TRACE METAL ANALYSIS OF FRESH AND CANNED FOOD SAMPLES BY ANODIC STRIPPING VOLTAMMETRY

by

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ABSTRACT

TRACE METAL ANALYSIS OF FRESH AND CANNED FOOD SAMPLES BY ANODIC STRIPPING VOLTAMMETRY

The objectives of this study were to develop the parameters of an electroanalytical method, DPASV, for the determination of trace elements Zn, Cu, Pb and Cd in fresh and canned food samples, and to compare the new method with the conventional one, ICP-OES. Fresh fish samples were purchased from the local markets of Gelibolu, Çanakkale, and from groceries in Istanbul. Fish and vegetable samples in canned packages were analyzed. Samples were weighed in three replicates of about 1.50 – 2.00 g, and air dried. Samples were digested in nitric acid (HNO_3) and nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). $HNO_3/HClO_4$ combination was found to be the most suitable to destroy the organic components of the food samples. DPASV parameters were optimized at 120 s of deposition time with Hanging Mercury Drop Electrode (HMDE), and 10 s of equilibration time and 1.8 s of voltage step time with Static Mercury Drop Electrode (SMDE). Supporting electrolytes of varying compositions at different pH levels (1.92, 4.60, and 8.40) were tested. Oxalate buffer, pH of 1.92, yielded the most precise and the accurate voltammetric peaks. In the presence of relatively high Zn and Cu concentrations, DPASV analyses were run separately by adjusting the corresponding deposition potential, and the mode of the mercury electrode. In the presence of relatively high Cu concentrations, DPASV analyses were done separately with the addition of a complexing agent, ethylenediaminetetraacetic acid (EDTA) at various concentration levels. Results of the ICP-OES and DPASV analyses were compared with each other; data sets were statistically analyzed with paired t-test. Statistical analysis at 95% confidence level showed that the results of the two methods were similar except the Pb contents of fresh and canned fish samples. Also, trace element concentrations in the food samples were investigated whether the recorded amounts were within the limits that were legislated by World Health Organization, European Union, and Turkish Food Codex or not.

ÖZET

ANODİK SIYIRMA YÖNTEMİ İLE KONSERVE VE TAZE GIDA ÖRNEKLERİNDE AĞIR METAL TAYİNİ

Bu çalışmanın amacı etkili bir elektroanalitik yöntem olan Anodik Sıyırma metodunun konserve ve taze gıda örneklerinde kullanımını geliştirmek ve bu yöntemle tespit edilen Zn, Cu, Pb ve Cd miktarlarını Endüktif Eşleşmiş Plazma Optik Emisyon Spektrometresi (ICP-OES) ile elde edilen sonuçlarla karşılaştırmaktır. Taze balık örnekleri Gelibolu'nun yerel marketlerinden, ve İstanbul'da bulunan marketlerden alınmıştır. Konserve olarak incelenen gıdalar ton balığı, hamsi, sardalya; mısır ve domates örnekleridir. Örnekler oda sıcaklığında bir gece kurutularak 1.50 2.00 g aralığında tartılmış, nitrik asit (HNO_3) ve nitric asit/perklorik asit ($HNO_3/HClO_4$, 5/1, v:v) karışımı ile öğütülmüştür. $HNO_3/HClO_4$ karışımının örneklerin organik içeriğini çözebilmek için en uygun ortam olduğu bulunmuştur. Anodik Sıyırma (DPASV) parametreleri Asılı Damla Cıva Elektrot (HMDE) için 120 s biriktirme süresi; Statik Damla Cıva Elektrot (SMDE) için ise 10 s dengeleme süresi ve 1.8 s voltaj bekleme süresi olarak belirlenmiştir. Tampon çözelti olarak çeşitli pH değerlerinde (1.92, 4.60, 8.40) kompozisyonlar kullanılmıştır. Oksalat çözeltisi (pH: 1.92) kullanılarak yapılan deneyler en kesin ve doğru voltammetrik sonuçları vermiştir. Zn ve Cu konsantrasyonlarının görece olarak yüksek bulunduğu durumlarda bu elementlerin voltammetrik analizleri, biriktirme potansiyeli ve uygun civa elektrodu modunu ayarlayarak, diğer üç elementin analizlerinden ayrı olarak gerçekleştirilmiştir. Yüksek Cu konsantrasyonlarında ise analizler kompleks yapıcı olarak kullanılan etilendiamintetraasetik asit (EDTA) eklenerek gerçekleştirilmiştir. ICP-OES ve DPASV metodları ile elde edilen sonuçlar eşleştirilmiş t-testi ile istatistiksel olarak analiz edilmiştir. Tespit edilen ağır metal miktarları Dünya Sağlık Örgütü, Avrupa Birliği ve Türk Gıda Kodeksi tarafından belirlenen ölçülerle karşılaştırılmıştır. İstatistiksel analiz %95 güven aralığında yapılmıştır. Konserve ve taze balık örneklerinde bulunan Pb miktarları dışında her iki metodun aynı değerleri verdiği bulunmuştur.

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A	Electrode Area
C_O	Concentration of the oxidized species
C_R	Concentration of the reduced species
D	Diffusion Coefficient
E	Applied Potential
$E_{1/2}$	Half-wave Potential
F	Faraday Constant
i_l	Limiting Current
t_d	Deposition Time
v	Potential Scan Rate
V_{Hg}	Volume of the Mercury Drop
ADI	Acceptable Daily Intake
AI	Adequate Intake
AE	Auxiliary Electrode
ATP	Adenosine Triphosphate
CB	Corn Brand
CFB	Canned Fish Brand
DME	Dropping Mercury Electrode
DPASV	Differential Pulse Anodic Stripping Voltammetry
DPCSV	Differential Pulse Cathodic Stripping Voltammetry
DRI	Dietary Reference Intake
EAR	Estimated Average Requirement
EPA	Environmental Protection Agency
FAAS	Flame Atomic Absorption Spectroscopy
FAO	Food and Agriculture Organization
FFB	Frozen Fish Brand
HMDE	Hanging Mercury Drop Electrode
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
IR	Induction Region
IRZ	Initial Radiation Zone

MFE	Mercury Film Electrode
MT	Metallothionein
NADPH	Nicotinamide adenine dinucleotide phosphate
NAZ	Normal Analytical Zone
PHZ	Preheating Zone
PMTDI	Permissible Maximum Tolerable Daily Intake
RDA	Recommended Daily Allowance
RDI	Recommended Daily Intake
RE	Reference Electrode
RF	Radiofrequency
RfD	Reference Dose
SD	Standard Deviation
SMDE	Static Mercury Drop Electrode
TTB	Canned Tomato Brand
UL	Upper Limit
WE	Working Electrode
WHO	World Health Organization

1. INTRODUCTION

Metals contribute to the regulation of biological functions in living organisms. Along with the plants and animals, the tissues of human body include a good deal of metals in trace amounts. A total adult body of 70 kg weight is considered to contain as 1 kg of calcium, 250 g of potassium, 150 g of sodium and 50 g of magnesium. Smaller amounts as 2 – 4 g of iron, 2 mg of selenium and other trace elements exist in human body [1].

Trace elements have received both scientific and legislative concern due to their nutritional and toxic features. Besides their nutritional and biological importance, exposure to metals in environment is a soaring problem. Metal contamination in environment follows various paths and processes as air pollution, water and soil contamination. Atmospheric emission is concerned as the greatest source of pollution [2]. Due to production based policies of industrial world large quantities of trace elements are accumulated and resulted in contamination in soils and water sources.

Water and soil are the main sources of metal contamination. Hence, food analysis became one of the major steps in investigation of metal uptakes by mankind. Food is a sophisticated non-homogenous mixture of chemical substances which is not easy to isolate and analyze. Appropriate methods regarding sample features, multi-element analysis, and laboratory equipments need to be improved.

The major step in food analysis is the preparation of the sample by investigation of the most suitable analytical technique. First of all, a representative sample should be prepared. Specimens should be handled with care, prevention of contamination is essential for the analyses. In food analysis, destruction of the organic material in sample matrices is crucial. Removal of the organic matter is generally carried out with the use of oxidizing agents in a wet digestion, or by dry ashing of the sample with air or pure oxygen. Various sample digestion techniques were studied for the best results [1, 3, 4].

Incremental attention on trace elements, their effects on living organisms and environment led to comprehensive studies. Governmental and international health

organizations arranged risk assessments in order to optimize the safe use of the chemicals and to detect the reliable limits of metals in nature and living organisms. The World Health Organization (WHO), Food and Agriculture Organization (FAO), and the U.S. Environmental Protection Agency (EPA) have set risk assessments of trace elements, since high intakes result in toxicity and low intakes cause nutritional deficiencies. Values for reference doses (RfDs), acceptable daily intakes (ADIs) and dietary reference intakes (DRIs) are calculated and the estimated values are arranged by commission regulations accordingly [5 - 8].

Fresh, frozen and canned fish samples and canned vegetable samples were analyzed for their Zn, Cu, Pb, and Cd contents. About 104 samples of canned fish, 62 samples of fresh fish, and 48 samples of canned vegetable samples were investigated for this purpose. Canned food samples of various brand names were selected, and canned fish samples were purchased from Istanbul and local markets in Gelibolu, Çanakkale. Fresh fish samples were purchased from markets in Istanbul and Gelibolu. Wet digestion technique with nitric acid (HNO_3), and nitric acid/perchloric acid compositions ($HNO_3/HClO_4$) was applied. Digestion time and the quantities of acid or acid mixture aliquots were optimized till clear digests were obtained.

The objectives of this study were to propose an electroanalytical method, Differential Pulse Anodic Stripping Voltammetry (DPASV) to detect the trace metal contents of Zn, Cu, Pb and Cd in the fresh and canned foods, and to evaluate the accuracy of the method by running parallel experiments with Inductively Coupled Argon Plasma Optical Emission Spectroscopy [9]. Method parameters of DPASV were optimized in terms of deposition time, deposition potential, and by using different buffer compositions as base electrolytes in voltammetric analyses. Simultaneous analysis of Zn, Cu, Pb and Cd was a challenging study, especially for the samples with high Zn and Cu contents. Therefore, suitable deposition potential ranges and the deposition time periods for metal-amalgam formations were searched. The voltammetric analysis of the Cu content required additional care and study due to its complex formation with chloride ions in the medium. Hence, DPASV method parameters were modified and the technique was improved by the addition of etylenediaminetetraacetic acid (EDTA) to the media in order to detect the Cu concentrations in food samples accurately.

Additionaly, Se content of several tuna and sardine samples were investigated by Differential Pulse Cathodic Stripping Voltammetry (DPCSV) [10].

The advantages and disadvantages of the DPASV method were determined through the comparison of the results revealed by the Stripping Voltammetry and Inductively Coupled Plasma Spectrometry. Data sets from both methods were statistically analyzed with paired sample t-test, by the software package, SPSS [11].

The results of this study were summarized in terms of corresponding Zn, Cu, Pb and Cd contents for each brand of sample that was investigated. They were compared with the limits set by the Health Organizations, Worldwide Commissions and Turkish Food Codex. Also, trace metal concentration levels of the investigated food samples were compared with the studies documented in the literature where Atomic Absorption Spectroscopic Methods of Analyses were used mainly [12-14].

2. TRACE METALS

2.1. Metals in Human Diet

Human nutrition requires adequate intake of metals as minerals, along with the major nutrients such as carbohydrates, fats, proteins and vitamins. Insufficient intakes end up with biological deficiencies and metabolic disturbances. A small number of these inorganic nutrients are significant on nutrition process; however, excess amounts of metals that are linked to contamination of the food supply chain accumulate in our body. The lack of metals in human diet may lead to significant biochemical issues, yet the present levels of metals in tissues determine their overall effect, whether they are classified as toxicants or not. The impact of metals on human health is detected at several different levels. Entry in the food chain can occur through plants and animal products, enhanced by supplementation and fortification, but also through environmental pollution.

2.2. Nutrient Metals

Considering the normal body functions, the variation of nutrient metals is divided into two classes:

2.2.1. Macronutrient Metals

This category includes metals as sodium, calcium, magnesium, potassium, phosphorus, chlorine and sulfur that are needed by the body in milligram amounts, daily.

2.2.2. Micronutrient Metals

Micronutrient metals are the minerals that metabolism needs in trace amounts, such as iron, zinc, copper, manganese, iodine, fluorine, boron, selenium, molybdenum, nickel, chromium, vanadium, silicon, arsenic, tin, cobalt, cadmium and lead. Besides the nutrient metals, living organisms are exposed to toxic metals such as beryllium, cadmium, lead, mercury; although cadmium and lead are listed as micronutrients. The margin between toxicity and essentiality is discussed in Section 2.5.

2.3. Trace Metals

The term ‘trace element’ is used to describe the amount of metals that belong to micronutrients group. Originally, the term defines diminutive amounts of metals in biological tissues below nanograms (10^{-9} g) down to picograms (10^{-12} g) which is hard to detect and quantify instrumentally. Today the term means that element occurs at a level of < 0.01% (< 100 μg/g) in biological tissues. ‘Ultra trace’ elements come up infrequently at a level of 0.01 μg/g [1]. For example, iron, copper and zinc are classified as trace elements, while ultra trace group includes chromium, manganese, fluorine, nickel, cadmium, lead, cobalt and selenium [15].

Inorganic macronutrients and micronutrients both participate in human body structure, exhibiting a wide range of biological functions. The macroelements are constituents of bone and teeth, as they help adjusting the composition of body fluids, while the microelements are components of enzymatic and redox systems and enzyme activators [1], [15]. Enzymes require additional chemical components called cofactors, one or more inorganic ions such as Mg^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+} or a complex organic or metallorganic molecule called coenzyme [16]. Further classification of trace metals concerns: i. Elements essential in diet: calcium, cobalt, chromium (III), copper, fluorine, iodine, iron, magnesium, molybdenum, potassium, selenium, sodium, and zinc. ii. Elements with possible beneficial effects: boron, nickel, silicon, and vanadium. iii. Elements without any beneficial effects: aluminum, antimony, arsenic, barium, beryllium, cadmium, lead, mercury, silver, strontium, thallium, and tin. These elements exist in the environment, and the human exposure should be limited. Entrance of the trace elements into the living systems is generally schemed as in Figure 2.1.

Trace elements enter the living system by diffusion or transport proteins. They interact with the nicotinamide adenine dinucleotide phosphate (NADPH) oxidase, facilitate the H_2O_2 production and the free radical formations. They disrupt the phospholipid bilayer due to lipid peroxidation and produce reactive oxygen species (ROS). ROS result in altered calcium homeostatis, and finally DNA damage. The toxicity of the elements is characterized by the effect of trace element on target molecules [42].

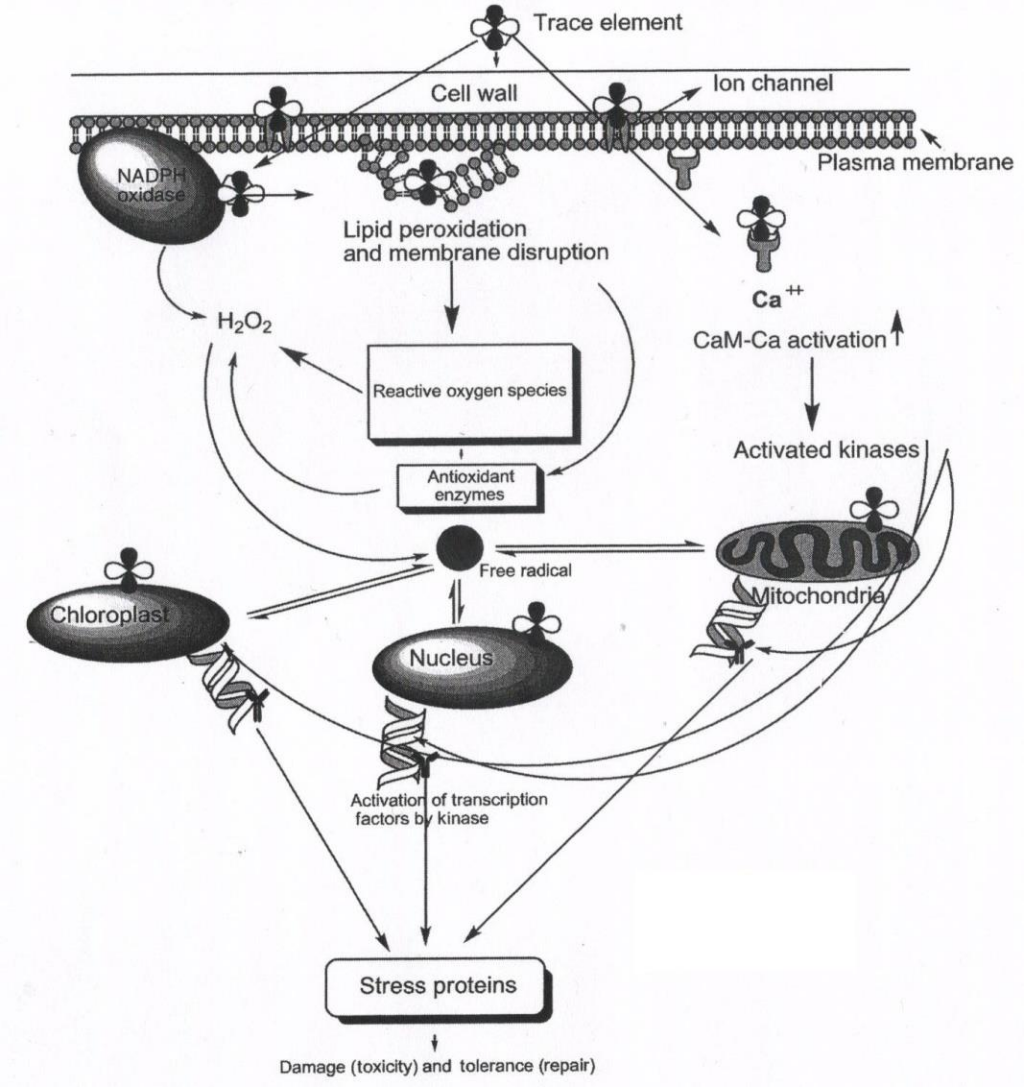

Figure 2.1. Trace element's entry in living organisms.

2.3.1. Essential Trace Metals

Currently, iron, zinc, copper, chromium, iodine, cobalt, molybdenum, and selenium are considered as essential for nutrition by World Health Organization (WHO), 2002. The elements silicon, manganese, nickel, boron, and vanadium are considered to be probably essential. Deficiency induces specific biochemical changes and results in suboptimal biological functions [17]. Nutritional requirements change for different organisms. However, regardless of the organisms, humans or animals, adequate intake of essential trace metals reduces and prevents biochemical abnormalities [18].

2.4. Toxic Metals

Within the essential trace metals, there is a group that can be regarded as toxic. However, distinction between the metals that play considerable roles in human metabolism and the hazardous category is not always obvious. For instance, in the case of selenium the difference between toxicity and sufficiency is very small. The attribute of a metal in the body depends on the other metals that are taken with, and on the synergestic or antagonistic effects between them. Therefore, it is hard to consider the effects of a single metal in isolation from the other metals and other components of the food. They interact with each other if consumed together. For instance, copper interacts with zinc, and high zinc intake inhibits intake of copper by competition for transpoters. Zinc also interferes with iron absorption. The toxicity and the other aspects of cadmium are related to the zincuptake. Similarly, cobalt and copper amount monitor the function of iron in the cells [1].

2.5. Toxicity and Essentiality

Toxicity of metals is affected by their interactions with micronutrients, as the effects of calcium on lead, phosphate on arsenate, and zinc on cadmium. Micronutrients can alter the body's response to toxic metals. For instance, cadmium has an inhibitory effect on zinc containing enzymes' activity. Disturbances in zinc metabolism may raise the toxic effects of cadmium. Copper intake also effects cadmium metabolism in diet. Studies reveal that lead absorption and toxicity decrease as dietary zinc increases. Additionally, selenium prevents the lead inhibition on certain enzymes. Adequate intake of micronutrients has a significant role in decreasing the disturbing effects of nonessential metals [19].

2.6. Trace Element Risk Assessment

The risk assessment of trace metals examines the two aspects of toxicity; intakes those are too high and result in toxicity, and intakes those are too low and associated with nutritional problems [6].

The U.S. Environmental Protection Agency (EPA), Food and Agriculture Organization (FAO) and The World Health Organization (WHO) have set values regarding the toxicity spectrum. Fundamental steps in risk assessments are hazard identification, dose-response assessment and exposure assessment. These steps assist risk characterization, which is connected with ongoing researches and risk management.

Biological effects of an element are related with its chemical and physical speciation. Development of risk assessment requires determination of chemical species of trace elements, since chemical species determine the amount and rate of trace element intake [5]. Metals can be in the forms of hydrated metal ions, inorganic and organic complexes, adsorbed on organic and inorganic colloidal particles in environmental samples. Its physicochemical form affects the toxicity of a trace metal [20].

2.6.1. Toxicity Risk Assessment

2.6.1.1. RfD. EPA's reference dose is an ''estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure to which the human population (including sensitive subpopulations) may be continually exposed over a lifetime without an appreciable risk of deleterious effect'' [21]. Highest dose level with no critical adverse effect (NOAEL) and lowest dose level with a critical adverse effect are estimated by examining many human and animal studies. The RfD is not a definite marker of risk but a reference point, yet, as the measure of exposure beating the RfD increases, the possibility of adverse effects also rise [6].

2.6.1.2. ADI. Acceptable Daily Intake of a chemical is the estimate of the amount of a substance in food or drinking water, expressed on a body weight basis that can be ingested daily over a lifetime without appreciable risk [22]. It is calculated with the same approach as EPA's RfD.

2.6.1.3. PMTDI. Permissible Maximum Tolerable Daily Intake by WHO is the bearable value of a substance that naturally exists in food and drinking water [23].

2.6.2. Nutritional Deficiency Risk Assessment

2.6.2.1. DRI. Dietary Reference Intakes are quantitative estimates of average daily nutrient intakes that are used for assessing diets for individuals. These values include Recommended Daily Allowances, Estimated Average Requirements and Adequate Intakes [7].

2.6.2.2. RDA and RDI. Recommended Daily Allowance is the average daily dietary nutrient intake level set by Europe that is sufficient to meet the nutrient requirement of nearly all (97 to 98 %) healthy individuals in a particular life stage and gender group [7]. RDA provides an adequate nutrition in humans. Recommended Daily Intake, RDI, is set by the U.S. for vitamins and elements in the early 1990s, and it is analogous to RDA of Europe.

2.6.2.3. EAR. Estimated Average Requirement is the average daily nutrient intake level estimated to meet the requirement of half the healthy individuals in a particular life stage and gender group. EAR is the basis for RDA [7]:

$$RDA = EAR + 2\ SD_{EAR}$$

2.6.2.4. AI. Adequate Intake is used when an RDA cannot be determined and sufficient scientific evidence is not available to calculate an EAR.

2.6.2.5. UL. Tolerable Upper Intake Level is the highest average daily nutrient intake level that is likely to pose no risk of adverse health effects to almost all individuals in the general population. The potential for adverse effects increases when intake increases above the UL [6].

2.7. Metals in Food

Metal accumulation in our body reflects the food we consume, which is also related to the environment we live in. Turkish Food Codex monitors levels of metals and hazardous substances [24], as similar legislations in other countries. The worldwide

collection of data assists to demonstrate and publish the scientific literature, which helps us to obtain an overall idea of levels of metals in foods consumed. Data from different countries generally represents similar values of element intakes of commonly consumed foods [17], [25], therefore this similarity shows that dietary intake of trace metals will have relative and comparable values in different regions of the world.

2.7.1. Sources of Metals in Food

The significance of chemical speciation of trace elements was mentioned earlier, most of the data that published in scientific literature refer to total concentration of trace metals in food. Yet, whatever chemical form it has, soil and water are the primary sources of metal content in foods. It is crucial to identify the origins of metals in food and how it contributes to ingredients. Mainly the sources of trace elements are: (i) Natural sources as rock outcroppings, geologic parent materials, volcanic eruptions, sea sprays from marine ecosystems to terrestrial environments [26]. (ii) Agricultural sources as inorganic and organic fertilizers, irrigation waters and pesticides, sewage sludge [27]. (iii) Industrial sources as mine wastes, refinement, energy supplying power stations, processing of plastics, textiles, microelectronics and paper [28]. (iv) Domestic effluents as waste substances of sewage outfalls, enzyme detergents containing trace metals [29]. (v) Atmospheric sources as geothermal activities, soil dust, coal burning [30].

Trace elements from these sources accumulate in the air, soil and water before their transfer to animal tissues and plants.

2.7.1.1. Air. Trace metal release to the environment results from natural sources such as windblown dust, volcanoes, forest fires, sea spray; anthropogenic sources as iron and steel production, metal finishing industry, municipal incinerators, refining and industrial use of metals, and coal burning [1].

2.7.1.2. Soil. Soil functions like a storage for the trace elements both as micronutrients and as pollutants. Trace elements in soils according to their sources are: (i) Lithogenic: Absorbed from parent material, lithosphere. (ii) Pedogenic: Originated from lithosphere,

but they change forms due to soil forming processes. (iii) Anthropogenic: Elements deposited onto soils because of human activities [31].

US E.P.A. states 13 metals in priority pollutant list which includes Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn. Mostly the origins of such metals are anthropogenic sources that include commercial fertilizers, liming materials, sewage sludge, manure, pesticides, coal combustion residues, metal smelting industries and transport emissions [32]. The stance and bioavailability of trace elements are ordinarily affected by the source. For instance, in well aerated acid soils, trace elements as Cd and Zn are mobile and their transfer to plants happens readily. In poorly aerated neutral or alkaline soils, the transfer is less available [33].

Elucidation of the key points of plant metal accumulation might help understanding the phytoavailability and bioavailability of trace elements.

2.7.1.3. Water. Water is the main carrier for all chemical elements, its composition controls the air-soil-water cycle. It governs the forms of trace elements; therefore it is the most studied medium as a metal source. Concentration of trace metals depends on the water source, i.e., sea water has higher concentrations than river. Mostly trace elements are not in soluble forms in waters; mainly they appear in suspended colloids, mineral and organic matters [31].

The riverine fluxes and anthropogenic activities are the main sources of trace elements in sea and ocean basins. Although the trace element amounts change with respect to the water source, the total contribution of anthropogenic sources is genuinely significant. Some average values for different systems are estimated considering the seasons and local conditions [34, 35].

2.8. Trace Elements as Contaminants and Nutrients

2.8.1. Zinc

Zinc exists in almost all tissues of the human body; it is a structural component of over 300 enzymes, which include the ribonucleic polymerases, alcohol dehydrogenase, carbonic anhydrase, and alkaline phosphatase [36]. It has an essential role in the metabolisms of macromolecules, and gene expression. Approximately 10% of proteins have zinc binding potential, in the human genome [37]. Zinc in food and beverages are provided by animal products, such as meat. Most sea foods and liver are rich in zinc content.

The evidences of zinc deficiency are loss of appetite, retardation of growth and reproduction, scaly skin, and immunological abnormalities. Especially in poorer and developing countries, people suffer from severe zinc deficiency, resulting in anemia, hypogonadism, and depressed immunity. Therefore, the recommended daily allowance (RDA) was set for zinc by investigating the minimal quantity of absorbed zinc which is adequate to match endogenous losses of zinc. An estimated average requirement (EAR) for zinc is calculated as 9.4 mg/day for males and 6.8 mg/day for females. RDA is 11 mg/day for males and 8 mg/day for females, and RDI is 15 mg/day.

Studies have investigated the toxic effects of zinc as nausea, vomiting, diarrhea, lethargy, and fever. Zinc salts are intestinal irritants, intake of 300 mg/day of zinc sulfate for 6 weeks caused disturbance in immune system [38]. The upper level (UL) for the zinc is determined as 40 mg/day for individuals older than 19 years.

2.8.2. Copper

Most of the copper in human body is bound to proteins, several of these works as enzymes, as catalytic cofactor. They involve in ATP production with cytochrome *c* oxidase, superoxide dismutase, oxygen metabolism, iron transport as caeruloplasmin, maturation of extracellular matrix. All these enzymes and their activities are maintained by

the copper metabolism in human body [1]. Copper generally present in all foods, yet, nuts, cereals, mushrooms, legumes, and shellfish are best sources [39].

The symptoms of copper deficiency are cardiac disfunction, increased low-density lipoprotein, and decreased high density lipoprotein cholesterol, decreased methionine, and leucine enkephalins, anemia, neutropenia, and bone mineralization. However, the dietary lack of copper generally has not been observed in adults. EAR for copper was calculated as 0.7 mg/day for both men and women. RDA is set as 0.9 mg/day for adults, and RDI is 2.0 mg/day [6].

The high levels of copper inhibit sulfhydryl groups on enzymes, which protect cell from damage of free radicals [39]. Dose over 200 mg kg^{-1} by day might be fatal. Ingestion of large quantities of copper sulfate results in acute copper poisoning, which causes the erosion of the lining of the gastrointestinal tract and a blue – green mucosa [40]. In Wilson's disease, body cannot metabolize and eliminate copper, and copper accumulates in brain, kidneys, and liver [41]. Exceeding levels of copper in human body also cause abdominal pain, cramps, nausea, diarrhea, and vomiting. The upper level (UL) for copper is determined as 10 mg/day, based on a critical point of liver damage [6]. Maximum acceptable daily load is 0.5 mg kg^{-1} body weight.

2.8.3. Lead

Lead is commonly found in soils such as black organic shales. Food industry and governments try to decrease the lead levels in human diet because of its danger and risks especially for children. Lead levels are significantly high in beef, pork, cattle kidney, and offal, wine, and home-grown vegetables. Also, foods packed in cans contain higher levels of lead than frozen or fresh foods. Mostly, lead is found in every tissue of human body. Lead uptake is carried by ingestion of food and drink, and balanced with calcium amount in the body. Diets with lower calcium intakes have the risk of high absorption of lead. Human body accumulates the lead in teeth, bones, and hair.

The symptoms of acute lead poisoning are generally gastrointestinal effects. General weakness, fatigue, and malaise are also marked. Effects of chronic low-level lead

poisoning are mild anemia, peripheral neuropathy, abdominal colic and pain. In the long run, lead poisoning results in neurophysical defects, reproduction failures, renal damage, and hypertension [1]. Provisional Tolerable Weekly Intake (PTWI) for lead is 1.75 mg, for a 70 kg adult [42]. For children aged about 1 – 4 years, the mean dietary exposure is estimated as 0.03 to 9 µg kg^{-1} body weights per day, and for adults the values are determined as 0.02 to 3 µg kg^{-1} body weights [43].

2.8.4. Cadmium

Cadmium generally comes as a bi-product of zinc smelters, and the sludge of electrolytic refining of zinc. It is a nonessential element which is found in leafy vegetables and root crops, rather than fruits or seeds. The high contents of cadmium in vegetables are generally associated with contaminated fertilizers, and contaminated sewage sludge to agricultural soils and industrial pollution. Consumption of fish products is one of the major sources of cadmium in metabolism [44].

Cadmium absorption is carried by the gut; its transport to the blood induces the synthesis of metallothionein (MT). MT is a protein that involves in transport and storage of various metals in human body. Cadmium competes for the binding sites of the MT with zinc, iron and copper.

The ingestion of cadmium results in nausea, vomiting, abdominal cramp and headaches. Fruit drinks that stored in galvanized vessels cause poisoning. Long term poisoning of cadmium affects mostly the kidney, which impairs re-absorption of protein, sugars and amino acids. Chronic accumulation of cadmium leads to osteomalaica and bone fractures. A known disease related with cadmium poisoning is Itai itai disease in Japan, consumption of the rice irrigated with industrially polluted water, accumulated with cadmium up to 1 mg kg^{-1}. Its symptoms were associated with deficiencies of calcium, iron, zinc, protein, and vitamin D [45]. Cadmium bioavailability is reduced by zinc; the high levels of zinc act as protective Cd-blocking agent.

Countries and health organizations regulate the cadmium concentration in food with maximum permitted amounts and guidelines. A corresponding cadmium exposure of 0.8

μg kg^{-1} body weight per day, or, 25 μg kg^{-1} body weight per month was estimated [43]. The upper limit for the cadmium intake is 0.49 mg per week, for a 70 kg adult [42].

2.8.5. Selenium

Selenium naturally exists in sedimentary rocks, limestone, coal, shale, soils, and crops. Exposure to selenium generally occurs through food, its distribution in nature is carried with agriculture, disposal of drainage water, and it is also used extensively as an additive in animal feeds, a dietary supplement and as a fertilizer. Beef, poultry, brown rice, whole grains, offal, Brazil nuts are main sources of selenium.

After its absorption by body, selenium is reduced to selenide within red blood cells, and it incorporates into specific selenoproteins and forms selenocysteine [46]. Several selenoproteins defend against oxidative stress, and regulate thyroid hormone metabolism and redox status of vitamin C [6]. Low selenium status is associated with cardiomyopathy that leads to heart failure, especially affects the young children and women of child bearing age [47]. Major symptoms of selenium deficiency are poor growth, loss of pigmentation of hair and skin, muscle pain and weakness. According to the studies, 200 μg of selenium per day decreases these diseases [48].

Selenium toxicity, which is called selenosis, results in hair and nail loss, skin rash, nausea, vomiting, nervous system abnormalities, paresthesia, interference in sulfur metabolism, inhibition of protein synthesis [49]. Studies showed that selenosis symptoms are observed for a person who consumed 1 mg of selenium per day as sodium selenite for more than 2 years. An EAR of 0.045 mg per day was calculated for average, RDA is set as 0.055 mg per day [36], and RDI for selenium is 0.035 mg per day. Upper limit (UL) was set as 0.4 mg per day by The Institute of Medicine.

Summary of the element properties were given with legislated amounts and dietary limits (Table 2.2) [42].

Table 2.2. Summary of Element Properties: Sources, Effects and Dietary Limits.

Element	Source in Food Chain	Effects of Deficiency	Symptoms of Toxicity	RDA (EU)	RDI (US)	UL
Zinc	Beef, pork, seafood,	Growth retardation, reproductive problems	Reduced copper status	15 mg	15 mg	40–45 mg
Copper	Shellfish, nuts, seeds, liver,	High blood pressure, fatigue, anemia, fragile bones	Nausea, muscle pain	1.15 mg	1.4 mg	10 mg
Lead	Potatoes, wine, fish, meat	Depressed growth, altered iron metabolism	Gastrointestinal effects, fatigue, malaise,	-	-	1.75 mg / week
Cadmium	Cereals, fruits and vegetables, meat and fish	Depressed growth	Nausea, vomiting, abdominal cramp, headache	-	-	0.49 mg / week
Selenium	Beef, poultry, brown rice	Muscle weakness and fatique	Fatigue, hair loss, nausea	55 µg	35 µg	400 µg / day

3. THEORY OF ANALYTICAL TECHNIQUES

3.1. Voltammetric Methods of Analysis

The requirements for an analytical technique to be useful are generally sensitivity, precision, accuracy, dynamic range, ease of pretreatment and sample preparation, cost and applicability of to a wide range of substances [50]. These conditions are fulfilled by voltammetric analysis technique.

Voltammetry is the electroanalytical technique in which the current is measured as a function of applied potential to the electrode. This applied potential, *E*, controls the reducing or oxidizing strength of the electrode, in other words, the concentration of the electroactive species.

$$O + ne \rightleftharpoons R \tag{3.1}$$

According to the Nernst equation,

$$E = E^{o} - \frac{0.059}{n} \log \frac{C_R}{C_o} \tag{3.2}$$

where C_o and C_R are the concentrations of oxidized and reduced forms of the electroactive species, *n* is the number of transferred electrons in the reaction at the electrode surface (at 25 ^{o}C). The change in the oxidation state of the species results in *faradaic current*, which is a direct measure of the rate of the redox reaction. Faradaic current depends on mass transport and the charge transfer. Mass transport is the rate of the species that moves from the bulk of the solution to the electrode, and charge transfer is the rate at which electrons move from electrode to the solution.

In addition, there is another type of current which is called *non-faradaic current*, also known as *charging current*, that results from the charging of the double layer which forms at the electrode-solution interface. It is called as non-faradaic since electrons are not transferred across the electrode-solution interface [51].

The concentration of the analyte in the solution is proportional to the magnitude of the peak current. The current vs. potential is called voltammogram. Current is displayed on the vertical axis, where the potential is on the horizontal axis. The wave- or peak- shaped plots are obtained; the shape of the voltammogram is dependent on the processes in the electrode reaction [52].

The detection range for the voltammetric analysis is from sub-ppb to ppm, or higher concentrations. Direct measurement by differential pulse voltammetry or square-wave voltammetry is possible for the higher concentrations. For the lower concentrations, the techniques are enriched by the pre-concentration step, which is referred to stripping method [50].

3.2. Excitation Signals in Voltammetry

In voltammetry, several different voltage-time functions can be applied to the electrode, this voltage is called the excitation signal. The voltage of the electrode is varied, and the current response is measured. The waveforms of four most common excitation signals are; Linear Scan, Differential Pulse, Square-wave and Triangular, which form the Linear Scan (Polarography), Differential Pulse, Square-wave and Cyclic Voltammetry [53]. Figure 3.1 shows the types of excitation signals.

3.2.1. Linear Scan Voltammetry

Linear sweep voltammetry is the simplest voltammetric method. The potential of the working electrode is increased or decreased at a typical rate of 2 to 5 mVs^{-1} [53].

In the reaction of,

$$A + ne^- \rightleftharpoons P \qquad (3.3)$$

where analyte A is reduced to give the product P, the electrode is assumed to be connected to the negative terminal of the linear sweep generator. Therefore, the applied potentials are given in negative sign (Figure 3.2). Cathodic currents are positive, where anodic currents are negative.

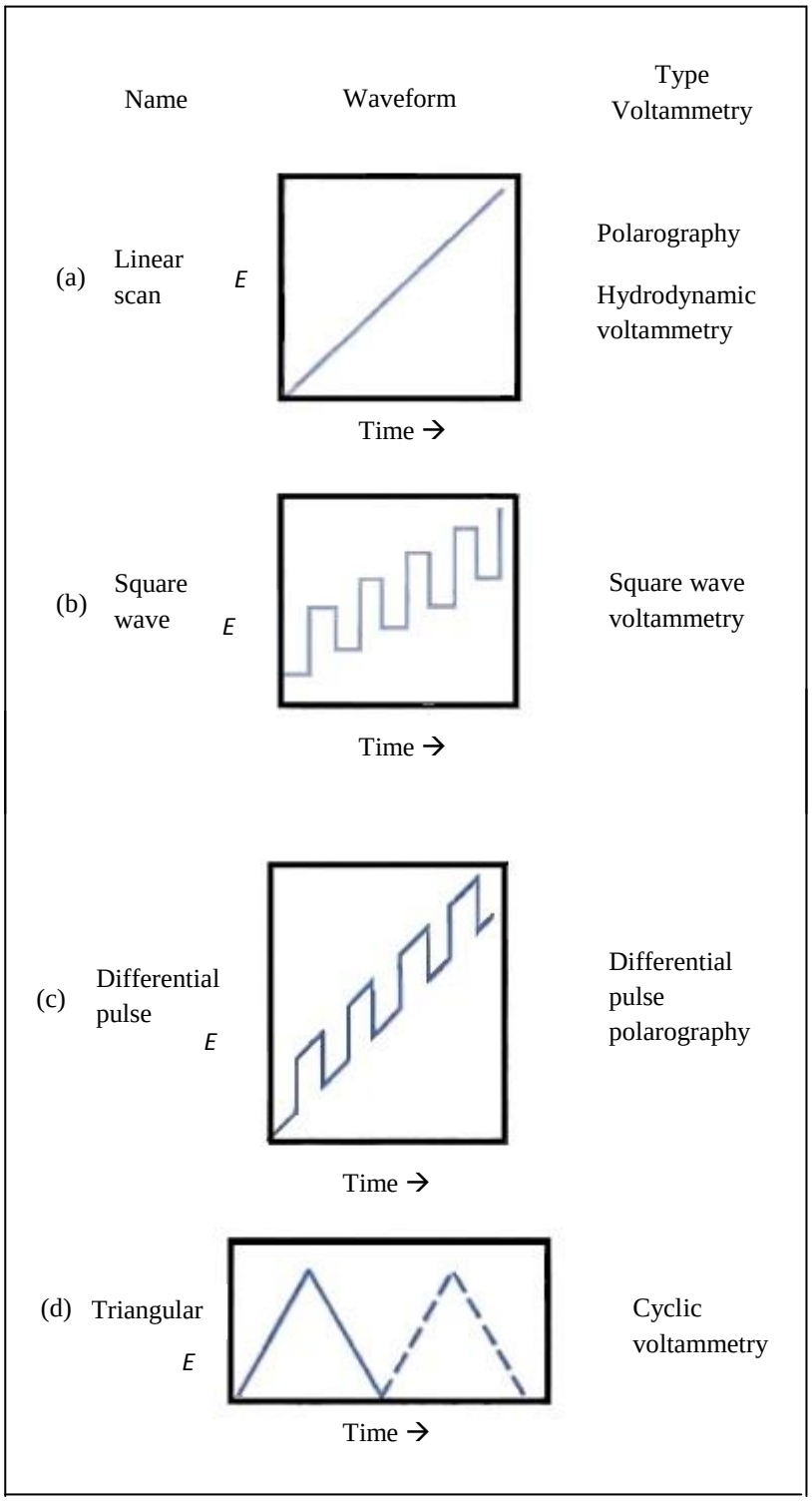

Figure 3.1. Excitation signals in voltammetry.

The voltammetric waves of linear sweep voltammograms have the shape of a sigmoidal curve. As the applied potential is increased from zero, the current flow will be observed. The further increase in the potential increases the reduction rate, therefore, the

current increases more. In classical polarography, the ions arrive at the Dropping Mercury Electrode (DME) only by natural diffusion; hence a point is reached at which the ions are reduced as fast as they diffuse to the electrode surface. Therefore, the current i_l is limited by the diffusion rate [54].

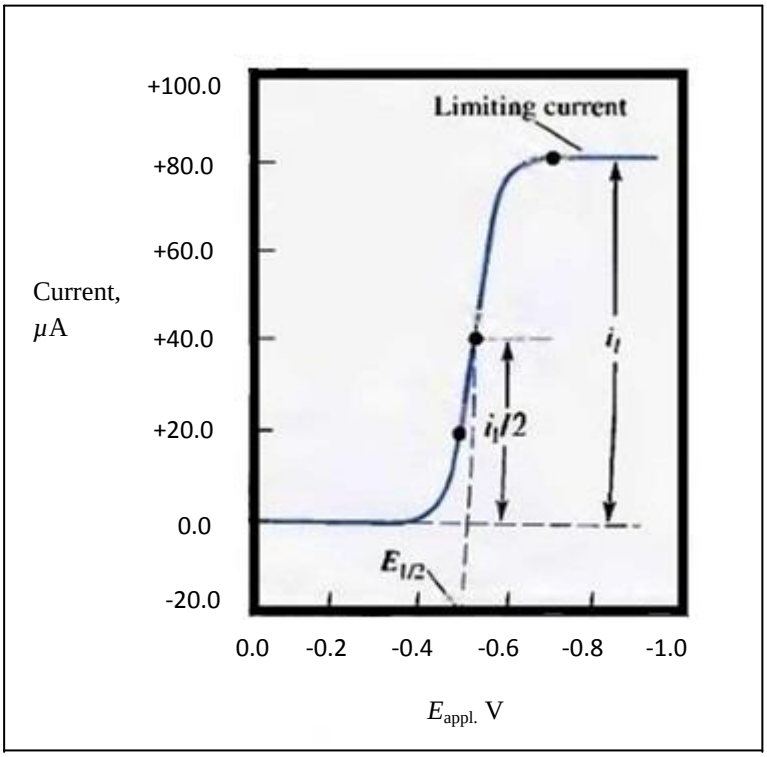

Figure 3.2. Linear scan voltammogram.

The potential at the mid-point of the wave at the half the limiting current, i_l, is known as the half-wave potential, $E_{1/2}$. The half-wave potential of a particular species is characteristic under fixed solution conditions, which is regarded as a ‘‘fingerprint’’. The limiting current is directly proportional to the concentration of the species,

$$i_l = kc_A \tag{3.4}$$

where c_A is the concentration of the analyte and k is constant.

Linear scan voltammetry is of two types, hydrodynamic voltammetry and polarography. In hydrodynamic voltammetry, the solution is stirred or microelectrode is kept in continuous motion. During electrolysis, the mass transfer to the electrode surface includes three factors (Figure 3.3), (i) *diffusion*, the spontaneous movement dependent on

the concentration gradient, independent of applied voltage, (ii) *migration*, the movement of particles along an electrical field, (iii) *convection*, the transport to the electrode by a physical movement [51].

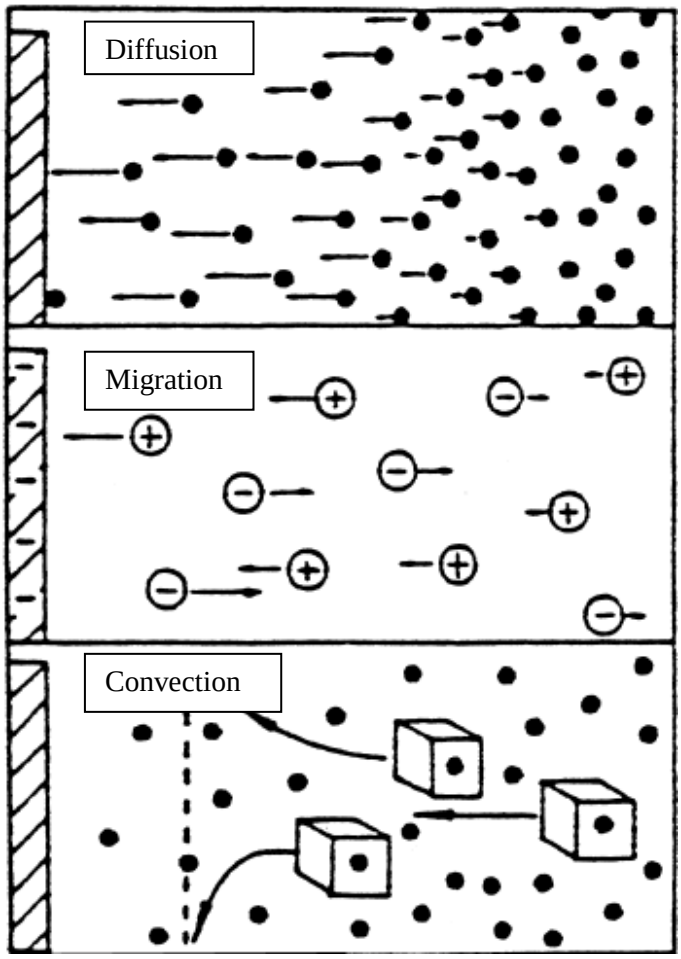

Figure 3.3. Types of mass transport.

The other type of linear scan voltammetry uses fast scan rates (1 V s^{-1} or greater) without stirring the analyte solution. Fast linear scans may lead to significant errors because of large faradaic currents and large capacitive currents [55].

3.2.2. Pulse Voltammetry

The limitations of the linear scan voltammetry such as slowness, inconvenient apparatus and poor detection limits were overcome by pulse methods. Differential pulse and square-wave voltammetry are two most common types of pulse voltammetry [56].

Differential pulse voltammetry is more sensitive than the normal polarography, also has significantly lower detection limits. By increasing the ratio between the faradaic and non faradaic currents, the measurement of the concentrations down to 10^{-8} M became possible [51]. Differential pulse polarography provides well defined peaks at a concentration level that is 500 times lower than normal polarography. One more advantage is that, the differential pulse voltammetry is able to differentiate the half-wave potentials by as little as 0.04 to 0.05 V; whereas the classical polarography needs 0.20 V for resolution of waves [53].

The trace levels of organic and inorganic species can easily be measured by differential pulse voltammetry. The fixed magnitude pulses are applied to the working electrode, just before the end of the drop (Figure 3.4). The current is measured twice, (i) before the pulse application and (ii) late in the pulse life. The first current is substracted from the second. The current difference versus the applied potential is plotted (Figure 3.5).

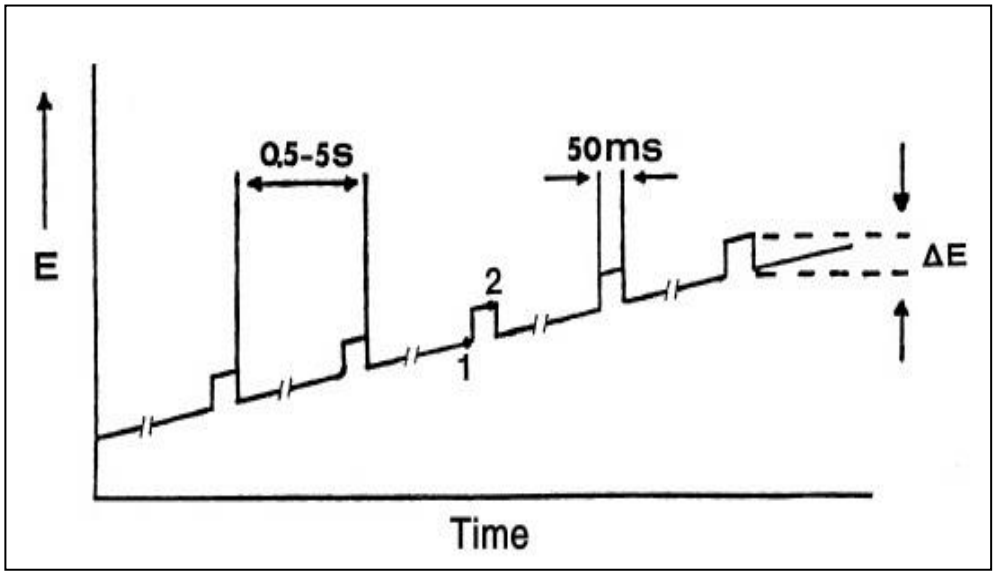

Figure 3.4. Excitation signal for differential pulse voltammetry.

The peaks in differential pulse voltammograms reveal the improvement in resolution of two species with similar redox potentials [51].

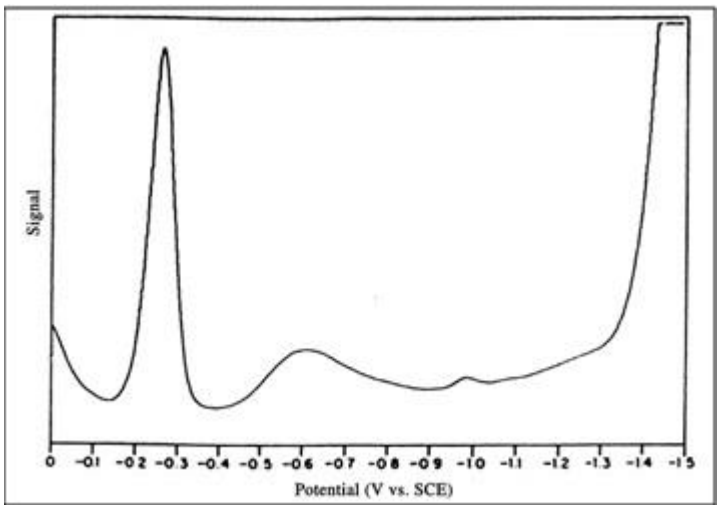

Figure 3.5. Differential pulse voltammogram.

3.3. Stripping Voltammetry

Stripping voltammetry is the electroanalytical technique which generates a favorable faradaic-to-non faradaic current ratio. The large faradaic currents per unit concentration give rise to low detection limits [57]. Four to six metals can be measured simultaneously at concentration levels down to 10^{-10} M, by stripping analysis.

Electroanalytical stripping comprises the oxidative or reductive removal of atoms, ions or compounds from the electrode. Two steps take place the stripping voltammetry, first one is the accumulation of the dissolved analyte onto the surface of the working electrode, and the second one is the removal of the accumulated substance into the solution. The activity of the accumulated substance is related with the concentration of the analyte in the sample. In addition, the accumulated substance activity is in correlation with maximum stripping current. Therefore, the electrode capacity is limited for the analyte accumulation, and the linearity is achieved well below the electrode saturation. Therefore, stripping voltammetry is used generally in trace analysis [58].

The use of stripping voltammetry is a widespread technique in environmental investigations. There are different versions of stripping analysis, according to the nature of the analyte and measurement steps.

3.3.1. Anodic Stripping Voltammetry

Anodic stripping voltammetry is suitable for the metal deposits as amalgams and adsorbed organic molecules. In anodic stripping voltammetry, ASV, the metals are pre-concentrated onto small volume mercury electrode. Accumulation of the metal is achieved by cathodic deposition at a controlled time and potential. Choice of the electro-deposition potential, $E_{d,}$ is made by estimating the deposition potential about 0.3 to 0.4 V more negative than the half-wave potential $E_{1/2}$ [59].

The metal ions transport to the electrode surface by convection and diffusion, and they concentrate as amalgams.

$$M^{n+} + ne^- + Hg \rightarrow M(Hg) \qquad (3.5)$$

The concentration of the metal in the amalgam, C_{Hg}, is calculated as,

$$C_{Hg} = \frac{i_l t_d}{nFV_{Hg}} \qquad (3.6)$$

where i_l is the limiting current for metal deposition, t_d is the deposition time period, V_{Hg} is the volume of the mercury electrode, F is 96,500 Coulomb per mole of electrons, and n is the number of electrons exchanged. The amalgam concentration is proportional to the deposition time, at very high and very low values of t_d the proportionality between concentration and deposition time is disturbed.

After the pre-concentration step, the amalgamated metals are re-oxidized, and stripped out of the electrode.

$$M(Hg) \rightarrow M^{n+} + ne^- + Hg \qquad (3.7)$$

A homogenous amalgam concentration can be achieved with a proper rest period between the deposition and the stripping processes.

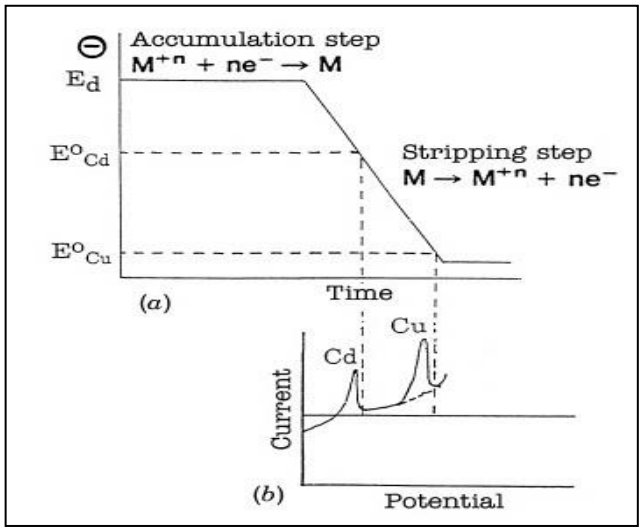

Figure 3.6. Anodic stripping voltammetry a) excitation signal, b) corresponding voltammogram.

The accumulated metal is stripped from the electrode surface and yields a peak height for each analyte (Figure 3.6). The peak current is linearly proportional to the analyte concentration and to the deposition time. However, long durations for accumulation step lead to overload on the electrode surface and miscalculations of concentrations of electro-active compounds [60].

Mostly encountered interferences in ASV are overlapping stripping peaks because of the similar oxidation potentials of some elements (e.g., of the Pb, Tl, Cd, Sn or Bi, Cu, Sb groups), and the formation of the inter-metallic compounds (e.g., Cu-Zn).

3.3.2. Cathodic Stripping Voltammetry

Cathodic stripping voltammetry is applied to the oxides, mercuric and mercurious salts and reducible organic molecules. Cathodic stripping voltammetry, CSV is carried out with anodic deposition of the analyte, and stripping in a negative potential scan. The reaction in the deposition step is as following,

$$A^{n-} + Hg \rightarrow HgA + ne^- \qquad (3.8)$$

The deposit is stripped off from the electrode as in the reaction:

$$HgA + ne^- \rightarrow A^{n-} + Hg \qquad (3.9)$$

3.3.3. Quantitative Analysis

Both in anodic and cathodic stripping voltammetry, the voltammetric peak reveal the concentration of the metal with respect to time. Peak potentials help identification of the metals in sample. The peak current depends on parameters of deposition and stripping steps. For hanging drop mercury electrode, the peak current is given by

$$i_p = 2.72 \times 10^5 \, n^{3/2} A D^{1/2} v^{1/2} C_{Hg} \qquad (3.10)$$

where n is the number of electrons involved in the reaction, A is the electrode area in cm^2, D is the diffusion coefficient for the metal on the mercury drop, in cm^2/s, v is the potential scan rate in V/s, and C_{Hg} is the concentration of the metal in the amalgam [51].

Peak recognition is achieved by delivering the minima and the maxima. After measuring the maxima and the minima values, the peak voltage and peak width values are determined for each peak, and then the base-line is constructed. The value of the peak maximum minus the value of the base-line at the position of the peak voltage reveals the peak height (Figure 3.7).

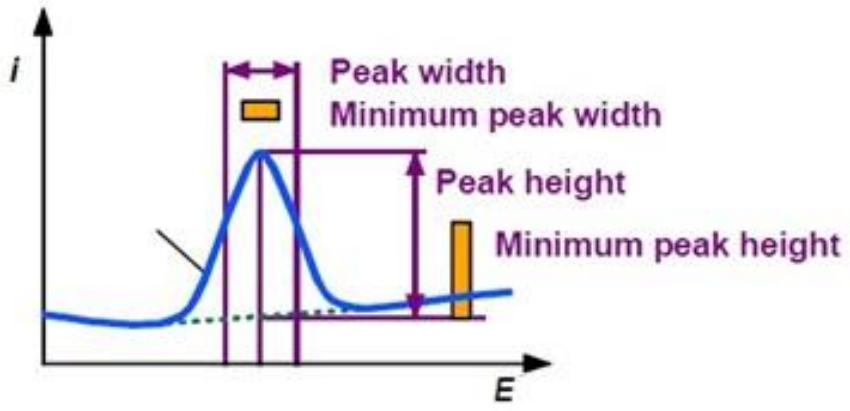

Figure 3.7. Recognition of a voltammetric peak.

The measured height, area, or derivative of a substance is proportional to its mass concentration. The relation between the evaluated peak height and mass concentration is determined by a calibration with reference solutions, that is, standard additions. In standard addition method, a known amount of analyte is added several times to the sample. The sample solution with the unknown mass concentration *c(s)* is measured one or more times and the evaluation quantity of the sample is recorded with mean and standard deviation values. Then the standard solution with known concentration is added to the analyte, and the evaluation quantity of the analyte with the known concentration *c(n)* is measured. Difference in the mass concentrations between added sample and the original sample solution gives the sample concentration. Determination of the standard addition curve is carried with the linear regression curve of the sample and the standard additions (Figure 3.8).

