34 , 58.85 ± 0.31 , and 71.57 ± 0.28 ppb as depicted in Figure 3. These results show that solar irradiation over 6 hours has a significant effect upon analysis results of the 4 tested heavy metals. The effect is largest in case of lead, where we found almost the same concentration as compared to the *UV Sample*, which served as the reference. The effect of 6 hours of solar irradiation was smaller for zinc and copper, However, even here, the results were much better than in case of the *Original Sample*. These findings can probably be addressed to matrix components that form complexes with these 3 metal ions. The irradiation effect was smallest for cadmium, which seems to be less prone to complexation by components present in this river water matrix.

The recovery rates were calculated by adding known concentrations of the metal ions to the three different sample categories in the very beginning. This experiment was used to evaluate the data obtained by means of stripping voltammetry in the various sample treatment procedures under consideration. The results obtained in this experiment are given in Table 2. For all 4 metals tested, the worst recovery rate was found for the *Original Sample*, that is, without any irradiation pretreatment. In case of zinc, the best recovery rate was obtained by solar irradiation treatment.

Interestingly, the recovery rate for copper was above 100% for all three kinds of samples. This corresponds to the observed decrease in slope of the standard addition function (Figure 3). Seemingly, the sensitivity in presence of

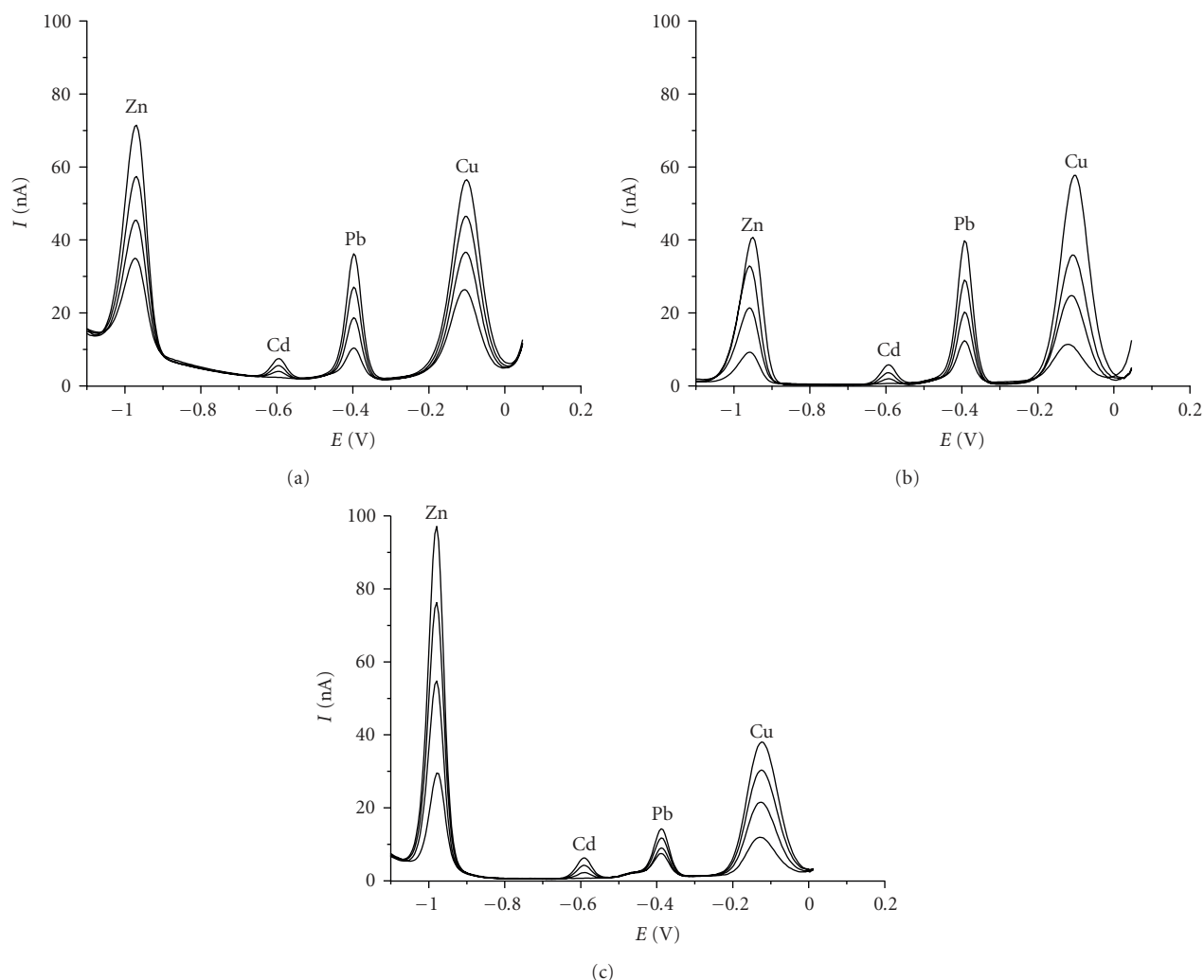


FIGURE 1: DP stripping voltammograms recorded for (a) the *Original Sample*, (b) the *SoUV Sample*, and (c) the *UV Sample*, with additions of 10, 20, 30 ppb for Zn and Cu, 3, 6, and 9 ppb for Pb, and 1, 2, and 3 ppb for Cd.

TABLE 2: Concentration and recovery rates measured for Zn, Cd, Pb, and Cu in *Original Sample*, *SoUV Sample* and *UV Sample* of Warnow River.

