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DETERMINATION OF HEAVY METALS IN WASTE ENERGETIC MATERIALS WITH USING SEQUENTIAL EXTRACTION

STANOVENÍ TĚŽKÝCH KOVŮ V ODPADNÍCH ENERGETICKÝCH MATERIÁLECH S VYUŽITÍM SEKVENČNÍ EXTRAKCE

DIPLOMOVÁ PRÁCE
MASTER'S THESIS

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ABSTRACT

This diploma thesis deals about determination of metal in energetic waste, such as fly ash, scoria, dross, loge ash and product of desulphurization, etc., coming from four Moravian heating plants. Extraction of metals was performed according to Tessier. As extraction agents were used magnesium chloride ($MgCl_2$), sodium acetate (CH_3COONa), hydroxylamin hydrochloride in acetic acid ($NH_2OH.HCl$ in CH_3COOH), hydrogen peroxide in nitric acid (H_2O_2 in HNO_3) and hydrofluoric acid (HF). Extraction proceeded at temperatures of 25°C and 40°C. Lead, copper and cadmium were determined on atomic absorption spectrometer (F AAS and ET AAS) and mercury was determined on AMA 254 in all fractions.

ABSTRAKT

Tato diplomová práce pojednává o stanovení vybraných kovů v energetických odpadech, jako je úletový popílek, škvára, struska, ložový popel, produkt odsíření apod., které pocházejí ze čtyř moravských tepláren. Extrakce kovů z energetických materiálů byla provedena Tessierovou extrakcí. Za tímto účelem byla použita extrakční činidla chlorid hořečnatý ($MgCl_2$), octan sodný (CH_3COONa), hydroxylamin hydrochlorid v kyselině octové ($NH_2OH.HCl$ v CH_3COOH), peroxid vodíku v kyselině dusičné (H_2O_2 v HNO_3) a kyselina fluorovodíková (HF). Extrakce probíhala při teplotách 25°C a 40°C. Ve všech frakcích byly stanoveny olovo, měď a kadmium s využitím atomové absorpční spektrometrie (F AAS, ET AAS) a rtuť metodou AMA 254.

KEYWORDS

Extraction, Tessier´s extraction, Atomic absorption spectrometry, F AAS, ET AAS, AMA 254, Lead, Copper, Mercury, Cadmium

KLÍČOVÁ SLOVA

Extrakce, Tessierova extrakce, Atomová absorpční spektrometrie, F AAS, ET AAS, AMA 254, Olovo, Měď, Rtuť, Kadmium

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DECLARATION

I declare that the diploma thesis has been worked out by myself and that all the quotations from the used literary sources are accurate and complete. The content of the diploma thesis is the property of the Faculty of Chemistry of Brno University of Technology and all commercial uses are allowed only if approved by both the supervisor and the dean of the Faculty of Chemistry, BUT.

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Tuto práci bych chtěla věnovat dvěma úžasným osobnostem, které již nejsou mezi námi, ale v našich srdcích zůstanou už napořád.

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1 INTRODUCTION

The Environmental pollution is today a global problem and people on the whole as well as individuals have been facing a challenge to stop this destruction as soon as possible. People know that in the environment there are a lot of pollutants from human activities (mainly from industry, transport, etc.) which negatively affect nature and our lives. In recent years more and more emphasis and attention has been put on the environmental protection of current and past pollution.

Now it is for many countries important to improve the legislation for more environmental protection and then to penalize non-compliance with them. It is very important to improve conditions in the industry and to reduce the production of pollutants into the environment. The fact still is that pollution exists and its consequences concern everyone. It is necessary to continue in the remedy of nature and in the development of new, cleaner and nature friendly technologies.

In this work, air pollution from some heat plants and their production of hazardous metals such as lead, copper, cadmium and mercury was chosen. These hazardous metals do not stay in the air for a long time, but their danger is increasing with rain and other meteorological conditions. After that metals penetrate into the fauna and flora and negatively affect people, animals and plants.

2 THEORETICAL PART

2.1 Energetic waste

Complementary products are produced as waste in the energy production processes, which are formed when solid fuel is burned and after that the combustion products are cleaned. This process makes ash, fly-ash, scoria, energo light spar, products of desulphurization etc.

2.1.1 Creation of energetic waste

Burning is chemical oxidation process, when chemical energy, bonded with burn fuel, is turned on heat energy. This process is the simplest term change of fuels, in condition of oxygen. Main product of this process, heat energy, is used for heating, warming of water and produce of electric energy.

A combustion equipment has a lot of parts, but the main part is a boiler, where the chemical energy is transformed to heat energy. Heat goes into work medium, mostly water, and the products are vapour, warm water (maximal temperature 110°C) and hot water (temperature upward 110°C).

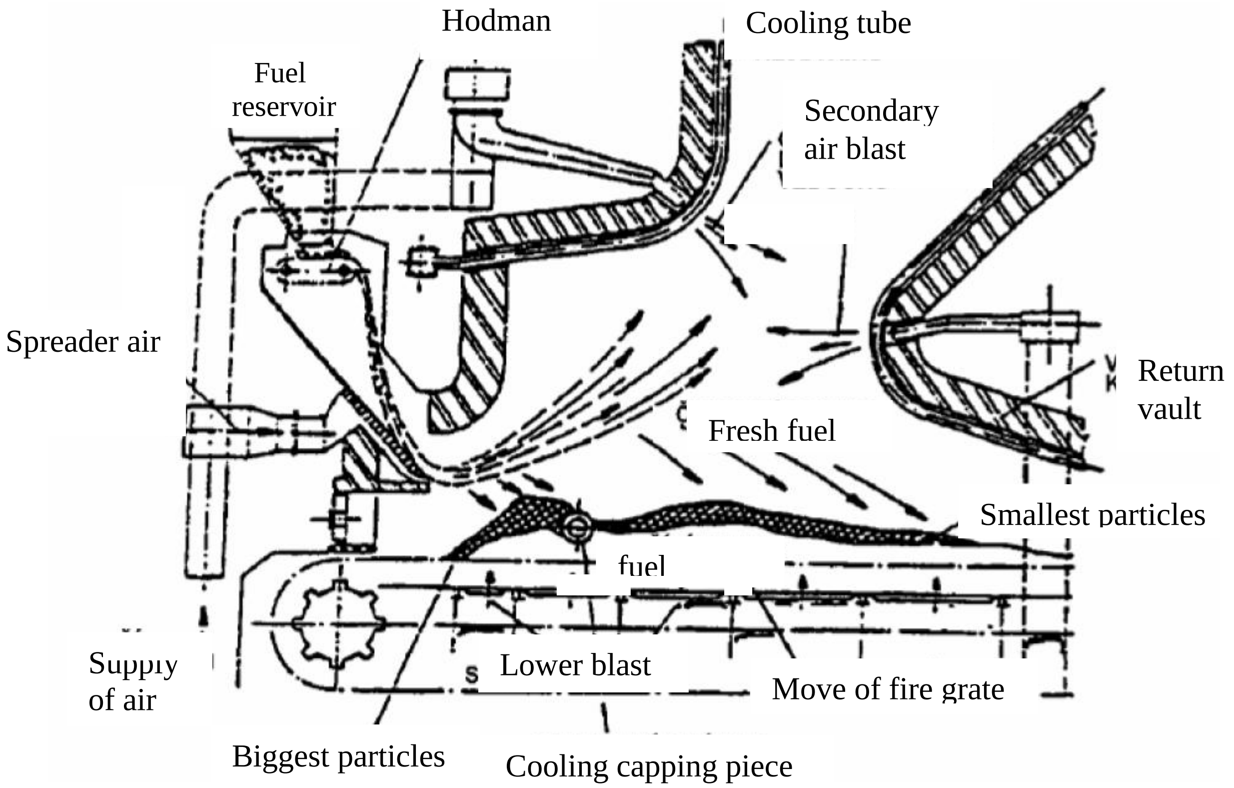
Boilers are divided (it depends on the method of fuel combustions):

- fluidized-bed boiler
- stoker fired boiler
- pulverized coal fired boiler [1]

2.1.1.1 **Stoker fired boiler**

These boilers are used for burning lump fuels. Burning in stoker fired boilers is on fire grate and in the space above the fuel, which is the biggest, when the fuel is more volatile constituent.

Picture 1: Diagram of a classical stoker fired boiler



Fuel passes through these characteristic parts:

- drying – fuel is in this part warmed and water is eliminated
- degassing – more intensive is at the temperature of 250°C

- combustion of volatile constituent and inflammation of solid part of flammable matters
- afterburning of solid phase and cooling the rest

In this time these boilers are used for combustion of biomass and wastes. [1]

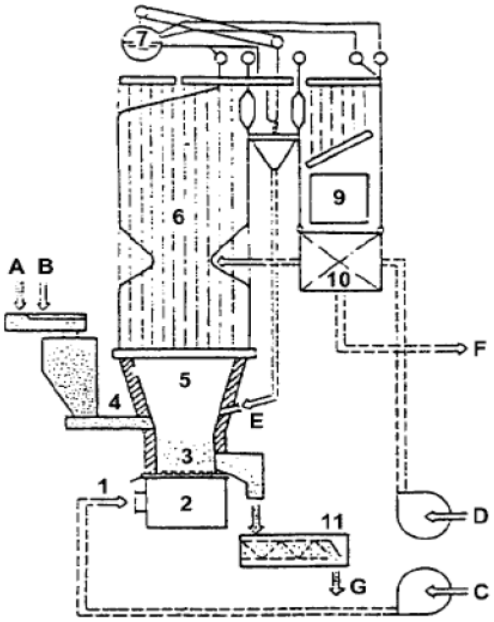
2.1.1.2 Fluidized-bed boiler

This boiler is based on fuel grinding of big particles, which are in flow of air in burning space and the behaviour of particles is like boiling liquid. The fluid layer does dispersion system, which is made by flowing gas, it goes across layer particles on the porous bed (fluid grate). Fuel particles are covered by air, so the process of combustion is faster and the regulation is easier. Temperature of this combustion is 700 – 900°C, this high temperature suppresses the production of nitrogen oxides (NO_x) and sulphurous oxide, which can be bonded on grind limestone.

Types of atmospheric fluid boilers:

- Atmospheric fluid boiler with stationary fluid layer (AFB): main part is bubbling fluid layer with clear surface

Picture 2: Diagram of an atmospheric fluid boiler AFB

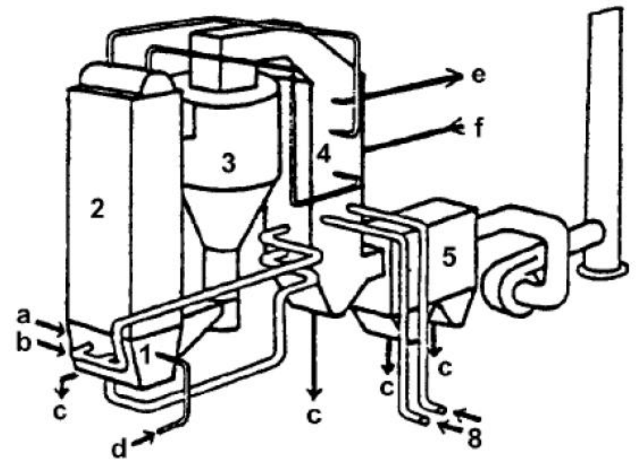


1. Fluid grate
2. Air chamber
3. Fluid layer
4. Feeder
5. Fluid reactor
6. Combustion chamber
7. Drum
8. Warmer of vapour
9. Warmer of water
10. Warmer of air
11. Cooling feeder of ash

A, B	Fuel
C	Primary air
D	Secondary air
E	Return of ash
F	Exit of combustion products
G	Exit of heat

- Atmospheric fluid boiler with circulate fluid layer (ACFB): combustion products go from the furnace across cyclone, where the biggest particles are returned back into the fluid furnace by the centrifugal force. Positive of this boiler is, that the particles stay longer in the combustion space, and it causes better desulphurization and better burning of carbon.

Picture 3: Diagram of an atmospheric fluid boiler ACFB



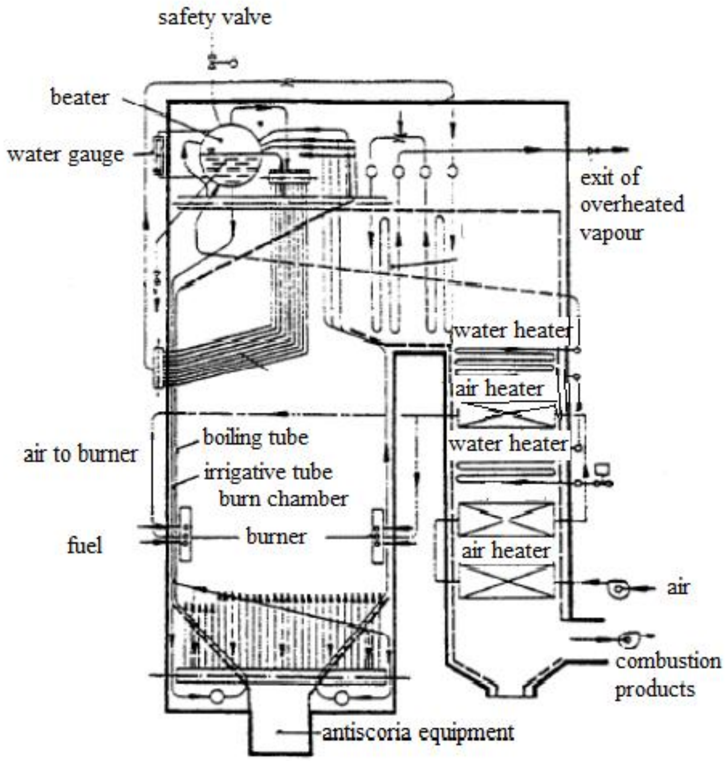
a	crush coal
b	additive
c	ash
d	lighting fuel
e	vapour
f	water
g	gas

1	fluid furnace
2	vapour system
3	cyclone
4	supplement of boiler

2.1.1.3 **Pulverized coal fired boiler**

In pulverized coal fired boiler there is fuel burnt, which is ground into powder with particles with the size of around 1mm. Load-bearing medium, takes grind fuel to the furnace, it is air or combustion products, sometimes a mixture of that. Its burning time is for 1 – 3 second.

Picture 4: Diagram of a pulverized coal fired boiler



Two types of the pulverized coal fired boiler are known:

- Granulation – there is a dry exit of solid products from the furnace in the form of dross. Combustion is in relatively low temperatures, and this boiler is suitable for brown coal.
- Melt – there is a wet exit of solid products from the furnace in the form of scoria. Suitable for coal with the biggest combustion temperature, it means for high quality black coal. [2]

2.2 Speciation analysis and fractionation

Speciation analysis is determination presence of different forms of metals, because metals have variety of different properties and toxicity of different compounds of the same metal. The exact name of terms stated International Union of Applied Chemistry:

a) Chemical species are a specific forms of element which are defined as the isotopic composition, electron or oxidation state of complexes or molecular structure
b) Speciation analysis (analytical chemistry) is analytical work to identify one or more individual chemical speciation in sample.
c) Speciation of elements is description of element on defined speciation in the system.

The fractionation is used, when is not possible chemical speciation. According to IUPAC fractionation is defined as classification of analytes or group of analytes in sample according to chemical (reactivity) or physical properties (solubility).

2.3 Extraction

Extraction is a separation process which consists in the separation of an analyte from a matrix. It may refer to:

a) Liquid - liquid extraction - known as solvent extraction. This is a method to separate compounds based on their relative solubility in two different immiscible liquids (usually water and organic solvent). It goes on principle, that one liquid (phase 1) is extraction into another liquid (phase 2).
   This extraction can be used in non – aqueous systems, like molten metal in contact with molten salt.
b) Solid phase extraction – in this separation process there is one compound (phase 1) which is dissolved in the liquid mixture (phase 2). The separation goes according to chemical and physical properties of all the phases of the system.

In few last years there have been used simple and sequence extraction. These methods are based on interaction between a solid phase and liquid leaching agent and after the samples are analyzed in the leaching liquid. These type of extractions show mobility of contaminants, their risks for the environment and people, etc. [9] [10]

2.3.1 Simple extraction

Simple extraction is the simplest method how an analyte can leach into the liquid. This method is very often used for metals, which are in contaminated soils or sediments. It means metals which are hazardous for plants.[17]

The most important indicator is liquid – to – solid ratio (L/S), which is chosen very similar to the natural environment (for soils is L/S lower, between 2-10).

The simplest leaching agent is distilled water. Solutions of inorganic salts, which are similar to soil water, are used for the measure of metals (ion-exchangeable reaction).

2.3.1.1 **Extraction by water solvents**

Extraction by water solvents is often used for determination of bioavailability of porous water. Catching of porous water is a very difficult process, so we use water solvents for determination of chemical substances concentration in soil solution. [34]

Porous water

Effects of polycyclic aromatic compound (PACs), when separate rates soil – porous water is used. They were studying relative toxicity PAHs and N-, S-, O-monosubstitute PACs for Enchytraeidae. Sverdrup used relation (coefficient 0,016 is organic carbon in their tested soil), when is big, than an element is more bond, so it´s less bioavailable.

Substances (for example PACs) have similar toxicity in different soils when they are determinate by maximal concentration in soil (mg/kg), but when we use equilibrium concentration in porous water, we will have substances with different toxicity. Toxicity depends on substances and soils properties.

Hydroxylpropyl-β-cyclodextrin extraction (HPCD)

This technique was used for PAHs. HPCD is cyclic oligosaccharide with hydrophilic surface and circular nonpolar hollow. HPCD with PAHs are turned in water solubility inclusions (PAHs are bonded in nonpolar hollow of HPCD). It depends on PAH´s properties and concentration of HPCD which must be much bigger than concentration of PAHs. HPCD regeneration is very bad, and this technique is really expensive. [35]

Extraction with $CaCl_2$

Extraction with 0,01M $CaCl_2$ can be used for bioavailability of herbicides and metals. 0,01M $CaCl_2$ is mixed with tested soil a few hours, it´s an alternative method for organic solvents. This extraction depends on pH of soil, and extraction can take long time.

2.3.1.2 **Extraction by organic solvents**

Extraction by organic solvents is used for the study of non polar compounds, and strong or weak solvents are used in different reaction conditions. [34]

Maximal (hard) extraction

These methods (are called hard) are still in our legislative for monitoring of quality of soils and potential leakage of elements in groundwater. Soxhlet extraction, Soxtec extraction or shaking with strong organic solvents (DCM, hexane or ethanol) are hard methods, also derivatization of soils (for example silylation). These methods give information about the total concentration of pollution in soils.

Soft (weak) extraction

This method is very often tested in these days and is very discussed because the adsorbed amount in biological tests and the mineralized amount were not equate in extractions with different solvents. But on the other hand there are many solvents which have equal results with biological tests. A lot of different solvents with different properties (like polarity) are the main positive of this extraction. [38]

Supercritical fluid extraction

Supercritical fluid extraction (SFE), with clear carbon dioxide, is used for characterization of sorption and desorption behavior of organic compounds in nature soils. Main benefits of this method are: adaptation power of extraction by modification of temperature or density of solvent, the minimal effect on compactness of matrix organic material, supercritical carbon dioxide is hydrophobic and can be displaced like HOC.

Another type of supercritical fluid extraction is SFE with supercritical water. This water is effective for extraction of organic compounds in wide spectrum matrixes, but applying is limited because of high temperature (more than 374°C) and pressure (more than 218 atm.) during extraction. These conditions affect the samples. [36]

2.3.1.3 **Solid phase extraction**

This extraction method is divided in two types: in wet soil or in soil suspension on SPE equipment during a fixed time. The concentration of the compound is similar to the concentration in porous water, so the bioavailability can be determined. The choice of the solid phase and the amount of the sample depends on polarity, properties and the amount of the soil etc.

Solid phase microextraction (SPME)

This method imitates dividing of chemical compound between porous water and an organism. SPME involves the use of a fiber coated with an extracting phase, that can be a liquid (polymer) or a solid (sorbent) which extracts different kinds of analytes from different kinds of media (liquid or gas phase). After extraction, the SPME fiber is put to the injection port of separating instruments, like Gas Chromatograph. The attraction of SPME is that the extraction is fast and simple and can be done without solvents, has great potential for field applications

Tenax

Tenax is a porous polymer (2,6-difenyl-p-fenylenoxide) used for desorption of analytes from soils. Tenax is hydrophobic and need really a long time for equilibrium. Benefits of Tenax: the properties of Tenax are similar to the properties of organisms and there is an easy separation from the matrix. [37]

Resin XAD

This method is used for the study of bioavailability and biodegradation, are known a lot of resins which have different properties. Globular resin particles have netting structure and huge surface, so the adsorption is very fast and gives information about bioavailability.

C18 membranes

These membranes use principle of free solved compounds (but there is necessary bigger volume than in SPME extraction).

Polyethylene tube dialysis (PTD)

PTD method means close sediment or solution of salt in the polyethylene tube (without air). The studies are not compared with biotests, so there have not been guarantees for bioavailability yet. [34]

2.3.2 Sequence extraction

This second type of extraction is more complicated than the first one, but they are more selectivity of the particular extraction procedures and sequenced (the probability of the redistribution of metals due to their readsorption on the active phases in the course of extraction procedures). Several types of leaching agents are used in these extractions. Sequence extraction analysis (SEA) is based on stepwise reactions sample with leaching agents, whose power is rising. [12] [14] [18]

Fractionations of metals are methods for description of distribution elements in soils. Methods of separation techniques used for the speciation analysis and fractionation are simple and sequence extraction, microwave extraction, solid phase extraction, ion exchangeable, difuze gradient technique, flow inject analysis, etc. The system of speciation and fractionation techniques was very difficult and therefore European commission was given in programme Standards, Measurement and Testing Programme (formal BCR) right procedure and describes three types of soils use like reference material.

Table 1: Schemes of sequence extractions

In different order (than order in the table) is the order write as capital letter in the superscript.
Residual fraction is not in the table. [50]

year	founded	A exchangeable	B dissolve in acids	C easy reducible	D easy oxidizable	E moderately reduscible	F oxidizable oxides and sulfides	G weak reducible
1973	MacLaren and Crawford	$CaCl_2$	HOAc	-	$K_4P_2O_7$	NH_4Ox/HOx	-	DCB
1977	Gibbs	$MgCl_2$	-	-	$NaOCl/DCB^C$	-	-	DCB^B
1977	Engler et at.	NH_4OAC	-	$NH_2OH.HCl$	-	-	$H_2O_2/$ NH4OAc	-
1979	Tessier et at.	$MgCl_2$	NaOAc	-	-	$NH_2OH.HCl/HOAc$	H_2O_2/NH_4OAc	-
1983	Meguellati et at.	$BaCl_2$	$NaOAc^C$	-	-	$NH_2OH.HCl/HOAc^D$	H_2O_2/NH_4OAc^B	-
1983	Shuman	$Mg(NO_3)_2$	-	$NH_2OH.HCl^C$	$NaOCl^B$	NH_4Ox/HOx	-	-
1984	Salomons and Fortsner	NH_4OAc	NaOAc	$NH_2OH.HCl$	-	NH_4Ox/HOx	H_2O_2/NH_4OAc	-
1986	Miller e at.	$Ca(NO_3)_2/Pb(NO_3)_2$	$HOAc/Ca(NO_3)_2$	$NH_2OH.HCl$	$K_4P_2O_7$	NH_4Ox/HOx	-	NH_4Ox/HOx
1990	Elliot et at.	$MgCl_2$	NaOAc	-	$Na_4P_2O_7^D$	NH_4Ox/HOx^C	-	-
1993	Ure et at. (BCR)	-	HOAc	$NH_2OH.HCl$	-	-	H_2O_2/NH_4OAc	-
1995	Krishnamurti et at.	$Mg(NO_3)_2$	NaOAc	$NH_2OH.HCl^D$	$Na_4P_2O_7^C$	NH_4Ox^F	$H_2O_2/Mg(NO_3)_2^E$	NH_4Ox/AA
1995	Campanella et at.	-	NH_4OAc	$NH_2OH.HCl/HOAc$	-	-	$HCl^C/NaOH^D/HNO_3^E$	-

A) Exchangeable fraction
   In this fraction are weak bonded speciation of metals which are bonded on surface of soils by weak electrostatic interactions. Bonds are broken by ionic exchangeable processes which are caused by electrolytes (salts of strong or weak acids, base with pH = 7) in the water solution.
   Leaching agents: chlorides ($MgCl_2$, $BaCl_2$, $CaCl_2$, NH_4Cl_2), acetates, nitrates ($Mg(NO_3)_2$, KNO_3, NH_4NO_3)
B) Fraction bonded on carbonates
   Metals are release in pH almost 5 and this fraction is very sensitive on pH changes. Dissolve effect depends on concentration of carbonates in sample (Tessier), grain size, size of sample (recommended ratio solid part: liquid part is 1:25)
   Leaching agents: buffered acetic acid, sodium acetate, EDTA
C) Fraction bonded on oxides and hydroxides of Iron and Manganese
   The best leaching agents of this fraction are reducing agent with ligand able to keep the loose ion in the solution.
   Leaching agents: hydroxylamine, oxalic acid, dithionites sodium
D) Fraction bonded on organic mass and sulfides
   Organic mass in soils are polymers, known as humic substances or carbohydrates, proteins, amino acids, fats or oils. Organic mass under oxidation conditions is degraded and release sorbed metals. Oxidation agents are used to extract the fraction.
   Leaching agents: hydrogen peroxides, sodium hypochlorite, sodium hydroxide, sodium diphosphate or potassium diphosphate
E) Residual fraction
   The main parts of this fraction are primary and secondary minerals with metals in crystalline structure which can be disrupt by strong acids. Metals in this fraction could not pollute the environment under natural conditions.
   Leaching agents: hydrofluoric acid, hydrochloric acid, perchloric acid or nitric acid

2.3.2.1 **Sequence extraction according to Tessier [16]**

All sequence extractions are based on this technique, which was described in 1979 by Tessier and col. [11]

Sequence extraction according to Tessier is based on 5 steps, whereas every step breakdown of materials into varied fractions (they are dissolved (selectively) by using different extraction agents):

a) Exchangeable fraction – fraction of metals, which are absorbed on soil complex. Leaching agent is neutral (pH=7) and changes are affect by sorption – desorption process.
   The magnesium chloride ($MgCl_2$) is most often use for this extraction, because it combines strong ionex capacity of Mg^{2+} with weak complexing ability of Cl^- and does not attack sulfides of metals, organic mass or silicates.
b) Fraction bonded on carbonates – metals dissolve in soft acidic conditions (pH=5 – simulation of rain water). This fraction can contain low concentrations of heavy metal, like lead, cadmium, and zinc.
   This extraction is appropriate for soils with low concentration of carbonates. In higher concentrations of carbonates are not dissolved all carbonates and therefore carbonates dissolving continue in the next step and it cause overestimation of reduce fraction.
c) Fraction bonded on oxides and hydroxides of iron and manganese – it is the first fraction where metals are bonded with very strong bonds, but trace metals are thermodynamically unstable under anoxic conditions. It can be named reducing stage.
   The hydroxylamine is the reduce agent and its effect depends on pH, concentration, time of extraction and temperature. The acetate acid prevents resorption usage of complexing properties of acetate ions.
d) Fraction bonded on organic mass and sulfides – fraction of metals unbend in strong oxidizing conditions (it can be named oxidizing stage).
   Hydrogen peroxide does not completely decompose organic mass and sulfides and oxalic acid which dissolves iron oxides is created during the reaction. Courturas et al. gives method for better relevance of results, it is acidification by nitric acid.

e) Residual fraction – it´s the rest of metals bonded in silicate residue.

