APPLICATION OF EMULSION LIQUID MEMBRANES IN THE EXTRACTION OF RHODIUM FROM MINING AND METAL REFINERY EFFLUENT

Report to the
Water Research Commission

by

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WRC Report No. 2011/1/13
ISBN 978-1-4312-0477-9

November 2013

Obtainable from

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EXECUTIVE SUMMARY

BACKGROUND

The platinum group metals (PGMs) constitute the backbone of the economy in South Africa. The mining and related metal refinery operations contribute a significant portion to the gross domestic product and the employment in the country. Thus the optimisation of the PGM extraction processes from the mined ore materials is critical to the ongoing development of the PGM mining sector. The emulsion liquid membranes are a relatively old technology which has been successfully used to the extraction of base metals from acidic media. Its advantage over the classical metal solvent extraction is that is integrates loading and stripping phases of the extracted metal into one step. This in turn increases the efficiency of the PGM production process. However, to this date and the best of the authors' knowledge no data is available on the application of the emulsion liquid membranes in the public membranes. This project set out to investigate the application of emulsion liquid membranes (ELMs) in PGMs from the aqueous by-products of PGM refining. The by-products are generated as side-streams which require storage and reprocessing. Of the PGMs, rhodium (Rh) is one of the more inert and therefore difficult to extract.

Membranes have historically been viewed as the semipermeable barriers between two adjacent phases (Kislik, 2009). From the operational point of view, membranes are easy to bring to the industrial scale for the following reasons (Kislik, 2009): the underlying scientific concepts are relatively simple, their operation and scale-up is uncomplicated to achieve, they are environmentally-friendly and low-cost from the energy point of view. Membranes can consist of polymer films and liquids (Kislik, 2009). If the membrane system is based on a liquid matrix, then it is called a liquid membrane (Tandlich, 2009). Liquid membrane systems involve contacting of an immiscible organic liquid (named the diluent) with a feed phase (i.e. the treated side-stream; Noble *et al*., 1987; Araki and Tsukube, 1990; Bartsch and Way, 1996).

The emulsion liquid membrane (ELM) is a specific case of the liquid membrane where the diluent layer contains dispersed microdroplets of the stripping phase (Kislik, 2009). The stripping phase forms a receiving phase of the extracted species, i.e. the solvent extraction and stripping of the loaded organic solvent are performed in one step. Application of emulsion liquid membranes (ELMs) reduces energy and financial costs and the time for the metal solvent extraction (Busca *et al*., 2008). This is caused by the faster kinetics of extraction with ELMs and higher extraction yields in comparison with the classical solvent extraction (Tandlich, 2009). Problems include the lack of stability of the ELM droplets at high shear stresses inside the extraction contactors (Park, 2006). The fundamental trigger for this drawback is the swelling of ELM microdroplets from water absorption when in contact with the treated side-stream (Park, 2006). Partial solution is to increase the surfactant concentrations inside the ELM (Tandlich, 2009). This leads to improvement of the microdroplet stability, but also increases the viscosity of the ELM (Groenweg *et al*., 1994). As a result, the higher ELM concentrations of surfactants decrease in the mass transfer rates of the extracted metal, i.e. prolonging the extraction process (Park, 2006). A solution is the application of non-Newtonian ELMs (Park, 2006).

RESULTS AND CONCLUSIONS

Results show that the complete extraction of Rh is possible from model side-streams from metal refinery operations, namely hydrochloric acid (HCl) solutions containing 7 mg/L of Rh (see Table below). This is achieved by the use of the optimised ELM where the diluent was 30% solution of toluene in kerosene and the other component concentrations were as follows: 30.000 g/L (w/v) PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80. This diluent phase was then mixed with 2 M HNO_3 (stripping phase) in a ratio of 2:1. The volumetric ratio of treated side-stream and the ELM was 5:1 and 98.7 to 108.7% of the initial Rh amount was recovered in the stripping phase after chemical demulsification. This was performed with polyethylene glycol with molecular weight of 400 g/mol (this chemical will be designated as PEG in further text, see list of abbreviations for further details) at 50 ± 1°C for 24 hours. Major carryover of the diluent components into the stripping phase and side-stream was observed. Using the COD digestion stoichiometry, the aqueous solubilities and the measured ELM components concentrations, it is estimate that the carry-over

was mostly from the TOA, toluene and PEG. The final spent side-stream should not be discharged into the environment as the acute *Daphnia pulex* toxicity testing results have shown.

Extraction efficiency of Rh at varying pH values of the spent side-stream for consecutive ELM extractions in the Taylor-vortex column.

pH[a]	C_0(Rh) [b] (µg/mL)	M_0(Rh)[c] (µg)	M_1(Rh)[d] (µg)	M_2(Rh)[e] (µg)	M_3(Rh)[f] (µg)	P_2(Rh)[g] (%)	P_3(Rh)[h] (%)
2.01	7.00	350	205	366	376	104.4	107.3
3.08	7.00	350	185	345	380	98.7	108.7

[a] Initial pH value of the treated side-stream
[b] Initial Rh concentration in the treated side-stream
[c] Initial Rh amount
[d] Rh amount extracted after one extraction
[e] Rh amount extracted after two extractions
[f] Rh amount extracted after three extractions
[g] Percentage Rh amount extracted after two extractions
[h] Percentage Rh amount extracted after two extractions

Complete extraction of Rh is possible from model side-streams, namely hydrochloric acid (HCl) solutions containing 7 mg/L of Rh. This was achieved by the use of the optimised ELM where the diluent was 30% solution of toluene in kerosene and the other component concentrations were as follows: 30.000 g/L (w/v) PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80. This diluent phase was then mixed with 2 M HNO_3 (stripping phase) in a ratio of 2:1. The volumetric ratio of treated side-stream and the ELM was 5:1 and 98.7 to 108.7% of the initial Rh amount was recovered in the stripping phase after chemical demulsification. Stripping was performed with polyethylene glycol (PEG) with a molecular weight of 400 g/mol at 50 ± 1°C for 24 hours. Major carryover of the diluent components into the stripping phase and side-stream was observed. Using the COD digestion stoichiometry, the aqueous solubilities and the measured ELM components concentrations, it is estimate that the carry-over was mostly from the TOA, toluene and PEG. The final spent side-stream should not be discharged into the environment, as the acute *Daphnia pulex* toxicity testing results have shown.

RECOMMENDATIONS

Commercial use of the ELMs in extraction processes is often hindered by in the instability of the stripping phase microdroplets due to the absorption of water from the feed phase into the ELM matrix. The classical solution is to increase the surfactant concentration in the ELM. This increases the stability of the microdroplets, but also leads to a decrease in mass transfer rates during metal extraction. Thus a novel solution must be found to address this problem. One of the potential solutions listed in literature for the extraction of base metals is the use of non-Newtonian liquids as ELMs. The simplest way to construct a non-Newtonian ELM is the addition of a polymer such as polyisobutylene (PIB) to the ELM diluent.

ACKNOWLEDGEMENTS

The project team wishes to thank the following people for their contributions to the project:

Dr Jo Burgess	Water Research Commission (Chairperson)
Dr Vermont Somerset	CSIR NRE, Stellenbosch
Dr Patrick Ndungu	University of KwaZulu-Natal, Durban
Ms Kerry Slatter	Anglo American Platinum/Independent Consultant

At the same time, the support of Rhodes University and the National Research Foundation is acknowledged for providing bursaries to Catherine D. Luyt, Francis Moyo and Khokela L. Tyalana,

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ACRONYMS AND ABBREVIATIONS

COD	Chemical Oxygen Demand
ELM(s)	Emulsion Liquid Membrane(s)
KHP	Potassium hydrogen phthalate
PEG	Polyethylene glycol with molecular weight of 400
PGM(s)	Platinum Group Metal(s)
PIB	Polyisobutylene
Rh	Rhodium
TBP	Tributylphosphate
TOA	Trioctyl amine

CHAPTER 1: BACKGROUND

1.1 INTRODUCTION

This project set out to investigate the application of ELMs in removing platinum group metals (PGMs) from the aqueous by-products of PGM refining. The by-products are generated as side-streams which require storage and reprocessing. The platinum group metals (PGMs) constitute the backbone of the economy in South Africa. The mining and related metal refinery operations contribute a significant portion to the gross domestic product and the employment in the country. Thus the optimisation of the PGM extraction processes from the mined ore materials is critical to the ongoing development of the PGM mining sector. The emulsion liquid membranes are a relatively old technology which has been successfully used to the extraction of base metals from acidic media. Its advantage over the classical metal solvent extraction is that is integrates loading and stripping phases of the extracted metal into one step. This in turn increases the efficiency of the PGM production process. However, to this date and the best of the authors' knowledge no data is available on the application of the emulsion liquid membranes in the public membranes. This project set out to investigate the application of emulsion liquid membranes (ELMs) in PGMs from the aqueous by-products of PGM refining. The by-products are generated as side-streams which require storage and reprocessing. Of the PGMs, rhodium (Rh) is one of the more inert and therefore difficult to extract.

Membranes have historically been viewed as the semipermeable barriers between two adjacent phases (Kislik, 2009). From the operational point of view, membranes are easy to apply at industrial scale for the following reasons (Kislik, 2009): the underlying scientific concepts are relatively simple, their operation and scale-up is uncomplicated to achieve, they are environmentally-friendly, and low-cost from the energy point of view. This type of semipermeable barrier can consist of polymer films and liquids (Kislik, 2009). If the membrane system is based on a liquid matrix, then it is called a liquid membrane (Tandlich, 2009). Such systems involve the contacting of an immiscible organic liquid (named the diluent) with a feed phase (i.e. the treated side-stream (Noble *et al*., 1987; Araki and Tsukube, 1990; Bartsch and Way, 1996)). During the interphase contact, the metal or pollutant of interest is extracted from the feed phase into the diluent and finally sequestered inside separate aqueous phase called the stripping phase (Noble *et al*., 1987; Araki and Tsukube, 1990; Bartsch and Way, 1996). A specific example of the liquid membrane is the emulsion liquid membrane (ELM), as shown in Figure 1.1.

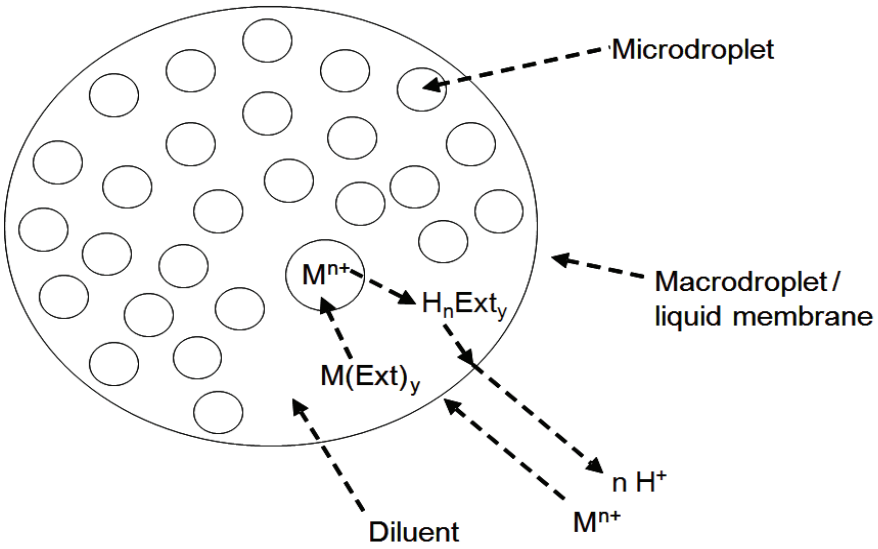


Figure 1.1 Schematic representation of the emulsion liquid membrane (ELM; adapted from Tandlich, 2009). The symbol M^{n+} stands for the dominant metal ion extracted from the treated metal refining side-stream, while the $M(Ext)_y$ is the complexed form of the extracted metal in the diluent part of the ELM.

An ELM contains the following components (Tandlich, 2009): a diluent, a modifier, a synthetic surfactant, an extractant and a stripping phase. These components are mixed together to form a stable emulsion with

droplets ranging from 1 to 10 mm in diameter (Busca *et al*., 2008). Inside a given ELM droplet are smaller microdroplets with diameters of 1-3 µm (Tandlich, 2009). If the ELM is put into contact with a side-stream containing finite concentrations of metals, the ELM technology can be successfully applied to the recovery of such metals (Kislik, 2009). Contrary to the classical metal solvent extraction (MacKenzie, 1998), solvent extraction from the treated side-stream and stripping of the metal from the loaded diluent are performed in one step (Park, 2006). This increases the speed and lowers the cost of extraction (Tandlich, 2009). During the extraction process, the ELM is contacted with the metal refinery side-stream (the feed phase). Extraction is conducted under steering conditions and so the ELM is dispersed throughout the volume of side-stream. The metal of interest/metal aqueous complex diffuses to the interface between the feed solution and the ELM. The metal cation M^{n+} forms a complex with the extractant molecule M(Ext)y (see Figure 1.1 for details).

The M(Ext)y diffuses through the ELM to the interface between the diluent and the stripping phase microdroplets. There M^{n+} is released from the M(Ext)y complex and sequestered in the stripping phase. To preserve electroneutrality, nH^+ are transported from the stripping phase into the feed solution. The driving force of the metal extraction from the side-stream is the chemical potential gradient of H^+ between the stripping solution and the feed phase (Tandlich, 2009). Therefore the metal can be extracted from the solution at trace concentrations and against its concentration gradient between the stripping solution and the feed phase (Chiarizia and Danesi, 1987). To achieve this, the pH value of the stripping phase must be kept below the pH of the feed phase. After extraction, phase separation between the ELM and the feed phase follows. Metal is recovered from the ELM by demulsificaton which can be performed electrochemically and using microwave radiation (Tandlich, 2009); or chemical reagents such as polyethylene glycol (PEG) can be applied (Little, 1981). After demulsification, the ELM phase is easily reconstituted and can be reused in another extraction.

Application of ELM reduces energy and financial costs and the time for the metal solvent extraction (Busca *et al*., 2008). This is caused by the fast kinetics of extraction with ELMs and high extraction yields in comparison with classical solvent extraction (Tandlich, 2009). Problems in applying ELMs include the lack of stability of the ELM droplets at high shear stresses inside the extraction contactors (Park, 2006). The fundamental trigger for this drawback is the swelling of ELM microdroplets from water absorption when in contact with the side-stream (Park, 2006). A partial solution lies in increasing the surfactant concentrations inside the ELM (Tandlich, 2009). This leads to improved microdroplet stability, but also increases the viscosity of the ELM (Groenweg *et al*., 1994). As a result, the higher ELM concentrations of surfactants decrease in the mass transfer rates of the extracted metal, i.e. prolonging the extraction process (Park, 2006). A solution is the application of non-Newtonian ELMs (Park, 2006).

Non-Newtonian behaviour of the ELM can be obtained by addition of a polymer such as polyisobutylene (PIB; Park, 2006). If the concentration of this polymer in the ELM is kept below a critical concentration, then the surfactant addition increases stability of the ELM without compromising the mass transfer rates of extracted compounds (Skelland and Meng, 1996). The critical concentration of the polymer can be calculated using Eq. (1).

$$C_{\text{critical}} = 228 \times \frac{\left(M_{\text{sru}}\right)^{\frac{5}{3}}}{V_{\text{sru}} \times \left(M_{\text{p}}\right)^{\frac{2}{3}}} \qquad (1)$$

Where:
C_{critical} = critical polymer concentration ($g.cm^{-3}$) and
M_{sru} = molecular weight of the pure liquid monomeric unit of the polymer added ($g.mol^{-1}$)
V_{sru} = molar volume of the pure liquid monomeric unit of the polymer ($cm^3.mol^{-1}$)
Mp = average molecular weight of the polymer ($g.mol^{-1}$)

To optimise the energy distribution during the extraction and simplify the scale-up any successful ELM extraction technology, the Taylor-vortex column was proposed as the extraction apparatus (Park, 2006). It is depicted in Figure 1.2. In a Taylor-vortex column, the power input is evenly distributed throughout the entire volume of the contactor, and the rotor and tank stirrers are roughly equal in diameter (Tandlich, 2009). The maximum shear that the extracted liquid is exposed to is one to two orders of magnitude lower than in a

continuously stirred contactor (Tandlich, 2009). In line with the general properties of the membrane-based technologies, combination of the ELM and the Taylor-vortex column can be easily scaled-up from bench to industrial settings by maintaining a constant value of the Taylor number which is defined in Eq. (2) (see Tandlich, 2009 for further details).

$$Ta = \frac{2\pi \times N}{\varphi}\left(R_{\text{rotor}}\right)^{\frac{1}{2}} \times \left(d_{\text{ag}}\right)^{\frac{3}{2}} \tag{2}$$

Where:
R_{rotor} = the radius of the inner cylinder of the Taylor column (m) and
N = the rotational speed of the inner cylinder of the Taylor-vortex column (s^{-1}) and
d_{ag} = the width of the space between the inner and the outer cylinders of the Taylor-vortex column (m) and
φ = for the kinematic viscosity of the liquid inside the Taylor-vortex column ($m^2.s^{-1}$).

The above-mentioned combination of the ELM and the Taylor-vortex column has been shown to extract up to 96 % of Zn, Pb, Ni and Cd from synthetic side-stream (Park, 2006). Such base metals are often found in the metal refinery side-streams which also contain the platinum group metals (PGM/PGMs). Given the principle of zero-discharge and the economic value of the recovery of PGMs from such liquid matrices, it is an attractive research and potentially operational idea to investigate the use of ELMs for the recovery of PGMs from metal refinery side-streams. However, the Taylor-vortex column has not yet been applied to the extraction of PGMs from these types of side-streams. Thus the main aim of this project was to address this knowledge gap using the Taylor-vortex column with non-Newtonian ELMs. The last PGM to be extracted from the PGM bearing raw materials is generally Rh due its complicated chemistry (Barbosa et al., 2007). It is therefore used in this project as the model extractant.

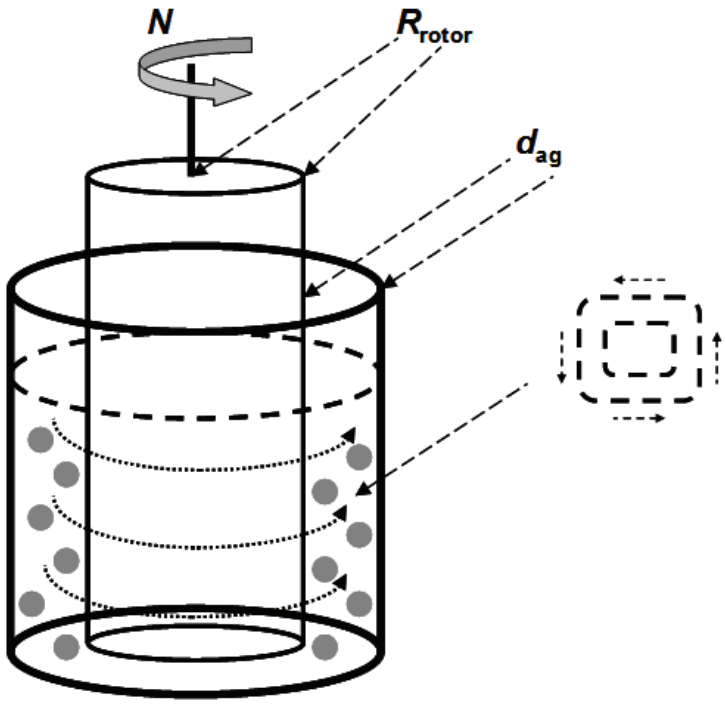


Figure 1.2. The Taylor-vortex column. The ELM microdroplets (●) are dispersed in the feed phase of the system via the rotation of the inner cylinder of the Taylor-vortex column, and the flow pattern, depicted by the dashed lines on the right-hand side of this figure, is established.

1.2 PROJECT AIMS

The project aim was broken down into four objectives:

1. To investigate the feasibility of using a combination of the Taylor-vortex column for and the emulsion liquid membranes in the extraction of rhodium (Rh) from the model metal refinery side-streams (see Introduction to Chapter 2 for details).
2. To investigate the use of kerosene and tributylphosphate (TBP) as diluent for the ELMs and the trioctyl amine (TOA) as the extractant in the emulsion liquid membrane,
3. Investigate the influence of the side-stream composition on the extraction efficiency of Rh.
4. To investigate the scale-up of the optimised system to industrial scale.

Aim 1 was accomplished, but limited success was observed with using the original diluent. Toluene had to be used instead of TBP in the ELM development. The pH of the aqueous phase was found to influence the extraction efficiency and the temperature of extraction showed a strong influence on the stability of the ELM. The scale-up considerations were only accomplished in the theoretical domain, but temperature of extraction and the chemical demulsification were optimised for upgrade in the future. Complete extraction of Rh from the model side-stream has been achieved, thus aims 1 to 3 of the project have been achieved. The pursuit of aim 4 was contingent upon positive, conclusive results being generated in the preceding aims. Since the results are conclusive but not positive, aim 4 could not be completed.

1.3 SCOPE AND LIMITATIONS

Metal extraction and refining activities form a substantial part of South Africa's gross domestic product. Thus development of novel and faster and/or more cost-effective extraction processes for metal separation is always desired. This is due to potential development of specific and high-value added know-how; and the increased yields of PGMs. The ELMs have been used in the processing of various chemical classes of compounds such as organic acids and base metals. Their advantages in comparison to the classical solvent extractions include faster kinetics of extraction and the performance of extraction and metal stripping in a single step (Kislik 2009, Tandlich 2009). These features make them highly attractive for PGM processing, but no such applications have been documented in the scientific literature/public domain to date. The scope of this project was to address this knowledge gap with Rh as the model PGM. The choice of Rh is by virtue of the facts that it is generally the last metal to be extracted from PGM-bearing materials, and its solution chemistry is the most complicated one from all the PGMs.

Commercial use of ELMs in extraction processes is often hindered by the instability of the stripping phase microdroplets due to the absorption of water from the feed phase into the ELM matrix. The classical solution is to increase the surfactant concentration in the ELM. This increases the stability of the microdroplets, but also leads to a decrease in mass transfer rates during metal extraction. Thus a novel solution must be found to address this problem. One of the solutions proposed in literature for the extraction of base metals is the use of non-Newtonian liquids as ELMs. The simplest way to construct a non-Newtonian ELM is by the addition of a polymer such as polyisobutylene (PIB) to the ELM diluent. The shear stress is further decreased by the extraction contactor being the Taylor-vortex column (Figure 1.1).

