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Towards continuous online oil-in-water measurement for regulatory purposes

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Towards Continuous Online Oil-in-Water Measurement for Regulatory Purposes

By

Zak Latif

EngD

January 2020

Towards Continuous Online Oil-in-Water Measurement for Regulatory Purposes

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A thesis submitted in partial fulfilment of the University's requirements for the Degree of Doctor of Engineering

Certificate of Ethical Approval

Applicant:

Zak Latif

Project Title:

Towards Continuous Online Oil-in-Water Measurement for Regulatory Purposes

This is to certify that the above named applicant has completed the Coventry University Ethical Approval process and their project has been confirmed and approved as Low Risk

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Abstract

For every barrel of crude oil extracted, four barrels of water is also produced (Robertson & Jahsen, 2006). This water, known as produced water, is found within reservoirs alongside the oil, gas and sand. In all situations, the measurement of oil-in-water concentration is important. For discharge, the measurement of oil-in-water is governed by environmental regulations depending on the location of the field. With the global interest turning towards cleaner sources of energy and reducing environmental impact, regulations relating to crude oil discharge are becoming stricter. Due to the challenges with conventional sampling techniques, alternative methods to measure oil-in-water concentration for regulatory compliance need to be considered. The use of online techniques to replace laboratory analysis has been a growing trend throughout most industries, with the need to gather more data on a continuous basis. However, the use of online techniques for measuring oil-in-water comes with many challenges. Two are stated below:

- Being able to demonstrate that an online technique is capable of measuring oil-in-water concentration which is statistically equivalent or better than currently accepted reference methods.
- Lack of knowledge surrounding measurement uncertainty in both the offline reference techniques and the online methods.

To overcome these challenges, the research focuses on both online oil-in-water measurement techniques and the current laboratory reference methods. As an outcome of the research, the following contributions to knowledge in this topic are summarised.

- The design and construction of a novel facility at NEL, capable of simulating produced water conditions to allow testing of online measurement techniques, was successfully completed.
- Significant parameter effects on several oil-in-water continuous measurement techniques were determined, showing gaps in established measurement principles.
- The effect of droplet size on Laser Induced Fluorescence was characterised, allowing for an empirical based relationship based on droplet size, concentration and temperature to be developed. A reduction of uncertainty from up to ±80% to ±8.5% at ideal conditions was noted.
- Development of a novel method for calibrating and verifying online techniques using fluorescent tracers to reduce uncertainties and improve reliability of methods.
- Undertaken an uncertainty analysis of reference techniques and online measurements, demonstrating significant increase of uncertainty due to sampling. Several experiments were also conducted to determine the impact of various parameters on the overall uncertainty of offline oil-in-water concentration measurement due to sampling.
- Methodology for calibrating online methods using a dosing method to counteract issues with current techniques due to high uncertainties with reference methodology is proposed.

This thesis ultimately provides guidance for continuous online oil-in-water measurement as a method for regulatory reporting as current UK guidance is currently lacking several elements.

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Abbreviations

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BAT	Best Available Technology
BEIS	Department for Business, Energy and Industrial Strategy
BEP	Best Environmental Practice
BSI	British Standards Institution
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CCD	Charge-Coupled Device
COD	Chemical Oxygen Demand
CV	Coefficient of Variation
DAQ	Data Acquisition
DECC	Department of Energy and Climate Change
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
GC	Gas Chromatography
IMO	International Maritime Organization
IR	Infrared
ISO	International Organization for Standardization
LED	Light-Emitting Diode
LIF	Laser Induced Fluorescence
MARPOL	Maritime Pollution
NEL	National Engineering Laboratory
NMR	Nuclear Magnetic Resonance
NPD	Norwegian Petroleum Directorate
OIW	Oil in Water
OSPAR	Oslo/Paris Convention
PAH	Polyaromatic Hydrocarbons
ROV	Remotely Operated Underwater Vehicle
RSD	Relative Standard Deviation
SPE	Solid Phase Extraction
TEX	Toluene, Ethylbenzene and Xylene
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TTCE	Tetrachloroethylene
UNEP	United Nations Environment Programme
UV	Ultraviolet

1 Introduction

Even as global interest turns towards renewable sources, most of the world's energy demands are still covered by crude oil and natural gas (BP, 2019). Due to this, the Oil and Gas Industry continues to be one of the largest energy producers globally. The processes involved in the production of crude oil and natural gas create large amounts of waste streams that need to be considered. These sources of waste vary from field to field, with environmental regulations controlling the eventual discharge of the sources.