Table 2: Experimental protocol of Tessier extraction

Tessier		
step	***leaching agent***	
1	$MgCl_2$	magnesium chloride
2	CH_3COONa	sodium acetate
3	$NH_2OH.HCl$ in 25% CH_3COOH	hydroxylamine hydrochloride in acetic acid
4	H_2O_2 with HNO_3	hydrogen peroxide in nitric acid
5	HF	hydrofluoric acid

2.3.2.2 **BCR sequence extraction**

Similar method, like Tessier, is BCR. This is the newest and simplest method which is a 3 step sequence extraction and was developed in programme Standards, Measurement and Testing Program (before BCR, but the name stays on). [13]

Three steps of BCR:

a) Exchangeable fraction
b) Reduced fraction
c) Oxide fraction

Table 3: Experimental protocol for BCR

BCR		
step	***leaching agent***	
1	CH_3COOH	acetic acid
2	$NH_2OH.HCl$	hydroxylamine hydrochloride
3	H_2O_2 and after that H_3COONH_4	hydrogen peroxide and after that ammonium acetate

2.3.3 Extraction by microwave

This method uses microwave radiation which increases temperature and pressure. The sample and reagents are introduced into a pressure vessel and thanks to microwave radiation are heated (pressure is rising, too). The extraction times are shorter than in the conventional methods.

2.4 Enviromental impact of hazardous metals

2.4.1 Lead (Pb)

Lead has a chemical symbol Pb (Latin: Plumbum) and it is a grey heavy metal. This toxic metal is known from ancient era because lead has low melting temperature, is very forging and it is water resistant.

Lead is the most widespread metal on the world and in small quantities can be toxic for organisms. The most important source of environment contamination are lead mining, ore processing, batteries, pipes for drinking water and production of paint colours, in the past from combustion of fuel (more than 30m from the road).

Heavy metals can stay in the atmosphere for a long time and migrate on a long distance. Contamination of soil can be thousands kilometres from the source of pollution. Most interesting is that fishermen and hunters spoil the environment with thousands of tons of lead. [25]

Lead absorption by plants (accumulate in roots) is reduce by reducing the acidity of calcareous and it can form complexes with humic substances and prevents any movement in the soil layers.

Physiological and environmental effects

Lead belongs to a group of toxic elements. It is most toxic for infant organisms and the chronic contact causes retardation of mental development and changes of behaviour. Lead goes in organisms mainly by lungs, is accumulated in the bones and blood and damage mainly central nerve system.

Symptoms of poisoning are whiteness colour in the face and on the lips, constipation, anaemia, headache, nephritis, disturbances of central nerve system, etc. [23]

Carcinogenicity of lead is known in animals, but in humans has not been confirmed.

2.4.2 Copper (Cu)

Copper is a very old metal, which was used in every period of our history. Cu (from Latin Cuprum) is the symbol of this metal. It has a reddish colour, very good electric conduction and is resistant against the atmospheric influence. This heavy metal has a lot of alloys, as bronze and brass, and compounds which have so many colours. [20]

The concentration of copper in soils depends on pH and organic mass. Amount of copper in soil water is very toxic for plants, it can be prevent by liming and organic fertilizers.

Physiological and environmental effects

Copper is a very important element for alive organisms which is participating on many enzymatic reactions and cycles necessary for function and health condition of organisms. It is a centre of compound hemocyanin, which transports oxygen in mollusces and articulates bodies.

Overage of Copper is venomous and causes serious health problems even death. The death is not so common because in the food Copper causes uncomfortable taste and is uneatable.

The acute intoxication causes metal fever which is manifest as flu and usually disappears within 24hours. The chronic intoxication is known just for employees working with mixture $CuSO_4$ and $Ca(OH)_2$ (known as “Bordeaux mixture”) on vineyards more than 43years.

Children whose have been exposed by a food and drinking water with high concentration of copper lost weight and had diarrhea but livers was not damage.

We know a very uncommon illness, Wilsons illness, when the body could not metabolize well copper from food, and it is accumulated in the tissues. Children have damaged liver, suffered with dementia and convulsions. [24]

2.4.3 Cadmium (Cd)

Cadmium is a soft, easily fusible toxic metal with a Latin name Cadmium (the symbol is Cd). Cd is used as protection of many alloys and metals, because the properties are better, but is very toxic. [26] Cadmium has low boiling point and is necessary for metallurgical work to clean gas exhalations or as electrodes in the alkali accumulators. Smokers are in bigger danger than non – smokers.

Cd can be bond on ash and soil particles, which can stay in the atmosphere for more than a week (it depends on pH, redox potential, concentration of Cl^- anions), and after that falls down with wet deposition. After that cadmium is cumulated in waters and soils (cadmium is immobile in alkaline soils) and is part of food chain, it caused accumulation in organisms (bio cumulative) – mainly toxic for water organisms. [29]

Physiological and environmental effects

We have known that Cadmium is very negative for plants and human organism. The main problem is that Cadmium is so similar to Zinc which is an essential element for organisms (cadmium can block the insulin cycle and it causes serious health problems). [27]

Another problem is that it is very cumulative poison (mainly in testes, lungs, livers and kidneys), but it depends on organism, age, sex (female are more sensitive for cadmium). Elimination is very problematic. The toxic effect depends on absorption, accumulation, metabolism and excretion and this effect begins when the concentration reaches to the critical value. Some reversible and irreversible changes are observed.

Symptoms of chronic poisoning are damage of lungs, kidneys and livers, anaemia, osteoporosis, influence on metabolism of calcium, lower function and quality of sperm etc., in generally cadmium is toxic for all organ systems in organism. If cadmium ions damage central and peripheral nervous system it cause slowing of reflexes and muscles twitching, Cadmium accumulate in the heart and blood vessels cause heart failure and disorders of blood circulation. Cadmium is strong carcinogen and teratogene.

Symptoms of acute poisoning are stomach ache, diarrhoea and vomitting. Lungs are very important organ cadmium poisoning and it cause severe irritation of the respiratory tract followed by cough, headache, dizziness, weakness and respiratory disorders. [28]

Lethal concentration of cadmium oxide fume is 5mg/m^3 for 8hours exposure and in oral intake is 350 – 8900mg for human. The most dangerous is a very long decay time, up to 20years.

No – effect level is around 3mg.

2.4.4 Mercury (Hg)

Mercury (Latin Hydrargyrum, symbol Hg) is a heavy and toxic metal with wide usage, as a part of alloys, filling for thermometers, etc. It is good at electric conductivity. [32]

Anthropogenic sources of Mercury in the environment are mining, burning of coal and waste, production of paints, accumulators and fluorescent tubes, industry of paper, cosmetics and crematories, from dentist and pharmaceutical industry.

Mercury has one of the highest rates of accumulation and therefore is liable to accumulate in sediments and subsequently in the flora and fauna.

Physiological and environmental effects

Mercury is a very strong toxic contaminant of the environment, especially for water organisms (mainly in sediment) whose are eaten by biggest organisms and these organisms are eaten by fishes where mercury is accumulated. After that lead goes in the food chain.

Concentration of mercury in soils depends on microorganisms and pH. In generally, due to the volatilization of Hg increase content in surface horizons (especially in higher alkalinity and warmer climates). Chronic exposition causes damage of the peripheral central nerve system (neurotoxic), immunity and hepatotoxic, symptoms are irritation, tiredness, sleeplessness and mental diseases (like decrease of IQ). [33]

Elementary mercury

In acute toxicity are damaged lungs and central nerve system. Symptoms are nausea, vomiting and strong diarrhea. Main important is metal taste in mouth, swelling of jaws follows by falling of teeth.

Lead causes damage of brain, tremors and muscle vibration in whole body (begins in fingers and lips) in chronic exposition. Typical is weakness, headache, dizziness, loss of appetite and loss of weight.

Inorganic compounds of mercury

These compounds cause on kidneys and digestive tract in acute exposition. Already ingestion of the toxic dose (0,2 - 1g) cause bloody vomiting after that comes abdominal pain associated with bloody diarrhea and collapse due to dehydration.

The chronic poisoning is not probably.

Organic compounds of mercury

Intoxication is across placenta and cause cerebral lesions with motor and mental disorders. Inhalation of mercury damages lungs.

The main risk group is pregnant women, because mercury passes across placenta to the foetus. It can cause defects of its development, hearing, sight, talking and thinking. [31]

2.5 Method for determination of metals

2.5.1 Atomic absorption spectrometer

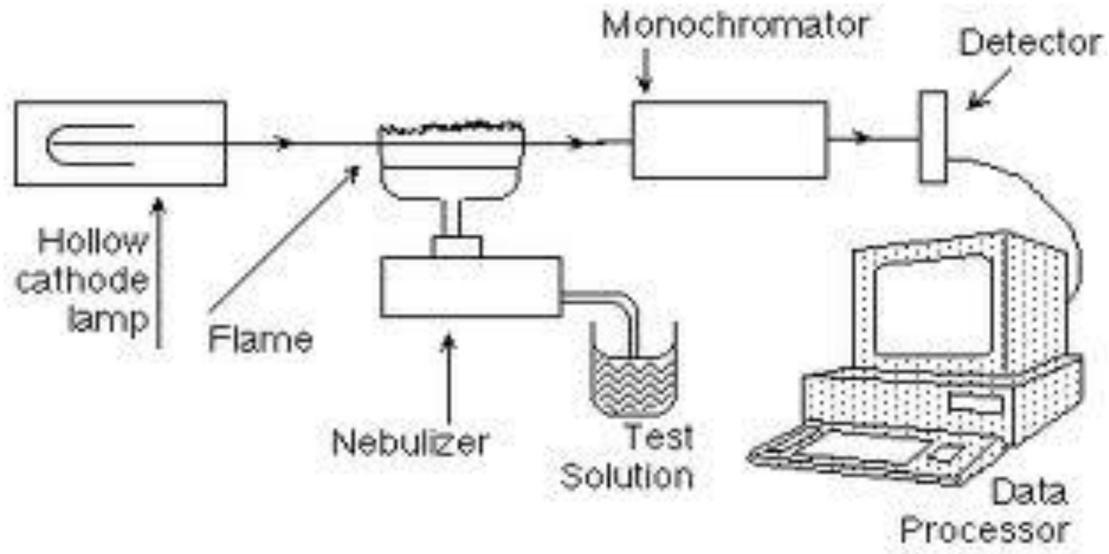
Principe

Atomic absorption spectrometry (AAS) is the most frequent analytic method in these days.

The principle of this method is absorption of right electromagnetic radiation by free atoms in gaseous state. Free atoms absorb photons definite energy, radiation of exact wavelength, which is characteristic for definite atoms. This method can be used for more than sixty elements. [39]

The radiation, which will be absorbed, must realize the condition: — — etc. (is the energy of the basic shell, and are energies of excitation shells) and the source of radiation must be the same element as the determination one. [40]

Picture 5: Atomic absorption spectrometer



Line source of monochromatic radiation

a) A lamp with a hollow cathode: the cathode is a hollow cylinder from the same metal as the determination one (full of neon or argon) and the anode is wolfram or a molybdenum needle. The lamp contains argon with the pressure of 1kPa. The tension of 400V causes glow discharge and the creation of ionize atoms of the inert gas, which strafes the metal. Vacant atoms of the metal are excited and they send radiation.
b) A multi – element lamp: has an alloy cathode. This lamp can analyse eight elements, but it is less sensitive.
c) A shielded cathode: cathodes have a shape of a hollow cylinder (the cathode and anode are isolated by ceramic material) and radiation is just inside the cylinder
d) A lamp with a high radiation: excitation of atoms is in discharge between helpful electrodes. It is for volatile elements, like sillicium, titanium etc.
e) An electrodeless discharge lamp: the principle is highfrequency electromagnetic field. The source of radiation is silicium flask. There is inert gas and little bit of volatile compound of determing element inside. The flask is on inductor of highfrequency source (frequency 27MHz), and after the supply of energy it creates ring discharge. It can be used just for volatile elements.

Atomizers

Atomizer is changing sample into free atoms. It need temperature for atomization, but lower one than it is needed for excitation of atoms, the temperature is around 2000-3000°C.

A) Flame

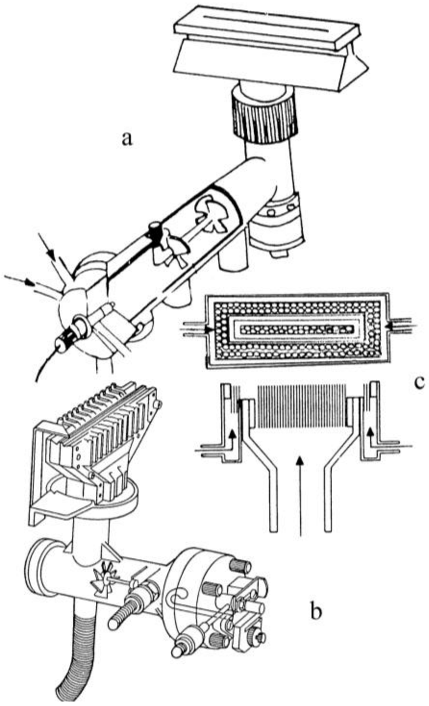
The flame atomizer works on principle of pneumatic steamer or ultrasonic spray, which sprays some solution of the sample. The sample, an oxide agent and heat gas are mixed and go in the flame, where is atomized.

1) Burners

   Long singlesplit or multisplit burners are from titan or anticorrosive materials. They are acceptable for laminar flames with a front – end steam chamber.

   The threesplit burner has a better rate signal/noise and we can use it for steaming of solutions with high concentration of salts. [43][44]

Picture 6: Burners a) the single split, b) the profile split, c) Mékere burner



2) Steamers

   Solution of the sample is sucked up by capillary in the pneumatic steamer thanks to the underpressure from jetting gas. This solution goes in the flame like aerosol, one part is coagulated in the stream chamber and just a small part of the solution (5-20%) goes in the flame.

3) Flame

   Creation of atoms in the flame is a very difficult process. Quantity of atoms in the flame, depend on all parts of the solution.

   The flame must be transparent for light, and cannot absorb radiation. Liquid or solid participations can cause dispersion of radiation and non – dissociated molecule can cause nonspecific absorption of radiation. Gases in lamination flames are mixed before burning. Rate C_2H_2/air and C_2H_2/N_2O are used most frequently as a flame.

Table 4: Flame temperatures in flame atomizer

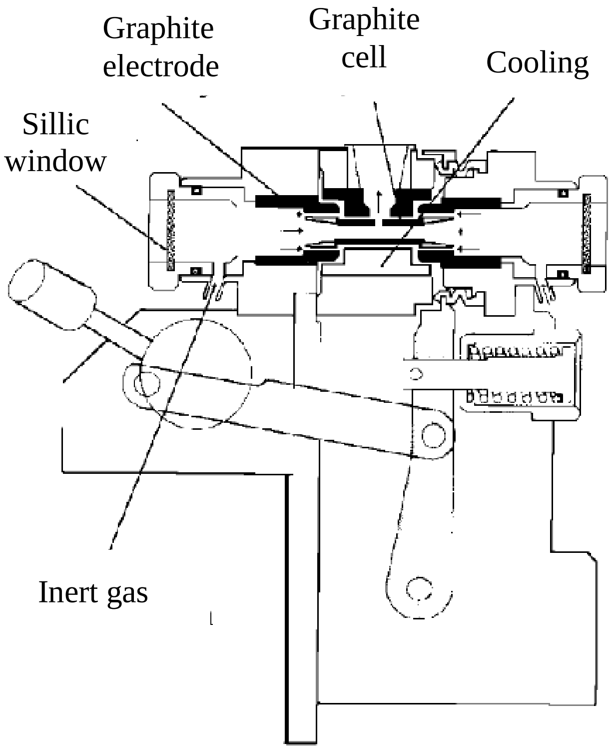
fuel	***oxide agent***	***temperature (°C)***
propane	air	1900
acetylene	air	2300
acetylene	oxygen	3100
acetylene	nitrogen monoxide	3000
hydrogen	oxygen	2600

Metal elements with low concentration are quantitatively analyzed by atomic absorption spectrometer. Lamb – Beer law is realized for the concentrations of 0,1 - 100µg/ml for the atomic absorption spectrometer with flame atomizer.

B) Electro thermal

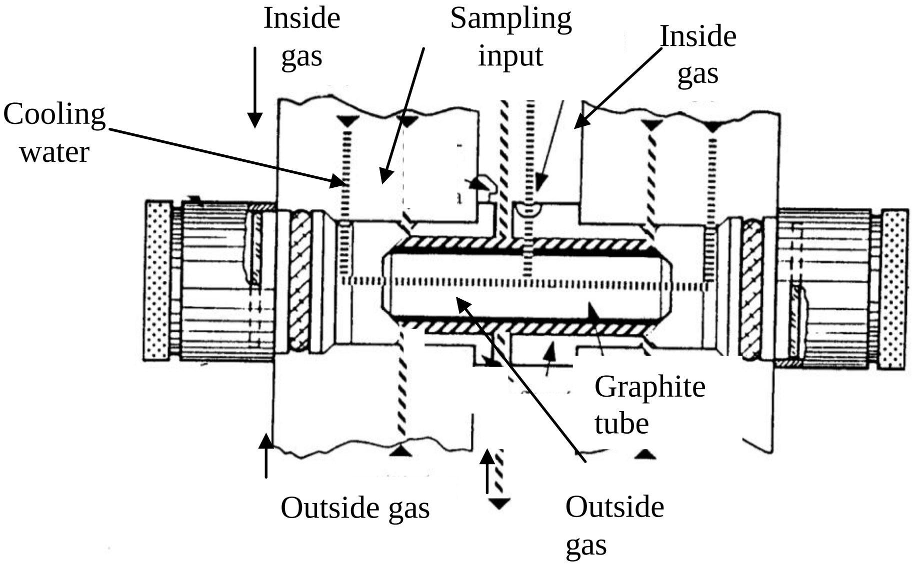
Electro thermal atomizer is equipment heated by the way through of electric current. Heating is by resistance (most frequently used), inductive or capacitive.

Picture 7: The head of an electro thermal atomizer



A lot of types of electro thermal atomizers are known. They are differentiated in material, construction, temperatures, heat speeds, and other properties.

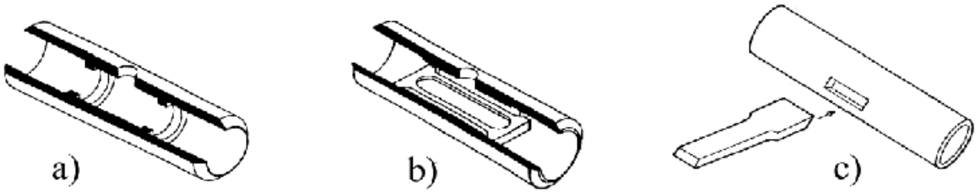
Picture 8: An electro thermal graphite atomizer HGA

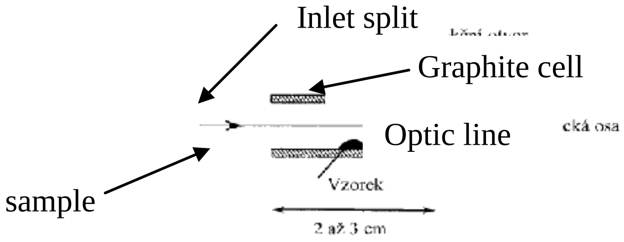


The graphite tube is the basic part of this atomizer. Argon goes inside (it goes from the beginning to the middle and leads away the waste product from the atomizer) and outside (protection against oxygen from the atmosphere).

The sample is dosed on the graphite cell and atomization is done by heating of the cell by electric current.[43][44]

Picture 9: Graphite cells: a) standard, b) with the platform, c) with the sond





Salts are destructed by dissociation or reducing. Drying, pyrolysis or atomization can be pre – set, all phases are characterized by heat speed, time of heating, gas – flow etc.

Drying of the sample is the first phase. The temperatures are, in general, chosen a little bit over a boiling point of the leaching agent or drying must proceed in more steps (for example for blood serum – 2 steps). It depends on volume of the sample. The sample must be totally dry, because the sample shortage of weight in an opposite case.

Pyrolysis is the second phase, it changes the analyte and sample matrix to another form. The best way is, when the matrix of the sample is taken out, but the analyte stays there. The maximum temperature is identified from Decomposition curve. It is constructed from repeated measurements, when atomizing is at the constant temperature. The optimal temperature is 50 – 100°C under the break on the curve.

The analyte signal is logged in the *atomized* phase. The optimal temperature of this phase is identified from Atomized curve, which has a constant temperature for pyrolysis, and this temperature must be 50 – 100°C higher than the constant temperature on this curve. Important properties are the heat speed and the flow of gas.

Cleaning of the atomizer from the sample (the temperature and time are chosen with the view to the age of the atomizer) and cooling are the last parts of this process. [45]

Monochromator

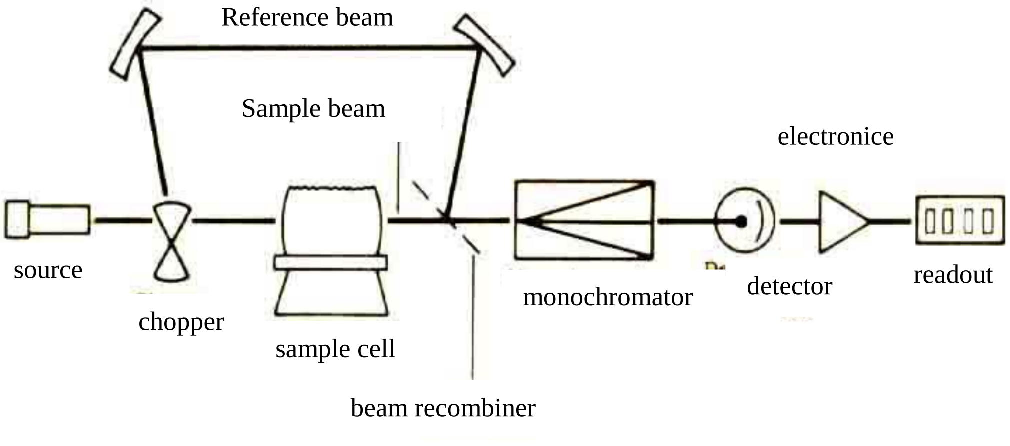
Detector

Detector is photomultiplier and it is connected to the computer. [39]

Atomic absorption spectrometer can be:

a) Single beam
b) Double beam – the beam of rays is divided by rotate mirror in two parallel beams, which alternatively come on slit of monochromator.

Picture 10: An atomic absorption spectrometer - double beam



2.5.2 Analyzer AMA 254

Concentration of mercury (in solid or liquid state) is determined by Analyzer AMA 254 and there are not necessary chemical changes before determination. This instrument is dedicated for mercury. [48]

Feeder[1] and *feeding boat*[21] put a sample into the instrument. The first part of the *burning tube*[2] is for thermal decline of the sample and the second part is filled by catalyst, heated on the constant temperature of 550°C by the catalytic furnace[3].

