Methods for improving solvent properties

ABSTRACT

In hydrometallurgical processes, the separation of nickel and cobalt is challenging. Cyanex 272 dialkyl phosphinic acid is generally used to separate these elements. The most effective separation requires that the reaction mixture be as pure as possible from various interferences such as carboxylic acids. This thesis investigates various possibilities for removing carboxylic acids from the extraction mixture.

Possibility of utilizing different pH isotherms and different water solubilities of carboxylic acids and Cyanex 272 for separation was investigated. Normal phase chromatography was attempted with one minute fractioning and finally molecular catcher was tested. Separation of extractants in these experiments, with these parameters failed.

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

<u>EXPERIMENTAL</u>

LIST OF ABBREVIATIONS

α — Separation factor in chromatography

A — Aqueous

(A336)(CA-12) — [tricaprylmethylammonium][sec-octylphenoxy acetate]

Acorga M5640 — 5-nonylsalicylaldoxime

Acorga P1 — 5-nonyl-salicylaldoxime

ATPS — Aqueous two-phase system

BTMBBA — Bis(2,4,4-trimethylpentyl) phosphinic acid

Cyanex 272 — Bis(2,4,4-trimethylpentyl)phosphinic acid

Cyanex 471 — tri-isobutyl phosphine sulphide

DE2HPA — Di-2-ethylhexyl phoshoric acid

E — Extraction factor

GC-FID — Gas chromatography - Flame Ionization Detector

GC-MS — Gas chromatography – Mass Spectrometry

HPLC — High performance liquid chromatography

ICP-OES — Inductive coupling plasma - Optical emission spectroscopy

IL — Ionic liquid

LCST — Lower critical solution temperature

LIX-622	5-dodecylsalicylaldoxime with tridecanol
LIX-860	5-dodecylsalicylaldoxime
k	Retention factor
MOAH	Mineral oil aromatic hydrocarbon
MOSH	Mineral oil saturated hydrocarbon
N	Plate number
NNH	Norilsk Nickel Harjavalta Oy
NPC	Normal phase liquid chromatography
O	Organic
OPPA	Di-p-octylphenyl phosphoric acid
PTMBBA	(2,4,4-trimethylpentyl) phosphonic acid
RPLC	Reverse phase liquid chromatography
SEC	Size exclusion chromatography
t	Retention time
TBP	tri-n-nbutyl phosphate
TOC	Total Organic Carbon
UCST	Upper critical solution temperature
Versatic 10	Neodecanoic acid
W	Peak width

1 INTRODUCTION

The chemical separation of nickel and cobalt is problematic as their chemical properties are similar. However, liquid-liquid extraction provides a method that enables cobalt-nickel separation. Commonly dialkylphosphinic acid Cyanex 272 is used.[1]

The organic mixture circulates in the process for decades, allowing it to accumulate impurities from the process. W.A. Rickelton, A.J. Robertson and J.H Hillhouse have found out in their article "The significanse of diluent oxidation in cobalt-nickel separation" that cobalt can also oxidize solvent. Oxidation products include e.g. carboxylic acids, which have been shown to impair the cobalt-nickel separation factor.[2]

$$RCH_3 \rightarrow RCH_2OOH \rightarrow RCH_2OH \rightarrow RCOH \rightarrow RCO_2H,$$
$$Alkane \rightarrow Hydroperoxide \rightarrow Alcohol \rightarrow Aldehyde \rightarrow Acid \tag{1}$$
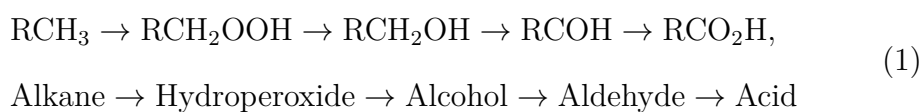
Reaction 1 can be inhibited by adding substance which reacts with the hydroperoxide radical.[2]

Nornickel Harjavalta (NNH) has made it possible to map out different ways in which such an organic mixture could be purified and thus restore its separation efficiency of cobalt and nickel to its original level.

Nornickel Harjavalta is a factory in Harjavalta, Finland which is part of the MMC Norilsk Nickel Group. NNH produces metallic nickel, nickel chemicals, and cobalt chemicals.[3]

2 LIQUID-LIQUID EXTRACTION

As early as 1872, Berthelot and Jungfleisch formulated the theory of the distribution of metals between two immiscible solutions. Thereafter, the liquid-liquid extraction has advanced remarkably and is now applied as part of a number of hydrometallurgical processes.[4] Today, there are more than 40 different kinds of extracts, of which about a dozen are in everyday use.[5]

2.1 Theory

The extraction process can be described by a simple equation 2

$$M + \overline{E} \rightleftharpoons \overline{ME}, \tag{2}$$

wherein the M metal ion is transferred from the aqueous phase E to the organic phase described by the length marker. Almost all processes are based on the manipulation of this equilibrium reaction, whereby by changing the extractant and the aqueous phase composition, the metals can be transferred between the aqueous phase and the organic phase as desired.
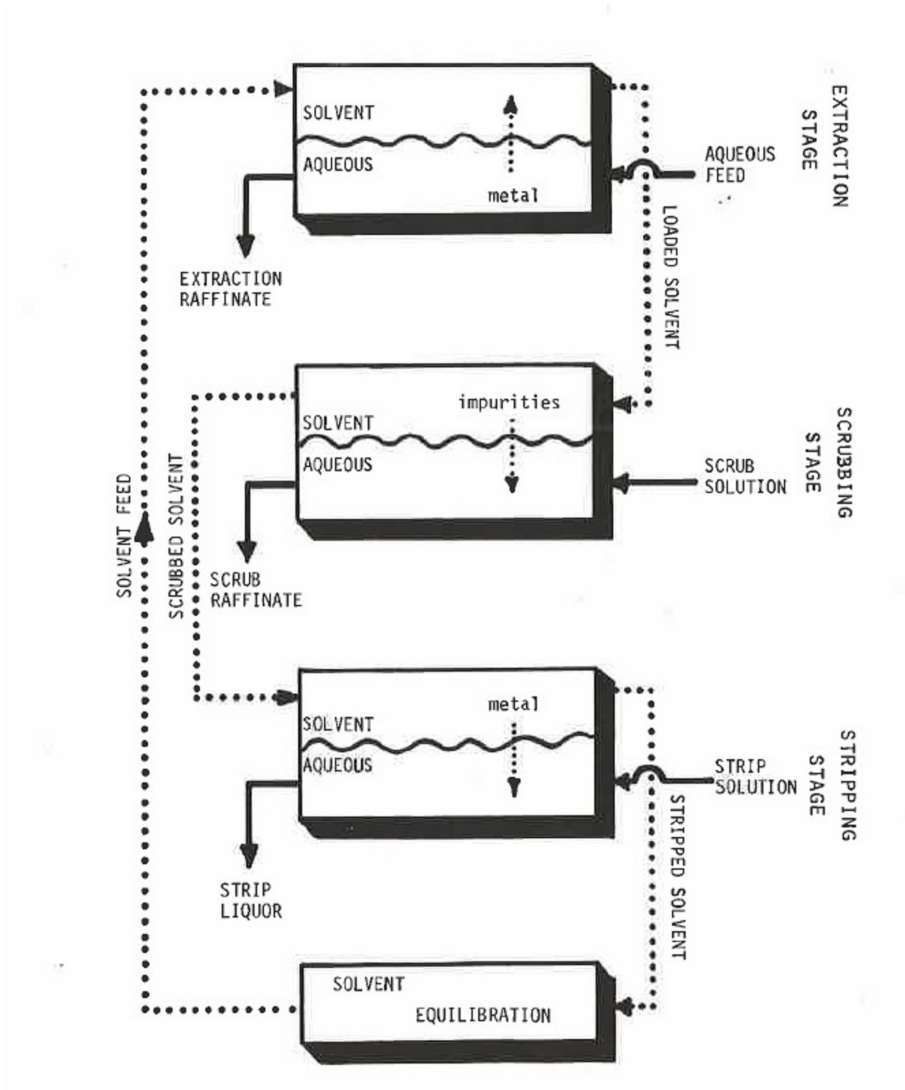
Figure 1: The practical process of solvent extraction.[4]

In the figure, 1 at its simplest is the extraction process. The metal-containing aqueous phase is mixed with the organic phase, the metal-loaded extract mixture is washed away with impurities, after which the metal is transferred back to the aqueous phase. The organic phase can then be directed back to the extraction step.[4 p.2-3]

2.1.1 Extraction coefficient

The extraction factor E depicts how well the metal is extracted from the solution. It is the ratio of metal concentrations present in different phases and is influenced by, for example, water and organic phase ratio, temperature, concentrations, pH, and metal complexation in phases. With the help of the extraction factor, the separation factor SF can be calculated with equation 3

$$\mathrm{SF} = \frac{\mathrm{E}_A}{\mathrm{E}_B}, \tag{3}$$

wherein subcripts A and B refer to extraction factors for different metals. When the value of the resolution factor is greater than 1, it indicates that the metals can be separated, but not yet how easily, or how many contacts are required for separation.[4 p.34]

2.1.2 Extractant concentration

The extraction factor increases as the concentration of the extractant increases as long as the concentration of the metals does not increase too high. The metal distribution curve shifts to a lower pH range.[4 p.26-37]

2.1.3   pH

pH value decreases with all the exctractants that release H^+ whereby a larger amount of the extracted metal leads to a lower pH value, which in turn reduces the extraction of the metals. This equilibrium reaction is represented by the equation 4

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{MA_n} + nH^+. \tag{4}$$

With balanced extractant concentration E increases as the pH increases, assuming that there are no reactions in the aqueous phase that change the conditions in a direction less favorable to the extraction conditions. The pH value's change also depends on the oxidation rate of the metal and the type of extractant used. If the metal binds to more than one hydrogen or if the metal forms a complex with more than one extractant, more hydrogen is released and the pH changes more in relation to the concentration of the extracted metal. The pH of the system affects both the metal and the extractant. The metal can be hydrolyzed at high pH or form an unrefined complex at low pH. The extractant can be protonated at low pH so that it cannot form a complex with the metal. pH is probably the most important parameter when designing extraction reactions.[4 p.38-42]

2.1.4   Aqueous phase composition

It can generally be said that if the metal-aqueous phase complex is more stable than the metal and the extractant complex, no extraction occurs. This can also be utilized to reduce the amount of anion forming the complex in the aqueous phase, thereby enhancing extraction.[4 p.42]

2.1.5 Metal ion concentration

Metal ion concentration effect is well illustrated by the equation of free extractant 5

$$(HA)_F = (HA)_T - (M \cdot nA), \tag{5}$$

wherein HA_T is the total concentration of the extractant and $(M \cdot nA)$ represents the metal bound to extractant. As a result, the increase in the concentration of the metal ion is directly proportional to amount of extractable metal. However, after the organic is phase 100 % loaded or near to 100%, increasing the metal ion is no longer increasing the amount of organic metal, it remains constant. On the other hand, the increase in the amount of metal in the aqueous phase results in a lower E value.[4 p.45]

2.1.6 Extractant loading

This parameter is essential when planning the extraction process. Generally speaking, it is not advisable to operate with a 100 % loading level because of the increased viscosity of the solution can make it difficult to handle, the desired metal can exit the system with the raffinate, and metals that are not wanted to be extracted, might be extracted. The maximum loading rate depends, among other things, on the amount of extractant and the solubility of the metal complex. The solubility is affected by the solvent used and the modifier. Extraction of the metal does not necessarily increase linearly by only adding the extractant, because the extractant molecules can react with each other to form dimers or polymers. The theoretical 100% charge can be lowered by assuming that all the metal reacts with all the available extractant, but in practice it rarely happens, especially at higher concentrations.[4 p.46-47]

2.1.7 Calculations and values

The previously mentioned SF value can be used to compare the separation of metals as a function of pH to describe the results of selectivity tests. $pH_{1/2}$-values can be used to compare the extraction of metals from different extracts in relation to pH and salt concentration. In addition, the acidity of the different extracts can be compared.

Extraction can be described by many different graphs and distributions, in this thesis a graph is used in which SF values are plotted as a function of pH values. This gives us a good opinion of how well the solutions of the different tests differ at different pH values.

2.1.8 Requirements of extractant

The criteria for selecting a good extract are listed in Gordon M. Ritcey's book Solvent extraction, principles and application to process metallurgy. A good extractant choice should be cheap, has low solubility to aqueous phase, is chemically stable, will not form emulsion, is able to load a lot of metal, relinquishes easily loaded metal, non-flammable, non-volatile and non-toxic, easily soluble in aliphatic and aromatic solvents and reacts kinetically in a desirable manner.[44 p.70]

2.1.9 Diluent and diluent properties

The organic mixture used in the extraction generally consists of an extractant, a possible modifier and a solvent. The solvent may be polar or nonpolar. Generally speaking, in the more polar solvent, less polymerization of the

extractant occurs. The solvent should be readily available, cheap and meet the chemical and safety requirements set by the extraction process. The flash point of the solvent should be as high as possible and the evaporation rate as low as possible. In regards to solvent density, it should be taken into account, that the density of the organic mixture is not too close to the density of the aqueous phase, thus slowing the phase separation. The loading of metals may increase the viscosity of the solvent, whereby the extraction must be operated at a higher temperature. The potential for interaction with the extractant must be taken into account in the polarity of the solvent, this can lead to reduced leaching stability.[4 p.186-197] Increasing the dielectric constant often weakens metal extraction.[6,7] In the solvent, the aliphatic moiety achieves good reaction kinetics, but it is good to have an aromatic portion of reducing the extractant loss to the aqueous phase.[8] There is no need for a solvent, but in the solutions used in this work, the solvent is always present in 75 - 98 w-% of the organic mixture.

2.1.10   3-phase system and modifiers

The 3-phase system is generated when the solubility of the metal extract agent in the polar hydrocarbon solvent is exceeded. One of the organic phases consists almost entirely of the solvent. In industry, 3-phase systems are generally avoided, but in this thesis, in one experiment, it is intentionally created.[4] Modifiers are used to improve phase separation, as well as to improve the solubility of the metal complexes, i.e. to prevent emulsion and 3-phase system. Modifiers have also been found to weaken, for example, the selectivity of Ni/Co in the use of Cyanex 272, probably because the modifier interacted with the extractant which reduces the extractant for cobalt extraction.[4 p.215-218]

2.1.11 Crud

In many liquid-liquid extraction processes, one of the problems is the multiphase emulsion, crud, formed in the process. Crud formation is a complex process, that can be formed by organic, water and solid phases as well as air. The formation of crud is positively influenced by e.g. purity of the organic phase extractant and solvent relative to other hydrocarbons, for example kerosene often contains unsaturated hydrocarbons. In addition, small particles may have air adsorbed, which can lead to local specific gravity reduction and induce crud formation.[9]

2.2 Extractants

Different types of extractives are listed in table 1

Table 1: Solvent extraction reagents[5]

Class of extractant	Type	Examples	Manufacturers	Commercial uses
Acid extractants	Carboxylic acids	Naphthenic acids, Versatic acids	Shell Chemical Co.	Copper/nickel separation, nickel extraction, yttrium recovery
	Alkyl phosphoric acids	Dialkyl phosphoric acids and sulphur analogues	Daihachi Chemical Industry Co Ltd (DP-8R, DP-10R, TR-83, MSP-8); Bayer AG (BaySolvex D2EHPA pure); Albright & Wilson Americas (DEHPA).	Uranium extraction, rare earth extraction, cobalt/nickel separation, zinc extraction, etc.
	Alkylphosphonic acids	2-ethylhexyl phosphonic acid 2-ethylhexyl ester and sulphur analogues	Daihachi Chemical Industry Co Ltd (PC-88A); Albright & Wilson Americas (Ionquest 801), Tianjin Beichen, China (P507).	Cobalt/nickel separation, rare earth separation
	Alkyl phosphinic acids	Dialkyl phosphinic acids and sulphur analogues	Cytec Inc. (CYANEX 272, 302 and 301); Daihachi Chemical Industry Co Ltd (PIA-8)	Cobalt/nickel separation, zinc and iron extraction, rare earth separation
	Aryl sulphonic acids	Dinonyl naphthalene sulphonic acid	King Industries Inc. (Synex 1051)	Magnesium extraction
Acid chelating extractants	Hydroxyoximes	Alpha alkaryl hydroxyoximes, beta alkaryl hydroxyoximes	Cognis Inc. (LIX reagents); Cytec Inc. (Acorga reagents)	Copper extraction, nickel extraction
	Beta diketones	LIX 54	Cognis Inc.	Copper extraction from ammoniacal solution
	Hydroxamic acids	LIX 1104	Cognis Inc.	Proposed for nuclear fuel reprocessing, iron extraction and As, Sb and Bi extraction from copper tankhouse electrolytes
Basic extractants	Primary amines	Primene JMT, Primene 81R	Rohm & Haas.	No known commercial use
	Secondary amines	LA-1, LA-2.	Rohm & Haas.	Uranium extraction, proposed for vanadium and tungsten extraction
	Tertiary amines	Various Alamines, in particular Alamine 336.	Cognis Inc.	Uranium extraction, cobalt extraction from chloride media, tungsten extraction, vanadium extraction, etc.
	Quaternary amines	Aliquat 336,	Cognis Inc.	Vanadium extraction, other possible uses for chromium, tungsten, uranium, etc.
	Mono N-substituted amide			Iridium separation from rhodium
	Trialkyl guanidine	LIX 79	Cognis Inc.	Gold extraction from cyanide solution
Solvating extractants and chelating non-ionic extractants	Phosphoric, phosphonic and phosphinic acid esters and thio analogues	TBP, DBBP, TOPO, CYANEX 921, CYANEX 923, CYANEX 471X.	Union Carbide, Albright & Wilson, Daihachi Chemical Industry Co Ltd, Cytec Inc.	Refining of U_3O_8, nuclear fuel reprocessing, Fe extraction, Zr/Hf separation, Nb/Ta separation, rare earth separation, gold extraction
	Various alcohols, ketones, esters, ethers, etc.	MIBK etc	Various.	Nb/Ta separation, Zr/Hf separation
	Alkyl and aryl sulphoxides	?	?	?
	Alkyl and aryl sulphides	di-n-octyl and di-n-hexyl sulphides	Daihachi Chemical Industry Co Ltd (SFI-6), others.	Palladium extraction in PGM refining

2.2.1 Acidic extractants

The extracting agents that make up the compounds, can be further divided into two subgroups according to their reaction mechanism, others react acidically with a cation exchange mechanism and others form a bidentate chelate with metal ions. Acidic reactants react by changing the hydrogen ion to the metal ion.[4 p.71] This group also includes Cyanex 272 and Versatic 10, which are the main subjects of interest in this research.

$$\text{M}^{n+} + \overline{nHA} \leftrightarrow \overline{MA}_n + \text{nH}^+ \tag{6}$$

In figure 2 and figure 3 are examples of acidic extractant structures.
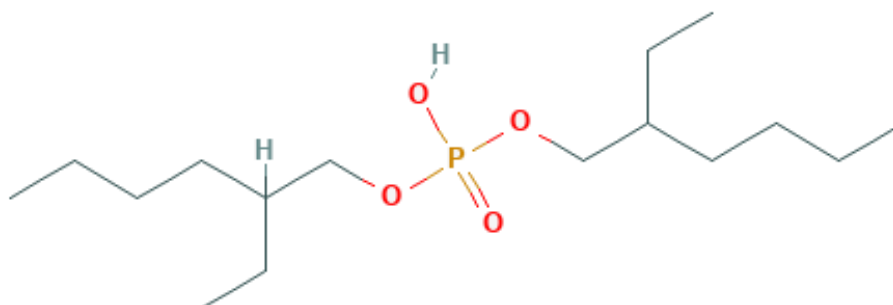
Figure 2: Di-2-ethylhexyl phoshoric acid (D2EHPA)
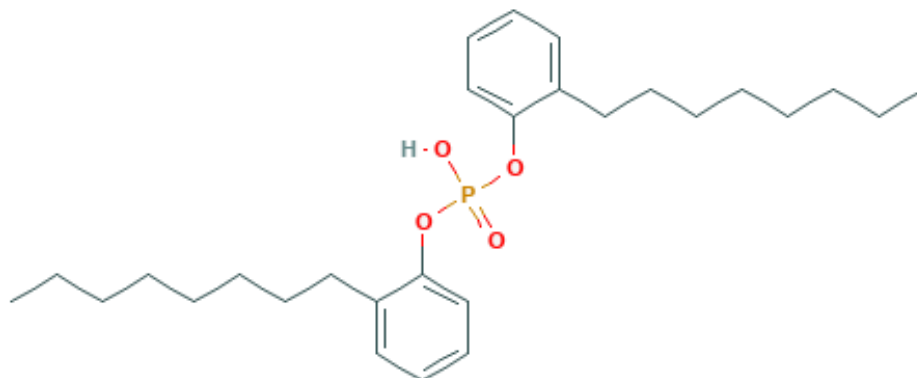
Figure 3: Di-p-octylphenyl phosphoric acid (OPPA)

2.2.2 Chelating extractants

Chelating excipients are capable of forming a bidental ligand with metal ions. These are often used in analytical applications because of their higher cost, but are currently used, for example in the copper industry.[5] For example, in a study by V. Ramosh and G. N. Rao, metal extraction with commercial LIX 622 was investigated. According to the results, copper was completely extracted[10] In addition, e.g. F. J. Alguacil, A. Cobo and M. Alonso investigated copper extraction from nitrate/nitric acid matrix with Acorga M5640 extract, and they got good results at pH 2.[11] In addition, other commercial chelating agents are e.g. Kelex and MSE product groups. In figure 4 and figure 5 are structures of two chelating extractants.
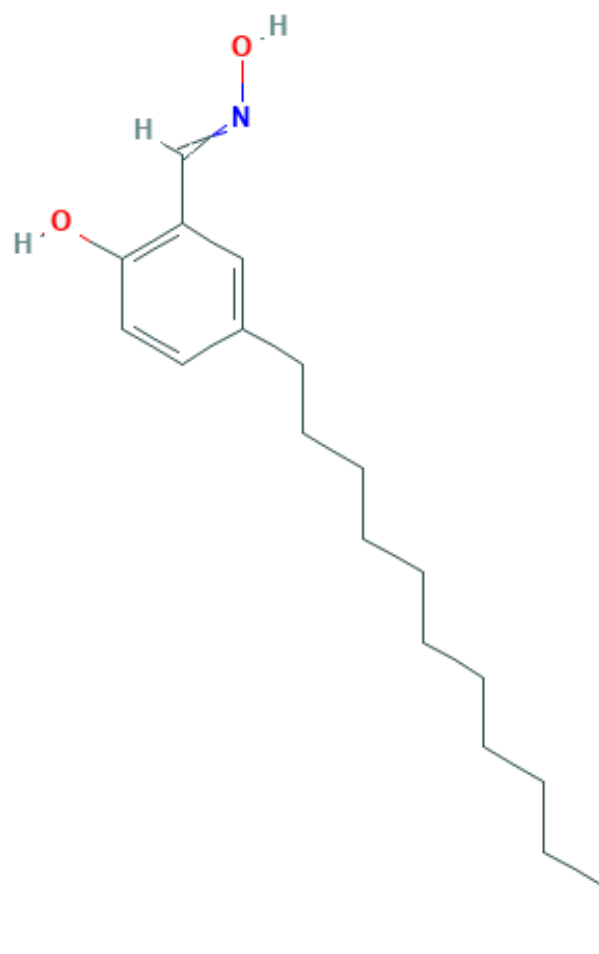
Figure 4: 5-dodecylsalicylaldoxime (LIX 860)
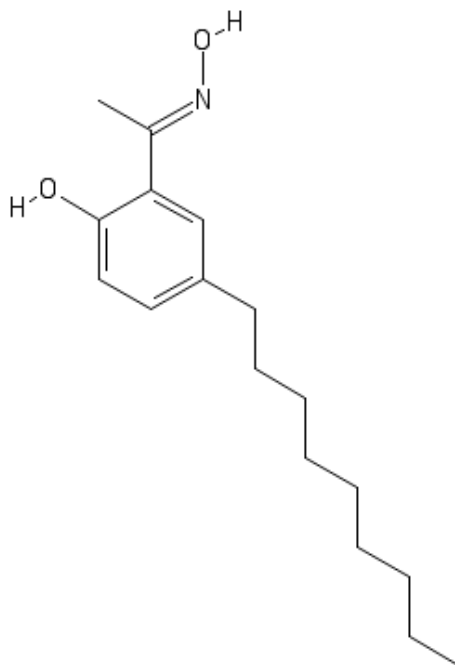
Figure 5: 5-nonyl-salicylaldoxime (Acorga P1)

2.2.3 Extractants involving ion association

For commercial use, the basic extractans are amines and quaternary ammonium halides. The utility of amines depends on the ability of the metal to form an anion complex in the aqueous phase. The amines first turn into a suitable amine salt according to the reaction 7 in the organic phase,

$$R_3N + HX \rightleftharpoons \overline{R_3N + H \cdot X^-}, \tag{7}$$
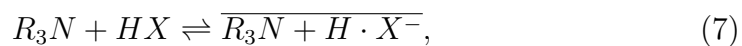
followed by the exchange reaction 8 with the metal-containing aqueous phase.[4 p.128]

$$\overline{R_3N + H \cdot X^-} + MY^- \rightleftharpoons \overline{R_3N + H \cdot MY^-} + X^-. \tag{8}$$
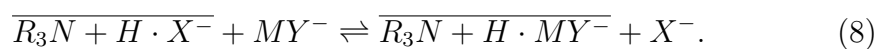
2.2.4 Extractants involving solvation