Element	Concentration (ppb)			Recovery rate		
	Original sample	SoUV sample	UV sample	Original sample	SoUV sample	UV sample(%)
Zinc	17.17 ± 0.43	22.86 ± 0.41	26.67 ± 0.40	88.81 ± 0.20	95.91 ± 0.13	92.90 ± 0.21
Cadmium	0.03 ± 0.001	0.05 ± 0.003	0.05 ± 0.005	75.32 ± 0.15	87.11 ± 0.22	93.66 ± 0.11
Lead	4.36 ± 0.05	7.07 ± 0.02	7.50 ± 0.01	84.21 ± 0.32	90.32	94.14 ± 0.31
Copper	32.20 ± 0.34	58.85 ± 0.31	73.57 ± 0.28	133.59 ± 0.42	112.75 ± 0.37	104.16 ± 0.35

organic river water matrix is slightly higher compared with both irradiation-treated samples. This would mean that the complexing matrix components lead to increased stripping signals, which on the other hand, leads to incorrect analysis results. The absolute stripping signals are, however, larger for the irradiated samples. The unusual recovery rate of 133.6% for the *Original Sample* in case of copper may also have to do with the considerable complexing effects. The latter is confirmed by pseudopolarographic studies as described below and in Figure 7.

The nature of matrix-complexed zinc and copper ions was studied by means of pseudopolarography of the three different kinds of samples. Figure 6 exhibits such pseudopolarograms for zinc. The main effect of irradiation treatment is a significant increase in peak currents that are plotted here versus deposition potentials. This means that after UV or solar irradiation, more metal ions are available for reduction during the deposition step. Obviously, the irradiative digestion treatment is more complete for artificial UV light; however, also solar irradiation reveals remarkable release of

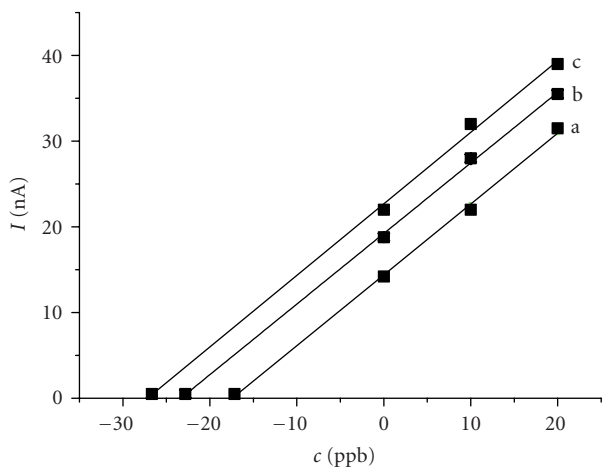


FIGURE 2: Standard addition for zinc in (a) *Original Sample*, (b) *SoUV Sample*, and (c) *UV Sample*.

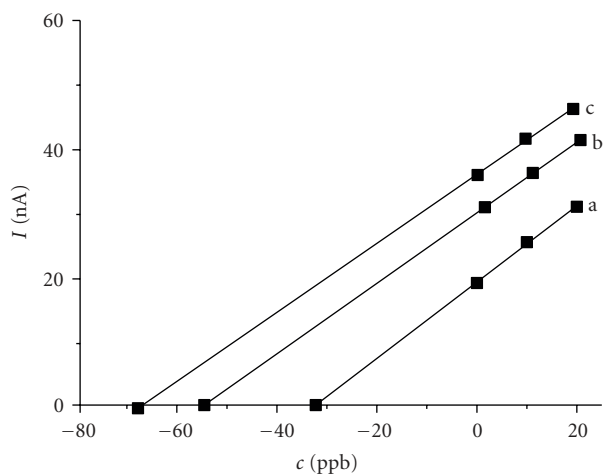


FIGURE 3: Standard addition for copper in (a) *Original Sample*, (b) *SoUV Sample*, and (c) *UV Sample*.