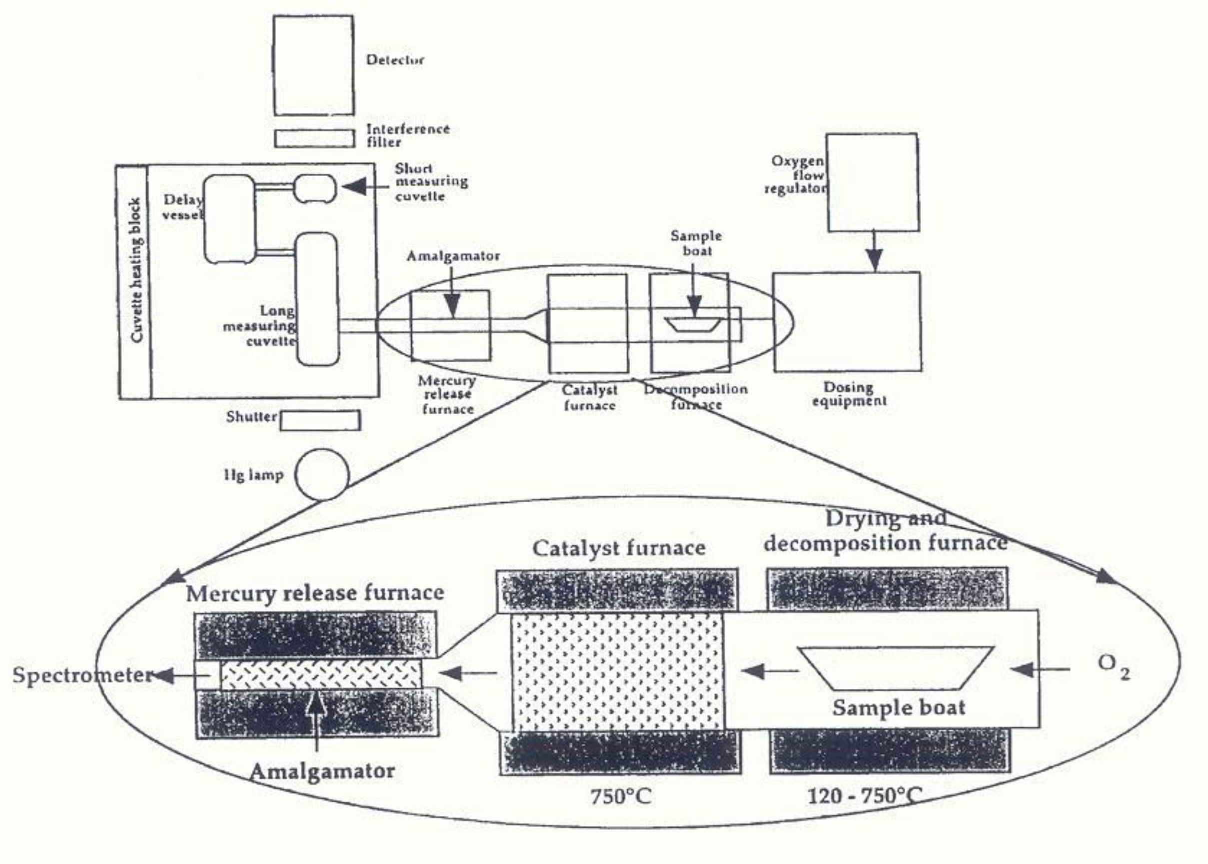
Mercury from the flow of gas products is caught in *amalgamator*[5] and after that it is desorbed by the *expel furnace*[6] (it heats amalgamator and it desorbs mercury). Measuring *cuvettes*[7] are in one bloc and they are heated up to 120°C by *heating block*[13]. Two cuvettes are connected by a serial connection. The first[14] and the second[16] cuvette are in the rate 10:1, and the *delaying cell*[15] is in the middle of them (out of the optic line) and has much more bigger volume than cuvettes. Thanks to this property, we can measure in double sensitivity, so we have two calibration ranges.

The low pressure *mercury discharge lamp*[8] is the source of radiation. The i*nterferential filter*[11], ionizes radiation 253,65 nm, is one part of the *detector*[10]. The c*ooling pump*[12] cools down amalgamator, the *analogue valve tube*[18] contains mercury discharge lamp, the source for the digital part, switches etc.

Oxygen goes in the whole instrument (from the input[22] to the output[17]) and the *flow regulator*[20] regulates oxygen flowage on a constant value.

Drying, decomposition and delay are basic setting properties of it. The time of drying depends on the type and quantity of the sample – liquids must be perfectly dry. [49] [47]

Picture 11: Scheme of analyzator AMA 254



3 EXPERIMENTAL PART

3.1 Samples

Samples were from one Moravian energetic companies from four heating plants. Most of the companies had a request that their name will not be published.

Identification of samples is in the table Table 5: The table of heating plants and terminology (nomenclature) of samples.

Table 5: The table of heating plants and terminology (nomenclature) of samples.

Type of heating plant	***fuel***	***combustion apparatus***	***output from heating plant***	***nomenclature of samples***
A	brown coal biomass	atmospheric fluid-bed boiler	log ash	A1
			fly-ash	A2
B	black coal biomass	pulverized coal fired boiler	fly-ash	B1
			hydromixture of ash and dross	B2
C	brown coal biomass	pulverized coal fired boiler	scoria	C1
			fly-ash	C2
			product from desuphurization	C3
D	black coal biomass brown coal	atmospheric fluid-bed boiler	log ash	D1
			fly-ash	D2
			-	-

3.1.1 Description of products from heating plant

The products from these heating plants are technological vapours, which are used for generation of electric energy, warm and hot water (used for heating).

- Heating plant A

  Brown coal and biomass are combustion in the Heating plant A in two atmospheric fluid-bed boilers with circulation layer. The temperature of this process is 820-850°C. After the combustion of fuel in the burning place, log ash goes from the furnace to the bottom of the burning chamber and this log ash cools here. Then it goes on the vibration riddle and to the silo of log ash in the mixing centre.

  Fly-ash is caught in the collecting hopper and goes to two silos in the mixing centre.

  Limestone is added directly in the fluid bed in the burning chamber. The result is that it decreases emissions of sulphur oxides. Products (plaster and the rest of limestone) are removed with log ash and fly-ash.[5]

  Heating plant A gives two samples which are described in the Table 5: The table of heating plants and terminology (nomenclature) of samples.

Picture 12-13: Sample A1 and A2

- Heading plant B

  Biomass (maximum 10-15%) and black coal is combusted, in the Heating plant B, in four granulation boilers. Dross goes on the overflow edge, from where it falls to the crusher and after that to the sludge bed. The sludge bed is a place for ash and dross, taking off water causes that the mixture goes to the permanent chamber. [6]

  Heating plant B gives two samples which are described in the Table 5: The table of heating plants and terminology (nomenclature) of samples.

Picture 14 - 15: Sample B1 and B2

- Heating plant C

  Brown coal and biomass are burnt in the Heating plant C in three granulation boilers, it is necessary that there is the maximum of 10% biomass in the mixture.

  There is a leaker under every boiler. The leaker takes dross, cools it in the water and puts the dross in the container. The dross is taken from the container put on the manipulation place near the mixture centre.

  The separator is behind every boiler where solid contaminants are caught from combustion products. Ash is caught in the separator too and after that it is taken to the mixture centre.

  Combustion products are desulphurization half-dry methods by limestone calcite. After desulphurization the combustion products go through fabric (textile) filter, which catches the product (from desulphurization). This product goes in the mixture centre. [7]

  Heating plant C gives three samples which are described in the Table 5: The table of heating plants and terminology (nomenclature) of samples.

Picture 16 - 18: Sample C1, C2 and C3

- <u>Heating plant D</u>
  Brown coal, black coal and biomass are combusted, in the Heating plant D, in two atmospheric fluid-bed boilers. Fly-ash is caught on fabric filter and then it is transported to the mixture centre. [8]
  Desulphurization is realizing of limestone direct dosing in the combustion chamber. [5]
  Heating plant D gives two samples which are described in the Table 5: The table of heating plants and terminology (nomenclature) of samples.

Picture 19 - 20: D1 and D2

3.2 Methods of extraction

The Tessier method was used for sequentional extraction. This extractions were performed at two temperature, at laboratory temperature (22±2°C) and 40±1°C.

The equipment used for the sequential extraction procedure was 50mL polyethylene (PE) or glass vessel and into the sample (2 g) was put. The sample and extraction solution were mixed by using a rotation machine and the heating equipment was water bath. Samples were stored in polyethylene bags in laboratory and all solutions and extraction solutions were stored at 4°C in laboratory refrigerator.

Deionized water was used for the preparation of stock solutions and in each step of the leaching procedure there it was obtained from a Millipore Milli-Q system. All glassware used for the experiments was previously rinsed in 5% HNO_3, and washed with deionized water. All reagents used in this study were of analytical grade and were checked for possible metal contamination.

After extraction the solution containing extraction agents and samples were filtered with using vacuum filtration apparatus Supelco with membrane filter Pragopore 5.

3.2.1 Procedure of extraction

1) *Exchangeable fraction:* The sediment was extracted at room temperature (25°C) for 24 hours with 20 ml of magnesium chloride solution (1 M $MgCl_2$, pH 7) with continuous agitation. Next steps were filtration on membrane filters and drying to the constant weight in the dessicator.

Picture 21: Sample and the leaching agent

Picture 22: Samples in shaker

2) *Fraction bonded on carbonates:* The residue from the exchangeable fraction was leached at the room temperature (25°C) with 20 ml of 1 M sodium acetate adjusted to pH 5 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for the complete extraction was 24 hours. The sample was dried in dessicator to the constant weight after filtration.

3)

Picture 23: Filtration of samples

4) *Fraction bonded on Iron or Manganese oxides or hydroxides:* The residue from fraction bonded on carbonates was extracted with 20 ml of 0.1 M hydroxylamine hydrochloride in 25% acetic acid with continuous agitation (the room temperature - 25°C) and the time of leaching was 24 hours. [41] Next steps were filtration and drying.

Picture24 - 25: Samples in the dessicator

5) *Fraction bonded on organic matter and sulfides:* To the residue from fraction bonded on Iron or Manganese oxides or hydroxides were added 7,5 ml of 65% M $HN0_3$ and 12,5 ml of 30% H_2O_2 and the mixture was agitated for 24 hours at the room temperature (25°C). [40] Samples were filtrated and dried in dessicator after agitation.

6) *Residual fraction:* The residue from the fraction bonded on organic matter and sulfides was mixed with 10 ml of hydrofluoric acid (in plastic flask) and was agitated 24 hours at the room temperature of 25°C. The time of agitation was 24 hours. This mixture was evaporated and dissolved in 2 M nitric acid.

Picture 26: The evaporation

3.3 Methods of determination

3.3.1 Calculation of Limit of detection and Limit of quantification

Limit of detection (LOD)

LOD is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value).

Calculation: —— S ... sensitivity (direction of calibration curve)
... standard deviation of the blank signal

Definition: it is absolute amount or concentration of analyte that gives a signal equal to three times the standard deviation of background signal.

Limit of quantification (LOQ)

LOQ is the smallest quantity of the analyte, which can be acceptable measurement. The standard solution is used for it.

Calculation: —— S ... sensitivity (direction of calibration curve)
... standard deviation of the blank signal

Definition: it is absolute amount or concentration of analyte that gives a signal equal to ten times the standard deviation of background signal.

3.3.2 Determination of mercury

The AMA 254 and computer with the right software were switched on according to the user manual. Oxygen was turned on and equipment was heated for 10-15 minutes. After that a cleaning programme was switched on (Table 6: Program of cleaning and analysis) with 100ml of deionized water. The cleaning process was repeated until the absorption was under 0,005.

The next step was the analysis with parameters in Table 7: Conditions of lead and copper during the measurement. The sample (50mg) was put on feeding cell and the analysis was switched on. The results, the units of the measurement (the concentration of mercury) were in ng, and for one sample it was done three times.

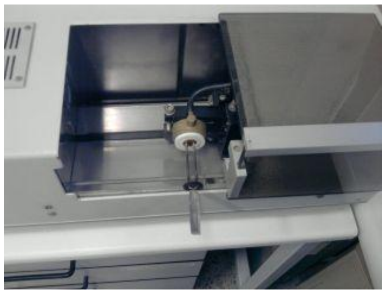
Table 6: Program of cleaning and analysis

process	***time (s)***	
	cleaning	***analysis***
drying	60	150
decomposition	90	200
waiting	45	45

After the end of the analysis was the supply of oxygen and computer switched off, but the equipment was switched off after 30minutes.

Picture 27: The AMA 254

Picture 28: The feeding cell of AMA 254



3.3.3 Determination of lead and copper

The computer with the software and acetylene were switched on. After that the equipment SpectrAA 30 was turned on and the flame was lighted up. Calibration solutions were measured in the same conditions as samples. The next step was to measure the solutions of samples.

Table 7: Conditions of lead and copper during the measurement

element	***current I (mA)***	***slit width (nm)***	***wavelength (nm)***	***flow of air/acetylene (l/min)***
Pb	10	1	217	3,5/1,5
Cu	6	0,5	324,8	3,5/1,5

Picture 29: The SpectrAA 30

Picture 30 - 31: The flame a) without a sample, b) with a sample

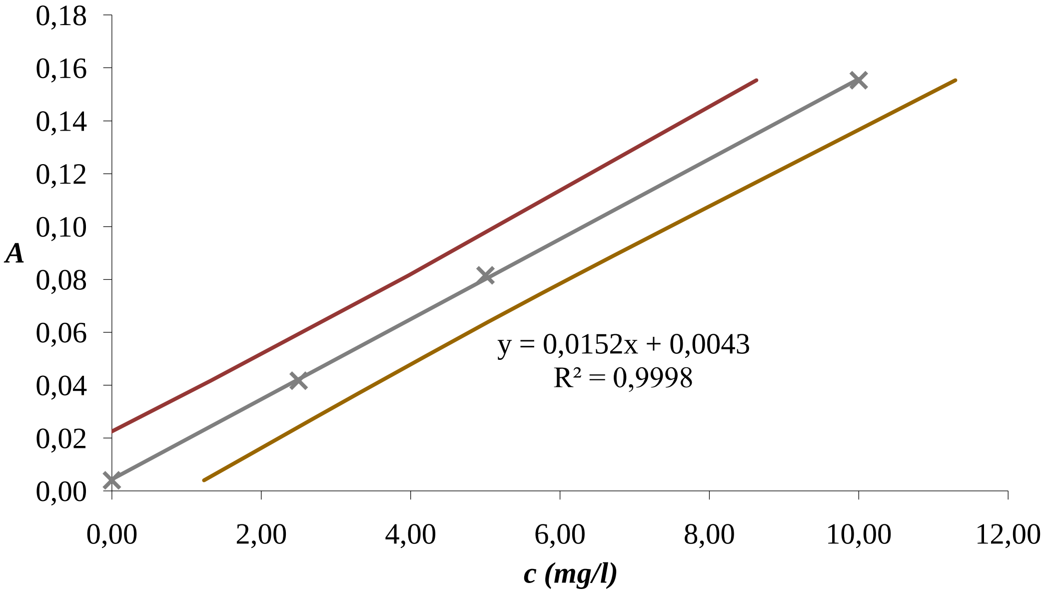
Table 8: Calibration solutions for lead

Pb	
concentration (mg/l)	***absorbance***
0	0,0040
2,5	0,0417
5	0,0815
10	0,1553

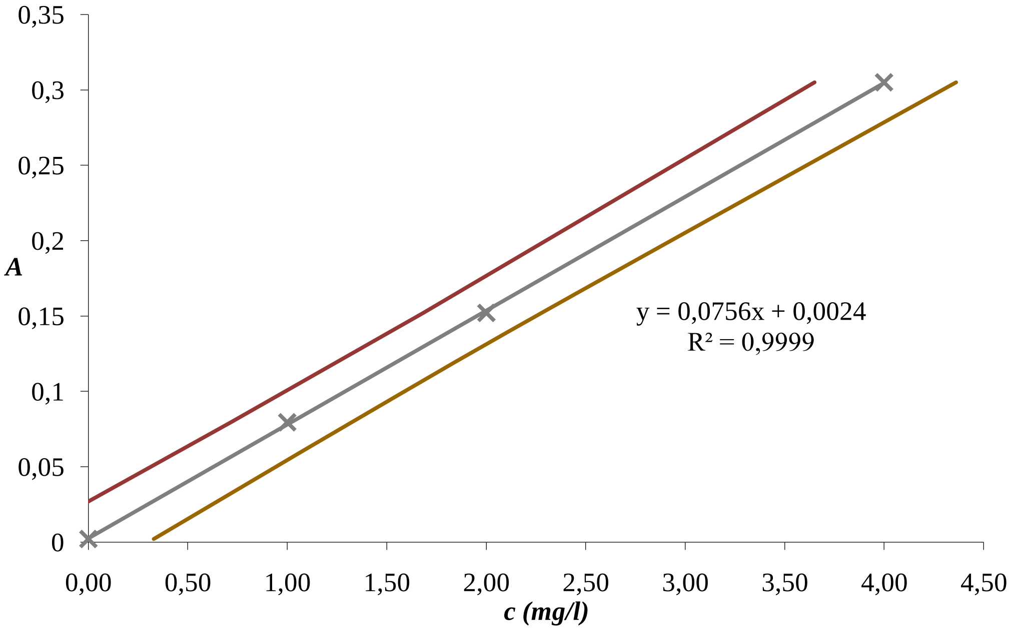
Table 9: Calibration solutions for copper

Cu	
concentration (mg/l)	***absorbance***
0	0,005
1	0,079
2	0,152
4	0,305

Graph 1: The calibration curve for lead



Graph 2: The calibration curve for copper



3.3.4 Determination of cadmium

The computer with the software and argon were switched on before the measurement. After that the equipment AAS-Zeenit 60 was turned on.

Table 10: The conditions of cadmium during the measurement

element	***current I (mA)***	***slit width (nm)***	***wavelength (nm)***	***flow of argon (l/min)***
Cd	3	0,5	228,8	48nl/h

Calibration solutions were mixed from the standard solution with concentration 1±0,002 g/l and were measured in the same conditions as samples.

Table 11: Temperature (furnace) program of ET-AAS during the measurement of cadmium

process	***temperature (°C)***	***ramp (°C/s)***	***hold time (s)***	***time (s)***	***flow of inert gas (argon)***
drying	90	5	20	34	max
drying	105	3	20	25	max
drying	110	2	10	12,5	max
pyrolyses	300	250	10	10,8	max
AZ*	300	0	4	4	stop
atomization	1000	1000	3	3,7	stop
cleanout	2200	500	4	6,6	max

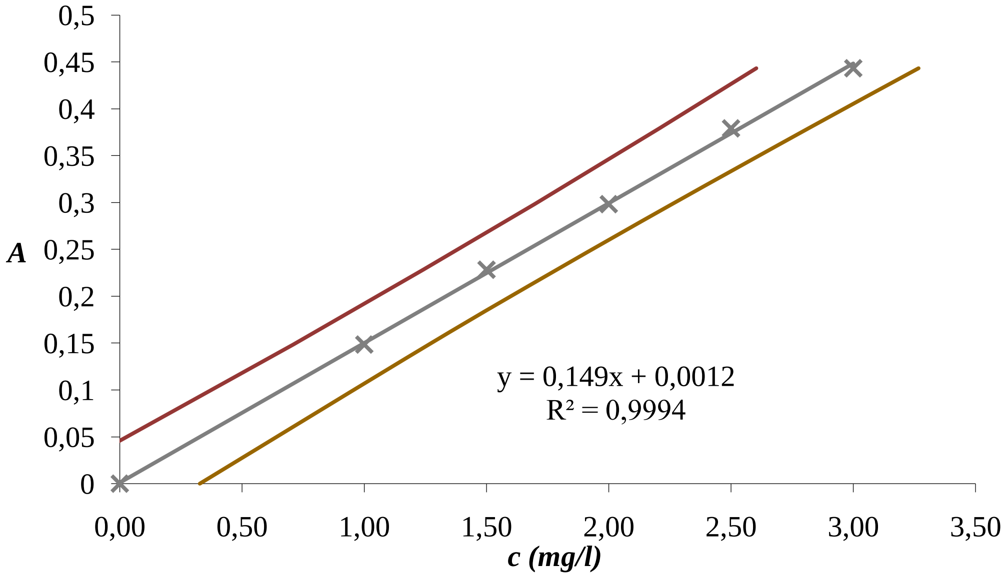
AZ* - autozero

Picture 32: The AAS ZEENIT 60

Table 12: Calibration solutions for cadmium

Cd	
concentration (µg/l)	***absorbance***
0	0
1	0,1485
1,5	0,2283
2	0,2984
2,5	0,3792
3	0,4432

Graph 3: The calibration curve for cadmium

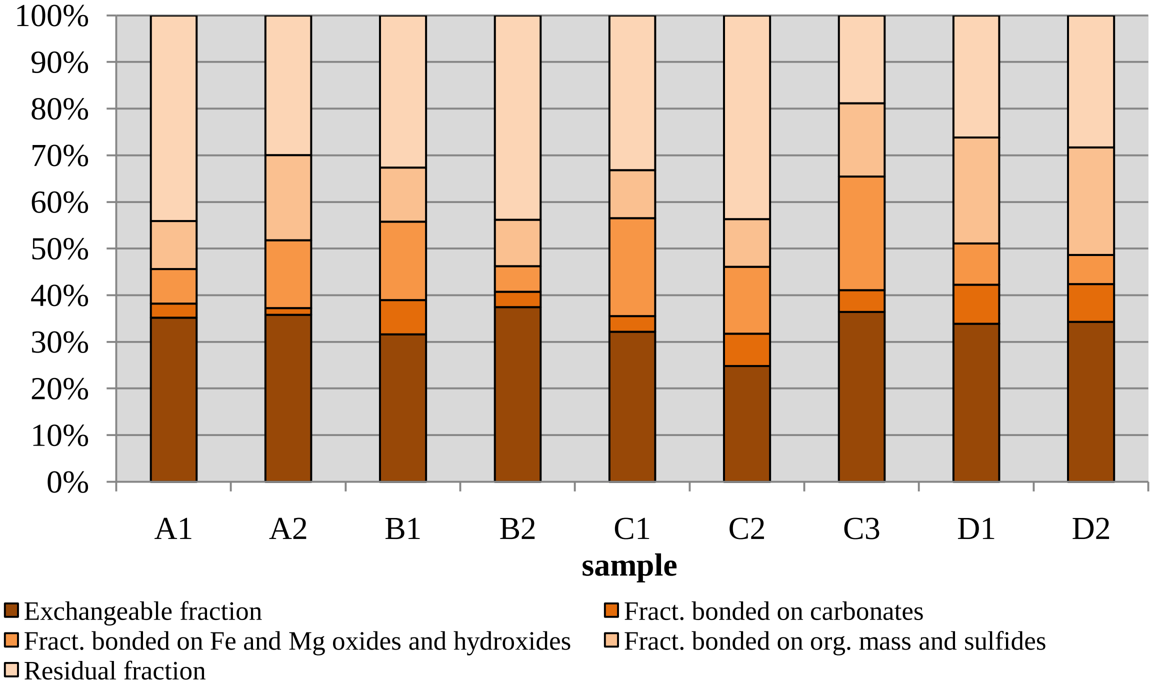


4 RESULTS AND DISCUSSION

4.1 Determination of lead

Lead was extracted in two temperatures (25°C and 40°C) in all samples of energetic wastes. The Graph 4: Amount of lead at the temperature of 25°C for all samples represents the results.

Graph 4: Amount of lead at the temperature of 25°C for all samples

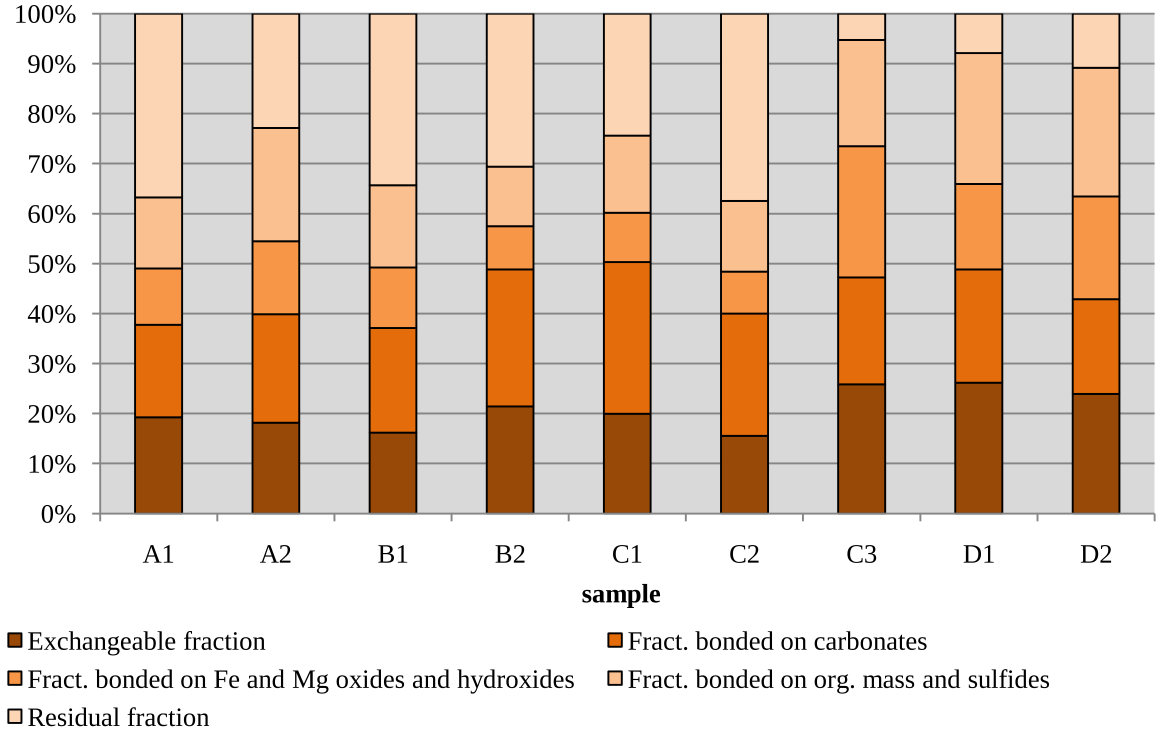


All samples had the higher amount of lead at the temperature of 25°C in the first fraction, the exchangeable fraction (28-40%), and in the last, the residual, fraction (25-45%). It means that lead can be changed very easily for another metal and entered into environmental components. Because the temperature was 25°C, similar as the room and nature temperature, is possible to say, that lead in this energetic waste is really dangerous for the nature in moderate climate in summer days (the mean temperature is around 25°C). The lowest concentration of lead was in the second step, the fraction bonded on carbonates (0-9%). In other fractions there were concentrations of lead low, around 10 %, it means that lead is not bonded on carbonates, Fe and Mg oxides and hydroxides or sulfides so much.

The lead extracted at the temperature of 40°C had not maximal concentration just in the one fraction, but had similar amounts in every step (mainly in samples C3, D1 and D2 –deviation was maximal 5% except the last, the residual, fraction).

Concentrations in the first fraction decreased in extraction at the temperature of 40°C from 28-40% on values 15-23%, on the other hand concentrations in the fraction bonded on carbonates was higher in 40°C than at the temperature of 25°C (0-9% increase on 25-30%). The higher temperature unbind lead mainly from carbonates, so in warmer locality is more dangerous lead bonded on carbonates than lead bonded in the exchangeable fraction, like in extraction at 25°C (moderate climate). In the third fraction (5-20%) and the fourth fraction (10-23%) had samples similar concentrations in both temperatures.