The electron donation mechanisms can be divided into two main groups according to their structure. Carbon-bound to oxygen and sulfur or oxygen bound to phosphorus. Both act by increasing the solubility of the inorganic material by organic solvation, but with different mechanisms. The phosphorus-bound groups are highly polar and able to compete with water around the metal. On the other hand, ketones and ethers need water to form an organometallic complex.[4 p.142] In figure 6 and figure 7 are example structures of extractants involving solvation.
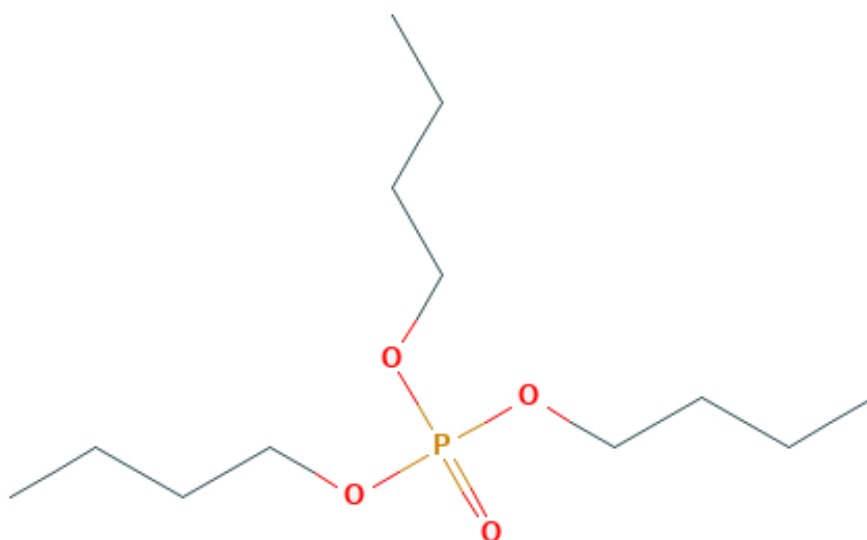
Figure 6: tri-n-nbutyl phosphate (TBP)
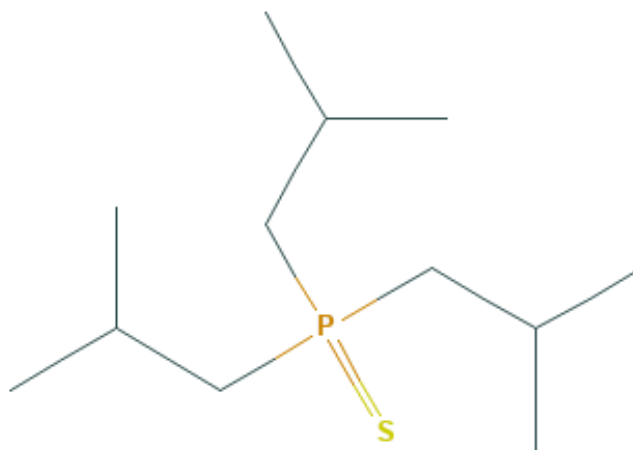
Figure 7: tri-isobutyl phosphine sulphide (Cyanex 471)

2.2.5 Ionic liquids as extractant

Ionic liquids could be a good alternative to traditional extractives. They are stable, non-volatile, non-flammable and can be controlled and adjusted to the desired properties regarding miscibility and polarity. By adjusting the structure of ionic liquids and increasing "trapping" molecules, their suitability for example extraction reactions can be improved. There is still much to be studied in ionic fluids before applying them to the industrial scale.[12] Main problems currently are water solubility. With fluorine IL's can be made more hydrophobic, but fluorine is expensive and can form highly dangerous hydrofluoric acid vapour with water. In addition because of the high viscosity of ionic liquids organic solvents must be used. An aqueous two-phase system

(ATPS) can be used to resolve these issues. In ATPS if temperature is higher than upper critical solution temperature (UCST) or lower than lower critical system temperature (LCST) IL is miscible with water. This allows reaction to occur with metal and IL without diffusing from aquoeus layer to organic phase. Upon cooling (or heating) phases separate and metal is extracted to organic phase. Temperature dependant phase transitions are capable of selectively extracting metals.[13]

In the study "Separation of cobalt and nickel using a thermomorphic ionic-liquid-based aqueous biphasic system" by Bieke Onghena, Tomas Opsomera and Koen Binnemans, tributyl(tetradecyl)phosphonium chloride as a IL and NaCl as a salting out agent were used to separate cobalt from nickel in chlorine base mixture. Result shows that cobalt extraction was increased by increasing salting out component and it did not have effect on nickel extraction.[14] In figure 8 and figure 9 are structures of two ionic liquid extractants.
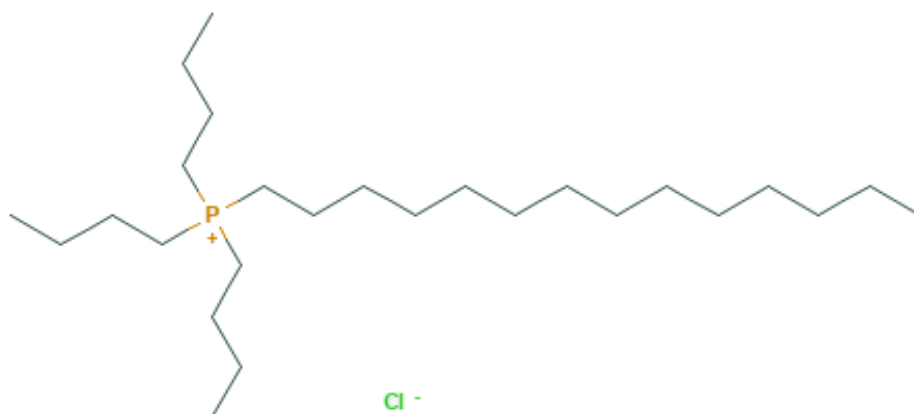
Figure 8: tributyl(tetradecyl)phosphonium chloride
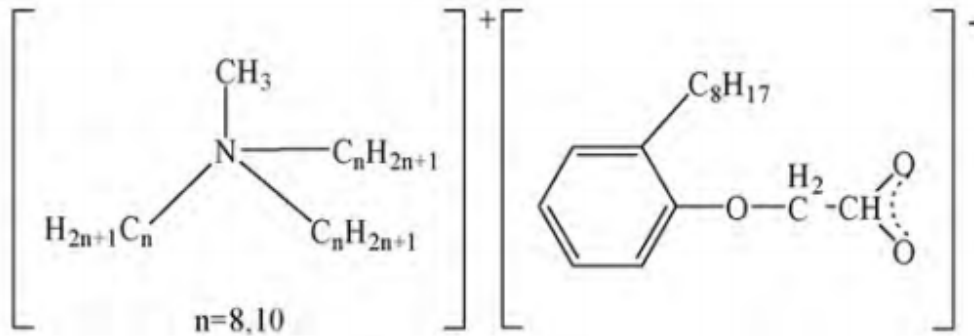
Figure 9: [tricaprylmethylammonium][sec-octylphenoxy acetate] ([A336][CA-12])

2.3 Separation of cobalt and nickel

Separation of cobalt and nickel by hydrometallurgical processes is difficult, but phosphorus-based extracts can be used to separate, up to 1:100 small cobalt concentrations.[5]

2.3.1 Phosphinic acid-based extractants

For example Cyanex extractives are based on phosphine PH_3. After commercial production of phosphines became possible, it opened the potential of producing phosphine derivatives. Phosphine oxides can be prepared by reactions 9 and 10[5]

$$3\,C_8H_{16} + PH_3 \longrightarrow (C_8H_{17})_3P \tag{9}$$

$$(C_8H_{17})_3P + H_2O_2 \longrightarrow (C_8H_{17})_3P(O) + H_2O \tag{10}$$
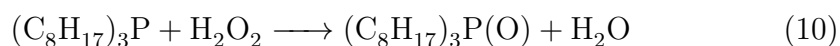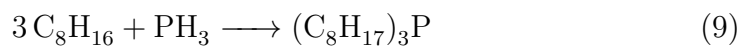
Mono and dialkylphosphine oxides are obtained by using sterically hindered alkenes or by using a pressure above 4 MPa. Monoalkylphosphine derivatives are treated with hydrogen peroxide to give mono- and dialkylphosphine acids and as an impurity trialkylphosphine.

2.3.1.1   Cyanex 272

Cyanex 272 is currently the best choice when it comes to separating cobalt from nickel and is currently producing a large part of the world's cobalt, but other cations can also be extracted at different pH. The active component of Cyanex 272 is phosphinic acid, so the reaction mechanism is cation exchange. It is readily soluble in many of the solvents in use and is chemically very stable. It is colorless to slightly yellowish orange, has a molecular weight of 290 g/mol, a density of 0.92 kg/dm^3 and boiling point above 300 °C Cyanex 272 consists of 85 % bis (2,4,4-trimethylpentyl) phosphine acid which is its active component.[15] The figure 10 shows the molecular structure and in the figure 11 the pH isotherm in the sulfate solution.
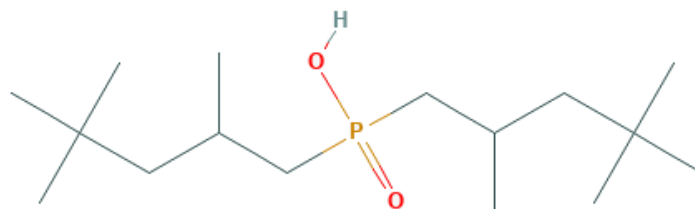
Figure 10: bis 2,4,4-trimethylpentyl phosphinic acid (Cyanex 272)[15]
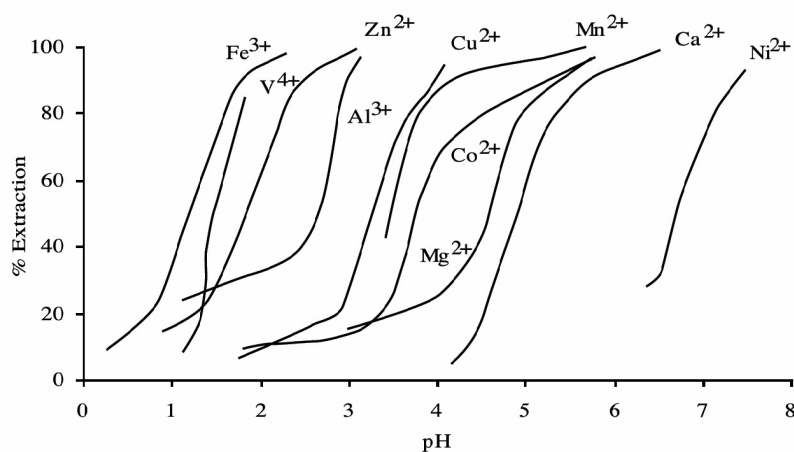
Figure 11: Cyanex 272 pH isotherm in sulphatic solution[15]

2.3.2 Carboxylic acids

By looking for the physical and chemical differences between Cyanex 272 and carboxylic acids it might be possible to find one or more ways to separate them. In this thesis Versatic 10 was chosen as a carboxylic acid source. Mainly

20

because it is one of the commercial mixture of acids that have been shown
to reduce extraction effiency of Cyanex 272.

2.3.2.1 Versatic 10

Versatic 10 also know as neodecanoic acid is a mixture of carboxylic
acids, that include for example 2,2,3,5-tetramethylhexanoic acid, 2,4-
Dimethyl-2-isopropylpentanoic acid, 2,5-Dimethyl-2-ethylhexanoic acid, 2,2-
Dimethyloctanoic acid and 2,2-Diethylhexanoic acid.[16] In figures 12 and 13
are two of aforementioned structures illustrated and in the figure 14 the pH
isotherm in the sulfate solution.
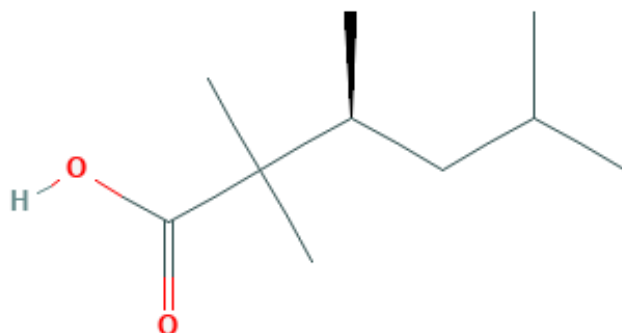
Figure 12: 2,2,3,5-tetramethylhexanoic acid
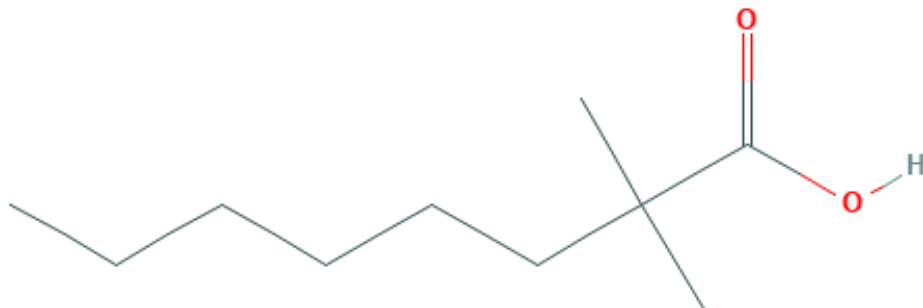
Figure 13: 2,2-Dimethyloctanoic acid
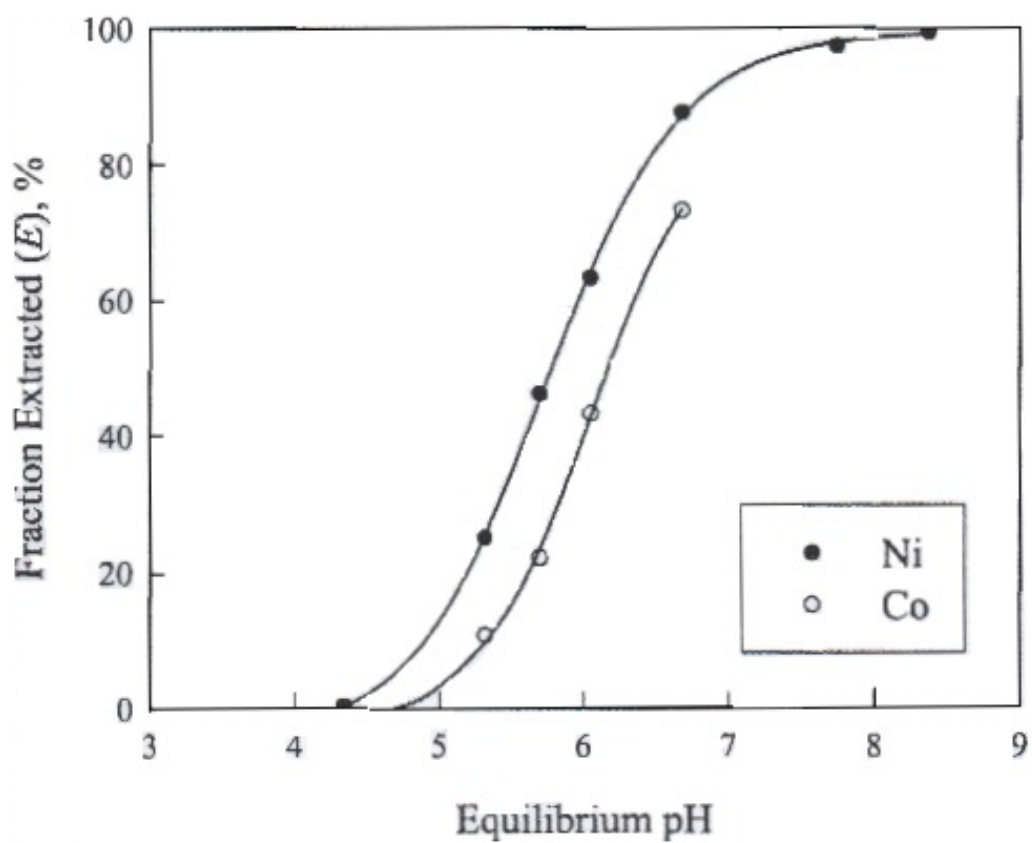
Figure 14: Versatic pH isotherm in sulphatic solution[17]

2.3.3 Isooctane solvent

Isooctane i.e. 2,2,4- trimethylpentane is clear, colorless, non-polar solvent with density of $0.69g/dm^3$ and molecular weight 114,23 g/mol. In figure 15 is isooctanes structure.
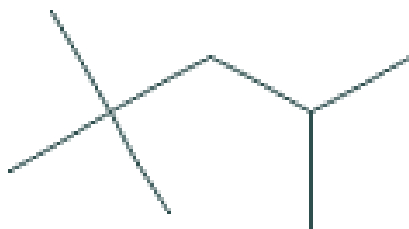
Figure 15: 2,2,4-trimethylpentane[18]

3 CHROMATOGRAPHY

Chromatography is a versatile analytical technique widely used in many areas of chemistry. Many substances in practice contain several different components. Chromatography can be used to separate these components using dispersion, hydrogen bond and dipole interactions. Once the mixture is decomposed into its basic components, components can be identified and even different component concentrations can be analyzed.[19 p.1-5]

3.1 Chromatography practice and instrumentation

A small sample volume is placed on a sample column, where the components pass with the mobile phase, the stationary phase slowing down different components at different times, whereby the elution of the samples, i.e. the output time, varies. The graph generated is called a chromatogram in which the detector response is plotted against time.[19 p.5-9] The chromatograph has a stationary phase inside the column wherethrough the mobile phase passes. After the column, there is usually a detector to provide a response to the different molecules. In the table 2 most common chromatography columns are listed.[19 p.8]

Table 2: Common RPLC and GC characteristics[19] p.9

	RPLC	GC (open tubular)
Column construction	Stainless steel	Quartz with a polyimide coating
Column length	20−250 mm	10−60 m
Column inner diameter	2.1− 4.6 mm	0.1−0.5 mm
Particle composition	Porous silica (SiO_2) particles	No particles − open tube
Particle size	1.8−5 μm	No particles − open tube
Mobile phase	Solvent mixture (e.g., water mixed with acetonitrile)	He, N_2, or H_2
Stationary phase location	Alkyl chains (C-8 and C-18) bonded to particle surface	Liquid-like polymer film bonded to capillary walls
Stationary phase chemistry	Relatively nonpolar and organic in nature	Polysiloxane polymer derivatized with organic moieties

3.1.1 Chromatographic calculations

From the chromatograms, the distribution constant can be calculated using the standard equation 11

$$K = \frac{[A]_s}{[A]_m},\tag{11}$$

wherein A_s describes specific analyte in stationary phase and A_m in mobile phase. The time taken for each sample to be injected, from the moment of injection, to the detection time is called the retention time, which is calculated

by the equation 12

$$[t]_r = [t]_s + [t]_m. \tag{12}$$

The retention time is the most important value obtained from the chromatogram. Retention time varies with different columns and different flow rates give different retention times, but their mutual ratio, i.e., the retention factor, is an independent measure of the apparatus calculated by the equation 13

$$k = \frac{[t]_r - [t]_m}{[t]_m}. \tag{13}$$

Generally, the retention of a single component is not the most important thing, but the separation of different components. The degree of separation can be quantified with equation 14

$$\alpha = \frac{[k]_B}{[k]_A}, \tag{14}$$

wherein α is separation factor. Higher separation factor indicates better separation.[19 p.13-22]

3.1.2 Resolution

Peak resolution is important in order to better quantify different peaks. Overlapping peaks cause distorted results. In practice, overlapping peaks are difficult to detect and almost impossible to quantify except for example with a mass spectrometer. The peak width is usually examined as either a spike or a mid-peak width. In the figure 16 $W_{1/2}$ is width of the peak at half of maximum signal and W_b is baseline spike.[19 p.24-28] In order to make comparisons between different columns, we use theoretical plate number N. There are no actual plates in chromatography columns like in distillation, but it is
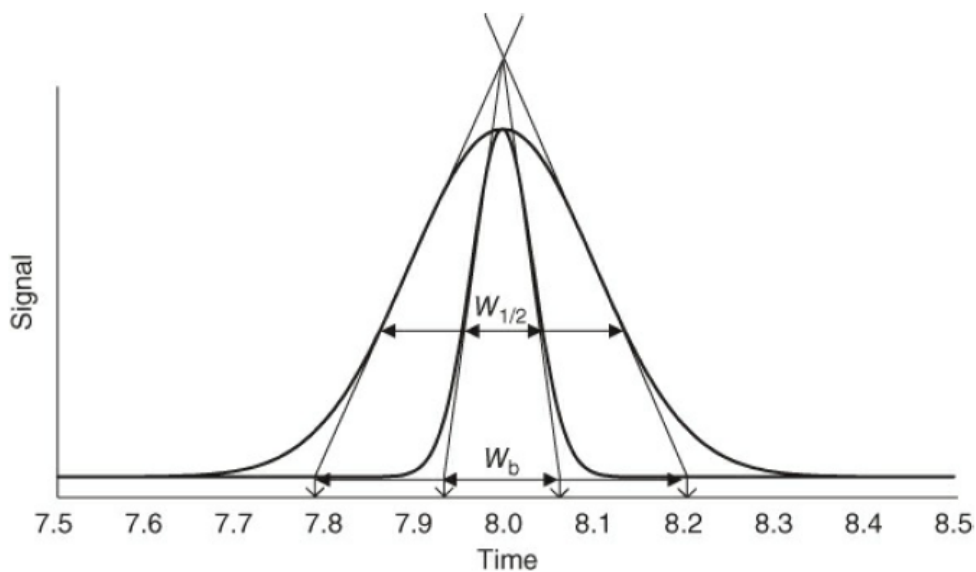
Figure 16: Illustration of peak[19]

a good way to measure and compare separation abilities. With equation 15

$$\text{N} = 5.54(\frac{[t]_r}{[W]_1/2})^2,\tag{15}$$

we can calculate the plate number.

3.1.3 Rate theory

It is commonly believed, that peak propagation is mainly influenced by four factors, diffusion in longitudinal and width direction, "paths" in the column where components pass at different rates, reactions with stationary phase affected by convection and diffusion interactions.[19] [p.36] Diffusion is the random

movement of molecules due to the kinetic energy according to the concentration gradient. The molecules in the stationary tube are distributed according to the normal distribution, the molecules have different diffusion coefficients, so the diffusion effect is also different. Generally speaking, small molecules are distributed more.[19] [p.36-40]

Rates in chromatography can be divided into three essential magnitudes, the rate at which a molecule that does not adhere to the stationary phase moves (i.e., the mobile phase rate) through the column, column diameter and a particle diameter. Molecules can move through columns at different routes at different velocities.[19] [p.42]

3.1.4 Open tube with thin stationary phase

In the parabolic flow, the middle molecules move faster, the parabolic effect increases as the pressure increases. If other factors affecting the movement of the molecule are not taken into consideration, the infinitely wide peaks should be taken into account. The speed of the molecules on the edges is practically zero, but according to the concentration gradient, the molecules on the edges tend to move towards the middle, i.e. the radial diffusion narrows the peaks and the faster moving phase expands them. As with many random movements, most molecules move at an average rate of molecules.[19] [p.42-45]

Longitudinal diffusion of the column expands the peaks, influenced by the diffusion rate of the molecule, and the time spent in the column. The effect of longitudinal diffusion in gas chromatography (GC) can be ignored, because the effect of diffusion in the stationary phase is insignificant compared to the diffusion in the mobile gas phase, this effect cannot be ignored in the liquid.[19] [p.47-48]

3.1.5 Packed column

The same phenomenas that are affecting open column, also affect the packed
column. However, there are some differences. The particles reduce longitudinal
diffusion, the stationary phase braking effect of the particles is determined
experimentally. The size, shape, and material of the particles are affecting
factors. The rate is influenced by the packing density and distribution of the
column, the molecules of different cavities can move at different speeds, and
this, on the other hand, increases the spike. The co-operation between the
two phenomena, on the other hand, narrows the peaks. Even on the path of
the molecule, the rate in the different parts of the column varies according to
figure 17. The slower the diffusion of the molecule radially, the less frequently
it changes the route, or moves to the particle retaining. Thus, the radial
diffusion of the molecule is inversely proportional to the peak width.[19 p.56-63]
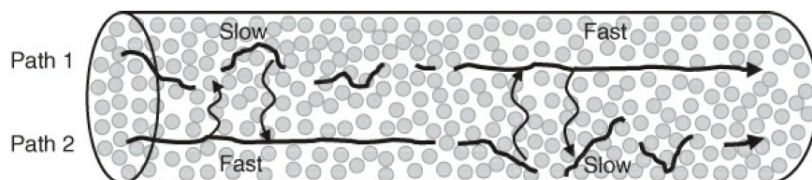
Figure 17: Illustration of molecule movement in packed column[19 p.61]

3.1.6 Modern liquid chromatography

The most significant change in modern liquid chromatography is that the par-
ticles are not solid-stationary-coated, but they are porous. Figure 18 describes
events in retention of solution. For solutes to be retained, they must move
close to solid particle and diffuse in the particle pores by diffusing through
stagnant mobile phase, then diffuse to stationary phase and finally diffuse

29
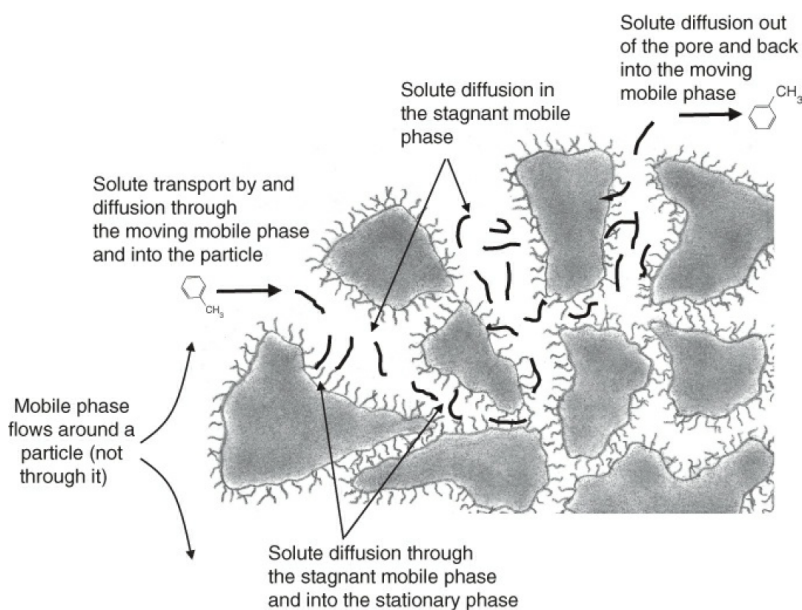
Figure 18: Illustration of molecule adsorbtion in porous adsorbents[19] p.70

back into the mobile phase.The faster these diffusion occur, the less peak broadening happens.

