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ORIGINAL ARTICLE

Determination of cadmium and lead in perch fish samples by differential pulse anodic stripping voltammetry and furnace atomic absorption spectrometry

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Abstract Lead and cadmium contents in the edible parts (muscle, fillet) of 17 commercially used fish species from South Egypt River Nile (Aswan) were determined by means of DPSAV (differential pulse stripping anodic voltammetry). In the sample preparation step, all fish samples were lyophilised, milled in a ball mill and finally decomposed by using mixed acid (HNO_3 + $HClO_4$). The accuracy of the concentrations determined in this study was checked by the measurements of the certified reference material CRM No. 422, cod muscle from the Commission of the European Communities, Community Bureau of Reference. All Pb^{2+} and Cd^{2+} concentrations observed from species of Egypt River Nile showed that fish from this area are a good source of these essential elements and the developed method is accepted as a good analytical routine method for these samples.

1. Introduction

Cadmium and lead were determined in fish samples from seven sampling stations of the Ria de Aveiro (Portugal) (Perez Cid et al., 2001; Vieira et al., 2011; Siavash Saei-Dehkordi et al., 2011). The species analyzed were *Anguilla anguilla*, *Mullus surmuletus*, *Trigla lucerna*, *Mugil cephalus*, *Chelon labrosus*, *Liza aurata* and *Dicentrarchus labrax*, all of which are used for human consumption. For this purpose, procedures for the electrothermal atomic absorption spectrometry determination of cadmium and lead in these samples were developed, as well as a microwave digestion method for obtaining a fast dissolution of the samples. The concentrations of metals found in the muscle of the fish species were very low. The minor contents corresponded to cadmium and lead with values smaller than 0.043 and 0.15 mg/g (wet weight), respectively. The accuracy of the analytical methodology employed was also evaluated through the analysis of two reference materials

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(NIST-1577b and IAEA-V10): good agreement was obtained between the experimental results and the certified values.

Studied levels of trace metals of canned fish samples collected from markets in Turkey were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion. The accuracy of the method was corrected by standard reference material (NRCC-DORM-2 Dogfish Muscle) (Ganjavi et al., 2010). The contents of the investigated trace metals in canned fish samples were found to be in the range of 0.09–0.40 lg/g for lead and 0.06–0.25 lg/g for cadmium. The results were compared with the literature values.

Ganjavi et al. (2010) (Meador et al., 2005), and (Mustafa and Mustafa, 2007) have studied the contents of Pb and Cd in two species of Iranian tuna fish (yellowfin and skipjack), which were caught from the Persian Gulf and the Oman Sea, and the effects of canning processing steps on their contents were assessed by electrothermal atomic absorption spectrometry. The results revealed that the levels of lead and cadmium throughout the processing steps in yellowfin were in the range of 0.154 ± 0.019–0.441 ± 0.025 μg/g and 0.029 ± 0.002–0.084 ± 0.0005 μg/g, respectively. Pb and Cd concentrations from received fish to final product in skipjack were found to be in range of 0.072 ± 0.031–0.218 ± 0.031 μg/g and 0.016 ± 0.001–0.062 ± 0.002 μg/g, respectively. The limits of detection for lead and cadmium were 0.058 μg/g (11.6022 μg/l) and 0.0007 μg/g (0.1485 μg/l), respectively. Results from paired sample t-test analysis showed that defrosting, cooking, and sterilisation by autoclave would reduce the contents of lead and cadmium, considerably.

Selected toxic (cadmium, lead) and essential (zinc and copper) trace metals were determined by means of differential pulse anodic stripping voltammetry (DPASV) in some different brands and kinds of fishery products purchased from the popular supermarkets of Turkey (Çelik and Oehlenschläger, 2007). Among the fishery products, the highest concentration of cadmium, lead, zinc and copper were found in the frozen anchovy (494.2 μg/kg, 314.2 μg/kg, 566 mg/kg, 45.7 mg/kg, respectively). While the canned anchovy fillet had the lowest cadmium (25.1 μg/kg), zinc (33.8 mg/kg) and copper (7.1 mg/kg) concentrations, canned tuna fish (Brand A) had the lowest lead (76.1 μg/kg). The concentrations of all toxic and essential elements in the selected products were high and often exceeded legal limits set by health authorities. Therefore these products must be monitored more often. The concentrations of selected metals, such as Hg, Cd, Pb, Cu and Zn, were determined in muscle and liver of perch (Perca fluviatilis) from the Pomeranian Bay and Szczecin Lagoon, southern Baltic.(Szefer et al., 2000).