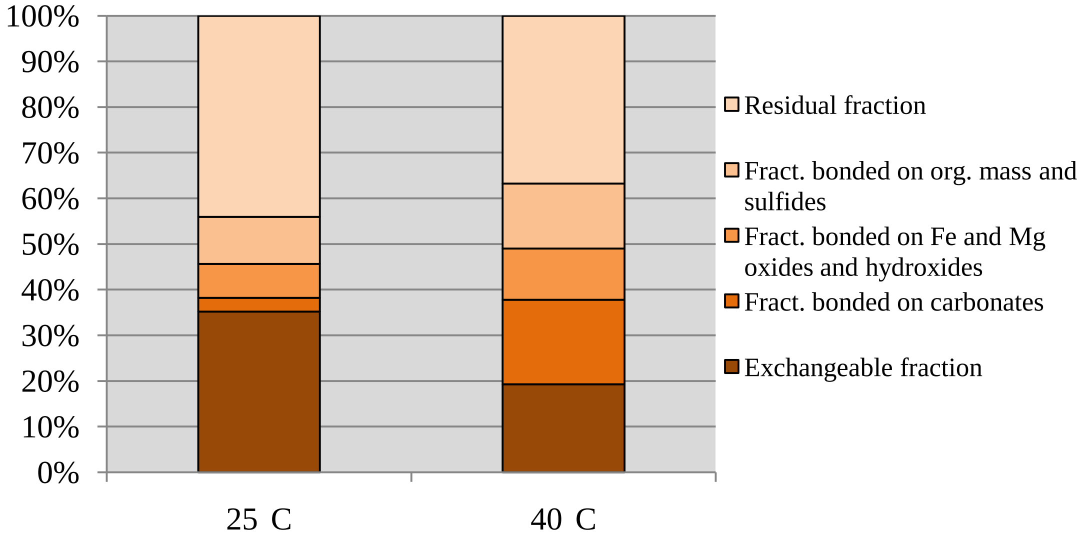
Graph 5: The amount of lead at the temperature of 40°C for all samples



4.1.1 Sample A1

This sample, log ash, was formatted in the atmospheric fluid-bed boiler from brown coal and biomass.

Graph 6: The amount of lead in sample A1 at the temperatures of 25°C and 40°C

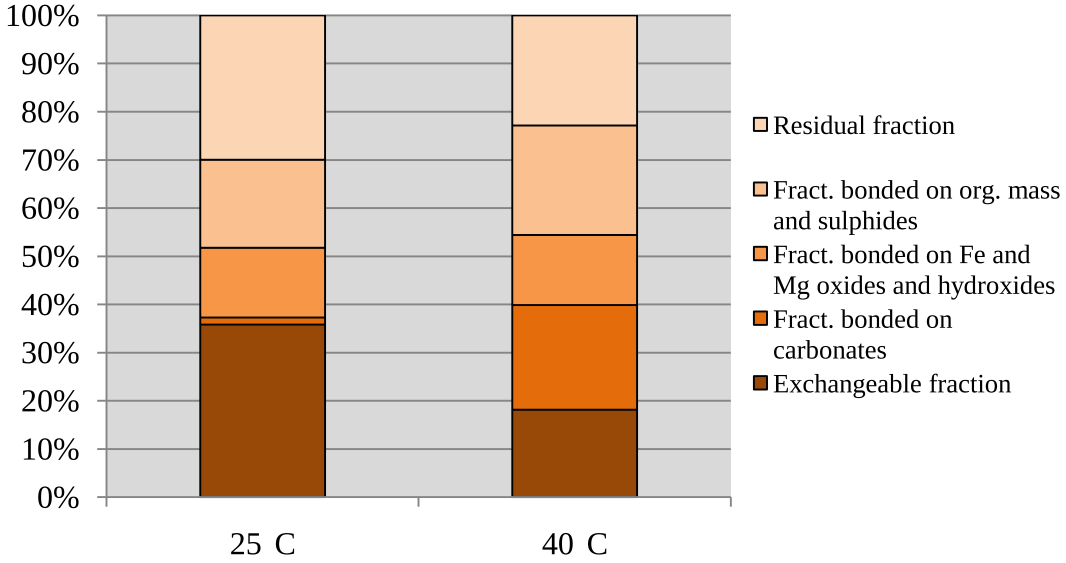


The highest concentration of lead is in the residual fraction (at 25°C it was 43% and at 40°C concentration was 38%). In the extraction at the temperature of 25°C there was the highest concentration of lead in the first step, the exchangeable fraction (35%), and the lowest concentration was in the fraction bonded on carbonates (3%). The third step is very similar as the fourth step (5-8%). On the other hand, at the temperature of 40°C there were the same concentration in the first (almost 20%, it is decreased in compare with 25°C) and the second steps (it is increased in compare with the lower temperature) which are the exchangeable fraction and the fraction bonded on carbonates. The concentration in the third and the fourth steps are similar (the fraction bonded on iron and manganese oxides and hydroxides and the fraction bonded on organic mass and sulfides), 11-13% and it is little bit higher concentration than at the temperature of 25°C (8-10%).

4.1.2 Sample A2

This fly ash was created by combusting of brown coal and biomass in the atmospheric fluid-bed boiler.

Graph 7: The amount of lead in sample A2 at the temperatures of 25°C and 40°C



The biggest concentration of lead in the fly ash at 25°C was in the exchangeable fraction (35%) and the lowest concentration was in the second step, in the fraction bonded on carbonates (approximately 1%). The third step was almost the same in both temperatures (14%), concentration in the fourth step is smaller at 25°C (19%) than at 40°C (23%).

At 40°C was concentration very similar in all steps (19-23%) of extraction according to Tessier. Little bit smaller amount of lead was in the third step, the fraction bonded on iron and manganese oxides and hydroxides (14%).

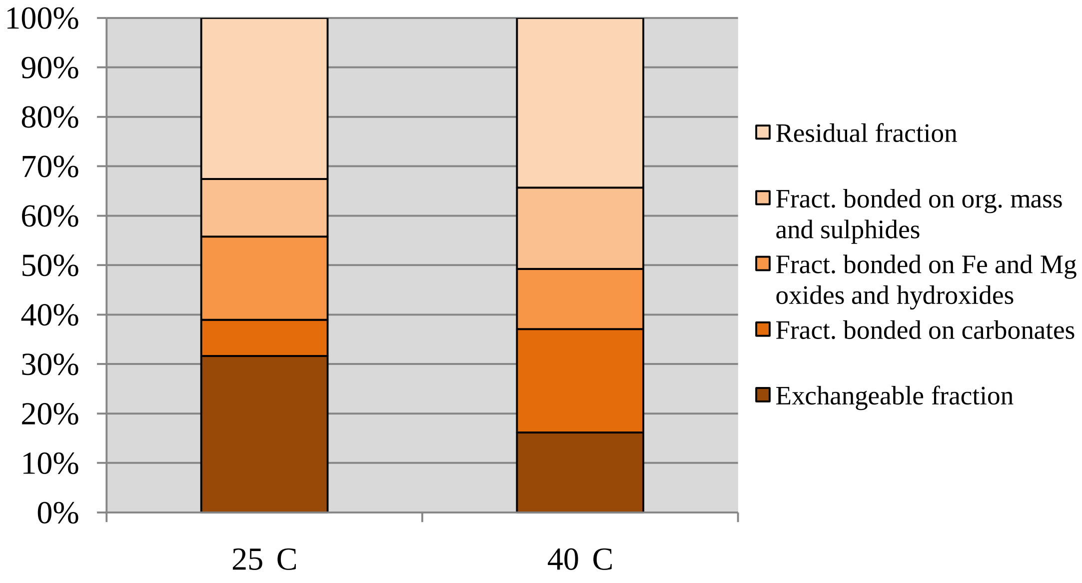
4.1.3 Sample B1

This sample is the fly ash. It was formatted by the pulverized coal fired boiler from biomass and black coal.

Fly ash had the highest concentration at 25°C in the first step, the exchangeable fraction – 31%, and the last step, the residual fraction – 32%. Very low amounts in the fraction bonded on carbonates (7%) and the fraction bonded on organic mass and sulfides (10%). The concentration in the fraction bonded on iron and manganese oxides and hydroxides was average (17%) and the bigger than at 40°C (10%).

At the temperature of 40°C there was the biggest amount in the residual fraction (33%, it is really as at the temperature of 25°C) and the second biggest concentration was in the second step, the fraction bonded on carbonates (20%, increased 13% than at 25°C). The first and the fourth fractions had similar concentrations (17% - the first fraction is smaller at 40°C than at 25°C, but the fourth fraction little bit increased in 40°C). The lowest concentration was in the fraction bonded on iron and manganese oxides and hydroxides (10%, it is decreased in compare with 25°C).

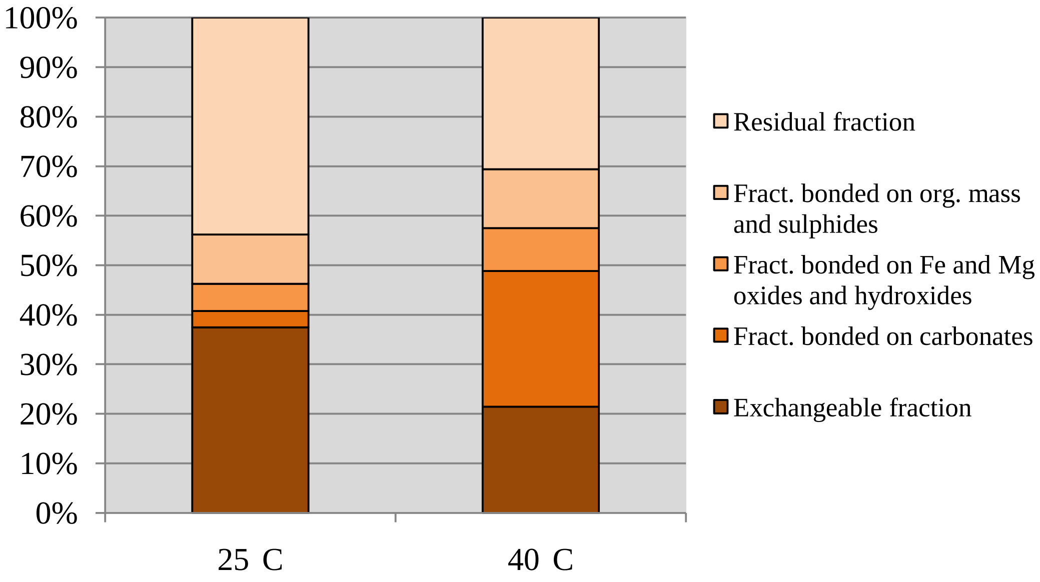
Graph 8: The amount of lead in sample B1 at the temperatures of 25°C and 40°C



4.1.4 Sample B2

Sample B2 is a hydromixture of ash and dross. This sample was created, as the same one sample B1, on the pulverized coal-fired boiler from black coal and biomass.

Graph 9: The amount of lead in sample B2 at temperatures of 25°C and 40°C

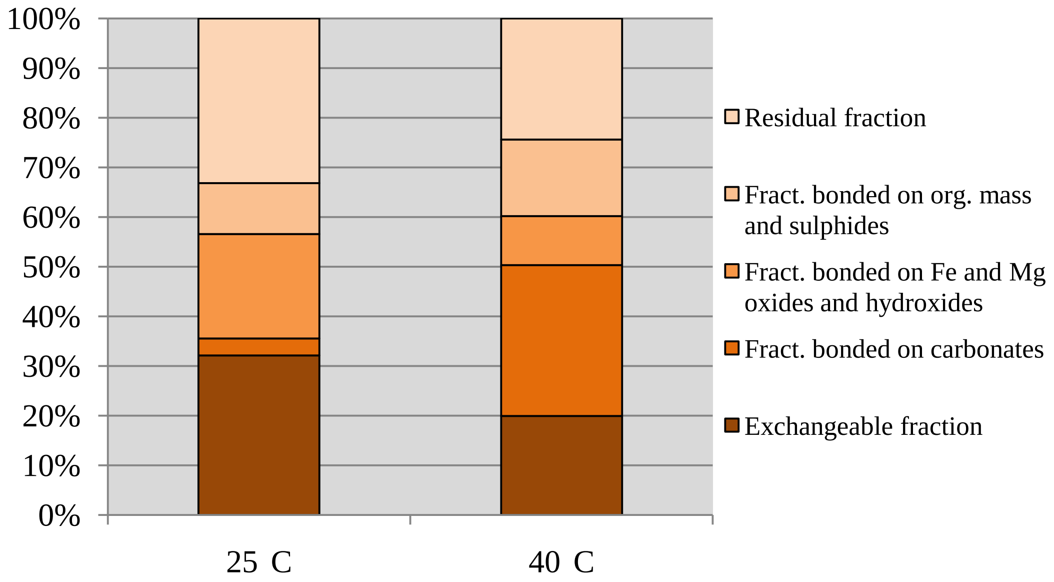


In sample B2 at 25°C was the biggest concentration in the exchangeable fraction (38%) and the residual fraction (43%) and very low in rest fractions (under 10%), on the other hand at 40°C concentrations the exchangeable fraction (21%) and the fraction bonded on carbonates (24%) were very similar, but the first fraction was much more lower than at 25°C and the second fraction at 40°C very increased in compare with 25°C. The third and the fourth steps had really the same amounts at temperatures of 25°C and 40°C (deviation was maximal 4%).

4.1.5 Sample C1

This sample is scoria from combustion of brown coal and biomass in the pulverized coal fired boiler.

Graph 10: The amount of lead in sample C1 at temperatures of 25°C and 40°C

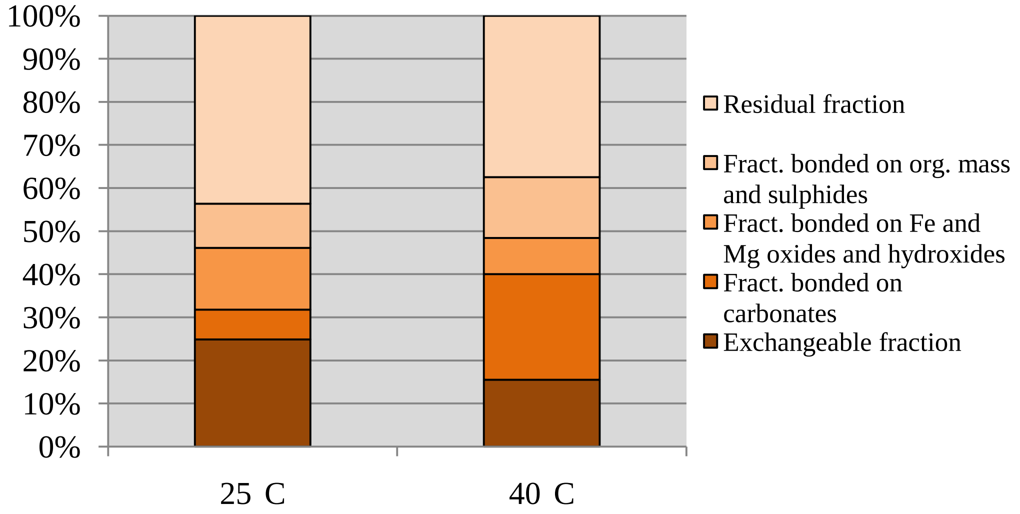


Scoria had at 25°C the biggest amount in the first step, the exchangeable fraction (33%), next concentraation was in the residual fraction (32%) and next in the fraction bonded on Fe and Mg oxides and hydroxides (20%). The lower concentration was in the second step, the fraction bonded on carbonates (3%). Sample had at 40°C the biggest concentration unlike extraction at 25°C in the fraction bonded on carbonates (31%) and the fraction bonded on organic mass and sulfides (15%). The lower concentrations were in the first (29%), the third (9%) and the last step (22%).

4.1.6 Sample C2

The sample is fly ash formed on pulverized coal fired boiler (from biomass and brown coal).

Graph 11: The amount of lead in sample C2 at temperatures of 25°C and 40°C



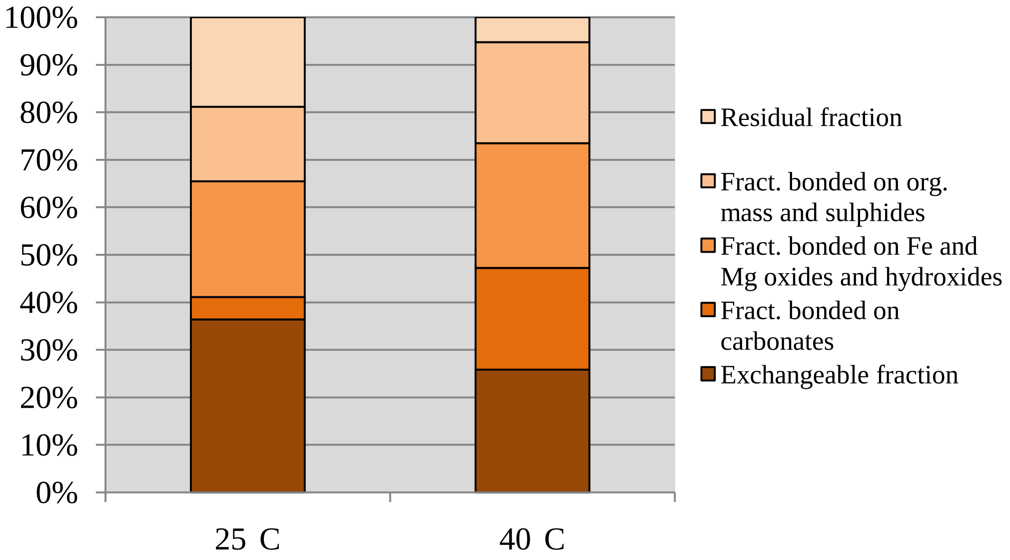
The biggest concentration of sample C2 at the temperature of 25°C there was in the last step, the residual fraction (44%), and in the first step, the exchangeable fraction 24%). The lowest concentration was in the second step (5%).

In 40°C was the biggest concentration in the residual fraction (38%) but in compare with 25°C this concentration little bit decreased (deviation was under 5%). The second highest concentration was in the second fraction (24%), which increased in compare with the temperature of 25°C. Concentration of the fraction bonded on organic mass and sulfides (13%) increased too, but the exchangeable fraction (16%) and the third fraction (8%) decreased.

4.1.7 Sample C3

This sample is the product of desulphurization. It was formed from biomass and brown coal in the pulverized coal fired boiler.

Graph 12: The amount of lead in sample C3 at temperatures of 25°C and 40°C



The highest amount was in the exchangeable fraction (37%) and the third step (24%), and the lowest was in the fraction bonded on carbonates (5%) at the temperature of 25°C. Very similar were concentrations in the fourth (15%) and the fifth (19%) steps.

In temperature of 40°C were concentrations of lead very similar in every step to Tessier´s extraction (21-26%), except to the residual fraction, which had lower concentration (4%). It means, that concentrations in the exchangeable fraction and the residual fraction decreased (around 11%), and in the fraction bonded on carbonates and in the fraction bonded on organic mass increased. The third fractions were similar in temperatures, 24% in 25°C and 25% in 40°C).

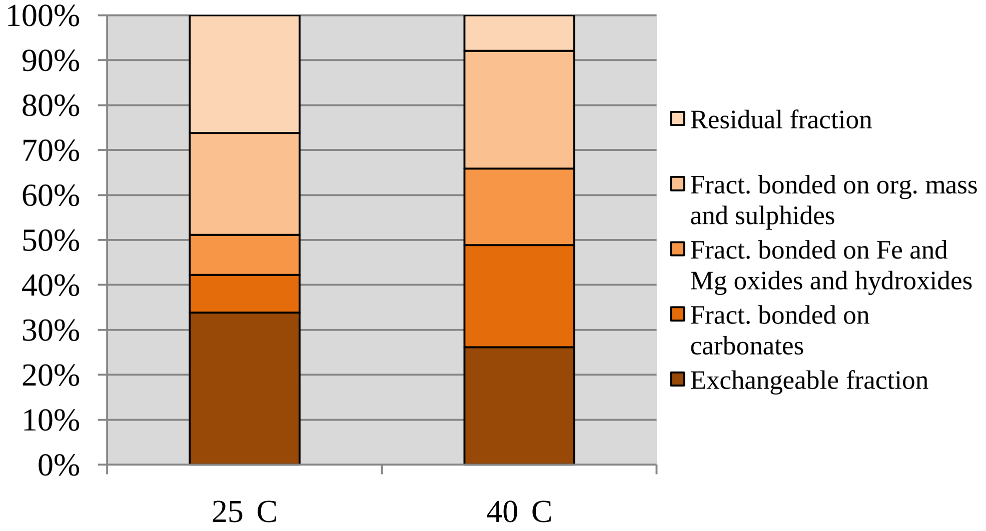
4.1.8 Sample D1

Biomass, black and brown coal was fired in the atmospheric fluid bed boiler and turned into log ash.

Log ash had the biggest amount in the exchangeable fraction (32%) and had really the same concentrations in steps two and three (10% in the fraction bonded on iron and manganese oxides and hydroxides and the fraction bonded on carbonates) and very similar concentrations in the fourth (21% in the fraction bonded on organic mass and sulfides) and the fifth (26% in the residual fraction) steps.

In temperature of 40°C were concentrations (20-26%) similar in all steps of extraction (the first and the fourth bigger than in the second and the third), except last one (8%), which had lower concentration than other. The exchangeable and the residual fraction decreased and the second, the third and the fourth steps increased in compare with concentrations at the temperature of 25°C.

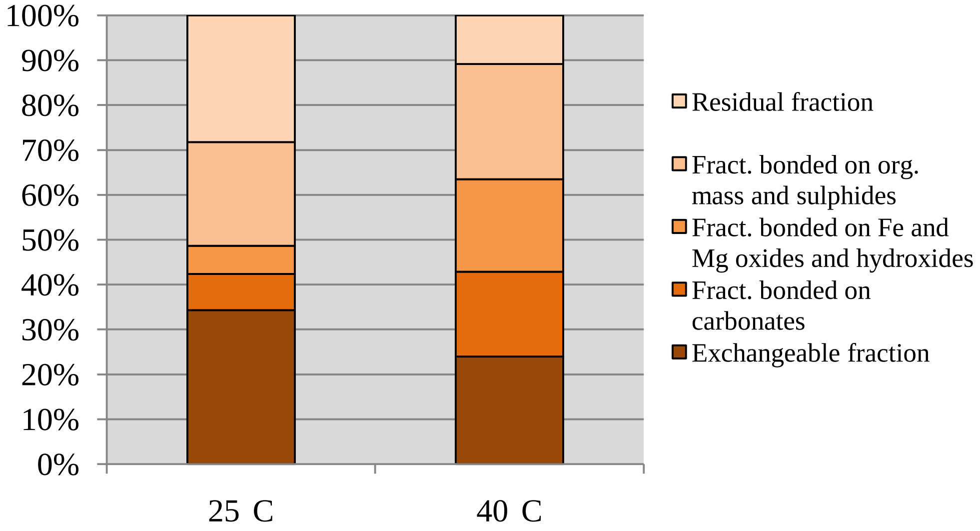
Graph 13: The amount of lead in sample D1 at temperatures of 25°C and 40°C



4.1.9 Sample D2

This sample is fly ash, which was created by combusting of biomass, black and brown coal in the atmospheric fluid bed boiler.

Graph 14: The amount of lead in sample D2 at temperatures of 25°C and 40°C



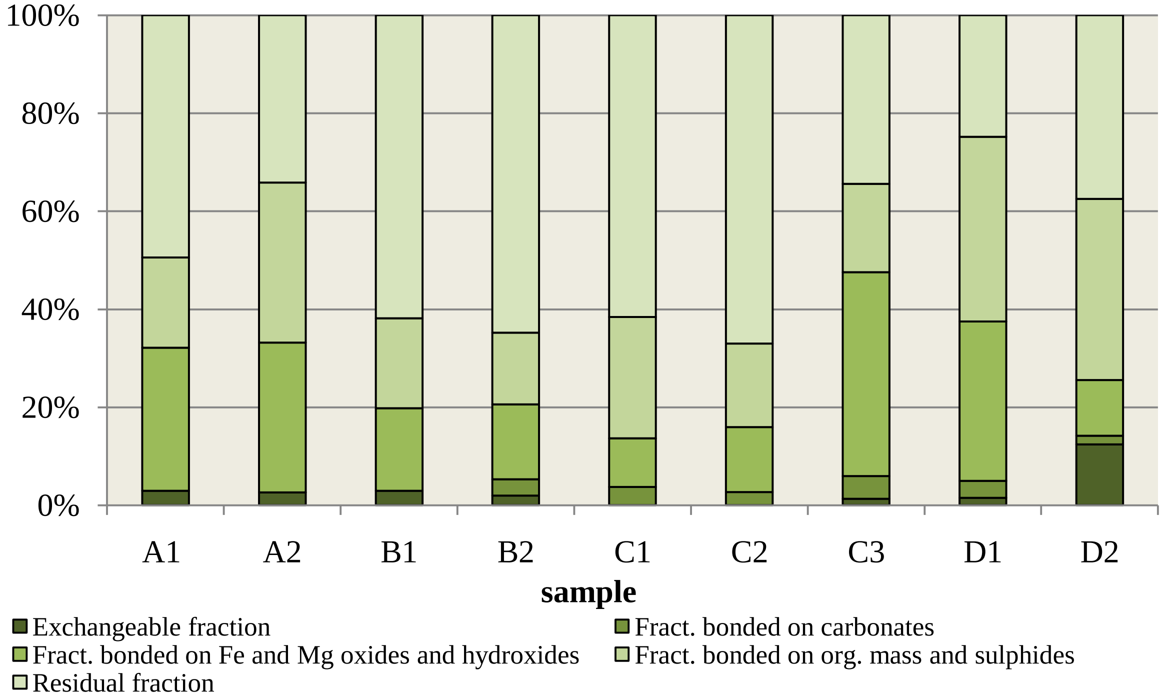
The biggest amount was in the exchangeable fraction (33%) and the smallest in the fraction bonded on carbonates (7%) and in the fraction bonded on iron and manganese oxides and hydroxides (6%), which were alike. The fraction bonded on organic mass and sulfides (24%) and the residual fraction (27%) are very similar in concentration.

At the temperature of 40°C there were all concentrations very similar (around 20-23%), but concentration in the fourth fraction was little bit higher (26%) and in the fifth step was little bit lower (11%) than in the other. In generally the first, the second and the third fractions were increased than at the temperature of 25°C. The fourth fractions were very similar and the last fraction decreased in compare with 25°C.

4.2 Determination of copper

Copper was extracted (as lead) in two temperatures of 25°C and 40°C.