For every barrel of crude oil extracted, a current estimate of 4 barrels of water is also produced (Robertson & Jahsen, 2006). This water, known as produced water, is found within reservoirs alongside the oil, gas and sand. Depending on the location and type of reservoir, the amount of water can vary, however as a field ages, the produced water typically increases. The water produced needs to be separated from the oil and/or gas, treated and then disposed of. Two main methods of disposal are used: re-injection or discharge. Re-injection involves injecting the produced water back into the reservoir, leading to increased reservoir pressure and therefore greater oil recovery. Discharge typically refers to offshore fields where the water is disposed of back into the ocean.

In all situations, the measurement of oil-in-water concentration is important. For re-injection scenarios, the oil-in-water concentration is required by reservoir engineers to ensure the well does not fracture or plug. For discharge, the measurement of oil-in-water is governed by strict environmental regulations depending on the location of the field. With the global interest turning towards cleaner sources of energy and reducing environmental impact, regulations relating to crude oil discharge are becoming stricter. At present, the oil-in-water concentration discharge limit for the North Sea is 30 mg/L (OSPAR, 2011), with varying levels depending on global location.

Oil-in-water concentration measurement is currently carried out by sampling the produced water flow, which is then analysed in a laboratory via an accepted reference technique. Depending on the amount of produced water being discharged, the number of samples required can vary. In the UK, the number of samples is covered by the regulatory guidance '*Methodology for Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges*' (BEIS, 2016), which states that manned installations discharging more than two tonnes of oil-in-water are required to collect at a minimum, two samples per day. These samples however only show a small window of the crude oil being discharged, which can vary throughout a given period. For unmanned and subsea applications, the method of sampling and laboratory analysis is very prohibitive, due to cost and availability.

Due to the challenges with conventional sampling techniques, alternative methods to measure oil-in-water concentration for regulatory compliance need to be considered. The use of online techniques to replace laboratory analysis has been a growing trend throughout most industries, with the need to gather more data and information on a continuous basis. This can by demonstrated for process control, for example, where data allows decisions to be made online, with unfavourable conditions being detected quicker. Similarly, the need for online crude oil measurements in water can be demonstrated throughout many parts of the oil and gas production process, such as droplet size detection for treatment processes through to oil-in-water concentration for discharge or re-injection. The use of online techniques for measuring oil-in-water comes with many challenges however. Two are stated below.

- Being able to demonstrate that an online technique is capable of measuring oil-in-water concentration which is statistically equivalent or better than currently accepted reference methods.
- Lack of knowledge surrounding measurement uncertainty in both the offline reference techniques and the online methods.

Both these challenges are related, as using online techniques for regulatory reporting cannot be achieved until these are met.

To overcome these challenges, this thesis initially investigates different online techniques, and their ability to measure oil-in-water concentration online for regulatory reporting. Undertaking this investigation allowed for several techniques to be further developed to improve online oil-in-water measurement under certain conditions. The second part of the thesis focusses on determining the uncertainty of reference techniques and online measurements. In this part, the key parameters contributing to the uncertainty of different methods are found and quantified. Using these, a method for lowering the total uncertainty of oil-in-water measurement is discussed.