Results show that the complete extraction of Rh is possible from model side-streams, namely hydrochloric acid (HCl) solutions containing 7 mg/L of Rh. This is achieved by the use of the optimised ELM where the diluent was 30% solution of toluene in kerosene and the other component concentrations were as follows: 30.000 g/L (w/v) PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80. This diluent phase was then mixed with 2 M HNO_3 (stripping phase) in a ratio of 2:1. The volumetric ratio of treated side-stream and the ELM was 5:1 and 98.7 to 108.7% of the initial Rh amount was recovered in the stripping phase after chemical demulsification. This was performed with polyethylene glycol with molecular weight of 400 g/mol (PEG) at 50 ± 1°C for 24 hours. Major carryover of the diluent components into the stripping phase and side-stream was observed. Using the COD digestion stoichiometry, the aqueous solubilities and the measured ELM components concentrations, it is estimate that the carry-over was mostly from the TOA, toluene and PEG. The final spent side-stream should not be discharged into the environment as the acute *Daphnia pulex* toxicity testing results have shown.

Limitations of the results from the project include the lack of competition studies, more in depth examination of Rh extraction from the real mining/metal refinery effluents and the lack distribution isotherm of Rh in the ELM/side-stream system. Competition studies will have to be performed with other PGMs before any scale-up or any industrial application of the optimised ELM and Taylor-vortex column can be launched. The

competition studies are currently underway and should be completed in the near future, as will be the distribution isotherm of Rh in the ELM./side-stream treatment system. Preliminary experiments have indicated that the extraction efficiency of Rh from side-streams is going to be influenced by the high concentrations of chloride anions and the sorption of the Rh-chloro complexes on the glass matrices of the extraction vessels. The nature of this effect should be addressed if future projects with similar scope are funded.

CHAPTER 2: ANALYTICAL TECHNIQUES

2.1 INTRODUCTION

In order to investigate the applicability of the Taylor-vortex column and non-Newtonian ELMs in the solvent extraction of PGMs, with Rh as the model compound, the first task of the project was to develop the relevant methods for the quantification of the components of a model metal refinery side-stream. The aim of the chapter is to develop methods to track the concentration of the components of the ELM throughout the extraction process. This will constitute the preparation of the model metal refinery side-stream and the quantification of the concentration of the ELM components in it. The model side-stream is based on the preliminary stability of the Rh solutions and the nature of its water chemistry (Barbosa et al., 2007). IN this case, Rh will be soluble in aqueous environments only if the pH of the aqueous phase is equal to 4.00 of lower. At the same time, the presence of chloride anions is essential in stabilization of the Rh cations in solution. Thus the model Rh refinery effluent was modelled as the Rh solution in HCl (hydrochloric acid). At the same time, the model metal refinery effluent will be assessed on the premise that the Rh metal refinery is working on the principle of zero discharge, i.e. no metal or organic species leave the production/metal refinery facility in question.

Most of the ELM components are organic chemicals and their procurement generally constitutes a major part of the operating costs of any metal refinery/metal solvent extraction process. Thus the exact amount of each of the components that are used and lost in any Rh extraction process must be known. Therefore validated methods of quantitative analyses must be available for each of the ELM components. Such methods are developed in the current chapter and will be used throughout the remainder of the study/report. Due to the complex nature of the treated side-stream a combination of colorimetry, gas chromatography, non-aqueous titration and the atomic absorption spectroscopy was chosen. The colorimetric methods were used to quantify chemical oxygen demand (COD), and concentrations of chlorides and nitrates. The non-aqueous titration with perchloric acid as the titrant was used to quantify trioctylamine (TOA). Gas chromatographic methods were used for the quantification of tributylphosphate, toluene and kerosene. The Rh concentrations were determined using induced-coupled plasma spectroscopy (ICP) and the atomic absorption spectroscopy.

2.2 CHEMICALS AND CONSUMABLES

The following items and consumables were purchased from Merck (Pty.) Ltd. (Johannesburg/Cape Town, South Africa): non-aqueous titrant of perchloric acid in acetic acid, nitrate kit (catalogue number: 1.09713.0001), chloride kit (catalogue number: 1.14897.0001), reagent A (catalogue number: 1.14679.0495) and B (catalogue number: 1.14679.0495) for the determination of COD in the ranges of 100-2000 and 500-10000 mg/L, KNO_3, potassium hydrogen phthalate (KHP), NaCl, toluene, acetic acid and HCl. The following items and consumables were purchased from Sigma-Aldrich (Johannesburg, South Africa): tributylphosphate, kerosene, TOA, ethanol, n-hexane, 2.0 mL clear glass GC vials with PTFE-lined silicone septa and the rhodium standardised solution.

2.3 MEASUREMENT OF CHEMICAL OXYGEN DEMAND

Chemical oxygen demand (COD) was measured using the closed-reflux colorimetric method (APHA *et al*., 1998) in the concentration ranges from 100 to 2000 and from 500 to 10000 mg/L. The KHP was used as the standard to prepare solutions and the COD values were converted into the KHP concentrations (mg KHP eq/L) based on Eq. (3).

$$C_8H_5O_4K + 3O_2 \rightarrow KOH + 8CO_2 + 2H_2O \quad (3)$$

The digestions were performed according to the manufacturer's instructions using the TR 300 thermoreactor (Merck Ltd., Johannesburg/Cape Town, South Africa). After completion of the digestions, the respective solutions were cooled down and the spectrophotometric measurements were performed using a Shimadzu UV-1601 spectrophotometer (Shimadzu, Johannesburg, South Africa). The measurements at six concentration levels with five replicates each were performed to construct the calibration curve. This was

then plotted as the dependence of the absorbance at 600 nm on the COD concentration in mg KHP eq/L. For the determination of limits of detection (LOD) and quantitation (LOQ), the COD concentration of 500 mg KHP eq/L was prepared for the 100-2000 mg KHP eq/L COD reagent range, while 750 mg KHP eq/L was prepared for the 500-10000 mg KHP eq/L COD reagent range. All samples were processed as the calibration curve solutions.

The U.S. EPA methodology for calculation of LOD and LOQ values was used (Tandlich, 2004). The LOD values were calculated using Eq. (4).

$$LOD(mg/L) = t(4;0.01) \times SD = 3.707 \times SD \quad (4)$$

In Eq. (4), t(4;0.01) is the *t*-test distribution value for 4 degrees of freedom at 1% level of significance (Tandlich and Zuma, 2012). The SD value is the standard deviation of the five replicate analysis at the 500 mg KHP eq/L level. The LOQ values were then calculated as five-times the LOD values as shown in Eq. (5). Calibration curve measured for the COD measurements is shown in Figures 2.1 and 2.2.

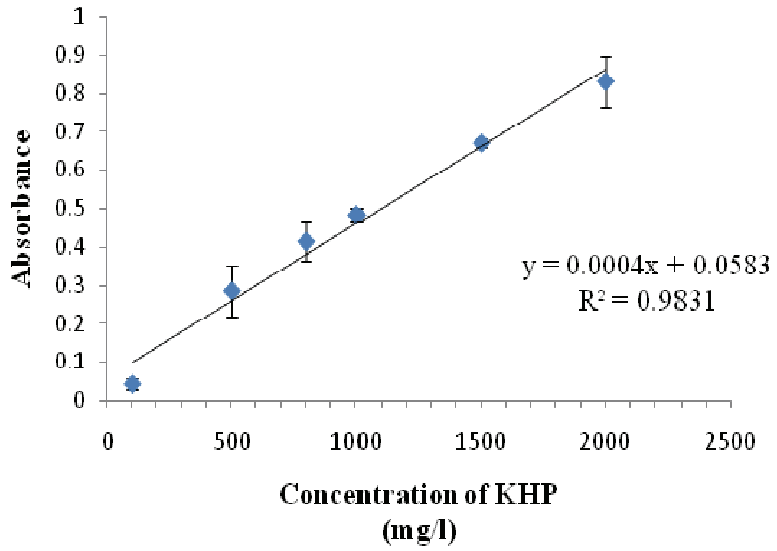


Figure 2.1. The COD calibration curve with a range of 100-2000 mg/L potassium hydrogen phthalate (KHP) as the standard solution.

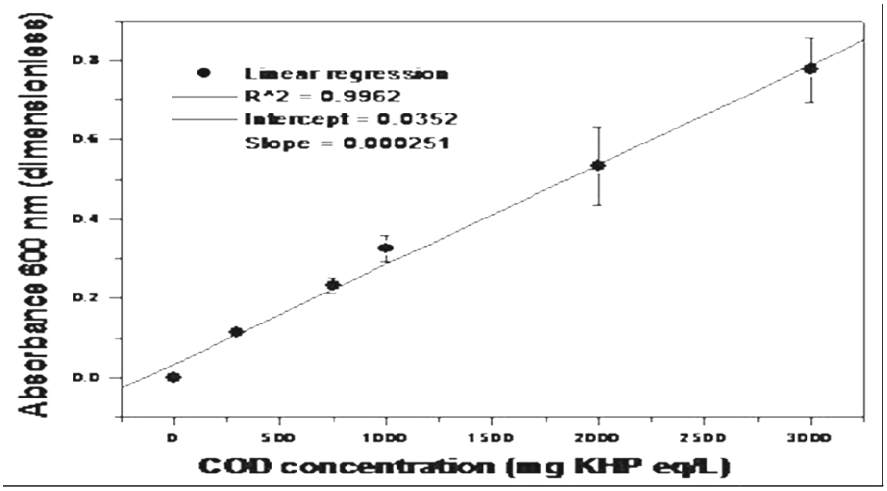


Figure 2.2. The COD calibration curve with a range of 500-10000 mg/L potassium hydrogen phthalate (KHP) as the standard solution.

$$LOQ(mg/L) = 5 \times LOD \quad (5)$$

Figures 2.1 and 2.2 demonstrate that the independent variable explains more than 98.31 and 99.62% of the variance of the dependent variable. The LOD value was equal to 200 and 880 mg/L for the two COD concentration ranges, respectively. At the same time, the LOQ values were 564 and 4340 mg/L. Precision of measurement ranged from 8 to 15% in the calibration range used in this study.

2.4 MEASUREMENT OF CHLORIDE CONCENTRATION

Chloride concentration was measured using the modified U.S. EPA method 325.1 (Cornerstone Laboratories LLC, 2004-5). The procedure was performed according to the manufacturer's instructions enclosed in the chloride kit and measurements were performed the Shimadzu UV-1601 spectrophotometer (Shimadzu, Johannesburg, South Africa). The calibration curve was constructed as a dependence of the absorbance at 480 nm on the chloride concentration in the concentration range from 0 to 250 mg/L. Five replicates measured at each level and NaCl was used as the standard. Values of LOD and LOQ were determined at the chloride concentration of 10 mg/L and using Eq.s (4) and (5). The calibration curve measured for chloride anions can be seen in Figure 2.3. Data in Figure 2.3 show that 99.8% of the variance of the dependent variable is explained through the variance in the chloride anions. The LOD value was equal to 48 mg/L and the LOQ value was equal to 235 mg/L. The precision ranged from 6 to 29% throughout the calibration range.

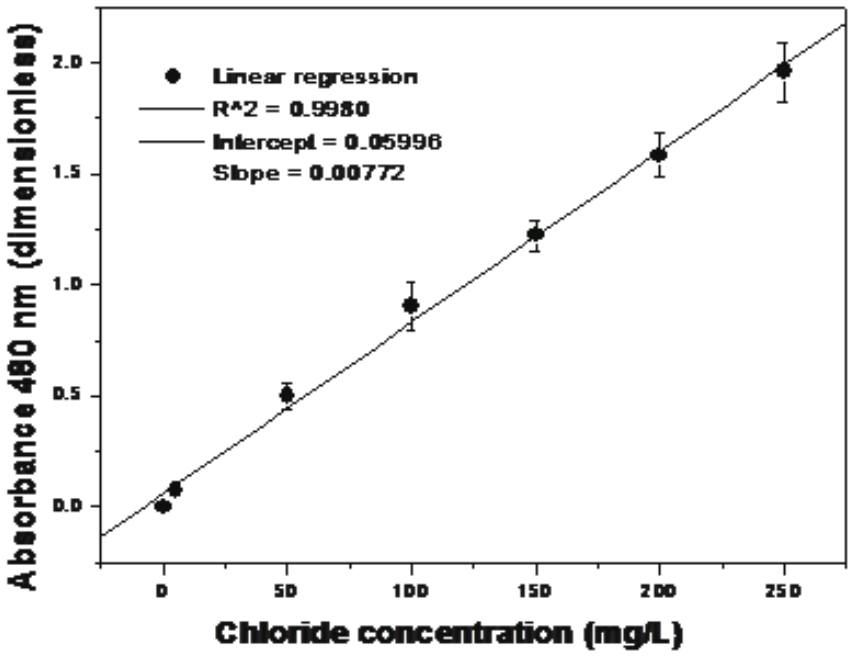


Figure 2.3. Calibration curve for the chloride anions quantitation using the Merck test kit.

2.5 MEASUREMENT OF NITRATE CONCENTRATION

The concentration of NO_3^- was measured using the modified ISO method 7890/1 (Merck Pty., Ltd., Johannesburg, South Africa) with KNO_3 as the standard. The procedure was performed using the respective nitrate kit from Merck Pty. Ltd. (Johannesburg, South Africa) and all measurements were performed using the Shimadzu UV-1601 spectrophotometer (Shimadzu, Johannesburg, South Africa). The calibration curve was constructed as a dependence of the absorbance at 540 nm for measurement at five concentration levels from 0 to 5.00 mg/L with five replicates measured at each level. LOD and LOQ were measured at 1.00 mg/L and calculated using Eq. (4) and (5). The nitrate calibration curve is shown in Figure 2.4. This calibration curve had an R^2 value 0.9740, i.e. 97.4% of the variance of the dependent variable is accounted for by the variance in the nitrate concentration. The LOD was equal to 0.29 mg/L, while the LOQ value was equal to 1.41 mg/L. Precision values varied between 1 and 20% inside the calibration curve interval.

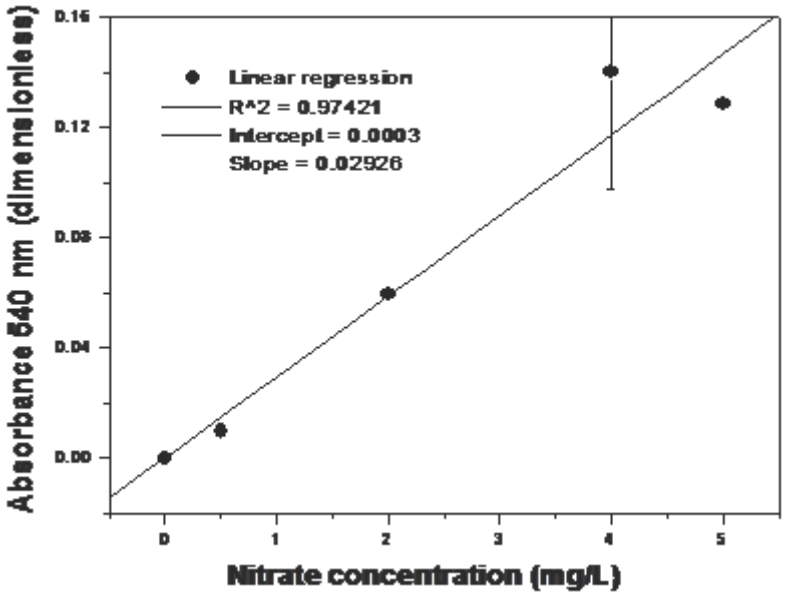


Figure 2.4. Calibration curve for nitrate quantitation using ISO method 7890/1.

2.6 QUANTITATION OF TRIBUTYLPHOSPHATE, TOLUENE AND KEROSENE

The method for quantitation of tributylphosphate and kerosene is a combination of liquid-liquid extraction and gas chromatography. For gas chromatography, the external standard method was used for quantitation of both components. For the preparation of the stock solution of both compounds, 40 mL of n-hexane was poured into a 50 mL volumetric flask. Accurate amounts of tributylphosphate and kerosene were then weighed analytically on the PA1214 (Pioneer™, Ohaus Corporation, Johannesburg, South Africa) and spiked into the layer of n-hexane in the 50 mL volumetric flask. The amount of each compound was adjusted to prepare a stock solution containing approximately 1.20 g/L of kerosene and 1.47 g/L of tributylphosphate. The flask was immediately stoppered and the contents mixed thoroughly by hand-shaking. Volume was filled up to the mark with n-hexane. Calibration solutions were then prepared in 2.0 mL GC vials by pipetting the required amount of the stock solution into n-hexane to obtain 1.5 mL of the respective calibration solution. The concentrations ranges of the calibration curves were as follows: 20-100 mg/L for tributylphosphate and 8.0-80 mg/L for kerosene. The calibration curves were constructed as the dependence of the peak area for a given compound on its concentration.

Peak areas were obtained by a splitless injection of 1.0 µL of each of the calibration solution using a 7693 autosampler attached to a 7890 gas chromatograph (Agilent, Johannesburg, South Africa) equipped with a DB 5 capillary GC column (30 m × 0.32 µm × 0.25 mm; Agilent, Johannesburg, South Africa) and a flame-ionisation detector. Helium was used as the mobile phase at a flowrate of 1.0 mL/min. The injector and detector temperatures were set to 300°C, and the oven temperature programme was as follows: initial temperature 40°C hold for 3 min, ramp to 180°C at 2.5°C/min, ramp to 250°C at 20°C/min and hold for 3 min. All gases were purchased in instrument grade from Afrox-Linde (Port Elizabeth, South Africa). The calibration curve for tributylphosphate is shown in Figure 2.5, and shows that the independent variable, i.e. the tributylphosphate concentration, explains 96.8% of the variability in the area of its chromatographic peak. Therefore the method can be deemed appropriate for analytical purposes in the scope of the ELM extraction. The calibration curve for kerosene followed a similar pattern and the R^2 value was equal to 0.998. Later in the project toluene was used as the modifier in the ELM instead of the tributylphosphate. This was caused by the acid hydrolysis of the TBP molecule which led to the decrease in the ELM stability (data not shown). The same gas chromatographic programme was used for toluene and the R^2 value of the calibration curve was equal to 0.993. The LOD values ranged from 1 to 5 mg/L for TBP, toluene and kerosene. At the same time, the respective LOQ values were equal to 5.7, 8.2 and 10.5 mg/L for TBP, toluene and kerosene.

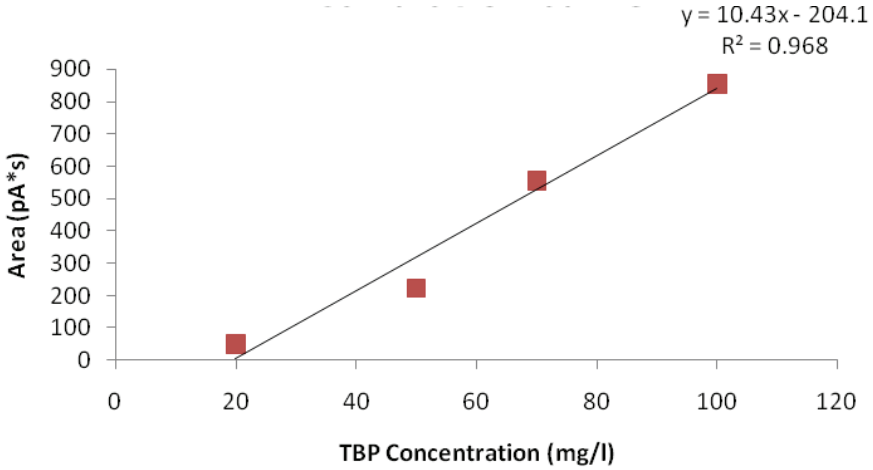


Figure 2.5. Calibration curve for tributylphosphate analysed using gas chromatography.

2.7 QUANTIFICATION OF RHODIUM

Calibration solutions were prepared by dilution of the standardised Rh stock solution with the concentration 999 ± 5 mg/L (Sigma-Aldrich, Johannesburg, South Africa). The calibration curves were prepared by dilution of the certified stock solution with 0.01 and 0.001 M HCl (diluted from the 32% commercially available solution; Sigma-Aldrich, Johannesburg, South Africa). The calibration range concentrations varied from 1 to 10 mg/L and the solutions were filtered through a 0.45 µm cellulose acetate filter (Spellbound, Port Elizabeth, South Africa) prior to analyses. The samples were analysed for Rh using the signal at 2334 nm and the Thermo/Finnagan ICP 7600 (Chemistry Department, Rhodes University). All readings were taken in triplicate. The calibration curves are shown in Figures 2.6 and 2.7. As can be seen, the R^2 values were equal to 0.997 in 0.01 M HCl and 0.999 in 0.001 M HCl. At the same time, the sensitivities of the analysis (slopes of the calibration curves) were independent on the pH value of the hydrochloric acid, as the slope of the calibration curve was equal to 466.8 in 0.01 M HCl and to 486.0 in 0.001 M HCl. The standard deviations of the individual concentration level signals were always below 5%. Thus the ICP method developed was deemed suitable for the determination of Rh concentrations in the extraction experiments. The LOD values were equal to 1.05 and 1.23 mg/L at pH = 2 and 3, respectively. At the same time, the LOQ values were equal to 2.61 and 3.11 mg/L. Due to the maintenance and performance issues with the ICP instrument, some of the samples were analysed using the commercial laboratory at the Chemtech Lab (Pretoria, South Africa). Here only the LOQ value was provided and it was equal to 0.058 mg/L.

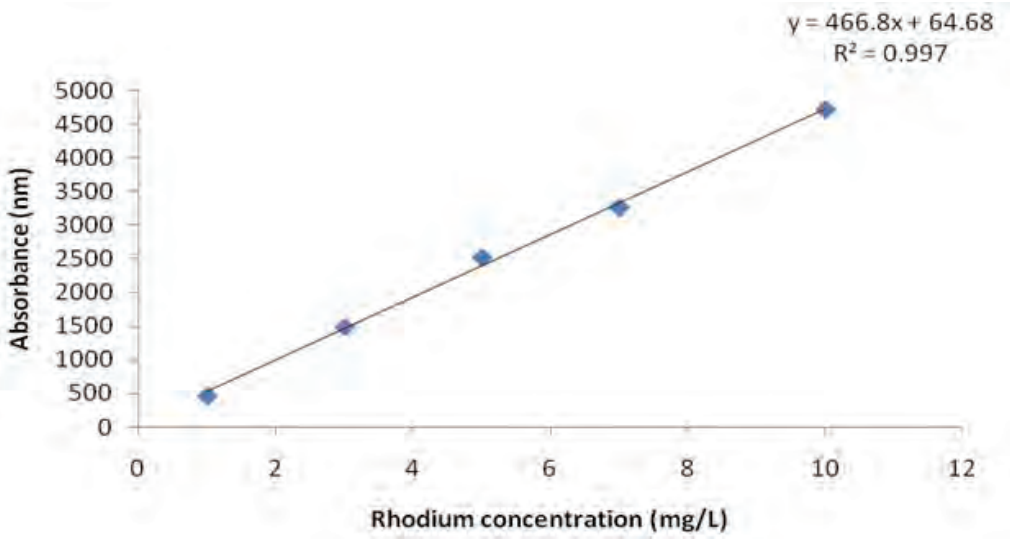


Figure 2.6. Calibration curve for Rh in 0.01 M HCl at a range of 1-10 mg/L at the 2334 nm signal.