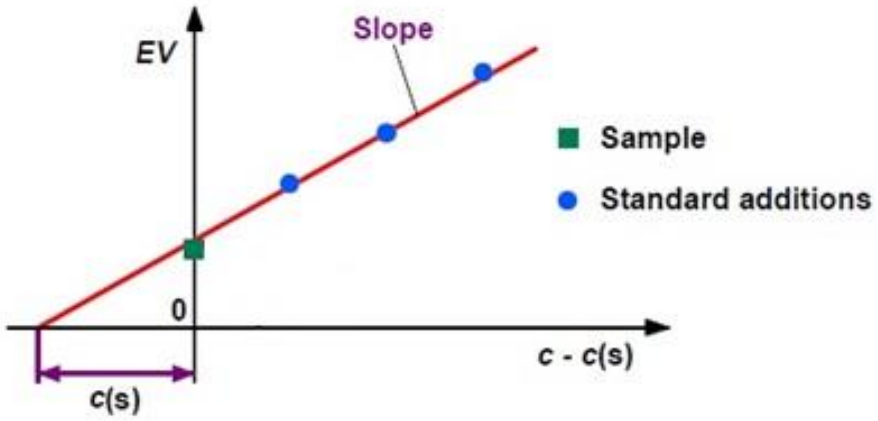

Figure 3.8. Voltammetric peak and the corresponding linear regression curve.

The advantage of the standard addition method is that its calibration takes place under real matrix conditions, and all measurement parameters remain unchanged. In order to decrease the scatter, number of replications should be as much as possible. The optimum standard addition ratio should be between 1:2 and 1:5; the standard addition amounts should be higher 2 to 5 times than the original sample solution [61].

3.4. Instrumentation in Voltammetry

Voltammetric measurements are carried out with the voltage source, voltammetric cell and voltammogram of measured species (Figure 3.9).

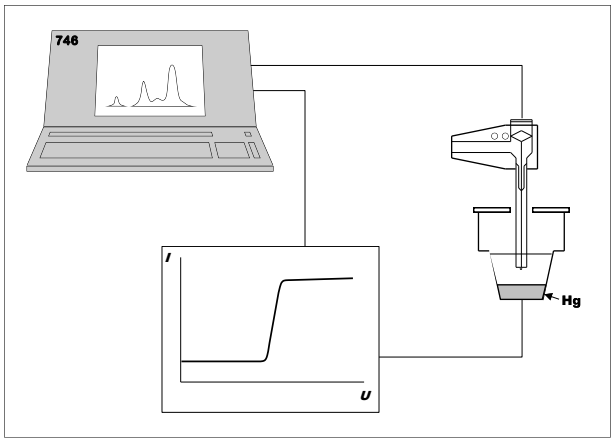

Figure 3.9. Instrumental set up for voltammetric determination.

3.4.1. Voltammetric Cell Components

Voltammetric measurements are carried out in an electrochemical cell, a glass, quartz or Teflon beaker. The cell contains three electrodes as working electrode (WE), reference electrode (RE) and auxiliary electrode (AE) (Figure 3.10). They are immersed in the sample solution in which the buffer and the electrolyte solutions are required [52].

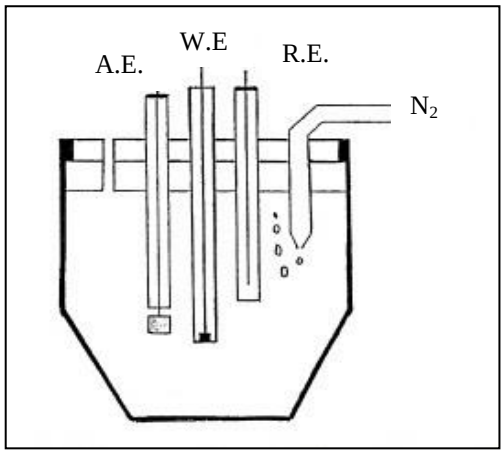

Figure 3.10. Schematic diagram of a cell for stripping analysis.

3.4.1.1. Electrodes in Voltammetry

The electrode is the integration of the electronic conductor with an ionic conductor. Electronic conductor can be a metal, or a semiconductor, the ionic conductor is usually an electrode solution. In analytical voltammetry, the analyte sample is generally dissolved in an electrolyte solution. The metallic conductor, as electrode, is immersed in an electrolyte solution. Dissolved electroactive ions change their charges by exchanging electrons with the conductor, at the surface of the electrode. The conductor is chemically inert, acts as sink of electrons [58].

3.4.1.1.1. Working Electrodes

The reaction occurs on the surface of the working electrode. The working electrode should provide high signal to noise ratio, in addition, it should minimize depletion of the analyte. In stripping analysis, generally two classes of working electrodes are used, mercury electrodes and inert solid electrodes [52].

Mercury Electrode: Mercury electrode has a high oxygen overvoltage, which extends the cathodic potential. It also generates reproducible and renewable smooth surface. There are several types of mercury electrodes, which are the dropping mercury electrode (DME), the hanging mercury drop electrode (HMDE), static mercury drop electrode (SMDE), and the mercury film electrode (MFE).

In DME, the mercury drop flows by gravity through the capillary at a steady rate, and the drop grows continuously (Figure 3.11). Detection limit is at parts per million levels (ppm). Controlling the flow of mercury drops is possible by HMDE, where detection limit is at parts per billion (ppb) and parts per trillion (ppt) levels [51]. The hanging dropping mercury electrode, HMDE, is a popular working electrode for stripping analysis. Stationary mercury drops are displaced from the reservoir through a vertical capillary.

The capillary should be filled with mercury and the air should be eliminated (Figure 3.12). The trapped air may lead non-reproducible drop sizes. The drop size can be controlled electronically.

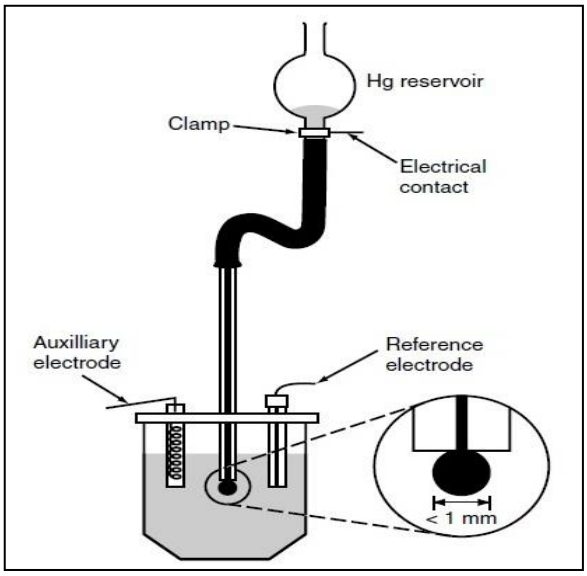

Figure 3.11. DME setup.

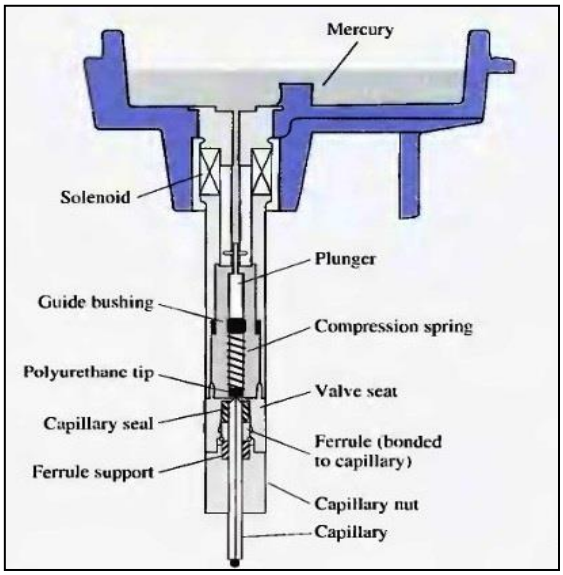

Figure 3.12. HMDE setup.

Highly reproducible surface area is achieved by static mercury drop electrode, SMDE, the drop hangs at the capillary tip until a drop knocker dislodges it. In addition, SMDE is generally used in detection of relatively higher concentrations of analyte, such as ppm or low ppm levels. Drop profiles of DME, SMDE and HMDE are given in Figure 3.13.

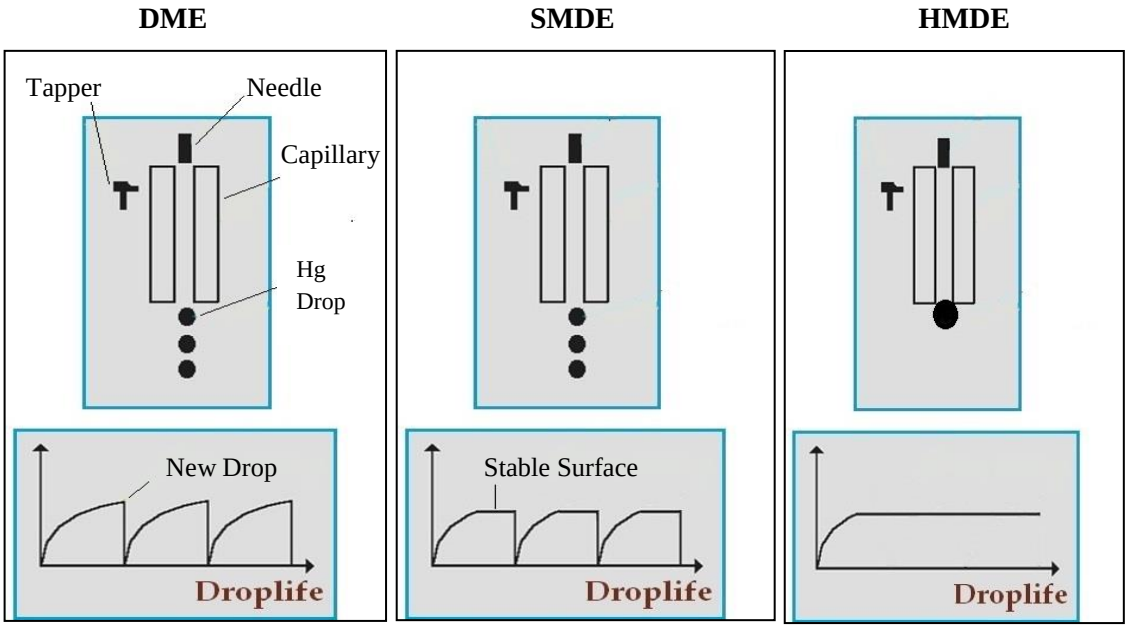

Figure 3.13. Drop profiles of mercury electrodes.

The mercury film electrode, MFE, consists of a very thin layer of mercury, covering a conducting and inert support. MFEs are used in cathodic deposition, and mostly, disk-shaped carbon electrodes are used to support the mercury film [51]. Detection limit is at parts per million (ppm) levels.

The elements with relatively positive redox potentials (i.e., Au, Hg) cannot be analyzed with mercury dropping or mercury film electrodes. Therefore, carbon (graphite) and/or noble metal (Pt, Au) electrodes are used. They are known as rotating disc electrodes. Glassy carbon electrode, for example, is used for the determination of silver and mercury. The carbon paste electrode is a mixture of graphite powder and a viscous organic binder, its non-faradaic current is very low.

Gold and platinum are commonly used rotating disc electrodes for stripping analyses. Yet they are not as inert as carbon electrodes, they may absorb hydrogen gas on their surfaces in acidic media. Also, the anodic potential range is restricted by the oxidation of the metal to complex chlorides, in acid chloride media. Gold film electrodes are used for the determination of arsenic, selenium, mercury, copper and silver. A disk-shaped solid electrode has been used in most cases [52].

3.4.1.1.2. Reference Electrode

Reference electrode implements a stable potential which is independent of the sample composition. The potential of the working electrode is compared with the potential of the reference electrode. Reference electrode remains unpolarized due to its constant composition, which serves as buffer against potential changes, as Ag/AgCl/KCl or saturated calomel electrode, Hg/Hg_2Cl_2. The reference electrode is separated from the sample solution, in order to minimize the contamination of the solution. The potential of the Ag/AgCl/KCl (3 mol L^{-1}) electrode is reproducible and the construction is very simple. The electrode net reaction is,

$$AgCl(s) + e^- \rightleftharpoons Ag^0(s) + Cl^- \qquad (3.11)$$

The electrode potential is 0.207 V at 25 ^oC. The electrode net reaction for the saturated calomel electrode can be formulated as:

$$\frac{1}{2}\ Hg_2Cl_2(s) + e^- \rightleftharpoons Hg^0(l) + Cl^- \quad (3.12)$$

The potential of the electrode is 0.244 V at 25 ^oC.

3.4.1.1.3. Auxiliary (Counter) Electrode

Auxiliary (counter) electrode minimizes the errors from cell resistance in controlling the potential of the working electrode. Inert conducting materials such as platinum wires or graphite rods are common counter electrodes in stripping analysis [52].

3.4.1.2. Supporting Electrolyte

In electroanalytical chemistry, the electrical migration of the metal ion caused by the electrical field should be minimized. Therefore, an excess of an inert supporting electrolyte is introduced into the sample solution. The solvent containing supporting electrolyte should have the electrical conductivity, electrochemical activity, and chemical reactivity. The supporting electrolyte should not get into reaction with the analyte [51].

The composition of the supporting electrolyte alters the pH of the medium, hence this affects the presicion of the result. The supporting electrolyte may be an inorganic salt, a mineral acid, or a base. The ideal electrolyte should give well-separated and well-shaped peaks [52]. Masking agents such as ethylenediaminetetraacetic acid (EDTA) may be used for the removal of interferences.

3.4.2. Removal of Oxygen

Dissolved oxygen interferes with the stripping analysis (Figure 3.14). The first step includes formation of the hydrogen peroxide, depending upon the pH, oxygen undergoes reduction in two steps:

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \text{ (acidic medium)} \quad (3.13)$$

$$O_2 + 2\ H_2O + 2e^- \rightleftharpoons H_2O_2 + 2OH^- \text{ (neutral or basic medium)} \quad (3.14)$$

Secondly, the peroxide reduces,

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \text{ (acidic medium)} \quad (3.15)$$

$$H_2O_2 + 2e^- \rightleftharpoons 2OH^- \text{ (neutral or basic medium)} \quad (3.16)$$

In the presence of oxygen, the metals may be oxidized in the electrode amalgam. In neutral or basic media, hydroxyl ions that formed during the reduction of oxygen can precipitate metal ions on the working electrode. Therefore the reduction of the oxygen is crucial for the analysis.

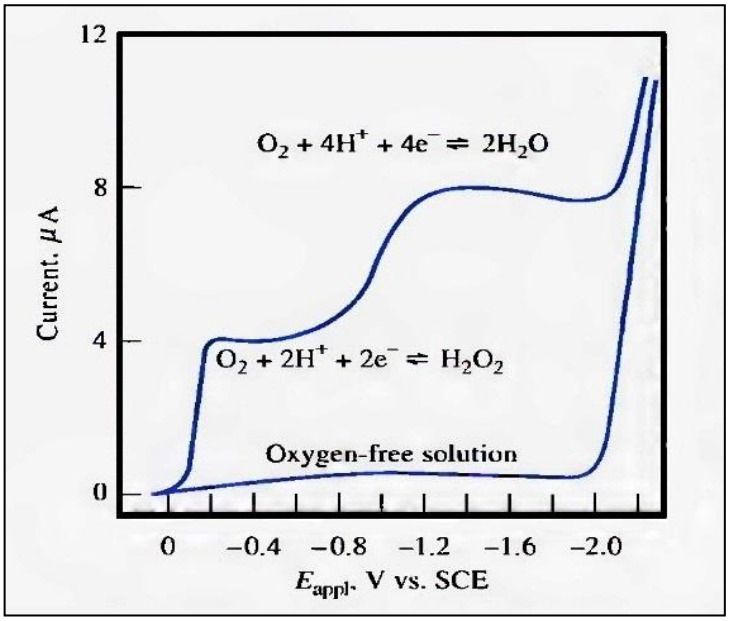

Figure 3.14. Oxygen peaks in voltammetry.

Removal of oxygen is generally performed with bubbling the solution with an inert gas i.e. nitrogen, argon. Nitrogen of 99.9% purity is mostly preferred because of its lower cost. Approximately 5-8 minutes is generally sufficient for the purge time [52].

3.5. Inductively Coupled Plasma Optical Emission Spectroscopy

The inductively coupled plasma optical emission spectroscopy (ICP-OES) is a widely used spectrochemical technique, especially in environmental science, it allows multielement quantitative analysis. The technique includes the injection of the liquid

sample into the radiofrequency-induced argon plasma. The sample solution is directed into the central channel of the plasma, after transformation to an aerosol. The aerosol is quickly vaporized at the core, since the temperature is approximately 10,000 ^{o}K. The elements in the analyte solution become free atoms. Excited atoms and ions emit photons in radio frequency discharge. The excited species relax to the ground state by the emission of a photon. The emission energies are quantized, thus the wavelength of the photons are characterized for each atom or ion (Figure 3.15) Furthermore, total number of photons reveals the concentration of the element in the analyte solution [62]. Schematic diagram of an ICP-OES instrument is given in Figure 3.16.

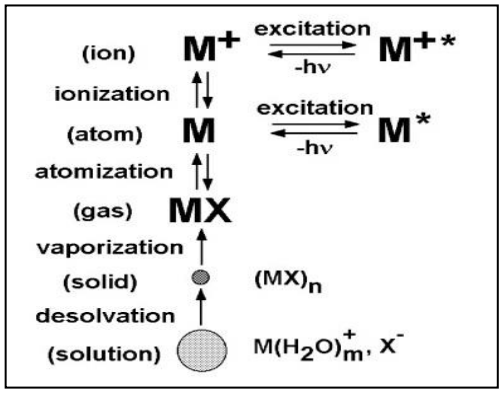

Figure 3.15. Process of a single sample droplet in ICP.

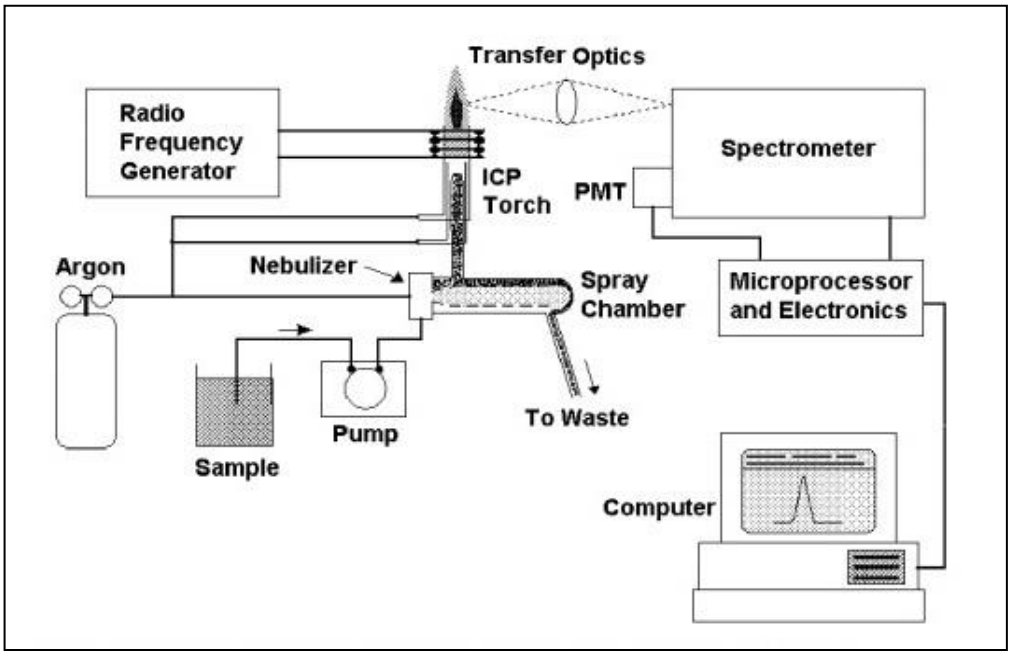

Figure 3.16. Major components of ICP-OES.

3.5.1. ICP-OES Torch

In ICP-OES, Argon gas is directed through a torch, which has three tubes made of quartz or some other suitable material (Figure 3.17). A copper coil (load coil) surrounds the edge of the torch and radiofrequency generator, RF power (700-1500 W) is applied to the copper coil, creating a changing magnetic field in the flowing gas inside the coil. This induces a circulating Eddy current in the gas, which in turn, heats it. Argon is not a conductor at room temperature, but it can be made electrically conducting by heating it. To initiate the ICP discharge, a discharge from a Tesla coil is applied to the flowing argon. Hence, in the induction region, IR, inductive energy is transferred from the coil to the plasma. The argon is quickly heated with a stable plasma being produced having a core temperature of about 10,000 K. As in Figure 3.18, a spark produces free electrons in the argon, which are accelerated by the RF.

The outer argon flow (10-15 L min^{-1}) conserves the high temperature; the sample aerosol is carried into the channel by the inner argon flow (0.5-1.5 L min^{-1}). In the preheating zone, PHZ, the aerosol vaporizes, then dissociates into atoms. The excitation and ionization process occur in the initial radiation zone, IRZ, and the normal analytical zone, NAZ.

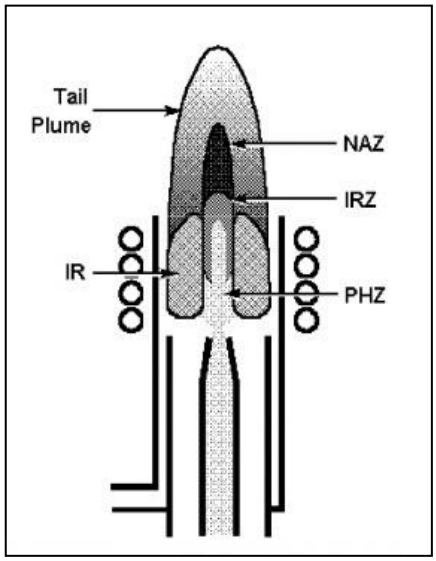

Figure 3.17. Zones of the ICP torch.

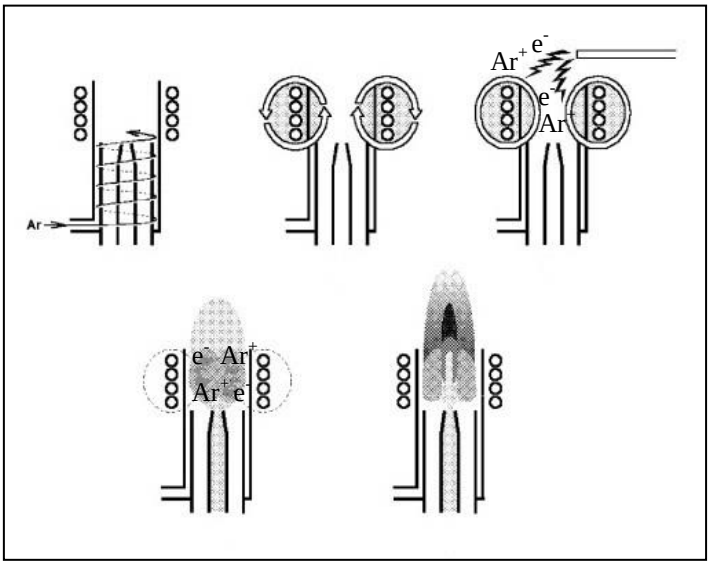

Figure 3.18. Cross section of an ICP torch.

3.5.2. Detection of Emission

In ICP-OES, the emitted light by the atoms and ions reveal information about the sample. Each species emit light at different wavelengths, therefore the emission from the plasma is polychromatic. The polychromatic radiation is sorted into individual wavelengths by a monochromator. After the separation of an individual wavelength, the actual detection of light is done by a photosensitive detector. 70 elements determined by the technique give at least 70,000 total emission lines in the wavelength range of 200-600 nm. Spectral interferences may occur in lower concentrations of elements.

Table 3.1. Emission wavelengths of Zn, Cd, Pb and Cu.

Element	Wavelength (nm)
Zn	206.200
Cd	228.802
Pb	220.353
Cu	327.393

3.5.3. Qualitative and Quantitative Analyses of the Sample

Identification of the emission wavelengths of the analyte sample reveals the characteristics of the elements. The relatively large number of the emission lines helps one to eliminate the interferences. Quantitative information is obtained by evaluation of the plots known as calibration curves (Figure 3.19). Standard solutions with known concentrations are introduced to the ICP-OES and intensity of the emission is recorded. The emission intensity versus concentration is plotted. Standard solutions with concentrations of 0.05, 0.1, 0.2, 0.5, 1.0 mg L^{-1} were used for low detection limits, and 1.0, 2.0, 3.0, 4.0, and 5.0 mg L^{-1} of standard solutions were used for higher detection limits.

The elements whose atoms have high excitation energies such as the halogens, Cl, Br and I are not determined at trace levels by ICP-OES [63].

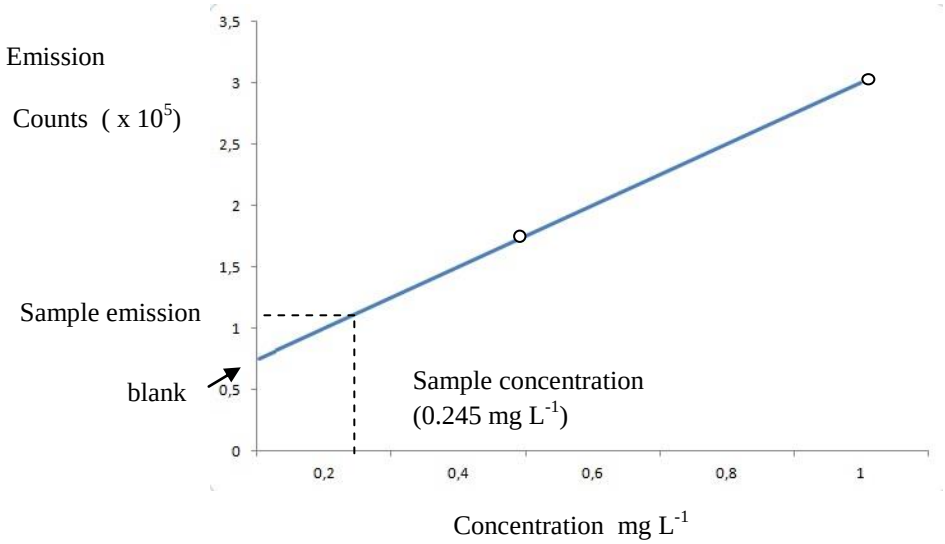

Figure 3.19. Calibration curve of ICP-OES.

In food science, plasma spectrometry has many applications with wide range of samples. However, the spectral overlap is an important challenge for ICP-OES. With complex matrices, interferences can occur. Examples of spectral interferences comprise the Cu interference on a sensitive Zn line at 213.85 nm, Mg on the 202.55 nm Zn line and Cr on the 206.20 nm Zn line [64].

The processes of sample collection and storage, preparation and pre-treatment have also significant effects on quality of ICP-OES analysis.

3.6. Comparison of Analytical Techniques DPASV and ICP-OES

With the improvement of analytical technology, the term ‘trace’ has been altered. The IUPAC Compendium of Chemical Terminology describes the trace element as ‘any element having an average concentration of less than 100 µg g^{-1}’ [65]. Yet, the detection capabilities have been developed, the upper limits for trace analysis transformed into ‘ultra trace’ boundaries.

Therefore, the analytical techniques for the detection of trace amounts were further investigated and compared. Electrochemical methods can be used in measuring either free ions in solution or ions bound in labile complexes. In DPASV, the accumulation step

increases the effectiveness of the method, and lowers the detection limit. It can be said that stripping voltammetry can achieve lower limit of detections than any other analytical technique. [66]. However, stripping voltammetry records the concentration values of free ions in solution and ions bound in labile complexes, but it is not very successful about assessing the concentration of elements that bound in compounds whose oxidation or reduction potentials were lower or higher than applied potential.

In atomic spectrometric techniques such as ICP-OES, ICP-MS, FAAS, there is no speciation of the elements, unless the technique is enriched with a chromatic process, they only reveal the total elemental content [67]. ICP-OES can detect many elements simultaneously; however, it is an expensive technique and can suffer from the interferences, particularly at lower concentrations [68].

When the spectroscopic methods were compared with electroanalytical methods, it can be seen that stripping analysis shows a good precision, accuracy and selectivity, with lower limits of detection and lower costs [69, 70].

For the elements investigated in this study, the detection limits were 10^{-8} M with HMDE mode, and 0.05 ppm for the ICP-OES analysis.

4. SAMPLE PREPARATION TECHNIQUES

4.1. Obtaining a Representative Sample

Proper sampling is the most fundamental aspect of food analysis, which provides accuracy. The care of the pre-analytical process is significant. First of all, homogenizing the foodstuff is essential. Portions of the sample should be taken in such a way that, each part of the material should have the same chance of appearing in the sample. Also, numbering the containers prevents miscalculation, and each portion selected represents the corresponded part of the bulk.

Both the animal and the plant tissues are naturally heterogeneous. Preparation of the sample requires a proper digestion technique. Additionally, the ways of contamination should be avoided by thoroughly cleaned glassware, blades, knives, sample containers, grinders, blenders the purity of chemical reagents and water, also thoroughly cleaned glassware [71].

4.2. Drying of Samples

When the fresh food samples need to be stored or homogenized in a ground mill, and a dry weight measurement is required, preparation of the sample is significant. This can be achieved by drying the samples in an air oven at 70-100 ^{o}C, in a vacuum oven within shorter time periods, or air-drying of the samples at 25 ^{o}C, overnight. The last method was applied to the food samples in this study [1].

4.3. Preparation of Samples Prior to Analysis

Canned and fresh fish and vegetable samples satisfy the energy and nutrition requirements, which include essential polyunsaturated fatty acids, essential aminoacids, minerals and vitamins. In order to be able to analyze the food samples properly, the destruction of the organic matter in the sample is essential. Otherwise, the organic residue in the sample may interfere with the analytical process. The removal of organic matter from the sample is carried out with the oxidation of the food either by the oxidizing acids

in the wet digestion or with air or pure oxygen by dry ashing. With respect to the metals to be analyzed, or the content of the food, the oxidation method varies [1].

In dry ashing method, the food samples are burned in a muffle furnace at temperatures between 400 and 600 ^{o}C. These temperatures are not suitable for volatile metals such as mercury, arsenic, selenium and lead. Moreover, incomplete combustion and adsorption on surfaces of incineration crucibles are disadvantages of this technique. Also, microwave digestion method is one of the pre-treatment techniques, which shortens the digestion time, and losses due to volatilization are minimized [3]. Electromagnetic energy brings the molecular motion and heating by the migration of ions and rotation of dipoles, without change in the molecular structure [72].

Wet digestion is one of the most applied techniques to dissociate the organic matrices in food and to obtain free ionic species. In this technique, strong oxidizing agents are used such as nitric, sulphuric and perchloric acid. The acids can be used either alone or in combinations .Wet digestion has flexibility for digestion of a wide range of organic matter. The detection limits in this method have been improved by more efficient sample oxidation with the use of pure reagents and by the dilution of the digests as little as possible. The food content alters the technique; carbohydrates are mineralized easier with nitric acid at 180 ^{o}C [73], while fats proteins and amino acids need further oxidizing agent such as perchloric acid [74].

4.3.1. Nitric Acid Digestion

Samples including zinc, lead and cadmium have convenient results with nitric acid digestion. In some cases, further oxidizing agents may be added in order to release the organic content of the sample, such as hydrogen peroxide [75]. However, because of the tendency of selenium for forming stable organic compounds in biological tissues, digestion of the sample with nitric acid only is not sufficient.

Meucci *et al*. prepared muscle samples according to the following several different methods: to 5 g of wet or dried muscle, 5 mL of 1N HNO_3 was added and heated up at 100 ^{o}C for 4 hours. Same procedure was repeated with the addition of 5 mL of HCl to 10 mLof

HNO_3. Moreover, the same digestion process was carried out with 10 mL of $HNO_3/HClO_4$ mixture (1:1, v/v) with the same digestion hours [76]. Studies showed that the addition of the stronger oxidizing agent helped the digestion process, detection of the Cd, Cu, Pb, and Hg by square-wave anodic stripping voltammetry were achieved successfully.

Djedjibegovic *et al*. had digested the fresh fish samples with 5 mL HNO_3 and 0.5 mL H_2O_2 mixture. Fish samples were approximately 0.25 g [77], the trace metal analysis was performed by ICP-MS. Kurun *et al*. digested the fish samples in HNO_3/H_2SO_4 mixture, AAS was used in the analyses [78]. Yet, the use of HNO_3/H_2SO_4 was less successful for the determination of selenium in food samples; the organic forms of selenium were resistant, and not broken down [79]. Also HNO_3/H_2SO_4 mixture was not convenient to be used for the determination of lead, due to the formation of insoluble lead sulphate [80].

4.3.2. Perchloric Acid Digestion

As in the work of Meucci *et al*., the addition of the perchloric acid, $HClO_4$ to the digestion medium as a further oxidizing agent enhanced the digestion process. Storelli *et al*. performed the wet acid digestion on fresh and canned tuna samples to investigated trace metals Hg, Cd and Pb. The acid digestion was carried with the addition of 11 mL of $HNO_3/HClO_4$ (8:3, v/v) to 1.0-2.0 g samples, and heated to 150 ^oC on a hot plate [81]. The best conditions for the voltammetric analysis of Zn, Cu, Cd and Pb were achieved with nitric acid/perchloric acid, $HNO_3/HClO_4$ mixture. The addition of perchloric acid improved the digestion process for the detection of Zn, Cu, Pb and Cd elements. However, the addition of the perchloric acid resulted in the loss of volatile elements such as chromium and selenium [82]. Therefore, an alternative digestion medium for those elements were searched.

5. EXPERIMENTAL APPROACHES

5.1. Reagents

5.1.1. Oxalate Buffer Solution

9.6 g of 142.11 g mol^{-1} extra pure di-ammoniumoxalate monohydrate ($C_2H_8N_2O_4$) and 4.6 g of 53.49 g mol^{-1} ammonium chloride (NH_4Cl) were dissolved in deionized water and 7.9 mL of 30% suprapur hydrochloric acid (HCl) was added in a 250 mL volumetric flask. All the reagents were supplied from Merck.

5.1.2. Acetic Acid Buffer Solution

74.9 mL of 25% suprapur ammonia (NH_3) and 118 mL of 100% suprapur acetic acid (CH_3COOH) were dissolved in a 1 L volumetric flask. Reagents were supplied from Merck.

5.1.3. Sodium Acetate Buffer Solution

5.9 g of 74.55 g mol^{-1} potassium chloride (KCl) and 20.5 g of 99% suprapur sodium acetate (CH_3COONa) were dissolved in deionized water and diluted in a 500 mL volumetric flask. Reagents were supplied from Merck.

5.1.4. Nitric Acid (HNO_3)

65% suprapur nitric acid was supplied from Merck. 10 – 20 mL aliquots of the acid solution were used for the wet digestion of food samples.

5.1.5. Perchloric Acid ($HClO_4$)

70% suprapur perchloric acid was supplied from Merck. 2 mL of the acid solution was used for the wet digestion of food samples.

5.1.6. EDTA Solution

0.372 g of ethylendinitrilotetraacetic disodium salt dihydrate was used to prepare 1 x 10^{-3} mol L^{-1} EDTA solution into 1 L volumetric flask. Reagent was supplied from Merck.

5.1.7. Potassium Chloride (KCl)

Potassium chloride solution of 3 mol L^{-1} was supplied from Metrohm and used for the voltammetric analyses.

5.1.8. Zinc Standard Solution

10 mL of 1001 ± 2 mg L^{-1} zinc stock solution supplied from Merck was diluted to 100 mL with deionized water in a volumetric flask in order to prepare 100 mg L^{-1} Zn standard solution.

5.1.9. Copper Standard Solution

1 mL of 10,000 mg L^{-1} copper stock solution supplied from BDH Chemicals was diluted to 100 mL with deionized water in a volumetric flask in order to prepare 100 mg L^{-1} Cu standard solution.

5.1.10. Lead Standard Solution

10 mL of 1000 ± 2 mg L^{-1} lead stock solution supplied from Merck was diluted to 100 mL with deionized water in a volumetric flask in order to prepare 100 mg L^{-1} Pb standard solution.

5.1.11. Cadmium Standard Solution

1001 ± 2 mg L^{-1} cadmium stock solution was supplied from Merck. 10 mL of was diluted to 100 mL with deionized water to prepare 100 mg L^{-1} Cd standard solution.

5.1.12. Selenium Standard Solution

10 mL of 1000 ± 5 mg L^{-1} selenium stock solution supplied from Merck was diluted to 100 mL with deionized water in a volumetric flask in order to prepare 100 mg L^{-1} Se standard solution.

5.2. Instruments

5.2.1. pH-meter

The pH-meter WTW Inolab pH/Cond 720 was used in analyses, the calibration of the pH-meter was carried with the buffer solutions of pH 4.00 and 7.00.

5.2.2. Voltammetric Analyzer

Metrohm 757 VA Computrace Voltammetric Analyzer was used for the voltammetric analyses. Mercury Drop Electrode with HMDE and SMDE modes was used as working electrode. Silver chloride, Ag/AgCl/KCl (3 mol L^{-1}) electrode was used as the reference electrode, and the platinum wire was used as the counter electrode.

The voltammetric cells were cleaned with 10% of HCl solution after each use.

5.2.3. Inductively Coupled Plasma Spectroscopy

ICP-OES Perkin Elmer Optima 2100 DV was used for the analysis of food samples. Working conditions were given in Table 3.1.

6. ANALYTICAL APPROACHES AND METHODOLOGY

Zn, Cd, Pb and Cu contents in various fish samples (fresh and canned) and in canned tomato and corn samples were analyzed by DPASV and ICP-OES methods. The following issues were taken into considerations: i. Effects of using HNO_3 and $HNO_3/HClO_4$ in the wet digestion process of food samples prior to analysis. ii. Effects of different supporting (base) electrolytes on the voltammetric analysis. iii. Effects of deposition time and deposition potential on the electrolytic deposition of trace metals onto electrode surface. iv. Effects of dilution factor of the digested samples on the voltammograms. v. Effects of the working -mode of Hg electrode as HMDE or SMDE in relation to the concentration of the metals in the digested samples. vi. Effects of EDTA on voltammetric determinations of Cu.

6.1. Acid Digestion of Food Samples

Most common sample pre-treatments include the use of concentrated acids in wet digestions, in order to break down the organic matter in fish and vegetable tissues.

In these laboratory experiments, fresh and canned fish samples and canned tomato and corn samples were investigated for their trace metal contents; Cd, Pb, Cu and Zn. Fresh fish samples such as anchovy and sardine were purchased from the local markets of Gelibolu, Çanakkale, while the bigger fish samples as seabass, bluefish, grey mullet, red mullet, horse mackerel, solefish, mackerel, mullet and goosefish were bought from groceries in Istanbul. Seven different brands of canned tuna samples as Kemerli, Superfresh, Alaeddin, Tamek, Ülker, Tonton and Pınar; canned anchovy samples of Yakşi brand and three different brands of frozen anchovy samples as Ayfrost, Pınar and Superfresh; four different brands of canned sardine samples as Yakşi, Alaeddin, Domes and Engin; Ayfrost brand musssel and Domes brand mackerel samples; four brands of canned tomato sauces and chopped tomato samples as Tamek, Tat, Demirci, Demko; five different brands of canned corn samples as Superfresh, Tat, Penguen, Tamek, Tukaş were analyzed.

Sample tissues for the analysis of sardine and anchovy samples were taken from both left and right sides of the fish spine and about one centimeter below the head. The bigger

fish samples were weighed in six replicates, and samples were taken from different parts of the same subject fish. Canned tuna, tomato and corn samples were collected in replicates from different parts of the same container.

Trace metal contents were determined by DPASV method and the results were compared from those obtained by ICP-OES. Test samples of 1.50 and 2.00 grams of weight were air dried. They were digested either in 20 mL of nitric acid (HNO_3) or in nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v) of 18 mL. Digestion period was kept between 18 hours and 26 hours in nitric acid alone, whereas it was about 20 hours in nitric acid/perchloric acid till clear solutions were obtained.

6.1.1. Nitric Acid Digeston of Canned Anchovy, Sardine, Corn and Tomato Samples

Anchovy samples of Yakşi Brand (Gelibolu) were taken out from the same can with a serial number of 008 and a production date of 08/10. Acid digestion was carried out in 20 mL of nitric acid (HNO_3) for about 18 hours. Clear digests were evaporated on hot plates and the excess acid was removed by replicate additions of deionized water. Each addition was followed by the evaporation of the digested sample to almost dryness. Then the samples were diluted to the final volume of 25.0 mL with deionized water. In DPASV analysis, voltammogram vessels contained 2 mL of the digested sample and 0.6–1.0 mL of buffer solutions, final volume was made up to 10.0 mL with deionized water. Since, DPASV method required the use of a supporting electrolyte for the transport of ions to the electrode surface, two different buffer compositions were tested, oxalate buffer and acetic acid potassium chloride buffer mixture (Table 6.1). Voltammograms were recorded in three replicates for each sample.

Table 6.1. Buffer compositions.

Buffer*	**Composition**	**pH**	**Volume in vessel (mL)**
Oxalate	$C_2H_8N_2O_4$ + NH_4Cl + HCl	1.92 ± 0.12	1.00
Acetic acid/ Potassium chloride	CH_3COOH + KCl	4.60 ± 0.05	0.60

*Quantities of Buffer Compositions are given on page 30.

The half-wave potentials ($E_{1/2}$) of the elements varied depending upon the composition of the buffer media that was used. Theoretically expected $E_{1/2}$ values are given in Table 6.2.

Table 6.2. Half-wave potentials ($E_{1/2}$,V) of metal ions [83].

Elements	**Oxalate Buffer**	**Acetic acid/ Potassium chloride**
Zn	-1.05	-0.98
Cd	-0.63	-0.56
Pb	-0.47	-0.38
Cu	-0.25	0.03

Generally, the results for the Zn contents as mg g^{-1} of anchovy samples from DPASV and ICP-OES were in good agreement with each other in oxalate and acetic acid plus potassium chloride buffers. Six different anchovy samples were analyzed and only the results of the triplicate analyses of the two (A_1 and A_2) were given in Table 6.3 and Table 6.4. Voltammograms were taken in the presence of 1.0 mL of oxalate buffer (Table 6.3).

Table 6.3. Zn contents of anchovy samples (Yakşi brand) in oxalate buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_1	177 ± 16	2.21 ± 0.22	9.04	216	2.70
A_2	91 ± 10	1.14 ± 0.10	11.0	127	1.59

Voltammograms were taken in the presence of 0.6 mL of acetic acid plus potassium chloride buffer (Table 6.4).

Table 6.4. Zn contents of anchovy samples (Yakşi brand) in acetic acid and potassium chloride.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_3	5.98 ± 0.28	0.075 ± 0.004	4.68	5.52	0.069
A_4	3.03 ± 0.11	0.038 ± 0.060	3.63	2.48	0.031

The corresponding Cu concentrations that were registered with DPASV method were not consistent with the values that were obtained with ICP-OES for samples A_1 and A_3 (Table 6.5, Table 6.6). Figure 6.1 represents the voltammogram of an anchovy sample, A_1, analyzed by DPASV method with oxalate buffer. The adjacent peak labeled as the unknown peak caused a shift in the baseline of the voltammogram. Hence, DPASV analysis did not give an accurate result for the Cu content. The voltammogram of the sample from the same can with acetic acid and potassium chloride buffer solution showed a shifted baseline and also a distorted and split peak (Figure 6.2). The corresponding half-wave potential values for the sample peak and the two consecutive standard addition peaks differed from each other. Thus, the result of the Cu concentration was not a reliable one.

Table 6.5. Cd, Pb, Cu contents of anchovy samples (Yakşi brand) in oxalate buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_1	Cd	11.9 ± 0.5	0.149 ± 0.006	4.20	12.6	0.158
	Pb	154 ± 3	1.92 ± 0.03	1.94	103	1.28
	Cu	1405 ± 105	17.5 ± 1.3	7.48	5914	73.8
A_2	Cd	9.55 ± 0.42	0.119 ± 0.005	4.35	12.6	0.157
	Pb	109 ± 5	1.36 ± 0.06	4.59	83.2	1.04
	Cu	1628 ± 79	20.3 ± 0.99	4.89	1377	17.2

Table 6.6. Cd, Pb, Cu Contents of anchovy samples (Yakşi brand) in acetic acid and potassium chloride buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_3	Cd	2.26 ± 0.22	0.028 ± 0.003	9.73	9.50	0.118
	Pb	65.2 ± 4.4	0.812 ± 0.054	6.75	67.1	0.836
	Cu	1746 ± 255	21.8 ± 3.2	14.6	288	3.59
A_4	Cd	43.5 ± 0.7	0.542 ± 0.009	1,61	44.3	0.552
	Pb	368 ± 7	4.58 ± 0.08	1.90	300	3.74
	Cu	95.8 ± 2.5	1.19 ± 0.03	2.61	140	1.74

The results of DPASV and ICP-OES methods for the Cd and Pb contents of samples agreed with one another, in both buffer media except for the sample A_3, where the Cd content as µg g^{-1} with DPASV method were rather lower than the ICP-OES result.

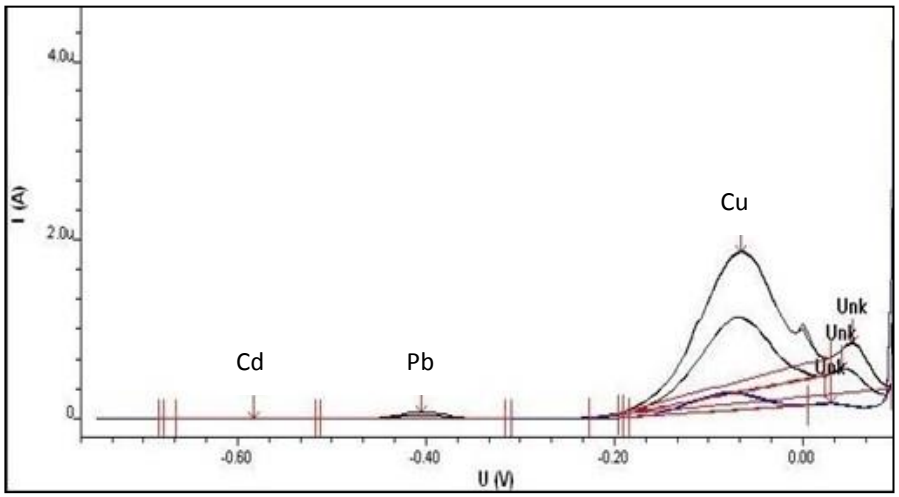

Figure 6.1. Voltammogram of sample A_1 with oxalate buffer.

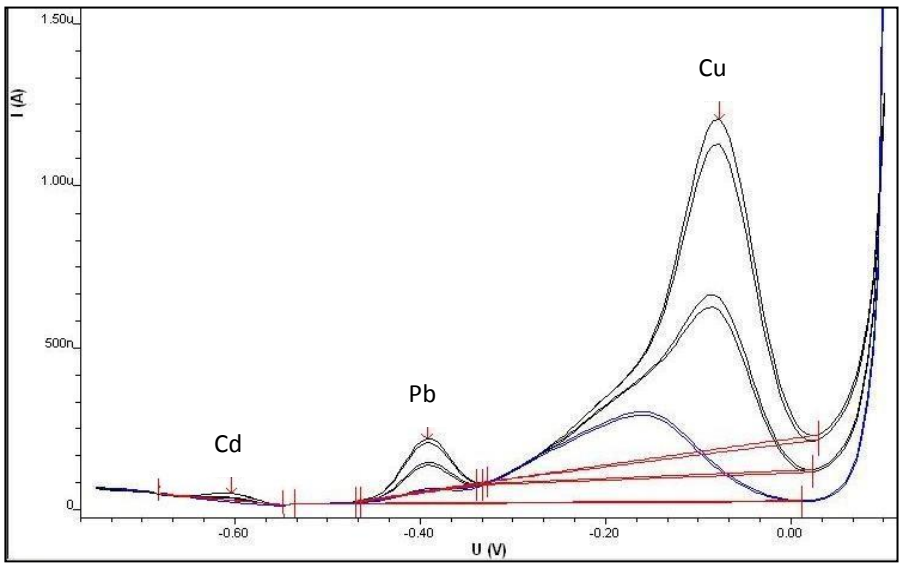

Figure 6.2. Voltammogram of sample A_3 with acetic acid and potassium chloride buffer.

The results of DPASV and ICP-OES analysis of anchovy samples were compared and the following conclusions were obtained: (i) The corresponding Zn contents (mg g^{-1}) of anchovy samples in DPASV and ICP-OES analyses were in agreement with each other in both buffer compositions. Voltammograms resulted in relatively small percent deviation values i.e., 4.78 % and 3.63 % for the samples A_3 and A_4, respectively. (ii) The

corresponding Cu concentration results of the DPASV method were not accurate due to the shifted base-lines in some samples. Also, the appearance of the split peaks indicated the presence of undestroyed organic matter and/or the unsuitable electrolyte media. iii. The corresponding concentrations of Cd and Pb in anchovy samples were generally lower than the corresponding Cu contents, except for the sample A_4 in which the Pb concentration was greater than that of Cu and Cd. The shifts in the base lines of Pb and Cd voltammograms were not observed in oxalate buffer.

It was rather difficult evaluate the efficiency of nitric acid in the digestion process of anchovy samples, and also to ascertain whether oxalate or acetic acid and potassium chloride buffer media was suitable. Furthermore, sardine samples were analyzed, and they were digested in nitric acid, also. The results of DPASV were not consistent with the ICP-OES analyses.

Seven sardine samples of Yakşi brand (Gelibolu) were taken from the same can with a serial number of 03 and a production date of 02/2012. Samples were digested in 20 mL of nitric acid for 20 hours. Voltammogram vessels contained 2 mL of the digested sample and 0.6 – 1.0 mL of buffer solutions which were either oxalate or acetic acid and potassium chloride mixture and the final volume was diluted to 10 mL with deionized water.

Table 6.7. Cd, Pb and Cu contents of sardine samples (Yakşi brand) in oxalate buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_1	Cd	0	0	-	7.76	0.096
	Pb	46.9 ± 2.9	0.580 ± 0.036	6.18	15.5	0.191
	Cu	102 ± 10	1.26 ± 0.13	9.80	30.4	0.375
S_2	Cd	0	0	-	17.5	1.39
	Pb	965 ± 160	11.9 ± 1.9	16.6	113	2.40
	Cu	0	0	-	194	2.39
S_3	Cd	0	0	-	8.54	0.105
	Pb	110 ± 3	1.36 ± 0.04	2.73	112	1.38
	Cu	1542 ± 85	19.0 ± 1.05	5.51	1549	19.1

Table 6.8. Zn contents of sardine samples (Yakşi brand) in oxalate buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_1	4.49 ± 0.12	0.055 ± 0.001	2.67	4.15	0.051
S_2	2.55 ± 0.05	0.032 ± 0.001	1.96	2.41	0.030
S_3	44.5 ± 3.1	0.550 ± 0.038	6.97	48.8	0.601

Table 6.9. Cd, Pb and Cu contents of sardine samples (Yakşi brand) in acetic acid and potassium chloride buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_1	Cd	0	0	-	7.76	0.096
	Pb	175 ± 8	2.16 ± 0.09	4.57	15.5	0.191
	Cu	0	0	-	30.4	0.375
S_2	Cd	0	0	-	17.5	1.39
	Pb	164 ± 18	2.02 ± 0.22	10.9	113	2.40
	Cu	0	0	-	194	2.39
S_3	Cd	0	0	-	8.54	0.105
	Pb	80.3 ± 11.5	0.991 ± 0.142	14.3	112	1.38
	Cu	580 ± 13	7.15 ± 0.16	2.25	1549	19.1

Table 6.10. Zn contents of sardine samples (Yakşi brand) in acetic acid and potassium chloride buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_1	4.82 ± 0.15	0.060 ± 0.002	3.11	4.15	0.051
S_2	0.345 ± 0.011	0.004 ± 0.000	3.18	2.41	0.030
S_3	30.1 ± 2.8	0.371 ± 0.034	9.30	48.8	0.601

DPASV analysis of sardine samples (S_1, S_2, S_3) did not detect the Cd content in either oxalate or acetic acid and potassium chloride buffer solutions, although they were detected by ICP-OES analysis. Also, DPASV analysis did not register the Cu contents of S_1 and S_2 in acetic acid plus potassium chloride medium, where the corresponding concentrations in ICP-OES analysis were 0.375 µg g^{-1} and 2.39 µg g^{-1}, respectively (Table 6.9). The same situation was experienced in sample S_2 in oxalate buffer for the Cu content (Table 6.7). Moreover, the recorded concentrations for both Pb and Cu in oxalate buffer were not consistent with the ICP-OES results, except for the sample S_3. Voltammograms of sample S_2 in both buffer media are given in Figure 6.3 and 6.4. Although the peaks in the DPASV analysis of sample S_2 in oxalate buffer were well separated, the recorded

amounts of Zn, Pb and Cu were not in agreement with the ICP-OES results. The Cu label on the right side of the voltammogram belongs to the Cu contents of the standard additions where the analyte peak was not observed (Figure 6.3).

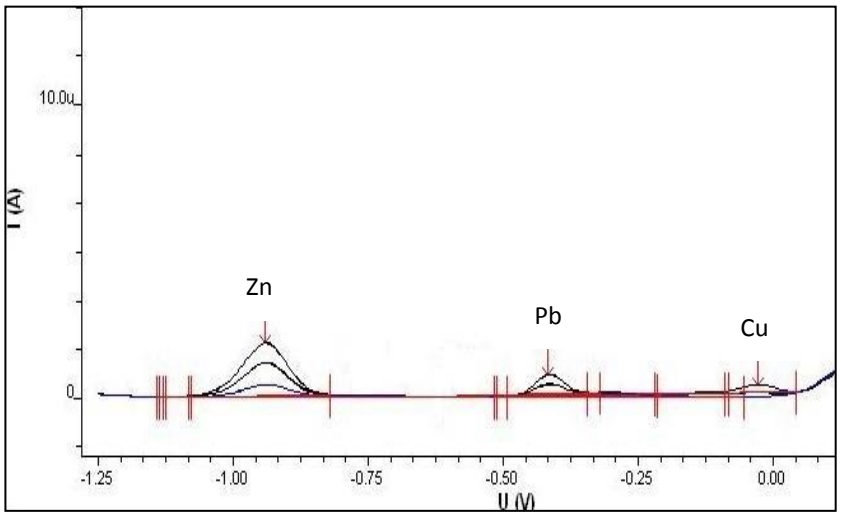

Figure 6.3. Voltammogram of sardine sample S_2 digested in oxalate buffer.

DPASV analysis of Zn contents in oxalate buffer were relatively similar to the ICP-OES results (Table 6.8), yet the Zn analysis in acetic acid and potassium chloride buffer did not reveal coherent results with the ICP-OES analysis (Table 6.10).

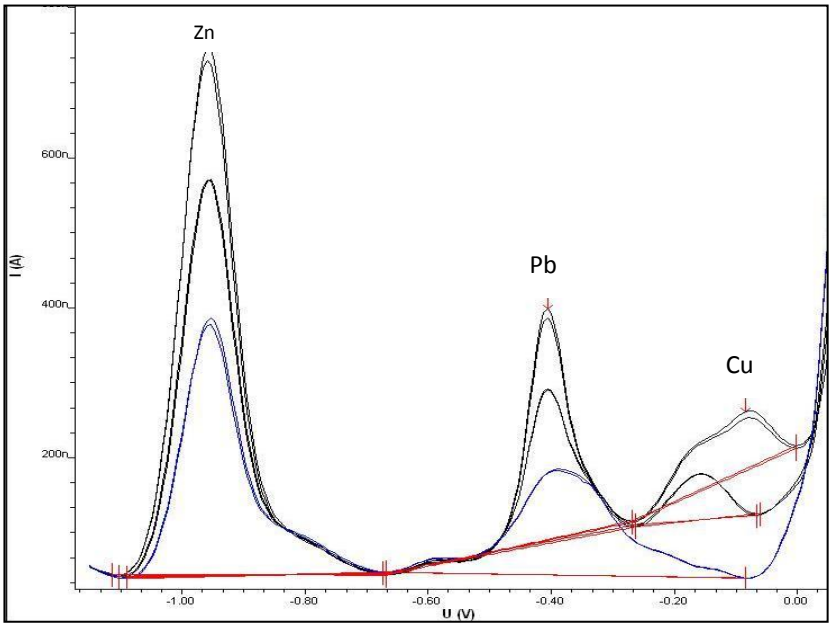

Figure 6.4. Voltammogram of sardine sample S_2 digested in acetic acid and potassium chloride buffer.

It was concluded that the digestion process carried out in nitric acid did not work well with sardine samples mostly due to their relatively high fatty contents. Trace quantities of Cd could not be determined in the presence of either of the two buffer solutions. Also, voltammograms of Pb and Cu peaks almost overlapped with each other in acetic acid and potassium chloride buffer medium. The standard addition method was not successful (Figure 6.4).

Some vegetable samples were also analyzed for their metal contents in nitric acid with longer digestion durations as 24 – 26 hours due to their high cellulose contents. Samples were prepared in the same way as the fish samples prior to analysis. Digestion was carried in 20 mL nitric acid. Digests were diluted to 10 mL after evaporation to almost dryness by the addition of deionized water.

Replicates of sweet corn samples were taken out from the same can, TAT brand with serial number of PN: 03 and production date of 01/2012, and from the same can, Tamek brand with serial number of PK 156.12.35 and the expiration date of 06/2015. 1 mL oxalate buffer was added to each 2 mL of the digested corn sample. DPASV results of samples C_2 (Tat brand) for the Cu and Zn contents in oxalate buffer; C_1 and C_2 (Tat brand) for the Cu content in acetic acid plus potassium chloride buffer; C_1 (Tat brand) for the Cd content in oxalate and acetic acid plus potassium chloride buffer media; C_3 and C_4 (Tamek brand) for the Cu content in oxalate buffer; C_3 (Tamek brand) for Zn content in oxalate buffer; C_4 (Tamek brand) for the Cu and Cd contents in oxalate buffer were not comparable with the ICP-OES results (Table 6.11 - 16).

Cd content could not be detected in DPASV analysis of C_4 (Tamek brand) where the ICP-OES analysis revealed a trace amount of Cd for the sample, i.e., 0.008 µg g^{-1}, which was a good indicator of an incomplete digestion process with nitric acid. The peak corresponding to Cd was hindered by the presence of Pb peak in the voltammogram.