3.2   Gas chromatography

Gas chromatography is an analysis method developed in the late 1940s to separate and quantify different molecules.[20]

3.2.1   Theory

When the sample moves through the column, it can interact with the stationary phase, whereby the net velocity of the sample at the interaction site is slightly smaller than the carrier gas. The different components are distributed differently between the stationary phase and the carrier gas, whereby they

elute at different times. In general, a column with liquid in the stationary phase is used.[21]

3.2.2 Sample preparation

In gas chromatography, it is essential that the sample is evaporated at a reasonable temperature. The sample is often subjected to pretreatment prior to gas chromatography analyzes, for example, its evaporation point can be lowered or increased as needed. The purpose of the so-called derivatization reaction is to change the analyte so that it is possible to detect or improve the detectable signal. Derivation reactions can be divided into three main groups: alkylation, acylation and silylation.[22] Alkylation is generally used to convert acids to esters by replacing the active hydrogen general reaction mechanism 16

$$RCOOH + PhCH_2X \longrightarrow RCOOCH_2Ph + HX. \qquad (16)$$

In silylation, the active hydrogen is replaced by a silyl group which reduces the hydrogen bonding of the molecule and thereby also reduces its boiling point. The silylation reaction acts as a nucleophilic attack of the silyl group as in the figure 19.
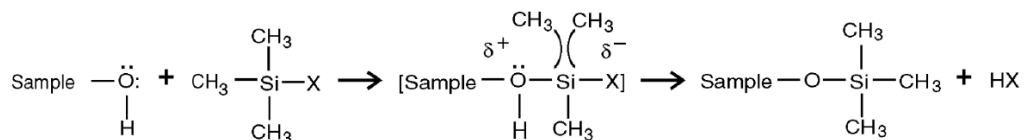
Figure 19: General reaction mechanism for the formation of trialkylsilyl[22]

31

Acylation involves attaching an acyl group to an organic molecule 17

$$RH_3OCOCOCH_3 + HOR \xrightarrow{H+catalyst} CH_3OCOR + HOCOCH_3 \qquad (17)$$
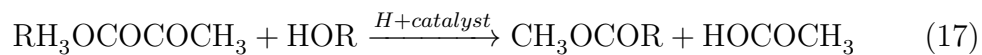
3.2.3 Detectors

One of the strengths of the GC is the low background disturbance of carrier gases, which allows many different detectors to be used for detection. The detectors are divided into selective or universal type by type. Selective detectors only detect certain molecules according to chemical or physical properties. In addition, some selective detectors may specifically detect different atoms or functional groups. The detectors can also be categorized according to whether they detect concentration or mass change between and are they destructive and non-destructive. There are differences between the detectors, also depending on how much samples they can detect, which is illustrated in figure 20.[23]
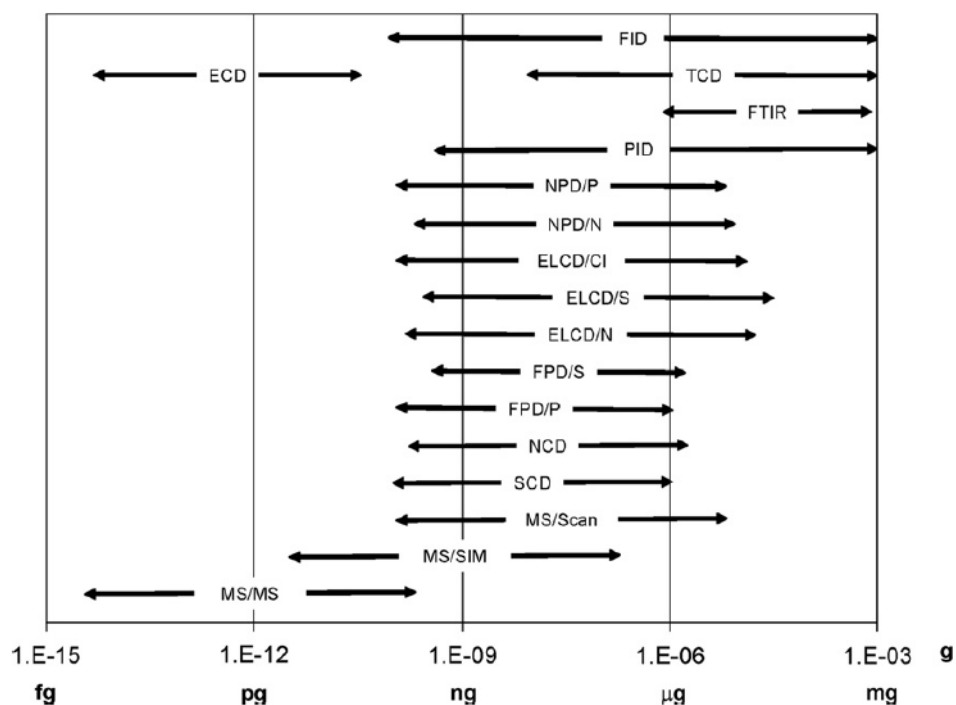
Figure 20: dynamic measuring areas of detectors

23

In this work, mainly flame ionization detector (FID) was used, but the mass spectrometer (MS) was also initially tested for analytical purposes.

3.2.4 Flame ionisation detector

FID is a mass-sensitive destructive detector that corresponds linearly to the amount of carbon flowing through. This accurate, structurally independent carbon detection results in the quantification of components without accurate calibration. For quantification, only one well-known reference sample is needed, which elutes at a different time from the samples. The lower peak of the chromatogram corresponds quite well to the percentage by mass of

33

the components in the mixture. Even without the known concentration, the areas of different peaks can be compared semi-quantitatively and their mass ratios are obtained.[24] In this thesis, data has been analyzed mainly semi-quantitatively, as it provided sufficient knowledge of the experiments. We can see from figure 20 that FID also has dynamic measuring area of seven orders of magnitude.

3.2.5 Inductively coupled mass spectrometer

Inductively coupled mass spectrometer (ICP-MS) is a plasma-based detector that can be used to identify and quantify all sample components. It provides accurate mass percentages of the different elements in the sample and can be detected in significantly smaller quantities than other detectors. In addition, when combined with GC, it generally receives a relatively pure sample for detection, which is directly gaseous.[25]

3.2.6 Method

The boiling points of the compounds studied at this work, are approximately 300°C, so derivatization was an essential part of sample processing. The basis for sample processing was the silylation recipe used by Anna-Maria Jäpölä in her master's thesis.[26] The gas chromatograph was the most practical instrument for analyzing the mixtures of extracts. The elution times of Versatic 10 and Cyanex 272 differed clearly and the method resulted in semi-quantitatively clear changes in the amounts of the excipients.

3.3   Liquid chromatography

Liquid chromatography was another of the main interests of the work. In the wood and paper industry, liquid chromatography has been studied as an analytical method for characterizing acids from a black solution, and they have been succesfully separated for analysis purposes.[27] For the needs of the food industry, mineral oil aromatic hydrocarbons have also been separated from the saturated hydrocarbons by column chromatography.[28]

3.3.1   Theory

Chromatography is generally described with either equilibrium or kinetic theory. The equilibrium theory operates when mass transfer events are so fast that there is a constant balance state between the stationary phase and the mobile phase. However, in most cases the processes are slow and even if almost immediate reactions occur on small molecules, kinetic theories offer more content and a new perspective.[29] Figure 21 illustrates basic partition between organic and aqueous phase. These studies, together with the basic theory of chromatography, provided the starting points for the chromatographic experiments of this work.

3.3.2   Macroscopic and microscopic kinetic theories

Macroscopic theories depict the events of the column as movement of the concentration regions. The column is considered as a a single entity and it is assumed that the stationary phase of the packed column is homogeneous, the temperature constant, the mobile phase is not compressed and the stationary
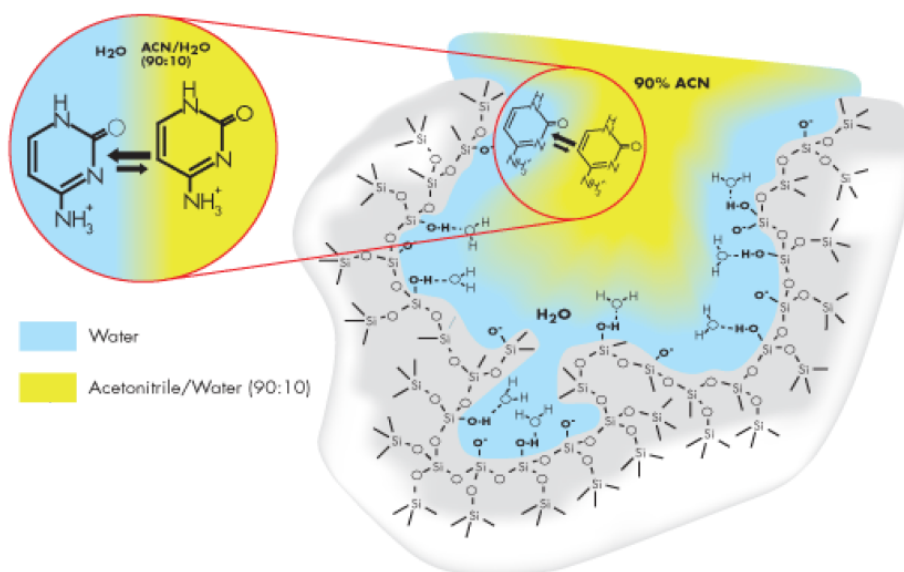
Figure 21: Partition between organic and aqueous phase.[30]

phase is not expected to diffuse. Microscopic theories describe the movement of a single molecule in a column. The model examines random movement in the mobile phase and random adsorption desorption reactions with the stationary phase.[29]

3.3.3 Instrumentation

The column should be chemically inert, withstand high pressures, smooth inside and the inside diameter variance must be small. Stainless steel 316 meets these criteria. The column selection is affected by the stationary phase particle size, the hardware and, of course, the analytics that is done. The column is generally 50 mm to 250 mm, usually plate number 5,000 to 10,000 enough for HPLC analysis. Different adsorbents can be packed on the column depending on the intended use, the table 3 lists the most common adsorbents and their properties.[31]

Types	Bulk structure	Surface chemistry	Synthesis routes Manufacture	Typical properties
POROUS OXIDES				
Silica, amorphous	Network of siloxane groups Disordered pore structure pH range of stability, 1−9	Silanol groups of various types	Sol-gel processing from tetraethoxysilane or highly pure colloidal silica	Hydrophilic, weakly acidic Weak cation exchanger pI = 2−3
Silica, ordered mesoporous	Long-range order Regular pore structure	Silanol groups of various types	Template assisted synthesis	Hydrophilic, weakly acidic Weak cation exchanger
Alumina	Gamma-alumina crystalline pH range of stability, 2−12	Broensted acid sites, Lewis acid, and Lewis basic sites	Controlled thermal decomposition of gibbsite or boehmite	Amphoteric, anionic and cationic exchange properties pI = 7
Titania	Anatas, rutile Both crystalline, pH range of stability, 1−14	Broensted and Lewis acid and basic sites	Agglomeration of nanoparticles by spray drying	Amphoteric anionic and cationic exchange properties pI = 5
Zirconia	Crystalline pH range of stability, 1−14	Broensted and Lewis acid and basic sites	Sol-gel processes (hydrolysis of zirconium compounds, colloidal zirconia) polymerization induces colloidal aggregation processes (coacervation, microencapsulation	Amphoteric anionic and cationic exchange properties pI = 10−13
Porous (graphitized) carbon	Graphitic structure, mesopores	Graphitelike surface structure with pronounced hydrophobicity	Thermal decomposition of polymers at inert atmosphere to active	Strongly hydrophobic surface properties π-π-interactions
Hydroxyapatite	Calciumhydroxy-phosphate crystalline	Cation exchange properties	Agglomeration of nanocrystals	Separation of biopolymers by ion exchange
CROSS-LINKED ORGANIC POLYMERS				
Poly(acrylamides)	Acrylamide and cross-linker pH range of stability, 0−14		Emulsion polymerization	Hydrophilic
Poly(styrene divinylbenzene)	Styrene and cross-linker, pH range of stability, 0−14		Emulsion polymerization	Hydrophobic
Poly(methacrylates)	Methylmethacrylate and cross-linker, pH range of stability, 2−12		Emulsion polymerization	Hydrophilic to hydrophobic
Poly (saccharides)	Cross-linked agarose and dextrans, cellulose pH range of stability, 0−14	Hydrophilic to hydrophobic depending on the terminating bonded ligands		Hydrophilic
Poly(vinylalcohols)	Vinylalcohol and cross-linker, pH range of stability, 2−12		Emulsion polymerization	Hydrophilic
SILICA-ORGANO HYBRIDS				
Poly(acrylamide)-poly(styrene) coated silica composite	Gel in a shell structure			
Silica-organic composites	Amorphous silica with bonded organo constituents	Surface functionality depends on the organic group R	Cohydrolysis and Co-condensation of tetraethoxysilane and organotriethythoxysilanes	Hydrophilic to hydrophobic

Modern liquid chromatography uses porous adsorbents with a high reaction area relative to volume. The reaction surface increases retention and separation of the analytes. In porous materials, the size of the cavities must also

be taken into account, as a basic rule it may be considered that the organic molecule requires a cavity of 8 times the volume of the molecule to allow the molecule to interact in the cavity.[31]

3.3.4 Normal phase chromatography

In normal phase chromatography (NPC), the column is packed with polar inorganic particles and less polar solvent is introduced into the column. Modern columns generally have silica having a silanol on the surface. Silanols are proton donors and they retain molecules with a dipole moment. In the retention process, the molecules and analytes of the solvent compete for positions on the surface of the silica. The mobile phase is generally a mixture of polar and non-polar solvent, whereby adjusting the separation ratio of the solvents of the mixture provides controlled separation. Polar molecules can cling to the stationary phase strongly leading to localization, i.e. hydrogen bonding with silanol. Due to localization, by adjusting the mobile phase ratios, it is possible to selectively separate the molecules.[32]

3.3.5 Gradient operation with normal phase chromatography

The gradient run is an high performance liquid chromatography (HPLC) process in which the ratio of solvents is changed as a function of time. Run begins with a nonpolar eluent and gradually the proportion of polar solvent is increased. Gradient NPC analysis is harder to predict and repeat than reverse phase chromatography (RPC). Eluent is more readily reacted with the column adsorbent, which may cause the eluent to be demixed, however with temperature control and dry solvents, good reproducibility can be achieved.[33]

3.3.6 Detectors

HPLC can be detected using many different detectors, the choice depends on the intended use. The UV-Vis absorption spetrometer is currently used as a general detector. In table 4 are listed the most commonly used HPLC detectors. In addition to direct detection, fractions can be recovered from the run at specific time intervals, and the fractions are treated so that otherwise invisible analytes can be analyzed.[34]

Table 4: Commonly used detectors[34]

Detector	Selectivity	Gradients?	LDR	LOD	Notes
UV−Vis	Broad	Yes	10^4	pg - ng	Near universal detection of organic compounds at low wavelengths. PDA allows for real-time spectra−peak purity.
RI	Very broad	No	10^3	ng - µg	Useful for nontrace analyses of analytes lacking chromophores (e.g., carbohydrates, lipids, and polymers). Requires a very stable HPLC system.
ELSD	Very broad	Yes	10^2	pg - ng	Requires nonvolatile analytes and volatile mobile phases. Condensation nucleation modification improves detection limits. Nonlinear calibrations may be needed.
CAD	Very broad	Yes	10^3	pg - ng	Requires nonvolatile analytes and volatile mobile phases. Larger LDR than ELSD. Nonlinear calibrations may be needed.
Conductivity	Selective	Yes (if suppressed)	10^3	ng - µg	Near universal detection of ionic compounds. Suppression required for optimal detection limits and gradient use.
Fluorescence	Very selective	Yes	10^4	fg - pg	Limited to natively fluorescent or derivatized analytes. Laser-induced fluorescence detection required for optimal detection limits.
ECD	Very selective	Limited	10^5	fg - pg	Limited to oxidizable or reducible compounds. Excellent sensitivity and linearity. Gradients can degrade sensitivity.

3.3.7   Ultra violet and visible light spectrometer

The UV-VIS spectrophotometer is a device that measures the intensity of light passing through the sample and compares it with the reference. The difference in intensity gives an absorbance as a result.[35,34]

4   ADDITIONAL EXPERIMENTS AND CONSIDERATIONS

Separating extractants using different washing techniques and normal phase liquid chromatography were largely emphasized in this thesis, however a molecular catcher technique was tested and a few other methods for separating extractives were considered.

4.1   Molecular catcher

The University of Jyväskylä is able to produce so-called molecular catcher with a 3-D printer. The idea is that a functional group that reacts with the element to be recovered from the solution is immersed in the catcher.

In this thesis, an attempt was made to use metallic zinc as a functional group. The hypothesis was that zinc could react with Versatic 10 to reduce its amount in solution, although the problem might be that Cyanex 272 is also able to react with zinc. The goal was to reduce only Versatic 10 concentration.

Molecular catcher has been successfully used for palladium capture in a study where two different oxidation states of palladium at 30 ppm were obtained

with 100 % yield.[36] In this work, however, no attempt was made to capture the metal, but to use metal as a catcher.

4.2   Size exclusion chromatography

Size exclusion chromatography is a method of separating molecules by their size. The column is packed with a porous material in which the size of the cavity is determined by the size of the separatable molecule. Large molecules do not fit in cavities and elude first. The counter on the Nanocomposix website is used to calculate the molecular size.[37,38] According to the counter, the Versatic 10 diameter would be about 8.4 Å and Cyanex 272 10 Å. Therefore, a molecular sieve or packing material on a column with 9 Å cavities would not slow down Cyanex 272, but might be able to retain the smaller Versatic 10 molecules.

4.3   Reverse phase chromatography

In reverse phase chromatography eluent is more polar than stationary phase and therefore polar compounds elute faster. RPLC is the most commonly used chromatography technique.

4.4   Super critical fluid chromatography

The use of supercritical carbon dioxide as a mobile phase brings a few advantages over conventional liquid chromatography. It works like normal phase chromatography, but it is more effective because of better diffusion and mass transfer. It is generally used with analytes with low water solubility, such as

fatty acids or oil fractions. The sample fraction recovery is easier because the carbon dioxide evaporates after the column. Supercritical fluid poses challenges especially for pump technology, but in principle the same equipment can be used as for liquid chromatography.[39,40,41]

The supercritical fluid is, in a way, an intermediate between liquid chromatography and gas chromatography, during the work it was found that the liquid chromatographic separation was not successful but gas chromatography was successful. In practice, replacing this work with carbon dioxide in hexane could perhaps help succesfully separate the extractants.

5 ANALYTICAL METHODS

5.1 pH

The pH value generally refers to the acidity / alkalinity of the aqueous phase. It is measured on a scale from 0 to 14 and can be interpreted as the activity of the hydrogen ions of the sample if necessary, usually in the aqueous phase and generally as an oxonium ion concentration.[42] The approximation of the pH value of the sample can be calculated by the equation

$$pH \approx -\log[H^+], \tag{18}$$

where $[H^+]$ represents the hydrogen ion concentration.[42]

In this work, the theoretical distribution of metals during the experiments was monitored by the pH value, in addition to the selectivity tests, the metal separation factor was interpreted as a function of pH.

5.2 ICP-OES

Frequently used atomic absorption techniques are good when analyzing metals, semi-metals and some non-metals. However, atomic absorption technology cannot analyze one element at a time. Atomic emission technology can simultaneously analyze multiple elements, because it does not require an atomic-specific radiation source. The strengths of the method further include: the concentration range is broad ppb to percent, linear ranges are broad, low assay limits, good repeatability and reproducibility, multiple anions can be analyzed, background disturbance is minimal. In a typical apparatus, the

sample is fed to the ICP by means of a peristaltic pump into a nebulizer which also flows argon gas. The sample is aerosolized in a nebulizer that flows into the nebulizer chamber. In the atomizer chamber, too large droplets run directly through the waste hose into the waste bin and 1-2 % of the sample flows up into the plasma flame.[43]

With ICP-OES, it is attempted to atomize the sample in the plasma flame, excite the atoms and finally, when the electrons of the atom return to basic state, the atom emits electromagnetic radiation at a specific wavelength. The emission of the sample is spread with prism by different wavelengths, signals of different wavelengths are amplified and detected by a CCD cell as shown in figure 22. The strength of the signal obtained from the cells is compared to known concentrations or directly calibrated directly to calculate the concentration of the sample.
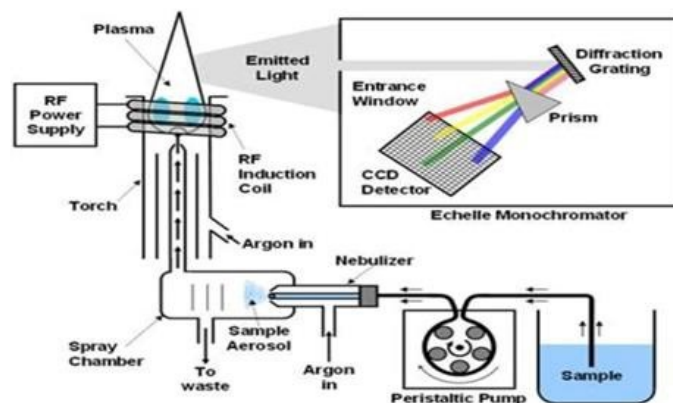

Figure 22: ICP-OES principle[43]

NNH laboratory performed analyzes of samples from different experiments on a Spectro Argos with pre-made methods with a suitable sample matrix. An extra monitoring solution was prepared to refine the results of high cobalt con-

tent. From the results, metal distributions between the organic and aqueous phases were determined and these results were used e.g. selectivity tests.

5.3   Selectivity tests

By using ICP results, the equation 3 can be used to calculate the separation factor at different pHs and to evaluate the effectiveness of the various novel mixtures in the separation of cobalt and nickel, for example with an extractant mixture of about 20 wt-% active Cyanex at pH 4.7. At equilibrium cobalt was analysed 8977,38 mg/l in organic phase, 655,98 mg/l in aqueous phase and nickel 288,32 mg/l organic phase and 107155 mg/l in aqueous phase

$$5086,24 = \frac{\frac{8977,38}{655,98}}{\frac{288,32}{107155}},\tag{19}$$

we can calculate that SF at pH 4.7 is 5086,24.

5.4   GC-FID/MS

Extractant mixtures were analyzed on GC-FID/MS device Shimadzu GC-2010 with column Agilent HP-5 19091J-413E with physical measures lenght 30 m, internal diameter of 0.32 mm and film thickness 0.25 µm. Injector temperature was 290 °C, detector 300 °C, oven's starting temperature was 100 °C with delay time 1.5 minutes. Temperature was ramped up with initial ramping of 6 °C/min to °C 180 and after that 4 °C/min to 290 °C. Total analysis time was 62.33 min. The GC-FID device yielded sufficiently accurate results. With pure substances good measuring response was achieved with Versatic 10 and Cyanex 272 and no overlapping signals were measured from derivatization reagents or solvent, results are listed in appendix A pages 75

to 78.

5.4.1   Sample derivatization

Cyanex 272 and Versatic 10 required derivatization. Samples were diluted
with n-hexane and dried with rotavapor. 200 µl 8:2 BSTFA-TMCS and 600
µl pyridine was added to sample and closed tightly. Samples were heated at
70 °celcius for 30 minutes. Afterwards treated samples were analysed with
GC-FID.

