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Determination and Speciation of Trace Heavy Metals in Natural Water by DPASV

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1. Introduction

The aim of water preservation within each country seeks to be achieved through the increased concern about the water, which often means controlling of the water quality. Chemical analysis and speciation of traces of heavy metals such as lead, cadmium, zinc, copper, etc. is of great importance.

The heavy metals also includes number of physiologically important elements such as Cu, Fe, Zn; than the highly toxic Pb, Mn, Cd, hg, As, Sb and less toxic as Au, Ag and Cr, etc. [1]

The most important anthropogenic sources of metals in aquatic ecosystem are certainly wastewaters, that are being discharged untreated or with different levels of purity, so they can cause many changes in the stream / recipient. Heavy metals pass go through biogeochemical process with different retention time in different parts of atmosphere. They do not decompose and have the ability of bioaccumulation, because they are being retained in plants, animals and nature in general. This is an extremely heterogeneous group of elements in terms of biological and ecological effects. Large numbers of metals is essential for proper functioning of the human body and appertain to the group of essential elements. A deficiency of heavy metals on one side can lead to serious symptoms; and on the other, their presence in slightly elevated concentrations can lead to serious illnesses. Their toxicity depends on concentration, and the allowed concentration range varies from metal to metal. Concentrations in which heavy metals can occur depend from source of pollution and features of system in which they are found, so they can range from traces to very high concentrations. Water, as well as air can receive large amounts of pollutants, but beside ability of self-cleaning, some pollutants among which are also heavy metals leads to modification of water quality to that level that it becomes useless for many purposes. From that reason most of European countries have issued maximum allowed amount of heavy metals in industrial waters that are being discharged into natural flow. Some of those values are given in table 1.

According to the data in table 1, Belgium has the most rigorous regulations regarding maximum allowance of heavy metal concentration.

In water, heavy metals are being rapidly degraded and sediment in the form of hard soluble carbons, sulphats and sulphids on the bottom. At the time when the absorptive capacity of sediment is exhausted, the concentration of metal ions in water is increasing. (Goletić 2005).

Features of these dissolved metals in water will depend on nature of other metal components dissolved in the water. Heavy metals in water appear in different chemical forms and in different oxidizing conditions, so their toxicity is changing depending on chemical form in which they are found. Therefore, the knowledge of total concentration of metals in contaminated water is often insufficient for the proper information regarding their harmful effect. Toxicity, biodegradability, bioaccumulation, mobility, solubility, as well as number of other important characteristics in particular depend on specific physical - chemical form in which the metal is found. Most studies on the topic of toxicity of heavy metals shows that the free hydrated metal ion is the most toxic form,^[2] because the free metal ion is significantly easier and faster absorbed on suspended particles or colloids.

Metal	Germany	Slovenia	Hungary	Italia	Belgium
Pb	0,5	0,5	0,05-0,2	0,2	0,05
Cd	0,1	0,5	0,005-0,01	0,02	0,005
Cu	0,5	0,5	0,5 -2,0	0,1	0,05
Zn	-	1,0	1,0-5,0	0,5	0,3
As	-	0,1	0,05	0,5	0,05
Fe	-	2,0	10-20	2,0	-
Cr	0,5	1,0	0,2-1,0	2,0	0,05

Table 1. Maximum allowed concentrations (mg/l) in industrial wastewaters of some European countries.

Heavy metals can also appear in the form of inorganic and organic complexes, tied to colloid fraction (as polyhydroxid complex and polysilicate), as polymers and pseudocolloids (metal hydroxides, humic acid) and tied on suspended particles or live organisms (e.g. Microorganisms). Appearance of different heavy metal chemical forms will depend also from chemical nature of given heavy metal, conditions of environment, presence of complexation substances, colloid dispersion, etc.^[3] To what extent will heavy metals in water be mobile, depends from number of parameters:

- pH of water
- Presence of carbonates and phosphates
- Hydrated oxides of iron and manages
- Content of organic mater
- Sulphideions and pirit(significant for mobilization process of heavy metals in water environment).

Migration of metals and way of their allocation in water systems is controlled primarily by sediment character in water mass. Intensity of reaching metals from sediment into water depends from its physical structure and chemical nature, since they determine power (strength, binding) force of chemical elements. This means that transport of pollutants in hydrosphere goes through physical - chemical processes in water and sediment.

Chemical characteristics of heavy metals offer information regarding their mobility, relative to the extent of their availability in live organisms. In order to determine it, it is necessary to examine kinetic, thermodynamic, chemical balance, stability constant of metal complex, and do the chemical speciation.

Several methods are appropriate for the speciation of metals. From electrochemical methods those are anodic and cathodic stripping voltammetry and potentiometry; and from analytical methods, beside separation technique based on ionic exchange, extraction, dialysis and ultrafiltration are being used, as well.

In this chapter, importance of monitoring of heavy metals in natural waters and their speciation using differential pulse anodic stripping voltammetry (DPASV) are going to be pointed out. The DPASV provides the capacity of determining very low concentrations, even up to 10^{-12} mol/l.

Natural water contains various organic and inorganic species, where heavy metals build complexes with both. Today, more and more experiments related to formed mixed ligand complexes are being performed. These complexes contain more than one type of ligand, which differs from solvent molecule, and which is being located in inner coordination sphere around the central metal ion.

In this chapter, the results of examination of Modrac Lake water, used as a source of drinking water, is going to be presented. Examination is conducted in order to determine concentration and speciation of heavy metal traces (Zn, Cu and Cd). The DPASV was applied for determination of the total concentrations and stable chemical forms, while for determination of labile chemical forms software programs MINTEQA2, CHEQA and HYDRUS were used.

Analyzed water samples of lake Modrac were taken through period of four seasons and from four different characteristic locations. The experiments have shown that concentration of Cd was very low ($<10^{-11}$ mol/l), while concentrations of Cu and Zn were around 10^{-8} mol/l. The constant stability and capacity of complexation of Cu was determined, in order to observe ecological status of the water from Lake Modrac from chemical analysis aspect.

2. Importance determination of content copper, zinc and cadmium in natural water

The pollution increase, caused by heavy metals and organometallic compounds is one of the today's most serious problems. Conditionally said, the examined heavy metals are incorporated in drinking water and in entire food chain. Heavy metals, as toxic and hazardous pollutants are also present in the pesticides which are used in agriculture. The common characteristic is that all are insoluble and have tendency to accumulate in vital organs. Zinc and copper fall into metalloids category, i.e. metals of essential importance necessary for different biochemical and psychological processes in the organism and toxic only above the "exactly" determined concentration. The "concentration window" of these heavy metals is somewhere around toxic and maximum allowed limit, and it is very slight. The toxicity level of metals significantly differs and depends on their physical-chemical form. According to the World Health Organization (WHO), about 400 million people in developing countries suffer from the diseases which are caused by use of contaminated drinking water.^[4] In table 2.1. the critical concentrations of heavy metals in natural waters by EPA.^[6] are given.

Metal	Maximum allowed concentration ($\mu\text{gr/l}$)
Mercury	0.002
Arsenic	0.5
Lead	0.5
Copper	0.6
Zinc	5
Cadmium	0.04

Table 2.1 Critical concentrations of heavy metals in natural water by EPA

2.1 Copper

Copper belongs to IB group of periodic system of elements, which is characterized by electronic configuration with one unpaired element. As a result, the two compounds have a high melting and boiling point. In natural waters, copper appears during dissolution of minerals and in the range of 1-10 $\mu\text{g/l}$. The main sources of copper are wastewaters from process of manufacturing copper, refining, copper processing, and manufacturing of steel.

In water environment, copper is found in three main forms: suspend, colloid and as dissolved. Dissolved form implies free copper ions and complexes with organic and inorganic ligands. Neutral ligands, such as ethilendiamin or pirid form complexes with copper that are typical for four-coordinated compounds. Moreover, they form complexes with humic substances (in fresh water over 90% is tied to these complexes, and in salt water only 10%). This low percentage of binding in sea water is result of its replacement with calcium and magnesium. The amount of copper tied to solid particles can range up to 97% of total content in fresh water. Intensive sorption of copper is the cause of its high content in the sediment, where the intensity of sorption depends from content of humic acids, fulvic acids, pH, iron oxide and manganese, etc. When the chloride content is increased, the sorption of copper is reduced due to formation of chloride complexes, results in higher solubility and mobility. Concentrations of copper and bioavailability to aquatic system also depends on many parameters such as hardness of water, alkalinity, ionic strength, pH, redox potential, amount of present complex ligands, suspended matters and interaction of water and sediment.

2.1.1 Eco-toxicity of copper

It is generally known that copper does not represent big eco-toxicity problem. However, taking into account that copper is very widespread, and given to its big exposition from exhaust gases, it is very important is structuring of ecosystem. In small quantities copper represents an essential heavy metal necessary for proper functioning of organisms, and for activity of different enzymes.

In aquatic environment, copper accumulation results in primary exposure of aquatic organisms. Aquatic organisms can accumulate dissolved copper by direct absorption through the skin, while particles are absorbed through the food chain. When it comes to plant aquatic life, copper is absorbed in ionic form and in helatnoj form. Normal concentrations of copper in plant are generally very low, ranging from 2-20 $\mu\text{g/g}$ of dry mass. In higher concentrations they are toxic, and toxicity is more expressed with low values

of pH. However, their main source comes from wastewaters resulting from the process of copper manufacturing, refining, procession go copper and manufacture of steel. It is essential element, but in large quantities causes, so called, Wilson disease. In natural waters copper appears due to dissolution of minerals, at around of 1 - 10 μ g/l.^[5]

2.2 Cadmium

Cadmium represents one of the most toxic metals. It is usually brought into organism through an thropogenic source. It belongs to the IIB group of transition elements, which are characterized by availability of *s* and *d* orbitals. This availability explains stability of elements of this group, as well as their different physical features, compared to other transition elements.

The standard redox potential of cadmium has negative value which indicates that cadmium relatively easy oxidizes in water solutions. Especially interesting are halogen complexes of cadmium, whose formation is caused by higher cadmium concentration. These complexes are not very stable, and the most stable is tetrajodocadmiat. whose constant of stability is 10⁶dm¹²/mol. ,^[6]. In the organism, Cadmium accumulates and causes weakness or total loss of kidney, liver and pancreas functions. Furthermore, it destroys DNA and leads to damage of the red blood cells. The basis of psychological influence of cadmium has its similarity with zinc in so that cadmium replaces zinc as microelement in some enzymes which then leads to complete change of enzymes stereo-structure and its characteristic features. The researches have shown that on the bioavailability of cadmium influences also other constituents in water and food; like calcium, phosphor and steel.

