LAPPEENRANNAN TEKNILLINEN YLIOPISTO

Faculty of Technology

Master's Degree Program in Chemical Engineering

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On-line determination of residual collector concentration in flotation process

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PREFACE

This Master's thesis was done in Lappeenranta University of Technology in the Laboratory of Chemistry in co-operation with Outotec Finland.

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Lappeenranta 1.4.2014
Jesse Tikka

ABSTRACT

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Faculty of Technology
LUT Chemistry

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On-line determination of residual collector concentration in flotation process

Master's thesis

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63 pages, 30 figures, 9 tables and 3 appendices

Examiners: Docent Satu-Pia Reinikainen
Ph.D. Jaakko Leppinen

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Valuable minerals can be recovered by using froth flotation. This is a widely used separation technique in mineral processing. In a flotation cell hydrophobic particles attach on air bubbles dispersed in the slurry and rise on the top of the cell. Valuable particles are made hydrophobic by adding collector chemicals in the slurry. With the help of a frother reagent a stable froth forms on the top of the cell and the froth with valuable minerals, i.e. the concentrate, can be removed for further processing. Normally the collector is dosed on the basis of the feed rate of the flotation circuit and the head grade of the valuable metal. However, also the mineral composition of the ore affects the consumption of the collector, i.e. how much is adsorbed on the mineral surfaces. Therefore it is worth monitoring the residual collector concentration in the flotation tailings. Excess usage of collector causes unnecessary costs and may even disturb the process.

In the literature part of the Master's thesis the basics of flotation process and collector chemicals are introduced. Capillary electrophoresis (CE), an analytical technique suitable for detecting collector chemicals, is also reviewed. In the experimental part of the thesis the development of an on-line CE method for monitoring the

concentration of collector chemicals in a flotation process and the results of a measurement campaign are presented. It was possible to determine the quality and quantity of collector chemicals in nickel flotation tailings at a concentrator plant with the developed on-line CE method. Sodium ethyl xanthate and sodium isopropyl xanthate residuals were found in the tailings and slight correlation between the measured concentrations and the dosage amounts could be seen.

TIIVISTELMÄ

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Teknillinen tiedekunta
LUT Kemia

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Kokoojakemikaalien jäännöspitoisuuksien on-line määrittäminen flotaatioprosessissa

Diplomityö

2014

63 sivua, 30 kuvaa, 9 taulukkoa and 3 liitettä

Tarkastajat: Dosentti Satu-Pia Reinikainen
FT Jaakko Leppinen

Avainsanat: on-line, kapillaarielektroforeesi, ksantaatti, flotaatio, kokooja kemikaali

Arvokkaat mineraalit voidaan ottaa talteen vaahdotuksen avulla. Tämä on yleisesti käytetty erotustekniikka mineraalien prosessoinnissa. Vaahdotuskennossa hydrofobiset partikkelit kiinnittyvät dispegoituihin ilmakupliin ja nousevat niiden avulla kennon huipulle. Arvokkaat partikkelit muutetaan hydrofobisiksi lisäämällä kokoojakemikaaleja lietteeseen. Vaahdote reagenssien avulla stabiili vaahtokerros muodostuu kennon yläosaan ja vaahto, joka sisältää arvokkaat mineraalit, ts. rikaste, voidaan poistaa jatkoprosessointia varten. Normaalisti kokoojakemikaalien annostus riippuu vaahdotuspiirin syöttömäärästä ja arvokkaiden metallien pitoisuudesta syötteessä. Kuitenkin myös syötteen mineraalikoostumus vaikuttaa kulutukseen, eli siihen paljonko kemikaalia adsorboituu mineraalipinnoille. Siksi kokoojakemikaalien jäännöspitoisuuksia kannattaa mitata vaahdotuksen jätteissä. Ylimääräinen kokoojakemikaalien käyttö aiheuttaa ylimääräisiä kustannuksia ja saattaa jopa haitata prosessia.

Diplomityön kirjallisuusosassa esitellään vaahdotuksen perusteet, kokoojakemikaalit, sekä kapillaarielektroforeesi (CE), kokoojakemikaalien määrittämiseen sopiva

analyyttinen menetelmä. Diplomityön kokeellisessa osassa kuvataan vaahdotusprosessin kooojakemikaalien havaitsemiseen soveltuva on-line-CE-menetelmän kehitys ja tulokset mittauskampanjasta. Myös kokoojakemikaalien havaitsemis- ja määritysrajat esitetään. Kehitetyllä menetelmällä oli mahdollista määrittää kokoojakemikaalien määrä ja laatu nikkelivaahdotuksen jätteestä rikastamolla. Havaitut kokoojakemikaalit olivat natrium-etyyli-ksantaatti ja natrium-isopropyyli-ksantaatti. Mitattujen kokoojakemikaalikonsentraatioiden ja annostusten välillä oli havaittavissa lievää korrelaatiota.

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APPENDIX I:	Electropherograms of SIPX, SEX and Aerophine calibration in filtered nickel tailings
APPENDIX II:	Electropherograms of concentrator measurements
APPENDIX III:	Measured SIPX and SEX migration time, peak area and concentration

Theoretical part

1 Introduction

Valuable minerals are separated from ore in a froth flotation process. Before flotation the ore is crushed and ground in order to liberate the valuable minerals. Ground ore is mixed with water and treated in a flotation cell where reagents such as collector chemicals, activating agents and depressants contribute to the separation process. Collector chemicals attach to the surface of the minerals rendering them hydrophobic. Hydrophobic particles attach to gas bubbles enabling selective separation of the desired minerals from the gangue. These particles accumulate on the surface of the cell as a froth layer. Frothers are used to aid the formation and stabilization of froths. The desired minerals are removed from the surface of the flotation cell with froth for further processing. [1-3]

Collector chemicals which are commonly used to process sulphide minerals are thiols or they can hydrolyse to thiols. Alkyl xanthates and dithiophosphates are the most commonly used collector chemicals for sulphide minerals. Collectors attach to the minerals by either chemisorption or physisorption forming a monolayer to the particle surface thus making them hydrophobic with their non-polar hydrocarbon ends. [3, 4]

The purpose of this work was to develop a capillary electrophoresis (CE) monitoring system for the amounts of collector chemicals used in mineral processing. Tuomas Sihvonen [5] and Jussi Kemppinen [6] had previously studied the detection of collector chemicals with capillary electrophoresis. The aim of this study was to develop an on-line CE method for monitoring concentration of sodium isopropyl xanthate, sodium ethyl xanthate and sodium di-isobutyldithiophosphinate in flotation tailings.

In the literature part the basics of froth flotation, collector chemicals and capillary electrophoresis are presented. In the experimental part instrumentation and reagents,

method development, concentrator plant measurements and conclusions are presented.

2 Froth flotation

Froth flotation is a separation method where the desired particles are removed from gangue. The process is widely used in mineral applications but it is not limited to those only. Non-mineral applications include processes such as de-inking of recycled paper. The process is based on differences in in the surface chemistry of particles that affects their ability to attach air bubbles. Hydrophobic particles adhere to air bubbles contrary to hydrophilic particles which stay in contact with water. Since froth flotation is a process which includes solid, liquid and gas phases, the process is considered to be rather complex. The process includes a variety of interrelated variables, and changing one of them could result in effects in another. A schematic of interrelated variables is presented in Figure 1. [1-3, 7]

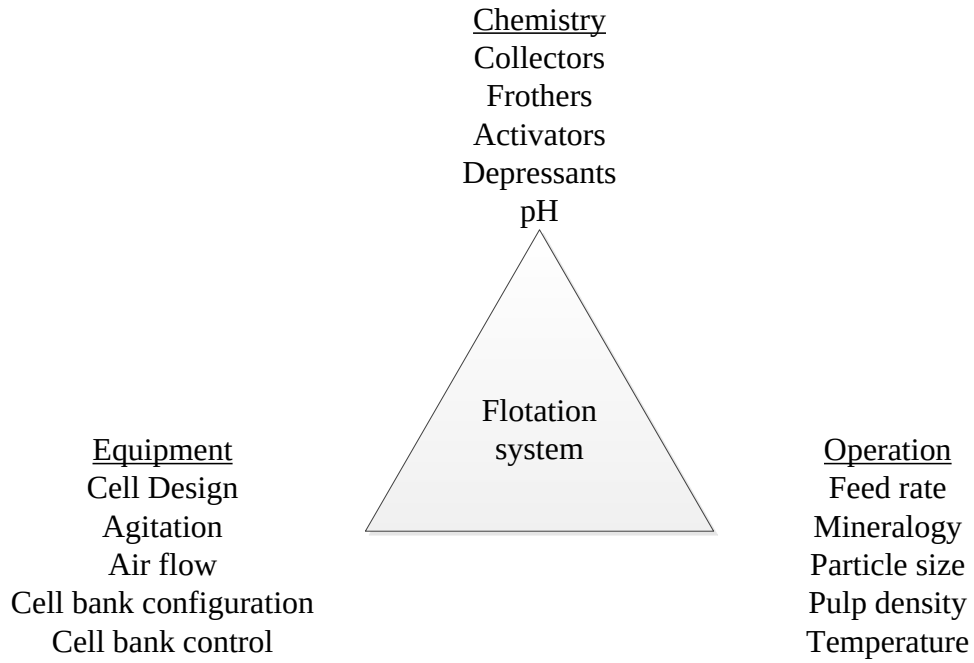


Figure 1 Froth flotation variables [3]

Floatable minerals can be categorized in to two groups which are polar and non-polar minerals. Non-polar minerals form relatively weak molecular bonds and thus are difficult to hydrate unlike polar minerals. Due to this non-polar minerals are hydrophobic and polar minerals are hydrophilic. [1] Most minerals are hydrophilic and thus need to be treated with chemicals to make them reject water. Some minerals are naturally hydrophobic. These include minerals such as graphite, sulfur, antimonite (Sb_2S_3), molybdenite (MoS_2), talc and high rank coals such as anthracite. Even though some minerals are naturally hydrophobic, they still usually need additional boost to separate them from gangue. This is done by using oil-based collectors such as petroleum oils. [1, 2]

2.1 Flotation Cell

In order to separate the desired minerals from ore it first needs to be crushed and ground into finer particles. The particles are then mixed with water and treated with specific reagents. The mixture is then fed to an aggregated flotation cell where the separation on desired particles takes place. [2, 8] A picture of a flotation cell is presented in Figure 2.

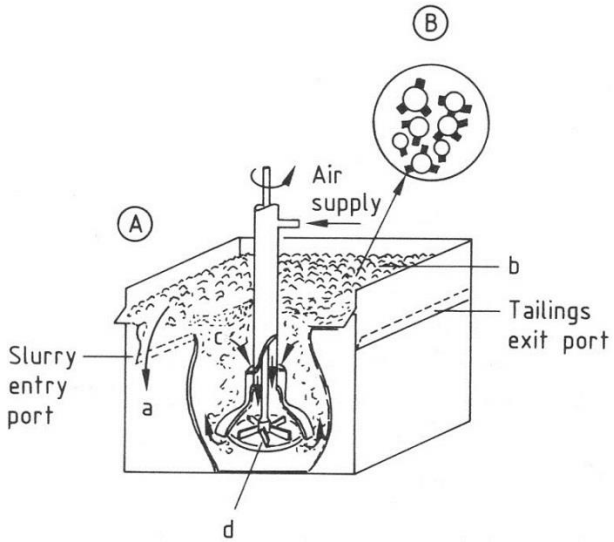


Figure 2 A flotation cell where: A Flotation cell, a froth exit point, B Minerals attached to air bubbles, b Froth layer, c Pulp, d Cell agitator [2]

Mixing the slurry with the presence of air bubbles ensures that the surface activated minerals come in contact with bubbles thus making the separation possible. Air bubbles transport the desired minerals to the top of the cell where they are removed for further processing. Unwanted gangue exits from the bottom of the cell. To ensure high recovery of desired minerals, several cells are usually needed. In this case they are installed in a series. Flotation cells are conventionally assembled in a multi-stage circuit, which includes rougher, cleaner and scavenger cells. The slurry, which contains coarser particles, is fed to rougher flotation cell. The rougher emphasizes in high mineral recovery without achieving the final concentration. The particles in rougher froth are commonly ground finer and fed to a cleaner cell which separates the final concentrate from the gangue which is fed back to rougher flotation. The rougher tail is fed to a scavenger cell which returns its concentrate back to circulation while removing the gangue from the process. The arrangement of these flotation cells is presented in Figure 3. There are a great number of different configurations of process flow sheets and this is one simplified example. [1, 2, 8, 9]

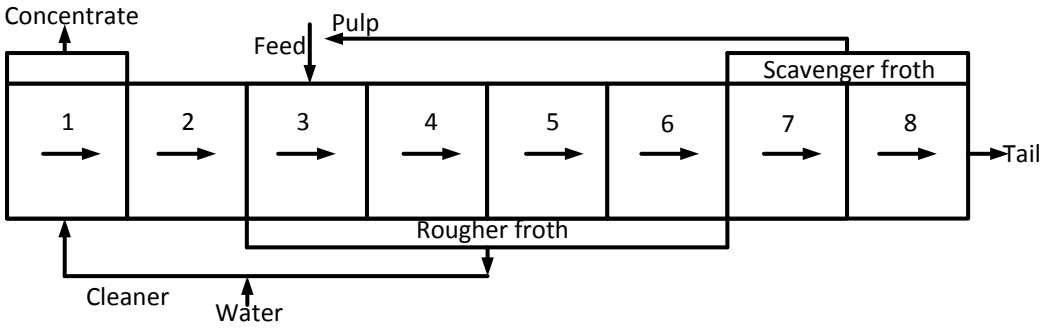


Figure 3 Typical flotation cell arrangement [1]

2.2 Flotation reagents

Flotation reagents are usually classified by their function or chemistry in the process. It is commonly considered that there are five functions which classify the reagents: collectors, frothers, modifiers, activators and depressants. Collectors coat and/or react with mineral surfaces thus making them hydrophobic. Common collectors are xanthates, amines and dithiophosphates. [1-3]

Frothers aid in the formation and stabilization of air-induced flotation froths. Often two or more frothers are used in conjunction. This is done because one must complement the collector to form complexes with minerals and one must aid in the formation of a mechanically satisfactory froth since flotation efficiency depends on it. [1-3, 10]

Modifiers influence the way that collectors attach to particle surfaces. Modifiers may increase or prevent the adsorption of collector onto minerals. Activators increase and depressants prevent the adsorption. Activators enable collector adsorption to minerals which normally would not be possible. For example copper sulfate can be used as an activator for sphalerite (ZnS) with xanthate collectors. Xanthate is not able to attach to sphalerite since the thermodynamic stability of zinc xanthate is low. In this case copper sulfate can be used as an activator since it forms a thin copper sulfide film on top of sphalerite which allows xanthate attachment thus rendering the particle floatable. Other metals, such as silver and lead, can be used instead of copper but copper is less toxic than lead and cheaper than silver. Depressants are usually based on increasing selectivity by preventing one mineral from attaching to collectors while allowing another mineral to attach and float unimpeded. [1-3, 11]

The boundary of these functions is not always clear, since some of these components can have several functions at the same time. For example lime can be used to modify pH but the calcium cation in lime can also act as a depressant for pyrite in copper

flotation. Commonly used organic flotation collectors are presented in Table I. Inorganic auxiliary flotation reagents are shown in Table II. [1-3]

Table I Commonly used organic flotation collectors [2]

Compound	**Area of application**
Primary amine salts	silica, silicates, sylvite
Quaternary ammonium salts	silicates, oxides, clays
p-Tolyarsonic acid	cassiterite
Sodium salts of carboxylic acids	oxides, carbonates, apatite, iron ore, chromite, scheelite
Alkyldithiocarbamates	sulfides, metallic minerals
Dixanthogens	sulfides, metallic minerals
Hydrocarbon oils [a]	coal, molybdenite, colemanite with sulfonates, iron ores, wolframite, cassiterite
Napthenic acids	fluorapatite, colemanite
Oximes	chrysocolla, cassiterite
Alkylsulfates and -sulfonates	iron ores, beach sand cleaning, borates, carbonates, fluorite
Sodium 2-(Methyloleylamino) ethylsulfonate	celestite
O-Ethyl isopropyl thionocarbamate	copper sulfides
Thionocarbanilide	sulfide minerals
Alkyldithiocarbonates (xanthates)	sulfide minerals, gold
Xanthogen formates [b]	sulfide minerals
Dialkyl-dithiophosphates [c]	sulfide minerals, native gold, copper
[a] Vapor oils, kerosine, fuel oils, [b] Trade name: Minerec, [c] Trade name: Aerofloat	

Table II Inorganic flotation reagents [2]

Compound	Composition	Common applications
Lime	CaO	pH regulator depressant
Sodium carbonate (soda ash)	Na_2CO_3	pH regulator depressant
Sodium hydroxide (caustic soda)	NaOH	pH regulator depressant
Sodium sulfide	Na_2S	sulfide depressant and ore sulfidizer
Sodium bisulfide	NaHS	sulfide depressant and ore sulfidizer
Sulfuric acid	H_2SO_4	pH regulator
Sodium cyanide	NaCN	sulfide depressant
Calcium cyanide	$Ca(CN)_2$	sulfide depressant
Sodium dichromate	$Na_2Cr_2O_7$	PbS depressant
Cupric sulfate	$CuSO_4$	ZnS, FeAsS, Sb_2S_3 activator
Lead acetate	$Pb(CH_3COO)_2$	Sb_2S_3 activator
Sodium ferrocyanide	$Na_4Fe(CN)_6$	depressant in Cu-Mo sulfide circuits
Potassium permanganate	$KMnO_4$	FeS_2 depressant in FeAsS flotation
Sulfur dioxide	SO_2	activated ZnS depressant
Sodum thiosulfate	$Na_2S_2O_3$	SO_2 source in acid circuits
Sodium silicate	Na_2SiO_3	siliceous gangue dispersant
Sodium fluosilicate	Na_2SiF_6	depressant in iron-flotation circuits
Sodium polyphosphates	e.g. $(NaPO_3)_6$	dispersant
Sodium fluoride	NaF	activator in silicate flotation
Nokes reagent	Complex mixture of P_2S_5, As_2O_3, Sb_2O_3, NaOH, etc.	flotation circuits except for MoS_2

3 Collector chemicals

Collector chemical molecular structure can be divided into two parts: polar and non-polar part. The non-polar part (hydrocarbon radical) of a collector gives the hydrophobic properties to it. The polar part can react with water and adsorb to a mineral surface thus orienting the hydrophobic hydrocarbon radical outwards the mineral making the compound repel water. Collectors bond to a mineral by either chemisorption or physisorption. In chemisorption the polar part of the collector undergoes a chemical reaction thus becoming irreversibly bonded. Since a chemical

reaction is specific to certain atoms, chemisorption is highly selective. In physisorption collectors attach to minerals reversibly due to Van Der Waals bonding or electrostatic attraction. Collectors can adsorb to any surface that have the right degree of natural hydrophobicity or electrical charge thus making physisorption less selective than chemisorption. [3, 12, 13] Sodium oleate which has a typical collector structure is presented in Figure 4.

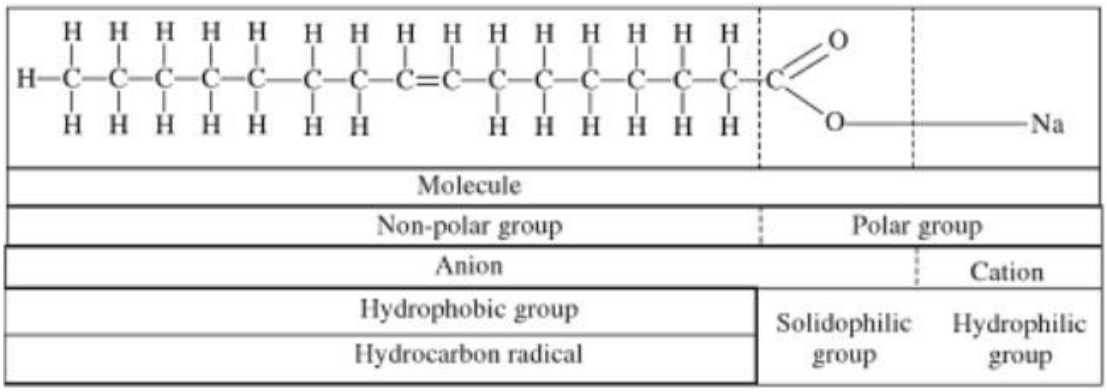


Figure 4 Sodium oleate molecule structure [14]

3.1 Collector classification

Collectors can be classified according to ability to dissociate into ion in water solutions. The ion which causes the hydrophobic properties to the mineral is called active repellant ion. The ion which does not give repellant properties is called non-active ion. Collectors cannot directly adsorb to minerals. Solidophilic group, which is attached to the hydrocarbon radical chain, forms a connection between the collector and the mineral once the collector has been dissociated to water. Collectors are classified into two groups: ionizing and non-ionizing. The ionizing group is further classified into anionic and cationic group according to which ion gives the hydrophobic properties to the mineral. Anionic collectors, which are the most used collectors in flotation, are subdivided according to their solidophilic group structure into oxhydryl (based on organic and sulfo-acid ions) and sulfhydryl (contains bivalent sulfur) collectors. Collector chemical classification is presented in Figure 5. [3, 14]

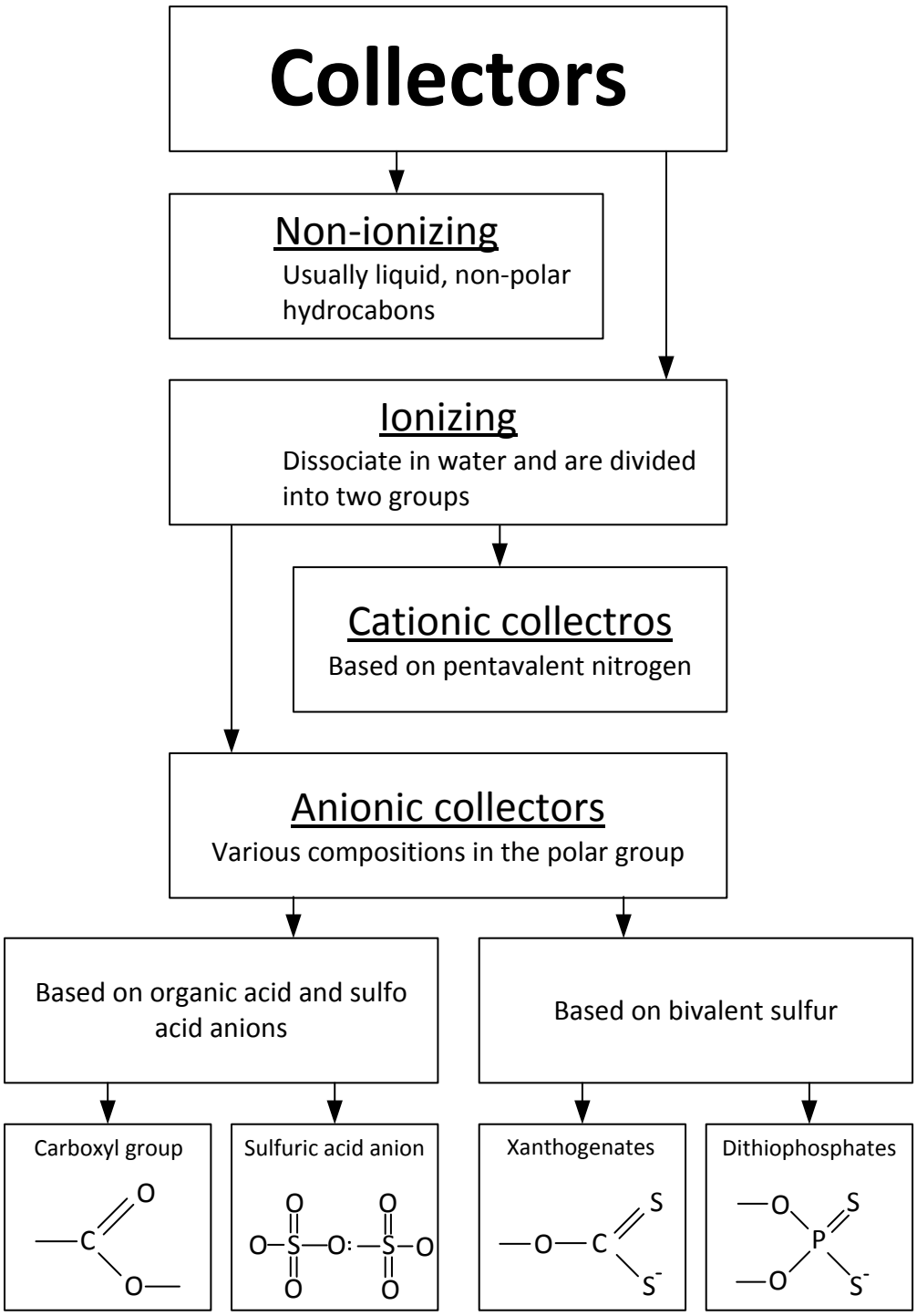
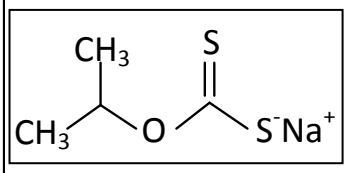
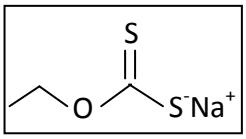
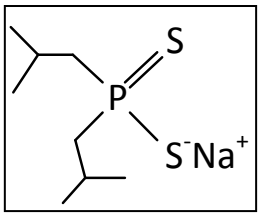


Figure 5 Collector chemical classification [14]

3.2 Thiol collectors

Thiol collectors operate mainly as collectors for metallic sulfides in froth flotation and they include minimum of one sulfur atom which is not bonded with oxygen. Thiol collectors include compounds such as xanthates, dithiophosphates and dithiophosphinates. [1,15] Although xanthate is the most preferred thiol collector, these are often used in conjunction with each other's since it has been noted that mixtures often result in higher recoveries and grades than single component collectors [16]. For example Bagci et al. [15] have studied the adsorption of isopropyl xanthates (SIPX) and di(isobutyl) dithiophosphinate (DTPI) mixture on chalcopyrite. They found two ratios for the maximum collector adsorption amount. The first ratio was 30:70 DTPI:SIPX when DTPI was added first. The second one was 50:50 SIPX:DTPI when the collectors were added together. This thesis will mainly focus on xanthates over dithiophosphates and dithiophosphinates. The collectors used in the experimental part are presented in Table III.