5.5   Titration of extractants

Concentrations of one extractant can be determined by titrating the poten-
tiometric acid-base distillation with its active moiety. The acidic Cyanex 272
active moiety bis(2,4,4-trimethylpentyl) phosphinic acid (BTMPPA) hydrox-
ide group can be titrated with sodium hydroxide. The other OH group of the
inactive portion (2,4,4-trimethylpentyl) phosphonic acid (TMPPA) also has
an equivalent point at the same pH. The second OH group of the inactive
portion is only titrated at a higher pH. The calculation is based on the volume
of titrant at the first equivalent point where hydroxyl group of BTMPPA is
active[44] Example of titrations and titration values are listed in appendix B

5.6   Total organic carbon

The organic content of the samples can also be measured by TOC analysis.
In the analysis, the sample is burned so that all of its carbon is converted to
carbon dioxide, which is analyzed by an IR cell. The IR cell signal is compared

to a known standard[45]

The analysis thus determines the organic carbon content and can be used to estimate the total organic matter. A very useful analysis when looking at the relative change of organic matter in the aqueous phase at different points.

6 EXPERIMENTS

The experiments were conducted between the summer of 2018 and spring 2019 at the Norilsk Nickel Harjavalta Research Laboratory and the Department of Applied Chemistry at the University of Jyväskylä. Tests can be divided into three main groups: washing of the extract mixtures, chromatographic separation, and separation using a molecular scraper.

6.1 Initial tests and preparations

Baseline selectivity test was made with pure 22,5 w-% Cyanex272 diluted in isooctane (SUL) and synthetic aqueous (NISO$_4$). Also to confirm previous results, SUL with 1,5 w-% added Versatic 10 (SULV1.5) was used as an organic phase. All organic solutions were stripped with dilute H$_2$SO$_4$ solution in order to remove impurities.

Solutions for the experimentations are listed in table 5. All organic solutions are diluted with isooctane.

Table 5: Solutions for first experimentations

	Solution	Concentration	Abbreviation
Synthetic organic	Cyanex 272	22 w-%	SUL
Synthetic organic with versatic	Cyanex 272 / Versatic 10	22 w-% / 1,5 w-%	SULV1.5
Synthetic aqueous	Ni / Co	120 g/l / 8,3 gl	$NiSO_4$
Natrium sulphate solution	Na	100 g/l	Na_2SO_4
Zinc sulphate solution	Zn	25 g/l	$ZnSO_4$
Magnesium sulphate solution	Mg	10g/l	$MgSO_4$
Sulphuric acid	H_2SO_4	200 g/l	H_2SO_4
Natrium hydroxide	NaOH	50 g/l	NaOH
SULV1.5 with zinc loading	SULV1.5 + Zn(stripped)	-	SULV1.5Zn
SULV1.5 with mg loading	SULV1.5 + Mg(stripped)	-	SULV1.5Mg
SULV1.5 with 1 contacts	SULV1.5	-	SULV1.5C1
SULV1.5 with 10 contacts	SULV1.5	-	SULV1.5C10

6.2 Using different pH isotherms

The hypothesis was that we could complex Cyanex 272 with zinc or magnesium at a pH where Versatic 10 would not yet form a complex with these metal ions. Then raise the pH as much as possible with the above limitation in mind. Higher pH also increases Versatic 10's water solubility and it may have been possible to transfer it from organic phase to aqueous phase. Additionally experiments without loading process were made with different number of contacts.

6.2.1 Zinc and magnesium loading processes

Loading processes and selectivity tests were conducted in a 1 dm^3 glass reactor with built-in heating mantle and flow disturbance plates. Stirring

was implemented with four bladed teflon propeller which was mounted to an electric mixer. Temperature was controlled with water bath which circulated the water through the reactors mantle. Default settings in all the tests were temperature 50 degree celcius, A:O phase ratio 1:1 and stirring rate at 500 rpm. pH value was measured with handheld pH meter from the aqueous phase samples and it was adjusted with 50 g/l NaOH and H_2SO_4 on about 15 minute intervals. For the loading processes 300 ml of aqueous and organic phases were used to make sure that there was enough solution for the selectivity tests.

SULV1.5 was stirred with $ZnSO_4$ solution and pH value was raised to 3.1. When desired pH value was reached, aqueous phase was removed and organic phase was washed two times with deionised water, the pH of which was adjusted to 8.0. After washing, Zn was stripped with 200g/l H_2SO_4 and selectivity tests were performed. Mg was processed in similar fashion, but pH value was raised to 6.1. Both pH values were chosen from Cyanex 272 and Versatic 10 pH isotherms. From these experiments SULV1.5Zn and SULV1.5Mg were produced.

Additionally experiments without metal shielding were made by substituting $ZnSO_4$ with Na_2SO_4 and washing one time and 10 times with deionised water, the pH of which was adjusted to 8.0. From these experiments SULV1.5C1 and SULV1.5C10 were produced.

6.2.2 Selectivity tests and analysis

The selectivity experiments were carried out with all the different organic materials and the synthetic nickel cobalt mixture ($NiSO_4$).All the selectivity tests were similar to one another, except for the first equilibrium pH which had

50

fluctuation between experiments. Aqueous solution was first added to reactor and stirred. Organic phase was slowly added and stirred with NiSO$_4$ solution for 15 min. The equilibrium pH was measured and 0-sample taken from both aqueous and organic phase. After that pH value was slowly raised and samples taken from points 4.4-5.8 with 0.3 increments except the last two points witch were 5.6 and 5.8. ICP analysis with both organic and aqueous methods were performed and results were used to calculate Co/Ni SFs with equation 3. With these results pH isotherms were drawn and compared. Results are listed in appendix D.
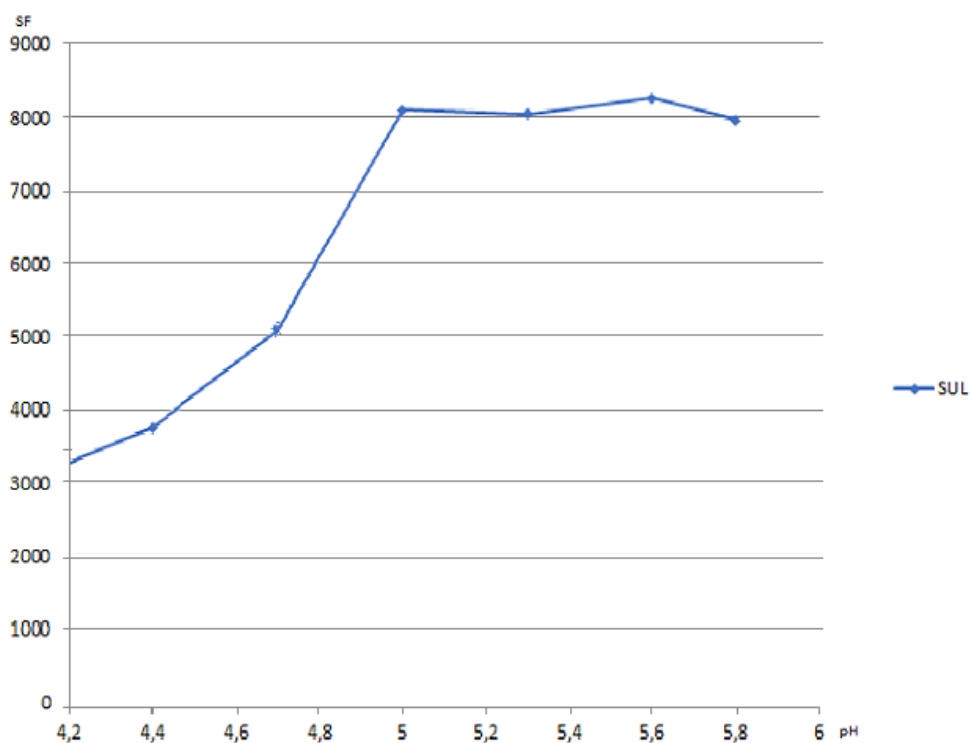
Figure 23: Co/Ni isotherm with 22w-% Cyanex 272

With SUL pH isotherm in figure 23 we noticed that pH value 5.0 and above

51

gives the best separation factor, which is confirmed in the literature[15]
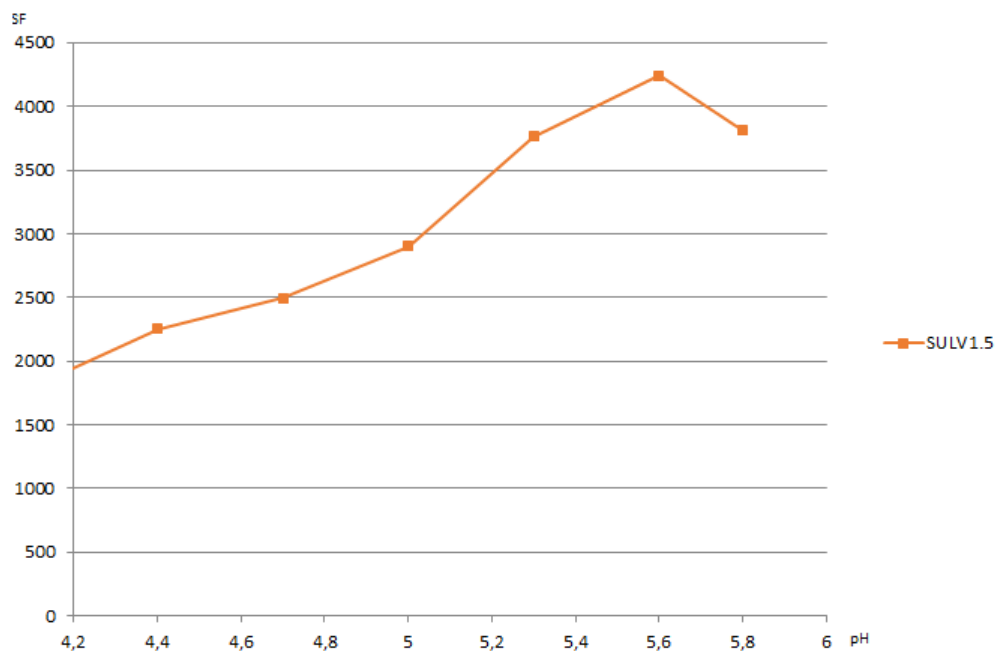

Figure 24: Co/Ni isotherm with 22w-% Cyanex 272 1,5w-% Versatic 10

Increasing concentration of carboxylic acids in solvent lowers Co/Ni separation factor in isotherm in figure 24 which is confirmed in the literature.[2]
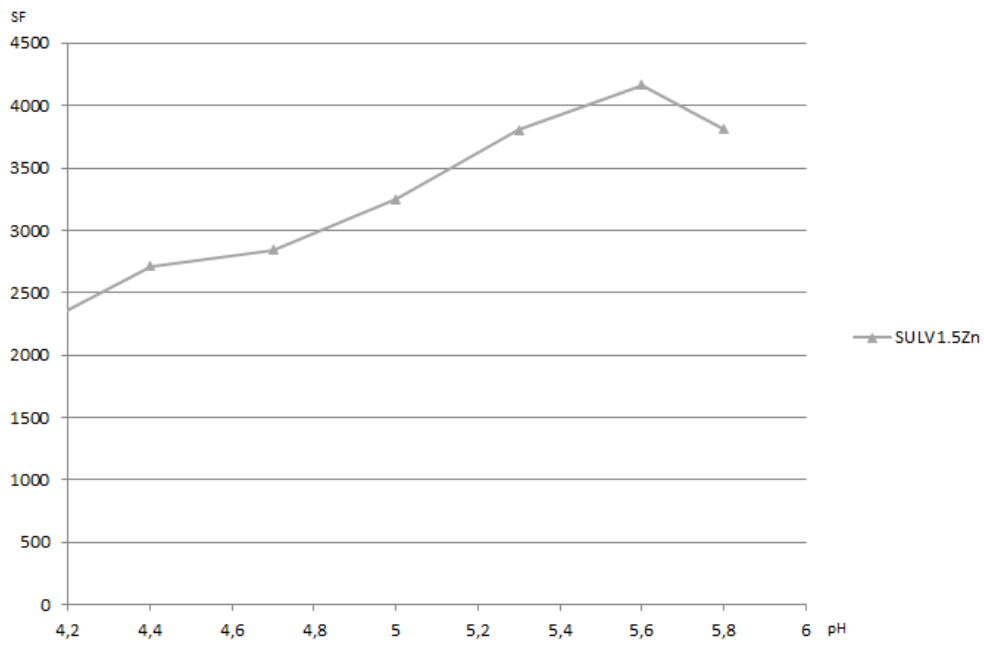
Figure 25: Co/Ni isotherm with zinc treated solvent

According to figure 25 zinc treatment of the solvent did not seem to have effect on separation factor compared to the isotherm presented in figure24
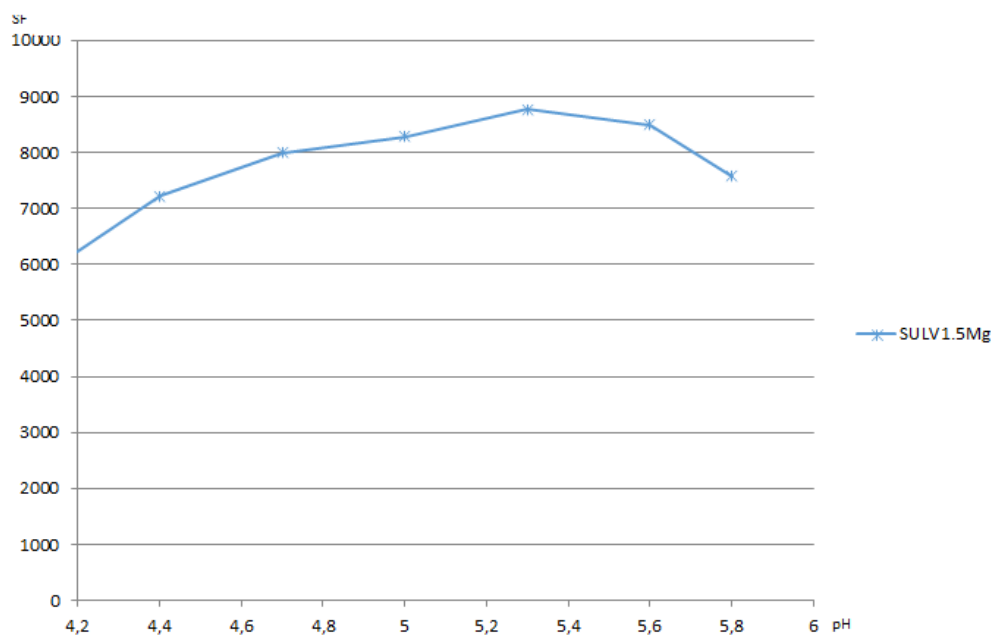
Figure 26: Co/Ni isotherm with magnesium treated solvent

	Versatic Area	STD Area
SUL1.5V	2026	2152
SUL1.5V Mg	2091	2152

Table 6: GC-FID peak ares for SULV1.5 and SULV1.5 Mg

Magnesium treatment of the solvent in isotherm presented in the figure 26 resulted in higher separation factor than in the experiment with only Cyanex 272 in the figure 23 which induced retesting the results and more detailed analysis of the samples with GC-FID. Results are shown in figure 6. Heneicosane acid was used as a standard. A more detailed analysis of ICP results revealed that more cobalt was loaded in to the solvent than in Cyanex 272 isotherm in the figure 23.
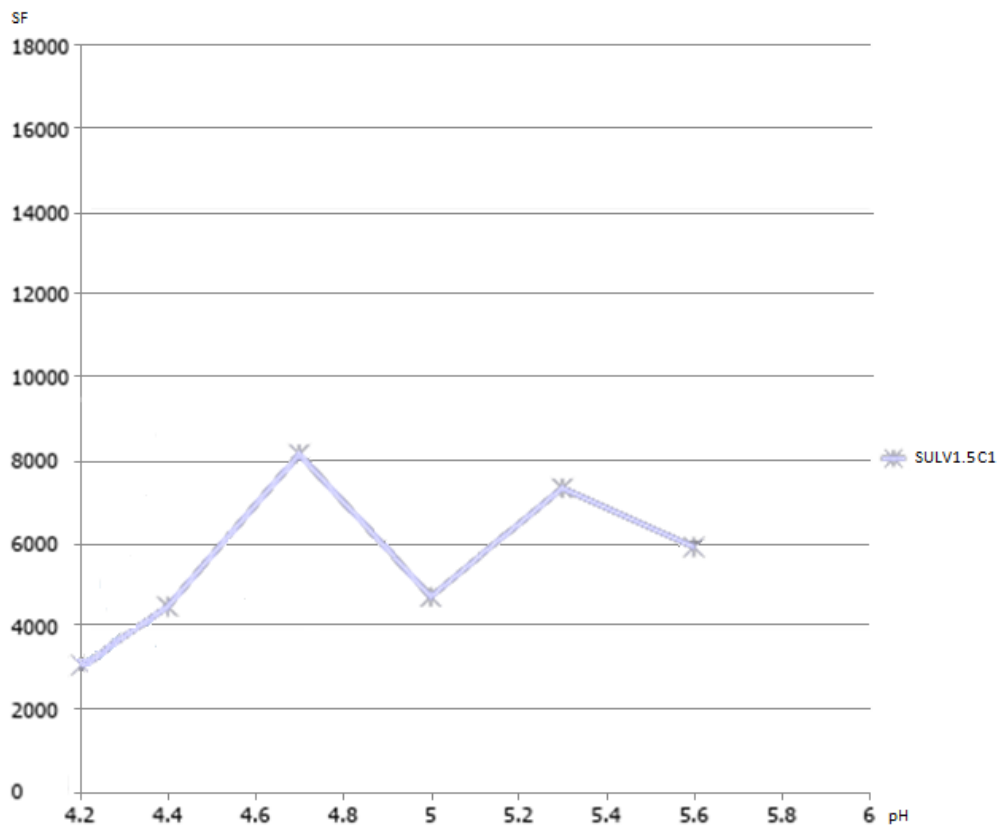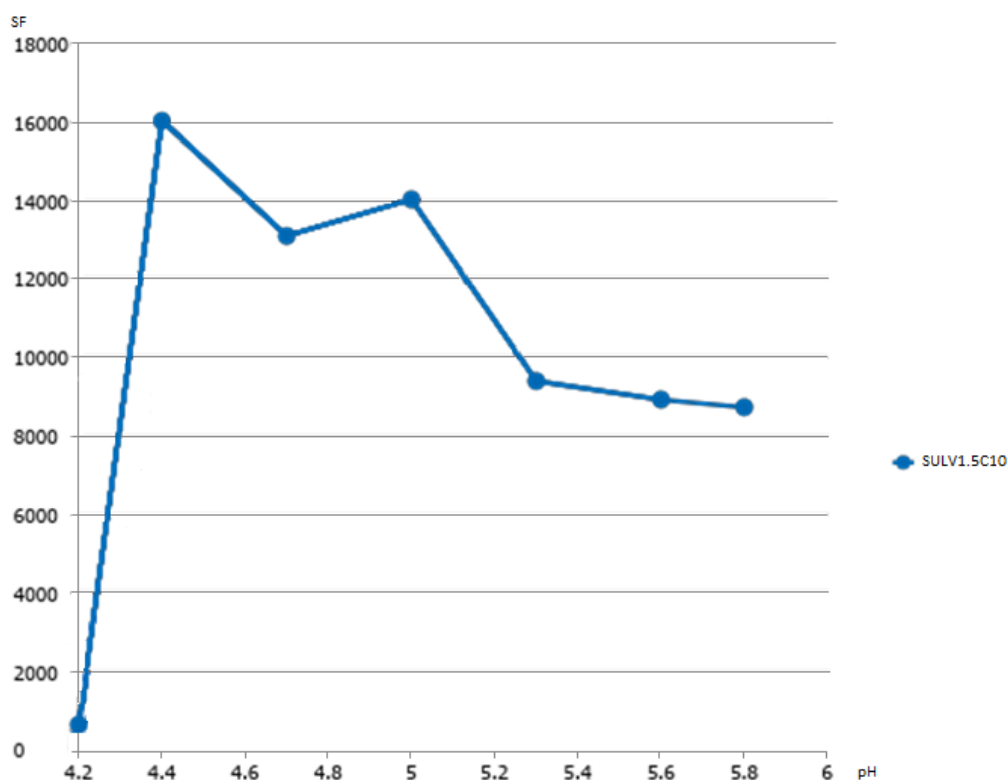
Figure 27: Co/Ni isotherm with single wash

Figure 28: Co/Ni isotherm with 10 wash

Both washing experiment isotherms presented in the figures 27 and 28 resulted in larger than expected values with separation factor. A more detailed analysis of ICP results revealed that significantly less nickel was loaded in to the solvent than in Cyanex 272 isotherm in the figure 23.

6.3 Using different water solubilities of extractants to separate them

Water solubilities of Cyanex 272 and Versatic 10 increase as the pH value increases. Hypothesis was that water solubility of Versatic 10 would be higher

at lower pH, than Cyanex 272, therefore, enabling washing at that pH. Experiments were conducted with Cyanex 272, Versatic 10 and with different mixtures of these extractants. Solutions for these experiments are listed in table 7. Pure solvents were analysed with titration, mixtures with GC-FID and aqueous layer for total organic carbon.

Table 7: Solutions for second experimentations

	Solution	Concentration (w-%)	Abbreviation
40 w-% Versatic 10	Versatic 10	40	V40
25 w-% Cyanex 272	Cyanex 272	25	C25
25 w-% Cyanex 272 10 w-% Versatic 10	Cyanex 272 / Versatic 10	25 / 10	C25V10
25 w-% Cyanex 272 10 w-% Versatic 10	Cyanex 272 / Versatic 10	25 / 1,5	C25V1.5

6.3.1   Experiments and analysis

Experiments were conducted with similar equipment as the selectivity tests. pH value was increased in 1.0 increments. In the first test pH was increased from 3.0 to 8.0 and samples were taken from each point. In second test steps from 8.0 to 12.0 were tried, but pH value changed from 8.0 to 12.0 with a single small NaOH addition. Titration results are listed in appendix C and TOC results in appendix D.
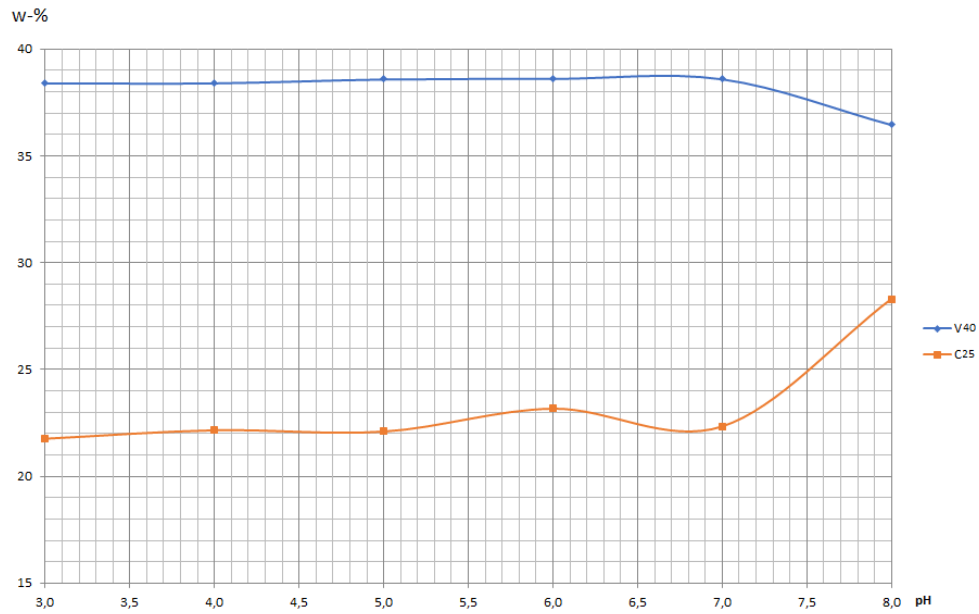
Figure 29: Extractant concentration titration vs pH graph

In the figure 29 are presented the extractant concentrations of the pure Cyanex 272 and Versatic 10 solvents. with Versatic 10 we measure downward trend in concentration at pH values higher than 7.0. In Cyanex 272 there is clear uptrend.
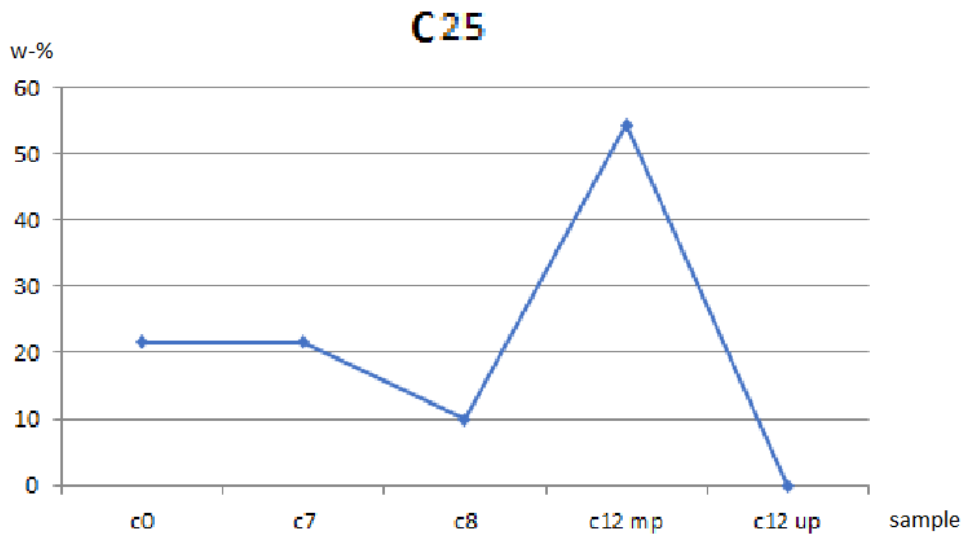
Figure 30: C25 concentration titration vs pH graph