The concentrations of Hg in muscle and Cd, Pb and Cu in liver increased with the age of the specimens analyzed. The positive relationship between muscle Hg and age (weight-length) is probably attributed to the specific bioaffinity for organic matter of CH_3Hg with a high biological half-life, which generally constitutes the dominant pool of the total Hg in the fish muscle. ANOVA analysis clearly demonstrated that in the Pomeranian Bay there were significant seasonal variations of muscle Hg and hepatic Cd, Pb and Cu. Factor analysis supported seasonal differences in muscle and especially hepatic samples; specifically, summer muscles were clearly separated from winter ones. Muscle samples corresponding to the winter season had relatively high concentrations of Hg, Cd and Pb. The concentrations of muscle Hg (corresponding to 70–105 μg CH_3Hg eaten weekly) are comparable to the PTWI (permissible tolerable weekly intake) recommended by WHO (200 μg CH_3Hg). The muscle Cd^{2+} and Pb^{2+} levels are significantly lower than the PTWI's and do not constitute any threat for man.

The relationships between chronic liver diseases and trace heavy metal contents in blood are debatable and have not been understood clearly (Mohamed et al., 2010).The present study is undertaken to determine Co, Fe, and Ni concentrations in sera from viral hepatitis patients .In all eighty patients with chronic hepatitis (B, C) and 29 healthy individuals were chosen forth in this study. Donors were selected from different environmental areas, including Aswan, KomOmbo, and Edfu as polluted areas, and Daraw as an unpolluted area. Co, Fe, and Ni concentrations in patient and healthy blood serum were measured by two different analytical techniques: differential pulse adsorptive stripping voltammetry (DPAdSV) and atomic absorption spectrophotometer (AAS). A comparative study was carried out between the results using DPAdSV and AAS techniques, which are in very good agreement.

A highly sensitive and selective voltammetric procedure is described for the simultaneous determination of eleven elements (Cd, Pb, Cu, Sb, Bi, Se, Zn, Mn, Ni, Co and Fe) in water samples. Firstly, differential pulse anodic stripping voltammetry (DPASV) with a hanging mercury drop electrode (HMDE) is used for the direct simultaneous determination of Cd, Pb, Cu, Sb and Bi in 0.1 M HCl solution (pH = 1) containing 2 M NaCl. Then, differential pulse cathodic stripping voltammetry (DPCSV) is used for the determination of Se in the same solution. Zn is subsequently determined by DPASV after raising the pH of the same solution to pH = 4 (Ghoneim et al., 2000).

The use of some fish parasites as bioindicators of heavy metal pollution has been demonstrated as particularly adequate due to their capacity of bioconcentration.(Eira et al., 2009) This study evaluated the effect of *Proteocephalus macrocephalus* on the accumulation of trace elements in the edible fish, *A. anguilla*, in a contaminated area in Portugal (Ria de Aveiro). Also, the model *P. macrocephalus*/*A. anguilla* was assessed as a bioindicator system in the presence of the highly prevalent nematode *Anguillicola crassus*. Samples (kidney, liver, muscle, *A. crassus* and *P. macrocephalus*) of 20 eels harboring *A. crassus* and another 20 harboring both *A. crassus* and *P. macrocephalus* were selected for elemental analysis by ICP-MS. The highest concentrations of Cr, Ni and Zn were detected in *P. macrocephalus*.

The highly sensitive determination of lead (Pb(II)) and cadmium (Cd(II)) ions, with a limit of detection of 0.01 μg L^{-1} for Pb(II) and Cd(II), by on-line preconcentration and anodic stripping voltammetry (ASV) controlled by a sequential injection system (SIA) is reported here. (Meucci et al., 2009; Augelli et al., 2007; Sherigara et al., 2007) An optimized digestion method coupled to electrochemical detection to monitor lead, copper, cadmium and mercury in fish tissues was developed. Square wave anodic stripping voltammetry (SWASV) coupled to disposable screen-printed electrodes (SPEs) was employed as a fast and sensitive electroanalytical method for heavy metal detection. Different approaches in digestion protocols were assessed. The study was focused on Atlantic lake fillets because of their wide diffusion in the human nutrition. Best results were obtained by digesting fish tissue with hydrogen peroxide/hydrochloric acid mixture coupled to solid phase (SP)

purification of the digested material. This combined treatment allowed quantitative extraction from fish tissue (muscle) of the target analytes, with fast execution times, high sensitivity and avoiding organic residues eventually affecting electrochemical measurements. Finally, the method has been validated with reference to standard materials such as dogfish muscle (DORM-2) and mussel tissues (NIST 2977) (Ninwong et al., 2012; Mahesar et al., 2010).

