Lappeenranta University of Technology
Faculty of Technology
Master's Degree Programme in Chemical Engineering

Heikki Kettunen

FEASIBILITY OF CAPILLARY ELECTROPHORESIS AS AN ON-LINE METHOD FOR MONITORING RESIDUAL COLLECTOR CONCENTRATIONS AT A FLOTATION PLANT

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ABSTRACT

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FEASIBILITY OF CAPILLARY ELECTROPHORESIS AS AN ON-LINE METHOD FOR MONITORING RESIDUAL COLLECTOR CONSENTRATIONS AT A FLOTATION PLANT

Master's thesis

2017

69 pages, 62 figures, 4 tables

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M.Sc. (tech.) Annukka Aaltonen

Keywords: On-line, Capillary electrophoresis, Flotation

The aim of this Master's thesis was to evaluate the technical feasibility of a capillary electrophoresis (CE) method as an on-line or an at-site instrument providing information of concentrations of sodium isopropyl xanthate (SIPX), sodium ethyl xanthate (SEX) and sodium di-isobutyldithiophosphinate (Aerophine 3814A). In the literature part of this thesis there is a short introduction to flotation process, a way to make representative process sampling, information about capillary electrophoresis and capillary electrophoresis as an online method is discussed. In the experimental part of the thesis there is a description of equipment used, a presentation of the sampling systems, results of the study, the feasibility of the method is discussed and suggestions for further development are given.

The study revealed that the method is specific for the measurands, and that the CE equipment is a minor cause of uncertainty in the monitoring system. The system was able to detect down to 1 ppm concentrations of collector chemicals in process waters. The main uncertainty originated from the function of the pre-analytical

sampling phase, and the sample handling is the most critical issue to be improved in the on-line procedure.

This study proved that the CE method applied in on-line monitoring the flotation reagent concentrations can be a commercially potential technology in future. However, more extensive research work will be needed in co-operation with instrument and process automation system manufacturers. In addition to the sample chain optimization, an automated inner validation procedure should be developed and integrated to assure the validity of the measurements.

TIIVISTELMÄ

Lappeenrannan teknillinen yliopisto
Teknillinen tiedekunta
Kemiantekniikan koulutusohjelma

Heikki Kettunen

KAPILLAARIELEKTROFOREESIMENETELMÄN SOVELTUVUUS KOKOOJIEN JÄÄNNÖSPITOISUUKSIEN JATKUVATOIMISEEN SEURANTAAN

Diplomityö

2017

69 sivua, 62 kuvaa, 4 taulukkoa

Tarkastajat: Dosentti Satu-Pia Reinikainen
DI Annukka Aaltonen

Avainsanat: kapillaarielektroforeesi, jatkuvatoiminen, vaahdotus

Diplomityön tavoitteena oli määrittää ja tarkastella kapillaarielektroforeesilaitteen soveltuvuutta natriumisopropyyliksantaatin (SIPX), natriumetyyliksantaatin (SEX) ja natriumdi-isobutyyliditiofosfinaatin (Aerophine 3814A) jatkuvatoimiseen mittaamiseen prosessiolosuhteissa. Kirjallisuusosassa käsitellään vaahdotusprosessista, edustavan prosessinäytteen ottamista sekä esitellään kapillaarielektroforeesimittausta ja jatkuvatoimisen mittauksen erikoistarpeita. Kokeellisessa osassa esitellään mittalaite ja näytteenottojärjestelmät, sekä tulokset. Lopussa on arvio mittauksen soveltuvuudesta nykyisessä muodossa ja lisäksi kehitysideoita järjestelmän parantamiseen.

Mittaussarjat osoittivat mittausmenetelmän olevan riippuvainen näytteiden käsittelystä, ja että mittalaite aiheuttaa myös jonkin verran epävarmuustekijöitä tuloksiin. Mittauksissa prosessivesistä havaittiin kokoojien pitoisuuksia aina 1 ppm asti. Eniten mittaukseen epävarmuutta lisäsi näytteen esikäsittely. Kapillaarielektroforeesi on kehityskelpoinen mittausmenetelmä, mutta nykyinen laitteisto vaatii vielä lisää kehitystä ollakseen kaupallisesti käytettävä järjestelmä.

Näytteenottoa tulisi kehittää vähemmän selektiiviseksi ja samalla näytteen kuljetus mittalaiteelle ei saisi muuttaa näytteen rakennetta esimerkiksi erottelemalla sitä.

Käytetty laitteisto, joka on kehitetty laboratorio-olosuhteissa tehtävään analytiikkaan, tarvitsee kehitystyötä erityisesti näytteenotossa ja menetelmän automatisoidussa validoinnissa ennen kuin se soveltuu laadun valvontaan jatkuvatoimisena mittauksena prosessiympäristössä.

PREFACE

This thesis was made in Lappeenranta University of Technology in the co-operation with Outotec (Finland) Oy. I would like to thank my supervisors, Satu-Pia Reinikainen, Annukka Aaltonen and Jaakko Leppinen, for all the support during this work. I would also like to especially thank Jouni Majaniemi from Berner Oy for the technical support for the equipment, Anssi Seppänen and Vesa Rantalainen from Outotec (Finland) Oy for support with instrumentation and Tomi Maksimainen from New Boliden for the opportunity to run tests in Kevitsa mine. Lastly, I would thank my family, Sari, Eppu and Elmeri for all the support during my studies.

Lappeenranta 31.3.2017
Heikki Kettunen

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1. INTRODUCTION

Analysing and controlling of the process through timely measurements are needed to confirm the maximum recovery of valuable material and the quality and of the final product of a plant. Digitalisation and automation are entering into the process control systems increasing demand of on-line measurement technologies. Increase in production rate and aim for higher efficiency while lowering costs structure calls for innovative systems to gather valid information from process flows. /1, 2/ Processes are developed towards sustainable production through e.g., closed water circulation. As a consequence, the chemicals used in the process accumulate in the circulation and may cause challenges to control the process. /3-5/

The purpose of this Master's thesis is to evaluate the technical feasibility of a capillary electrophoresis (CE) method as an on-line or at-site instrument providing information of concentrations of certain measurands. In the course of the study an existing CE method /6-8/ was first validated in a laboratory environment, and then installed into a process environment. Several test series were done to validate the durability and usability of the equipment and instrumentation in a process environment. This was done to estimate robustness of the analytical technique and the instrumentation, and to identify the critical features that need development. The method is novel /9/, and the present application can be seen as one of the first attempts for on-line monitoring using the CE measurement method.

2. PROCESS

The process that is studied in this thesis is froth flotation that is used to separate precious minerals from gangue. Flotation has been used over a century for minerals separation /10, 11/. The challenge in the froth flotation process is the complexity of the electrochemical reactions between the minerals, air and chemicals mixed in the slurry /11, 12/. A block diagram of a typical concentration process is presented in Figure 1.

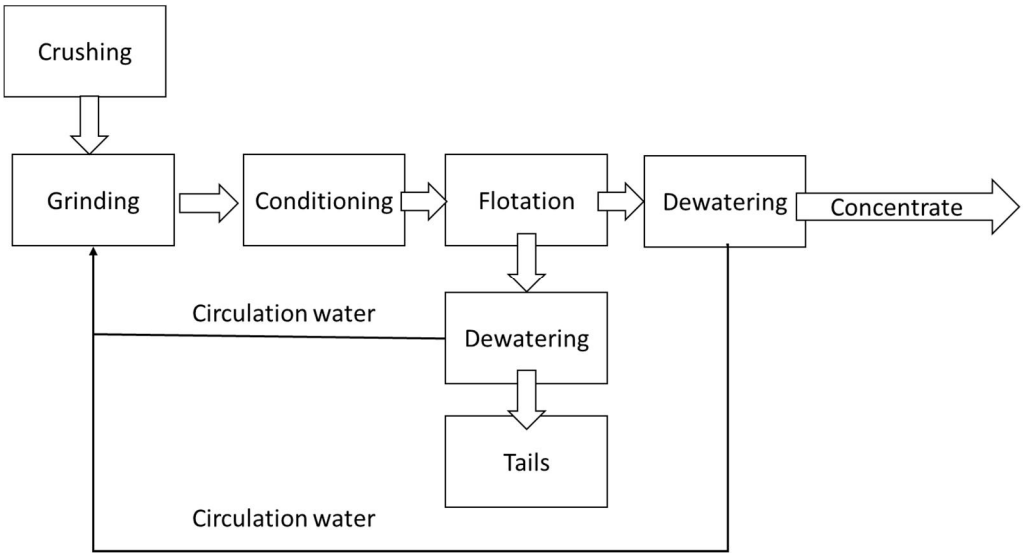

Figure 1. General flow chart of metal concentration plant.

There are several stages before the actual froth flotation. Firstly, the ore is mined. Second stage is crushing of the ore. After crushing there is a grinding stage where the ore is mixed with water to create slurry. Slurry is then sent to the conditioning stage where chemicals are mixed into the slurry. /11, 13/

Flotation reagents such as collector chemicals, activating agents and depressants are added to the separation process. The collector chemicals are used to make the valuable minerals hydrophobic. Hydrophobic minerals attach to gas bubbles and rise on the surface of the flotation cell into the froth that is collected from the cells. /11, 14/ The key points in flotation process are visualized in Figure 2.

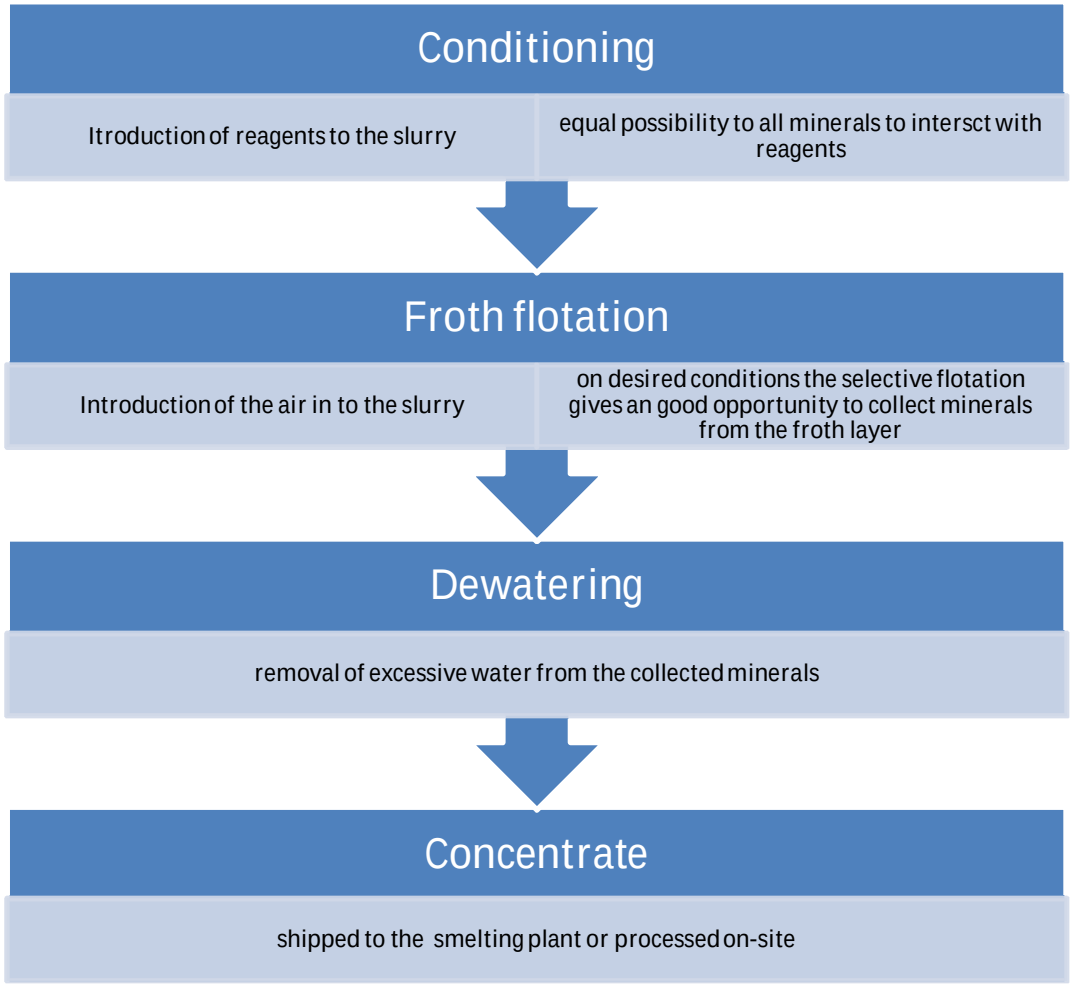

Figure 2. Step by step main line process from conditioning to concentrate.

Collectors

The flotation collectors are in generally organic compounds, which contains polar and non-polar compounds. The polar parts of the compounds are reactive with water. The non-polar parts has different hydrocarbon free radicals that are not reactive with water. /15/

The selection of the collector is based to the mineral that is processed. For instance in case of sulphide minerals a thiol collector chemical is chosen as the collector chemical. If the mineral is a non-sulphide the collector can be carboxylate or sulfonate. The non-metallic minerals are collected with carboxylates, alkyl amines or alkyl sulphates.

The Metallic sulphides are the most common group of raw material in mineral processing. Which had led to the thiol collector as the standard selection among collector chemicals. /15-17/

Thiols used as collector have at least one sulphur in their structure that is not bonded with oxygen. The non-polar part is commonly hydrocarbon, ethyl for example. The thiol collectors contain such compound groups as dialkyl dithiocarbamates, dialkyl dithiophosphate and xanthates. The xanthates are the most commonly used of the thiol collectors. /15-17/

The length of hydrocarbon chain has an effect on the success of the flotation.

The practical application test have shown that the xanthates with different hydrocarbon chains have selectivity for different kind of sulphide minerals. /15,17/

Frothers

Role of the frother chemicals in the flotation cell is to help forming the froth. The secondary part is to stabilize the froth. The frothers works as concentrator agent to the water-air mix and prevents the bubbles collapsing. Also the frothers decrease surface tension of the water. In practice selecting the right kind of frother is difficult as the complex nature of flotation process is hard to estimate effect of selected frother. The frother chemicals include alcohols and other weakly soluble chemicals. /18/

Modifiers

The modifiers or regulators, are a set of compounds that are used to adjust the flotation conditions, the behaviour of the collector chemicals and impurities. The impurities might have an effect to cationic or anionic reactions on the mineral surface. They affect the flotation process and create difficulties./19/

These modifiers are added to control the impurities they still can work as activators and depressants for the mineral systems. This is useful in the separation of the different mineral types. This is the main reason, why the regulators have important role in the flotation./19/

3. REPRESENTATIVE PROCESS SAMPLING

Sampling requirements for the process industry usually arise from the need to run and control the process at hand. Only way to certainly know what is the state of the process is to take representative samples and analyse them. /20/ All sampling have to start with a question for what purpose is this sample needed. In order to prepare and analyse one have to know what it is for. /21/

Then there is the determination what kind of the sample is needed to the analysis required in order obtain the required information. Also the physical for of the sample will dictate the sampling procedure needed. The representative sample equals something that is the portion of material at selected time that characterises the state of the process. In order to get good result from the representative sample all three points have to be taken care of./22/ Those steps are taking the sample, transportation of the sample and preparation of the sample. First the actual sampling should be taken from a place where the flow of the process is homogenous or that all parts of the flow has an equal possibility be selected as a part of the sample. In the second part the transportation of the sample requirements are that the sample does not change its physical state or separate to fractions or sieves. The third part is the pre-treatment of the sample prior the measurement. If milling, screening, filtration or any other physical change to the sample is required then it is important to make sure that it does not change the original condition of the sample, introduce any contamination or change the chemical condition of the sample./22,23/ In the sampling theory Pierre Gy /24/ defines uncertainties for the sampling. In the table 1 there is some sources of uncertainty in the sampling and the sample preparation.

Table 1 Some sources of uncertainty in the sampling and the sample preparation /25/

Sampling	**Preparation of the sample**
• Heterogeneity	• Homogenisation effects

• Effects of specific sampling strategy • Effects of movement of bulk medium • Physical state of bulk • Temperature and pressure effects • Effects of sampling process on composition • Transportation and preservation of sample	• Sub-sampling effects • Drying • Milling • Dissolution • Extraction • Contamination • Chemical effects • Dilution errors • pre-Concentration

A total sampling error is also described on the sampling theory. The total sampling error is a sum of analytical error from the measurement and the sampling errors that are caused by different parts of the sampling procedures./24/ As analytical method the capillary electrophoresis is seldom used as an on-line instrument to measure the process condition. The Capillary electrophoresis is rather sensitive to the environmental change and requirements of the sample preparation in order to get good repeatability. The requirements for the CE are described in the chapter 4 in this thesis.

The sampling strategy is different when the sample is measured in the on-line analysis as compared to the regular laboratory sample./25/ On preparation of a laboratory sample there is usually more time and possibilities to ensure the purity of the sample. Also it is possible to make all required pre-treatments to obtain the best possible result. Online analysis is always time critical due the nature of the process will need the control information as soon as possible. This leads into more crucial approach to the actual sampling. There is no time to homogenise the sample if the sampling creates heterogenic portions of the process. The dilution and the filtration has to be made with extra care as the possibility to introduce contamination sources is bigger on no laboratory environment. Any alternation of the samples chemical and physical structure will create the possible errors in the result. Also the transportation distances of the sample should be kept as short as possible as all pumping has a risk to separate and modify the samples structure./21, 26/

4 CAPILLARY ELECTROPHORESIS

The advantages of capillary electrophoresis as an analysis technique are its simplicity compared to other separation methods. It requires little instrumentation and can run the analysis on small amount of the sample. The measuring ability varies from the inorganic ions to the big organic molecules. As analytical method the capillary electrophoresis has been used for 35 years. /27/

Measurement in the capillary electrophoresis is an electro static separation of the compounds in a silica capillary under an electric field. The capillaries have inner diameter from 25 to 100 μm and length of 10 to 100 cm. The silica capillaries are used for UV transparency, and are easy to manufacture. Outside of the capillaries are coated with a polyamide polymer for flexibility and prevent breaking. The coating is removed, usually with heating the chosen part for the creation of the detection window. The window is situated at the desired length of the capillary. The electrical field is used in the separation is created with a high voltage, usually from using 10-30 kV. This enables a short analysis times and good efficiency. /28/

The short analysis time and the minimal sample consumption in the capillary electrophoresis are advantageous while comparing to a high performance liquid chromatography as a separation method./29/

The problems of capillary electrophoresis are methods reproducibility, sensitivity, and injection accuracy. /30/ For example the solution adsorption to the capillary walls and variable migration times can cause errors. These issues can be treated with a careful adjustment of the sample introduction and the separation conditions. Also the sample treatment has to be extremely carefully as all foreign material can cause pollution or may interfere the measurement. Instrumentation of the capillary electrophoresis contains a high voltage power supply, two electrodes, a capillary, a sampling system, a detector, an instrument control and a data collection with a computer. The basic arrangement of the main components of the CE apparatus are in figure 3 The capillary electrophoresis equipment have been commercially available since early 1980’s, but there is also a variety of non-commercial units and kits available. /31/

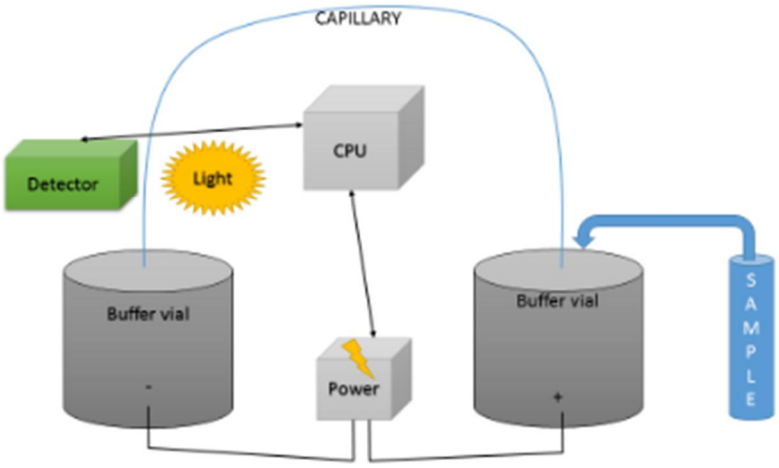

Figure 3. Main components of the CE apparatus.

Theory behind the CE measurement is introduced and thoroughly explained in several different publications such as /27,29,31/ also including this work /9/. As all analytical methods the CE has some common causes to disturb or fail the measurement. In table 2 there are some insights to common faults and what might have been the cause and also most importantly measures to resolve the symptoms encountered in the CE experiments./32/

Table 2 Symptom check list for common CE measurement errors.

Symptom	**Check list**	**to do list**
Current based no current	capillary empty no buffer solution wrong vials electrode not submerged capillary clogged	fill capillary fill vials change the sequence for right buffer vials or insert vials on correct locations fill vials or buffer reservoirs change new capillary
current is lost or unstable	air bubbles in capillary broken or shattered capillary voltage leak	buffer wash capillary and degas buffer with ultrasound buffer wash capillary check current flow again if shattered washing with pressure breaks the capillary -> new capillary dry the vial caps, reservoir lids and check if any leakages from sampling
Unstable baseline		buffer filtration and ultrasonic mixing
spikes in baseline	buffer solution is contaminated or precipitation occurred	check the aperture if broken change new capillary
noisy baseline	optical aperture broken or capillary misaligned light level dropped	check the calibration of light source (deuterium) check the condition of the lens for the light -> replace light if necessary

flat baseline	capillary misaligned	check the capillary assembly is firmly in place and light source is connected
	no voltage	check the power source setting and parameters
	no sample injected	ensure the sample vial does have sample inside and it is on correct spot according the measurement sequence

5 CE AS ONLINE METHOD

5.1 Current State of Art

There are several producers of the Capillary electrophoresis equipment in the world the main difference on these are the aim of usage of the equipment. Roughly the equipment can be put in three different sub categories based on the aim of the manufacturer's interest group./33/ The groups are clinical industry, research groups and education. The clinical aimed equipment are meant to be used in the study of the chemical purity and standard for the pharmaceutical industry and other manufacturers of the fine chemicals./34/ The research equipment are more flexible but also more difficult to maintain and use as they have all the development options enabled. The equipment for education are simplified and does not include automatic sample handling or multiple capillary systems./33/ None of the companies find or contacted are not currently offering a non-laboratory environment system. The system that can operate in the process like conditions where the explosion to the dust, vibration or change of the temperature and humidity is possible. There are at least one manufacturer that offers a modular system for the CE /35/

5.2 SWOT

Developing the CE system to an independent standalone unit requires a lot of R&D work due the nature of the process environments and facilities. In table 3 there is some ideas what an on-line CE apparatus could base on./27,29,31,34,36/

Table 3 Some sources of uncertainty in sampling and sample preparation

Strengths • efficient system for small concentrations • known technology • good selectivity • Possibility to continuous running • multiple capillary systems • out sourced calculation • infinite possibilities of re-analyses	Weaknesses • capillary life span • Drifting i.e. measurement time changes due wear • Dependency on environmental change • Purity requirements high
Opportunities • a novel method, no competition • suitable for most chemical components • only small amount of sample is required • Possibility to integrate to existing system • Basic results from online extra with data collection	Threads • market potential • R&D price of new system • application of results

6 EXPERIMENTS AND RESULTS

The experimental part of this thesis were conducted at the New Bolidens Kevitsa mine in Sodankylä Figure 4. The measurements were made in a three separate periods from November 2016 to February 2017. The studied method and measuring sequence has been previously developed in a three different thesis works and introduced in an article. In this work the method and the chemicals were used as described on previous works. Some minor changes have to be made to the operation sequence of the CE control program in order to get better run ability on the system. During the experimental part there were several test for the calibration of the CE equipment and runs to test the online measurement capabilities of the both sampling systems detailed introduced in chapter 7.2. The results of these experiments are displayed in chapter 7.3.