2.3 Zinc

Zinc, like cadmium, has negative redox potential and ability to easy oxidize in water solution. It is essential element and has important role in biological process in organism. In water solutions, zinc behaves as very strong acidic metal, binding halogenid ions in series F⁻ > Cl⁻ > Br⁻ > J⁻. At pH 6.7, zinc in water is in divalent form which is available for sorption and forming complexes with organic substances. Same as lead and cadmium, zinc also has ability of bioaccumulation to some extent, especially in fish. Level of bioaccumulation also depends from the exposure time and conditions that are present in aquatic environment. Conditions that may influence to the toxicity of zinc in aquatic environment are water hardness (content of Ca, Mg), alkalinity, and content of humic substances. In all concentrations, higher than 100 ppm, zinc is fitotoxic.

2.4 Complex compounds of heavy metals in natural waters

Natural and synthetic organic ligands and chloride complex of metal poor sorption and increase time of deposition in water layer. Biological systems have significant impact on chemical reactions of heavy metals in water. Water plants and animals are using nutrients, excreted metabolic products, while in their organism occurs bio-concentration of heavy metals. Moreover, during microbiological degradation of organic substances, complexing agents are formed, which directly influence mobility of heavy metals in aquatic environment.

Solubility of metals in natural waters are determined and in some way controlled by three factors:

1. pH
2. type and concentration of ligand and chelating complex
3. oxidizing state of mineral components and redox environment of system

It is already stated above that metal in traces can be in suspended, colloid or in dissolved form. Suspended particles are in fact those whose diameter is higher than $100\mu\text{m}$, dissolved are those whose diameter is lower than $1\mu\text{m}$, and colloid are those whose diameter is in range from $1\text{-}100\ \mu\text{m}$. Colloid and suspended particles can consist of 1) heterogeneous mixture of metals in form of hydroxide, sulfide oxide or silicates or 2) organic matters which are tied to metal ion by absorption, ionic exchange or complexation. Besides these forms, metals in water can be also in the form of free metal ions, surrounded by coordinative molecules of water, in form of anions (OH^- , CO_4^{2-} , Cl^-) or in a form of organic or inorganic complexes with hydrated metal ion that substitutes coordinative water.

Variations in speciation of heavy metals, as well as change of their oxidation state can significantly influence their biodegradability, and therefore toxicity. Thus, for example, As (III) is much more toxic than As (V). Significant changes in nutrition can also lead to decline in biodegradability of organic compounds of heavy metals, so for example, high fiber food and proteins absorb essential elements and can cause lack of minerals. In case of copper, hydroxyl complexes are also toxic even though in lesser measures. Strong complexes and particles associated on colloid particles are usually nontoxic.

Unpolluted sea or fresh water contains very low concentrations of heavy metals like Cu, Cd, Zn, Pb, etc, mostly dissolved and absorbed on organic and inorganic colloid substances. Namely, human by itself makes toxic form, and as such release directly into waterway or causing decrease of pH transform it into reactive metal form. The table 2.4.1 provides for possible physical-chemical forms of Zn, Cu and Cd.

Physical-chemical form	Possible complex	Average diameter (nm)
Particles	Held on the filter $0,45\mu\text{m}$	>450
Simple hydrated metal ions	$\text{Cd}(\text{H}_2\text{O})_6^{2+}$	0.8
Simple organic complex	Cu -glycinat	1-2
Stabile inorganic complex	ZnCO_3	1-2
Stabile organic complex	Cu -fulvate	2-4
Absorbed on inorganic colloid	$\text{Cu}^{2+}\text{-Fe}_2\text{O}_3$	10-500
Absorbed on organic colloid	Cu - hum. Acid	10-500
Absorbed on compound of organic/inorganic colloid	Cu - hum. acid/ Fe_2O_3	10 -500

Table 2.4.1. Possible physical-chemical forms of Zn, Cu and Cd. .[7]

As seen from the table, metal ions can complex with organic and inorganic ligands through chemical reactions similar to reaction of hydrolysis of metal ions. As a result, soluble and insoluble complexes can occur, which depends on concentration of metal, ligand concentration and pH value of water.

Inorganic ligands are usually present in natural waters in much higher concentrations than from metal with which will form complexes. Every metal ion has specific behavior model in aquatic system which depends from 1) tendencies of metal ion to form complexes with inorganic ligands 2) stability of products incurred with hydrolyze reaction. Ions like Cd or Zn ions form series of complexes in presence of Cl⁻ and/or SO₄²⁻ in conditions when concentration is approximate to concentration of sea water. Metal ions can be tied to artificial organic substances and form organometal compounds, than carboxyl groups forming salts of organic acids, electron donor atoms O,N,P,S forming coordinative complexes.

Nowadays, researches related to metal behavior test in natural waters usually includes calculation of thermodynamic balance in model systems of metal and ligands, inside volume of pH which is characteristic for natural water (5 - 9,5).

Taking into account that natural water is complex and unbalanced redox environment to the behavior of metal, significant impact has also redox conditions. Impact of these conditions can be expressed through 1) direct change of oxidation stage of metal ion and 2) change of redox in availability and competition of ligands.

Nowadays inorganic complex of heavy metals is being the most studied one. However for proper comprehension of biodegradability, toxicity and geochemical reactivity, the smallest particles present in the water must be taken into account and knowledge of organic complexation of heavy metal traces is necessary. Taking this into account, this chapter will provide mechanism of metal concentration.

2.5 Differential Pulse Anodic Stripping Voltammetry (DPASV)

Electroanalytical methods are widely used in scientific studies and monitoring of industrial materials and the environment. One of the most widespread electroanalytical methods is voltammetry (polarography).

Various voltammetry techniques have simple laws and theoretical relations that in detail describe and represent different aspects of dependence $i - E$ such as the shape of curve, height and position of peak.

Nowadays, voltammetry unite large number of instrumental techniques such as anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV), adsorbed voltammetry (DPAV), differential pulse anodic stripping voltammetry (DPASV), which due to its large sensibility more and more suppresses classic techniques.

Stripping methods belongs to the electroanalytical methods group with pre-concentration, and these methods have the lowest detection border, so they are applicable for the analysis of media with very low concentrations ranging from 10⁻¹⁰ to 10⁻¹²M,^[8]. All stripping methods are based on two-stage process.

I-stage is pre-concentration of analytes from the tested sample solution on the surface of the working mercury electrode by oxidation or reduction, at a constant potential deposition E_d . This step can include anode or cathode process. Pre-concentration stage usually lasts 5 to 30 minutes, and with longer disposition time leads to higher signal and lower detection border.

II-stage is dissolution of tested electro-active species from surface of working electrode with potential scan. Process of dissolution can be done by changing potential of working electrode or by applying controlled electric pulses. During this stage, solution is in phase of inaction. As response, electrical signal caused by dissolution process is registered. It can be either current or potential, and depending on the type of signal, we distinguish several types of stripping methods.

The electrical signal (response) obtained in this way is directly proportional to the concentration of metal, and the position of the half-wave peak potential is identified by tested metal.

On the other side, by using pulse methods, it is possible to overcome the deficiency of voltammetry (polarography) with linear change of potential, like complex apparatus or a low detection border. Pulse techniques are intended to reinforce Faraday's current in relation to charging current, which results in increasing detection limit of ion species.

The excitation signal in differential pulse polarography represents linearly increasing potential pulse, on which is superimposed small square pulse potential with amplitude of 10 to 100mV.

As result, curve $i - E$ is obtained, with the height of power peak directly proportional to the concentrations and potential is directly proportional to the half-wave potential.

On figure 2.5.1. voltamogram appearance in linear change of potential is given.

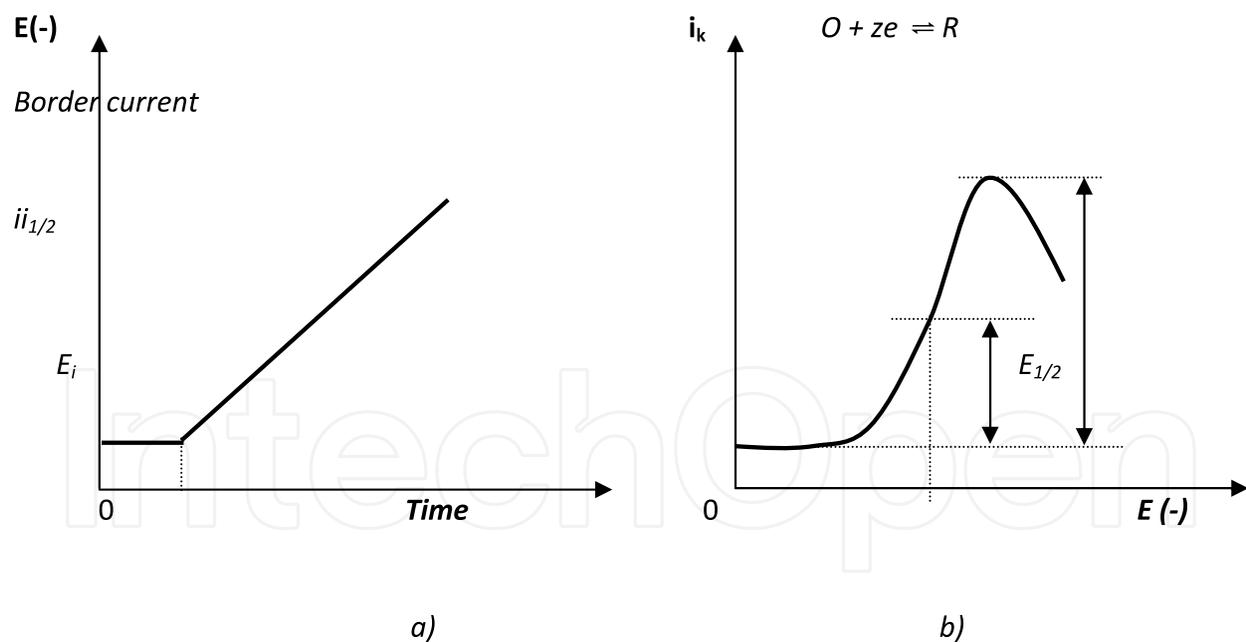


Fig. 2.5.1. (a) Excitation signal, (b) Response signal (voltamogram) in linear change of potential

Potential in maxim is given by equatation:

$$E_{\max.} = E_{1/2} - \frac{\Delta E}{2}$$

In this potential, current of differential pulse voltamogram is :

$$(\Delta i)_{\max.} = \frac{z \cdot F \cdot A \cdot D^{1/2} \cdot c_0}{p^{1/2} t_m^{1/2}} \cdot \frac{1-s}{1+s} \quad 2.5.1$$

where:

- s – function of amplitude of pulse potential;
- D – coefficient of diffusion;
- A – surface of electrode.

Quantitative parameter is maximum height and can be changed by this method in order to improve sensitivity. With change of height current peak, sensitivity can be adjusted, which is important analytical mean.

The source of information in voltammetric technique is always an electrochemical reaction. If reaction is reversible, the peak of potential is equal to standard potential of reaction. In the case of irreversible electrode reaction, position of maximum current peak is shifted toward negative values in relation to formal electrode potential of tested redox system.