The aim of this study was to determine Cadmium and lead contents in the muscle of edible parts of 51 commercially used fish species from the Egypt River Nile (Aswan) and to develop a routine analytical method for the determination of cadmium and lead using DPASV, Differential Pulse Anodic Stripping Voltammetry, using an auto sampler (Locatelli et al., 2001; Nrünberg, 1983; Stoeppler and Näurnberg, 1979).

2. Experimental

2.1. Recommended procedure for determination of cadmium and lead in fish samples by Differential Pulse Anodic Stripping Voltammetry DPASV

Many studies have already been published on the preparation of samples for wet chemical analysis. Two main techniques have been used: alkali fusion and acidic decomposition or extraction. Alkali fusion induces high blank levels and high detection limits. Due to the small amounts of particulate matter, acidic methods are more suitable. There are many ways to proceed with acids. In addition, various parameters, such as the method of heating, working pressure, and acids, has a role to play in the digestion efficiency. The use of low quantities of acid allows small volumes of final solution to be handled and the detection limits to be improved. The principal acids used for particle digestion are HNO_3, HCl, $HClO_4$, HF, and H_2SO_4 (Hseu et al., 2002). However, the use of HF leads to long, dangerous, and cumbersome schemes and it is not recommended for routine analysis. Thus, in environmental analytical chemistry, acid leaching has become a common procedure as an alternative to total digestion. Five grams of muscles of each sample (different weight and length) was weighted in Petri dishes which were put in a closed low temperature (41–45 °C) in an electrical furnace for 24 h and then ground in an agate mortar. The experimental conditions for the determination of cadmium and lead by differential pulse anodic stripping voltammetry are shown in Table 1. The powders of River Nile samples (S_1–S_{17}) and Lake Nasser samples (S_1–S_{12}) were transferred into 100-ml beaker and are mixed with 50 ml (1:1) mixed acid (HNO_3 + $HClO_4$) and evaporated to near dryness. The samples were transferred into a 100-ml measuring flask and diluted to the required volume (100 ml) by bidistilled water. All glassware and polyethylene bottles were soaked in 2 M nitric acid for at least 1 week, washed three times with bidistilled water, and finally soaked in 0.1 M hydrochloric acid until being ready for use (Liu et al., 1997).

2.2. Apparatus

In this study, DPASV, i.e. differential pulse anodic stripping voltammetry with an EG&G Princeton Applied Research Corp. microprocessor controlled: (PAR) Model 264A stripping analyzer, coupled with a PAR 303A Static Mercury Drop Electrode SMDE, (drop size: medium, area of the drop: 0.014 cm^2). The polarographic cell bottom (PAR Model K 0060) was fitted with an Ag/AgCl saturated KCl, reference electrode, working electrode: HMDE (Hanging Mercury Drop Electrode) and a platinum wire were used as a counter electrode. A PAR 305 stirrer was connected to the 303A SMDE. A PAR Model RE 0089 X–Y recorders were used for the collection of the experimental data for the determination of trace elements. Stirring was performed with a Teflon-coated bar at approximately 400 rpm using a magnetic stirrer (KIKA Labortechinik, Germany). A Pyrex glass cell was used for the measurements with magnetic fusion energy (MFE). pH measurements were made with an Orion model 601 digital pH meter. All solutions were prepared with deionised water. Certified atomic absorption spectroscopic standard solutions (1 mg/ml) for cadmium and lead were purchased from BDH (UK). Working standard solutions were prepared by appropriate dilution of the stock solutions. A SP1900Pye Unicam Recording Flame Atomic Absorption Spectrophotometer was utilized to measure the concentrations of cadmium and lead Using Pye Unicam Single element hollow cathode lamps (Mohamed, 1999).

Table 1 Experimental condition for the simultaneous determination of Cd^{2+} and Pb^{+2} by differential pulse anodic stripping voltammetry (DPASV).

Condition of DPASV	Cd^{2+}	Pb^{2+}
Deposition potential	−580 mV	−330 mV
Final potential	−450 mV	−100 mV
Deposition time	130 s	120 s
Delay time before potential sweep	10 s	10 s
Potential scan rate	10 mV/s	10 mv/s
Stirring rate	2000 rpm	2000 rpm

Supporting electrolyte: 0.1 M HCl. Working electrode: Hanging Mercury Drop Electrode (HMDE) (Christopher et al., 1993).

