

## Electroanalytical Determination of Cadmium and Lead in Marine Samples\*

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The possibilities of cadmium and lead determination by electroanalytical methods such as differential pulse anodic stripping voltammetry, square wave anodic stripping voltammetry, potentiometric stripping analysis and constant current stripping potentiometry in sea water, algae, bivalves, fish and seal samples after different digestion methods (UV, PTFE-bomb and high pressure) have been presented. The comparison with ICP-MS and ET-AAS demonstrated the possibilities and limitations of these electroanalytical approaches with respect to the trace element determination in real samples from marine ecosystem.

### INTRODUCTION

The chemical species and the binding state in which metals exist in the sea is of particular significance, because these are taken up by organisms and thus enter into the marine food webs. Although normal levels of cadmium and lead ions dissolved in sea water are very low (typically 100 ng/L to less than 0.1 ng/L) they are of great significance as they are accumulated by adsorption on suspended particulate inorganic and organic matter; they interact with and are incorporated in marine sediments and marine organisms. Cadmium and lead enter the marine food chain and are significantly accumulated at the lowest trophic level (ng/L) from which they are transferred to the higher trophic levels (mg/kg).

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\* Dedicated to Marko Branica on the occasion of his 65<sup>th</sup> birthday.

Electroanalytical techniques offer indeed exceptional possibilities for the determination, speciation, and physicochemical characterization of cadmium and lead in sea water, particular matter, sediments, and marine organisms.<sup>1</sup> A number of literature exist, which describe the use of electroanalytical techniques in lead and cadmium determination in marine ecosystem.<sup>2</sup> Because of differences in methods used in preparation and determination, it is difficult to compare all the data and conclude about the kind of samples from marine ecosystem suitable for the determination of lead and cadmium by electroanalytical techniques.

From the experiences of over 10 years in using different analytical methods (ET-AAS, SS-AAS, IDMS, ICP-MS) for the determination of different elements in environmental samples, only the results of cadmium and lead determination by different electroanalytical techniques in real marine samples will be presented. Sample collection and preparation are two of many factors which can influence the accuracy of analytical data. The importance of electroanalytical techniques in routine cadmium and lead determination in samples from marine ecosystem will be demonstrated.

### *Method Description*

*Anodic stripping voltammetry* (ASV) is the most widely used form of stripping analysis. In this case, the metals are preconcentrated by electrodeposition into a small-volume mercury electrode (a thin mercury film [MFE] or a hanging mercury drop [HMDE]). The preconcentration is done by cathodic deposition at a controlled time and potential. The deposition potential is usually 0.3–0.5 V more negative than  $E^\circ$  for the least easily reduced metal ion (e.g. zinc, cadmium, lead, and copper) to be determined. The metal ions reach the mercury electrode by diffusion and convection. The convective transport is achieved by electrode rotation (for MFE) or solution stirring (for MFE or HMDE). The duration of the deposition step is selected according to the concentration of the metal ions in question, i.e. 0.5 min deposition at the  $10^{-7}$  M to 10 min (for HMDE) or 30 min (for MFE) at the  $10^{-11}$  M solutions. Following the preselected time of deposition, the forced convection is stopped, and the potential is scanned anodically, linearly, or in a more sensitive potential-time (pulse) waveform that discriminates against the charging background current (usually square wave [SW-ASV] or differential-pulse [DP-ASV] ramps). During this anodic scan, the amalgamated metals are re-oxidized, stripped out of the electrode, which produces an electric current. The voltammetric peaks (potential-time curve) reflects the time-dependent concentration gradient of the metal in the mercury electrode during the potential scan. Peak potential serve to identify the metals at the sample and peak current the concentration.

*Potentiometric stripping analysis* (PSA), differs from ASV in the method used for stripping the amalgamated metals. In this case, the potentiostatic

control is disconnected, and the preconcentrated metals are reoxidized by an oxidizing agent (e.g., oxygen, mercury ions) which is present in the solution. During the oxidation step, the change of the working electrode potential *vs.* time is recorded. A sharp potential steps accompanies the depletion of each metal from the electrode. The time needed for the oxidation (transition time) of a given metal is a quantitative measure of the metal concentration in the sample. Modern PSA instruments use microcomputers to register fast stripping events (as time can be monitored with extremely high resolution by the computer clock) and to convert the wave-shaped response to a more convenient peak over a flat baseline. The use of nondeaerated samples represent an important advantage of PSA. In addition, this method can accommodate electrodes of any size, thus eliminating the need for amplification when microelectrodes are used.