Anode stripping voltammetry is also known as *inverse voltammetry*, and given the high sensitivity, it is suitable for analysis of low metal concentrations in different matrices. Anode stripping voltammetry is carried out through two stages:

The first stage is cathode deposition from solution to the surface of working electrode with appliance suitable negative potential [9]. If mercury electrode is used as working electrode and if metal in mercury is soluble, amalgam will arise. Concentration of metal ions in mercury film depends from concentration of M^{n+} ions in the solution, time of electrolyze and speed of mixing.



In this phase, anodic current of dissociation in function of the amount or concentration of metal in tested sample is registered.

Cathodic deposition is usually performed at potential which is 300 – 400 mV more negative than polarographic half-wave potential of tested metal. Maximum potential of deposition depends on the type of material of working electrode. Mercury electrodes have shown to be most suitable, since they allow simultaneous determination of a larger number of different metal ions in one tested sample.

Reproducibility of measurements depends from hydrodynamic conditions within the solution. Process of cathode deposition is carried out through inert conditions without presence of oxygen.

In «stripping» phase or in anodic dissolution phase, the response is obtained, i.e. curve $i - E$ whose shape depends from used electrode and the speed of change of potential. If the speed of change in potential is small enough, then the height of the peak/spade signal is directly proportional to the speed of change of potential. Current in peaked wave is then given by proposition 2.5.2:

$$i_p = \frac{z^2 F^2 v \cdot l \cdot A \cdot c}{2,7 \cdot R \cdot T} \quad 2.5.2.$$

Where: F – Faraday's constant, v – speed of change of potential, l – thickness of mercury, A – surface of electrode, c – concentration of separated metal in mercury, z – charging.

While processing obtained voltamograms, graphical methods are used, where the height of current peak/spade i_p is directly proportional to the concentration of deposited metal. If the mercury-film electrode is used as working electrode, then the integration of current (surface) below the voltamogram is performed. The relation between height of maximum and concentration for tested metal is determined by method of standard supplement/addition or by method of standard sample.

The great variety of electrode reactions, electrode materials (including solids studies), electrode designs, and conditions of electrode polarization determines a wide field of stripping electroanalytical methods application. Essential advantages of stripping electroanalytical methods over other methods used to determine trace concentration of inorganic and organic substances in solutions and to analyze and study solids are:

- High selectivity, good accuracy and reproducibility
- The possibility of determining a considerable number of chemical elements and many organic substances
- Low detection limits (10^{-10} M)
- The possibility of determining correlation of the „ composition – property for the solid substances and materials analyzed and of studying structural peculiarities of this entities
- Relative simplicity and low price

Beside Anodic Stripping Voltammetry (ASV), Differential Pulse Anodic Stripping Voltammetry (DPASV), is the most applied technique nowadays for determination of different heavy metals chemical forms. With these techniques, it is possible to separate species based on their redox potential and determine labile or electro active complexes and free ions. DPASV falls into electro analytical methods which are based on direct dependence of measured electro chemical magnitude of tested system concentration.^[10] By applying DPASV, it is possible to get three types of information regarding tested system:

- Regarding thermodynamic magnitudes
- Regarding setting up mechanism of electrode process and reactions which precede reduction
- Regarding qualitative and quantitative analytical parameters

It is important for pulse measurements that their sensitivity depends from usage of pure solvents and chemicals used as base electrolytes, and whose concentration is generally about 10 times lower than in the field of electrolytes, used in DC – polarography. Beside water, as solvents in differential – pulse analysis can be also used non-aqueous solvents, with which it is possible to determine electro active species that are infusible in water. The selection by itself, of carrying electrolyte, influences to the selectivity of method. On figure 2.5.2 use of voltamogram polarographic techniques is given.

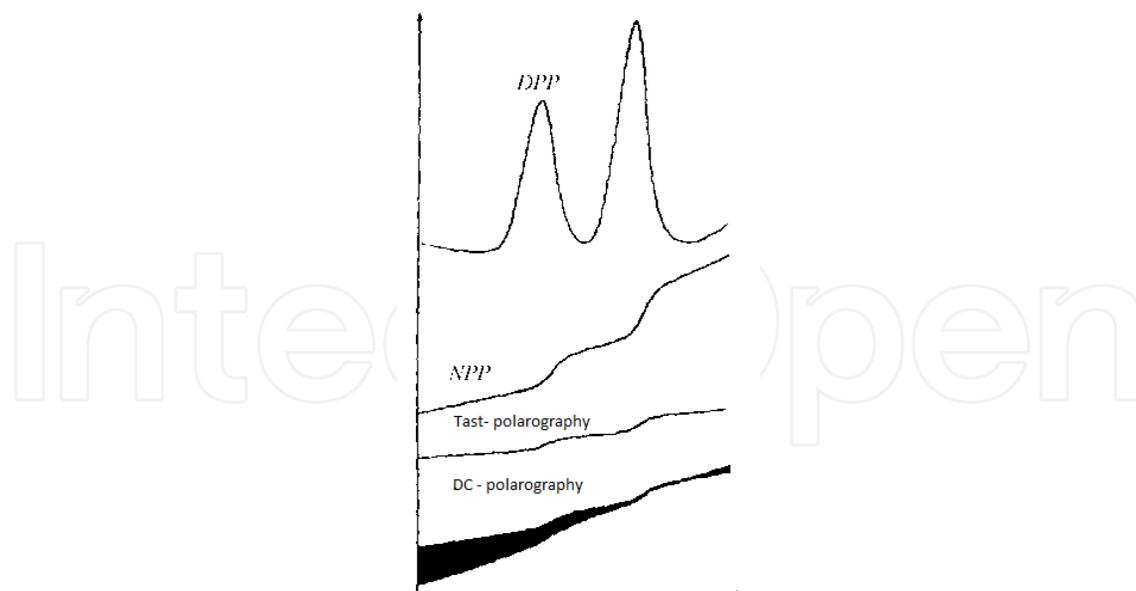
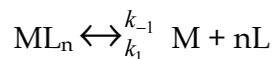


Fig. 2.5.2. Use of voltamogram polarographic techniques for Pb and Cd in 0,1 M HNO₃.

The intense sensitivity of differential pulse anode stripping voltammetry is great advantage in analysis of natural waters. The possibilities of this technique lie in the fact that the amount of metal (M) which is being sedimented on electrode during level of deposition depends among other things on deposition rate (k_{-1}) complex metal species (ML_n) on intermediate stages of electrodes - solution:



The amount of metal M that is being sedimented depends also from parameters like: total metal concentration, time of deposition, surface of electrodes and temperature.

However, contribution of metal complexes in height of the ASV- peak does not depend from these parameters, but only from k_{-1} and thickness of diffuse layer. This fact has lead to the widespread use of term "ASV - labile metal" in analysis of water, i.e. concentration of metals that are determined with ASV in natural pH of water or in slightly acidic solutions (acetic puffer pH 4,7); which makes ASV and DPASV methods unique in monitoring of metal traces speciation.

The ability of DPASV method to measure labile metals, as well as great sensibility (around $10^{-10}M$) for four most common toxic heavy metals: Cu, Cd, Pb and Zn , constitutes the powerful instrument in metal traces speciation.

It is evidently that in the near future, legislative for heavy metal in water will also include need for determination of speciation. Besides that, capacity of complexion can also be included into criteria of water quality.

There are various procedures by which stripping analysis can be used in order to obtain information about metal speciation using method of titration. When metal is used as titration means, than "capacity of complexion" for given metal is being determined. Titrimetric stripping procedures include direct determination of conditioned stability

constants for metal complex – ligand. Direct stripping procedure can be set to measure total metal concentration or labile fraction.

Labile metal fraction represents part of total dissolved metal determined by stripping analysis – in well defined experimental conditions, in natural pH of water. This fraction also includes free hydrated metal ions, labile metal complexes.

Labile metal complexes represent bio – available toxic fraction. The advantage of measurements by stripping labile metal fraction is in minimal pretreatment of sample.

Non - labile metal fraction also include metals that are tied in complexes or absorbed on colloid mater with speed of dissociation that is slower than stripping measurements time scale. This method is characterized by adequate «detection window» for monitoring and determination of speciation of metal traces, as well as constants of complex stability. The scope of detection window depends from interaction of metal – ligand in solution of sample and is determined by stability and adsorptivity of these surface-active metal complexes. Detection window depends from potential of disposition and detention time of inert complex molecules in diffusive layer during electrochemical deposition.

Opportunities and accuracy of DPASV – method, as well as reproducibility to the extent of concentration of metal traces of $10^{-10}M$, is completely satisfactory for all three tested metals, as given in table 2.5.1..^[11].

<i>Cu</i>	<i>Cd</i>	<i>Zn</i>
0,2 - 0,02ppb	0,2 - 0,02ppb	0,2 - 0,02ppb
±5-10%	±2,5%	±2,5%

Table 2.5.1. Scope of concentrations and accuracy

2.6 Chemical speciation

One of the most important voltammetry appliances in environment analysis is for speciation testing. Speciation analysis is defined as determination of concentration of different chemicals forms of elements that make up the total concentration in sample.

Since toxicity of every metal ion depends on physical – chemical form and that the most toxic form of metal ion is hydrated or free metal ion, it is important to do the chemical speciation.

Metal speciation, either in sea or in natural water is different because of:

- Different ionic strength
- Different concentration of metal ion
- Different concentrations of cations and anions
- Higher concentration of organic ligand in natural (clean) water
- Lower content of adsorbent in sea water

The least toxic forms are stable metal complexes and metal absorbed on colloid particles. Metal complexes with highly lipophylic organic ligands are also very toxic.

Concentration of electro-active oxidation state can be determined with measurements of total concentration of metal ion following conversion from electro-inactive to electro-active

stage because it is possible to measure concentrations of metals only in ionic form, and not individual species like PbCl^- , CuCl^- and others.

Labile species are those that can be detected with DPASV, like hydrated metal ion or metal ion that is dissociated from poorly tied inorganic complex or weakly absorbed on colloid particle. This is the first (I) - phase of speciation.

Chemical speciation of water in lake Modrac refers primarily to determination of chemical forms of heavy metals, copper, cadmium and zinc; whereby copper is separated because of the lake surroundings and high exposure, and its capacity of complexations determined.

In the first (I) phase, based on the obtained experimented results and with application of software programs MINTQ^{61,62} and HIDRA chemical forms of tested metals are determined; taking into account pH of the lake, ionic strength and water temperature.

In second (II) phase, concentration of inert metal complex is determined. The content of inert complex is such that the particles does not dissociate under given conditions. That is why the water sample is subject to extended UV-radiation in duration of three hours in acidic environment that accelerates the dissociation from all types of ligands and colloids. The assumption is that complexed metal does not reduce directly during deposition.