2.3. Samples collected and procedure

In this work, seventeen fish samples of individuals (S_1–S_{17}), belonging to Nile perch fish family *Lates niloticus* from the River Nile in Aswan city (Upper Egypt) and twelve *L. niloticus* samples (S_1–S_{12}) from Lake Nasser were collected onboard the fishery research vessel, in June 2007. The three parts of each perch fish sample (head, medium and tail) from South River Nile (Aswan) and Lake Nasser were immediately frozen after suitable preparation onboard and kept in the deep freezer before analyzing. All chemical used were of A.R grade (99.9%) and purchased from BDH, Aldrich, Sigma and Merck.

3. Results and discussion

3.1. Optimization of the solution conditions

From the previous studies (Ghoneim et al., 2000) hydrochloric acid is considered as the most suitable supporting electrolyte for the determination of Cd^{2+} and Pb^{2+} by DPASV, because it forms chlorocomplexes with these metal ions at low pH values. These chlorocomplexes have different formation constants

and hence they will be reduced to their metallic forms at different electrodeposition potentials and then the metals are stripped off the mercury electrode by oxidation. By increasing the concentration of HCl, separation between the peak potentials (E_p) of Cd^{2+} and Pb^{2+} increases gradually up to 0.1 M HCl (pH = 1) which provides the best peak resolution. This medium is found to be most suitable for the determination of Cd^{2+} and Pb^{2+} with good peak separation. The effect of chloride ion concentration on the peak separation was studied as a function of NaCl concentration. It is clear that by increasing the chloride ion concentration, the E_p of Cd^{2+} shifts to more positive values. The resolution of the peak of Cd^{2+} is found to increase with increasing the NaCl concentration up to 2 M, where the best peak resolution is obtained. This means that the optimal supporting electrolyte for the determination of Cd^{2+} and Pb^{2+} by DPASV consists of 0.1 M HCl (pH = 1) and 2 M NaCl. The NaCl added has no effect on the peak resolution of the other elements under investigation.

In this highly acidic medium, a major problem is that the oxidation peak of Cd^{2+} is masked by the hydrogen evolution. Accordingly, Cd^{2+} was determined by the same technique (DPASV) after raising the pH of the medium to 2 by adding ammonia/ammonium chloride (as a basic solution).

3.2. Optimization of the instrumentation conditions

The most reasonable scan rates for the determination of the two elements are found to be 5–10 mV/s, depending on the element determined. The electrode position potentials (E_d) of the two elements were studied separately, and plotted against the peak current (i_p) values to make it easy to select the optimal deposition potential for each metal ion Fig. 1. The optimal deposition potentials for metal ions under investigation in the specified solution and instrumental conditions were determined. The relation between the peak current (i_p) and deposition time (t_d) is studied separately for the two metal ions. The linearity is valid for the investigated metal ions through long periods within the concentration levels normally found in fish samples.

3.3. Recommended analysis scheme

The concentrations of the two elements Cd^{2+} and Pb^{2+} dissolved in fish samples can be determined by the method of standard addition under the optimal conditions described above, according to the following analysis scheme:

1- After filtration and acidification of the fish samples to 0.1 M HCl (pH = 1), NaCl was added up to 2 M, the investigated solution was deoxygenated for 10 min by purified nitrogen while stirring. Since the metal ions of Pb^{2+} dissolve in mercury by forming amalgams, they can be determined by DPASV. Preconcentration of this metal is carried out at a potential of −0.35 V (vs. Ag/AgCl) at a suitable deposition time, according to the following reaction:

$$Pb^{2+} + 2e^- + Hg \rightarrow Pb(Hg)(\text{Preconcentration step})$$

At the end of the deposition period, the stirring is stopped and after a small rest period (30 s) the potential is scanned anodically to-0.1 V with a scan rate of 10 mV/s for Pb^{2+} and a pulse height of 25 mV, the dissolved amalgam is then reoxidized back to the following equation:

$$Pb(Hg) \rightarrow Pb^{2+} + 2e^- + Hg(\text{DPASV step})$$

1- The pH of the solution is raised up to 2.0 by adding ammonia/ammonium chloride solution (as a basic solution) and then the concentration of Cd^{2+} can be determined by DPASV after preconcentration at E_d of −0.68 V. After a rest period of 30 s, the voltammogram is then recorded anodically within the potential range −0.75 to −0.45 V with a scan rate of 10 mV/s and a pulse height of 25 mV:

$$Cd^{2+} + 2e^- + Hg \rightarrow Cd(Hg)(\text{Preconcentration step})$$
$$Cd(Hg) \rightarrow Cd^{2+} + 2e^- + Hg(\text{DPASV step})$$

3.4. Test of linearity of calibration plots

The linearity between i_p and concentration C was tested for the investigated elements by the standard addition method under the optimal conditions Fig. 2. Satisfactory linearity was obtained over the concentration range generally found in the fish samples for all investigated elements. The slope values of the calibration curves of the investigated elements are reported in Table 2.