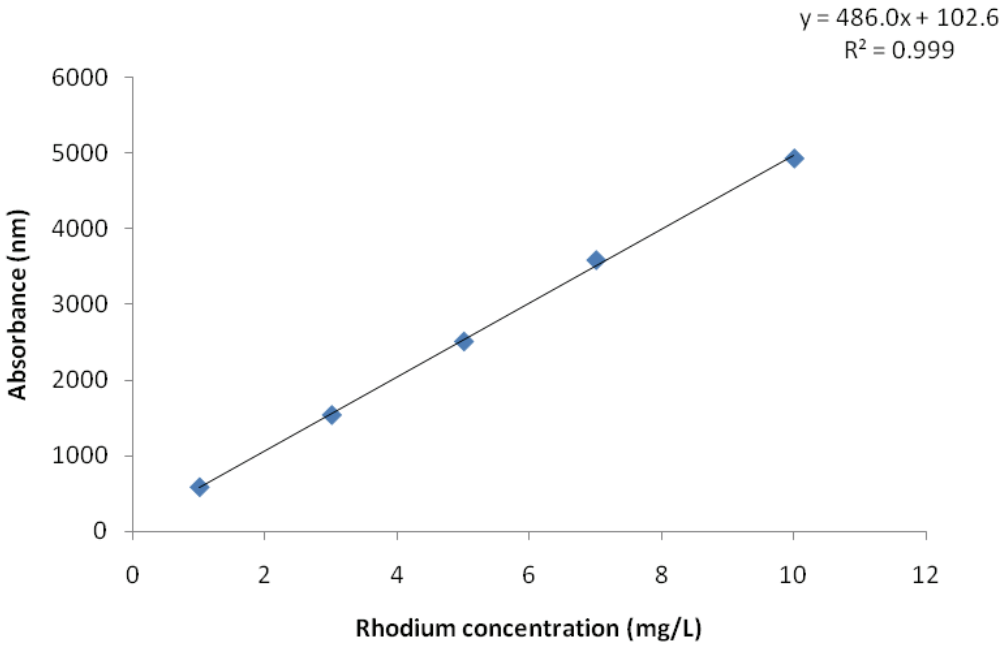
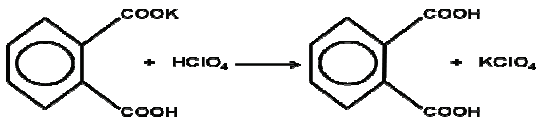


Figure 2.7. Calibration curve for Rh in 0.001 M HCl at a range of 1-10 mg/L at the 2334 nm signal.

2.8 QUANTIFICATION OF TRIOCTYL AMINE

The titration method by Kar (2005) was used as the basis for the quantification of TOA. Firstly, the standardisation of the approximately 0.1 M perchloric acid solution was performed against KHP. For this, 2.0400 g of KHP was accurately weighed out using a PA1214 Pioneer™ (Ohaus Corporation, Johannesburg, South Africa) and the powder was transferred quantitatively into a clean 100 mL volumetric flask. The KHP was quantitatively dissolved in 100 mL glacial acetic acid to give a solution with concentration of 0.1000 M. Before bringing the solution to the final volume with acetic acid, the flask content was heated upon needed to achieve complete dissolution of KHP crystals. Then 25 mL of this solution was transferred into a 250 mL titration flask and three drops of 0.5% crystal violet in glacial acetic acid was added to the solution. Aliquot of the KHP solution was then titrated with 0.1 M perchloric acid (solution in acetic acid) until the blue colour of the solution changed to a green/yellow colour. All titrations were performed in triplicate and the respective calculations were done according to Eq. (6).



(6)

After standardisation of the titrant, the TOA solutions with concentrations of 0.01 and 0.10 M were prepared in a simulated ELM, i.e. a 10% solution of tributylphosphate (TBP) in kerosene or the 30% toluene solution in kerosene. These solutions are termed the test samples in the text below and they were prepared in the following manner. Eighty millilitres of the simulated ELM was transferred into a 100 mL volumetric flask using a 250 mL graduated cylinder. This was placed onto a PA1214 Pioneer™ analytical balance and the balance was tared. The volumetric flask was then removed and 3.5367 g of the neat liquid TOA was pipetted into the volumetric flask into the ELM diluent by submerging the pipette tip and dispensing the TOA into the diluent layer. The volumetric flask was stoppered and the outside was wiped off with a paper towel to ensure that excess TOA or the simulated ELM did not contaminate the outside of the volumetric flask. The flask was placed onto the PA1214 Pioneer™ analytical balance and the accurate weight of TOA was recorded.

The solution inside the flask was mixed thoroughly by hand-shaking and the volume was made up to the 100 mL mark by a 10% TBP in kerosene solution. To prepare 0.01 M TOA solution, 10 mL of the previous test sample was pipetted accurately into a clean 100 mL volumetric flask and diluted to volume with the

simulated ELM. Next the test samples were assayed as with the standardisation (see previous paragraph) and the exact concentration of the TOA solutions was calculated based on the stoichiometry in Eq. (7).

$$HClO_4 + N(C_8H_{17})_3 \rightarrow ClO_4^- + N(C_8H_{17})_3H^+ \quad (7)$$

Standardisation of three individual batches of the perchloric acid titrant showed that the average concentration was equal to 0.0950 ± 0.0017 M with a coefficient of variation of 1.8%. Analysis of the test samples showed at 0.10 M solution of TOA, the measured concentration was equal to 0.0950 ± 0.0039 M, while at the 0.01 M level the actual concentration was recorded at 0.0120 ± 0.0028 M. This gives precision of 4.1% and 23%; and accuracy values were equal to 95 and 120% respectively. These results are comparable to the U.S. EPA criteria for suitable analytical methodologies (Tandlich, 2004). Volume expansion of the titrant had no influence on the independent of the results of the TOA determination between 20 and 35°C (Kar, 2005). With the negative control (a 10% solution of TBP in kerosene or 30% solution of toluene in kerosene), the diluent did not interfere with the TOA determination.

CHAPTER 3: OPTIMISATION OF THE EMULSION LIQUID MEMBRANE COMPOSITION AND DEMULSIFICATION

3.1 INTRODUCTION

After the analytical methods of the ELM components were optimised, the next step of the project was to optimise the ELM composition, preparation and the demulsification procedure. The crucial part of this process was to achieve an ELM composition which would guarantee that the stripping phase microdroplets diameter was 1-3 µm (Tandlich, 2009). This is critical for optimum mass transfer characteristics, i.e. optimum kinetics of Rh extraction from the side-streams, as the interface for the Rh transport will reach maximum mass transfer rates if the microdroplet diameter lies inside this range (Kislik 2009). To obtain the optimum composition, the concentrations of the diluent, the modifiers, polyisobutylene, the surfactant SPAN 80 and the extractant were varied. The particle size was analysed using optical microscopy. Once the optimum composition of the ELM was obtained, the demulsification options for the recovery of Rh from the stripping phase were investigated. Electrochemical demulsification equipment was too costly for the budget of the current project. On the other hand, preliminary experiments with the microwave radiation indicated that the phase separation between the treated side-stream and the ELM was a problem. Therefore thermal demulsification and chemical demulsification with addition of PEG were investigated as an alternative.

3.2 MATERIALS AND METHODS

3.2.1 Apparatus and chemicals

Kerosene, PIB, and TOA were purchased from Sigma Aldrich (Johannesburg, South Africa), Saarchem brand HNO_3 was purchased from Merck Chemicals Pty. Ltd. (Merck, Port Elizabeth, South Africa), SPAN 80 and TBP from Fluka Analytical (Johannesburg, South Africa). An Olympus UCMAD3 microscope mounted with an Olympus ultra 20 soft imaging system UTVX-2 was used for all microscopic work (Institute for Water Research, Rhodes University, South Africa). Absorbances for COD were measured using a UV spectrophotometer model UV-1201 Shimadzu Corporation (Japan). The Labcon COD thermoreactor model D60 (Merck Pty. Ltd., Johannesburg, South Africa) was used for the COD digestions. All glassware was purchased from the Sigma-Aldrich (Johannesburg, South Africa).

3.2.2 Optimisation of the stripping phase microdroplet size

Composition of the ELM and the preparation procedure will have a significant influence on the microdroplet size (Tandlich, 2009). Therefore the concentrations of the individual components need to be optimised first before any extraction experiment is attempted. In this section, various protocols of ELM preparation are used and their influence on the microdroplet diameter evaluated. Differences in the individual protocols originate from the use of mechanical shaking and sonication; and varying concentrations of TBP, PIB, TOA and SPAN 80 used. The subsections will be entitled based on the composition of the diluent/organic phase of the ELM and the method of the ELM preparation used.

3.2.2.1 Kerosene-TBP diluent and sonication

For diluent preparation, 10 mL of TBP was pipetted into a 100 mL volumetric flask and kerosene was added to bring the volume to the 100 mL mark. In this way, a 10% TBP solution in kerosene was obtained and it was used as the diluent for the ELM. The diluent was mixed with 2 M HNO_3 in the ratios 1:1 (20 mL of HNO_3: 20 mL of the diluent), 1:2 (20 mL of HNO_3: 40 mL of the diluent) and 1:3 (20 mL of HNO_3: 60 mL of the diluent). The mixtures were sonicated for 10 minutes using the BRANSON 8510 ultrasonication bath (LASEC SA, Port Elizabeth, South Africa) to obtain the ELMs. After sonication, the ELMs were left to stand on a laboratory bench top and at 20 ± 2°C. Sonication was repeated for the same preparations for 20 minutes.

3.2.2.2 The kerosene-TBP-PIB-TOA diluent and sonication

The diluent in this experiment consisted of kerosene, TBP and PIB, while TOA was used as the extractant. Firstly, 5 g PIB was weighed analytically using the PA1214 analytical balance (Pioneer™, Ohaus Corporation, Johannesburg, South Africa). The weighed amount was transferred quantitatively into a 250 mL volumetric flask. The PIB was completely dissolved in 150 mL of Kerosene and 25 mL of TBP. Then with 2.5670 g of TOA was weighed out using the PA214 analytical balance and the entire amount of the extractant was quantitatively dissolved in the diluent components. The entire content of the flask was homogenised by hand-shaking. Next, 12.5060 g of SPAN 80 was weighed out as with TOA and PIB; and added to the volumetric flask. After dissolution of the surfactant, Kerosene was used to bring the volume to the 250 mL mark. The following concentrations of the individual components were obtained in the solution: 20.000 g/L of PIB, 10.268 g/L for TOA and 50.024 g/L for SPAN 80. The solution was mixed with 2 M HNO_3 in the same proportions as described in section 3.1.2.1. The resulting mixtures were sonicated using the BRANSON 8510 ultrasonication bath for 10 minutes. The mixtures were left to stand at 21 ± 2°C.

3.2.2.3 Kerosene-TBP-PIB-TOA diluent and orbital shaking 1

The diluent with extractant addition was prepared in the same way as in section 3.2.2.2. The diluent was then mixed with HNO_3 as described in section 3.2.2.1 for the ELM preparation. This was achieved by orbital shaking of the diluent/extractant/HNO_3 mixture on the Chiltern orbital shaker SS70 (Slough, Berkshire, Chiltern Scientific, United Kingdom) at 600 rpm for varying periods of time.

3.2.2.4 Kerosene-toluene-PIB-TOA diluent and orbital shaking 2

In this experiment, the diluent with extractant contained 5 g PIB which was dissolved in 100 mL of Kerosene inside a 250 mL volumetric flask. To it, 30 mL of toluene (Johannesburg, Sigma-Aldrich, South Africa) was added, together with 2.5390 g of TOA and 12.4936 g of SPAN 80. Both TOA and SPAN 80 were weighed out analytically on the PA214 balance and completely dissolved in the kerosene-toluene mixture. Then Kerosene was used to make up the volume to 250 mL to obtain the final ELM concentrations as follows: 20.000 g/L (m/v) of PIB, 10.156 g/L (m/v) TOA and 49.972 g/L (m/v) of SPAN 80. The resulting diluent with extractant was mixed with 2 M HNO_3 in the ratios 1:1, 1:2, 1:3 as described in section 3.2.2.1; and in a ratio of 1:4 (20 mL of HNO_3: 80 mL of diluent with extractant).

These mixtures were shaken using the Chiltern orbital shaker at 600 rpm for 20 minutes. The ELM microdroplet size distribution was examined using optical microscopy magnification of 400 ×. The mixtures were left to stand and the time for phase separation was noted. The ELMs were reconstituted and left in the fridge at 5 ± 2°C for 24 hours. The ELMs were re-shaken again and the microdroplet size was re-examined using optical microscopy. The point of this experiment was to investigate the reusability of the ELM between extractions and possible storage in the refrigerator on different days.

3.2.2.5 Kerosene-toluene-PIB-TOA diluent and orbital shaking 3

The varying concentration of PIB in the diluent was achieved in the following manner. Firstly, 2 g of PIB was dissolved in a mixture of 50 mL of kerosene and 30 mL toluene inside a 100 mL volumetric flask. Then 1.0250 g of TOA and 5.0201 g of SPAN 80 was added. Kerosene was then added to the 100 mL mark to make 20.000 g/L (m/v) of PIB, 10.250 g/L (m/v) of TOA and 50.201 g/L (m/v) of SPAN 80. The ELM were then prepared in one of the following ways:

a) The diluent with extractant addition was mixed with 2 M HNO_3 in the ratios 1:1 (10 mL of HNO_3: 10 mL of diluent) and 1:2 (10 mL of HNO_3: 20 mL of the diluent). These mixtures were shaken using the Chiltern orbital shaker SS70 at 600 rpm for 20 minutes. The microdroplet distribution was examined under the microscope at the magnification of 400 x. After the measurement, the ELMs were left to stand at 22 ± 1°C and were monitored for phase separation. The time when significant phase separation occurred was noted. Finally, the ELMs were re-constituted as described in the previous section and incubated at 5 ± 2°C. The microdroplet size distribution was re-examined microscopically after 12 to 24 hours. This experiment was performed to examine the effect of temperature and the time for phase separation to occur was noted;

b) A new set of the ELMs was prepared using the same protocol as in paragraph a), the ELM constitution was performed by shaking for 40 minutes. The resulting ELMs were subsequently examined for the microdroplet diameter using optical microscopy (see above for details). After the diameter measurement the ELM were re-shaken at 600 rpm using the orbital shaker for additional 40 minutes and stored at 5 ± 2°C. The phase separation time at 5 ± 2°C was again noted. The microdroplet size distribution was re-examined microscopically after 12 to 24 hours of storage at 5 ± 2°C; and bringing to 22 ± 1°C before microscopic examination.

3.2.2.6 The kerosene-toluene-PIB-TOA diluent and orbital shaking 4

Diluent with extractant addition was added in this experiment was prepared by dissolution of 3 g of PIB in a mixture of 50 mL of kerosene and 30 mL toluene inside a 100 mL volumetric flask. Then 1.0870 g of TOA was added, along with 5.1001 g of SPAN 80. The volume was made up to 100 mL with kerosene to obtain the following concentrations: 30.000 g/L (m/v) of PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80. The diluent with extractant addition was subsequently mixed with 2 M HNO_3 in the ratios 1:1 (10 mL of HNO_3: 10 mL of diluent) and 1:2 (10 mL of HNO_3: 20 mL of the diluent). These were shaken for 40 minutes using the Chiltern orbital shaker SS70 at 600 rpm. The resulting ELMs were then examined using optical microscopy at 400 x. After diameter of the microdroplets had been measured, the ELMs were left standing at 21 ± 2°C and monitored for phase separation. The time when significant phase separation occurred was noted. The ELMs were re-constituted by orbital-shaking and placed in the refrigerator at 5 ± 2°C. The temperature stability was examined by measuring the time until phase separation was noted.

3.2.3 Demulsification of the ELMs

3.2.3.1 Thermal demulsification at 35.0 ± 0.5°C

Several diluents with extractant addition were prepared and tested. Firstly, 3 g of PIB was dissolved in a mixture of 50 mL of kerosene and 30 mL toluene inside a 100 mL volumetric flask. Next 1.0370 g of TOA was added and mixed with 5.0510 g of SPAN 80. Kerosene was used to make the volume to 100 mL to get 30.00 g/L (m/v) of PIB, 10.37 g/L (m/v) of TOA and 50.51 g/L (m/v) of SPAN 80. This solution constituted the first diluent. The next version of the diluent with TOA was prepared by dissolution of 2 g of PIB in a mixture of 50 mL of kerosene and 30 mL toluene inside a 100 mL volumetric flask. Then TOA was added in the amount of 1.0460 g and the solution composition was completed with addition of 5.0331 g SPAN 80. Both the extractant and SPAN 80 were completely dissolved and the volume was made up to 100 mL with kerosene. The final concentrations of the individual components in the resulting solution were as follows: 20.000 g/L (m/v) of PIB, 10.460 g/L (m/v) of TOA and 50.331 g/L (m/v) of SPAN 80.

Using the above-mentioned diluents with extractant additions, the ELMs were prepared by applying the following protocol. The diluent with extractant addition and 3 g of PIB was mixed with 2 M HNO_3 in the ratios 1:2 (20 mL of HNO_3: 40 mL of diluent) to form two 1:2 emulsions in separate 250 mL Erlenmeyer flasks. One flask was shaken for 20 minutes and the other flask was shaken for 40 minutes at 600 rpm using the Chiltern Orbital Shaker. On the other hand, the diluent containing 2 g of PIB was mixed with 2 M HNO_3 in the ratios 1:2 as above. Two 1:2 emulsions were formed and they were treated as above. All the four emulsions were demulsified in the incubator at 35.0 ± 0.5°C for 24 hours. Unless stated otherwise, all incubations in Chapter 3 were performed in one of the following incubators: the Labcon incubator Model FSIM B (Labmark, Johannesburg, RSA), the TS 606/3-I incubator (WTW, Weilheim, Germany), the Labcon low temperature incubator LTIE 10 (Labmark, Johannesburg, RSA); and/or the Heraeus Model FT 420 (Heraeus Kulzer GmbH, Dormagen, Germany).

3.2.3.2 Thermal demulsification at 45.0 ± 0.5°C

The above experiment was repeated with 4 new ELMs, two had the PIB concentration of 20.000 g/L (m/v) an two contained 30.000 g/L (m/v) of PIB. These were placed in the UFE 700 oven (Memmert, Schwabach, Germany) at 45.0 ± 0.5°C for 24 hours for demulsification.

3.2.3.3 Chemical demulsification at 70.0 ± 1.0°C

In this experiment, the first diluent was prepared by mixing 5 g of PIB and completely dissolving it in the mixture of 150 mL of kerosene and 75 mL toluene inside a 250 mL volumetric flask. This was combined with 2.576 g of TOA and 12.543 g of SPAN 80 was added. Kerosene was then added to the 250 mL mark to make 20.000 g/L (m/v) of PIB, 10.304 g/L (m/v) of TOA and 50.172 g/L (m/v) of SPAN 80. The next diluent contained of 7 g of PIB and 2.537 g of TOA were dissolved in a mixture of 150 mL of kerosene and 75 mL toluene inside a 250 mL volumetric flask. Subsequently, 12.538 g of SPAN 80 was added and kerosene was used to make up the volume to 250 mL. In this way, the following final concentrations were obtained: 28.000 g/L (m/v) of PIB, 10.148 g/L (m/v) of TOA and 50.152 g/L (m/v) of SPAN 80.

For the ELM preparation, the diluent with extractant addition and the PIB concentration of 20.000 g/L was mixed with 2 M HNO_3 in the ratios 1:2 (20 mL of HNO_3: 40 mL of diluent) to form 1:2 emulsions in a 150 mL Erlenmeyer flask. The flask was shaken using the Chiltern orbital shaker SS70 at 600 rpm for 40 minutes. Five more emulsions were prepared in the same way. For chemical demulsification, PEG (Sigma-Aldrich, Johannesburg, South Africa) was added as shown in Table 3.1 into the six emulsions.

Table 3.1. The PEG weights used in chemical demulsification.

Emulsion	PEG added (g)
1	0
2	1
3	2
4	4
5	6
6	10

The ELMs which contained 28.000 g/L of PIB were prepared in an analogical fashion and the same amounts of PEG were added as in Table 3.1. This resulted in 12 ELMs which were subsequently statically and chemically demulsified using the UFE 700 oven, with the demulsification temperature set to 70 ± 1.0°C and the incubation period equal to 24 hours. The bottom layer was pipette and COD was carried out to determine how much of the diluent is in the aqueous phase (see section 2.3 for details).

3.2.3.4 Chemical demulsification at 70.0 ± 1.0°C and ELM carry-over

The first diluent was prepared by dissolution of 5 g of PIB in a mixture of 150 mL of kerosene and 75 mL toluene inside a 250 mL volumetric flask, with addition of 2.5020 g of TOA. This was followed by addition of 12.5090 g of SPAN 80 to the mixture and kerosene used to make up the volume to 250 mL. The respective final concentrations were then as follows: 20.000 g/L (m/v) of PIB, 10.008 g/L (m/v) of TOA and 50.036 g/L (m/v) of SPAN 80. The next diluent composition was prepared by weighing out 7 g of PIB and completely dissolving it in the same kerosene/toluene mixture as with the first diluent. The identical TOA concentration was used, but the SPAN 80 amount was increased to 12.5550 g. This was dissolved in kerosene which was used to make up the total volume to 250 mL. The final component concentrations were equal: 28.000 g/L (m/v) of PIB, 10.084 g/L (m/v) of TOA and 50.22 g/L (m/v) of SPAN 80.

The respective ELMs was prepared by mixing the diluent containing 20.000 g/L of PIB with 2 M HNO_3 in a ratio of 1:2 (20 mL of HNO_3: 40 mL of diluent) in a 150 mL Erlenmeyer flask. The flask was shaken for 40 minutes using the Chiltern orbital shaker SS70 at 600 rpm. Two more ELMs were prepared in the same way and then increasing amounts of PEG were added to the individual ELMs as shown in Table 3.2. The ELMs prepared with 28.000 g/L of PIB were made in the same way as the ELMs containing 20.000 g/L of PIB (see above). Then the same PEG amounts were added and the chemical demulsification was performed by incubating the ELMs in the UFE 700 oven at 70°C for 24 hours.

Table 3.2. The PEG weights used in chemical demulsification and ELM carry-over.