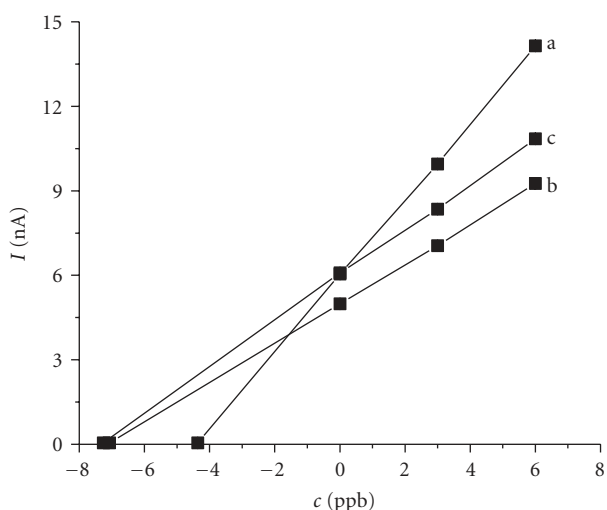


FIGURE 4: Standard addition calibration curve for lead in (a) *Original Sample*, (b) *SoUV Sample*, and (c) *UV Sample*.

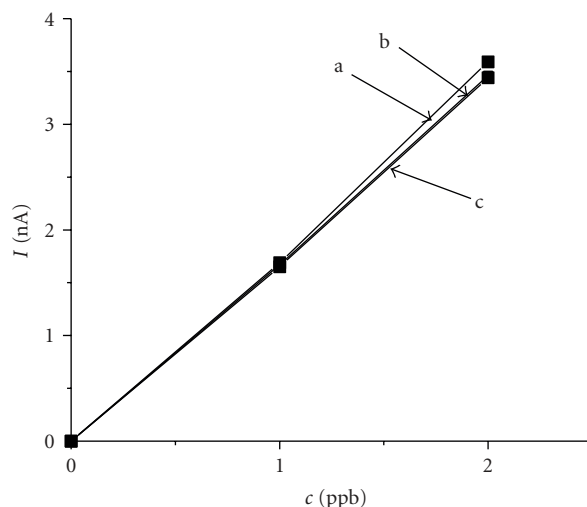


FIGURE 5: Calibration curve for cadmium in (a) *Original Sample*, (b) *SoUV Sample*, and (c) *UV Sample*.

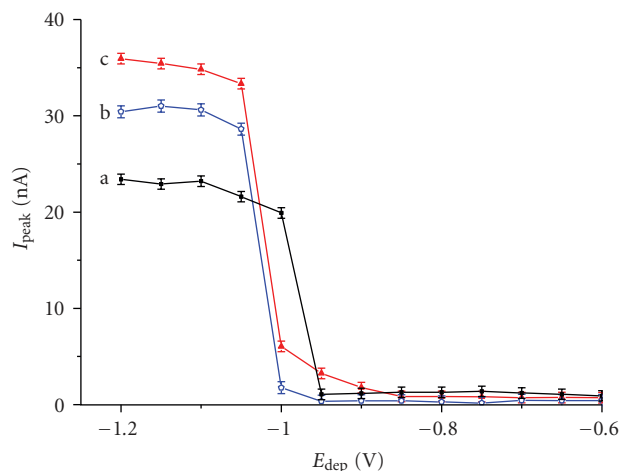


FIGURE 6: Pseudopolarograms of 10 ppb zinc in (a) *Original Sample*, (b) *SoUV Sample*, and (c) *UV Sample*; DPASV at HMDE, accumulation time 240 s, initial potential -1.2 V, final potential -0.70 V, scan increment 0.05 V, interval time 0.5 s, scan rate 10 mV/s, and 0.1 M acetate buffer containing 0.1 M KCl (pH = 4.6).

zinc ions from the matrix complexes by destruction of the organic ligands.

Figure 7 illustrates in case of copper the dramatic effect of both irradiation treatment methods tested in this study. Both the pseudopolarographic half-wave potential and the step height change considerably after treatment with either solar or artificial UV light.