During chemical speciation, it must be taken into account presence of organic substances that are naturally present in lake water, and which can lead to error in results of analysis and determination of total concentrations of heavy metals by DPASV. For this reason, pre-treatment of samples is necessary. For elimination of undesired effects surface - active substances and complexing ageneses, different methods can be used. One of these methods involves modification of media, namely the change of pH during deposition and stripping. There are three versions:

- Deposition and stripping at pH 7
- Deposition and stripping at pH 2
- Deposition at pH 7, and stripping at pH 2

In these experiments, when it comes to copper, deposition and stripping are performed at water pH 2, since some comparative studies have shown that change of media and pH leads to significant increase of concentrations of labile fraction. If it is known that metal ions which are incorporated into organic complexes are usually not toxic, than it is obvious why chemical speciation is important. The capacity of Cu complexion is determined by applying ASV titration of water samples with increasing concentrations of Cu^{2+} ions. End point of titration indicates the presence of free Cu ion in water. Based on obtained experimented data using method by Ruzic and equitation 2.6.1.capacity of complexion is calculated.

$$\frac{[M]}{(M_T - [M])} = \frac{[M]}{(C_M + \Delta_M - [M])} = \frac{([M] + 1/K)}{C_L} \quad 2.6.1.$$

Where:

- C_M i C_L - concentrations of metal and ligand present in the system

- M_T – total metal concentration
- Δ_M – concentration of added metal
- $[M]$ – concentration of non-complexed metal
- K – constant of stability of ML complex

Speciation of copper is interesting and important because of:

- Very wide application that inevitably makes it a component on water surface in concentrations that are significant for water ecosystem
- Known for its affinity toward natural complexing ageneses
- Organic Cu compounds have shown to be significantly less toxic than from free Cu ions or inorganic complexes [12].

Accuracy can be tested by using larger volume of deposition potentials and drawing curves $I = d(E_d)$. If ionic form of metal is only reduced, than current peak rise from 0 to the upper limit in small volume of potential; and if metal complex is directly reduced, than current peak continuously grows with potential of deposition. With these analyses it is recommended to use minimal deposition potential while measuring each metal, but sufficiently negative to give maximal anodic current, after which metals can be determined in individual experiments.

The advantage of chemical speciation using DPASV is that the labile fraction can well correlation with toxic fraction.

This method can also be combined with other methods of separation for the separation of labile and inert fraction, such as leakage through ion – exchange column.

3. Results

3.1 Method applied for analysis of results

For quantitative polarographic determinations in practice, usually three methods are used.[13]

- Method of calibration diagram
- Method of direct comparison
- Method of standard addition.

These methods allow calculating concentration of electro-active species in tested solution, based on the polarographic wave height. Most commonly applied method is method of standard addition since it is suitable for determination of small concentrations in small amounts of sample. In our researches, standard addition method is used.

Method of standard addition is often used for analysis of complex samples. It is based on successive addition of several portions of the standard solution of known concentration into tested sample, always in same amount. This process is known as sample “spiking”. It measures the current response for tested sample before addition of standard solution and after each adding. Volume of V_s standard addition shall not significantly influence to the volume of sample V_x . The obtained current response id proportional to the concentration of tested sample, so that:

$$S = \frac{k \cdot V_s \cdot c_s}{V_t} + \frac{k \cdot V_x \cdot c_x}{V_t} \quad 3.1.$$

Where:

- c_x – concentration of tested sample
- k – constant of proportionality
- c_s – concentration of standard addition
- V_s – volume of standard addition
- V_x – volume of tested sample.

Drawing $S = f(V_s)$ equation of direction is obtained:

$$S = mV_s + b \quad 3.2.$$

Where m is slope of direction, and b is section on y - axis so that:

$$m = \frac{k \cdot c_s}{V_t}; \text{ and } b = \frac{k \cdot V_x \cdot c_x}{V_t} \quad 3.3.$$

Rearranging, concentration of tested sample is obtained

$$c_x = \frac{b \cdot c_s}{m \cdot V_x} \quad 3.4.$$

The figure 3.1.gives a graphical display of standard addition method.

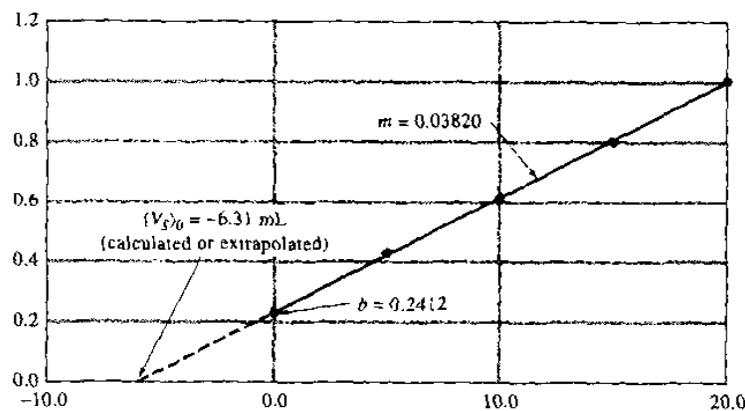


Fig. 3.1.1. Standard addition method

In the process of preparing and analysis of samples, used chemicals where of high purity level (Merck); HNO_3 , HClO_4 , HCl i KNO_3 .

All samples were prepared in redistilled water, obtained by triple distilled process whereby second and third level was performed in rock ristaly aparatures.

Standard analyzed metal solutions (Cu, Cd and Zn) were prepared in "concentrations" from 10^{-4} to 10^{-5} mol/l from supra pure salts of nitrate metal ions.

- Copper – standard solution $\text{Cu}(\text{NO}_3)_2$ in HNO_3 , $c(\text{Cu}) = 1\text{g/l}$
- Zinc – standard solution $\text{Zn}(\text{NO}_3)_2$, in HNO_3 $c(\text{Zn}) = 1\text{g/l}$
- Cadmium – standard solution $\text{Cd}(\text{NO}_3)_2$ in HNO_3 $c(\text{Cd}) = 1\text{g/l}$

Glassware and electro analytical cells were kept for 24 hours in 6 M HNO_3 , after which they were flushed with distilled and redistilled water. As carrying electrolyte 0.1M KNO_3 was chosen which was prepared from salts of KNO_3 supra pure. All metals were determined individually.

The water samples of lake Modrac were taken from four characteristic places during four seasons, from the depth of 2,5 m.

- Place A – area around entrance into area around dam
- Place B – area on the middle of lake
- Place C – area around the mouth of river Tinja
- Place D – area around the mouth of river Spreca

Instrumental parameters for determination of concentrations of Cu, Cd and Zn in water were as follows:

- Working electrode HMDE
- Auxiliary electrode – platinum wire
- Reference electrode Ag/AgCl ($E=0,222\text{V}$)
- Cleaning time (nitrogen deaeration) 120 sec
- Sleep time 15 sec
- Scanning rate 2 mV/sec
- Time of deposition 300 sec

Half-wave potential for each metal is given in table 3.1.1.

Metal	Initial potential (mV)	Final potential (mV)
Cu	-0,45; -0,35	0; 0,05
Cd	-0,9	-0,6
Zn	-1,2	-0,9

Table 3.1.1. Potential of deposition

Results of water analysis samples for free/labile metal ion

In first phase are the concentrations of Cu, Zn and Cd and their labile chemical forms present in the water of lake Modrac. One part of water samples was acidified on the spot with concentrated HCl. In these samples, total concentrations of free metal ion or metal ion that was tied to in labile inorganic complex, were determined. The second part of samples was frozen to -20°C and analyzed in second phase of experimental work in order to determine total concentrations of metals that were tied in stabile organic complex with ligand; which is naturally present in water lake Modrac, as well as capacity of complexation

of Cu. Applying standard addition method in Mathcad program, concentrations of heavy metal traces (Cu, Cd and Zn) in tested samples were determined. On figure 3.2., 3.3. and 3.4. are given voltamograms obtained for Cu, Cd and Zn applying standard addition method.

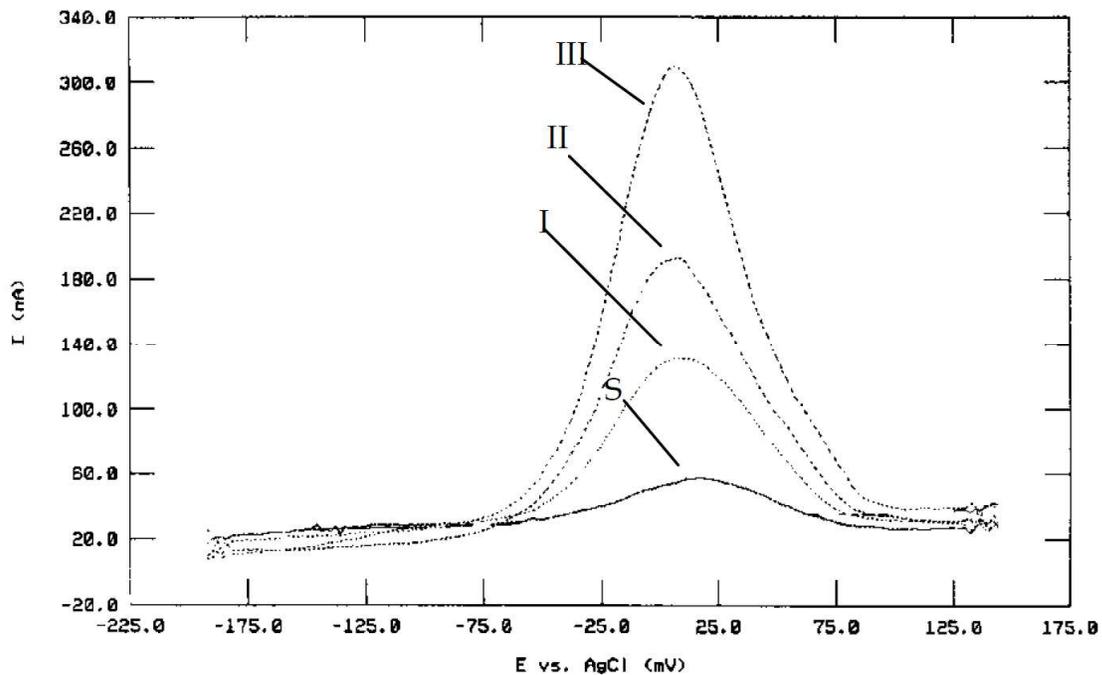


Fig. 3.2. Copper in water of lake Modrac - standard addition method (I - first addition, II- second addition, III - third addition, S - sample)