This thesis provides guidance for continuous online oil-in-water measurement as a method for regulatory reporting. Globally, the guidance will differ, however this work focuses on the regulations in the UK and North Sea. Typically, regulations from different countries have been based on the recommendations from the UK, which are generally stricter than other locations. Current guidance provided for the measurement of oil-in-water is currently lacking several elements, which this research looks to improve upon. Two key parameters are discussed as part of the guidance; online techniques and measurement uncertainty, however the information provided is limited and can be difficult for end users to interpret. The research provided in this report is intended to be submitted to the UK regulator, BEIS, as an official Guidance Note.

1.1 Drivers

Oil-in-water concentration is required to be measured in several industries, such as: Oil and Gas, Petrochemical, Agriculture and Pharmaceutical. Given the large number of applications that require oil-in-water measurement, there is increased demand for accuracy, reliability and speed of measurement. For the oil and gas industry, oil-in-water concentration is primarily used for produced water, which is typically either re-injection or discharged. In both situations, the concentration of oil-in-water is a critical parameter, i.e. for well protection (Turnbull & Yang, 1992) and oil contamination (Yang, 2011) respectively .

Other than decreasing uncertainty, there are other drivers towards the movement from conventional sampling to online techniques. Online measurements give continuous data which allow for operators to set-up better process control on their produced water treatment systems. This improvement in process control can allow for a decrease in oil-in-water concentration which reduces the requirement for expensive polishing treatment options.

Presently, only periodic sample information is reported to the regulators which can have bias and skewed data profiles. Data from online measurements negates this bias by reporting oil-in-water discharge data from a continuous measurement rather than spot samples. An increase of data collected by the regulators can also be an issue for some operators or applications, as accurate discharge information could lead to the average oil discharge for a platform or reservoir being increased, requiring further treatment. The challenge of how to report the continuous data also needs to be considered, as variations in measured oil-in-water concentration may change depending on what other processes are taking place. Fluctuations from the measuring instruments may also occur, depending on the technology used. Therefore, how to properly interpret and report the results needs be carefully considered. The current methodology of averaging the data points over a month would result in peak measurements being lost in the data. The guidance from regulators would also need to be considered when deciding how to report continuous oil-in-water measurements, as current monthly limits may be not be suitable for all situations.

Depending on the online technique used, the size of the oil droplets can be measured as part of the overall oil-in-water concentration. Oil droplet size information is critical for a number of aspects. Several produced water treatment techniques are based on separation, where droplet size is a key parameter on the effectiveness and speed of separation (Young, et al., 1994). In Produced Water re-injection, the oil concentration, along with solid concentration is often crucial to determine if the well will plug or be damaged (Barkman, 1972). The size distribution of oil droplets can affect how oil sheens are formed (ERIN; OCL, 2002).

With a low oil price, the economic viable price per barrel of oil produced needs to be carefully considered in new developments. With the world’s oil supply reducing, the ability to tap into new reservoirs in challenging conditions is becoming essential. One of the challenges currently facing the oil and gas industry is the ability to use unmanned installations, which can significantly reduce costs and allow marginal fields to be economically viable. The most challenging installation of this kind is in subsea environments, where the oil and gas are separated from the water and pumped back to topside. The water is then treated and re-injection back into the reservoir or discharged. This however leads to a key problem, the ability to measure oil-in-water concentration in unmanned platforms. For typical installations, the regulators in the UK allow samples to be collected on every visit in a specified pre-agreed frequency. This however cannot be achieved in subsea situations, where the ability to take samples is extremely limited. To collect samples subsea, a remotely operated vehicle (ROV) is required to be deployed at a cost of up to £250k per sample collected (Yang, 2017). To overcome this, an online oil-in-water monitor would be able to determine the concentration continuously and therefore significantly fewer samples would be required. The requirement of sampling has been known to be a limiting factor towards subsea development in the oil and gas industry.

1.2 Research Questions

This thesis aims to explore the use of online techniques for regulatory compliance monitoring of produced water, where current practice decrees only offline laboratory techniques suitable. This overall research goal is broken down into five research questions, which are as follows:

1. Can we simulate stable produced water conditions in an experimental facility? Can the droplet size be controlled to be within specified diameter ranges?