## EXPERIMENTAL

*Samples and sample pretreatment.* Surface sea water samples were taken in conditioned 2 L polyethylene bottles from different sampling areas 6 times in the year. Water samples were filtered directly after sampling (0.45  $\mu\text{m}$  filters) and the filtrate was acidified to pH 2 with HCl (suprapur Merck). Samples were deep frozen at  $-20\text{ }^{\circ}\text{C}$  for transportation and stored at this temperature until thawing overnight before electrochemical determination.

At the collection sites the environmental samples are prepared in mobile laboratories, for instance dissection of fishess, following by immediate storage in special containers above liquid nitrogen. After that the cryogenic chain which provides temperatures below  $-150\text{ }^{\circ}\text{C}$  is not interrupted including final storage at the Environmental Specimen Bank facility in Jülich.<sup>3</sup> This procedure reduces chemical alteration to a minimum. After grinding, homogenization and aliquotation most of the powder subsamples are stored in the bank. Some subsamples are used for an initial analytical characterization with respect to selected organic and inorganic compounds, species and elements.

Harbour seals study was based on two groups of samples collected at the University of Kiel in autumn of 1982 at the Schleswig-Holstein coast (»blank values«). It consists of 9 livers and 9 kidneys from different seals and one liver and kidney from the same animal. From these, 19 seals, one was found dead and 18 were shot. The samples were stored at  $-20\text{ }^{\circ}\text{C}$ . The age was determined by counting annual growth layers in teeth cementum. The second group of material were collected during summer 1988. The seven seals found dead in Schleswig-Holstein were autopsized and the liver and kidney samples were collected and frozen. The age of this animals was determined only approximately and all the animals were classified into the three age groups: < 12 months, < 24 months and > 24 months.

Sea water samples were digested by UV irradiation before voltammetric determination.

Fresh powder samples were investigated for mercury and mercury species by using cold vapor atomic absorption spectrometry as detection technique. The other pro-

cedures are applied after freeze-drying of the material. Solid samples were analyzed directly by solid sampling AAS and instrumental neutron activation. The other method requires dissolution of the powders by means of pressurized or even high-pressure digestion.

*Equipment.* TraceLab with SAC80 Sample Changer and ABU93 Triburette (Radiometer, Germany) was used for potentiometric stripping analysis (PSA). 693 VA Processor with 695 Autosampler (Metrohm, German) was used for differential pulse anodic stripping voltammetry (DPASV). Model 384B Polarographic Analyzer with 303A SDME (EG&G, Germany) was used for square wave ASV determination. High pressure asher (HPA, Kürner, Rosenheim, Germany) and PTFE bomb (Prawol, Fleischhacker, Germany) were used for sample digestion.

*Chemicals.* Nitric acid was subboiled before use for digestion. All other chemicals were of suprapure quality. Water from a Milli-Q-System (Millipore, Germany) was used in cleaning, dilution and determination steps.

*Digestion procedures.* One of the most prominent decomposition methods during the past years has been the wet chemical decomposition with nitric acid in PTFE bombs. Bomb decomposition offers a great advantage that many substances which are inert towards nitric acid at lower temperatures may be attacked successfully at higher temperatures, and also an additional bonus is that the loss of volatile reaction products is avoided, unless of course there is an escape of gases when the bomb is opened after cooling. This method however is hampered by a major disadvantage. The decomposition temperature can not exceed 200 °C because there is loss of the mechanical stability of PTFE at high temperatures. Frequently, the decomposition process at this temperature proceeds sluggishly and is incomplete. This digested solution can not be used for subsequent voltammetric determination. However, in some matrices it is possible to determine lead and cadmium by PSA.

To avoid the problem of the loss of mechanical stability at high temperature, vessels made from quartz is used in a new pressure decomposition system (high pressure ashing, HPA).<sup>4</sup> Different sizes of vessels (2–70 mL) are available to optimally decompose samples varying in weight from few mg to 1.2 g. Depending upon the size of the digestion vessel up to seven units are placed inside the autoclave. A micro-processor temperature control allows a wide variety of temperature programs.