Graph 15: The amount of copper in temperature of 25°C for all samples



The biggest amount of copper was in the last step, the residual fraction, in most of samples (all samples had concentration around 50-68% except A2 - 34%, C3 - 35%, D1 – 26% and D2 – 39%). It means, that copper is very strong bonded in sample and could not contaminate environment so easily at the room temperature (moderate climate in nature).

The second biggest concentration was in the fraction bonded on organic mass and sulfides (23-37%) and the third step, the fraction bonded on iron and manganese oxides and hydroxides (8-15% in most of samples, 29-39% in sample A1, A2, C3 and D1).

The amount of copper in the first step, the exchangeable fraction, was in samples C1 and C2 zero, in samples A1, A2, B1, B2, C3 and D1 were concentrations under 3% and just in sample D2 concentration was 11%). The second step, the fraction bonded on carbonates had in samples A1, A2 and B1 zero concentrations and in the remaining samples were concentration lower than 6%. The first and the second steps could be neglect.

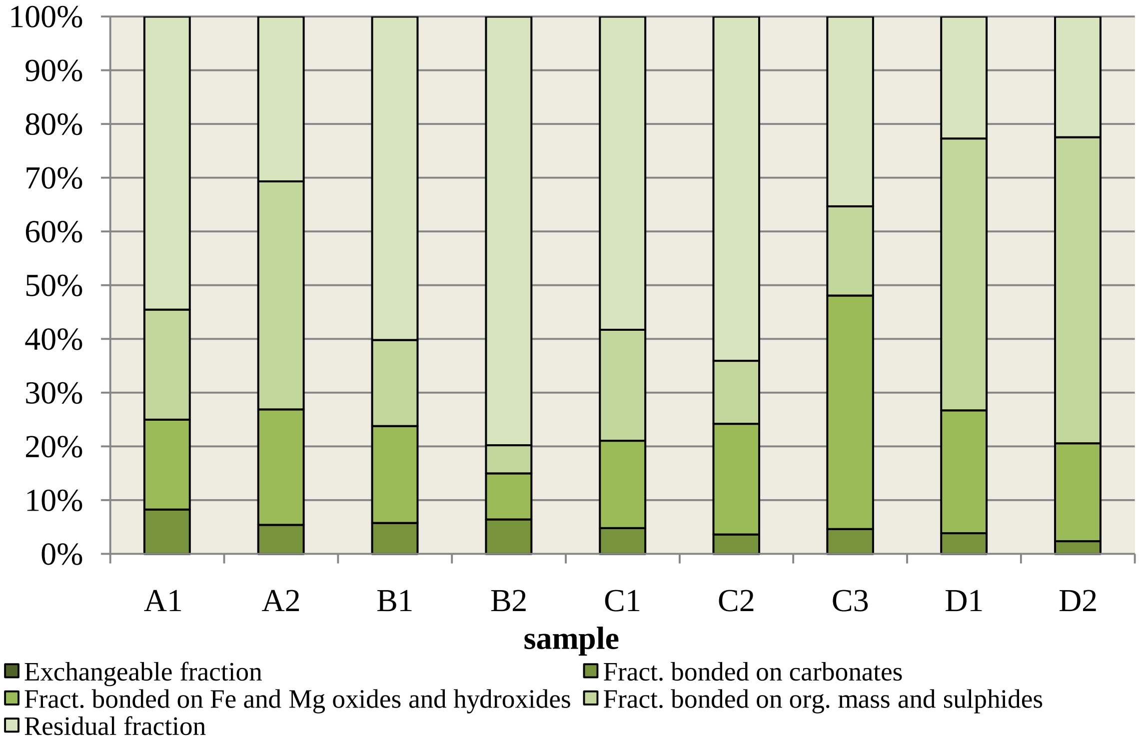
At the temperature of 40°C had half of samples the biggest amount in the last step, residual fraction (56-79%). It means that copper, in 40°C, had very strong bonds on energetic waste, so in warmer climates copper stay in sample and it is not so much danger for environment. The second part of samples (A2, D1 and D2) had not the highest concentration in the last part, but in the fourth part, the fraction bonded on organic mass and sulfides (41-50%). The sample C3 had the main concentration in the third step (39%).

Concentrations in the fourth steps (except A2, D1 and D2) were 8-20%. The sample B2 in the fraction bonded on organic mass and sulfides had amount of copper just 6% of the total concentration.

The third fractions had really similar concentrations (9-20%), except the sample C3 which had in this fraction concentration 41%.

All samples had in the fractions bonded on carbonates very low concentrations (under 8%) and the exchangeable fractions were absent.

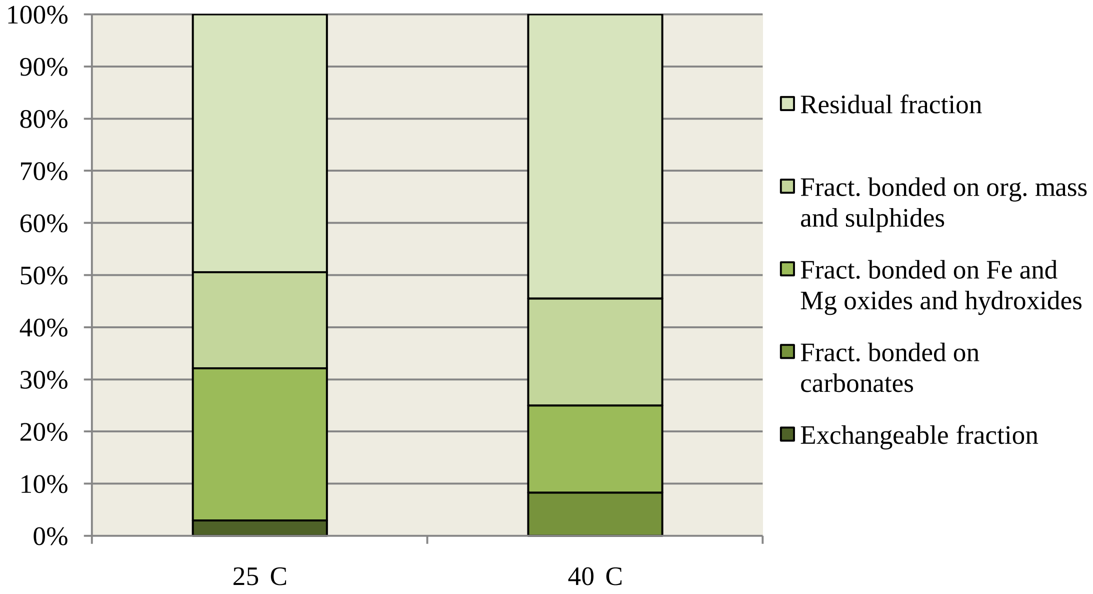
Graph 16: The amount of copper in temperature of 40°C for all samples



The biggest difference was that at the temperature of 25°C there was not in most of samples the second fraction, the fraction bonded on carbonates, and at the temperature of 40°C there was not the first step, the exchangeable fraction. The behavior of samples was very different in this temperature and is not possible to comprehensively evaluate all samples for comparison with the temperature of 25°C.

4.2.1 Sample A1

Graph 17: The amount of copper in sample A1 at temperatures of 25°C and 40°C



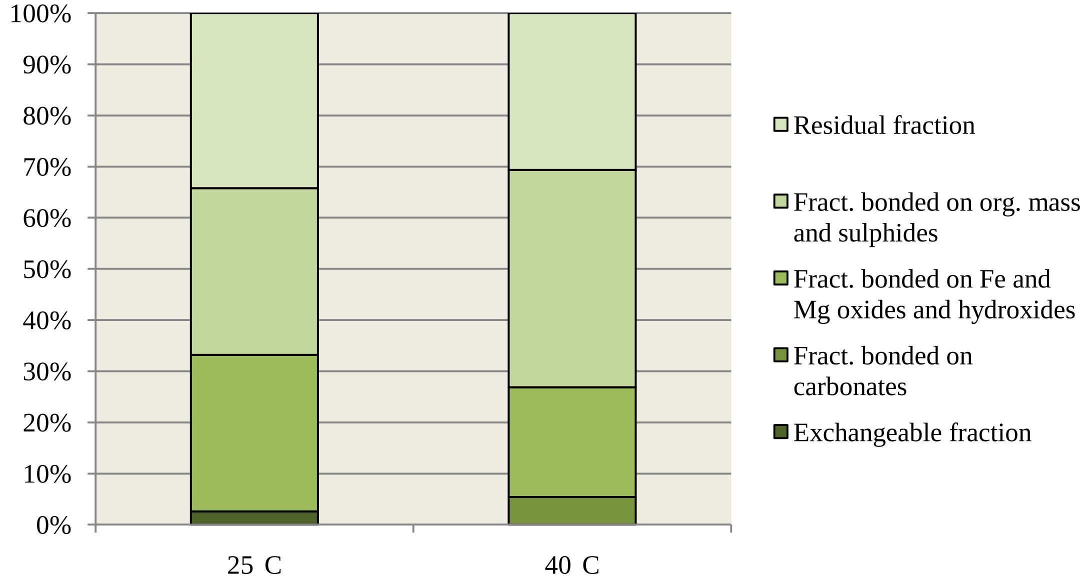
This sample had the biggest concentration in the last part (the residual fraction) 49% at the temperature of 25°C and 53% at the temperature of 40°C. The second highest concentration was at the temperature of 25°C in third part which is fraction bonded on iron and manganese oxides and hydroxides (30%). At the temperature of 25°C there was absent the fraction bonded on carbonates and the exchangeable fraction was very low, less than 4%.

On the other hand at the temperature of 40°C the concentrations in fraction bonded on iron and manganese oxides and hydroxides (19% it is decreased in compare with 25°C) and fraction bonded on organic mass and sulfides (21%) were very similar. In the 40°C was not the exchangeable fraction, the first step, and the second fraction was under 8%.

The fourth fractions were very similar in both temperatures (in 25°C it was 19% and in the 40°C it was 21%).

4.2.2 Sample A2

Graph 18: The amount of copper in sample A2 at temperatures of 25°C and 40°C



The sample A2 had at 25°C in the third (26% - the fraction bonded on iron and manganese oxides and hydroxides), the fourth (32% - the fraction bonded on organic mass and sulfides) and the fifth (32% - the residual fraction) steps very closely concentrations. In the first step was very small concentration, less than 3%, so it could be neglect. The fraction bonded on carbonates was not here.

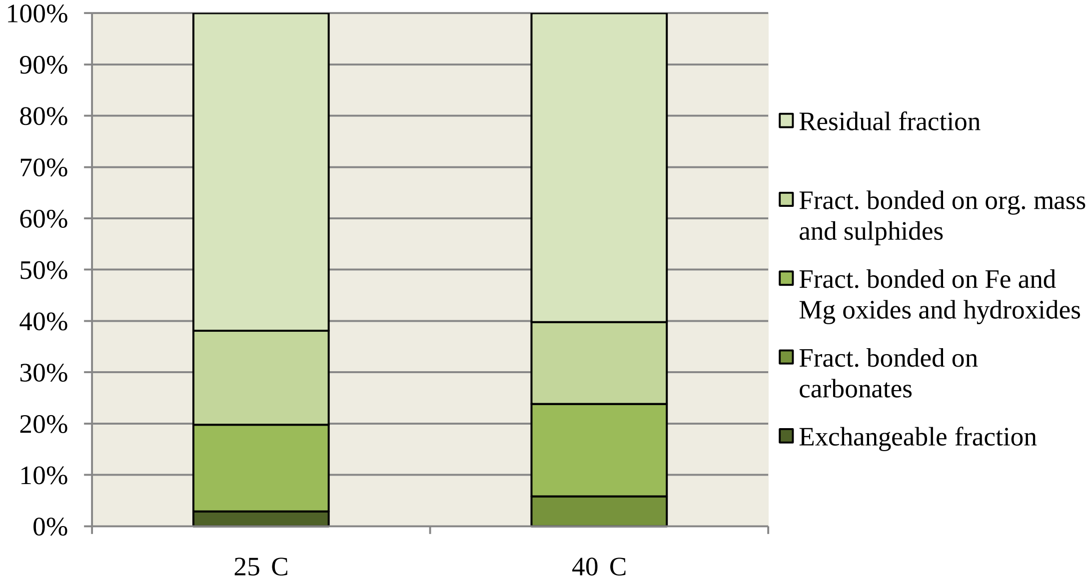
At the temperature of 40°C there was the biggest concentration (40%) in the fraction bonded on organic mass and sulfides, the fourth step, the concentration increased with the temperature. The smaller concentration than at the temperature of 25°C there was in the residual fraction (31%) and in the third step (20%). The fraction bonded on carbonates (the second step) had very low concentration (less than5%) and the first step (exchangeable fraction) was absent.

4.2.3 Sample B1

This fly ash had similar distribution in both temperatures (25°C and 40°C). The biggest concentrations were in the last step, the residual fraction (61%), and very similar concentrations in fractions bonded on organic mass and sulfides (15% and 18%) and fractions bonded on iron and manganese oxides and hydroxides (17% in 25°C and 19% at the temperature of 40°C).

The same as in samples A1 and A2, the sample B1 at the temperature of 25°C had not copper bonded on carbonates (6% in 40°C), and at the temperature of 40°C had not copper bonded in the exchangeable fraction (3% at the temperature of 25°C).

Graph 19: The amount of copper in sample B1 at temperatures of 25°C and 40°C

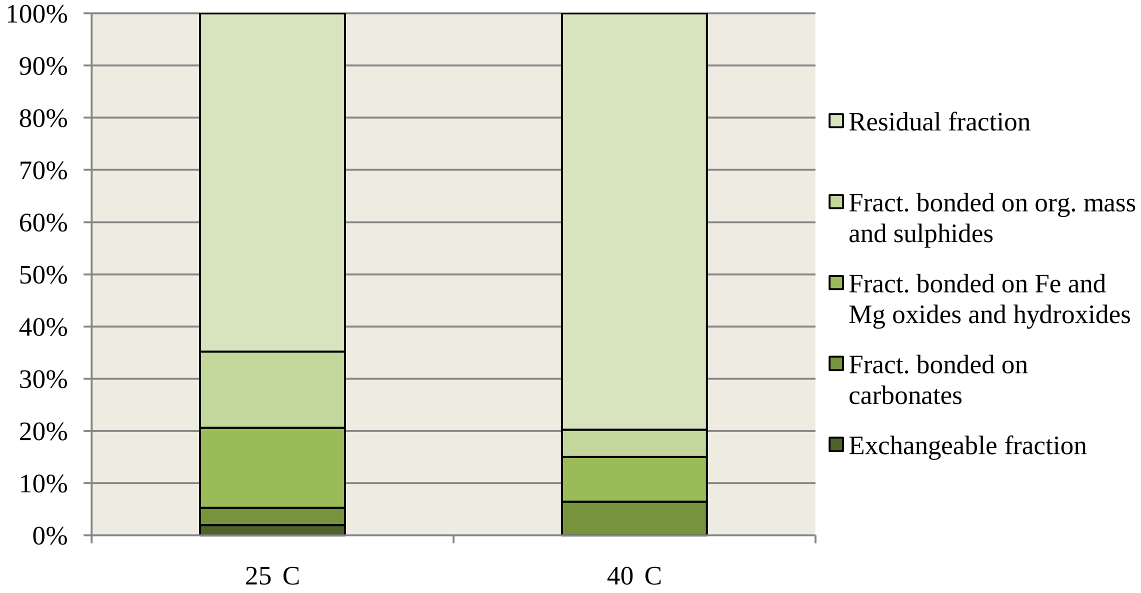


4.2.4 Sample B2

In sample B2 were the biggest concentrations in the residual fractions (65%). At the temperature of 25°C there was really similar concentrations in the third and the fourth steps (approximately 15%) and similar in the first and the second steps (2%). The main difference is that this sample was present in the fraction bonded on carbonates at the temperature of 25°C.

In 40°C was the highest concentration in the residual fraction (80% it increased) and concentration of the fraction bonded on organic mass and sulfides (little bit increased, deviation was 4%). The fraction bonded on iron and manganese oxides and hydroxides (decreased in compare with 25°C), and the fraction bonded on carbonates (decreased in compare with temperature of 25°C) were very similar (4-9%). The concentration of the exchangeable fraction was zero, but in 25°C it was 2%.

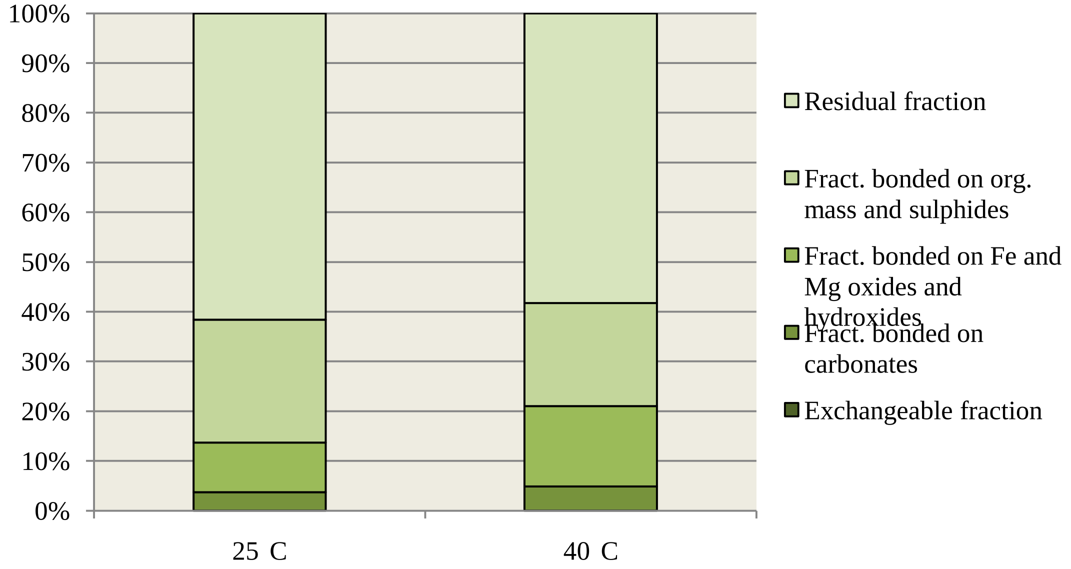
Graph 20: The amount of copper in sample B2 at temperatures of 25°C and 40°C



4.2.5 Sample C1

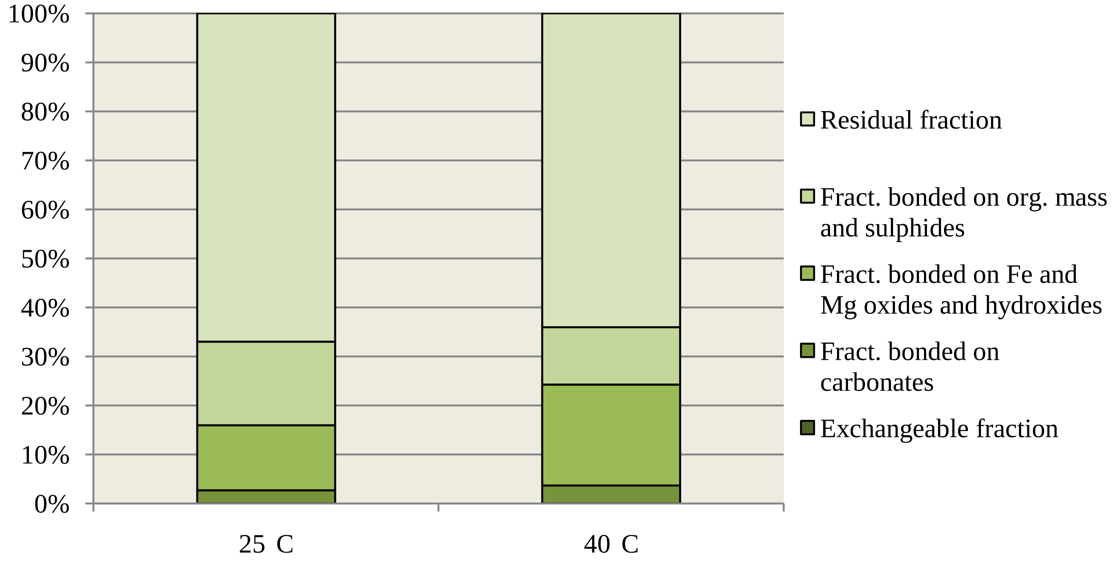
Scoria had similar concentrations in the residual fraction (59% at the temperature of 25°C and 61% in 40°C) and in the fraction bonded on organic mass and sulfides (22% and 20%) in both temperatures. The concentration in the third step was little bit smaller at the temperature of 25°C than in 40°C (approximately 5% less in 25°C). The amount of copper in the fraction bonded on carbonates was similar (around 5% at temperatures of 25°C and 40°C) and the exchangeable fraction was missing in both temperatures.

Graph 21: The amount of copper in sample C1 at temperatures of 25°C and 40°C



4.2.6 Sample C2

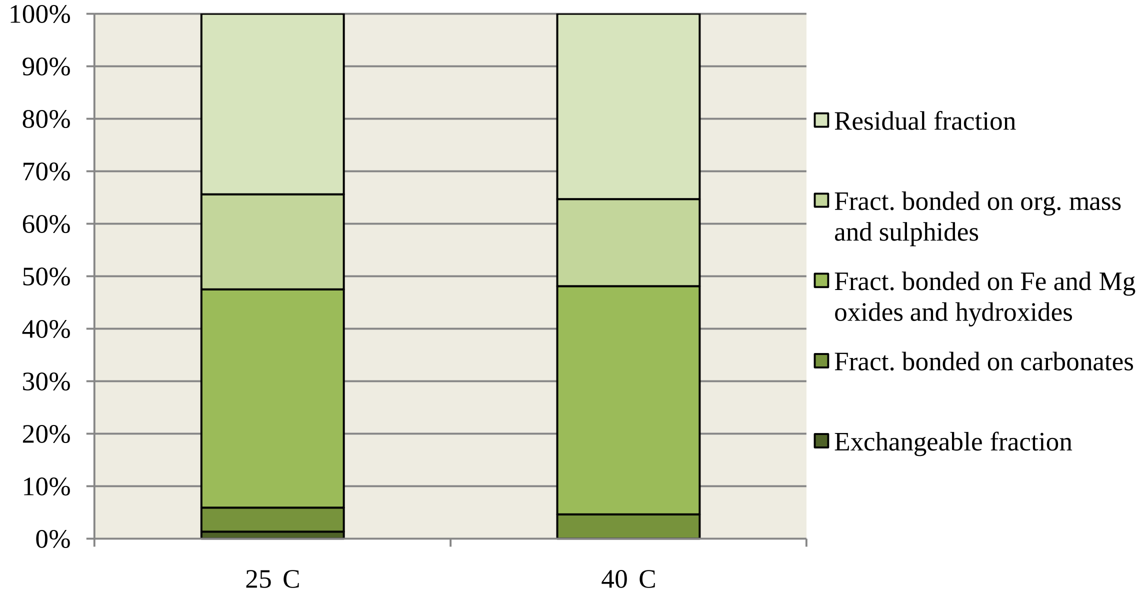
Graph 22: The amount of copper in sample C2 at temperatures of 25°C and 40°C



The biggest concentrations of sample C2, fly ash, was in the last step (the residual fraction – 64% in 25°C and 67% in 40°C) and the smallest amount was in the second step (the fraction bonded on carbonates – less than 4%). The concentration of first step is zero in both temperatures, so copper is not in the exchangeable fraction. Other concentrations are really similar (around 13-20%), but at the temperature of 40°C the concentration decreased in the fraction bonded on organic mass and sulfides and increased in the third fraction in compare with the temperature of 25°C.

4.2.7 Sample C3

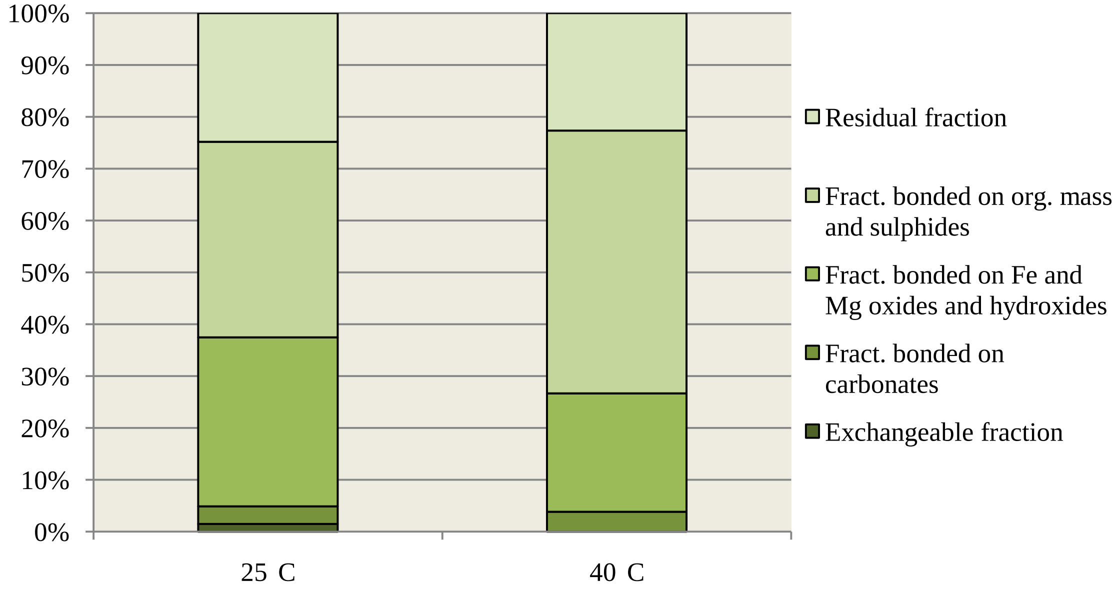
Graph 23: The amount of copper in sample C3 at temperatures of 25°C and 40°C



The amount of copper in sample C3 was very similar in both temperatures. The highest concentration was in the third step (the fraction bonded on iron and manganese oxides and hydroxides – around 40%) and the lowest concentration was in the fraction bonded on carbonates in the temperature of 25°C was lower concentration (deviation was maximal 2% of total concentration). The fourth steps had concentration 18% in 25°C and 17% in 40°C, and residual fractions were same (33%). The first step, the exchangeable fraction, was not at the temperature of 40°C and in 25°C it was less than 1%, so it could be neglect.