In additional experiments with the first C25 solution at pH 8.0-12.0 in figure 30 a 3-phase system is generated clearly after 8.0. At pH 8.0 results contradict with the previous experiment where there was a rising trend in concentration. Results indicate that Cyanex 272 concentration has increased in the middle phase and decreased in the uppermost phase.
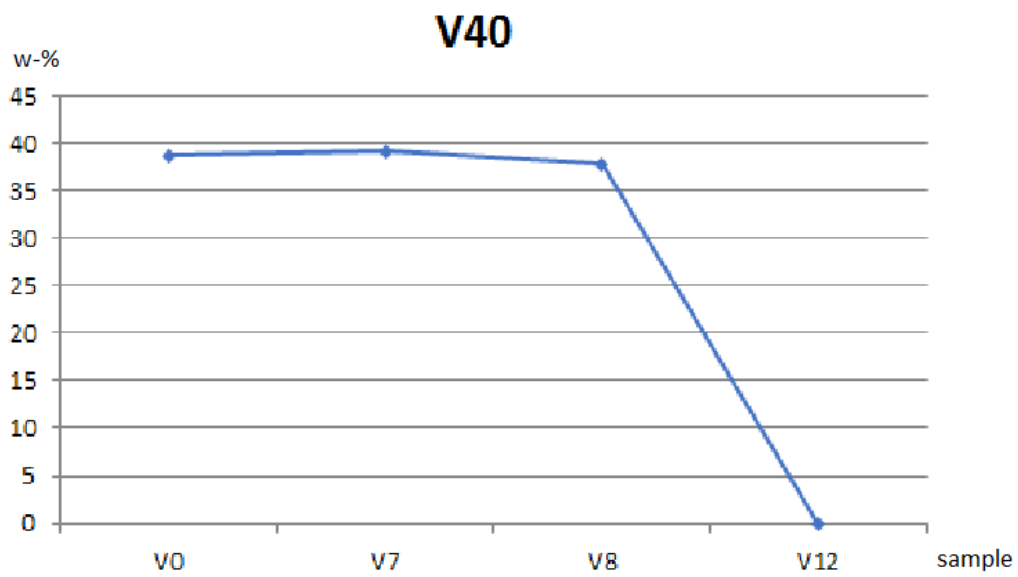
Figure 31: V40 concentration titration vs pH graph

In figure 31 are presented the results of the titration test for solvent containing 40 w-% Versatic 10. It is clear, that all Versatic 10 migrates to aqueous phase.
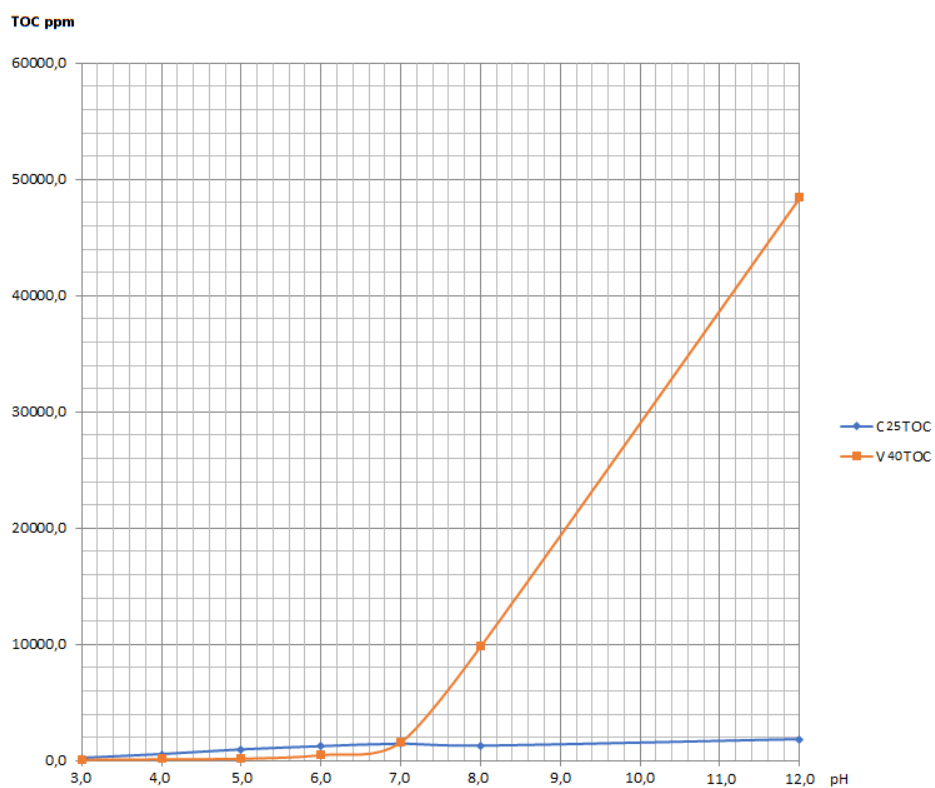
Figure 32: Aqueous TOC vs pH graph

In figure 32 are presented the TOC analysis results of aqueous phase at different pH values. Solvents contained 25 w-% Cyanex 272 and 40 w-% Versatic 10. TOC results show similar trends as the titration results. Versatic concentration increases significantly at pH 8.0.
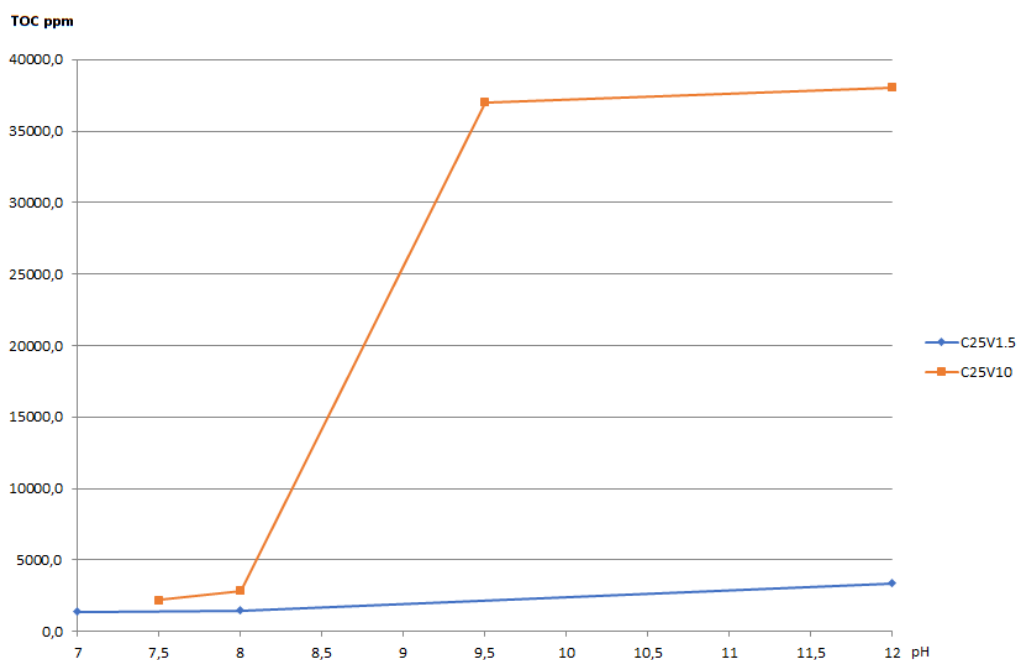
61

Figure 33: C25V1.5 and C25V10 vs pH graph

In figure 33 are presented TOC results aqueous phase at different pH values. One mixture of extractants contained 25 w-% Cyanex 272 and 10 w-% Versatic 10 and the other 25 w-% Cyanex 272 and 1.5 w-% Versatic 10. Organic phase analysis were carried out with GC-FID, results are listed in appendix A pages 79 to 85.

6.4 Separating Cyanex 272 from Versatic 10 with liquid chromatography

Hypothesis was that, bulkier Cyanex 272 would have been less polar, therefore separation with liquid chromatography would have been possible.

6.4.1 Experiments and analysis

Experiments were performed with Hewlett Packard 1100 series HPLC system and Luna 2u Silica (2) 100A column. Gradient method started at point 100:0 % hexane to methanol ratio. Mixture was then changed by incrementally adding methanol concentration. Two methods produced similar results which are illustrated in figure 34.Blue and orage colored boxes represent a time window when both extractants eluated. At first detection was tried with UV-VIS, but no clear signal was produced with either Cyanex 272 or Versatic 10. Samples were taken with fractioning and analysed with GC-FID. Initially, tests with pure solvents were carried out to ensure that both reagents eluated within allotted timeframe. It was concluded that with this experimental setup separation was not possible.
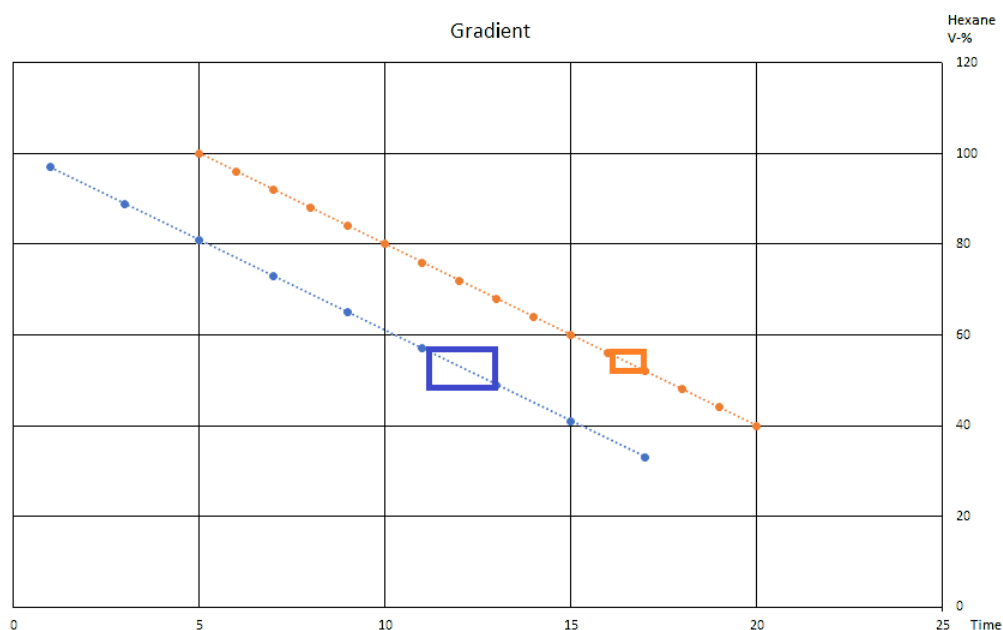

Figure 34: HPLC gradient method illustration

63

6.5 Removing Versatic 10 with 3-D manufactured molecular catcher

Hypothesis was that Versatic 10 would react with zinc thus reducing its concentration.

6.5.1 Experiments and analysis

In Jyväskylä University's chemistry department, a molecular catcher was produced. Solutions in table 8 were prepared and forced through molecular catcher.

Table 8: Solutions for third experimentations

	Solution	Concentration (w-%)	Abbreviation
10 w-% Versatic 10	Versatic 10	10	V10
Synthetic organic with versatic	Cyanex 272 / Versatic 10	22 w-% / 1,5 w-%	SULV1.5
SULV1.5 with pH adjusted to 5.5	Cyanex 272 / Versatic 10	22 w-% / 1,5 w-%	SULV1.5ph55
SULV1.5 with cyanex-zinc complexation	Cyanex 272 / Versatic 10	22 w-% / 1,5 w-%	SULV1.5Zn

GC-FID Analysis in appendix A showed no change in extractant concentrations before or after the filtration.

7 RESULTS ANALYSIS AND SUMMARY

None of the experiments produced the desired outcome, however there where some interesting observations made.
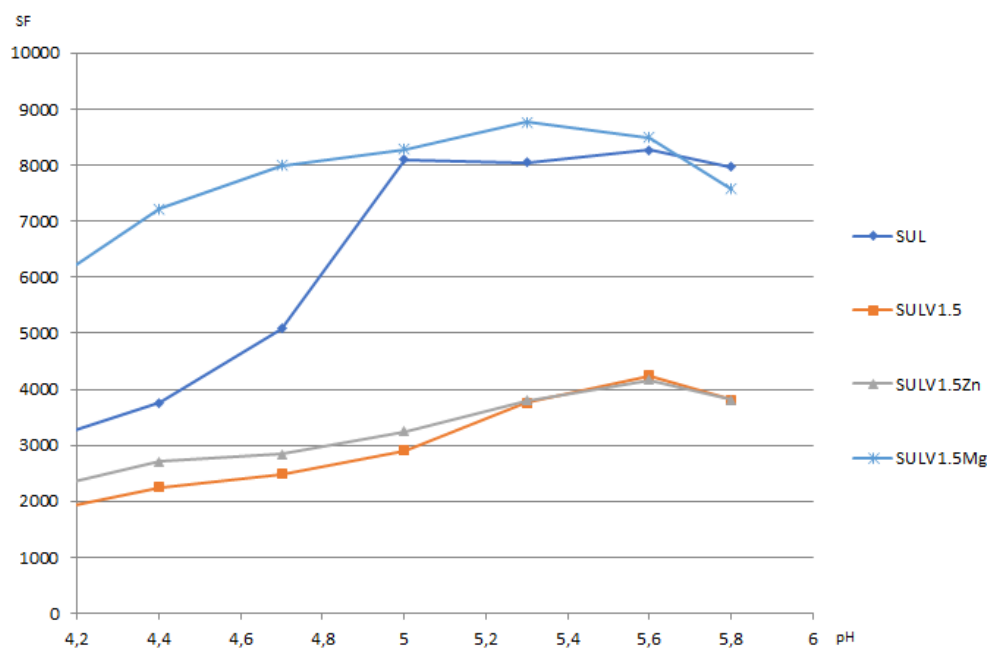
Figure 35: Co/Ni isotherms with loading experiment results

Figure 35 indicated, that magnesium handling would improve separation factor beyond pure Cyanex 272. Also from figures 27 and 28 we also find interestingly high separation factors. From figures 32 and 29, we can deduce, that some organic carbon is transferring to aqueous layer even at pH values 4-6, however no loss in Cyanex 272 concentration is detected. In the future, if similar experiments are made experimenter should observe volume changes in organic phase.

In water solubility experiments contradicting results were propably caused by slightly erroneus sampling. In second test, we found that 3-phase system was produced, it is likely that at pH value 8, there already were three phases even if they were nearly homogenous. And in the first test, sample was taken from the middle phase and in the second from the upper phase. In future tests,

it should be noted that with derivatization there were slight change in color of samples where there were Cyanex 272 and Versatic. It would be useful to know, if both of them caused the coloring or only other one. This might create an opportunity to analyze samples with UV-Vis after derivatization or perhaps some other reagents.

In order to succesfully separate extractants I recommend following procedures. Chromatographic techniques size exclusion, supercritical CO_2 chromatography and if possible reverse phase chromatography. TGA analysis and mathematical modeling of system might produce useful information. To continue water solubility experiments with focus on pH range 8-12, there might be a zone where only versatic migrates to aqueous layer. Finally molecular catcher could work with experiment parameters where catcher is imbued with functional group that is able to react with metal part of the metal-versatic complex.

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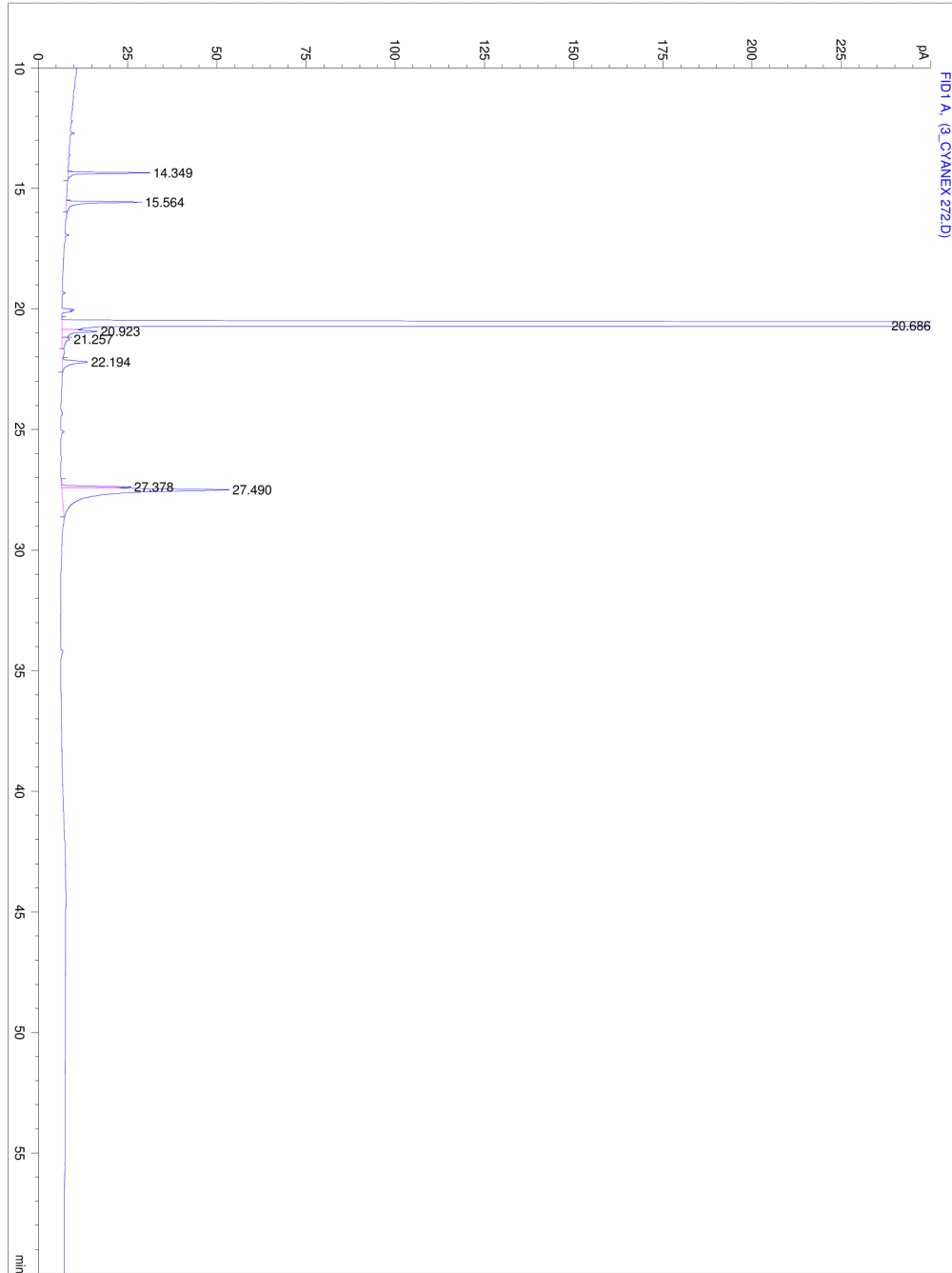[45] Lenarita Koski-Tuuri. Total organic carbon analysis. *Norilsk Nickel Harjavallan laboratorion työohje*, 2009.
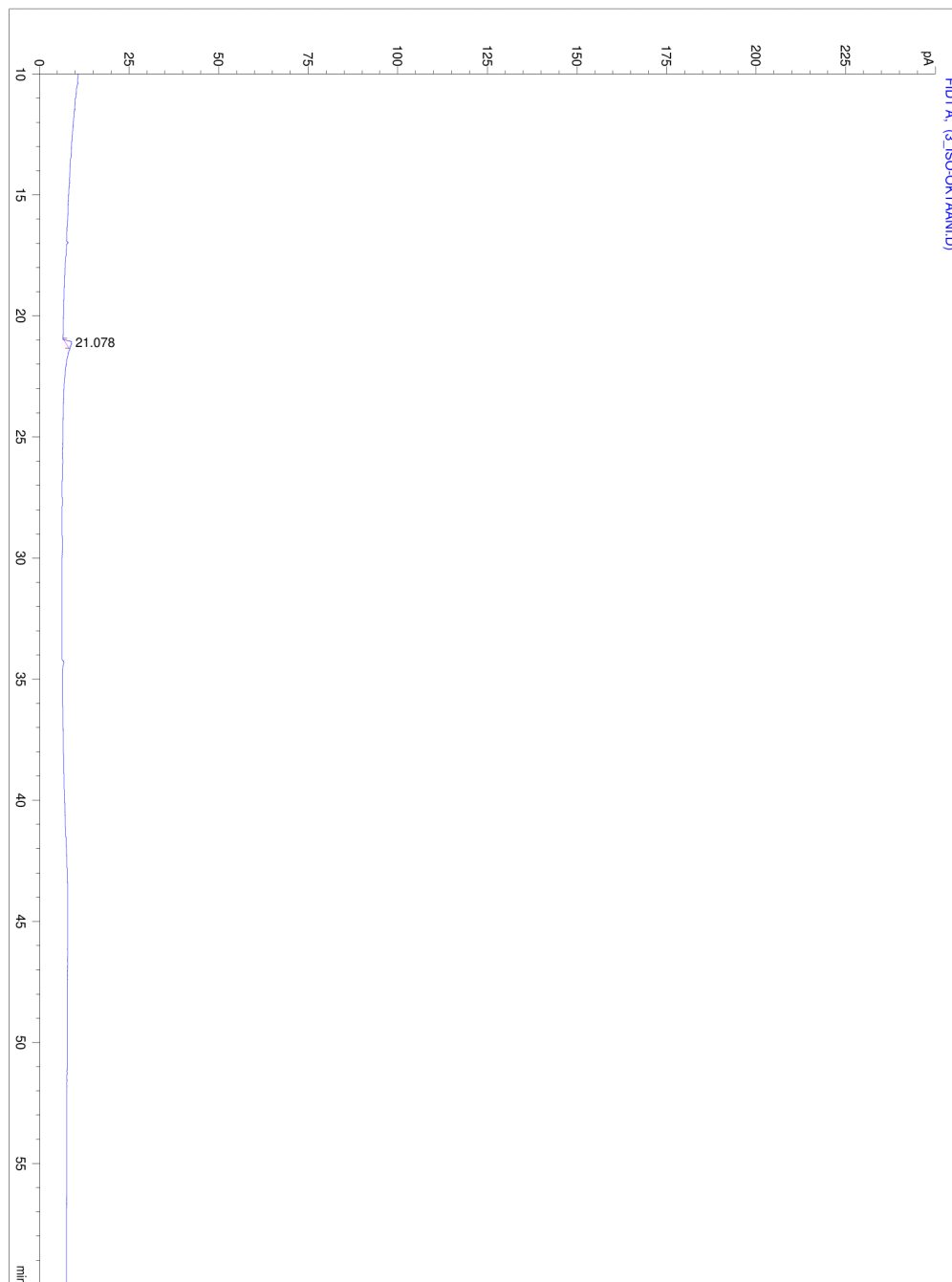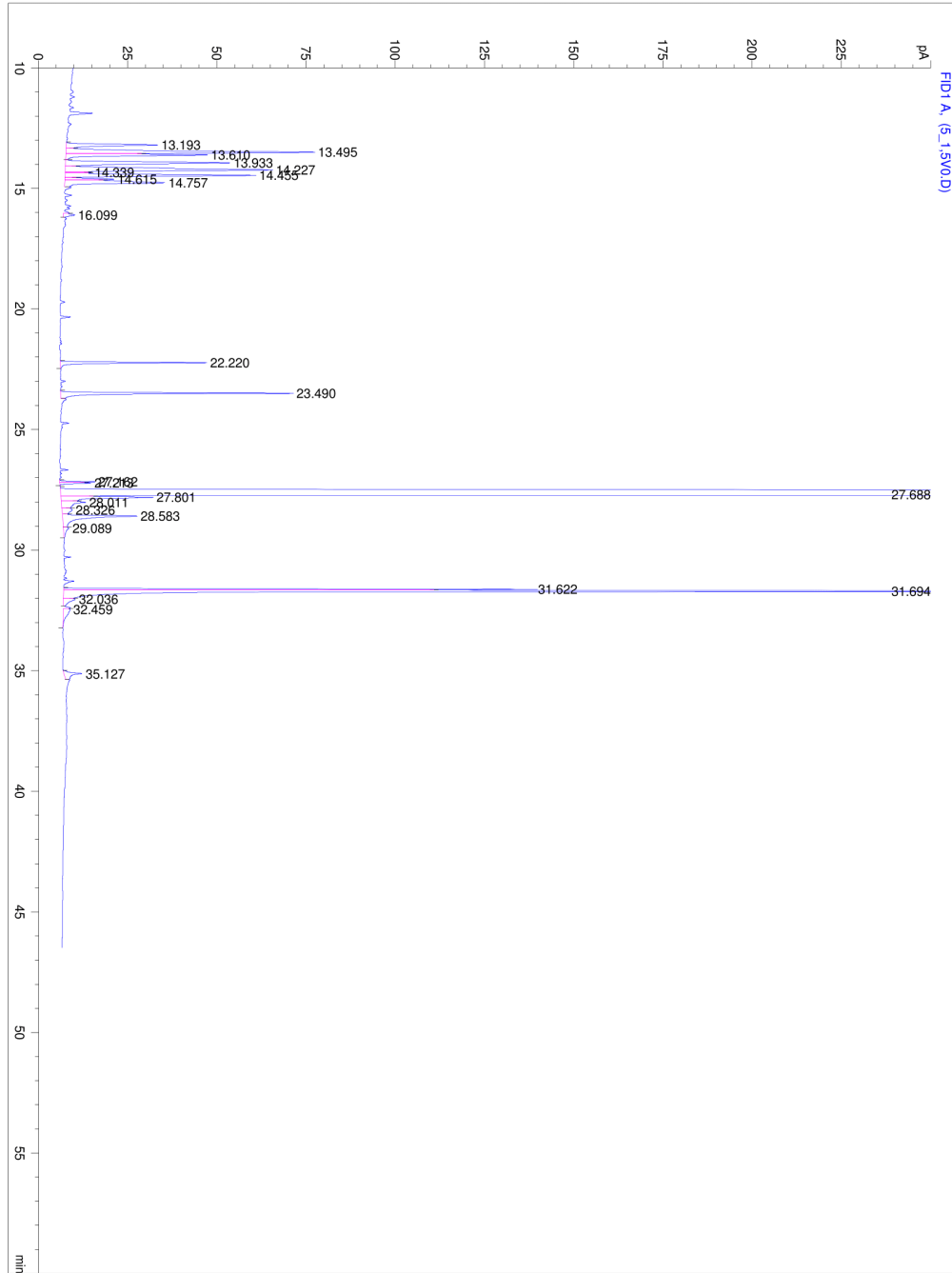
Appendices