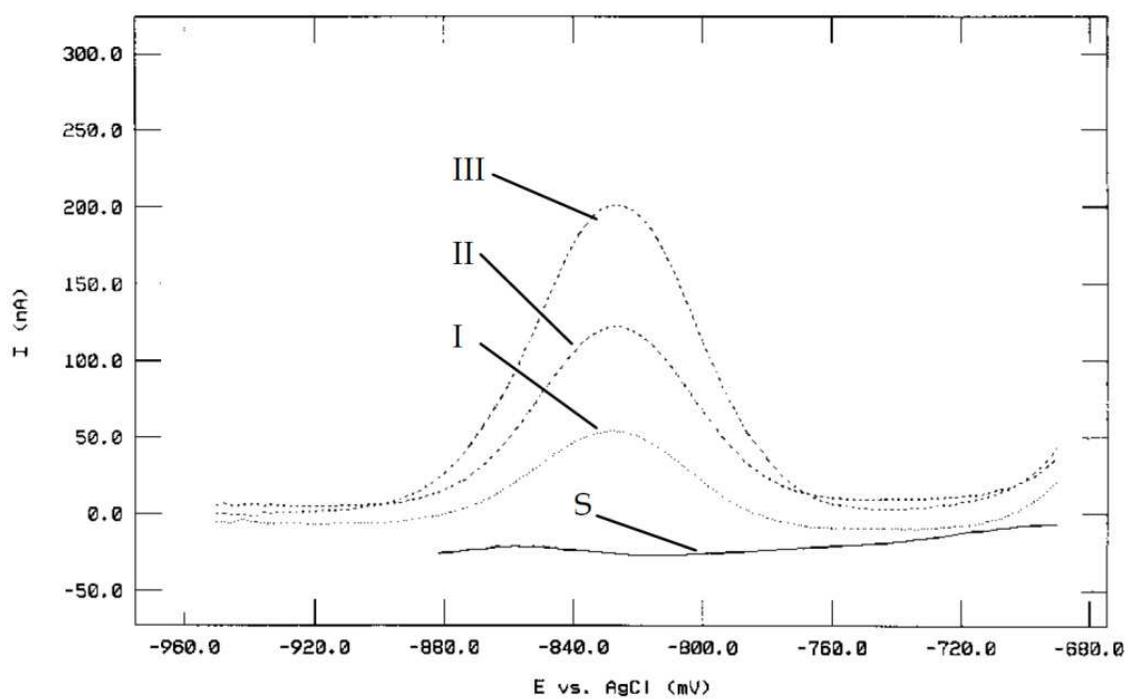


Fig. 3.3. Cadmium in water of lake Modrac - standard addition method (I - first addition, II- second addition, III - third addition, S - sample)

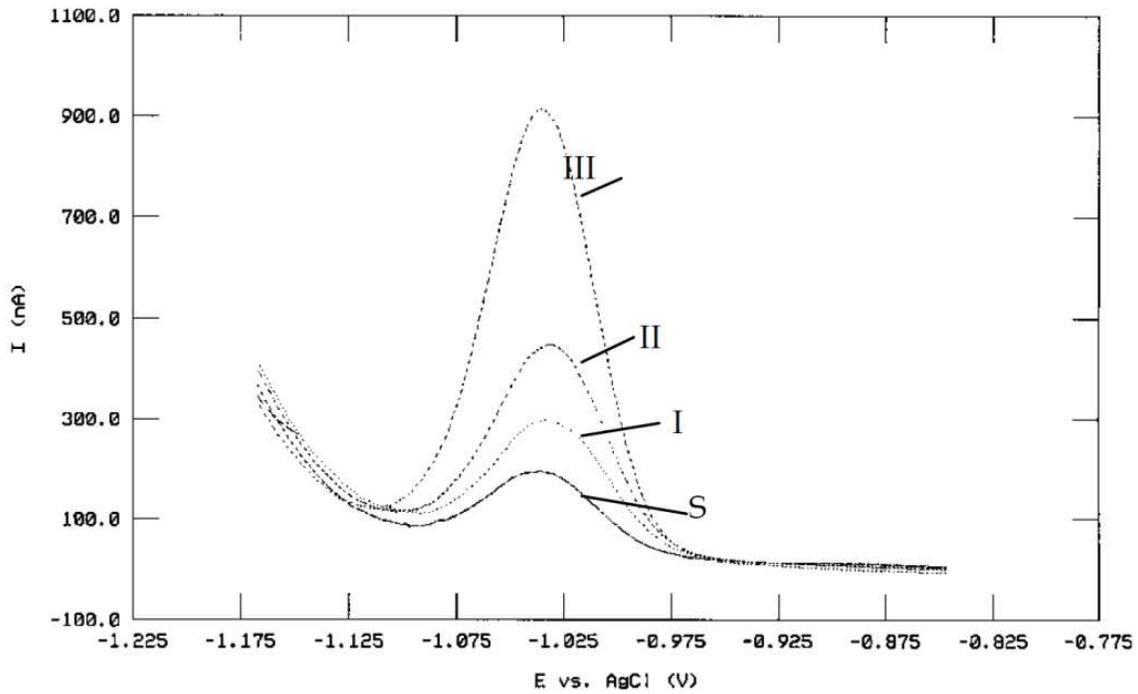


Fig. 3.4. Zinc in water of lake Modrac – standard addition methods(I – first addition, II- second addition, III – third addition, S – sample)

On figure - diagrams 3.5., 3.6., and 3.7., are given average calculated concentrations of Cu, Cd and Zn during four seasons in Lake Modrac.

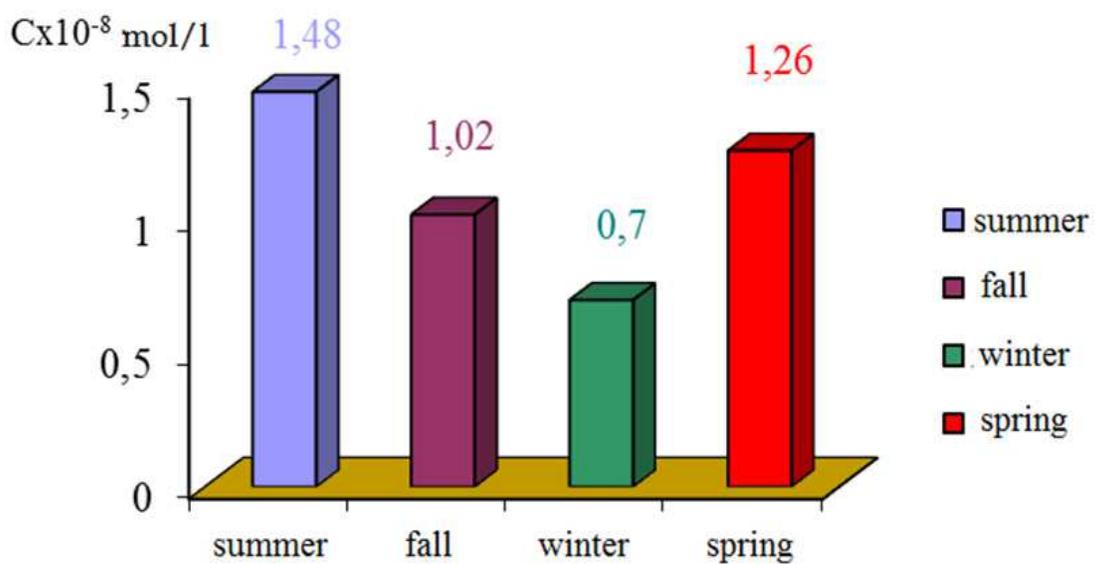


Fig. 3.5. Average amounts of copper during four seasons in Lake Modrac

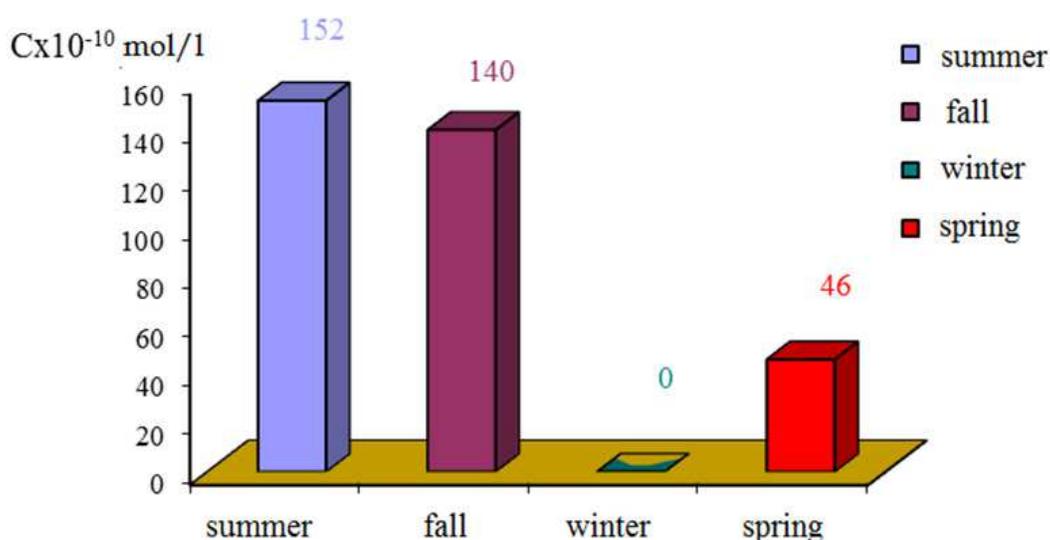


Fig. 3.6. Average amounts of cadmium during four season in Lake Modrac 10⁻¹⁰

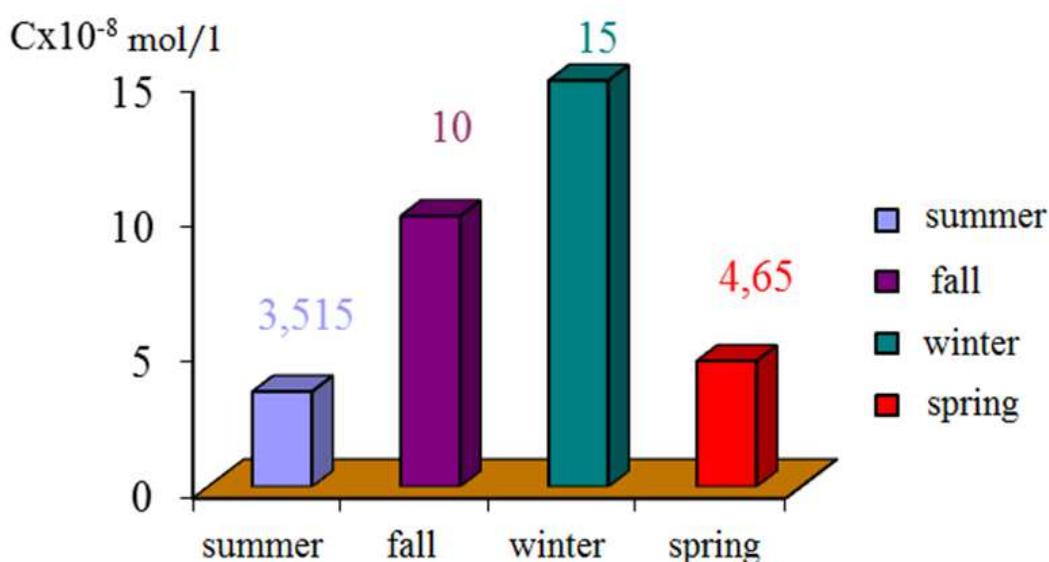


Fig. 3.7. Average amounts of zinc during four season in Lake Modrac

Metal	Season			
	Summer	Autumn	Winter	Spring
Cu	94•10 ⁻⁵ (mg/l)	64,81•10 ⁻⁵ (mg/l)	44,48•10 ⁻⁵ (mg/l)	80,06•10 ⁻⁵ (mg/l)
Cd	1,78•10 ⁻³ (mg/l)	1,573•10 ⁻³ (mg/l)	<10 ⁻⁶ (mg/l)	5,17•10 ⁻⁴ (mg/l)
Zn	2,29•10 ⁻³ (mg/l)	6,54•10 ⁻³ (mg/l)	9,811•10 ⁻³ (mg/l)	3,041•10 ⁻³ (mg/l)

Table 3.2. Summary of calculated average concentrations of Cu, Cd and Zn

In table 3.3. Percentage representation of certain metal complexes of copper obtained by application of software programs HIDRA and MINTQ.