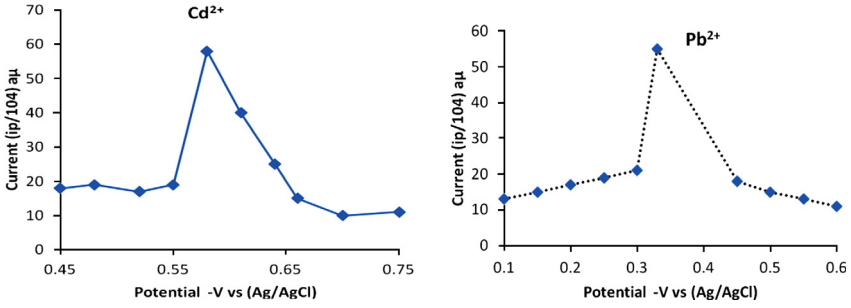

Figure 1 Relation i_p/E_d plot of 0.01 mg/L Cd^{2+} and Pb^{2+} in [0.1 M HCl + 2 M NaCl, pH = 2 and 1, scan rate = 10 mV/s and t_d = 120 s].

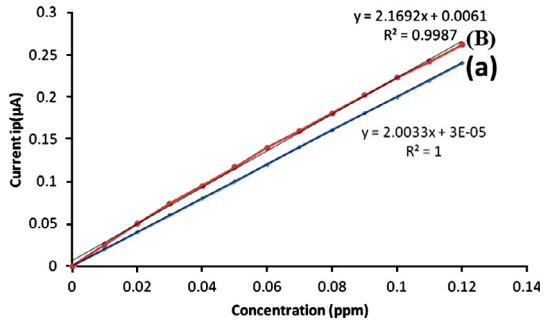

Figure 2 Calibration plot (i_p/c) of Cd^{2+} obtained by standard addition method at Ed = −0.58 V, t_d = 120 s and pulse height = 25 mV for (a) the element present alone in the solution and (b) the element mixed with 0.1 mg/L of the Pb^{2+} investigated element.

3.5. Intermetallic compound formation

The formation of intermetallic compounds between the investigated metal ions may cause an error in their determination. This aspect was investigated by comparing the slopes of the i_p/concentration plots for each metal present in the solution separately and mixed with 0.1 mg/l of the other investigated metals. Table 2 shows that slope value (a) of the calibration plot of the pure element solution and slope value (b) of the plot of the element mixed with the other investigated element is not significantly different. This indicated that the intermetallic compound formation between the investigated elements in the mercury drop electrode under the optimal conditions of the proposed analysis scheme is small and can be neglected.

3.6. Precision, accuracy, detection limits and quantification limit

Precision and accuracy were determined as relative standard deviation (RSD) and relative error (RE), respectively, by analyzing the same reference standard solution five times for various concentration levels. Table 2 shows RSD and RE for five concentration levels of each element. The detection limits D_L of the investigated metals, defined as the metal concentration yielding an analytical peak equal to the minimum detectable one, can be calculated as.(Smith and Osteryoung, 1978) $D_L = 5(S_d/m)$ Where S_d is the standard deviation of the blank and m is the slope of the calibration line. Table 2 shows the calculated detection limits of all elements under study. The given detection limits of the elements under investigation revealed that the proposed scheme of analysis under the optimal conditions is very sensitive and very useful for ultra trace determination of elements.

The detection and quantification limits have been established as the concentration expressed in nanograms of the element per gram of sample, giving a current reading statistically different from that of the blank, and they have been calculated by dividing 5 and 10 times the standard deviation of the current readings of the blank by the slope of the analytical curve, respectively. From these values, and taking into account the dilution and sample size, the detection and quantification limit in nanograms per gram of sample have been calculated. The values obtained are shown in Table 2. Precision of the method has been estimated from the standard deviation and the correlation coefficient for five replicate analyses of sample solutions, and it provides values greater than 0.006 and 0.99 for all metals, respectively.

3.7. Application

Cadmium and lead concentrations of the edible muscle parts of *L. niloticus* fish belonging to Nile perch family from South River Nile were determined by using DPASV in Fig. 3(a–b). Cadmium concentrations of the South Egypt Nile (Aswan) fishes investigated are given in Table 3.