A

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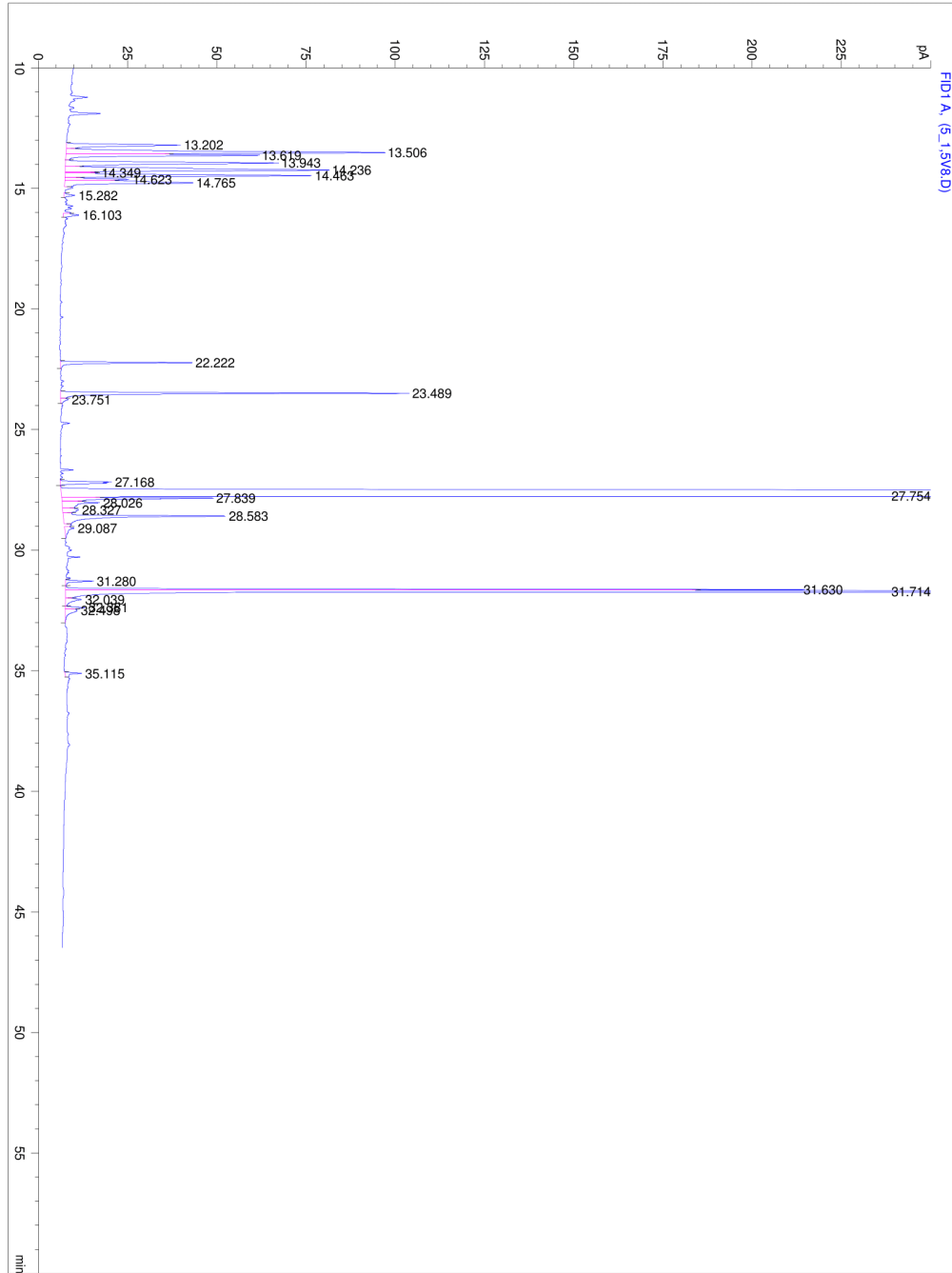
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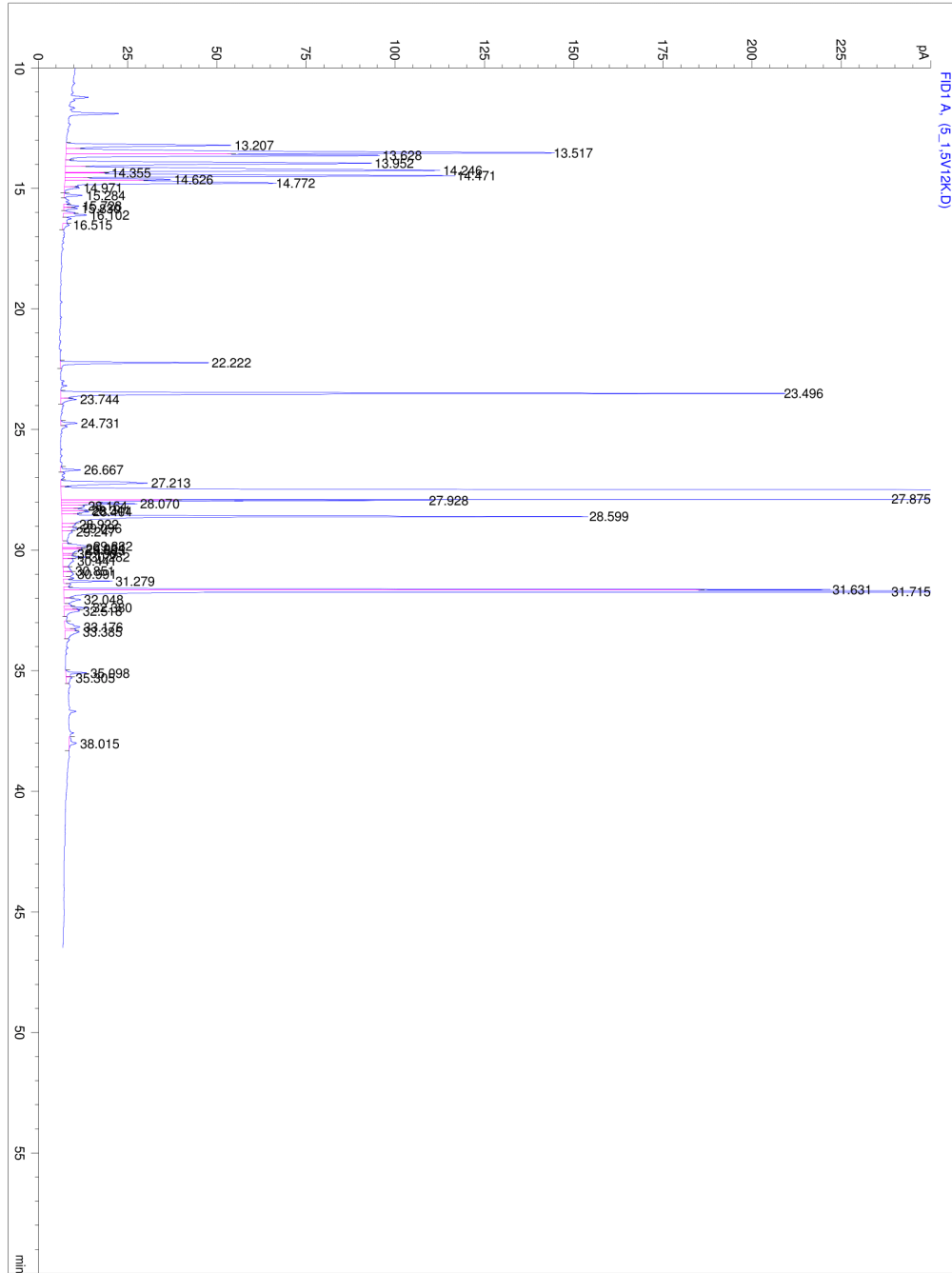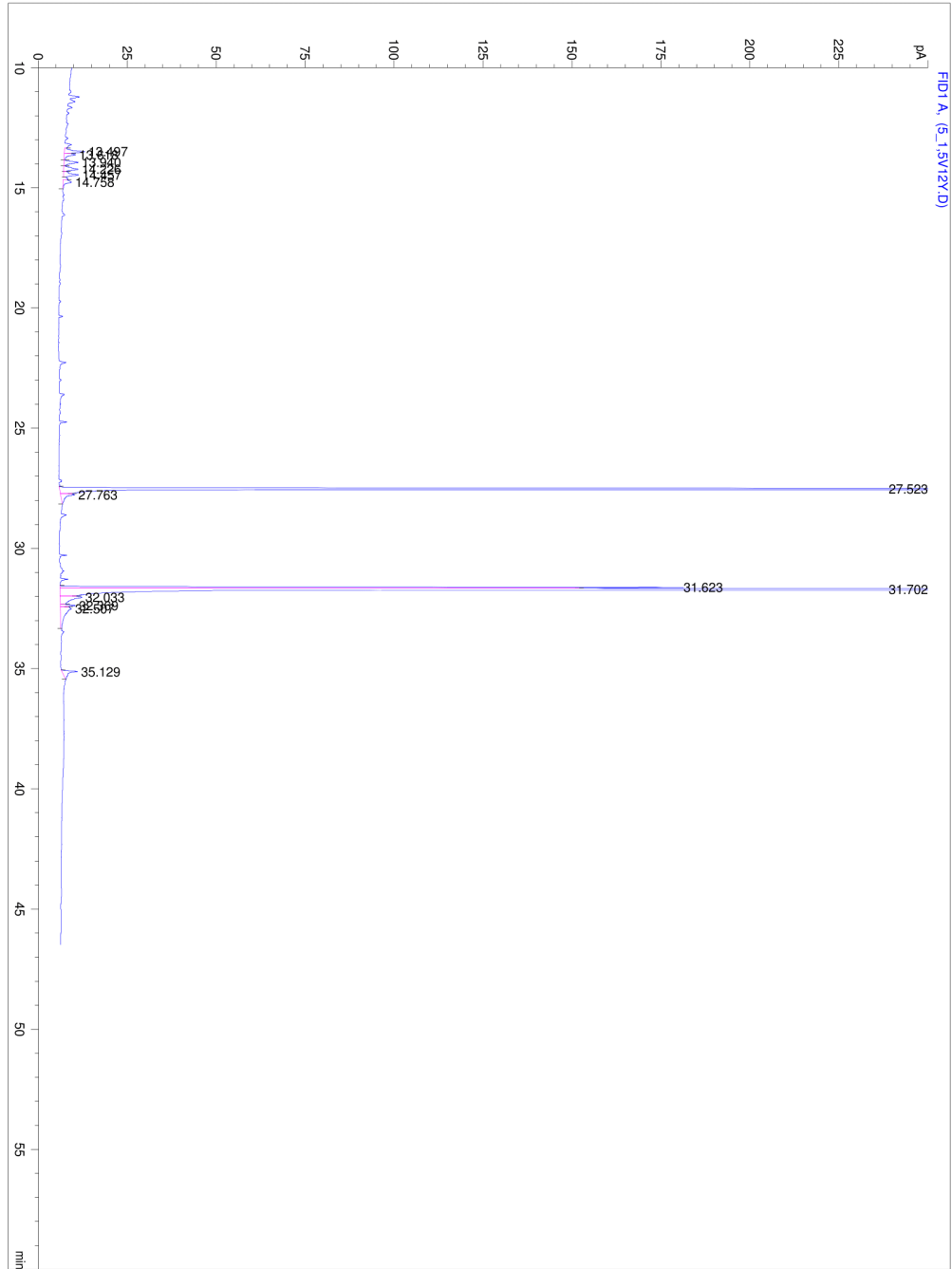
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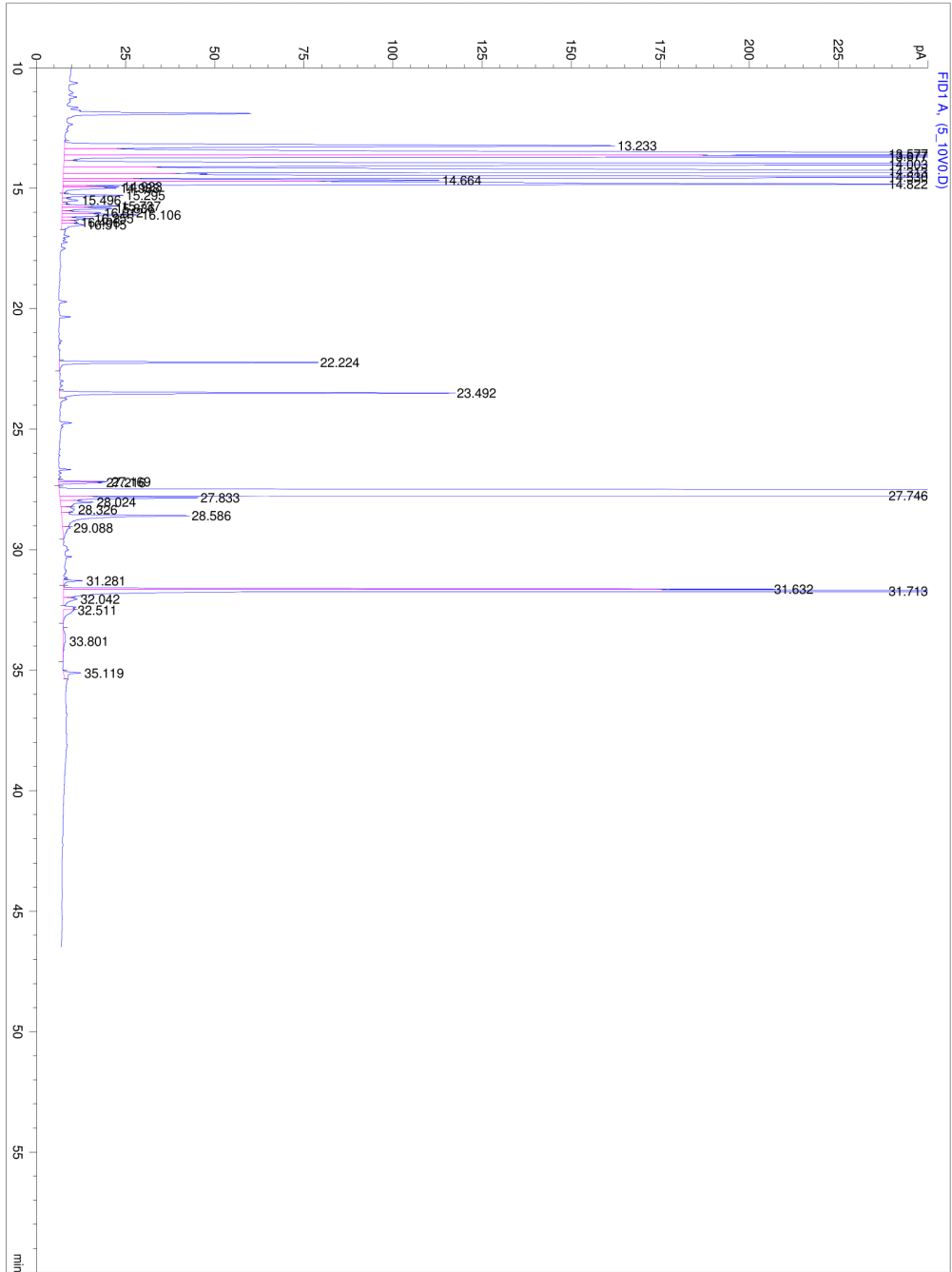
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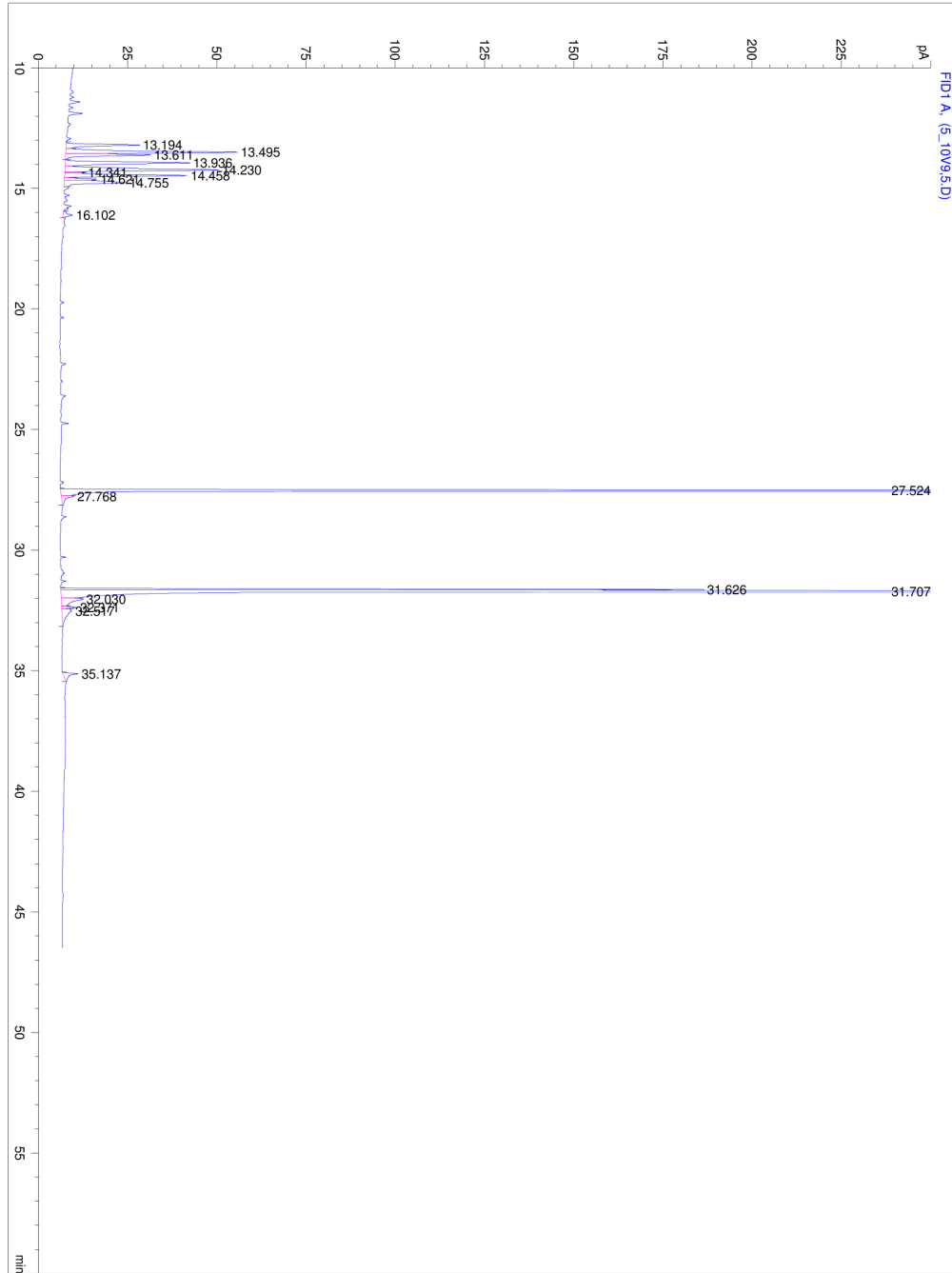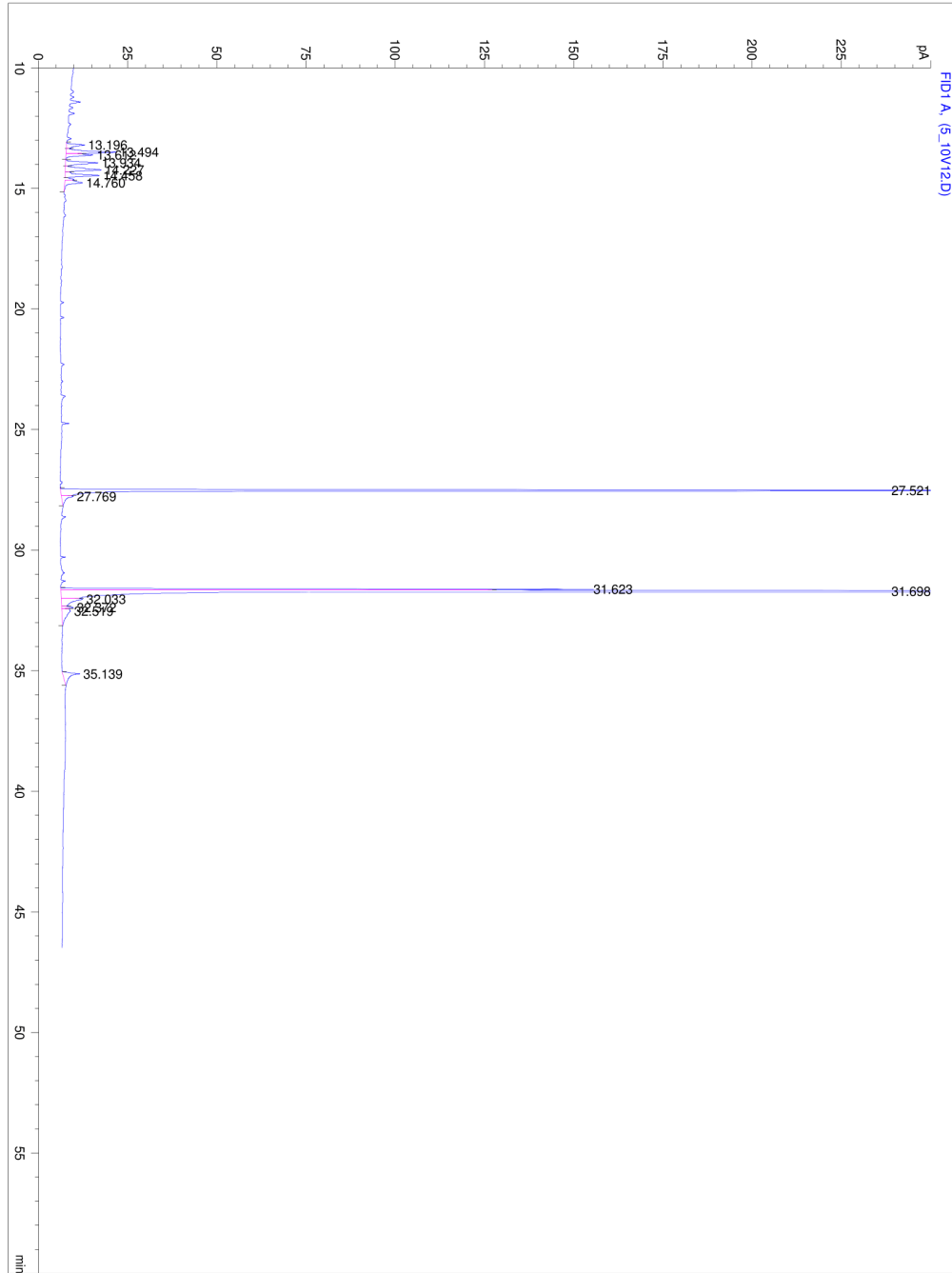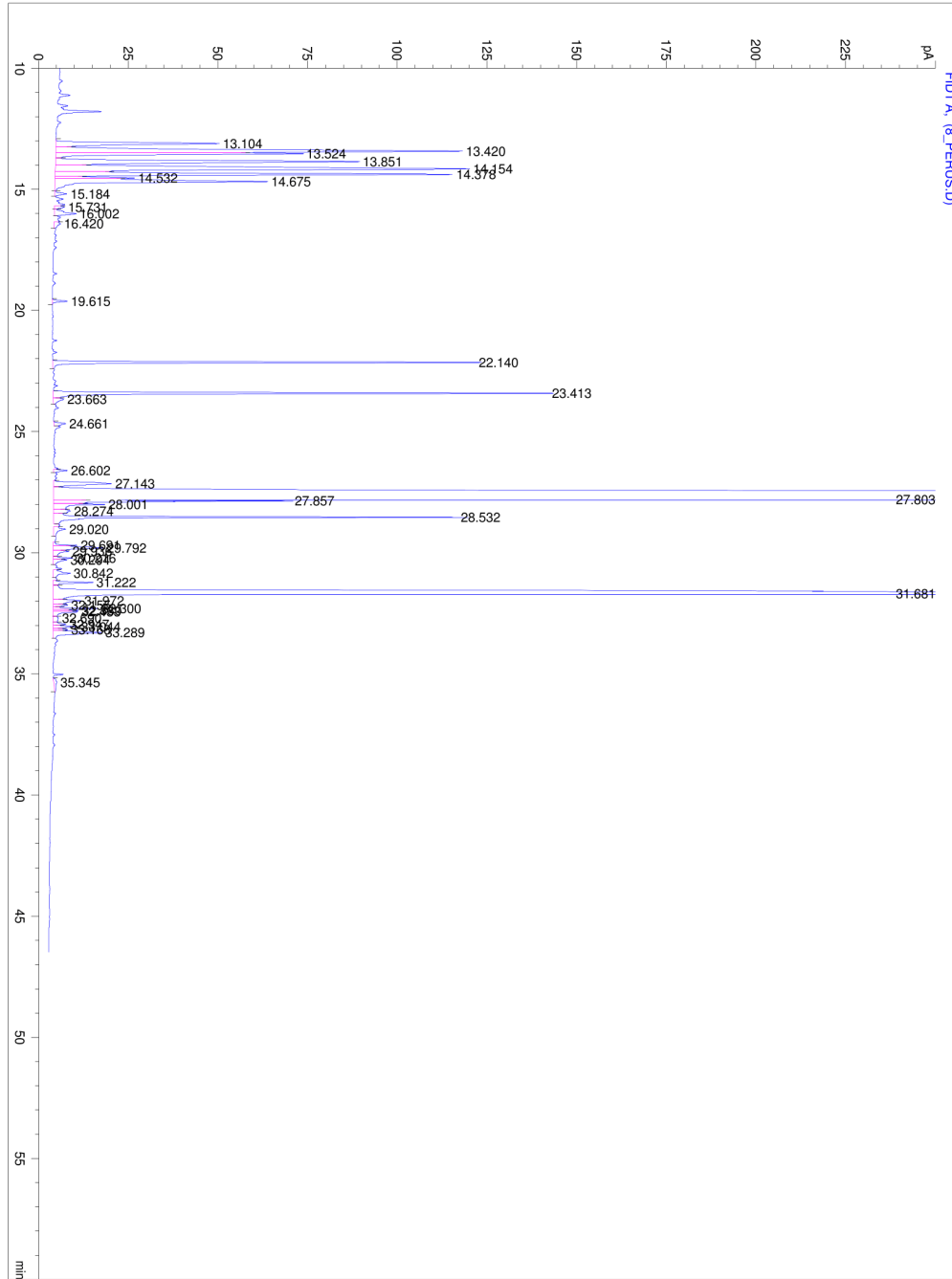