Emulsion	PEG added (g)
1	2
2	4
3	6

After chemical demulsification, organic (diluent) layer from the given ELM was removed using a 10 mL glass pipette. Then the bottom/stripping layer from each ELM was transferred into a clean COD tube and was centrifuged at 3000 g using the Allegra X-15 benchtop centrifuge (Beckman Coulter, Johannesburg, South Africa). Once the centrifugation was finished, the COD concentration was measured in the stripping phase (bottom layer; see section 2.3 for details). The aim of the measurement was to determine the carry-over of the diluent components, extractant and the SPAN 80 into the stripping phase. Subsamples of the stripping phase were removed and examined for the presence of the trace emulsion globules under the microscope magnification of 400 x. This would provide an indication about the completeness of phase separation, i.e. the effectiveness of the demulsification process.

To try to identify which of the ELM components were responsible for the COD concentrations measured in the stripping phase (see section 3.2 for details). Firstly, the structures and aqueous solubilities of the individual ELM components were examined. SPAN 80 is otherwise known as sorbitan mono-oleate and it is only dispersible and non-soluble in water (SPAN 80, 2013). At the same time, kerosene contains mostly hydrocarbons which have limited or negligible aqueous solubility (Kerosene, 2013). This was proven by extraction of the stripping phase and the measurement of kerosene levels below the LOD of the gas chromatographic method (data not shown). Given the structure of TOA and the highly acidic pH of the aqueous phase, it is possible for TOA molecules to partition into the stripping phase by formation of the ion pairs with the nitrate anions from HNO_3 molecules. Molecules of toluene have been shown to undergo hydrogen bonding with molecules of water and its aqueous solubility has been shown to be around 526 mg/L (Tandlich and Zuma, 2012). Therefore these two compounds are the most likely to contribute significantly to any carry-over of ELM components into the stripping phase during demulsification.

The following experiment was performed to measure the actual contribution of TOA and toluene to the COD in the stripping phase after demulsification. A fresh batch of the ELM mentioned above was prepared and demulsified in the same fashion. Next, the aqueous phase was placed in a 250 mL separating funnel and 20 mL of n-hexane was added. The contents of the funnel were vigorously hand-shaken for 5 minutes to achieve extraction of organic components. The funnel was left to stand until phase separation was observed and the n-hexane layer was collected into a 100 mL volumetric flask. This was then stoppered and extraction was repeated two more times with fresh 20 mL aliquots of n-hexane. The three n-hexane extracts were combined and dried with 2.00 g of anhydrous $MgSO_4$ (Sigma-Aldrich, Johannesburg, South Africa). Then 20 mL of the organic extract was pipetted into a clean 250 mL Erlenmeyer flask and solution was titrated for the TOA content (see section 2.8 for details). The remainder of the organic extract was concentrated under gentle stream of nitrogen to 1 mL and transferred into a 2 mL GC vial. The content of toluene was determined using GC analysis (see section 2.6 for details).

3.2.3.5 Chemical demulsification at 50.0 ± 1.0°C and ELM carry-over

The diluents with extractant addition from section 3.2.3.4 were used in this experiment. The diluent with 20.000 g/L of PIB was mixed with 2 M HNO_3 in the ratios 1:2 (20 mL of HNO_3: 40 mL of diluent) to form 1:2 emulsions in 150 mL Erlenmeyer flasks. The flask was shaken for 40 minutes using the Chiltern orbital shaker SS70 at 600 rpm. Then 20 g of PEG was added and the ELM was again shaken for another 75 minutes. The ELM containing 28.000 g/L of PIB was made and treated with PEG in the same way. The two ELMs were placed in an UFE 700 oven and the chemical demulsification was performed at 50 ± 1°C for 24 hours. The completeness of the separation and the potential carry-over of diluent components into the stripping phase were examined in analogical fashion as in section 3.2.3.4.

3.3 RESULTS FOR EMULSION LIQUID MEMBRANE OPTIMISATION AND DEMULSIFICATION

3.3.1 Stability of emulsion liquid membranes prepared by sonication

This section presents the results of the experiments described in section 3.2.2.1 and 3.2.2.2. No stable ELMs were formed with the kerosene-TBP diluent after 20 minutes of sonication. This was based on the limited phase mixing and the observation that complete phase separation of the diluent layer from the stripping phase occurred after 5 minutes or less of the ELM standing at ambient temperature. With the kerosene-TBP-PIB-TOA diluent, complete phase separation was observed for the 1:1 preparation after 167 minutes, for the 1:2 ELM after 92 minutes and 55 minutes for the 1:3 ELM. Thus sonication and the diluents from sections 3.2.2.1 and 3.2.2.2 were not suitable for application in extraction of Rh from side-streams.

3.3.2 Stability and microdroplet sizes of ELMs prepared by orbital shaking 1

Here the ELM stability and microdroplet diameters are described for the diluents and preparation by orbital shaking as outlined in sections 3.2.2.3 and 3.2.2.4. The aqueous phase and the diluent (organic) phase mixed completely to form milky white ELMs. After the first round of shaking, all ELMs remained stable for 3 hours and then phase separation took place. Re-emulsification occurred after the shaking was repeated. The 1:1 and 1:2 ELMs subsequently remained stable for 7 hours and the phase separation took place again. The 1:3 and the 1:4 ELMs remained stable for 12 hours, after which separation again occurred. No ELMs were stable beyond 24 hours when stored at 5 ± 2°C. Thus the ELMs for extraction will have to be prepared on the extraction day and as close to the start of the Rh extraction as possible. Microdroplet size distribution, as determined using optical microscopy, is shown in Fig. 3.1. The average globule diameters of 1:1, 1:2, 1:3 and 1:4 were as follows (µm): 10.8 ± 2.8; 4.2 ± 1.6; 11.4 ± 4.6 and 14.8 ± 6.7. This was outside of the optimum 1-3 m range and therefore the mass transfer characteristics of these ELMs would not be favourable for Rh extraction from metal refinery side-streams.

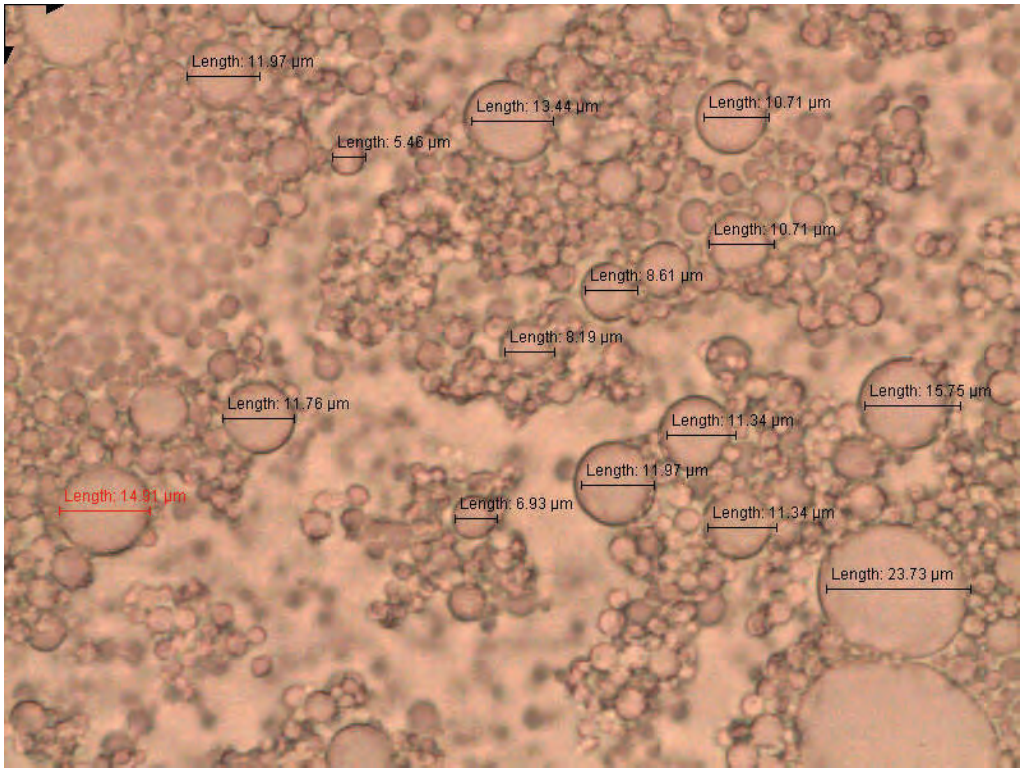
3.3.3 Stability and microdroplet sizes of ELMs prepared by orbital shaking 2

Experiments from section 3.2.2.5 when the orbital shaking lasted 20 minutes during the ELM preparation resulted in the milky water-in-oil (W/O) ELMs were formed. Stable ELMs were observed visually for the diluent-stripping-phase-volumetric ratios of 1:1 and 1:2, as no phase separation was observed at 22 ± 1°C after 12 hours. Micrographs of the microdroplets are shown in Figure 3.2. The microdroplet size distribution indicated that the average diameters of the 1:1 ELMs were 5.2 ± 1.5 µm after storage at 22 ± 1°C after 12 hours. This value increased slightly to 6.1 ± 2.9 µm after re-shaking and storage at 5 ± 2°C for up to 24 hours (see section 3.2.2.5 for details).

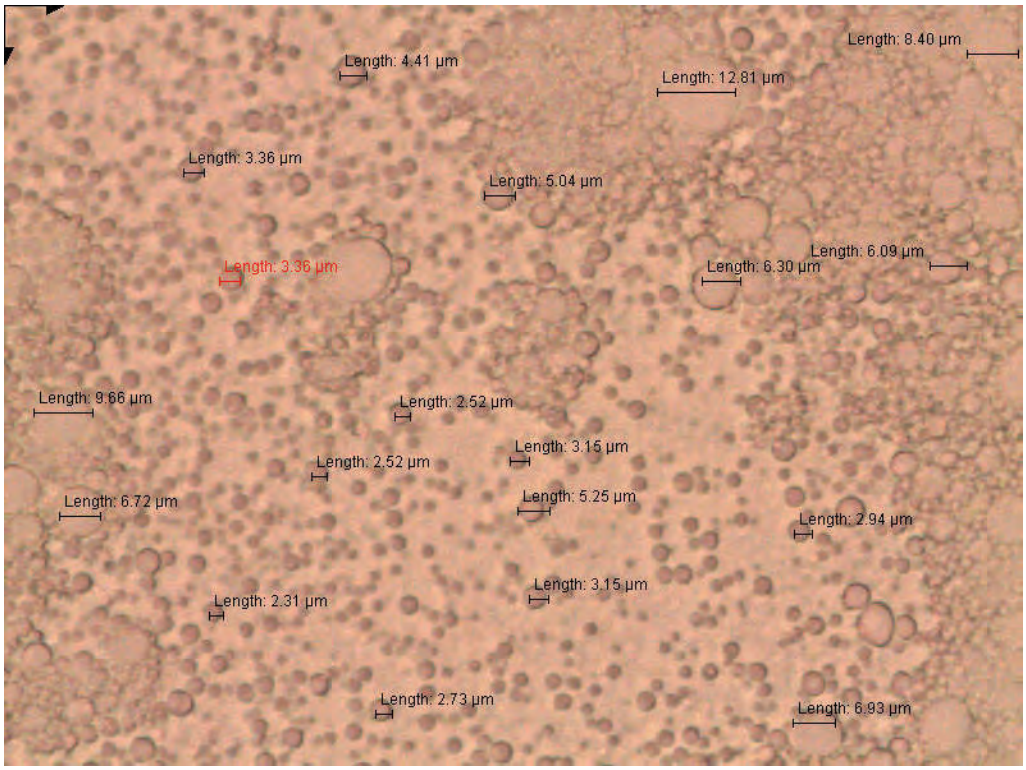
The average diameters of the microdroplets with the 1:2 ELMs were 3.5 ± 1.0 µm and 3.4 ± 0.8 µm. The first value is reported for the ELM storage at 22 ± 1°C after 12 hours, while the second describes the microdroplet size distribution after re-constitution of the ELMs through the second shaking for 20 minutes and storage at 5 ± 2°C for up to 24 hours. When the shaking time during the ELM preparation was extended to 40 minutes (see section 3.2.2.5b for details), the milky water-in-oil (W/O) ELMs were formed and again visually stable for the diluent:HNO_3 ratios of 1:1 and 1:2 (v/v) emulsions at 22 ± 1°C for up to 12 hours. Figure 3.3 shows the images of the microdroplet size distribution as determined using optical microscopy and the 400x magnification.

The average microdroplet diameters of the 1:1 ELMs were 3.1 ± 0.9 µm and 3.5 ± 0.9 µm. The average diameters of the microdroplets of the 1:2 ELMs were 3.3 ± 0.5 µm and 2.9 ± 1.0 µm. In both cases, the first average value is reported for the ELM storage at 22 ± 1°C after 12 hours, while the second describes the microdroplet size distribution after re-constitution of the ELMs through the second shaking for 20 minutes and storage at 5 ± 2°C for up to 24 hours. The increase in the mixing time brought the microdroplet diameter closer to the optimum range for metal extraction. From the data measured in section 3.2.2.5, it can be clearly seen that the diluent with extractant addition and the following composition (g/L): 20.000 PIB, 10.250 TOA and 50.201 SPAN 80, resulted in a stable ELM if mixed on an orbital shaker for 20 minutes with 2 M HNO_3 in the volumetric ratios of 1:1 and 1:2.

If these ELMs are prepared on the same day, they can be used for up to 12 hours after preparation, before re-shaking and ELM reconstitution become necessary.

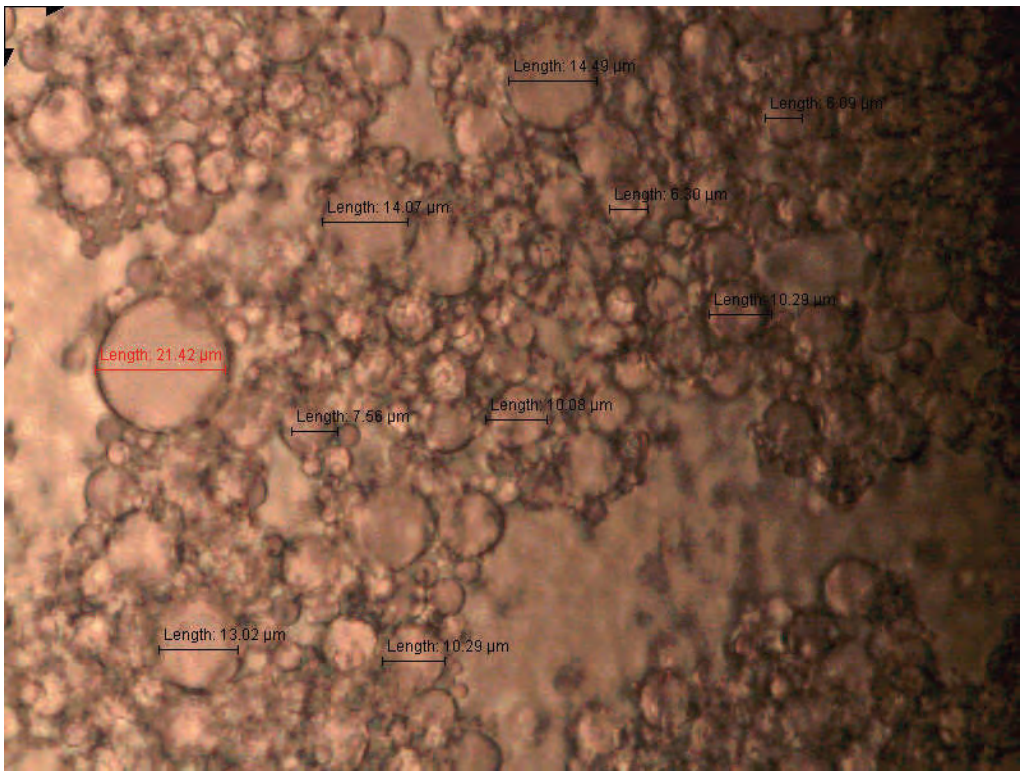


(a)

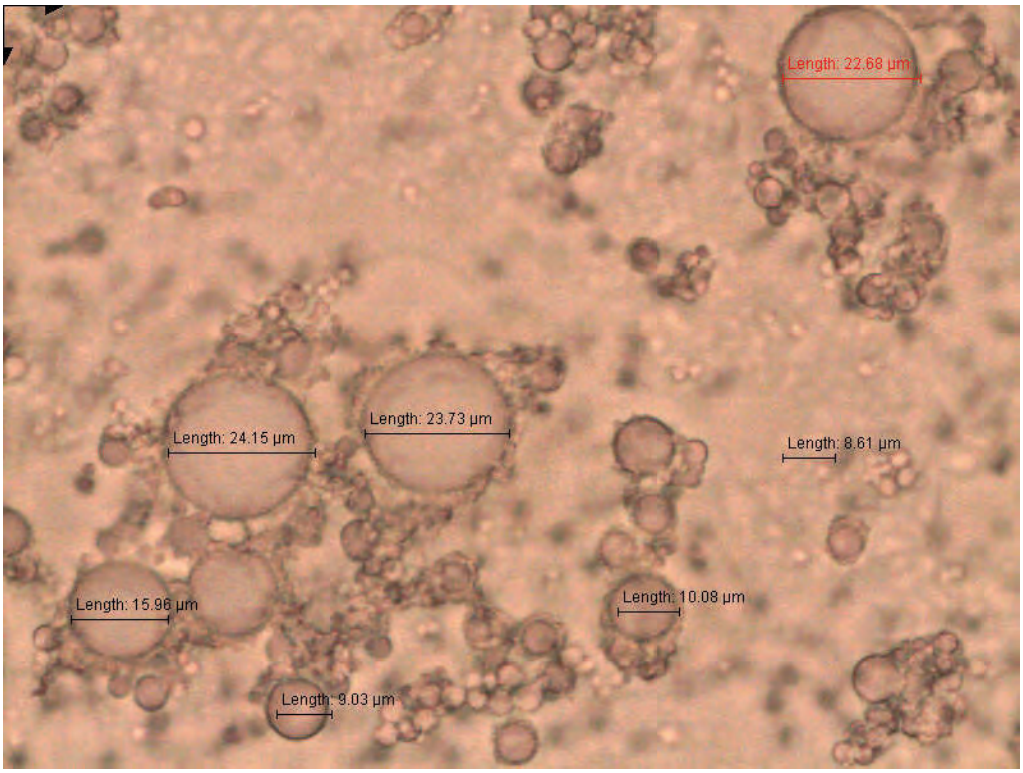


(b)

Figure 3.1. The microdroplet diameter distribution of the 1:1 ELM (a), the 1:2 ELMs (b), the 1:3 ELMs (c) and the 1:4 (d) prepared by 20 minutes of orbital shaking and using the diluents from sections 3.1.2.3 and 3.1.2.4.

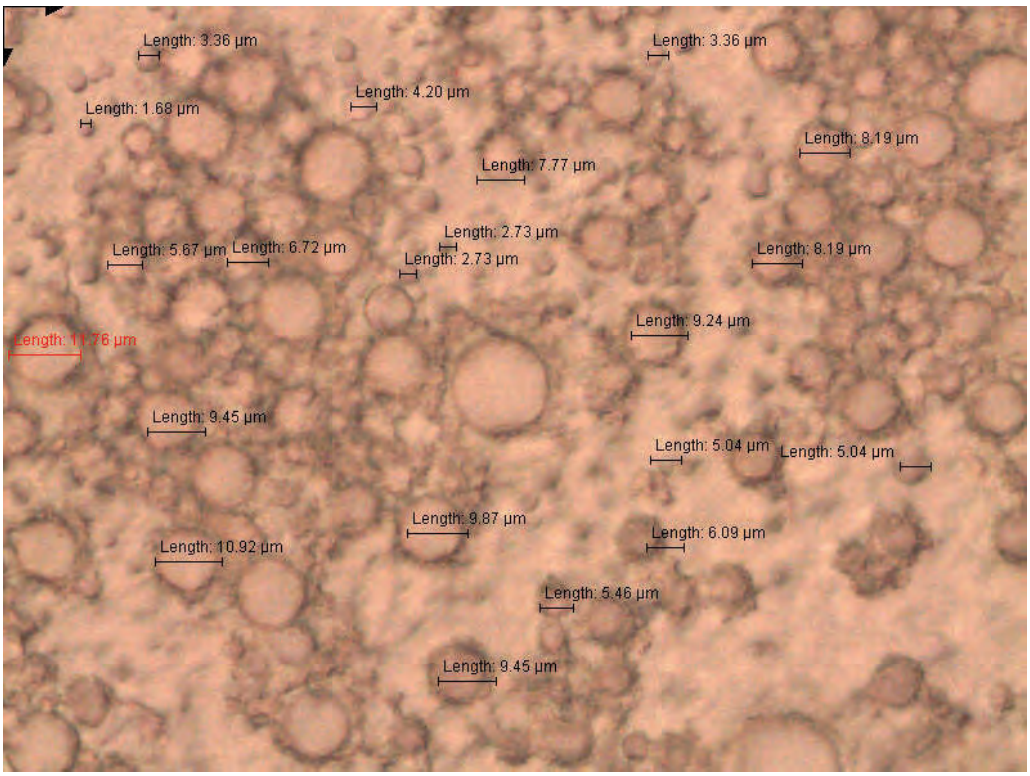


(c)

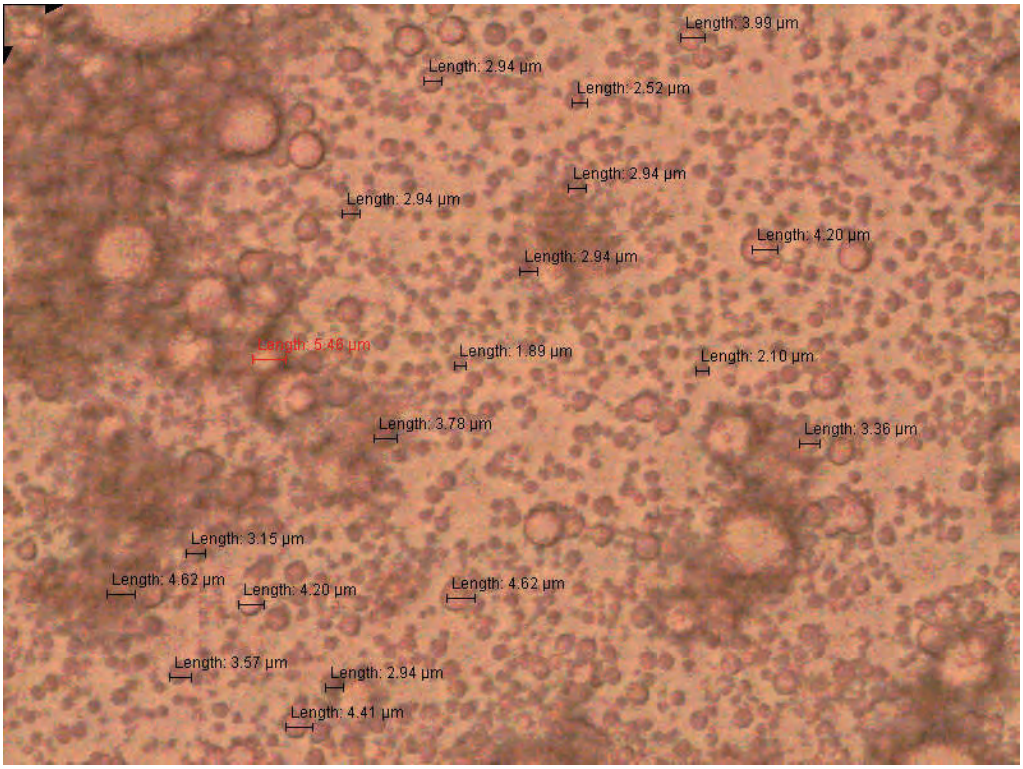


(d)

Figure 3.1. (Continued). The microdroplet diameter distribution of the 1:1 ELM (a), the 1:2 ELMs (b), the 1:3 ELMs (c) and the 1:4 (d) prepared by 20 minutes of orbital shaking and using the diluents from sections 3.1.2.3 and 3.1.2.4.