4.2.8 Sample D1

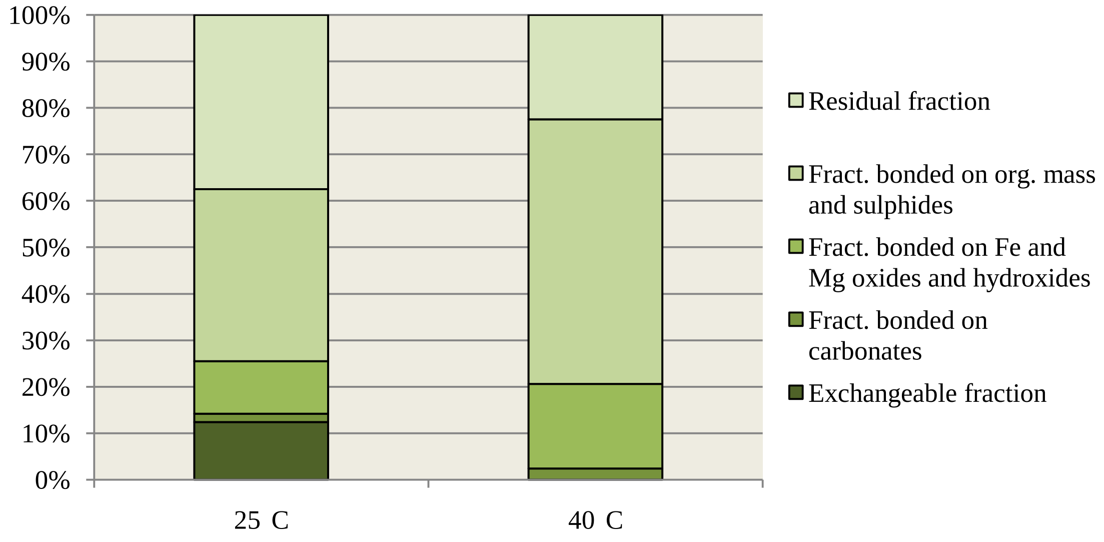
Graph 24: The amount of copper in sample D1 at temperatures of 25°C and 40°C



The loge ash (the sample D1) had similar behaviour in both temperatures, but little bit different from other samples. The biggest concentration was in the fraction bonded on organic mass and sulfides (38% at the temperature of 25°C and 50% in 40°C). Concentrations in the last steps at the temperature of 25°C increased little bit, but deviation was maximal 2% and in the third steps in 40°C concentration decreased around 7%, but in generally were similar (23-31%). The lowest concentration was in the fraction bonded on carbonates in temperature of 40°C and in temperature of 25°C was the lowest concentration in exchangeable fraction which was missing in the second extraction (40°C).

4.2.9 Sample D2

Graph 25: The amount of copper in sample D2 at temperatures of 25°C and 40°C



At the temperature of 25°C all steps were present. Concentrations in the residual fraction (39%) and in the fraction bonded on organic mass and sulfides (36%) were really the same and the biggest in this extraction. The fraction bonded on iron and manganese oxides and hydroxides (9%) and the exchangeable fraction (11% - it had very high concentration in this sample) had really similar concentrations. The lowest amount of copper was in the second step, fraction bonded on carbonates (less than 1%).

In 40°C the biggest concentration was in the fraction bonded on organic mass and sulfides (51% it increased in compare with the temperature of 25°C). The fraction bonded on carbonates had the lowest concentration (less than 1%), but it os really the same as at the temperature of 25°C. The exchangeable fraction was absent in this temperature. The concentrations of the third and the fifth steps were really similar (approximately 20%), but in the third fraction concentration decreased and in the fourth step the concentration increased in compare with the temperature of 25°C.

4.3 Determination of cadmium

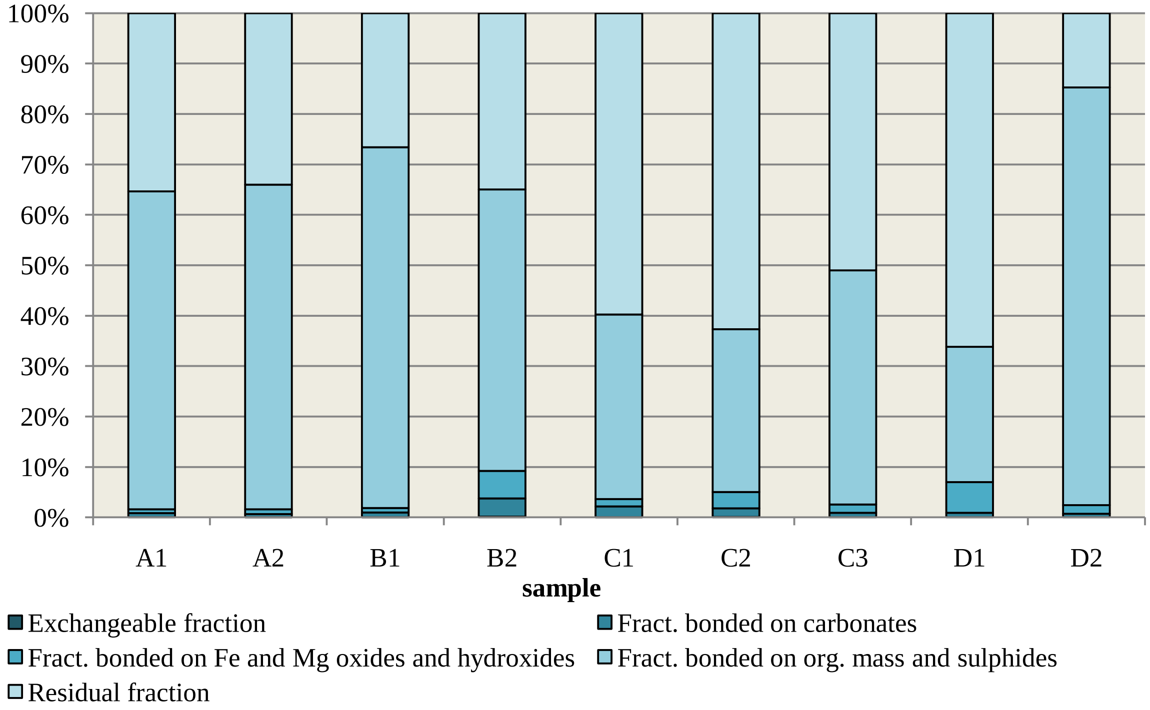
Cadmium was extracted and determined (as lead and copper) in two temperatures of 25°C and 40°C.

Cadmium in the exchangeable fractions was absent in all samples in 25°C, but the exchangeable fraction was at the temperature of 40°C (0-5% of total concentration). Concentrations in the second (0-1%) and the third (0-7%) steps were very small at the temperature of 25°C. Concentrations of the fraction bonded on carbonates (2-19%) were bigger than in 25°C and the third step (0-4%) concentrations decreased at the temperature of 40°C.

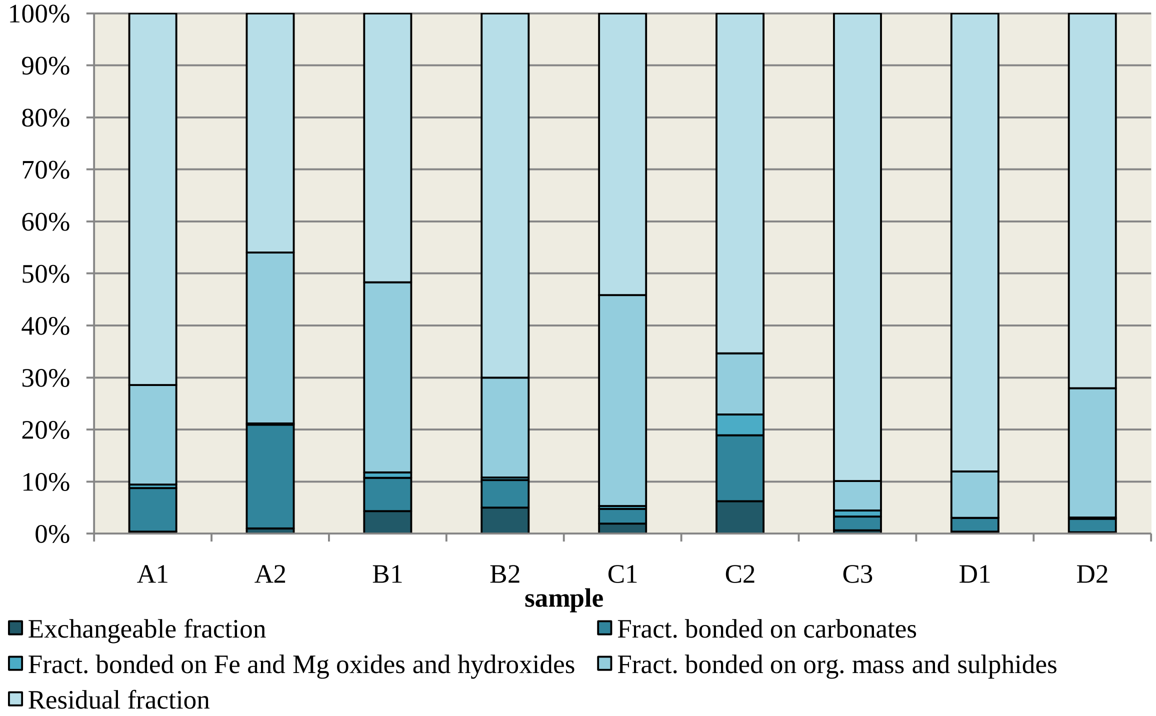
The fourth steps, the fraction bonded on organic mass and sulfides, had concentration 28-83% in 25°C, but it was 5-40% at the temperature of 40°C, so in higher temperature concentrations of this fraction were decreased.

The biggest concentration was in the residual fractions (47-90%) at the temperature of 40°C and at the temperature of 25°C there were the biggest concentrations in the fourth (28-83% of the total concentration) and the fifth steps (15-68%), it depends on the sample.

Graph 26: The amount of cadmium in temperature of 25°C for all samples



Graph 27: The amount of cadmium at the temperature of 40°C for all samples

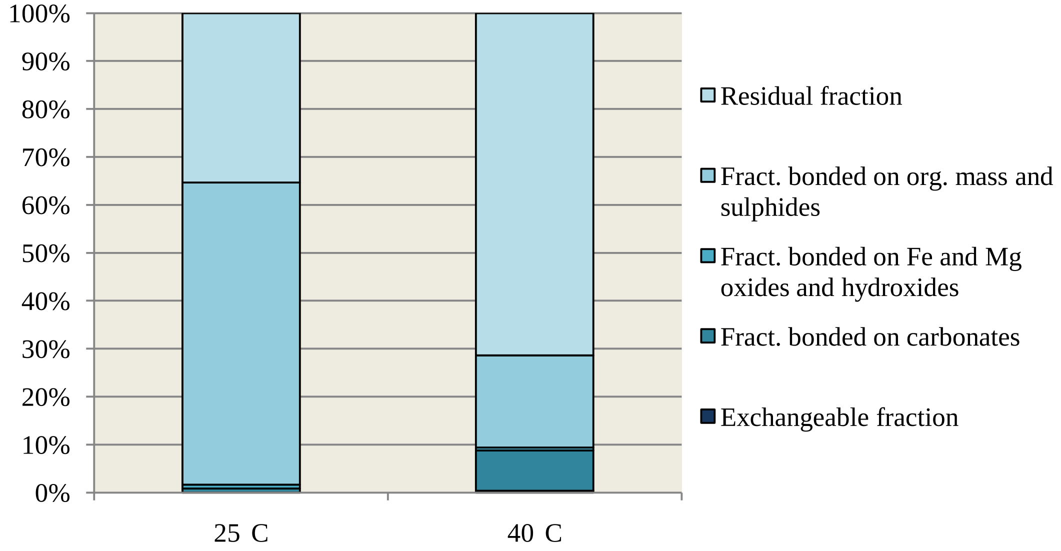


4.3.1 Sample A1

The exchangeable fraction was absent in both temperatures. The concentration in the second step was lower than 0,5% at the temperature of 25°C and almost 10% in 40°C, so this concentration was increased with the temperature. The third fractions were very low concentration (less than 0,5%), so it could be neglect.

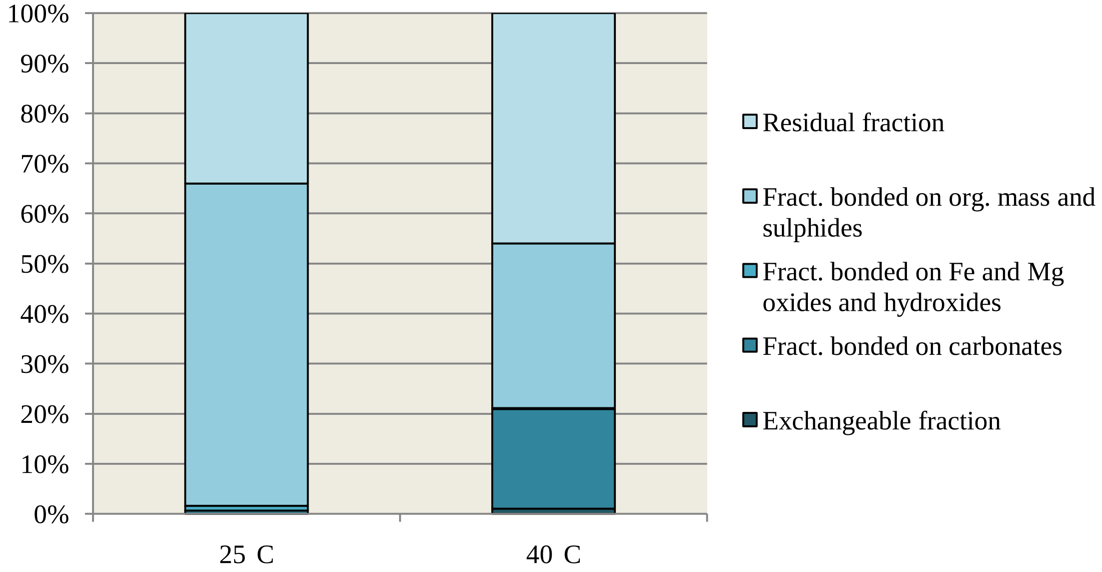
The fraction bonded on organic mass and sulfides was biggest in 25°C (62%) and the second biggest (21% - it decreased in compare with the temperature) in 40°C. On the other hand the biggest concentration at the temperature of 40°C there was in the residual fraction (72%) and it was lower in 25°C (33%).

Graph 28: The amount of cadmium in sample A1 at temperatures of 25°C and 40°C



4.3.2 Sample A2

Graph 29: The amount of cadmium in sample A2 at temperatures of 25°C and 40°C

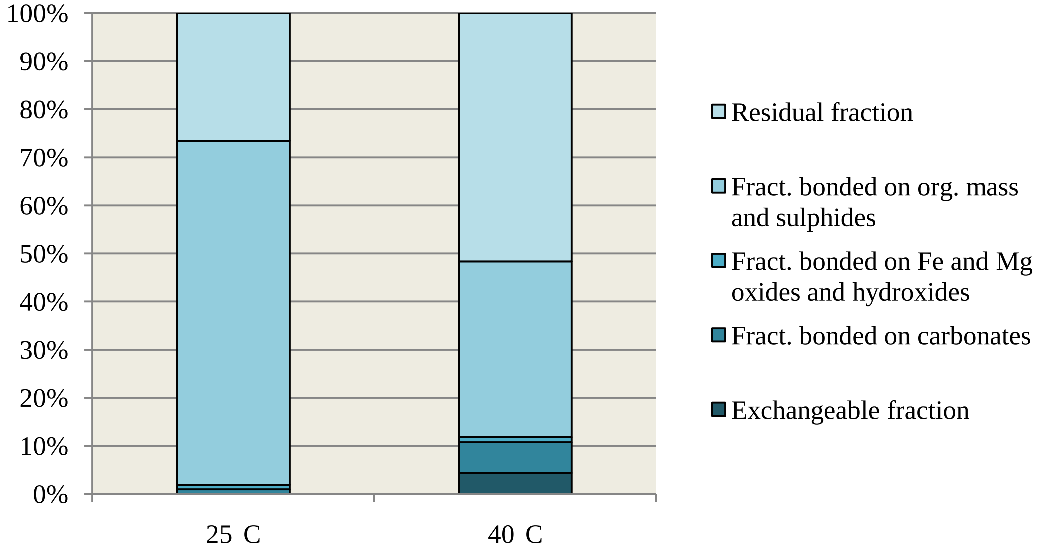


Concentrations in the first (less than 0,5%), the second (less than 0,5%) and the third steps (less than 0,5% again) were very small, almost zero and it could be neglect at the temperature of 25°C. It was same at the temperature of 40°C, just in the second fraction was concentration 20%, so concentration of the fraction bonded on carbonates is increased in compare with the temperature.

The biggest concentrations were in the fraction bonded on organic mass and sulfides (65%) in 25°C and in the residual fraction (47%) in 40°C. The residual fraction was lower (33%) at the temperature of 25°C than in the residual fraction in 40°C. The concentration of the fourth step decreased (on 32% in 40°C from 47% in 25°C) in compare with the temperature.

4.3.3 Sample B1

Graph 30: The amount of cadmium in sample B1 at temperatures of 25°C and 40°C

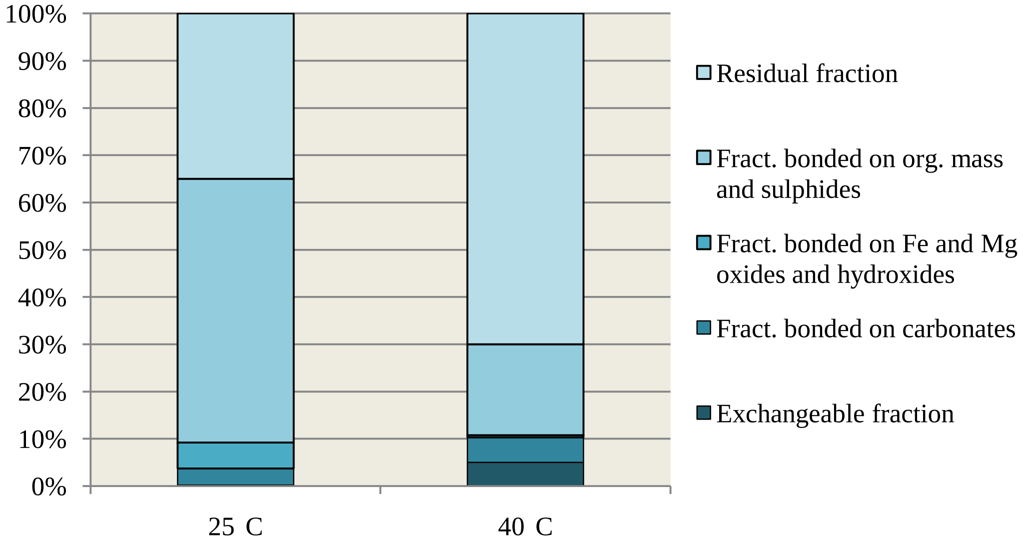


The exchangeable fraction and the third step had almost the same concentrations (less than 0,5%) and the second step was absent, so all these steps could be neglect at the temperature of 25°C. The third steps were the same in both temperatures (less than 0,5%). The first and the second steps had very similar concentration (4-6%) in 40°C.

The concentration of the fraction bonded on organic mass and sulfides decreased (71% at the temperature of 25°C - the biggest concentration in this temperature, and 36% in 40°C) and the concentration of the residual fraction increased (28% in 25°C and 53% in 40°C – the biggest amount at the temperature of 40°C) in compare with temperature.

4.3.4 Sample B2

Graph 31: The amount of cadmium in sample B2 at temperatures of 25°C and 40°C



The exchangeable fraction was absent at the temperature of 25°C, but concentration was 5% in 40°C. The second steps had very similar concentrations (around 5%) in both temperatures. The third steps were very low, 6% in 25°C and lower than 0,5% at the temperature of 40°C, so in this fraction concentration of cadmium decreased in compare with temperature.

The fraction bonded on organic mass and sulfides had the biggest concentration in 25°C (56%), in 40°C this concentration decreased on 19% (the second biggest concentration in extraction at the temperature of 40°C). The last step, the residual fraction, increased in compare with temperature, 34% in 25°C and 70% in 40°C.

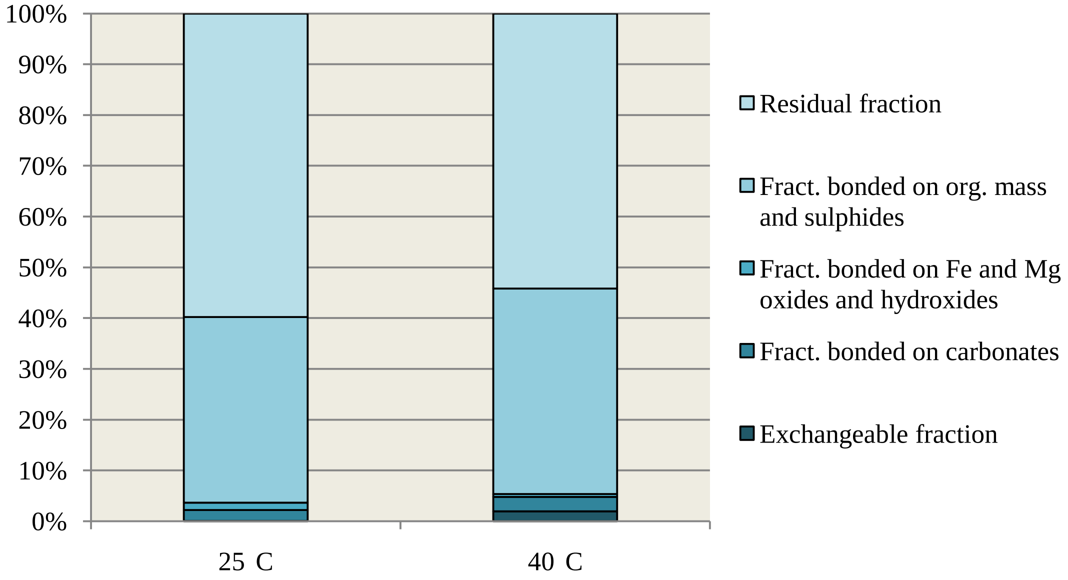
4.3.5 Sample C1

The first step, the exchangeable fraction, was absent in 25°C. This fraction was present in 40°C and the concentration was around 2% of the total concentration. The second (2%) and the third steps (1%) were almost the same in both temperatures.

In the fourth step (the fraction bonded on organic mass and sulfides) were concentrations very similar at temperatures of 25°C and 40°C and little bit increased in 40°C, from 37% at 25°C on 40% at the temperature of 40°C.

The biggest amounts of cadmium were in the residual fraction, the last step, in both temperatures (60% in 25°C and 55% in 40°C).

Graph 32: The amount of cadmium in sample C1 at temperatures of 25°C and 40°C

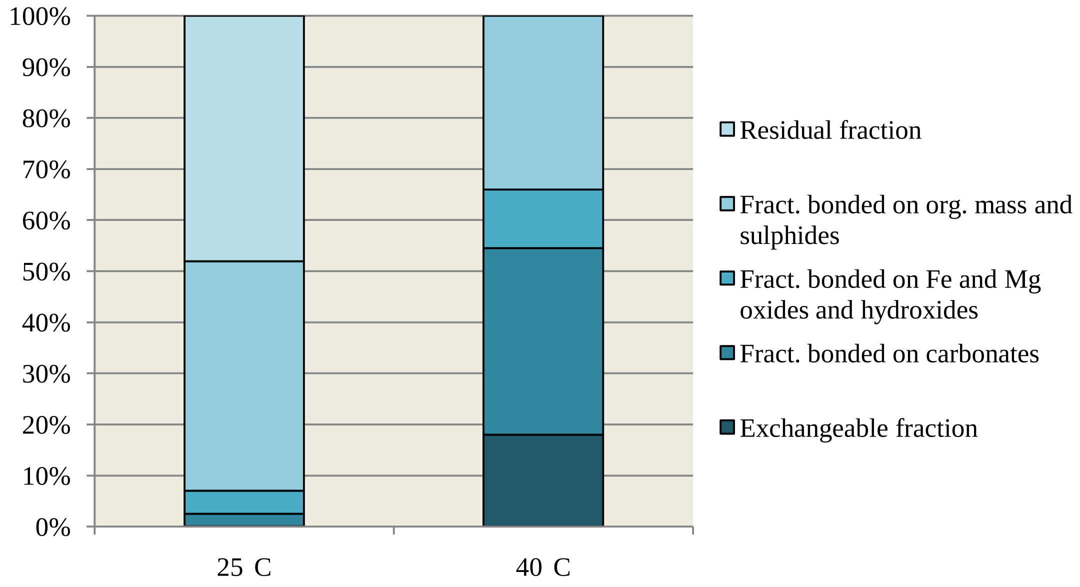


4.3.6 Sample C2

The exchangeable fraction was absent at the temperature of 25°C, but concentration was 18% in this fraction in 40°C. Concentrations in the second (3% in 25°C and 38% in 40°C – the biggest concentration in this extraction) and the third (5% at the temperature and 10% in 40°C) steps increased in compare with temperature, but amount in the fraction bonded on organic mass and sulfides decreased in higher temperature (43% in 25°C and 34% of the total concentration in 40°C).

The residual fraction, the fifth step, was absent in extraction in 40°C, but the concentration was biggest in this step in 25°C (49%).