Figure 4. A view toward the mine in Kevitsa.

6.1 Equipment and instrumentation

The CE apparatus used was a Beckman Coulter P/ACE MDQ, with the [UV/VIS] diode array detector. The diameter of the capillary was 50 µm. The length of

capillary was 60 cm and the length from injection to the detector was 50 cm. The capillary was manufactured by Polymicro technologies and it was fused silica coated with a polymer. The polymer was burned off to create a detection window. Ismatec model BVB Standard peristaltic pump with a multi-channel pump head CA-12, was used to transport samples to a sample container inside the CE apparatus. Two vial trays with buffer reservoirs (2 x 25 ml) were used for supply of the buffer solution.

A 20 µm stainless steel rod filter was used as a primary filter the samples. Secondary filtration was made with a filter cartridge 1 µm. The sampling was done with an automatic sampler which was rebuilt for this study parts are described more thoroughly in part 7.2.

6.2 Sample delimitation, extraction, transportation

The online measurement were divided into two different sample points which originally were intended to measure simultaneously. The selected points were a flotation feed for Tank cell 500 and the process circulation water (Figure 1). The aim at both of these sample points were to determine a presence of selected collector chemical in the process.

Sampling and measurement Setup 1

The primary sample was taken as automated sample from the courier multiplexer line 20. The flow chart of the Setup 1 is presented in figure 5. Once the process control system gives a signal for taking a sample from the line, the slurry pump will activate. The pump unit is shown in figure 6.

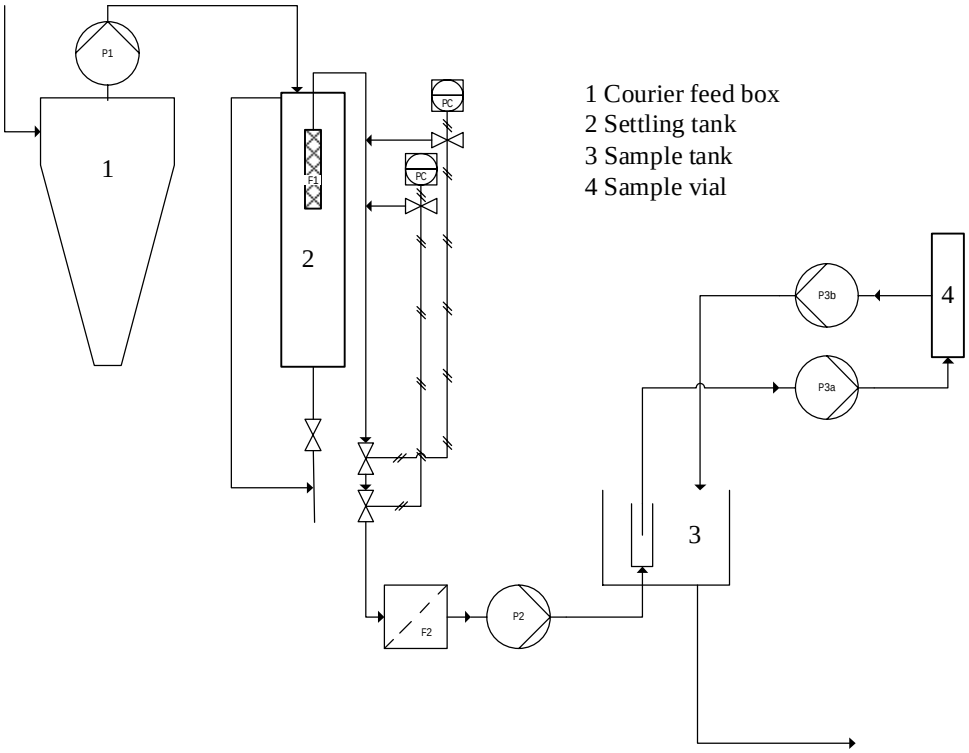

Figure 5. Flow chart of the Setup 1

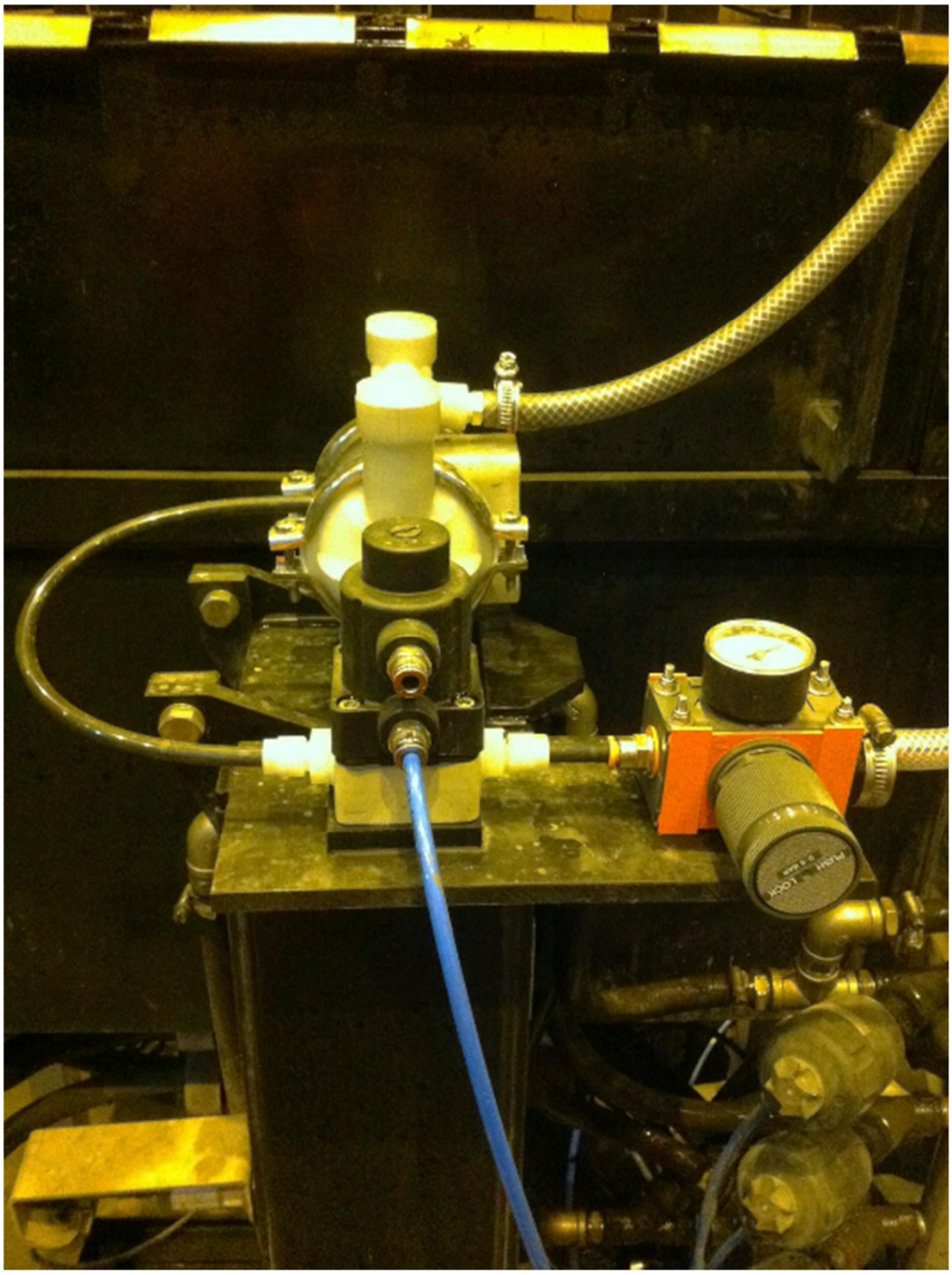

Figure 6. Sampling slurry pump unit to collect the sample from the multiplexer

Then the slurry pump runs a predetermined time controlled by a time relay (LIETE PPU), shown on figure 7 to fill a settling tank. The settling tank in shown in figure 8.

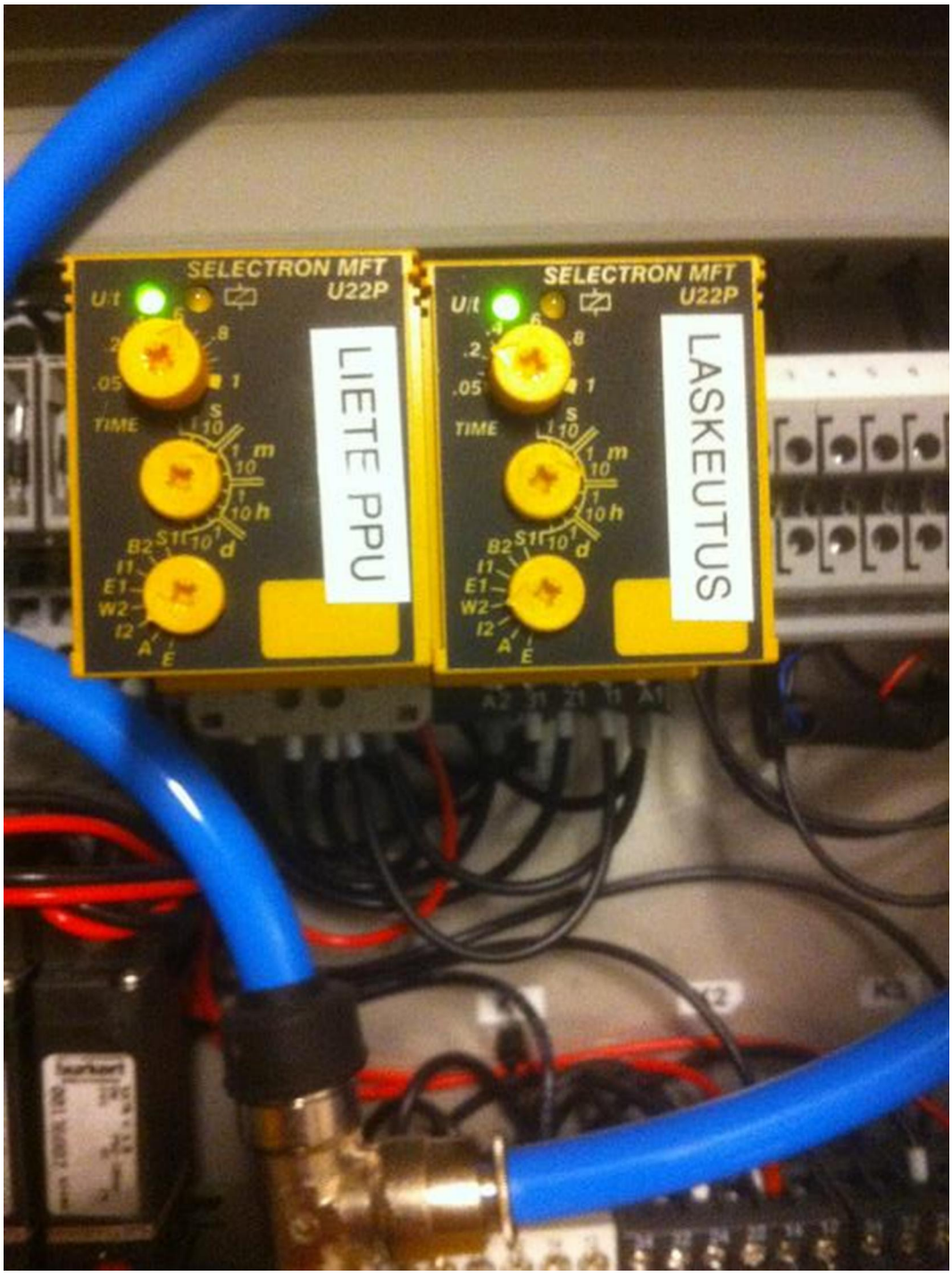

Figure 7. Relay units for slurry pump and settling tank and set times to control.

Once the settling tank is filled the time relay for the settling (LASKEUTUS) will begin. The relay is shown in figure 7. During the settling period the minerals and other solid particles in the slurry settle to the bottom of the tank. Inside the tank there is a wire mesh screen with nominal screening capacity of 20 μm. The picture of the screen is illustrated in figure 9. Screen is positioned at the upper half of the tank. In order to be inside the eluent fluid but not buried in to the settled solids.

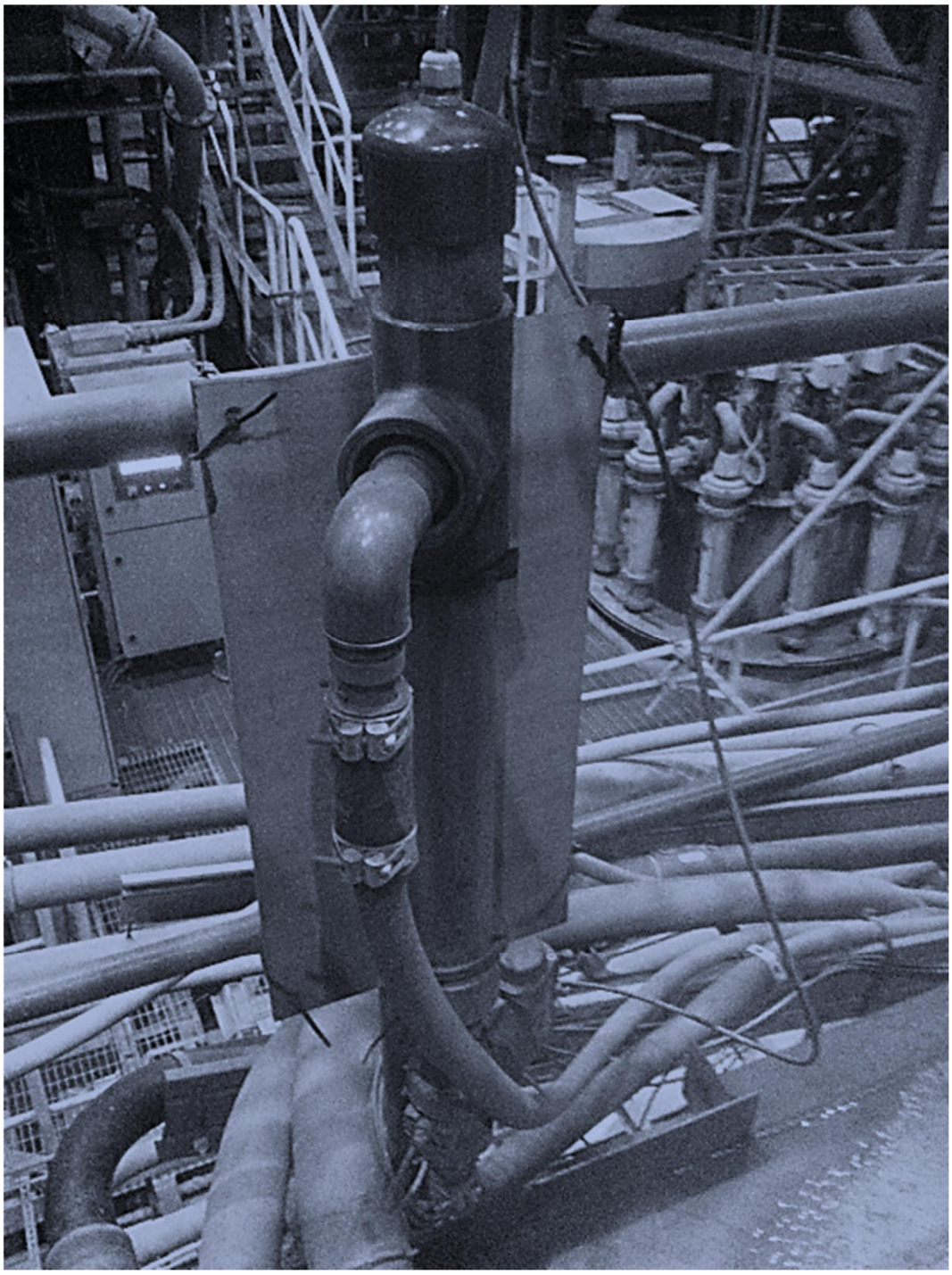

Figure 8. Settling tank, the feed line is at right side of the top. Overflow for the slurry is in front of the tank.

Figure 9. Wire mesh filter for nominal 20 μm particle size.

After the settling time relay (LASKEUTUS) has expired the relay for the secondary sampling pump (PPU), figure 10, will start pumping the sample through the primary wire mesh screen and the secondary nominal 1 µm filter screen to the sample basin (figure 11). The relay unit for PPU is visualized in figure 12

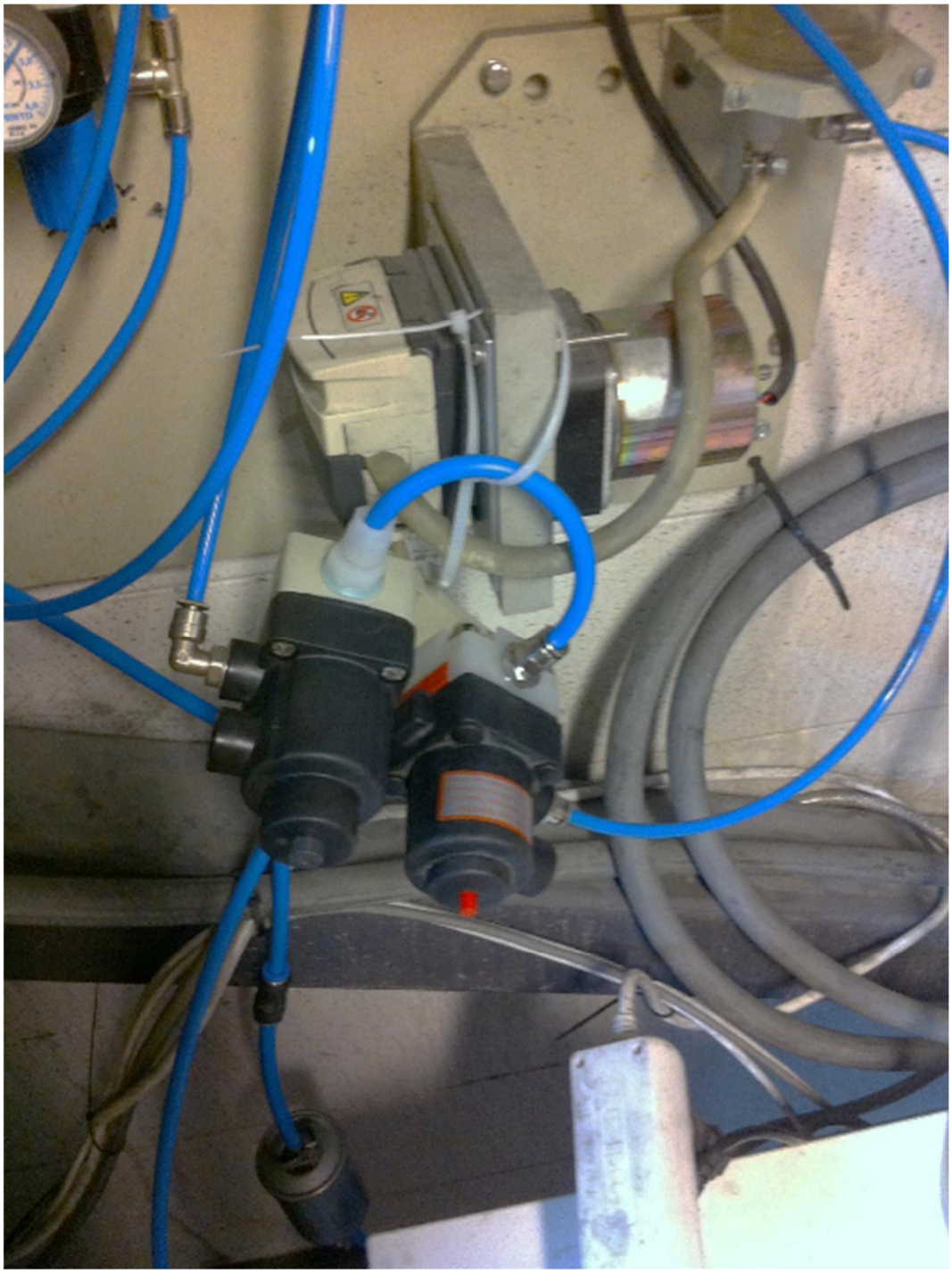

Figure 10. Sampling pump PPU takes the sample from the settling tank to the sampling basin

Figure 11. Filter cartridge setup to the sampling line for nominal up to 1 μm filtration.