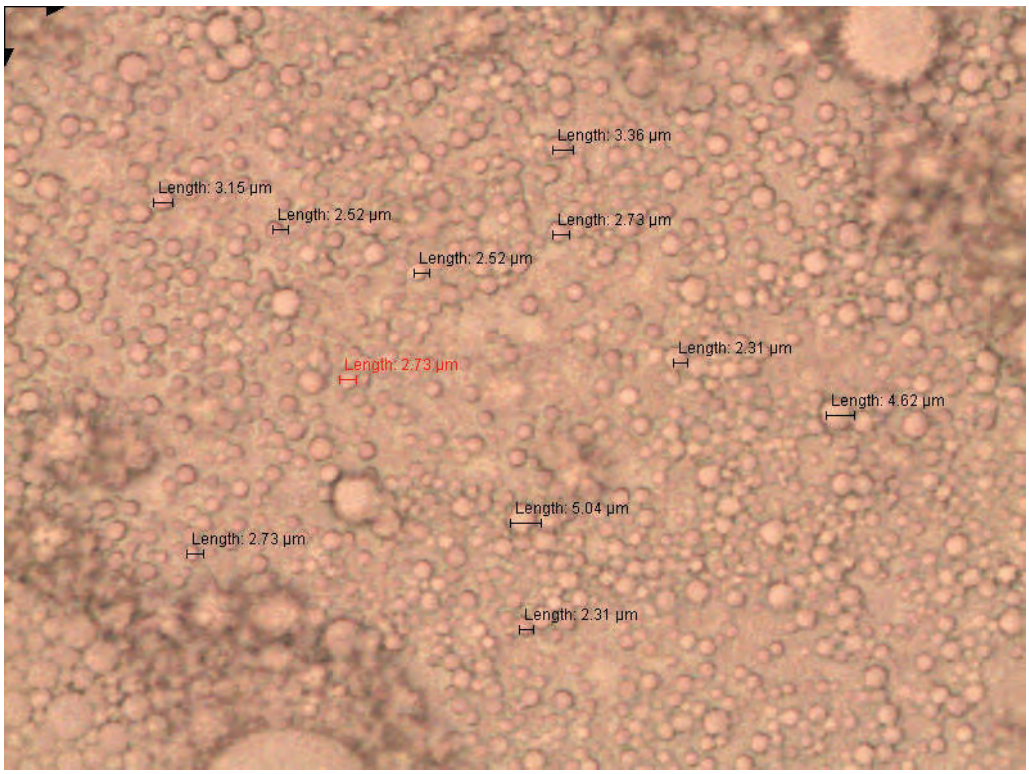


(a)

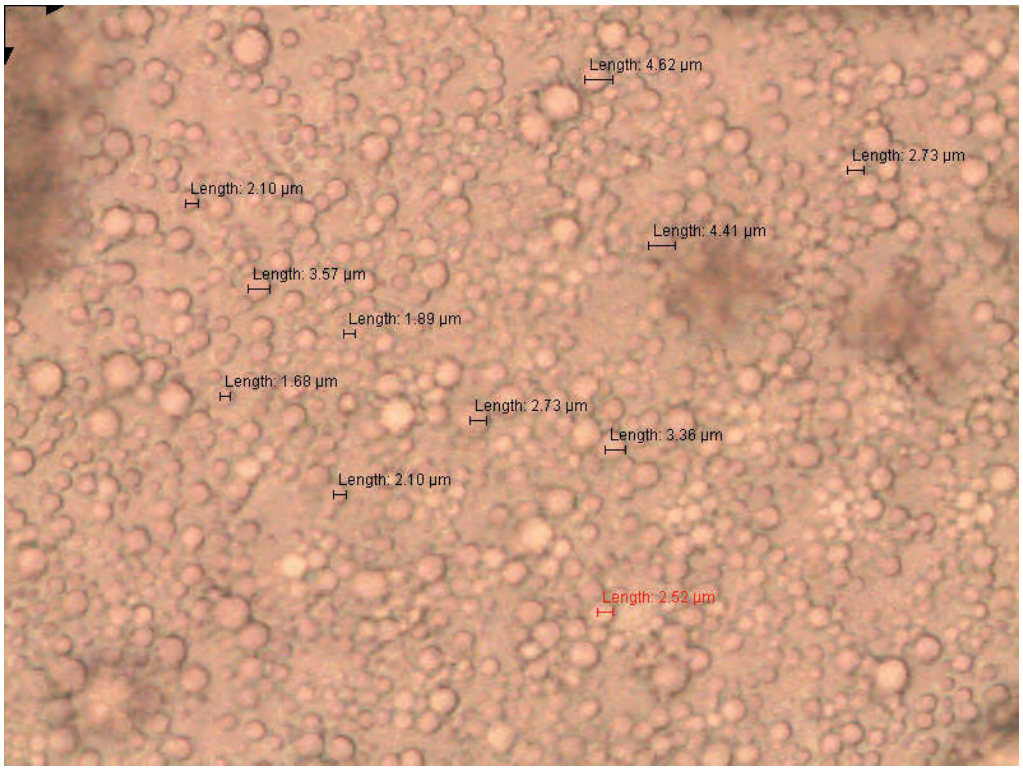


(b)

Figure 3.2. Examples of the microdroplet diameter distribution of the 1:1 ELM (a) and the 1:2 ELMs after 20 minutes of orbital shaking as described in section 3.2.2.5a.



(a)



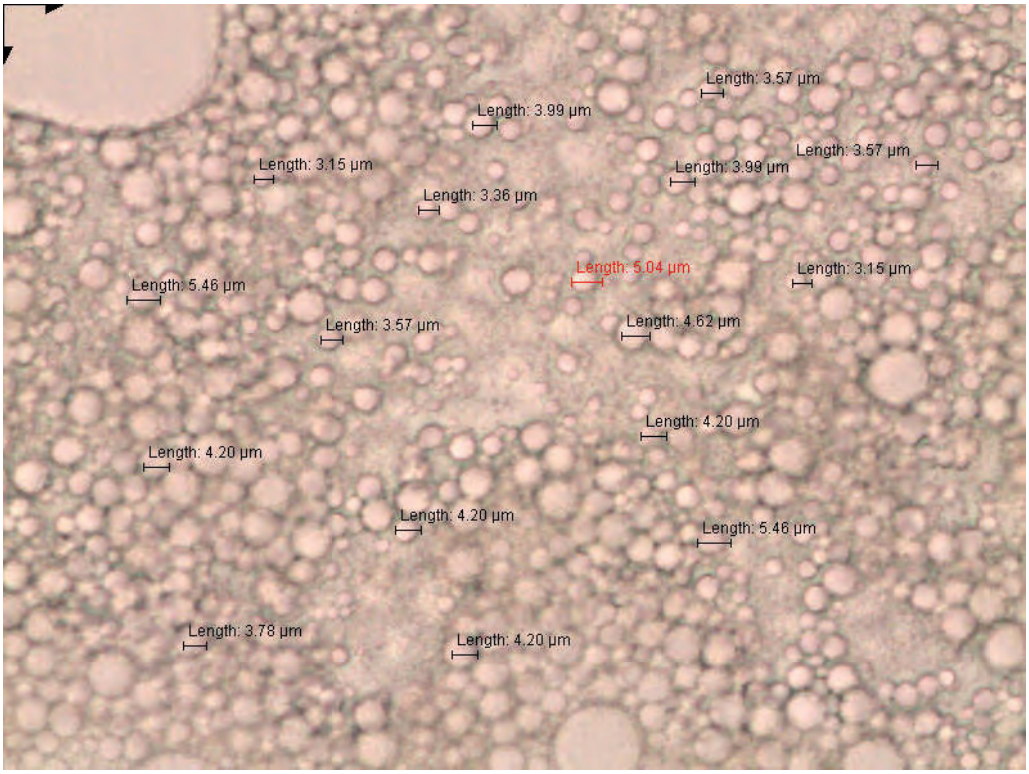
(b)

Figure 3.3. Examples of the microdroplet diameter distribution of the 1:1 ELM (a) and the 1:2 ELMs after 40 minutes of orbital shaking as described in section 3.2.2.5b.

Once the reconstituted ELM in question is prepared, it can be stored in the refrigerator and reused for up to 24 hours after reconstitution by orbital shaking. One major drawback still remains and it originates from the microdroplet average diameters which are just outside of the optimum range for Rh extraction, i.e. 1-3 µm. This is addressed in the next paragraph with same diluent:HNO_3 ratios, orbital mixing for 40 minutes and increasing the concentration of PIB to 30.000 g/L. Diluent containing 30.000 g/L (w/v) PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80 was mixed with 2 M HNO_3 in volumetric ratios of 1:1 (10 mL of HNO_3: 10 mL of diluent) and 1:2 (10 mL of HNO3: 20 mL of the diluent; see section 3.2.2.6 for details). The Chiltern SS70 orbital shaker was used and this approach resulted in the formation of milky water-in-oil (W/O) ELM. These were visually at 21 ± 2°C for up to 12 hours. The microdroplet size distribution can be seen in Figure 3.4.

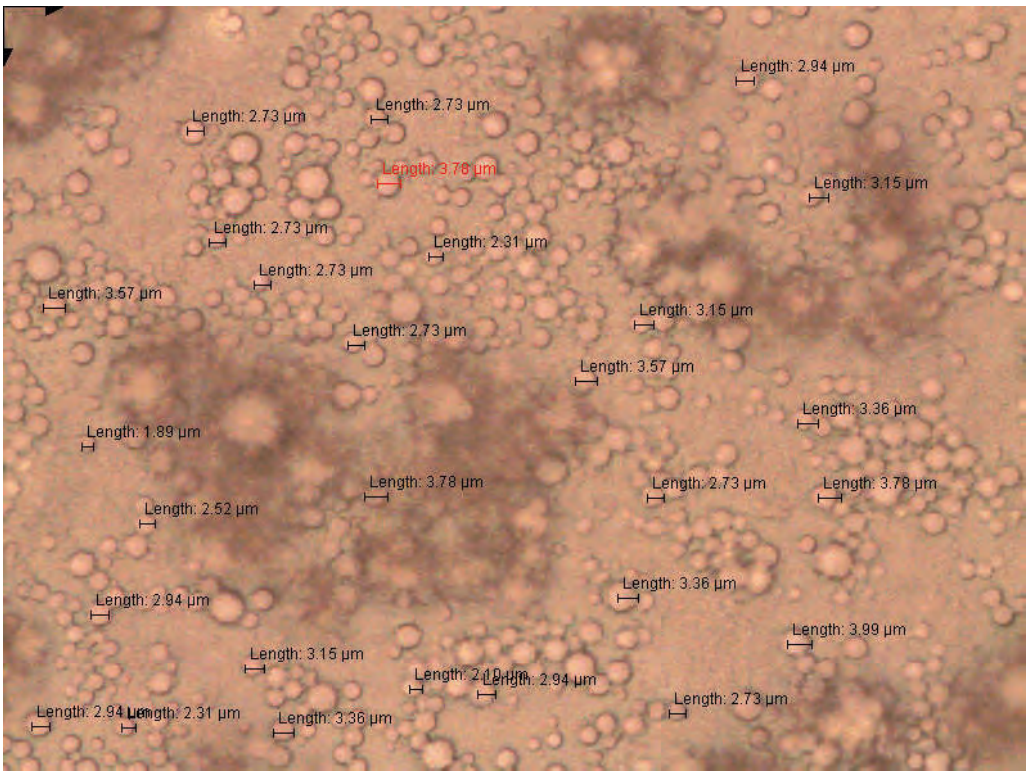
For the 1:1 ELMs, the average microdroplet diameters ranged from 3.0 ± 0.6 µm to 4.1 ± 0.7 µm. The respective values for the 1:2 ELM stood at 3.0 ± 0.5 µm; 2.8 ± 0.4 µm and 2.9 ± 1.0 µm. For both types of ELMs, the first average diameter represents the microdroplet size distribution right after the 12 hour storage at 21 ± 2°C. The second diameter indicates the microdroplet size distribution after the 12 hour storage at 21 ± 2°C and reconstitution of the ELMs. The last diameter described the changes of the microdroplet diameter distribution after the storage of the reconstituted ELM at 5 ± 2°C for 24 hours. Diluent which contains 30.000 g/L (w/v) PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80 when mixed with 2 M HNO_3 in volumetric ratios of 1:1 or 1:2 leads to the formation of stable ELMs which can be used for up to 12 hours without the need for reconstitution. Storage in the refrigerator is possible after reconstitution and reuse is feasible on two different days.

Taking the microdroplet diameter distributions into account, the best ELM for Rh extraction has the following diluent composition: 30.000 g/L (w/v) PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80; and mixed with 2 M HNO_3 in volumetric ratio of 1:2.



(a)

Figure 3.4 Examples of the microdroplet diameter distribution of the 1:1 ELM (a) and the 1:2 ELMs after 40 minutes of orbital shaking as described in section 3.2.2.6.



(b)

Figure 3.4 (continued) Examples of the microdroplet diameter distribution of the 1:1 ELM (a) and the 1:2 ELMs after 40 minutes of orbital shaking as described in section 3.2.2.6.

3.3.4 Demulsification results

Thermal demulsification at 35 ± 0.5°C and 45 ± 0.5°C for 24 hours resulted in limited or no phase separation as shown in Figures 3.5 and 3.6. The ELMs prepared for chemical demulsification with PEG led were (w/o) ELMs in appearance which did not change even after the addition of PEG (see Figure 3.7a and section 3.2.3 for further details). Phase separation was achieved after the PEG 400 addition and heating of the ELM at 70°C for 24 hours (examples can be seen in Figs. 3.7a and 3.7b). There was significant carry-over of the ELM diluent components into the stripping phase as demonstrated by the stripping phase COD concentrations shown in Tables 3.3 and 3.4. At the same time, no emulsion droplets were detected microscopically in either the stripping phase or the diluent layer.

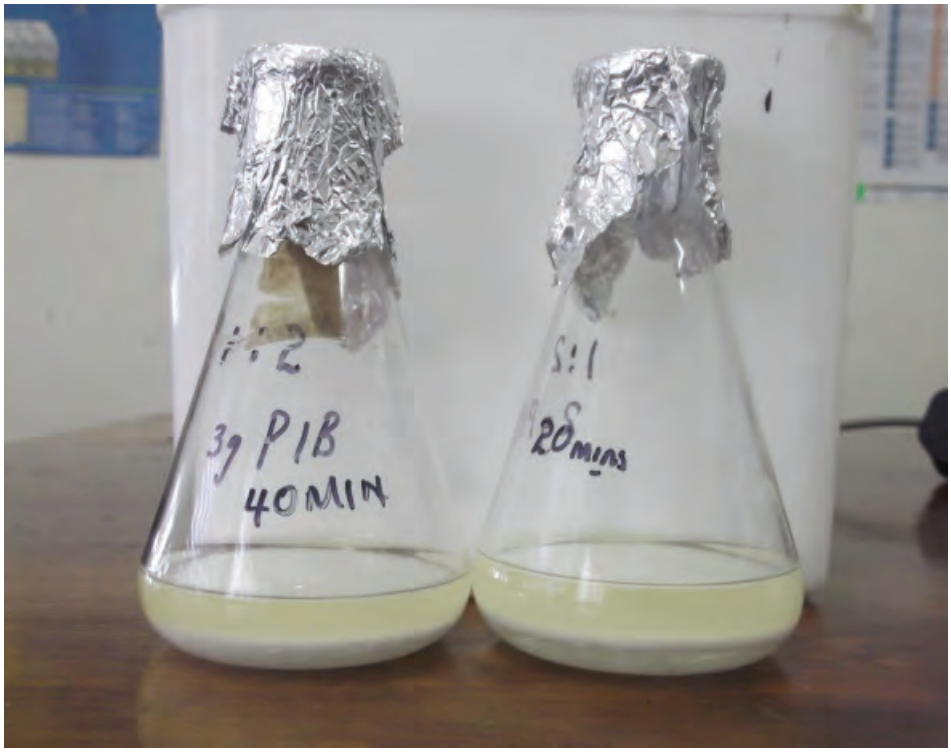
As it can be seen the COD in the stripping phase increased with increasing concentration of PIB in the ELM diluent and the increasing weights of PEG added to the ELM before the chemical demulsification. It has to be, however, stated that the carry-over of organic matter is variable. These data will be taken into account during further parts of the study as the loss of the diluent components will increase the cost of any developed ELM extraction method for Rh. The prices for the extractant, diluent and the chemical demulsifier do vary significantly and therefore it is critical to ascertain which one of these components is likely to contribute to the COD concentrations shown in Tables 3.3 and 3.4. This was done by considering the aqueous solubilities of the individual ELM components, their relationship to the structure of the compounds used and the stoichiometric equations. The results are described in the following paragraphs.

(a)

(b)

Figure 3.5. Results of thermal demulsification of ELMs at 35 ± 0.5°C for 24 hours with diluent containing 20.000 g/L PIB (a) and the diluent containing 30.000 g/L PIB (b).

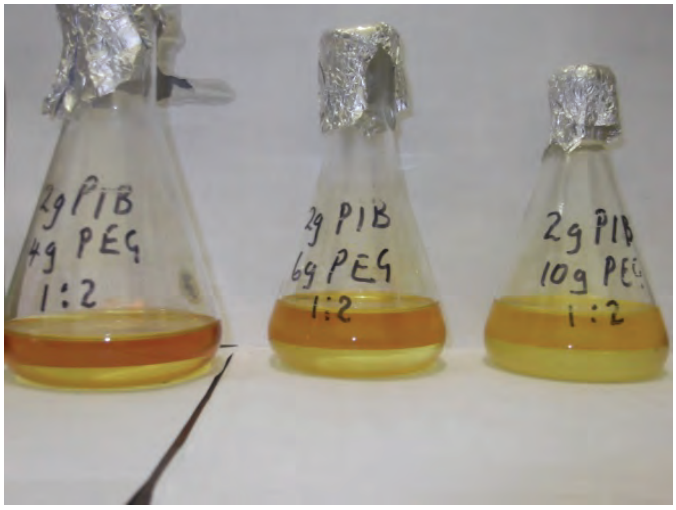
(a)



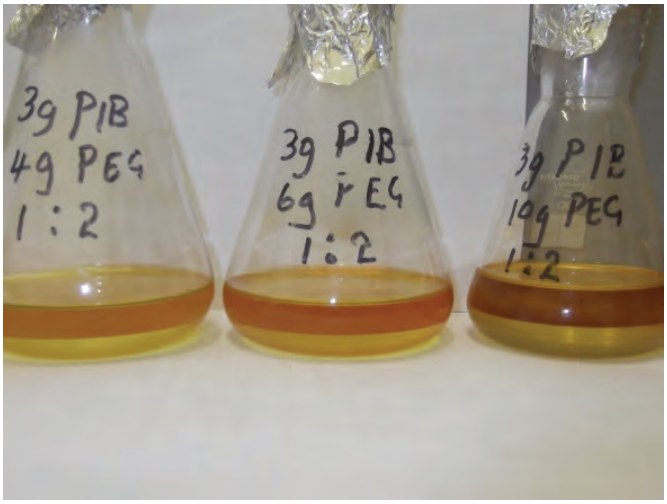
(b)

Figure 3.6. Results of thermal demulsification of ELMs at 45 ± 0.5°C for 24 hours with diluent containing 20.000 g/L PIB (a) and the diluent containing 30.000 g/L PIB (b).

(a)



(b)



(c)

Figure 3.7. Chemical demulsification: original ELMs right after the addition of varying PEG weights (a); after chemical demulsification at 70°C for 24 hours when the diluent contained 20.000 g/L PIB (b) and when the diluent contained 30.000 g/L (c).

Table 3.3. Residual COD concentrations in the stripping phase after demulsification at 70 ± 1°C for 24 hours from section 3.2.3.3.

Emulsion	COD (mg/L)
Emulsion with 1 g PEG- diluent has 2 g PIB	2130
Emulsion with 2 g PEG- diluent has 2 g PIB	2970
Emulsion with 10 g PEG- diluent has2 g PIB	3930
Emulsion with 1 g PEG- diluent has 3 g PIB	2890
Emulsion with 4 g PEG- diluent has 3 g PIB	3130
Emulsion with 10 g PEG- diluent has 3 g PIB	4380

Table 3.4. Residual COD concentrations in the stripping phase after demulsification at 70 ± 1°C for 24 hours from section 3.2.3.4.