Due to complete decomposition of organic substances, this digestion method is highly suitable for electrochemical determination. It is possible to determine Zn, Cd, Pb, Cu, Ni and Co in different matrices using HMDE or MFE with different electrochemical detection methods. Low element blanks by HPA digestion make it possible to determine these elements also at very low concentration level, as observed in some environmental matrices (e.g. fish).

For the digestion 0.2 g of dry sample was mixed with 2 mL of subboiled nitric acid in digestion vessel (made from quartz for HPA digestion or made from PTFE for Prawol system). After closing the vessels in appropriate devices the digestion was started. The end digestion temperature were 300 °C for HPA and 180 °C for PTFE-bomb. The colourless solutions has been transferred to a 10 mL volumetric flasks and diluted with water.

*Determination procedures.* Cadmium and lead were determined by square wave or differential pulse anodic stripping voltammetry as well as potentiometric stripping analysis (PSA). For voltammetric determination supporting electrolyte was 0.02 M



perchloric acid. Deposition potential was  $-0.9$  V *vs.* sat. Ag/AgCl electrode. PSA was used for cadmium and lead determination in samples after PTFE-bomb digestion. Supporting electrolyte was  $0.01$  M hydrochloric acid with  $80$  mg/L  $\text{Hg}^{2+}$ . Deposition potential was  $-1.15$  V *vs.* sat. Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode. Deposition time was correlated to the element concentrations in the sample.

## RESULTS AND DISCUSSION

### *Seawater*

Trace metals in water exist partly in solution and partly in suspension adsorbed to organic or inorganic particulate matter. In addition a certain amount of metal exists in colloids or chelates, which may be difficult to assign to either soluble or particulate fraction. The assignment of metals in water to soluble and particulate fraction is arbitrary, being based on whether the metal passes through or is retained by a filter of pore diameter of  $0.45$   $\mu\text{m}$ . The proportion and absolute amounts of metal in each fraction vary with the metal considered, the particulate content and its nature and the time and location of sampling (Table I). Data presented in Table I demonstrate a significant difference between cadmium and lead present in the solution and in the particular fraction.

In seawater the major portion of total cadmium content is present in the form of »free« ions. Only a small part of cadmium is bound to the particulate matter. For lead the opposite situation is observed. More than 90% of total lead content is bound to a particulate matter. The major disadvantage of water analysis as a means of comparing the degree of metal pollution, on different locations, is the large variation in concentration of metals found in water with differences in season, time of day, the extend of freshwater run-off, depth of sampling, intermitted flow of industrial effluent and hydro-

TABLE I

Relationship between element concentration in water and total element concentration ( $c_{\text{diss}}/c_{\text{total}}$ , %) in time and space.

Sampling area	Cuxhaven		Eckwarderhörne		Nordstrand		Sylt		Altenbruch	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
Sampling time										
February	63.7	1.7	57.1	1.1	91.8	6.1	47.5	0.8	28.0	0.9
April	75.9	2.3	53.5	3.3	78.9	3.3	66.4	1.9	25.2	3.0
June	15.8	1.1	28.6	3.5	86.2	15.3	58.1	9.2	31.6	0.9
August	95.0	10.3	96.1	13.2	80.0	6.8	22.8	1.6	82.8	2.8
October	77.3	30.9	61.3	1.4	82.1	31.4	72.5	0.6	78.5	2.4
December 89	95.1	10.2	57.6	2.5	90.2	11.7	35.3	12.5	27.3	8.1