From the data in Tables 3 and 4, it can be seen that, cadmium concentrations range from 12 ng g^{-1} to 16 ng g^{-1} (head part), from 6 ng g^{-1} to 24 ng g^{-1} (medium part) and from 4 ng g^{-1} to 16 ng g^{-1} (tail part) in the Nile Perch fish samples, while in the Lake Nasser Perch fish samples, it has been found that cadmium concentrations ranged from 14 ng g^{-1} to 24 ng g^{-1} (head part), from 6 ng g^{-1} to 16 ng g^{-1} (medium part) and from 8 ng g^{-1} to 18 ng g^{-1} (tail part). The concentration of cadmium in the Perch fish samples under study is in safety baseline levels. Extensive study has shown this to be one of the most toxic commonly encountered elements. It is taken into the body either through breathing contaminated air,

Table 2 Slopes of i_p/C, relative standard deviation (RSD), relative error (RE), calculated detection limit (D_L) values and quantification limits (Q_L) of various concentration levels of the investigated elements under the optimal conditions and t_d = 120 s.

Element	Slope (a)	Slope (b)	Taken (ppm)	Found (c)	RSD%	RE%	(D_L) ppb	(D_L) (M)	(Q_L) ppb	(Q_L) (M)	Technique	DPASV
Cd^{2+}	2.00	2.17	10.00	9.989	0.0778674	0.11	0.019816	1.69×10^{-10}	0.0396	3.37×10^{-10}		
			5.00	5.069	0.9625245	1.38						
			1.00	1.012	0.8384665	1.20						
			0.10	0.102	1.3864839	2.00						
			0.01	0.009	7.856742	10.0						
Pb^{2+}	1.74	1.83	10.00	10.08	0.5611959	0.80	0.022678	1.12×10^{-10}	0.0454	2.199×10^{-10}		
			5.00	4.998	0.0282956	0.04						
			1.00	1.014	0.9762816	1.40						
			0.10	0.099	0.7142493	1.00						
			0.01	0.011	6.4282435	10.0						

Slope (a) for the element present alone in the solution.
Slope (b) for the element mixed with 0.1 ppm of the other elements.
(c) Average of five experiments.

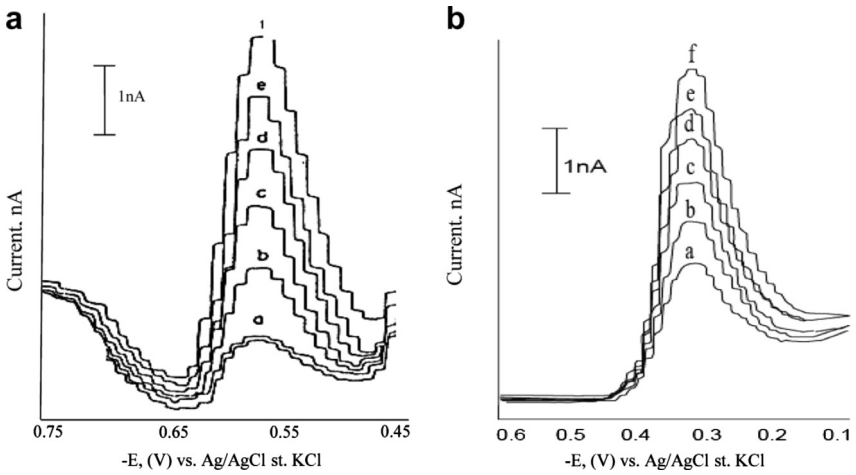

Figure 3 (a-b) DPAS Voltammograms for the determination of Cd^{2+} and Pb^{2+} in 225 g and 355 g (M), respectively. River Nile each with different concentrations of Cd^{2+} and Pb^{2+} ions in 0.056 M HNO_3, pH~2 at deposition potential −0.75 and −0.6 V and deposition time 120 s (medium part). (a) Sample 225and 355 (M) (b) S. + 1×10^{-9} and 2×10^{-8} (c) S. + 2×10^{-9} and 4×10^{-8} (d) S. + 3×10^{-9} and 6×10^{-8} (e) S. + 4×10^{-9} and 8×10^{-8} (f) S. + 5×10^{-9} and 1×10^{-7} M Cd^{2+} and Pb^{2+}, respectively.

Table 3 Cadmium concentrations of River Nile and Lake Nasser fishes ($ng \cdot g^{-1}$).