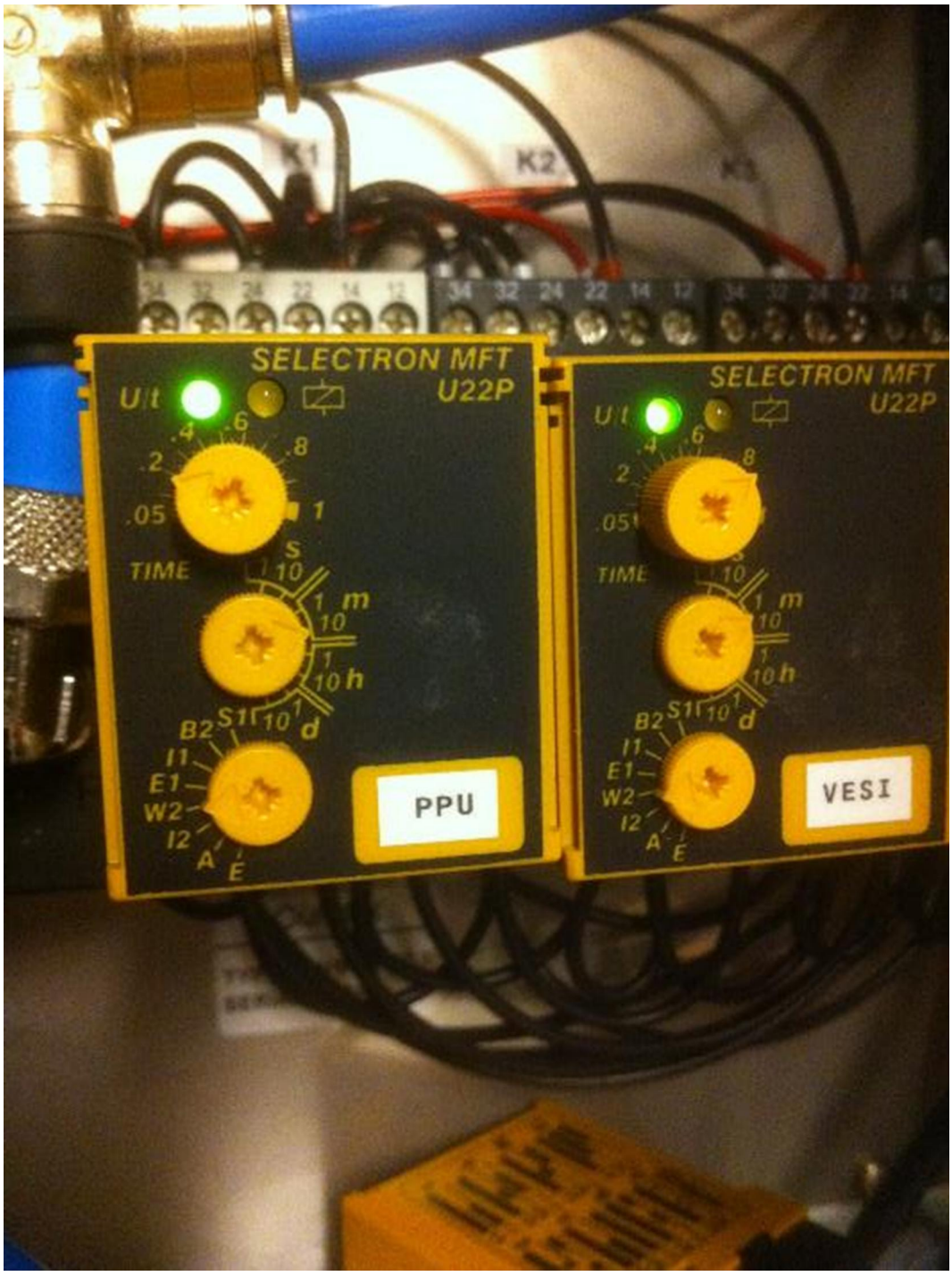

Figure 12. Time relay unit for PPU pump and valve VESI and time setup for the control.

The sample arrives to the sample basin shown in figure 13, and the pump continues to fill the sample basin. Excessive sample is removed trough an overflow to the drain. After this step the sampling is divided into a two different sequences.

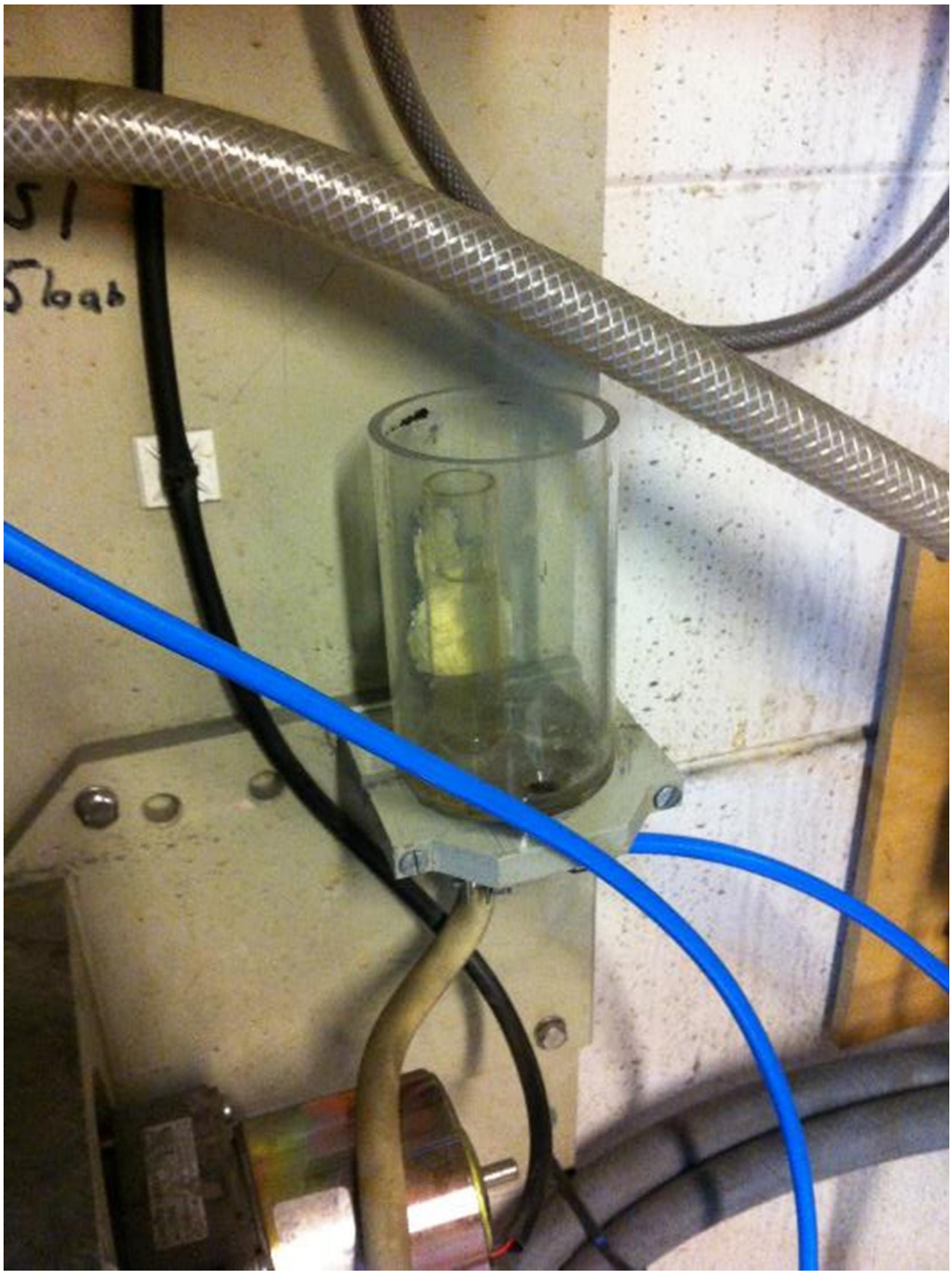

Figure 13. Sample basin is the smaller cylinder in the middle, feed is from the bottom. Container surrounding it works as a drain to remove excessive sample from the basin.

The sample that stay in the sample basin is pumped based on the control of the measurement sequence to the sample container inside the analyser (figure 14). The pumping is made with the peristatic pump so that there is a circulation of the sample flow through the sample container in portion of one pump for the inlet and two

pumps for outlets. The peristatic pump is shown in figure 15. The analyser takes an test sample from the sample container as part of the normal sampling sequence.

Figure 14. Sample is circulated into the sample container trough the pipes.

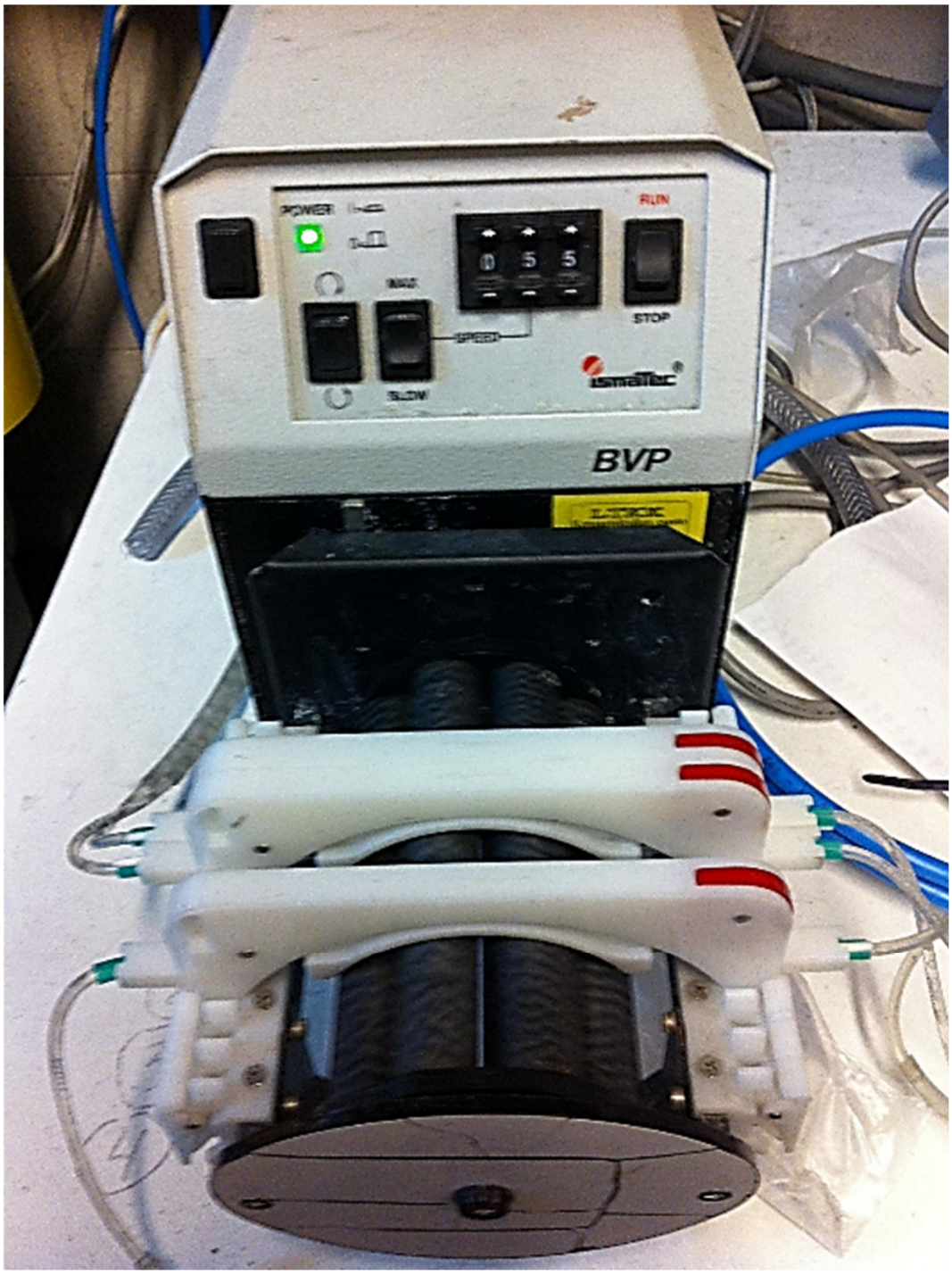

Figure 15. Peristatic pump feeds the analyser from the sample basin. With a single pump unit and circulates it back with two units. Setup for the rotation speed is seen on the pump.

The second part of the sampling sequence is the cleaning of the sample line between the PPU pump and the settling tank and rinsing the slurry out of the settling tank. This sequence in controlled by the time relays for the water feed valve VESI and the air feed valve ILMA. Picture of these relays and their setup times are shown in figures 12 and 16.

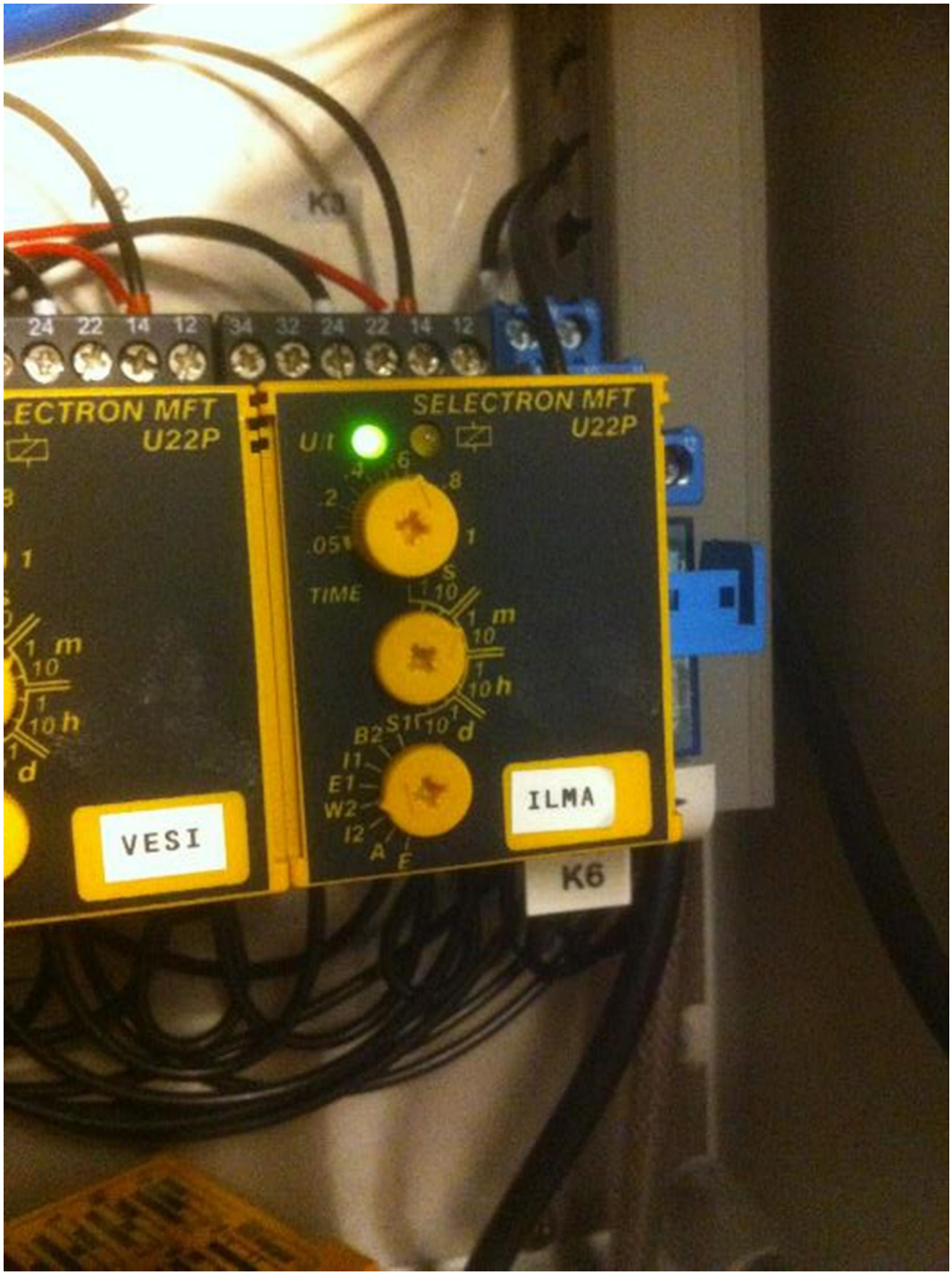

Figure 16. Time relay for air feed valve ILMA and time setup for the control.

Once the cleaning sequence is completed the relay for the slurry pump will hibernate until the next time activated by a control signal from the process control system. The setup of sample system 1 is a random sequence as the analyser does not have control over the time when the new sample in introduced, or the process

control system has no knowledge whether the previous sample is analysed before taking a new one.

Sampling and measurement Setup 2

The sample is taken as partial flow through a y-connector from the sealant water feed to the process pumps. The sampling point is shown in figure 18. The sample is the process circulation water from the pond outside of the facility. The flow chart for Setup 2 is presented in figure 17

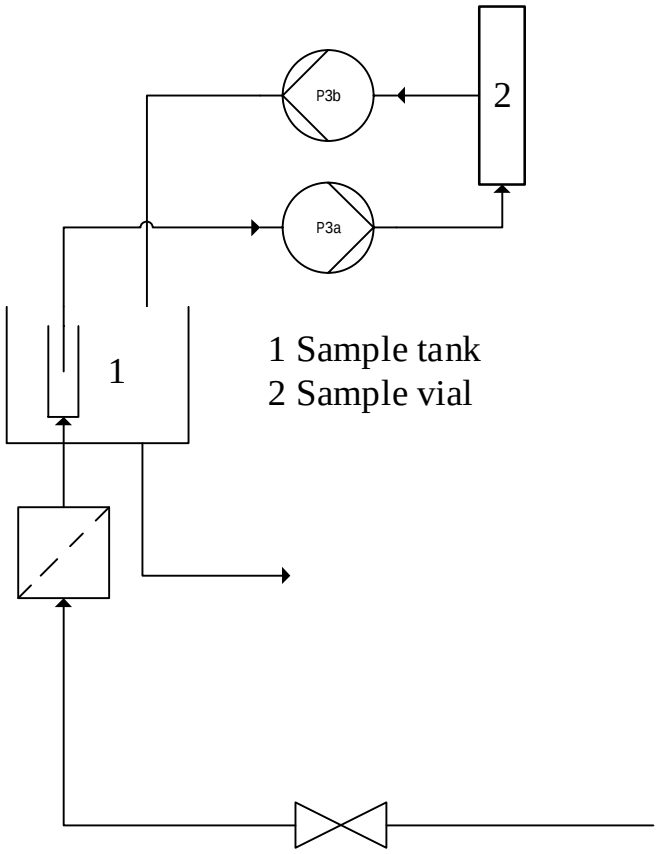

Figure 17. Flow chart of the Setup 2

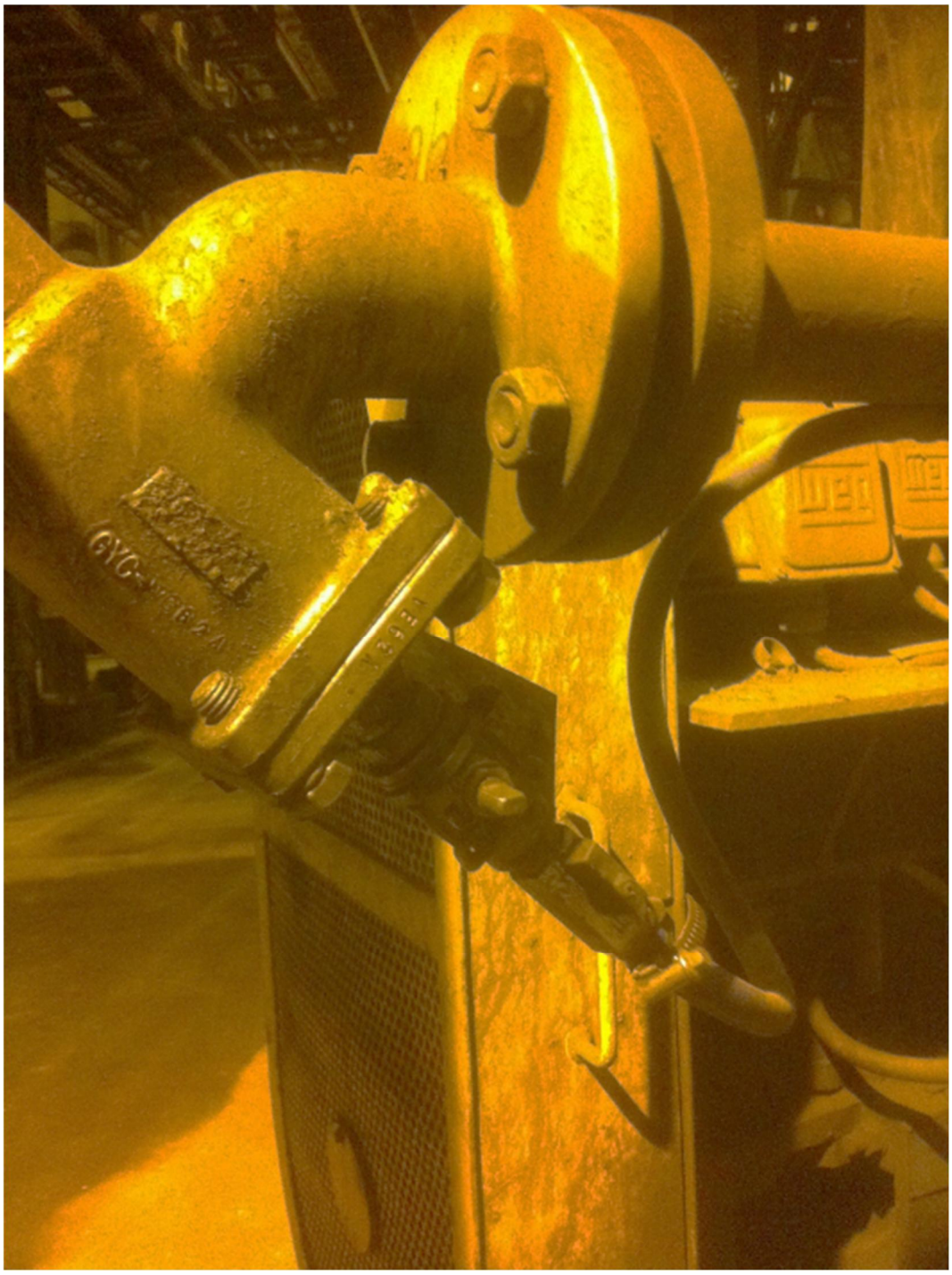

Figure 18. Sample point for the process water is through the valve seen in bottom of the connector.