Table 6.11. Cd, Pb and Cu contents of corn samples (Tat brand) in oxalate buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_1	Cd	13.1 ± 0.6	0.155 ± 0.007	4.58	7.12	0.084
	Pb	30.6 ± 0.9	0.364 ± 0.011	2.91	23.1	0.275
	Cu	28712 ± 777	341 ± 9	2.70	27410	325
C_2	Cd	0	0	-	0	0
	Pb	12.8 ± 0.7	0.153 ± 0.008	5.48	13.7	0.164
	Cu	156 ± 4	1.86 ± 0.06	2.56	873	10.4

Table 6.12. Zn contents of corn samples (Tat brand) in oxalate buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_1	98.9 ± 11.0	1.17 ± 0.13	11.2	70.4	0.836
C_2	15.9 ± 0.7	0.189 ± 0.008	4.40	211	2.51

Table 6.13. Cd, Pb and Cu contents of corn samples (Tat brand) in acetic acid and potassium chloride buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_1	Cd	15.9 ± 3.1	0.188 ± 0.037	19.5	7.12	0.084
	Pb	32.4 ± 4.2	0.385 ± 0.049	12.8	23.1	0.275
	Cu	15132 ± 1056	180 ± 12	6.98	27410	325
C_2	Cd	0	0	-	0	0
	Pb	16.9 ± 0.9	0.201 ± 0.011	5.32	13.7	0.164
	Cu	216 ± 14	2.57 ± 0.16	6.48	873	10.4

Table 6.14. Zn contents of corn samples (Tat brand) in acetic acid and potassium chloride buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_1	85.2 ± 7.9	1.01 ± 0.09	9.27	70.4	0.836
C_2	106 ± 13	1.27 ± 0.15	12.3	211	2.51

Table 6.15. Cd, Pb, Cu contents of corn samples (Tamek brand) in oxalate buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_3	Cd	0	0	-	0	0
	Pb	11.5 ± 0.7	0.193 ± 0.013	6.09	9.83	0.165
	Cu	291 ± 14	4.88 ± 0.23	4.81	119	2.00
C_4	Cd	0	0	-	0.477	0.008
	Pb	14.5 ± 1.8	0.242 ± 0.029	12.4	9.24	0.154
	Cu	536 ± 19	8.93 ± 0.32	3.56	225	3.74
C_5	Cd	0	0	-	0	0
	Pb	12.6 ± 2.1	0.211 ± 0.034	16.7	6.29	0.105
	Cu	322 ± 15	5.36 ± 0.24	4.66	392	6.54

Table 6.16. Zn Contents of corn samples (Tamek brand) in oxalate buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_3	1.07 ± 0.04	0.018 ± 0.001	3.72	0.508	0.008
C_4	8.21 ± 0.37	0.137 ± 0.006	4.51	11.8	0.197
C_5	6.93 ± 0.28	0.11 ± 0.005	4.05	8.55	0.142

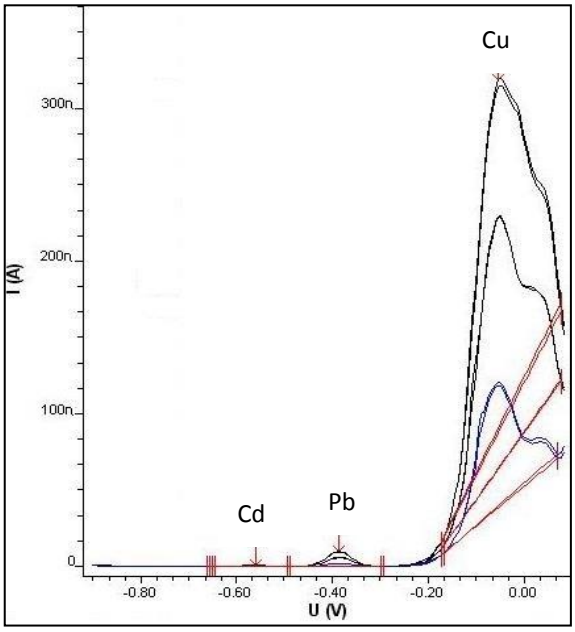

Figure 6.5. Voltammogram of sample C_2 in oxalate buffer.

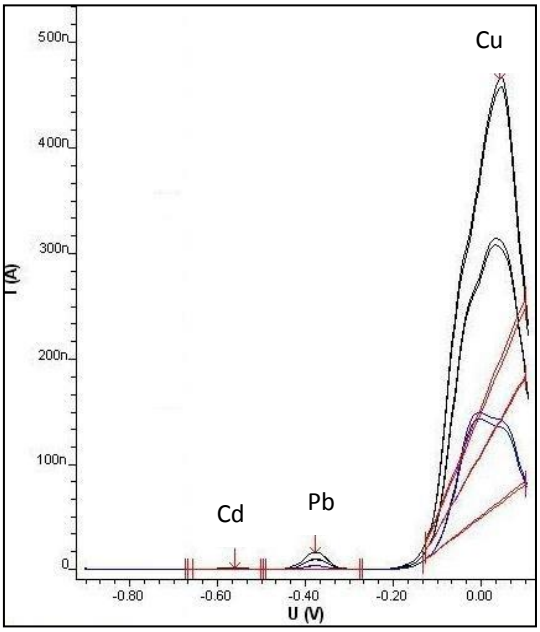

Figure 6.6. Voltammogram of sample C_2 in acetic acid and potassium chloride buffer.

Figures 6.5 and 6.6 show the voltammograms for Cd, Pb and Cu of corn sample C_2 in oxalate and acetic acid plus potassium chloride buffer media. The shifted base-lines of the Cu peaks in both buffer solutions were caused by the incomplete digestions in nitric acid.

Moreover, three replicates of chopped tomato samples were prepared from the same can in order to check the suitability of nitric acid for the digestion process. Chopped tomatoes were TAT Brand, with serial number of PN: 16 16:50 and expiration date of 08/2014. Digestion was carried in 20 mL of nitric acid. Samples were diluted to a final volume of 25 mL after evaporation to almost dryness. 1 mL oxalate buffer was used for each of the 2 mL digested chopped tomato sample, final volume was 11 mL in the vessel. Voltammogram of one of the digested tomato samples (TT_1) is shown in Figure 6.7. Neither the results of DPASV analyses with high standart deviation values nor the voltammograms with shifted base lines were satisfactory in both buffer media.

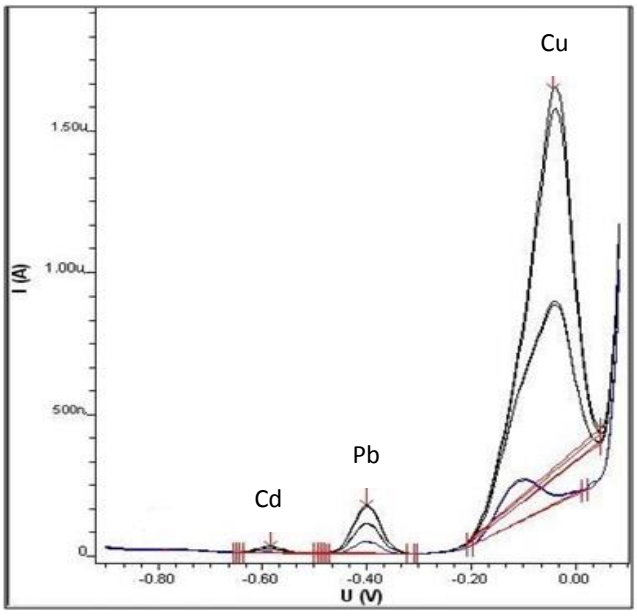

Figure 6.7. Voltammogram of chopped tomatoes TT_1 (Tat brand) in oxalate buffer.

Table 6.17. Zn contents of chopped tomato samples (Tat brand) in oxalate buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_1	103 ± 9	1.24 ± 0.11	8.74	112	1.34
TT_2	16.9 ± 0.8	0.184 ± 0.008	4.73	13.5	0.146
TT_3	4.05 ± 0.14	0.050 ± 0.002	3.46	3.82	0.048

Table 6.18. Cd, Pb and Cu contents of chopped tomato samples (Tat brand) in oxalate buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_1	Cd	5.04 ± 0.44	0.060 ± 0.005	8.73	2.21	0.026
	Pb	41.4 ± 2.0	0.502 ± 0.024	4.83	21.7	0.261
	Cu	1792 ± 180	21.5 ± 3.2	10.0	2853	34.2
TT_2	Cd	0	0	-	0	0
	Pb	65.3 ± 5.4	0.708 ± 0.059	8.27	10.5	0.114
	Cu	106 ± 7	1.15 ± 0.07	6.60	98.9	1.07
TT_3	Cd	1.82 ± 0.27	0.023 ± 0.003	14.9	0.559	0.007
	Pb	27.8 ± 1.3	0.346 ± 0.016	4.68	40.5	0.504
	Cu	110 ± 15	1.37 ± 0.191	13.6	188	2.34

Results for the Zn contents of Tat brand chopped tomato samples were close to one another in DPASV and ICP-OES analyses (Table 6.17). Relatively high value of standard deviations for the Cu concentrations in TT_1 and TT_3 were attributed to the shifted base-lines of the copper peak. In addition, the Pb concentration of the sample TT_2 recorded by the DPASV analysis was almost six times higher than the ICP-OES result (Table 6.18). Overall, digestion process of the chopped tomato samples in nitric acid was not successful. Clear digests were not obtained in every sample treatment.

Three replicates of tomato sauce samples, TAMEK Brand with the serial number of E49 L 112-2 and expiration date of 08/2014 were analyzed both in oxalate buffer and acetic acid and potassium chloride buffer mixture. Samples were digested in 20 mL nitric acid. DPASV results of the samples with oxalate buffer revealed smaller standard deviations, and similar results to the ICP-OES analyses (Table 6.19, 6.20). However, when acetic acid and potassium chloride buffer mixture was used, the differences between the results of DPASV and the ICP-OES analyses were increased (Table 6.21, 6.22).

Table 6.19. Zn contents of tomato sauce samples (Tamek brand) in oxalate buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_4	89.5 ± 4.1	0.959 ± 0.044	4.58	95.8	1.03
TT_5	3.65 ± 0.01	0.037 ± 0.001	0.27	2.00	0.020
TT_6	0.979 ± 0.041	0.010 ± 0.000	4.19	0.888	0.009

Table 6.20. Cd, Pb, Cu contents of tomato sauce samples (Tamek brand) in oxalate buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_4	Cd	6.58 ± 0.17	0.071 ± 0.002	2.58	5.18	0.055
	Pb	44.4 ± 1.1	0.477 ± 0.012	2.48	45.1	0.484
	Cu	5312 ± 137	56.9 ± 1.5	2.58	5549	59.5
TT_5	Cd	3.55 ± 0.21	0.036 ± 0.002	5.92	4.98	0.051
	Pb	19.1 ± 0.5	0.192 ± 0.005	2.62	16.3	0.164
	Cu	219 ± 4	2.19 ± 0.04	1.83	317	3.19
TT_6	Cd	7.04 ± 0.22	0.075 ± 0.002	3.12	5.75	0.061
	Pb	11.8 ± 0.6	0.125 ± 0.007	5.08	10.1	0.108
	Cu	320 ± 17	3.41 ± 0.18	5.31	319	3.39

Table 6.21. Zn contents of tomato sauce samples (Tamek brand) in acetic acid and potassium chloride buffer.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_4	63.2 ± 7.8	0.678 ± 0.084	12.4	95.8	1.03
TT_5	4.23 ± 0.37	0.042 ± 0.004	8.75	2.00	0.020
TT_6	1.14 ± 0.09	0.012 ± 0.001	7.89	0.888	0.009

Table 6.22. Cd, Pb, Cu contents of tomato sauce samples (Tamek brand) in acetic acid and potassium chloride buffer.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_4	Cd	7.99 ± 0.42	0.086 ± 0.004	5.26	5.18	0.055
	Pb	46.2 ± 1.1	0.496 ± 0.012	2.38	45.1	0.484
	Cu	2959 ± 103	31.7 ± 1.1	3.48	5549	59.5
TT_5	Cd	0	0	-	4.98	0.051
	Pb	106 ± 11	1.07 ± 0.11	10.4	16.3	0.164
	Cu	114 ± 7	1.15 ± 0.08	6.14	317	3.19
TT_6	Cd	8.51 ± 0.93	0.091 ± 0.009	10.9	5.75	0.061
	Pb	15.4 ± 1.5	0.164 ± 0.016	9.74	10.1	0.108
	Cu	156 ± 7	1.67 ± 0.08	4.49	319	3.39

Voltammograms of TT_5 in oxalate and in acetic acid plus potassium chloride media were compared (Figure 6.8 and Figure 6.9). The split Cu and Pb peaks indicated unsuccessful standard additions in the presence of acetic acid plus potassium chloride buffer.

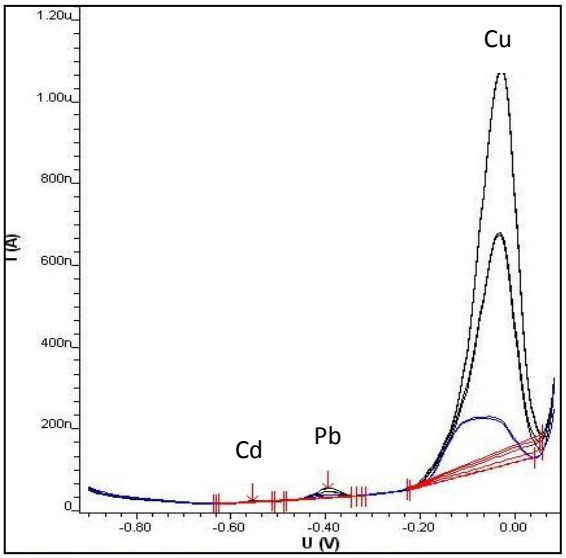

Figure 6.8. Voltammogram of sample TT_5 in oxalate buffer.

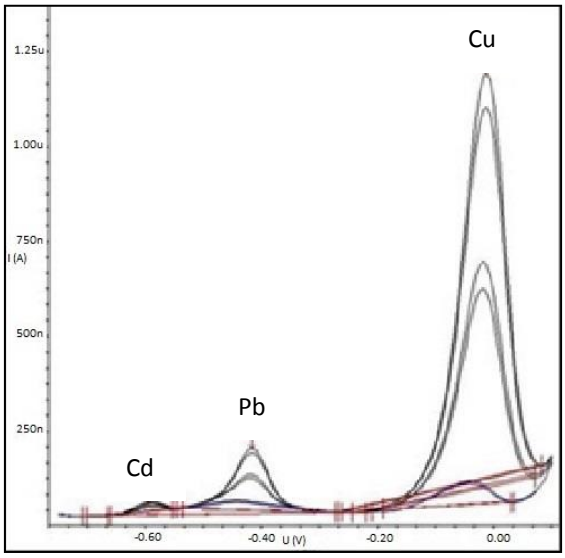

Figure 6.9. Voltammogram of sample TT_5 in acetic acid and potassium chloride.

The results of DPASV analysis of tomato sauce samples showed that in the presence of an oxalate buffer voltammograms of simultaneously determined peaks of Cd, Pb and Cu were separated well with respect to their half-wave potential values. Also, the replicate measurements for each sample resulted in relatively small standard deviations. DPASV results for Cd, Pb and Cu contents were in good agreement with ICP-OES analyses (Table 6.20). In acetic acid plus potassium chloride buffer solution, DPASV results of Cd, Pb, Cu, and Zn were incoherent with ICP-OES analysis (Table 6.21, 6.22). Cu contents that were recorded with DPASV analysis for samples TT_5 and TT_6 were lower almost by a factor of two with respect to ICP-OES results. The DPASV results of the Zn concentration values of both Tamek and Tat brand samples were in agreement with the results of ICP-OES analysis in oxalate buffer (Table 6.17, 6.19).

The overall conclusion was that the vegetable samples with long digestion durations up to 26 hours and fish samples with 20 hours in nitric acid did not always result in clear digests at the end of the process. In some cases Pb and Cu peaks and in others Zn and Cd peaks overlapped with each other. Therefore, the DPASV results were inconsistent with the ICP-OES results in such cases. Also, the shifted base-lines of the peaks and/or the split voltammograms were good indicators of the incomplete and insufficient digestion processes in nitric acid.

6.1.2. Perchloric Acid Digestion of Canned Tuna, Canned and Fresh Sardine and Anchovy and Canned Corn Samples

The DPASV analyses of some canned fish (anchovy and sardine), canned corn and tomato samples indicated that acetic acid plus potassium chloride buffer mixture was not always suitable as the supporting electrolyte in media, especially for Cu content determinations. Also, digestion processes of corn and tomato samples in nitric acid did not always result in clear digests. Hence, nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture in 5:1 (v/v) ratio was used in combination with oxalate buffer for the DPASV analysis. Five tuna samples were taken from the same can of Kemerli Ton with a production date of 05/10 which was also the serial number. The samples were drained, and weighed as 2.02 ± 0.05 g. Digestion with 18 mL of nitric acid/perchloric acid mixture was held for 20 hours. Excess acid was evaporated to almost dryness by the aid of successive additions of deionized water, and the tuna digests were diluted up to 25.0 mL of final volumes. Voltammogram vessels contained 2 mL of the digested sample with 1 mL oxalate buffer solution, finally diluted to 11 mL with deionized water.

Table 6.23. Cd, Pb and Cu contents of tuna samples (Kemerli brand) in nitric acid/perchloric acid.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_1	Cd	3.54 ± 0.12	0.044 ± 0.002	3.39	3.59	0.044
	Pb	38.2 ± 3.6	0.473 ± 0.044	9.42	33.6	0.415
	Cu	596 ± 54	7.37 ± 0.67	9.07	460	5.69
T_2	Cd	6.12 ± 0.51	0.075 ± 0.006	8.31	5.78	0.071
	Pb	54.7 ± 1.1	0.673 ± 0.013	2.01	45.4	0.559
	Cu	465 ± 26	5.73 ± 0.31	5.59	414	5.10
T_3	Cd	4.25 ± 0.35	0.052 ± 0.004	8.24	3.45	0.045
	Pb	39.7 ± 3.5	0.485 ± 0.043	8.82	37.2	0.454
	Cu	494 ± 50	6.02 ± 0.61	10.1	422	5.15
T_4	Cd	19.9 ± 1.0	0.245 ± 0.013	5.02	11.4	0.139
	Pb	46.8 ± 1.8	0.574 ± 0.022	3.69	51.6	0.632
	Cu	N.D.	N.D.	-	733	8.98
T_5	Cd	5.07 ± 0.17	0.062 ± 0.002	3.35	4.95	0.061
	Pb	20.9 ± 0.7	0.257 ± 0.008	3.35	19.8	0.242
	Cu	2108 ± 64	25.8 ± 0.8	3.04	2028	24.9

Table 6.24. Zn contents of tuna samples (Kemerli brand) in nitric acid/perchloric acid.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_1	15.6 ± 0.9	0.193 ± 0.012	5.77	15.2	0.188
T_2	1.45 ± 0.08	0.018 ± 0.001	5.52	1.09	0.013
T_3	12.7 ± 0.1	0.155 ± 0.001	0.79	11.3	0.138
T_4	8.45 ± 0.62	0.104 ± 0.008	7.33	7.22	0.088
T_5	72.2 ± 5.2	0.886 ± 0.064	7.20	76.2	0.934

The simultaneous analyses of Cd, Pb and Cu contents of canned tuna samples showed that the presence of a secondary powerful oxidizing agent in media affected the digestion process in a favorable way. The corresponding voltammograms of metal contents had become more definite and well separated from each other (Figure 6.10). The concentrations of the trace metal contents of tuna samples in the same can were varied between 0.044-0.245, 0.257-0.673, 5.73-25.8 in µg g^{-1} for Cd, Pb and Cu respectively. The Zn analysis revealed peaks with straight base-lines and the resultant concentrations were in good agreement with ICP-OES results (Figure 6.11). The corresponding Zn contents were within the range of 0.018-0.886 mg g^{-1}. The large fluctuations in each metal content of the same can indicated that tuna fish were sampled from very different sources.

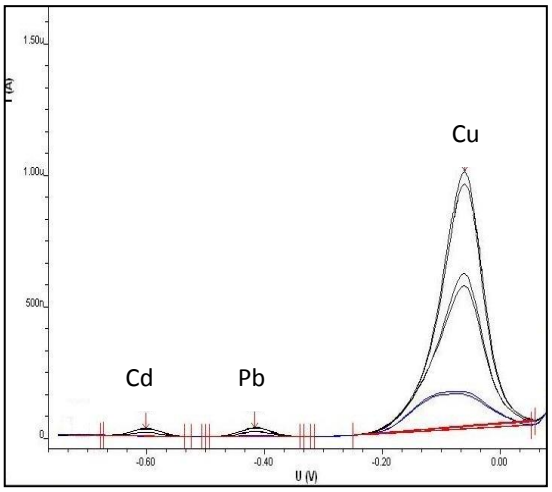

Figure 6.10. Voltammogram of sample T_2 in oxalate buffer.

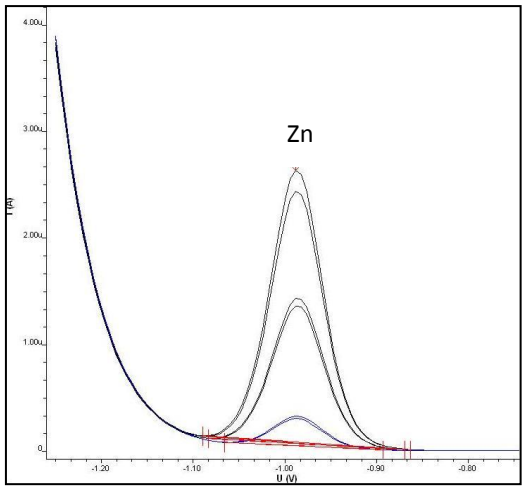

Figure 6.11. Voltammogram of sample T_2 in oxalate buffer.

Fresh sardines purchased from the local bazaar of Gelibolu were also analyzed by DPASV and the results were compared with ICP-OES analysis. Zn, Cd, Pb, Cu contents were in good agreement with ICP-OES results (Table 6.25, Table 6.26). The recorded

amounts for Cd, Pb and Cu elements in µg g^{-1} were between the range of 0-0.155; 0.103-0.994; and 0.72-15.8, respectively (Table 6.25). Voltammograms showed finely resolved and unsplitted peaks which indicated that organic matter was destroyed completely in nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1,v:v), supporting electrolyte (oxalate buffer) was suitable for the analysis and the standard additions were successful (Figure 6. 12, 6.13).

Table 6.25. Cd, Pb, Cu contents of fresh sardine samples in nitric acid/perchloric acid.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_4	Cd	10.3 ± 0.8	0.127 ± 0.009	7.77	12.0	0.148
	Pb	69.2 ± 5.3	0.855 ± 0.066	7.66	50.4	0.622
	Cu	323 ± 33	3.98 ± 0.41	10.1	297	3.66
S_5	Cd	6.22 ± 0.35	0.077 ± 0.004	5.63	7.86	0.097
	Pb	26.4 ± 0.8	0.326 ± 0.009	3.03	23.6	0.292
	Cu	235 ± 21	2.91 ± 0.26	8.93	207	2.56
S_6	Cd	12.5 ± 1.0	0.155 ± 0.012	8.00	12.5	0.155
	Pb	80.1 ± 4.5	0.994 ± 0.056	5.62	49.6	0.616
	Cu	772 ± 16	9.58 ± 0.20	2.07	938	11.6
S_7	Cd	3.08 ± 0.19	0.038 ± 0.002	6.17	5.64	0.069
	Pb	36.4 ± 0.4	0.449 ± 0.005	1.10	30.7	0.378
	Cu	309 ± 35	3.81 ± 0.43	11.3	298	3.68
S_8	Cd	3.85 ± 0.26	0.048 ± 0.003	6.75	5.81	0.072
	Pb	46.7 ± 1.0	0.578 ± 0.013	2.14	41.9	0.519
	Cu	570 ± 40	7.05 ± 0.49	7.02	486	6.01
S_9	Cd	4.77 ± 0.17	0.058 ± 0.002	3.56	4.10	0.049
	Pb	27.9 ± 0.4	0.338 ± 0.006	1.43	23.4	0.284
	Cu	1302 ± 17	15.8 ± 0.2	1.30	1040	12.6
S_{10}	Cd	4.88 ± 0.47	0.056 ± 0.006	9.63	6.55	0.076
	Pb	12.8 ± 0.9	0.148 ± 0.011	7.03	18.2	0.210
	Cu	628 ± 46	7.27 ± 0.53	2.71	682	7.89
S_{11}	Cd	4.84 ± 0.18	0.058 ± 0.002	3.72	4.56	0.054
	Pb	23.9 ± 0.9	0.284 ± 0.012	3.76	21.9	0.260
	Cu	N.D.*	N.D.*	-	253	3.01
S_{12}	Cd	0	0	-	0	0
	Pb	36 ± 1	0.602 ± 0.015	2.78	9.63	0.161
	Cu	394 ± 27	6.59 ± 0.46	6.85	228	3.82
S_{13}	Cd	1.46 ± 0.12	0.024 ± 0.002	8.22	2.99	0.048
	Pb	6.38 ± 4.44	0.103 ± 0.007	6.90	5.34	0.086
	Cu	44.5 ± 0.7	0.72 ± 0.01	1.57	46.2	0.746

*N.D.: Cu peak was distorted, standard additions were unsuccessful. The content could not be determined accurately.

Table 6.26. Zn contents of fresh sardine samples in nitric acid/perchloric acid.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_4	4.90 ± 0.09	0.061 ± 0.001	1.84	4.24	0.052
S_5	2.84 ± 0.07	0.035 ± 0.001	2.46	2.08	0.026
S_6	8.07 ± 0.54	0.100 ± 0.007	6.69	7.57	0.094
S_7	10.9 ± 0.5	0.136 ± 0.006	4.59	9.88	0.122
S_8	20.8 ± 1.0	0.257 ± 0.013	4.81	18.6	0.231
S_9	23.3 ± 0.1	0.282 ± 0.002	0.43	21.2	0.256
S_{10}	4.43 ± 0.19	0.051 ± 0.002	4.29	5.05	0.058
S_{11}	3.81 ± 0.09	0.045 ± 0.001	2.36	3.58	0.042
S_{12}	2.95 ± 0.11	0.049 ± 0.002	3.73	2.35	0.039
S_{13}	2.31 ± 0.01	0.038 ± 0.0002	0.43	2.16	0.035

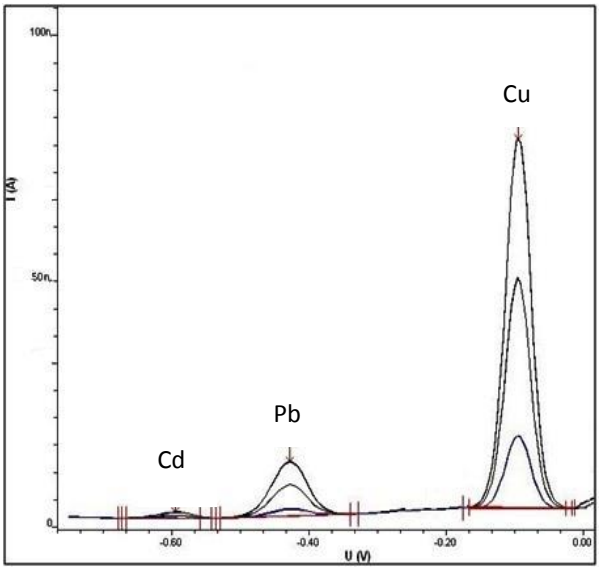

Figure 6.12. Voltammogram of the sample S_{13} digested in nitric acid/perchloric acid.

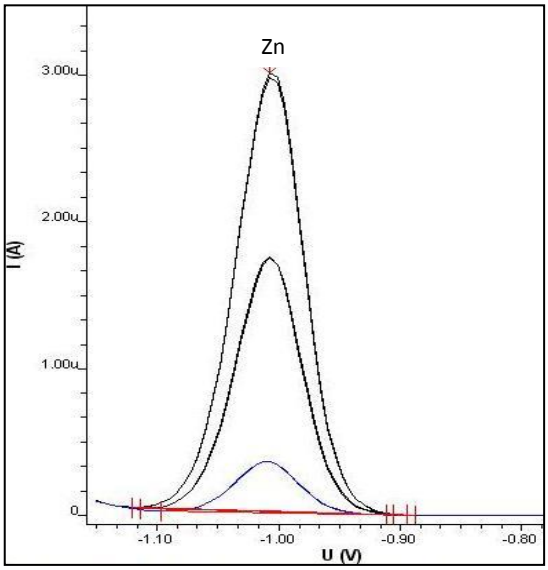

Figure 6.13. Voltammogram of the sample S_{10} digested in nitric acid/perchloric acid.

The Zn contents of fresh sardine samples were calculated in the 0.035 - 0.282 mg g^{-1} range (Table 6.26). In the presence of relatively high Zn concentrations (>1 mg L^{-1}), determinations were carried out separately. Deposition potential range for Zn was kept between -1.15 V and -0.75V. About 0.2 - 0.5 mL of clear digests with an oxalate buffer solution were put in a voltammogram vessel and diluted to 10 mL with deionized water. Figure 6.13 is a good example of a successful acid digestion and DPASV analysis of Zn element.

Although the majority of the DPASV results for the fish samples digested in nitric acid/perchloric acid were in good agreement with the ICP-OES analysis, in few cases problems arose about the detection of Cu. Cu peaks shifted towards more positive potentials as the analyte was spiked with aliquots of the metal standard. Hence, the half-wave potential for analyte peak differed from that of the standard addition peaks. Voltammograms of samples A_6 and A_7 are given in Figure 6.14 and Figure 6.15.

Table 6.27. Cd, Pb, Cu contents of anchovy samples (Yakşi brand) in nitric acid/perchloric acid.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_5	Cd	16.0 ± 0.8	0.199 ± 0.009	5.00	19.1	0.248
	Pb	72.0 ± 3.8	0.899 ± 0.047	5.28	77.8	0.972
	Cu	275 ± 13	3.43 ± 0.16	4.73	268	3.35
A_6	Cd	12.5 ± 1.1	0.156 ± 0.014	8.80	12.5	0.156
	Pb	72.5 ± 2.4	0.904 ± 0.029	3.32	55.8	0.696
	Cu	71.2 ± 6.0	0.887 ± 0.075	8.43	176	2.19
A_7	Cd	6.34 ± 0.34	0.078 ± 0.004	5.36	8.28	0.102
	Pb	68.6 ± 2.0	0.848 ± 0.025	2.92	43.7	0.539
	Cu	516 ± 9	6.38 ± 0.12	1.74	242	2.99

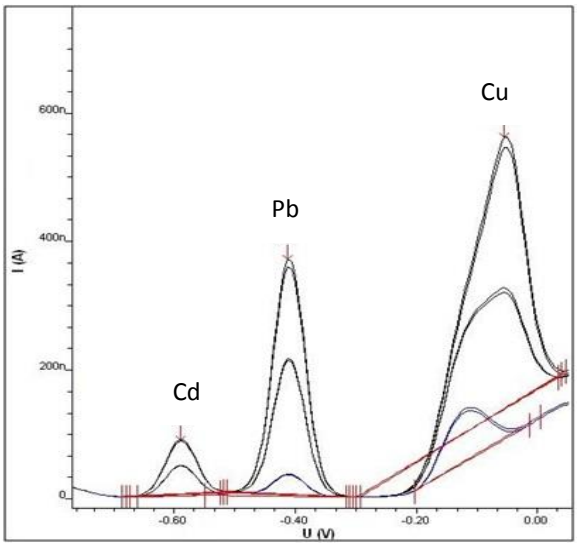

Figure 6.14. Voltammogram of the sample A_6 digested in nitric acid/perchloric acid.

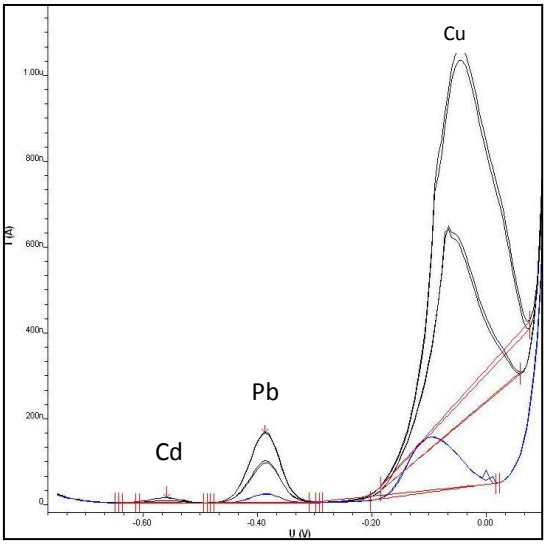

Figure 6.15. Voltammogram of the sample A_7 digested in nitric acid/perchloric acid.

The Cu contents of the sample A_6 and A_7 were not in agreement with ICP-OES results (Table 6.27). Despite its relatively smaller standard deviation, the Cu content of the

sample A_7 was twice as much as the value recorded by ICP-OES analysis. DPASV results of Zn contents of the anchovy samples were consistent with ICP-OES results. The range of the Zn content of samples taken from the same can was between 0.088-0.146 mg g^{-1} (Table 6.28).

Table 6.28. Zn contents of anchovy samples (Yakşi brand) in nitric acid/perchloric acid.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_5	11.7 ± 0.3	0.146 ± 0.003	2.56	10.2	0.127
A_6	10.2 ± 0.2	0.127 ± 0.002	1.96	9.91	0.123
A_7	7.13 ± 0.01	0.088 ± 0.000	0.15	7.74	0.096

Fresh anchovy samples were digested in nitric acid/perchloric acid also, and DPASV analysis was carried with oxalate buffer. Samples were prepared from separate anchovy fish species purchased from the local markets of Gelibolu, Çanakkale (Table 6.29, 6.30).

Table 6.29. Zn contents of fresh anchovy samples in nitric acid/perchloric acid.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_8	1.64 ± 0.03	0.019 ± 0.001	1.83	1.21	0.014
A_9	292 ± 3	3.38 ± 0.03	1.03	274	3.17
A_{10}	438 ± 5	5.14 ± 0.06	1.15	455	5.34
A_{11}	74.9 ± 0.3	0.892 ± 0.004	0.45	67.6	0.804
A_{12}	4.04 ± 0.07	0.048 ± 0.001	1.75	5.65	0.067
A_{13}	103 ± 1	1.24 ± 0.01	0.97	105	1.26
A_{14}	3.27 ± 0.45	0.040 ± 0.006	13.8	2.99	0.037
A_{15}	417 ± 2	4.93 ± 0.02	0.49	435	5.14
A_{16}	522 ± 25	6.33 ± 0.31	4.79	523	6.34
A_{17}	112 ± 1	1.37 ± 0.01	0.89	98.8	1.21
A_{18}	12.5 ± 0.5	0.203 ± 0008	4.00	14.1	0.230
A_{19}	1.28 ± 0.05	0.021 ± 0.001	3.91	0.988	0.016

Zn contents of the samples ranged between 0.019 µg g^{-1} and 6.33 µg g^{-1}(Table 6.29). Results for the Cu content of the fresh anchovy samples were between 1.28 - 39.6 µg g^{-1}. Amongst the twelve anchovy samples investigated, there was one irrelevant data; DPASV analysis result of Cu content for the sample A_{19} was much greater than that of the ICP-OES analysis (Table 6.30). The recorded amounts of Pb and Cd concentrations were between 0-1.59 and 0-0.276 µg g^{-1}, respectively. DPASV analyses results were in good agreement

with ICP-OES analyses. Generally, Cd contents of fresh anchovy samples were in smaller quantities than the canned anchovy samples.

Table 6.30. Cd, Pb, Cu contents of fresh anchovy samples in nitric acid/perchloric acid.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_8	Cd	0	0	-	0	0
	Pb	13.8 ± 0.9	0.163 ± 0.011	6.59	8.54	0.101
	Cu	108 ± 4	1.28 ± 0.05	3.70	85.7	1.01
A_9	Cd	9.01 ± 0.51	0.104 ± 0.006	5.66	10.9	0.126
	Pb	42.9 ± 2.3	0.496 ± 0.026	5.33	38.2	0.442
	Cu	1885 ± 85	21.8 ± 0.9	4.53	2279	26.3
A_{10}	Cd	89.8 ± 9.0	1.05 ± 0.11	10.0	74.6	0.875
	Pb	136 ± 2	1.59 ± 0.03	1.47	116	1.36
	Cu	3379 ± 75	39.6 ± 0.9	2.23	3522	41.3
A_{11}	Cd	0	0	-	0	0
	Pb	39.3 ± 1.2	0.467 ± 0.014	3.04	37.7	0.449
	Cu	725 ± 29	8.63 ± 0.35	4.00	777	9.24
A_{12}	Cd	10.2 ± 0.14	0.121 ± 0.002	1.38	9.17	0.109
	Pb	15.9 ± 0.5	0.188 ± 0.006	3.11	13.0	0.155
	Cu	189 ± 16	2.24 ± 0.18	8.46	176	2.08
A_{13}	Cd	7.48 ± 0.82	0.10 ± 0.01	11.0	11.2	0.135
	Pb	48.8 ± 2.4	0.588 ± 0.029	4.92	36.8	0.443
	Cu	1319 ± 107	15.9 ± 1.3	8.11	1375	16.6
A_{14}	Cd	0	0	-	0	0
	Pb	19.9 ± 0.6	0.244 ± 0.007	3.02	15.5	0.189
	Cu	189 ± 6	2.32 ± 0.08	3.17	121	1.48
A_{15}	Cd	7.78 ± 0.52	0.092 ± 0.006	6.63	9.63	0.114
	Pb	39.1 ± 3.1	0.462 ± 0.036	7.86	28.7	0.339
	Cu	2919 ± 252	34.5 ± 2.9	8.63	3328	39.3
A_{16}	Cd	22.8 ± 1.4	0.276 ± 0.017	6.14	26.8	0.325
	Pb	53.1 ± 2.4	0.643 ± 0.029	4.49	52.9	0.642
	Cu	1140 ± 50	13.8 ± 0.7	4.38	730	8.9
A_{17}	Cd	0	0	-	0	0
	Pb	20.9 ± 1.0	0.256 ± 0.013	4.78	22.2	0.272
	Cu	1158 ± 22	14.2 ± 0.3	1.90	1356	16.6
A_{18}	Cd	0	0	-	0	0
	Pb	15.4 ± 1.6	0.250 ± 0.026	10.4	18.2	0.290
	Cu	203 ± 19	3.31 ± 0.31	9.36	160	2.61
A_{19}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	596 ± 21	9.86 ± 0.35	3.52	90.8	1.50

Three replicates of corn samples of about 2.00 ± 0.05 g from the same can of Superfresh brand with the expiration date of 02/2015 and the serial number of L2158 were taken and digested with nitric acid/perchloric acid ($HNO_3/HClO_4$, 5:1, v/v) mixture of 18 mL for about 20 hours. Oxalate buffer was used in the analysis. The DPASV results for Cd, Pb, Cu and Zn analyses were consistent with ICP-OES results (Table 6.31, Table 6.32).

Table 6.31. Cd, Pb, Cu contents of corn samples (Superfresh brand) in nitric acid/perchloric acid.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD	µg L^{-1}	µg g^{-1}
C_6	Cd	4.5 ± 0.4	0.055 ± 0.005	8.89	2.76	0.034
	Pb	51.9 ± 1.6	0.634 ± 0.019	3.08	39.1	0.477
	Cu	3726 ± 187	45.5 ± 2.3	5.03	3280	40.1
C_7	Cd	2.66 ± 0.15	0.032 ± 0.002	5.64	1.28	0.016
	Pb	37.2 ± 1.3	0.453 ± 0.015	3.49	32.3	0.394
	Cu	1538 ± 123	18.7 ± 1.5	8.00	1548	18.8
C_8	Cd	0	0	-	0	0
	Pb	25.1 ± 1.6	0.299 ± 0.019	6.37	22.5	0.269
	Cu*	1388 ± 50	17.2 ± 0.6	3.60	873	10.4

*The analysis was repeated with the addition of 1 mL of 1 x 10^{-2} mol L^{-1} of EDTA, and discussed in Section 6.5.

Table 6.32. Zn contents of corn samples (Superfresh brand) in nitric acid/perchloric acid.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_6	27.6 ± 2.2	0.338 ± 0.028	7.97	26.4	0.323
C_7	63.4 ± 0.6	0.772 ± 0.008	0.95	75.3	0.917
C_8	5.96 ± 0.25	0.071 ± 0.003	4.19	5.63	0.067

Conclusions about the DPASV results of the experiments with fish and vegetable samples are summarized as; (i) Digestion processes of fish (tuna, anchovy, sardine), and canned corn samples resulted in completely colorless solutions in nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture. Hence, this combination was chosen to be the suitable medium for the wet digestion of fish and vegetable samples. (ii) DPASV analysis results for metal contents of Zn, Cu, Cd and Pb were in agreement with ICP-OES analysis in the

presence of oxalate buffer. In higher Zn concentrations, Zn was determined separately with shorter enrichment time or after being diluted to a greater extend, i.e. 0.2 mL diluted to 10 mL. (iii) Analyses were run in three replicates to check the reproducibility of the DPASV results. Small standard deviations indicated good repeatability of the method. (iv) Sample blanks were analyzed together with each sample batch. Metal concentrations in blanks were below the detection limits in all analyses, and they were considered to be equal to zero value.

6.2. Comparison of Buffer Solutions

Electroanalytical measurements are performed in a solvent containing medium as suppporting electrolyte. Buffer composition and supporting electrolyte influence the migration of reactants to electrode surface. The supporting electrolyte should not get into reaction with the analyte. It decreases the resistance of the analyte solution, eliminates the migration effect and maintains a constant ionic strength; also it keeps the pH value constant. An inorganic salt, a mineral acid or a buffer may be the inert supporting electrolyte. If water is used as solvent, potassium chloride or nitrate, ammonium chloride, sodium hydroxide, ammonia/ammonium chloride or hydrochloric acid are employed as supporting electrolyte [61]. The composition of the electrolyte and the buffer solution also affect the sensitivity of the measurement. The half-wave potentials ($E_{1/2}$) or peak potentials of metal ions change in different supporting electrolyte compositions. In cases where increasing background current of the supporting electrolyte exists, poor waves are obtained or quantitative evaluation becomes impossible. In some cases masking agents such as ethylenediaminetetraacetic acid (EDTA) can be used for removal of interferences [58].

Test samples were chosen randomly amongst the previously digested canned sardine, tuna, corn and tomato samples which were about 1.50-2.00 ± 0.05 g. Digestions were done in nitric acid/perchloric acid ($HNO_3/HClO_4$, 5:1, v/v) in a total volume of 18 mL. Digests were evaporated to almost dryness by successive additions of deionized water, and finally the volume was made up to 25 mL with deionized water. Metal contents of Zn, Cu, Pb and Cd were determined in four different buffer solutions; oxalate, acetic acid, acetic acid plus potassium chloride and sodium acetate. Deposition time was kept as 120 seconds.

Metal contents of Cd, Pb and Cu were determined simultaneously. Cu has a relatively low solubility in Hg [61]. Hence, it is considered to be an important parameter for the sensitivity of the analysis. Also, in the presence of chloride ions, copper forms complexes such as $CuCl_4^{2-}$ and $CuCl_2^-$, those are associated with a shift in the half-wave potential and the limiting current values, difficulties can arise in the peak evaluation [60].

Compositions of buffer solutions are as following:

Buffer I: Oxalate Buffer

Composition: $C_2H_8N_2O_4$ + NH_4Cl + HCl

Preparation: 9.6 g $C_2H_8N_2O_4$, 4.6 g NH_4Cl are dissolved in deionized water and 7.9 mL HCl (30%) is added in a 250 mL volumetric flask.

pH: 1.92 ± 0.12

Buffer II: Acetic acid Buffer

Composition: HAc + NH_3

Preparation: 74.9 mL NH_3 (25 %) and 118 mL $C_2H_4O_2$ are dissolved in a 1 L volumetric flask.

pH: 4.60 ± 0.05

Buffer III: Buffer II + KCl

Composition: HAc + NH_3 + KCl

Preparation: 74.9 mL NH_3 (25 %) and 118 mL $C_2H_4O_2$ are dissolved in a 1 L volumetric flask. 1 mL of 3 mol L^{-1}KCl solution was added to sample cell for each analysis.

pH: 4.60 ± 0.05

Buffer IV : Sodium acetate Buffer

Composition: KCl + NaOAc

Preparation: 5.9 g KCl and 20.5 g CH_3COONa are dissolved in deionized water and diluted in a 500 mL volumetric flask.

pH: 8.40 ± 0.08

Theoretical half-wave potential values ($E_{1/2}$) of metal ions are given in Table 6.33 [83].

Table 6.33. Half-wave potentials ($E_{1/2}$, V) of metal ions.

Elements	Buffer I	Buffer II, Buffer II+KCl	Buffer IV
Zn	-1.05	-0.98	-0.98
Cd	-0.63	-0.56	-0.56
Pb	-0.47	-0.38	-0.40
Cu	-0.25	0.03	-0.05

In each set, vessels were prepared as following:

(i) Cd, Pb and Cu analysis with Buffer I and Buffer IV:

1 mL of buffer solution was added to 2 mL digested sample and diluted to 11 mL of final volume.

(ii) Zn analysis with Buffer I and Buffer IV,

1 mL of buffer solution was added to 0.2 mL digested sample and diluted to 11 mL of final volume.

(iii) Cd, Pb and Cu analysis with Buffer II,

0.5 mL of buffer solution was added to 2 mL digested sample and diluted to 11.5 mL of final volume.

(iv) Zn analysis with Buffer II,

0.5 mL of buffer solution was added to 0.2 mL digested sample and diluted to 11.5 mL of final volume.

In additional studies, potassium chloride (KCl) was added to Buffer II. Sets were prepared as following:

(i) Cd, Pb and Cu analysis with Buffer III,

0.1 mL of 3 mol/L KCl solution and 0.5 mL of buffer solution was added to 2 mL digested sample and diluted to 11.6 mL of final volume.

(ii) Zn analysis with Buffer III,

0.1 mL of 3 mol L^{-1} KCl solution and 0.5 mL of buffer solution was added to 0.2 mL digested sample and diluted to 11.6 mL of final volume.

Peak positions of each metal ion, initial currents, currents after each standard addition, and the corresponding Δi values were recorded. The Δi is the average value of the increase in sample peak height after two subsequent additions of standard solutions. As the Δi values become closer to another, the precision of the method increases. The concentrations of metal ions in each sample were determined as µg L^{-1} and as µg or (mg) g^{-1} of original sample weight. DPASV results were checked with ICP-OES data sets, so that the comparison between the buffer solutions could be done.

In Buffer I, standard additions were done with 0.1 mg L^{-1} Cd, 0.2 mg L^{-1} Pb, 15 mg L^{-1} Cu; in Buffer II, with 0.1 mg L^{-1} Cd, 0.5 mg L^{-1} Pb, 25 mg L^{-1} Cu; in Buffer III, with 0.5 mg L^{-1} Cd, 0.75 mg L^{-1} Pb, 7.5 mg L^{-1} Cu; and for Buffer IV, 0.5 mg L^{-1} Cd, 0.75 mg L^{-1} Pb, 7.5 mg L^{-1} Cu were used. In the presence of relatively low concentrations of Zn (<1 mg L^{-1}) standard additions were done with 10 mg L^{-1}, and in the presence of relatively high Zn concentrations (>1 mg L^{-1}) standard additions were done with 25 mg L^{-1}, and 50 mg L^{-1} Zn.

6.2.1. Effects of Buffer Compositions in the Analysis of Canned Sardine, Tuna, Corn and Tomato Samples

The DPASV results of canned sardine, tuna and corn samples summarized in Table 6.34 to Table 6.45. Voltammograms and the corresponding observations were discussed below.

Sample S_{32} was an Engin Brand sardine sample with the expiration date of 04/2013 which was also the serial number. Among the four different buffer solutions, Buffer I gave the closest results of DPASV analyses for Cd, Pb and Cu to ICP-OES analyses although the smallest relative standard deviations were achieved for both Cd and Pb with Buffer III in replicate measurements. Nevertheless, DPASV result for Pb was twice as much as the ICP-OES result, and the DPASV result for Cd was six fold greater than the ICP-OES result

in Buffer III. As the experimental results of DPASV analysis for Cd, Pb and Cu were compared with the ICP-OES analysis, Buffer III showed the greatest discrepancy amongst the other buffer compositions. Addition of KCl to Buffer II affected the appearance of Cu peak as in Figure 6.16, 6.17. Formation of chloride complexes of copper ($CuCl_4^{2-}$, $CuCl_2^-$) caused the occurrence of an additional peak. Therefore, the highest relative standard deviation and the most unreliable data were obtained.

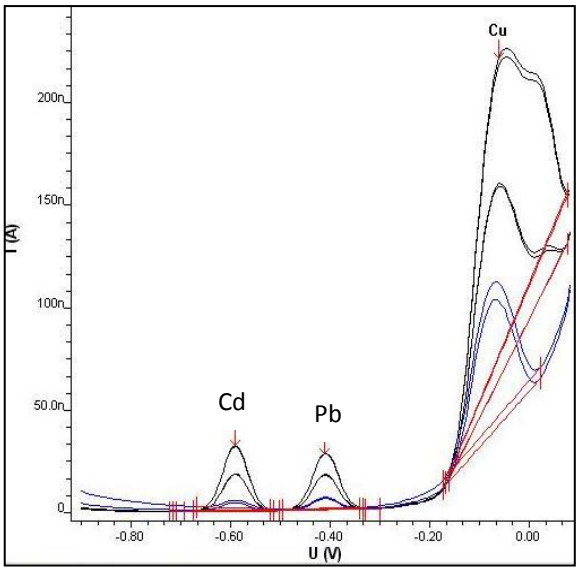

Figure 6.16. Voltammogram of S_{32} with Buffer III.

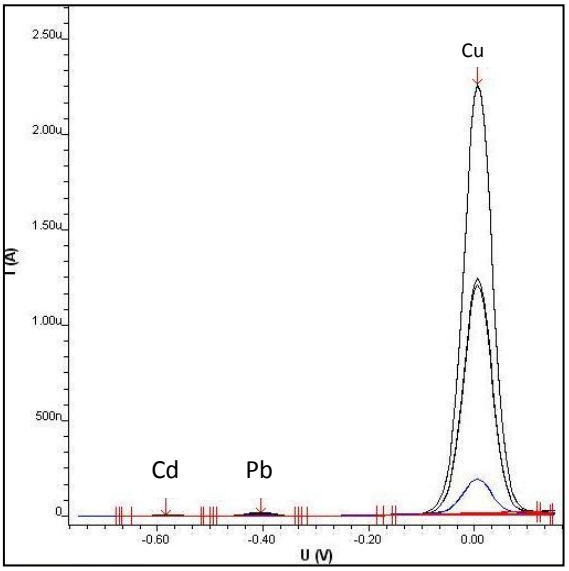

Figure 6.17. Voltammogram of S_{32} with Buffer II.

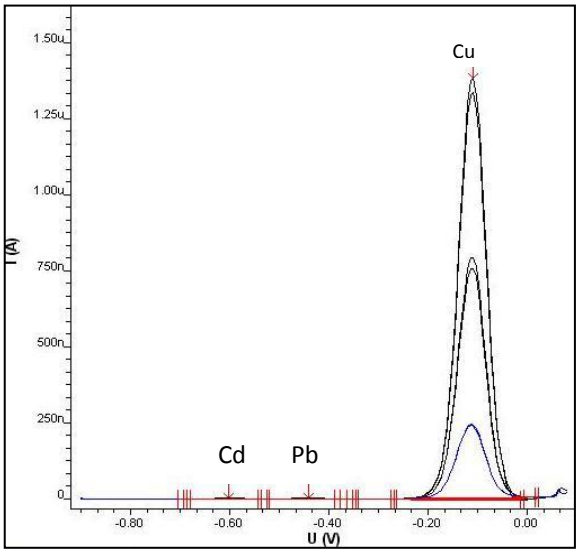

Figure 6.18. Voltammogram of S_{32} with Buffer I.

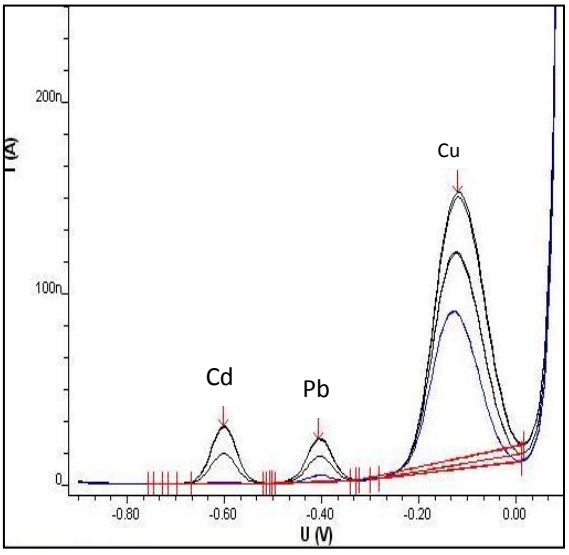

Figure 6.19. Voltammogram of S_{32} with Buffer IV.

The smallest differences in Δi values were obtained with Buffer I which indicated an elevated level of precision in the method. Evaluation of the Cu peaks were more difficult than that of the Cd and Pb peaks, since shifted base-lines or broad peaks were observed in analysis of some of the analytes. Reasonably smooth and a reliable Cu peak with a small relative standard deviation value, i.e., 2.27 % was achieved with Buffer I (Figure 6.18). The corresponding peak height after the last standard additions was almost three to five times higher than the sample peak, and this was the theoretically expected situation a successful standard addition in voltammetry.

Buffer II and Buffer IV both revealed relatively small standard deviation values for Cu analysis, yet the Cu peak with Buffer IV was not a reliable one because of the unsuccessful standard additions and a shifted baseline (Figure 6.17, 6.19). The difference in Δi values was 1.4 in the case of Buffer IV. However, there was no difference between Δi values in the case of Buffer II. Buffer II aroused an interest by introducing a smooth peak similar to that of Buffer I. Buffer compositions were listed with respect to their suitability in DPASV analysis for Cd, Pb and Cu contents of sardine samples as Buffer I > Buffer II > Buffer IV > Buffer III (Table 6.34).

Sardine samples with relatively high Zn contents; i.e., 1 mg L^{-1} – 25 mg L^{-1} were analyzed separately by arranging the deposition potential between – 1.15 V and – 0.75 V. Sample dilution was increased in the voltammetric cell. 0.2 mL of a sample was diluted to a final volume of 10 mL. Four different buffer compositions were tested. The results of the analyses with comparison to ICP-OES data set are given in Table 6.35.

Table 6.34. Cd, Pb and Cu contents of sardine sample S_{32} with four buffer solutions.

DPASV						
Buffer	Addition	Element	Peak Position (V)	Δi	µg L^{-1}	SD %
Buffer I	Sample	Cd	-0.602		0.953 ± 0.060	6.30
	Add.1		-0.599	2.14		
	Add.2		-0.599	2.19		
	Sample	Pb	-0.439		8.75 ± 0.59	6.72
	Add.1		-0.442	2.42		
	Add.2		-0.442	1.93		
	Sample	Cu	-0.108		280 ± 6	2.14
	Add.1		-0.108	0.533		
	Add.2		-0.108	0.591		
Buffer II	Sample	Cd	-0.583		2.38 ± 0.18	7.56
	Add.1		-0.583	3.24		
	Add.2		-0.583	2.90		
	Sample	Pb	-0.405		19.9 ± 0.9	4.52
	Add.1		-0.408	7.24		
	Add.2		-0.405	6.86		
	Sample	Cu	0.006		216 ± 4	1.85
	Add.1		0.006	1.03		
	Add.2		0.006	1.03		
Buffer III	Sample	Cd	-0.591		6.51 ± 0.19	2.92
	Add.1		-0.591	14.2		
	Add.2		-0.591	13.5		
	Sample	Pb	-0.412		17.3 ± 0.6	3.47
	Add.1		-0.412	11.5		
	Add.2		-0.412	10.4		
	Sample	Cu	-0.073		405 ± 50	12.3
	Add.1		-0.067	30.1		
	Add.2		-0.061	47.4		
Buffer IV	Sample	Cd	-0.599		1.87 ± 0.21	11.2
	Add.1		-0.622	14.7		
	Add.2		-0.622	14.0		
	Sample	Pb	-0.406		13.4 ± 0.6	4.48
	Add.1		-0.406	9.76		
	Add.2		-0.406	8.91		
	Sample	Cu	-0.126		327 ± 7	2.14
	Add.1		-0.126	28.5		
	Add.2		-0.126	27.1		

ICP results for Cd, Pb and Cu elements were 1.11, 9.08, 256 µg L^{-1}, respectively.

Table 6.35. Zn contents of sardine sample S_{32} with four buffer solutions.

DPASV						ICP-OES
Buffer	Addition	Peak Position (V)	Δi	mg L^{-1}	SD %	mg L^{-1}
Buffer I	Sample Add.1 Add.2	-1.025 -1.025 -1.025	 0.519 0.530	23.1 ± 0.2	0.86	22.4
Buffer II	Sample Add.1 Add.2	-0.995 -0.983 -0.983	 7.23 4.45	18.5 ± 2.0	10.8	
Buffer III	Sample Add.1 Add.2	-0.995 -0.989 -0.983	 6.82 5.16	16.9 ± 1.2	7.10	
Buffer IV	Sample Add.1 Add.2	-0.995 -0.997 -0.989	 6.45 5.08	17.1 ± 0.9	5.26	

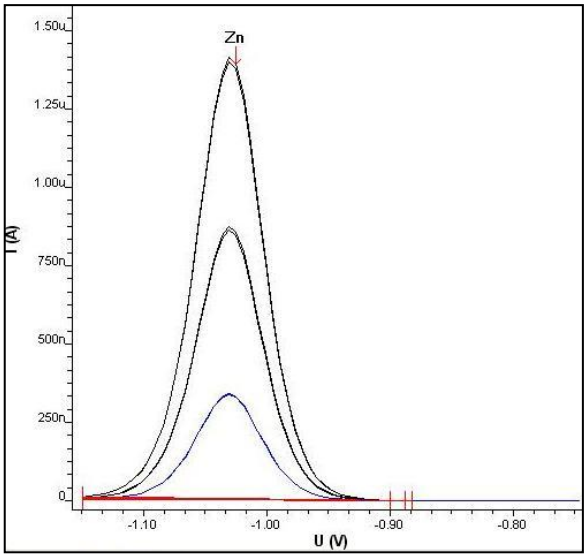

Figure 6.20. Voltammogram of S_{32} with Buffer I.