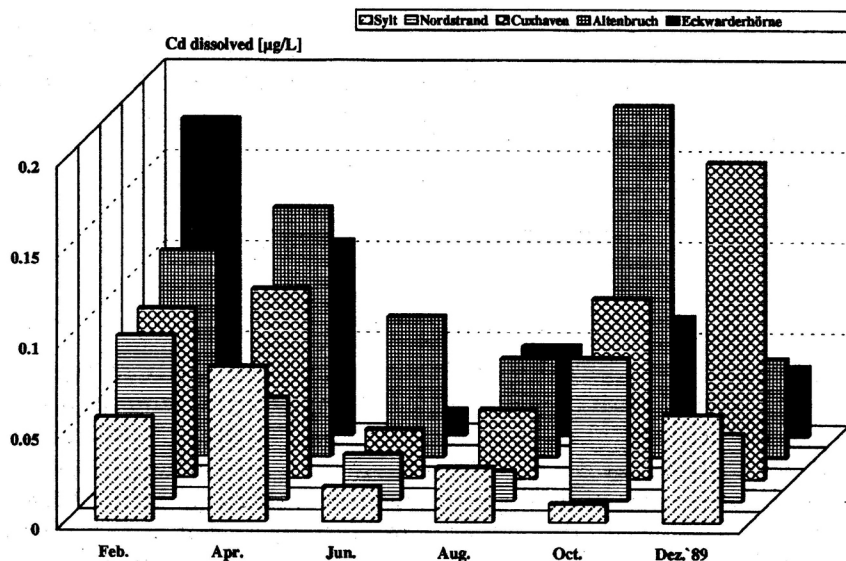


Figure 1. Change of dissolved ( $< 0.45 \mu\text{m}$ ) cadmium in sea water in time and space.

logical factors such as tides and currents. The variation of cadmium concentration with sampling time and sampling area has been presented in Figure 1 and it appears to be high.

Dissolved cadmium concentration changes from 0.002 to 0.09  $\mu\text{g/L}$  in one sampling area (Sylt) and from 0.001 to 0.2  $\mu\text{g/L}$  between different sampling areas.

### *Sediments*

Variations of trace element concentration found in marine sediments occur according to the rate of trace metal deposition, the rate of particle sedimentation, the particle size and the nature and the presence or absence of organic materials. For some non-nuclear analytical techniques the digestion of the sediment sample is necessary. The concentration of some elements found depends very strongly on digestion method used. Due to high silica content in sediment samples, hydrofluoric acid is employed for complete digestion. Data presented in the Figure 2 demonstrate that there are no large differences between cadmium and lead concentrations found by DPASV after high pressure digestion (HPA) or by PSA after digestion in PTFE-bomb. For cadmium and lead determination in sediment, a pressurized digestion with nitric acid only is sufficient to extract nearly all these elements from the sediment samples. The found concentrations agree well with certified values. For real sediment samples three major problems exist. Firstly, the ele-

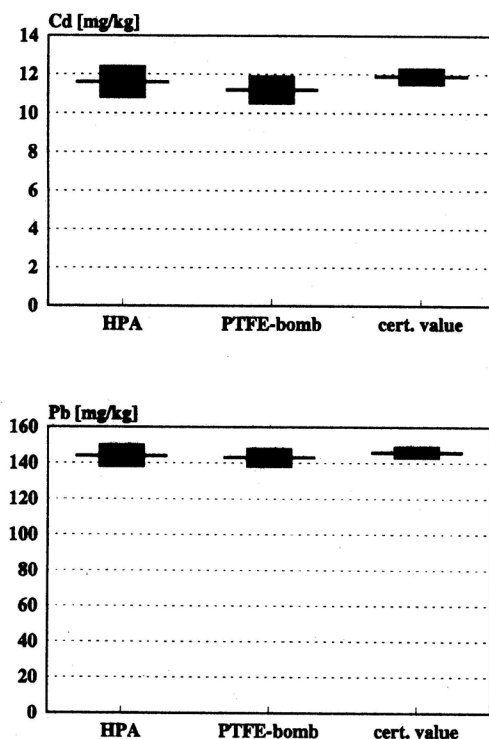


Figure 2. Cadmium and lead concentration found by electroanalytical methods in reference material Estuarine sediment BCR 277.

ment concentration change nearly linear with the particle size. It is very difficult to collect each time the samples with the same particle size distribution. Secondly, the concentration of a metal found in sediments increase in approximately linear fashion with increased organic content. Without the knowledge about the organic and total carbon content in the sediment sample, it is very difficult to interpret the analytical data. Thirdly, even if a complete and accurate data about the elemental concentration in sediments is available, no data exist about the biological availability of elements to the biota.