The sample is led through a filter similar to the one in figure 11 into the sampling basin for the process water (shown in figure 19). There is a constant overflow of the water. From the sampling basin for the process water the peristatic pump (figure 15) circulates the sample to the measurement container in the same manner as in

the Setup 1. In the Setup 2 the sampling works as a timed sequence as the sampling rate is controlled by the analyser, and it can be seen as a systematic sampling.

Figure 19. Process water sample basin is feed from the bottom of the basin with a constant over flow. Sample lines for the peristatic pump are also visible the one in the middle is the feed line and two from the side are the circulation lines.

6.3 Calibration and validation

The analytical method for the CE has been developed in the previous studies. The validation and primary the calibration were done in Ordior Oy:s Konala facility in Helsinki with a analyser specialist and an Process Metallurgist. The mechanical, electrical and optical functionality were tested to ensure that once the analyser was taken to site it would be in working order. The primary tests also included introduction of the calibration measurands, three different collector chemicals. These were measured in different dilutions with the selected test method. Also the test method was reviewed in case of features that might cause faults during the measurement runs. The device passed initial testing and reference values were taken to compare with the on-site measurements.

The site did not have any source for purified water so ultra-pure water originated (Elga, Centra-R 60/120) from the University of Lappeenranta to ensure the dilution of the reference material would be sufficient and free of contamination from the water. The dilutions were made in a three different ratios for each reference measurand. Then each of the references were measured with a five parallel samples and compared to the primary calibration values. From those measurement the calibration curves were calculated to estimate the amount of the collector chemicals in the process samples. The calibration curves for SIPX, SEX and Aerophine can be seen in figures 20, 21 and 22.

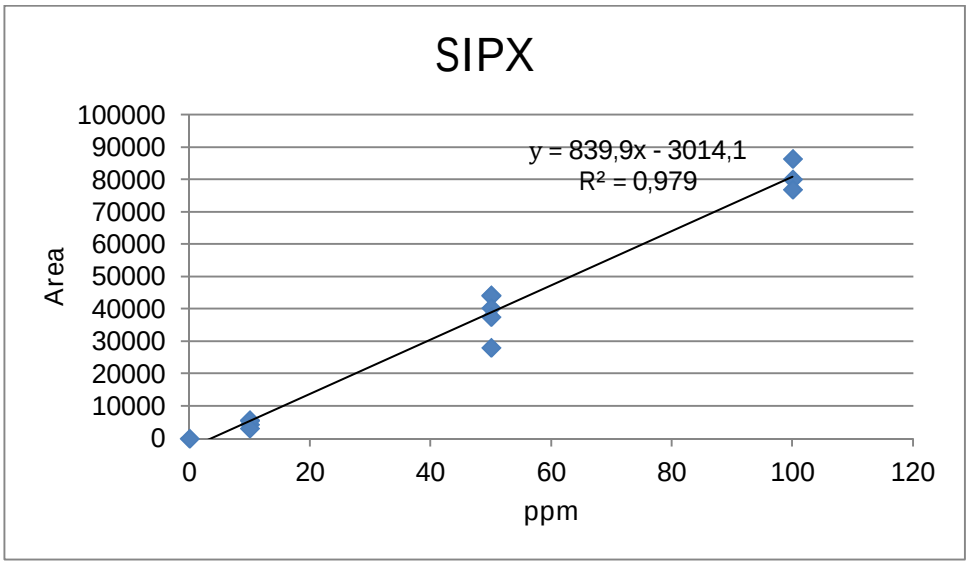

Figure 20. Calibration for SIPX from area to concentration.

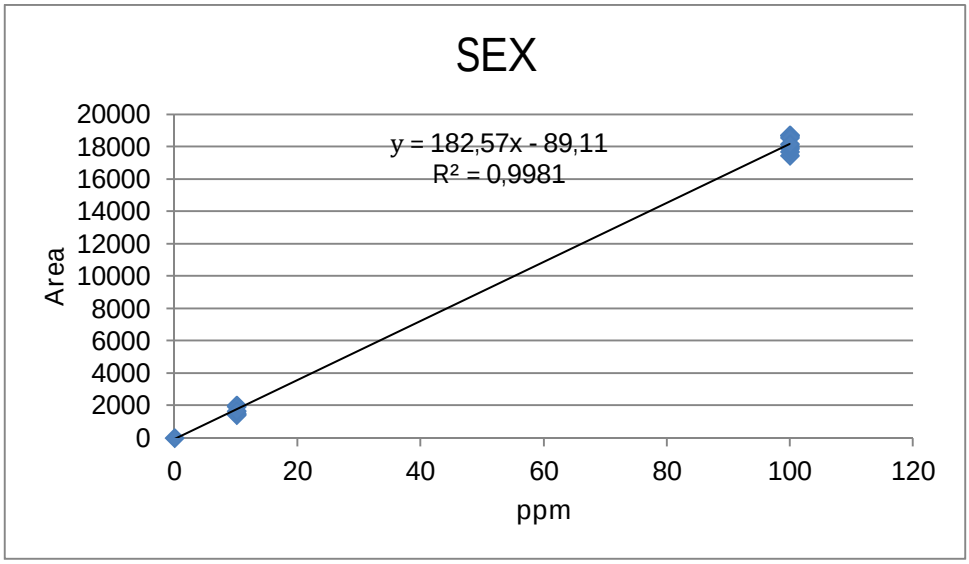

Figure 21. Calibration for SEX from area to concentration

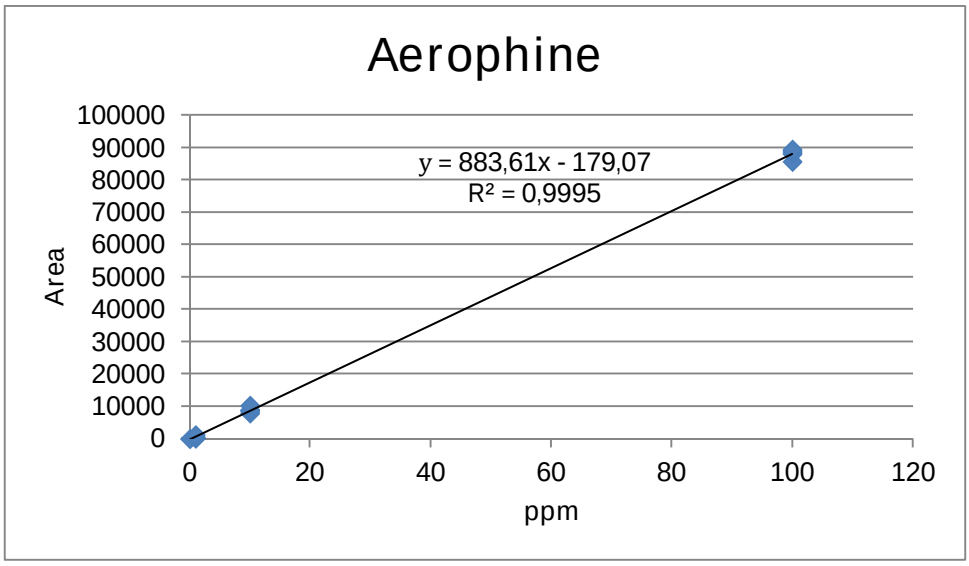

Figure 22. Calibration for Aerophine from area to concentration

After an analysis the currency diagram was used to check the condition of the measurement if the currency diagram showed the distinguished features of an EOF then the analysis was approved. In case of oddities in the curve the following procedure was made. First checking the sample tray if there were any signs of a leakage, secondly washing the buffer reservoirs and changing the buffer solutions. Running a test with clean buffer bottles that the capillary was intact. Running a reference material from the reference bottle. Replacing new a capillary and running conditioning the capillary with a buffer wash. Procedure is explained in figure 23.

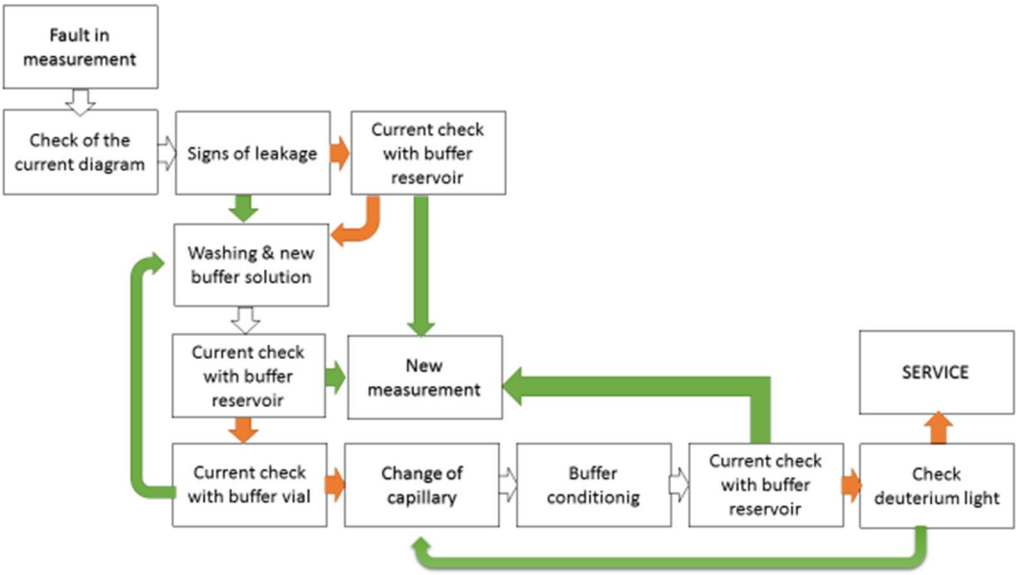

Figure 23. Diagnostic procedure after fault in measurement

The migration time for the component are often slightly changing due the nature of the CE measurement this is effected by the ongoing conditioning of the capillary and also the depletion of the buffer solution./37/ In process environment the shift of the migration time might be more severe. It was noticed that the typical 0.2 minutes detection window for constant the migration time was inadequate. On one hand the window should be wide enough to be able to find the peak. On the other hand a wide window increases the risk for false identification, and increases the background noise into the results. For example there is noticeable change in figure 48 (Chapter 7.4) where the migration time is shifting over a time. A dynamic system to update the migration time via a reference solution could be beneficial or even essential to establish to ensure the correct detection of measurands.

On a request of a customer the same CE method was used for a fourth collector by applying similar the calibration procedure to it as the three other calibration measurands. The R^2 value for that indicated a poor fit, and the calibration was non-significant statistically. In this case of the third xanthate, it was discovered that the measurand had two partially parallel peaks that were overlapping each other. In the time frame some test were made to get a better integration result for the surface area but the interface could not give a satisfactory results. This shows that the present method requires still work on the specificity although the selectivity is in reasonable level on the pure samples. Thus, the fourth measurand was removed from the calibration table. This example is brought out due to the need in developing the

method: even if the buffer solution and the detection is a good a combination for the selected measurand then the peak detection may still need a lot of work to ensure valid results from the system. As method development was not an aim of this study no additional measures were made to ensure a better classification of the fourth measurand.

6.4 Experiments in Process Environment

Eight runs with the Setup 1 were tested and seven runs with the Setup 2. There were several tries to do more runs but that will be discussed in part 7.5 in this work. In figure 24 there is visualization of a proper sample in with the detection of the xanthate. The analysis also produces a current diagram to verify the state of the measurement, figure 25.

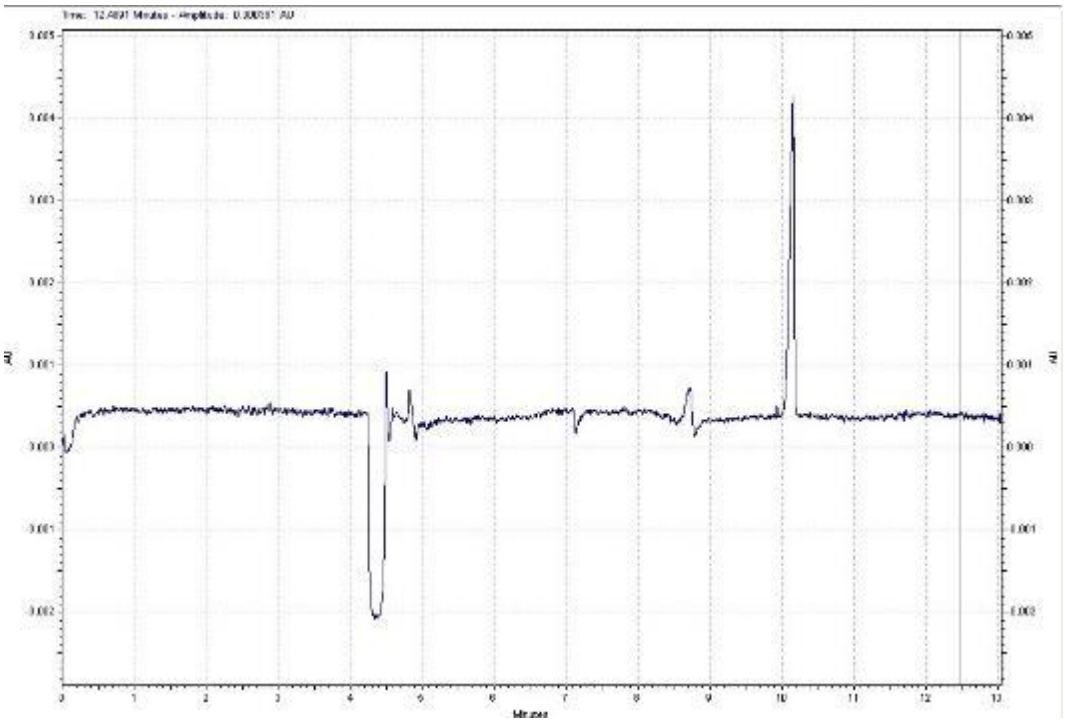

Figure 24. Peak of a xanthate specimen 100 ppm shown as a peak starting from 10 minutes mark.

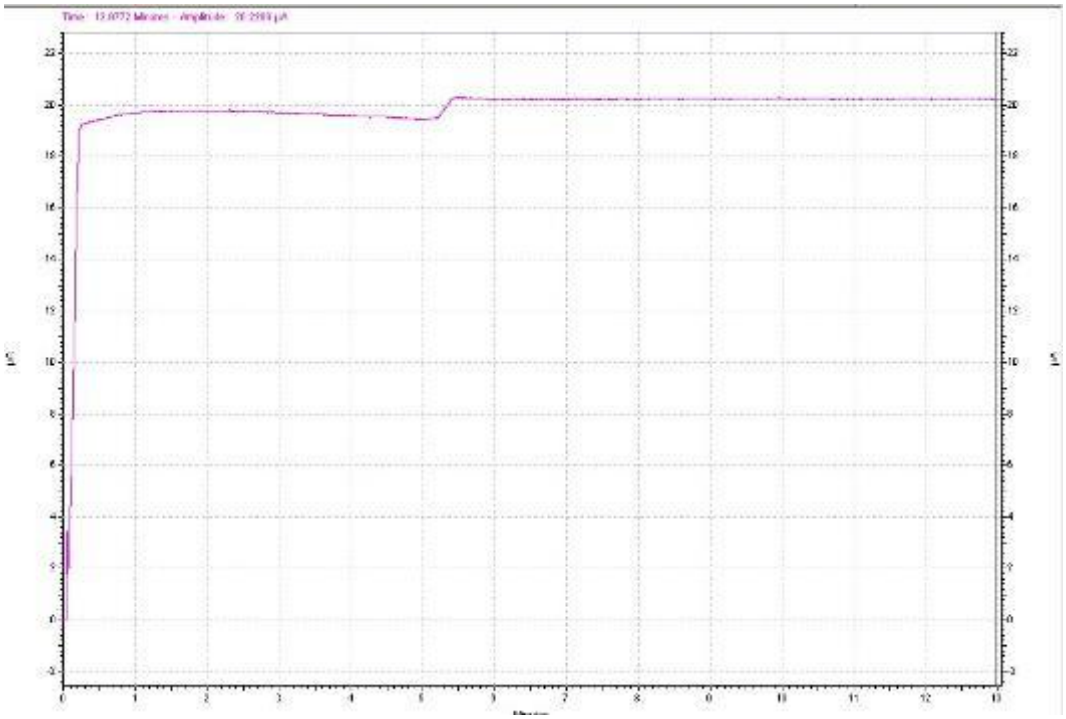

Figure 25. Example of a current diagram of successful measurement taken from same sample as shown in figure E1.

The results from the Setup 1 runs in a chronological order are presented in figures 26 to 41. The results are shown either form of chart in case the flotation chemicals were detected on the measurements or in form of a measurement diagram with the current diagrams for validation purposes in figures 26 to 41.

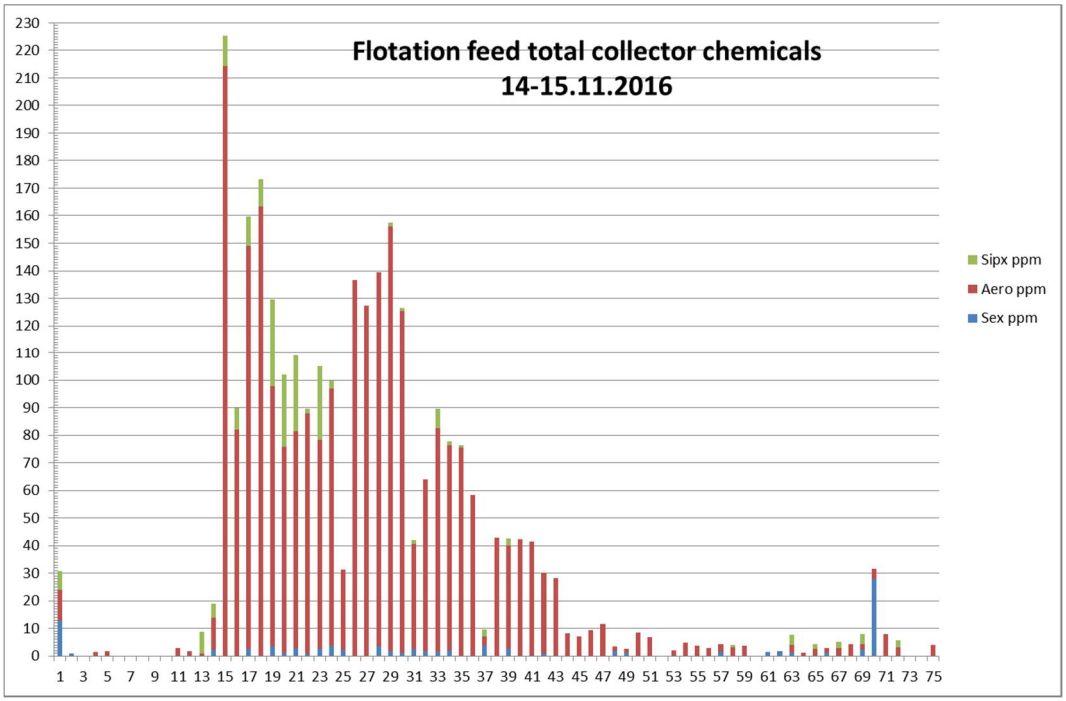

Figure 26. Amount of flotation chemicals, SIPX, Aerophine and SEX detected in measurements between 14-15.11.2016

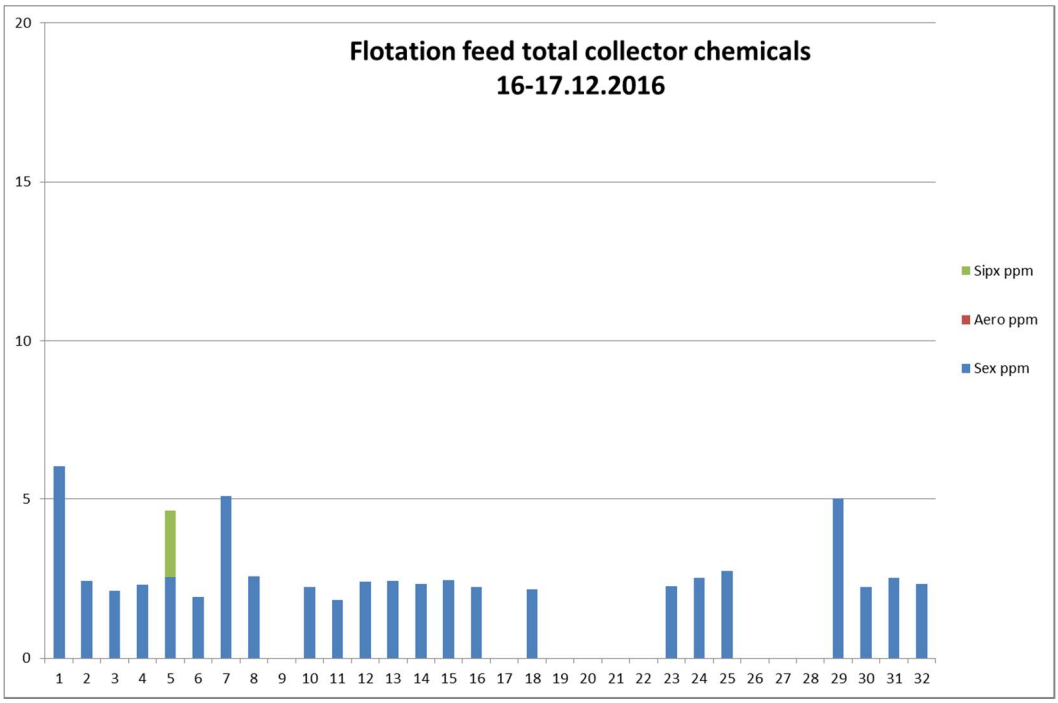

Figure 27. Amount of flotation chemicals, SIPX, Aerophine and SEX detected in measurements between 16-17.12.2016