Emulsion	COD (mg/L)
Emulsion with 2 g PEG- diluent has 2 g PIB	3007
Emulsion with 4 g PEG- diluent has 2 g PIB	4300
Emulsion with 6 g PEG- diluent has2 g PIB	6430
Emulsion with 2 g PEG- diluent has 3 g PIB	3180
Emulsion with 4 g PEG- diluent has 3 g PIB	4680
Emulsion with 6 g PEG- diluent has 3 g PIB	6880

The average TOA concentration in the stripping phase was equal to 0.172 g/L. The contribution of these TOA levels to the measured COD concentrations can be estimated using the stoichiometry of the TOA molecule during the COD digestions as shown in Eq. (8).

$$(C_8H_{17})_3N + 36O_2 \rightarrow NH_3 + 24CO_2 + 24H_2O \quad (8)$$

The average volume of stripping phase after demulsification was equal to 15 mL. Combining Eq. (8) with the molecular weights of TOA (353.68 g/mol) and O_2 (32 g/mol), the relationship between the TOA concentration and the COD contribution from TOA can be derived to obtain Eq. (9).

$$COD = 3.257 \times C(TOA) = 560\ mg/L \quad (9)$$

The concentration TOA is unlikely to be influenced by the weights of PEG added to the ELM prior to demulsification as this compound is miscible with water and TOA is highly hydrophobic. The average toluene concentration in the stripping phase was equal to 450 mg/L, but the concentrations varied by up to 30%. The toluene contribution to the measured COD concentrations can be estimated using the stoichiometric Eq. (10).

$$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O \quad (10)$$

The average volume of stripping phase after demulsification was equal to 15 mL. Combining Eq. (10) with the molecular weights of toluene (92.14 g/mol) and O2 (32 g/mol), the relationship between the stripping phase concentration of toluene and the respective COD levels takes the form of Eq. (11).

$$COD = 3.126 \times C(toluene) = 1410\ mg/L \quad (11)$$

The concentration TOA is unlikely to be influenced by the weights of PEG added to the ELM prior to demulsification as this compound has been shown to be miscible with water and thus will not influence the TOA mass transfer into the aqueous phase. Summation of the TOA and toluene contributions to the COD levels in the stripping phase account for 1970 mg/L. The remaining COD concentrations most likely originate from oxidation of PEG molecule which dissolves in water during chemical demulsification. When the chemical demulsification was performed by shaking at 600 rpm for 75 minutes and incubations at 50 ± 1°C, the ELMs lost their stability and complete phase separation was observed as shown in Figure 3.8. No ELM microdroplets were observed in the stripping phase or the diluent. Based on the results above the 1:2 ELM with 28.000-30.000 g/L were chosen for the extraction of Rh.

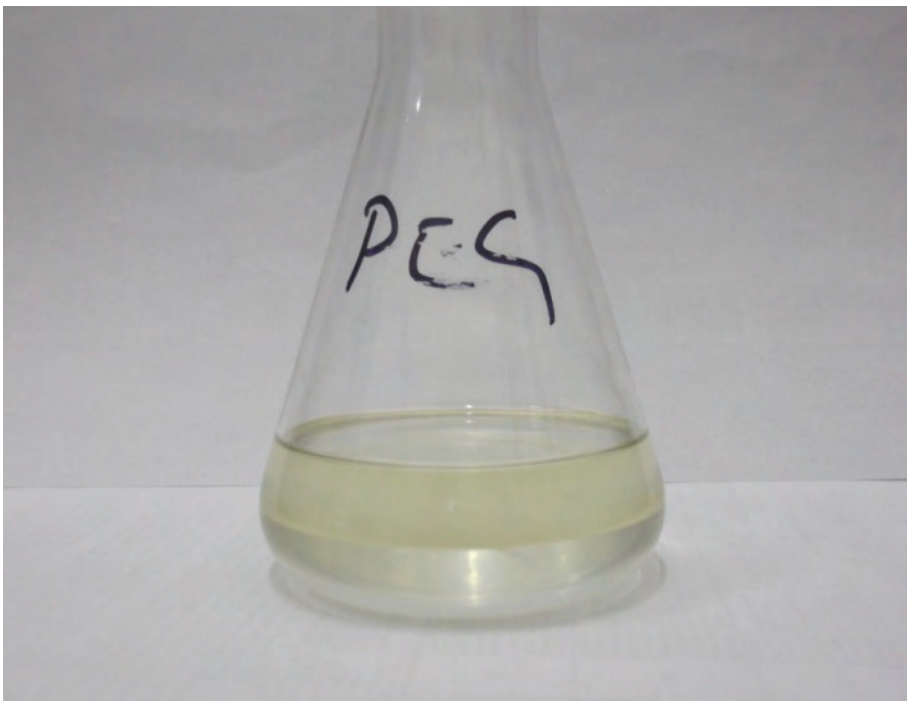


Figure 3.8. Demulsification of the 1:2 ELM containing 20.000 g/L with 20 g of PEG after incubation at 50 ± 1°C for 24 hours.

The colour of the ELM remained comparable to the original milky ELM formed right after the ELM preparation (compare Figures 3.5 and 3.8 for details). Extent of the colour change in question was quantified by measuring the absorbance of the solution at 490 nm. This was equal to 0.261 if the demulsification was performed at 70 ± 1°C. The absorbance was equal to 0.008 if the demulsification was performed at 50 ± 1°C. These results indicate that chemical changes might have taken place at the higher demulsification temperature. Based on this, chemical demulsification at 50 ± 1°C for 24 hours was more appropriate and was thus used in further experiments.

3.4 EXTRACTION OF RHODIUM FROM A MODEL REFINERY SIDE-STREAM

3.4.1 Methodology

Model metal refining side-streams were prepared in the following way. A solution of 7 mg/L of Rh was prepared by diluting the stock solution with the certified concentration 999 ± 5 mg/L in 0.01 M HCl (pH=1.87) and in 0.001 M HCl (pH = 2.92), respectively. Extraction of Rh with the optimised ELM was then performed using the Taylor-vortex column shown in Figure 3.9.

The ELMs with approximately 30 g/L PIB was prepared. For this, 7.5260 g of PIB was dissolved in a mixture of 150 mL of kerosene and 75 mL toluene. The PIB concentrations between 28.000 and 30.000 g/L provided the same results microdroplet diameter distribution (data not shown). Then 2.6031 g of TOA was added, along with 12.5320 g of SPAN 80. Kerosene was then added to the 250 mL mark to make 30.104 g/L (m/v) PIB, 10.412 g/L (m/v) TOA and 50.128 g/L (m/v) SPAN 80. This diluent was mixed with 2 M HNO_3 in the ratios 1:2 (125 mL of HNO_3: 250 mL of diluent) to form 1:2 ELMs in 500 mL Erlenmeyer flasks. The flask was shaken for 40 minutes using the orbital shaker at 600rpm.

The optimised ELM was mixed with the model side-stream in a ratio of 1:5 (10 mL ELM:50 mL model mining side-stream). The solution was then stirred in the Taylor-vortex column at 250 rpm and the temperature was held at 21 ± 1°C. After the extraction process had been completed, the ELM/side-stream mixture was taken out of the Taylor-vortex column. It was placed into a conical flask and then left to stand to allow separation of the aqueous phase (model of mining waste water) from the ELM. The ELM was removed and demulsified. The extraction procedure was repeated at pH = 1.87 for stirring times of 5, 7, 15, 25 and 30 minutes (experiment 1). The procedure was done for stirring time of 5, 10, 15, 20 and 30 minutes at pH = 2.92 (experiment 2). All extractions were repeated in duplicate. Demulsification of ELM in question was completed

by adding 10 g of PEG 400 to the loaded ELM. The mixture was subsequently shaken at 600 rpm on the Chiltern orbital shaker for 75 minutes and placed into the UFE 700 oven at 50 ± 1°C for 24 hours. The bottom layer was pipetted and analysed for Rh using the ICP.

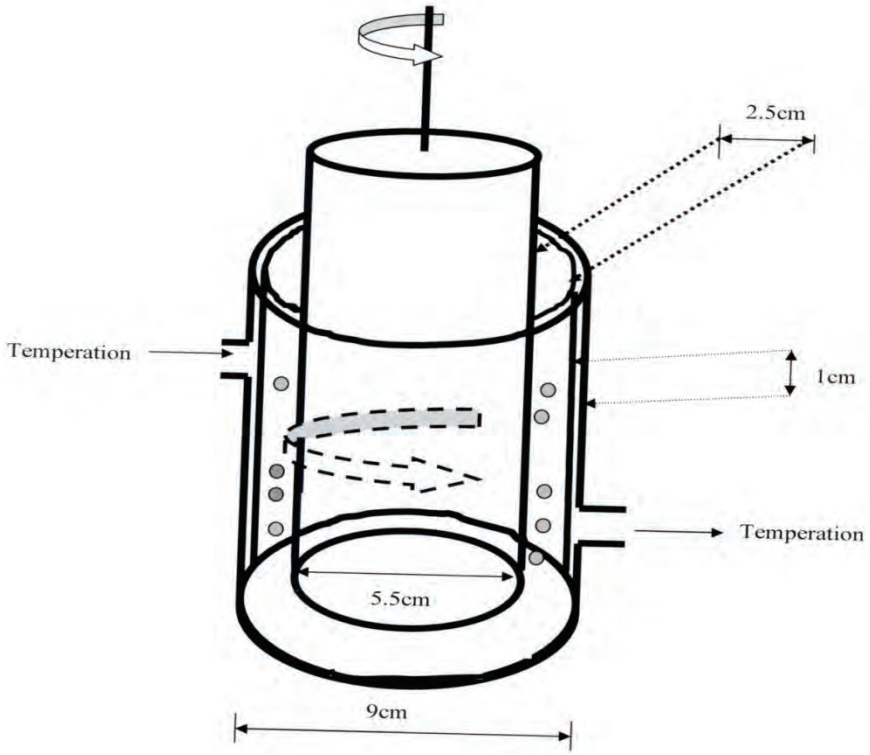


Figure 3.9. The Taylor-vortex column used in the extraction of Rh from model mining side-streams. The diameters of internal and external cylinders and the thickness of the external cylinder are shown in the diagram. The membrane globules (●) are dispersed in the feed phase of the system via the rotation of the inner cylinder of the Taylor-vortex column. The dotted arrow around the internal cylinder represent the stirring pattern due to the rotation of the inner cylinder, and point out the even distribution of energy in the entire volume of the ELM-side-stream mixture.

3.4.2 Results

Extraction efficiency results are shown in Tables 3.5 and 3.6. The recovery efficiency was calculated as a percentage of the initial Rh amount (mg) which was recovered in the stripping phase (mg). A maximum recovery of 41.7% was observed for the extraction stirring time of 30 minutes, if the pH of the treated side-stream/feed phase was equal to 1.87 (Table 3.5). At pH = 2.92, the maximum recovery of 46.2% was observed for the extraction stirring time of 30 minutes (Table 6). Mass balance of Rh for the whole ELM procedure ranged from 75 to 87%. The next step in the investigation of the Rh extraction using the optimised ELM is the effect of temperature on the stability of the ELM and the Rh extraction efficiency. This is discussed in the next section 3.5.

Table 3.5. Recovery efficiency of Rh from the aqueous phase of the ELM after demulsification at the feed phase; pH = 1.87.

Time (mins)	pH	Initial volume (mL)	Initial conc (mg/L)	Initial mass (mg)	Final volume (mL)	Final conc (mg/L)	Final mass (mg)	Recovery of Rh (%)
5	1.87	0.050	7	0.350	25	2.2	0.055	15.8
7	1.87	0.050	7	0.350	27	3.3	0.090	25.7
15	1.87	0.050	7	0.350	31	3.6	0.110	31.5
25	1.87	0.050	7	0.350	36	3.6	0.115	32.8
30	1.87	0.050	7	0.350	40	3.7	0.146	41.7

Table 3.6. Recovery efficiency of Rh from the aqueous phase of the ELM after demulsification at the feed phase; pH = 2.92.

Time (mins)	pH	Initial volume (L)	Initial conc (mg/L)	Initial mass (mg)	Final volume (L)	Final conc (mg/L)	Final mass (mg)	Recovery of Rh (%)
5	2.92	0.050	7	0.350	0.020	2.926	0.059	16.7
10	2.92	0.050	7	0.350	0.028	2.756	0.077	22.1
15	2.92	0.050	7	0.350	0.037	2.377	0.088	25.1
20	2.92	0.050	7	0.350	0.035	3.455	0.121	34.6
30	2.92	0.050	7	0.350	0.042	3.853	0.162	46.2

3.5 EFFECT OF TEMPERATURE ON THE ELM EXTRACTION OF Rh

3.5.1 Methodology

3.5.1.1 Apparatus and chemicals

Kerosene, PIB and TOA were purchased from Sigma-Aldrich (Johannesburg, Sigma Aldrich, South Africa), while Saarchem brand HNO_3 was purchased from Merck Chemicals Pty Ltd. (Port Elizabeth, South Africa) and SPAN 80 from Fluka Analytical (Johannesburg, South Africa). The Olympus UCMAD3 microscope mounted with an Olympus ultra 20 soft imaging system UTVX-2 was used for all microscopic work and the circulating water bath serial number 109046004 from Grant instruments (Cambridge) England.

3.5.1.2 Preparation of the ELM

The ELMs with approximately 30 g/L PIB was prepared. For this, 7.5260 g of PIB was dissolved in a mixture of 150 mL of kerosene and 75 mL toluene. Then 2.6031 g of TOA was added, along with 12.5320 g of SPAN 80. Kerosene was then added to the 250 mL mark to make 30.104 g/L (m/v) PIB, 10.412 g/L (m/v) TOA and 50.128 g/L (m/v) SPAN 80. This diluent was mixed with 2 M HNO_3 in the ratios 1:2 (125 mL of HNO_3: 250 mL of diluent) to form 1:2 emulsions in 500 mL Erlenmeyer flasks. The flask was shaken for 40 minutes using the orbital shaker at 600 rpm.

3.5.1.3 Temperature stability of the optimised ELM

Ten millilitres of the ELM was poured into the empty Taylor-vortex column and temperated at 40 ± 1°C or 50 ± 1°C for 5, 10, 15, 20 and 30 minutes. After the time period in question elapsed, samples of the ELM was removed and placed onto a microscopic slide and examined using the Olympus microscope at 400 × immediately. The diameter of the microdroplets was measured and the averages recorded for both examined for all incubation temperatures.

3.5.1.4 Effect of incubation temperature on the Rh Extraction

The model side-streams, i.e. solutions of 7 mg/L of Rh in 0.01 M HCl (pH = 2.04) and the 0.001 M HCl (pH = 3.14) were prepared in the same fashion as stated in section 3.3 (see above). Then 50 mL of the side-stream with a particular pH was placed in the Taylor-vortex column pre-heated to at 40 ± 1°C or 50 ± 1°C. Next, 10 mL of the optimised ELM was added and the stirring was started at 250 rpm for 5, 10, 15, 20 and 30 minutes. At each time point, a fresh aliquot of the optimised ELM was poured into the system and a fresh aliquot of un-extracted model side-stream was loaded as well for the Rh containing side-stream. At the given time point, the stirring was interrupted and the ELM/model side-stream mixture was then taken out of the column. It was then placed in a 500 mL Erlenmeyer flask and then left to stand to allow separation of the aqueous phase. The aqueous phase was removed and the loaded ELMs were demulsified. Demulsification was performed by first adding 10 g PEG to the loaded ELM and the resulting mixture was shaken at 600 rpm on the orbital shaker for 75 minutes. The emulsions were place in an oven at 50 ± 1°C for 24 hours. The bottom layer, i.e. stripping phase, was analysed for the Rh concentration using ICP. The spent

model side-stream was subsampled and also analysed for the Rh content. The resulting Rh concentrations were then used to calculate the mass balance of Rh using Eq. (12).

$$\% \text{ Mass balance} = \frac{[C_{elm} \times V_{elm} + C_{ww} \times V_{ww}]}{C_{in} \times V_{in}} \times 100 \quad (12)$$

In Eq. (12), C_{elm} and V_{elm} is the concentration of Rh recovered in the stripping phase of the ELM (mg/L) and the volume of the stripping phase after de-emulsification respectively (L). At the same time, C_{ww} and V_{ww} are analogical values for Rh in the spent model side-stream (unit of mg/L and L).

Finally, the stability of the ELM microdroplets was examined as a function of the extraction temperature, For this, The Taylor vortex column (TV) was connected to the Grant circulating water bath (Manufacturing and Laboratory Techniques, Raedene, USA) as shown in Figure 1 (see Introduction). The TV was filled with water and the temperature maintained at 40 ± 1°C or 50 ± 1°C (see Figure 3.9, page 29). Ten millilitres of the ELM were put in the empty TV which had been adjusted to the respective temperature. Samples of the ELM were removed after 5, 10, 15, 20 and 30 minutes; and the samples were then examined under the optical microscope for microdroplet size distribution.

3.5.1.5 Results

Extraction results are shown in Table 3.7. At pH = 2.04 and at 40 ± 1°C, the extracted amount of Rh increased with increasing time of extraction and the individual recoveries ranged from 21.6 to 38.1%. The maximum extraction efficiency was achieved after 30 minutes of extraction. The extraction fluctuated when the temperature of extraction was increased to 50 ± 1°C and maintaining the model side-stream pH at 2.04. The extracted recovery ranged from 13.8 to 41.8%, with the minimum extraction efficiency recorded after 10 minutes and the maximum observed after 20 minutes. At pH = 3.14 and at 40 ± 1°C, the extracted amount of Rh again fluctuated with time and the individual recoveries ranged from 20.6 to 37.2%. The maximum extraction efficiency was achieved after 20 minutes of extraction. For the same pH values of the feed phase, the Rh recovery ranged from 18.2 to 38.2% when the extraction temperature was raised to 50 ± 1°C.

Table 3.7. Extraction efficiencies of Rh at pH 2.04 or 3.14, and 40 ± 1°C or 50 ± 1°C

pH	Temperature (°C)	Time (mins)	Initial mass (mg)	Final volume (mL)	Final concentration (mg)	Final mass (mg)	Recovery of Rh (%)
2.04	40 ± 1	5	350	26	2.939	76.4	21.8
2.04	40 ± 1	10	350	24	3.143	75.4	21.6
2.04	40 ± 1	15	350	25	3.461	86.5	24.7
2.04	40 ± 1	20	350	28	3.643	102	29.2
2.04	40 ± 1	30	350	36	3.701	133	38.1
2.04	50 ± 1	5	350	27	2.436	65.8	18.8
2.04	50 ± 1	10	350	23	2.099	48.3	13.8
2.04	50 ± 1	15	350	25	4.525	113	32.3
2.04	50 ± 1	20	350	29	5.043	146	41.8
2.04	50 ± 1	30	350	33	4.228	140	39.9
3.14	40 ± 1	5	350	25	3.946	98.65	28.2
3.14	40 ± 1	10	350	28	2.573	72.044	20.6
3.14	40 ± 1	15	350	29	4.443	128.847	36.8
3.14	40 ± 1	20	350	32	4.069	130.208	37.2
3.14	40 ± 1	30	350	35	3.618	126.63	36.2
3.14	50 ± 1	5	350	21	3.895	81.795	23.4
3.14	50 ± 1	10	350	26	2.973	77.298	22.1
3.14	50 ± 1	15	350	24	2.656	63.744	18.2
3.14	50 ± 1	20	350	29	3.54	102.66	29.3
3.14	50 ± 1	30	350	32	4.172	133.504	38.2

The mass balance of Rh at pH = 2.04 and 40 ± 1°C ranged from 61.8 to 72.3%. The respective values the same pH and 50 ± 1°C ranged from 63.0 to 70.1% of the original Rh amount (data not shown). Therefore

increase in the extraction temperature resulted decreased maximum extraction efficiencies for Rh when the pH of the feed phase was around 2.00. The mass balance of Rh at pH = 3.14 ranged from 53.0 to 80.4% regardless of the extraction temperature. Therefore the Rh extraction performs best with the optimised ELM at 22 ± 1°C. A more detailed examination of the mass balance was conducted at 21 ± 1°C. The ELM with approximately 30 g/L PIB as described in section 3.5.1.2. The results are shown in Table 3.8.

Table 3.8. Percentage mass balance after extraction of rhodium using the ELM with 30 g/L PIB at pH = 2.04 or 3.14.

pH	Time (mins)	Initial mass (mg)	Final mass (mg) in the stripping phase	Final mass (mg) in Waste water	% Mass balance
2.04	5	350	91.0	157	70.8
2.04	10	350	95.1	140	67.1
2.04	15	350	113	141	72.4
2.04	20	350	133	94.1	64.9
2.04	30	350	183	77.7	74.6
3.14	5	350	78.7	157	67.2
3.14	10	350	93.9	142	67.5
3.14	15	350	108	136	69.7
3.14	20	350	139	124	75.2
3.14	30	350	188	98.7	81.8

As can be seen, the mass balances ranges from 61.9 to 81.8% of the initial Rh amount present in the model side-stream. The mass balance depends strongly on the stirring time and the pH of the feed phase. In comparison to the higher extraction temperatures, the percentage of Rh extracted from the spent side-stream at 21 ± 1°C increased as a function of time and reached a maximum after 30 minutes of extraction. This is probably going to make the extraction more predictable and thus the commercial process should be run at 21 ± 1°C. To investigate the reasons for the above-mentioned observations in more detail, micrographs of the microdroplets' structure were taken of the ELM samples incubated at 40 ± 1°C and 50 ± 1°C. The results are shown in Figures 3.10 and 3.11, depicting that the diameters of the microdroplets were outside of the ideal 1-3 µm interval (Tandlich, 2009). The average microdroplet diameter was 5.41 ± 1.03 µm, suggesting an increase in the average size of the microdroplets.

At the same time, more extreme diameters were observed as demonstrated by the highest diameter of 35.27 µm which was measured after extraction at 40 ± 1°C for 30 minutes. Similar observations were made at pH = 3.08 and for both pH values of the extracted side-stream 50 ± 1°C, with the average microdroplet size equal to 7.86 ± 2.67 µm (Figure 3.11). Besides this, the microdroplets were found to coalesce more than at 21 ± 1°C (see Figures 3.10 and 3.11). The increase in the microdroplet diameter was most likely caused by the absorption of increased volume of water by the stripping phase. On the other hand, the increased apparent coalescence of the microdroplets probably resulted in the decreased/more erratic interfacial area for the mass transfer of Rh through the diluent part of the ELM. This in turn could have contributed to the fluctuating dependence of Rh recovery on the extraction time. The increase in extraction temperature is likely to have led to rise in the vapour pressure of the kerosene and toluene (Tandlich and Zuma, 2012). This might have further compromised the stability of the ELM and led to the observed fluctuating and decreased extraction efficiencies for Rh. Thus any scale-up of the proposed technology will have to be conducted at ambient temperature.