Chemical form	Season			
	Summer %	Autumn %	Winter %	Spring %
Cu^{2+}	13,4	75	64	12
$\text{CuII}(\text{OH}^+)$	17,9	18,5	16	30
$\text{CuII}(\text{OH})_{\text{aq}}$	-	5,4	14	5
Cu II CO_3	37,12	-	14	-
CuSO_4	-	5,4	4	-

Table 3.3. Representation of chemical forms of Cu during four season expressed in percentages.

The table shows that chemical form of copper in summer and spring time varies more in relation to autumn, and especially to the winter. In fall and winter time, copper is mainly found in ionic form, which means in the most toxic form. This is explained with the higher pH value in this two seasons (7,5 – 8), since with higher pH values copper is easily dissociated and from label inorganic complexes goes into ionic form.

In table 3.4. balance constant of found copper complexes, calculated with software program CHEAQES are given.

Unorganic complexes	Real constante of balance (K)
$\text{CuII}(\text{OH})^+$	6,5
$\text{CuII}(\text{OH})_{2\text{aq}}$	11,8
$\text{CuII}(\text{SO}_4)_{\text{aq}}$	2,36
$\text{CuII}(\text{CO}_3)_{\text{aq}}$	6,7
$\text{CuIIC}(\text{HCO}_3)$	12,12

Table 3.4.

Cadmium is not found in water samples in winter period, not in any location. More accurate, those concentration were above 10^{-12} mol/l. Inorganic speciation has shown that cadmium is found same as zinc, mostly as free metal ion, even 90% and on all locations and during all four seasons.

Test results of some other authors have shown that cadmium requires higher pH value than copper; in order to occur adsorption to organic or inorganic particles [14]. This is probably reason why cadmium in lake Modrac is usually found in most toxic form. In table 3.5, representation of Cd chemicals forms during four seasons by percentage, obtained by application of software programs HIDRA and MINTQ, are given.

In the table 3.7 are given results obtained for Zinc. During all four season and on all places, zinc is found almost completely dissociated, i.e. in ionic form and one smaller portion in form of zinc-sulfate whose determined equilibrium constant ($K=2,3$) indicates that it is very unstable complex from which zinc easy dissociate and transforms into ionic form. This goes with results obtained by Figure and McDuffie by which Zn in natural waters is found mostly in very labile form. By Florenc, zinc is also found as free ion in fresh water for about

50%, while in the sea water is usually found in form of chlorine-complexes for about 47% and 27% as free ion.

Test for inorganic chemical speciation of zinc are controversial and with very different results which can be explained by the fact that zinc is component that is present in variety of materials that are being used in lab work, human skin, so that contamination of samples is much bigger problem than in other heavy metals.

Chemical form	Season			
	Summer %	Autumn %	Winter %	Spring %
Cd ²⁺	85	97	-	91
CdCl ⁻	9,6	-	-	1,4
Cd(SO ₄) _{aq}	7,0	6,0	-	7,5

Table 3.5. Representation of Cd chemical forms during four seasons expressed in percentages.

Inorganic complexes	Real constant of balance (K)
Cd(SO ₄) _{aq}	2,37
CdCl ⁺	1,98

Table 3.6. Equilibrium constants of found cadmium complexes, calculated using the software program CHEAQES.

Chemical form	Season			
	Summer %	Autumn %	Winter %	Spring %
Zn ²⁺	90	92,7	93	92
ZnHCO ₃ ⁻	-	-	-	-
Zn(SO ₄) _{aq}	7,5	6,4	5,1	6,9

Table 3.7. Representation of Zn chemical forms during all four seasons expressed in percentages, obtained by application of software programs HIDRA i MINTQ, are given.

Determination of complex capacity of copper in lake water Modrac

In second (II) phase complex capacity of copper was determined, as one of the possible parameters of natural water quality.

In second phase of speciation, water samples were first defrosted to room temperature, filtrated through sterile membrane filter of 0,45 µm pore diameter. Filtration was carried out in order to remove possible presence of colloid particles. After filtration samples were acidified to pH 2 with s.p. HCL and ventilated with UV radiation intensity 100 W during three hours. Radiation was performed in order to release metal ions tied into stabile organic complexes. Previously acidification was performed to achieve a faster release of metal ions from these complexes. Figure 3.8. represents voltamogram for copper before and after radiation.

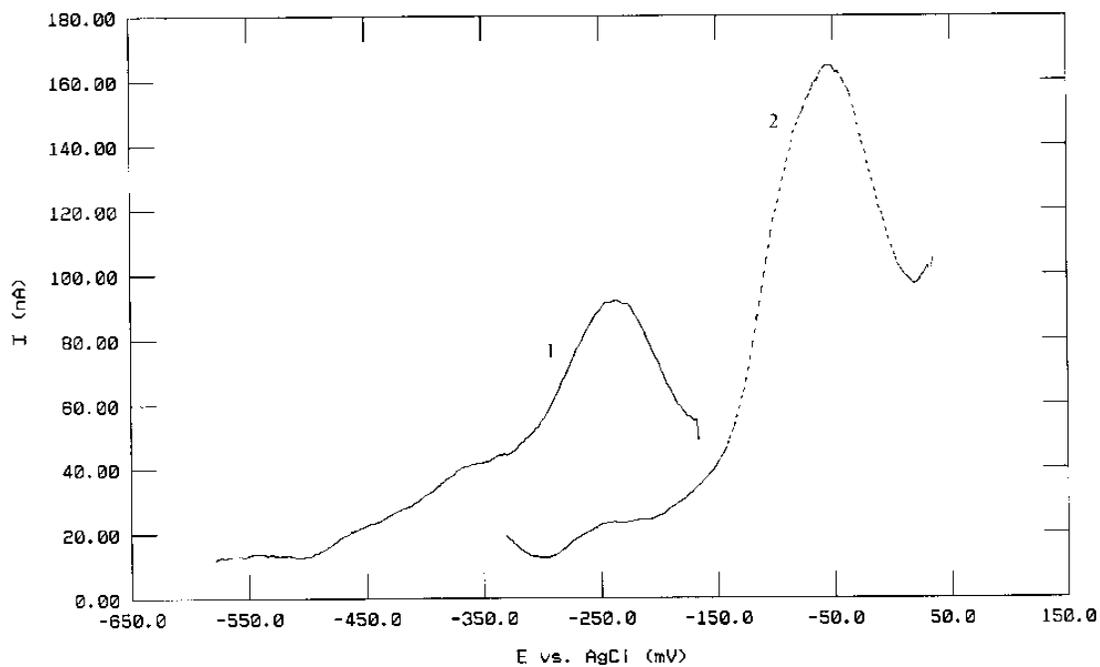


Fig. 3.8. Voltamogram of copper before (1) and after (2) radiation

The results obtained after radiation have shown that there was an increase in copper concentrations in all season, indicating a higher presence of copper, but in the form of stable organic complexes. Movements of half-wave potentials toward positive values are caused by change of pH values.

Results for copper with EDTA

In order to determine the complex capacity of copper, e.i. concentration of organic ligand naturally present in water that can tie copper into stable complexes, first were done test with known ligand, EDTA, which is by characteristic very similar to natural ligand. This was performed only for data reproducibility and greater accuracy.

Primary the calibration diagram was documented for known concentrations of copper and to the extent in which the concentrations of this metal ion was found in lake Modrac (1,6; 5; 8; 10; 14; 180 and 22) $\cdot 10^{-6}$ mol/l. Based on calibration diagram and from obtained equation of direction, concentration of non-complex copper ion of copper was calculated.

Capacity of complexation and constant of stability are calculated based on Ruzic method. On figure 3.2.1.obtained calibration diagram for copper is shown.

To determine the capacity of complexation of copper with EDTA in 6 copper samples of 10 ml, of above stated concentrations, EDTA concentration of $2,2 \cdot 10^{-6}$ mol/l was added. The samples were left in the sterile plastic bottles overnight, after which concentrations of non-complexing copper with EDTA was recorded, based on the differences in height of current peak for copper before and after EDTA adding. On figure 3.2.2.are given results obtained by linearization of data for height of current peaks for copper and EDTA. The ratio between concentrations of non-complex and complex copper in function of concentration non-complexing copper is given. From the slope of directions, capacity of CuEDTA complexion was determined, and stability constant of resulting complex from section.