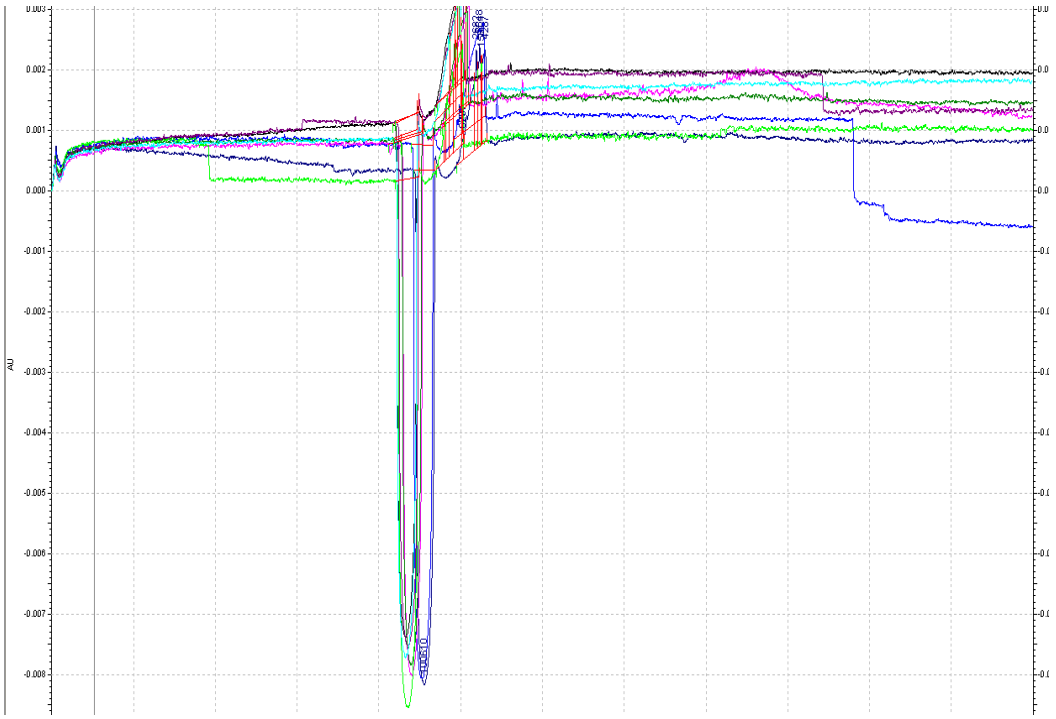

Figure 28. Flotation feed 18.12.2016 measurement diagrams

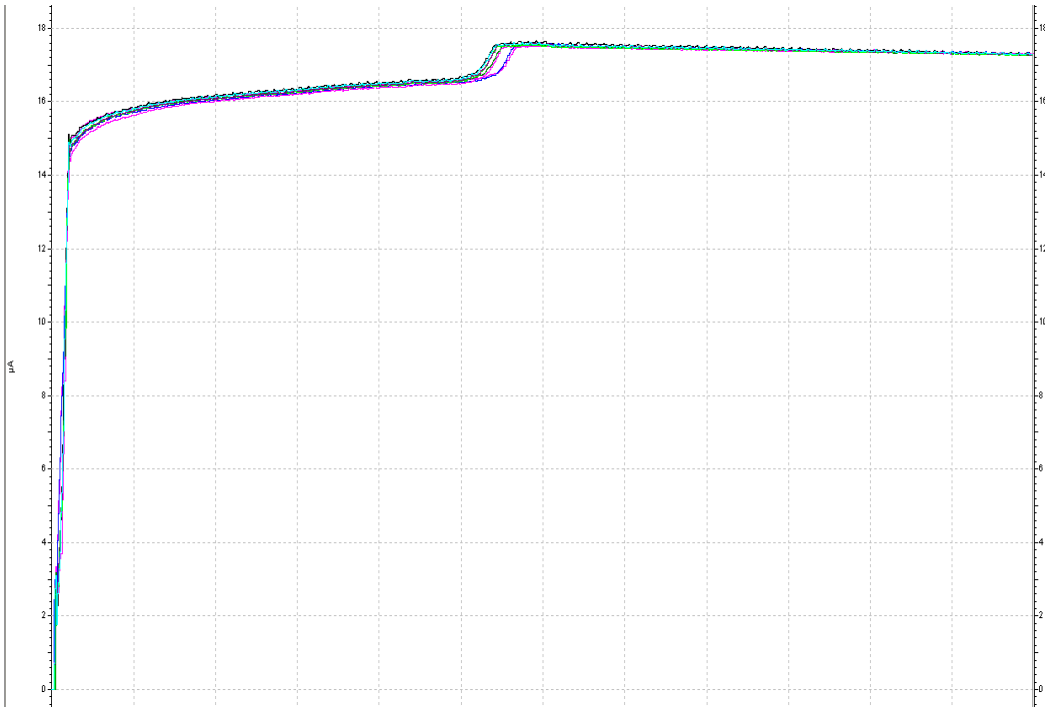

Figure 29. Flotation feed 18.12.2016 verification current diagrams

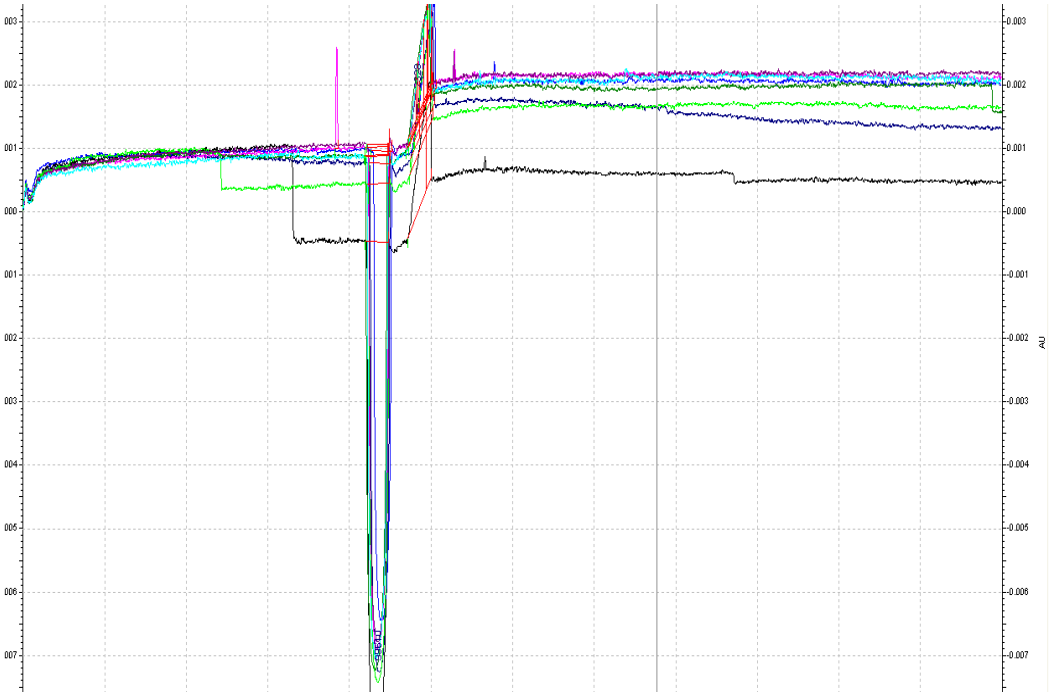

Figure 30. Flotation feed 19.12.2016 measurement diagrams

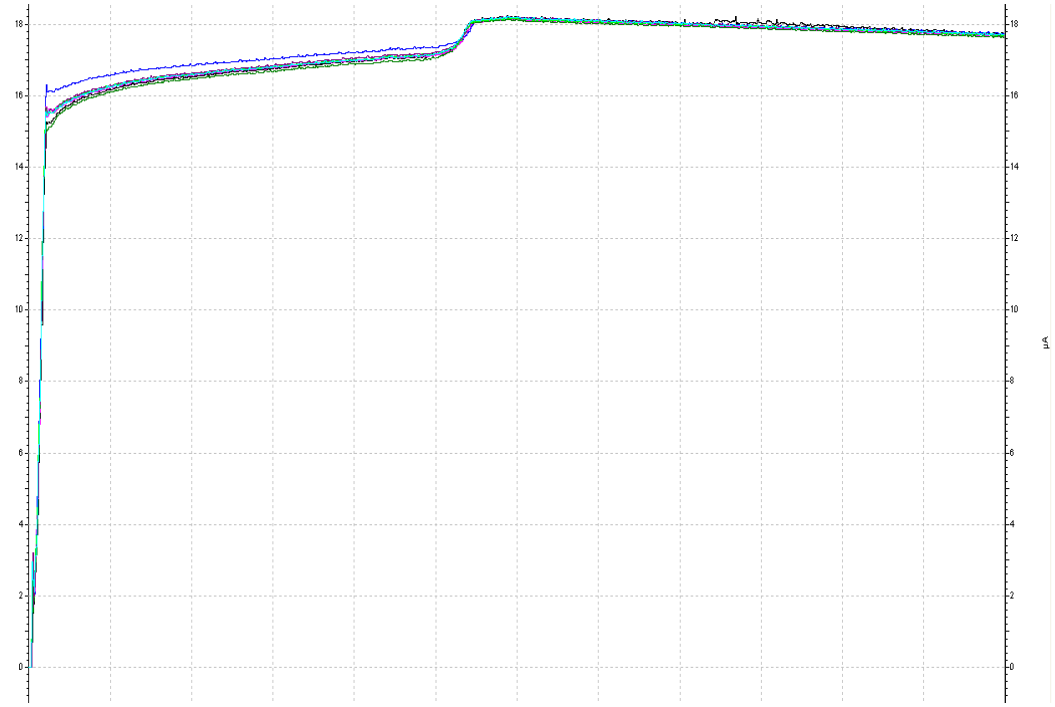

Figure 31. Flotation feed 19.12.2016 verification current diagrams

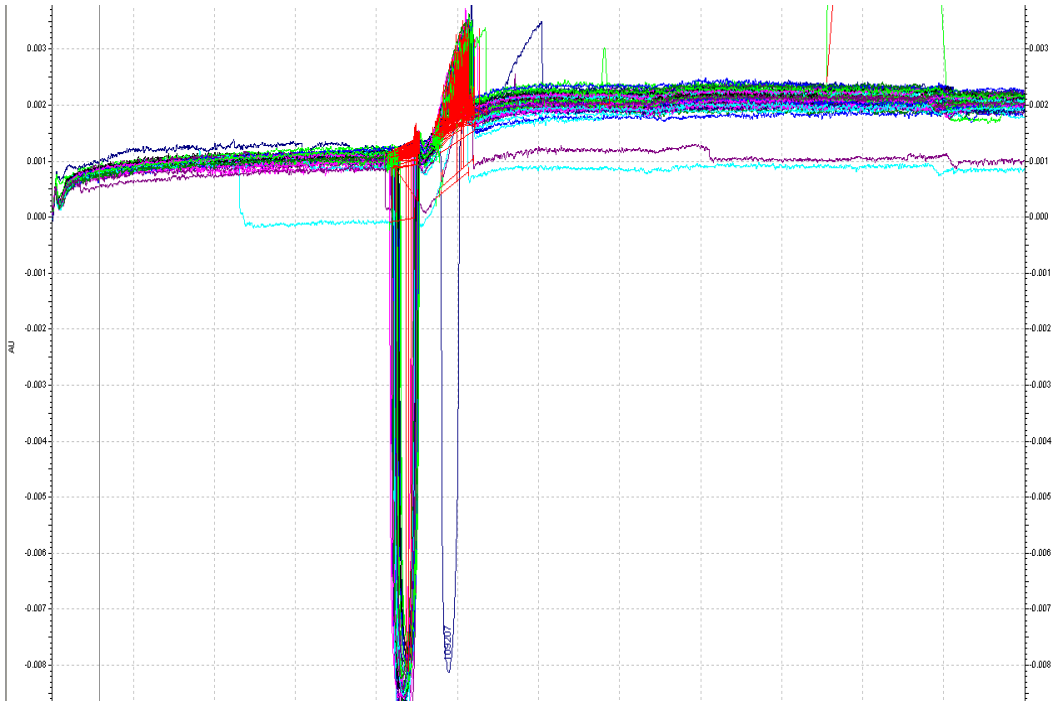

Figure 32. Flotation feed 19.01.2017 measurement diagrams

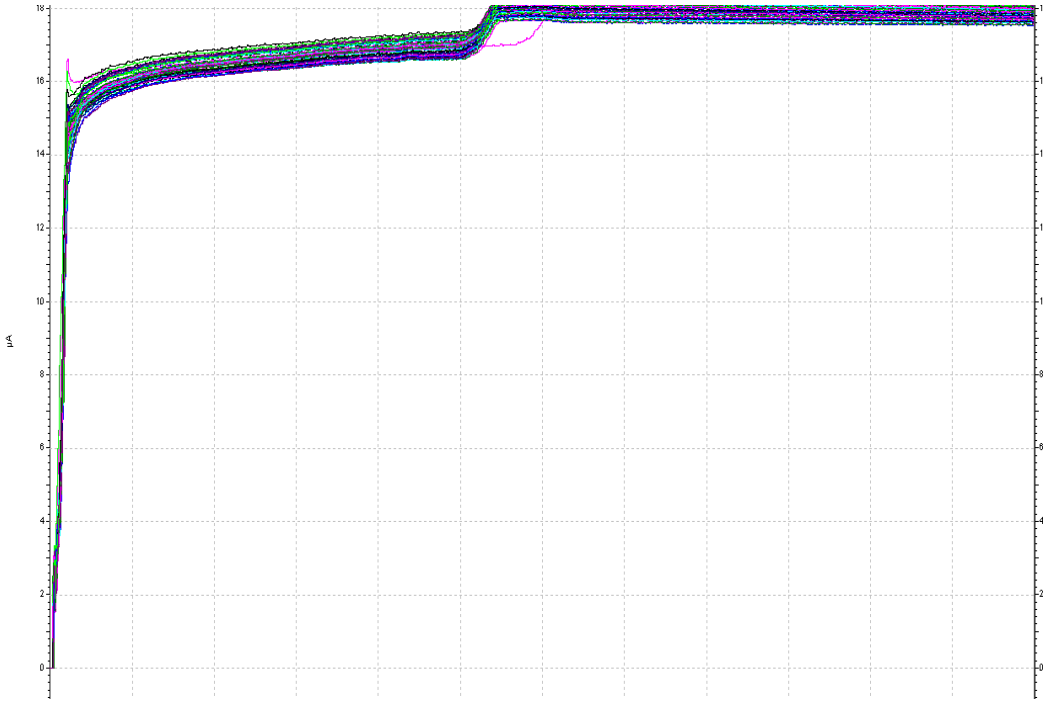

Figure 33. Flotation feed 19.01.2017 verification current diagrams

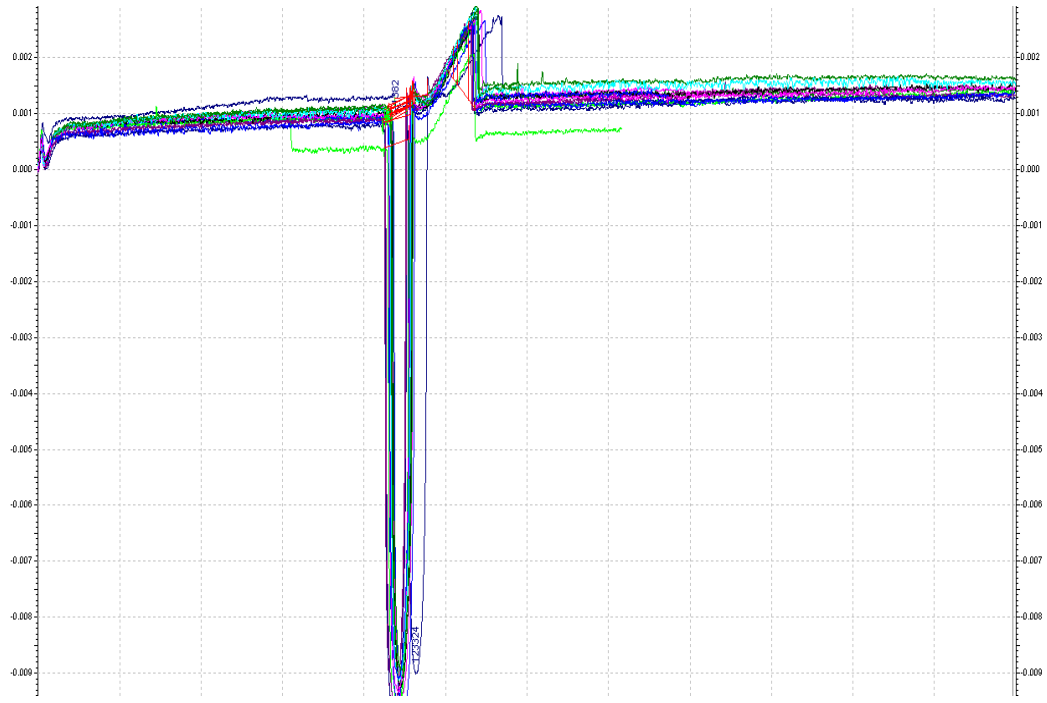

Figure 34. Flotation feed 22.01.2017 measurement diagrams

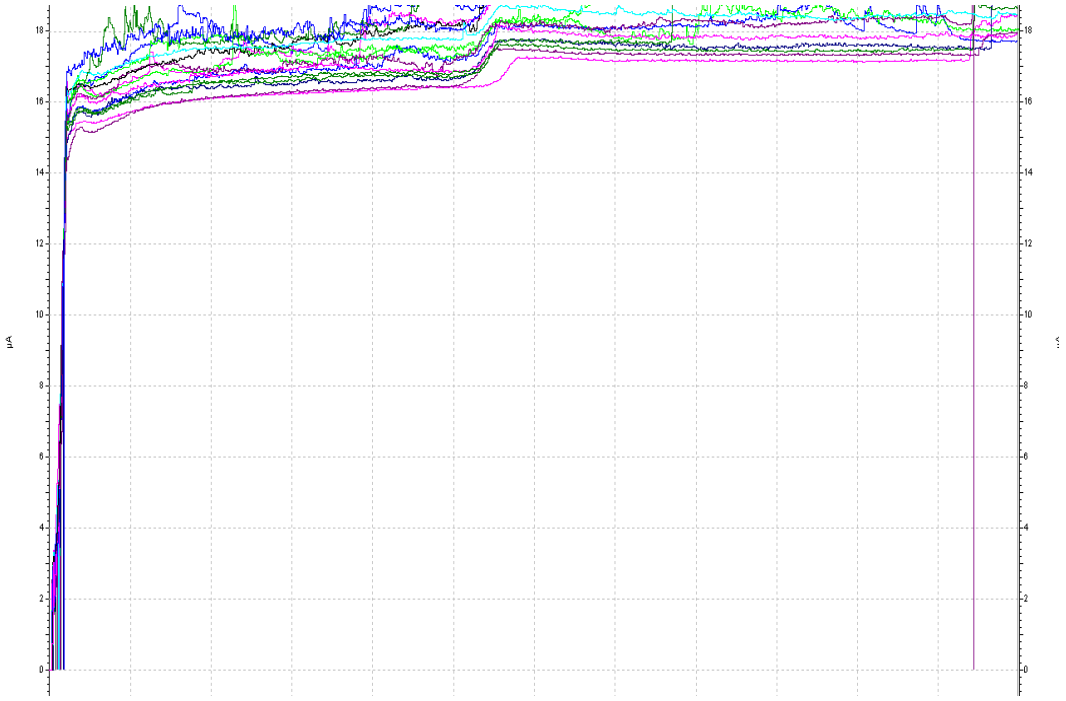

Figure 35. Flotation feed 22.01.2017 verification current diagrams

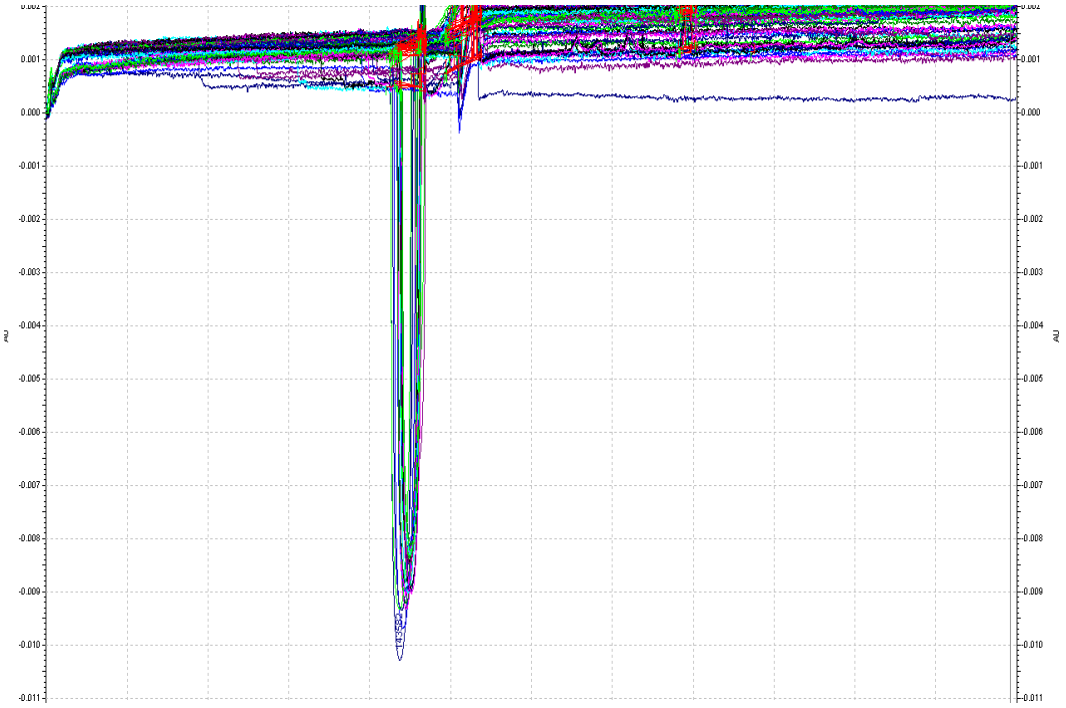

Figure 36. Flotation feed 23.01.2017 measurement diagrams

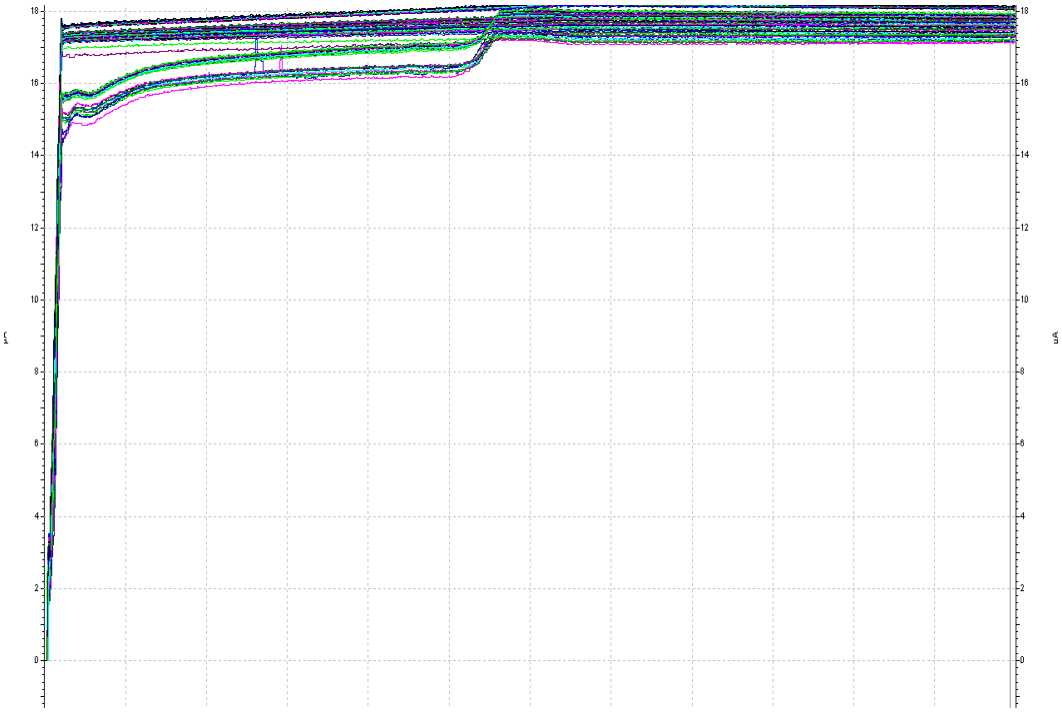

Figure 37. Flotation feed 23.01.2017 verification current diagrams

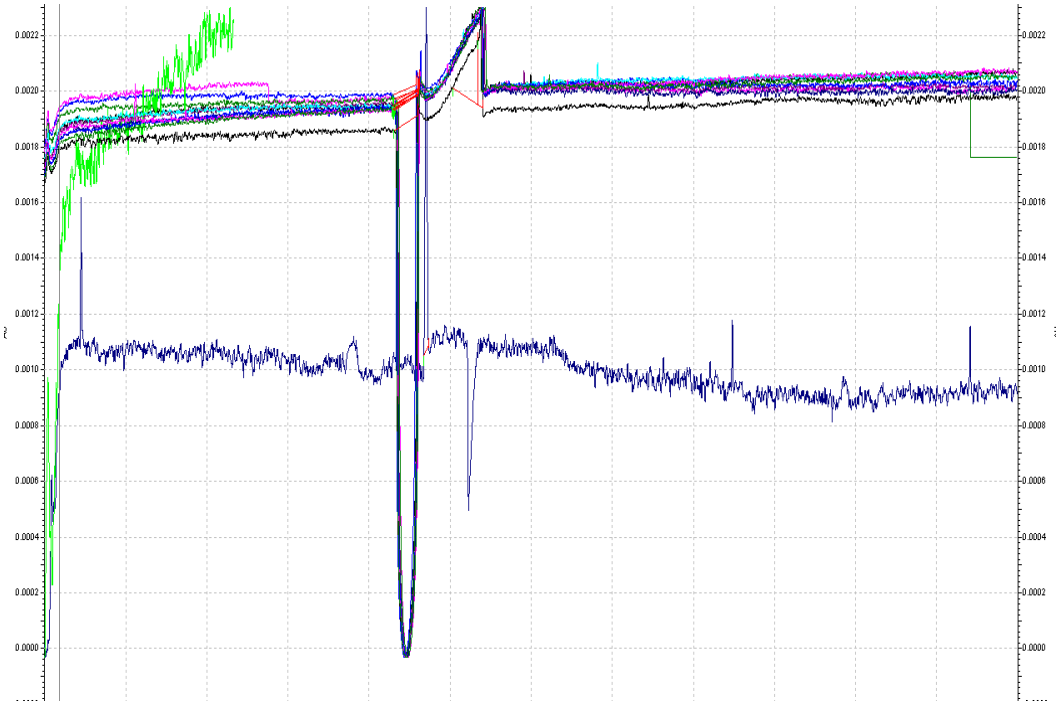

Figure 38. Flotation feed 24.01.2017 measurement diagrams

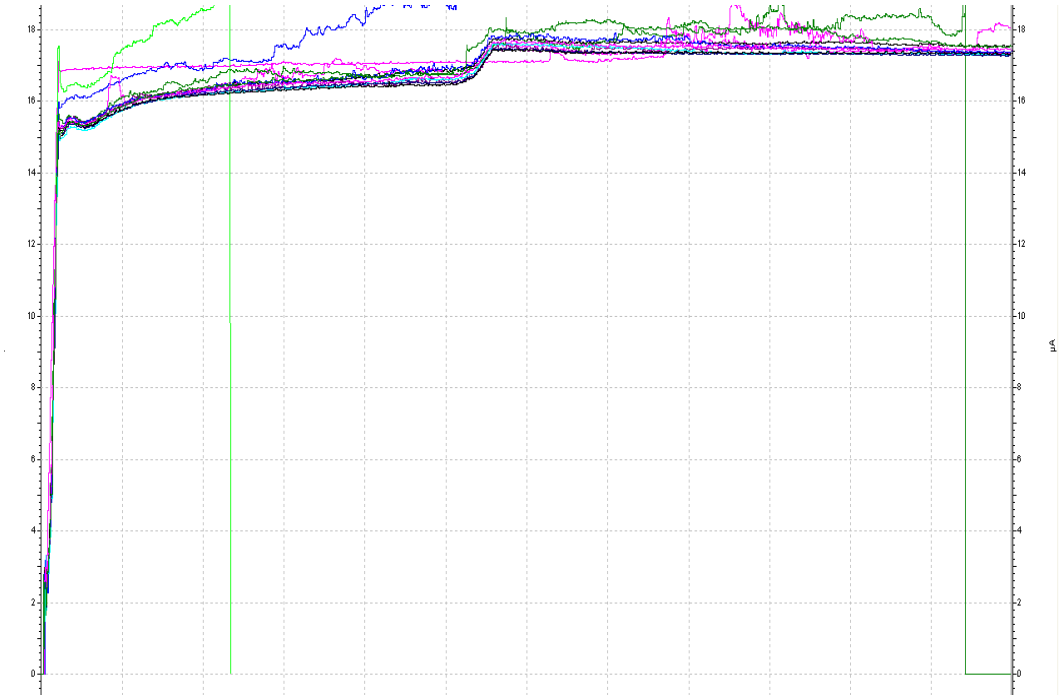

Figure 39. Flotation feed 24.01.2017 verification current diagrams

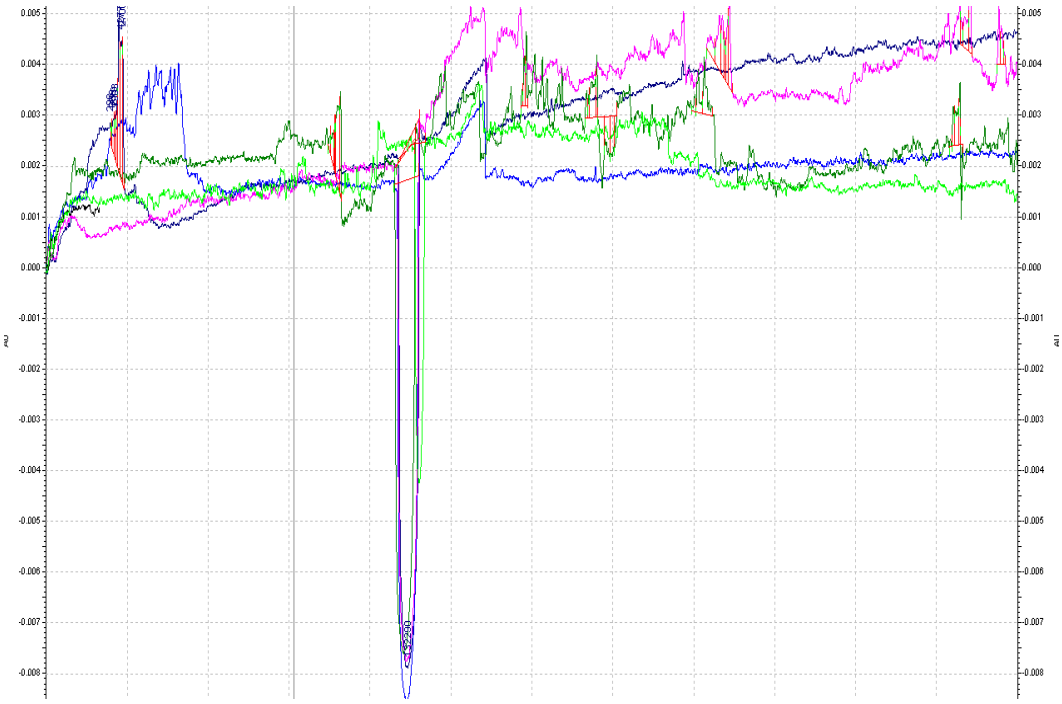

Figure 40. Flotation feed 25.01.2017 measurement diagrams

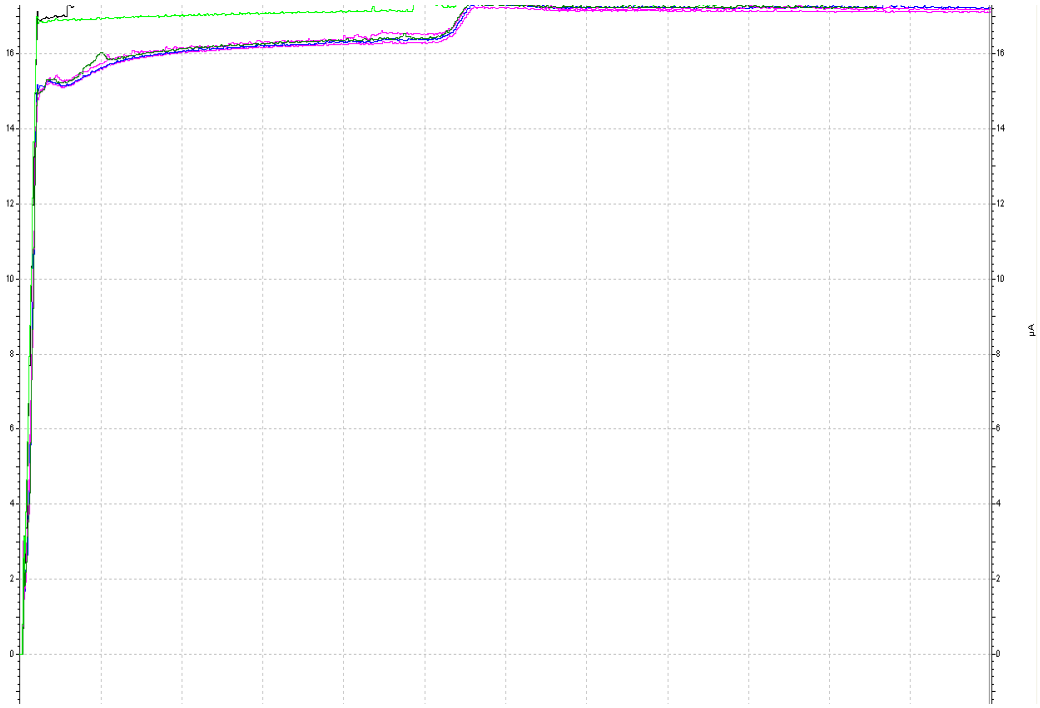