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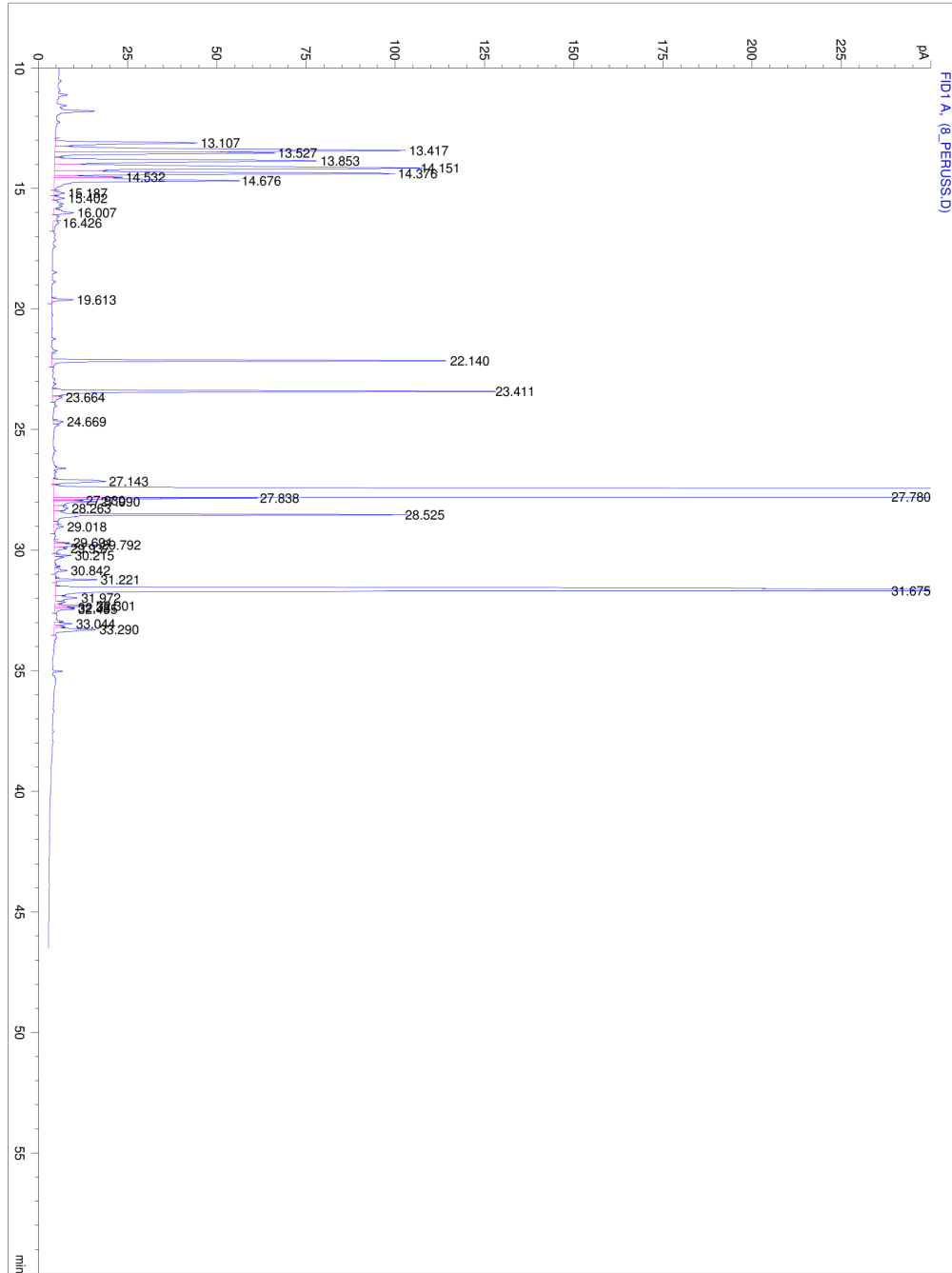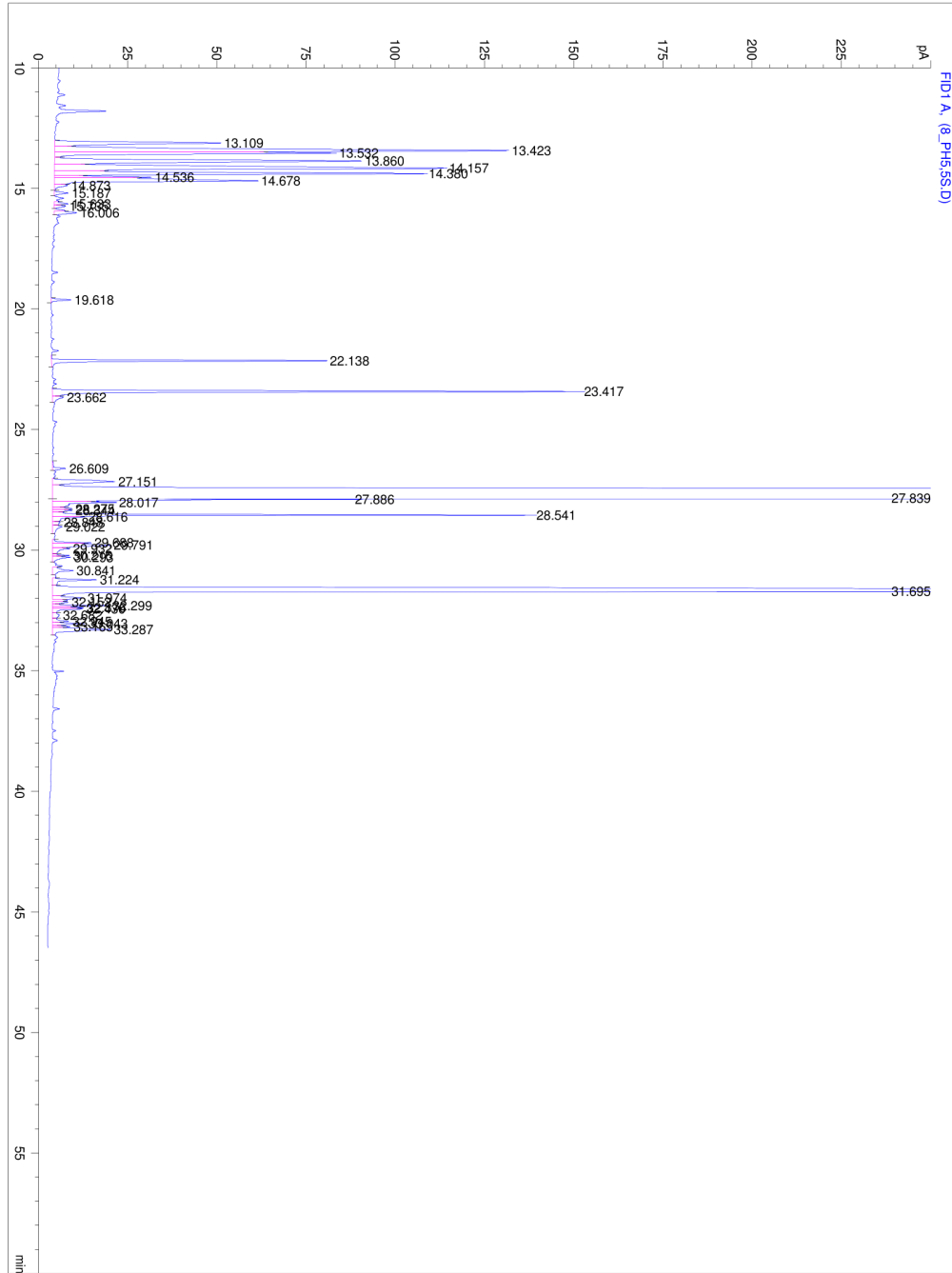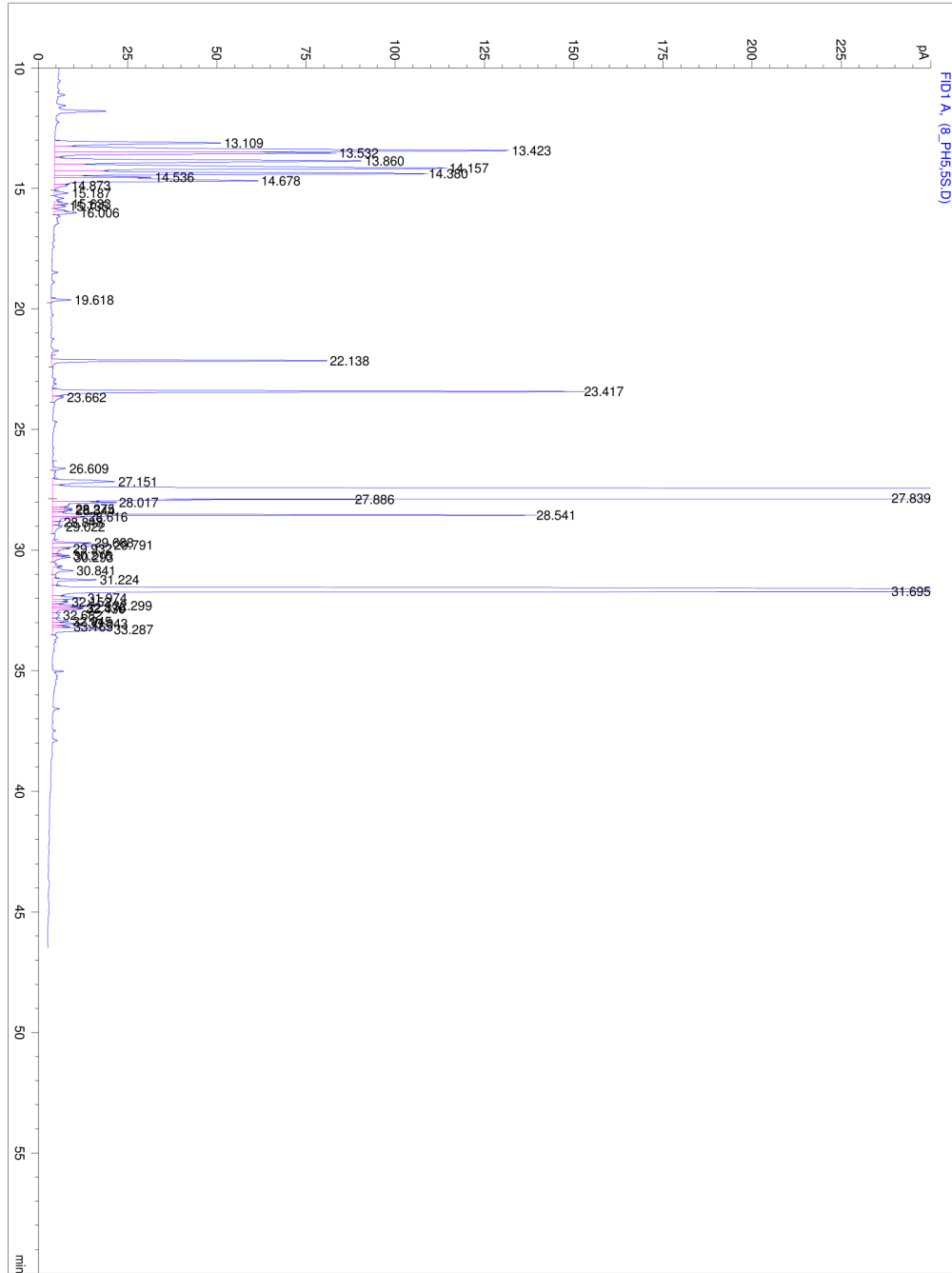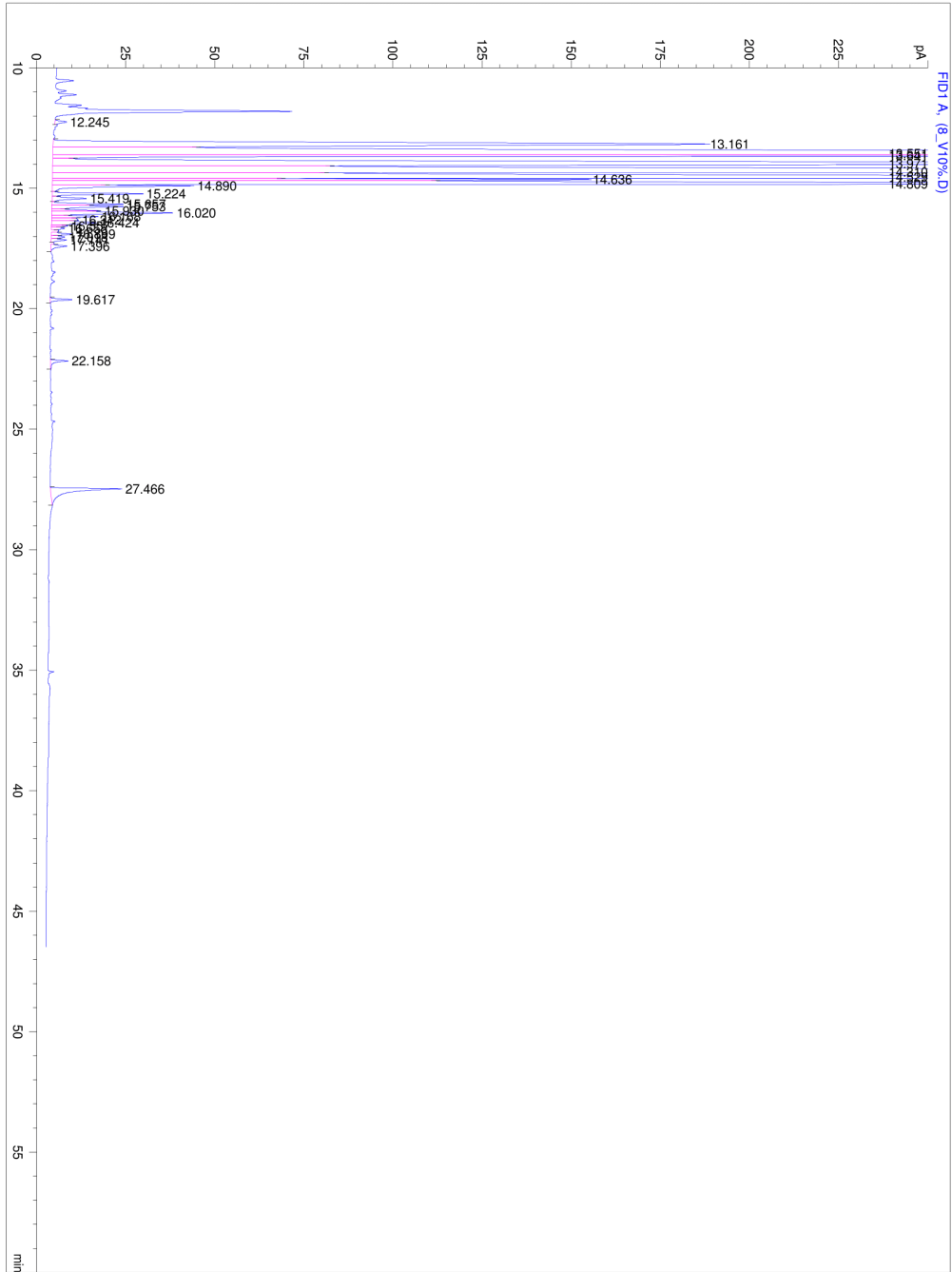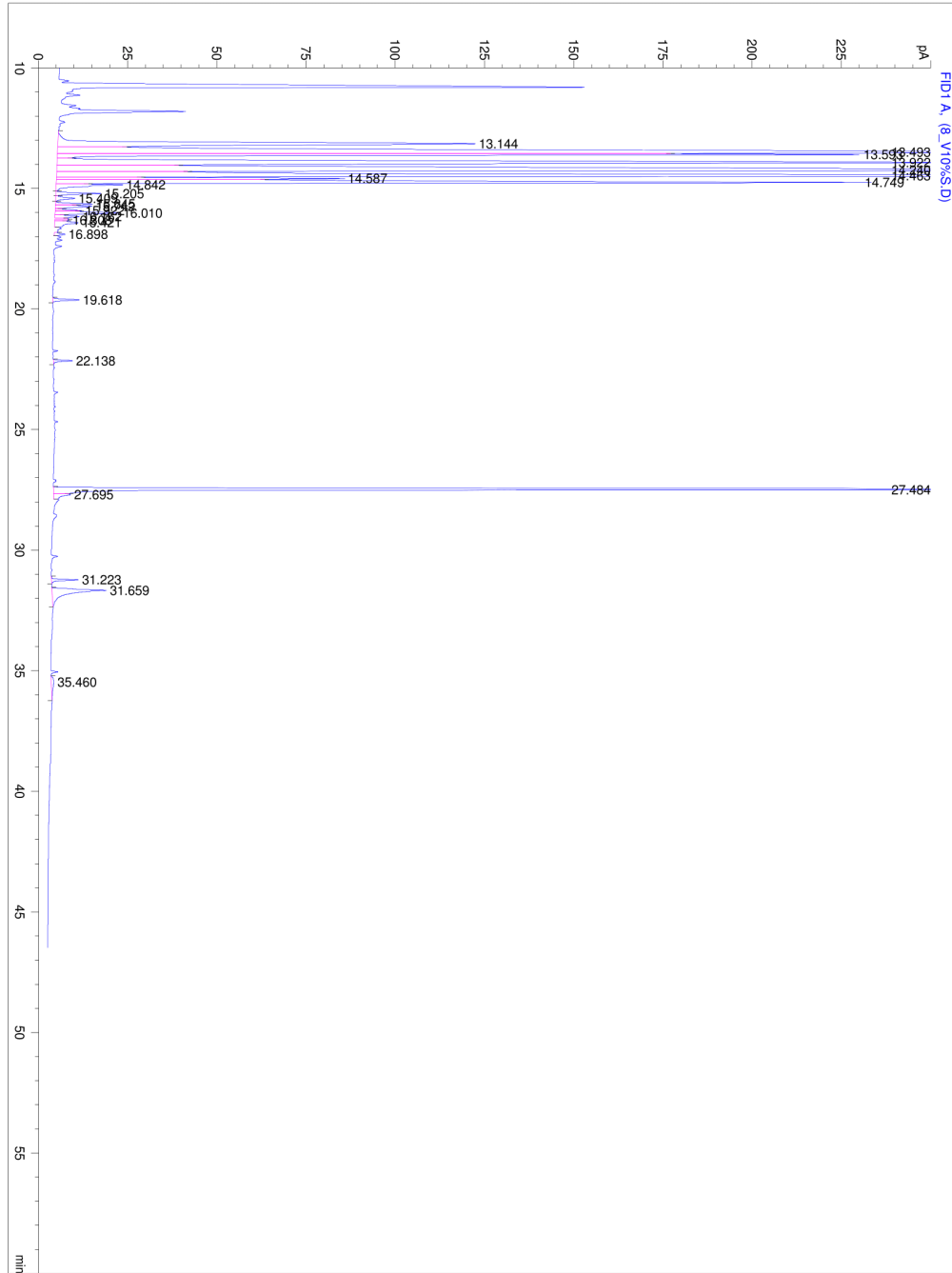
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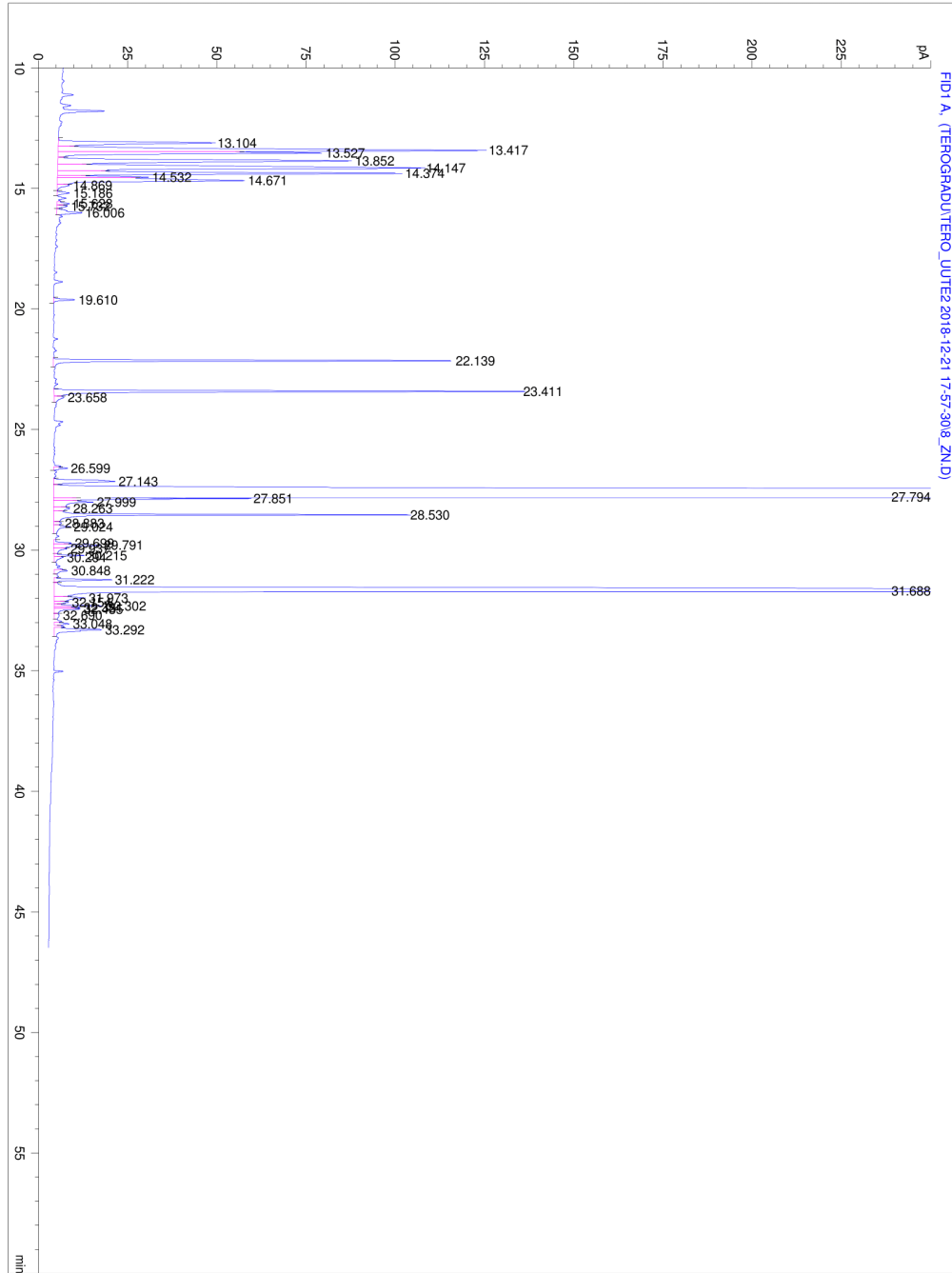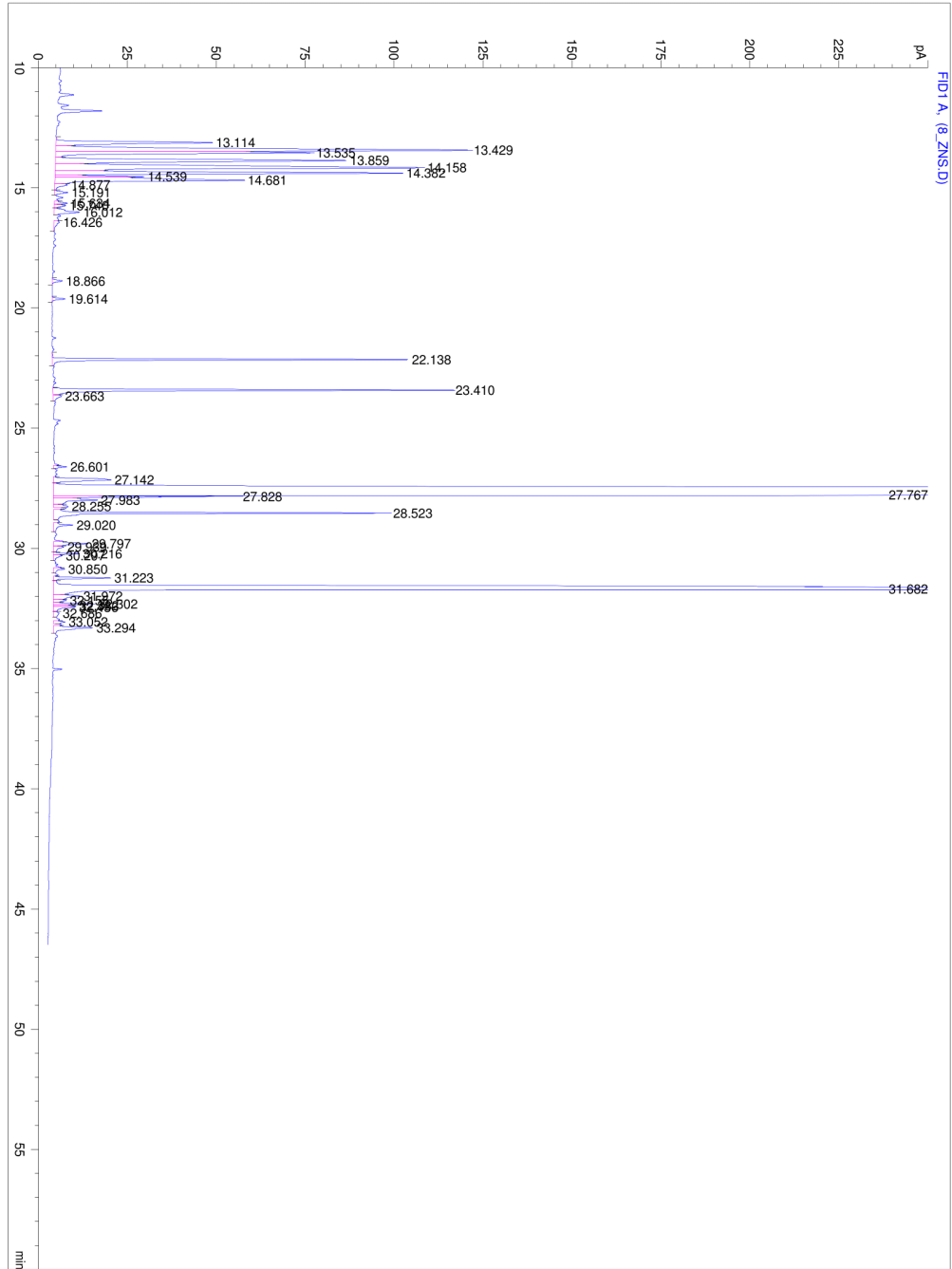
B