### *Macroalgae*

Chemical constituents and metal levels in algae may vary considerably between the different tissue type, age, and according to the microhabitat and season. Brown algae are known to have high metal accumulation abilities which reflects the ambient concentrations of dissolved metals in surrounding waters.<sup>2</sup>

Biological activity in the sea has an influence on the total concentration of elements in macroalgae. Cadmium and lead concentration in *Fucus vesiculosus* change with the season.<sup>3</sup> In months with high biological activity (summer) the concentration of lead and cadmium related to dry weight are less than in winter. This effect can reflect the concentration of lead and cadmium in surrounding water but also can reflect the effect of algae growth. Concentration levels for cadmium and lead observed in macroalgae (higher than 1 mg/kg dry weight) are suitable for the determination by all analytical techniques. In Table II some results of cadmium and lead determination in *Fucus vesiculosus* (North Sea) and *Ulva rigida* (Atlantic Ocean) in the interlaboratory comparison organized in 1994 are presented. The analytical results obtained by the both electroanalytical techniques (DPASV and PSA) are very similar to those found by other well established analytical methods.

TABLE II  
Interlaboratory comparison: cadmium and lead determination in  
*Fucus vesiculosus* and *Ulva rigida*.

		Determination methods				
		ET-AAS	ICP-MS	IDMS	DPASV	PSA
<i>Fucus vesiculosus</i>	Cd*	1.20 ± 0.10	1.27 ± 0.17	1.24 ± 0.04	1.26 ± 0.07	1.17 ± 0.09
	Pb*	2.90 ± 0.20	2.95 ± 0.05	2.87 ± 0.02	2.65 ± 0.16	2.82 ± 0.12
<i>Ulva rigida</i>	Cd*	120 ± 10	102 ± 4	108 ± 3	98 ± 7	95 ± 11
	Pb*	0.76 ± 0.07	0.88 ± 0.04	0.87 ± 0.02	0.94 ± 0.06	1.01 ± 0.09

ET-AAS: electrothermal atomic absorption spectrometry

ICP-MS: inductively coupled plasma – mass spectrometry

IDMS: isotope dilution mass spectrometry

DPASV: differential pulse anodic stripping voltammetry

PSA: potentiometric stripping analysis

\* Concentrations in mg/kg dry weight

### *Bivalves*

Because of their capacity to accumulate metals from the environment, bivalves have been widely used as qualitative biological indicators of metal pollution. Theoretically bivalves may also be used to quantify the degree of pollution to which they have been exposed. The quantification of pollution has two aspects: to assess relative degree of pollution by comparison of metal levels in the tissues of bivalves from different areas and to calculate average metal levels in the surrounding water by using rates of metal accumulation in bivalve tissue.<sup>5</sup> Due to two different accumulation ways (food chain and surrounding water) the change of element concentration with time is not as characteristic by bivalves, as by macroalgae. There are many biological, physical and chemical parameters which influence cadmium and lead concentration in bivalves.

Bivalves similar to macroalgae can be used for cadmium and lead monitoring in the sea. Figure 3 presents the cadmium distribution in *Fucus vesiculosus* and *Mytilus edulis* collected in different sampling areas in the North Sea.

Macroalgae represent mainly the situation in surrounding water whereas mussels indicate also other biological processes. From the measurements of collected bivalves samples in this ecosystem, cadmium and lead concentrations were found to be between 0.5 to 2.5 mg/kg and 1.5 to 2.5 respectively.

### Fish

Fish can accumulate elements only through the food chain. For bivalves, it was demonstrated<sup>6</sup> that the cadmium uptake via food played an insignificant role compared to direct uptake from ambient water. Due to this difference in accumulation ways, it can be expected that not only cadmium but

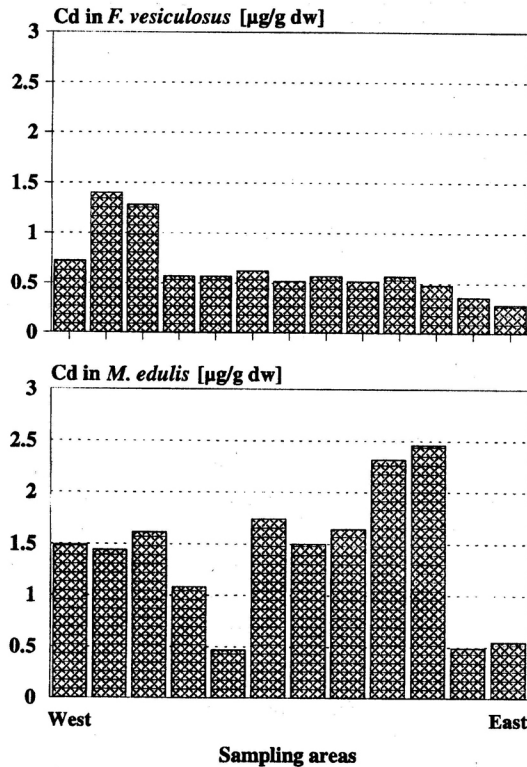


Figure 3. Cadmium concentrations in macroalgae and bivalves collected in the North Sea 1991.