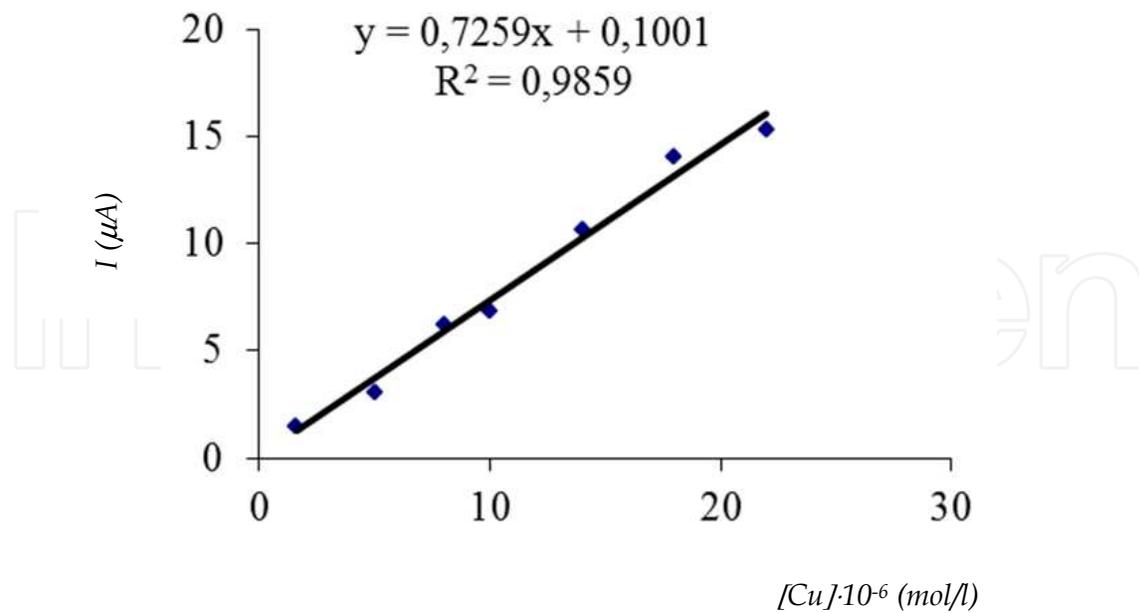


Fig. 3.2.1. Calibration diagram for Cu

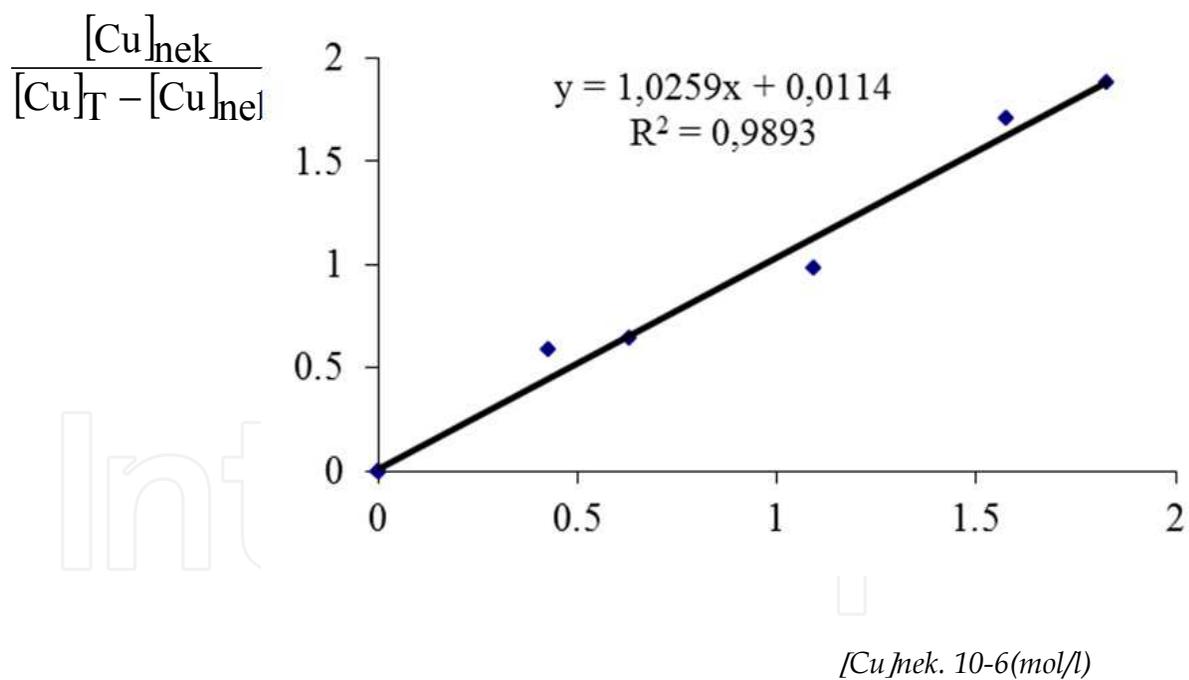


Fig. 3.2.2. Mathematical data processing for copper + EDTA

$$1/C_L = 1,0259 \cdot 10^{-6} mol/l ; C_L = 1/1,0259 = 0,974 \cdot 10^{-6} mol/l ; 1/K \cdot C_L = 0,0114 ;$$

$$K = 1/0,0114 \cdot 0,974 \cdot 10^{-6} = 1/0,0111 \cdot 10^{-6} ; K = 9,009 \cdot 10^7 ; \log K = 7,95$$

Obtained values capacity of complexation and stability constant explain good conformity with literature data.

Results for capacity of complexation of copper in water of lake Modrac

Due to results reproducibility, capacity of complexation for copper in water of lake Modrac was not performed at natural pH value, rather the samples were acidified with 0.1 M HNO₃ right before recording so that the pH was 2,3.

First, the calibration diagram was recorded for concentrations that match the concentration of copper in lake water. Following copper concentrations was used (0.1; 0,5; 0,7; 1; 1,5; 2,5; 3; 5,5; 8,5)·10⁻⁸mol/l.

On figure 3.2.3. calibration diagram for copper is given.

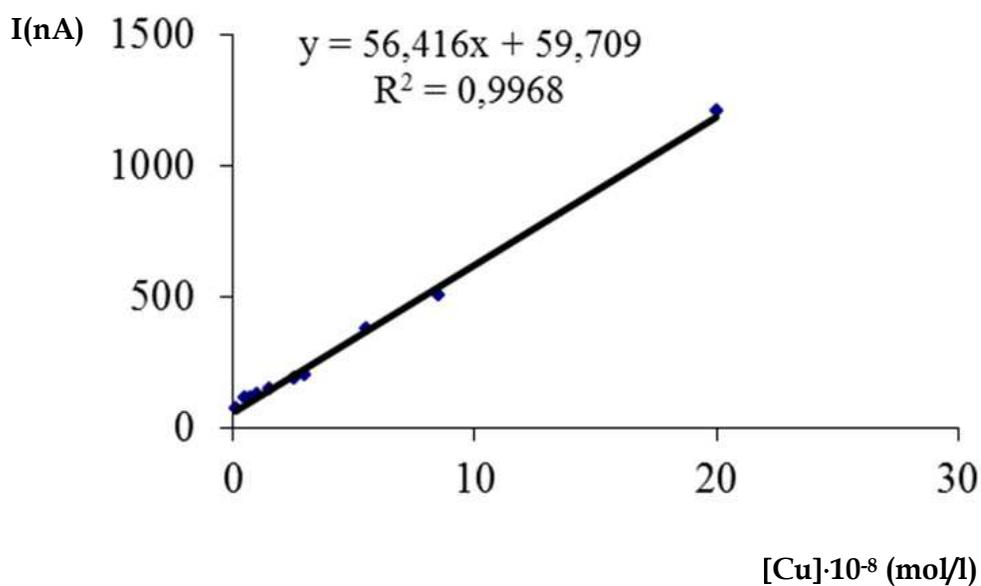


Fig. 3.2.3. Calibration diagram for copper

For analysis, 100 ml of untreated lake water is taken and divided into 10 sterile bottles of 10 ml. into samples increasing concentrations of copper was added; the same concentration by which calibration diagram was constructed. Samples were left overnight to make the maximum absorption of copper into water, after which concentrations of non-complexing copper with natural ligand from water were recorded. From calibration diagram, Fig. 4.3.5. concentrations of non-complexing copper were calculated. From the difference of total concentration of copper [Cu]_T and concentration of non-complexing copper [Cu]_{nek}, concentration of complexed copper [Cu]_{kom} was calculated.

$$[Cu]_T = C_{Cu} + \Delta Cu \quad 3.2.$$

C_{Pb} - concentration of copper found in lake; ΔCu - added concentration of copper.

Linearization of data, from the relationship between concentrations of non-complexing and complexing copper in function of non-complexing copper, the complex capacity in water of lake Modrac from the slope of direction was calculated; and stability constant of resulting complex was calculated from the section. On Figure 3.2.4 diagram $[Cu]_{nek} / [Cu]_T - [Cu]_{nek} = f([Cu]_{nek})$ is given.

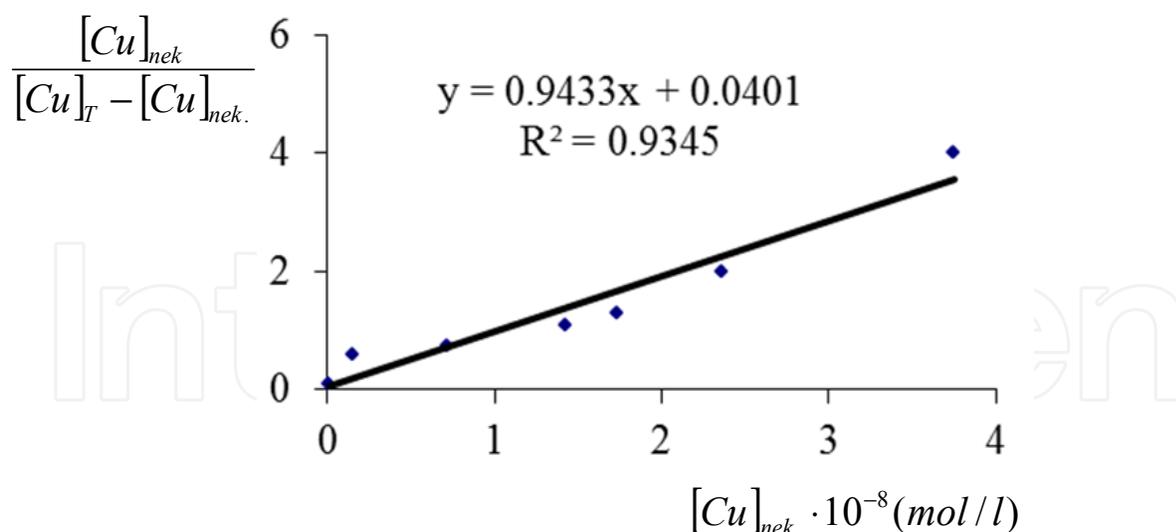


Fig. 3.2.4. Data obtained using mathematical processing of data for complex capacity of copper into water of lake Modrac

From equation $y = 0,9433 \cdot x + 0,0401$; ($R^2 = 0,9345$) capacity of complexation and stability constant for copper were calculated:

$$1/C_L = 0,9433; C_L = 1/0,9433 = 1,06 \cdot 10^{-8} mol/l.$$

$$1/K \cdot C_L = 0,0401; K = 1/0,0401 \cdot 1,06 \cdot 10^{-8} = 2,5 \cdot 10^9$$

$$C_L = 1,06 \cdot 10^{-8} mol/l; K = 2,5 \cdot 10^9, \log K = 9,4$$

4. Conclusion

Results of copper testing have shown that this metal in lake water is found mostly in « medium » labile and « poor » labile inorganic form. Copper is usually found in inorganic complexes and smaller percentage in form of free metal ion. The results indicated that dominant chemical form varies depending on season and locality. So that, during summer and spring for which is characteristic neutral pH value, copper is usually found at labile hydroxide complex about 30% and as carbonate about 50%. On the other side, during autumn and winter copper is usually found in the form of free metal ion. Similar results were obtained by Florence.^[15] for sea and fresh water, where copper is found about 50% as $CuCO_3$ and 40% as $Cu(OH)$.