Table III Collectors used in the experimental part of this Master's thesis

Name	Sodium isopropyl xanthate	Sodium ethyl xanthate	Sodium di(isobutyl) dithiophosphinate
Trademark	FLOMIn C-3330	FloMin C-3200	Aerophine 3418A
Abbreviation	SIPX	SEX	DTPINa
CAS no.	140-93-2	140-90-9	13360-78-6
Structure			

3.3 Xanthates

Xanthates (IUPAC chemical name O-Alkyl carbonodithioate) are the most abundantly used thiol collectors for sulfide ore treatment. They are commercially available as solutions, powders and pellet from which pellets are mostly favored since they have less problems with dusting and have better storage stability. Xanthates decompose in the presence of moisture. One of the decomposition products of xanthates is carbon disulfide which is highly flammable. That is why good ventilation should be taken in consideration when storing xanthates. Xanthates dissolve in water fairly well. However the solubility decreases with the chain length. Xanthate ions absorb UV light at the wave length of 226 and 301 nm latter showing higher values. Xanthates are produced by reacting alkyl alcohol and alkali hydroxide following by addition of carbon disulfide. [1, 15, 17] The reactions are shown in equations 1 and 2.

$$R - OH + NaOH \rightarrow R - ONa + \mathrm{H_2O} \quad (1)$$

$$R - ONa + CS_2 \rightarrow ROCS_2Na \quad (2)$$

Purity of commercial xanthates is usually less that 85-90 %. Impurities may include production of by-products such as residual alcohol or alkali hydroxide. Alkali hydroxide may be purposely added to the commercial xanthate since it slows down the thermal decomposition of xanthates during storage. In storage xanthate decomposition rates are usually below 1 % per day. The stability of xanthates has an effect on the process which is why the decomposition mechanism is good to know. Below pH 3, half-life of xanthates is reduced to minutes. [1, 15]

Z. Sun et al. [13] have studied the degradation of ethyl-xanthate as a function of pH in different temperatures and media by UV-visible spectrophotometry. They came to the conclusion that the degradation increases with decreasing pH when pH<7. Xanthates have the maximum half-life at pH 7-8. The degradation increases at pH 9-10 but the half-life increases after pH 10. Lower temperatures increased the half-life of xanthates. The half-life of xanthates was higher in pure water unlike in waters

where agents such as $NaNO_3$ and NaCl were added or in supernant of flotation tailings. The half-live of xanthate is presented in Figure 6 as a function of pH in three different temperatures. Xanthate and its main degradation products are presented in Table IV. [17]

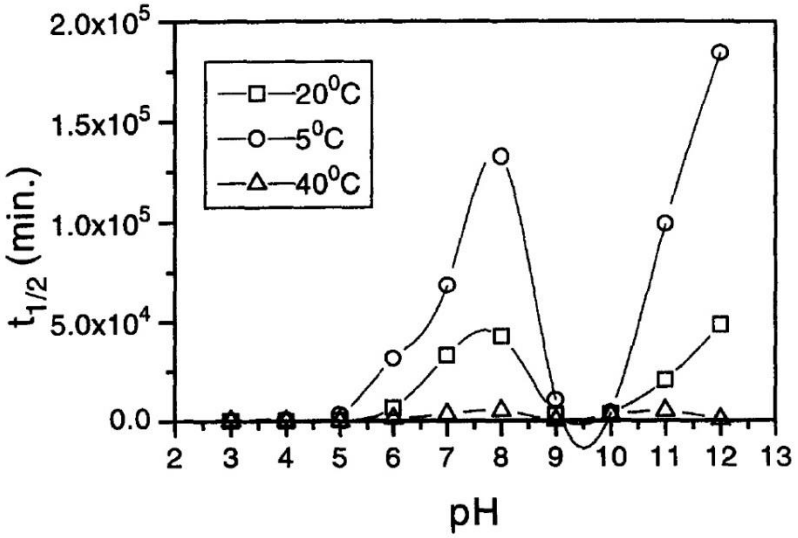


Figure 6 Half-life of xanthate as a function of pH in three different temperatures 5, 20 and 40 °C. [17]

Table IV Xanthate and its main degradation products and forming pHs [17]

Agent		**UV-light adsorption wavelength, nm**	**Formation pH**
Xanthate	$ROCS_2^-$	226 & 301	-
Carbon disulfide	CS_2	206,5	3-5
Monothiocarbonate	$ROCSO^-$	223	6-12
Dixanthogen	$(ROCS_2)_2$	238 & 283	6-12
Xanthic acid	$ROCS_2H$	270	3-5
Perxanthate	$ROCS_2O^-$	348	9-11

Since froth flotation is usually conducted in pH above 5, the most interesting decomposition products are monothiocarbonate, dixanthogen and perxanthate. For the sake of process control, knowledge of xanthate decomposition is of interest. Minerals also have an effect on xanthate decomposition by providing alternative paths to decomposition on the mineral surfaces. Hao et al. [19] have characterized different pathways for xanthate decomposition by oxidation on mineral surfaces. Different pathways are presented in Figure 7.

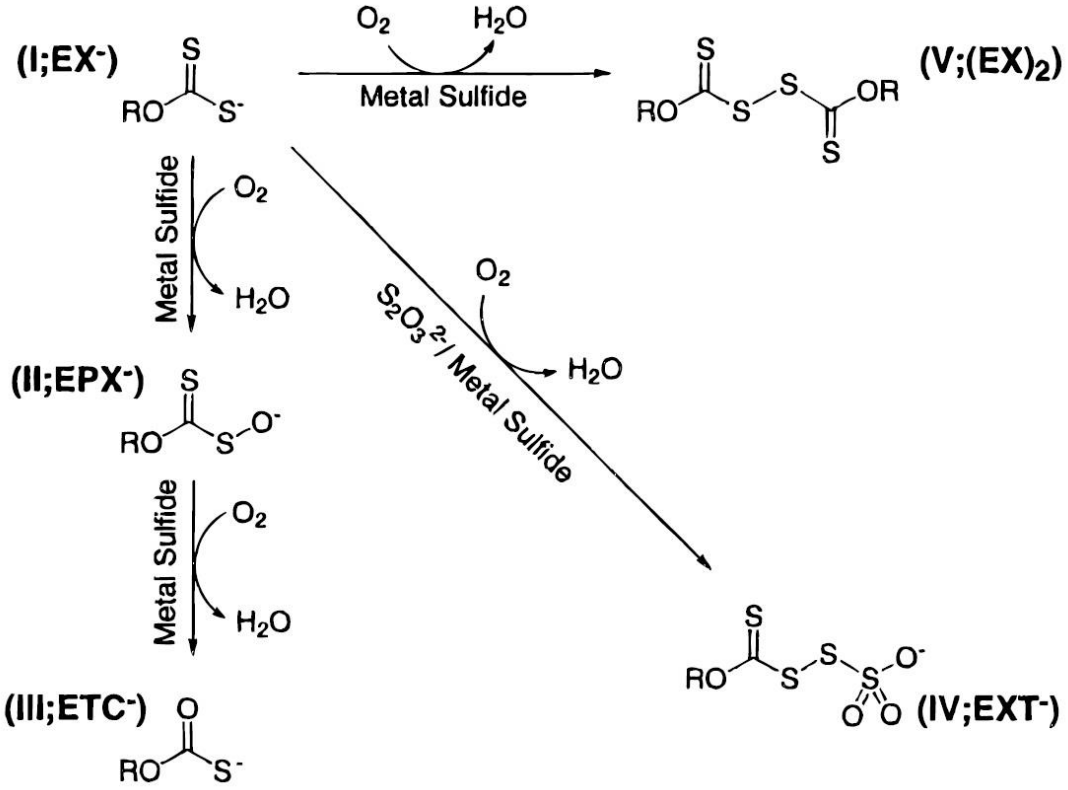


Figure 7 Pathways for xanthate decomposition on mineral surfaces where $I;EX^-$ is ethyl xanthate, $II;EPX^-$ is ethyl perxanthate, III; ETC^- is ethyl monothiocarbonate, IV; EXT^- is ethyl xanthyl thiosulfate and $V;(EX)_2$ is diethyl dixanthogen. [19]

Xanthates are able to form metal-xanthate complexes with metals which can be often found in flotation process waters. The complexes can be soluble (ionic) or insoluble. Ionic complexes are either cationic $M(X)^{(n-m)+}$ or anionic $M(X)_m^{(m-n)-}$ (M^{n+} metal cation, X^- xanthate ion). Anionic complexes are formed when amount of metal ions is

lower than xanthate ions and cationic complexes are formed when the amount of metal ions is higher than xanthate ions. Insoluble metal xanthates are formed when xanthate and metal ions react in stoichiometric concentrations. Xanthates are able to form 1:1 complexes with Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+} and Cu^{2+}. Other metal-xanthate complexes may also occur. Xanthate metal complexes have quite low solubilities e.g. $Zn(EtX)_2$ has a solubitity of $9.0*10^{-4}$ mol/L in 20°C water. [15]

4 Capillary electrophoresis

Electrophoresis is the movement of ions in an electric field. This often performed by applying a current across a narrow-bore open capillary where the separation of substances takes place. Other electrophoresis techniques include methods such as slab gel electrophoresis, but it has lower separation efficiency and longer analysis time. High separation efficiency of capillary electrophoresis (CE) is based on large surface area to volume ratio and the minimizing of peak widening due to thermal reasons. The advantages and disadvantages of capillary electrophoresis are presented in Table V. [20-25]

Table V Advantages and disadvantages of capillary electrophoresis [20-23, 25]

Advantages	**Disadvantages**
High efficiency	Method reproducibility
Short analysis time	Sensitivity
Small samples needed (1-50nl)	Injection accuracy
Produces small amount of analysis waist	
Wide range of applications	
Operates in aqueous media	
Method development is relatively simple	
Automated instrumentation	

The capillary is fused silica with bore diameter varying between 20-200 µm. The length of the capillary varies often between 20-100 cm.. Capillaries can be made from glass or Teflon but silica usually preferred since it has certain advantages over glass and Teflon e.g. it won't break so easily as glass. High voltage (10-30 kV) is applied across the capillary ends which generates electro-osmotic (EOF) and electrophoretic flows that transport substances in different velocities according to their charge density. Thus the substances arrive in different order to the detector where migration time and absorbance level can are measured. [20-23]

The detector is usually based on absorbance of ultraviolet (UV) -light, but other detectors are also sometimes used. These include detectors such as laser-induced fluorescence, conductivity, electrochemical, mass spectrophotometry, radioactivity and refractive index detectors. The absorbance of UV light is done through a capillary window, where the polymer coating over the capillary has been removed. Substances which don't absorb UV-light can also be detected with a UV absorbance detector by using a buffer which absorbs light strongly. When the substance zone arrives to the detector it is recognized by its ability to not absorb light. In other words the absorbance level decreases below the zero level. This occurs every time when zones of substances that don't absorb UV-light arrive to the detector. [23, 26, 26]

Capillary electrophoresis instrumentation setup consists of inlet and outlet buffer electrolyte reservoirs, sample reservoir, high voltage power supply, capillary, detector and a computer control. The capillary is coated with a polymer to protect it. The polymer is removed where the detector is since the detection is made through the capillary usually with a UV-detector. CE instrumentation setup is presented in Figure 8.

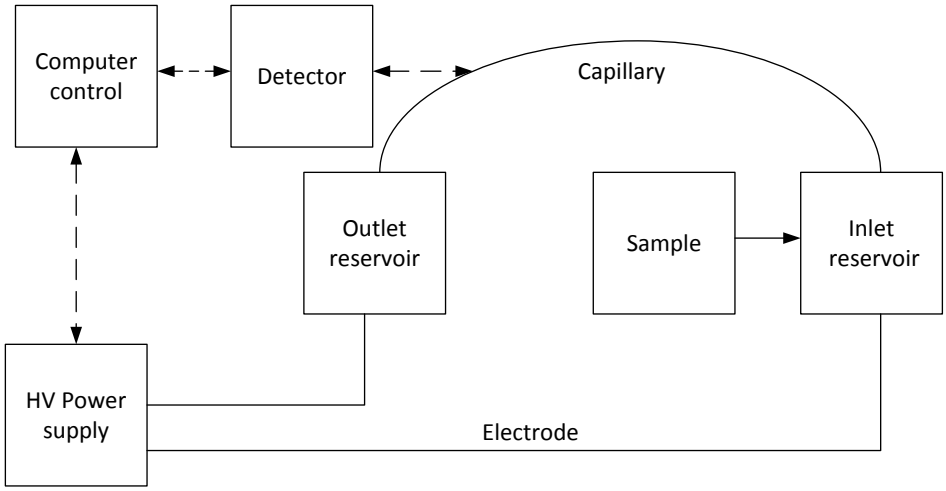


Figure 8 CE instrumentation setup [21]

4.1 Electrophoresis and electro-osmosis

The capillary is filled with a background electrolyte (buffer). Sample is introduced to the capillary by inserting the capillary inlet end from the buffer vial to the sample vial. Sample is injected by using different methods to the capillary. The inlet end of the capillary is inserted back to the buffer vial after which voltage is turned on between the capillary ends. The outlet of the capillary is usually in the same vial as the negative electrode. This is called normal polarity. When the outlet is in the same vial as the positive electrode the setup is called reversed polarity. Positively charged ions are attracted to the negative electrode and start to move towards it. Negative ions are attracted to the positive electrode. This movement caused by electrical voltage is called electrophoretic flow (EPF). When the pH of the buffer is above 2 the silica capillary becomes ionized and is negatively charged. Thus the positively charged ions accumulate as a layer on top of the silica surface forming an electrical double layer (Stern layer). A diffusion layer, forming of mainly positively charged ions, is stratified loosely on top of the Stern layer. When a voltage is applied to the capillary negatively charged ions pull the loose positively charged ions with them. This movement is called electro-osmotic flow. If EOF is greater than the repulsion of

positively charged ions towards the positively charged electrode caused by electrophoretic force, the positively charged ions will also move forward towards the detector. [20-23] The mobility of analytes has been expressed in formula 3. [27]

$$\mu_a = \mu_{EP} \pm \mu_{EO} \quad (3)$$

Where μ_a apparent mobility

μ_{EP} electrophoretic mobility

μ_{EO} electro-osmotic mobility

With cations μ_{EP} and μ_{EO} are parallel and with anions vice versa if the system has been setup as normal polarity. Anions will go through the capillary only if μ_{EO} is larger than μ_{EP}. Apparent mobility is calculated with formula 4.

$$\mu_a = \frac{L_t L_d}{tU} \quad (4)$$

Where L_d capillary length to detector

L_t capillary total length

t migration time

U applied voltage between capillary ends

Electro-osmotic mobility can also be calculated with the previous by replacing migration time with EOF peak time.

4.2 Sample injection

Samples are introduces to the capillary by replacing the capillary inlet vial from the buffer vial to the sample vial. The length of sample zone injected should be less than 1-2 % of the total length of the capillary. Hydrodynamic sample injection is the most preferred injection method available. Sample is introduced to the capillary by the means of either pressure from the inlet, by vacuum from the outlet or by siphoning. Hydrodynamic injection is almost independent from the sample matrix. That is why it is often preferred over others injection methods. [20-22]

Electrokinetic sample injection, which is often called field amplified sample injection (FASI), is another method for sample injection. Capillary inlet is placed in to the sample vial and voltage is applied between the capillary ends. Analytes move to the capillary due to electrophoretic flow. EOF can help to inject the analytes to the capillary if EOF moves towards the outlet. If EOF moves to the opposite direction, it will hinder the injection. Molecules with high electrophoretic mobilities will migrate to the capillary more rapidly. That is why FASI will not give a uniform injection. Field strengths are often 3-5 times lower than the field strengths used in separation. Injection times are usually 10-30 s. Pressure and voltage are many times used in combination to inject the sample to the capillary. In this case the injection method is called pressure assisted field amplified sample injection (PA-FASI). This combination can be used if EOF migrates the analytes away from the capillary to overcome this problem. PA-FASI has the same problem as FASI as the molecules with higher electrophoretic mobilities will migrate more rapidly, the injection will not be uniform. [20-23, 28]

Stacking is a method where sample that has a much lower conductivity than the buffer electrolyte is injected to the capillary hydrodynamically. Ions of the sample are stacked (compressed) into zones in the sample region near the buffer region. Opposite polarity is turned on to push the end of the sample matrix out of the capillary while the stacked ions of the sample stay near to the buffer region. After this the inlet end of

the capillary is set in the buffer vial and normal separation voltage is applied. Stacking requires filling the capillary up to two thirds of the total capillary length. [5, 20, 21, 29, 30]

4.3 Modes of operation

Capillary electrophoresis has a group of operation modes which have divergent operative and separative characteristics. The modes are capillary zone electrophoresis (CZE), capillary isoelectric focusing (CIEF), capillary gel electrophoresis (CGE), capillary isotachophoresis (CITP), micellar electro kinetic capillary chromatography (MEKC) and capillary electro chromatography (CEC). Since the focus of this research was on CZE, it and only two of the previously mentioned modes are shortly described below to give some kind of a view of these modes and how the differ from one another. [20, 22]

Capillary zone electrophoresis is the simplest form of CE and it is also the mode which was used in the experimental part of this research. The capillary is filled with a homogenous buffer solution after which sample is injected to it. Constant field strength is applied throughout the length of the capillary which causes analytes to migrate in to different zones due to EOF and EPF. [20, 22]

Molecules will stop migrating if they become neutral in an electric field. Capillary isoelectric focusing is performed in a pH gradient. The pH is high at the cathode and low at the anode end. Carrier ampholytes applied in a series generate the pH gradient. Ampholytes migrate in the capillary, when voltage is applied, according to their charge towards different electrodes. When ampholytes reach their isoelectric point they will stop migrating, since they will become neutral. Thus the molecules will be in different zones. [20, 22, 31]

Capillary isotachophoresis is carried out by filling the capillary with a leading buffer solution which has higher mobility that any of the analytes. Sample is the injected to

the capillary after which a terminating buffer is introduced to the end of the capillary. The terminating buffer has a lower mobility than any of the analytes. Thus the analytes will separate between the leading and terminating buffer. [20, 22, 32] An illustration of how analytes separate in different zones when using CZE, CIEF and CITP is expressed in Figure 9.

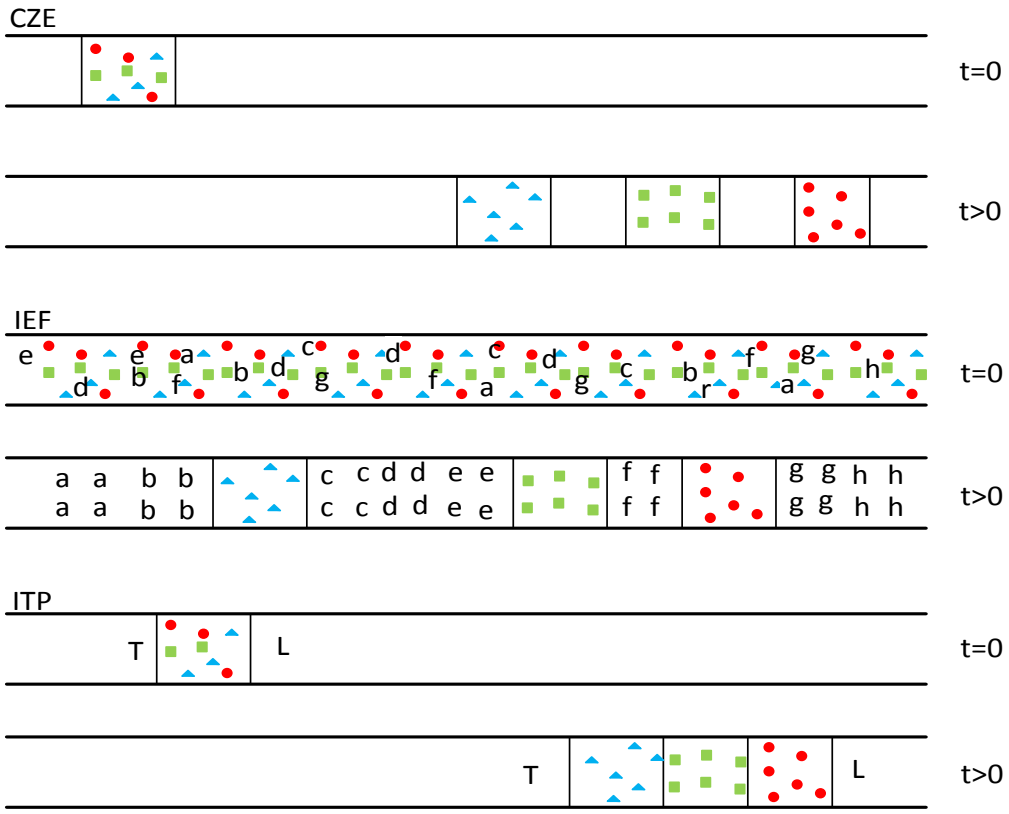


Figure 9 Illustration of CZE, CIEF and CITP zonal separation [20]

5 On-line measuring

On-line monitoring of environmental or process samples can help control and understand processes better. The word "on-line" in this context means that sampling and analysis is automated while sample transport is integrated. If compared to e.g. off-line monitoring, sampling is manual, analysis is manual or automated and sample transport is done in a remote or centralized laboratory. Different classes of process analyzers are presented in Table VI. [33]

Table VI Classes of process analyzers [33]

Process analyzer	Sampling	Sample transport	Analysis
Off-line	manual	to remote or centralized laboratory	automated/manual
At-line	discontinuous/manual	to logical analytical equipment	automated/manual quick check
On-line	automated	Integrated	automated
In-line	integrated	no transport	automated
Noninvasive	no contact	no transport	automated

Physical parameters, such as temperature, pressure and density, may have an effect on chemical reactions. These are often more easily measured on-line, than chemical parameters, but they do not explain the overall process. An on-line chemical measurement method is needed to determine variables that physical parameter measurements cannot explain such as chemical composition. This requires a fast and reliable analysis method to able to intervene the process according to the situation. On-line measurements can aid in the following issues: [33]

- Making the process more efficient
- Ensure and enhance product quality and uniformity
- Comprehension of the process
- Increasing safety by monitoring process and reactor conditions
- Saving raw materials, labor costs, process waste and etc.
- Saving time for analysis and sample transport

On-line monitoring of chemical reactions includes methods which are based on techniques such as ultrasound, dielectric spectroscopy, optical spectroscopy, particle size analysis, chromatography, electroanalytical methods, mass spectrometry, rheometry, NMR spectroscopy and etc. [33] An on-line Capillary electrophoresis system has been used previously to e.g. monitor the production of carboxylic acid by yeast in bioreactor cultivations [34] and to monitor water-soluble ions in pulp and paper machine waters [35].

H. Turkia et al. [34] developed a method where a sample was pumped from a bioreactor, through a filter, to a CE flow-through sample vial. CE measured the production of carboxylic acid by two yeast, K. lactis and S. serevisiae. The sampling interval was either once per hour or once per every two hours and system was able to run automatically and continuously up to six days. The system setup of the on-line CE monitoring method which H. Turkia et al. used is presented in Figure 10.

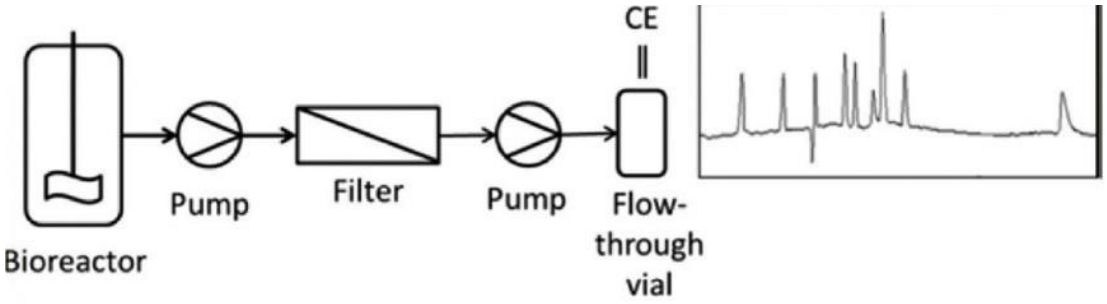


Figure 10 Schematic of the on-line monitoring system used to produce carboxylic acid [34]

R. Kokkonen et al. [35] used an on-line CE system to monitor water-soluble ions in pulp and paper machine waters. Requirements for water circulation have increased which means the concentrations of water-soluble compounds will increase also. It is highly likely that this will lead to chemical precipitation and equipment corrosion. A batch-type feeding unit was used in the CE unit to refill the samples. The system was suitable for the task and it could run continuously up to one week.

S.Luukkanen et al. [36] developed a method for measuring xanthate concentrations from flotation tailings with an on-line potentiometric titration system (Murtac OMT 20 DX). They conducted a two-week measuring experiment in in Pyhäsalmi Finland concentrating plant. The tailings slurry was directed through several clarifying stages before filtering it by using a CERAMEC filter. The clarifying stages were used since the pulp density in the tailings was high and because of this the filter would have been blocked rapidly. Thus the sample would not have been able to be transported to

the analyzer. The xanthate amounts in the flotation tailings varied between 3-11 ppm during a two-week measuring period.

A method, which used similar titrator as S. Luukkanen et al. used, was previously operated in Siilijärvi Finland concentration plant to measure seasonal fluctuations of species which dissolved from minerals and air (Ca^{2+}, CO_3^{2-} and HCO_3^-) to a flotation pond by P. Stén et al. [37] A sintered alumina CERAMEC filter proved to be a sufficient way to clear the sample from the pond.

Xanthates have also been analyzed, in a laboratory scale, by using an on-line UV-spectrometer system. F. Hao et al. [38] used a method where they pumped solution from a flotation cell through a micro filter with a peristaltic pump to a UV-spectrometer. The UV-spectrometer was able to measure the sum of xanthates used since no separation was done. The system could be used successfully for 50 minutes at a time without blocking the filter.

In this research an on-line monitoring CE system was developed to measure collector chemicals from flotation tailings. An automatic sampling unit and a CE method were developed for this purpose. Normally the dosage of the collector depends on the feed rate of the flotation circuit and the head grade of the valuable metal, but these variables do not reveal the changes taking place in mineral composition of the ore. Therefore it is worth monitoring the residual collector concentration in the flotation tailings since excess usage of collector causes unnecessary costs and may even disturb the process. The method development is presented in the experimental part of the thesis.

Experimental part

6 Instrumentation and reagents

The aim of the experimental part of the thesis was to develop an on-line CE method that is able to measure the concentration of collector chemicals from nickel flotation tailings. Water used in these experiments was purified by Elga Centra R 60/120 water purification system. This water is referred as pure water. Process water was received from FQM Kevitsa Mining Oy in Finland as well as the tailings slurry from nickel flotation with ca. 25 % solids. The ionic strength of samples affects the CE analyses. Since collector concentrations were designed to be measured from nickel tailings, the tailings were used as sample matrix when calibration standards were created. Hence the ionic strength is closely the same.

Beckman Coulter P/ACE MDQ, with UV/vis diode array detection, capillary electrophoresis was used to analyze all samples. The diameter of the capillary was 49 µm. The total length of capillary was 60 cm and the length to the detector was 50 cm. The capillary was manufactured by Polymicro technologies and it was fused silica coated with a polymer. The polymer was burned off at the detection window. A peristaltic pump manufactured by Ismatec model BVB Standard with a multi-channel pump head Ismatec CA-12, was used during on-line experiments to transport samples to a flow-through vial inside the capillary electrophoresis. The pump was controlled with a relay through the CE program. Two vial trays which had two large buffer reservoirs (2 x 30 ml) were used since during long runs the buffer started to deplete. Also the operator would not have to fill several small vials instead of a few large ones. A vial tray which has two large buffer reservoirs is presented in Figure 11.