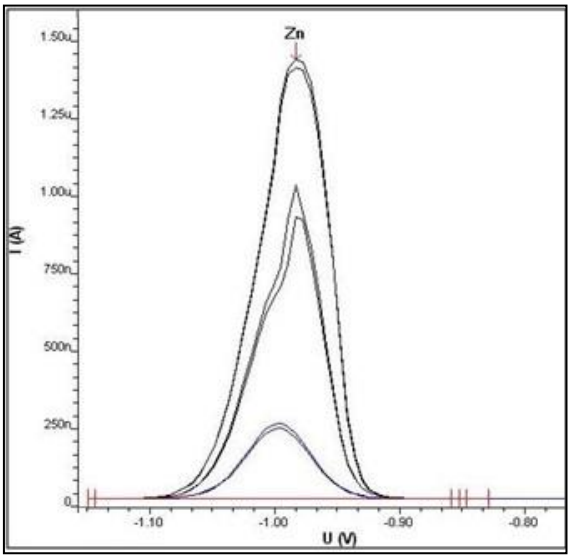

Figure 6.21. Voltammogram of S_{32} with Buffer II.

DPASV with Buffer I yielded the closest result to ICP-OES for the Zn determination, also with the smallest relative standard deviation i.e. 0.86 %. The Δi values were in good agreement for the first and the second standard additions. Half-wave ($E_{1/2}$) potential values for the original sample and the two consequent standard additions were the same i.e., -1.025 V. Voltammetric peak was not distorted and the base-line was not shifted (Figure 6.20).

Since the voltammetric data with the Buffer II medium appeared to be the second closest set to the ICP-OES result; Buffer III and Buffer IV compositions were not taken into consideration. Also, the distorted voltammetric peak with the highly different Δi values indicated that Buffer II was not a good choice for Zn determination (Figure 6.21).

Although Buffer I composition was the most suitable one for Cd, Pb and Cu determinations, in some fish, corn and tomato samples, determination of the Cu content was challenging. Especially, at relatively high concentrations (> 1 mg L^{-1}), split peaks, shifted base lines or rather different Δi values for the subsequent standard additions were experienced. In such instances, Cu voltammograms were investigated separately by isolating the deposition potential between -0.25 V and 0.10 V. Canned sardine sample, S_{36} was one of the analytes, and the tests were run in four different buffer compositions (Table 6.36). DPASV analyses of sardine fish samples from the same can showed that the best results for the unshifted base-lines, and the closest Δi values were obtained in Buffer I (Figure 6.22). Also, the voltammetric result of Buffer I was in good agreement with ICP-OES data (Table 6.36).

Table 6.36. Cu contents of Sardine sample S_{36} with four buffer solutions.

DPASV						ICP-OES
Buffer	Addition	Peak Position (V)	Δi	mg L^{-1}	SD %	mg L^{-1}
Buffer I	Sample Add.1 Add.2	-0.134 -0.134 -0.134	 2.90 2.43	7.79 ± 0.30	3.84	7.60
Buffer II	Sample Add.1 Add.2	0.002 0.002 0.002	 80.8 123	5.51 ± 0.58	10.5	
Buffer III	Sample Add.1 Add.2	0.002 0.002 0.002	 0.46 0.63	5.59 ± 0.55	9.87	
Buffer IV	Sample Add.1 Add.2	-0.009 -0.061 -0.054	 54.7 288	11.5 ± 2.9	25.2	

Voltammetric peak of the Cu element in Buffer II and in Buffer III exhibited half-wave potentials at 0.002 V which were towards positive potentials with respect to the ones in Buffer I and Buffer IV (Table 6.36). The DPASV analysis in Buffer II resulted in split peaks with highly different Δi values (Figure 6.23), while the unknown peak that appeared

in Buffer III was most probably due to $CuCl_2^-$ or $CuCl_4^{2-}$ complex formations which caused the DPASV result to differ from the ICP-OES analysis (Figure 6.24). Also, the voltammogram of Cu in Buffer IV had a shifted base-line (Figure 6.25).

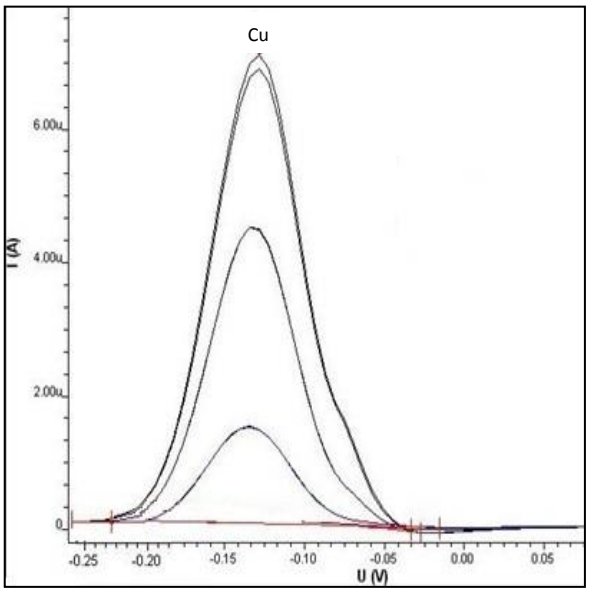

Figure 6.22. Voltammogram of S_{36} with Buffer I.

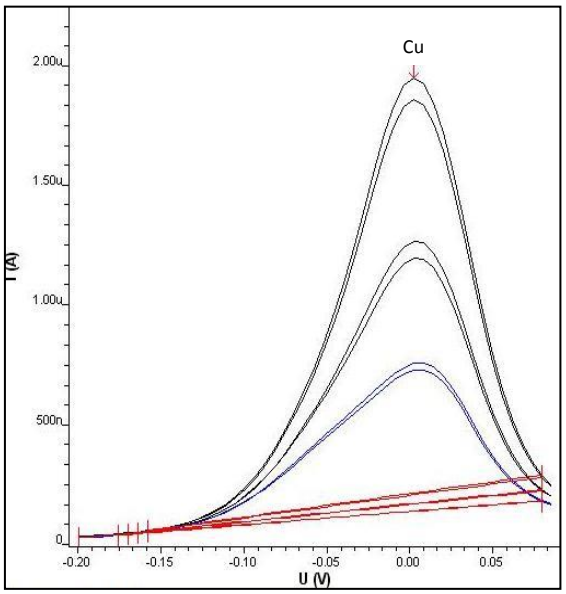

Figure 6.23. Voltammogram of S_{36} with Buffer II.

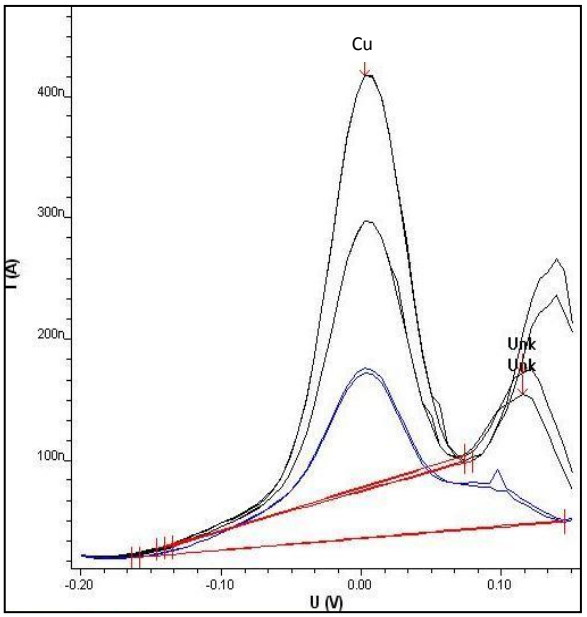

Figure 6.24. Voltammogram of S_{36} with Buffer III.

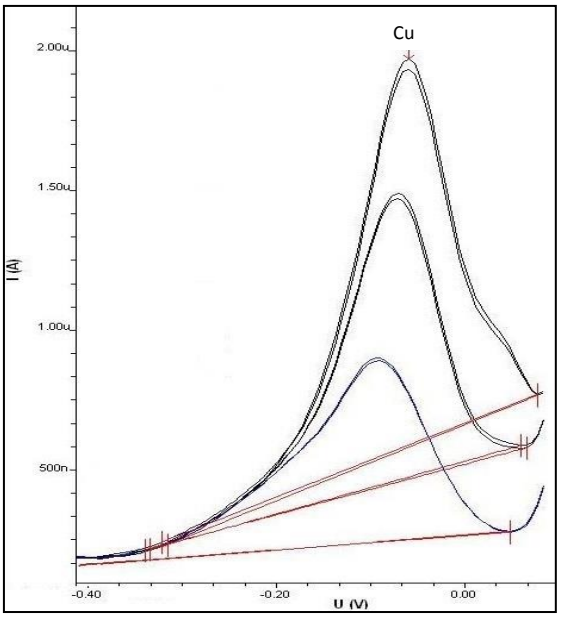

Figure 6.25. Voltammogram of S_{36} with Buffer IV.

Buffer tests were run on numerous fresh and canned sardine samples and the following conclusions were obtained:

Buffer I resulted in smooth voltammetric peaks with unshifted base lines for Cd, Pb, Cu and Zn. Also, standard additions were successful with the smallest deviations between the Δi values.

In Buffer II, voltammetric peaks for Cd and Pb were split, which resulted in highly deviated Δi values. Yet the recorded amounts of Cd and Pb were not always in agreement with ICP-OES data. Cu peaks showed smooth and acceptable voltammograms in some cases, but in others highly shifted base lines were observed.

Buffer III resulted in unknown peaks adjacent to Cu peaks in some samples and in others broad peaks were observed. Mostly, the Δi values were rather different from each other for the subsequent standard additions. The results of DPASV analysis were not always in agreement with ICP-OES analysis. Smooth voltammetric peaks were observed for Cd and Pb.

In Buffer IV, voltammetric peaks for Cu, Cd and Pb were broad and slightly split in most of the cases, and in others Cu content could not be determined due to unsuccessful standard additions or else Cu voltammograms were masked totally.

Buffer solutions were also tested for the tuna samples, labeled as $T_{6,}$ T_{36}, and T_{37}. Table 6.37 shows the results of the study with canned tuna of Superfresh brand with production date of 06/2012 and serial number of DGL 2163, sample labeled as T_6. As the DPASV data were compared with ICP-OES data, the collaborative trials for the buffer tests resulted differently for each element. The order of the increasing efficiency in use of different buffer compositions in DPASV analysis of Cd, Pb, and Cu was the following:

Cd: Buffer I > Buffer III > Buffer IV > Buffer II
Pb: Buffer I > Buffer IV > Buffer II > Buffer III
Cu: Buffer I > Buffer II > Buffer IV > Buffer III

Zn contents of tuna samples were determined separately, 0.1 mL sample solutions were diluted to 10 mL in the vessel. Deposition potential range was kept between -1.15 V and -0.75 V as in the case of sardine samples. Standard additions were done with 50 mg L^{-1} Zn for Buffer II, Buffer III, and Buffer IV; and 100 mg L^{-1} Zn for Buffer I. Zn content of the sample $T_{6,}$ 112 mg L^{-1}, revealed the smallest standard deviation in Buffer I (Table 6.37). Although, the results of DPASV in Buffer III appeared to be the closest to ICP-OES, the peak was distorted after the second addition (Figure 6.26).

Table 6.37. Zn content of tuna sample T_6 with four buffer solutions.

DPASV						ICP-OES
Buffer	Addition	Peak Position (V)	Δi	mg L^{-1}	SD %	mg L^{-1}
Buffer I	Sample Add.1 Add.2	-1.031 -1.031 -1.025	 0.516 0.515	112 ± 3	2.68	104
Buffer II	Sample Add.1 Add.2	-0.995 -0.989 -0.983	 6.60 3.04	57.2 ± 8.7	15.3	
Buffer III	Sample Add.1 Add.2	-0.995 -0.986 -0.989	 2.52 5.03	57.0 ± 24.2	42.4	
Buffer IV	Sample Add.1 Add.2	-0.995 -0.995 -0.995	 2.66 2.66	107 ± 3	2.80	

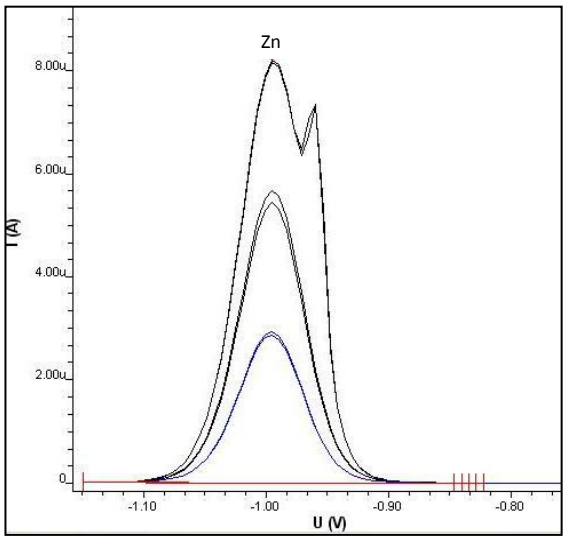

Figure 6.26. Voltammogram of T_6 with Buffer IV.

The results of DPASV analysis for tuna sample T_6 are given in Table 6.38. ICP-OES results for Cd, Pb and Cu elements were 45.0, 33.8, 1403 µg L^{-1}, respectively, and the concentrations of Cd, Pb and Cu in Buffer I were 48.6, 35.5, and 1315 µg L^{-1}. Hence, it was decided that Buffer I was the most suitable medium for the analyses of those elements

Table 6.38. Cd, Pb and Cu contents of tuna sample T_6 with four buffer solutions.

DPASV						
Buffer	Addition	Element	Peak Position (V)	Δi	µg L^{-1}	SD %
Buffer I	Sample	Cd	-0.601		48.6 ± 0.8	1.65
	Add.1		-0.601	49.1		
	Add.2		-0.601	49.1		
	Sample	Pb	-0.429		35.5 ± 0.5	1.41
	Add.1		-0.429	43.6		
	Add.2		-0.429	41.7		
	Sample	Cu	-0.089		1315 ± 14	1.06
	Add.1		-0.089	1.67		
	Add.2		-0.089	1.58		
Buffer II	Sample	Cd	-0.589		64.4 ± 1.4	2.17
	Add.1		-0.589	93.3		
	Add.2		-0.589	86.8		
	Sample	Pb	-0.417		50.9 ± 1.9	3.73
	Add.1		-0.417	29.6		
	Add.2		-0.417	31.9		
	Sample	Cu	0.000		1208 ± 70	5.78
	Add.1		0.000	104		
	Add.2		0.000	116		
Buffer III	Sample	Cd	-0.595		55.3 ± 1.9	3.44
	Add.1		-0.595	43.1		
	Add.2		-0.595	41.5		
	Sample	Pb	-0.423		57.9 ± 5.0	8.64
	Add.1		-0.423	37.3		
	Add.2		-0.417	38.1		
	Sample	Cu	-0.012		838 ± 42	5.01
	Add.1		-0.006	1.16		
	Add.2		-0.006	1.14		
Buffer IV	Sample	Cd	-0.607		55.4 ± 0.9	1.62
	Add.1		-0.607	42.6		
	Add.2		-0.607	38.2		
	Sample	Pb	-0.435		31.3 ± 0.8	2.55
	Add.1		-0.429	32.7		
	Add.2		-0.429	29.3		
	Sample	Cu	-0.101		1766 ± 19	1.08
	Add.1		-0.083	314		
	Add.2		-0.078	290		

Table 6.39 shows the Cd, Pb and Cu contents of Ülker Brand canned tuna with the production date of 26/06/2012 and the serial number of DG L 2179, sample labeled as T_{36}.

Table 6.39. Cd, Pb and Cu contents of tuna sample T_{36} with buffer solutions.

DPASV						
Buffer	Addition	Element	Peak Position (V)	Δi	μg L^{-1}	SD %
Buffer I	Sample	Cd	-0.585		4.29 ± 0.25	5.83
	Add.1		-0.591	4.46		
	Add.2		-0.591	4.44		
	Sample	Pb	-0.418		10.5 ± 0.7	6.67
	Add.1		-0.418	8.84		
	Add.2		-0.418	8.13		
	Sample	Cu	-0.079		332 ± 10	3.01
	Add.1		-0.079	0.845		
	Add.2		-0.079	0.734		
Buffer II	Sample	Cd	-0.588		3.06 ± 0.50	16.3
	Add.1		-0.585	2.34		
	Add.2		-0.585	2.65		
	Sample	Pb	-0.412		14.2 ± 2.3	16.2
	Add.1		-0.406	8.68		
	Add.2		-0.406	9.45		
	Sample	Cu	0.052		62.5 ± 9.2	14.7
	Add.1		0.070	44.5		
	Add.2		0.005	25.4		
Buffer III	Sample	Cd	-0.588		2.25 ± 0.08	3.56
	Add.1		-0.591	5.15		
	Add.2		-0.591	4.93		
	Sample	Pb	-0.418		9.02 ± 1.31	14.5
	Add.1		-0.412	8.16		
	Add.2		-0.412	8.87		
	Sample	Cu	-0.228		161 ± 33	20.5
	Add.1		-0.195	16.5		
	Add.2		-0.129	3.62		
Buffer IV	Sample	Cd	-0.599		1.44 ± 0.23	16.0
	Add.1		-0.602	5.23		
	Add.2		-0.602	5.38		
	Sample	Pb	-0.415		5.12 ± 2.22	43.4
	Add.1		-0.406	8.07		
	Add.2		-0.400	9.86		
	Sample	Cu	-0.288		87.6 ± 7.2	8.22
	Add.1		-0.192	17.14		
	Add.2		-0.159	19.13		

ICP-OES results for Cd, Pb and Cu elements were 3.78, 7.05, 369 μg L^{-1}, respectively. Buffer I revealed the most relevant DPASV result with ICP-OES analysis in

case of Cu determination. Buffer IV revealed the most irrelevant DPASV result with ICP-OES in case of Cd and the second most irrelevant DPASV result in case of Cu.

In Buffer IV, the standard deviation value related to Pb determination was 43.4 % which indicated unsuccessful standard additions. In Buffer III, the standard deviation value for Cu determination, i.e., 20 % was beyond the acceptable limits. Also, the Cu content was almost half of its value obtained from ICP-OES analysis. Buffer II resulted in high standard deviation values for all of the three elements investigated; Pb 16.4%, Cd 16.4% and Cu 14.8%. Also, irrelevant Δi values were registered for the subsequent standard additions in Cu determination. Moreover, DPASV analysis for Pb and Cu contents were not in good agreement with ICP-OES analysis.

Furthermore, DPASV analyses of fish samples were continued without Buffer IV as the supporting electrolyte. Hence, canned tuna sample, T_{37}, Ülker brand, was chosen randomly for investigating the buffer effect with Buffer I, Buffer II and Buffer III compositions (Table 6.40, 6.41). DPASV analysis of Zn with Buffer II and Buffer III both exhibited high standard deviation values and the least accurate results with respect to the ICP-OES results (Table 6.40). The change in the peak potentials in each addition of standards affected the Δi values and increased the value of standard deviation. Buffer I yielded the best result for Zn analysis in tuna samples. Highly distorted voltammetric peak of Zn yielded in the presence of Buffer II as shown in Figure 6.27.

Table 6.40. Zn contents of tuna sample T_{37} with three buffer solutions.

DPASV						ICP-OES
Buffer	Addition	Peak Position (V)	Δi	mg L^{-1}	SD %	mg L^{-1}
Buffer I	Sample Add.1 Add.2	-1.028 -1.028 -1.028	 0.516 0.515	65.5 ± 0.7	1.07	67.2
Buffer II	Sample Add.1 Add.2	-0.971 -1.001 -0.989	 2.501 4.471	24.9 ± 24.6	98.8	
Buffer III	Sample Add.1 Add.2	-0.983 -0.983 -0.983	 11.7 7.55	99.5 ± 8.5	8.55	

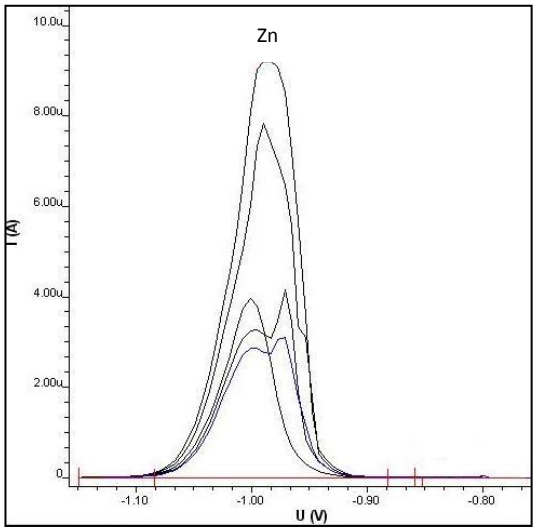

Figure 6.27. Voltammogram of T_{37} with Buffer II.

Table 6.41. Cd, Pb and Cu contents of tuna sample T_{37} with three buffer solutions.

DPASV						
Buffer	Addition	Element	Peak Position (V)	Δi	µg L^{-1}	SD %
Buffer I	Sample	Cd	-0.602		4.24 ± 0.33	7.78
	Add.1		-0.602	5.21		
	Add.2		-0.602	5.55		
	Sample	Pb	-0.442		43.8 ± 2.5	5.70
	Add.1		-0.442	32.3		
	Add.2		-0.442	32.2		
	Sample	Cu	-0.163		1123 ± 38	3.38
	Add.1		-0.163	4.06		
	Add.2		-0.163	3.64		
Buffer II	Sample	Cd	-0.590		2.46 ± 0.64	25.9
	Add.1		-0.584	16.2		
	Add.2		-0.581	11.8		
	Sample	Pb	-0.411		3.93 ± 0.18	4.58
	Add.1		-0.408	63.3		
	Add.2		-0.408	59.1		
	Sample	Cu	0.002		1083 ± 79	7.29
	Add.1		0.002	167		
	Add.2		0.002	115		
Buffer III	Sample	Cd	-0.591		4.94 ± 0.30	6.07
	Add.1		-0.591	8.03		
	Add.2		-0.591	6.92		
	Sample	Pb	-0.412		20.7 ± 1.9	9.18
	Add.1		-0.412	36.8		
	Add.2		-0.412	29.8		
	Sample	Cu	-0.005		607 ± 74	12.2
	Add.1		-0.002	0.621		
	Add.2		-0.002	0.597		

ICP-OES results of Cd, Pb and Cu elements for tuna sample T_{37} were 3.47, 34.4, 1212 µg L^{-1}, respectively. Although the smallest relative standard deviation in the detection of Cd content was achieved with Buffer III solution, the closeness of the DPASV results to ICP-OES and the similarity of Δi values for the subsequent standard additions in each element determination showed that Buffer I was the best composition (Table 6.41). In the case of Pb analysis, Buffer II revealed the most irrelevant data with ICP-OES analysis. Also, Buffer III exhibited the most irrelevant data for Cu determination, although the corresponding standard deviation was relatively small, i.e. 1.22 %.

Experiments on fish samples with four different buffer compositions indicated that the most suitable electrolyte medium was established with Buffer I composition. Additionally, analyses with those four buffer solutions were run for the vegetable samples (Table 6.42-6.45). Tukaş brand canned corn samples with a serial number of PN 246-2-19:19-11 and the expiration date of 03/03/2015, labeled as C_{19} and C_{23} (Table 6.42 and Table 6.43) and diced tomato samples which were Demko Brand with a serial number of 24911 20 01 and the expiration date of 06/09/2014, labeled as TT_{18} and TT_{19} (Table 6.44 and Table 6.45) were analyzed in four different buffer media. Zn analysis data revealed that Buffer I composition was the best with the lowest standard deviation value and the coherent Δi values (Table 6.42).

Table 6.42. Zn contents of corn sample C_{19} with different buffer compositions.

DPASV						ICP-OES
Buffer	Addition	Peak Position (V)	Δi	mg L^{-1}	SD %	mg L^{-1}
Buffer I	Sample	-1.025				
	Add.1	-1.025	3.07	2.13 ± 0.06	2.81	
	Add.2	-1.025	2.91			
Buffer II	Sample	-1.001				
	Add.1	-0.995	2.10	0.517 ± 0.097	18.8	
	Add.2	-0.995	1.51			1.67
Buffer III	Sample	-0.995				
	Add.1	-0.995	2.84	2.11 ± 0.18	8.53	
	Add.2	-0.995	3.22			
Buffer IV	Sample	-0.995				
	Add.1	-0.995	2.60	2.57 ± 0.19	7.39	
	Add.2	-0.995	2.59			

Table 6.43. Cd, Pb and Cu contents of corn sample C_{23} with different buffer compositions.

DPASV						
Buffer	Addition	Element	Peak Position (V)	Δi	µg L^{-1}	SD %
Buffer I	Sample	Cd	-0.599		3.59 ± 0.12	3.34
	Add.1		-0.599	6.72		
	Add.2		-0.599	6.23		
	Sample	Pb	-0.460		37.8 ± 0.2	0.53
	Add.1		-0.460	24.9		
	Add.2		-0.460	24.5		
	Sample	Cu	-0.081		7997 ± 63	0.79
	Add.1		-0.081	1.02		
	Add.2		-0.081	0.99		
Buffer II	Sample	Cd	-0.580		3.35 ± 0.78	23.4
	Add.1		-0.583	6.20		
	Add.2		-0.583	7.84		
	Sample	Pb	-0.414		30.5 ± 2.8	9.18
	Add.1		-0.411	16.1		
	Add.2		-0.411	17.2		
	Sample	Cu	0.006		10222 ± 903	8.83
	Add.1		0.006	2.57		
	Add.2		0.006	3.06		
Buffer III	Sample	Cd	-0.591		3.89 ± 0.16	4.11
	Add.1		-0.594	7.04		
	Add.2		-0.591	6.46		
	Sample	Pb	-0.418		33.3 ± 1.3	3.90
	Add.1		-0.418	17.5		
	Add.2		-0.418	15.4		
	Sample	Cu	0.005		15719 ± 1730	11.0
	Add.1		0.011	2.82		
	Add.2		0.016	1.40		
Buffer IV	Sample	Cd	-0.607		13.4 ± 6.2	46.3
	Add.1		-0.604	2.09		
	Add.2		-0.601	6.64		
	Sample	Pb	-0.417		21.9 ± 9.0	41.1
	Add.1		-0.414	6.71		
	Add.2		-0.411	5.14		
	Sample	Cu	-0.095		7325 ± 648	8.84
	Add.1		-0.086	0.563		
	Add.2		-0.083	0.557		

ICP-OES results for Cd, Pb and Cu elements were 2.85, 26.5, 7414 µg L^{-1}, respectively. DPASV with Buffer I yielded the closest results to ICP-OES analysis for Cd and Cu for the corn sample C_{23} (Table 6.43). Also, standard deviation values were the smallest, and Δi values for the standard additions were the closest among the others. Buffer

II and Buffer III showed highly different DPASV results for Cu with respect to ICP-OES analysis. DPASV analysis with Buffer IV resulted in irrelevant data for Cd content as compared to ICP-OES.

Table 6.44. Cd, Pb and Cu contents of tomato sample TT_{18}.

DPASV						
Buffer	Addition	Element	Peak Position (V)	Δi	µg L^{-1}	SD %
Buffer I	Sample	Cd	-0.626		6.44 ± 0.32	4.97
	Add.1		-0.626	15.9		
	Add.2		-0.626	14.1		
	Sample	Pb	-0.477		5.73 ± 0.46	8.03
	Add.1		-0.477	2.62		
	Add.2		-0.477	2.44		
	Sample	Cu	-0.168		81.3 ± 2.8	3.44
	Add.1		-0.162	0.461		
	Add.2		-0.162	0.440		
Buffer II	Sample	Cd	-0.583		7.10 ± 0.45	6.37
	Add.1		-0.586	13.8		
	Add.2		-0.589	14.4		
	Sample	Pb	-0.420		9.62 ± 0.92	9.57
	Add.1		-0.417	5.59		
	Add.2		-0.417	4.66		
	Sample	Cu	0.000		110 ± 3	2.70
	Add.1		0.000	93.8		
	Add.2		0.000	81.0		
Buffer III	Sample	Cd	-0.596		18.6 ± 44.7	241
	Add.1		-0.579	3.54		
	Add.2		-0.596	-1.27		
	Sample	Pb	-0.418		8.14 ± 11.7	144
	Add.1		-0.421	2.02		
	Add.2		-0.382	0.72		
	Sample	Cu	-0.091		203 ± 15	7.23
	Add.1		-0.073	48.0		
	Add.2		-0.049	53.8		
Buffer IV	Sample	Cd	-0.604		7.95 ± 0.68	8.56
	Add.1		-0.601	13.8		
	Add.2		-0.601	13.9		
	Sample	Pb	-0.411		11.7 ± 2.2	18.8
	Add.1		-0.414	4.61		
	Add.2		-0.417	4.15		
	Sample	Cu	-0.143		97.4 ± 14.6	15.0
	Add.1		-0.143	28.1		
	Add.2		-0.143	36.9		

ICP-OES results for Cd, Pb and Cu elements were 5.48, 5.40, 71.9 µg L^{-1}, respectively. DPASV results with Buffer I for Cu, Cd and Pb contents were the best in the analysis of tomato sample, TT_{18} (Table 6.44, Figure 6.28). DPASV analysis with Buffer III and Buffer IV showed experimental results which were rather different than the ICP-OES analysis. The greatest difference between the two methods was registered in Buffer III for Cu determination, i.e., 203 µg L^{-1} in DPASV.

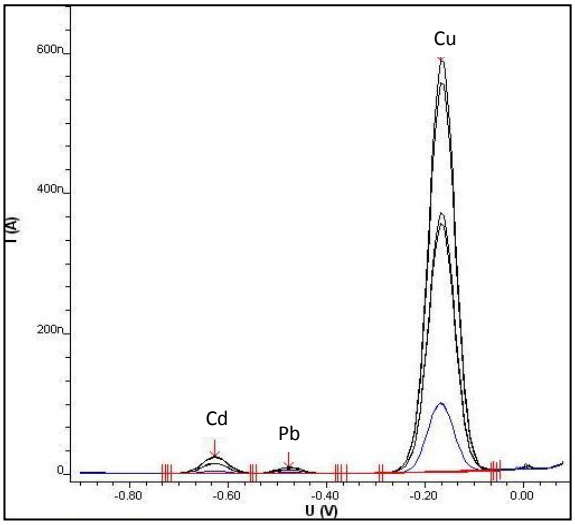

Figure 6.28. Voltammogram of TT_{18} with Buffer I.

The best result for Zn content of TT_{19} was obtained in Buffer I, with small standard deviation value and coherent Δi values (Table 6.45).

Table 6.45. Zn contents of tomato sample TT_{19} with four buffer solutions.

DPASV						ICP-OES
Buffer	Addition	Peak Position (V)	Δi	mg L^{-1}	SD %	mg L^{-1}
Buffer I	Sample Add.1 Add.2	-1.025 -1.025 -1.025	 1.09 1.06	2.08 ± 0.02	0.98	2.03
Buffer II	Sample Add.1 Add.2	-1.001 -1.001 -1.001	 13.3 16.9	0.969 ± 0.07	7.22	
Buffer III	Sample Add.1 Add.2	-1.001 -0.998 -0.995	 1.14 1.11	1.15 ± 0.07	6.08	
Buffer IV	Sample Add.1 Add.2	-0.995 -0.995 -0.980	 2.78 6.05	3.36 ± 0.79	23.5	

In voltammetry, the peak height depends on the amount of metal deposited on the electrode and is a function of many parameters. In order to be able to correlate the peak height with the original concentration of the test material in the solution, the deposited fraction of the metal must be constant in all measurements that are to be compared. This can be achieved by keeping constant the pre-electrolysis time (deposition time) and potential, the convection conditions, solution composition, and stripping conditions (scan rate, pulse amplitude, etc.). Also, it is required that a sufficient amount of base electrolyte should be added to the sample medium. Voltammetric studies about the effect of buffer compositions in the analyses of fish, corn tomato samples showed that the most suitable base electrolyte that matched with the nature of the analyte and the character of the sample matrix was Buffer I, oxalate composition.

6.3. Deposition Time and Deposition Potential

The pre-concentration step in DPASV involves electrolytic deposition of the chemical species onto electrode surface at a definite DC potential. A negative potential is applied to the working electrode in order to reduce the metal ion to the metal, which forms an amalgam with the mercury electrode. The measured peak current is linearly proportional to the analyte concentration and to the deposition time [59]. Too rapid and short time periods for the deposition are not sufficient for proper accumulation, while long durations for accumulation step lead overload on the electrode surface and miscalculations of concentrations of electroactive compounds.

Cd, Pb and Cu are mostly determined in acidic solutions (pH ~ 2) simultaneously. Cu has a low solubility in Hg, only a small amount of deposited Cu forms an amalgam during the pre-electrolysis. It is necessary to shorten the pre-electrolysis time after the individual additions of the standard. With small amounts of copper the pre-electrolysis time should be as short as possible and the instrument sensibility must be high, since the deposited amount of copper is small and thus all the mercury forms an amalgam.

In order to enhance the sensivity of voltammetry, the signal-to-noise ratio i_d/i_c, diffusion current per capacity current, should be increased. If the i_d and i_c are measured by the end of the drop time τ, the i_d/i_c would be at its maximum value [84]. Signal to noise

ratio is improved by depositing the analyte electronically on the working electrode (Hanging Mercury Dropping Electrode), and the selectivity is controlled by choosing the solution composition (electrolyte, buffer and pH value), deposition potential and the deposition time. For mercury electrodes, a direct relationship is observed between the maximum of the registered current of oxidation of the metal deposited on the electrode and the concentration of the metal ions in the solution over a broad concentration interval [85].

The amount of the amalgam formed is proportional to the metal concentration in the sample solution and the deposition time; shortening of the deposition time will cause the amount of the amalgam to be virtually constant in all measurements, thus eliminating possible interference caused by the formation of intermetallic compounds. The original concentration of the metal in the sample is calculated from the relationship

$$c = \frac{m i_s}{w \, \Delta i} \qquad (6.1)$$

where m is the Standard addition in ng, w is the mass of water sample in the vessel in g, i_s is the height of the sample peak and Δi is the average value of the increase in sample peak height after two subsequent additions of the standard solution [53].

6.3.1. Effects of Deposition Potential, Deposition Time and Sample Dilution Factor in the Analysis of Canned Sardine, Anchovy and Corn Samples

Engin brand canned sardine sample, S_{32} was weighed about 1.50 g. It was digested in nitric acid/perchloric acid ($HNO_3/HClO_4$, 5:1, v/v) mixture for 15 hours. Treatment of the sample prior to DPASV analysis was the same as the others. Digests were diluted to a final volume of 10 mL. Voltammogram vessels contained 2 mL of sample and 1 mL of Buffer I.

Table 6.46 shows the results of the analysis of Cd, Pb and Cu elements in Engin Brand canned sardine sample S_{32} with various deposition times as 90, 120, 150 and 180 seconds in Buffer I. The highest standard deviations were observed for the deposition time of 180 seconds, for the three elements. Best results were achieved when deposition time was set to 120 seconds; DPASV and ICP-OES results were in agreement with one another,

and the standard deviations were relatively small. The corresponding Δi values for 120 seconds were close to each other, except for the analysis of Pb, which might have been due to the insufficient concentrations of standard addition solutions.

Table 6.46. Cd, Pb and Cu contents of sardine sample S_{32}.

DPASV							ICP-OES
Dep. Time (s)	Element	Addition	Mean Current	Δi	µg L^{-1}	SD %	µg L^{-1}
90	Cd	Sample Add.1 Add.2	0.513 nA 2.135 nA 3.701 nA	 1.622 1.566	1.50 ± 0.4	26.3	1.11
120	Cd	Sample Add.1 Add.2	0.465 nA 2.610 nA 4.798 nA	 2.145 2.188	0.953±0.065	6.82	
150	Cd	Sample Add.1 Add.2	0.621 nA 3.505 nA 6.213 nA	 2.884 2.709	1.54 ± 0.19	12.3	
180	Cd	Sample Add.1 Add.2	0.338 nA 3.708 nA 0.436 nA	 3.369 -3.372	121 ± 2340	1933	
90	Pb	Sample Add.1 Add.2	0.414 nA 2.836 nA 4.770 nA	 2.422 1.934	2.07 ± 0.45	21.9	9.81
120	Pb	Sample Add.1 Add.2	1.076 nA 2.621 nA 3.554 nA	 1.545 0.933	8.75 ± 0.59	6.72	
150	Pb	Sample Add.1 Add.2	0.79 nA 9.40 nA 16.6 nA	 8.61 7.23	2.81 ± 1.42	50.3	
180	Pb	Sample Add.1 Add.2	0.22 nA 14.9 nA 2.14 nA	 14.76 -12.84	117 ± 647	552	
90	Cu	Sample Add.1 Add.2	0.238 uA 0.771 uA 1.362 uA	 0.533 0.591	306 ± 14	4.58	256
120	Cu	Sample Add.1 Add.2	0.187 uA 0.665 uA 1.135 uA	 0.478 0.470	280 ± 6	2.14	
150	Cu	Sample Add.1 Add.2	0.289 uA 1.171 uA 1.994 uA	 0.882 0.773	324 ± 8	2.47	
180	Cu	Sample Add.1 Add.2	0.359 uA 1.350 uA 1.932 uA	 0.991 0.582	302 ± 30	9.93	

In order to see the effect of the deposition time in the presence of relatively low concentrations of Cd, Pb, and Cu, Engin Brand canned sardine S_{33} was analyzed (Table 6.47).

Table 6.47. Cd, Pb and Cu contents of sardine sample S_{33}.

DPASV							ICP-OES
Dep. Time (s)	Element	Addition	Mean Current	Δi	µg L^{-1}	SD %	µg L^{-1}
90	Cd	Sample Add.1 Add.2	0	0	0	-	0
120	Cd	Sample Add.1 Add.2	0	0	0	-	
150	Cd	Sample Add.1 Add.2	0	0	0	-	
180	Cd	Sample Add.1 Add.2	0	0	0	-	
90	Pb	Sample Add.1 Add.2	2.32 nA 8.24 nA 13.4 nA	 5.92 5.14	10.2 ± 0.7	6.86	8.73
120	Pb	Sample Add.1 Add.2	2.87 nA 10.2 nA 16.4 nA	 7.33 6.21	10.3 ± 0.5	4.85	
150	Pb	Sample Add.1 Add.2	3.77 nA 16.8 nA 30.3 nA	 13.0 13.5	11.4 ± 1.93	16.9	
180	Pb	Sample Add.1 Add.2	5.26 nA 21.3 nA 35.7 nA	 16.0 14.4	12.2 ± 1.1	9.01	
90	Cu	Sample Add.1 Add.2	0.304 uA 0.764 uA 1.174 uA	 0.460 0.410	484 ± 8	1.65	414
120	Cu	Sample Add.1 Add.2	0.367 uA 0.926 uA 1.443 uA	 0.559 0.517	475 ± 6	1.27	
150	Cu	Sample Add.1 Add.2	0.421 uA 1.143 uA 1.917 uA	 0.722 0.774	536 ± 22	4.09	
180	Cu	Sample Add.1 Add.2	0.517 uA 1.277 uA 1.956 uA	 0.761 0.678	663 ± 36	5.43	

In this particular sample, Cd did not exist. The aim was to investigate whether the deposition time of 120 seconds would be still effective or not in the absence of one element. Results showed that both 90 seconds and 120 seconds of deposition periods yielded the closest results for Pb and Cu to ICP-OES analysis. Also, the DPASV analysis revealed that the results were not significantly different from one another at 90 seconds and 120 seconds. Although, the deposition time of 120 seconds resulted in relatively smaller standard deviation values.

Zn contents of the sample S_{32} was determined separately due to its high concentration (Table 6.48). Deposition time of 120 seconds revealed the closest Δi values for the subsequent standard additions and the smallest relative standard deviation. Dilution factor was set to 0.2/10.

Table 6.48. Zn contents of sardine sample S_{32}.

DPASV						ICP-OES
Dep. Time (s)	Addition	Mean Current	Δi	mg L^{-1}	SD %	mg L^{-1}
90	Sample Add.1 Add.2	0.265 uA 0.487 uA 0.711 uA	 221.4 224.4	29.0 ± 0.4	1.38	22.4
120	Sample Add.1 Add.2	0.328 uA 0.848 uA 1.378 uA	 0.519 0.530	23.1 ± 0.2	0.86	
150	Sample Add.1 Add.2	0.308 uA 1.008 uA 1.650 uA	 0.701 0.642	22.2 ± 5.4	24.6	
180	Sample Add.1 Add.2	0.465 uA 1.407 uA 2.236 uA	 0.942 0.829	25.3 ± 0.6	2.57	

Analyses on vegetable samples were also carried out with canned corn sample, C_{20}, Tukaş Brand with the serial no of PN 246-2-19:19-11 and the expiration date of 03/03/2015 (Table 6.49). The DPASV analysis with 90 seconds of pre-concentration time gave the smallest standard deviation value; however, the recorded concentration value for Cd concentration was not in agreement with ICP-OES result. The results of Pb and Cu analyses at 120 seconds of deposition time gave the closest results to ICP-OES analyses although the standard deviation values were higher than the ones at 90 seconds of

deposition time. Cu content of the sample was determined separately, with the dilution factor of 0.5/10.

Table 6.49. Cd, Pb and Cu contents of corn sample C_{20}.

DPASV							ICP-OES
Dep. Time (s)	Element	Addition	Mean Current	Δi	µg L^{-1}	SD %	µg L^{-1}
90	Cd	Sample Add.1 Add.2	11.26 38.78 63.38	 27.52 24.60	20.5 ± 0.5	2.44	10.8
120	Cd	Sample Add.1 Add.2	7.11 39.2 69.1	 32.11 29.91	10.9 ± 0.6	5.50	
150	Cd	Sample Add.1 Add.2	7.09 54.25 91.12	 47.16 36.86	7.89 ± 5.2	65.9	
180	Cd	Sample Add.1 Add.2	16.8 64.1 114.7	 47.3 50.6	16.8 ± 0.6	3.57	
90	Pb	Sample Add.1 Add.2	58.5 159.9 243.3	 101.4 83.4	222 ± 11	4.91	119.3
120	Pb	Sample Add.1 Add.2	30.3 78.4 117.1	 48.1 38.7	130 ± 9	6.92	
150	Pb	Sample Add.1 Add.2	83.9 232.4 363.1	 148.5 130.6	212 ± 6	2.83	
180	Pb	Sample Add.1 Add.2	101.5 281.7 453.9	 180.3 172.1	206 ± 5	2.43	
90	Cu	Sample Add.1 Add.2	0.775 2.061 3.270	 1.287 1.208	4819 ± 52	1.08	4116
120	Cu	Sample Add.1 Add.2	1.175 3.411 5.202	 2.236 1.791	4543 ± 175	3.85	
150	Cu	Sample Add.1 Add.2	1.136 2.821 4.216	 1.685 1.395	5633 ± 230	4.08	
180	Cu	Sample Add.1 Add.2	1.641 3.834 5.281	 2.193 1.447	6745 ± 550	8.16	

Once again, in the vegetable sample batches, Zn contents were analyzed separately. Zn content of Demko Brand canned tomato sample with the serial number of 24911 20 01 and the expiration date of 06/09/2014 was analyzed in Buffer I. Sample preparation was the same as in canned corn samples. 120 seconds of deposition time was the most suitable one since it was the closest to the ICP-OES result and had similar Δi values (Table 6.50). 0.2 mL of the sample was diluted to 10 mL of final volume.

Table 6.50. Zn contents of tomato sample TT_{20}.

DPASV						ICP-OES
Dep. Time (s)	Addition	Mean Current	Δi	mg L^{-1}	SD %	mg L^{-1}
90	Sample Add.1 Add.2	-1.031 uA -1.031 uA -1.031 uA	 89.3 105.7	0.970 ± 0.048	4.95	0.594
120	Sample Add.1 Add.2	-1.031 uA -1.031 uA -1.031 uA	 124.7 125.5	0.570 ± 0.039	6.84	
150	Sample Add.1 Add.2	-1.025 uA -1.025 uA -1.025 uA	 132.3 140.4	0.747 ± 0.019	2.54	
180	Sample Add.1 Add.2	-1.025 uA -1.025 uA -1.025 uA	 169.3 169.1	0.673 ± 0.017	2.52	

The second main step in anodic stripping voltammetry is the oxidation step of the deposited concentrate back to the bulk solution. The deposition potential was arranged in order to adapt the linear relationship between the maximum stripping current and the accumulated substance activity. Electrochemical accumulation depends on the electrode potential. However, this relationship may vary from one sample to another due to the differences of sample matrices [61]. The activity of accumulated substance is a time-dependent fact, and also cannot be considered without the effect of adjusted potential.

First of all, a simultaneous analysis of Zn, Cd, Pb and Cu elements was done with Yakşi Brand canned anchovy sample, digested for about 18 hours in nitric acid/perchloric acid (HNO3/$HClO_4$, 5:1, v/v) medium. Deposition time was set to 120 seconds, starting potential was -1.25V and the ending potential was 0.1V. As can be seen in Figure 6.28, the Zn content of the sample was too high to be detected accurately along with the other three

elements. As a matter of fact, Cd peak was suppressed in the presence of high concentration (>1 mg L^{-1}) of Zn. Furthermore, standard addition for the Zn analysis was not successful since the experimental detection limits were exceeded. So, Zn analysis had to be carried out separately, with a higher dilution factor of the analyte in the voltammetric vessel. Additionally, in the determination of copper and zinc, the formation of intermetallic compounds (CuZn, $CuZn_2$, $CuZn_3$) may interfere, leading to an increase in the height of the copper stripping peak and a decrease in that of zinc. Since these compounds oxidize at a close potential to that of a copper stripping potential, they may increase the copper current and decrease the zinc current [53].

Recorded amount of Zn content in Figure 6.29 was 5.94 ± 0.62 mg L^{-1} where the ICP-OES analysis revealed the concentration as 9.91 mg L^{-1}. Standard additions were done with 20 mg L^{-1} Zn, the first standard addition peak overlapped with the analyte peak whereas the expected increase in the current was not in the order of 2 to 5 with respect to the sample peak. Also, the second standard addition peak overlapped with the first one whereas doubling in the current value was expected with respect to the first addition. This indicated that the Hg drop of the working electrode was overloaded, and the corresponding concentration of Zn beyond its detection limit. An alternative approach for the accurate analysis was sought. The solution was either to increase the dilution factor of the sample in the vessel or to change the mode of the electrode from HMDE to SMDE.

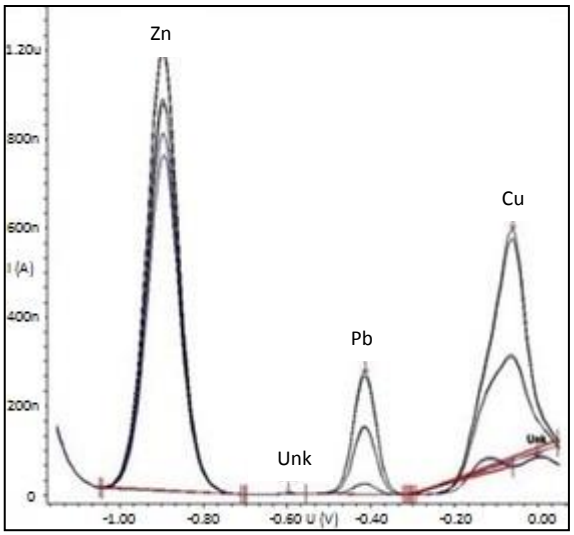

Figure 6.29. Voltammogram of an anchovy sample A_6.

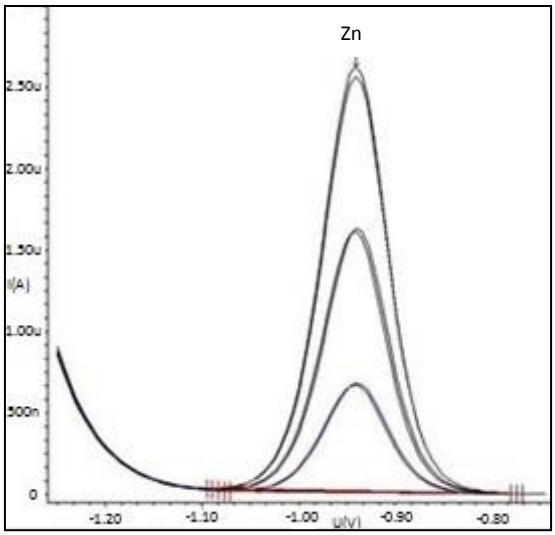

Figure 6.30. Voltammogram of an anchovy sample A_6.

Hence, the Zn content analysis was repeated with the dilution of 0.2 mL anchovy sample to 10 mL final volume with the addition of 1 mL Buffer I. The starting potential was set to -1.15V, while the ending potential was set to -0.75V. The result was more satisfactory with the standard addition of 40 mg L^{-1} Zn (Figure 6.30). Zinc amount was recorded as 10.2 ± 0.2 mg L^{-1}.

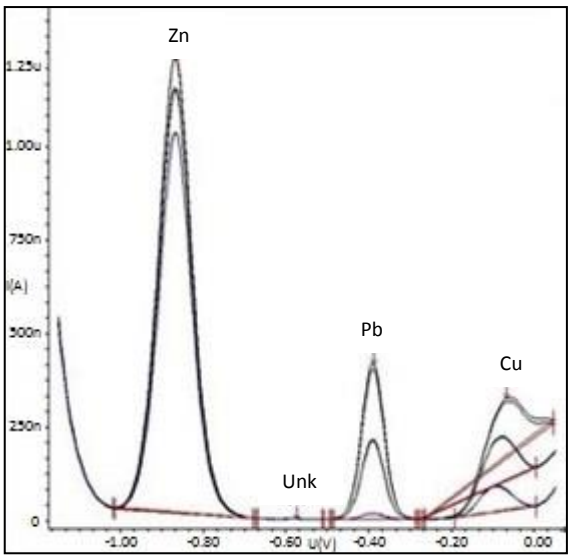

Figure 6.31. Voltammogram of canned sardine sample S_{18}.

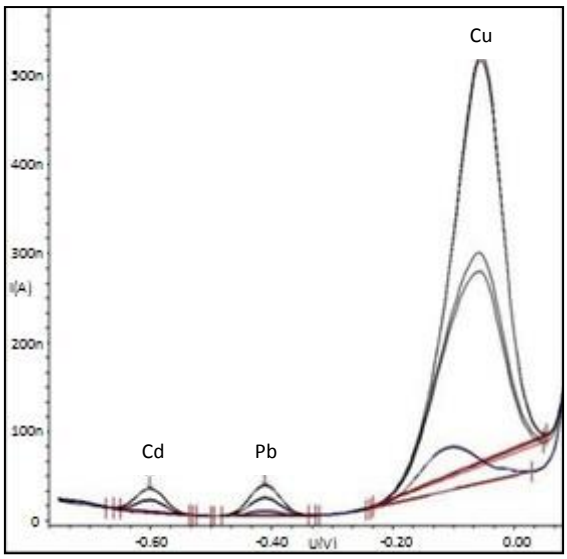

Figure 6.32. Voltammogram of canned sardine sample S_{18}.

Figure 6.31 is Yakşi Brand canned sardine sample with a serial number of 03 and the production date of 02/2012. Four elements were detected simultaneously, but as in the case of anchovy, the Zn amount was over the detection limits, and dominated over the Cd peak, hence concentration of Cd could not be detected. DPASV analysis recorded the corresponding concentrations as 7.66 ± 0.28 mg L^{-1} for Zn, 53.0 ± 1.3 and 705 ± 69 µg L^{-1} for Pb and Cu respectively, where the ICP-OES results were as 2.13 mg L^{-1} for Zn, 6.18 µg L^{-1} for Cd, 89.5 µg L^{-1} for Pb, 380 µg L^{-1} for Cu.

The voltammogram for the separated analysis of Cd, Pb and Cu is in Figure 6.32. The starting potential was -0.75V and the ending potential was 0.08V. The DPASV results were in good agreement with the ICP-OES results. DPASV analysis revealed concentrations as 5.98 ± 0.44 µg L^{-1} for Cd, 114 ± 3 µg L^{-1} for Pb and 302 ± 26 µg L^{-1} for Cu.

When the Cu amounts in the analytes were in relatively high concentrations (> 1 mg L^{-1}), voltammograms of Cu peaks were distorted. Therefore, the analyses of the Cu contents at high concentrations were needed to be done separately by adjusting the deposition and the stripping potentials accordingly.

Tukaş Brand canned corn sample C_{23} with the deposition potential started at -0.75V and ended with 0.08V was a good example to this case (Figure 6.33). Relatively high amount of Cu in the sample could not be detected accurately under these conditions. DPASV analysis was carried with the dilution factor of 2/10. The measured amounts of Cd, Pb and Cu in µg L^{-1} were 3.81 ± 0.12, 40.3 ± 0.9, 14284 ± 1089, respectively. The Cu peak supressed the Cd and Pb peaks, so that they could not be observed in detail, in the voltammogram. The results of the ICP-OES analysis were 2.85, 26.5, and 7414 µg L^{-1} for Cd, Pb, and Cu, respectively.

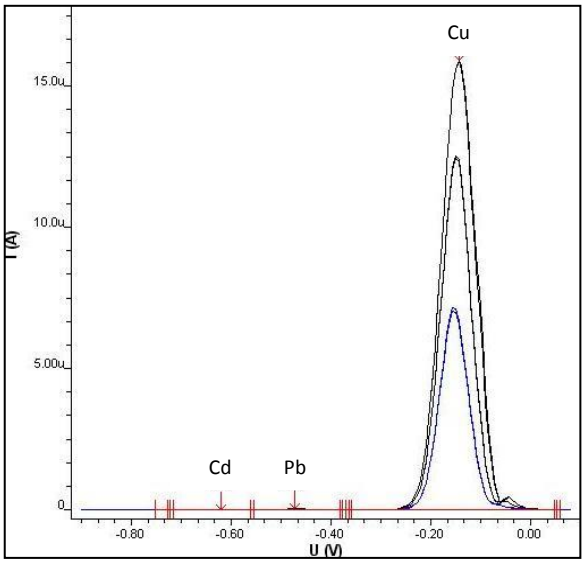

Figure 6.33. Voltammogram of the canned corn sample C_{23}.

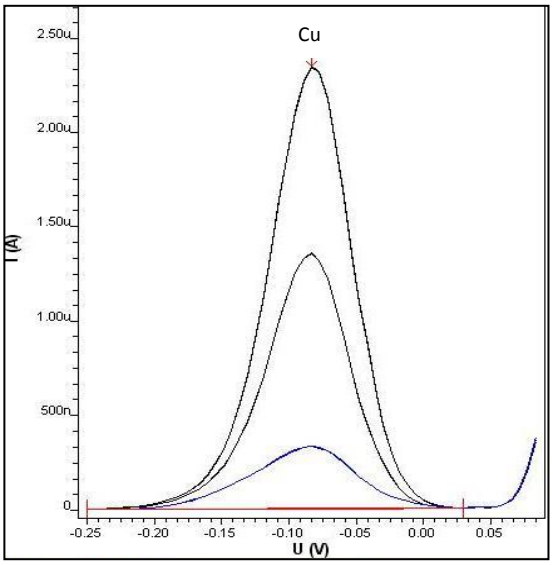

Figure 6.34. Voltammogram of canned corn sample C_{23}.

When the Cu analysis was run separately within the potential range between -0.25 V to 0.08 V, with the dilution factor of 0.5/10, the Cu content was recorded as 7997 ± 63 µg L^{-1} (Figure 6.34). The potentials were kept between -0.90 V to -0.25 V for the Cd and Pb analysis (Figure 6.35), and the results were coherent with the ICP-OES results (Table 6.41), 3.59 ± 0.12 and 37.8 ± 0.2 µg L^{-1} were detected for Cd and Pb, respectively.

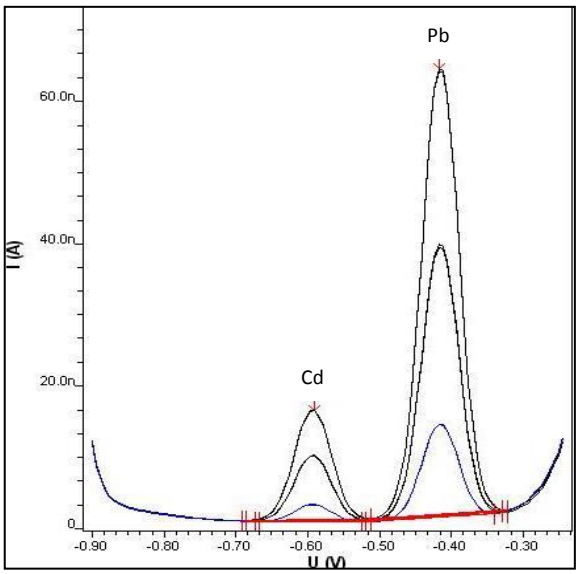

Figure 6.35. Voltammogram of canned corn sample C_{23}.

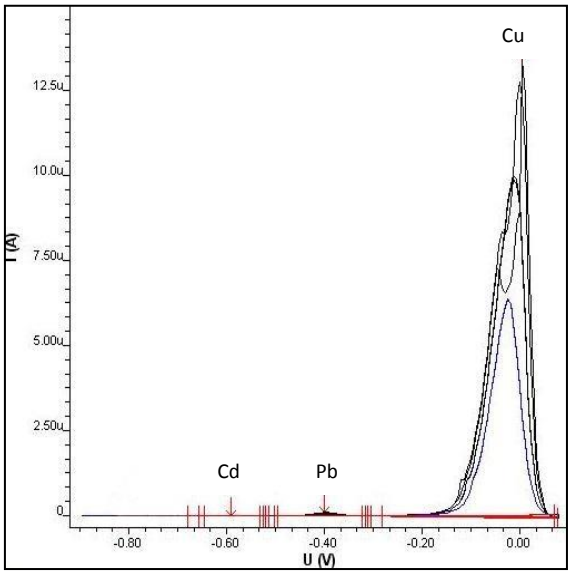

Figure 6.36. Voltammogram of canned sardine sample S_{36}.

Canned sardine sample S_{36} of the Engin brand was analyzed with the starting potential of -0.75 V and the ending potential of 0.08V for its Cd, Pb, and Cu contents with the dilution factor of 2/10. Again, the high amount of Cu content in the sample caused distorted peaks in the voltammogram, and the standard additions were unsuccessful (Figure 6.36). Although, the results were not accurate, the following data were registered as 6.01 ± 1.78, 62.2 ± 2.2, 12575 ± 528, respectively.