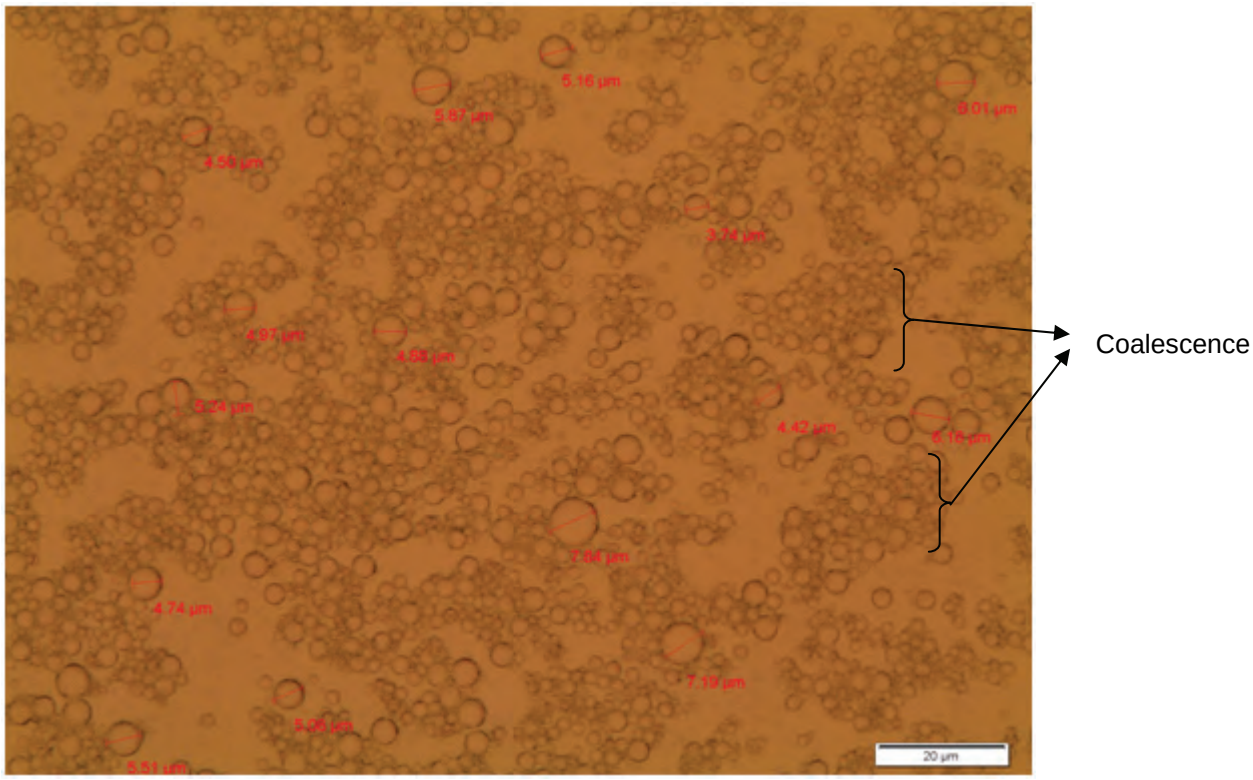
The final experiment in the extraction of Rh from model side-streams was the assessment of multiple extractions performed at 21 ± 1°C. Two or three consecutive extractions were done with the optimised 30.000 g/L PIB ELM as described in section 3.3. Fresh ELM was used in each consecutive extraction at pH 2.01 and 3.08. The loaded ELM was demulsified at 50 ± 1°C for 24 hours, and the addition of PEG was equal to 10 *g*. The results of the ICP analyses are shown in Table 3.9.

Table 3.9 shows that complete removal of Rh from the treated side-stream was achieved after two extraction steps with the optimised ELM.

Table 3.9. Extraction efficiency of Rh at varying pH values of the spent side-stream for consecutive ELM extractions in the Taylor-vortex column.

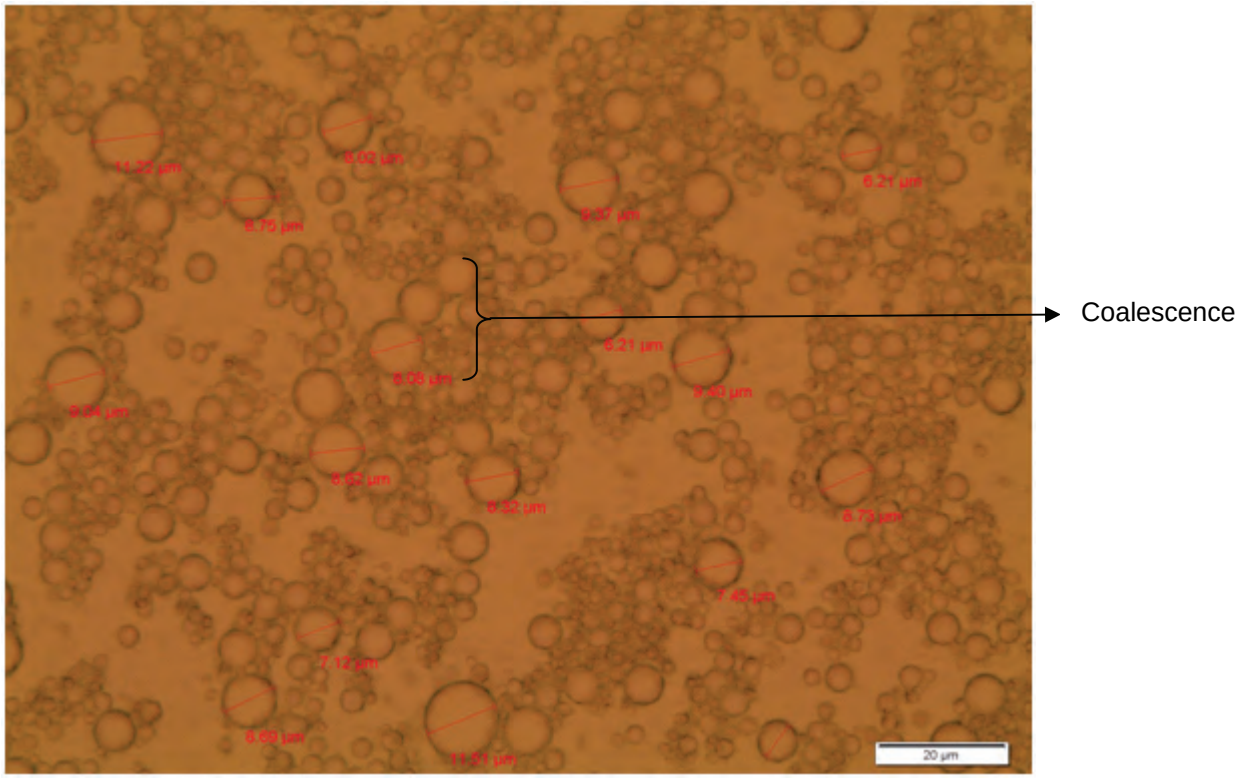
pH[a]	C_0(Rh) [b] (µg/mL)	M_0(Rh)[c] (µg)	M_1(Rh)[d] (µg)	M_2(Rh)[e] (µg)	M_3(Rh)[f] (µg)	P_2(Rh)[g] (%)	P_3(Rh)[h] (%)
2.01	7.00	350	205	366	376	104.4	107.3
3.08	7.00	350	185	345	380	98.7	108.7

[a] Initial pH value of the treated side-stream
[b] Initial Rh concentration in the treated side-stream
[c] Initial Rh amount
[d] Rh amount extracted after one extraction
[e] Rh amount extracted after two extractions
[f] Rh amount extracted after three extractions
[g] Percentage Rh amount extracted after two extractions
[h] Percentage Rh amount extracted after two extractions

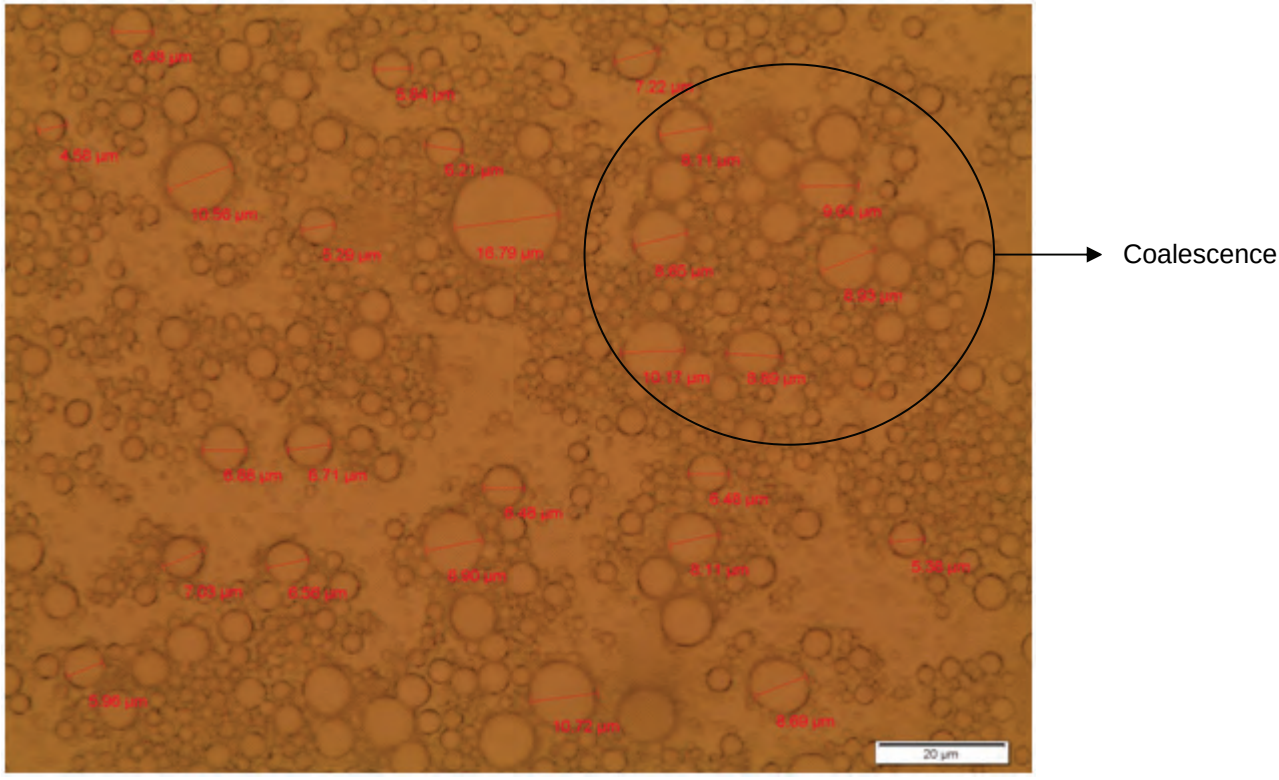


(a)

Figure 3.10. The micro-droplet sizes of ELM at 40 ± 1°C with side-stream pH equal to 1.87 after 5 minutes of extraction (a), 10 minutes of extraction (b), 15 minutes of extraction (c), 20 minutes of extraction (d) and 30 minutes of extraction (e).

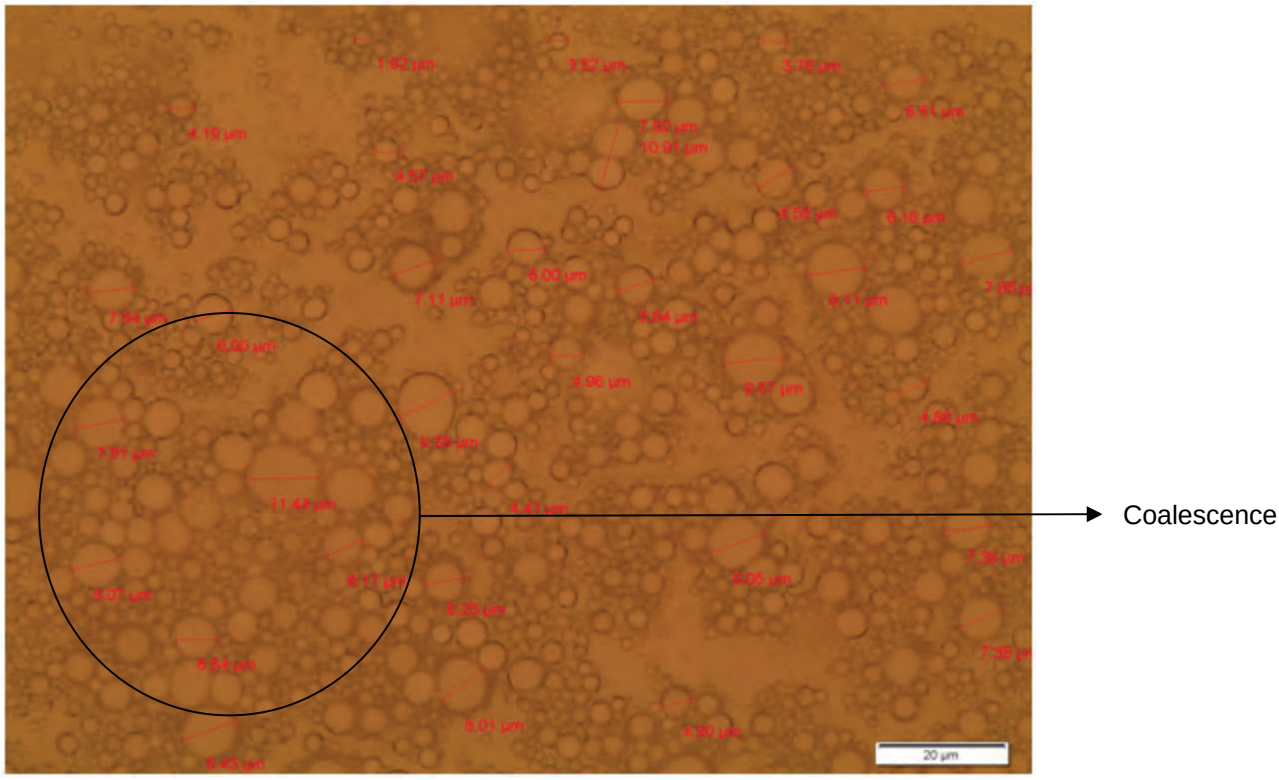


(b)

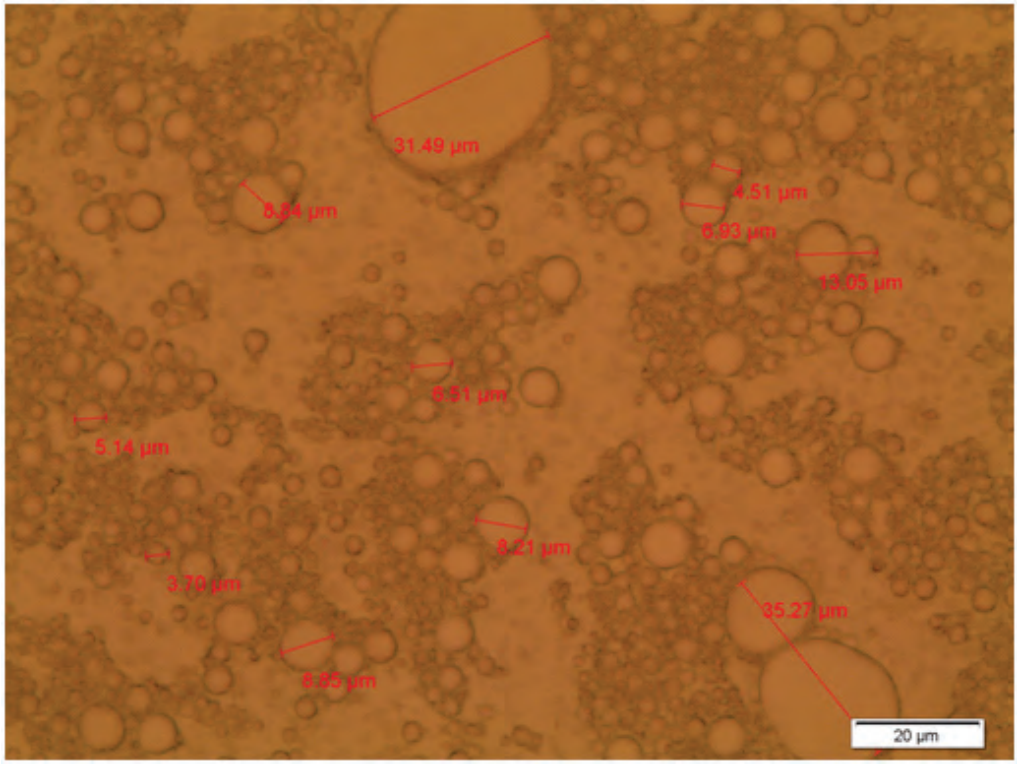


(c)

Figure 3.10 (Continued). The micro-droplet sizes of ELM at 40 ± 1°C with side-stream pH equal to 1.87 after 5 minutes of extraction (a), 10 minutes of extraction (b), 15 minutes of extraction (c), 20 minutes of extraction (d) and 30 minutes of extraction (e).

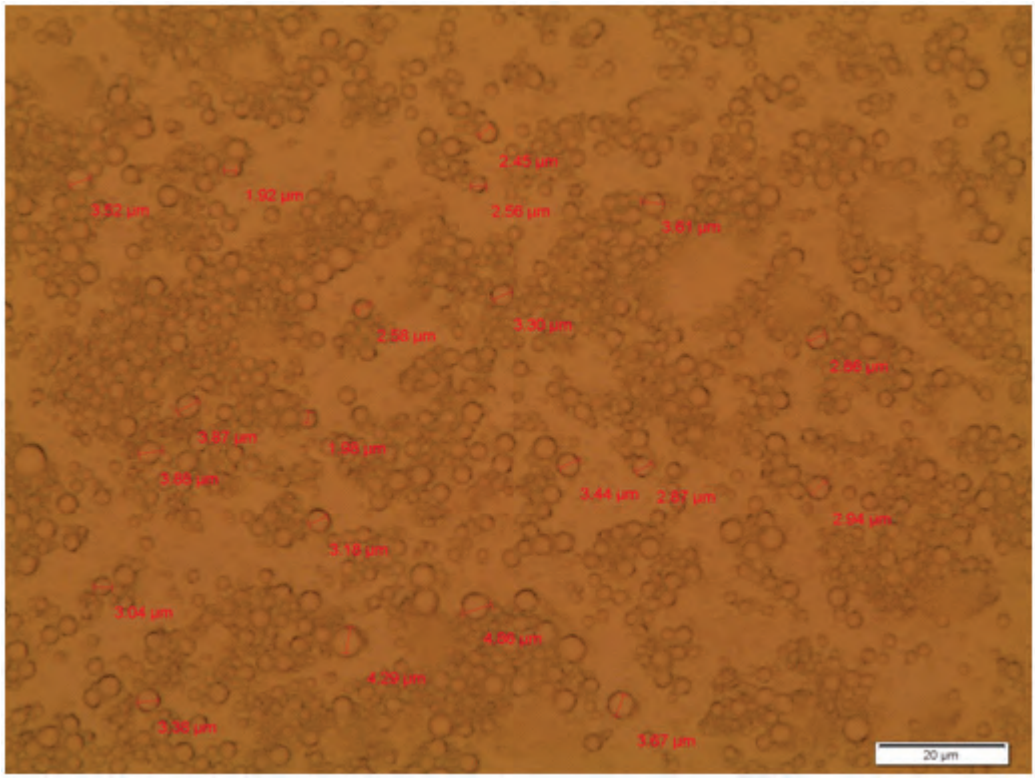


(d)

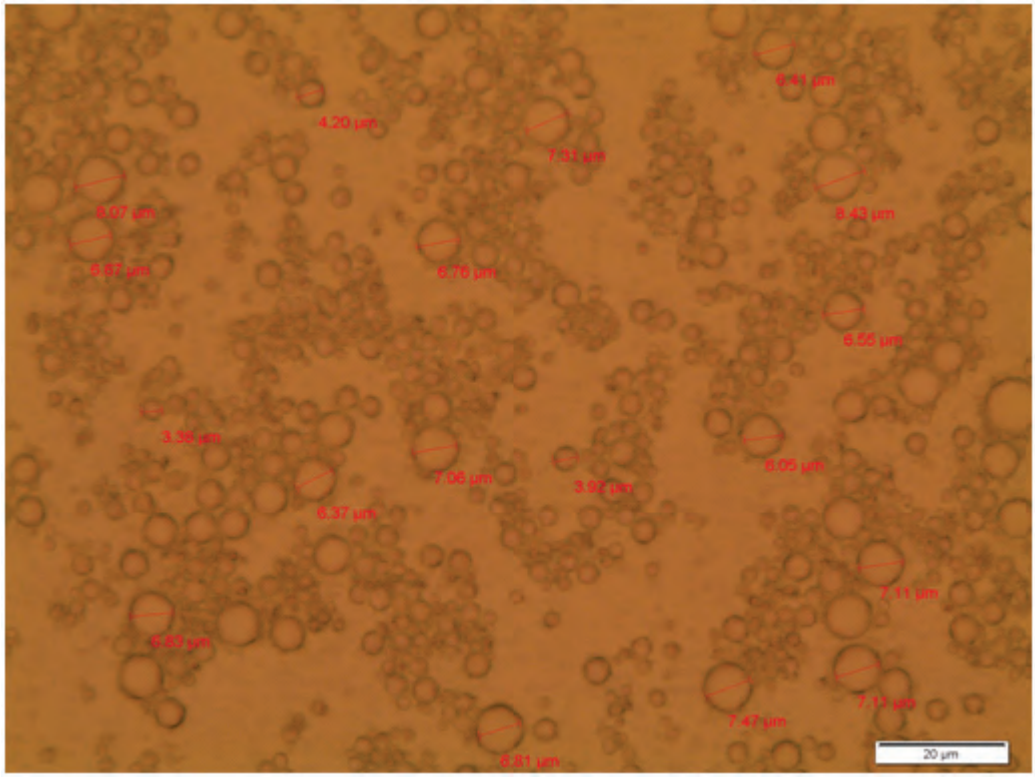


(e)

Figure 3.10 (Continued). The micro-droplet sizes of ELM at 40 ± 1°C with side-stream pH equal to 1.87 after 5 minutes of extraction (a), 10 minutes of extraction (b), 15 minutes of extraction (c), 20 minutes of extraction (d) and 30 minutes of extraction (e).