Location	*n*	M	Mean ± SD			Minimum			Maximum		
			H	M	T	H	M	T	H	M	T
River Nile (Aswan)	17	DPASV	13.84 ± 1.95	10.19 ± 5.75	9.37 ± 3.32	11.62	5.97	3.96	16.32	23.91	15.97
		FAAS	13.78 ± 1.86	10.22 ± 5.78	9.33 ± 3.32	12.00	6.00	4.03	16.18	24.00	16.06
Lake Nasser	12	DPASV	18.43 ± 2.82	11.76 ± 3.23	12.10 ± 2.65	13.75	6.00	7.98	23.98	16.09	17.56
		FAAS	18.45 ± 2.79	11.78 ± 3.23	12.22 ± 2.73	14.00	6.00	8.00	24.00	16.00	18.00

or by ingested contaminated food and beverages. Cadmium also can be found in water supplies through dumping of industrial wastes as well as other mechanisms.(Schroeder and Balassa, 1963) Its compounds are used as pigments, fungicides and anthelminties. Once ingested, a number of symptoms may occur including hypertension and interference with iron metabolism. (Underwood, 1971)

Lead concentrations in the Nile Perch fish samples ranged from 26 $ng \cdot g^{-1}$ to 168 $ng \cdot g^{-1}$ (head part), in the medium sample, lead disappeared in all weights except in the 310 g weight (250 $ng \cdot g^{-1}$), 355 g weight (24 $ng \cdot g^{-1}$), 660 g (124 $ng \cdot g^{-1}$), and 825–1400 g weight (4 $ng \cdot g^{-1}$), while in the tail sample lead was observed only in two samples, 660 g (22 $ng \cdot g^{-1}$) and 1400 g (10 $ng \cdot g^{-1}$). In Lake Nasser Perch fish samples, lead ranged from 80 $ng \cdot g^{-1}$ to 286 $ng \cdot g^{-1}$ (head part), from 38 $ng \cdot g^{-1}$ to 120 $ng \cdot g^{-1}$ (medium part) and from 16 $ng \cdot g^{-1}$ to 94 $ng \cdot g^{-1}$ (tail part). It can be observed that, lead was found in all head samples through Nile and Lake samples, was also found in higher concentration values in the Lake samples than the Nile samples, this may be due to the water nature in the Nile and the Lake. Lead is a toxic element and is known to react with free sulfhydryl groups which make them unavailable for certain enzyme catalyzed reactions and as a result interferes with the production of heme, and it accumulates in both plants and animals tissues (Khana et al., 1976). The variations in the correlation coefficient (trace elements) between Perch fish samples may be attributed to accommodation of these elements within minerals, already exist in the deposits particle through the Nile and the Lake.

3.8. Environmental effects

Lead in the environment is mainly particulate bound with relatively low mobility and bioavailability. Lead bioaccumulates

Table 4 Lead concentrations of River Nile and Lake Nasser fishes ($ng \cdot g^{-1}$).

Location	*n*	M	Mean ± SD			Minimum			Maximum		
			H	M	T	H	M	T	H	M	T
River Nile (Aswan)	17	DPASV	100.31 ± 48.02	45.32 ± 86.67	3.67 ± 7.91	26.03	0	0	166.92	250.09	22.85
		FAAS	100.44 ± 48.14	45.11 ± 86.72	3.56 ± 7.67	26.00	0	0	168.00	250.00	22.00
Lake Nasser	12	DPASV	180.99 ± 66.42	59.79 ± 35.41	48.25 ± 27.43	80.00	0.0096	15.89	285.37	121.12	93.26
		FAAS	180.89 ± 66.68	59.56 ± 35.03	48.22 ± 27.43	8.00	0	16.00	286.00	120.00	94.00

H: Head of fish M: Medium T: Tail.

Table 5 Toxicity of lead in aquatic environments and bio-concentration factors.

Species, effect	Concentration (mg/kg)
Toxicity in fresh water	
Plankton algae (EC_{50}-growth rate, etc.)	140–11.000
Crustaceans (Chronic)	10–200
Crustaceans (acute)	100–224.00
Fish (chronic)	0.4–220
Fish (acute)	1.00–540.00

in most organisms, in particular in biota feeding primarily on particles, e.g. mussels and worms. In general there is no increase in the concentration of the metal in food chains (biomagnification). Whereas many metals are converted to organic forms by microorganisms in the soil, there is little evidence to suggest that the natural production of methylated lead has any general environmental significance. The distribution of lead within animals is closely associated with calcium metabolism. In shellfish, lead concentrations are higher in the calcium-rich shell than in the soft tissue. In dolphins, lead is transferred from mothers to offspring during fetal development and breast-feeding. Lead accumulates in the bones of animals like it does in humans. The following information has largely been extracted from the IPCS monograph/WHO 1989 (WHO, 1990; FAO-WHO, 1972; FAO-WHO, 1989)/ unless otherwise indicated Table 5.