Sample S_{36} was analyzed once again, the deposition potential range for Cd and Pb was kept between from -0.90 V to -0.25 V, with dilution factor of 2/10, in which Cd and Pb contents were recorded as 3.89 ± 0.31 µg L^{-1} and 63.9 ± 2.6 µg L^{-1}, respectively (Figure 6.37). The concentration values that were recorded by ICP-OES analysis were as 3.38 µg L^{-1}, and 59.2 µg L^{-1} for Cd and Pb, respectively. The DPASV analysis of Cu at deposition potentials between -0.20 V and 0.08 V with the dilution factor of 0.5/10, resulted in 7787 ± 299 µg L^{-1}, and the corresponding ICP-OES analysis was 7596 µg L^{-1} (Figure 6.38).

Experiments indicated that as Zn and Cu existed at high levels in the analytes they were needed to be analyzed separately by adjusting the deposition potentials, and the dilution factor of the samples in the vessels was needed to be increased from 2 mL: 10 mL

to 0.2 mL: 10 mL for Zn and from 2 mL:10 mL to 0.5 mL: 10 mL for Cu (sample volume: total volume).

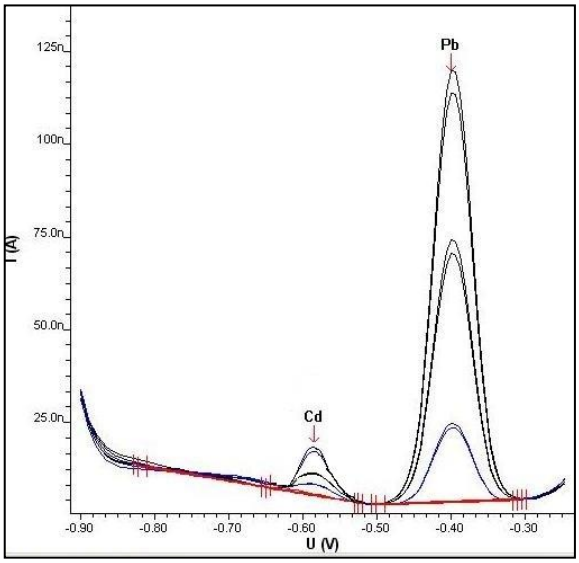

Figure 6.37. Voltammogram of canned sardine sample S_{36}.

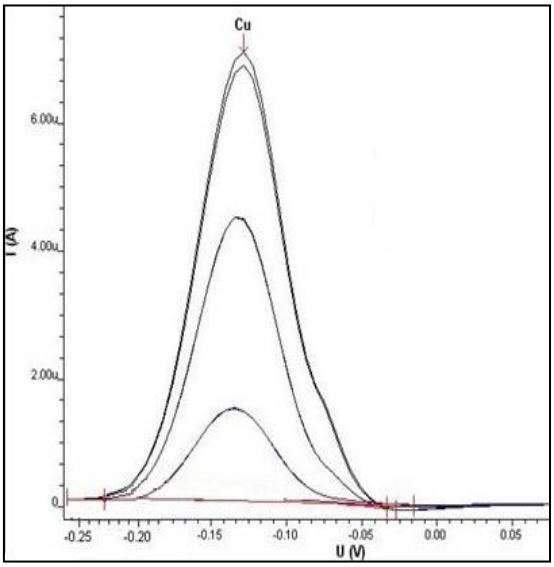

Figure 6.38. Voltammogram of canned sardine sample S_{36}.

Synthetically prepared solutions of Cu at 300, 1000, and 2000 µg L^{-1} levels were tested in order to optimize the experimental parameters by taking into account the effects of deposition potential and the sample dilution factor (Table 6.51). Aliquots of samples were taken as indicated in Table 6.51, and they were diluted to 10 mL of final volume in the voltammetric vessel. Deposition time was kept at 120 seconds. Measurements were run in three replicates.

Samples $St._1$ and $St._2$ with relatively low Cu concentrations were tested within the deposition potential range from -0.75 V to 0.08 V. In voltammetric analysis, it is well known that accuracy of the measurements is elevated by increasing the volume of the analyte in the vessel, especially at low ppm levels. However, the analyses showed that doubling the sample volume in the vessel by keeping the ratio between the sample and the buffer constant did not alter the recorded concentration value, and the corresponding standard deviation values were almost the same. Standard additions were done with 25 mg L^{-1} and 30 mg L^{-1} of copper standards for $St._1$ and $St._2$. Additionally, relatively high Cu concentrations of $St._3$, $St._4$ and $St._5$ were examined. 75, 15 and 100 mg L^{-1} standard

solutions of copper were used in the analysis, respectively. Recorded concentration for the Cu content in $St._5$ was three fold of the original content of synthetic solution; also the relative standard deviation value was too high. The result of sample $St._4$ was within the acceptable limits, and the corresponding relative error was 1.20 %.

Table 6.51. DPASV results of the synthetic solutions.

Sample	Start Potential (V)	End Potential (V)	Synthetic Sample ($\mu g\ L^{-1}$)	Sample Volume (mL)	Buffer Volume (mL)	Recorded Concentration $\mu g\ L^{-1}$	SD %
$St._1$	-0.75	0.08	300	2	1	273 ± 6	2.26
$St._2$	-0.75	0.08	300	4	2	274 ± 9	3.21
$St._3$	-0.25	0.08	1000	2	1	1592 ± 166	10.4
$St._4$	-0.25	0.08	1000	0.5	1	1012 ± 12	1.20
$St._5$	-0.75	0.08	2000	2	1	6924 ± 1524	22.0
$St._6$	-0.25	0.08	2000	2	1	4396 ± 768	17.5
$St._7$	-0.25	0.08	2000	0.5	1	2030 ± 30	1.50

The result of $St._7$ yielded 1.5 % of relative error. 30 mg L^{-1} of copper standard solution was used. The deposition potential range and the sample dilution factor were the same as in case $St._4$. It was concluded that higher dilution factors for the samples with relatively high Cu contents were essential in voltammetric analysis.

In some cases of food analyses, Cd content was too low to be detected accurately; high values of standard deviations were obtained. Since, the half-wave potentials ($E_{1/2}$) of Cd and Pb were close to one another (Table 6.2) the possibilities were either the Cd peak would have been masked totally by Pb or Cd, or Pb voltammograms would have overlapped with each other in the presence of high Pb concentration. Therefore the sample analysis was carried out by increasing the sample volume in the cell, from 2 mL to 4 mL and diluting to the final volume of 10 mL. The volume of the buffer solution in the samples was also adjusted with respect to the dilution factor of the samples. The ratio of the sample and buffer volume was optimized.

Tests were run on sardine, anchovy, and tomato samples and the following conclusions were made: (i) Doubling the volume of buffer to 2 mL and the volume of the sample to 4 mL did not change the recorded data for the Cd-content of sardine and anchovy samples as compared to 1 mL buffer and 2 mL of sample combinations. Corresponding standard deviation values for analyses ranged between 5 % and 15%. Overlapping of the Cd and Pb peaks was not observed. (ii) Trace quantities of Cd as low as 2 μg L^{-1} were determined in tomato samples in the presence of relatively high concentrations of Pb, i.e., 36 μg L^{-1}. Overlapping of the peaks was not observed. Sample volume was doubled to 4 mL and the buffer volume was kept at 1 mL. Corresponding standard deviation values were as low as 4 % and the data of DPASV analysis were in good agreement with ICP-OES anlaysis. (iii) Doubling the volume of sample to 4 mL and keeping the buffer volume at 2 mL resulted in split peaks with high standard deviation values in tomato samples. (iv) Doubling the volume of sample to 4 mL and keeping the buffer volume at 4 mL resulted in split peaks and high standard deviation values, i.e., 27% in tomato samples.

Therefore, the volume ratios of sample solution to buffer differed with respect to the nature of analyte whether it was fish or vegetable origin. A 2:1 (v:v) ratio of sample to buffer was utilized in determining trace quantities of Cd in fish samples. Whereas, sample to buffer (v:v) ratio was 4:1 in the analysis of vegetable samples. Also, in most cases Cd was analyzed separately by appliying the deposition potential between -0.90 V and -0.40 V

6.4. Electrode Mode

Mostly, Zn content of the samples existed in relatively high amounts (>1 mg L^{-1}), therefore its detection required high dilution factors. 0.2 mL of each food sample was diluted to the final volume of 10 mL and 1 mL buffer solution was added, the analyses were done with Hanging Mercury Drop Electrode (HMDE) mode. However, in some cases where the Zn content of the samples existed even in higher amounts (>10 mg L^{-1}), Static Mercury Drop Electrode (SMDE) mode was used. 0.05 mL to 0.5 mL of each food sample was diluted to the final volume of 10 mL and 1 mL buffer solution was added, the analyses were done with the SMDE mode.

Figure 6.39 represents Alaeddin brand tuna sample with the Serial Number of 0.81.2 AYT and the expiration date of 03/2016. DPASV analysis with 0.2 mL of sample diluted to the final volume of 10 mL recorded the concentration as 144 ± 18 mg L^{-1}, while its ICP-OES result was 322 mg L^{-1}. Starting potential was -1.25 V while the end potential was set to -0.75 V. Because of the overloaded concentration of zinc on the mercury electrode, the Zn peak was distorted.

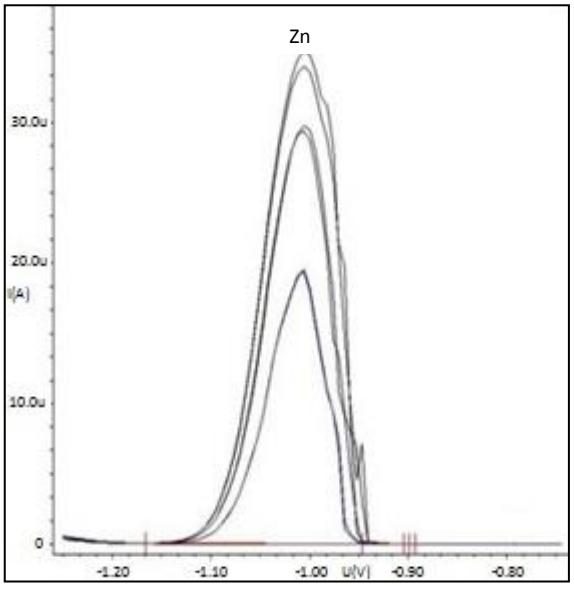

Figure 6.39. Voltammogram of canned tuna sample T_{14} with HMDE mode.

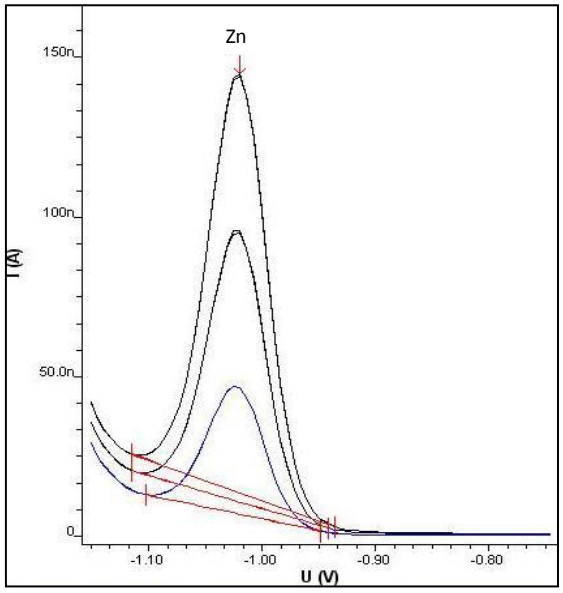

Figure 6.40. Voltammogram of canned tuna sample T_{14} with SMDE mode.

Analysis was repeated with 0.1 mL of sample diluted to the final volume of 10 mL with SMDE mode. Zn concentration was recorded as 341 ± 4 mg L^{-1} (Figure 6.40).

The sensitivity of the HMDE mode was useful and reliable within the range of 0.5 - 10 mg L^{-1} concentration of Zn while the volume of sample was kept between 0.2 mL – 0.5 mL with the addition of 1 mL of buffer in 10 mL deionized water. However, when the Zn amount was above these limits, distorted peaks with high standard deviation values appeared. To be able to detect the Zn amount in the sample accurately, sample aliquots were taken in 0.2 mL amounts, and SMDE mode of the electrode was used.

Superfresh Brand corn sample C_7 with the expiration date of 02/2015 and the serial number of L2158 was analyzed to record the Zn content. In the first place, HMDE mode of

DPASV was applied to the sample solution. Measured value was 55.5 ± 5.6 mg L^{-1} with the standard deviation value of 10.6 % (Figure 6.41). Analysis was repeated with SMDE mode, 63.4 ± 0.6 mg L^{-1} of zinc was detected (Figure 6.42), while the ICP-OES analysis revealed the concentration value as 75.3 mg L^{-1}. The difference between the measured amounts of zinc in DPASV and ICP-OES analysis was due to the low sensitivity of ICP-OES in the presence of relatively high amounts of zinc content. Since the detection limit of ICP-OES for Zn was in the range of 1 – 5 mg L^{-1}, in some fish and corn samples, dilution factors of 1/50 to 1/100 were necessary. In turn, the sensitivity of ICP-OES measurements was lowered.

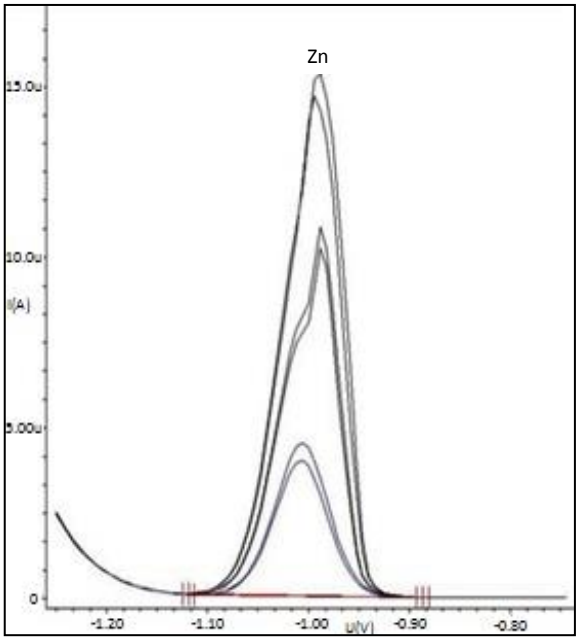

Figure 6.41. Voltammogram of canned corn sample C_7 with HMDE mode.

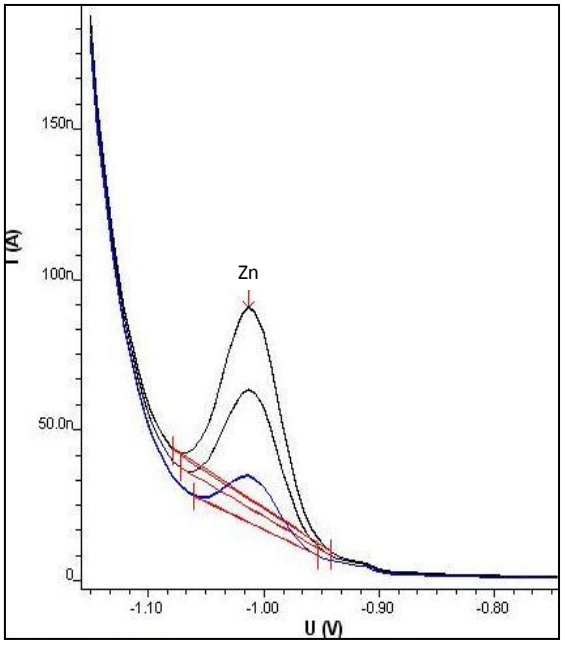

Figure 6.42. Voltammogram of canned corn sample C_7 with SMDE mode.

In order to be able to establish the optimum working conditions for Static Mercury Dropping Electrode, synthetic solutions of Zn were prepared and tested with varying parameters. Equilibration time was set to two different values for the complete deposition onto electrode surface. Equilibration time of SMDE mode was equivalent to the deposition time in HMDE mode. Voltage step time was also arranged, which was the required time for the two consecutive mercury drops.

Table 6.52. Experimental parameters for SMDE mode of mercury electrode.

Sample Solutions* mg L^{-1}	Equilibriation Time (s)	Voltage Step Time (s)	Measured Concentration (mg L^{-1})	SD %
500	10	0.6	491.3 ± 7.8	1.61
500	30	0.6	487.5 ± 2.1	2.35
500	10	1.8	494.8 ± 9.4	1.91
500	30	1.8	492.4 ± 9.9	2.01
200	10	0.6	189.1 ± 3.5	1.85
200	10	1.8	193.3 ±2.9	1.55

*They were prepared from a stock solution of 1000 mg L^{-1} of Zn standard.

Samples in the voltammetric vessels were prepared by the dilution of 50 µL of synthetic sample and 1 mL of buffer to the final volume of 11 mL with deionized water. Deposition potential was arranged by setting the starting potential to -1.15 V and ending potential to -0.75 V. Results of the DPASV analysis of synthetic solutions revealed that the closest results to the actual synthetic solution concentrations with the lowest standard deviation values were achieved with 10 s of equilibration time and 1.8 s of voltage step time. Hence, analytes with Zn concentrations exceeding 10 mg L^{-1} were determined with SMDE mode instead of HMDE mode, and with the combination of parameters given in Table 6.52. The Zn content analysis of food samples were carried with such combination of parameters.

6.5. Voltammetric Determination of Cu with EDTA

The composition of the analysis solution determines the forms and half-wave potentials of the peaks of analyzed metals. In this situation, complex formation alters the half-wave potential and the limiting current; difficulties can arise in the peak evaluation. Hence, these difficulties must be eliminated by appropriate changes in the composition of the supporting electrolyte.

In chloride-containing solutions, copper can occur both as a $CuCl_4^{2-}$ and a $CuCl_2^-$ complex. These complexes generally give peaks near each other. In such cases,

determination of copper becomes impossible, and inaccurate results are obtained [60]. Therefore, Ethylenediaminetetraacetic acid (EDTA), which is a commonly used complexometric titrant, was used as a complexing agent. The EDTA (H_4Y) molecule has four carbonyl groups and the two amino groups with an unshared pair of electrons (Figure 5.43), it has six potential sites for bonding a metal ion [53].

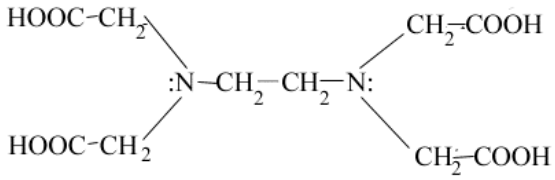

Figure 6.43. Structure of EDTA (H_4Y).

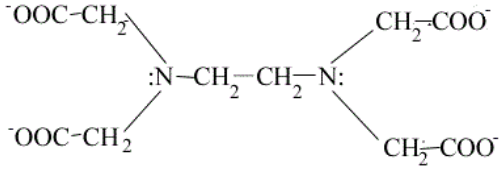

Figure 6.44. Fully deprotonated form of EDTA (Y^{4-}).

EDTA is a useful titrant since the reagent combines with metal ions in a 1:1 ratio, independent of the charge of the cation. In general, the reaction of the Y^{4-} anion (Figure 6.44) with a metal ion M^{n+} as:

$$M^{n+} + Y \rightleftharpoons M(Y)^{(n-4)} \tag{6.2}$$

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\,[Y^{4-}]} \tag{6.3}$$

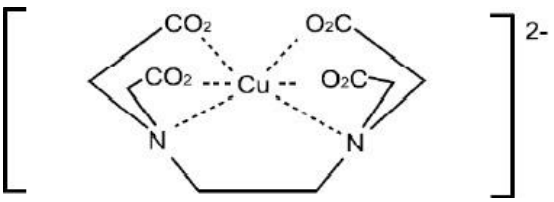

Figure 6.45. Structure of $Cu(Y)^{2-}$ complex.

The formation constants for Cu-EDTA complex are [53], [92]:

$$K_{Cu(Y)^{2-}} = 6.3 \times 10^{18} \quad (6.4)$$

$$\text{Log } K_{Cu(Y)^{2-}} = 18.80 \quad (6.5)$$

$$K_{(CuCl_2)^-} = 3.2 \times 10^{5} \quad (6.6)$$

$$\text{Log } K_{(CuCl_2)^-} = 5.50 \quad (6.7)$$

$$K_{(CuCl_4)^{2-}} = 1.26 \times 10^{13} \quad (6.8)$$

$$\text{Log } K_{(CuCl_4)^{2-}} = 13.1 \quad (6.9)$$

$Cu(Y)^{2-}$ complex formation is more favorable than the $CuCl_2^-$ and $CuCl_4^{2-}$ formations, also CuY^{2-} complexes are stable within pH range of 3 to 7 (Figure 6.46).

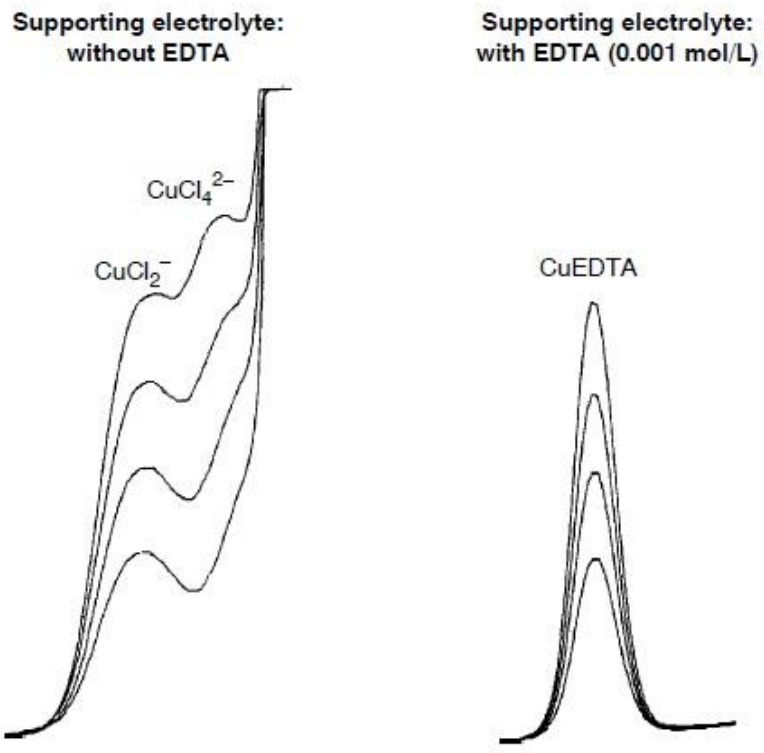

Figure 6.46. Voltammograms of copper chloride complexes.

Copper-chloride complex formations were expected to be hindered in the presence of EDTA. The most suitable supporting electrolyte was searched in the presence of EDTA. Buffer I and Buffer III compositions were analyzed. Tests were run in the presence of 1×10^{-3}, 5×10^{-3}, 1×10^{-2}, 5×10^{-2} mol L^{-1} concentrations of EDTA. 1×10^{-3} mol L^{-1} EDTA

solution was prepared by the dissolution of 0.372 g of sodium EDTA in 1 L of deionized water. The volume (mL) of the EDTA solution needed for 1:1 complexation with copper was investigated. In the test runs Penguen brand canned corn sample C_{26} with the serial number of SNF1431 and expiration date of 05/2015 was analyzed, the results of the DPASV analysis were compared with ICP-OES analysis. 2 mL of the previously digested sample with 1 mL of Buffer I and 0.6 mL of Buffer III were diluted to 10 mL of final volume with the addition of deionized water. Standard additions were done with 0.2 mg L^{-1} of Cd, 1 mg L^{-1} of Pb, 7.5 mg L^{-1} of Cu. Simultaneous analysis of Cd, Pb and Cu elements were run with and without EDTA additions (Table 6.53).

Table 6.53. Cd, Pb and Cu determination of C_{26} in the presence of EDTA.

Element	EDTA mol L^{-1}	EDTA mL	Buffer	µg L^{-1}	µg g^{-1}	SD %
Cd	0	0	Oxalate	3.03 ± 0.15	0.049 ± 0.002	5.02
Pb	0	0	Oxalate	27.9 ± 1.8	0.456 ± 0.029	6.55
Cu	0	0	Oxalate	288 ± 29	4.70 ± 0.5	9.94
Cd	$1 \times 10^{3-}$	0.4	Oxalate	3.45 ± 0.20	0.056 ± 0.003	5.85
Pb	$1 \times 10^{3-}$	0.4	Oxalate	27.2 ± 1.18	0.445 ± 0.019	4.32
Cu	$1 \times 10^{3-}$	0.4	Oxalate	417 ± 70	6.82 ± 1.15	16.8
Cd	$1 \times 10^{3-}$	1	Oxalate	0	0	-
Pb	$1 \times 10^{3-}$	1	Oxalate	20.2 ± 2.9	0.330 ± 0.048	14.4
Cu	$1 \times 10^{3-}$	1	Oxalate	255 ± 19	4.16 ± 0.32	7.63
Cd	$1 \times 10^{3-}$	1.5	Oxalate	7.13 ± 3.15	0.116 ± 0.051	44.2
Pb	$1 \times 10^{3-}$	1.5	Oxalate	39.8 ± 14.7	0.65 ± 0.24	36.9
Cu	$1 \times 10^{3-}$	1.5	Oxalate	239 ± 20	3.91 ± 0.33	8.46
Cd	0	0	HAc+KCl	22.8 ± 9.1	0.373 ± 0.148	39.7
Pb	0	0	HAc+KCl	47.6 ± 0.4	0.777 ± 0.006	0.78
Cu	0	0	HAc+KCl	307 ± 18	5.02 ± 0.29	5.93
Cd	$1 \times 10^{3-}$	1	HAc+KCl	0	0	-
Pb	$1 \times 10^{3-}$	1	HAc+KCl	46.4 ± 0.9	0.758 ± 0.015	2.01
Cu	$1 \times 10^{3-}$	1	HAc+KCl	143 ± 5	2.33 ± 0.09	3.91
Cd	$1 \times 10^{3-}$	1.5	HAc+KCl	0	0	-
Pb	$1 \times 10^{3-}$	1.5	HAc+KCl	50.6 ± 1.6	0.826 ± 0.027	3.28
Cu	$1 \times 10^{3-}$	1.5	HAc+KCl	133 ± 6	2.18 ± 0.09	4.30

Results of ICP-OES analysis for Cd and Pb were 4.06 µg L^{-1} and 31.4 µg L^{-1}, respectively. Results of the tests with Buffer I were summarized as followings: (i) The closest DPASV result for Cd to ICP-OES was achieved in the presence of 0.4 mL of EDTA addition. The result obtained without EDTA was also considerably close to ICP-OES. However, the trials were unsuccessful as the EDTA additions were increased to 1 mL

and 1.5 mL. (ii) In the case of Pb determinations, the closest voltammetric data were obtained as 27.2 µg L^{-1} and 27.9 µg L^{-1} with 0.4 mL EDTA and without EDTA, respectively. It was assumed that the difference between the two results was not significant. Although, the DPASV result for Pb was 39.8 ± 14.7 µg L^{-1} in the presence of 1.5 mL EDTA, the standard deviation value, SD was increased up to 36.9 %, which was totally unacceptable. (iii) Cu-peak was distorted under all of the experimental conditions as given in Table 6.53. Figures 6.47, 6.48, 6.49, 6.50 exhibited the voltammograms with and without EDTA additions in Buffer I. The ICP-OES analysis recorded 196 µg L^{-1} for the Cu concentration, and the closest DPASV data to this result was obtained in the presence of 1.5 mL, i.e., 239 ± 20 µg L^{-1} with 8.46 % standard deviation. However, the unknown peak besides the Cu peak did not disappear as the EDTA additions were increased from 0.4 mL to 1.5 mL. The unknown peak was interpreted as the peak which belonged to the Cu-chloride complex formation.

Results of the tests with Buffer III were summarized below and the voltammograms were given in Figures 6.51, 6.52, 6.53 and 6.54: (i) DPASV results for the Cd concentrations were not taken into consideration, since they were registered as 0 µg L^{-1} and 22.8 ± 9.1 µg L^{-1} with and without EDTA, respectively. (ii) In the presence of 1.0 mL of EDTA, the closest DPASV result for Pb to ICP-OES was obtained as 46.4 ± 0.9 µg L^{-1}. However, it was still not as close as the one obtained in the presence of Buffer I with 0.4 mL of EDTA addition. (iii) Cu content of the sample was detected as 143 ± 5 µg L^{-1} in the presence of 1.0 mL of EDTA, which was a relatively close result to ICP-OES analysis. The unknown peak of Cu-chloride complex was overcome, but the base-line shift still remained (Figure 6.52). In order to be able to overcome this problem, Cu peak was analyzed separately, 1 mL of sample and 0.6 mL of Buffer III were diluted to the final volume of 10 mL, and the deposition potential was kept between -0.40 V and 0.10 V. The result of the analysis was 183 ± 9 µg L^{-1} which was in agreement with ICP-OES result, 196 µg L^{-1} (Figure 6.54).

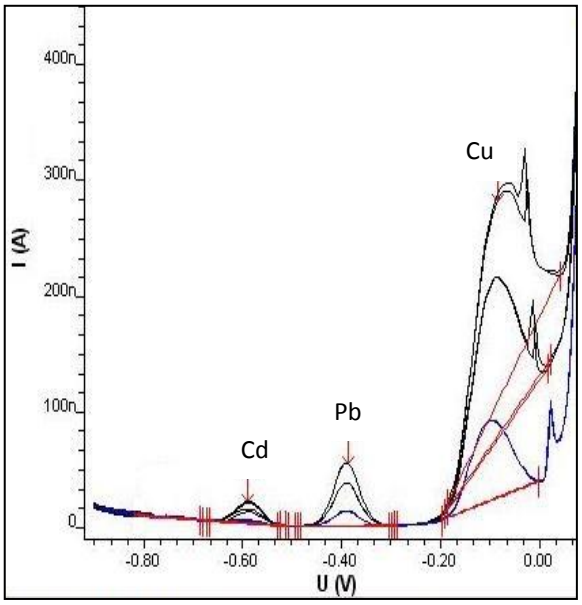

Figure 6.47. Voltammogram of corn sample C_{27} in Buffer I.

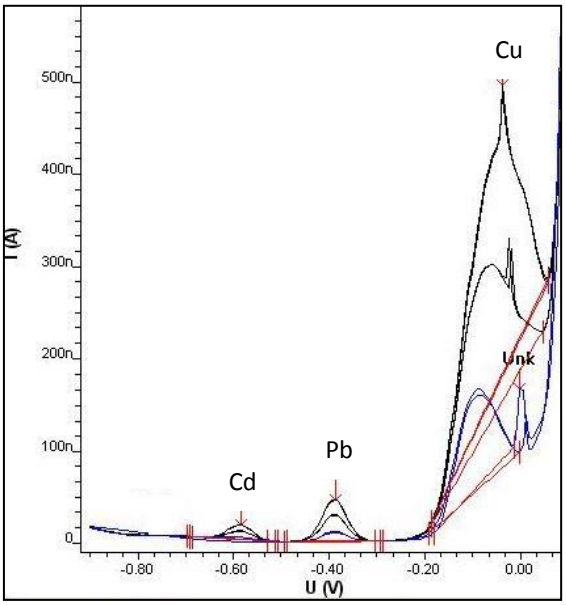

Figure 6.48. Voltammogram of corn sample C_{27} in Buffer I + 0.4 mL of EDTA.

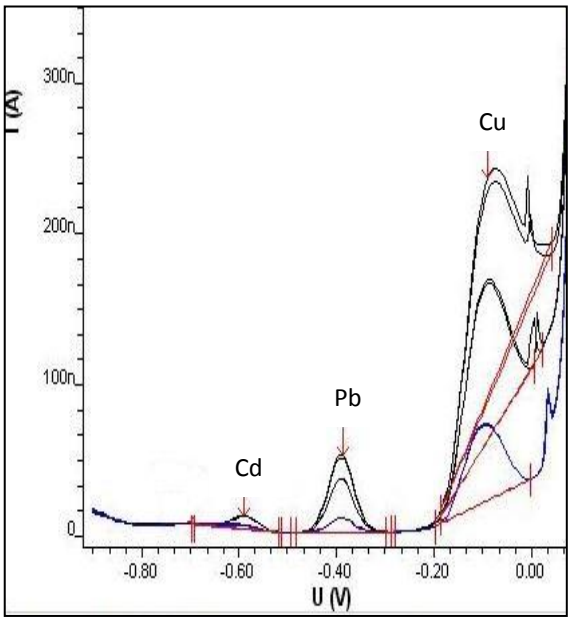

Figure 6.49. Voltammogram of corn sample C_{27} in Buffer I + 1.0 mL of EDTA.

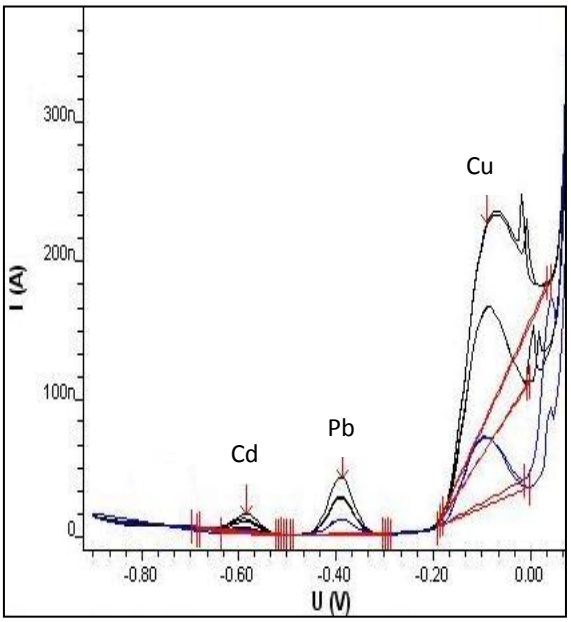

Figure 6.50. Voltammogram of corn sample C_{27} in Buffer I + 1.5 mL of EDTA.

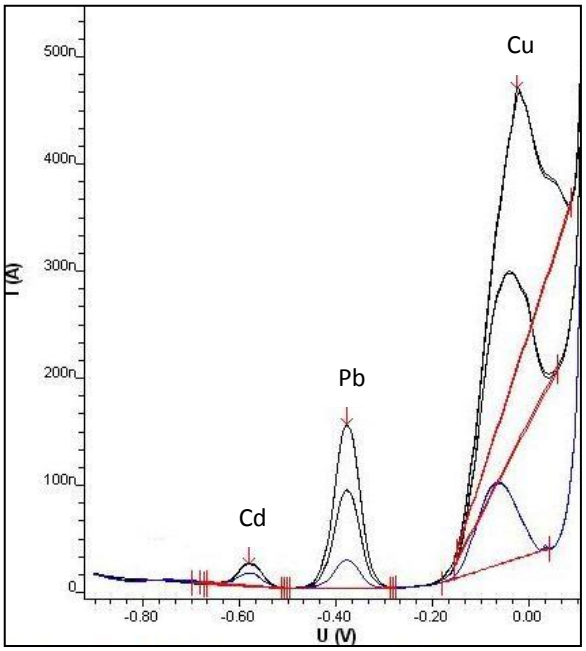

Figure 6.51. Voltammogram of corn sample C_{27} in Buffer III.

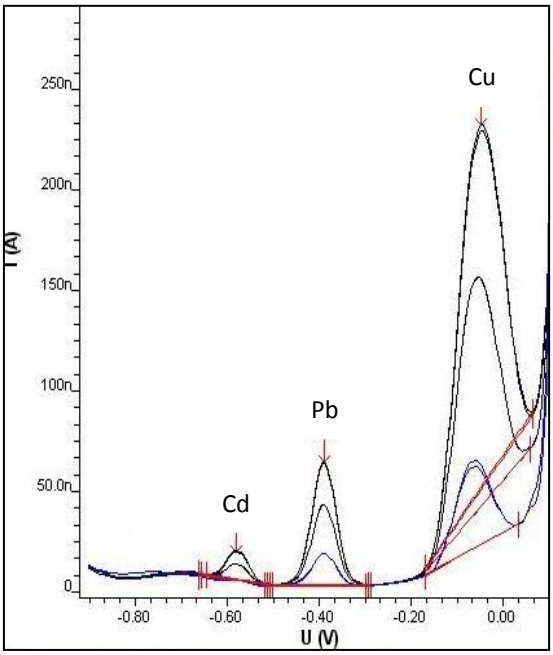

Figure 6.52. Voltammogram of corn sample C_{27} in Buffer III + 1.0 mL of EDTA.

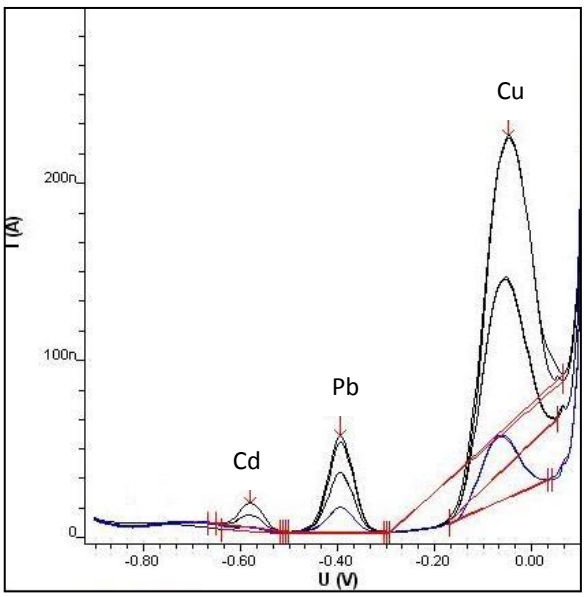

Figure 6.53. Voltammogram of corn sample C_{27} in Buffer III + 1.5 mL of EDTA.

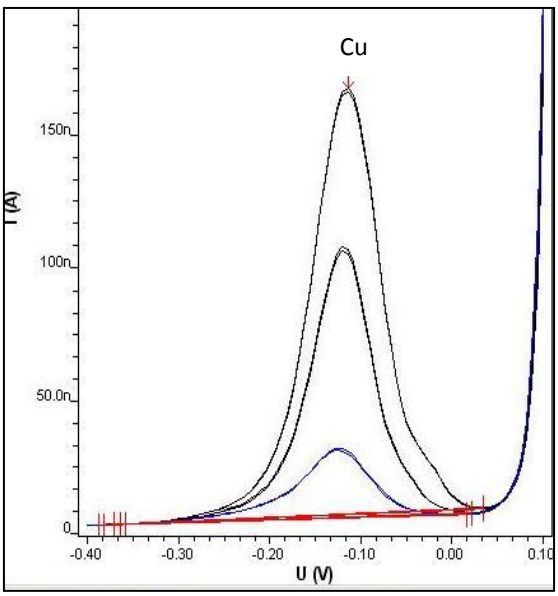

Figure 6.54. Voltammogram of corn sample C_{27} in Buffer III + 1.0 mL of EDTA.

In a separate experiment, Tamek brand corn sample C_{12} with a serial number of PK 156.12.35 and the expiration date of 06/2015 was analyzed. The simultaneous analysis of Cd, Pb and Cu contents of the sample was carried with 2 mL of the previously digested sample, and 1 mL Buffer I which were diluted to the final volume of 10 mL with deionized water. First analysis was done without the addition of EDTA; standard additions were done with 0.1 mg L^{-1} of Cd, 0.5 mg L^{-1} of Pb and 10 mg L^{-1} of Cu. The Cu peak was shifted (Figure 6.55).

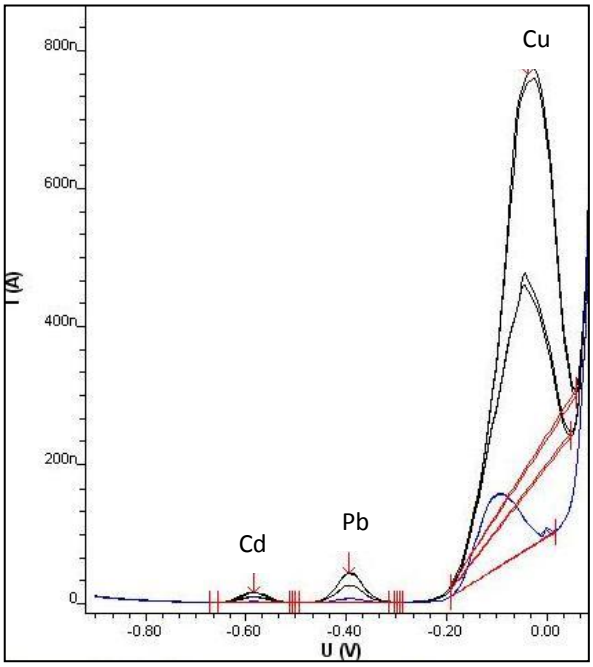

Figure 6.55. Voltammogram of corn sample C_{12} in Buffer I.

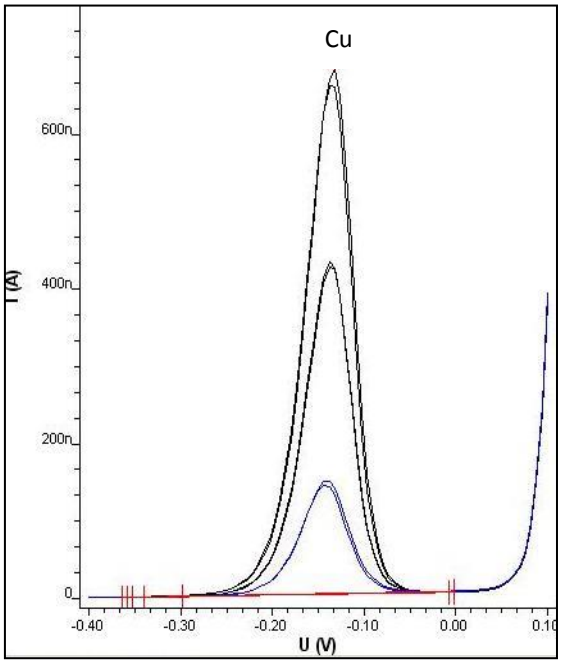

Figure 6.56. Voltammogram of corn sample C_{12} in Buffer III + 1.0 mL of EDTA.

Recorded amounts for Cd, Pb and Cu contents with DPASV analysis were 1.21 ± 0.11 µg L^{-1}, 14.1 ± 0.5 µg L^{-1}, 342 ± 21 µg L^{-1}, respectively, where the ICP-OES analysis revealed the concentrations in as 1.06 µg L^{-1}, 13.4 µg L^{-1}, 256 µg L^{-1} . So, Cu analysis of the sample was repeated with 1 mL of the sample, 0.6 mL of Buffer III, and 1 mL 1 x 10^{-3} mol L^{-1} of EDTA. Standard additions were done with 0.1 mg L^{-1} of Cd, 0.5 mg L^{-1} of Pb, and 10 mg L^{-1} of Cu. The result of the DPASV analysis was 247 ± 18 µg L^{-1}, which was in good agreement with ICP-OES result (Figure 6.56). Deposition potential for the analysis was set between -0.40 V and 0.10 V. The half-wave potential value of the element shifted towards more negative values, i.e., -0.14 V, due to the formation of Cu-EDTA complex.

Tukaş brand canned corn sample, C_{18} with the serial number of PN 246-2-19:19-11 and the expiration date of 03/03/2015 was also analyzed. Cu content of the sample with Buffer I was 183 ± 9 µg L^{-1} (SD 4.97%), and every broad voltammetric peak gave an inaccurate result (Figure 6.57). The ICP-OES result of the Cu analysis was 83.6 µg L^{-1}. The result of the DPASV analysis of Cu content after the addition of 1 mL, 1 x 10^{-3} mol L^{-1} EDTA in the presence of Buffer III was 78.6 ± 1.9 µg L^{-1} (SD 2.40%), (Figure 6.58). Standard additions were done with 5 µg L^{-1} of Cu.

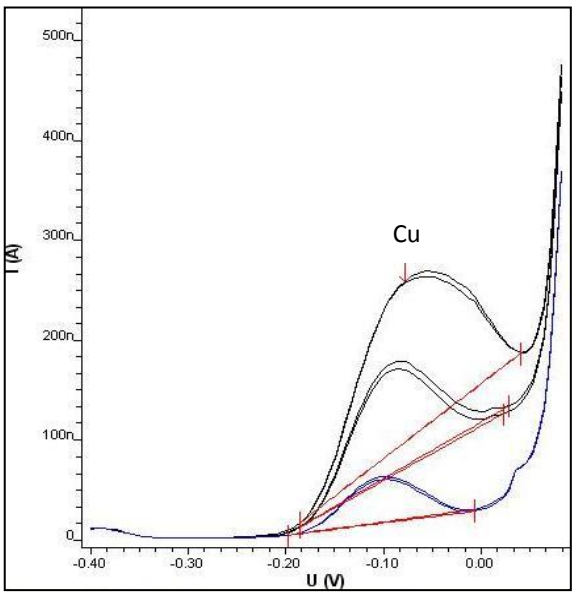

Figure 6.57. Voltammogram of corn sample C_{18} with Buffer I.

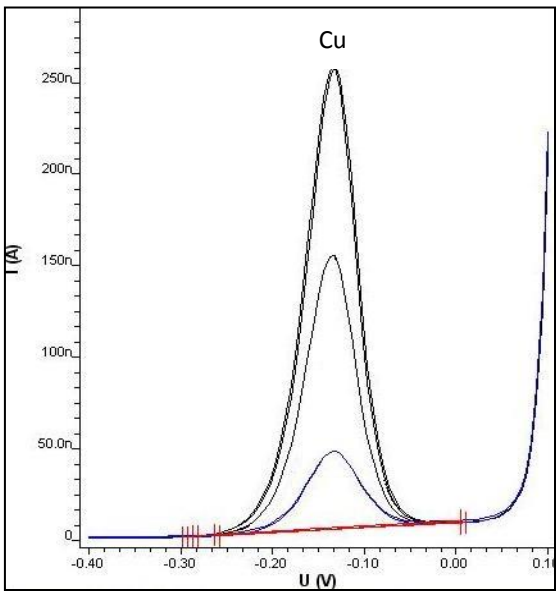

Figure 6.58. Voltammogram of corn sample C_{18} in Buffer III + 1.0 mL of EDTA.

However, EDTA of 1 x 10^{-3} mol L^{-1} did not give accurate results for Cu concentrations greater than about 250 µg L^{-1}. Canned corn sample, C_{11}, Tat brand with the serial number of PN: 03 and production date of 01/2012 was analyzed. Cu content was determined separately, the DPASV result was 255 ± 39 µg L^{-1} (SD 15.3%), in Buffer I (Figure 6.59), where the result of the ICP-OES analysis for the Cu content was 305 µg L^{-1}. In order to overcome the base-line shift and the distortions of the peak, 1 mL of 1 x 10^{-3} mol L^{-1} EDTA was added to 1 mL of sample in 0.6 mL of Buffer III composition. The base-line shift could not be overcome (Figure 6.60), moreover, the recorded concentration for the Cu amount was 130 ± 1 µg L^{-1} (SD 1.10%). Therefore, the concentration of the EDTA solution needed to be increased. Same procedure was repeated this time with 1 mL of 5 x 10^{-3} mol L^{-1} of EDTA. Standard additions were done with 10 mg L^{-1} of Cu. The

base-line shift for the Cu peak no longer existed, the result was 280 ± 5 µg L^{-1} (SD 1.77%), (Figure 6.61).

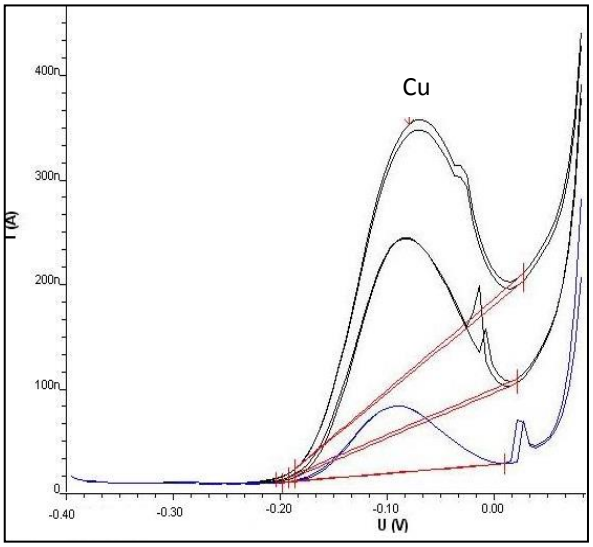

Figure 6.59. Voltammogram of corn sample C_{11} in Buffer I.

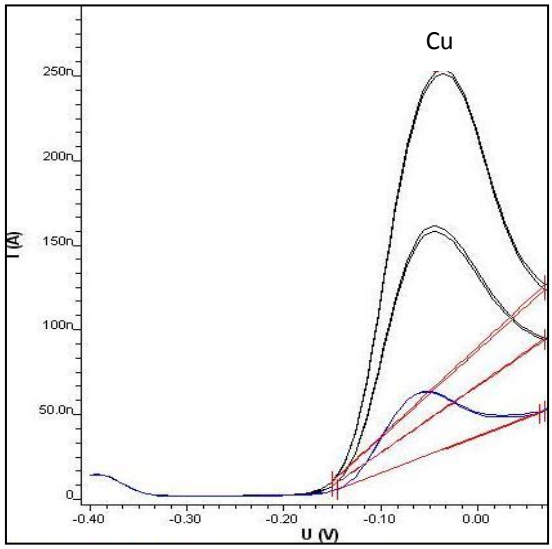

Figure 6.60. Voltammogram of corn sample C_{11} in Buffer III + 1.0 mL of EDTA, 1 x 10^{-3} mol L^{-1}.

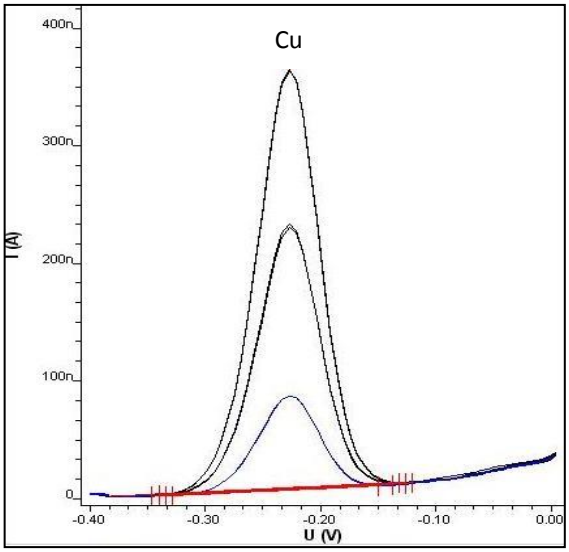

Figure 6.61. Voltammogram of corn sample C_{11} in Buffer III + 1.0 mL of EDTA, 5 x 10^{-3} mol L^{-1}.

Anchovy sample $A_{25,}$ Ayfrost brand with the serial number of 01113321 and the expiration date of 06/2013 was analyzed. The Cu analysis of the sample with Buffer I revealed the concentration as 221 ± 35 µg L^{-1} (SD 16.0 %), and a shifted base-line (Figure

6.62). With the addition of 1 mL of 1 x 10^{-3} mol L^{-1} of EDTA, concentration of the Cu content was recorded as 286 ± 9 µg L^{-1} (SD 3.14 %), where the ICP-OES result was 244 µg L^{-1} (Figure 6.63). The Cu content of the sample was analyzed again with 1 mL of 5 x 10^{-3} mol L^{-1} of EDTA, in order to prevent the occurrence of the broad peak. Standard additions were done with 10 mg L^{-1} of Cu. Recorded value of Cu content was 240 ± 6 µg L^{-1} (SD 2.70 %), (Figure 6.64).

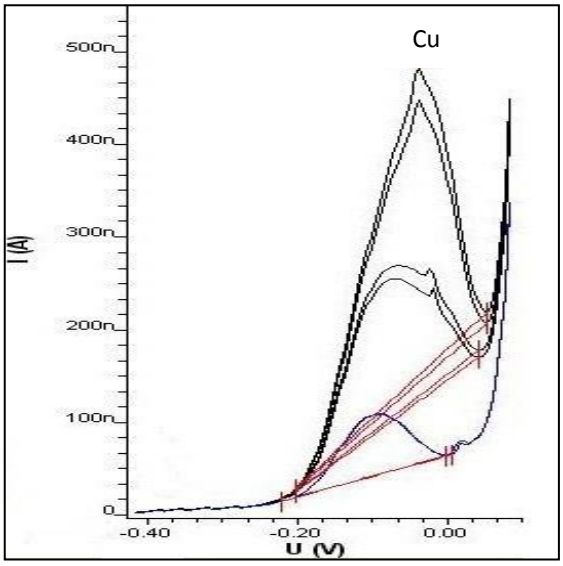

Figure 6.62. Voltammogram of anchovy sample A_{25} in Buffer I.

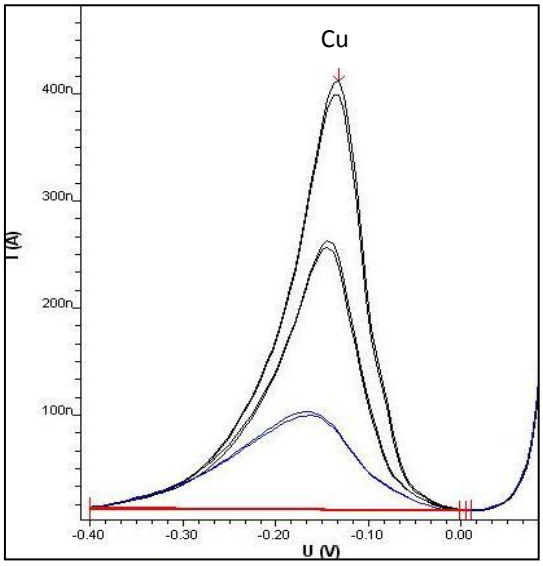

Figure 6.63. Voltammogram of anchovy sample A_{25} in Buffer III + 1.0 mL of EDTA, 1 x 10^{-3} mol L^{-1}.

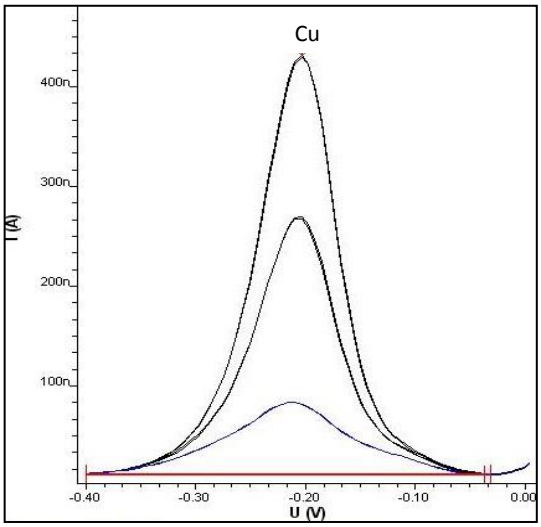

Figure 6.64. Voltammogram of anchovy sample A_{25} in Buffer III + 1.0 mL of EDTA, 5 x 10^{-3} mol L^{-1}.

Canned corn sample C_{10}, Tat brand with the serial number of PN: 03 and production date of 01/2012 was analyzed. When the DPASV analysis was carried with Buffer I, the Cu peak had a shifted base-line and the recorded value was 344 ± 32 µg L^{-1} (SD 9.33%), (Figure 6.65). The ICP-OES result for the Cu concentration was recorded as 565 µg L^{-1}.

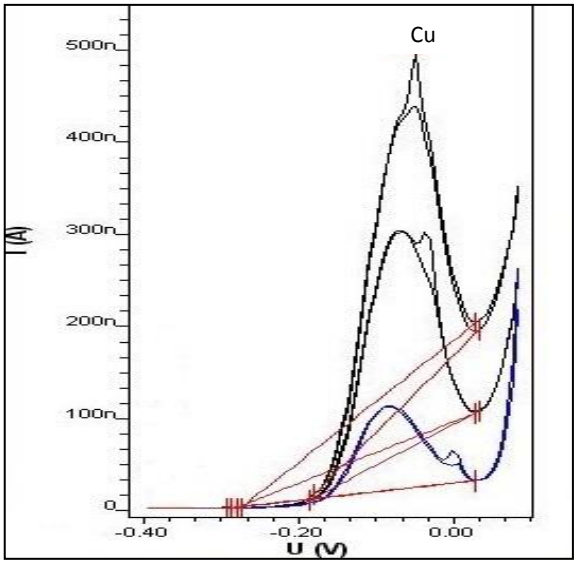

Figure 6.65. Voltammogram of the corn sample C_{10} with Buffer I.

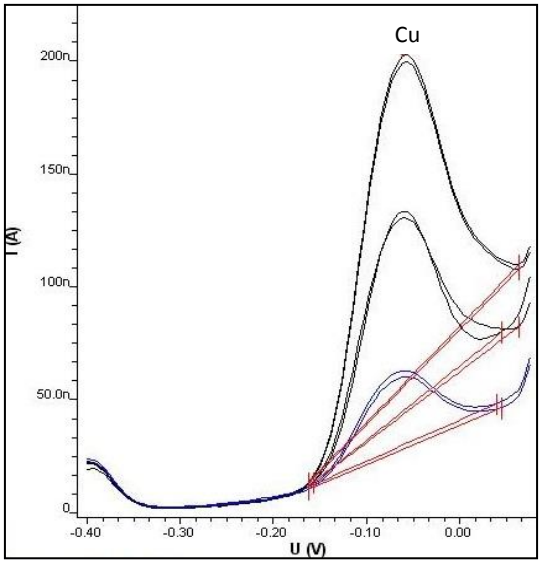

Figure 6.66. Voltammogram of anchovy sample C_{10} in Buffer III + 1.0 mL of EDTA, 1 x 10^{-3} mol L^{-1}.

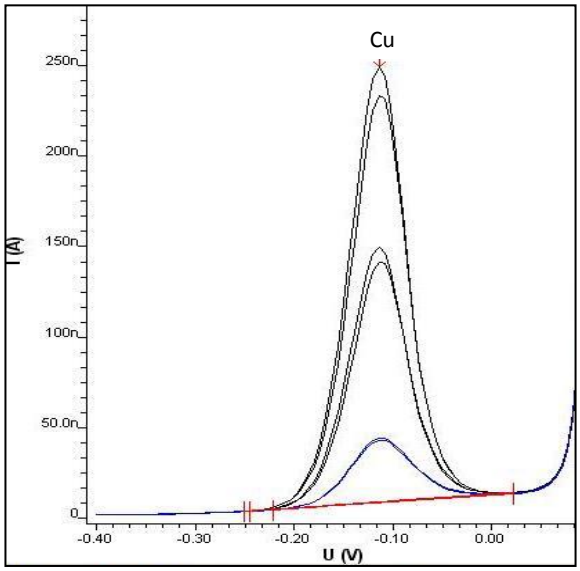

Figure 6.67. Voltammogram of anchovy sample C_{10} in Buffer III + 1.0 mL of EDTA, 5 x 10^{-3} mol L^{-1}.