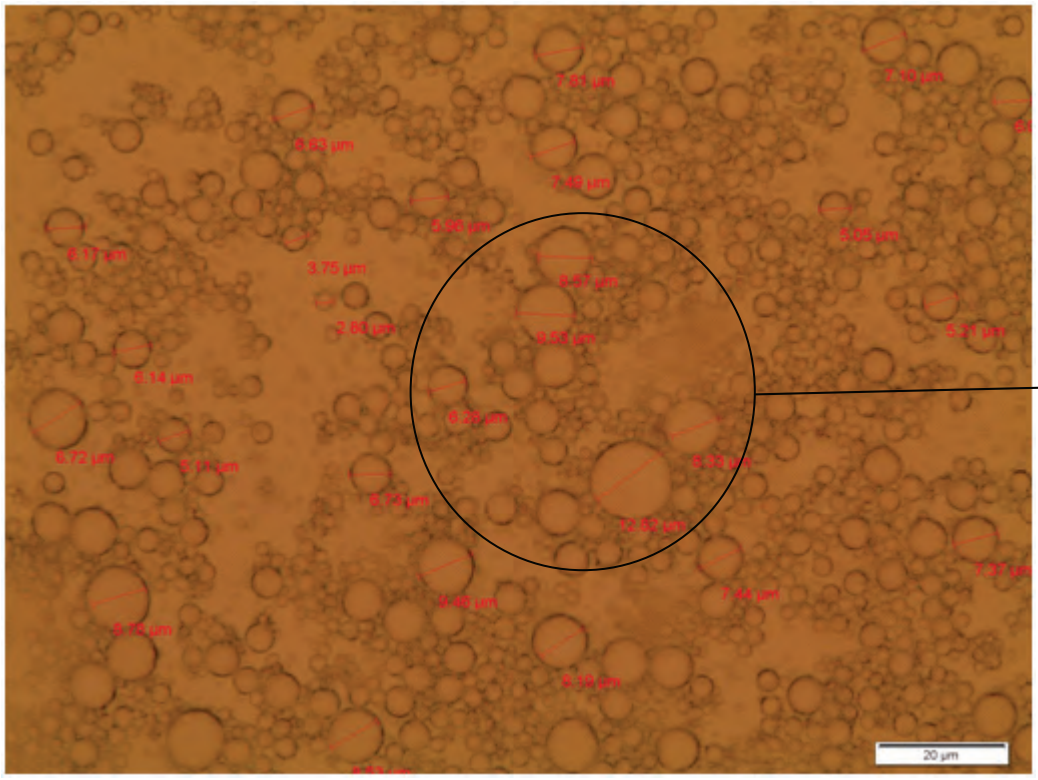


(a)

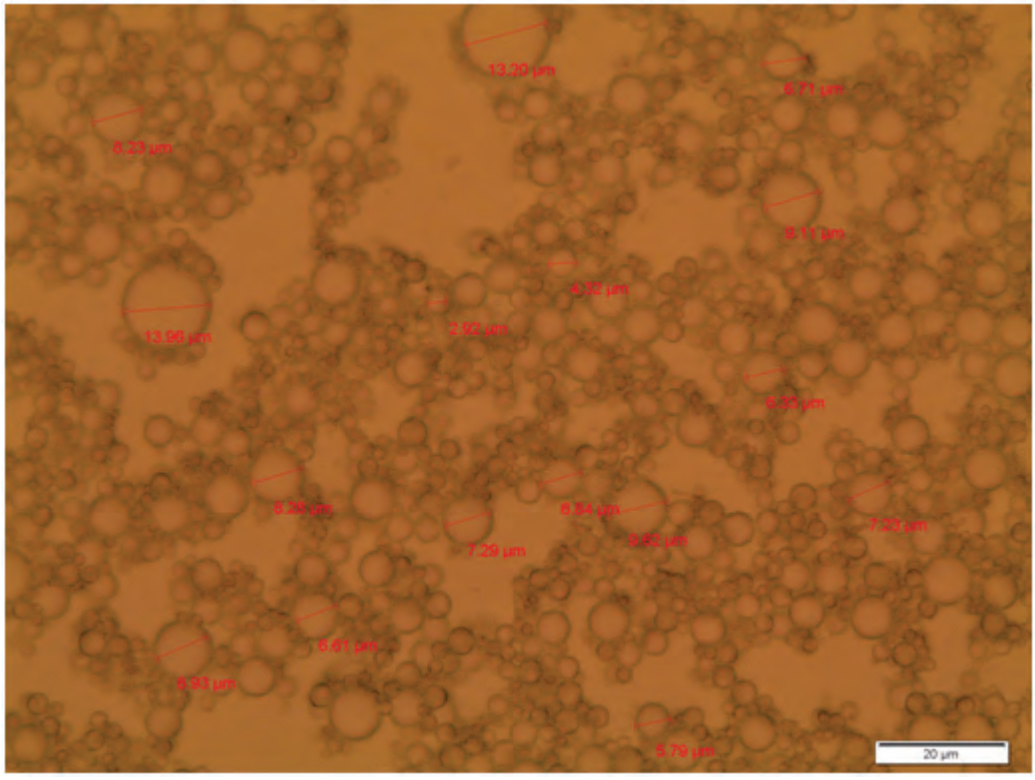


(b)

Figure 3.11. The micro-droplet sizes of ELM at 50 ± 1°C with side-stream pH equal to 1.87 after 5 minutes of extraction (a), 10 minutes of extraction (b), 15 minutes of extraction (c), 20 minutes of extraction (d) and 30 minutes of extraction (e).

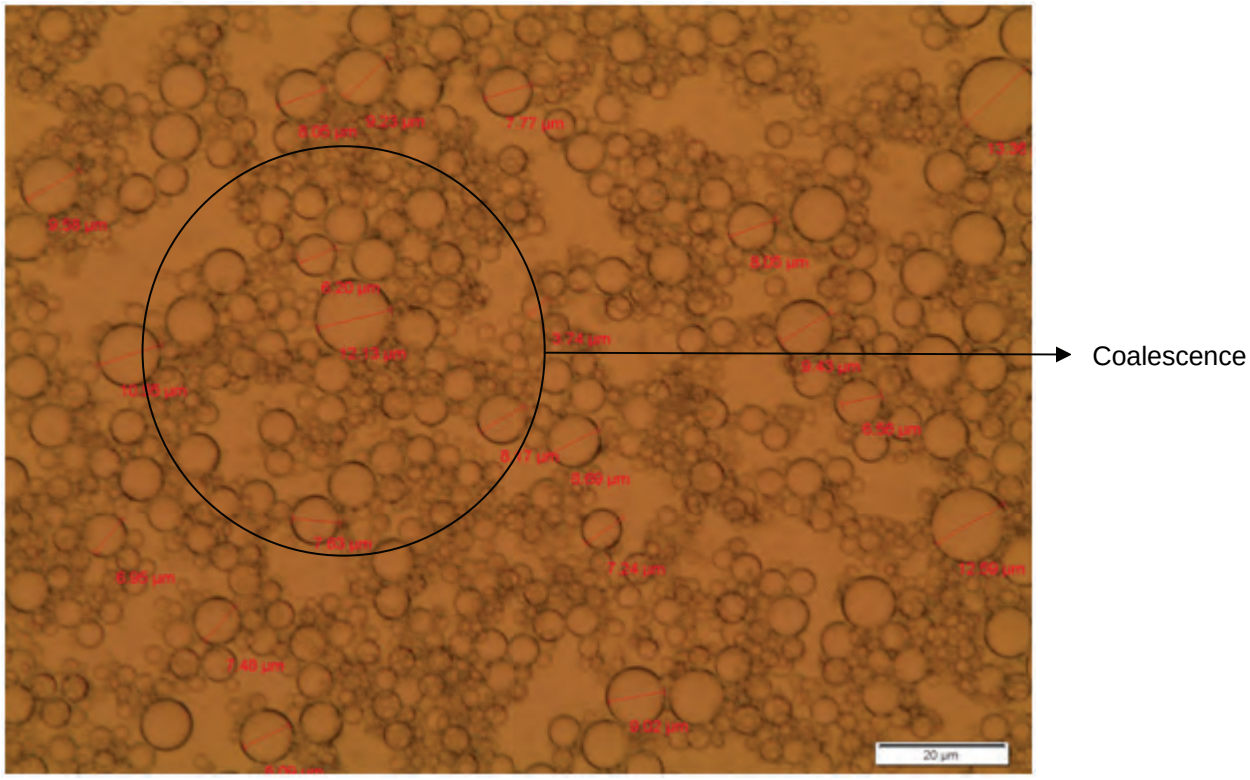


(c)



(d)

Figure 3.11 (Continued). The micro-droplet sizes of ELM at 50 ± 1°C with side-stream pH equal to 1.87 after 5 minutes of extraction (a), 10 minutes of extraction (b), 15 minutes of extraction (c), 20 minutes of extraction (d) and 30 minutes of extraction (e).



(e)

Figure 3.11 (Continued). The micro-droplet sizes of ELM at 50 ± 1°C with side-stream pH equal to 1.87 after 5 minutes of extraction (a), 10 minutes of extraction (b), 15 minutes of extraction (c), 20 minutes of extraction (d) and 30 minutes of extraction (e).

CHAPTER 4: SCALE-UP CONSIDERATIONS

Figure 3.9 contains a detailed description of the Taylor-vortex column used in the extraction experiments. Based on the discussion above, the scaled-up form of the instrument will be optimally run at 20°C. Given the nature of the apparatus, the mass balances and the percentage of Rh extracted in a single-step extraction, the scaled-up process will have to be run as a sequential arrangement of two to three single ELM based extraction. Such experiments are currently underway and will be reported upon in the final report from the project. Any such scale up will be simple from the constancy of the Taylor criterion (*Ta*) as defined in Eq. (13).

$$Ta = \frac{2\pi N}{\phi}\left(R_{\text{rotor}}\right)^{1/2}\left(d_{\text{ag}}\right)^{2/3} \tag{13}$$

In Eq. (13), where R_{rotor} is the radius of the inner cylinder of the Taylor column, that is, rotor (m), N is the rotational speed (s^{-1}), dag is the diameter of the space between the inner and the outer cylinders of the Taylor-vortex column (m). Given the information in Figure 3.9 and using assuming that the kinematic viscosity of the ELM is equal to that of kerosene (0.0037 Pa.s; Roymech, 2013), the Ta for the system used in this study will be equal to 24.1. Parameters that will change with scale-up are the energy requirements. These will originate from the mixing during ELM preparation and demulsification, stirring during the extraction process and the heating of the loaded ELM during demulsification and rhodium recovery. Therefore the energy requirements for the scaled-up version of the Taylor-vortex column in Figure 3.9 will be as follows.

$$P = \frac{\left\lfloor V_{\text{scale-up}} \right\rfloor}{\left\lfloor V_{\text{laboratory}} \right\rfloor} \times \left(P_{\text{shaker}} \times t_{\text{shaker}} + P_{\text{stirrer}} \times t_{\text{stirrer}} + P_{\text{oven}} \times t_{\text{oven}}\right) \tag{14}$$

In Eq. (14), the terms P stand for the work done by a given instrument (Watts) and the terms t stand for the time required to perform a given operation (hours). The first fraction in Eq. (9) stands for the size factor with V representing volume of the operation (dm^3). Subscript of scale-up stands for volume of the treated side-stream in the scaled-up version of the Taylor-vortex column, while the subscript laboratory stands for the volume in its laboratory version. Stirrer stands for the extraction apparatus, oven for the demulsification oven and the shaker for the shaking.

The energy requirements for 50 mL of the model side-stream are based on the following figures: 115 minutes/1.92 hours for the shaking, 24 hours for the oven and 30 minutes for the stirrer. The respective work values are 60 Watts for the shaker and the stirrer; and 250 W for the oven. Thus the energy consumption for the 50 mL of the model side-stream is equal to 145 Wh. Using Eq. (14), the energy consumption for the extraction of 10000 litres can be estimated at 2.9 × 104 kWh.

CHAPTER 5: TOXICITY TESTING

5.1 INTRODUCTION

Ethylenediaminetetraacetic acid tetrasodium salt dihydrate (EDTA) is a mono- to tetradentate ligand depending on the pH of the aqueous phase (Kari and Giger, 1996; Repo *et al*., 2011). It has a high affinity for heavy metals (e.g., Cu, Fe, Pb and Co), which are widely used in industries and agriculture (Wu *et al*., 2011). EDTA is used to prevent precipitation of metals at high pH through chelation (Kołodyńska *et al*., 2008). This should include Rh as it is precipitated if the pH of the aqueous phase increases above 4.00 (Barbosa *et al*., 2007). EDTA may affect the results of metal toxicity which will be considered in data evaluation from the *Daphnia pulex* acute test (Bergers and de Groot, 1994; Guilhermino *et al*., 1997). However, it is not possible to use the standard microbial toxicity tests, such as Microtox and Biotox, to assess the toxicity of the final effluent/spent side-stream after the ELM extraction of Rh from this matrix. The pH adjustment to neutral values is needed and the EDTA chelation is needed to stabilise the Rh solution at these pH values.

At the same time, mammalian (including human) toxicity of EDTA is low due to its low absorptivity and this chemical compound is not a carcinogen (Kari and Giger, 1996; Sorvari and Sillanpää, 1996). Thus even though the toxicity of spent side-stream after the ELM extraction process will be affected by the EDTA, if this influence is quantified and taken into account, a general estimate about the Rh toxicity to environmental compartments it is discharged into should be feasible. The preliminary toxicity assessment of the Rh spent side-stream is performed in this chapter using the acute *Daphnia pulex* toxicity test. The appropriateness of the acute testing is that most metal refinery operations aim to work on the zero-discharge principle, i.e. any spillage of the Rh-bearing materials and side-streams into the environmental will be the result of industrial accidents.

5.2 CHEMICALS AND TEST ORGANISM

The EDTA and the standardised Rh were purchased from Sigma-Aldrich (Johannesburg, South Africa), while the *Daphnia pulex,* chemicals, and consumables for the 48 hour acute *Daphnia pulex* toxicity test were purchased from the Institute for Water Research at Rhodes University (Grahamstown, South Africa. For the acute 48-hour toxicity testing, the *Daphnia pulex* was cultivated in the dilution water described in ISO 6341 in the temperature of 20 ± 2°C in the light rhythm of 16 hours light and 8 hours dark. The green alga *Chlorella* sp. was used as a food source. The cultures were prepared in 2 L containers, with an initial population density of one daphnid per 100 mL. The neonates were separated and used for toxicity determination. The organisms were not fed during the experiments.

5.3 STABILIZATION OF RH AT NEUTRAL pH

Preliminary experiments indicates that Rh was unstable in solutions when the pH of the aqueous phase increased above 3.14. This confirmed the literature data (see section 5.1 for details). On the other hand, the Daphnia pulex acute toxicity test is conducted at neutral pH values. Thus the first partial task in the toxicity testing part of this deliverable was to stabilise the concentrations of Rh in its aqueous solutions around pH 7.00. For this purpose, solutions of EDTA in MilliQ water with the EDTA concentrations ranging from 0 to 3 g/L were prepared by dissolving between 0.0000 and 0.7500 g of EDTA in 100 mL of 0.01 M HCl and transferred into a 250 mL volumetric flask. The volume was made up to mark with 0.01 M HCl and 50 mL of this solution was put into the Erlenmeyer flask and 5 mL of 1000 mg/L standardised Rh solution was added.

The solution was stored at 20 ± 2°C for 72 hours and ICP readings were then taken from this solution for Rh concentration, and any precipitation was observed visually. Another solution was prepared in the same fashion as stated above, but the pH of the final solution was adjusted to 8.4 with 2.5 M NaOH. The solution was incubated at 20 ± 2°C for up to 3 days. Precipitation and Rh concentrations were assayed periodically over the 72-hour period. No precipitation was observed in any of the solutions and the Rh concentration remained stable within 20% of the initial value only if the concentration of EDTA was equal to 3 g/L. Therefore the solution prepared in this manner was considered suitable for use in the acute *Daphnia pulex* test.

5.4 PREPARATION OF THE MODEL MINING SIDE-STREAM

The first model mining side-stream was a solution of 7 mg/L of Rh which was prepared in 0.01 M HCl (pH 1.87) by dilution of the standardised Rh solution with initial concentration of 1000 mg/L. A second model mining side-stream was prepared in the same fashion, but 0.001 M HCl (pH = 2.92) was used as the solvent. The model mining side-streams containing Rh were mixed with the optimised ELM with 30.000 g/L PIB (see section 3 for details) and both were put into the Taylor-vortex column in the ratio 1:5 (10 mL ELM : 50 mL the model mining side-stream). The solutions were then stirred in the Taylor vortex column using a speed of 250 rpm for 30 minutes. The ELM/feed phase mixture was then taken out of the column and placed in a conical flask. It was allowed to stand at 21 ± 2°C until phase separation was observed between the spent model mining side-stream and the loaded ELM. The spent mining effluent was always put aside and stored at 5 ± 2°C until the ICP mass balance analyses and the toxicity testing could be conducted. The procedure was repeated until 250 mL of the aqueous phase was collected for both model mining side-streams. All samples were always analysed within 72 hours of production.

5.5 STOCK SOLUTIONS FOR THE *DAPHNIA PULEX* TOXICITY DETERMINATION

For each of the model mining side-streams, 200 mL of the spent effluent was brought to room temperature and transferred into a 1000 mL acid-washed glass beaker. Then 3 g of EDTA was added to each of the solutions and salt crystals were completely dissolved. The volume was made up to approximately 900 mL with MilliQ water and pH was adjusted to 6.8 using 2.5 M NaOH. The solutions were then transferred into the acid-washed 1000 mL volumetric flask and the volume was made up to the mark with MilliQ water. Each of the two solutions had a final pH of around 6.90. Both solutions were then stored at 5 ± 2°C for 120 hours. They were examined under optical microscope at magnification of 400 x for any traces of crystals forming and ICP readings were taken to confirm the concentration. No crystal formation was observed and the Rh concentration remained within 20% of the initial value.

Toxicity of the mining effluents had to be evaluated in comparison to the EDTA baseline (see section 3.2 for details). Therefore 1000 mL of a 3 g/L EDTA solution in MilliQ water was prepared. The pH was adjusted to 6.90 with 5 M HCl and this value remained stable at 5 ± 2°C for 120 hours. It was thus used in further toxicity testing without any further modifications.

The test concentration of both mining effluents and the EDTA solution, 25 mL of each of the stock solutions (see previous section) was pipetted into an acid-washed 200 mL volumetric flask. All three solutions were then made up to the mark using the *Daphnia pulex* growth medium to make a concentration of 12.5% of the stock solution. The resulting mixtures were hand-shaken to achieve complete content's mixing and then further subdivided into four batches of 50 mL each. Each of the 50 mL aliquots was poured into a separate 100 mL beaker and 5 Daphnids were put into each solution. This procedure was repeated using 25%, 50%, 62.5%, 87.5% and 100% of each of the spent mining effluent solutions. Next all Daphnids were exposed to the test solutions for 48 hours. Their survival was inspected after 24 hours of exposure and again after 48 hours, when counting of results was again performed. A control experiment was set up in analogical fashion but the *Daphnia pulex* growth medium was the only one. All toxicity experiments were performed in duplicate.

5.6 ACUTE TOXICITY TESTING RESULTS

Results for the EDTA solution and the spent mining effluents are shown in Tables 5.1-5.3. The Daphnids were well adapted to the test conditions as 100% survival was observed in the control experiment. The data clearly shows that the addition of 3 g/L of EDTA led to minor toxicity to *Daphnia pulex* as only the undiluted solution led to complete die-off of the Daphnids (see Table 5.1 for details). All test organisms died after 48 hours of exposure to the mining effluent with the original pH = 1.87, while 10-60% survival rates were observed at the mining spent effluent with original pH of 2.92 if the strength of the effluent ranged from 12.5 to 62.5% (see Tables 5.2 and 5.3).

Table 5.1. The percentage survival of *Daphnia pulex* after 24 hours and 48 hours after exposure to 3 g/L EDTA.

Test concentration (%)	% survival after 24 hrs	% survival after 48 hrs
12.5	100	100
25	100	95
50	85	70
62.5	70	50
87.5	45	25
100	30	0
control	100	100

Table 5.2. The percentage survival of *Daphnia pulex* after 24 hours and 48 hours after exposure to aqueous phase effluent of mining waste water made by a solution of Rh at pH = 1.87 after extraction of Rh using the ELM.

Test concentration (%)	% survival after 24 hrs	% survival after 48 hrs
12.5	85	0
25	90	0
50	70	0
62.5	45	0
87.5	15	0
100	0	0
control	100	100

Table 5.3. The percentage survival of *Daphnia pulex* after 24 hours and 48 hours after exposure to aqueous phase effluent of mining waste water made by a solution of Rh at pH = 2.92 after extraction of Rh using the ELM

Test concentration (%)	% survival after 24 hrs	% survival after 48 hrs
12.5	100	65
25	90	45
50	65	20
62.5	45	10
87.5	15	0
100	0	0
Control	100	100

The concentration of Rh was comparable in both solutions and averaged 2.5 ± 0.8 mg/L. The extraction efficiencies between pH of 1.87 and 2.92 were also comparable (see previous section). Therefore it can be concluded that some organic components of the ELM, most probably toluene, the molecules carried over into the spent mining effluent and caused the observed die off. This was probably observed to a higher extent at pH of 1.87 then at pH of 2.92, providing an explanation of the results in Tables 5.2 and 5.3. The discharge of the spent Rh side-stream should thus be discouraged and prevented at all costs.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

Results show that the complete extraction of Rh is possible from model side-streams, namely hydrochloric acid (HCl) solutions containing 7 mg/L of Rh. This is achieved by the use of the optimised ELM where the diluent was 30% solution of toluene in kerosene and the other component concentrations were as follows: 30.000 g/L (w/v) PIB, 10.870 g/L (m/v) of TOA and 51.001 g/L (m/v) of SPAN 80. This diluent phase was then mixed with 2 M HNO_3 (stripping phase) in a ratio of 2:1. The volumetric ratio of treated side-stream and the ELM was 5:1 and 98.7 to 108.7% of the initial Rh amount was recovered in the stripping phase after chemical demulsification. This was performed with polyethylene glycol with molecular weight of 400 g/mol (PEG) at 50 ± 1°C for 24 hours. Major carryover of the diluent components into the stripping phase and side-stream was observed. Using the COD digestion stoichiometry, the aqueous solubilities and the measured ELM components concentrations, it is estimate that the carry-over was mostly from the TOA, toluene and PEG. The final spent side-stream should not be discharged into the environment as the acute *Daphnia pulex* toxicity testing results have shown.

6.2 RECOMMENDATIONS

Commercial use of the ELMs in extraction processes is often hindered by the instability of the stripping phase microdroplets, due to the absorption of water from the feed phase into the ELM matrix. The classical solution is to increase the surfactant concentration in the ELM. This increases the stability of the microdroplets, but also leads to a decrease in mass transfer rates during metal extraction. Thus a novel solution must be found to address this problem. One of the solutions listed in literature for the extraction of base metals is the use of non-Newtonian liquids as ELMs. The simplest way to construct a non-Newtonian is the addition of a polymer such as polyisobutylene (PIB) to the ELM diluent. The shear stress is further decreased by the extraction contactor being the Taylor-vortex column (see Figure 1.1 for details)

Limitations of the results from the project include the lack of competition studies, more in depth examination of Rh extraction from the real mining/metal refinery effluents and the lack distribution isotherm of Rh in the ELM/side-stream system. Competition studies will have to be performed with other PGMs before any scale-up or any industrial application of the optimised ELM and Taylor-vortex column can be launched. The competition studies are currently underway and should be completed in the near future, as will be the distribution isotherm of Rh in the ELM/side-stream treatment system. Preliminary experiments have indicated that the extraction efficiency of Rh from side-streams is going to be influenced by the high concentrations of chloride anions and the sorption of the Rh-chloro complexes on the glass matrices of the extraction vessels. The nature of this effect should be addressed if future projects with similar scope are funded.

CHAPTER 7: REFERENCES

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