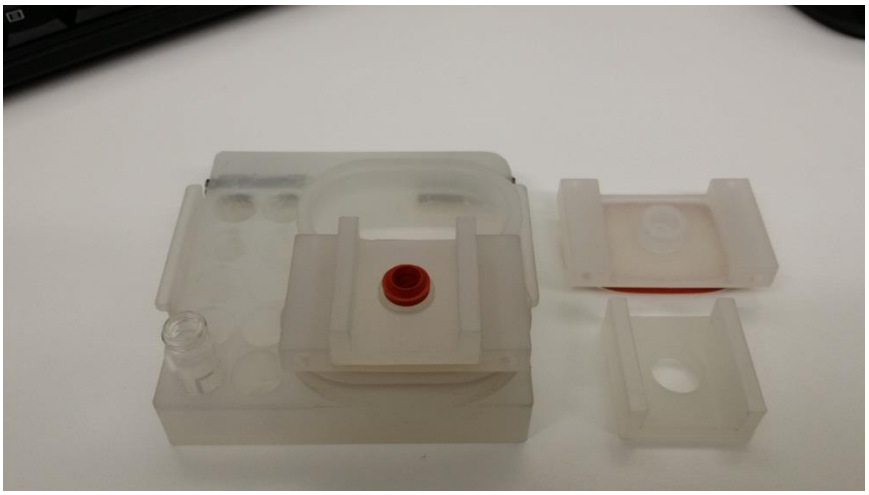


Figure 11 A vial tray with two large buffer reservoirs

A 10 µm Metrohm stainless steel rod filter, in conjunction with a settling tank, was used to filter the samples for the capillary electrophoresis. Sampling was done with an automated system which was specifically built for this study. The system is presented in method development section.

Preliminary experiments were made in Lappeenranta University of Technology before the concentrator measurement campaign. Sodium isopropyl xanthate (SIPX) and sodium di(isobutyl) dithiophosphinate (Aerophine) were measured during these test. Sodium ethyl xanthate (SEX) was included to the experiments during the concentrator measurement campaign. The purities and the providers of the reagents are shown in Table VII.

Table VII Reagents used in the experiments

Chemical	Abbreviation	Purity	Provider
Sodium isopropyl xanthate	SIPX	87-89 %	Flomin Inc.
Sodium di(isobutyl) dithiophosphinate	Aerophine 3418A	50-52 % (aq)	Cytec Industries Inc.
Sodium ethyl xanthate	SEX	90 %	Flomin Inc.

The background electrolyte solution (buffer) used was the same that Tuomas Sihvonen [5] and Jussi Kemppinen [6] had used in their theses. The buffer was a 60 mM CAPS (3-(cyclohexylamino)propane-1-sulfonic acid) and 40 mM NaOH

solution. The solution was prepared by dissolving and mixing the substances to pure water in an ultrasonic bath. The electrolyte solution seemed to keep relatively stable for a long period of time. During the preliminary tests it was stored in a fridge and before experiments the solution was allowed to warm to room temperature and it was mixed in an ultrasonic bath. When the experiments were made during the concentrator measurement campaign there was no ultrasonic bath available to mix the solution. Instead, it was mixed manually, by shaking it in a bottle.

7. Preliminary experiments and method optimization

The validation process utilized in the experimental part is expressed in Figure 12.

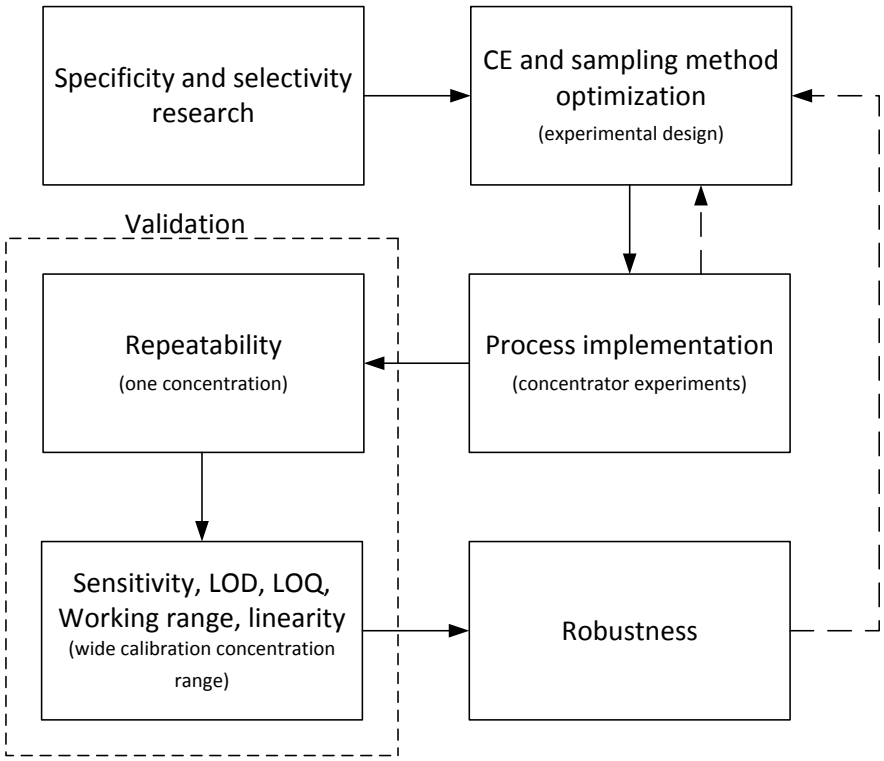


Figure 12 A schematic of the utilized validation process

The method development was mainly made on the basis of preliminary experiments. Before a two-week concentrator plant measurement campaign, experiments were made in Lappeenranta University of Technology in Finland. Beckman Coulter P/ACE MDQ capillary electrophoresis analyzer was used during the preliminary tests. However, the CE broke before the concentrator measurement campaign and a similar replacement instrument had to be used during the two-week measurement campaign. A few experiments were made, with the replacement device, before the campaign to see if the device would give similar results as previously and thus if it could be used. The surface area of electro-osmotic flow peak was much lower on the replacement CE and the peak did not stand out from the base line as clearly as with the first CE used. This likely refers that less sample was injected to the capillary. However it is likely that the surface areas are not compatible across devices. None the less, collector chemicals could be qualified and quantified with the replacement device with adequate precision.

Validation factors and components that affect them:

- Specificity and selectivity
    - Sample matrix
    - Background electrolyte solution (buffer)
    - Method parameters
    - Chemical characteristics
- Repeatability
    - Stability of chemicals used
    - Storage conditions
    - Ambient conditions
- LOD & LOQ
    - Separation efficiency
    - Baseline noise
    - Peak identification and integration
    - Chemical characteristics
    - Detection method

- Sensitivity, working range and linearity
    - Calibration concentration range
    - Calibration correlation

7.1. Method optimization: operating parameters

The first experiments were done off-line before switching to on-line. Experiments started with the same method as T. Sihvonen et al. [39] had used in their tests. During the injection negative voltage was applied to concentrate anions and external pressure was added to exceed EOF. Process water and the filtrated tailings of nickel circulation were tested with a capillary that had an effective range (length from inlet to detection window) of 50 cm. The tailings sample was filtered with a 0.45 µm syringe filter since otherwise the solid particles might have blocked the capillary.

The capillary was introduced by washing it first by pressure with NaOH for 10 min, pure water 10 min and finally with the CAPS-buffer for 10 min. After this the actual method was started. The method included three steps: buffer washing 3 min, injection 1 min and separation 10-20 min. Several runs were made with this method, which is why there had to be a buffer wash between runs. The washing pressure was 40 psi. The injection was done with a pressure assisted field amplified sample injection (PA-FASI) method. The injection pressure was 1.5 psi and the voltage was 15 kV. The polarity was on reverse. Once the separation started, the polarity was switched to normal and the separation voltage was set to 20 kV. This method was tried on the process water and filtered nickel flotation tailings. Process water did not show traces of SIPX or Aerophine since the base line of CE graph was almost completely flat (i.e. no spikes were shown). SIPX was found on the nickel flotation tailings, but no Aerophine was detected. The peaks were identified by spiking i.e. adding reagents to the sample matrix and seeing which peak grows. The method parameters, from where the development was started, are presented in Table VII. CE graphs of process water and nickel flotation tailings are presented in Figures 13 and 14.

Table VII Instrument parameters

Relay 2 on (pump)	Time from start	2.9 min
Buffer wash	Time Pressure	3 min 40 psi
Injection	Voltage Pressure Time Polarity	15 kV 1.5 psi 1 min reverse
Separation	Voltage Time Temperature Polarity	20 kV 10-20 min 20 °C normal
Detection	Wavelength	214, 225 and 301 nm

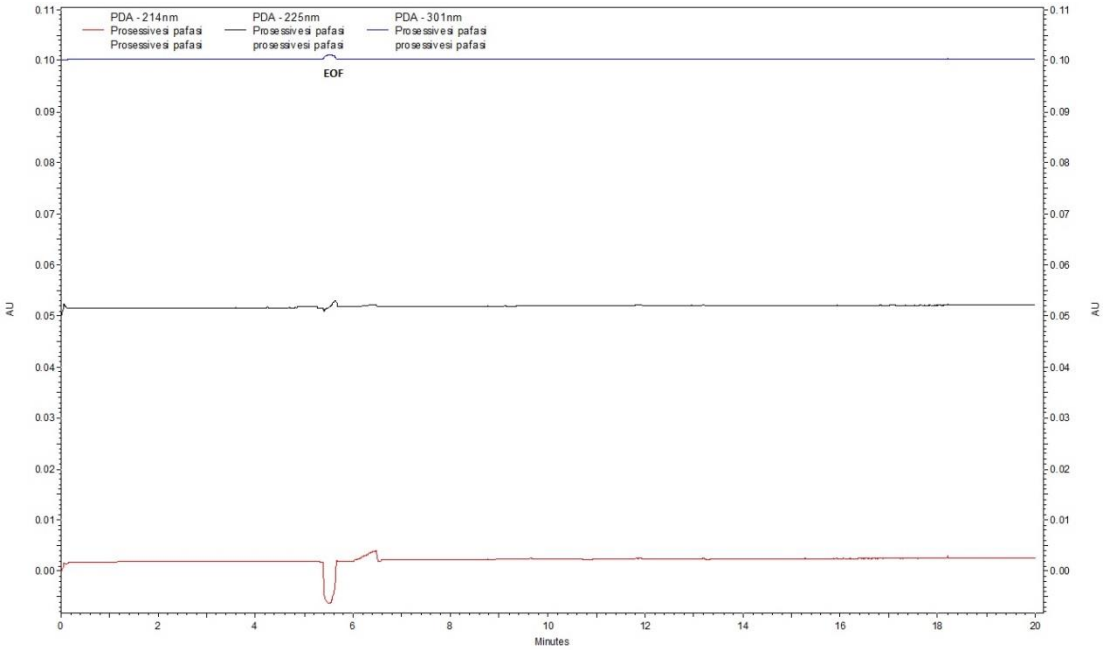


Figure 13 Process water CE graph. Applied wavelengths were 301 nm (blue/top line), 225 nm (black/mid line) and 214 nm (red/bottom line). EOF-peak can be seen approximately at time 5.5 min. Injection was done with pressure and voltage. Separation voltage was 20 kV.

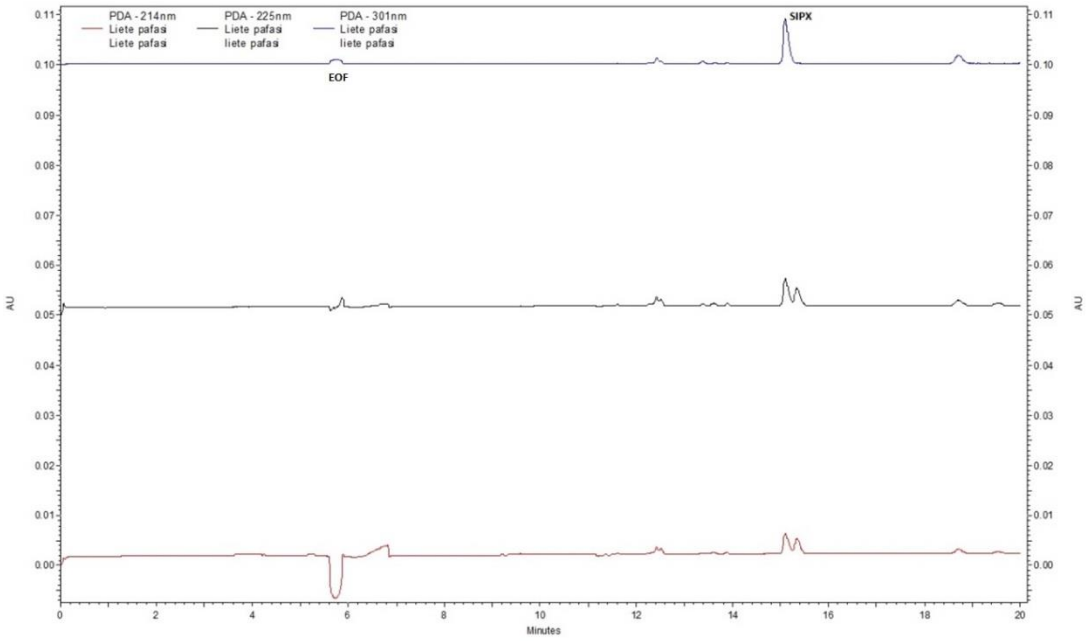


Figure 14 Filtered nickel circulation tailings CE graph. Applied wavelengths were 301 nm (blue/top line), 225 nm (black/mid line) and 214 nm (red/bottom line). EOF-peak can be seen approximately at time 5.5 min. SIPX can be seen clearly from the blue/top line approximately slightly after 15 min mark. Injection was done with pressure and voltage. Separation voltage was 20 kV.

SIPX and Aerophine peaks could be clearly seen from the sample matrix, when they were added into it, even with relatively low concentrations. This indicated that the injection seemed to be working. The peaks could also be seen during on-line tests. Higher separation voltages were tried to make the method faster. The maximum allowed separation voltage which could be set on the device was 30 kV. With this voltage peaks still clearly separated from each other and the separation was made faster. SIPX peak came approximately five minutes faster, during on-line tests, on 30 kV separation voltage when compared with 20 kV separation voltage. Because of this it was decided to use the 30 kV voltage. Using higher separation voltages also makes CE spikes higher and narrower which facilitates analyzing.

During on-line tests, a peristaltic pump was used to transport samples to a flow-through sample vial. Sample was circulated from a beaker glass to the vial and back. The circulation was first set to be on the whole method. The pump speed was set to be relatively low since otherwise it would spit some of the samples out from the flow-

through vial inside the CE and could cause problems with electricity. Capillary electrophoresis gave several errors due to pressure and voltage leakage during injection. Since the injection was done with a pressure assisted field amplified sample injection method, it was deduced that pressure and voltage might leak because of the flow through vial. Injection was set to be done with vacuum and voltage, instead of pressure and voltage. By using vacuum, pressure could not leak since the inlet end of the capillary was under the sample surface in the flow-through vial. Sample circulation was set to be on only during the buffer wash which stopped voltage from leaking.

Two vial trays with two large 30 ml buffer reservoirs (Figure 11) were acquired, since during long runs the buffer started to deplete. The manufacturer announced in the user manual that the reservoirs could hold up to 30 ml of solution. However, when experiments were made by adding 30 ml of buffer to the reservoirs, they slightly flood over. If the reservoirs were filled too full, some electrical discharges could be seen during usage and the experiment had to be immediately stopped. It was noted that when 15 ml of buffer was added in a reservoir, no electrical discharges could be seen. Since the reservoirs were relatively large, some power was sure to be leaked and the device informed about it. An “external adapter” option had to be selected from the device program to bypass this problem.

Repetition experiments were made with nickel circulation tailings where SIPX and Aerophine were added to see how the depletion of buffer affects the analysis. This was done with the special vial trays, where the buffer reservoirs were filled with 15 ml of buffer. It was noted that after 30 runs, each having a 20 min separation phase, the area of SIPX peak was approximately 80 % of the first run.

The nickel circulation tailings had to be filtered since otherwise the solids would have blocked the 50 µm diameter capillary. The slurry contained 25 % of solids and the experiments made used mainly tailings which were filtered with a 0.45 µm syringe filter. No solids could be seen in the filtered matrix. Samples which were filtered with the 10 µm rod filter contained some solids. The filter was able to remove approximately 99 % of solids and the matrix was slightly dark. The slurry, filtered

with the 10 µm rod filter, was analyzed with CE to see if the non-filtered solids would interfere the analysis. A few small sharp peaks could be seen in the CE graph on all applied wavelengths, which implies that solid particles pass the detector. This did not seem to disturb the analysis, even when several repetitions were made.

As an outline optimization to operating parameters was done to the following issues:

- Separation voltage
- Flow-through vial pump speed
- Injection pressure
    - Pressure was reversed to vacuum
- CE program configuration
    - "External adapter" option was selected to bypass current leakage
- Amount of runs that can be done before the buffer depletes

7.2 Method optimization: sampling procedure

Approximately 40 liters of nickel circulation tailings slurry was obtained for preliminary experiments. During the transportation and storing most of the solids had settled to the bottom of the storage barrel and the surface of the slurry was clear. The settled solids had a clay-like feeling when trying the bottom with a stick. The slurry was mixed with a 3-blade propeller. Since the concentration of solids was high, 25 % in mass, the slurry had to be left to mix overnight so that it would be homogenous once filtrated.

A peristaltic pump, with a capacity of 320 ml/min (theoretical value, real value with water 250 ml/min), and a 20 µm stainless steel rod filter were used in filtration tests. The filter was attached to the other end of a 3 m tube, with a 4 mm diameter, and the pump was installed to the other. However, once the filter was sunk under the mixed slurry and the pump was turned on, the speed of the filtration was so low that it was decided to get a pump with a larger 1.2 l/min capacity. Also the 20 µm rod filter

seemed to let through a relatively large amount of solids which could be seen with the human eye. The filtrate was relatively dark in the beginning of the filtration, before a cake was formed on top of the filter and started to do most of the filtration. Therefore a filter with a smaller 10 µm mesh size was tested. The higher 1.2 l/min capacity was theoretically possible with no counter pressure. However, it was able to pump water, with a 3 m hose attached and no filter, approximately only 330 ml/min. When the mixed tailings slurry was filtered with the higher capacity pump and a smaller mesh size rod filter the speed of the filtration was approximately 19 ml/min. The filtrate was quite clear since the filter removed approximately 99 % of solids. The filtrate became even clearer during the filtration since a cake was formed on top of the filter and started to do most of the filtration. The hose and filter were backwashed with water for 10 s time and with air for 5 s time to remove the formed cake on top from the filter and to clear the hose from filtrate and washing water. This was done since after a few minutes of filtration, the cake became so thick that it restricted too much of the flow and it was not reasonable to continue the filtration with such a slow speed. The filtration volume in relation to filtration time is illustrated in Figure 15.

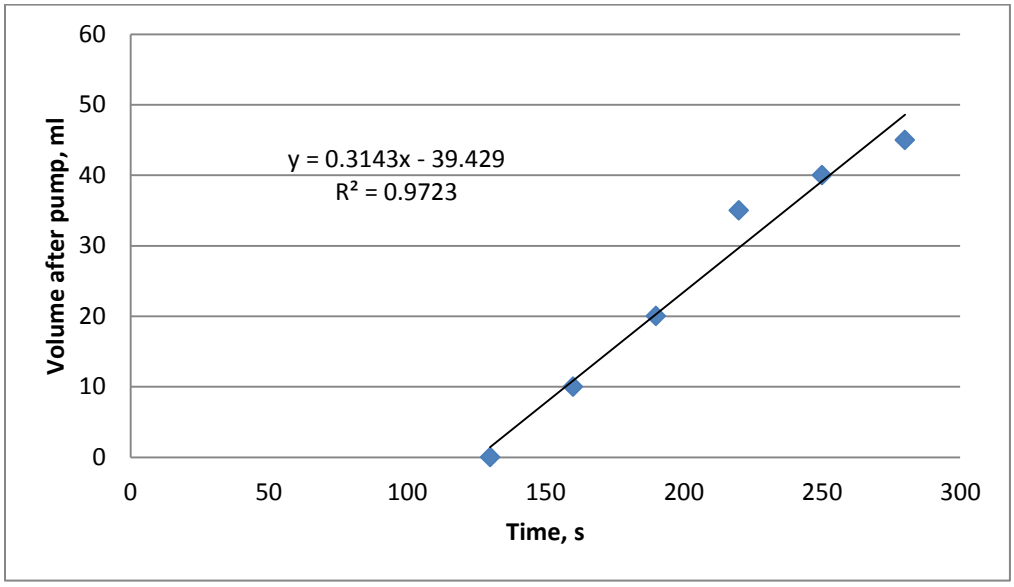


Figure 15 Filtration volume expressed as a relation to filtration time. The graph starts at 130 s time since it took that much time to fill the 3 m hose between the filter and the pump. The filtration speed calculated from the slope is approximately 19 ml/min.

Next, a 10 minute settling was tried prior filtration to see if it would speed up the filtering. It was concluded that a single-stage sample preparation by filtration would be too slow. For this reason an estimate for settling speed had to be determined. A measuring cylinder was filled with the mixed slurry and the time which the solids settled was measured. In the beginning the settling speed was slightly above 0.2 cm/min but after 162 min of settling it had dropped down to 0.13 cm/min. The solids settled relatively slowly, but there was a clear cut between the two phases. The settling in a measuring cylinder is shown in Figure 16.

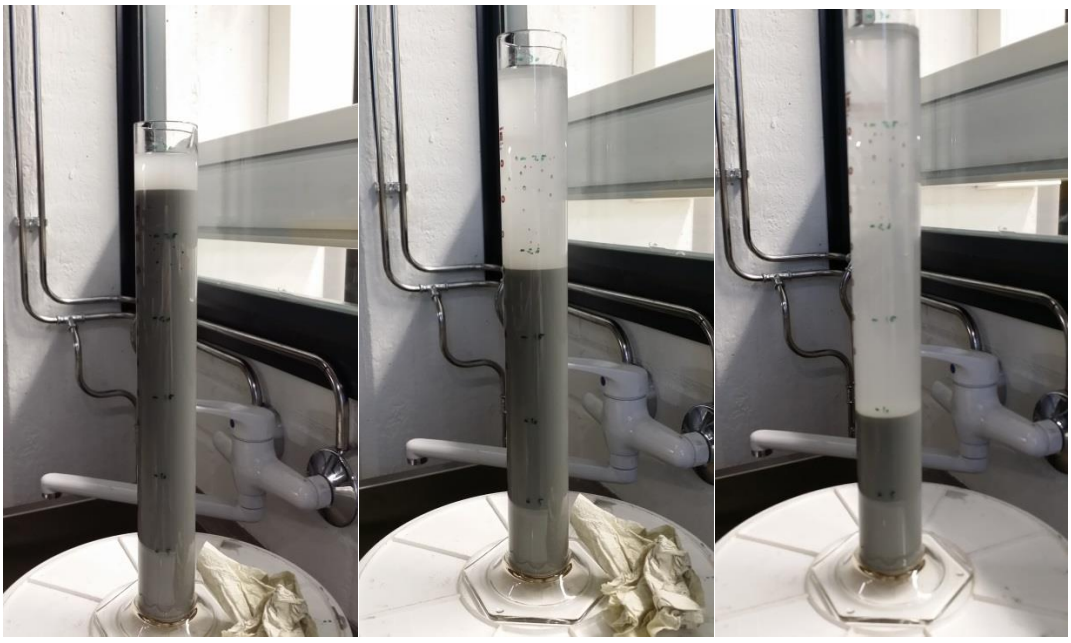


Figure 16 Settling of the nickel circulation tailings. Settling times from left to right: 12, 67 and 137 min.

Sampling was planned to be done from Multiplexer, used as a sampler for the Courier analyzer, manufactured by Outotec, in a real flotation process at FQM Kevitsa Mining Oy. Courier is an on-line analyzer that measures element grades from process streams. The results from Courier can be used to control the process. It uses wavelength dispersive x-ray fluorescence (WDXRF) as a measuring technique and can give for example the copper grade (%) in a process sample. Process samples are fed to Courier from sample Multiplexer (MXA), which selects one sample at a time to be analyzed. The sample, for measuring collector chemicals, was taken

automatically from Courier feed box at the MXA, when the tailings from nickel flotation was fed to the box. The flow chart is presented in Figure 17 after which the process is described.

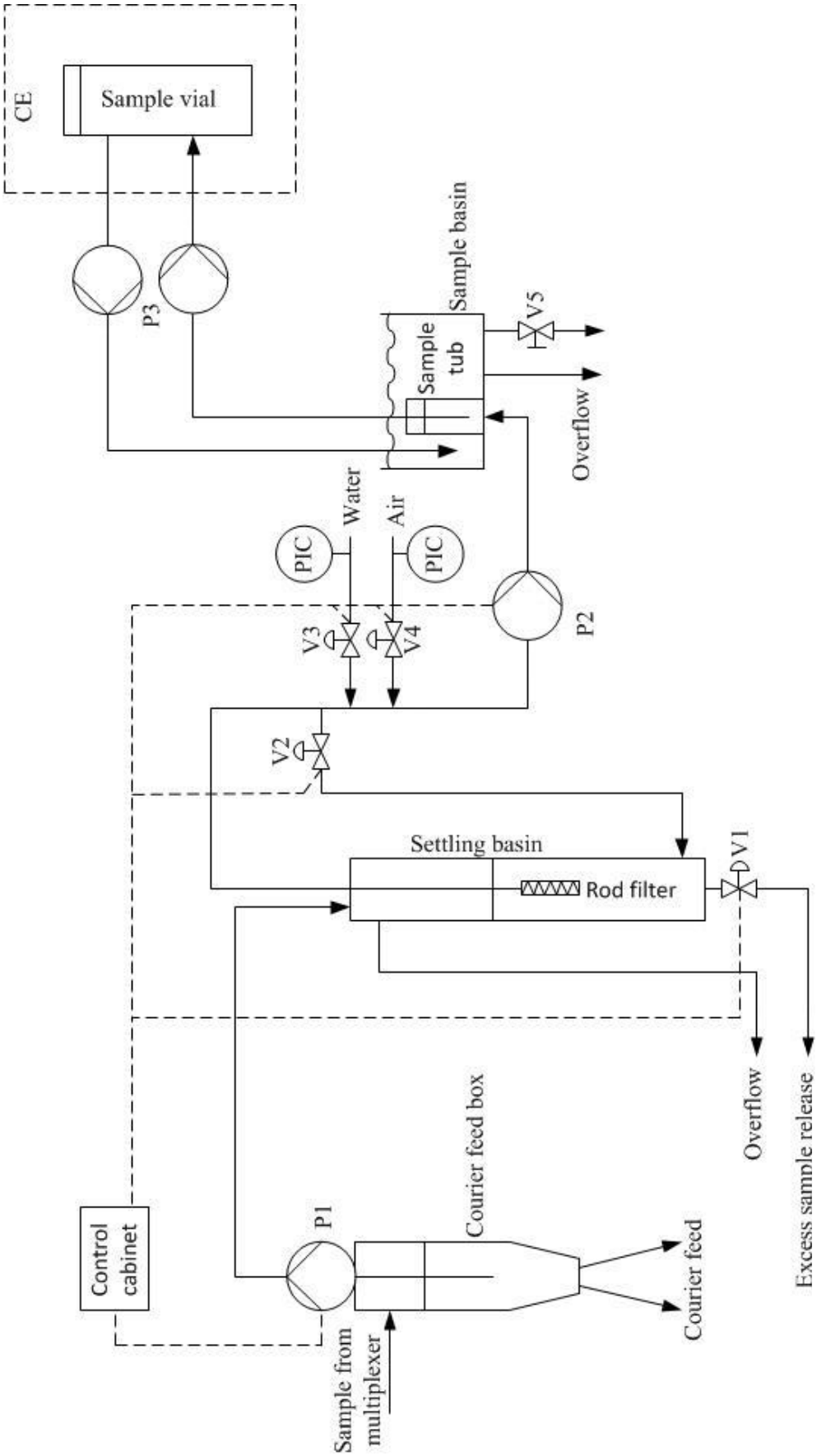


Figure 17 System flow chart

Slurry is pumped via pump P1, which is a diaphragm pump, to a settling tank for 48 seconds. The slurry is left to settle for 24 minutes. After settling it is pumped, via 10 µm rod filter, with a peristaltic pump P2 to a sample tub inside the sample basin for 3 minutes. Following the filtration, valves V3 and V2 open automatically and back-wash the pipelines, filter and bottom of the settling tank, are backwashed for 18 seconds after which the valves close. The water used for washing is the concentrator's raw water. Next the pipelines and filter are cleared with air and the bottom of the settling unit opens clearing the tank of excess sample. Valves V1 and V4 open automatically for 24 seconds. The automation is done by using time relays. Valve V5 can be manually opened if the sample tank needs to be cleared. CE and the multi-channel peristaltic pump P3 work independently regardless of the sample preparation unit. CE sends a command to pump P3, once previous analysis is done, to start pump sample from the sample reservoir inside the sample tank to the flow-through sample vial. Sample tub overflow is led out of the system from the bottom of the sample basin. Settling basin and units prior that, were one floor up from the rest of the system which were in the same booth as the Courier analyzer unit. A Schematic diagram of the Courier installation layout is presented in Figure 18.