The DPASV analysis of the sample with 1 mL of 1 x 10^{-3} mol L^{-1} EDTA revealed the concentration as 232 ± 32 µg L^{-1} (SD 1.81 %), (Figure 6.66). Therefore, the analysis was carried out with 1 mL of 5 x 10^{-3} mol L^{-1} of EDTA. Standard additions were done with 20 mg L^{-1}. The recorded Cu concentration was 520 ± 22 µg L^{-1} (S.D. 4.28 %), and the base-line shift did not exist any longer (Figure 6.67).

Ayfrost brand mussel sample, M_{11}, with the serial number of 02536011 and the expiration date of 12/2013 was analyzed. The Cu content analysis with Buffer I revealed the concentration as 816 ± 54 µg L^{-1} (SD 6.62%), (Figure 6.68). 1 mL of 5 x 10^{-3} mol L^{-1} of EDTA was used with Buffer III composition in order to prevent the distortion on the Cu peak. Yet, the shift of the half-wave potential of the Cu-peak with each addition of the standard Cu solution could not be prevented (Figure 6.69). The result was 675 ± 31 µg L^{-1} (SD 4.59 %) of Cu. Therefore, concentration was increased in parallel to the increasing Cu concentration of the analyte. 1 mL of 1 x 10^{-2} mol L^{-1} of EDTA was used, and the recorded concentration of Cu content with DPASV analysis was 583 ± 11 µg L^{-1} (SD 1.82 %), while the result of the ICP-OES analysis was 600 µg L^{-1} (Figure 6.70). Standard additions were done with 20 mg L^{-1} of Cu.

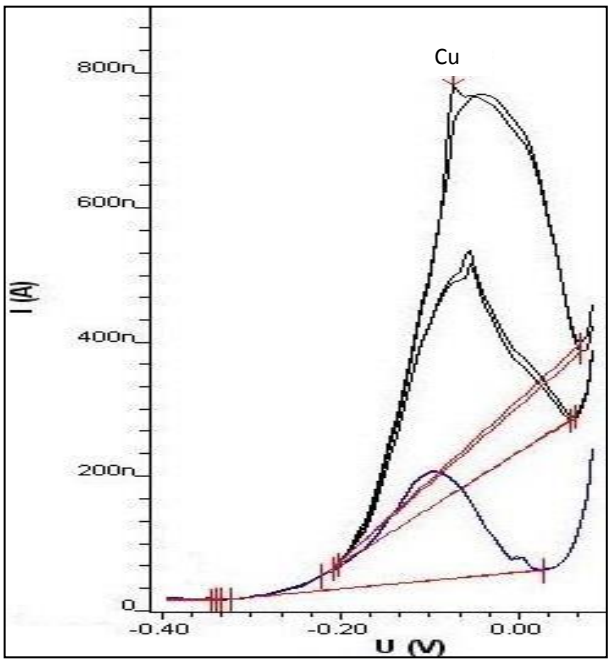

Figure 6.68. Voltammogram of mussel sample M_{11} with Buffer I.

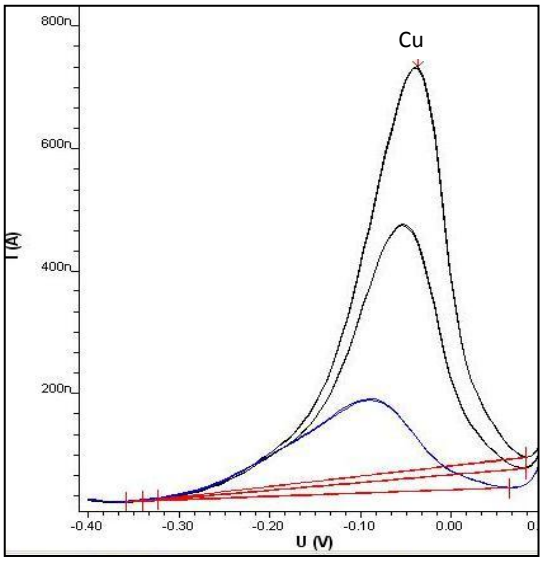

Figure 6.69. Voltammogram of mussel sample M_{11} in Buffer III + 1.0 mL of EDTA, 5 x 10^{-3} mol L^{-1}.

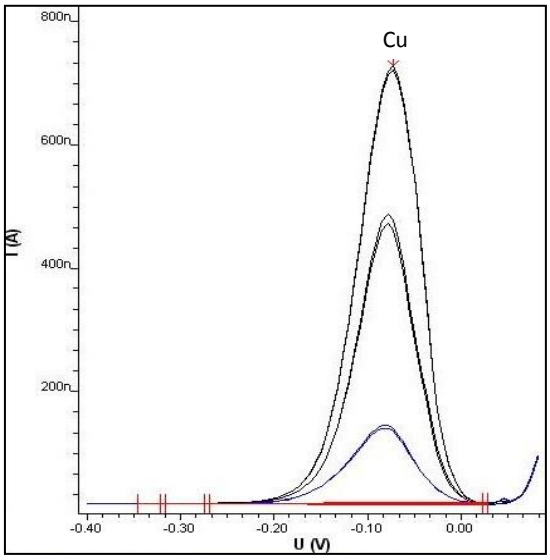

Figure 6.70. Voltammogram of mussel sample M_{11} in Buffer III + 1.0 mL of EDTA, 1 x 10^{-2} mol L^{-1}.

Canned tuna sample T_4, Kemerli brand with a production date of 05/10 which was also the serial number, was analyzed. The Cu content was recorded as 365 ± 25 µg L^{-1} (SD 6.89%) with Buffer I (Figure 6.71). 1 mL of 5 x 10^{-3} mol L^{-1} of EDTA was used to overcome the base-line shift and distortion of the Cu peak. The recorded concentration for Cu content was 1064 ± 45 µg L^{-1} (SD 4.26%), and the ICP-OES result of the Cu concentration was 733 µg L^{-1}. However, the shift in the base-lines could not be prevented (Figure 6.72).

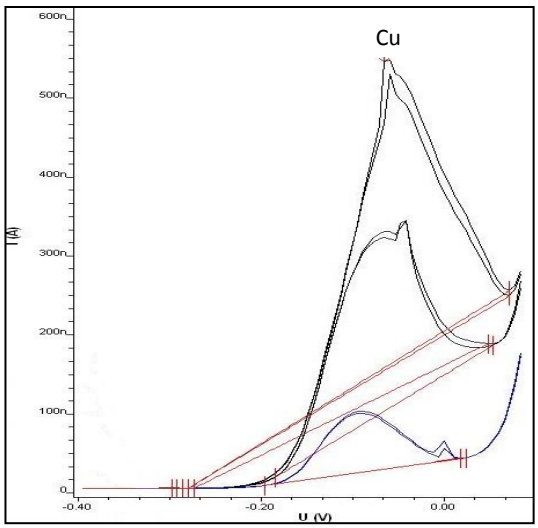

Figure 6.71. Voltammogram of tuna sample T_4 with Buffer I.

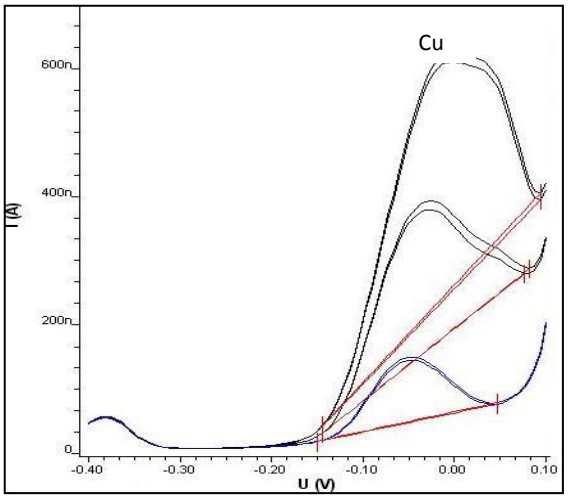

Figure 6.72. Voltammogram of tuna sample T_4 in Buffer III + 1.0 mL of EDTA, 5 x 10^{-3} mol L^{-1}.

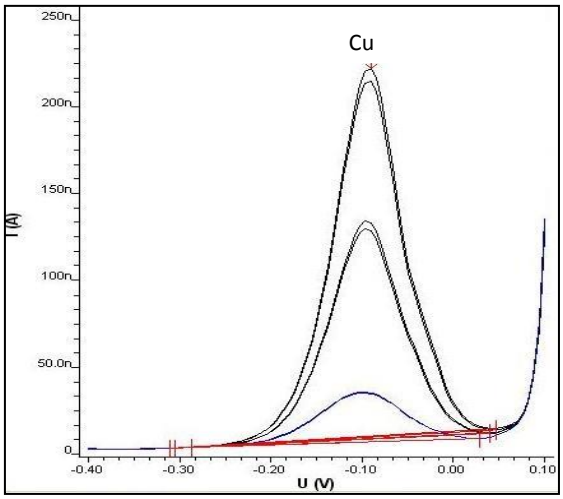

Figure 6.73. Voltammogram of tuna sample T_4 in Buffer III + 1.0 mL of EDTA, 1 x 10^{-2} mol L^{-1}.

Hence, the analysis was carried out with 1 mL of 1 x 10^{-2} mol L^{-1} of EDTA. Standard additions were done with 25 mg L^{-1} of Cu. The result was in good agreement with the ICP-OES analysis. 765 ± 23 µg L^{-1} (SD 3.00 %) of Cu content was recorded (Figure 6.73).

Canned corn sample C_8, Superfresh brand with the expiration date of 02/2015 and the serial number of L2158 was taken and firstly analyzed with Buffer I. Shifted base-lines and split peaks were observed. The DPASV result for the Cu detection was 1388 ± 50 µg L^{-1}, (SD 3.61%). Although the standard deviation value was lower, the result was unreliable (Figure 6.74).

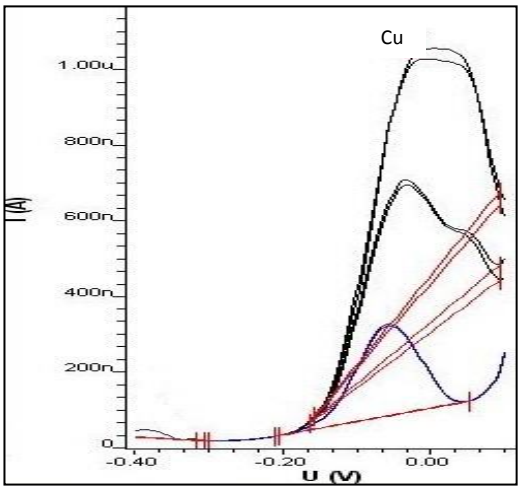

Figure 6.74. Voltammogram of corn sample C_8 with Buffer I.

The analysis with 1 mL of 5 x 10^{-3} mol L^{-1} of EDTA with Buffer III concentration revealed the Cu concentration as 1801 ± 84 µg L^{-1}, (SD 4.67%), (Figure 6.75), where the result of the ICP-OES analysis was 873 µg L^{-1}. The analysis was performed with 1 mL of 1 x 10^{-2} mol L^{-1} of EDTA in order to obtain a reliable result, and the recorded concentration was 883 ± 16 µg L^{-1}, (SD 1.81%), (Figure 6.76). Standard additions were done with 25 mg L^{-1} of Cu.

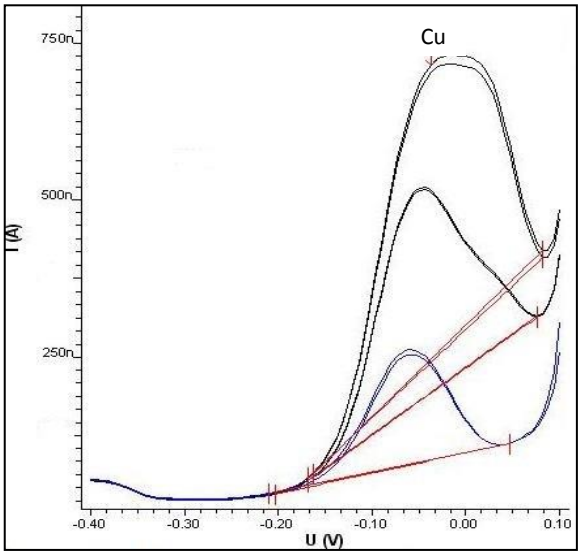

Figure 6.75. Voltammogram of corn sample C_8 in Buffer III + 1.0 mL of EDTA 5 x 10^{-3} mol L^{-1}.

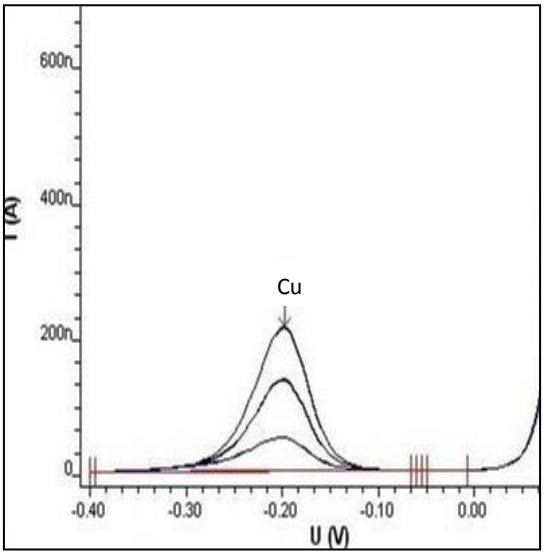

Figure 6.76. Voltammogram of corn sample C_8 in Buffer III + 1.0 mL of EDTA, 1 x 10^{-2} mol L^{-1}.

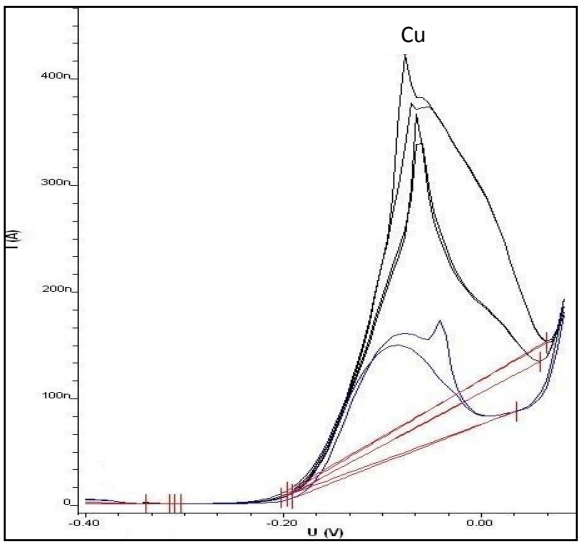

Figure 6.77. Voltammogram of tuna sample T_5 with Buffer I.

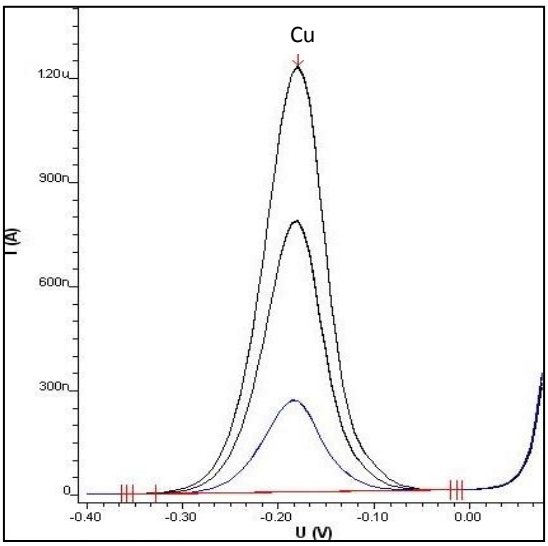

Figure 6.78. Voltammogram of sample T_5 in Buffer III + 1 mL of 5 x 10^{-2} mol L^{-1} EDTA.

Kemerli brand tuna sample T_5 with a production date of 05/10 which was also the serial number was analyzed. The recorded Cu concentration with Buffer I was 874 ± 198 µg L^{-1} (SD 22.7%), (Figure 6.77). The recorded concentration of Cu content by ICP-OES analysis was 2028 µg L^{-1}. Therefore, considering the correlation between the EDTA concentration and the Cu content in the sample, the concentration of the EDTA was increased. 1 mL of 5 x 10^{-2} mol L^{-1} of EDTA was used with Buffer III composition, standard additions were done with 50 mg L^{-1} of Cu. Measured amount of the Cu content was, 2108 ± 64 µg L^{-1}, (SD 3.04%). The peak height after each subsequent standard addition was 3 to 4 times of the analyte peak, and the voltammogram of the Cu appeared to be a smooth and a well shaped peak (Figure 6.78).

Elements which investigated the effects of base electrolytes had indicated that Buffer I (oxalate) was the most suitable composition for the DPASV analysis of Zn, Cd, Pb and Cu in fresh and canned fish, canned corn, and canned tomato samples (Section 6.2). Under the circumstances where the corresponding Cu concentration was around 75 µg L^{-1} level and above, shifts in the half-wave potential values during the standard additions occurred. In turn, distorted voltammetric peaks were observed, and inaccurate quantitative data were obtained. Trial test runs confirmed that the shifted baselines and/or the distorted voltammograms for the Cu peaks could be modified in the presence of Buffer III with EDTA addition. An aliquot of 1 mL of the digested sample, 1 mL of Buffer III, and 1 mL of EDTA within the the concentration range of 1 x 10^{-3} mol L^{-1} and 5 x 10^{-2} mol L^{-1} were put in a voltammetric vessel, and the final volume was diluted to 10 mL prior to analysis.

In voltammetric determinations of Cu-chloride complex formations were possible due to two main reasons: (i) Perchloric acid, $HClO_4$(aq), which was used in the digestion process, (ii) HAc + NH_3 + KCl (Buffer III) which was used as supporting electrolyte in media.

Samples were chosen among the corn, anchovy, tuna and mussel sets of which the corresponding Cu, Cd and Pb contents were already determined by ICP-OES analyses. Samples were screened, and the concentration ranges where the DPASV analysis encountered difficulties were selected. Experimental results suggested the following EDTA concentrations for the analysis of Cu at the given concentration ranges:

1×10^{-3} mol L^{-1} EDTA was suitable at 90 µg $L^{-1} \leq [Cu^{2+}] < 600$ µg L^{-1},
1×10^{-2} mol L^{-1} EDTA was suitable at 600 µg $L^{-1} \leq [Cu^{2+}] < 900$ µg L^{-1},
5×10^{-2} mol L^{-1} EDTA was suitable at 900 µg $L^{-1} \leq [Cu^{2+}] < 2500$ µg L^{-1}.

6.6. Voltammetric Determination of Selenium

Selenium determination of food is enabled by Cathodic Stripping Voltammetry (CSV). Se(IV) is the only electrochemically active substance, yet, it is also possible to detect Se(II) and Se(VI), if the sample is properly prepared. The reagents were prepared as following:

3.72 g of $Na_2EDTA.2H_2O$ were dissolved in 100 mL ultrapure water to obtain 0.1 mol L^{-1} of EDTA-solution. 0.098 mL of 96% H_2SO_4 was dissolved in 500 mL ultrapure water in order to get 0.01 mol L^{-1} of H_2SO_4. 0.1 g L^{-1} of Cu solution and 1 mg L^{-1} of Se (IV) solution were prepared as diluting the concentrated Cu and Se standard solutions with 0.01 mol L^{-1} of H_2SO_4, respectively [10].

An aliquot of 2 mL of sample was diluted to 10 mL in the voltammetric vessel. A 3.3. g of ammonium sulphate was added and dissolved, followed by addition of 1 mL of Cu solution and 1 mL of EDTA. The pH value of the solution was adjusted to 2.2 ± 0.1 with sulphuric acid.

Tuna sample, $T_{40,}$ Tonton brand with the serial number of TR 17.50 and the expiration date of 08/2016 was analyzed. Standard additions were done with 1 mg L^{-1} of Se standard solution. Se content was recorded as 91.0 ± 10.1 µg L^{-1} (Figure 6.79).

In order to adjust the sample dilution factor, same procedure was repeated with dilution of 0.5 mL of sample solution to the final volume of 10 mL with deionized water. Since the standard addition of 1 mg L^{-1} of Se was not adequate in the previous determination, 10 mg L^{-1} standard solution of Se was added to the voltammetric vessel. However, the determination of Se could not be achieved due to the high dilution factor of sample (Figure 6.80).

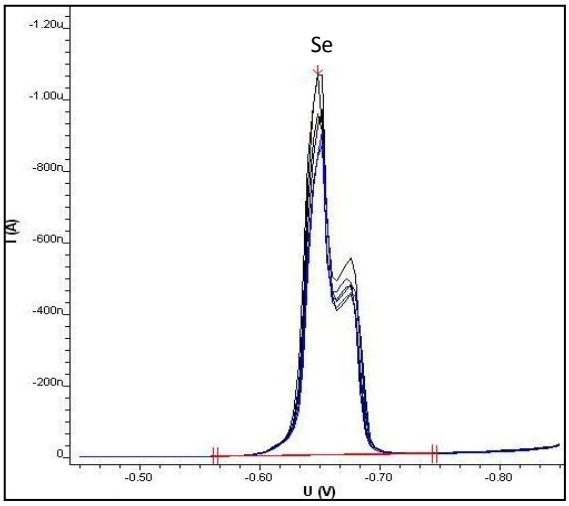

Figure 6.79. Voltammogram of 2 mL of of sample T_{40} diluted to 10 mL.

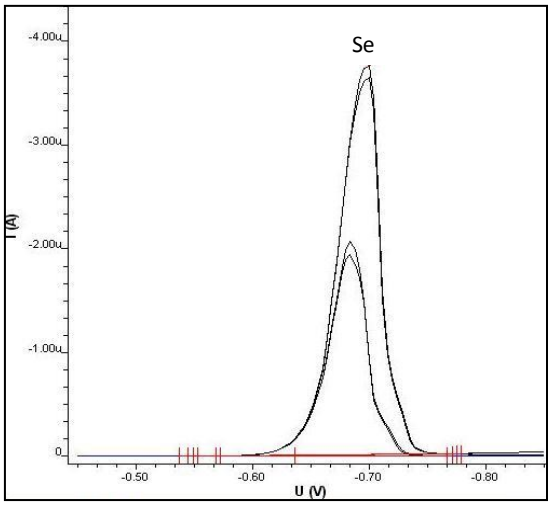

Figure 6.80. Voltammogram of 0.5 mL of sample T_{40} diluted to 10 mL.

The Se analysis of the tuna samples continued with sample T_{41}, 1 mL of the sample was diluted to 10 mL of final volume. The standard additions were done with 4 mg L^{-1} of Se (Figure 6.81). Recorded value by the DPCSV anlaysis was 40.6 ± 0.5 µg L^{-1}. The analysis was repeated with the same dilution factor but decreasing the standard solution to 2 mg L^{-1} of Se (Figure 6.82). The DPCSV result of the analysis was 39.8 ± 2.7 µg L^{-1}.

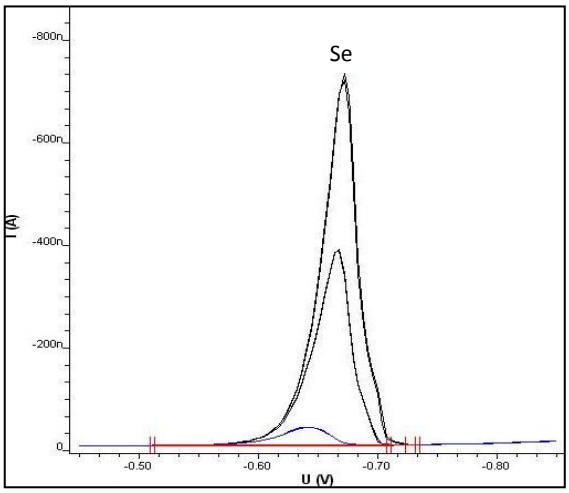

Figure 6.81. Voltammogram of 1 mL of sample T_{41} diluted to 10 mL.

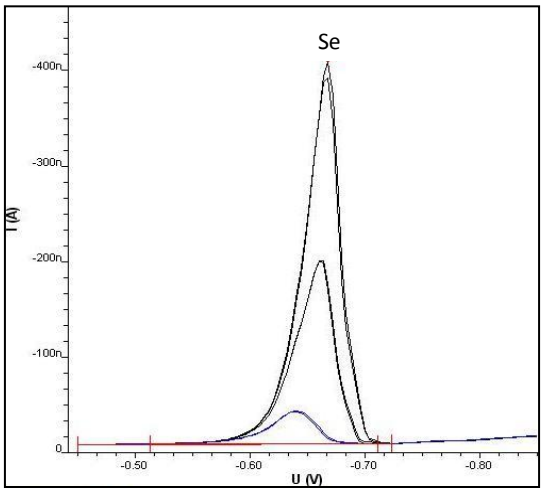

Figure 6.82. Voltammogram of 1 mL of sample T_{41} diluted to 10 mL.

Sample T_{42} was analyzed with the dilution of 1 mL of analyte to the final volume of 10 mL. 1 mg L^{-1} standard solution of Se was used (Figure 6.83). Se content was recorded

as 45.6 ± 4.5 µg L^{-1} by DPCSV. 5 mg L^{-1} of standard solution of Se was used in order to detect the Se content of the sample T_{45} (Figure 6.84), 200 ± 6 µg L^{-1} of Se was recorded.

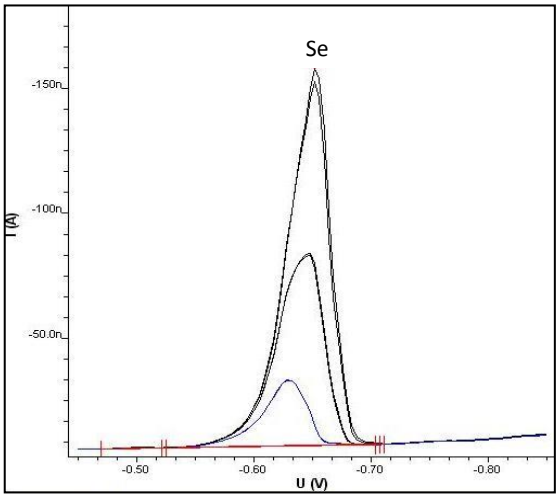

Figure 6.83. Voltammogram of 1 mL of sample T_{42} diluted to 10 mL.

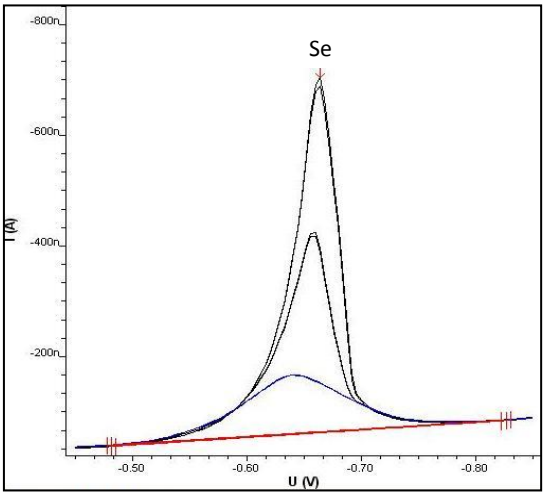

Figure 6.84. Voltammogram of 1 mL of sample T_{45} diluted to 10 mL.

Relatively lower concentrations of standard solutions were used in order to detect Se contents of the samples. Tuna samples of Ülker Light brand with the serial number of DGL 2129 and the expiration date of 05/2017 were analyzed. 1 mL of sample T_{48} was diluted to 10 mL and 0.3 mg L^{-1} of Se solution was used in standard additions. DPCSV analysis recorded the Se concentration as 13.9 ± 0.9 µg L^{-1}. Samples T_{50} and T_{51} were analyzed. 1 mL of each analyte was diluted to 10 mL of final volume and the standard additions were done with 0.5 mg L^{-1} of Se solution. Se contents of the samples were 19.6 ± 0.9 µg L^{-1} and 25.4 ± 1.5 µg L^{-1}, respectively.

In cases where the Se content of the sample was rather in smaller quantities i.e., <10 µg L^{-1}, 4 mL of the analyte solution was diluted to 10 mL of final volume. Samples T_{43} and T_{44} were analyzed in this manner. DPCSV analysis recorded the Se concentrations as 4.27 ± 0.3 µg L^{-1} and 3.32 ± 0.09 µg L^{-1}, respectively. Some of the sardine samples were also analyzed in their Se content. Engin Brand sardine samples with the expiration date of 04/2013 which was also the serial number were investigated. The selenium concentrations were higher than the results of the tuna samples. Overall results of the analyses were given in Section 6, Tables 6.70 – 6.73. Advanced researches on cathodic stripping analysis can be investigated in further studies.

7. RESULTS AND DISCUSSION

DPASV method parameters were set for the quantitative analyses of Zn, Cd, Pb and Cu in fish, canned corn, and tomato samples with Buffer I as given in Table 7.1.

Table 7.1. Voltammetric parameters for Zn, Cd, Pb and Cu analysis.

Deposition Potential (V)	-0.9
Deposition Time (s)	120
Equilibrium Time (s)	5
Start Potential (V)	-1.25
End Potential (V)	0.08
Voltage Step (V)	0.006
Pulse Amplitude (V)	0.05
Pulse Time (s)	0.04
Voltage Step Time (s)	0.2
Sweep Rate (V/s)	0.0298

Table 7.2. Determination Parameters.

Cell Volume (mL)	11.0 – 11.6
Sample Volume (mL)	0.05 – 2.00
Addition Purge Time (s)	10
Blank Purge Time (s)	300
Number of Additions	2
Number of Replications	3

When Zn determination was carried alone, deposition potential was set as -1.25 V to -0.75 V. In some cases, Cu contents of the samples were determined alone, the deposition potential was set as -0.25 V V to 0.08 V. Also, deposition potential was set as -0.90 V to -0.40 V for separate determination of Cd content whenever it was necessary. In some cases, Cu determination was performed with EDTA addition in Buffer III and the cell volume was increased up to 11.6 mL instead of 10 mL. Generally, sample volumes in the voltammetric vessels were between 0.05 mL and 2 mL, in detection of Zn and Cu.

Standard additions were done with Zn of 10.0, 25.0, 50.0, 75.0 and 100.0 mg L^{-1}, Cd of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mg L^{-1}, Pb of 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 3.0 and 5.0 mg L^{-1}, Cu of 5.0, 7.5, 10.0, 15.0, 25.0, 50.0, 75.0 and 100.0 mg L^{-1}.

Metal concentrations in blanks were determined; they were below the detection limits in all analyses. The ratio of sample volume to the total volume in the voltammetric vessel was indicated as the dilution factor.

7.1. Analysis of Sardine Samples

Fresh sardine samples purchased from local markets of Gelibolu and Çanakkale and the canned sardine samples of several different brands were analyzed. Analyses of samples S_4-S_{11} were carried with 2.00 ± 0.05 g of sardine specimens. Each sample referred to the dry weight measurement of an individual sardine specimen, and the digestion took place with 18 mL of nitric acid/perchloric acid (HNO_3/$HClO_4$) mixture (5/1, v:v) for approximately 20 hours. Samples S_{12}-S_{36} were weighed 1.50 ± 0.02 g, each sardine was digested for about 15 hours in nitric acid/perchloric acid mixture of 12 mL (5/1, v:v). All determinations were done with 2 mL of sample solution for Cd, Pb and Cu; and 0.2 mL of sample for Zn, by HMDE mode of mercury electrode. Circumstances where the SMDE mode of the electrode or other dilution factors were in use, they were specified along the analysis.

7.1.1. Fresh Sardine Samples

The Cd amount in the fresh sardine samples was in the range of 0 – 0.155 µg g^{-1}; Pb content was between the ranges of 0.103 – 0.994 µg g^{-1}; Cu content was in the range of 0.720 – 15.8 µg g^{-1} (Table 7.3). Cu determination of sample S_9 was done separately, and the dilution factor was 0.5/10. Also, the analysis of the samples S_8 and S_{12} were performed 5 times. The most precise results with relatively small standard deviation values, and also closest to the results of the ICP-OES analyses, were considered.

Table 7.3. Cd, Pb and Cu contents of fresh sardine samples.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_4	Cd	10.3 ± 0.8	0.127 ± 0.009	7.84	12.0	0.148
	Pb	69.2 ± 5.3	0.855 ± 0.066	7.71	50.4	0.622
	Cu	323 ± 33	3.98 ± 0.41	10.3	297	3.66
S_5	Cd	6.22 ± 0.35	0.077 ± 0.004	5.71	7.86	0.097
	Pb	26.4 ± 0.8	0.326 ± 0.009	2.90	23.6	0.292
	Cu	235 ± 21	2.91 ± 0.26	8.89	207	2.56
S_6	Cd	12.5 ± 1.0	0.155 ± 0.012	8.04	12.5	0.155
	Pb	80.1 ± 4.5	0.994 ± 0.056	5.65	49.6	0.616
	Cu*	772 ± 16	9.58 ± 0.20	2.12	938	11.6
S_7	Cd	3.08 ± 0.19	0.038 ± 0.002	6.32	5.64	0.069
	Pb	36.4 ± 0.4	0.449 ± 0.005	1.03	30.7	0.378
	Cu	309 ± 35	3.81 ± 0.43	11.4	298	3.68
S_8	Cd	3.85 ± 0.26	0.048 ± 0.003	6.65	5.81	0.072
	Pb	46.7 ± 1.0	0.578 ± 0.013	2.19	41.9	0.519
	Cu	570 ± 40	7.05 ± 0.49	7.00	486	6.01
S_9	Cd	4.77 ± 0.17	0.058 ± 0.002	3.50	4.10	0.049
	Pb	27.9 ± 0.4	0.338 ± 0.006	1.63	23.4	0.284
	Cu	1302 ± 17	15.8 ± 0.2	1.30	1040	12.6
S_{10}	Cd	4.88 ± 0.47	0.056 ± 0.006	9.79	6.55	0.076
	Pb	12.8 ± 0.9	0.148 ± 0.011	7.38	18.2	0.210
	Cu	628 ± 46	7.27 ± 0.53	7.34	682	7.89
S_{11}	Cd	4.84 ± 0.18	0.058 ± 0.002	3.74	4.56	0.054
	Pb	23.9 ± 0.9	0.284 ± 0.012	4.18	21.9	0.260
	Cu**	210 ± 4	2.50 ± 0.048	1.90	253	3.01
S_{12}	Cd	0	0	-	0	0
	Pb	36 ± 1	0.602 ± 0.015	2.47	9.63	0.161
	Cu	394 ± 27	6.59 ± 0.46	6.98	228	3.82
S_{13}	Cd	1.46 ± 0.12	0.024 ± 0.002	8.09	2.99	0.048
	Pb	6.38 ± 0.44	0.103 ± 0.007	6.96	5.34	0.086
	Cu	44.5 ± 0.7	0.720 ± 0.010	1.56	46.2	0.746

* Cu detection was carried with 1 mL of 1 x 10^{-2} of EDTA with 1 mL of sample.

** Cu detection was carried with 1 mL of 1 x 10^{-3} of EDTA with 1 mL of sample.

The results of the analyses of fresh sardine specimens showed that the Zn contents of the samples ranged between 0.035 mg g^{-1} and 0.282 mg g^{-1}. DPASV results were in agreement with the results of ICP-OES analyses (Table 7.4). Zn determinations of samples were performed with HMDE mode of mercury electrode with dilution factor of 0.2/10,

except the samples S_8 and S_9 which were analyzed by SMDE mode. The dilution factor was 0.5/10, and deposition potential range was between -1.15 V and -0.75 V.

Table 7.4. Zn contents of fresh sardine samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_4	4.90 ± 0.09	0.061 ± 0.001	1.77	4.24	0.052
S_5	2.84 ± 0.07	0.035 ± 0.001	2.58	2.08	0.026
S_6	8.07 ± 0.54	0.100 ± 0.007	6.71	7.57	0.094
S_7	10.9 ± 0.5	0.136 ± 0.006	4.39	9.88	0.122
S_8	20.8 ± 1.0	0.257 ± 0.013	4.94	18.6	0.231
S_9	23.3 ± 0.1	0.282 ± 0.002	0.58	21.2	0.256
S_{10}	4.43 ± 0.19	0.051 ± 0.002	4.48	5.05	0.058
S_{11}	3.81 ± 0.09	0.045 ± 0.001	2.29	3.58	0.042
S_{12}	2.95 ± 0.11	0.049 ± 0.002	3.75	2.35	0.039
S_{13}	2.31 ± 0.01	0.038 ± 0.0002	0.65	2.16	0.035

7.1.2. Canned Sardine Samples

Four different brands of canned sardine samples; CFB1, CFB2, CFB3 and CFB4 were analyzed. Canned sardine samples had higher contents of Pb and Cu concentrations than fresh sardine samples. However, the corresponding metal contents for the replicate fish species taken from the same can were so diversified that the average value of the metal contents was not possible to calculate. In order to compare the trace amounts of metals in samples, the upper and lower limits of measured concentrations were compared with each other.

CFB1 sardine samples with a serial number of 03 and the production date of 02/2012 were analyzed. Cd contents were in the range of 0.063 – 0.134 µg g^{-1}; Pb amounts had been recorded as 0.709 – 1.44 µg g^{-1}; and the Cu contents were measured in the range of 3.27 – 10.9 µg g^{-1}. Also, Cu contents were recorded as 34.8 µg g^{-1} and 62.1 µg g^{-1} for two of the sardine samples which were rather higher than the rest (Table 7.5). Cu contents of the samples S_{14} and S_{15} were determined separately, with dilution factor of 0.5/10.

Table 7.5. Cd, Pb and Cu contents of sardine samples CFB1 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_{14}	Cd	10.5 ± 1.0	0.13 ± 0.01	9.72	11.8	0.146
	Pb	116 ± 2	1.44 ± 0.02	1.55	98.9	1.23
	Cu	2804 ± 122	34.8 ± 1.5	4.34	2544	31.6
S_{15}	Cd	7.37 ± 0.29	0.091 ± 0.004	4.04	8.76	0.108
	Pb	67.8 ± 2.4	0.839 ± 0.029	3.56	58.0	0.719
	Cu	5010 ± 214	62.1 ± 2.6	4.27	5114	63.4
S_{16}	Cd	5.04 ± 0.36	0.063 ± 0.004	7.12	4.72	0.059
	Pb	57 ± 2	0.709 ± 0.024	3.36	49.9	0.620
	Cu	882 ± 76	10.9 ± 0.9	8.56	543	6.76
S_{17}	Cd	10.8 ± 0.5	0.134 ± 0.006	4.83	13.9	0.171
	Pb	57.2 ± 1.3	0.706 ± 0.016	2.27	53.6	0.661
	Cu	265 ± 17	3.27 ± 0.21	6.35	196	2.42
S_{18}	Cd	5.98 ± 0.44	0.074 ± 0.005	7.36	6.18	0.076
	Pb	114 ± 3	1.41 ± 0.03	2.34	89.5	1.10
	Cu	302 ± 26	3.73 ± 0.32	8.65	380	4.69

Zn concentrations were in the range of 0.009 – 0.131 mg g^{-1}, yet, 0.676 mg g^{-1} of Zn was recorded for one of the sardine samples (Table 7.6). In DPASV analysis, low standard deviation values were achieved by using the SMDE mode of the mercury electrode. Samples S_{14} and S_{15} were analyzed by SMDE mode with dilution factors of 0.5/10 and 0.2/10, respectively.

Table 7.6. Zn contents of sardine samples CFB1 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_{14}	10.6 ± 0.06	0.131 ± 0.001	0.57	11.3	0.140
S_{15}	54.5 ± 0.9	0.676 ± 0.011	1.67	51.3	0.636
S_{16}	5.63 ± 0.04	0.070 ± 0.001	0.74	5.49	0.068
S_{17}	0.710 ± 0.008	0.009 ± 0.0001	1.11	0.638	0.008
S_{18}	2.09 ± 0.06	0.026 ± 0.001	2.65	2.13	0.026

Sardine samples CFB2 brand with a serial number of 233.1 and the expiration date of 08/2017 were analyzed. Cd contents were in the range of 0.018 – 0.312 µg g^{-1}, and two of the sardine samples did not contain any Cd. Pb amounts had been recorded as 0.201 – 0.614 µg g^{-1}, and one sardine sample did not reveal any Pb content. Cu concentration was

measured in the range of 2.84 – 51.2 µg g^{-1} (Table 7.7). Cu contents of the samples S_{21}, S_{23}, S_{25} were determined separately. The dilution factor was 0.5/10.

Table 7.7. Cd, Pb and Cu contents of sardine samples CFB2 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_{19}	Cd	19.3 ± 0.2	0.312 ± 0.004	1.24	23.2	0.376
	Pb	25.7 ± 0.3	0.416 ± 0.005	1.24	19.8	0.321
	Cu	708 ± 4	11.5 ± 0.1	0.66	572	9.28
S_{20}	Cd	6.49 ± 0.46	0.107 ± 0.008	7.09	8.84	0.146
	Pb	0	0	-	0	0
	Cu	421 ± 11	6.93 ± 0.18	2.59	308	5.08
S_{21}	Cd	7.89 ± 0.34	0.129 ± 0.006	4.29	11.8	0.194
	Pb	22 ± 1	0.362 ± 0.017	4.77	17.2	0.283
	Cu	2291 ± 78	37.7 ± 1.3	3.39	2342	38.5
S_{22}	Cd	5.43 ± 0.42	0.089 ± 0.007	7.68	7.79	0.127
	Pb	12.3 ± 0.7	0.201 ± 0.011	5.47	11.9	0.195
	Cu	246 ± 7	4.02 ± 0.12	3.09	284	4.64
S_{23}	Cd	0	0	-	0	0
	Pb	36.9 ± 2.8	0.614 ± 0.046	7.49	33.9	0.562
	Cu	3082 ± 161	51.2 ± 2.7	5.24	2908	48.3
S_{24}	Cd	4.49 ± 0.42	0.074 ± 0.007	9.35	5.89	0.101
	Pb	32.2 ± 1.5	0.532 ± 0.025	4.70	31.8	0.526
	Cu	172 ± 8	2.84 ± 0.13	4.59	173	2.86
S_{25}	Cd	1.08 ± 0.04	0.018 ± 0.001	3.71	0	0
	Pb	29.9 ± 2.1	0.497 ± 0.035	7.00	26.9	0.445
	Cu	1059 ± 53	17.6 ± 0.9	5.01	838	13.9

The range for Zn concentrations of CFB2 brand canned sardine was 0.061 – 0.285 mg g^{-1}, higher than the Zn contents of CFB1 brand. The highest concentration values of 0.854 mg g^{-1} and 0.890 mg g^{-1} were recorded for two of the sardine samples (Table 7.8).

Table 7.8. Zn contents of sardine samples CFB2 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_{19}	54.9 ± 1.9	0.890 ± 0.031	3.49	58.9	0.956
S_{20}	6.12 ± 0.36	0.101 ± 0.006	5.85	4.99	0.082
S_{21}	17.3 ± 0.2	0.285 ± 0.003	1.22	17.0	0.280
S_{22}	15.1 ± 0.8	0.247 ± 0.012	5.00	13.1	0.214
S_{23}	17.6 ± 0.1	0.292 ± 0.002	0.74	15.3	0.254
S_{24}	3.70 ± 0.26	0.061 ± 0.004	6.91	3.17	0.052
S_{25}	51.5 ± 0.8	0.854 ± 0.014	1.69	50.9	0.845

Zn contents of the samples were determined by SMDE mode except for the samples S_{20} and S_{24}. Dilution factor was 0.2/10 for the samples S_{19} and S_{25}, and 0.5/10 for $S_{21,}$ S_{22}, and S_{23}.

CFB3 brand sardine samples with a serial number of 364/1 and the expiration date of 12/16 were analyzed. The range of Cd content was between 0.129 – 0.173 µg g^{-1}; Pb contents were between 0.142 – 0.485 µg g^{-1}, which were the lowest concentrations recorded for the Pb content in sardine samples, also in one of the samples Pb did not exist at all. The Cu contents were measured in the range of 1.95 – 9.31 µg g^{-1} (Table 7.9), which were lower than the Cu concentrations of the other canned CFB2 brand sardine samples.

Table 7.9. Cd, Pb and Cu contents of sardine samples CFB2 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_{26}	Cd	10.7 ± 0.7	0.173 ± 0.012	6.88	14.5	0.235
	Pb	29.9 ± 1.1	0.485 ± 0.018	3.82	21.1	0.341
	Cu	575 ± 34	9.31 ± 0.55	5.88	625	10.1
S_{27}	Cd	8.16 ± 0.51	0.129 ± 0.008	6.29	6.29	0.099
	Pb	8.97 ± 0.49	0.142 ± 0.008	5.49	8.61	0.137
	Cu	123 ± 11	1.95 ± 0.17	8.92	133	2.11
S_{28}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	278 ± 18	4.31 ± 0.29	6.66	266	4.13
S_{29}	Cd	0	0	0	0	0
	Pb	12.9 ± 0.8	0.199 ± 0.012	6.29	10.0	0.154
	Cu	343 ± 16	5.29 ± 0.25	4.79	432	6.66
S_{30}	Cd	0	0	-	0	0
	Pb	10.2 ± 1.1	0.162 ± 0.018	11.0	7.28	0.115
	Cu	283 ± 2	4.49 ± 0.04	0.84	272	4.31

The range for the Zn contents of CFB3 brand was similar to that of CFB2 brand; it was between 0.038 mg g^{-1} and 0.275 mg g^{-1} (Table 7.10). SMDE mode was used for the determination of the Zn contents of the samples S_{28}, S_{29} and S_{30} with dilution factor of 0.5/10.

Table 7.10. Zn contents of sardine samples CFB3 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_{26}	4.22 ± 0.04	0.068 ± 0.001	0.87	4.43	0.072
S_{27}	2.39 ± 0.09	0.038 ± 0.002	4.00	2.14	0.034
S_{28}	13.9 ± 0.2	0.215 ± 0.003	1.35	12.7	0.196
S_{29}	17.8 ± 0.7	0.275 ± 0.011	3.89	21.9	0.339
S_{30}	12.6 ± 0.7	0.200 ± 0.012	5.83	10.2	0.162

CFB4 brand sardine samples with the expiration date of 04/2013 which was also the serial number were analyzed. Zn content was in the range between 0.042 – 0.384 mg g^{-1} with one exception that was 8.01 mg g^{-1} of Zn (Table 7.11). The difference between the results of DPASV and ICP-OES analyses of sample S_{36} stems from the high dilution factor in ICP-OES analysis. SMDE mode of electrode was used with the sample S_{36}, and the dilution factor was 0.05/10.

Table 7.11. Zn contents of sardine samples CFB4 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
S_{31}	3.71 ± 0.05	0.062 ± 0.001	1.45	3.45	0.057
S_{32}	23.1 ± 0.2	0.384 ± 0.003	0.86	22.4	0.373
S_{33}	8.22 ± 0.13	0.137 ± 0.002	1.56	7.42	0.124
S_{34}	2.52 ± 0.02	0.042 ± 0.0003	0.77	2.24	0.037
S_{35}	2.76 ± 0.02	0.046 ± 0.0002	0.56	2.57	0.042
S_{36}	481 ± 11	8.01 ± 0.19	2.35	468	7.80

Mostly the Cd content was recorded as 0, yet two sardine samples had the Cd concentrations as 0.016 µg g^{-1} and 0.065 µg g^{-1}, it has shown that the samples of CFB4 brand had the lowest concentrations of Cd. Pb concentrations were in the range of 0.084 – 0.269 µg g^{-1}, while the Pb concentrations of two sardine samples were recorded as 0 and 1.06 µg g^{-1}. Cu concentrations were measured between 2.59 – 13.9 µg g^{-1}, yet one of the samples revealed the Cu concentration as 130 µg g^{-1} (Table 7.12). Cu detection was carried separately with sample S_{36}. Dilution factor was 0.5/10.

Table 7.12. Cd, Pb and Cu contents of sardine samples CFB4 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
S_{31}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	839 ± 42	13.9 ± 0.7	4.98	759	12.6
S_{32}	Cd	0.953 ± 0.065	0.016 ± 0.001	6.82	1.11	0.018
	Pb	8.75 ± 0.59	0.146 ± 0.009	6.72	9.08	0.164
	Cu*	280 ± 6	4.68 ± 0.106	2.27	256	4.28
S_{33}	Cd	0	0	-	0	0
	Pb	10.3 ± 0.5	0.172 ± 0.009	5.13	8.73	0.145
	Cu	475 ± 6	7.91 ± 0.10	1.27	414	6.90
S_{34}	Cd	0	0	-	0	0
	Pb	7.13 ± 0.41	0.113 ± 0.018	5.75	8.69	0.144
	Cu	360 ± 39	5.96 ± 0.64	10.8	330	5.45
S_{35}	Cd	0	0	-	0	0
	Pb	16.3 ± 1.1	0.269 ± 0.018	6.84	13.2	0.218
	Cu	157 ± 9	2.59 ± 0.14	5.51	137	2.27
S_{36}	Cd	3.89 ± 0.31	0.065 ± 0.005	7.93	3.38	0.056
	Pb	63.9 ± 2.6	1.06 ± 0.04	4.02	59.2	0.986
	Cu	7787 ± 299	130 ± 5	3.84	7596	126

* Cu detection was carried with 1 mL of 1 x 10^{-3} of EDTA with Buffer II + KCl.

Trace metal contents in canned sardine samples exhibited variations in the corresponding concentrations. This indicated that the fish were collected from various sources and regions, and packaged together in the same can.

7.2. Analysis of Tuna Samples

Six brands of tuna samples were investigated; CFB2, CFB5, CFB6, CFB7, CFB8 and CFB9. Replicate samples were taken from different parts within the same container. Fish were packed in chunks in the cans so, specimens were collected from the sites of as many different chunks as possible. Samples were weighed as 1.50 ± 0.02 g and they were digested in 12 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v) for approximately 15 hours. DPASV determinations were done with 2 mL sample solution for Cd, Pb and Cu; and 0.2 mL sample for Zn by HMDE mode of the electrode. Irregular cases were specified along the analyses.

7.2.1. Canned Tuna Samples

Tuna samples CFB5 brand with the production date of 05/10, which was also the serial number, were analyzed. Cd contents were between 0.044 µg g^{-1} and 0.075 µg g^{-1} and one of the replicates was recorded as 0.245 µg g^{-1}. Recorded amounts of Pb content were between 0.257 µg g^{-1} and 0.673 µg L^{-1}; and the Cu content range was 5.73 – 25.8 µg g^{-1} (Table 7.13). Zn contents were in the range of 0.018 – 0.193 mg g^{-1} (Table 7.14). The results of DPASV analysis were consistent with the ICP-OES results.

Table 7.13. Cd, Pb and Cu contents of tuna samples CFB5 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_1	Cd	3.54 ± 0.12	0.044 ± 0.002	3.45	3.59	0.044
	Pb	38.2 ± 3.6	0.473 ± 0.044	9.34	33.6	0.415
	Cu	596 ± 54	7.37 ± 0.67	9.07	460	5.69
T_2	Cd	6.12 ± 0.51	0.075 ± 0.006	8.31	5.78	0.071
	Pb	54.7 ± 1.1	0.673 ± 0.013	1.97	45.4	0.559
	Cu	465 ± 26	5.73 ± 0.31	5.49	414	5.10
T_3	Cd	4.25 ± 0.35	0.052 ± 0.004	8.28	3.45	0.045
	Pb	39.7 ± 3.5	0.485 ± 0.043	8.88	37.2	0.454
	Cu	494 ± 50	6.02 ± 0.61	10.1	422	5.15
T_4	Cd	19.9 ± 1.0	0.245 ± 0.013	5.15	11.4	0.139
	Pb	46.8 ± 1.8	0.574 ± 0.022	3.82	51.6	0.632
	Cu*	765 ± 23	9.38 ± 0.280	2.98	733	8.98
T_5	Cd	5.07 ± 0.17	0.062 ± 0.002	3.32	4.95	0.061
	Pb	20.9 ± 0.7	0.257 ± 0.008	3.50	19.8	0.242
	Cu**	2108 ± 64	25.8 ± 0.8	3.04	2028	24.9

* Cu determination was performed with 1 x 10^{-2} mol L^{-1} of EDTA with 1 mL of sample.

** Cu determination was performed with 5 x 10^{-2} mol L^{-1} of EDTA with 1 mL of sample.

Table 7.14. Zn contents of tuna samples CFB5 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_1	15.6 ± 0.9	0.193 ± 0.012	6.12	15.2	0.188
T_2	1.45 ± 0.08	0.018 ± 0.001	5.38	1.09	0.013
T_3	12.7 ± 0.1	0.155 ± 0.001	0.83	11.3	0.138
T_4	8.45 ± 0.62	0.104 ± 0.008	7.33	7.22	0.088
T_5	72.2 ± 5.2	0.886 ± 0.064	7.25	76.2	0.934

Zn determination was performed with SMDE mode of electrode for $T_{1,}$ T_3, with dilution factor of 0.5/10 and T_5 with dilution factor of 0.2/10.

Tuna samples CFB6 brand with the serial number of DGL 2163 and the production date of 06/2012 were analyzed. Cd contents of the tuna samples were between 0.022 µg g^{-1} and 1.16 µg g^{-1}, and the Cd amount of one of the samples was recorded as 0. Measured Pb range was 0.169 – 1.77 µg g^{-1}. The corresponding Cu concentrations also varied, mainly Cu contents were between 0.529 µg g^{-1} and 3.96 µg g^{-1}, yet three of the samples revealed the Cu concentration as 17.4, 21.5 and 52.5 µg g^{-1} (Table 7.15). Cu concentrations of the samples T_6, T_{11}, and T_{12} were determined separately, with dilution factor of 0.5/10.

Table 7.15. Cd, Pb and Cu contents of tuna samples CFB6 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_6	Cd	48.6 ± 0.8	0.793 ± 0.013	1.61	45.0	0.735
	Pb	35.5 ± 0.5	0.579 ± 0.009	1.55	33.8	0.552
	Cu	1315 ± 14	21.5 ± 0.2	1.05	1403	22.9
T_7	Cd	3.29 ± 0.29	0.054 ± 0.005	8.83	4.68	0.077
	Pb	11.8 ± 1.1	0.194 ± 0.018	9.00	9.39	0.154
	Cu	241 ± 13	3.96 ± 0.21	5.42	288	4.72
T_8	Cd	1.35 ± 0.08	0.022 ± 0.001	5.85	1.68	0.028
	Pb	10.2 ± 0.4	0.169 ± 0.007	4.04	14.7	0.243
	Cu	31.9 ± 2.2	0.529 ± 0.037	7.06	44.1	0.731
T_9	Cd	2.60 ± 0.12	0.043 ± 0.002	4.49	3.52	0.058
	Pb	13.4 ± 0.5	0.222 ± 0.008	3.50	6.80	0.113
	Cu	67.9 ± 5.9	1.12 ± 0.09	8.64	39.4	0.654
T_{10}	Cd	0	0	-	0	0
	Pb	11.6 ± 0.4	0.192 ± 0.006	3.36	11.1	0.185
	Cu	42.4 ± 2.7	0.704 ± 0.044	6.27	68.8	1.14
T_{11}	Cd	5.43 ± 0.37	0.088 ± 0.006	6.75	4.96	0.081
	Pb	36.8 ± 1.9	0.598 ± 0.032	5.41	31.4	0.510
	Cu	3230 ± 222	52.5 ± 3.6	6.87	3794	61.6
T_{12}	Cd	70.7 ± 1.7	1.16 ± 0.03	2.46	59.6	0.976
	Pb	108 ± 2	1.77 ± 0.03	1.91	67.5	1.11
	Cu	1064 ± 91	17.4 ± 1.5	8.55	824	13.5

In three out of four tuna samples, Zn contents were higher than the rest, i.e. 1.83, 1.94 and 3.14 mg g^{-1} (Table 7.16). Samples T_6, T_{11}, and T_{12} were analyzed with SMDE mode with dilution factor of 0.1/10, and sample T_7 was also determined by SMDE mode

with dilution factor of 0.5/10. The discrepancies between the concentrations were related to the packaging processes and the compositions of tuna fish collected from various sources.

Table 7.16. Zn contents of tuna samples CFB6 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_6	112 ± 3	1.83 ± 0.05	2.62	104	1.71
T_7	17.0 ± 1.4	0.279 ± 0.024	8.50	20.8	0.341
T_8	1.00 ± 0.03	0.017 ± 0.001	3.35	0.722	0.012
T_9	0.899 ± 0.059	0.015 ± 0.001	6.59	0.759	0.012
T_{10}	2.33 ± 0.051	0.039 ± 0.001	2.19	2.16	0.037
T_{11}	193 ± 9	3.14 ± 0.15	4.90	192	3.12
T_{12}	118 ± 8	1.94 ± 0.13	6.59	139	2.29

Tuna samples CFB2 brand with the serial number of 0.81.2 AYT and the expiration date of 03/2016 were analyzed. Zn contents of the samples were between 0.024 mg g^{-1} and 0.322 mg L^{-1}. Concentrations of the two samples were recorded as 3.51 mg g^{-1} and 5.65 mg g^{-1} (Table 7.17). Zn determinations of the samples $T_{13,}$ T_{14}, and T_{15} were performed with SMDE mode, in which the dilution factors were 0.5/10 for T_{13} and 0.1/10 for T_{14} and T_{15}.

Table 7.17. Zn contents of tuna samples CFB2 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_{13}	19.5 ± 0.6	0.322 ± 0.010	3.11	18.8	0.310
T_{14}	341 ± 4	5.65 ± 0.07	1.22	322	5.34
T_{15}	220 ± 7	3.51 ± 0.12	3.46	205	3.28
T_{16}	1.48 ± 0.03	0.024 ± 0.0005	2.00	1.40	0.023
T_{17}	7.09 ± 0.42	0.114 ± 0.007	6.00	9.02	0.145
T_{18}	10.2 ± 0.3	0.169 ± 0.005	3.00	12.1	0.201

Cd contents of the tuna samples were between 0.052 – 0.075 µg g^{-1}, except the one, T_{14}, which was 0.521 µg g^{-1}. Pb contents were more or less the same; they were in the range of 0.194 µg g^{-1} and 0.341 µg g^{-1} (Table 7.18). Higher standard deviation value for the Pb content of the sample T_{13} was due to the splitted peak which normally did not occur in voltammetric analysis of Pb. However, in this particular sample it was observed. Three of the samples exhibited Cu concentrations between 1.55 µg g^{-1} and 5.93 µg g^{-1}, while samples T_{14} and T_{15} revealed the concentrations as 37.9 µg g^{-1} and 63.9 µg g^{-1}. Cu contents of the samples T_{14} and T_{15} were determined separately, with the dilution factor of 0.5/10.