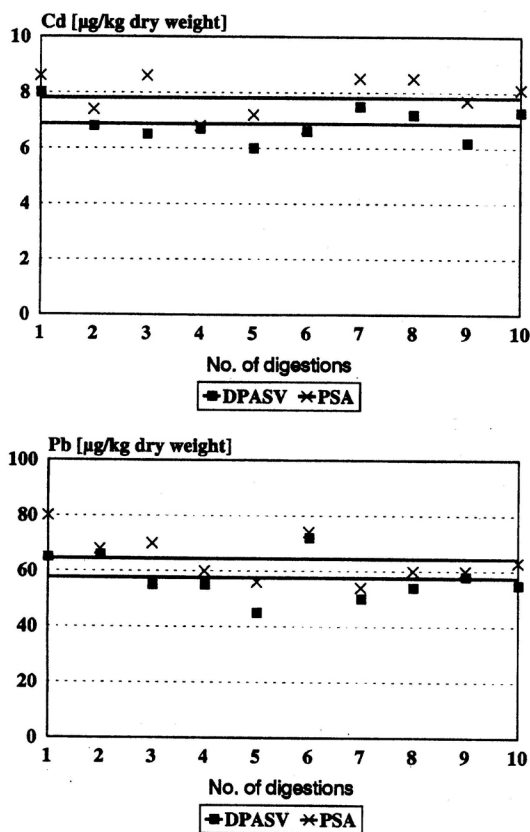


Figure 4. Reproducibility of cadmium and lead determination by PSA and DPAS in fish tissue after HPA digestion.

also lead concentration in fish tissue is very low. Only in the fish kidney or liver higher concentrations of these elements could be found. PSA and differential pulse anodic stripping voltammetry (DPASV) were used for cadmium and lead determination in fish muscle samples. Figure 4 present the reproducibility and comparability of PSA and DPASV determination at low  $\mu\text{g/kg}$  level in the internal reference material »fish muscle«.

### *Harbor Seals*

After the seal catastrophe in Denmark in the Kattegatt area, perhaps in February 1988, the first signs of an unusually high mortality rate were found in March 1988, close to the Danish border. This rate started to increase rapidly in May 1988. The number of victims grew and the amount

per decade reached its peak in the middle of August 1988 with 877 seals dead. More than 6000 dead seals have been recorded at the west coast of Schleswig-Holstein in 1988.<sup>7</sup> It is well known that several metals and other environmental contaminants such as pesticides or PCB's accumulate in marine mammals.<sup>8</sup> The potential hazard of heavy metals to marine mammals is primarily through biological magnification in the oceans and seas, as residues of heavy metals bioaccumulate in marine mammals to levels that are often 100 to 1000 times greater than in lower marine life forms.

It has to be noted that sample pretreatments and analytical techniques used were often different and therefore quantitative results may vary considerably, especially when residue levels in tissues of seals originating from two sampling areas have to be tested. Therefore, the data from literature alone may lead to unreliable conclusions.

Age of mammals is a very important factor which can influence the element concentration in kidney and liver.<sup>9</sup> Only in one group of samples the age of seals was determined. Figure 5 presents the observed change of cadmium concentration in kidney.

There are three characteristic ranges. For very young seals, the cadmium concentration deposited in organs increase slowly. Probably during this time, the mothers milk is the most important part of the food chain. After this short period, the cadmium concentration change very rapidly and increase to a level of more than 1 mg/kg. This level of cadmium is then more or less stable, which indicates that the accumulation kinetic is similar to excretion kinetic and a dynamic equilibrium exists. Cadmium concentration observed in the kidney and liver samples collected in 1982 and in 1988 are similar.