Figure 41. Flotation feed 25.01.2017 verification current diagrams

As seen on the diagrams the detections of xanthates were only made during the first two runs on Setup 1. The last six runs were measured without any error signals from the analyser, but as seen from the current diagrams the buffer solution or some other thing was interfering with the measurement.

The setup 2 runs were intended to monitor possible flotation chemical circulation from the reservoir pond once the pond froze. The first four tests were measured during the pond was still unfrozen and during the last three pond was frozen. The results are shown either in the charts or in form of the diagrams and the current verification dependent whether the detection of the flotation chemicals were made. These results are displayed in figures 42 to 57 measurement diagrams

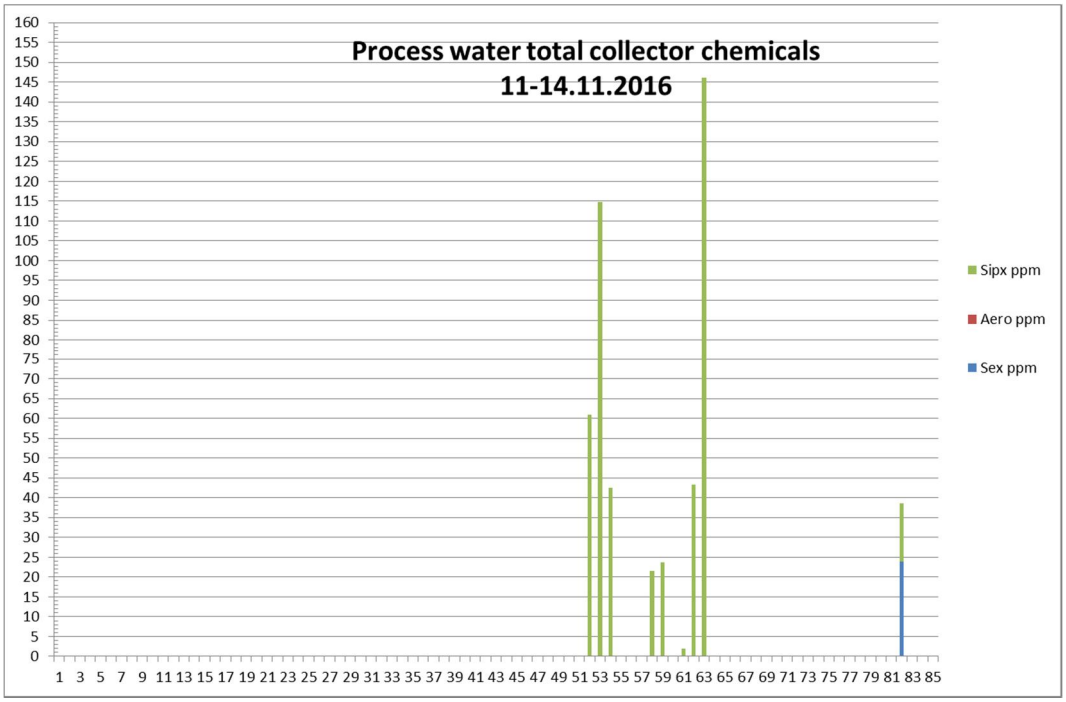

Figure 42 Amount of flotation chemicals, SIPX, Aerophine and SEX detected in process water measurements between 11-14.11.2016.

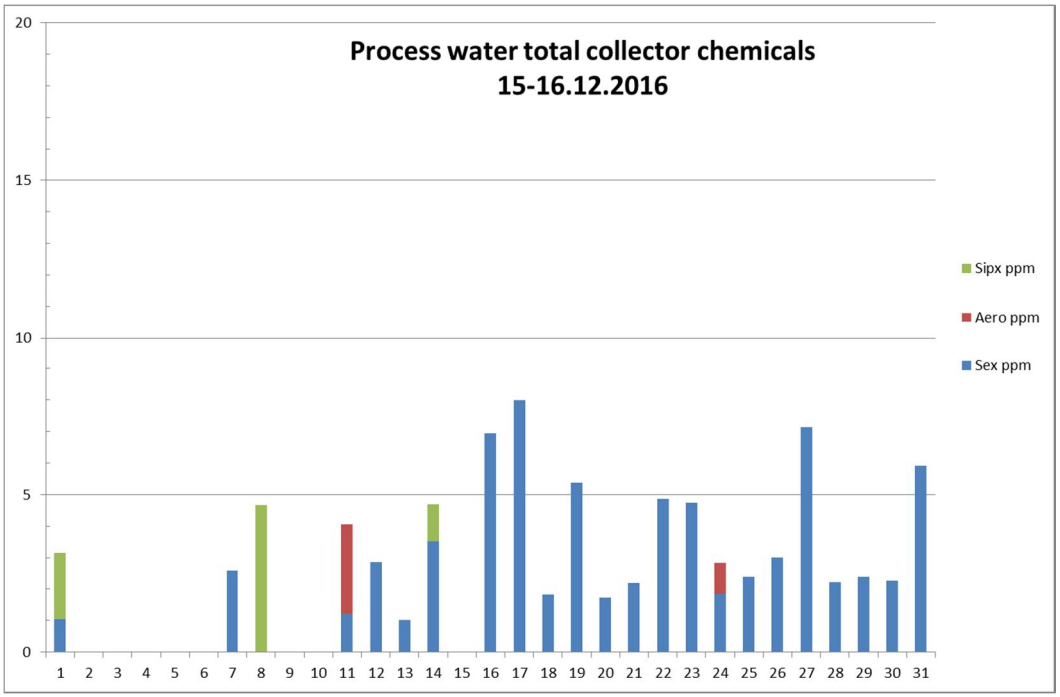

Figure 43 Amount of flotation chemicals, SIPX, Aerophine and SEX detected in process water measurements between 15-16.12.2016

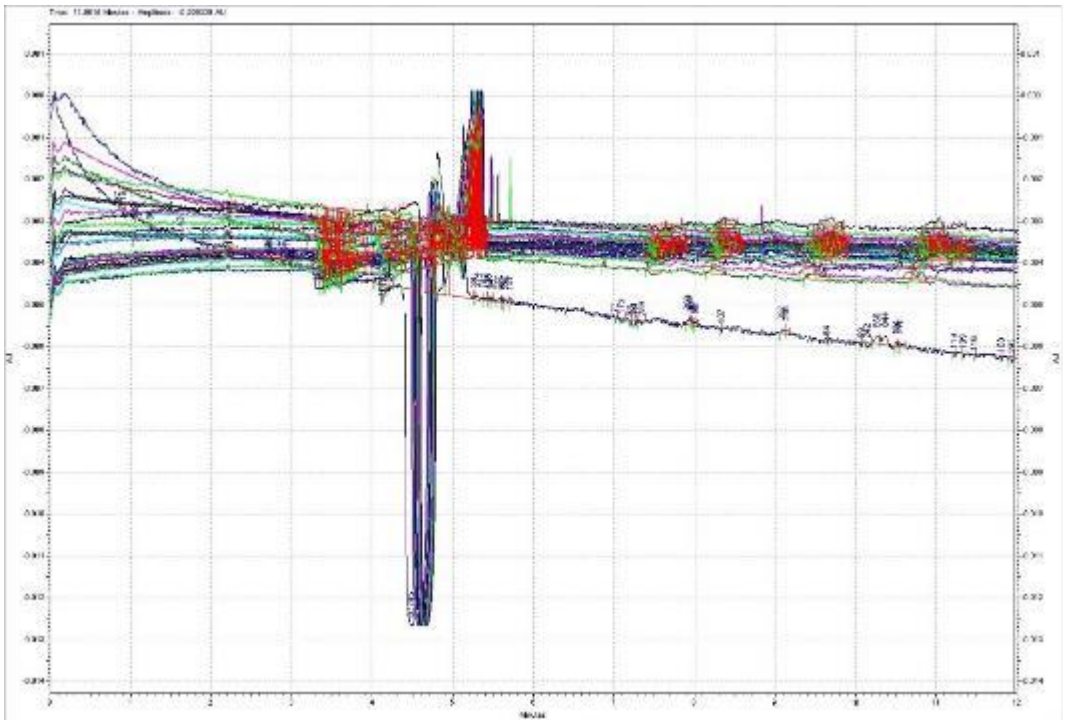

Figure 44 Process water 15-16.12.2016 measurement diagrams.

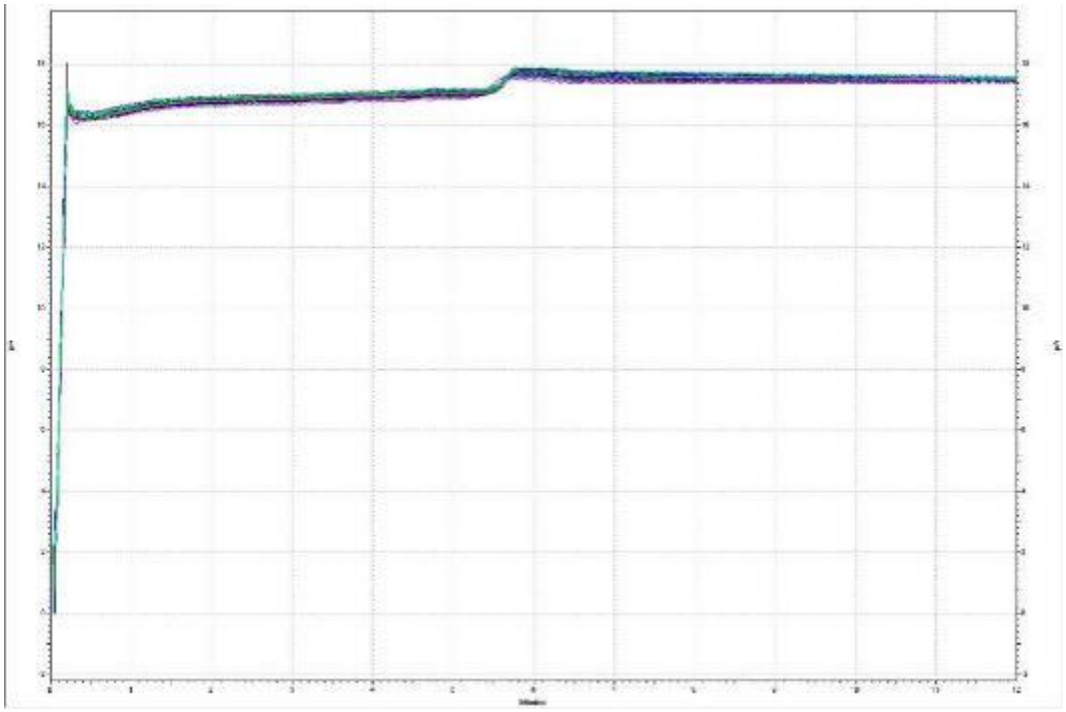

Figure 45 Process water 15-16.12.2016 verification current diagrams

Figure 46 Process water 17.12.2016 measurement diagrams.