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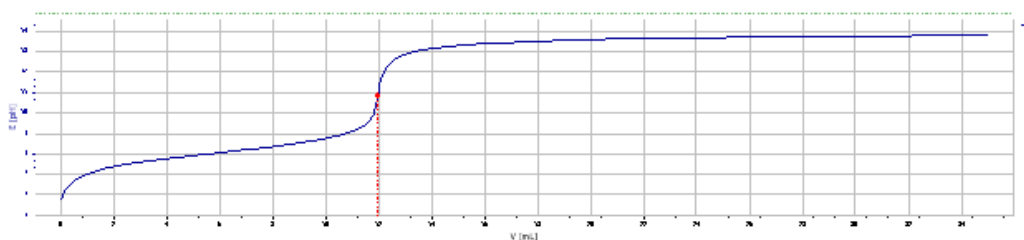
t [s]	V [mL]	E [pH]	dV/dt [mL/s]	T [°C]	dE/dV [pH/mL]	log dE/dV [log (pH/mL)]	EQP Name	BETA Name	Buffer capacity [mmol/(L*p H)]
0	0	5,759		25					
15	0,05	5,938	0,003	25					
24	0,1	6,078	0,005	25					
31	0,162	6,225	0,008	25					
38	0,229	6,338	0,01	25					
45	0,342	6,506	0,017	25	1,43	0,15			
50	0,445	6,621	0,019	25	1,16	0,07			
56	0,606	6,764	0,026	25	0,9	-0,04			
62	0,799	6,9	0,034	25	0,71	-0,15			
67	1,04	7,027	0,046	25	0,55	-0,26			
73	1,378	7,175	0,059	25	0,42	-0,38			
78	1,756	7,302	0,074	25	0,32	-0,49			
84	2,256	7,437	0,088	25	0,25	-0,6			
89	2,756	7,548	0,102	25	0,21	-0,69			
94	3,256	7,645	0,104	25	0,18	-0,75			
99	3,756	7,73	0,106	25	0,16	-0,79			
104	4,256	7,809	0,111	25	0,15	-0,82			
108	4,756	7,886	0,116	25	0,15	-0,83			
113	5,256	7,958	0,102	25	0,14	-0,85			
118	5,756	8,03	0,109	25	0,14	-0,85			
122	6,256	8,098	0,111	25	0,14	-0,85			
127	6,756	8,171	0,093	25	0,14	-0,84			
132	7,256	8,244	0,098	25	0,15	-0,83			
137	7,756	8,321	0,1	25	0,16	-0,81			

92

142	8,256	8,401	0,1	25	0,16	-0,78			
147	8,756	8,488	0,096	25	0,18	-0,75			
152	9,256	8,584	0,091	25	0,2	-0,69			
158	9,756	8,697	0,077	25	0,24	-0,61			
164	10,256	8,827	0,079	25	0,32	-0,5			
171	10,756	8,997	0,075	25	0,47	-0,33			
177	11,072	9,14	0,052	25	0,65	-0,19			
184	11,296	9,276	0,034	25	0,87	-0,06			
190	11,464	9,412	0,027	25	1,18	0,07			
198	11,589	9,547	0,016	25	1,68	0,23			
206	11,682	9,681	0,011	25	2,35	0,37			
216	11,753	9,828	0,007	25	3,05	0,48			
227	11,803	9,958	0,005	25	3,6	0,56			
241	11,853	10,127	0,004	25	4,6	0,66			
271	11,903	10,441	0,002	25	5,94	0,77			
301	11,953	10,793	0,002	25	6,68	0,82			
	11,964113	10,878					EQP1		
331	12,003	11,177	0,002	25	6,49	0,81			
362	12,053	11,509	0,002	25	5,46	0,74			
383	12,103	11,726	0,002	25	4,24	0,63			
395	12,153	11,868	0,004	25	3,38	0,53			
407	12,226	12,076	0,006	25	2,57	0,41			
416	12,276	12,198	0,005	25	2,26	0,35			
424	12,34	12,323	0,008	25	1,88	0,27			
431	12,426	12,453	0,012	25	1,53	0,18			
438	12,542	12,584	0,017	25	1,19	0,08			
445	12,703	12,719	0,023	25	0,87	-0,06			
451	12,919	12,847	0,034	25	0,63	-0,2			
458	13,239	12,978	0,046	25	0,42	-0,38			
464	13,724	13,108	0,078	25	0,26	-0,59			
470	14,224	13,203	0,082	25	0,17	-0,77			
476	14,724	13,276	0,086	25	0,13	-0,9			
481	15,224	13,334	0,093	25	0,1	-1			
486	15,724	13,38	0,093	25	0,08	-1,08			
491	16,224	13,418	0,096	25	0,07	-1,15			
496	16,724	13,453	0,102	25	0,06	-1,22			
500	17,224	13,481	0,122	25	0,05	-1,27			
504	17,724	13,507	0,116	25	0,04	-1,35			
508	18,224	13,529	0,125	25	0,04	-1,37			
511	18,724	13,547	0,147	25	0,04	-1,38			
515	19,224	13,567	0,119	25	0,04	-1,38			
518	19,724	13,582	0,156	25	0,04	-1,4			
546	20,224	13,619	0,018	25	0,04	-1,44			
549	20,724	13,627	0,156	25	0,03	-1,51			

552	21,224	13,638	0,152	25	0,03	-1,6		
555	21,724	13,65	0,152	25	0,02	-1,69		
558	22,224	13,66	0,147	25	0,02	-1,75		
561	22,724	13,67	0,147	25	0,02	-1,71		
564	23,224	13,68	0,147	25	0,02	-1,75		
568	23,724	13,688	0,143	25	0,02	-1,79		
570	24,224	13,696	0,2	25	0,02	-1,8		
574	24,724	13,703	0,139	25	0,02	-1,81		
577	25,224	13,711	0,192	25	0,01	-1,83		
580	25,724	13,718	0,185	25	0,01	-1,84		
583	26,224	13,728	0,172	25	0,01	-1,87		
586	26,724	13,731	0,172	25	0,01	-1,89		
589	27,224	13,738	0,167	25	0,01	-1,93		
592	27,724	13,744	0,167	25	0,01	-1,95		
595	28,224	13,75	0,167	25	0,01	-1,96		
598	28,724	13,755	0,161	25	0,01	-1,96		
601	29,224	13,76	0,161	25	0,01	-2,01		
604	29,724	13,765	0,156	25	0,01	-2,03		
607	30,224	13,77	0,156	25	0,01	-2,05		
610	30,724	13,774	0,152	25	0,01	-2,06		
613	31,224	13,778	0,152	25	0,01	-2,07		
616	31,724	13,782	0,147	25	0,01	-2,09		
619	32,224	13,787	0,147	25	0,01	-2,1		
622	32,724	13,791	0,147	25	0,01	-2,1		
626	33,224	13,794	0,143	25				
628	33,724	13,798	0,2	25				
632	34,224	13,802	0,139	25				
635	34,724	13,806	0,192	25				
638	35	13,808	0,102	25				

[Read-Only] - Results Editor LabX

Measured Values
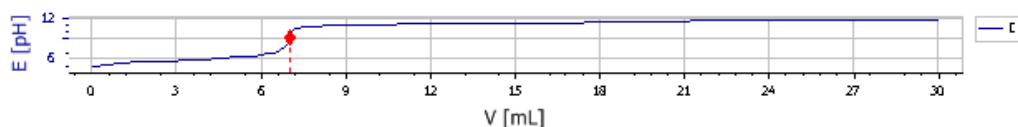
t [s]	V [mL]	E [pH]	dV/dt [mL/s]	T [°C]	dE/dV [pH/mL]	log dE/dV [log..]	EQP Name	BETA Name	Buffer capacity
0	0	4,817		25					
5	0,05	4,814	0,01	25					
8	0,1	4,826	0,016	25					
14	0,225	4,976	0,019	25					
19	0,275	5,015	0,01	25					
25	0,4	5,109	0,022	25	0,64	-0,19			
31	0,586	5,211	0,03	25	0,55	-0,26			
38	0,927	5,344	0,047	25	0,4	-0,4			
45	1,41	5,482	0,065	25	0,27	-0,57			
51	1,91	5,588	0,083	25	0,2	-0,69			
57	2,41	5,681	0,079	25	0,18	-0,75			
64	2,91	5,771	0,077	25	0,17	-0,77			
70	3,41	5,858	0,091	25	0,17	-0,76			
76	3,91	5,954	0,091	25	0,19	-0,71			
83	4,41	6,062	0,071	25	0,23	-0,64			
91	4,91	6,185	0,063	25	0,29	-0,53			
100	5,41	6,34	0,054	25	0,41	-0,39			
113	5,789	6,509	0,029	25	0,55	-0,26			
124	6,001	6,63	0,019	25	0,68	-0,16			
135	6,186	6,754	0,016	25	0,86	-0,07			
146	6,357	6,89	0,015	25	1,12	0,05			
158	6,501	7,032	0,012	25	1,49	0,17			
171	6,612	7,186	0,008	25	1,89	0,28			
186	6,681	7,327	0,005	25	2,31	0,36			
204	6,731	7,474	0,003	25	2,7	0,43			
220	6,781	7,621	0,003	25	2,97	0,47			
242	6,831	7,809	0,002	25	3,94	0,6			
249	6,881	7,906	0,007	25	5,89	0,77			
280	7,006	8,576	0,004	25	8,42	0,93			
	7,032436	8,999					EQP1		
310	7,056	9,377	0,002	25	7,6	0,88			
339	7,106	9,947	0,002	25	5,32	0,73			
367	7,156	10,256	0,002	25	4,54	0,66			

376	7,206	10,358	0,005	25	4,3	0,63			
387	7,331	10,517	0,011	25	2,63	0,42			
397	7,501	10,651	0,016	25	1,23	0,09			
403	7,78	10,744	0,048	25	0,55	-0,26			
409	8,28	10,865	0,082	25	0,21	-0,68			
414	8,78	10,94	0,104	25	0,1	-1,02			
422	9,28	10,988	0,067	25	0,06	-1,2			
425	9,78	10,972	0,192	25	0,07	-1,14			
430	10,28	11,016	0,1	25	0,09	-1,06			
440	10,78	11,096	0,052	25	0,1	-0,99			
445	11,28	11,147	0,1	25	0,11	-0,95			
452	11,78	11,218	0,077	25	0,1	-0,98			
455	12,28	11,238	0,185	25	0,04	-1,4			
458	12,78	11,246	0,185	25	-0,01	-2,01			
461	13,28	11,265	0,167	25	-0,04	-1,44			
464	13,78	11,226	0,161	25	-0,05	-1,32			
468	14,28	11,123	0,125	25	-0,04	-1,42			
471	14,78	11,188	0,147	25	-0,02	-1,73			
478	15,28	11,188	0,068	25	0	-3,21			
481	15,78	11,182	0,152	25	0,03	-1,53			
485	16,28	11,192	0,135	25	0,05	-1,29			
488	16,78	11,216	0,147	25	0,05	-1,31			
492	17,28	11,231	0,128	25	0,06	-1,22			
496	17,78	11,31	0,122	25	0,06	-1,26			
500	18,28	11,334	0,143	25	0,05	-1,27			
503	18,78	11,317	0,156	25	0,06	-1,24			
507	19,28	11,342	0,125	25	0,06	-1,22			
510	19,78	11,388	0,143	25	0,06	-1,21			
540	20,28	11,452	0,017	25	0,07	-1,16			
544	20,78	11,47	0,122	25	0,06	-1,26			
548	21,28	11,478	0,132	25	0,03	-1,5			
553	21,78	11,49	0,102	25	0,02	-1,69			
556	22,28	11,504	0,167	25	0,02	-1,71			
559	22,78	11,505	0,167	25	0,02	-1,62			
562	23,28	11,53	0,147	25	0,03	-1,59			
566	23,78	11,547	0,125	25	0,02	-1,7			
569	24,28	11,545	0,147	25	0,02	-1,79			
573	24,78	11,551	0,122	25	0,01	-1,98			
576	25,28	11,564	0,152	25	0	-2,81			
579	25,78	11,551	0,147	25	0	-3,3			
583	26,28	11,566	0,135	25	0	-2,95			
587	26,78	11,553	0,139	25	0	-2,52			
590	27,28	11,551	0,192	25	0	-3,44			

593	27,78	11,558	0,185	25	0,01	-2,27			
596	28,28	11,561	0,185	25					
600	28,78	11,565	0,128	25					
603	29,28	11,576	0,161	25					
606	29,78	11,581	0,161	25					
609	30	11,589	0,069	25					
				25					
580	25,724	13,718	0,185	25	0,01	-1,84			
583	26,224	13,728	0,172	25	0,01	-1,87			
586	26,724	13,731	0,172	25	0,01	-1,89			
589	27,224	13,738	0,167	25	0,01	-1,93			
592	27,724	13,744	0,167	25	0,01	-1,95			
595	28,224	13,75	0,167	25	0,01	-1,96			
598	28,724	13,755	0,161	25	0,01	-1,96			
601	29,224	13,76	0,161	25	0,01	-2,01			
604	29,724	13,765	0,156	25	0,01	-2,03			
607	30,224	13,77	0,156	25	0,01	-2,05			
610	30,724	13,774	0,152	25	0,01	-2,06			
613	31,224	13,778	0,152	25	0,01	-2,07			
616	31,724	13,782	0,147	25	0,01	-2,09			
619	32,224	13,787	0,147	25	0,01	-2,1			
622	32,724	13,791	0,147	25	0,01	-2,1			
626	33,224	13,794	0,143	25					
628	33,724	13,798	0,2	25					
632	34,224	13,802	0,139	25					
635	34,724	13,806	0,192	25					
638	35	13,808	0,102	25					

C

Titration results (w-%)							
Sample	pH	3,0	4,0	5,0	6,0	7,0	8,0
C25		21,77	22,16	22,1	23,17	22,34	28,28
V40		38,42	38,42	38,6	38,63	38,61	36,46
Additional experiments							
Sample	pH	3,0	7,0	8,0	12,0 mp	12,0 up	
C25		21,546	21,552	9,972	54,392	0	
V40		38,696	39,227	37,794	0		

D

Sample	Co	Ni	Sample	Co	Ni	Sample	Co	Ni
	mg/L	mg/L		mg/L	mg/L		mg/L	mg/L
Ni-Co	8674,49	123333	SULV1.5 0OF	135,17	12,75	SULV1.5C10 OF0	34,66	0,75
SUL0 OF	130,99	4,36	SULV1.5 0VF	8112,62	116303	SULV1.5C10 VF0	8169,67	114185
SUL0 VF	8063,88	113528	SULV1.5 1OF	7961,78	191,69	SULV1.5C10 OF1	6710,31	16,6
SUL1 OF	7844,58	135,93	SULV1.5 1VF	2064,66	111995	SULV1.5C10 VF1	2710,44	107517
SUL1 VF	1667,38	108601	SULV1.5 2OF	8593,27	319,51	SULV1.5C10 OF2	5087,68	10,88
SUL2 OF	8977,38	288,32	SULV1.5 2VF	1167,16	108136	SULV1.5C10 VF2	3659,68	102528
SUL2 VF	655,98	107155	SULV1.5 3OF	9441,87	364,15	SULV1.5C10 OF3	6705,74	19,17
SUL3 OF	9396,48	634,53	SULV1.5 3VF	980,76	109814	SULV1.5C10 VF3	2571,35	103149
SUL3 VF	193,2	105712	SULV1.5 4OF	10039,4	627,19	SULV1.5C10 OF4	8175,25	75,31
SUL4 OF	9624,75	753,67	SULV1.5 4VF	463,4	108911	SULV1.5C10 VF4	1212,23	104983
SUL4 VF	166,1	104634	SULV1.5 5OF	9977,32	802,95	SULV1.5C10 OF5	8059,72	89,98
SUL5 OF	10107,2	866,42	SULV1.5 5VF	317,84	108470	SULV1.5C10 VF5	1044,45	104141
SUL5 VF	147,32	104476	SULV1.5 6OF	10108,7	1526,07	SULV1.5C10 OF6	8404,4	102,71
SUL6 OF	9776,75	1019,39	SULV1.5 6VF	183,95	105783	SULV1.5C10 VF6	974,39	104013
SUL6 VF	121,8	101158	SULV1.5Zn 0OF	92,47	4,37	SULV1.5C1 OF0	2,8	25,78
SULV1.5Mg 0OF	214,13	10,5	SULV1.5Zn 0VF	8370,93	120865	SULV1.5C1 VF0	8021,25	111504
SULV1.5Mg 0VF	7722,6	111455	SULV1.5Zn 1OF	8719,85	178,64	SULV1.5C1 OF1	4330,35	33,84
SULV1.5Mg 1OF	8494,18	58,59	SULV1.5Zn 1VF	2003,3	111362	SULV1.5C1 VF1	4455,78	104494
SULV1.5Mg 1VF	1704,56	103592	SULV1.5Zn 2OF	9812,38	331,12	SULV1.5C1 OF2	7087,72	66,55
SULV1.5Mg 2OF	9601,75	97,19	SULV1.5Zn 2VF	1141,88	109505	SULV1.5C1 VF2	2386,14	99774
SULV1.5Mg 2VF	960,92	100430	SULV1.5Zn 3OF	10308,6	431,14	SULV1.5C1 OF3	8699,55	87,21
SULV1.5Mg 3OF	9885,5	129,35	SULV1.5Zn 3VF	800,71	108786	SULV1.5C1 VF3	1166,49	95177
SULV1.5Mg 3VF	725,93	101184	SULV1.5Zn 4OF	10622,2	583,11	SULV1.5C1 OF4	9508,07	316,27
SULV1.5Mg 4OF	10241,2	179,1	SULV1.5Zn 4VF	509,75	106430	SULV1.5C1 VF4	622,76	97165,1
SULV1.5Mg 4VF	513,08	101451	SULV1.5Zn 5OF	10992,9	815,69	SULV1.5C1 OF5	9767,38	154,42
SULV1.5Mg 5OF	10483,1	291,14	SULV1.5Zn 5VF	335,2	103638	SULV1.5C1 VF5	799,05	92389,4
SULV1.5Mg 5VF	329,97	99026,6	SULV1.5Zn 6OF	11209	1175,41	SULV1.5C1 OF6	9896,79	401,79
SULV1.5Mg 6OF	10701,4	528,74	SULV1.5Zn 6VF	256,11	102392	SULV1.5C1 VF6	386,48	92448,9
SULV1.5Mg 6VF	195,85	99392,8						

E

TOC	C25V1.5 0		TOC:189,4mg/L TC:190,9mg/L IC:1,505mg/L
TOC	C25V1.5 pH7		TOC:1534mg/L TC:1538mg/L IC:3,076mg/L
TOC	C25V1.5 pH8		TOC:1613mg/L TC:1628mg/L IC:15,15mg/L
TOC	C25V1.5 pH12		TOC:3755mg/L TC:3962mg/L IC:206,2mg/L
TOC	C25V10 0		TOC:222,0mg/L TC:223,6mg/L IC:1,556mg/L
TOC	C25V10 pH7.5		TOC:2465mg/L TC:2482mg/L IC:16,20mg/L
TOC	C25V10 pH8		TOC:3188mg/L TC:3188mg/L IC:0,000mg/L
TOC	C25V10 pH9.5		TOC:41505mg/L TC:41507mg/L IC:2,002mg/L
TOC	C25V10 pH12		TOC:42672mg/L TC:42677mg/L IC:5,336mg/L
TOC	TC100		TOC:111,8mg/L TC:111,9mg/L IC:0,08118mg/L
TOC	C25 pH3.0		TOC:247,2mg/L TC:248,5mg/L IC:1,235mg/L
TOC	C25 pH4.0		TOC:612,4mg/L TC:613,5mg/L IC:1,114mg/L
TOC	C25 pH5.0		TOC:1051mg/L TC:1052mg/L IC:1,269mg/L
TOC	C25 pH6.0		TOC:1353mg/L TC:1354mg/L IC:1,369mg/L
TOC	C25 pH7.0		TOC:1587mg/L TC:1590mg/L IC:3,141mg/L
TOC	C25 pH8.0		TOC:1405mg/L TC:1418mg/L IC:12,35mg/L
TOC	C25 pH7.0		TOC:1314mg/L TC:51,14mg/L IC:0,09105mg/L
TOC	C25 pH8.0		TOC:1326mg/L TC:51,82mg/L IC:0,2917mg/L
TOC	C25 pH12.0		TOC:1856mg/L TC:74,12mg/L IC:2,021mg/L
TOC	V40 pH3.0		TOC:148,6mg/L TC:149,2mg/L IC:0,6130mg/L
TOC	V40 pH4.0		TOC:194,9mg/L TC:195,6mg/L IC:0,7117mg/L
TOC	V40 pH5.0		TOC:243,6mg/L TC:244,5mg/L IC:0,8798mg/L
TOC	V40 pH6.0		TOC:583,9mg/L TC:584,9mg/L IC:1,043mg/L
TOC	V40 pH7.0		TOC:1805mg/L TC:1807mg/L IC:1,481mg/L
TOC	V40 pH8.0		TOC:10851mg/L TC:10855mg/L IC:4,325mg/L
TOC	TC100		TOC:110,4mg/L TC:110,4mg/L IC:0,04349mg/L
TOC	V40 pH7.0		TOC:2819,522mg/L TC:505,7mg/L IC:0,1653mg/L
TOC	V40 pH8.0		TOC: 13016,15mg/L TC:109,5mg/L IC:0,08037mg/L
TOC	V40 pH12.0		TOC:48433,99mg/L TC:1886mg/L IC:5,016mg/L
TOC	TC100		TOC:106,8mg/L TC:106,8mg/L IC:0,01505mg/L