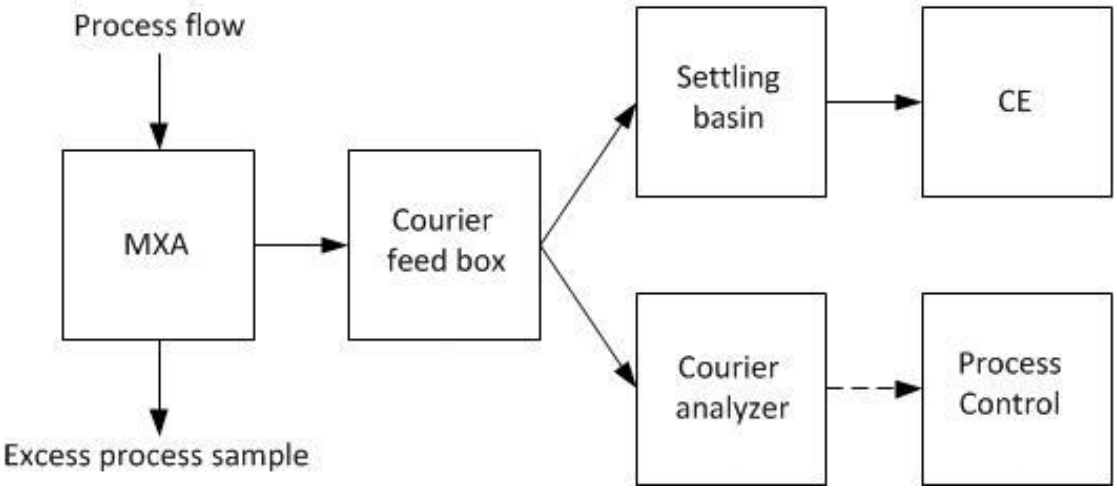


Figure 18 Courier installation layout

As an outline optimization to sampling procedure was done to the following issues:

- Filter mesh size
    - A smaller 10 µm mesh size rod filter was selected instead of a 20 µm filter since it would not have filtered the solids as well.
- The times of various stages
    - Filtration time
    - Counter-current water wash time
    - Counter-current air blow time
    - Settling time
    - Slurry pump (P1) operating time

8 Process implementation

A two-week measurement campaign was carried out in the end of January 2014 at FQM Kevitsa Mining Oy concentrator plant, in northern Finland. Kevitsa Mining Oy employs more than 300 workers and the estimated operating time is 29 years. The concentrator produces approximately 85 000 tons/year of nickel concentrate and 70 000 tons/year of copper concentrate. After the ore has gone through crushing and grinding, copper is recovered in several stages of flotation. The tailings of copper flotation are fed to nickel circuit and the tailings of nickel flotation are fed to pyrite flotation. SIPX and SEX are added to the beginning of nickel flotation. Aerophine is added to the beginning of copper circuit.

Sample pretreatment unit which was developed on the basis of preliminary experiments was introduced during these measurements. Before the campaign, the CE which was used in method development broke and experiments had to be done with a similar replacement device. SIPX and Aerophine collectors were tested during the preliminary tests. SEX was introduced in addition to these in the concentrator. There

was no previous experience on how SEX would behave during long period on-line runs with CE. T. Sihvonen [5] had studied Potassium-ethyl-xanthate off-line with CE in his studies.

Issues which needed to be taken in consideration while implementing the system are listed below:

- Sample pretreatment
    - Sample should be relatively clear (as little of solids as possible)
    - Sample is taken from the correct stream
- Sample feed
    - Enough sample is fed
- Process conditions
    - Humidity should not be too high.
    - CE should be placed on a stable platform (no vibration).
    - Temperature should be close to laboratory conditions.

8.1 Sample pretreatment

The automatic sampling system was introduced during the concentrator measurement campaign. The system was automated by using time relays. One of the relays was broken and thus the system skipped the last phase of the sampling loop. Because of this, during the first week of measurements, the system had to be partly manually operated. At the end of the first measurement week, a new relay arrived and after switching it with the broken one, there were no problems due to the relay.

The system was set to take a sample from the courier feed box when the tailings of nickel circulation arrived to it. However, the sample loop started quite often immediately after the previous had ended, even if the Courier feed box held a wrong sample. This was probably due to wrong parameters in Couriers program. New parameters were obtained at the end of the measurement campaign, but there was no

time to test them in action. The new parameters are expected to be tested during a second measurement which will be reported separately from this thesis. Approximately 1/3 of experiments went wrong due to wrong sample intake. During the campaign the system was set to do measurements over one night, which was the longest single run. The wrong samples could be seen from CE graphs since the graphs were much different from the nickel flotation tailings graphs.

Optimization of the sampling unit had to be mainly done in the amount of sample taken from the Courier feed box and the level of the filter in the settling tank. The amount of sample pumped to settling tank was relatively low. It was increased by raising the operating pressure of the slurry pump and increasing the pumping time. The amount of slurry pumped to the settling tank was also affected by the primary sample flow from the process to Multiplexer. However it was not possible to alter the amount of primary sample flow. The amount, and thus the level, of slurry pumped to the settling tank varied slightly between measurements. Because of this the filter had to put in a certain height, so that it would be under the slurry surface. If it would have been put too low, it would have clogged since a large amount of the solids settle to the bottom of the tank. A quite good height for the filter was found by trial and error.

8.2 On-line CE analyses

Capillary electrophoresis was used to qualify and quantify collector chemicals from the tailings of nickel circuit. Four collectors were used at the concentrator, which were SIPX, SEX, Aerophine and potassium-amyl-xanthate (PAX). PAX was not studied in either during the preliminary experiments or at the concentrator. PAX is used in sulfur flotation which is done after nickel flotation where the process sample was taken. SIPX and Aerophine had been examined before the concentrator measurement campaign. During the preliminary experiments SIPX was found from the tailings of nickel circuit unlike Aerophine. Aerophine is added to the beginning of copper flotation at low design rate and has thus quite possibly left the process before the end of nickel circuit.

SEX was measured for the first time with the developed method during the campaign. There was no previous experience how it would behave during long period on-line experiments. Two large spikes were seen on xanthate detection wavelength 301 nm. The peaks were distinguished by spiking, i.e. adding collector to the sample matrix and seeing which peak grows. Identifying was slightly problematic since when spiking was done with SIPX, both of the peaks grew. When spiking was done with SEX only the latter peak grew. It is possible that SIPX pellets, used for preparing the solution, contained also SEX as a production by-product of SIPX. SIPX came to the detector before SEX. The amount, of which SEX peak area grew when SIPX pellets were added, seemed to be rather constant in relation to the peak area which SIPX grew. This relation was used as a correction factor when SEX calibration curve was made, since the calibration curves of all three collectors were made in the same matrix (SIPX influenced SEX peak area) and the issue was noticed only after the calibration solutions had been made and analyzed. In addition, if the calibration curves had been made individually for all three collectors, it would have taken a too large portion of the time which was available at measurement campaign.

After identifying the spikes and creating a calibration curve for all three collectors, the sampling unit and analyzer were tested in conjunction and the results were compared with the dosage values of the collectors. Nickel flotation tailings, where 1 ppm of SIPX and SEX has been added, is presented In Figure 19. The analyzed tailings, used in Figure 18, were divided into two portions. To one portion a small amount of SEX was added. This is presented in Figure 20. SIPX was added to the second portion, which is presented in Figure 21.

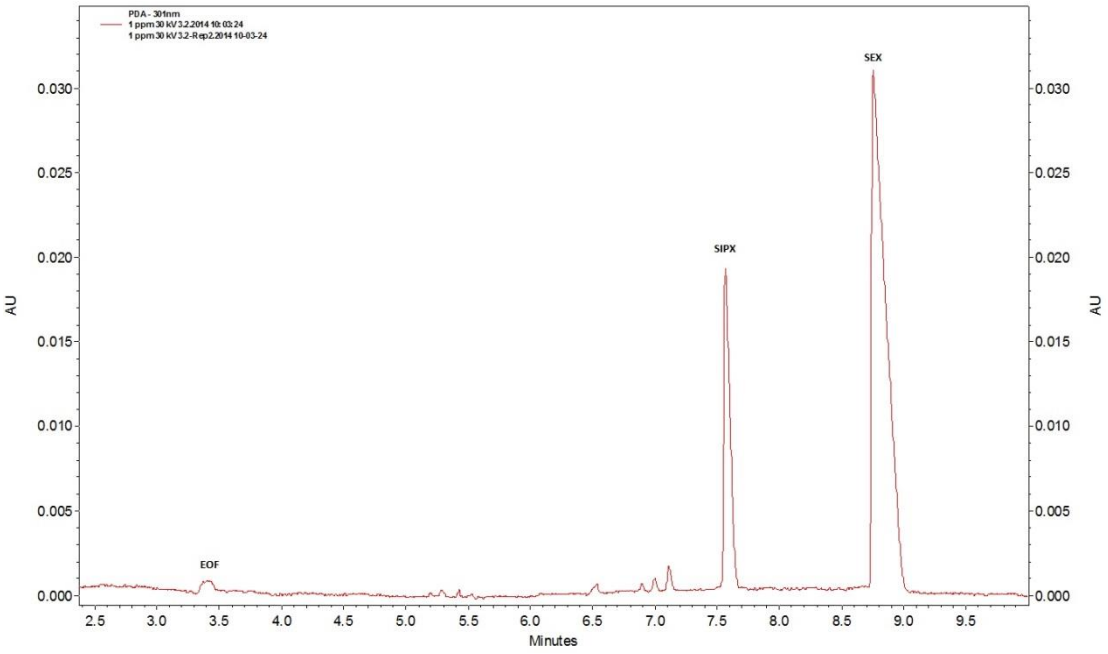


Figure 15 Nickel circulation tailings where 1 ppm of SIPX and SEX has been added. Detection wavelength is 301 nm.

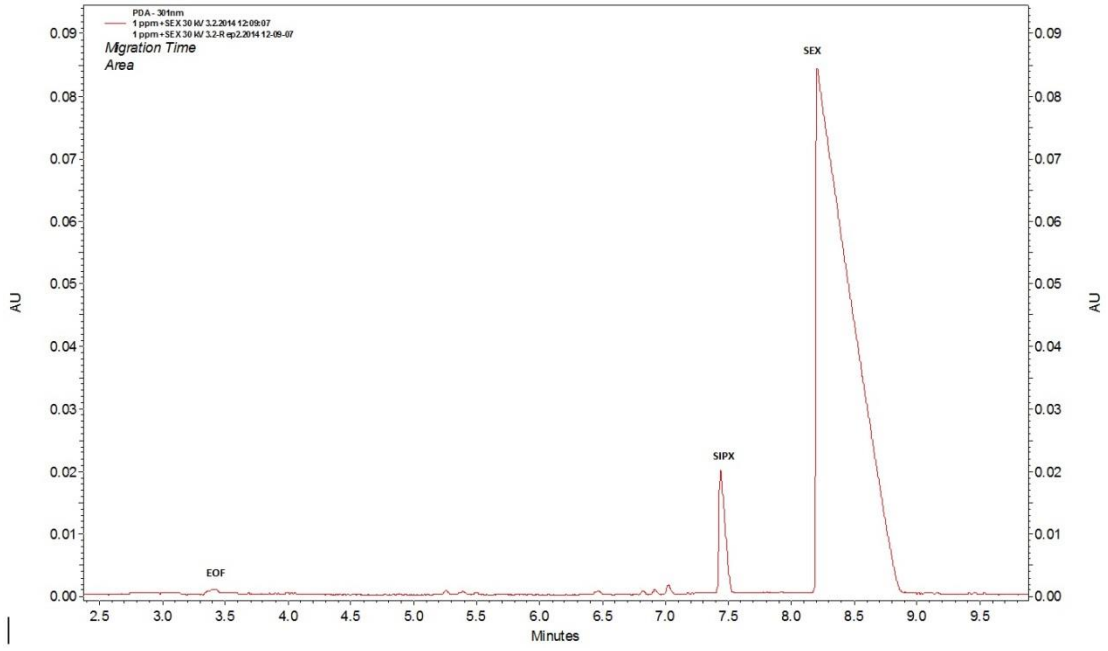


Figure 20 Nickel circulation tailings where a small amount of SEX has been added in addition to the 1 ppm addition of SIPX and SEX. Detection wavelength is 301 nm.

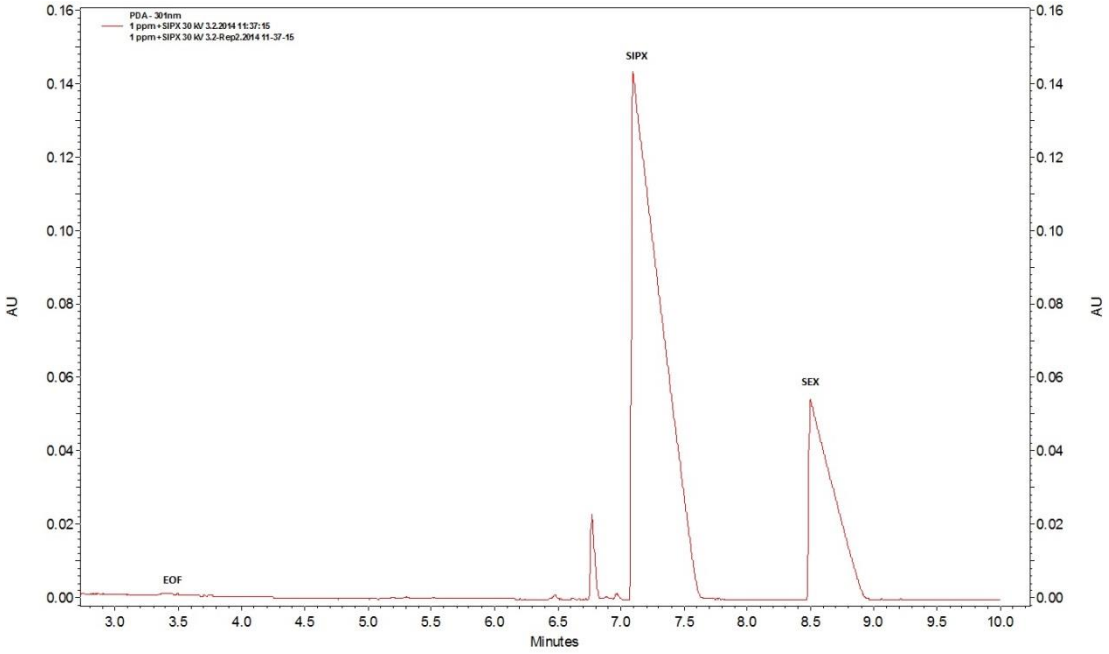


Figure 21 Nickel circulation tailings where a small amount of SIPX has been added in addition to the 1 ppm addition of SIPX and SEX. Detection wavelength is 301 nm.

It can be clearly seen that when SEX was added to the nickel circulation tailings in Figure 20, which included 1 ppm of SIPX and SEX, only the latter of the two large spikes grew. This obviously means that the latter spike represents SEX. But when SIPX was added to the tailings, both of the spikes grew. However, the first of the two large spikes grew more over the other.

The pressure used to wash the capillary during the preliminary experiments was set to 40 psi. However the replacement CE could not keep the pressure so high. The program stopped some of the runs due to this. The washing pressure was lowered to 30 psi which stopped the program from giving errors. The reduction did not seem to affect the analysis.

The sample tank had a small reservoir (a few tens of milliliters) inside of it where the filtrate was pumped. The filtrate overflow ran to the sample tank. The overflow filtrate was led out from the bottom of the tank. Since the volume of the reservoir was small, the time which the multi-channel peristaltic pump P3 operated had to be

decreased to one minute. The reservoir was drained empty during the one minute pumping but the pump did not unnecessarily operate as long as it did previously. Since the outlet of the flow-through vial was higher than the inlet, and the capillary and electrode sunk under the sample surface, it did not matter if the sample ran out from the reservoir inside the sample tank. The final method which was improved on the basis of preliminary experiments and concentrator measurements is presented in Table VIII.

Table VIII Final CE method

Relay 2 on (pump)	Time from start	1 min
Buffer wash	Time	3 min
	Pressure	30 psi
Injection	Voltage	15 kV
	Pressure	1.5 psi
	Time	1 min
	Polarity	reverse
Separation	Voltage	30 kV
	Time	10-20 min
	Temperature	20 °C
	Polarity	normal
Detection	Wavelength	214, 225 and 301 nm

9 Robustness

The results are given separately for preliminary and concentrator campaign experiments. A similar CE analyzer was used in both of the experiments but slight differences could be seen between them. The differences were mainly on the values of peak areas but it is likely that they are not compatible across devices. For example the peak area for EOF with the replacement device was approximately 1/5 of the area which the original device gave when using the same method off-line. Also the EOF peak could be more clearly seen, i.e. it stud out from the base line, with the CE used during the preliminary experiments. This implies that less sample is injected to the capillary.

9.1 Preliminary experiment results

Aerophine and SIPX were used during the preliminary experiments. The collectors were identified by spiking i.e. adding the measured substances and seeing which spike grows. It was known that xanthates are detected well at 301 nm wavelength and dithiophosphinates are detected well at 214 and 225 nm wavelengths. Since there were only two substances to be identified, the procedure was relatively simple. In Figure 22 the tailings of nickel circulation, where 1 ppm of SIPX and Aerophine was added, is presented. Aerophine spike can be seen on the graph on 214 nm and 225 nm detection wavelengths coming to the detector approximately at time point 11 min. SIPX can be seen with detection wavelength 301 nm coming to the detector slightly before 18 minutes has passed.

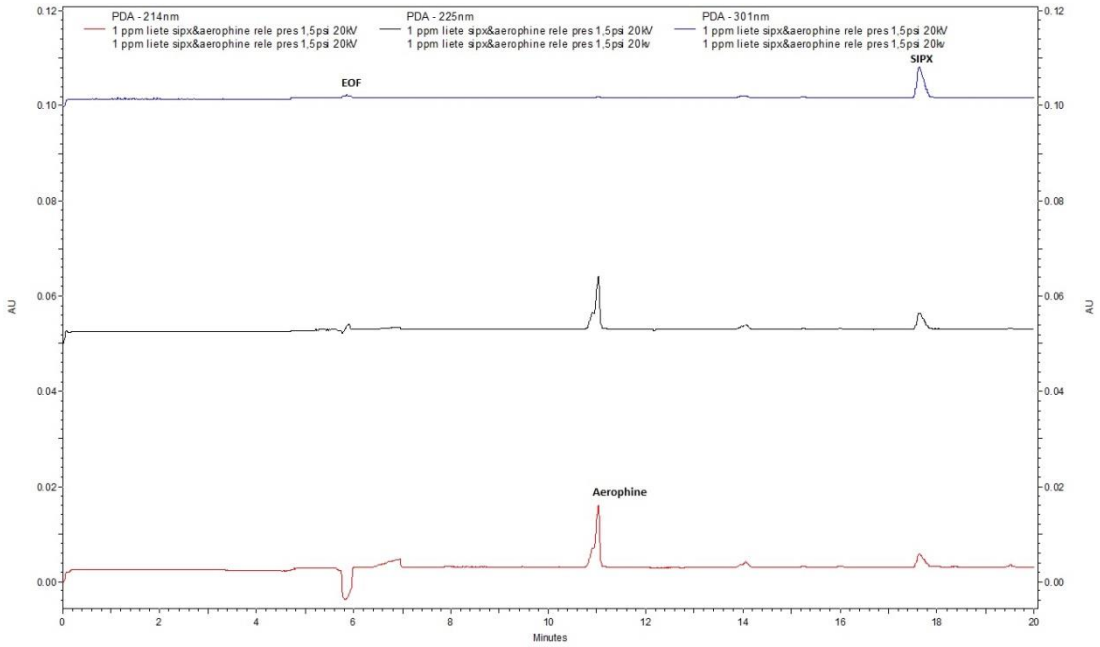


Figure 22 CE graph of nickel circulation tailings where 1 ppm of SIPX and Aerophine have been added. Injection was done with pressure and voltage. Separation voltage was set to 20 kV. Applied wavelengths were 301 nm (blue/top line), 225 nm (black/mid line) and 214 nm (red/bottom line).

During the first on-line experiments with CE, the instrument gave occasional errors due to electricity and pressure leakage. The electricity leakage stopped when the circulation in the flow-through vial was stopped during the injection. However this did not solve the leakage problem with the pressure used during injection. Vacuum was tried instead of pressure to exceed EOF. The injection done with vacuum and voltage gave a surface area for EOF peak which was approximately 1,3 times larger than the injection done with pressure and voltage. This implies that more analytes are injected to the capillary. Even if circulation is not on during injection, pressure might be pushed out slightly from the outlet of the flow-through vial.

Different separation voltages were tried mainly to test if the analysis could be made faster but also to see if any problems would occur. This way the problems could be avoided during the measurement campaign. Since SIPX came to the detector after Aerophine, analysis time depended on it. When a 15 kV separation voltage was applied, SIPX was not shown in the CE graph during a 20 minute separation phase.

However, when a 30 kV separation voltage was applied, SIPX was shown in the CE graph slightly before 12 minutes of separation voltage had passed.

Repetition experiments were made with nickel circulation tailings where SIPX and Aerophine were added to see how the depletion of buffer affects the analysis. This was done with the special vial trays, where the buffer reservoirs were filled with 15 ml of buffer. It was noted that after 30 runs, each having a 20 min separation phase, the area of SIPX peak was approximately 80 % of the first run. The depletion of the buffer is expressed as relative reduction of SIPX peak area as a function of repetitions in Figure 23.

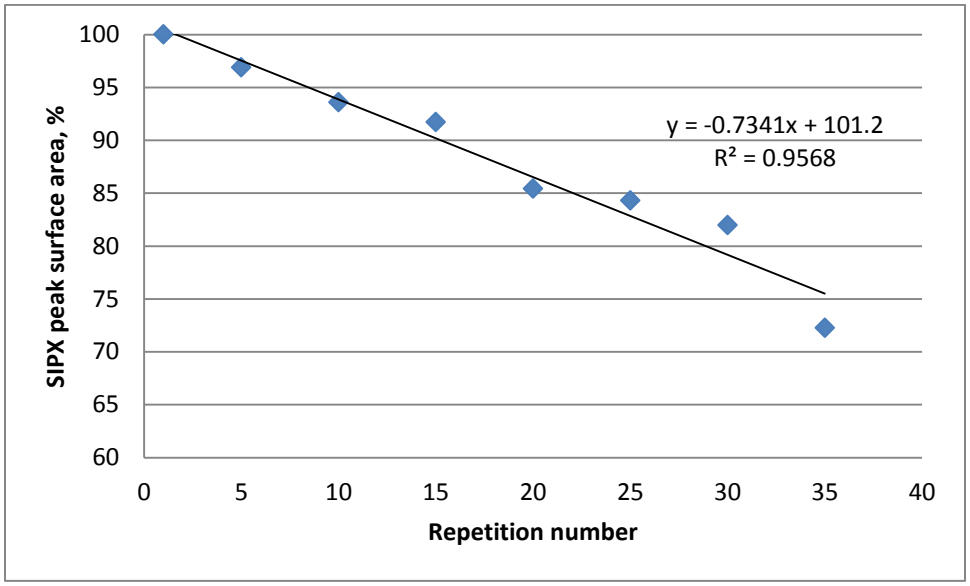


Figure 23 The depletion of the buffer expressed as SIPX peak surface area relative reduction as a function of repetitions

Since the 10 µm rod filter removed approximately 99 % of solids, the filtered tailings from nickel circuit had to be tested in case the non-filtered particles would interfere the analysis. A few small sharp peaks were shown on all applied detection wavelengths due to solid particles which passed the detector. However these particles did not seem to hinder the process even when several analysis repetitions of the filtrate were made. CE graphs of nickel circulation tailings filtrate, where SIPX and Aerophine have been added, are shown on in Figures 24 and 25 with two different detection wavelengths.

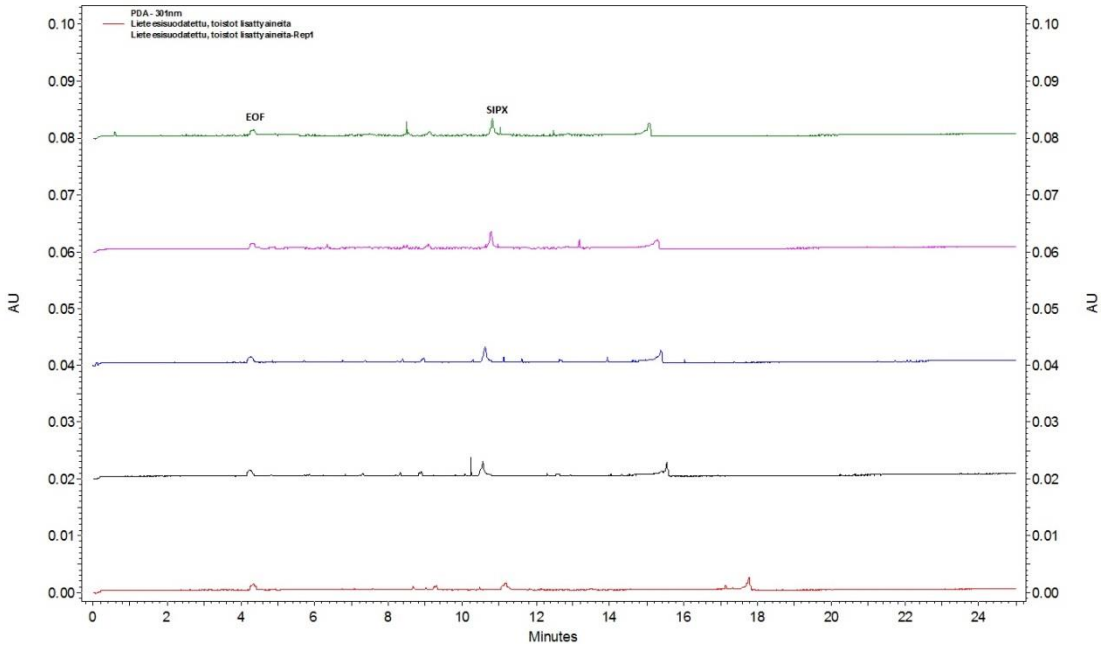


Figure 24 CE graph of filtered tailings from nickel circuit with 5 repetitions. 1 ppm of SIPX and Aerophine were added to the filtrate. Applied wavelength is 301 nm.