It can be estimated from Figure 8 that more than 1000 ppm humic acids (in a wide sense) have been present in the river water samples. For this estimation, UV/Vis spectra were taken for 1000- and 100-fold diluted original Warnow river water samples and then compared with 1 mg/L and 0.1 mg/L of an artificially prepared humic acid solution. This method was used to estimate the concentration of the most abundant UV/Vis-active organic matter (among them humic

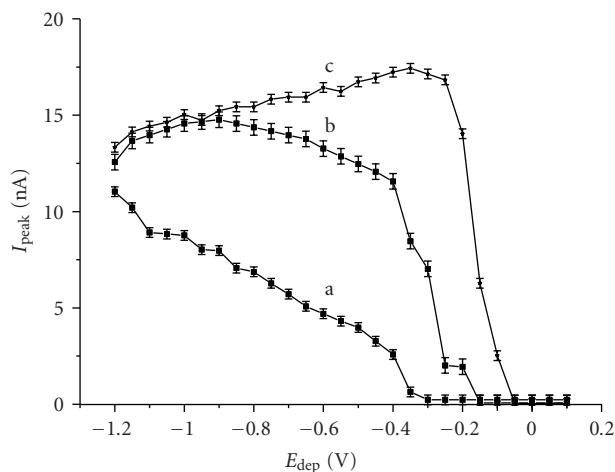


FIGURE 7: Pseudopolarograms of 10 ppb copper in (a) *Original Sample*, (b) *SoUV Sample*, and (c) *UV Sample*; DPASV at HMDE, accumulation time 240 s, initial potential -1.2 V, final potential 0.10 V, scan increment 0.05 mV, interval time 0.5 s, scan rate 10 mV/s, and 0.1 M acetate buffer with 0.1 M KCl ($\text{pH} = 4.5$).

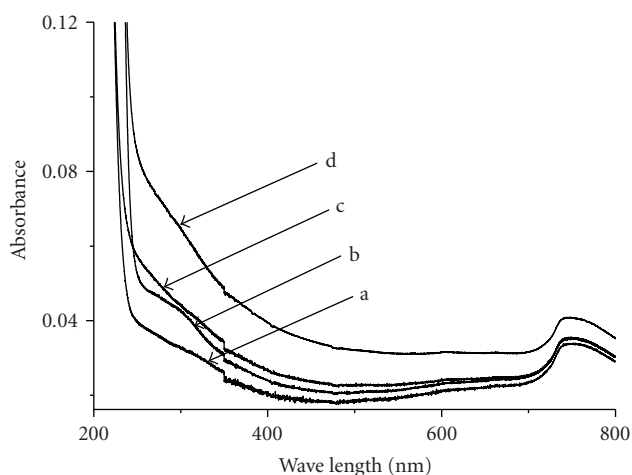


FIGURE 8: UV-VIS spectra of (a) 0.1 mg/L humic acid, (b) 1 mg/L humic acid, (c) Warnow river sample $1:1000$ diluted, and (d) Warnow river sample $1:100$ diluted.

acid) in the used water sample from river Warnow. The high level of organic matter explains the great effect of irradiation treatment.

4. Conclusions

This study demonstrates that solar irradiation assisted by low pH and addition of hydrogen peroxide can serve as a means for water sample digestion. All what is needed includes a few hours of solar irradiation, an aluminum reflector, and a PET plastic bottle. The presented protocol can be recommended for trace determinations of copper and zinc in river water at remote places in the environment or otherwise, where electric high-power UV lamps or commercial UV digestion units cannot be used. The method also works for lead and

cadmium; however, in these cases, 6 hours of sun irradiation seem too short to finish the process.

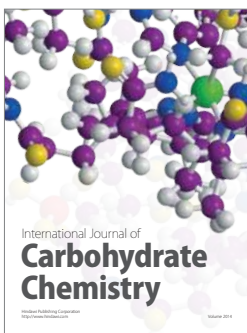
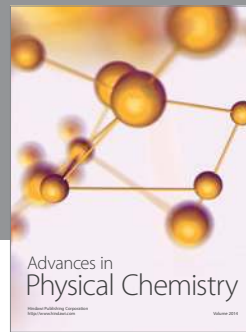
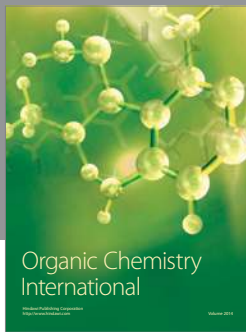
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