The dominance of free Cu ion in fall can be explained with chemical composition of water, which is characterized by total absence of carbonates. Calculated equilibrium constants using CHEAQS program also indicates that it is medium labile complexes, especially when it comes to hydroxide and carbonates ($K = 6,5$ and $6,7$).

On the diagrams 3.5 to 3.8 is given copper distribution and dominant labile inorganic forms in function of pH value, determined using software programs HIDRA and MINTQ.

The diagram shows that with pH increase, portion of copper free metal ion decreases and adsorption on inorganic molecules occurs, so that during the winter and spring there is

more in form of inorganic complexes while during autumn in the form of free ion. Chemical form of copper mostly varies during summer period from place to place. High percentage of free metal ion on place B, which represents middle area of the lake, can partly be explained with water currents which are expressed on minimum level, as well as lower concentrations of dissolved oxygen and decreased quantities of organic and inorganic matters as result of hydrologic characteristics. [16]

The determined Cu constant of stability and calculated capacity of complexation addresses that it is very stable/inert Cu organic complex, and that significant amount of organic active substance is present in the water of Lake Modrac. [16]

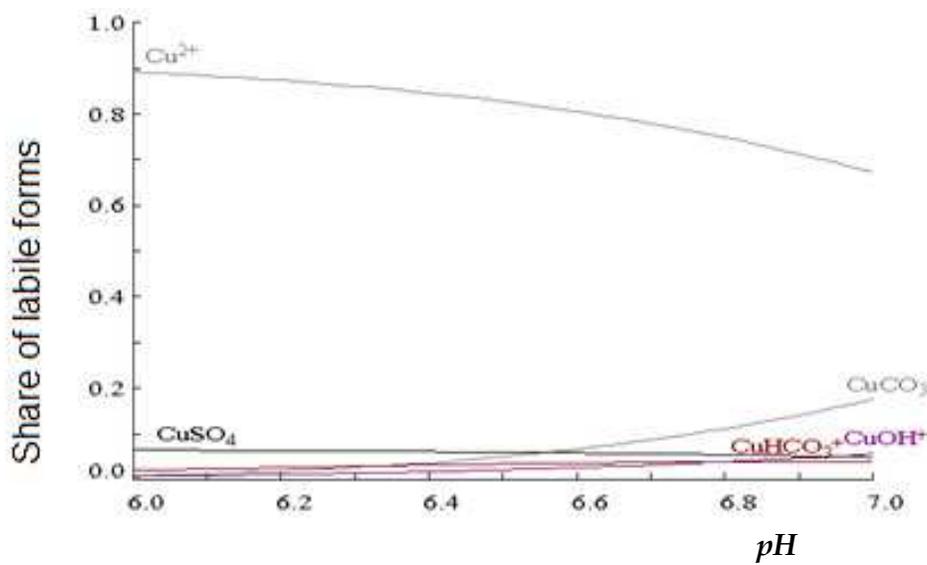


Fig. 3.5. Dominant labile copper forms in summer period

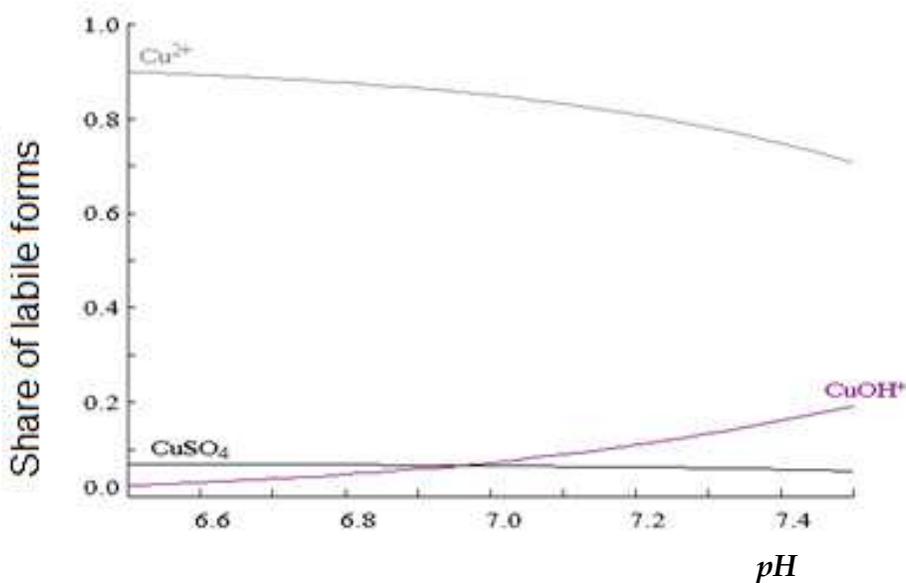


Fig. 3.6. Dominant labile copper forms in autumn period

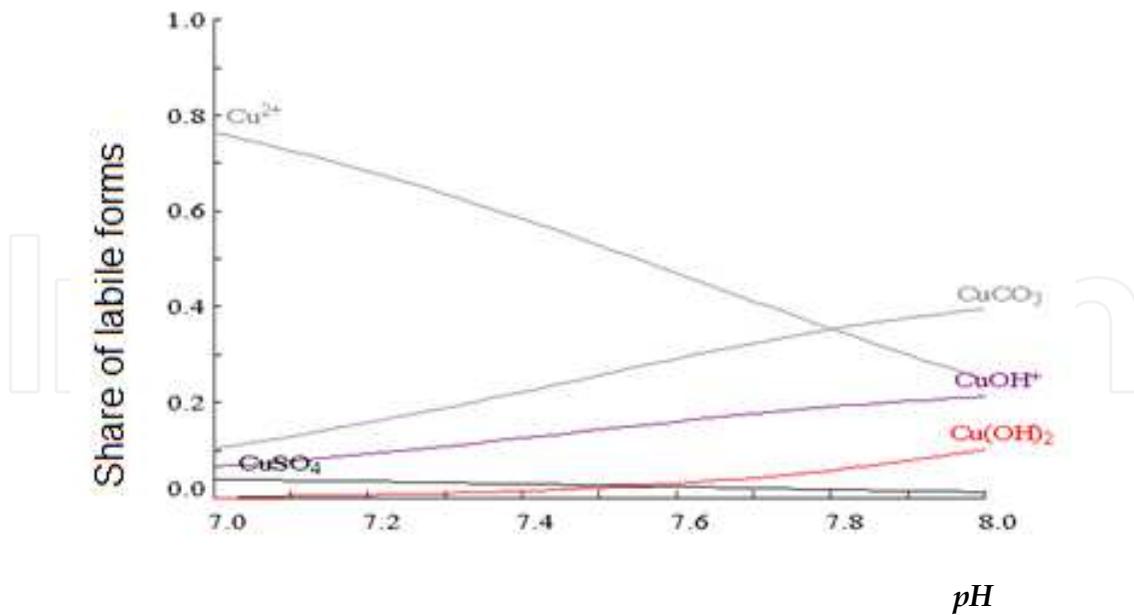


Fig. 3.7. Dominant labile copper forms in winter period

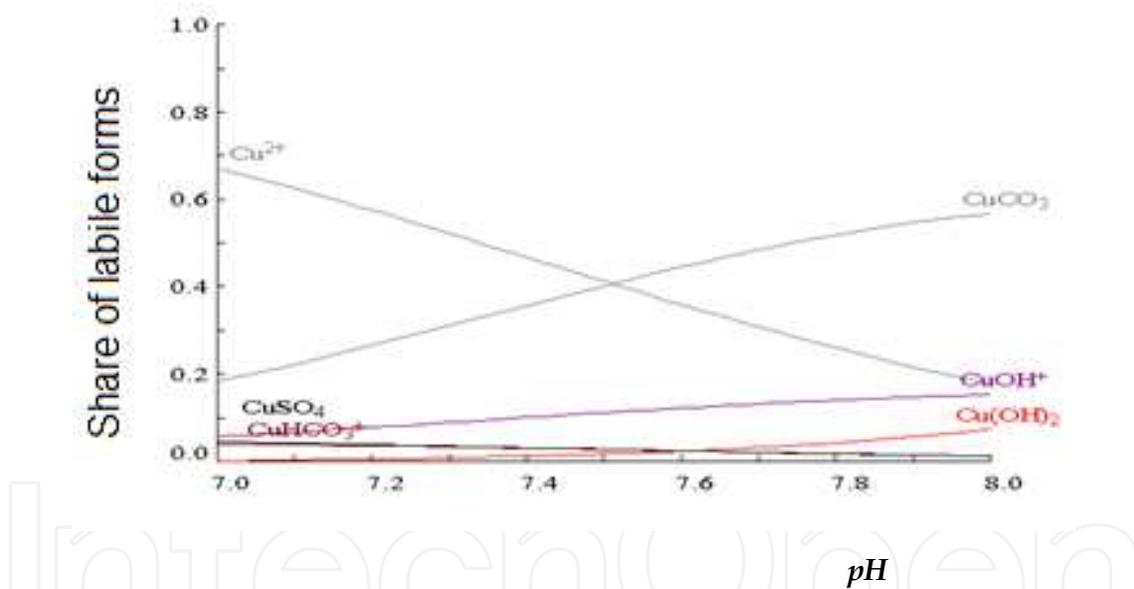


Fig. 3.8. Dominant labile copper forms in spring period

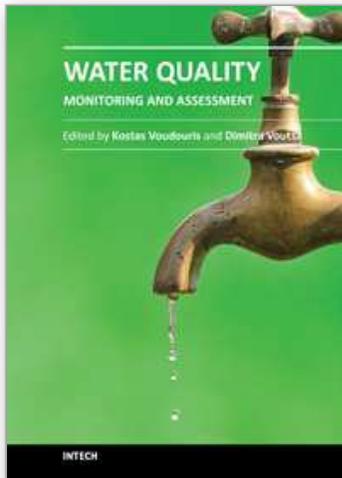
Performed testing have shown that DPASV method that was used as basic polarographic technique, with varying conditions and electrochemical parameters by type of determination, proved to be extremely accurate and sensitive and definitely economically most suitable.

Application of modeled polarographic DPASV technique offers possibility to determine speciation and capacity of complexation of natural waters. Moreover, it allows determination of total concentrations of tested metals in natural waters, sediments and aquatic ecosystem, by which this method, as optimal method, is recommended by all research cycles for this kind of testing.

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The book attempts to covers the main fields of water quality issues presenting case studies in various countries concerning the physicochemical characteristics of surface and groundwaters and possible pollution sources as well as methods and tools for the evaluation of water quality status. This book is divided into two sections: Statistical Analysis of Water Quality Data;Water Quality Monitoring Studies.

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