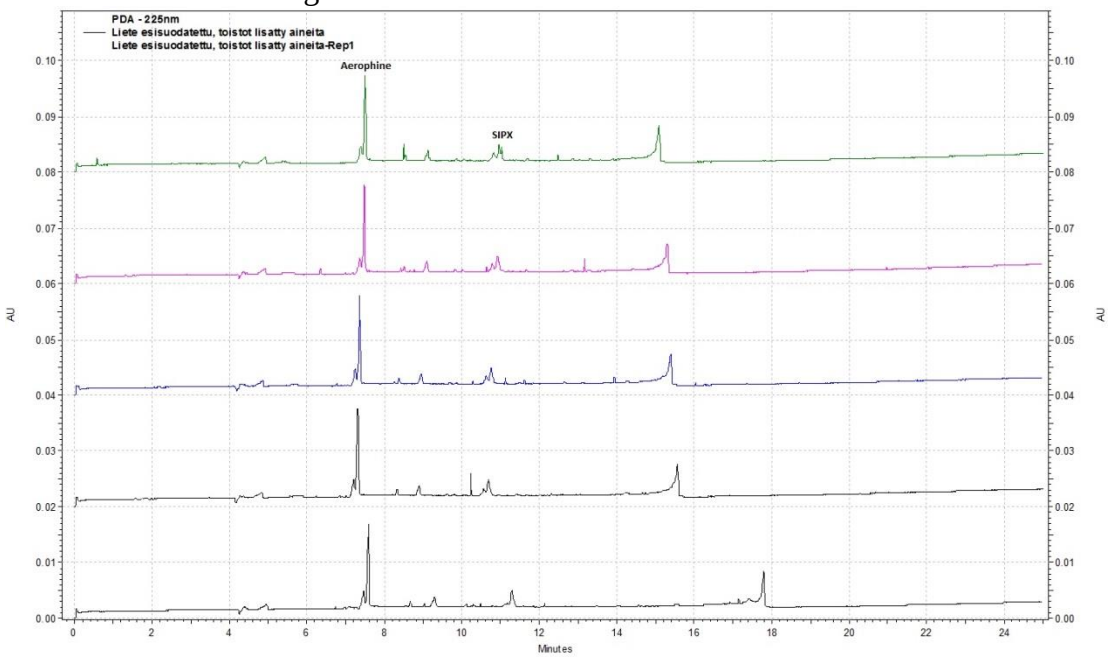


Figure 25 CE graph of filtered tailings from nickel circuit with 5 repetitions. SIPX and Aerophine were added to the filtrate. Applied wavelength is 225 nm.

9.2 Concentrator experiment results

Calibration curves for SIPX, SEX and Aerophine were made on-line with the CE method described in Table VIII. The standard solutions were made in the same matrix (nickel circulation tailings) as the measurements were done. This way the ionic strengths in the solutions should be close to same. Some variation might occur in the ionic strength of nickel circulation tailings for example due to changes in ore composition. Nonetheless this method should provide a good way to calculate accurate concentrations for the collectors used. Calibrations standards were made in the concentrations of 0.05; 0.1; 0.5; 1; 5; and 15 ppm. Since the tailings contained SIPX and SEX in itself, the absorbance response of the blank solution was reduced from the standard solutions. Also the constant was taken off from the calibration curves. The electropherograms from CE calibration curve runs are shown in APPENDIX I. The calibration curves for Aerophine, SIPX and SEX are presented in figures 26, 27 and 28.

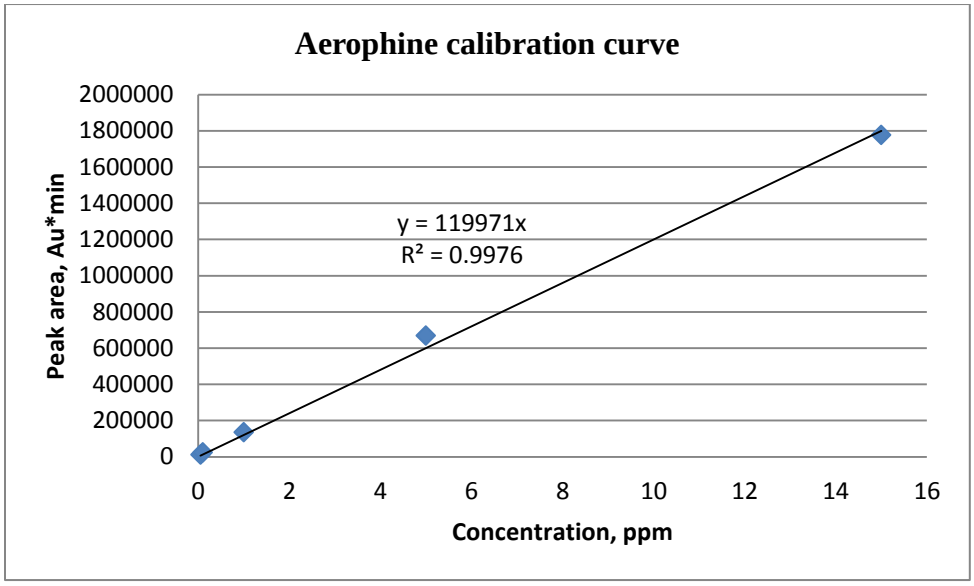


Figure 26 Aerophine calibration curve in nickel circulation tailings

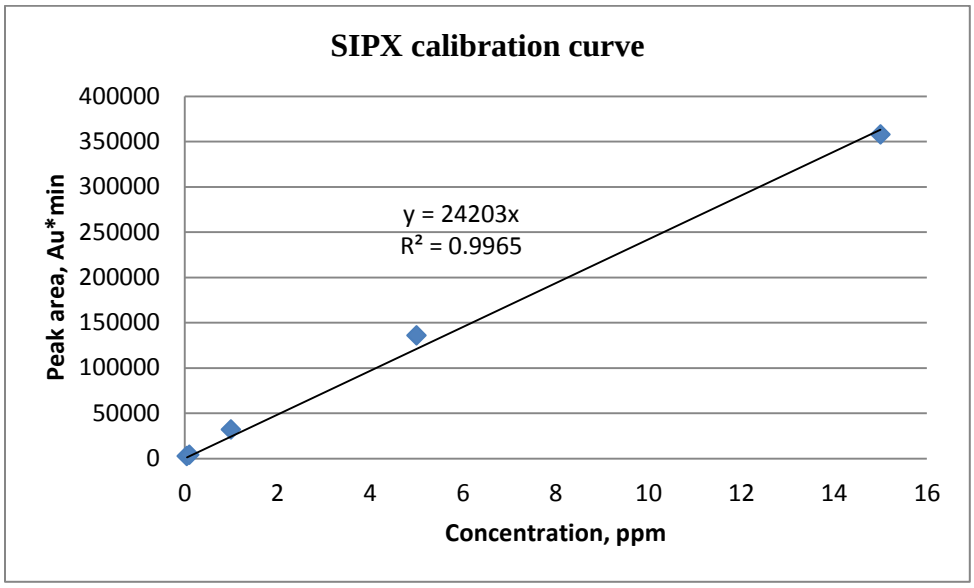


Figure 27 SIPX calibration curve in nickel circulation tailings

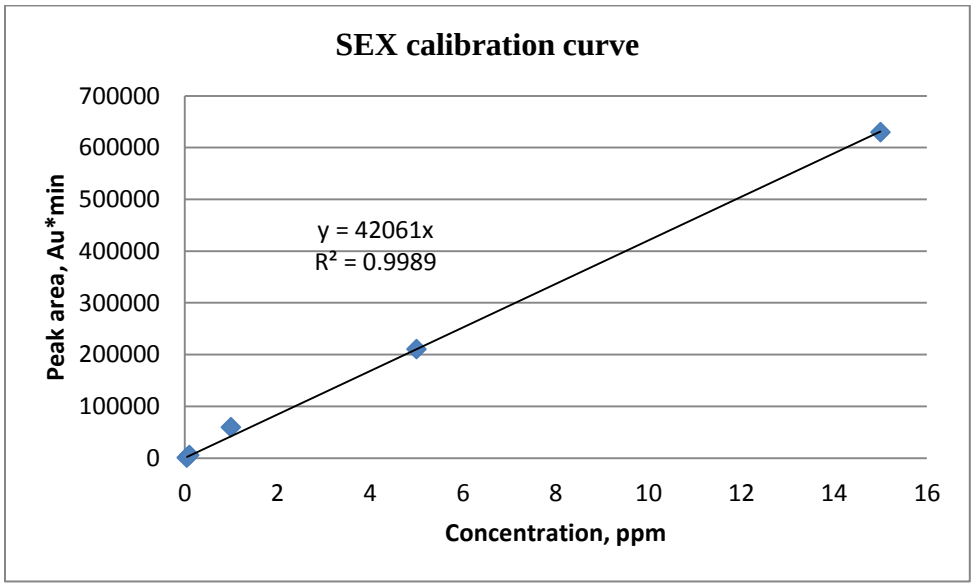


Figure 28 SEX calibration curve in nickel circulation tailings

The automated sampling unit in collaboration with CE was used to measure collector chemical concentrations in nickel circulation tailings. SIPX and SEX were seen in the tailings but Aerophine was not. The longest non-stop run was approximately 12 hours. The measured collector chemical concentration variations and relative addition amounts are presented in Figure 29.

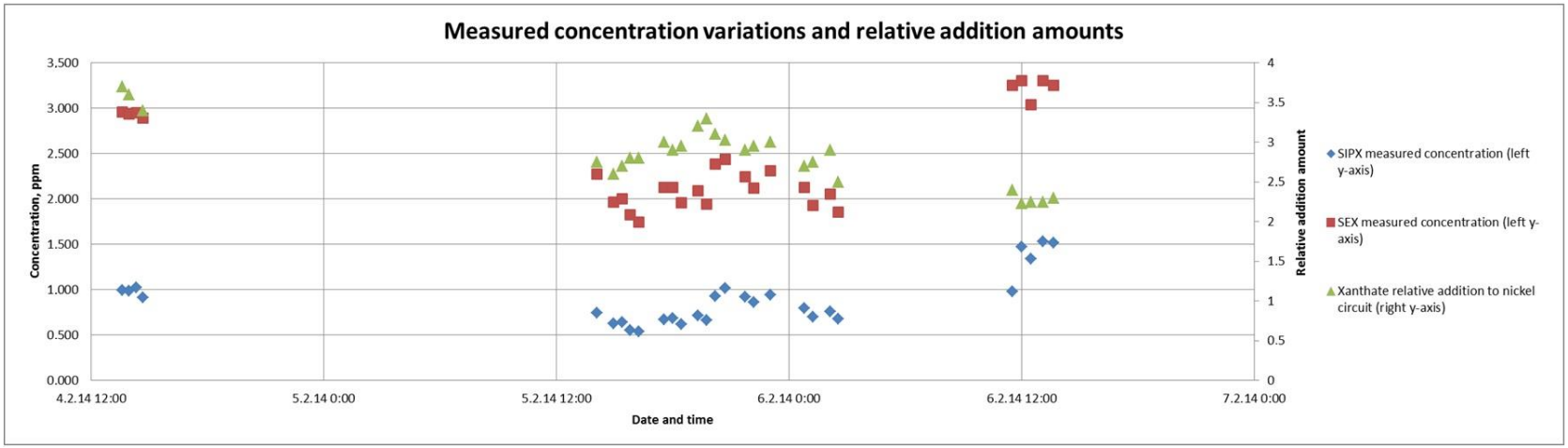


Figure 29 Measured concentrations and relative addition amounts of collector chemicals in the process

The electropherograms from concentrator measurements are shown in APPENDIX II. The values of migration time, peak area and concentration for each data point can seen in APPENDIX III. Some correlation can be seen between the measured concentrations and the relative addition amounts. During the longest single period 12-hour run the concentrations seem to follow the addition amounts with a slight delay. However if the individual runs are compared with each other's, the correlation cannot be seen. This might be explained for example due to buffer depletion or because the capillary needs to be rinsed with NaOH so that no precipitate accumulation will interfere the analysis. The capillary was rinsed in the beginning and end of each run with 0.1 M NaOH.

It was noticed that SIPX pellets contained SEX as well. When SIPX was added to the nickel circulation tailings the amount which SEX increased seemed to be rather constant. The amount, which SEX grew, was approximately 12 % of the increase amount of SIPX.

Limit of detection (LOD) and limit of quantification (LOQ) were calculated from signal areas. Signal for analyte peaks were obtained from the lowest calibration standards which had a signal to noise ratio larger than 10. The noise was obtained from the baseline by integrating several noise peaks and calculating an average of those. LOD was calculated as a signal area corresponding with the compound at the lowest concentration to receive signal to noise ratio equal to 3. LOQ was calculated the same way but with ratio 10. Electrophoretic mobilities for analytes were calculated with equations 3 and 4 for calibrations standards between concentration area of 0.05 ppm – 15 ppm. Relative standard deviation (RSD) for electrophoretic mobility was determined to describe the spread of data with respect to the mean. LOD, LOQ, μ_{ep} and RSD of μ_{ep} are presented in Table IX.

Table IX Validation measures LOD, LOQ, electrophoretic mobility and relative standard deviation for electrophoretic mobility, for each collector chemical

Collector chemical	LOD, ppm	LOQ, ppm	μ_{ep}, $10^{-8}m^2v^{-1}s^{-1}$	μ_{ep} RSD, %
SIPX	0.0076	0.0254	-2.184	3.02
SEX	0.0029	0.0096	-2.392	6.36
Aerophine	0.0005	0.0018	-1.638	4.11

The migration time of SIPX and SEX changed between runs and during long runs. Both collectors came to the detector faster over time as the run went forward. For example during a 12-hour run, SEX came to detector approximately in 8 minutes at the beginning. But after circa 12 hours had passed, SEX came to the detector more than a minute earlier. This is probably due to ionic strength changes in the buffer solution. Some shifting of the spikes, between different runs, could be seen during the measurement campaign. This is probably caused by temperature and ionic strength variations in the process. The used CE could control the temperature of the capillary and sample storage but it is probable that, since the measurements were done on-line, the samples did not have enough time to warm up to the set temperature. Migration time shift of SIPX and SEX during approximately a 12-hour run is presented in Figure 30 which can be used to estimate how the peaks will shift.

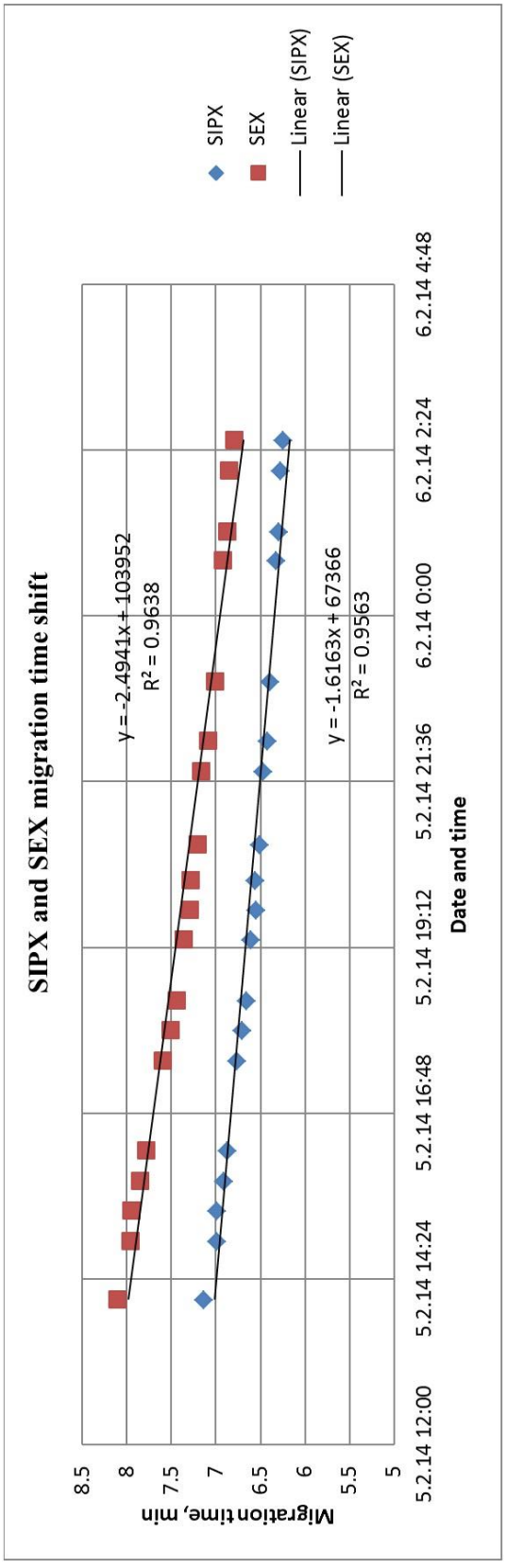


Figure 30 SIPX and SEX migration time shift during approximately 12 h run

10 Conclusions

The aim of this thesis was the development of an on-line capillary electrophoresis (CE) method for monitoring the behavior of collector chemicals in a flotation process. For this reason a pretreatment filtration unit had to be designed to remove solid particles, from nickel circulation tailings, which would otherwise interfere the CE analyses. High concentrations of solids would likely block the capillary and/or cause the CE graph to be un-interpretable due to additional spikes in the graph caused by the solid particles. Also, a CE method needed to developed, because of this. Collector chemicals had been examined previously by CE off-line. The method needed to be enhanced to be able to work on-line in a real industrial process for long periods of time. Method development was mainly done during preliminary experiments in Lappeenranta University of Technology. Some minor tweaks were done to the method when the system was tested in practice at a concentrator plant FQM Kevitsa Mining Oy in northern Finland during a two week measurement campaign.

The designed pretreatment filtration unit removed approximately 99 % of the solids in nickel circulation tailings. The remained particles did not hinder the analysis. The used 10 µm rod filter, in conjunction with a settling unit, seemed to be a robust way to filter the solid particles. In the beginning of the filtration more particles passed the filter since a cake had not formed on top of the filter, which later started to do most of the filtration. The system filtered a few deciliters of sample before the filter was almost completely clogged. The sample amount was more than enough which was needed for on-line CE analysis. The pretreatment filtration unit took samples automatically approximately once every 30 minutes when nickel circulation tailings came to the Courier multiplexer. However the system started to do another sampling loop relatively frequently after the correct sampling loop had ended. Therefore the system took a wrong sample to be analyzed. This effected approximately on one third of the samples taken and the reason for wrong sample intake was probably involved with the parameters set in the Courier program. The wrong samples could be clearly spotted from the CE graphs since they differed from the correct ones so dramatically.

New Courier parameters will be tested in the future which will hopefully stop this problem from occurring.

The developed CE method, described in Table VII, was able to detect sodium isopropyl xanthate (SIPX) and sodium ethyl xanthate (SEX) from nickel circulation tailings. Aerophine was not detected. This is likely due to the fact that Aerophine is added to the beginning of copper circulation, which is set before nickel circulation, and thus is removed before the end of nickel circulation. Limit of detection (LOD) and limit of quantification (LOQ) for SIPX was 0.0076 ppm and 0.0254 ppm, for SEX 0.0029 ppm and 0.0096 ppm and respectively for Aerophine 0.0005 ppm and 0.0018 ppm. The measured concentrations of SIPX and SEX were higher than LOD and LOQ. The analysis of these components was possible to be done in less than 15 minutes which was less than sampling time.

When the calibration curve for SEX was created, the CE peaks widened on higher concentrations and distinctly differed from the lower concentration peaks. High concentrations lead to broad cross-sectional flow profiles and thus can be seen as wide peaks. However when the wide peaks were integrated, the surface area values did not seem to differ from the calibration line drawn with lower concentrations i.e. the surface area values fitted to the line. This implies that the CE response taken from higher concentrations could be used in the concentration determination.

The system can operate approximately one day on its own. After this the operator mainly needs to change the buffer in the CE trays and check that the system is working properly. The CE trays which had large buffer trays proved to ease the workload of the operator since he did not have to fill several smaller vials instead of a few larger ones. The system can be made to operate at a longer period if the analysis interval is made longer. Collector chemical concentrations should not change in the system relatively suddenly which should make the interval change possible. However problems might still occur with the device itself since it is a relatively delicate analyzer. Therefore it is better if the operator checks the system condition at least once a day.

SIPX and SEX were added to the beginning of nickel flotation. During CE analyses, it was noticed that the SIPX pellets contained also SEX, which is likely a production by-product of SIPX. The amount, which SEX grew, was approximately 12 % of the increase amount of SIPX. This could partially explain why the amount of SEX in nickel circulation tailings was roughly 2-3 times the amount of SIPX. SIPX might also react more actively with minerals which could be why there would be less of it in the tailings of nickel circulation.

Slight correlation between the measured and addition amounts of collector chemicals can be seen in Figure 29. During the longest single period 12-hour run, the concentrations seemed to follow the addition amounts with a slight delay. However if the individual runs are compared with each other's, the correlation cannot be seen. This might be explained e.g. due to buffer depletion or because the capillary needs to be rinsed with NaOH so that no precipitate accumulation will interfere the analysis. The capillary was rinsed in the beginning and end of each run with 0.1 M NaOH. The correlation refers that the method seems to be working as intended. However more data is needed on this issue in order to insure this fact. For this reason more measurements will be made but they will be reported separately from this thesis.

In addition to the new Courier parameter tests and extra measurements, which should be made to ensure that the system is working as intended, the next step could be further automation in the CE program. In this research the CE spikes had to be manually integrated with the program and the spike surface area had to be compared to the calibration curve to get a concentration for each measurement and collector chemical. This was relatively time consuming for the operator. The program should be automated so that it would do this itself and send the data to the control room programs which operators could use to control the process. Some shifting of the spikes could be seen during the measurement campaign which might make automatic spike integration difficult. A way to predict the shifting should be looked into more closely. Also the on-line CE system could be altered so that it would measure the concentrations of collector chemicals form other streams in addition to the nickel

circuit tailings. Robustness in process conditions should also be looked more closely into.

Two electropherogram spikes came to the detector after SIPX and SEX nearly every time (can be seen in APPENDIX II). These spikes can be seen with detection wavelengths 214 and 225 nm. The spikes are likely degradation products of the collectors. Jussi Kemppinen [6] had examined degradation products of collectors in his Master's thesis. The electropherograms spike which follows SEX spike is likely ethyl thiocarbonate.

As a conclusion the developed on-line CE system proved to work in a real industrial process relatively well. However some further testing in a concentrator plant and development in CE program automation is needed so that the system would not be so dependent on operator service.