Graph 33: The amount of cadmium in sample C2 at temperatures of 25°C and 40°C

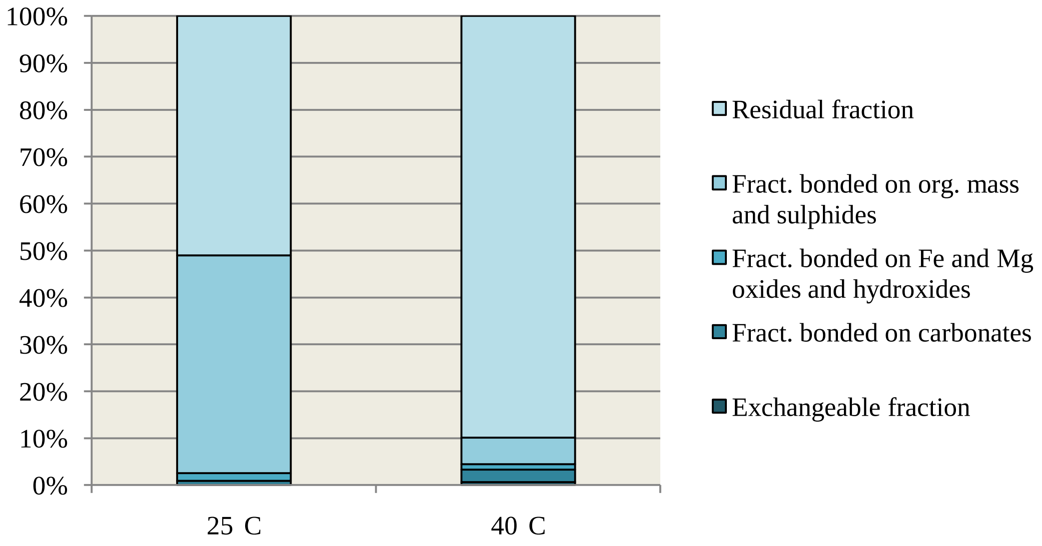


4.3.7 Sample C3

The first steps, the exchangeable fraction, were the same in both temperatures (less than 0,5% of the total concentration). The second steps were very similar to each other and to the first steps (0,5% at the temperature of 25°C and around 1% in 40°C). The fraction bonded on iron and manganese oxides and hydroxides were very low, lower than the first and the second steps in 40°C (less than 0,5%) and was absent at the temperature of 25°C.

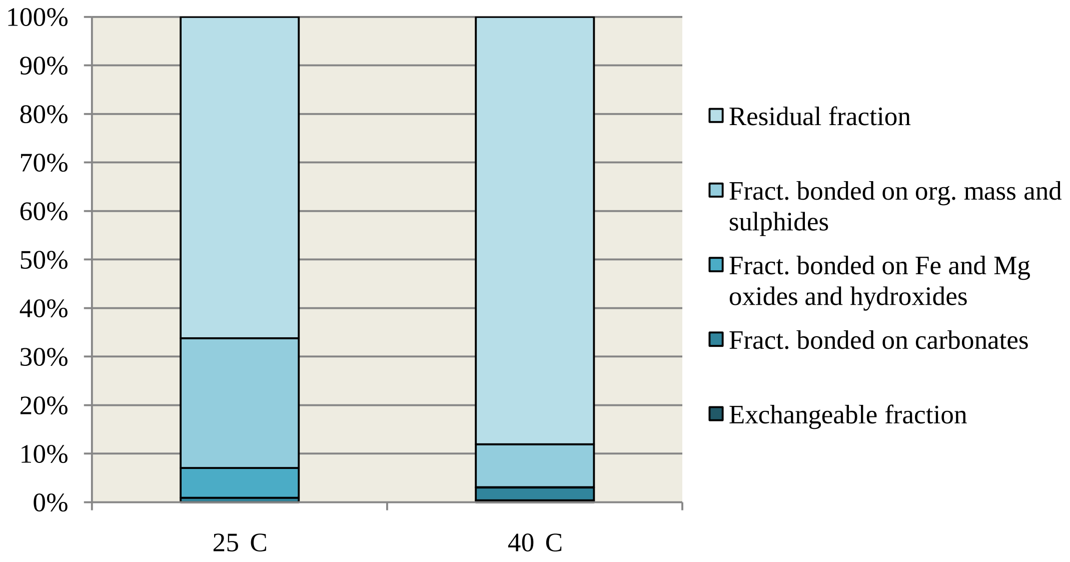
The fraction bonded on organic mass and sulfides was very high (48%) in 25°C, but still low (6%) at the temperature of 40°C. The biggest concentrations were in the last steps (the residual fraction) in both temperatures (51% in 25°C and 92% at the temperature of 40°C).

Graph 34: The amount of cadmium in sample C3 at temperatures of 25°C and 40°C



4.3.8 Sample D1

Graph 35: The amount of cadmium in sample D1 at temperatures of 25°C and 40°C



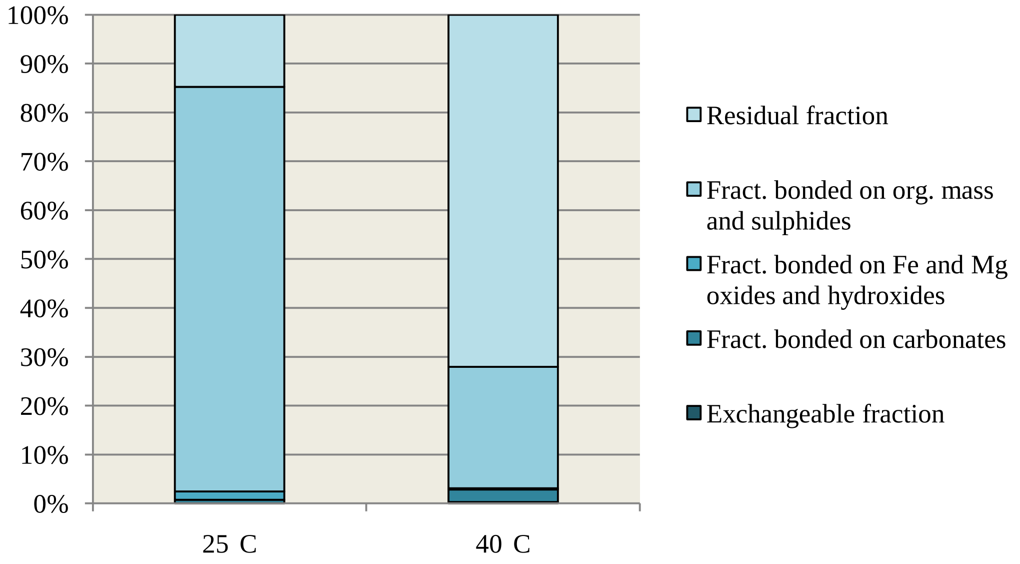
The exchangeable fraction was absent in 25°C and concentration was almost zero at the temperature of 40°C. Concentrations in the second step were very low (around 0,5% in 25°C and 2%of the total concentration at the temperature of 40°C).

The third step, the fraction bonded on iron and manganese oxides and hydroxides, was little bit bigger at the temperature of 25°C (6% at 25°C and almost zero at 40°C). Concentrations in the next step (fraction bonded on organic mass and sulfides) decreased in compare with temperature (26% at the temperature of 25°C and 10% at the temperature of 40°C).

The biggest amounts were in the last steps, in the residual fraction, and the concentration increase with the temperature – 68% in lower temperature and 88% of the total concentration in the higher temperature (40°C).

4.3.9 Sample D2

Graph 36: The amount of cadmium in sample D2 at temperatures of 25°C and 40°C



In the first (zero concentration - the exchangeable fraction), the second (concentrations were around 2% in the fraction bonded on carbonates) and in the third (concentrations were almost zero in the fraction bonded on iron and manganese oxides and hydroxides) steps were very similar concentrations in both temperatures.

The biggest concentration was in the fraction bonded on organic mass and sulfides at the temperature of 25°C, concentration decreased in compare with temperature (26% in 40°C).

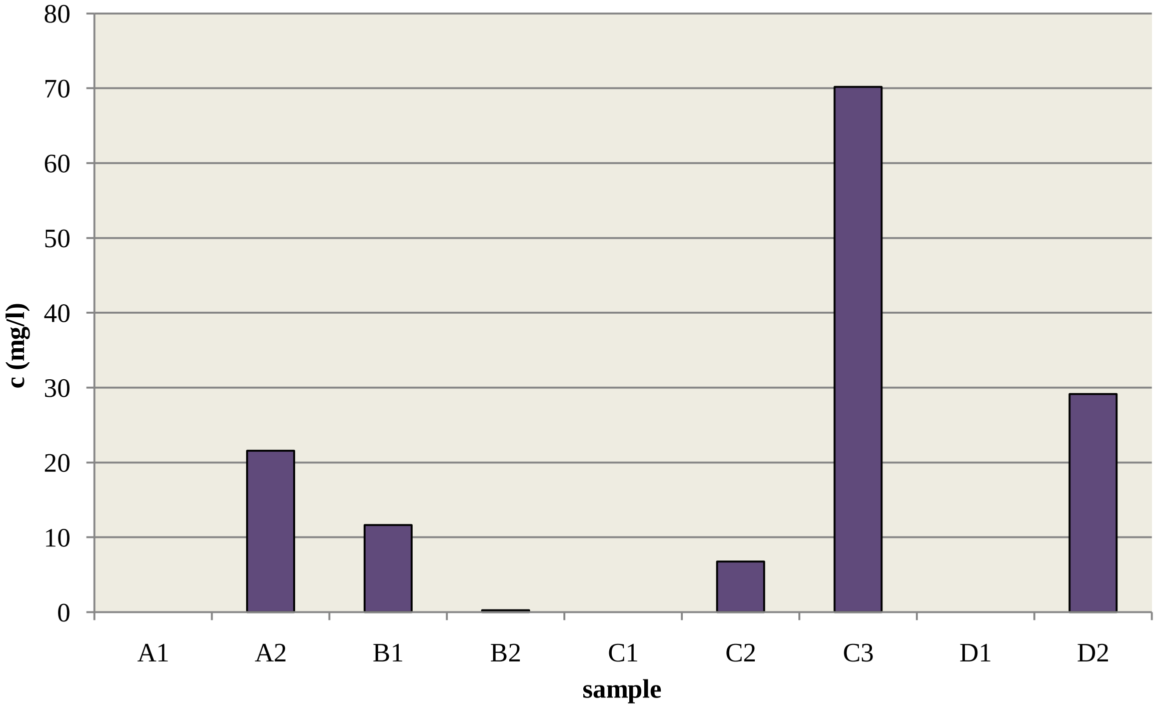
The residual fraction (the last step) had the biggest concentration at the temperature of 40°C (72%). The concentration increased with the temperature (14% in 25°C and 72% in 40°C).

4.4 Determination of mercury

The concentration of mercury depends on type of the sample (**Chyba! Nenalezen zdroj odkazů.**).

In generally the biggest concentration 70mg/l of mercury was in sample C3 (product from desuphurization). Similar concentrations were in fly ashes (samples A2 – 20mg/l, B1 – 10mg/l, C2 – 9mg/l and D2 – 28mg/l) and mercury was not in the other samples loge ash (A1, D1), hydromixture of ash and dross (B2) and scoria (C1).

Graph 37: The amount of mercury for all samples



5 CONCLUSION

This diploma thesis deals with the extraction according to Tessier and so it also deals with the determination of metals (lead, copper, cadmium and mercury) on the atomic absorption spectrometer (F AAS, ET AAS) and by mercury method AMA 254.

The theoretical part deals with energetic waste which was used for the extraction. The next chapter deals with the known extractions, their classification on the simple and sequenced extraction and with the impact of some hazardous metals (which were determined and they are - lead, copper, cadmium and mercury) on the environment.

The samples were described in the experimental part. Scoria, fly ash, dross, the product of desulphurization, loge ash and hydromixture of ash and dross became the samples.

The next chapter of the experimental part deals with the method of extraction. Extraction of metals was according to Tessier and it means that extraction goes in five steps with five different extraction agents and it was done at two temperatures, 25°C and 40°C. As extraction agents were used these compounds: 1M magnesium chloride ($MgCl_2$), 1M sodium acetate (CH_3COONa), 1M hydroxylamin hydrochloride in 25% acetic acid ($NH_2OH.HCl$ in CH_3COOH), hydrogen peroxide in nitric acid (H_2O_2 in HNO_3) and hydrofluoric acid (HF).

Lead and copper were determined on the atomic absorption spectrometer with flame atomization (F AAS), cadmium was determined on the atomic absorption spectrometer with electrothermal atomization (ET AAS) and mercury was determined by mercury method on AMA 254. All metals in all fractions were determined on these instruments.

The concentration of the individual metals depended on the type of the sample (ash, dross, scoria, etc.), on the temperature (a season of the year) and on the extraction agents and could not be comprehensively assessed. It is possible to say that heat plants did not pollute the environment so much and the filters and other cleaning elements are quite effective.

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The sample A1

The sample A2

The sample B1

The sample B2

The sample C1

The sample C2

The sample C3

The sample D1

The sample D2

APPENDIX A: Tables of values for lead

1. Fraction - 25°C

	concentration (mg/l)			*average*	*median*	*standard deviation*	*range*	
							min	*max*
A1	2,2800	2,2600	2,2700	2,4500	2,4350	0,1989	2,2600	2,6700
	2,6300	2,5900	2,6700					
A2	2,5400	2,4800	2,5300	2,4850	2,4800	0,0428	2,4400	2,5400
	2,4800	2,4400	2,4400					
B1	2,1400	2,2000	2,0400	2,1950	2,1950	0,0991	2,0400	2,3000
	2,1900	2,3000	2,3000					
B2	2,0500	2,1000	2,0700	2,0417	2,0600	0,0508	1,9700	2,1000
	2,0700	1,9700	1,9900					
C1	1,8800	1,8800	1,9400	1,7033	1,7400	0,2297	1,3700	1,9400
	1,6000	1,5500	1,3700					
C2	1,5600	1,5000	1,3700	1,4850	1,5250	0,0878	1,3700	1,5600
	1,5500	1,5500	1,3800					
C3	1,9300	1,7600	1,5800	1,6683	1,6350	0,1614	1,4700	1,9300
	1,6800	1,5900	1,4700					
D1	1,6800	1,6100	1,4100	1,3250	1,3400	0,3040	0,8900	1,6800
	1,2700	1,0900	0,8900					
D2	1,3400	1,3600	1,3500	1,3467	1,3500	0,0266	1,3000	1,3800
	1,3800	1,3000	1,3500					

1. Fraction - 40°C

	concentration (mg/l)			*average*	*median*	*standard deviation*	*range*	
							min	*max*
A1	1,2100	1,1200	1,2300	1,2167	1,2350	0,0497	1,1200	1,2500
	1,2500	1,2500	1,2400					
A2	1,1100	1,1400	1,1800	1,1733	1,1900	0,0398	1,1100	1,2100
	1,2100	1,2000	1,2000					
B1	1,0100	1,0400	1,0000	0,9913	0,9990	0,0376	0,9300	1,0400
	0,9300	0,9700	0,9980					
B2	1,1400	1,1100	1,1000	1,0917	1,0950	0,0343	1,0400	1,1400
	1,0400	1,0700	1,0900					
C1	0,9500	0,9000	0,9800	1,0133	1,0150	0,0838	0,9000	1,1200
	1,0800	1,1200	1,0500					
C2	1,0500	0,9400	0,9800	1,0017	1,0000	0,0736	0,9100	1,1100
	1,1100	0,9100	1,0200					
C3	1,4200	1,5200	1,4600	1,4383	1,4250	0,0475	1,3800	1,5200
	1,4300	1,3800	1,4200					
D1	1,3500	1,4100	1,3700	1,3850	1,3900	0,0226	1,3500	1,4100
	1,4000	1,4000	1,3800					
D2	1,6600	1,6200	1,6000	1,5367	1,5550	0,1140	1,3500	1,6600
	1,4800	1,3500	1,5100					

2. Fraction – 25°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,2200	0,2500	0,1800	0,2017	0,2000	0,0402	0,1600	0,2500
	0,1600	0,1600	0,2400					
A2	0,1300	0,1800	0,1300	0,0950	0,1100	0,0650	0,0100	0,1800
	0,0300	0,0100	0,0900					
B1	0,5000	0,5900	0,4000	0,5117	0,5400	0,0935	0,4000	0,6000
	0,5800	0,4000	0,6000					
B2	-0,0100	0,0500	0,0880	0,1797	0,0750	0,3059	-0,0100	0,8000
	0,0700	0,0800	0,8000					
C1	0,0600	0,1000	0,8000	0,1800	0,0700	0,3057	0,0000	0,8000
	0,0800	0,0000	0,0400					
C2	0,3000	0,3600	0,3500	0,4150	0,4000	0,1029	0,3000	0,5900
	0,4500	0,4400	0,5900					
C3	0,2400	0,2300	0,2300	0,2150	0,2150	0,0207	0,1900	0,2400
	0,2000	0,1900	0,2000					
D1	0,3400	0,3500	0,3500	0,3283	0,3450	0,0354	0,2700	0,3600
	0,2700	0,3000	0,3600					
D2	0,3200	0,3200	0,3100	0,3167	0,3200	0,0103	0,3000	0,3300
	0,3300	0,3000	0,3200					

2. Fraction – 40°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,8600	1,0100	0,9800	1,1700	1,1750	0,2482	0,8600	1,4400
	1,4400	1,3400	1,3900					
A2	1,4700	1,4500	1,4200	1,4017	1,4000	0,0556	1,3200	1,4700
	1,3200	1,3700	1,3800					
B1	1,2900	1,2200	1,3100	1,2783	1,2850	0,0306	1,2200	1,3100
	1,2800	1,2800	1,2900					
B2	1,3800	1,3300	1,3700	1,3967	1,3950	0,0480	1,3300	1,4700
	1,4200	1,4700	1,4100					
C1	1,4200	1,4500	1,5000	1,5417	1,5550	0,0970	1,4200	1,6400
	1,6300	1,6400	1,6100					
C2	1,5800	1,6500	1,6000	1,5750	1,5950	0,0896	1,4000	1,6500
	1,4000	1,6300	1,5900					
C3	1,2300	1,2200	1,2100	1,1883	1,1950	0,0387	1,1300	1,2300
	1,1600	1,1300	1,1800					
D1	1,1700	1,1700	1,1900	1,2017	1,1950	0,0325	1,1700	1,2500
	1,2500	1,2300	1,2000					
D2	1,1600	1,2800	1,2200	1,2132	1,2145	0,0418	1,1600	1,2800
	1,2300	1,1800	1,2090					

3. Fraction – 25°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,4700	0,5100	0,4500	0,5183	0,5200	0,0523	0,4500	0,5800
	0,5300	0,5700	0,5800					
A2	0,8600	0,7700	0,8600	1,0050	0,9550	0,2077	0,7700	1,2700
	1,0500	1,2200	1,2700					
B1	1,1600	1,0600	1,1800	1,1683	1,1850	0,0564	1,0600	1,2100
	1,1900	1,2100	1,2100					
B2	0,2900	0,3000	0,3100	0,2983	0,2950	0,0147	0,2800	0,3200
	0,2800	0,3200	0,2900					
C1	1,1400	1,1300	1,1700	1,1133	1,1150	0,0408	1,0600	1,1700
	1,1000	1,0800	1,0600					
C2	0,8400	0,8400	0,9000	0,8550	0,8500	0,0367	0,8000	0,9000
	0,8000	0,8900	0,8600					
C3	1,1700	1,1800	1,1800	1,1183	1,1250	0,0652	1,0400	1,1800
	1,0400	1,0800	1,0600					
D1	0,5900	0,4800	0,5000	0,3483	0,3350	0,1957	0,1500	0,5900
	0,1500	0,1900	0,1800					
D2	0,3500	0,3400	0,3400	0,2450	0,2500	0,1082	0,1300	0,3500
	0,1600	0,1300	0,1500					

3. Fraction – 40°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,7700	0,7400	0,7400	0,7100	0,7150	0,0482	0,6400	0,7700
	0,6400	0,6800	0,6900					
A2	0,8400	0,8900	0,9100	0,9433	0,9450	0,0747	0,8400	1,0300
	1,0100	1,0300	0,9800					
B1	0,7900	0,6900	0,7800	0,7420	0,7360	0,0375	0,6900	0,7900
	0,7400	0,7200	0,7320					
B2	0,5400	0,5200	0,5100	0,4433	0,4500	0,0903	0,3300	0,5400
	0,3700	0,3300	0,3900					
C1	0,4100	0,4700	0,4500	0,5000	0,5000	0,0669	0,4100	0,5800
	0,5800	0,5300	0,5600					
C2	0,5400	0,4300	0,5700	0,5400	0,5450	0,0657	0,4300	0,6300
	0,6300	0,5500	0,5200					
C3	1,7100	1,5500	1,5900	1,4617	1,4600	0,1844	1,2200	1,7100
	1,3700	1,2200	1,3300					
D1	0,9300	0,7300	0,8800	0,9033	0,9200	0,0987	0,7300	1,0300
	1,0300	0,9400	0,9100					
D2	1,4000	1,3500	1,3000	1,3217	1,3050	0,0462	1,2700	1,4000
	1,3000	1,2700	1,3100					

4. Fraction – 25°C

	concentration (mg/l)			*average*	*median*	*standard deviation*	*range*	
							min	*max*
A1	0,7100	0,7000	0,7000	0,7133	0,7150	0,0121	0,7000	0,7300
	0,7300	0,7200	0,7200					
A2	1,3200	1,1300	1,2200	1,2650	1,3000	0,0758	1,1300	1,3200
	1,3000	1,3200	1,3000					
B1	0,8600	0,9300	0,9000	0,8067	0,8100	0,1076	0,6500	0,9300
	0,7600	0,6500	0,7400					
B2	0,6200	0,5400	0,6000	0,5433	0,5450	0,0734	0,4100	0,6200
	0,5400	0,4100	0,5500					
C1	0,4600	0,4700	0,4700	0,5450	0,5350	0,0873	0,4600	0,6500
	0,6000	0,6500	0,6200					
C2	0,6200	0,6500	0,6200	0,6133	0,6250	0,0472	0,5200	0,6500
	0,6300	0,5200	0,6400					
C3	0,7100	0,7000	0,7100	0,7183	0,7100	0,0214	0,7000	0,7600
	0,7600	0,7100	0,7200					
D1	0,9700	0,9200	0,9000	0,8867	0,8900	0,0606	0,7900	0,9700
	0,7900	0,8600	0,8800					
D2	0,9300	1,0200	0,9200	0,9067	0,9050	0,0677	0,8300	1,0200
	0,8300	0,8500	0,8900					

4. Fraction – 40°C

	concentration (mg/l)			*average*	*median*	*standard deviation*	*range*	
							min	*max*
A1	0,8800	0,9300	0,9000	0,9000	0,9000	0,0190	0,8800	0,9300
	0,8800	0,9100	0,9000					
A2	1,4900	1,4400	1,4560	1,4643	1,4630	0,0228	1,4400	1,4900
	1,4400	1,4900	1,4700					
B1	1,1800	1,0800	1,0100	1,0050	0,9800	0,1093	0,8900	1,1800
	0,9200	0,8900	0,9500					
B2	0,6000	0,6700	0,6200	0,6062	0,5985	0,0357	0,5700	0,6700
	0,5700	0,5800	0,5970					
C1	0,7600	0,7900	0,7800	0,7817	0,7850	0,0194	0,7600	0,8100
	0,8100	0,7900	0,7600					
C2	0,9100	0,8800	0,8900	0,9100	0,9100	0,0228	0,8800	0,9400
	0,9400	0,9100	0,9300					
C3	1,2300	1,2700	1,2400	1,1833	1,1850	0,0726	1,0900	1,2700
	1,1400	1,0900	1,1300					
D1	1,3700	1,4000	1,3900	1,3867	1,3900	0,0103	1,3700	1,4000
	1,3900	1,3900	1,3800					
D2	1,6800	1,7200	1,6600	1,6500	1,6700	0,0825	1,4900	1,7200
	1,6500	1,4900	1,7000					

5. Fraction – 25°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	3,2200	2,9600	3,0100	3,0667	3,0500	0,0903	2,9600	3,2200
	3,0400	3,1100	3,0600					
A2	2,3400	2,2200	2,2000	2,0800	2,0900	0,2015	1,8300	2,3400
	1,9100	1,8300	1,9800					
B1	2,5600	2,6100	2,6000	2,2633	2,2550	0,3584	1,9200	2,6100
	1,9500	1,9200	1,9400					
B2	2,4800	2,5500	2,5000	2,3867	2,3750	0,1371	2,2600	2,5500
	2,2600	2,2600	2,2700					
C1	1,7900	1,8400	1,8100	1,7567	1,7600	0,0698	1,6500	1,8400
	1,7300	1,6500	1,7200					
C2	2,7300	2,7500	2,7100	2,6083	2,6150	0,1364	2,4400	2,7500
	2,5200	2,4400	2,5000					
C3	0,7700	0,8600	0,8000	0,8633	0,8650	0,0745	0,7700	0,9800
	0,8700	0,9800	0,9000					
D1	1,0600	0,9800	1,0100	1,0250	1,0200	0,0315	0,9800	1,0600
	1,0600	1,0100	1,0300					
D2	1,2600	1,1500	1,2000	1,1100	1,0850	0,1081	1,0100	1,2600
	1,0200	1,0100	1,0200					

5. Fraction – 40°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	2,8400	2,7900	2,8000	2,3233	2,3450	0,5356	1,7500	2,8400
	1,7500	1,9000	1,8600					
A2	1,3300	1,2700	1,3000	1,4783	1,4800	0,1972	1,2700	1,6900
	1,6300	1,6900	1,6500					
B1	2,6100	2,6500	2,6200	2,1017	2,1050	0,5755	1,5500	2,6500
	1,6000	1,5500	1,5800					
B2	1,9000	1,7500	1,7000	1,5600	1,5500	0,2573	1,2600	1,9000
	1,3500	1,2600	1,4000					
C1	1,2100	1,2700	1,2500	1,2400	1,2350	0,0410	1,1900	1,3000
	1,3000	1,1900	1,2200					
C2	2,3800	2,5200	2,4000	2,4133	2,3950	0,0572	2,3600	2,5200
	2,3600	2,3900	2,4300					
C3	0,3100	0,2900	0,3100	0,2917	0,3000	0,0271	0,2400	0,3100
	0,3100	0,2400	0,2900					
D1	0,4300	0,4000	0,4200	0,4188	0,4165	0,0144	0,4000	0,4400
	0,4100	0,4400	0,4130					
D2	0,6700	0,6300	0,6900	0,6950	0,6950	0,0428	0,6300	0,7500
	0,7300	0,7500	0,7000					