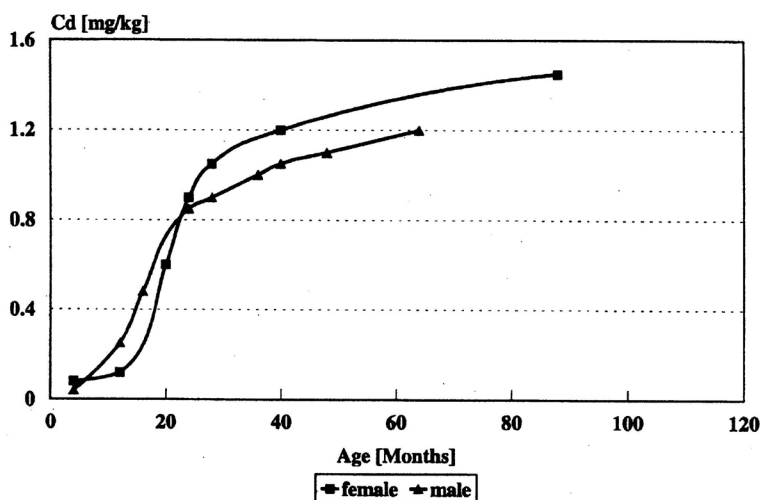


Fig. 5. Influence of the seals age to cadmium concentration in kidney samples.



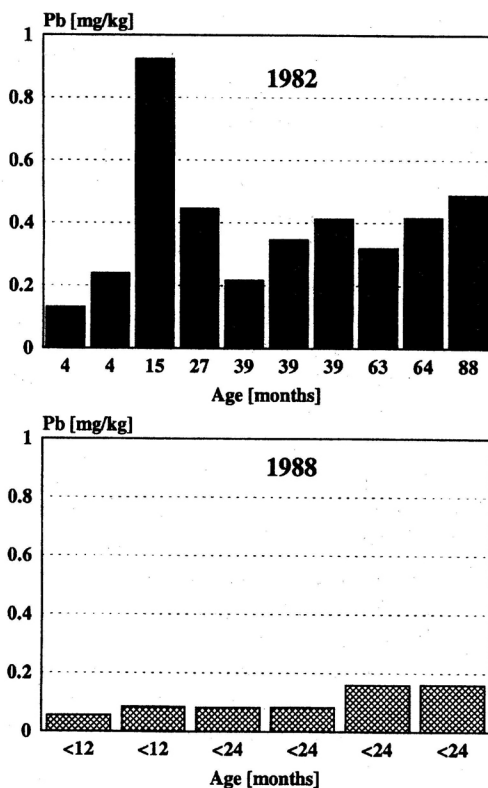


Fig. 6. Influence of the seals age to lead concentration in kidney samples in two sampling periods (1982 and 1988).

Age of the seals does not influence the lead concentration in liver and kidney samples (Figure 6). Lead concentration found in liver and also in the kidney samples, differ significantly in both groups. Lead concentration found in samples from 1988 are significantly lower than found in the samples from 1982. This difference can be due two reasons: first the lead concentration in the food chain changed significantly during the period 1982 to 1988, or second the contamination of kidney and liver by Pb, as the samples were collected by shooting the seals in 1982.

## CONCLUSIONS

Electroanalytical method like DPASV or PSA are able to determine cadmium and lead in all kinds of samples presented in the marine ecosystem. Appropriate determination procedures make it possible to determine elements

at concentration levels of a few ng/L in sea water, µg/kg dry weight in fish tissue or high mg/kg level in sediment or seal kidney samples. Equipment development with automation of all analytical steps make the electrochemical determination easy and does not depend on individuals. Completely digested samples are needed for the DPASV determination. By PSA, it is also possible to determine cadmium and lead after PTFE-bomb digestion or microwave digestion.

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## SAŽETAK

### Elektroanalitičko određivanje kadmija i olova u morskim uzorcima

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Prikazane su mogućnosti određivanja kadmija i olova elektroanalitičkim metodama kao što su diferencijalna pulsna i pravokutnovalna voltometrija s anodnim otapanjem te potenciometrijska analiza otapanja u morskoj vodi, algama, školjkama, ribi i uzorcima tuljana nakon primjene različitih postupaka razaranja (UV, teflonska bomba i visoki tlak). Usporedbom s ICP-MS i ET-AAS opisane su mogućnosti i ograničenja tih elektroanalitičkih postupaka s obzirom na određivanje tragova elemenata u stvarnim uzorcima iz morskog ekosustava.