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Electropherograms of SIPX, SEX and Aerophine calibration in filtered nickel tailings

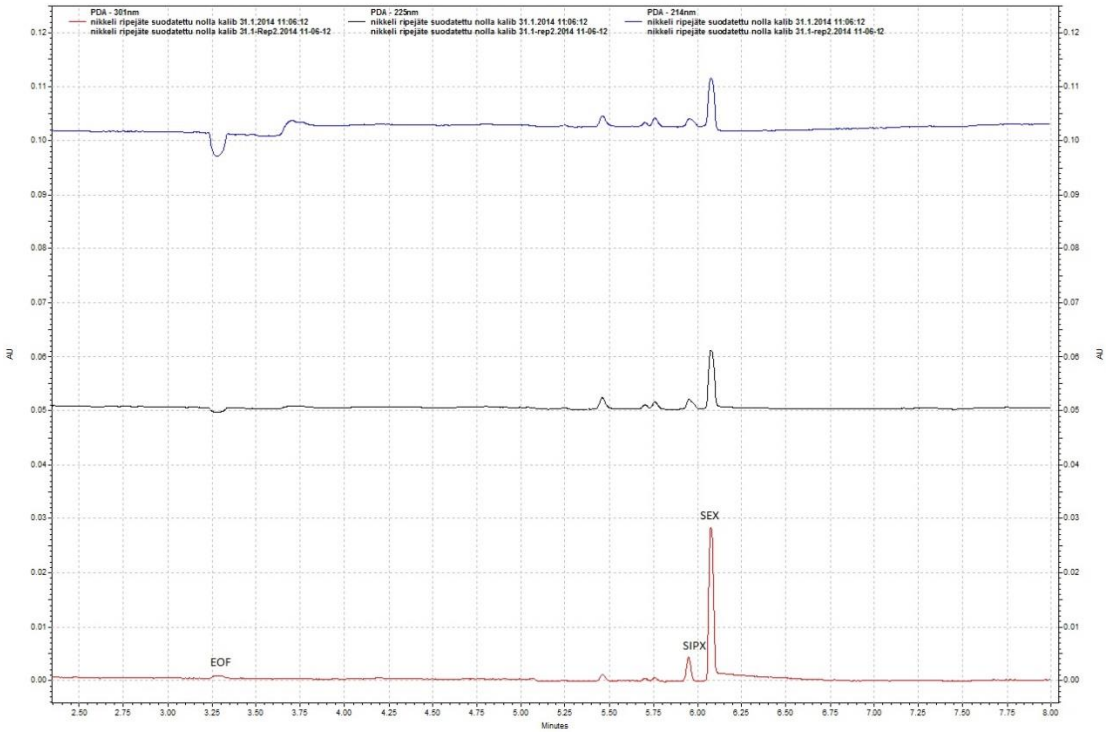

Figure 31 CE graph of nickel circulation tailings. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

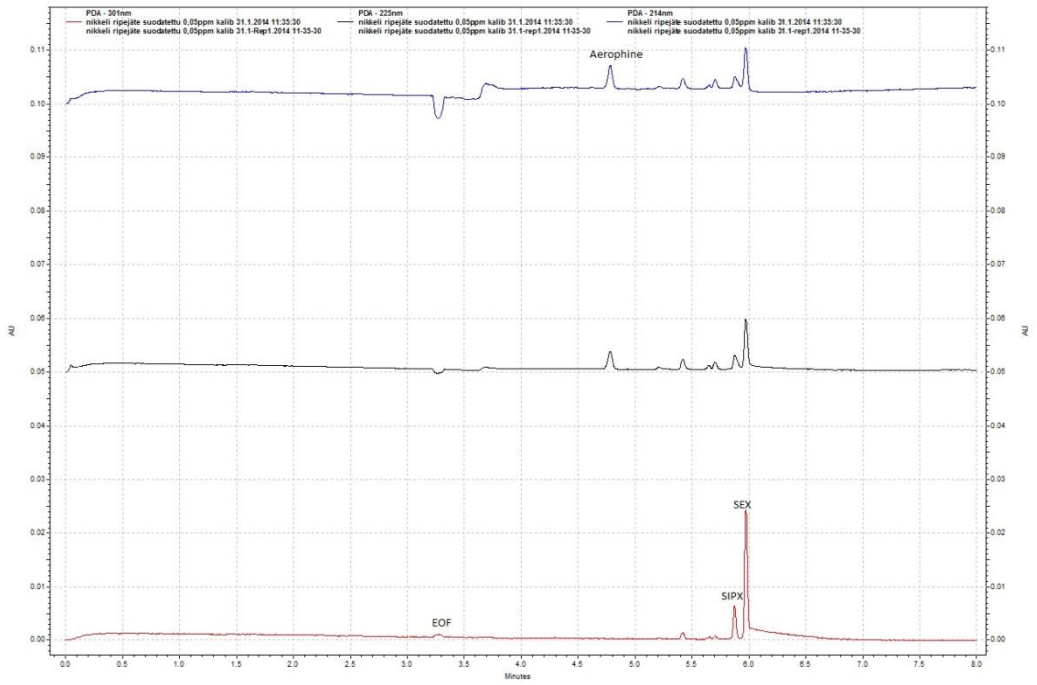

Figure 32 CE graph of nickel circulation tailings where 0,05 ppm of Aerophine, SIPX and SEX were added. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

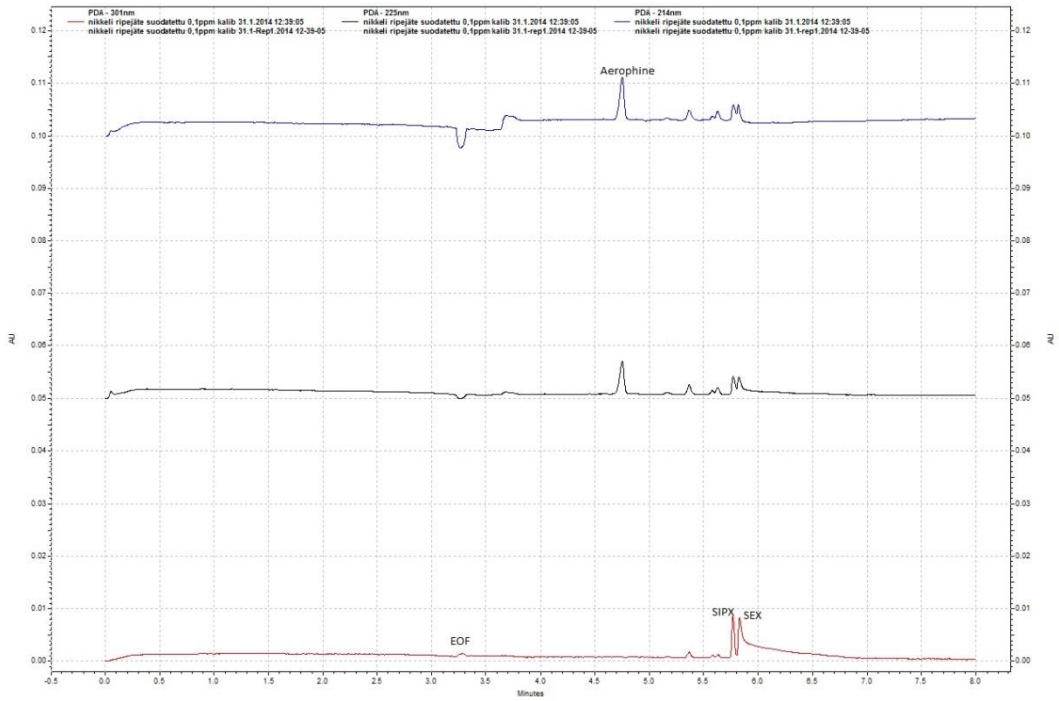

Figure 33 CE graph of nickel circulation tailings where 0,1 ppm of Aerophine, SIPX and SEX were added. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

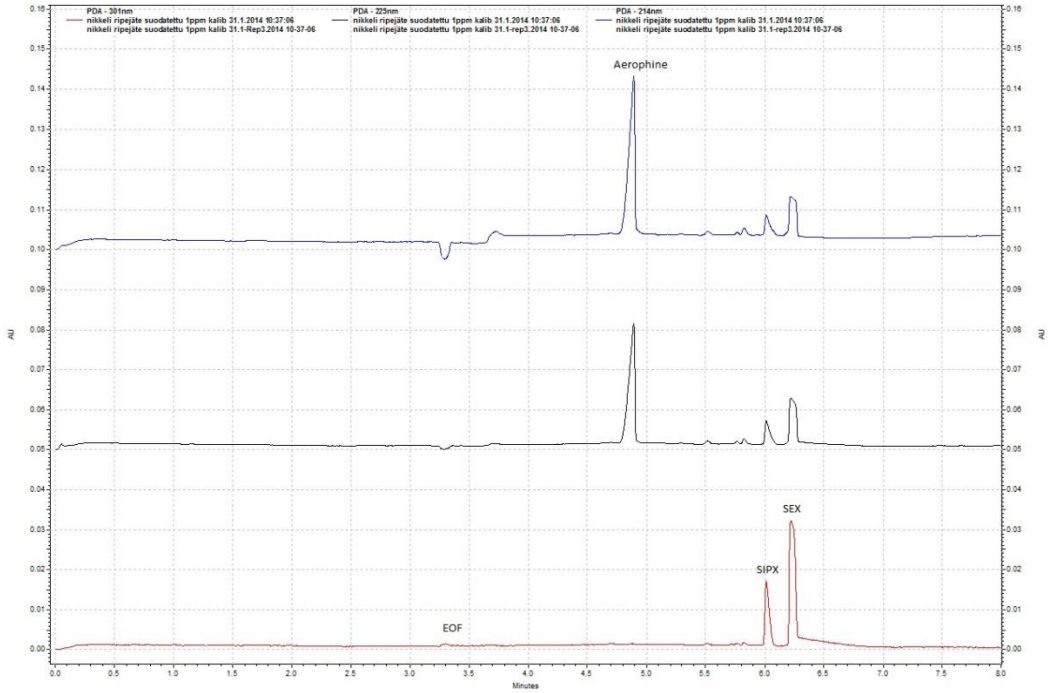

Figure 34 CE graph of nickel circulation tailings where 1 ppm of Aerophine, SIPX and SEX were added. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

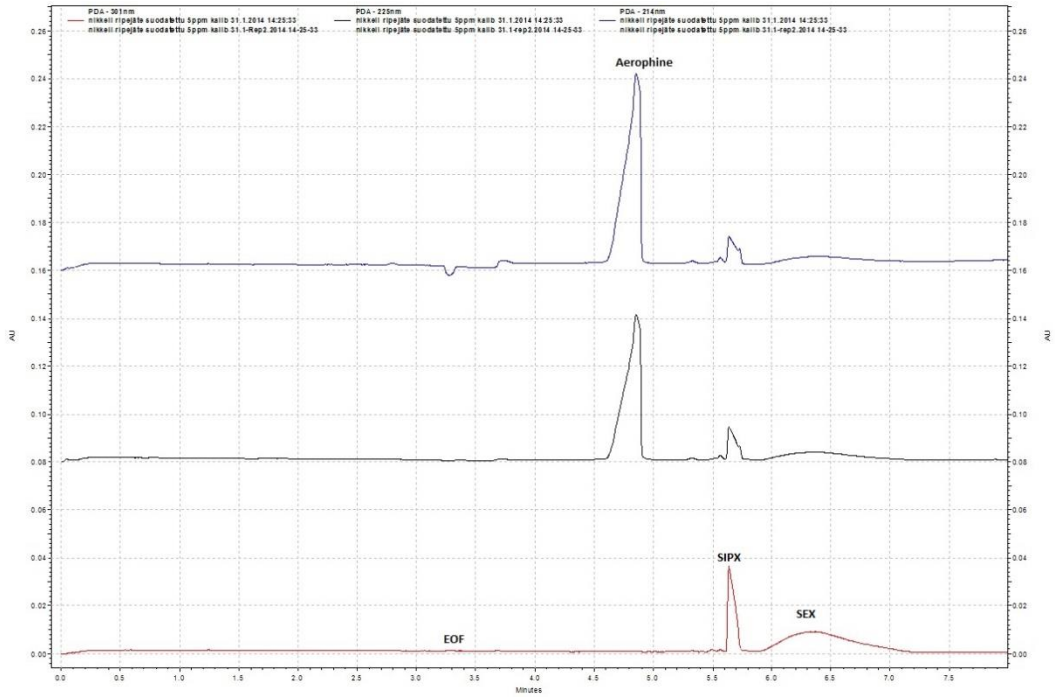

Figure 35 CE graph of nickel circulation tailings where 5 ppm of Aerophine, SIPX and SEX were added. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

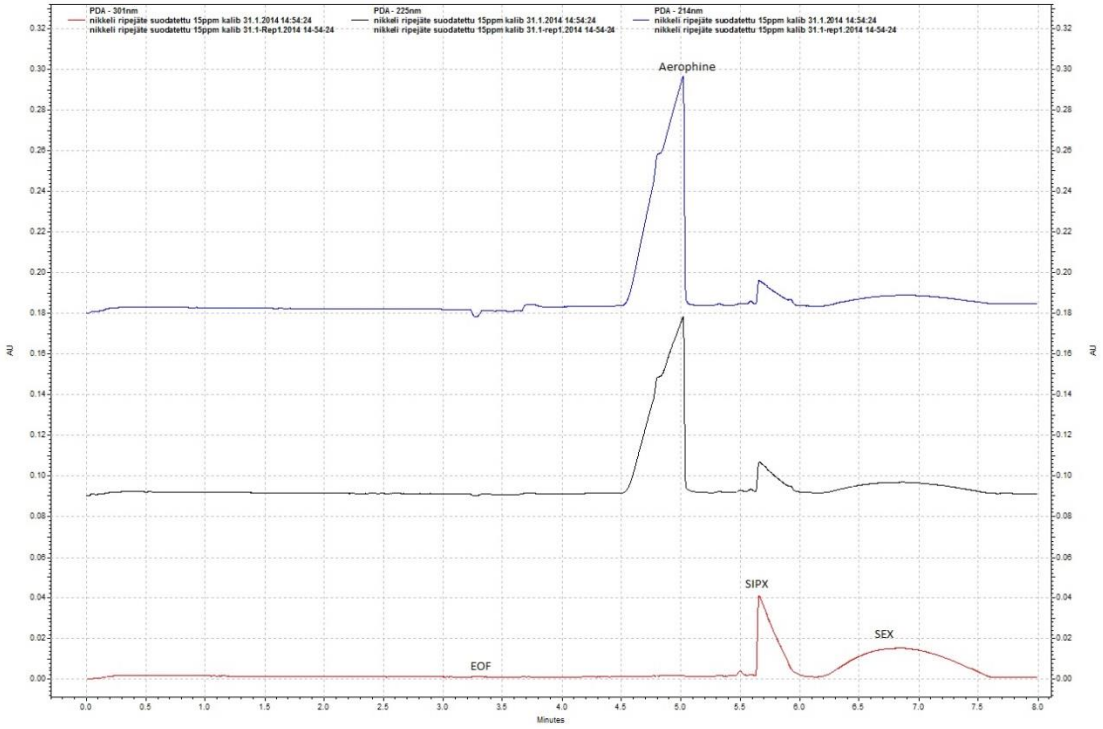

Figure 36 CE graph of nickel circulation tailings where 15 ppm of Aerophine, SIPX and SEX were added. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

Electropherograms of concentrator measurements

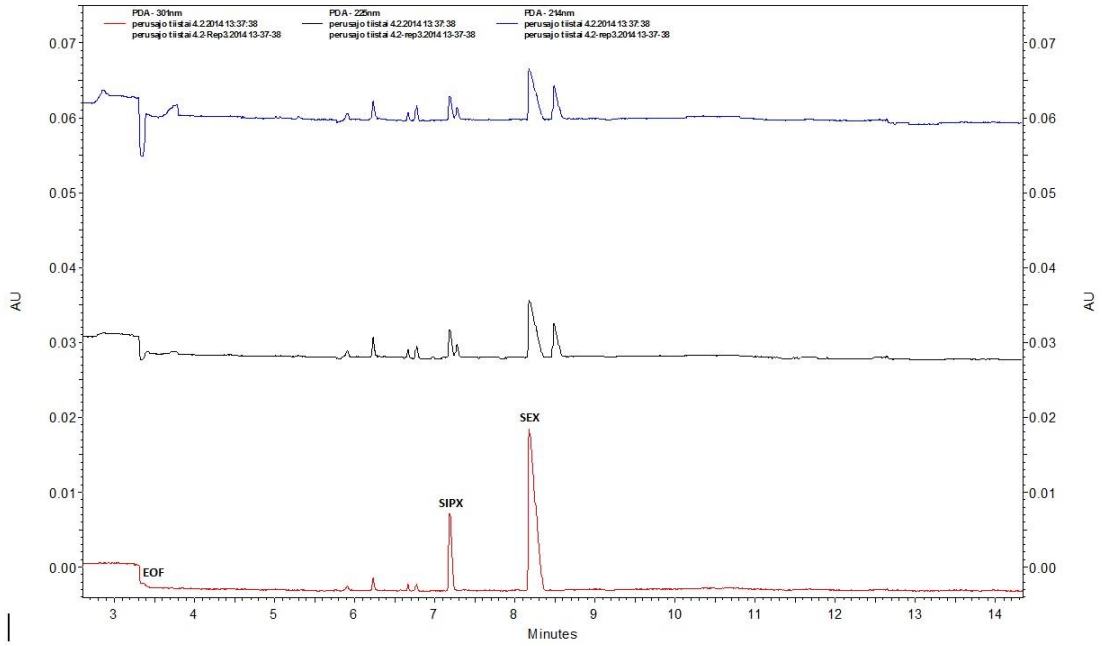

Figure 37 Electropherogram of nickel circulation tailings 4.2.2014 – 13:37. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

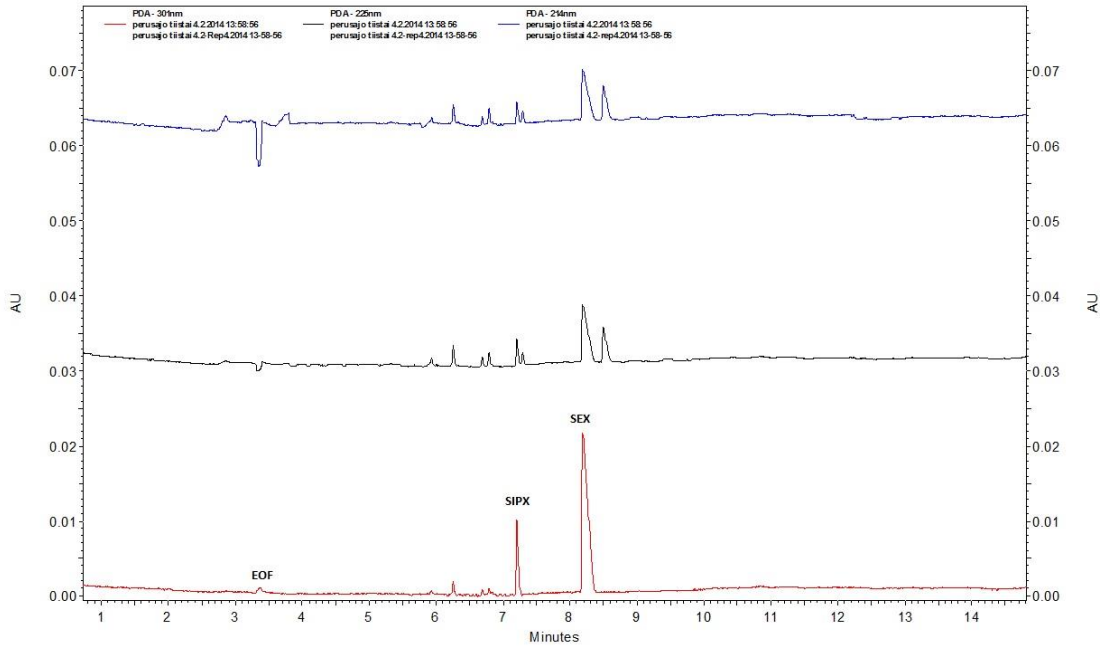

Figure 38 Electropherogram of nickel circulation tailings 4.2.2014 – 13:58. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

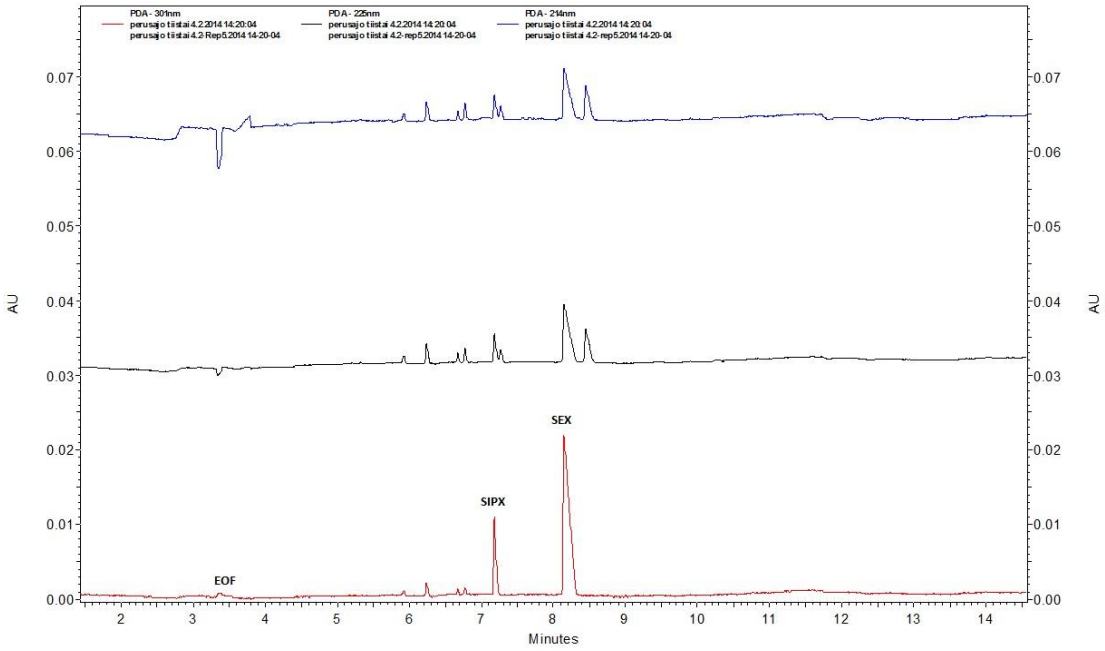

Figure 39 Electropherogram of nickel circulation tailings 4.2.2014 – 14:20. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

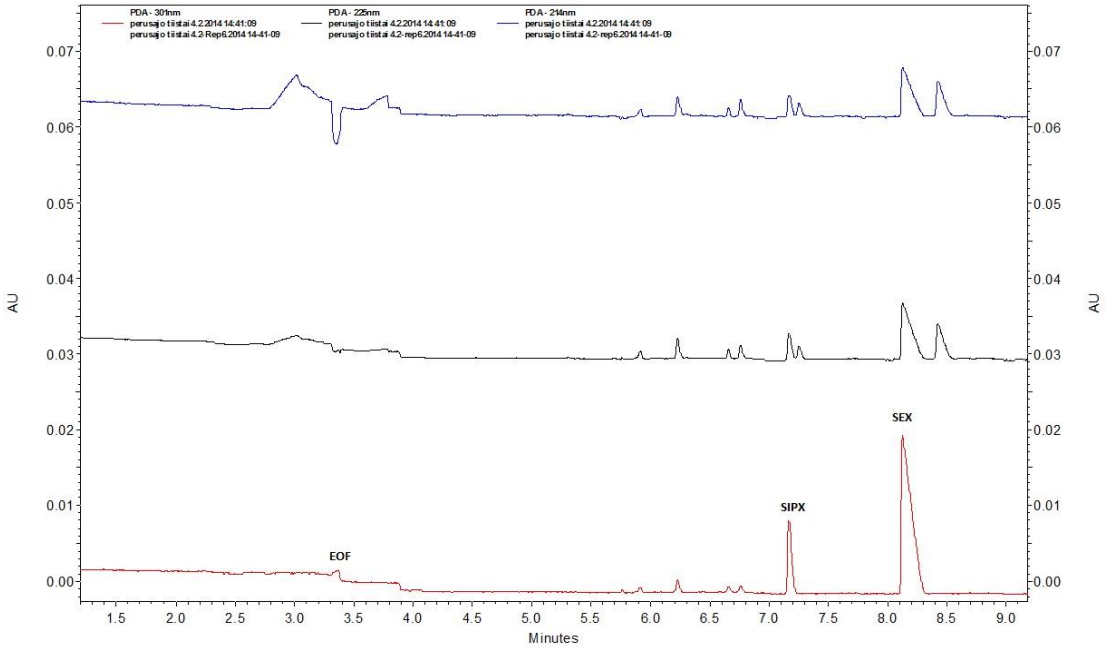

Figure 40 Electropherogram of nickel circulation tailings 4.2.2014 – 14:41. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

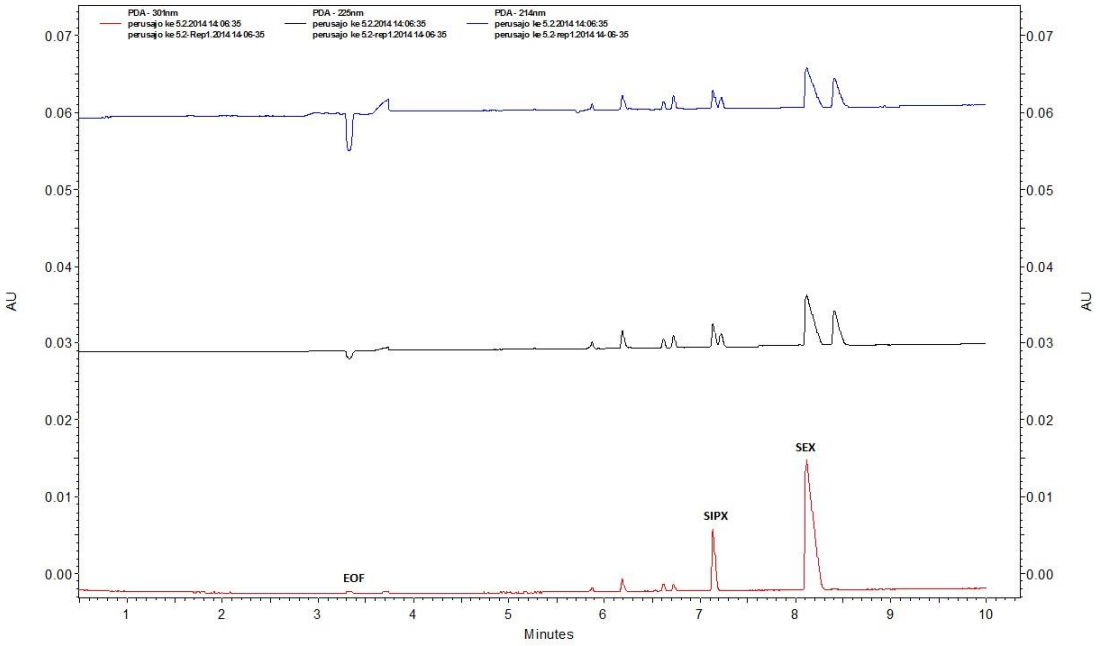

Figure 41 Electropherogram of nickel circulation tailings 5.2.2014 – 14:06. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

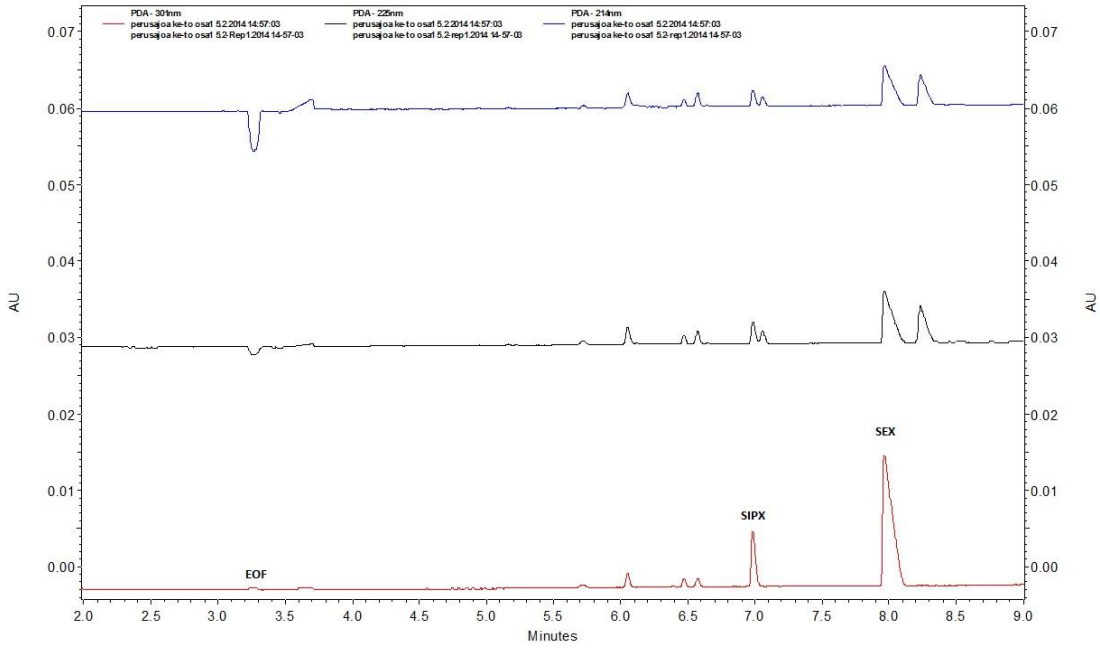

Figure 42 Electropherogram of nickel circulation tailings 5.2.2014 – 14:57. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

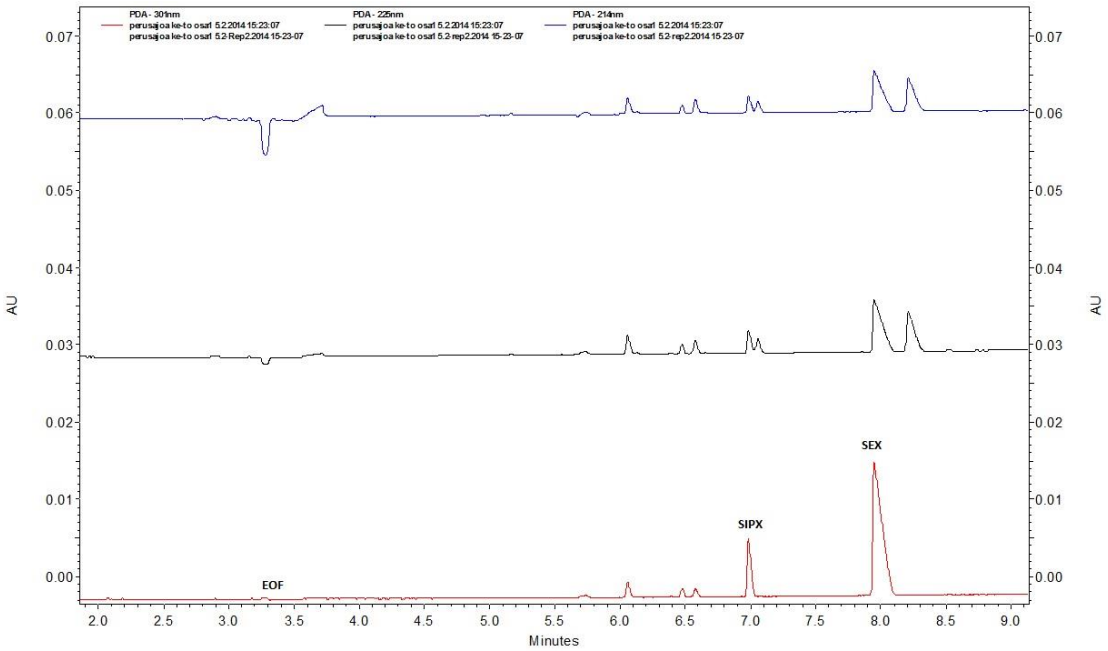

Figure 43 Electropherogram of nickel circulation tailings 5.2.2014 – 15:23. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