APPENDIX B: Tables of values for copper

1. Fraction - 25°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,0420	0,0386	0,0378	0,0499	0,0490	0,0118	0,0378	0,0640
	0,0560	0,0640	0,0610					
A2	0,0690	0,0760	0,0830	0,0715	0,0690	0,0067	0,0650	0,0830
	0,0650	0,0690	0,0670					
B1	0,0720	0,0530	0,0540	0,0603	0,0595	0,0084	0,0520	0,0720
	0,0660	0,0520	0,0650					
B2	0,0490	0,0420	0,0480	0,0395	0,0395	0,0083	0,0290	0,0490
	0,0290	0,0370	0,0320					
C1	0,0200	0,0130	0,0110	-0,0098	0,0105	0,0427	-0,0920	0,0200
	0,0100	-0,0920	-0,0210					
C2	-0,0320	-0,0250	-0,0170	-0,0228	-0,0240	0,0073	-0,0320	-0,0120
	-0,0230	-0,0280	-0,0120					
C3	0,0100	0,0220	0,0180	0,0160	0,0170	0,0051	0,0100	0,0220
	0,0100	0,0160	0,0200					
D1	0,0420	0,0390	0,0360	0,0280	0,0270	0,0122	0,0160	0,0420
	0,0170	0,0180	0,0160					
D2	0,2900	0,2890	0,2610	0,2788	0,2800	0,0108	0,2610	0,2900
	0,2810	0,2730	0,2790					

1. Fraction - 40°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	-0,0140	-0,0060	-0,0040	-0,0130	-0,0125	0,0078	-0,0250	-0,0040
	-0,0250	-0,0110	-0,0180					
A2	0,0020	-0,0010	-0,0020	-0,0088	-0,0070	0,0099	-0,0210	0,0020
	-0,0210	-0,0190	-0,0120					
B1	-0,0090	-0,0080	0,0100	-0,0152	-0,0165	0,0158	-0,0300	0,0100
	-0,0300	-0,0240	-0,0300					
B2	-0,0130	-0,0170	-0,0100	-0,0257	-0,0245	0,0146	-0,0470	-0,0100
	-0,0350	-0,0320	-0,0470					
C1	-0,0250	-0,0250	-0,0240	-0,0417	-0,0405	0,0187	-0,0620	-0,0240
	-0,0560	-0,0620	-0,0580					
C2	-0,0510	-0,0550	-0,0560	-0,0545	-0,0555	0,0034	-0,0590	-0,0500
	-0,0590	-0,0500	-0,0560					
C3	-0,0520	-0,0450	-0,0340	-0,0510	-0,0525	0,0103	-0,0620	-0,0340
	-0,0530	-0,0600	-0,0620					
D1	-0,0410	-0,0370	-0,0630	-0,0563	-0,0585	0,0157	-0,0800	-0,0370
	-0,0800	-0,0570	-0,0600					
D2	-0,0580	-0,0440	-0,0630	-0,0608	-0,0630	0,0096	-0,0730	-0,0440
	-0,0730	-0,0640	-0,0630					

2. Fraction - 25°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	-0,0180	-0,0430	-0,0410	-0,0453	-0,0485	0,0153	-0,0590	-0,0180
	-0,0590	-0,0540	-0,0570					
A2	-0,0600	-0,0630	-0,0540	-0,0652	-0,0670	0,0074	-0,0720	-0,0540
	-0,0710	-0,0720	-0,0710					
B1	-0,0840	-0,0840	-0,1000	-0,0532	-0,0545	0,0405	-0,1000	-0,0070
	-0,0070	-0,0190	-0,0250					
B2	0,0730	0,0670	0,0700	0,0680	0,0690	0,0044	0,0600	0,0730
	0,0600	0,0690	0,0690					
C1	0,0730	0,0740	0,0840	0,0672	0,0670	0,0117	0,0540	0,0840
	0,0570	0,0540	0,0610					
C2	0,0690	0,0570	0,0680	0,0622	0,0640	0,0072	0,0510	0,0690
	0,0670	0,0610	0,0510					
C3	0,0580	0,0660	0,0630	0,0562	0,0580	0,0085	0,0450	0,0660
	0,0580	0,0470	0,0450					
D1	0,0490	0,0710	0,0600	0,0637	0,0620	0,0100	0,0490	0,0780
	0,0780	0,0610	0,0630					
D2	0,0460	0,0430	0,0520	0,0398	0,0405	0,0091	0,0270	0,0520
	0,0380	0,0270	0,0330					

2. Fraction - 40°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,1160	0,1010	0,1070	0,1205	0,1215	0,0157	0,1010	0,1440
	0,1270	0,1440	0,1280					
A2	0,1210	0,1370	0,1340	0,1302	0,1290	0,0096	0,1210	0,1440
	0,1440	0,1240	0,1210					
B1	0,1070	0,1180	0,0970	0,1073	0,1075	0,0077	0,0970	0,1180
	0,1080	0,1010	0,1130					
B2	0,1040	0,0990	0,0940	0,1080	0,1075	0,0112	0,0940	0,1240
	0,1160	0,1240	0,1110					
C1	0,0810	0,0640	0,0820	0,0765	0,0780	0,0074	0,0640	0,0840
	0,0730	0,0840	0,0750					
C2	0,0960	0,0790	0,0870	0,0878	0,0880	0,0109	0,0730	0,1030
	0,0890	0,0730	0,1030					
C3	0,0570	0,0690	0,0570	0,0618	0,0615	0,0049	0,0570	0,0690
	0,0590	0,0650	0,0640					
D1	0,1080	0,0930	0,0830	0,0818	0,0795	0,0168	0,0610	0,1080
	0,0610	0,0700	0,0760					
D2	0,0760	0,0870	0,0750	0,0808	0,0815	0,0091	0,0680	0,0910
	0,0680	0,0880	0,0910					

3. Fraction - 25°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,4790	0,4550	0,5040	0,4960	0,4915	0,0306	0,4550	0,5320
	0,5280	0,4780	0,5320					
A2	0,7240	0,7290	0,7440	0,8328	0,7935	0,1209	0,7240	0,9850
	0,9720	0,9850	0,8430					
B1	0,3810	0,3780	0,4240	0,3462	0,3445	0,0561	0,2800	0,4240
	0,3030	0,2800	0,3110					
B2	0,3020	0,3420	0,3770	0,3102	0,3015	0,0453	0,2440	0,3770
	0,3010	0,2440	0,2950					
C1	0,1510	0,1600	0,1920	0,1805	0,1770	0,0282	0,1510	0,2260
	0,2260	0,1920	0,1620					
C2	0,2710	0,2390	0,2440	0,3060	0,3110	0,0615	0,2390	0,3760
	0,3550	0,3760	0,3510					
C3	0,5570	0,5240	0,4940	0,5082	0,4975	0,0280	0,4790	0,5570
	0,4790	0,5000	0,4950					
D1	0,4990	0,5410	0,5180	0,6048	0,5720	0,1062	0,4990	0,7430
	0,6030	0,7430	0,7250					
D2	0,0361	0,3460	0,3700	0,2545	0,2595	0,1179	0,0361	0,3700
	0,2560	0,2560	0,2630					

3. Fraction - 40°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,3540	0,3600	0,3710	0,2428	0,2545	0,1317	0,0950	0,3710
	0,1550	0,1220	0,0950					
A2	0,4610	0,4980	0,4060	0,5172	0,5085	0,0935	0,4060	0,6830
	0,5190	0,6830	0,5360					
B1	0,3160	0,3310	0,3090	0,3328	0,3340	0,0183	0,3090	0,3580
	0,3370	0,3580	0,3460					
B2	0,1300	0,1580	0,1710	0,1437	0,1375	0,0176	0,1280	0,1710
	0,1440	0,1280	0,1310					
C1	0,3300	0,3150	0,3370	0,2558	0,2600	0,0795	0,1700	0,3370
	0,1780	0,1700	0,2050					
C2	0,3050	0,3050	0,3190	0,4927	0,4895	0,2008	0,3050	0,6900
	0,6770	0,6900	0,6600					
C3	0,3080	0,2870	0,3910	0,5768	0,5770	0,2765	0,2870	0,8770
	0,7630	0,8350	0,8770					
D1	0,5850	0,5760	0,0,559	0,4666	0,4990	0,1238	0,3220	0,5850
	0,4990	0,3510	0,3220					
D2	0,6780	0,6090	0,6400	0,6217	0,6185	0,0365	0,5700	0,6780
	0,6050	0,5700	0,6280					

4. Fraction - 25°C

	concentration (mg/l)			*average*	*median*	*standard deviation*	*range*	
							min	*max*
A1	0,2430	0,2760	0,2770	0,3130	0,2955	0,0603	0,2430	0,4000
	0,3140	0,3680	0,4000					
A2	0,8470	0,8370	0,8600	0,8903	0,8940	0,0471	0,8370	0,9380
	0,9280	0,9320	0,9380					
B1	0,3720	0,3640	0,3970	0,3775	0,3765	0,0140	0,3620	0,3970
	0,3810	0,3620	0,3890					
B2	0,2610	0,2830	0,2750	0,2967	0,2985	0,0272	0,2610	0,3280
	0,3190	0,3140	0,3280					
C1	0,4200	0,4710	0,4090	0,4480	0,4555	0,0276	0,4090	0,4770
	0,4770	0,4590	0,4520					
C2	0,4010	0,4250	0,4390	0,3950	0,3910	0,0327	0,3550	0,4390
	0,3550	0,3690	0,3810					
C3	0,1500	0,2000	0,2090	0,2208	0,2190	0,0478	0,1500	0,2930
	0,2290	0,2440	0,2930					
D1	0,7080	0,0,711	0,7220	0,6982	0,6900	0,0164	0,6820	0,7220
	0,6820	0,6900	0,6890					
D2	0,9130	0,9390	0,9240	0,8313	0,8335	0,1037	0,7270	0,9390
	0,7270	0,7310	0,7540					

4. Fraction - 40°C

	concentration (mg/l)			*average*	*median*	*standard deviation*	*range*	
							min	*max*
A1	0,3290	0,2570	0,2670	0,2977	0,3055	0,0300	0,2570	0,3290
	0,3220	0,2950	0,3160					
A2	0,8780	0,8550	0,8920	1,0223	1,0225	0,1622	0,8550	1,1880
	1,1530	1,1680	1,1880					
B1	0,2470	0,2400	0,2210	0,2957	0,2960	0,0664	0,2210	0,3700
	0,3450	0,3510	0,3700					
B2	0,0950	0,1030	0,1200	0,0873	0,0850	0,0223	0,0630	0,1200
	0,0750	0,0630	0,0680					
C1	0,3630	0,3500	0,3450	0,3268	0,3290	0,0301	0,2870	0,3630
	0,3030	0,2870	0,3130					
C2	0,2820	0,2530	0,2530	0,2813	0,2850	0,0248	0,2530	0,3160
	0,2880	0,2960	0,3160					
C3	0,2730	0,2330	0,2590	0,2207	0,2190	0,0413	0,1700	0,2730
	0,1840	0,1700	0,2050					
D1	1,0780	1,0480	1,0550	1,0753	1,0735	0,0225	1,0480	1,1010
	1,1010	1,0690	1,1010					
D2	1,9920	1,9780	2,0130	1,9393	1,9600	0,0697	1,8390	2,0130
	1,8390	1,9420	1,8720					

5. Fraction - 25°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,8410	0,8190	0,7980	0,8395	0,8480	0,0264	0,7980	0,8690
	0,8690	0,8550	0,8550					
A2	0,8970	0,9270	0,9200	0,9323	0,9325	0,0233	0,8970	0,9640
	0,9380	0,9640	0,9480					
B1	1,3090	1,3230	1,3340	1,2710	1,2770	0,0581	1,2040	1,3340
	1,2040	1,2110	1,2450					
B2	1,3640	1,3750	1,4280	1,3155	1,3170	0,0852	1,2150	1,4280
	1,2150	1,2410	1,2700					
C1	1,2010	1,2070	1,2080	1,1163	1,1225	0,0980	1,0180	1,2080
	1,0200	1,0180	1,0440					
C2	1,6290	1,6970	1,6330	1,5488	1,5445	0,1170	1,4300	1,6970
	1,4300	1,4440	1,4600					
C3	0,3820	0,3690	0,3710	0,4202	0,4200	0,0511	0,3690	0,4760
	0,4580	0,4650	0,4760					
D1	0,4940	0,4800	0,4900	0,4613	0,4590	0,0297	0,4300	0,4940
	0,4360	0,4300	0,4380					
D2	0,9550	0,9610	0,9600	0,8423	0,8430	0,1275	0,7230	0,9610
	0,7230	0,7310	0,7240					

5. Fraction - 40°C

	concentration (mg/l)			***average***	***median***	***standard deviation***	***range***	
							min	***max***
A1	0,8160	0,8000	0,8120	0,7917	0,7930	0,0219	0,7590	0,8160
	0,7860	0,7770	0,7590					
A2	0,7080	0,7270	0,7160	0,7383	0,7375	0,0255	0,7080	0,7740
	0,7740	0,7480	0,7570					
B1	1,3150	1,3490	1,3440	1,1120	1,1075	0,2457	0,8790	1,3490
	0,9000	0,8850	0,8790					
B2	1,3510	1,3660	1,3790	1,3372	1,3330	0,0326	1,2990	1,3790
	1,2990	1,3150	1,3130					
C1	0,9090	0,9050	0,9100	0,9197	0,9185	0,0132	0,9050	0,9360
	0,9310	0,9360	0,9270					
C2	1,5470	1,5640	1,5550	1,5343	1,5355	0,0243	1,5070	1,5640
	1,5070	1,5090	1,5240					
C3	0,4440	0,4650	0,4450	0,4687	0,4735	0,0206	0,4440	0,4900
	0,4860	0,4900	0,4820					
D1	0,4540	0,4820	0,4690	0,4815	0,4845	0,0187	0,4540	0,5090
	0,4880	0,4870	0,5090					
D2	0,7700	0,7580	0,7700	0,7642	0,7670	0,0073	0,7530	0,7700
	0,7530	0,7700	0,7640					

APPENDIX C: Tables of values for cadmium

1. Fraction - 25°C

	concentration (μg/l)		*average*	*median*	*standard deviation*	*range*	
						min	*max*
A1	-0,0023	0,0490	-0,0009	-0,0107	0,0353	-0,0312	0,0490
	-0,0312	-0,0190					
A2	-0,0260	-0,0536	0,0114	-0,0374	0,1091	-0,0536	0,1741
	0,1741	-0,0488					
B1	0,0021	-0,0002	0,0158	0,0092	0,0207	-0,0002	0,0449
	0,0449	0,0163					
B2	0,0441	0,0718	0,0666	0,0663	0,0191	0,0441	0,0896
	0,0608	0,0896					
C1	-0,0016	-0,0055	0,0166	0,0170	0,0234	-0,0055	0,0380
	0,0380	0,0355					
C2	0,0265	0,0187	0,0263	0,0269	0,0057	0,0187	0,0326
	0,0273	0,0326					
C3	-0,0219	-0,0219	-0,0121	-0,0157	0,0127	-0,0219	0,0048
	-0,0096	0,0048					
D1	-0,0026	-0,0047	-0,0070	-0,0041	0,0070	-0,0174	-0,0026
	-0,0035	-0,0174					
D2	-0,0117	-0,0153	-0,0159	-0,0166	0,0032	-0,0188	-0,0117
	-0,0179	-0,0188					

1. Fraction - 40°C

	concentration (μg/l)		*average*	*median*	*standard deviation*	*range*	
						min	*max*
A1	0,0906	0,1075	0,1886	0,1767	0,1070	0,0906	0,3106
	0,2459	0,3106					
A2	0,5398	0,4436	0,4553	0,4404	0,0593	0,4009	0,5398
	0,4372	0,4009					
B1	1,0863	1,4806	1,0941	1,0050	0,2720	0,8856	1,4806
	0,8856	0,9238					
B2	2,1675	2,2106	1,8583	2,0519	0,5075	1,1188	2,2106
	1,1188	1,9363					
C1	0,8025	0,4279	0,4595	0,4025	0,2435	0,2306	0,8025
	0,3771	0,2306					
C2	2,6281	2,5350	1,5203	1,5101	1,2262	0,4329	2,6281
	0,4852	0,4329					
C3	1,0388	0,2465	0,4050	0,2282	0,4255	0,1251	1,0388
	0,1251	0,2098					
D1	0,2523	0,1604	0,1956	0,1848	0,0417	0,1604	0,2523
	0,1684	0,2013					
D2	0,1245	0,1436	0,1234	0,1316	0,0257	0,0868	0,1436
	0,0868	0,1387					

2. Fraction - 25°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	0,9128	0,9256	1,0045	0,9218	0,1714	0,9128	1,2615
	0,9179	1,2615					
A2	1,0913	1,1772	0,7965	0,8009	0,3939	0,4069	1,1772
	0,5105	0,4069					
B1	0,6308	0,7744	0,8996	0,9037	0,2405	0,6308	1,1600
	1,1600	1,0331					
B2	2,3462	2,1821	1,3785	1,3435	1,0248	0,4810	2,3462
	0,5049	0,4810					
C1	2,0718	2,1554	1,5854	1,5774	0,6112	1,0315	2,1554
	1,0315	1,0831					
C2	1,0549	0,9854	0,7994	0,7892	0,2568	0,5641	1,0549
	0,5931	0,5641					
C3	0,9682	0,9867	0,7254	0,7262	0,2912	0,4628	0,9867
	0,4628	0,4841					
D1	0,9579	0,9033	0,5520	0,5604	0,4392	0,1294	0,9579
	0,1294	0,2174					
D2	0,7510	0,7705	0,6491	0,6444	0,1292	0,5372	0,7705
	0,5377	0,5372					

2. Fraction - 40°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	3,1481	3,4669	3,9675	3,3084	1,4329	3,1481	6,1050
	6,1050	3,1500					
A2	16,5313	17,0500	8,9106	8,9606	9,1062	0,6713	17,0500
	1,3900	0,6713					
B1	2,3050	2,2544	1,6083	1,6084	0,7758	0,9113	2,3050
	0,9113	0,9625					
B2	1,9669	2,0188	1,9777	1,9928	0,1052	1,8381	2,0869
	1,8381	2,0869					
C1	0,8813	0,7531	0,6871	0,6727	0,1617	0,5217	0,8813
	0,5217	0,5923					
C2	5,0763	5,4219	3,0803	3,0328	2,5090	0,8338	5,4219
	0,9894	0,8338					
C3	2,4738	2,3331	1,6278	1,6319	0,8997	0,7738	2,4738
	0,7738	0,9306					
D1	0,9563	0,8419	1,4623	1,3953	0,6705	0,8419	2,2169
	2,2169	1,8344					
D2	1,7975	1,2813	1,1167	0,9913	0,5316	0,6869	1,7975
	0,7013	0,6869					

3. Fraction - 25°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	1,0880	1,1467	0,9892	0,9923	0,1527	0,8253	1,1467
	0,8967	0,8253					
A2	1,6833	1,6227	1,0984	1,1011	0,6415	0,5081	1,6833
	0,5795	0,5081					
B1	0,8060	0,7640	0,8502	0,8603	0,0772	0,7640	0,9160
	0,9160	0,9147					
B2	1,0807	1,1067	2,1058	1,0937	2,4096	0,5372	5,6987
	0,5372	5,6987					
C1	1,5113	1,5193	1,0780	1,0860	0,5053	0,6207	1,5193
	0,6607	0,6207					
C2	2,6493	1,3673	1,5028	1,1977	0,7844	0,9667	2,6493
	0,9667	1,0280					
C3	1,1140	1,1527	1,2778	1,2793	0,1681	1,1140	1,4387
	1,4060	1,4387					
D1	1,3753	13,5667	3,7851	0,7802	6,5491	0,0131	13,5667
	0,0131	0,1851					
D2	0,9120	0,8873	1,5183	1,5173	0,7145	0,8873	2,1513
	2,1513	2,1227					

3. Fraction - 40°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	0,3144	0,3205	0,3104	0,3141	0,0121	0,2928	0,3205
	0,2928	0,3138					
A2	0,0989	0,1001	0,1011	0,0995	0,0106	0,0900	0,1156
	0,1156	0,0900					
B1	0,3487	0,3374	0,2566	0,2556	0,1000	0,1667	0,3487
	0,1737	0,1667					
B2	0,2095	0,1964	0,1737	0,1748	0,0349	0,1358	0,2095
	0,1533	0,1358					
C1	0,1497	0,1442	0,1299	0,1296	0,0199	0,1107	0,1497
	0,1151	0,1107					
C2	0,3913	0,3764	0,9604	0,9626	0,6658	0,3764	1,5400
	1,5400	1,5338					
C3	0,8946	0,9592	0,7267	0,7158	0,2329	0,5159	0,9592
	0,5159	0,5369					
D1	0,0300	0,0397	0,0345	0,0341	0,0044	0,0300	0,0397
	0,0318	0,0363					
D2	0,1239	0,1342	0,1230	0,1231	0,0092	0,1116	0,1342
	0,1116	0,1223					

4. Fraction - 25°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	96,3400	84,6000	77,2400	74,9600	16,0466	62,7000	96,3400
	62,7000	65,3200					
A2	85,4700	74,9400	76,7575	74,5800	5,9059	72,4000	85,4700
	72,4000	74,2200					
B1	49,6400	47,2100	67,0475	67,6350	21,5263	47,2100	85,7100
	85,7100	85,6300					
B2	26,5500	28,9500	21,5675	21,0900	7,2086	15,1400	28,9500
	15,6300	15,1400					
C1	33,8700	27,5300	26,8400	26,2250	5,3921	21,0400	33,8700
	24,9200	21,0400					
C2	20,1800	17,0400	14,8400	14,3200	4,5586	10,5400	20,1800
	11,6000	10,5400					
C3	60,4700	63,0000	36,4700	35,9200	29,1921	11,0400	63,0000
	11,3700	11,0400					
D1	25,2900	24,5400	16,5323	16,4080	9,6850	8,0230	25,2900
	8,2760	8,0230					
D2	25,2300	20,3200	74,3875	75,4650	59,6312	20,3200	126,3000
	125,7000	126,3000					

4. Fraction - 40°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	7,2063	8,3188	9,0906	9,0125	1,7019	7,2063	11,1313
	11,1313	9,7063					
A2	15,8250	16,2438	14,7328	14,6438	1,5128	13,4000	16,2438
	13,4625	13,4000					
B1	5,6775	5,9069	9,1945	9,0566	3,9427	5,6775	12,9875
	12,9875	12,2063					
B2	5,4663	5,8913	7,1613	7,1269	1,7359	5,4663	8,9250
	8,9250	8,3625					
C1	9,6938	8,9750	9,7266	9,8781	0,5416	8,9750	10,1750
	10,1750	10,0625					
C2	3,0119	2,8875	2,8716	2,8494	0,1045	2,7756	3,0119
	2,7756	2,8113					
C3	4,7175	5,5600	3,4805	3,3441	1,9492	1,6738	5,5600
	1,6738	1,9706					
D1	4,3794	4,6925	4,9127	4,9184	0,4686	4,3794	5,4344
	5,1444	5,4344					
D2	10,6688	9,9688	10,7938	10,9500	0,6192	9,9688	11,3063
	11,2313	11,3063					

5. Fraction - 25°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	43,930	41,740	43,300	43,590	1,130	41,740	44,290
	44,290	43,240					
A2	40,510	40,260	40,560	40,390	0,460	40,240	41,220
	41,220	40,240					
B1	20,990	23,760	24,910	25,320	3,170	20,990	28,010
	26,880	28,010					
B2	12,400	12,380	13,520	13,490	1,310	12,380	14,730
	14,730	14,570					
C1	31,610	119,900	43,890	21,920	51,510	11,830	119,900
	12,220	11,830					
C2	28,840	27,860	28,830	28,850	0,780	27,860	29,770
	29,770	28,850					
C3	74,520	63,610	40,110	37,430	33,730	11,050	74,520
	11,050	11,250					
D1	11,490	10,990	40,880	36,680	34,950	10,990	79,170
	61,870	79,170					
D2	13,280	10,680	13,260	13,780	1,830	10,680	14,780
	14,780	14,280					

5. Fraction - 40°C

	concentration (μg/l)		***average***	***median***	***standard deviation***	***range***	
						min	***max***
A1	59,138	31,981	33,858	27,131	17,478	22,031	59,138
	22,031	22,281					
A2	19,325	18,831	20,592	20,672	1,761	18,831	22,194
	22,194	22,019					
B1	14,188	13,550	13,003	12,925	1,041	11,975	14,188
	11,975	12,300					
B2	10,600	10,413	26,111	25,891	18,024	10,413	42,250
	41,181	42,250					
C1	8,188	7,688	13,000	13,125	5,849	7,688	18,063
	18,063	18,063					
C2	16,175	15,906	15,895	15,875	0,215	15,656	16,175
	15,656	15,844					
C3	55,013	58,294	55,298	54,794	2,123	53,313	58,294
	54,575	53,313					
D1	44,875	44,813	48,597	48,516	4,337	44,813	52,544
	52,544	52,156					
D2	56,3438	56,150	31,378	31,350	28,716	6,469	56,344
	6,4688	6,550					

APPENDIX D: Tables of values for mercury

	concentration (mg/l)			*average*	*median*	*standard deviation*	*range*	
							min	*max*
A1	-0,1913	-0,1756	-0,1786	-0,1818	-0,1786	0,008334	-0,1913	-0,1756
A2	21,6269	21,4575	21,6431	21,5758	21,6269	0,102799	21,4575	21,6431
B1	11,5020	11,7897	11,6658	11,6525	11,6658	0,14431	11,5020	11,7897
B2	0,2331	0,1917	0,3136	0,2461	0,2331	0,061986	0,1917	0,3136
C1	-0,0987	-0,0730	-0,0725	-0,0814	-0,0730	0,014984	-0,0987	-0,0725
C2	6,7200	6,7157	6,8610	6,7656	6,7200	0,082676	6,7157	6,8610
C3	69,9233	70,7310	69,8952	70,1832	69,9233	0,474646	69,8952	70,7310
D1	-0,2817	-0,2602	-0,2598	-0,2672	-0,2602	0,01253	-0,2817	-0,2598
D2	29,4462	28,9103	29,1038	29,1534	29,1038	0,271376	28,9103	29,4462