3.9. Cadmium Suppin et al. (2005)

In previous work, Cadmium and lead were determined in different tissues (muscle, gill, stomach, intestine, liver, vertebral column and scales) of Tilapia nilotica from the High Dam Lake, Aswan (Egypt) to assess the lake water pollution with those toxic metals. Fish samples were chosen to be analyzed along with samples of the aquatic plant (Najas armeta), sediment and lake water. The results showed that cadmium and lead concentrations were higher in fish scales and the vertebral column than in the other parts of the fish. The higher concentrations of cadmium and lead in Lake Nasser perch fish (Tilapia nilotica) were a result of the pollution which uptake from aquatic plants, sediments and gasoline containing lead that leaks from fishery boats. Tilapia nilotica fish was used as a good bio-assay indicator for lake pollution with cadmium and lead. The fish muscles in these studies were in the safety baseline levels for human consumption (Rashed, 2001). Cadmium levels in fish from the two locations were well below the normal range (0.02 μg/g) The PTWI (permissible tolerable weekly intake) of cadmium has been set at 7 μg/kg body weight (FAO-WHO 1989, 1972), equaling 420 μg cadmium/week for a 60-kg person. In our observation, the metal cadmium was also below the normal estimated values as shown in Table 3.

3.10. Lead Atuanya et al. (2011)

Fish are a high-protein, low-fat food that provide a range of health benefits. Fish are lower in fat than any other source of animal protein, and oily fish are high in omega-3 fatty acids. As our body does not make significant amounts of these nutrients, fish are an important source. However, most fish nowadays have lost their nutritional values due to environmental pollution. The impact of pollution on fish and the potential health implications of eating contaminated fish are areas of considerable concern for the government bodies and general public. Fish consumes much of the toxic wastes which are polluted materials discharged into their ambient environment. These toxic wastes are usually industrial wastes, sewage, pesticides and heavy metals such as mercury and cadmium.

Lead absorption may constitute a serious risk to public health. Lead may induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular diseases in adults. Over the past decade the levels in food have decreased significantly owing to the awareness of lead as a health problem and source related efforts to reduce the emission of lead. The EC concluded in its opinion of 19th June 1992, that whereas the mean level of lead in foodstuffs does not seem to be a cause for alarm, long-term action should follow with the objective of further lowering the mean levels of lead in foodstuffs. Therefore, the maximum levels should be as low as reasonably achievable. Similarly, levels of lead in fish from four locations were also below the permissible level which is 1.5 μg/g. FAO of the United Nations and WHO (1990) has established a provisional tolerable weekly intake (PTWI) of lead as 25 μg/kg body weight for humans, equaling 1,500 μg/g lead/week for a 60-kg person. It was observed that the intake of lead through fish from the locations such as the Aswan city and the Lake Nasser was well below this limit as shown in Table 4.

4. Conclusions

In the present study, the samples were lyophilized, milled and then mineralized in a closed low temperature microwave oven. Then the mineralized samples were dissolved in mixed acid (HNO_3 + $HClO_4$) and Zinc and Copper concentrations were determined by DPASV, differential pulse anodic stripping voltammetry by Hanging Mercury drop electrode (HMDE), using an auto sampler. DPASV has some important advantages, such as simultaneous determination of up to 4 elements, low contamination risk and high precision (Celik and Oehlenschläger, 2004).

In addition, it was found that the stripping voltammetry results indicate that the mean levels of Cd^{2+} and Pb^{2+} ions ranged from 5.97 $ng{\cdot}g^{-1}$ to 23.90 $ng{\cdot}g^{-1}$ and from 4.03 $ng{\cdot}g^{-1}$ to 250.00 $ng{\cdot}g^{-1}$ (Nile medium parts) and also, from 6.00 $ng{\cdot}g^{-1}$ to 16.09 $ng{\cdot}g^{-1}$ and from 37.88 $ng{\cdot}g^{-1}$ to 121.12 $ng{\cdot}g^{-1}$ (Lake medium parts), respectively. On the other hand, the mean levels obtained using atomic absorption spectrometry of the same elements mentioned above ranged from 6 $ng{\cdot}g^{-1}$ to 24 $ng{\cdot}g^{-1}$ (Cd) in the Nile medium parts of the Perch fishes, also, there is no lead detected in the Nile medium parts except in the weights of 310–355 g and from 6 $ng{\cdot}g^{-1}$ to 16 $ng{\cdot}g^{-1}$ and 38 $ng{\cdot}g^{-1}$ to 120 $ng{\cdot}g^{-1}$ (Cd and Pb) in the Lake Nasser medium parts of Perch fishes.

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