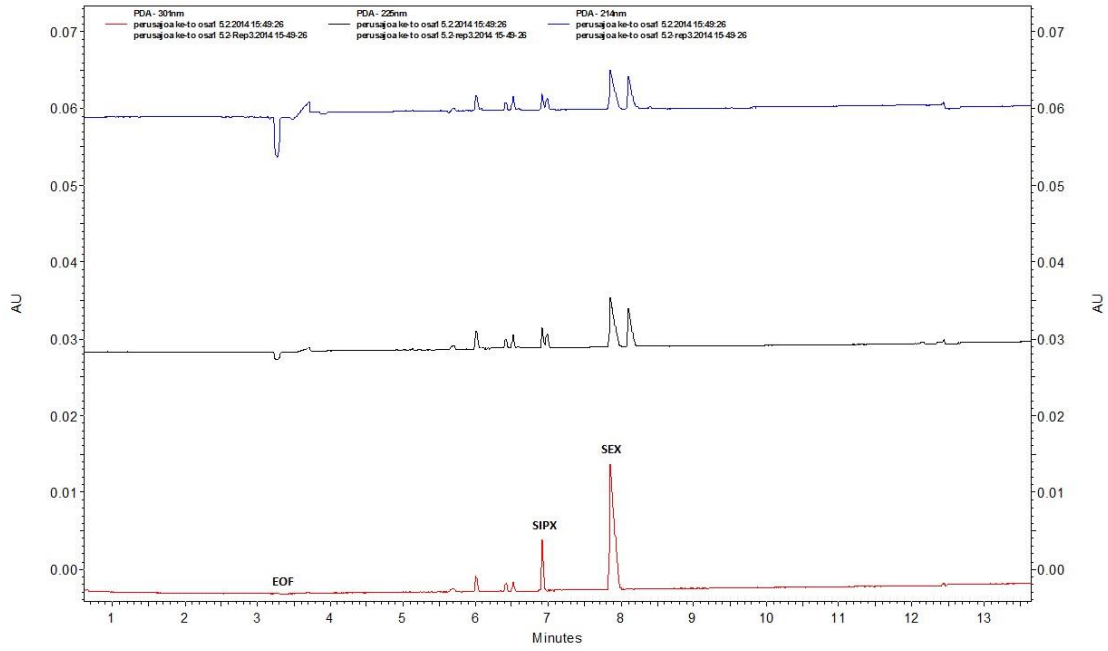

Figure 44 Electropherogram of nickel circulation tailings 5.2.2014 – 15:49. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

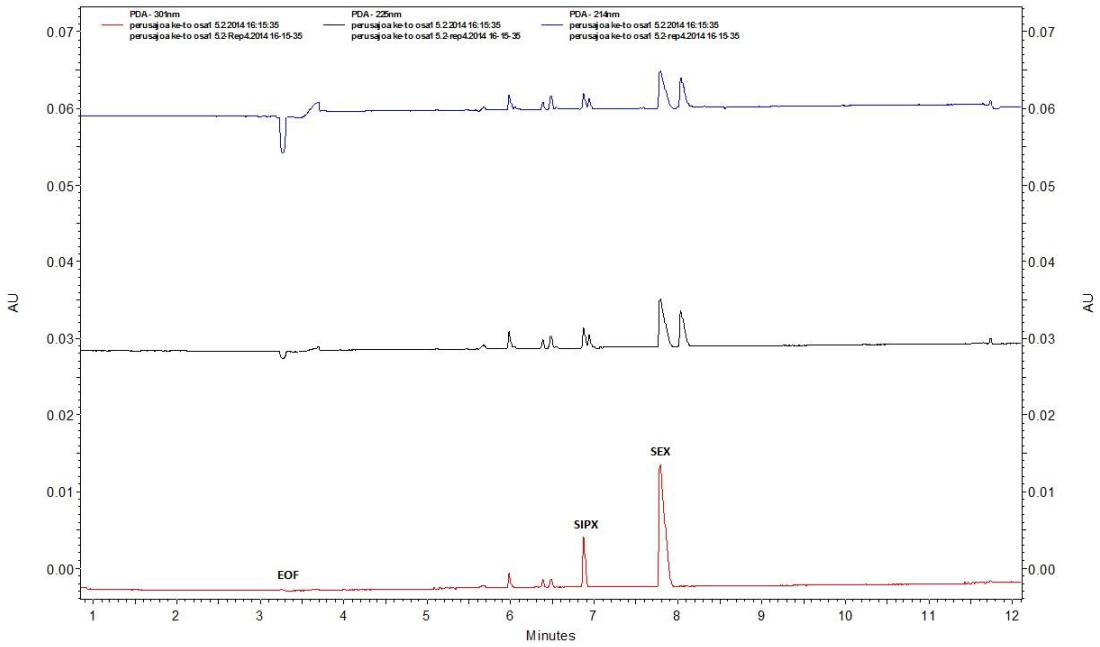

Figure 45 Electropherogram of nickel circulation tailings 5.2.2014 – 16:15. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

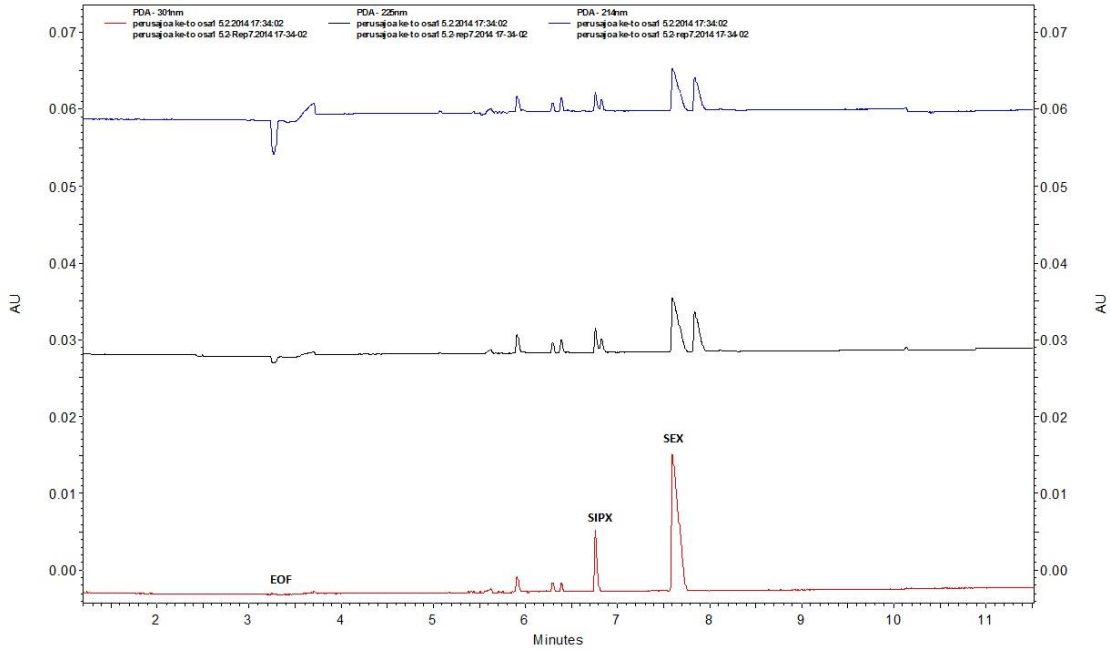

Figure 46 Electropherogram of nickel circulation tailings 5.2.2014 – 17:34. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

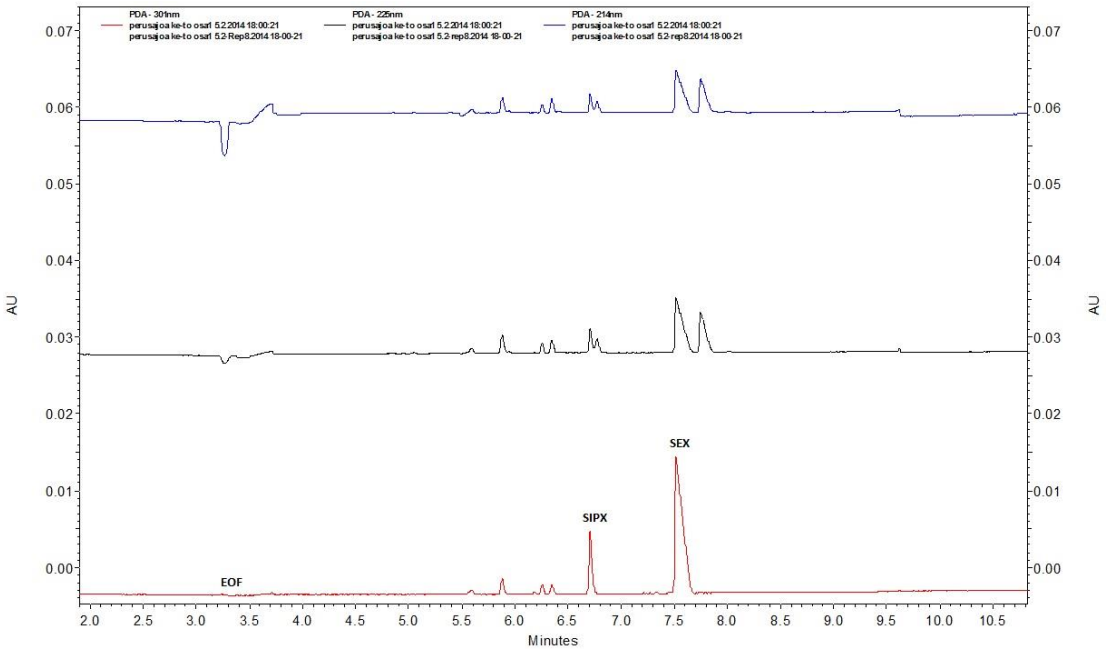

Figure 47 Electropherogram of nickel circulation tailings 5.2.2014 – 18:00. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

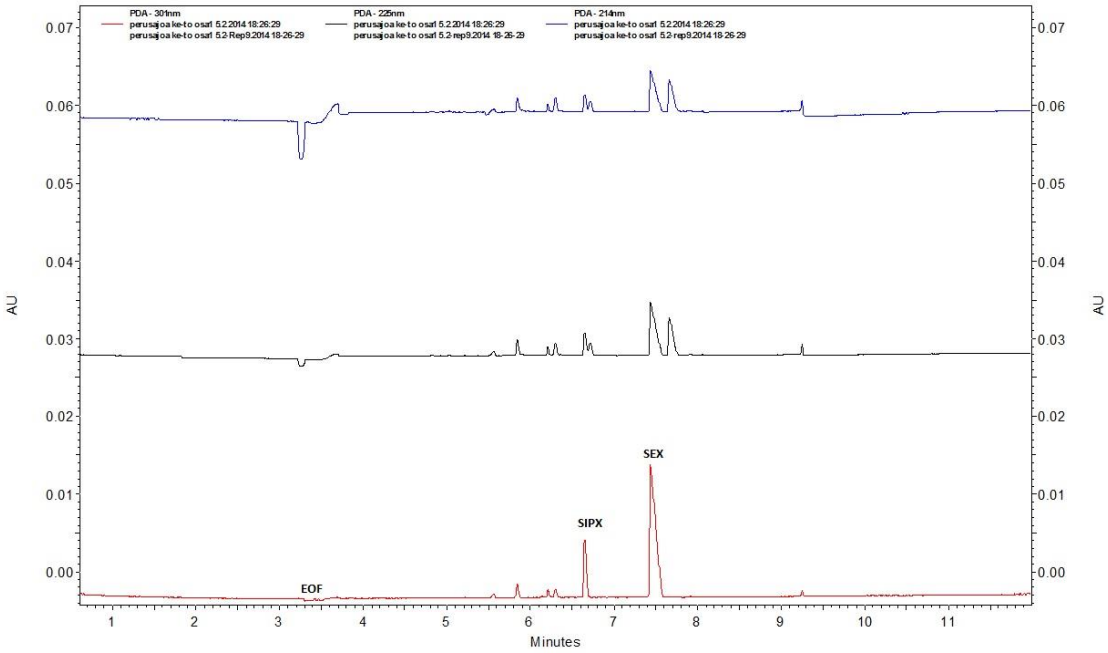

Figure 48 Electropherogram of nickel circulation tailings 5.2.2014 – 18:26. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

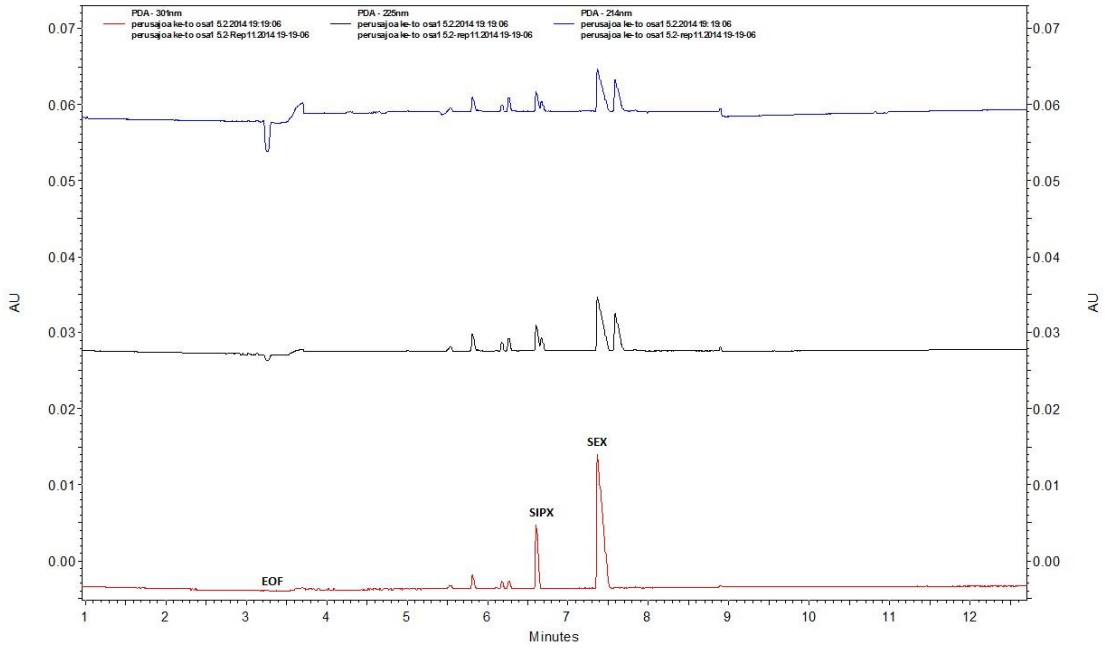

Figure 49 Electropherogram of nickel circulation tailings 5.2.2014 – 19:19. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

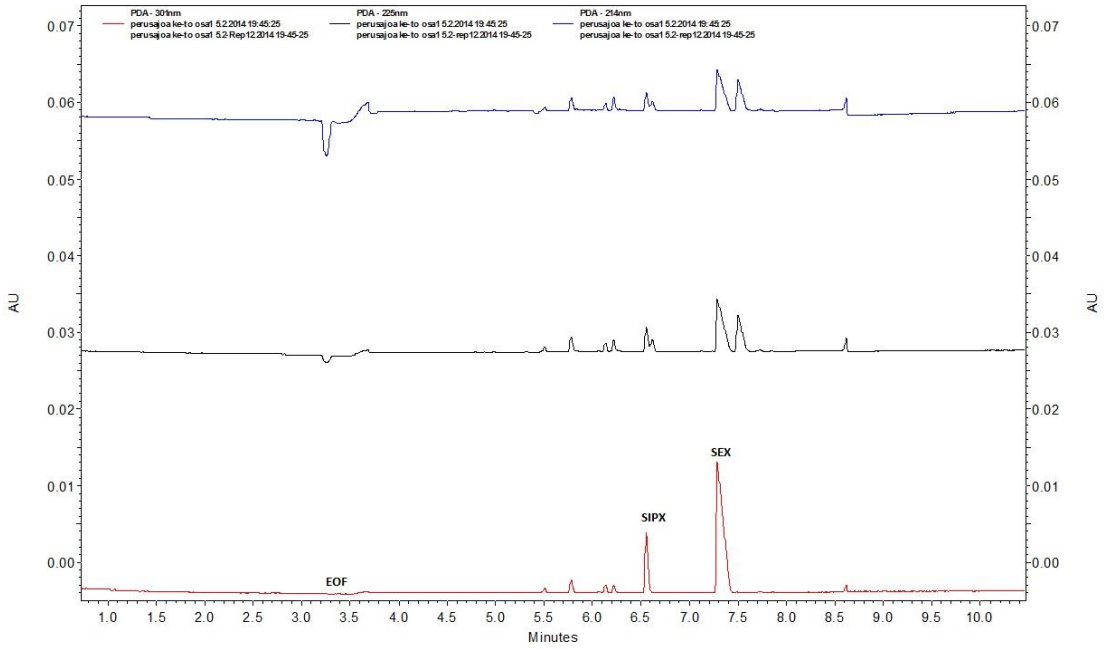

Figure 50 Electropherogram of nickel circulation tailings 5.2.2014 – 19:45. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

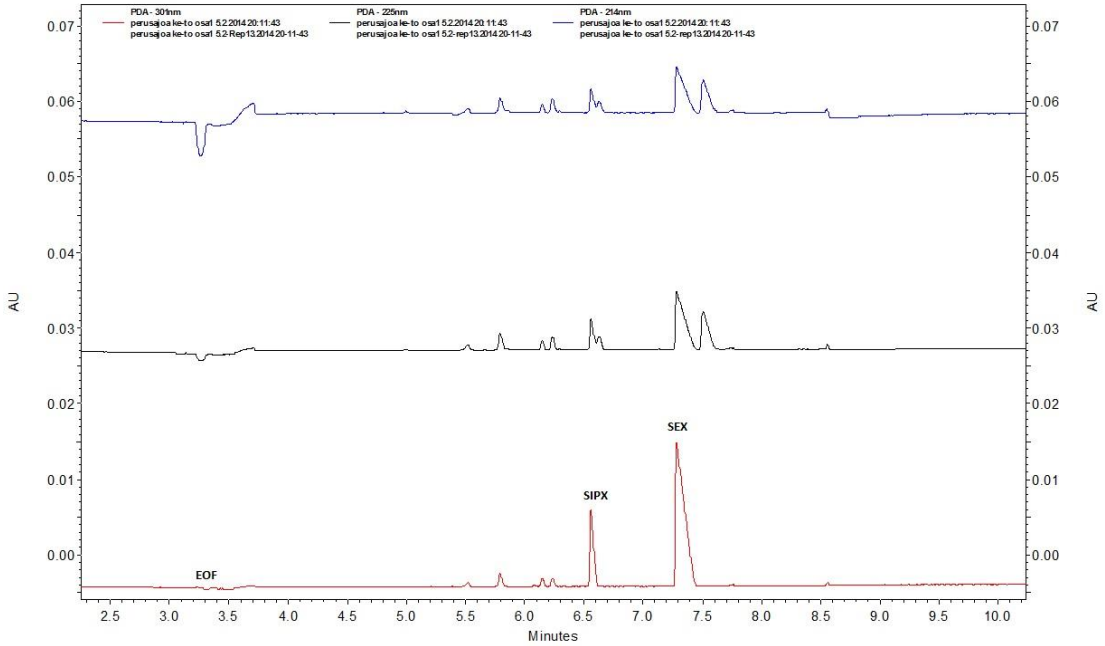

Figure 51 Electropherogram of nickel circulation tailings 5.2.2014 – 20:11. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

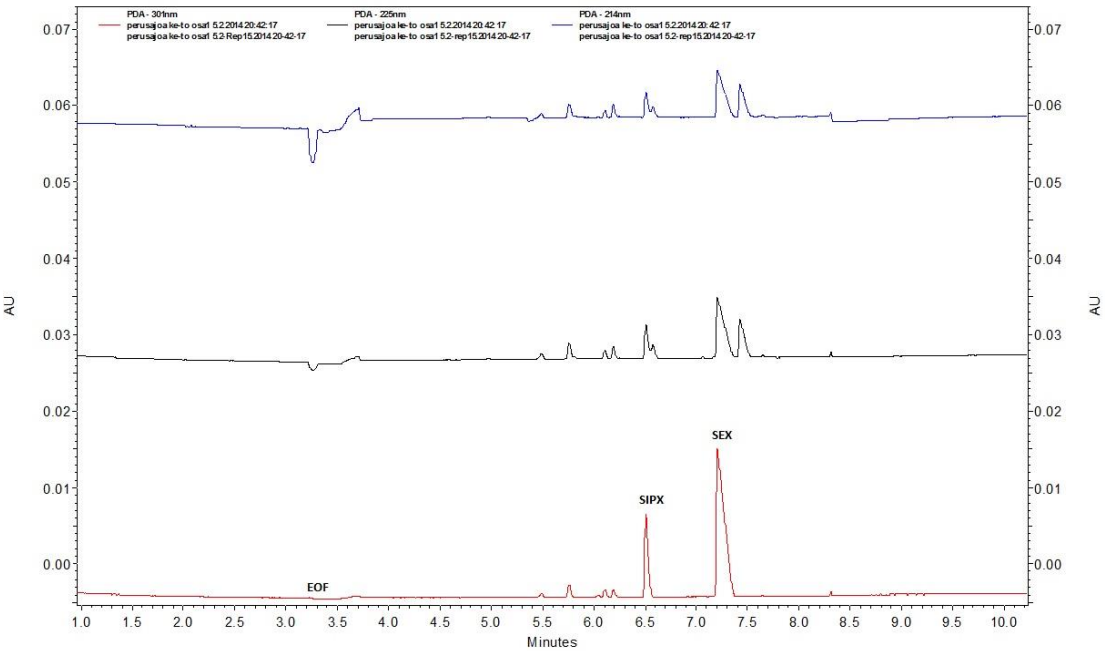

Figure 52 Electropherogram of nickel circulation tailings 5.2.2014 – 20:42. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

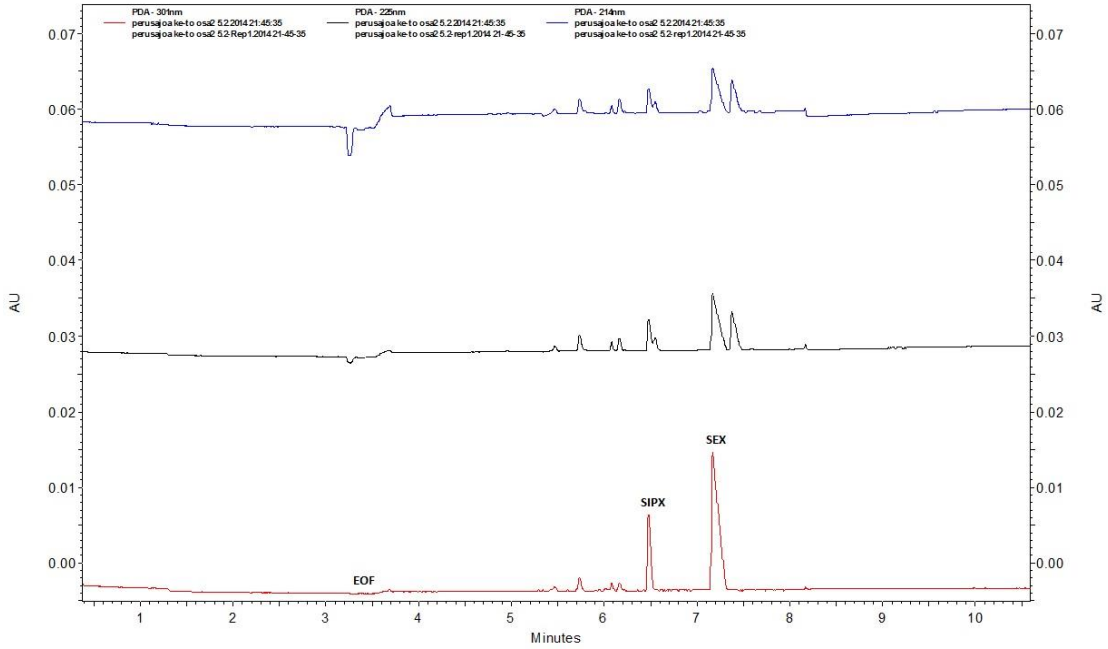

Figure 53 Electropherogram of nickel circulation tailings 5.2.2014 – 21:45. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

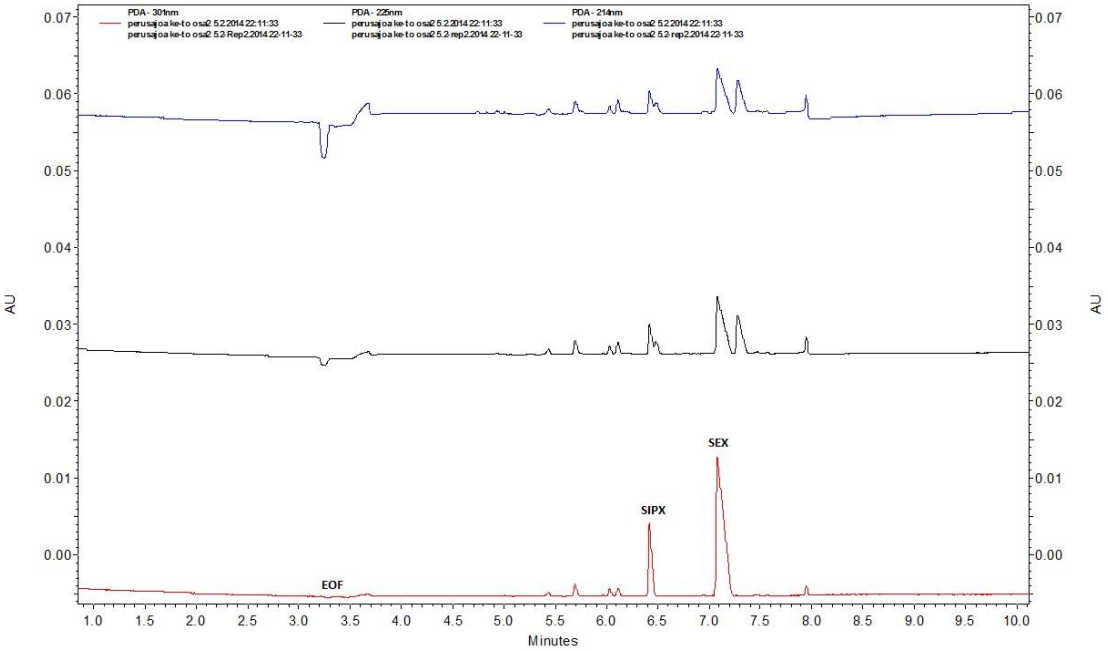

Figure 54 Electropherogram of nickel circulation tailings 5.2.2014 – 22:11. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