Table 7.18. Cd, Pb and Cu contents of tuna samples CFB2 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_{13}	Cd	3.79 ± 0.26	0.063 ± 0.004	6.91	4.23	0.069
	Pb	11.8 ± 1.0	0.194 ± 0.017	8.47	11.9	0.198
	Cu	359 ± 26	5.93 ± 0.43	7.28	417	6.88
T_{14}	Cd	31.0 ± 1.0	0.521 ± 0.018	3.48	27.9	0.461
	Pb	18.2 ± 1.1	0.301 ± 0.019	6.21	16.0	0.265
	Cu	2291 ± 155	37.9 ± 2.5	6.77	1925	31.8
T_{15}	Cd	4.69 ± 0.26	0.075 ± 0.004	5.65	5.66	0.090
	Pb	21.3 ± 0.5	0.341 ± 0.008	2.54	14.8	0.236
	Cu	4002 ± 226	63.9 ± 3.6	5.66	3784	60.5
T_{16}	Cd	3.23 ± 0.26	0.053 ± 0.004	8.16	4.63	0.075
	Pb	13.2 ± 1.0	0.214 ± 0.017	7.78	9.49	0.154
	Cu	95.4 ± 2.7	1.55 ± 0.004	2.87	82.3	1.34
T_{17}	Cd	4.39 ± 0.51	0.071 ± 0.008	11.5	4.35	0.070
	Pb	12.3 ± 0.3	0.198 ± 0.005	2.79	10.0	0.161
	Cu	195 ± 11	3.14 ± 0.18	5.87	162	2.62
T_{18}	Cd	3.12 ± 0.24	0.052 ± 0.004	7.77	3.84	0.064
	Pb	20.1 ± 1.7	0.333 ± 0.029	8.77	17.2	0.284
	Cu	154 ± 6	2.55 ± 0.10	4.09	189	3.14

Tuna samples CFB7 brand with the expiration date of 08/2016, which was also the serial number, were analyzed. Tuna samples of CFB7 brand had the highest Zn concentrations, ranging between 0.423 mg g^{-1} and 3.54 mg g^{-1}, and Zn content of one of the samples, T_{19} had been recorded as 0.031 mg g^{-1} (Table 7.19). All the Zn content measurements were performed with SMDE mode except for T_{19}, the dilution factor was 0.1/10 for T_{20}, $T_{21,}$ T_{23}, and T_{24}; and it was 0.5/10 for T_{22}.

Table 7.19. Zn contents of tuna samples CFB7 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_{19}	1.86 ± 0.06	0.031 ± 0.001	3.29	1.82	0.030
T_{20}	206 ± 99	3.38 ± 0.162	4.79	197	3.24
T_{21}	118 ± 6	1.97 ± 0.107	5.42	108	1.79
T_{22}	25.7 ± 1.7	0.423 ± 0.029	6.77	29.3	0.483
T_{23}	141 ± 3	2.35 ± 0.053	2.25	146	2.45
T_{24}	214 ± 7	3.54 ± 0.120	3.39	220	3.64

Cd amount of the samples were generally in the range of 0 – 0.094 µg g^{-1}, yet one of the samples, T_{23} had been recorded as 0.293 µg g^{-1}. The Pb concentrations were close to each other, they varied between 0.176 µg g^{-1} and 0.730 µg g^{-1}. Cu concentrations ranged

from 2.01 µg g^{-1} to 54.4 µg g^{-1} (Table 7.20). Cu contents of the samples except for T_{19} and T_{22} were determined separately, with dilution factor of 0.5/10.

Table 7.20. Cd, Pb and Cu contents of tuna samples CFB7 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_{19}	Cd	4.68 ± 0.23	0.077 ± 0.004	4.83	3.54	0.058
	Pb	10.7 ± 0.6	0.176 ± 0.009	5.49	9.65	0.159
	Cu	122 ± 10	2.01 ± 0.16	8.15	82.2	1.35
T_{20}	Cd	5.75 ± 0.19	0.094 ± 0.003	3.44	3.53	0.058
	Pb	30.6 ± 0.7	0.503 ± 0.012	2.34	23.7	0.390
	Cu	2346 ± 73	38.5 ± 1.2	3.12	2784	45.7
T_{21}	Cd	0	0	-	0	0
	Pb	30.4 ± 2.3	0.505 ± 0.038	7.58	28.2	0.469
	Cu	3271 ± 244	54.4 ± 4.1	7.46	3598	59.9
T_{22}	Cd	4.36 ± 0.33	0.072 ± 0.005	7.58	4.81	0.079
	Pb	26.7 ± 0.6	0.439 ± 0.010	2.35	24.6	0.406
	Cu	470 ± 18	7.73 ± 0.30	3.93	588	9.69
T_{23}	Cd	17.6 ± 0.6	0.293 ± 0.010	3.48	11.8	0.197
	Pb	34.9 ± 1.4	0.582 ± 0.024	4.17	30.1	0.501
	Cu	1148 ± 66	19.1 ± 1 .1	5.76	1292	21.5
T_{24}	Cd	1.91 ± 0.16	0.032 ± 0.003	8.60	1.05	0.017
	Pb	44.1 ± 1.2	0.73 ± 0.02	2.81	20.6	0.341
	Cu	2239 ± 168	37.1 ± 2.8	7.52	2508	41.5

Tuna samples CFB8 brand with a serial number of DGL 2179 and the production date of 06/2012 were analyzed. Zn concentrations were recorded from 0.169 mg g^{-1} to 0.613 mg g^{-1}. All of the Zn content analyses were performed with SMDE mode electrode with the dilution factor of 0.5/10 (Table 7.21).

Table 7.21. Zn contents of CFB8 brand tuna samples

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_{25}	33.6 ± 3.9	0.548 ± 0.065	11.8	39.4	0.642
T_{26}	37.1 ± 0.5	0.613 ± 0.008	1.31	35.3	0.583
T_{27}	26.1 ± 0.3	0.433 ± 0.006	1.15	26.9	0.447
T_{28}	10.2 ± 0.2	0.169 ± 0.004	2.23	10.9	0.181
T_{29}	19.6 ± 0.2	0.326 ± 0.037	11.3	18.4	0.306

Cd contents of the samples resembled to the results of the other brands of canned tuna samples, ranging between 0 – 0.113 µg g^{-1}. Pb contents were between the range of

0.290 µg g^{-1} and 0.517 µg g^{-1}. Cu contents were between the range of 2.40 µg g^{-1} and 25.8 µg g^{-1} (Table 7.22). Cu contents of the samples T_{26} and T_{29} were determined separately with the dilution factor of 0.5/10.

Table 7.22. Cd, Pb and Cu contents of tuna samples CFB8 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_{25}	Cd	0.831 ± 0.064	0.014 ± 0.001	7.70	0.742	0.012
	Pb	17.8 ± 0.3	0.290 ± 0.005	1.95	13.9	0.228
	Cu	473 ± 24	7.72 ± 0.38	5.04	606	9.88
T_{26}	Cd	3.54 ± 0.19	0.058 ± 0.003	5.51	3.55	0.058
	Pb	31.2 ± 0.31	0.517 ± 0.005	0.98	26.1	0.431
	Cu	1264 ± 344	20.9 ± 0.5	2.72	1090	18.0
T_{27}	Cd	0	0	-	0	0
	Pb	18.9 ± 1.9	0.314 ± 0.033	10.6	12.2	0.202
	Cu	275 ± 15	4.56 ± 0.25	5.41	295	4.89
T_{28}	Cd	6.85 ± 0.64	0.113 ± 0.011	9.30	6.15	0.102
	Pb	26.1 ± 1.3	0.432 ± 0.022	5.02	21.9	0.364
	Cu	145 ± 6	2.40 ± 0.1	4.12	232	3.84
T_{29}	Cd	0	0	-	0	0
	Pb	22.7 ± 1.8	0.377 ± 0.030	8.07	17.1	0.285
	Cu	1550 ± 125	25.8 ± 2.1	8.08	1643	27.3

CFB9 brand tuna samples with the serial number of TR 17.50 and the expiration date of 08/2016 were analyzed. DPASV analyses of Zn concentrations were in agreement with ICP-OES results. The content range was between 0.028 mg g^{-1} and 0.945 mg g^{-1} (Table 7.23). Analyses of the samples $T_{31,}$ T_{32}, T_{33}, and T_{35} were performed with SMDE mode with the dilution factor of 0.5/10.

Table 7.23. Zn contents of tuna samples CFB9 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_{30}	2.98 ± 0.17	0.049 ± 0.003	5.77	2.42	0.040
T_{31}	57.6 ± 4.4	0.945 ± 0.072	7.61	55.3	0.907
T_{32}	34.8 ± 1.4	0.565 ± 0.022	4.00	37.9	0.616
T_{33}	11.0 ± 0.1	0.183 ± 0.002	1.32	13.5	0.224
T_{34}	1.72 ± 0.13	0.028 ± 0.002	7.64	1.69	0.028
T_{35}	25.5 ± 0.2	0.415 ± 0.004	0.93	24.2	0.395

Cd concentrations of the samples were 0 µg g^{-1}, except for the one, T_{33} which contained 0.028 µg g^{-1} of Cd. These values were the lowest Cd concentrations that were

measured amongst the canned tuna fish samples. Pb concentrations were recorded between 0.206 µg g^{-1} and 0.678 µg g^{-1}, one of the samples had the Pb content as 0 µg g^{-1}. Cu concentrations were rather in the similar range, they were measured from 1.34 µg g^{-1} to 13.8 µg g^{-1}. DPASV analyses of each of the samples T_{31}-T_{33} were performed three times till peak splitting or shifted base-lines were not observed for Cu analysis (Table 7.24).

Table 7.24. Cd, Pb and Cu contents of tuna samples CFB9 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_{30}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	836 ± 41	13.8 ± 0.7	4.87	886	14.7
T_{31}	Cd	0	0	-	0	0
	Pb	41.3 ± 0.7	0.678 ± 0.011	1.66	29.6	0.485
	Cu	484 ± 28	7.94 ± 0.45	5.70	687	11.3
T_{32}	Cd	0	0	-	0	0
	Pb	31.4 ± 0.9	0.509 ± 0.016	3.11	25.2	0.409
	Cu	619 ± 14	10.1 ± 0.2	2.36	869	14.1
T_{33}	Cd	1.69 ± 0.15	0.028 ± 0.002	8.72	1.23	0.020
	Pb	18.1 ± 0.9	0.30 ± 0.02	5.08	12.4	0.205
	Cu	376 ± 13	6.24 ± 0.21	3.44	469	7.79
T_{34}	Cd	0	0	-	0	0
	Pb	12.6 ± 1.0	0.206 ± 0.016	8.00	10.7	0.175
	Cu	81.9 ± 7.7	1.34 ± 0.12	9.39	94.4	1.54
T_{35}	Cd	0	0	-	0	0
	Pb	39.2 ± 1.4	0.639 ± 0.023	3.54	31.0	0.504
	Cu	678 ± 29	11.0 ± 0.5	4.34	658	10.8

Second can of the CFB8 brand tuna samples with the serial number of DGL 2179 and the production date of 06/2012 were analyzed. The Zn contents of the samples were rather lower than the first can of the same brand, the highest recorded amount was 1.09 mg g^{-1}, where 0.021 mg g^{-1} of Zn was measured as the lowest amount (Table 7.25). Zn content analysis of the sample T_{37} was performed by SMDE mode, with dilution factor of 0.2/10.

Table 7.25. Zn contents of tuna samples CFB8 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
T_{36}	1.32 ± 0.03	0.022 ± 0.0004	2.07	1.23	0.020
T_{37}	65.5 ± 0.7	1.09 ± 0.01	1.14	67.2	1.12
T_{38}	8.59 ± 0.08	0.143 ± 0.001	0.89	7.07	0.118
T_{39}	1.25 ± 0.03	0.021 ± 0.0005	2.24	0.864	0.014

Cd concentrations of the tuna samples were measured 0.070 µg g^{-1} and 0.071 µg g^{-1}, while two of the samples were recorded as 0 µg g^{-1} of Cd. Pb contents were between 0.106 µg g^{-1} and 0.727 µg g^{-1}, Cu concentrations were measured between 1.56 µg g^{-1} and 18.6 µg g^{-1} (Table 7.26). Cu content of the sample T_{37} was determined separately, with the dilution factor of 0.5/10.

Table 7.26. Cd, Pb and Cu contents of tuna samples CFB8 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
T_{36}	Cd	4.29 ± 0.25	0.071 ± 0.004	5.91	3.78	0.062
	Pb	10.5 ± 0.74	0.172 ± 0.012	7.08	7.05	0.116
	Cu	332 ± 10	5.45 ± 0.17	3.05	369	6.07
T_{37}	Cd	4.24 ± 0.33	0.070 ± 0.005	7.71	3.47	0.058
	Pb	43.8 ± 2.5	0.727 ± 0.041	5.63	34.4	0.571
	Cu	1123 ± 38	18.6 ± 0.6	3.41	1212	20.2
T_{38}	Cd	0	0	-	0	0
	Pb	14.2 ± 0.5	0.236 ± 0.008	3.32	9.26	0.154
	Cu	145 ± 4	2.41 ± 0.06	2.44	173	2.88
T_{39}	Cd	0	0	-	0	0
	Pb	6.44 ± 0.78	0.106 ± 0.013	12.1	5.53	0.091
	Cu	95.2 ± 8.1	1.56 ± 0.13	8.56	69.8	1.15

7.3. Analysis of Anchovy Samples

Fresh anchovy fish purchased from Gelibolu, Çanakkale and frozen and canned samples purchased from groceries in Istanbul, were analyzed. Each sample represented the whole anchovy fish, and the sample tissues were taken from both left and right sides of its spine. 1.50 ± 0.02 g of samples were weighed and they were digested in in 12 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v) for approximately 15 hours. DPASV determinations were done with 2 mL sample solution for Cd, Pb and Cu; and 0.2 mL sample for Zn by HMDE mode of the electrode. Irregular cases were specified along the analyses.

7.3.1. Fresh Anchovy Samples

Cd contents of the fresh anchovy samples were in a wide range (Table 7.27), six out of twelve samples had the Cd concentration as 0 µg g^{-1}, for the others Cd range was 0.092-

1.05 µg g^{-1}. The Pb content varied between 0 and 1.59 µg g^{-1}. Cu concentrations were between 1.28 µg g^{-1} and 8.63 µg g^{-1}, and 13.8 µg g^{-1} – 39.6 µg g^{-1}. Cu contents of the samples A_9, $A_{10,}$ A_{13}, A_{15}, $A_{16,}$ and A_{17} were determined separately, with the dilution factor of 0.5/10.

Table 7.27. Cd, Pb and Cu contents of fresh anchovy samples.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_8	Cd	0	0	-	0	0
	Pb	13.8 ± 0.9	0.163 ± 0.011	6.59	8.54	0.101
	Cu	108 ± 4	1.28 ± 0.05	3.65	85.7	1.01
A_9	Cd	9.01 ± 0.51	0.104 ± 0.006	5.60	10.9	0.126
	Pb	42.9 ± 2.3	0.496 ± 0.026	5.33	38.2	0.442
	Cu	1885 ± 85	21.8 ± 0.9	4.53	2279	26.3
A_{10}	Cd	89.8 ± 9.0	1.05 ± 0.11	10.0	74.6	0.875
	Pb	136 ± 2	1.59 ± 0.03	1.68	116	1.36
	Cu	3379 ± 75	39.6 ± 0.9	2.23	3522	41.3
A_{11}	Cd	0	0	-	0	0
	Pb	39.3 ± 1.2	0.467 ± 0.014	3.04	37.7	0.449
	Cu	725 ± 29	8.63 ± 0.35	4.09	777	9.24
A_{12}	Cd	10.2 ± 0.14	0.121 ± 0.002	1.38	9.17	0.109
	Pb	15.9 ± 0.5	0.188 ± 0.006	3.11	13.0	0.155
	Cu	189 ± 16	2.24 ± 0.18	8.23	176	2.08
A_{13}	Cd	7.48 ± 0.82	0.10 ± 0.01	11.0	11.2	0.135
	Pb	48.8 ± 2.4	0.588 ± 0.029	4.98	36.8	0.443
	Cu	1319 ± 107	15.9 ± 1.3	8.08	1375	16.6
A_{14}	Cd	0	0	-	0	0
	Pb	19.9 ± 0.6	0.244 ± 0.007	2.80	15.5	0.189
	Cu	189 ± 6	2.24 ± 0.08	3.33	121	1.48
A_{15}	Cd	7.78 ± 0.52	0.092 ± 0.006	6.63	9.63	0.114
	Pb	39.1 ± 3.1	0.462 ± 0.036	7.86	28.7	0.339
	Cu	2919 ± 252	34.5 ± 2.9	8.63	3328	39.3
A_{16}	Cd	22.8 ± 1.4	0.276 ± 0.017	6.14	26.8	0.325
	Pb	53.1 ± 2.4	0.643 ± 0.029	4.49	52.9	0.642
	Cu	1140 ± 50	13.8 ± 0.7	5.02	730	8.9
A_{17}	Cd	0	0	-	0	0
	Pb	20.9 ± 1.0	0.256 ± 0.013	5.03	22.2	0.272
	Cu	1158 ± 22	14.2 ± 0.3	1.88	1356	16.6
A_{18}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	203 ± 19	3.31 ± 0.31	9.48	160	2.61
A_{19}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	596 ± 21	9.86 ± 0.35	3.54	90.8	1.50

Zn concentrations of the samples were diversified in a wide range; they were classified in between 0.021 mg g^{-1} – 0.203 mg g^{-1} and 0.892 mg g^{-1} – 6.33 mg g^{-1} (Table 7.28). Zn concentrations of the samples were determined by SMDE mode, except the samples A_8, A_{12}, A_{14}, and A_{19}. Dilution factor was 0.5/10 for the sample A_{18}, 0.2/10 for A_{11}, 0.1/10 for A_9, A_{13}, and A_{17}, 0.05 for A_{10}, A_{15}, and A_{16}.

Table 7.28. Zn contents of fresh anchovy samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_8	1.64 ± 0.03	0.019 ± 0.001	1.92	1.21	0.014
A_9	292 ± 3	3.38 ± 0.03	0.96	274	3.17
A_{10}	438 ± 5	5.14 ± 0.06	1.15	455	5.34
A_{11}	74.9 ± 0.3	0.892 ± 0.004	0.45	67.6	0.804
A_{12}	4.04 ± 0.07	0.048 ± 0.001	1.75	5.65	0.067
A_{13}	103 ± 1	1.24 ± 0.01	0.88	105	1.26
A_{14}	3.27 ± 0.45	0.040 ± 0.006	13.8	2.99	0.037
A_{15}	417 ± 2	4.93 ± 0.02	0.49	435	5.14
A_{16}	522 ± 25	6.33 ± 0.31	4.85	523	6.34
A_{17}	112 ± 1	1.37 ± 0.01	0.55	98.8	1.21
A_{18}	12.5 ± 0.5	0.203 ± 0008	3.89	14.1	0.230
A_{19}	1.28 ± 0.05	0.021 ± 0.001	4.03	0.988	0.016

7.3.2. Canned and Frozen Anchovy Samples

Yakşi brand of canned anchovy samples and three different brands of frozen samples, FFB1, FFB2 and FFB3 were investigated. Canned anchovy samples CFB1 brand with the serial number of 008 and a production date of 08/10 were analyzed. The Zn range of anchovy samples of CFB1 brand was between 0.088 mg g^{-1} and 0.146 mg g^{-1} (Table 7.29). ICP-OES and DPASV results were in good agreement with each other.

Zn determinations of the samples were performed with HMDE mode. Dilution factor was 0.2/10.

Table 7.29. Zn contents of the anchovy samples CFB1 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_5	11.7 ± 0.3	0.146 ± 0.003	2.30	10.2	0.127
A_6	10.2 ± 0.2	0.127 ± 0.002	1.79	9.91	0.123
A_7	7.13 ± 0.01	0.088 ± 0.000	0.15	7.74	0.096

Cd contents of the samples were measured between 0.078 µg g^{-1} and 0.199 µg g^{-1}, Pb concentrations were in the range of 0.848 µg g^{-1} and 0.904 µg g^{-1}, and Cu concentrations were recorded between 0.887 µg g^{-1} and 6.38 µg g^{-1}. (Table 7.30). Inconsistency between the results of DPASV and ICP-OES analyses of Cu content for samples A_6 and A_7 had been tried to be diminished; however, the DPASV analyses could not be repeated with EDTA due to the lack of sample stock.

Table 7.30. Cd, Pb and Cu contents of anchovy samples CFB1 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_5	Cd	16.0 ± 0.8	0.199 ± 0.009	4.98	19.1	0.248
	Pb	72.0 ± 3.8	0.899 ± 0.047	5.24	77.8	0.972
	Cu	275 ± 13	3.43 ± 0.16	4.66	268	3.35
A_6	Cd	12.5 ± 1.1	0.156 ± 0.014	8.82	12.5	0.156
	Pb	72.5 ± 2.4	0.904 ± 0.029	3.32	55.8	0.696
	Cu	71.2 ± 6.0	0.887 ± 0.075	8.45	176	2.19
A_7	Cd	6.34 ± 0.34	0.078 ± 0.004	5.36	8.28	0.102
	Pb	68.6 ± 2.0	0.848 ± 0.025	2.97	43.7	0.539
	Cu	516 ± 9	6.38 ± 0.12	1.82	242	2.99

Frozen anchovy samples FFB1 brand with the serial number of 01113321 and the expiration date of 06/2013 were analyzed. Zn concentrations were measured between 0.067 - 0.214 mg L^{-1} and 0.489 – 1.49 mg g^{-1} (Table 7.31). Analyses of the samples A_{21}, and A_{23}, were performed with SMDE mode and the dilution factor of 0.5/10, where the dilution factor was 0.2/10 for the sample A_{22}, with SMDE mode.

Cd contents of the samples were recorded as 0 µg g^{-1}, except for the sample A_{21}, which was measured as 0.046 µg g^{-1}. Pb concentrations were between 0 – 0.382 µg g^{-1}, which were lower than the canned anchovy samples. Cu contents of the samples were in the range between 2.51 µg g^{-1} and 11.3 µg g^{-1} (Table 7.32). The DPASV analysis of Cu for the sample A_{25} was carried with 5 x 10^{-3} mol L^{-1} of EDTA. Sample volume was taken as1 mL.

Table 7.31. Zn contents of Anchovy samples FFB1 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_{20}	5.13 ± 0.4	0.084 ± 0.006	7.40	4.45	0.073
A_{21}	12.9 ± 0.4	0.214 ± 0.007	3.33	8.71	0.144
A_{22}	92.4 ± 0.8	1.49 ± 0.01	0.91	105	1.69
A_{23}	30.4 ± 0.2	0.489 ± 0.003	0.62	28.3	0.454
A_{24}	11.3 ± 0.3	0.184 ± 0.005	2.93	11.7	0.190
A_{25}	4.02 ± 0.26	0.067 ± 0.004	6.60	4.27	0.071

Table 7.32. Cd, Pb and Cu contents of anchovy samples FFB1 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_{20}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	371 ± 26	6.11 ± 0.4	7.03	322	5.30
A_{21}	Cd	2.81 ± 0.24	0.046 ± 0.004	8.64	1.33	0.022
	Pb	23.2 ± 1.3	0.382 ± 0.022	5.71	17.5	0.289
	Cu	452 ± 20	7.44 ± 0.33	4.38	452	7.45
A_{22}	Cd	0	0	-	0	0
	Pb	16.4 ± 1.1	0.266 ± 0.018	6.82	11.7	0.190
	Cu	170 ± 3	2.74 ± 0.05	1.74	222	3.59
A_{23}	Cd	0	0	-	0	0
	Pb	16.1 ± 1.5	0.259 ± 0.024	9.35	12.5	0.201
	Cu	705 ± 56	11.3 ± 0.9	7.96	743	11.9
A_{24}	Cd	0	0	-	0	0
	Pb	8.01 ± 0.60	0.131 ± 0.009	7.53	7.98	0.130
	Cu	154 ± 10	2.51 ± 0.16	6.51	201	3.28
A_{25}	Cd	0	0	-	0	0
	Pb	21.8 ± 1.8	0.362 ± 0.029	8.06	20.8	0.345
	Cu*	240 ± 6	3.97 ± 0.11	2.70	244	4.04

Anchovy samples FFB2 brand with the serial number of L212031 and the expiration date of 04/2014 were analyzed. Cd amounts of the samples were between 0 and 0.104 µg g^{-1}, also they were in good agreement with ICP-OES results. The results of the DPASV analyses of Pb contents showed that samples contained Pb in the range of 0.066 µg g^{-1} and 0.249 µg g^{-1}, which were the lowest Pb concentrations recorded amongst the other anchovy samples. Cu concentrations were between 1.78 µg g^{-1} and 12.3 µg g^{-1} (Table 7.33).

Table 7.33. Cd, Pb and Cu contents anchovy samples FFB2 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_{26}	Cd	0.849 ± 0.039	0.014 ± 0.001	4.62	0.809	0.014
	Pb	4.65 ± 0.11	0.077 ± 0.002	2.43	3.32	0.055
	Cu	417 ± 34	6.96 ± 0.56	8.11	456	7.6
A_{27}	Cd	0	0	-	0	0
	Pb	9.59 ± 0.16	0.161 ± 0.003	1.65	7.62	0.123
	Cu	361 ± 32	6.04 ± 0.53	8.80	366	6.12
A_{28}	Cd	0	0	-	0	0
	Pb	7.55 ± 0.37	0.118 ± 0.006	4.94	7.66	0.119
	Cu	236 ± 19	3.69 ± 0.29	8.10	242	3.77
A_{29}	Cd	5.22 ± 0.11	0.088 ± 0.002	2.03	4.76	0.080
	Pb	14.9 ± 0.7	0.249 ± 0.012	4.85	16.4	0.276
	Cu	106 ± 8	1.78 ± 0.13	7.54	129	2.17
A_{30}	Cd	2.58 ± 0.09	0.041 ± 0.001	3.38	4.72	0.075
	Pb	7.76 ± 0.18	0.124 ± 0.003	2.28	7.45	0.118
	Cu	126 ± 5	2.01 ± 0.08	3.74	155	2.47
A_{31}	Cd	6.16 ± 0.53	0.104 ± 0.009	8.58	8.45	0.142
	Pb	3.93 ± 0.26	0.066 ± 0.004	6.74	4.71	0.079
	Cu	727 ± 45	12.3 ± 0.7	6.16	900	15.2
A_{32}	Cd	2.87 ± 0.11	0.048 ± 0.002	3.87	3.56	0.059
	Pb	7.15 ± 0.21	0.119 ± 0.004	2.98	6.94	0.116
	Cu	203 ± 11	3.39 ± 0.19	5.57	177	2.96
A_{33}	Cd	2.98 ± 0.23	0.048 ± 0.004	7.78	2.59	0.041
	Pb	7.52 ± 0.61	0.120 ± 0.009	8.15	5.16	0.082
	Cu	112 ± 17	1.79 ± 0.28	15.7	133	2.12

Table 7.34. Zn contents of anchovy samples FFB2 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_{26}	33.7 ± 0.2	0.561 ± 0.003	0.61	34.8	0.581
A_{27}	6.0 ± 0.6	0.100 ± 0.011	11.0	4.29	0.072
A_{28}	2.89 ± 0.16	0.045 ± 0.002	5.73	2.92	45.5
A_{29}	3.08 ± 0.23	0.05 ± 0.004	7.57	2.67	0.045
A_{30}	3.98 ± 0.22	0.063 ± 0.004	5.54	3.68	0.058
A_{31}	16.0 ± 0.1	0.270 ± 0.002	0.90	18.7	0.314
A_{32}	3.36 ± 0.09	0.056 ± 0.001	2.60	3.68	0.061
A_{33}	3.35 ± 0.21	0.053 ± 0.003	6.29	3.27	0.052

Zn concentrations of the samples were mostly between 0.045 – 0.063 mg g^{-1}, but two of the samples indicated the corresponding Zn concentrations as 0.270 mg g^{-1} and 0.561 mg g^{-1}. Zn content determination of the samples A_{26} and A_{31} was performed by SMDE mode, with the dilution factor of 0.5/10 (Table 7.34).

Frozen anchovy samples of FFB3 brand with the serial number of PK09604 and the expiration date of 12/2012 were analyzed. Cd contents of the samples were between 0 – 0.026 µg g^{-1}. DPASV results of the Pb analyses revealed the concentrations between 0 – 0.307 µg g^{-1}, and Cu contents were between 0.731 µg g^{-1} – 4.88 µg g^{-1} and 20.5 – 21.5 µg g^{-1} (Table 7.35). Cu contents of the samples A_{39}, A_{41}, and A_{42} were determined separately, with the dilution factor of 0.5/10. Sample A_{35} was analyzed with $1x10^{-2}$ mol L^{-1} of EDTA.

Table 7.35. Cd, Pb and Cu contents of anchovy samples FFB3 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
A_{34}	Cd	0	0	-	0	0
	Pb	11.8 ± 0.3	0.195 ± 0.005	2.65	10.4	0.172
	Cu	224 ± 12	3.72 ± 0.19	5.33	254	4.20
A_{35}	Cd	1.71 ± 0.09	0.026 ± 0.001	5.28	1.73	0.026
	Pb	11.5 ± 0.2	0.178 ± 0.003	1.73	9.73	0.151
	Cu	118 ± 1	1.83 ± 0.016	0.016	97.3	1.51
A_{36}	Cd	0	0	-	0	0
	Pb	5.92 ± 0.24	0.099 ± 0.004	4.05	6.80	0.114
	Cu	292 ± 21	4.88 ± 0.36	7.33	298	4.97
A_{37}	Cd	0	0	-	0	0
	Pb	18.6 ± 0.6	0.307 ± 0.009	3.24	22.6	0.374
	Cu	218 ± 5	3.59 ± 0.07	2.15	230	3.79
A_{38}	Cd	0.532 ± 0.056	0.009 ± 0.001	10.5	0.550	0.013
	Pb	6.52 ± 0.49	0.108 ± 0,008	7.56	5.49	0.090
	Cu	44.3 ± 4.7	0.731 ± 0.078	10.6	55.1	0.909
A_{39}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	1281 ± 26	21.5 ± 0.4	2.04	1599	26.8
A_{40}	Cd	0	0	-	0	0
	Pb	10.5 ± 0.5	0.173 ± 0.008	4.59	10.9	0.180
	Cu	251 ± 5.3	4.14 ± 0.09	2.11	120	1.98
A_{41}	Cd	0	0	-	0	0
	Pb	0	0	-	0	0
	Cu	1234 ± 77	20.5 ± 1.3	6.27	1045	17.4
A_{42}	Cd	0	0	-	0	0
	Pb	15.5 ± 0.9	0.249 ± 0.014	5.67	11.8	0.989
	Cu	1279 ± 10	20.9 ± 0.1	0.79	1434	23.1

Table 7.36. Zn contents of anchovy samples FFB3 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
A_{34}	23.8 ± 0.2	0.395 ± 0.003	0.75	25.1	0.416
A_{35}	4.03 ± 0.14	0.063 ± 0.002	3.55	3.75	0.058
A_{36}	2.64 ± 0. 10	0.044 ± 0.002	3.88	2.86	0.048
A_{37}	21.3 ± 0.3	0.352 ± 0.005	1.45	25.2	0.416
A_{38}	3.69 ± 0.06	60.9 ± 1.1	1.75	3.99	0.066
A_{39}	72.2 ± 0.7	1.21 ± 0.012	0.97	86.4	1.45
A_{40}	18.5 ± 1.2	0.307 ± 0.019	6.35	16.8	0.278
A_{41}	2.79 ± 0.14	0.046 ± 0.002	5.03	2.20	0.037
A_{42}	81.4 ± 0.7	1.31 ± 0.01	0.97	91.4	1.47

Zn concentrations of the anchovy samples FFB3 brand were between 0.044 -0.063 mg g^{-1} and 0.307 – 1.31 mg g^{-1} (Table 7.36). Zn contents of the samples $A_{34,}$ A_{37}, and A_{40} were determined by SMDE mode with the dilution factor of 0.5/10, and the samples A_{39} and A_{42} were analyzed by SMDE with dilution factor of 0.2/10.

7.4. Analysis of Corn Samples

Canned corn samples of five different brands that have been purchased from groceries were analyzed. The brands were CB1, CB2, CB3, CB4 and CB5. Analyses were performed with 1.50 ± 0.02 g of air dried sweet corn samples. They were digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Sample dilution factors were between 0.2/10 and 2/10 range.

7.4.1. Canned Corn Samples

Corn samples CB1 brand with the expiration date of 02/2015 and the serial number of L2158 were analyzed. Cd contents of the samples were between 0 µg g^{-1} and 0.055 µg g^{-1}. Pb concentrations were in the range of 0.299 µg g^{-1} and 0.634 µg g^{-1}, where measured amounts of Cu contents were between 10.6 – 45.5 µg g^{-1}. Cu determination of the sample C_8 was performed with 1 x 10^{-2} mol L^{-1} of EDTA in order to obtain a more accurate result (Table 7.37). Also, Cu contents of the samples C_6 and C_7 were determined separately with the dilution factor of 0.5/10.

Table 7.37. Cd, Pb and Cu contents of corn samples CB1 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_6	Cd	4.50 ± 0.40	0.055 ± 0.005	8.78	2.76	0.034
	Pb	51.9 ± 1.6	0.634 ± 0.019	3.10	39.1	0.477
	Cu	3726 ± 187	45.5 ± 2.3	5.03	3280	40.1
C_7	Cd	2.66 ± 0.15	0.032 ± 0.002	5.56	1.28	0.016
	Pb	37.2 ± 1.3	0.453 ± 0.015	3.41	32.3	0.394
	Cu	1538 ± 123	18.7 ± 1.5	8.00	1548	18.8
C_8	Cd	0	0	-	0	0
	Pb	25.1 ± 1.6	0.299 ± 0.019	6.23	22.5	0.269
	Cu*	883 ± 16	10.6 ± 0.2	1.81	873	10.4

*Cu determination was performed with 1 x 10^{-2} mol L^{-1} of EDTA with 1 mL of sample.

Zn concentrations of the samples were between 0.071 mg g^{-1} – 0.772 mg g^{-1}, which were consistent with ICP-OES results (Table 7.38). Samples C_6 and C_7 were analyzed by SMDE mode, with the dilution factors of 0.5/10 and 0.2/10, respectively.

Table 7.38. Zn contents of corn sample CB1 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_6	27.6 ± 2.2	0.338 ± 0.028	8.15	26.4	0.323
C_7	63.4 ± 0.6	0.772 ± 0.008	0.97	75.3	0.917
C_8	5.96 ± 0.25	0.071 ± 0.003	4.27	5.63	0.067

Corn samples of CB2 Brand with the serial number of PN:03 and production date of 01/2012 were analyzed. Cd contents recorded by the ICP-OES were approximately half of the values that the DPASV analysis measured. The corresponding Cu contents of the samples were relatively high, so the samples were diluted by a factor of ten. Inconsistency of the Cd concentrations between DPASV and ICP-OES analyses was related to this situation. Under the stated conditions, voltammograms of Cu had shifted base-lines and split peaks in some of the measurements. Hence, the Cu concentration of the sample C_9 was determined with 5 x 10^{-2} mol L^{-1} of EDTA, where samples C_{10} and C_{11} were analyzed with 5 x 10^{-3} mol L^{-1} of EDTA. Cu contents were measured between 3.36 µg g^{-1} and 21.4 µg g^{-1}. Cd contents were registered between 0.026 µg g^{-1} and 0.065 µg g^{-1}; Pb concentrations were recorded in the range of 0.232 - 0.506 µg g^{-1} (Table 7.39).

Table 7.39. Cd, Pb and Cu contents of corn samples CB2 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_9	Cd	2.19 ± 0.12	0.026 ± 0.001	5.61	1.58	0.019
	Pb	19.4 ± 0.6	0.232 ± 0.007	3.28	18.2	0.217
	Cu	1794 ± 26	21.4 ± 0.3	1.45	1406	16.8
C_{10}	Cd	5.49 ± 0.36	0.065 ± 0.004	6.61	2.39	0.028
	Pb	42.6 ± 2.5	0.506 ± 0.029	5.93	37.5	0.445
	Cu	520 ± 22	6.17 ± 0.26	4.28	565	6.70
C_{11}	Cd	3.89 ± 0.20	0.047 ± 0.002	5.19	1.72	0.021
	Pb	30.5 ± 1.1	0.366 ± 0.013	3.58	26.0	0.312
	Cu	280 ± 5	3.36 ± 0.061	0.18	305	3.65

Zn concentrations of the samples were recorded between 0.022 mg g^{-1} and 0.384 mg g^{-1}, agreement with the ICP-OES results were achieved (Table 7.40). Zn content analysis of the sample C_9 was performed by SMDE mode, with the dilution factor of 0.5/10.

Table 7.40. Zn contents of corn samples CB2 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_9	32.2 ± 0.3	0.384 ± 0.041	10.6	29.9	0.357
C_{10}	3.48 ± 0.05	0.041 ± 0.001	1.36	3.51	0.042
C_{11}	1.85 ± 0.02	0.022 ± 0.0002	0.97	1.72	0.021

Corn samples CB3 brand with the serial number of PK 156.12.35 and the expiration date of 06/2015 were analyzed. Zn contents of the samples were between 0.012 – 0.057 µg g^{-1} (Table 7.41).

Table 7.41. Zn contents of corn samples CB3 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_{12}	3.47 ± 0.29	0.057 ± 0.005	8.25	2.54	0.042
C_{13}	0.759 ± 0.018	0.012 ± 0.0003	2.43	0.718	0.012
C_{14}	1.61 ± 0.12	0.026 ± 0.002	7.74	1.96	0.032
C_{15}	1.58 ± 0.027	0.025 ± 0.0001	1.71	1.74	0.028
C_{16}	2.37 ± 0.26	0.039 ± 0.004	11.1	2.40	0.039
C_{17}	2.47 ± 0.08	0.041 ± 0.001	3.35	2.68	0.045

Cd concentrations were recorded mostly between 0 – 0.041 µg g^{-1}, except for the sample C_{15} the corresponding Cd concentration was relatively high, i.e., 0.166 µg g^{-1}. Pb contents were between 0.194 – 0.899 µg g^{-1}; Cu concentrations were recorded from 1.18 µg g^{-1} to 5.24 µg g^{-1} (Table 7.42).

Table 7.42. Cd, Pb and Cu contents of corn samples CB3 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_{12}	Cd	1.21 ± 0.11	0.020 ± 0.002	8.83	1.06	0.018
	Pb	14.1 ± 0.5	0.233 ± 0.008	3.45	13.4	0.222
	Cu*	247 ± 18	4.09 ± 0.303	7.39	256	4.24
C_{13}	Cd	1.55 ± 0.13	0.026 ± 0.002	8.51	1.64	0.027
	Pb	14.3 ± 1.07	0.237 ± 0.018	7.45	18.2	0.302
	Cu	71.3 ± 2.7	1.18 ± 0.04	3.84	48.7	0.807
C_{14}	Cd	0	0	-	0	0
	Pb	55.4 ± 1.9	0.898 ± 0.031	3.40	63.9	1.04
	Cu	323 ± 28	5.24 ± 0.45	8.56	340	5.52
C_{15}	Cd	10.5 ± 0.3	0.166 ± 0.004	2.74	11.3	0.180
	Pb	56.7 ± 5.9	0.899 ± 0.094	10.5	91.3	1.45
	Cu	314 ± 19	5.00 ± 0.31	6.29	342	5.42
C_{16}	Cd	2.48 ± 0.11	0.041 ± 0.002	4.39	2.24	0.037
	Pb	14.6 ± 0.4	0.239 ± 0.006	2.51	12.3	0.202
	Cu	223 ± 10	3.66 ± 0.16	4.41	197	3.23
C_{17}	Cd	0	0	-	0	0
	Pb	11.6 ± 0.6	0.194 ± 0.010	5.36	21.3	0.355
	Cu	150 ± 21	2.51 ± 0.34	13.7	180	3.01

* Cu determination was performed with 5 x 10^{-3} mol L^{-1} of EDTA with 1 mL of sample.

Canned corn samples CB4 brand with a serial number of PN 246-2-19:19-11 and the expiration date of 03/03/2015 were analyzed. Cd concentrations of the samples were recorded as 0 – 0.184 µg g^{-1}, only for the sample C_{25} the result of the DPASV analysis was not consistent with ICP-OES results. Pb concentrations were recorded in the range of 0.071 µg g^{-1} and 2.18 µg g^{-1}; Cu contents were mostly between 1.16 µg g^{-1} and 15.0 µg g^{-1} while samples C_{20} and C_{23} were recorded as 76.1 µg g^{-1} and 132 µg g^{-1}, respectively (Table 7.43). Cu detection of the samples C_{20} and C_{23} were done separately, and the dilution factor was 0.5/10. Samples C_{18} and C_{25} were analyzed with Buffer III composition and 1 mL of 1 x 10^{-3} mol L^{-1} of EDTA.

Table 7.43. Cd, Pb and Cu contents of corn samples CB4 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_{18}	Cd	0	0	-	0	0
	Pb	9.34 ± 1.12	0.155 ± 0.018	12.0	9.51	0.158
	Cu*	78.6 ± 1.9	1.31 ± 0.03	2.40	83.6	1.39
C_{19}	Cd	0	0	-	0	0
	Pb	6.36 ± 0.52	0.105 ± 0.008	8.13	9.34	0.154
	Cu	70.5 ± 3.3	1.16 ± 0.05	4.70	84.7	1.39
C_{20}	Cd	10.9 ± 0.6	0.184 ± 0.011	5.84	10.8	0.182
	Pb	130 ± 9	2.18 ± 0.16	7.29	119	1.99
	Cu	4543 ± 175	76.1 ± 2.9	3.85	4116	69
C_{21}	Cd	0	0	-	0	0
	Pb	6.15 ± 0.34	0.102 ± 0.006	5.51	5.785	0.096
	Cu	94.0 ± 8.0	1.57 ± 0.13	8.51	88.8	1.482
C_{22}	Cd	1.55 ± 0.13	0.026 ± 0.002	8.62	0.912	0.015
	Pb	13.4 ± 0.4	0.224 ± 0.007	3.26	8.25	0.137
	Cu	885 ± 23	15.0 ± 0.4	2.64	704	11.7
C_{23}	Cd	3.59 ± 0.12	0.060 ± 0.002	3.22	2.85	0.047
	Pb	37.8 ± 0.2	0.626 ± 0.004	0.67	26.5	0.439
	Cu	7997 ± 63	132 ± 1.05	0.79	7414	123
C_{24}	Cd	0	0	-	0	0
	Pb	4.38 ± 0.30	0.071 ± 0.005	6.85	3.07	0.050
	Cu	296 ± 25	4.80 ± 0.40	8.36	271.9	4.39
C_{25}	Cd	1.24 ± 0.11	0.020 ± 0.002	8.85	0.445	0.007
	Pb	5.64 ± 0.32	0.093 ± 0.005	5.64	4.21	0.069
	Cu*	78.5 ± 6.2	1.29 ± 0.10	7.86	69.9	1.15

Table 7.44. Zn contents of the corn samples CB4 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_{18}	2.51 ± 0.07	0.042 ± 0.001	2.82	2.435	0.040
C_{19}	2.13 ± 0.06	0.035 ± 0.001	2.64	1.67	0.027
C_{20}	33.5 ± 0.2	0.562 ± 0.004	0.71	25.6	0.429
C_{21}	1.89 ± 0.15	0.031 ± 0.002	7.88	1.82	0.030
C_{22}	8.54 ± 0.33	0.142 ± 0.006	3.91	8.95	0.149
C_{23}	51.5 ± 1.3	0.852 ± 0.022	2.56	45.3	0.749
C_{24}	4.68 ± 0.09	0.076 ± 0.001	2.06	4.05	0.066
C_{25}	2.00 ± 0.04	0.033 ± 0.001	2.14	2.02	0.033

Zn concentrations of the samples were within the range of 0.031 mg g^{-1} and 0.142 mg g^{-1}, except for the samples C_{20} and C_{23}, which were 0.562 mg g^{-1} and 0.852 mg g^{-1} (Table 7.44). In DPASV analysis of C_{20} and C_{23}, SMDE mode was used, and the dilution factor of the analyte was 0.5 /10.

Corn samples CB5 brand with the serial number of SNF1431 and expiration date of 05/2015 were analyzed. Cd contents were recorded between 0.034 µg g^{-1} and 0.077 µg g^{-1}; Pb concentrations were between 0.306 µg g^{-1} and 0.456 µg g^{-1}; Cu concentrations were between 1.04 µg g^{-1} and 4.32 µg g^{-1} (Table 7.45). Cu detection of the sample C_{27} was carried with 1 mL of 1 x 10^{-3} of EDTA with Buffer III.

Table 7.45. Cd, Pb and Cu contents of corn samples CB5 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
C_{26}	Cd	2.05 ± 0.14	0.034 ± 0.002	6.83	1.87	0.031
	Pb	18.4 ± 0.5	0.306 ± 0.009	2.95	15.2	0.252
	Cu	62.5 ± 2.1	1.04 ± 0.04	3.37	82.1	1.37
C_{27}	Cd	3.03 ± 0.15	0.049 ± 0.002	5.02	3.55	0.057
	Pb	27.9 ± 1.8	0.456 ± 0.029	6.55	32.8	0.536
	Cu	183 ± 9	2.98 ± 0.16	4.91	196	3.19
C_{28}	Cd	4.69 ± 0.25	0.077 ± 0.004	5.25	4.08	0.067
	Pb	23.4 ± 0.5	0.386 ± 0.008	1.99	17.8	0.294
	Cu	262 ± 53	4.32 ± 0.878	20.3	263	4.34

Results of the Zn detection in the samples showed that the corn samples of CB5 brand had the Zn concentration between 0.034 mg g^{-1} and 0.041 mg g^{-1} (Table 7.46).

Table 7.46. Zn contents of corn samples CB5 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
C_{25}	2.47 ± 0.06	0.041 ± 0.001	2.46	2.39	0.040
C_{26}	2.11 ± 0.03	0.034 ± 0.0004	1.29	2.40	0.040
C_{27}	2.07 ± 0.03	0.034 ± 0.0004	1.27	3.02	0.049

7.5. Analysis of Tomato Samples

Canned - chopped tomatoes and canned tomato sauces purchased from the groceries in Istanbul were analyzed. The brands were TTB1, TTB2, TTB3 and TTB4. Each sample was taken as 1.50 ± 0.02 grams of wet weight. Samples were digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Sample dilution factors were within 0.1 mL:10 mL and 2 mL:10 mL range. HMDE mode of electrode was used unless stated otherwise.

7.5.1. Canned Tomato Samples

Tomato sauce samples TTB1 brand with the serial number of E49 L 112-2 and expiration date of 08/2014 were analyzed. Cd range of the samples was 0.028 – 0.089 µg g^{-1}; Pb range was 0.274 – 0.928 µg g^{-1}; Cu range was 4.46 – 98.4 µg g^{-1} (Table 7.47); Zn range was 0.212 – 1.10 mg g^{-1} (Table 7.48). Cu detections of the samples TT_7 and TT_8 were performed separately, with dilution factor of 0.5/10. Zn analysis was carried with SMDE mode with the dilution factor of 0.2/10.

Table 6.47. Cd, Pb and Cu contents of tomato sauce samples TTB1 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_7	Cd	6.64 ± 0.54	0.073 ± 0.006	8.14	4.01	0.044
	Pb	29.2 ± 1.2	0.324 ± 0.013	3.98	27.9	0.311
	Cu	2237 ± 55	24.8 ± 0.6	2.46	2690	29.9
TT_8	Cd	8.07 ± 0.79	0.089 ± 0.009	9.75	10.4	0.116
	Pb	83.3 ± 6.3	0.928 ± 0.071	7.64	74.3	0.827
	Cu	8839 ± 423	98.4 ± 4.7	4.79	9637	107
TT_9	Cd	2.71 ± 0.11	0.028 ± 0.001	3.95	2.91	0.029
	Pb	26.9 ± 2.2	0.274 ± 0.022	8.00	23.7	0.242
	Cu	438 ± 31	4.46 ± 0.32	7.18	419	4.27

Table 7.48. Zn contents of tomato sauce samples TTB1 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_7	99.4 ± 1.0	1.10 ± 0.01	1.01	110	1.23
TT_8	93.3 ± 1.6	1.04 ± 0.02	1.68	101	1.13
TT_9	20.8 ± 1.8	0.212 ± 0.019	8.89	14.6	0.149

Chopped tomato samples TTB2 brand with serial number of PN: 16 16:50 and expiration date of 08/2014 were analyzed. Zn concentrations were between 0.029 mg g^{-1} and 0.088 mg g^{-1} (Table 7.49). Cd and Pb contents of the samples had the similar range with that of tomato sauce samples of TTB1 brand. Cd amounts were recorded between 0.039 µg g^{-1} and 0.071 µg g^{-1}; Pb concentrations were measured in the range of 0.253 µg g^{-1} – 0.504 µg g^{-1}; Cu range was between 1.45 – 5.96 µg g^{-1} (Table 7.50).

Table 7.49. Zn contents of chopped tomato samples TTB2 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_{10}	2.53 ± 0.01	0.029 ± 0.0002	0.61	2.23	0.025
TT_{11}	7.96 ± 0.42	0.088 ± 0.005	5.35	7.59	0.084
TT_{12}	2.59 ± 0.139	0.032 ± 0.002	5.36	2.42	0.030

Table 7.50. Cd, Pb and Cu contents of chopped tomato samples TTB2 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_{10}	Cd	6.23 ± 0.56	0.071 ± 0.006	8.89	5.92	0.068
	Pb	44.1 ± 2.1	0.504 ± 0.025	4.88	35.9	0.412
	Cu	135 ± 3	1.45 ± 0.04	2.63	131	1.50
TT_{11}	Cd	3.44 ± 0.32	0.038 ± 0.003	9.26	1.59	0.02
	Pb	21.7 ± 1.4	0.239 ± 0.016	6.52	18.3	0.202
	Cu	339 ± 16	3.74 ± 0.17	4.67	399	4.41
TT_{12}	Cd	3.22 ± 0.13	0.039 ± 0.002	4.16	3.621	0.045
	Pb	20.5 ± 0.7	0.253 ± 0.009	3.48	21.2	0.261
	Cu	483 ± 18	5.96 ± 0.23	3.84	431	5.32

Tomato sauce samples TTB2 brand with the serial number of PN:11 and the production date of 09/2011 were analyzed. Zn concentrations were between 0.016 mg g^{-1} and 0.204 mg g^{-1} (Table 7.51).

Table 7.51. Zn contents of tomato sauce TTB2 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_{13}	1.02 ± 0.08	0.016 ± 0.001	7.61	0.753	0.012
TT_{14}	10.6 ± 0.2	0.177 ± 0.004	2.10	13.4	0.224
TT_{15}	12.4 ± 0.5	0.204 ± 0.009	4.50	10.5	0.173

Cd amounts were recorded between 0.076 µg g^{-1} and 0.150 µg g^{-1}; Pb concentrations were measured in the range of 0.208 – 0.223 µg g^{-1}; Cu range was between 5.90 – 6.53 µg g^{-1} (Table 7.52).

Table 7.52. Cd, Pb and Cu contnets of tomato sauce TTB2 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_{13}	Cd	6.31 ± 0.54	0.103 ± 0.009	8.64	5.36	0.087
	Pb	13.7 ± 1.4	0.223 ± 0.023	10.3	15.9	0.259
	Cu	369 ± 18	6.01 ± 0.29	4.95	393	6.40
TT_{14}	Cd	4.58 ± 0.44	0.076 ± 0.007	9.74	1.96	0.033
	Pb	12.4 ± 1.1	0.208 ± 0.017	8.40	11.6	0.194
	Cu	353 ± 22	5.90 ± 0.37	6.32	291	4.86
TT_{15}	Cd	9.15 ± 0.48	0.150 ± 0.008	5.30	8.98	0.148
	Pb	12.5 ± 1.4	0.205 ± 0.023	11.0	11.0	0.181
	Cu	398 ± 18	6.53 ± 0.30	4.59	483	7.93

Tomato sauce samples TTB3 brand with the serial number of 249112001, and the expiration date of 09/2014 were analyzed. Zn concentrations were between 0.009 mg g^{-1} and 0.441 mg g^{-1} (Table 7.53). Zn content determination of the samples TT_{16}, TT_{18}, TT_{21}, and TT_{25} was performed by SMDE mode and the dilution factor was 0.5/10.

Table 7.53. Zn contents of tomato sauce TTB3 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_{16}	18.5 ± 0.9	0.306 ± 0.015	5.07	16.8	0.277
TT_{17}	6.73 ± 0.42	0.105 ± 0.007	6.31	6.32	0.103
TT_{18}	26.3 ± 0.1	0.441 ± 0.002	0.45	21.7	0.364
TT_{19}	2.08 ± 0.02	0.034 ± 0.0003	0.98	2.03	0.034
TT_{20}	0.570 ± 0.04	0.009 ± 0.001	6.81	0.593	0.009
TT_{21}	25.1 ± 0.4	0.368 ± 0.006	1.64	23.4	0.343
TT_{22}	3.36 ± 0.06	0.056 ± 0.001	1.85	3.37	0.06
TT_{23}	4.02 ± 0.05	0.060 ± 0.001	1.27	3.79	0.057
TT_{24}	6.85 ± 0.07	0.105 ± 0.001	1.08	6.08	0.094
TT_{25}	25.2 ± 1.0	0.406 ± 0.02	4.12	23.8	0.384

Cd concentrations of the samples were between 0 µg g^{-1} and 0.162 µg g^{-1}; Pb concentrations were measured in the range of 0.078 µg g^{-1} – 0.473 µg g^{-1}; Cu range was between 0.858 – 7.31 µg g^{-1} (Table 7.54). Cu determination of the sample TT_{19} was performed with 1 mL of 1 x 10^{-3} mol L^{-1} of EDTA with 1 mL of sample.

Table 7.54. Cd, Pb and Cu contents of tomato sauce TTB3 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_{16}	Cd	3.24 ± 0.22	0.053 ± 0.004	6.92	2.98	0.049
	Pb	5.27 ± 0.38	0.087 ± 0.006	7.31	3.97	0.066
	Cu	442 ± 13	7.31 ± 0.22	3.09	564	9.32
TT_{17}	Cd	3.07 ± 0.21	0.050 ± 0.003	6.79	2.21	0.036
	Pb	10.1 ± 0.5	0.164 ± 0.008	5.06	6.25	0.102
	Cu	123 ± 4	2.01 ± 0.06	2.80	118	1.93
TT_{18}	Cd	6.44 ± 0.32	0.108 ± 0.005	4.97	5.48	0.092
	Pb	5.73 ± 0.46	0.096 ± 0.008	8.03	5.40	0.090
	Cu	81.3 ± 2.8	1.40 ± 0.05	3.44	71.9	1.20
TT_{19}	Cd	0	0	-	0	0
	Pb	10.9 ± 0.6	0.18 ± 0.01	5.81	2.14	0.036
	Cu	63.0 ± 1.7	1.04 ± 0.03	2.67	89.9	1.49
TT_{20}	Cd	3.49 ± 0.16	0.056 ± 0.003	4.69	2.19	0.035
	Pb	5.74 ± 0.36	0.093 ± 0.006	6.36	4.82	0.078
	Cu	99.8 ± 5.5	1.62 ± 0.09	5.57	97.9	1.58
TT_{21}	Cd	2.33 ± 0.11	0.034 ± 0.001	4.67	2.56	0.037
	Pb	16.1 ± 1.2	0.235 ± 0.018	7.69	12.4	0.182
	Cu	113 ± 3	1.65 ± 0.04	2.52	124	1.81
TT_{22}	Cd	0	0	-	0	0
	Pb	16.4 ± 1.2	0.273 ± 0.021	7.55	14.8	0.246
	Cu	245 ± 14	4.07 ± 0.23	5.61	243	4.04
TT_{23}	Cd	0	0	-	0	0
	Pb	5.21 ± 0.22	0.078 ± 0.003	4.24	4.87	0.073
	Cu	57.1 ± 1.2	0.858 ± 0.019	2.17	50.7	0.762
TT_{24}	Cd	0	0	-	0	0
	Pb	5.42 ± 0.17	0.083 ± 0.003	3.12	4.57	0.070
	Cu	123 ± 1	1.89 ± 0.01	0.60	111	1.71
TT_{25}	Cd	10.1 ± 0.61	0.162 ± 0.009	7.27	12.1	0.195
	Pb	29.4 ± 2.1	0.473 ± 0.034	7.27	27.5	0.443
	Cu	263 ± 5	4.23 ± 0.85	2.00	232	3.74

Tomato sauce samples TTB4 brand with the serial number of IH261011-2 and the expiration date of 12/2013 were analyzed. Cd concentrations of the samples were generally 0 µg g^{-1}, yet one sample, TT_{30}, were measured as 0.099 µg g^{-1}; Pb concentrations were measured in the range of 0.314 – 0.878 µg g^{-1}; Cu range was between 7.99 – 46.6 µg g^{-1} (Table 7.55). Cu contents of the samples TT_{26}, TT_{28}, TT_{29}, and TT_{30} were determined separately, with dilution factor of 0.5/10.

Table 7.55. Cd, Pb and Cu contents of tomato sauce TTB4 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
TT_{26}	Cd	0	0	-	0	0
	Pb	37.5 ± 0.9	0.592 ± 0.015	2.51	30.5	0.483
	Cu	2946 ± 48	46.6 ± 0.7	1.63	2966	46.9
TT_{27}	Cd	0	0	-	0	0
	Pb	19.7 ± 0.4	0.314 ± 0.006	2.02	15.8	0.251
	Cu	503 ± 41	7.99 ± 0.66	8.15	568	9.03
TT_{28}	Cd	0	0	-	0	0
	Pb	25.7 ± 0.6	0.389 ± 0.009	2.38	24.0	0.364
	Cu	2189 ± 44	33.2 ± 0.6	2.00	2316	35.2
TT_{39}	Cd	0	0	-	0	0
	Pb	19.7 ± 0.5	0.295 ± 0.008	2.85	22.2	0.332
	Cu	1573 ± 40	23.5 ± 0.6	2.56	1679	25.1
TT_{30}	Cd	6.14 ± 0.26	0.099 ± 0.004	4.18	6.27	0.101
	Pb	54.4 ± 0.9	0.878 ± 0.015	1.75	50.8	0.818
	Cu	2280 ± 200	36.8 ± 3.2	8.77	1881	30.3
TT_{31}	Cd	0	0	-	0	0
	Pb	18.9 ± 0.4	0.322 ± 0.007	2.27	16.3	0.277
	Cu	499 ± 25	8.50 ± 0.43	5.08	520	8.86

Zn concentrations were between 0.244 mg g^{-1} and 2.14 mg g^{-1} (Table 7.56). Zn content analysis of the samples was performed by SMDE mode, the dilution factor was 0.1/10 for TT_{26}, and 0.5/10 for the rest of the samples.