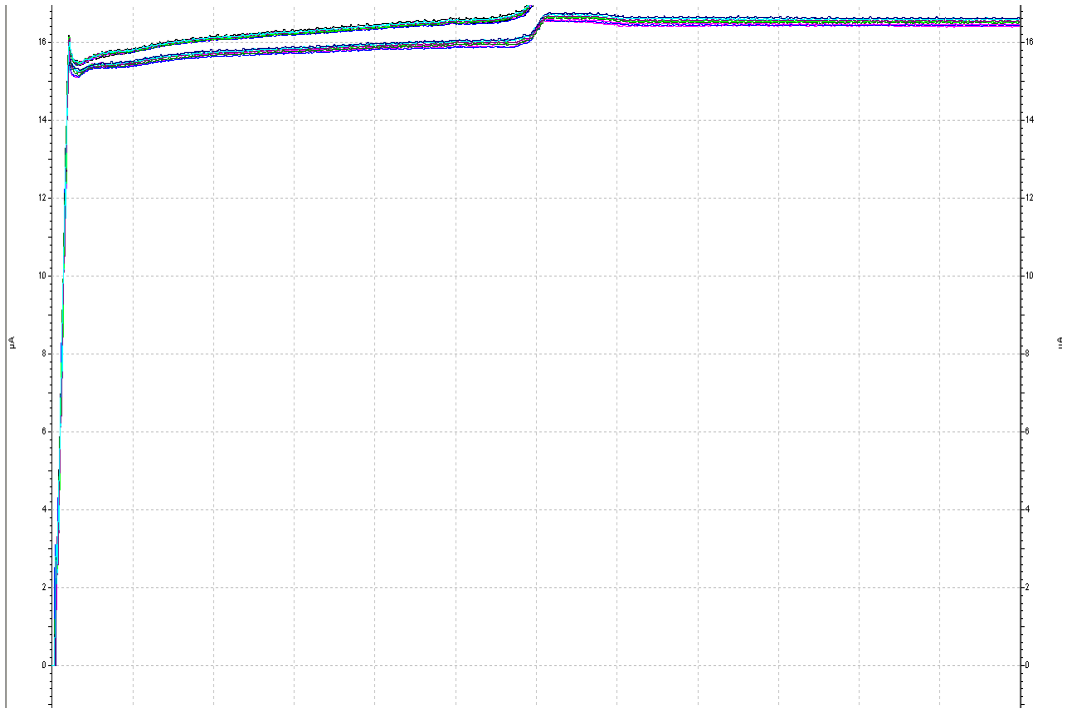

Figure 47 Process water 17.12.2016 verification current diagrams

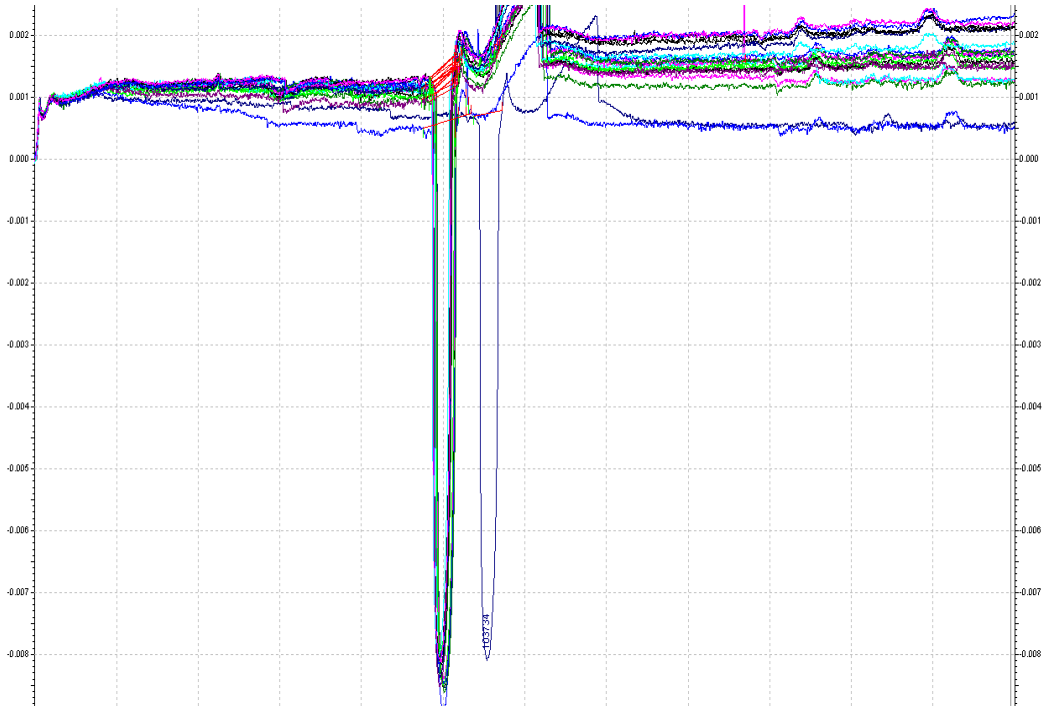

Figure 48 Process water 18.01.2017 measurement diagrams.

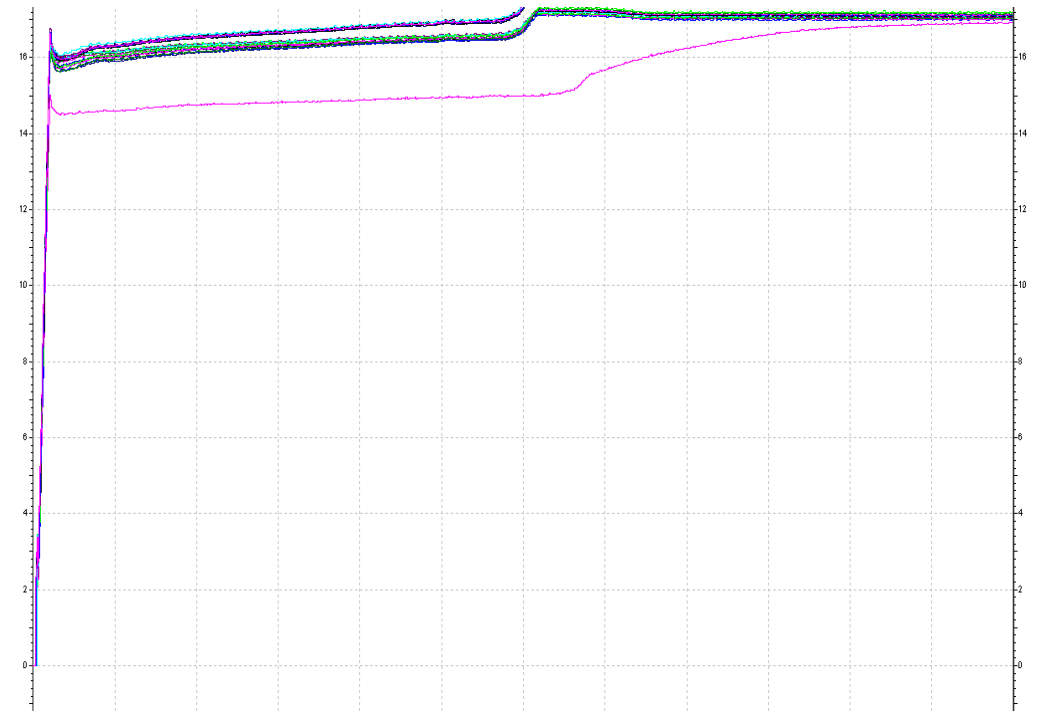

Figure 49 Process water 18.01.2017 verification current diagrams

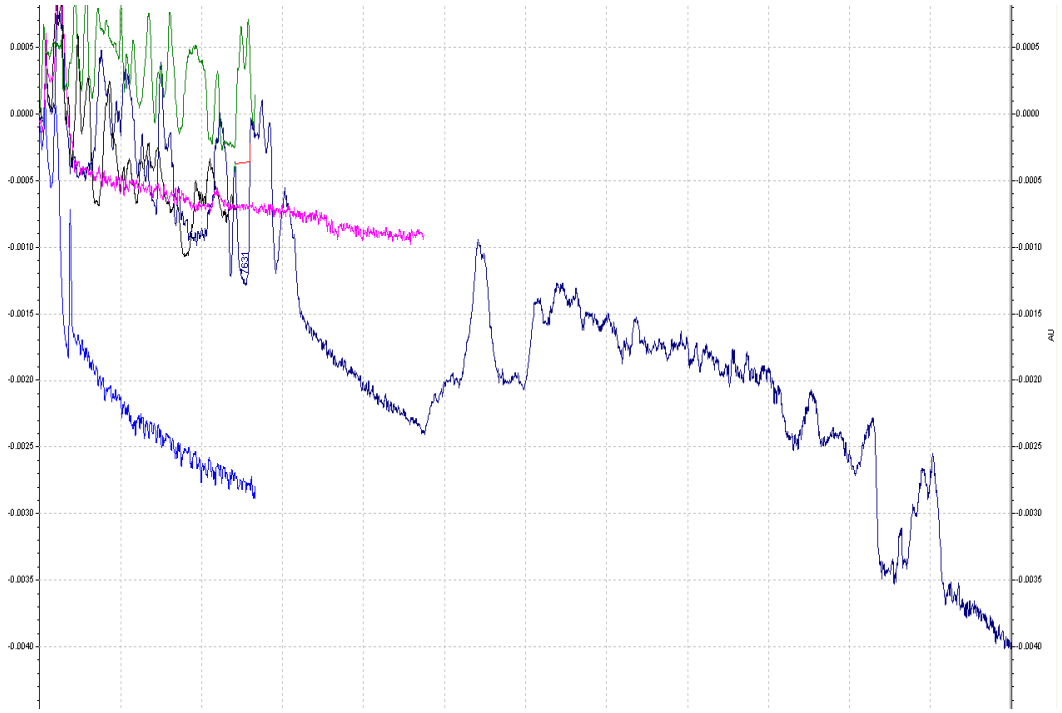

Figure 50 Process water 20.01.2017 measurement diagrams.

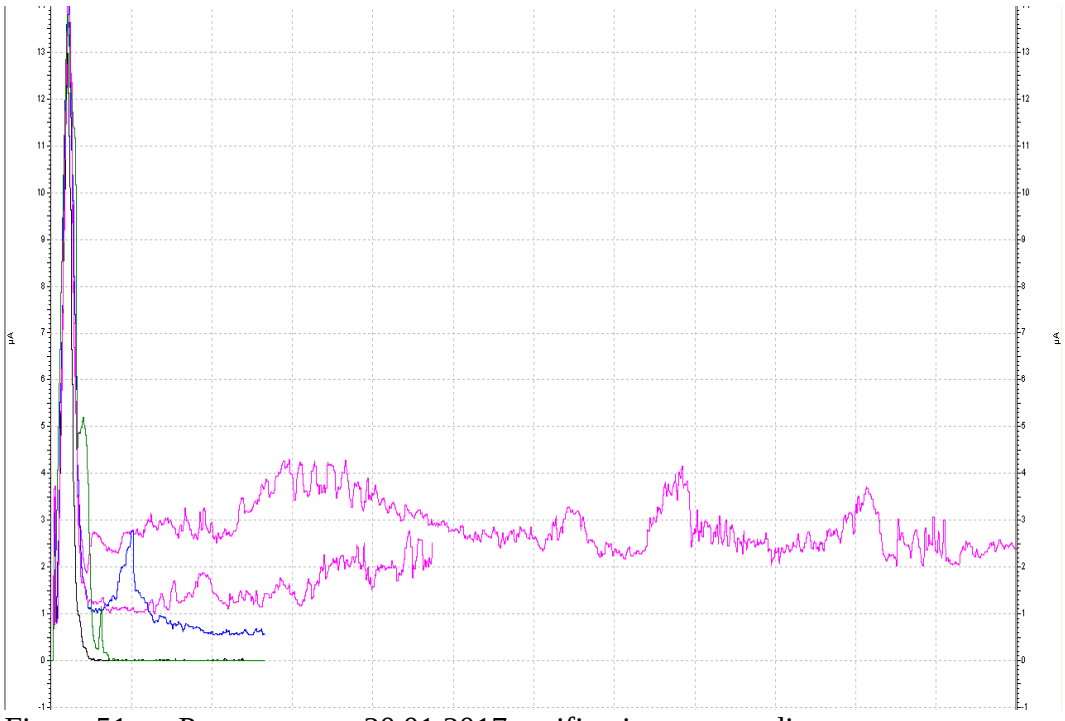

Figure 51 Process water 20.01.2017 verification current diagrams

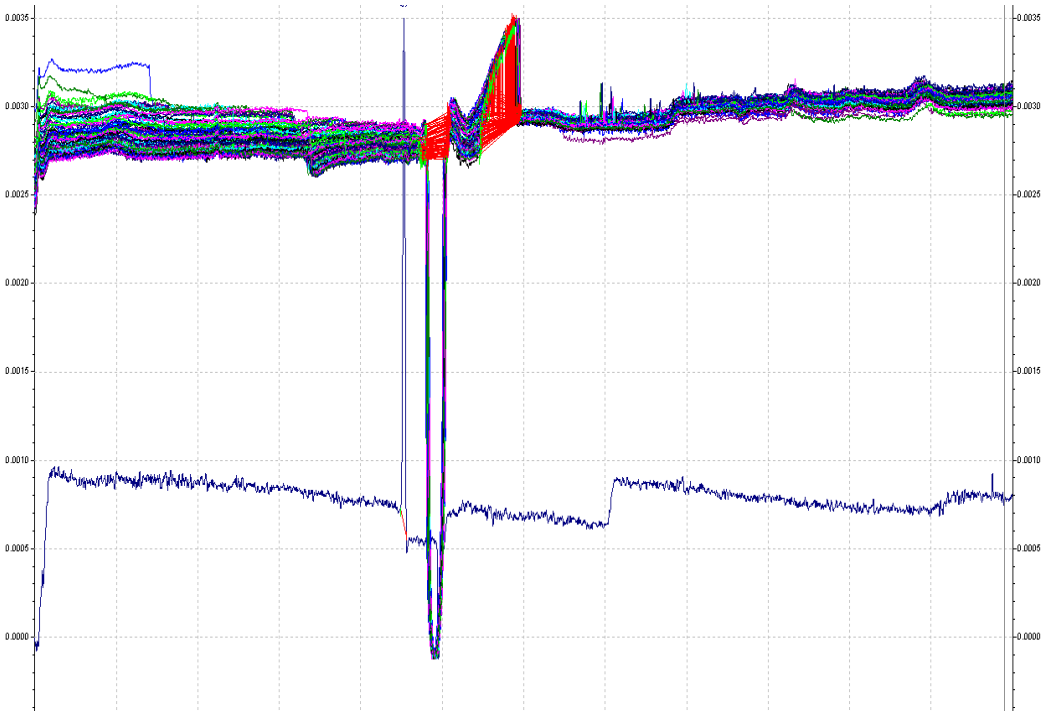

Figure 52 Process water 21.01.2017 measurement diagrams.

Figure 53 Process water 21.01.2017 verification current diagrams

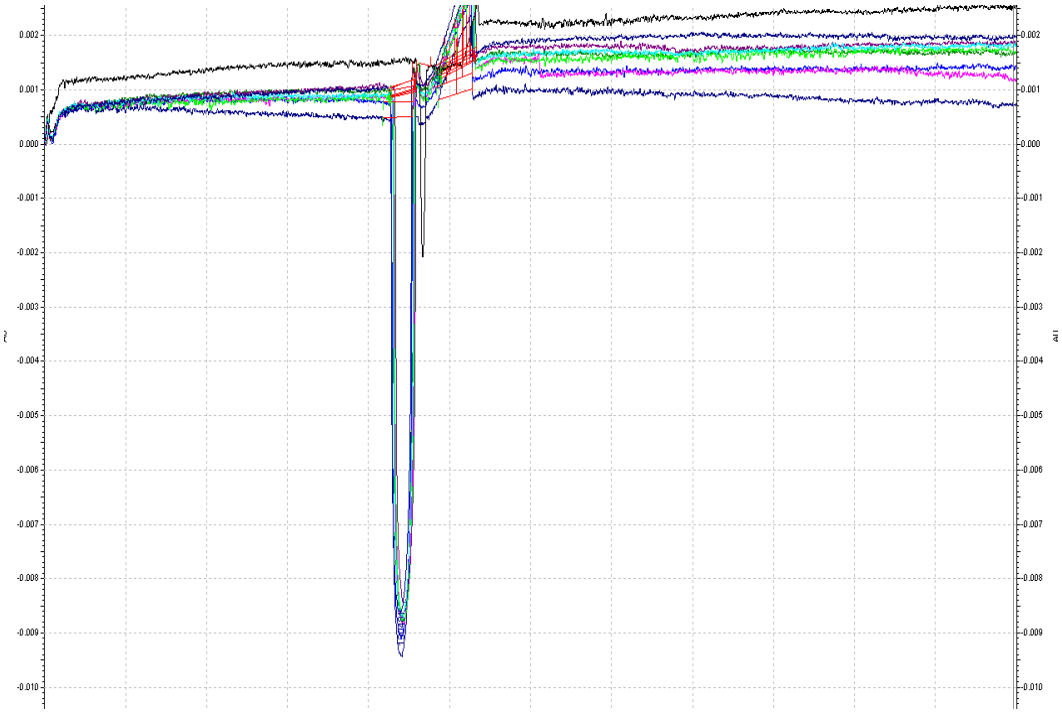

Figure 54 Process water 25.01.2017 measurement diagrams.

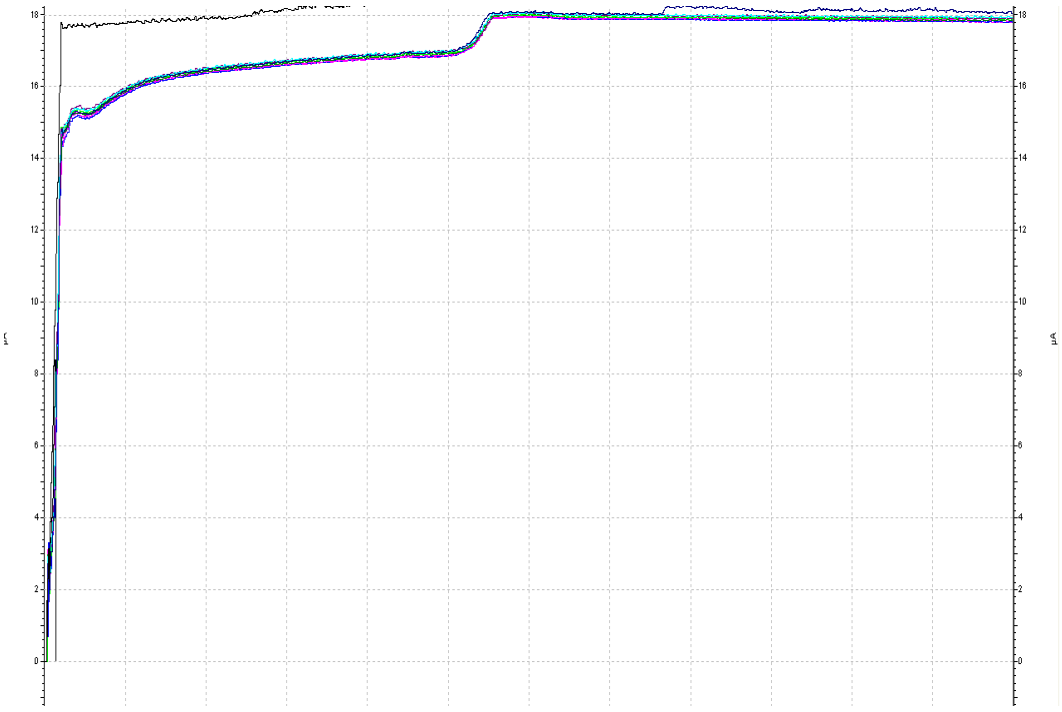

Figure 55 Process water 25.01.2017 verification current diagrams

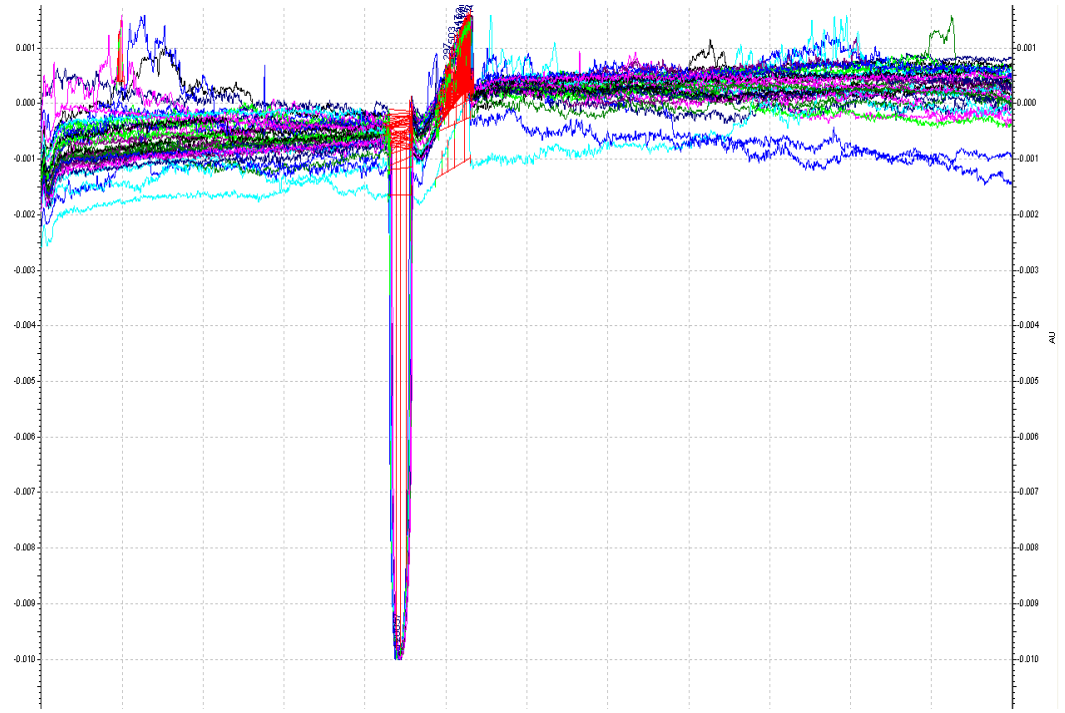

Figure 56 Process water 26.01.2017 measurement diagrams.