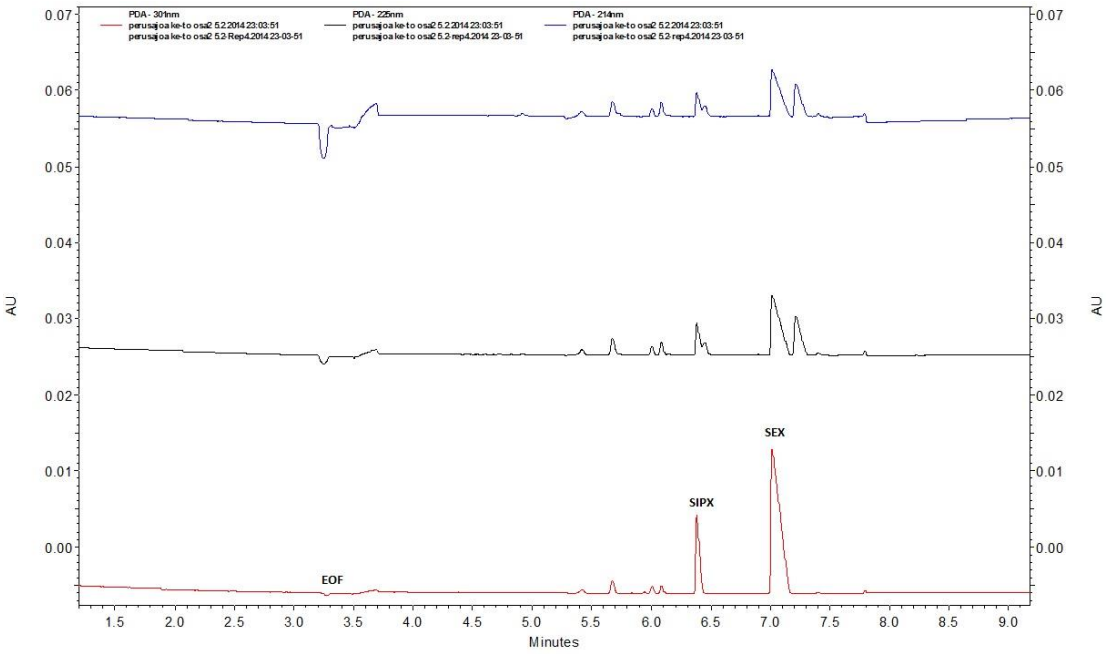

Figure 55 Electropherogram of nickel circulation tailings 5.2.2014 – 23:03. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

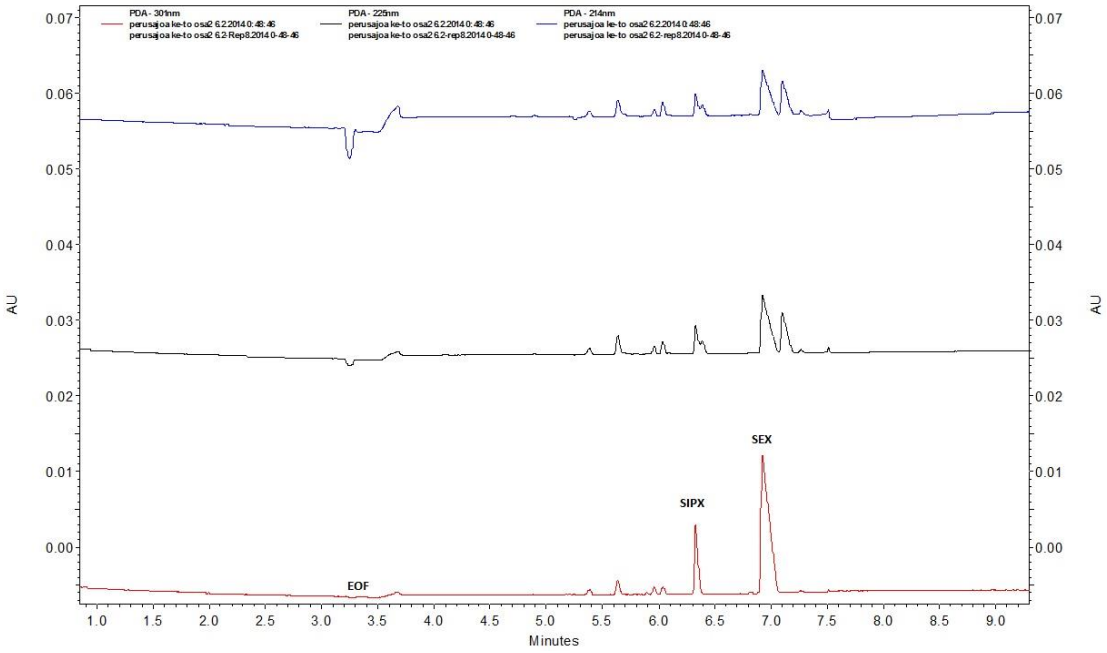

Figure 56 Electropherogram of nickel circulation tailings 6.2.2014 – 00:48. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

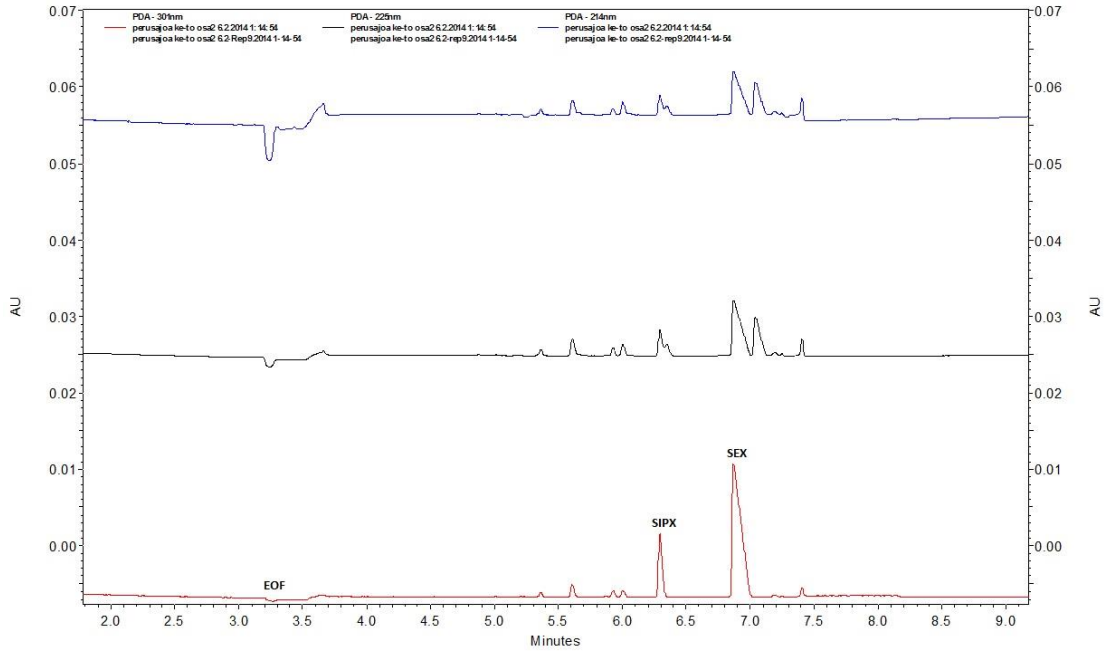

Figure 57 Electropherogram of nickel circulation tailings 6.2.2014 – 01:14. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

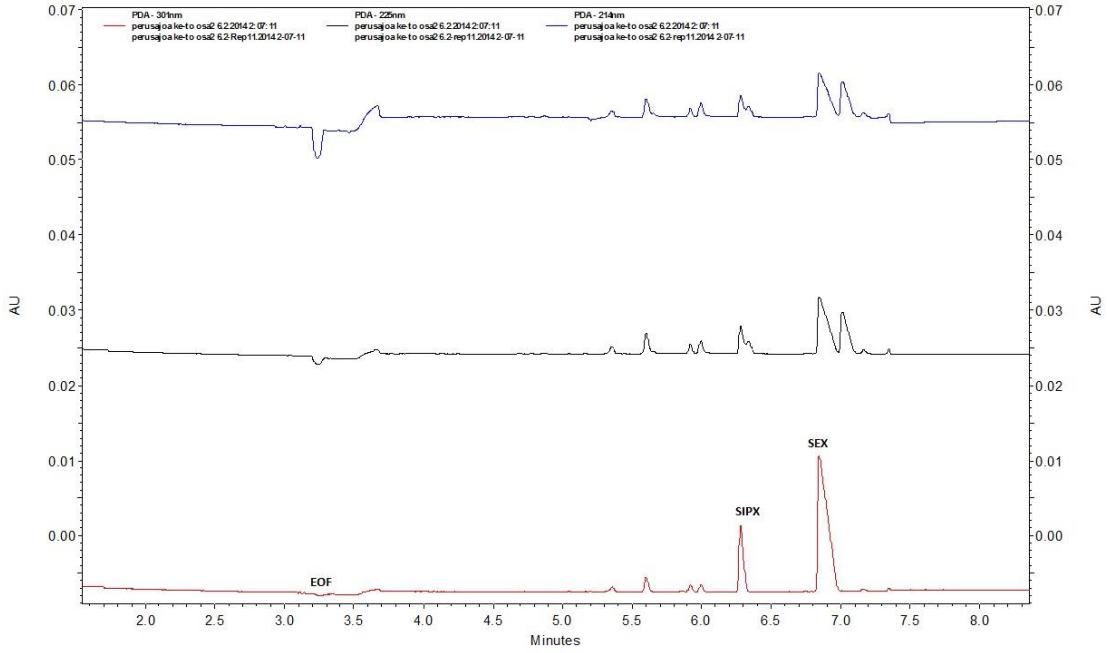

Figure 58 Electropherogram of nickel circulation tailings 6.2.2014 – 02:07. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

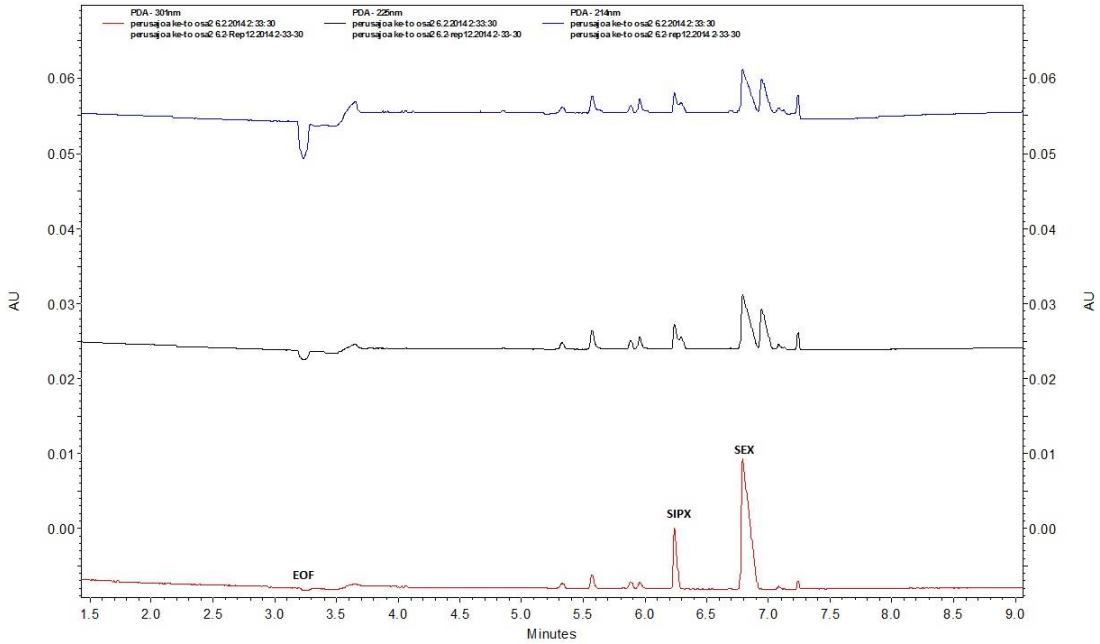

Figure 59 Electropherogram of nickel circulation tailings 6.2.2014 – 02:33. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

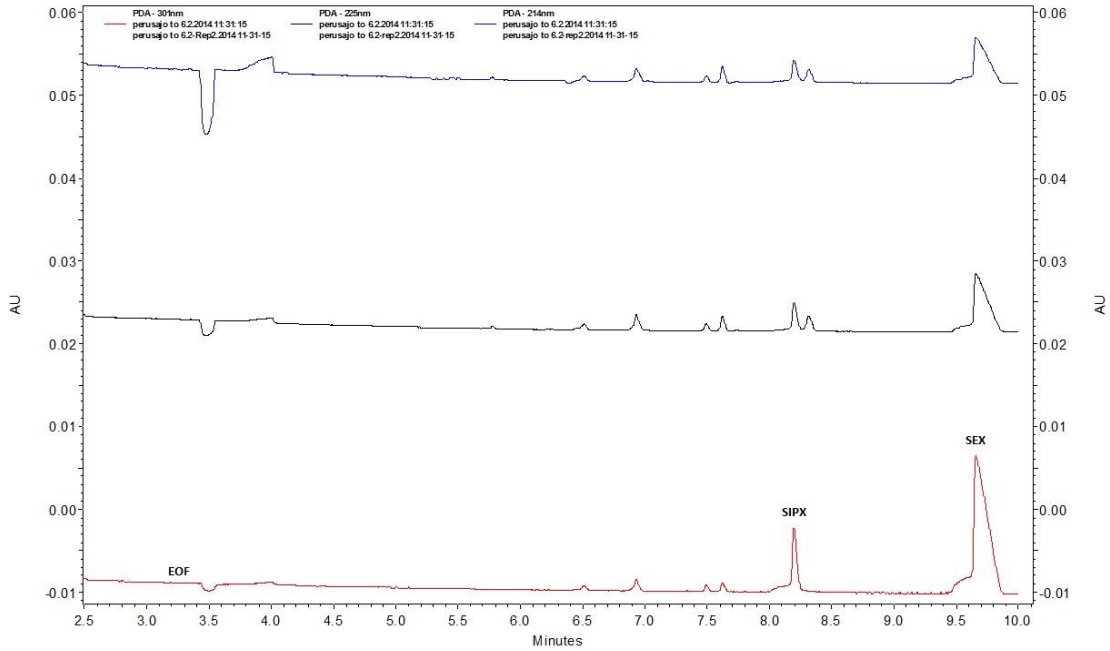

Figure 60 Electropherogram of nickel circulation tailings 6.2.2014 – 11:31. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

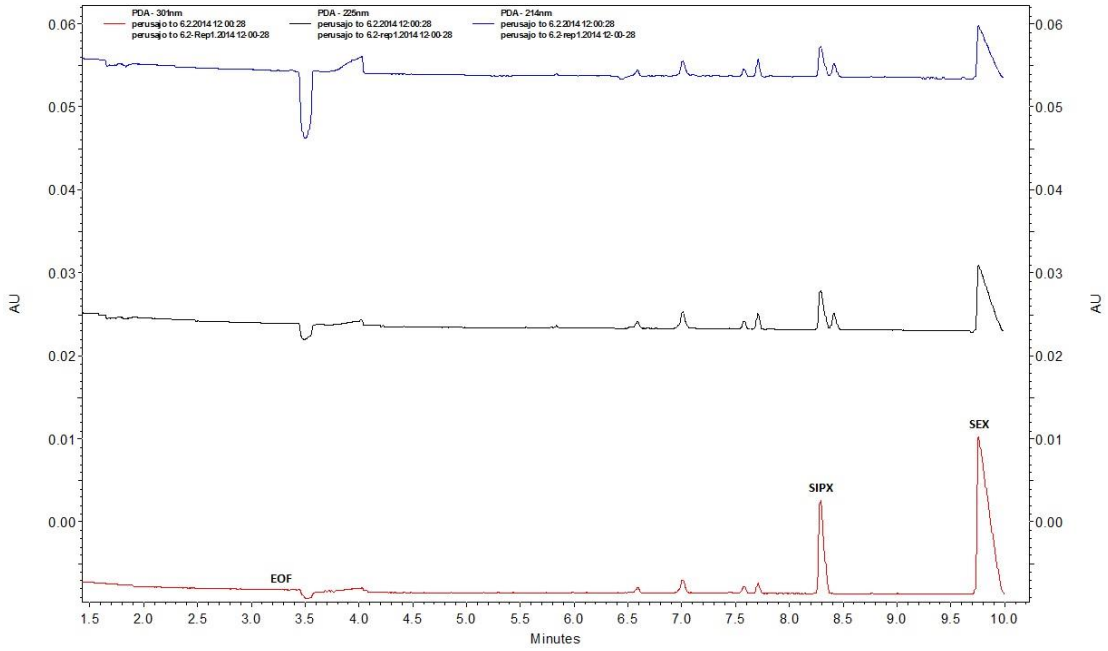

Figure 61 Electropherogram of nickel circulation tailings 6.2.2014 – 12:00. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

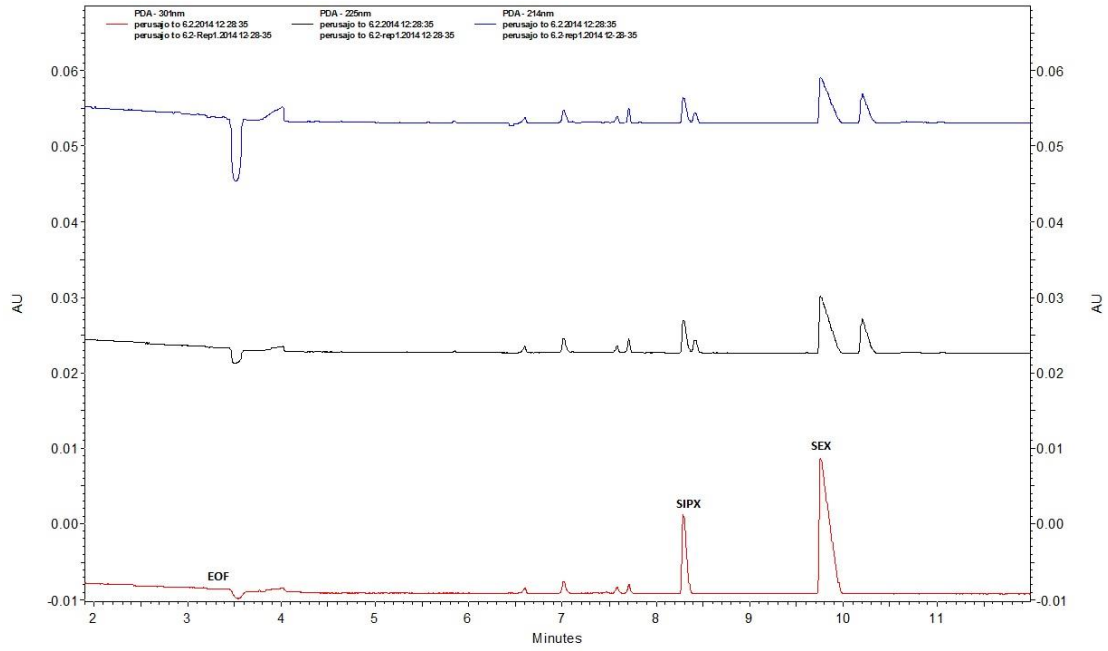

Figure 62 Electropherogram of nickel circulation tailings 6.2.2014 – 12:28. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

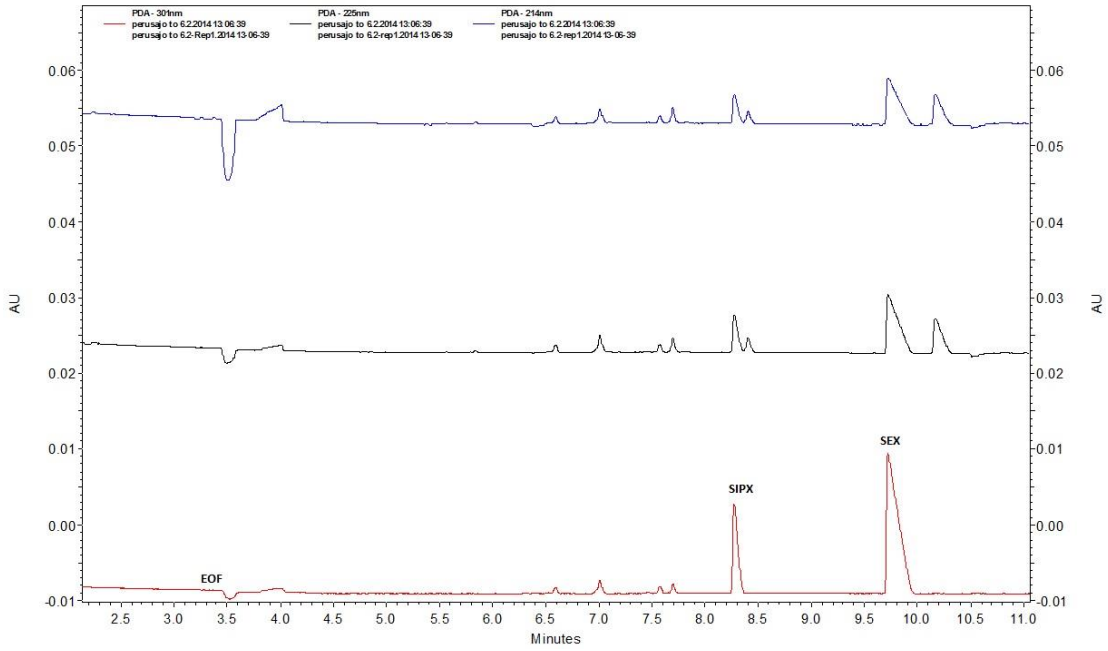

Figure 63 Electropherogram of nickel circulation tailings 6.2.2014 – 13:06. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

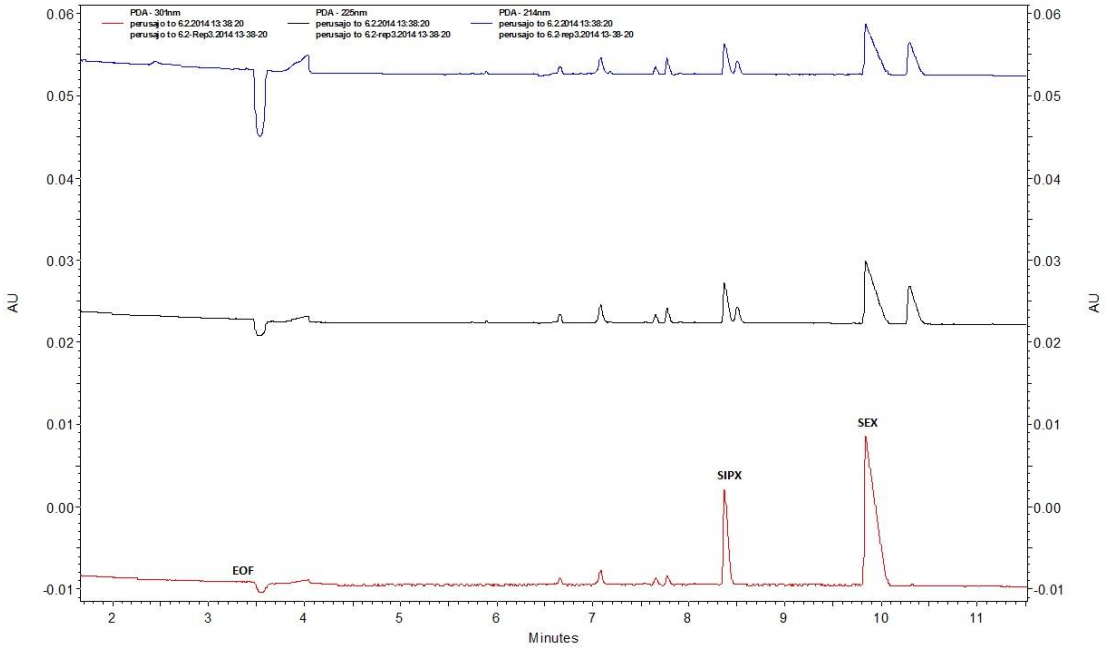

Figure 64 Electropherogram of nickel circulation tailings 6.2.2014 – 13:38. Applied wavelengths were 214 nm (blue/top line), 225 nm (black/mid line) and 301 nm (red/bottom line).

Measured SIPX and SEX migration time, peak area and concentration

Measurement time	Measurement date	SIPX migration time, min	SIPX peak area, Au*min	SIPX concentration, ppm	SEX migration time, min	SEX peak area, Au*min	SEX concentration, ppm
13:37	4.2.2014	7.19	24150	1.00	8.18	124483	2.96
13:58	4.2.2014	7.20	23960	0.99	8.19	123603	2.94
14:20	4.2.2014	7.18	24774	1.02	8.14	123966	2.95
14:41	4.2.2014	7.17	22199	0.92	8.13	121482	2.89
14:06	5.2.2014	7.14	18083	0.75	8.11	95666	2.27
14:57	5.2.2014	6.98	15148	0.63	7.97	82700	1.97
15:23	5.2.2014	6.99	15462	0.64	7.95	84064	2.00
15:49	5.2.2014	6.92	13463	0.56	7.85	76834	1.83
16:15	5.2.2014	6.87	12972	0.54	7.79	73477	1.75
17:34	5.2.2014	6.76	16219	0.67	7.60	89356	2.12
18:00	5.2.2014	6.71	16532	0.68	7.52	89567	2.13
18:26	5.2.2014	6.65	14942	0.62	7.44	82280	1.96
19:19	5.2.2014	6.61	17362	0.72	7.37	87918	2.09
19:45	5.2.2014	6.55	16000	0.66	7.29	81862	1.95
20:11	5.2.2014	6.56	22538	0.93	7.28	100373	2.39
20:42	5.2.2014	6.51	24551	1.01	7.20	102363	2.43
21:45	5.2.2014	6.48	22264	0.92	7.17	94309	2.24
22:11	5.2.2014	6.42	20790	0.86	7.08	89221	2.12
23:03	5.2.2014	6.38	22769	0.94	7.02	97141	2.31
0:48	6.2.2014	6.33	19309	0.80	6.92	89395	2.13
1:14	6.2.2014	6.29	17001	0.70	6.87	81033	1.93
2:07	6.2.2014	6.28	18325	0.76	6.85	86285	2.05
2:33	6.2.2014	6.24	16444	0.68	6.79	77997	1.85
11:31	6.2.2014	8.20	23767	0.98	9.66	136897	3.25
12:00	6.2.2014	8.29	35673	1.47	9.76	138806	3.30
12:28	6.2.2014	8.29	32481	1.34	9.76	127762	3.04
13:06	6.2.2014	8.28	37109	1.53	9.72	138839	3.30
13:38	6.2.2014	8.37	36685	1.52	9.84	136869	3.25

Table X Measured SIPX and SEX migration time, peak area and concentration