Table 7.56. Zn contents of tomato sauce TTB4 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
TT_{26}	135 ± 1	2.14 ± 0.02	0.71	133	2.12
TT_{27}	16.8 ± 1.4	0.267 ± 0.022	8.06	16.1	0.257
TT_{28}	49.3 ± 1.1	0.748 ± 0.016	2.21	50.5	0.768
TT_{29}	16.3 ± 0.1	0.244 ± 0.001	0.42	17.3	0.258
TT_{30}	79.9 ± 0.9	1.29 ± 0.01	1.13	81.2	1.31
TT_{31}	21.5 ± 0.2	0.367 ± 0.004	1.02	22.4	0.381

7.6. Analysis of Mussel Samples

Frozen mussel samples, FFB1 brand with a serial number of 02536011 and a expiration date of 12/2013 were analyzed. Each sample was weighed as 1.50 ± 0.02 g on the basis of dried mussels, two or three of the mussels needed to be gathered in order to be weighed as 1.50 grams. Samples were digested for about 15 hours in 18 mL of nitric

acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). SMDE and HMDE modes of electrodes were used.

DPASV analysis of the Zn concentrations resulted in various amounts, ranging between 0.041 – 1.48 mg g^{-1} and 4.38 – 10.9 mg g^{-1}, which were in agreement with the ICP-OES results (Table 7.57). Zn content determination was performed by the SMDE mode, dilution factor was 0.05/10 for the sample M_3, 0.1/10 for M_2 and M_9, 0.2/10 for M_6, 0.5/10 for M_4, M_8, M_{10} and M_{12}.

Table 7.57. Zn contents of mussel sample FFB1 brand.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
M_1	9.40 ± 0.24	0.155 ± 0.004	2.51	9.20	0.151
M_2	263 ± 1	4.38 ± 0.0002	0.47	271	4.5
M_3	679 ± 7	10.9 ± 0.1	1.02	691	11.1
M_4	12.9 ± 0.3	0.208 ± 0.004	2.20	13.9	0.224
M_5	3.35 ± 0.23	0.055 ± 0.004	6.94	3.02	0.050
M_6	89.8 ± 0.9	1.48 ± 0.02	0.98	104	1.72
M_7	2.46 ± 0.09	0.041 ± 0.002	3.64	2.11	0.035
M_8	51.6 ± 0.3	0.853 ± 0.005	0.63	60.4	0.997
M_9	288 ± 4	4.66 ± 0.001	1.37	275	4.44
M_{10}	42.4 ± 0.1	0.704 ± 0.002	0.22	43.8	0.728
M_{11}	2.69 ± 0.03	0.043 ± 0.001	1.26	2.38	0.038
M_{12}	37.8 ± 0.4	0.610 ± 0.006	1.03	41.9	0.676

Cd contents of the mussel samples were mainly between 0.130 - 0.794 µg g^{-1}, sample M_1 was recorded as 0 µg g^{-1} of Cd content. Pb concentrations were measured in the range of 0.135 – 5.29 µg g^{-1}; Cu range was between 5.22 – 255 µg g^{-1} (Table 7.58). Cu contents of the samples M_2, M_3, M_5, M_6, and M_9 were determined separately, with the dilution factor of 0.5/10, except for the sample M_3, in which the dilution factor was 0.2/10. Samples M_4, M_{10}, and M_{11} were analyzed with EDTA for their Cu contents. 1 mL of 1 x 10^{-2} mol L^{-1} of EDTA was used for the analyses of M_{10} and M_{11}, and 1 mL of 5 x 10^{-2} mol L^{-1} of EDTA was used for the analysis of M_4.

Table 7.58. Cd, Pb and Cu contents of mussel sample FFB1 brand.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
M_1	Cd	0	0	-	0	0
	Pb	22.1 ± 1.2	0.364 ± 0.020	5.43	24.3	0.400
	Cu	317 ± 28	5.22 ± 0.46	8.83	338	5.56
M_2	Cd	25.4 ± 0.5	0.424 ± 0.008	1.92	32.3	0.540
	Pb	0	0	-	0	0
	Cu	7019 ± 614	119 ± 10	8.64	6014	100
M_3	Cd	24.6 ± 0.9	0.396 ± 0.016	4.05	27.9	0.451
	Pb	62.5 ± 3.2	1.01 ± 0.05	5.14	56.1	0.904
	Cu	15793 ±1090	255 ± 18	6.90	15479	250
M_4	Cd	31.8 ± 3.6	0.513 ± 0.058	11.3	38.1	0.615
	Pb	23.9 ± 1.8	0.386 ± 0.028	7.36	25.9	0.417
	Cu	1235 ± 100	19.9 ± 1.6	8.13	1466	23.6
M_5	Cd	29.4 ± 0.6	0.486 ± 0.010	2.02	27.6	0.455
	Pb	24.0 ± 0.6	0.396 ± 0.011	2.76	47.6	0.786
	Cu	1219 ± 99	20.1 ± 1.6	8.18	1409	23.2
M_6	Cd	21.4 ± 0.7	0.354 ± 0.012	3.30	21.6	0.357
	Pb	26.8 ± 1.2	0.444 ± 0.020	4.46	20.1	0.332
	Cu	1181 ± 19	19.5 ± 0.3	1.60	1227	20.3
M_7	Cd	18.0 ± 0.3	0.302 ± 0.005	1.70	11.1	0.187
	Pb	10.3 ± 0.4	0.172 ± 0.007	4.01	8.99	0.151
	Cu	446 ± 15	7.48 ± 0.26	3.51	387	6.49
M_8	Cd	16.4 ± 0.4	0.270 ± 0.007	2.59	17.3	0.286
	Pb	29.8 ± 0.6	0.493 ± 0.009	1.90	23.4	0.387
	Cu	562 ± 7	9.28 ± 0.13	1.37	582	9.61
M_9	Cd	49.1 ± 0.9	0.794 ± 0.016	1.98	47.7	0.770
	Pb	327 ± 9	5.29 ± 0.15	2.82	247	4.00
	Cu	7266 ± 407	117 ± 66	5.60	7807	126
M_{10}	Cd	15.9 ± 1.4	0.264 ± 0.022	8.56	15.6	0.250
	Pb	21.6 ± 0.9	0.358 ± 0.016	4.41	23.9	0.397
	Cu	896 ± 81	14.9 ± 1.4	9.09	826	13.7
M_{11}	Cd	29.8 ± 2.5	0.478 ± 0.040	8.39	21.3	0.354
	Pb	8.39 ± 0.61	0.135 ± 0.010	7.24	10.9	0.175
	Cu	583 ± 11	9.36 ± 0.17	1.82	600	9.98
M_{12}	Cd	8.08 ± 0.19	0.130 ± 0.003	2.40	9.16	0.148
	Pb	12.6 ± 0.4	0.203 ± 0.006	2.85	8.75	0.141
	Cu	410 ± 5	6.62 ± 0.08	1.17	492	7.93

7.7. Analysis of Horse Mackerel Samples

Fresh horse mackerels purchased from a market in Istanbul, each analysis was carried with a different fish sample. Sample tissues were taken from both left and right sides of the spine and about one centimeter below the head. Test samples of 2.00 ± 0.05 grams of weight were air dried. Horse mackerels were about 14.2 to 15.9 centimeters of length. Samples were digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Aliquots of samples were diluted by a factor of 2 mL:10 mL for Cd, Pb and Cu determinations unless stated otherwise. Zn contents were determined by the dilution factor of 0.2 mL:10 mL and HMDE mode of electrode was used unless stated otherwise.

Zn concentrations of the horse mackerel samples were in the range of 0.039 mg g^{-1} – 2.06 mg g^{-1} (Table 7.59). In DPSAV analysis of Zn contents, SMDE mode was used for samples HM_1, HM_6, HM_7 and HM_9. The dilution factor was 0.1/10 for the samples HM_1, HM_7, and HM_9; and 0.5/10 for the sample HM_6.

Table 7.59. Zn contents of fresh horse mackerel samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
HM_1	124 ± 5	2.02 ± 0.09	4.40	111	1.82
HM_2	8.36 ± 0.06	0.137 ± 0.001	0.78	9.55	0.156
HM_3	6.77 ± 0.58	0.112 ± 0.009	8.53	5.97	0.099
HM_4	2.93 ± 0.18	0.048 ± 0.003	6.09	2.59	0.042
HM_5	5.25 ± 0.27	0.065 ± 0.003	5.12	5.00	0.062
HM_6	11.3 ± 0.9	0.147 ± 0.013	8.85	10.3	0.134
HM_7	122 ± 1	1.57 ± 0.01	0.96	131	1.68
HM_8	3.04 ± 0.18	0.039 ± 0.002	6.09	2.85	0.037
HM_9	164 ± 2	2.06 ± 0.03	1.41	182	2.29

The range for Cd content was 0 – 1.15 µg g^{-1}; 0 – 0.750 µg g^{-1} for Pb; and 0.777 µg g^{-1} – 63.5 µg g^{-1} for Cu (Table 7.60). Cu contents of the samples HM_1, HM_7, and HM_9 were analyzed separately with the dilution factor of 0.5/10.

Table 7.60. Cd, Pb and Cu contents of fresh horse mackerel samples.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
HM_1	Cd	22.5 ± 0.2	0.367 ± 0.003	0.89	27.3	0.446
	Pb	0	0	-	0	0
	Cu	1104 ± 66	18 ± 1	6.30	1159	18.9
HM_2	Cd	3.09 ± 0.19	0.051 ± 0.003	6.26	1.62	0.026
	Pb	20.4 ± 0.5	0.334 ± 0.009	2.71	15.7	0.257
	Cu	70.6 ± 6.64	1.15 ± 0.109	9.41	92.1	1.51
HM_3	Cd	0	0	-	0	0
	Pb	13.3 ± 0.8	0.219 ± 0.014	6.45	14.2	0.234
	Cu	189 ± 22	3.13 ± 0.37	11.8	120	1.98
HM_4	Cd	4.05 ± 0.34	0.066 ± 0.005	8.27	2.78	0.046
	Pb	45.9 ± 0.9	0.750 ± 0.020	2.11	47.4	0.777
	Cu	181 ± 34	2.96 ± 0.56	19	102	1.66
HM_5	Cd	1.89 ± 0.07	0.023 ± 0.001	3.69	1.38	0.017
	Pb	10.2 ± 0.1	0.126 ± 0.002	1.45	10.7	0.132
	Cu	62.7 ± 5.6	0.777 ± 0.070	9.01	66.4	0.822
HM_6	Cd	0	0	-	0	0
	Pb	8.89 ± 0.45	0.115 ± 0.006	5.02	7.23	0.094
	Cu	258 ± 38	3.35 ± 0.49	14.6	315	4.09
HM_7	Cd	3.16 ± 0.21	0.041 ± 0.003	6.78	3.08	0.040
	Pb	26.4 ± 0.6	0.34 ± 0.01	2.27	20.8	0.268
	Cu	2725 ± 23	35.1 ± 0.3	0.84	3120	40.2
HM_8	Cd	1.61 ± 0.13	0.021 ± 0.002	7.85	2.21	0.029
	Pb	9.95 ± 0.74	0.128 ± 0.009	7.42	8.13	0.105
	Cu	259 ± 28	3.35 ± 0.37	11	212	2.72
HM_9	Cd	91.2 ± 0.8	1.15 ± 0.01	0.93	80.1	1.01
	Pb	0	0	-	0	0
	Cu	5041 ± 106	63.5 ± 1.3	2.09	6447	81.2

7.8. Analysis of Mullet Samples

Six pieces of mullet samples were purchased from a market in Istanbul. The length of the samples varied between from 16.0 and 18.0 centimeters. 1.50 ± 0.02 grams of air dried samples were weighed and digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Samples Ml_2,Ml_3, Ml_4,Ml_5; and Ml_8,Ml_9 were prepared from the left and right sides of the spines of three different mullets. Ml_1, Ml_6, and Ml_7 represented the samples taken from one side of three different mullets. HMDE mode of the electrode was used unless stated otherwise. Sample dilution factors were 2 mL:10 mL and 4 mL:10 mL.

The range for Cd content was 0 – 0.116 µg g^{-1}; 0.097 – 0.535 µg g^{-1} for Pb; and 1.83 µg g^{-1} – 83.4 µg g^{-1} (Table 7.61). Cd determinations of the samples Ml_2 and Ml_9 were performed separately, with the dilution factor of 4/10. Cu contents of the samples Ml_4 and Ml_6 were also determined separately, with the dilution factor of 0.5/10.

Table 7.61. Cd, Pb and Cu contents of fresh mullet samples.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
Ml_1	Cd	1.16 ± 0.05	0.019 ± 0.001	4.67	1.87	0.030
	Pb	8.99 ± 0.18	0.147 ± 0.003	2.06	7.64	0.125
	Cu	264 ± 11	4.32 ± 0.18	4.20	226	3.70
Ml_2	Cd	0.899 ± 0.062	0.015 ± 0.001	6.93	0.905	0.016
	Pb	7.98 ± 0.44	0.132 ± 0.007	5.47	5.59	0.092
	Cu	138 ± 2	2.27 ± 0.03	1.38	101	1.68
Ml_3	Cd	1.88 ± 0.07	0.031 ± 0.001	3.72	0.917	0.015
	Pb	10.7 ± 0.3	0.174 ± 0.005	2.72	7.86	0.128
	Cu	408 ± 12	6.62 ± 0.20	3.04	738	11.9
Ml_4	Cd	0	0	-	0	0
	Pb	18.8 ± 2.17	0.295 ± 0.034	11.5	13.8	0.217
	Cu	1898 ± 39	29.8 ± 0.6	2.04	2207	34.6
Ml_5	Cd	2.19 ± 0.13	0.036 ± 0.002	6.10	1.11	0.018
	Pb	5.96 ± 0.21	0.097 ± 0.003	3.44	4.55	0.074
	Cu	182 ± 2	2.97 ± 0.03	1.12	144	2.34
Ml_6	Cd	4.53 ± 0.17	0.070 ± 0.003	3.77	5.26	0.082
	Pb	34.4 ± 0.8	0.535 ± 0.013	2.39	33.0	0.512
	Cu	5364 ± 259	83.4 ± 4.0	4.82	6338	98.5
Ml_7	Cd	1.42 ± 0.08	0.023 ± 0.001	6.01	2.97	0.047
	Pb	17.4 ± 0.6	0.278 ± 0.009	3.34	14.6	0.234
	Cu	157 ± 8	2.51 ± 0.13	5.03	139	2.22
Ml_8	Cd	7.08 ± 0.68	0.116 ± 0.011	9.56	6.25	0.102
	Pb	22.8 ± 0.4	0.372 ± 0.007	1.90	59.4	0.970
	Cu	234 ± 6	3.82 ± 0.09	2.43	192	3.14
Ml_9	Cd	0.945 ± 0.091	0.015 ± 0.001	9.65	0.840	0.010
	Pb	8.31 ± 0.45	0.135 ± 0.007	5.40	6.18	0.100
	Cu	113 ± 14	1.83 ± 0.23	12.4	91.6	1.48

Zn concentrations of the mullet samples were in the range of 0.026 mg g^{-1} – 3.12 mg g^{-1} (Table 7.62). Samples Ml_3, Ml_4, Ml_6, Ml_7, and Ml_8 were analyzed by SMDE mode. Dilution factor was 0.5/10 for Ml_3 and Ml_7; and it was 0.1/10 for Ml_4, Ml_6, and Ml_8.

Table 7.62. Zn contents of fresh mullet samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
Ml_1	5.24 ± 0.36	0.086 ± 0.006	6.98	4.70	0.077
Ml_2	3.09 ± 0.15	0.051 ± 0.002	4.81	2.71	0.045
Ml_3	53.5 ± 0.3	0.868 ± 0.005	0.58	74.1	1.20
Ml_4	199 ± 0.5	3.12 ± 0.01	0.26	211	3.30
Ml_5	1.58 ± 0.02	0.026 ± 0.0003	1.07	2.56	0.042
Ml_6	272 ± 1	4.23 ± 0.02	0.48	258	4.02
Ml_7	13.8 ± 1	0.221 ± 0.016	7.38	10.9	0.174
Ml_8	105 ± 1	1.72 ± 0.02	1.26	96.4	1.57
Ml_9	5.61 ± 0.44	0.091 ± 0.007	7.87	4.37	0.071

7.9. Analysis of Grey Mullet Samples

Fresh grey mullet was purchased from a market in Istanbul. 1.70 ± 0.02 grams of air dried samples were weighed and digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Samples GM_1 – GM_6 were from the left side of the spine, and samples GM_7-GM_{11} were from the right side of the spine of the same grey mullet. Dilution factor of the samples was 2/10 for Cd, Pb and Cu detection, and 0.2/10 for the Zn analysis, unless stated otherwise. HMDE mode of the electrode was used. SMDE mode applications were specified.

Table 7.63. Zn contents of fresh grey mullet samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD %	mg L^{-1}	mg g^{-1}
GM_1	58.5 ± 0.4	0.847 ± 0.006	0.74	60.2	0.871
GM_2	16 ± 1	0.238 ± 0.013	5.60	14.9	0.221
GM_3	89.3 ± 1.6	1.32 ± 0.02	1.76	79.8	1.18
GM_4	2.21 ± 0.13	0.031 ± 0.002	6.06	2.02	0.029
GM_5	2.19 ± 0.10	0.031 ± 0.002	4.96	1.99	0.030
GM_6	3.88 ± 0.26	0.057 ± 0.004	6.79	3.58	0.053
GM_7	5.79 ± 0.31	0.075 ± 0.004	5.38	4.02	0.052
GM_8	5.04 ± 0.37	0.065 ± 0.005	7.38	4.84	0.062
GM_9	2.45 ± 0.22	0.029 ± 0.003	8.92	2.09	0.026
GM_{10}	88.1 ± 0.6	1.09 ± 0.01	0.68	84.5	1.05
GM_{11}	16.2 ± 0.1	0.207 ± 0.001	0.47	17.4	0.222

Zn concentrations of the grey mullet samples were between 0.031 mg g^{-1} – 1.32 mg g^{-1} (Table 7.63). Zn contents of the samples $GM_{1,}$ GM_3, GM_{10} and GM_{11} were determined by the SMDE mode. Dilution factor for the analytes was 0.5/10 for $GM_{1,}$ and GM_{11}, and it was 0.2/10 for GM_3 and GM_{10}.

Table 7.64. Cd, Pb and Cu contents of fresh grey mullet samples.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
GM_1	Cd	23.9 ± 0.4	0.346 ± 0.005	1.51	30.2	0.437
	Pb	0	0	-	0	0
	Cu	927 ± 34	13.4 ± 0.5	3.64	1228	17.8
GM_2	Cd	4.70 ± 0.43	0.069 ± 0.006	9.21	3.14	0.047
	Pb	39.4 ± 1.6	0.584 ± 0.023	3.97	32.4	0.481
	Cu	206 ± 18	3.06 ± 0.27	8.85	176	2.61
GM_3	Cd	7.09 ± 0.30	0.105 ± 0.004	4.25	6.42	0.095
	Pb	63 ± 2	0.934 ± 0.030	3.21	58.5	0.867
	Cu	3734 ± 246	55.4 ± 3.6	6.59	3744	55.5
GM_4	Cd	1.85 ± 0.08	0.027 ± 0.001	4.21	1.16	0.016
	Pb	25.0 ± 0.5	0.359 ± 0.008	2.11	19.4	0.279
	Cu	63.6 ± 1.8	0.913 ± 0.026	2.82	55.4	0.796
GM_5	Cd	1.81 ± 0.11	0.027 ± 0.002	5.85	1.55	0.023
	Pb	21.9 ± 0.2	0.327 ± 0.003	0.81	18.5	0.276
	Cu	136 ± 11	2.03 ± 0.16	8.12	113	1.70
GM_6	Cd	2.81 ± 0.19	0.042 ± 0.003	6.79	2.19	0.032
	Pb	20.8 ± 0.7	0.307 ± 0.011	3.63	15.5	0.229
	Cu	141 ± 5	2.08 ± 0.07	3.3	124	1.83
GM_7	Cd	0	0	-	0	0
	Pb	118 ± 4	1.53 ± 0.05	3.3	95.1	1.23
	Cu	110 ± 5	1.43 ± 0.06	4.53	96.2	1.24
GM_8	Cd	0	0	-	0	0
	Pb	51.5 ± 0.8	0.662 ± 0.009	1.49	40.3	0.518
	Cu	96.6 ± 12.4	1.24 ± 0.16	12.8	79.0	1.02
GM_9	Cd	1.95 ± 0.16	0.024 ± 0.002	7.95	1.28	0.016
	Pb	22.7 ± 0.3	0.278 ± 0.004	1.50	19.0	0.233
	Cu	129 ± 8	1.58 ± 0.09	6.20	83.0	1.02
GM_{10}	Cd	37.1 ± 0.8	0.461 ± 0.009	2.09	47.3	0.588
	Pb	0	0	-	0	0
	Cu	2056 ± 151	25.5 ± 1.9	7.33	2224	27.9
GM_{11}	Cd	3.31 ± 0.23	0.042 ± 0.003	6.98	3.40	0.043
	Pb	67.2 ± 1.5	0.86 ± 0.02	2.21	56.5	0.723
	Cu	2333 ± 35	29.8 ± 0.4	1.52	2835	36.3

Cd range for the samples was 0 - 0.461 µg g^{-1}; Pb contents were between 0 – 1.53 µg g^{-1}; Cu concentrations were recorded between 0.913 µg g^{-1} – 55.4 µg g^{-1} (Table 7.64). Cu contents of the samples $GM_{3,}$ GM_{10}, and GM_{11} were determined separately; the dilution factor was 0.5/10.

7.10. Analysis of Red Mullet Samples

Fresh red mullet samples were purchased from a market in Istanbul. 2.00 ± 0.05 grams of air dried samples were weighed and digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Samples were taken left and right sides of the spines of three different red mullets. RM_1-RM_2, RM_3-RM_4, RM_5-RM_6 are pairs of three samples. Dilution factor of the samples was 2/10 for Cd, Pb and Cu detection, and 0.2/10 for the Zn analysis, unless stated otherwise. HMDE mode of the electrode was used. SMDE mode applications were specified.

Table 7.65. Cd, Pb and Cu contents of fresh red mullet samples.

DPASV					ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
RM_1	Cd	2.98 ± 0.14	0.037 ± 0.002	4.66	3.14	0.038
	Pb	23.2 ± 1.2	0.278 ± 0.014	5.23	19.5	0.234
	Cu	67.8 ± 5.4	0.814 ± 0.064	7.91	55.8	0.670
RM_2	Cd	1.61 ± 0.09	0.020 ± 0.001	6.13	1.72	0.022
	Pb	15.1 ± 0.9	0.190 ± 0.012	6.26	12.0	0.151
	Cu	71.7 ± 3.8	0.899 ± 0.048	5.36	38.4	0.482
RM_3	Cd	1.82 ± 0.06	0.022 ± 0.001	3.18	1.14	0.014
	Pb	14.7 ± 0.2	0.182 ± 0.003	1.54	17.8	0.220
	Cu	49.4 ± 3.8	0.611 ± 0.048	7.79	37.8	0.467
RM_4	Cd	3.29 ± 0.16	0.040 ± 0.002	4.98	3.96	0.048
	Pb	74.7 ± 2.1	0.915 ± 0.025	2.76	51.3	0.629
	Cu	514 ± 35	6.31 ± 0.43	6.78	504	6.18
RM_5	Cd	0.94 ± 0.08	0.012 ± 0.001	8.11	0.559	0.007
	Pb	120 ± 3	1.50 ± 0.03	2.22	108	1.35
	Cu	18.6 ± 1.2	0.233 ± 0.014	6.19	16.7	0.209
RM_6	Cd	3.93 ± 0.30	0.049 ± 0.004	7.66	4.64	0.058
	Pb	26.6 ± 1.1	0.33 ± 0.01	4.22	21.6	0.268
	Cu	274 ± 10	3.41 ± 0.13	3.75	229	2.85

Cd range for the samples was 0.012 - 0.049 µg g^{-1}; Pb contents were between 0.182 – 1.50 µg g^{-1}; Cu concentrations were recorded between 0.233 µg g^{-1} – 6.31 µg g^{-1} (Table 7.65). Zn concentrations of the red mullet samples were between 0.007 mg g^{-1} – 0.136 mg g^{-1} (Table 7.66). Zn content of the sample RM_6 was determined by SMDE mode; the dilution factor was 0.5/10.

Table 7.66. Zn contents of fresh red mullet samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD	mg L^{-1}	mg g^{-1}
RM_1	1.05 ± 0.10	0.013 ± 0.001	9.49	0.988	0.012
RM_2	1.26 ± 0.09	0.016 ± 0.001	7.06	1.39	0.017
RM_3	0.578 ± 0.046	0.007 ± 0.0006	7.93	0.564	0.007
RM_4	7.22 ± 0.04	0.088 ± 0.0005	0.63	7.82	0.096
RM_5	0.281 ± 0.022	0.003 ± 0.0002	7.85	0.334	0.004
RM_6	10.9 ± 0.6	0.136 ± 0.007	5.29	10.3	0.128

7.11. Analysis of Seabass Samples

Fresh seabass samples were purchased from a market in Istanbul. Each sample represented a different seabass, dry weight of 2.00 ± 0.02 grams. Samples were digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Sample dilution factors were within 0.2/10 and 2/10. Zn concentrations of the red mullet samples were between 0.015 mg g^{-1} – 0.392 mg g^{-1} (Table 7.67). In DPASV analysis of the samples SB_4 and SB_6, SMDE mode was used with the dilution factor of 0.5/10.

Table 7.67. Zn contents of fresh seabass samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD	mg L^{-1}	mg g^{-1}
SB_1	4.21 ± 0.12	0.053 ± 0.001	2.82	4.51	0.057
SB_2	7.68 ± 0.68	0.096 ± 0.009	8.92	7.48	0.094
SB_3	2.63 ± 0.19	0.033 ± 0.002	7.46	2.38	0.030
SB_4	28.7 ± 0.5	0.354 ± 0.006	1.64	30.4	0.374
SB_5	1.23 ± 0.02	0.015 ± 0.0003	1.92	1.36	0.017
SB_6	30.9 ± 0.4	0.392 ± 0.006	1.47	32.6	0.412

Cd range for the samples was 0 - 0.072 µg g^{-1}; Pb contents were between 0.198 – 0.858 µg g^{-1}; Cu concentrations were recorded between 0.568 µg g^{-1} – 22.3 µg g^{-1} (Table 7.68). Cu content of the sample SB_6 was determined separately, with the dilution factor of 0.5/10.

Table 7.68. Cd, Pb and Cu contents of fresh seabass samples.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
SB_1	Cd	3.55 ± 0.28	0.045 ± 0.003	7.75	2.43	0.030
	Pb	16.4 ± 0.6	0.206 ± 0.007	3.52	12.9	0.162
	Cu	77.1 ± 8.3	0.97 ± 0.10	10.8	64.3	0.810
SB_2	Cd	0	0	-	0	0
	Pb	33.9 ± 1.6	0.426 ± 0.020	4.78	29.0	0.365
	Cu	152 ± 9	1.91 ± 0.11	5.78	142	1.79
SB_3	Cd	0	0	-	0	0
	Pb	15.8 ± 1.3	0.198 ± 0.016	8.26	8.50	0.106
	Cu	45.3 ± 2.8	0.568 ± 0.035	6.21	34.0	0.426
SB_4	Cd	5.84 ± 0.46	0.072 ± 0.006	7.87	4.71	0.058
	Pb	69.6 ± 1.6	0.858 ± 0.019	2.23	56.0	0.690
	Cu	286 ± 27	3.52 ± 0.33	9.34	267	3.30
SB_5	Cd	0	0	-	0	0
	Pb	20.8 ± 0.6	0.259 ± 0.008	3.06	23.6	0.295
	Cu	73.4 ± 5.8	0.917 ± 0.072	7.89	86.0	1.07
SB_6	Cd	0	0	-	0	0
	Pb	19.4 ± 0.7	0.246 ± 0.009	3.54	15.3	0.194
	Cu	1763 ± 176	22.3 ± 2.2	9.98	1948	24.7

7.12. Analysis of Goosefish Samples

Fresh goosefish samples were purchased from a market in Istanbul, samples were taken left and right sides of the spine of a goosefish, and weighed 2.00 ± 0.02 grams. They were digested for about 15 hours in 18 mL of nitric acid/perchloric acid ($HNO_3/HClO_4$) mixture (5/1, v:v). Sample dilution factors were between 0.2/10 and 2/10. Cd range for the samples was 0.010 - 0.051 µg g^{-1}; Pb contents were between 0.509 – 1.17 µg g^{-1}; Cu concentrations were recorded between 0.519 – 8.69 µg g^{-1} (Table 7.69). Cu content of the sample GF_4 was determined separately, with the dilution factor of 0.5/10.

Table 7.69. Cd, Pb and Cu contents of fresh goosefish samples.

		DPASV			ICP-OES	
Sample	Element	µg L^{-1}	µg g^{-1}	SD %	µg L^{-1}	µg g^{-1}
GF_1	Cd	0.808 ± 0.064	0.010 ± 0.0008	7.92	1.12	0.015
	Pb	77.7 ± 1.3	0.991 ± 0.016	1.67	71.2	0.908
	Cu	280 ± 19	3.57 ± 0.24	6.78	250	3.19
GF_2	Cd	1.47 ± 0.074	0.018 ± 0.001	5.02	1.92	0.024
	Pb	69.1 ± 1.1	0.871 ± 0.014	1.59	81.3	1.02
	Cu	188 ± 16	2.37 ± 0.20	8.51	215	2.71
GF_3	Cd	1.46 ± 0.11	0.018 ± 0.001	7.53	2.15	0.026
	Pb	41.4 ± 0.9	0.509 ± 0.011	2.17	50.8	0.625
	Cu	42.2 ± 2.2	0.519 ± 0.027	5.21	59.8	0.736
GF_4	Cd	3.21 ± 0.3	0.037 ± 0.003	9.34	3.63	0.042
	Pb	66.7 ± 0.9	0.768 ± 0.010	1.35	71.1	0.819
	Cu	755 ± 24	8.69 ± 0.276	3.18	810	9.33
GF_5	Cd	1.33 ± 0.08	0.016 ± 0.001	6.02	1.77	0.022
	Pb	68.1 ±1.7	0.844 ± 0.021	2.50	75.2	0.932
	Cu	45.4 ± 2.4	0.562 ± 0.030	5.29	58.4	0.723
GF_6	Cd	4.12 ± 0.27	0.051 ± 0.003	6.55	5.15	0.064
	Pb	94.3 ± 6.2	1.17 ± 0.08	6.57	109	1.35
	Cu	355 ± 27	4.40 ± 0.33	7.60	321	3.97

Zn concentrations of the red mullet samples were between 0.020 mg g^{-1} – 0.892 mg g^{-1} (Table 7.70). Zn content of the sample GF_4 was determined by SMDE mode, and the dilution factor was 0.2/10.

Table 7.70. Zn contents of fresh goosefish samples.

	DPASV			ICP-OES	
Sample	mg L^{-1}	mg g^{-1}	SD	mg L^{-1}	mg g^{-1}
GF_1	3.98 ± 0.28	0.051 ± 0.004	7.24	3.16	0.040
GF_2	6.15 ± 0.41	0.077 ± 0.005	6.74	5.98	0.075
GF_3	1.66 ± 0.11	0.020 ± 0.001	6.50	1.55	0.019
GF_4	77.5 ± 0.8	0.892 ± 0.010	1.12	79.9	0.921
GF_5	1.72 ± 0.04	0.021 ± 0.001	2.44	1.88	0.023
GF_6	2.27 ± 0.10	0.028 ± 0.001	4.54	2.45	0.030

7.13. Analysis of Selenium contents in Tuna and Sardine samples

Tuna samples of Tonton brand with the serial number of TR 17.50 and the expiration date of 08/2016, Ülker Light brand with the serial number of DGL 2129 and the expiration

date of 05/2017, Superfresh brand with the serial number of DGL 2035 and the expiration date of 02/2017, and sardine samples of Engin brand with the expiration date of 04/2013 which was also the serial number, were analyzed for their Se content. 10 mL diluted sample was investigated with the addition of 3.3 g of ammonium sulphate, 1 mL of 0.1 mol L^{-1} of EDTA, and 1 mL of 0.1 g L^{-1} of Cu solution. pH of each sample was adjusted to 2.2 ± 0.1 by concentrated H_2SO_4. Standard additions were done with 0.3, 0.5, 1, 2, 4, 5, 10 mg L^{-1} of Se solution. HMDE mode of electrode was used. Voltammetric parameters for Se detection were as given:

Table 7.71. Voltammetric parameters of Se determination.

Deposition Potential (V)	-0.4
Deposition Time (s)	90
Equilibrium Time (s)	10
Start Potential (V)	-0.45
End Potential (V)	-0.85
Voltage Step (V)	0.004
Pulse Amplitude (V)	0.08
Pulse Time (s)	0.04
Voltage Step Time (s)	0.1
Sweep Rate (V/s)	0.04

Se contents of the tuna samples were between 0.054 µg g^{-1} and 3.27 µg g^{-1} (Table 7.73 – 7.75).

Table 7.72. Se contents of tuna samples (CFB9 brand).

DPCSV			
Sample	µg L^{-1}	µg g^{-1}	SD %
T_{41}	39.8 ± 2.7	0.662 ± 0.045	6.78
T_{42}	45.6 ± 4.5	0.753 ± 0.074	9.87
T_{43}	4.27 ± 0.28	0.071 ± 0.004	6.56
T_{44}	3.32 ± 0.09	0.054 ± 0.001	2.71
T_{45}	200 ± 6	3.27 ± 0.09	3.00

Table 7.73. Se contents of tuna samples CFB8 brand.

DPCSV			
Sample	µg L^{-1}	µg g^{-1}	SD %
T_{46}	20.4 ± 1.1	0.337 ± 0.018	5.39
T_{47}	31.2 ± 3.8	0.517 ± 0.063	12.2
T_{48}	13.9 ± 0.9	0.230 ± 0.015	6.47
T_{49}	37.1 ± 4.2	0.618 ± 0.070	11.3
T_{50}	19.6 ± 0.9	0.326 ± 0.015	4.59
T_{51}	25.4 ± 1.5	0.421 ± 0.025	5.90

Table 7.74. Se contents of tuna samples CFB6 brand.

DPCSV			
Sample	µg L^{-1}	µg g^{-1}	SD %
T_{52}	24.1 ± 0.9	0.399 ± 0.015	3.73
T_{53}	12.9 ± 0.8	0.213 ± 0.013	6.20
T_{54}	51.2 ± 4.6	0.838 ± 0.075	8.98
T_{55}	135 ± 13	2.25 ± 0.22	9.63
T_{56}	47.8 ± 2.7	0.797 ± 0.045	5.65
T_{57}	75.6 ± 1.0	1.26 ± 0.017	1.32

Se contents of the sardine samples were between 0.903 µg g^{-1} and 2.92 µg g^{-1} (Table 7.75).

Table 7.75. Se contents of sardine samples CFB4 brand.

DPCSV			
Sample	µg L^{-1}	µg g^{-1}	SD %
S_{32}	73.6 ± 7.9	1.23 ± 0.13	10.7
S_{33}	175 ± 3	2.92 ± 0.05	1.71
S_{34}	54.2 ± 3.9	0.903 ± 0.065	7.20
S_{35}	107 ± 5	1.78 ± 0.08	4.67
S_{36}	167 ± 11	2.78 ± 0.18	6.59

8. COMPARISONS OF REGULATED CONCENTRATIONS OF TRACE ELEMENTS WITH THE EXPERIMENTAL RESULTS

Maximum levels of allowed concentrations of Zn, Cu, Pb and Cd by World Health Organization (WHO), Food and Agriculture Organization (FAO), and European Union (EU) Commissions in fresh, frozen and canned fish and vegetables are given in Table 8.1 and Table 8.2. The regulations for trace metal concentrations are compared with those limits set by Turkish Food Codex.

Table 8.1. Maximum level of trace elements in fish and mollusks.

Element	**Maximum Level (μg g^{-1})**	
	FAO/WHO/EU	**Turkish Food Codex [89]**
Zn	50 [86]	50
Cu	20 [86]	20
Pb	0.3 [87] 0.4* [88] 1.5** [88]	0.2*** 0.4* 1.5**
Cd	0.1 [88] 2.0** [87]	0.05*** 0.1* 1.0**

*Grey Mullet, Horse Mackerel, Sardine, and Tuna.

Bivalve Molluscs. ***** Frozen and Processed Fish.

Table 8.2. Maximum level of trace elements in vegetables.

Element	**Maximum Level (μg g^{-1})**	
	FAO/WHO	**Turkish Food Codex [89]**
Zn	50 [86]	Not defined
Cu	20 [86]	Not defined
Pb	0.1 [87] 1.0* [87] 1.5**	0.1 1.0*
Cd	0.05 [87]	0.05

*Canned vegetables. ** Processed concentrates of vegetables.

8.1. Zinc Contents

Experimental results for Zn, Cu, Pb and Cd contents of the vegetable, canned and fresh fish samples were classified according to their brands. The Zn contents were summarized it Tables 8.3 – 8.7. Recorded concentrations were compared with the regulated amounts set by Health Organizations and Governments. Zn concentrations were above the limits both for the corn and tomato samples, exclusive of the Corn Brand 1 (CB1) corn sample. The maximum concentrations detected for the fish samples exceed the regulated amounts, also. Detailed explanations are given in the conclusion part, Section 10.

Table 8.3. Zn concentration limits of canned corn samples.

Brand	**Concentration mg g^{-1}**
CB1	0.071 – 0.772
CB2	0.022 – 0.384
CB3	0.012 – 0.057
CB4	0.031 – 0.852
CB5	0.034 – 0.041

Table 8.4. Zn concentration limits of canned tomato sauce and chopped tomato samples.

Brand	**Concentration mg g^{-1}**
TTB1 (sauce)	0.212 – 1.10
TTB2 (chopped)	0.029 – 0.088
TTB2 (sauce)	0.016 – 0.204
TTB3 (sauce)	0.009 – 0.441
TTB4 (sauce)	0.267 – 2.14

Table 8.5. Zn concentration limits of frozen fish and mussel samples.

Brand	**Concentration mg g^{-1}**
FFB1 (anchovy)	0.067 – 1.49
FFB2 (anchovy)	0.045 – 0.561
FFB3 (anchovy)	0.044 – 1.21
FFB1 (mussel)	0.041 – 10.9

Table 8.6. Zn concentration limits of fresh fish samples.

Species	**Concentration mg g^{-1}**
Sardine	0.035 – 0.282
Anchovy	0.019 – 6.33
Horse Mackerel	0.048 – 2.02
Mullet	0.026 – 4.23
Grey Mullet	0.031 – 1.32
Red Mullet	0.003 – 0.136
Seabass	0.015 – 0.354
Goosefish	0.020 – 0.892

Table 8.7. Zn concentration limits of canned fish samples.

Brand	**Concentration mg g^{-1}**
CFB1 (sardine)	0.009 – 0.131
CFB2 (sardine)	0.061 – 0.890
CFB3 (sardine)	0.038 – 0.275
CFB4 (sardine)	0.042 – 8.01
CFB4 (tuna)	0.018 – 0.886
CFB5 (tuna)	0.015 – 3.14
CFB2 (tuna)	0.024 – 5.65
CFB7 (tuna)	0.031 – 3.54
CFB8 (tuna)	0.021 – 1.09
CFB9 (tuna)	0.028 – 0.945
CFB1 (anchovy)	0.088 – 0.146

8.2. Copper Contents

Experimental results are summarized in Tables 8.8 – 8.12. Detailed explanations of the experimental data are given in conclusion part, Section 10.

Table 8.8. Cu concentration limits of canned corn samples.

Brand	Concentration µg g^{-1}
CB1	10.6 – 45.5
CB2	3.36 – 21.4
CB3	1.18 – 5.24
CB4	1.16 – 132
CB5	1.04 – 4.32

Table 8.9. Cu concentration limits of canned tomato sauce and chopped tomato samples.

Brand	Concentration µg g^{-1}
TTB1 (sauce)	4.46 – 98.4
TTB2 (chopped)	1.45 – 5.96
TTB2 (sauce)	5.90 – 6.53
TTB3 (sauce)	0.858–7.31
TTB4 (sauce)	7.99 - 46.6

Table 8.10. Cu concentration limits of canned fish samples.

Brand	Concentration µg g^{-1}
CFB1 (sardine)	3.27 – 62.1
CFB2 (sardine)	2.84 – 51.2
CFB3 (sardine)	1.95 – 9.31
CFB4 (sardine)	2.59 – 130
CFB4 (tuna)	5.73 – 25.8
CFB5 (tuna)	0.529–52.5
CFB2 (tuna)	1.55 – 63.9
CFB7 (tuna)	2.01 – 54.4
CFB8 (tuna)	1.56 – 25.8
CFB9 (tuna)	1.34 – 13.8
CFB1 (anchovy)	0.887–6.38

Table 8.11. Cu concentration limits of fresh fish samples.

Species	**Concentration µg g^{-1}**
Sardine	0.720 – 15.8
Anchovy	1.28 – 39.6
Horse Mackerel	0.777 – 63.5
Mullet	1.83 – 83.4
Grey Mullet	0.913 – 55.4
Red Mullet	0.233 – 6.31
Seabass	0.568 – 22.3
Goosefish	0.519 – 8.69

Table 8.12. Cu concentration limits of frozen fish and mussel samples.

Brand	**Concentration µg g^{-1}**
FFB1 (anchovy)	2.51 – 11.3
FFB2 (anchovy)	1.78 – 12.3
FFB3 (anchovy)	0.731–21.5
FFB1 (mussel)	5.22 - 255

8.3. Lead Contents

Experimental results are summarized in Tables 8.13 – 8.17. Detailed explanations are given in conclusion part, Section 10.

Table 8.13. Pb concentration limits of canned corn samples.

Brand	**Concentration µg g^{-1}**
CB1	0.299 – 0.634
CB2	0.232 – 0.506
CB3	0.194 – 0.899
CB4	0.071 – 2.18
CB5	0.306 – 0.456

Table 8.14. Pb concentration limits of canned tomato sauce and chopped tomato samples.

Brand	Concentration µg g^{-1}
TTB1 (sauce)	0.274 – 0.928
TTB2 (chopped)	0.239 – 0.504
TTB2 (sauce)	0.205 – 0.223
TTB3 (sauce)	0.078 – 0.473
TTB4 (sauce)	0.295 – 0.878

Table 8.15. Pb concentration limits of fresh fish samples.

Species	Concentration µg g^{-1}
Sardine	0.103 – 0.994
Anchovy	0 – 1.59
Horse Mackerel	0 – 0.750
Mullet	0.097 – 0.535
Grey Mullet	0 – 1.53
Red Mullet	0.182 – 1.50
Seabass	0.198 – 0.858
Goosefish	0.509 – 1.17

Table 8.16. Pb concentration limits of canned fish samples.

Brand	Concentration µg g^{-1}
CFB1 (sardine)	0.706 – 1.44
CFB2 (sardine)	0 – 0.614
CFB3 (sardine)	0 – 0.485
CFB4 (sardine)	0 – 1.06
CFB4 (tuna)	0.257 – 0.673
CFB5 (tuna)	0.169 – 1.77
CFB2 (tuna)	0.194 – 0.341
CFB7 (tuna)	0.176 – 0.730
CFB8 (tuna)	0.290 – 0.517
CFB9 (tuna)	0 – 0.727
CFB1 (anchovy)	0.848 – 0.904

Table 8.17. Pb concentration limits of frozen fish and mussel samples.

Brand	Concentration µg g^{-1}
FFB1 (anchovy)	0 – 0.382
FFB2 (anchovy)	0.066 – 0.249
FFB3 (anchovy)	0 – 0.307
FFB1 (mussel)	0.135 – 5.29

8.4. Cadmium Contents

Experimental results are summarized in Tables 8.18 – 8.22. Detailed explanations are given in conclusion part, Section 10.

Table 8.18. Cd concentration limits of canned corn samples.

Brand	Concentration µg g^{-1}
CB1	0 – 0.055
CB2	0.026 – 0.065
CB3	0 – 0.166
CB4	0 – 0.184
CB5	0.034 – 0.077

Table 8.19. Cd concentration limits of canned tomato sauce and chopped tomato samples.

Brand	Concentration µg g^{-1}
TTB1 (sauce)	0.028 – 0.073
TTB2 (chopped)	0.038 – 0.071
TTB2 (sauce)	0.076 – 0.150
TTB3 (sauce)	0 – 0.161
TTB4 (sauce)	0 – 0.099

Table 8.20. Cd concentration limits of fresh fish samples.

Species	Concentration µg g^{-1}
Sardine	0 – 0.155
Anchovy	0 – 0.276
Horse Mackerel	0 – 1.15
Mullet	0 – 0.116
Grey Mullet	0 – 0.461
Red Mullet	0.012 – 0.049
Seabass	0 – 0.072
Goosefish	0.010 – 0.051

Table 8.21. Cd concentration limits of frozen fish and mussel samples.

Brand	Concentration µg g^{-1}
FFB1 (anchovy)	0 – 0.046
FFB2 (anchovy)	0 – 0.104
FFB3 (anchovy)	0 – 0.026
FFB1 (mussel)	0 – 0.794

Table 8.22. Cd concentration limits of canned fish samples.

Brand	Concentration µg g^{-1}
CFB1 (sardine)	0.063 – 0.134
CFB2 (sardine)	0 – 0.312
CFB3 (sardine)	0 – 0.173
CFB4 (sardine)	0 – 0.065
CFB4 (tuna)	0.044 – 0.245
CFB5 (tuna)	0 – 1.16
CFB2 (tuna)	0.052 – 0.521
CFB7 (tuna)	0 – 0.293
CFB8 (tuna)	0 – 0.113
CFB9 (tuna)	0 – 0.028
CFB1 (anchovy)	0.078 – 0.199

8.5. Selenium Contents

The DPCSV analysis of Se contents of food samples were carried out by using only the tuna and sardine samples. The limited number of samples was analyzed. Further studies are needed to develop the method parameters in voltammetry. In 1987, World Health Organization (WHO) stated the Se levels for organ meat and seafood as 0.4 to 1.5 µg g^{-1}, and for fruits and vegetables as 0.1 µg g^{-1} [90]. However, Turkish Food Codex does not reveal the Se concentration for vegetables or seafood. The codex only exhibits the maximum Se concentration in drinking water [91].

Table 8.23. Se concentration limits of canned fish samples.

Brand	**Concentration µg g^{-1}**
CF4 (sardine)	0.903 – 2.92
CF6 (tuna)	0.213 – 2.25
CF8 (tuna)	0.230 – 0.618
CF9 (tuna)	0.054 – 3.27

Tuna samples of CFB9 and CFB8 brands exhibited the Se content within the accepted limits.

Results of the analyses showed that the Zn amount of most of the vegetable and fish products exceed the permitted concentration regulated by Turkish Food Codex and European Union Regulations. Detailed explanation of Zn, Cu, Pb and Cd contents of the samples is given in Section 10. These concentrations may be reduced by careful handling of the products, or toxic element analysis prior to processing. Also, Turkish Food Codex has an insufficient regulation of the trace elements regarding the vegetables.

9. STATISTICAL ANALYSIS

The results of the two methods, ICP-OES and DPASV were analyzed with paired samples test, by the software package, SPSS version 21. Statistical analysis was carried with gathering the samples into three groups as vegetables, fresh fish and canned fish samples. The results of the paired t-tests for the groups revealed that significance level was greater than 0.05 at 95 % confidence interval, which proved that DPASV results were not statistically different than the results of conventional ICP-OES for Zn, Cu and Cd determinations.

Table 9.1. Paired samples test for vegetable samples.

Element	N	Paired Differences		t	df	Sig. (2-tailed)
		95% Confidence Interval of the Difference				
		Lower	Upper			
Zn	48	-0.892	1.026	0.141	47	0.889
Cu	48	-46.891	72.121	0.426	47	0.672
Pb	48	-0.490	3.534	1.522	47	0.135
Cd	48	0.076	0.660	2.537	47	0.015

In the analyses of Pb for fresh and canned fish samples, the differences in the results of the two methods were statistically significant. Significant levels for the Pb analyses were 0.009 and 0.000 for canned and fresh fish samples, respectively.

Table 9.2. Paired samples test for canned fish samples.

Element	N	Paired Differences		t	df	Sig. (2-tailed)
		95% Confidence Interval of the Difference				
		Lower	Upper			
Zn	104	-1.910	0.476	-1.191	103	0.236
Cu	104	-92.777	3.631	-1.835	103	0.070
Pb	104	-0.729	4.942	2.670	103	0.009
Cd	104	-0.677	0.433	-0.436	103	0.664

Table 9.3. Paired samples test for fresh fish samples.

Element	N	Paired Differences		t	df	Sig. (2-tailed)
		95% Confidence Interval of the Difference				
		Lower	Upper			
Zn	62	-0.773	1.885	0.836	61	0.406
Cu	62	-38.758	36.393	-0.063	61	0.950
Pb	62	3.107	5.709	6.775	61	0.000
Cd	62	-0.395	0.805	0.684	61	0.497

10. CONCLUSIONS

Acid digestion of food samples was carried with nitric acid, perchloric acid $HNO_3/HClO_4$ (5/1, v:v) mixture with the digestion time of average 20 hours. Four different buffer mixtures were investigated as supporting electrolytes in DPASV analyses. Buffer composition with di-ammonium oxalate monohydrate, ($C_2H_8N_2O_4$), ammonium chloride, (NH_4Cl) and hydrochloric acid (HCl) mixture was found to be most suitable one, since the requirements for a precise and an accurate voltammetric measurement were satisfied. The criteria were to obtain smooth peaks at the expected half-wave, $E_{1/2}$, potential values, non-shifted base lines and coherent Δi values for the subsequent standart additions. In order to enhance the voltammetric parameters of the Anodic Stripping method, necessary modifications were made in the deposition time, deposition potential, and the mode of the working electrode.

There is a direct relationship between the maximum current of the oxidation of the metal deposited onto the electrode surface and the concentration of trace metal ions in the solution in DPASV method. Also, the amount of amalgam formed between the Hg electrode and metal ions in the analyte is proportional to the metal concentration in solution and the deposition time. In this study, deposition time of 120 seconds was found to be the most suitable.

The deposition potential was arranged so that a linear relationship existed between the maximum stripping current of the deposited amalgam and the concentration of the deposited element onto electrode surface. Multielement analysis of Zn, Cu, Pb and Cd was carried between -1.25 V and 0.1 V. Multielement analysis of Pb, Cu and Cd was carried between -0.75 V and 0.08 V. Samples with relatively high Zn contents were investigated separately between potentials -1.25 V and -0.75 V. Also, in cases where voltammetric determinations of Cu was run separately, deposition and stripping potentials were set between -0.25 V and 0.08 V; the potentials were kept between -0.90 V and -0.25 V for the simultaneous analysis of Cd and Pb. Concentration levels of trace metals in media governed the mode of the Hg electrode that must have been used; ppb, ppt, and low ppm levels required the use of HMDE mode whereas SMDE mode was used at relatively higher

ppm levels. Hence, high dilution factors were omitted by using the SMDE mode of the electrode in the presence of Zn concentrations greater than 10 mg L^{-1}.

Cu contents of the samples were analyzed with the help of EDTA additions of various concentrations:

1×10^{-3} mol L^{-1} EDTA was suitable at 90 µg $L^{-1} \leq [Cu^{2+}] < 600$ µg L^{-1},
1×10^{-2} mol L^{-1} EDTA was suitable at 600 µg $L^{-1} \leq [Cu^{2+}] < 900$ µg L^{-1},
5×10^{-2} mol L^{-1} EDTA was suitable at 900 µg $L^{-1} \leq [Cu^{2+}] < 2500$ µg L^{-1}

DPCSV method was used for the detection of Se content for a limited number of samples. The results of the Se analysis revealed that the corresponding concentrations were within the safe margine of the restricted limits.

Fresh and canned fish species were investigated in three replicates for about 180 samples. The results of 166 analytes were given, the rest were not taken into considerations; either voltammetric peaks were distorted due to incomplete digests or standard additions were not accurate. Canned corn and tomato samples were run in three replicates and about 60 samples were investigated. Only, the results of 48 were given due to the same reasons indicated above.

Zn contents of the fresh and canned fish samples at their recorded outmost levels were above the limits set by FAO/WHO/EU and Turkish Food Codex. The Zn contents of anchovy samples of the brands FFB1, sardines of CFB1 and CFB2 brands were above the regulated limits even at their lowest concentration values. Zn contents of the investigated canned corn samples were within the acceptable limits in their lowest concentration levels except for the CB1 brand. Excluding the CB3 and CB5 brands of canned corn samples, the outmost Zn concentration values of the other brands were above the regulated limits. The investigated brands of canned tomato sauce and chopped tomato samples exhibited Zn contents above the regulated limits. The low concentration values of the samples were within the limits except for TTB1 and TTB4 tomato sauces.

Assuming the average consumption of 500 g of fish and 800 g of vegetables per week, following results were obtained for Zn intake. The RDA value of Zn was set as 15 mg, and it is 105 mg per week [42]. Canned corn samples of CB3 and CB5 brands, tomato sauce samples of TTB2 brand, sardine and anchovy samples of CFB1 brand and fresh red mullet samples had their maximum Zn content within the safe limits. Weekly consumptions of all other canned corn, canned tomato, fresh, frozen and canned fish brands were found to be above the recommended limits.

Cu contents of the fresh fish samples were above the limits legislated by FAO/WHO/EU and Turkish Food Codex except for sardine, red mullet, seabass and goosefish. Frozen fish samples of all brands revealed the Cu concentration below the limits; however, the Cu contents of frozen mussel samples of FFB1 brand were above the limits. Investigated canned fish samples exhibited the Cu concentrations above the limits except for the CFB3, CFB9 and CFB1 brands, which were purchased from the markets of Çanakkale. Cu contents of CB1 and CB4 brands of canned corn samples were above the legislated limits, the brands of CB2, CB3 and CB5 were within the acceptable limits. Investigated samples of canned tomato sauce and chopped tomatoes of TTB2 and TTB3 brands exhibited the Cu contents below the limits. Canned tomato sauce samples of TTB1 and TTB4 brands were above the acceptable limis.

The RDA value of Cu is 1.15 mg, and it is 8.05 mg per week. The results of the analyses showed that canned corn samples of CB3 and CB5 brands, tomato sauces of TTB2 and TTB3 brands, sardine samples of CFB3 brand, tuna samples of CFB9 brand, anchovy samples of CFB1 brand, frozen anchovies of FFB1 and FFB2 brands, fresh sardine, red mullet and goosefish had their Cu limits within the safe limits. All the other canned fish, vegetable and fresh fish samples were above the recommended limits.

High concentrations of Pb contents of fresh fish samples were above the limits for all of the investigated species. Besides, all of the frozen and fresh fish samples revealed their Pb concentrations within the acceptable limits according to Turkish Food Codex, except for the frozen mussel sample of FFB1 brand. Analyses of canned corn, chopped tomato and canned tomato sauce samples exhibited the Pb concentrations within the legislated limits, except for CB4 brand corn samples.

The upper limit (UL) was estimated as 1.75 mg per week for Pb intake. All the fresh fish samples, frozen and canned fish and vegetable samples were determined to be safe except for CB4 brand canned corn and FFB1 mussel samples; considered 500 g of fish or 800 g of vegetable was consumed for a week.

Cd contents of fresh fish samples were above the acceptable limits set by FAO/WHO/EU and Turkish Food Codex, except for the red mullet seabass, and goosefish samples. Investigated frozen fish and mussel samples revealed the Cd concentration below the legislated limits except for the FFB2 brand anchovy samples. Cd contents of canned fish samples were above the regulated limits except for the CFB9 brand. The sardine samples of CFB4 brand exhibited the Cd contents within the acceptable limits of FAO/WHO/EU, but they exceeded the limits set by Turkish Food Codex. All of the investigated samples of canned corn, canned tomato sauce and chopped tomato samples were above the limits of Cd legislation set by FAO/WHO/EU and Turkish Food Codex, except for canned corns of CB1 brand.

The upper limit (UL) for Cd intake was determined as 0.49 mg per week. Anyone consumed 500 g fish or 8000 g canned vegetable for a week would be in the safe consumption limits. Yet, eating mussels more than 400 g per week would exceed the upper limit of Cd intake.

Two methods of trace element analysis, ICP-OES and DPASV were compared with each other. DPASV method is economically more convenient. Statistical analysis of two methods showed that they both revealed the similar results, except for the Pb content of the fish samples.

ICP-OES emission wavelengths of Pb and Cd are 220.353 and 228.802 nm, respectively. Several advantages are associated with the plasma source. They stem from the high stability of the plasma temperature, low noise, low background as it is free of argon lines, chemically inert environment, and small or nonexistent ionization interference effects because of the large concentration of electrons from the ionization of argon. Also, calibration curves tend to remain linear over several orders of magnitude of concentration.

Half-wave potentials, $E_{1/2}$, of Pb and Cd in Buffer I media are -0.47 V and -0.63 V, respectively. Generally, 0.1 to 0.2 V is required if the more reducible species undergoes a two-electron reduction. Hence, the single voltammogram should permit the quantitative determination of Pb and Cd accurately since there is sufficient difference between succeeding half-wave potentials.

The reason for statistically revealed difference in Pb contents of the fish samples between DPASV and ICP-OES methods could not be explained clearly. Also, no significant differences were revealed in Pb contents of vegetable samples.

11. SUGGESTIONS FOR FUTURE WORK

A comprehensive study should be performed for the voltammetric analysis of Se. During the the digestion process of food samples, Se vaporizes easily with the use of strong oxidizing agent such as perchloric acid, $HClO_4$. Moreover, working parameters such as deposition time, deposition potential, and buffer medium should be improved.

Fresh and canned fish samples should be analyzed for their Hg levels, since the Hg content of the fish samples monitor the contamination level of marine environments.

Turkish Food Codex lacks the information about Zn and Cu contents of fruit and vegetable samples. Further investigations can be done regarding this issue.

A comprehensive study should be performed according to the dietary habits, age, gender, social and economical life regarding the amounts of canned or fresh fish and vegetables that we consume in our everyday diet.

12. PRODUCTS OF THE STUDY

1. Las Vegas, USA, International Conference and Exhibition on Analytical and Bioanalytical Techniques IV, October 2013, Oral Presentation

2. Warsaw, Poland, Euroanalysis XVII, August 2013, Poster Presentation

3. Istanbul, Turkey, Bogazici University Chemistry Symposium II, May 2012, Poster Presentation

4. Mugla, Turkey, National Chemistry Congress XXVI, September 2012, Poster Presentation

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