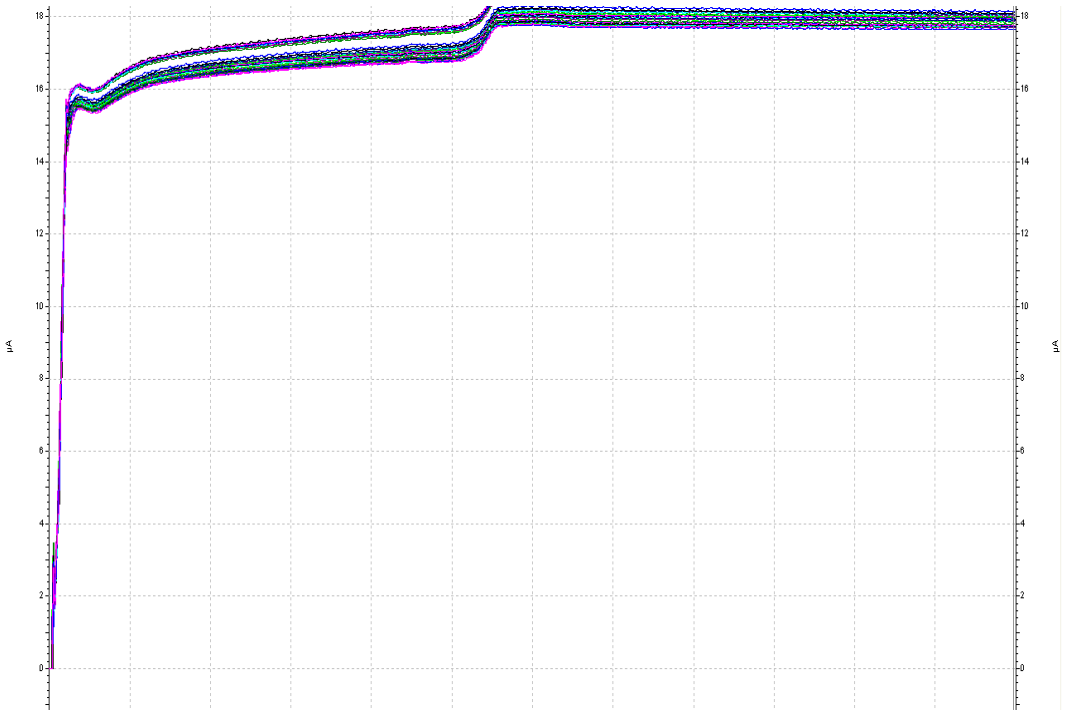

Figure 57 Process water 26.01.2017 verification current diagrams

As seen from the charts there were only a few occasions when the flotation chemicals were present on the process water while running tests with the Setup 2. When comparing the verification current diagrams it is shown that the measurement while running without an error messages from the analyser there has been several

issues during the measurement. One of the most notable thing is a fluctuation on the 26.1.2017 measurements base line that could indicate a possible contamination inside the capillary or on the buffer solution.

All the test series were run as with a daily maintenance routines. Before starting a new test series the buffer reservoirs were washed with the deionised water and dried. The new buffer solution was degassed put into the reservoirs. The filters cartridges (figure 11) were cleaned with a counter current washing in both the Setup 1 and the Setup 2. On the Setup 1 the feed pump (Figure 6) for the settling tank were rinsed with a bucket full of water operating the pump manually. The wire mesh filter was first counter current washed but as it was insufficient to clean the filter, it was then cleaned in an ultrasonic bath as many times as necessary to get it clean. Usually it took up to three times 4 minutes to unclog the wire mesh. A one 12 minutes cycle did not clean the filter as well as the three separate ones with change of clean the washing liquid.

6.5 Process variation

There was a test to use the both lines at same time but that lead constant errors with a current leakage alarms due to the overflow of the sampling container (figures 58 and 59) even with a slow speed of the feeding pump. Although the constant maintenance routines helped the running the system was still occasionally running with errors.

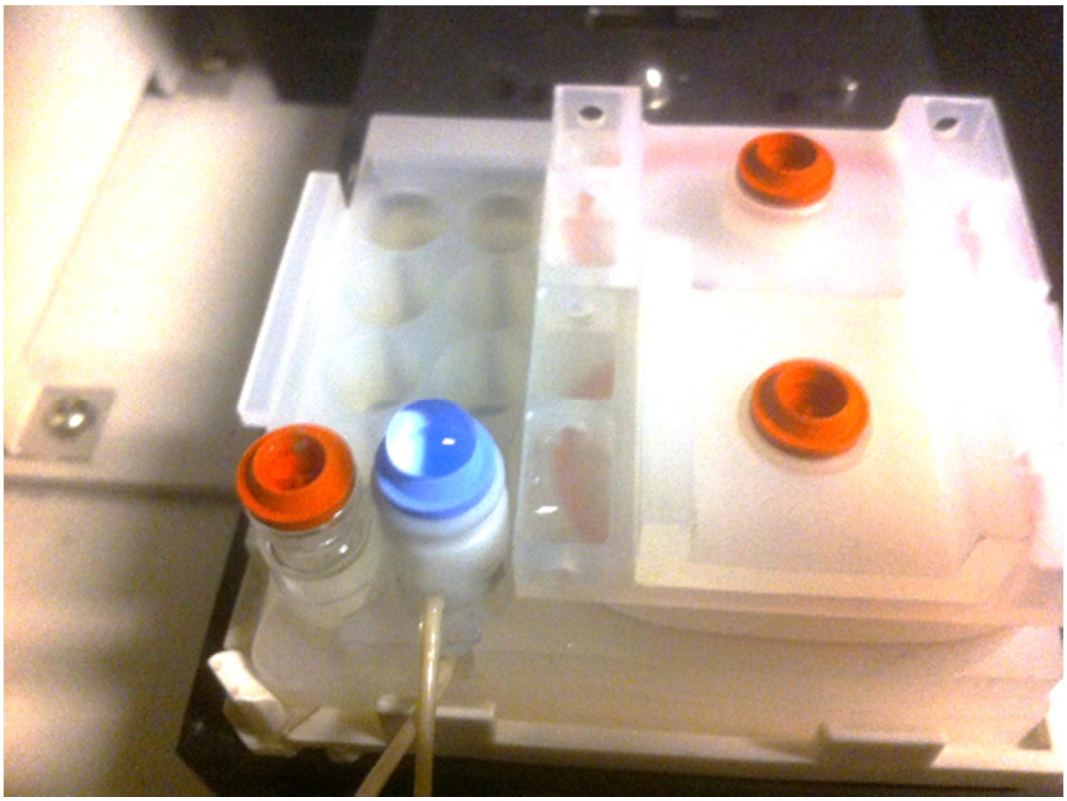

Figure 58 Air bubble causes the sample vial to overflow.

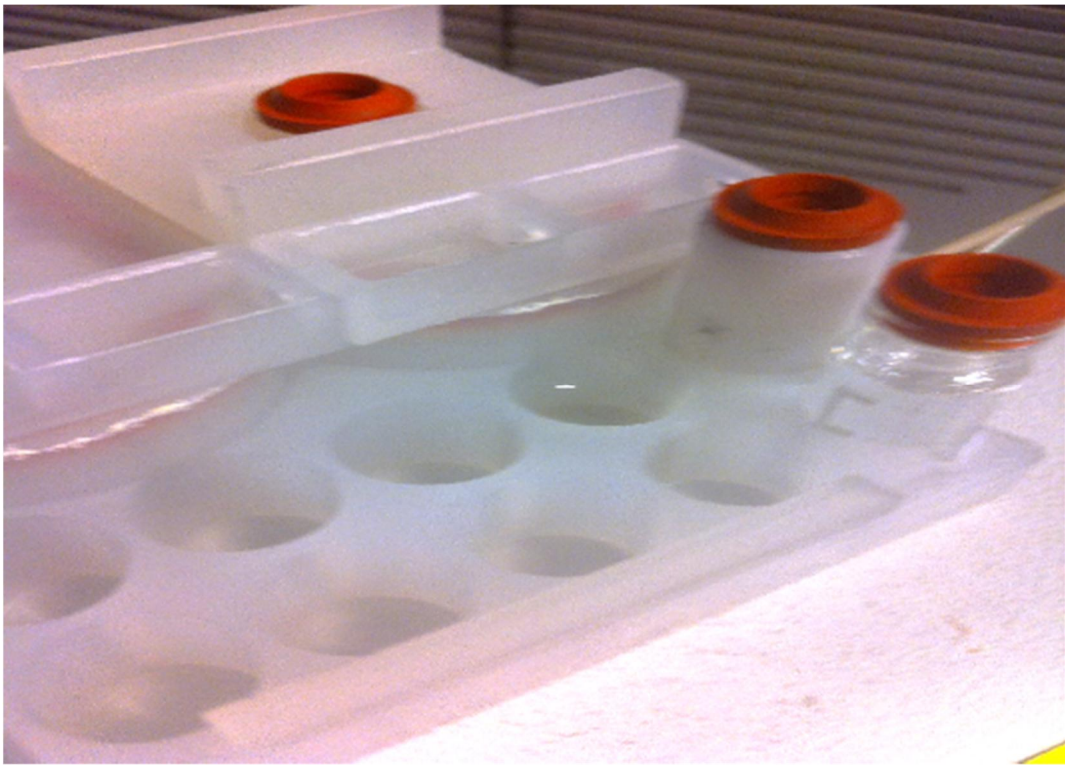

Figure 59 After the vial has overflown current leakages are likely to happen.

Variations in Setup 1

The feeding pump to the settling tank was clogged few times. This was caused by the left over sample in the tube between the tank and pump. This could be removed by adding a rinsing valve to the pump feed. The settling tank as itself worked flawlessly the issue with the settling tank were caused by the wire mesh filter inside the tank. The filter had a tendency to clog after 12 hours of running. The filter has the counter currency rinse and air burst to keep the mesh open but it seems to be still insufficient. The only way to wash the wire mesh clean was the ultrasonic bath. In future the addition of either an ultrasonic transducer to the filter could be applied to keep it clean. Other possibility would be a primary settling tank for the eluent to be pumped before the filtration as now the filter is exposed to the slurry every time. The original setup did not include the valves to prevent the flow to the sample tank during the counter current wash and in use of the air bursts. This lead the sample inside to the tank to be sprayed to the walls. In this event there were no sample left to measure. This was handled with an addition of two valves (figure 10) to close the feed line towards the secondary filter. As the control of the sampling sequence is based on timed operations there is a lot of work in timing and to set the events to smooth the sampling procedure. To ensure a faster modification of the sequence all the valves and the pumps should be manually controllable. This would also help on the diagnostic work during an error situation. One of the sources of variation is the multiplexer sampling device. There were several occasions as the pump took the sample but the settling tank were only filled halfway. That would lead to situation that the sampling pump would take fresh water from the line instead of the sample and that would become the sample measured instead of the real process sample. The multiplexer had also feeding issues as the sample line to the multiplexer was either offline or clogged. The sampling procedure would require a control system that would monitor either the levels at the tanks and flowrate on the pumps. Another option would be that the analyser would be controlled by the sampling procedure to ensure that if there is no valid sample on the system there would be no analysis done. As all sophisticated online systems the control of the measurement should be integrated to the process control system and monitored on both levels when to measure and include some validation for the result before implementation to the control sequence.

Variations in Setup 2

Major variations to the Setup 2 was caused the process itself as the process water contained occasionally large amounts of solids. The system of sample extraction from the line (figure 18) collects solid particles and that caused issues with the mesh wire filter. That led to the breakages of several capillaries. When the filter cartridge was installed instead of the wire mesh filter, the variations were not any more effecting the capillaries. Only once there were a severe process condition as an excessive amount of solid were in the process water. The whole filter cartridge was filled with a fine grit. This was noted as the overflow suddenly stopped. The solids also have a possibility to bind the flotation chemicals in the flow and alter the result.

Variations in CE measurement and software

Some of the measurement uncertainties can be pointed to the CE apparatus. There was some failures to measure cases as the analyser controlling program just hang up. The mechanical sequence in the analyser worked through but the software did not record anything or start a new measurement from the sequence.

The light value of the deuterium (figure 60) light source checked in calibration in Ordior started to diminish. This could have caused some of the detection problems during the measurements. During the second measurement period light source was changed to a new one (figure 61), still it seemed that the optical path to the detector were quite dirty. The analyser expert advised against to the cleaning of the lenses with a conventional means as it might scratch or blur the lenses altogether. The cleaning of lenses should be done as in-house service by experts.

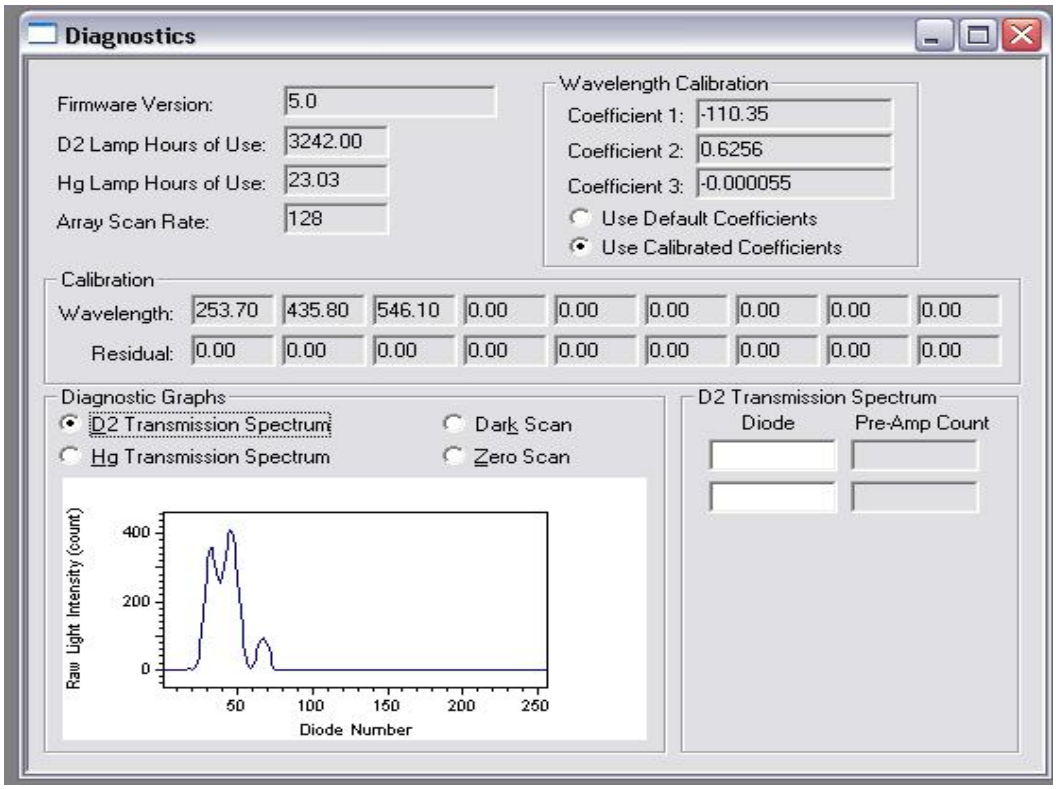

Figure 60 Light intensity diagram for the deuterium light source prior the lamp change.

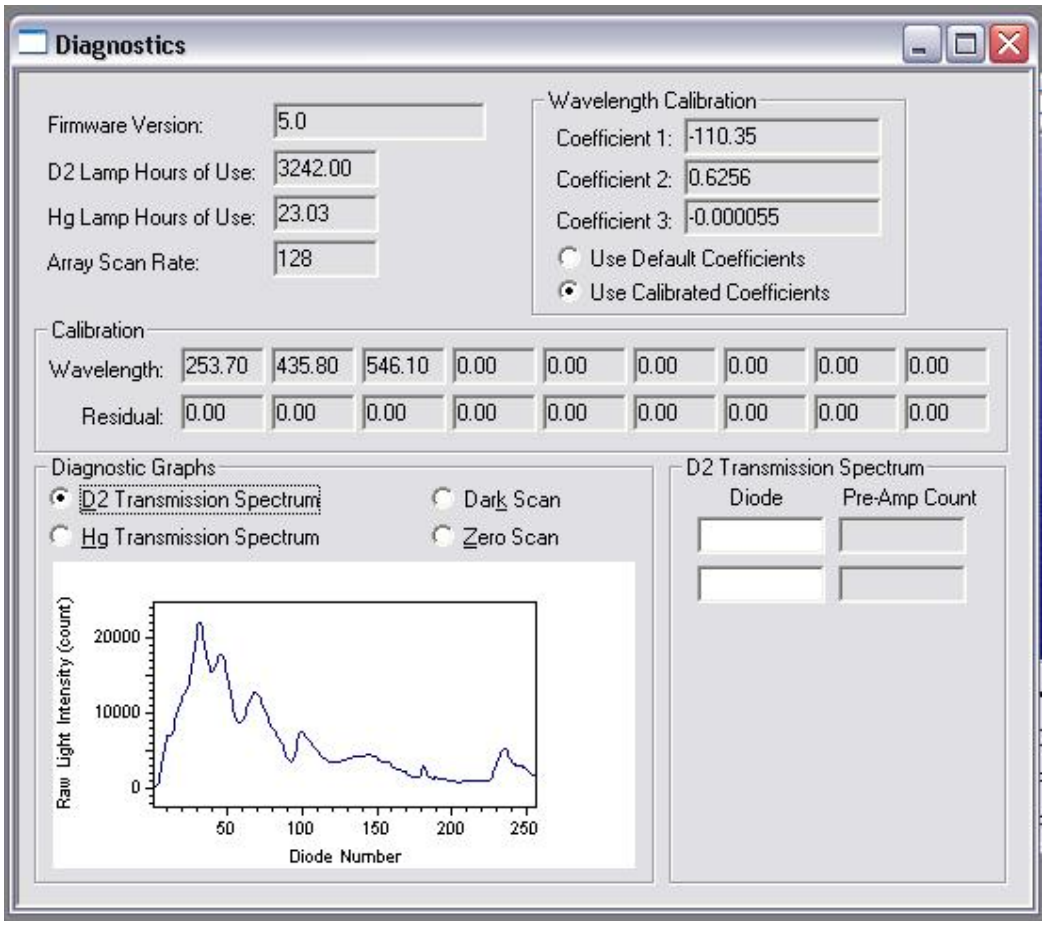

Figure 61 Light intensity diagram for the deuterium light source after the lamp change.

Also there were several mechanical related measurement failures as an example during the measurement system could give an alarm for the sample robotic table as seen in figure 62. The fault was related to the analyser cover sensor that was not detecting the magnet all the time as it was attached to the cover by a piece of duct tape. As a summary the analyser itself is at end of its lifespan and would require a complete overhaul to make certain it would work as it should. The one source of uncertainty is the preparing the capillary cassette to the measurement. In order to keep good repeatability it is necessary to prepare the capillary always to the same length and ensure that the window in the capillary is clean after the burning process. The change of the capillary requires a lot of experience and the environment to do this should be dust free.

Figure 62 Sample table robot gives an error message due the cover open detection signal is no functioning correctly.

6.6 Technical Feasibility of the method

On table 4 there is feasibility chart for CE apparatus in perspective of different variables in system and process environment.

Table 4 The CE apparatus feasibility as on-line measurement

	Pro	**Con**	**Development aspects**
Process	Process technology and theories is well-established and well-known.	Chemistry is known but not completely understood in flotation.	Determination of the sampling points to ensure most detailed information of the process flow. In case absolute values are not available, the relative change can be monitored
Interface and peripheral devices	Computer aided measurement has a potential for fast extensive analysis. Current interface does not require a lot of experience for basic control.	System provides too complicated and extensive information in perspective of monitoring. User interface is open to all access possibility to alter sequence unintentionally.	Novel simplified user interface for operators (with ability to export required values and figures). Peripheral devices should be environment resistant and usable also with gloves.

Instrumentation and control system	Basic transportation of samples is well handled. Synchronisation with courier system as provider of the sample feed worked well during the trials.	Pipelines in sampling chain are long causing segregation and settling of sample, as well as other technical problems in transportation of sample (e.g., pumping). Delay from sampling to process control signal via analytics is unacceptably long (20-30 min)	Shorter lines would decrease segregation, and delay. Sampling and sample preparation procedure could be developed to support faster process control with specific sampling lines with filtering. Targets for sampling or analytics could be re-defined to support needs of the quality control: point estimates or composite sample.
Equipment	Method is developed with current equipment that ensures functioning of the measurement when the measurands detection is properly calibrated.	Equipment is mechanically old and needs constant maintenance. Risk of internal failure lowers the repeatability of the measurement and increases down time for the measurement	Modular measuring unit, that is specially developed handling for sample and other utilities, would increase the usability and increase the service intervals.
Environment	Challenges of process environment are well-defined: dust, vibration, temperature gradients, and moisture fluctuation	Sensitivity for interferences that are present in process environment. The results and analytical procedure might be severely altered by the environmental impact.	Impact of process environment should be minimized via selecting proper location. Uncertainty factors cannot be totally removed but they can be minimized by isolating the equipment from altering process environment.

7 CONCLUSIONS

As the provider of the process knowledge the CE measurement has a potential to become an integrated part of the process control. The applicability of the results and the information of the process conditions accumulated from the measurement should be evaluated and further discussed. The target of the measurements should be clarified or in other words the present application is not developed for the customers' needs, and their interests and motivations should be met in the finalized product. If the application is developed for the monitoring of the residual chemicals in the waste waters there will be markets for these the analyses with a control application and interphase.

As proven in previous studies the CE method functions well with the selected flotation chemicals tested during the method development phase. However, the online implementation will require extensive research and development work on the sample preparation and handling as it is the main source of uncertainties on the system. The analyser has to be developed and built rugged to withstand changes of the process environment. The scope to further development should be aimed to get an improved understanding of the process environments impact to the CE measurement. An automatic and dynamic calibration system should be developed to ensure that the migration time shift detection as is an inseparable part of the CE measurement, and can be taken into account and then controlled. There should be a provider of fresh buffer solution and other utility chemicals for the washing and the regeneration of the capillary. Also the development of the analytical chain should concentrate on creating a system that ensures an equal possibility for each unit to be selected as a part of the sample. The second critical requirement of the sampling procedure is that the sample should not change its physical state or segregate in transportation

As shown in this study the changes in the process environment has an immense effect to the CE measurement. If the control aspect of the measurement is not critical and the delay for the results can be allowed to be more than 30 minutes, then the method can be considered. As an alternative to the process environment, an

option to create a sampling system that would collect samples that could be further analysed in a less hostile environment.

The results show that the method and the system are promising for at-site monitoring rather than online monitoring.

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