The first question is based upon whether it is possible to simulate produced water in an experimental facility. The composition of produced water can vary depending on reservoir location, age of reservoir, enhanced oil recovery techniques, presence of production chemicals, and a number of other factors. Due to this, the key factors in oil-in-water measurement for simulation purposes can be simplified to oil-in-water concentration and oil droplet size. To effectively simulate produced water conditions, the ability to control oil concentration and droplet size, along with the ability to generate stable mixtures for pre-specified lengths of time, is key to be able to accurately simulate characteristics of produced water. Can these key conditions that reproduce typical produced water conditions be experimentally simulated?

2. What techniques are available that can detect oil-in-water at concentrations below 30 mg/L? In addition, can the impact of typical parameters found in produced water applications be quantified for individual techniques?

The second research question is split into two further questions. The first of these asks which technologies are currently available that can detect current produced water discharge conditions of 30 mg/l oil-in-water concentration. Different technologies and devices will have their own advantages and disadvantages; therefore, a selection of techniques needs to be considered. The second question poses a more difficult challenge. After demonstrating that online techniques can measure oil-in-water concentration in ideal scenarios, the next step is to demonstrate this ability with other varying, commonly seen, parameters. This question asks whether it is possible to quantify the impact of each parameters on the selected technologies.

3. Can improvements be made to current online techniques or methods, to improve performance of measuring oil-in-water concentration?

The third research question asks whether improvements can be made to current online oil-in-water measurement methods. Depending on the outcome of the second research question, the impact on certain parameters may cause increased uncertainty for the online methods. To answer this question, physical or theoretical methods will be considered to reduce the uncertainty of online techniques and allow them to measure closer to the reference value.

4. Can we determine the uncertainty of reference techniques typically used to measure oil-in-water concentration? In addition, can we predict the impact of uncertainty due to sampling? If so, what sampling parameters have the largest contribution?

The fourth research question looks at whether it is possible to determine the uncertainty of the measurement for current oil-in-water concentration reference methods. The uncertainty of the measurement can be split into two parts. The first is the measurement uncertainty due to the reference technique, and the second is due to sampling. As all reference methods require sampling, the second part of the research question asks if the sources of uncertainty for sampling can be identified, and how do they contribute into the uncertainty of the overall measurement.

5. Can online techniques be used for produced water regulatory compliance monitoring? What methods are required to demonstrate this ability?

The fifth research question focuses on the use of online techniques for regulatory compliance of produced water discharges. Currently only accepted offline reference methods can be used for regulatory reported purposes, the question asks if it is possible to demonstrate that online methods can replace current offline techniques. Can this be demonstrated, and what methodology would have to be undertaken to achieve this.

1.3 Thesis Structure

The thesis is structured into 8 chapters, as shown in the list below.

- **Chapter 1:** Introduction
- **Chapter 2:** Literature Review
- **Chapter 3:** Produced Water Facility Development
- **Chapter 4:** Produced Water Parameter Characterisation
- **Chapter 5:** Improvements to Current Online Methods
- **Chapter 6:** Measurement Uncertainty
- **Chapter 7:** Conclusions
- **Chapter 8:** Future Work

Chapters 1 introduces the thesis and the give the reasons why the research is being carried out. Chapter 2 describes the gap analysis undertaken to qualify different online technologies selected to be evaluated as part of this work and gives background to the principles and regulations surrounding oil in water measurement. Chapter 3 describes the design and development of the produced water test facility which forms the basis for the majority of experimental work completed. Chapter 4 focuses on the impact of individual parameters on the selected online technologies, to determine correlations between specific variables and the oil-in-water concentration measurement. Chapter 5 describes improvements found based upon the correlations made in the previous chapter and discusses novel methods for measurement verification. Chapter 6 focusses on the measurement uncertainty associated with oil-in-water measurements. This chapter is split into three parts; the first describing the initial experimental work to determine the uncertainty of current reference methods. The second section investigates this further by analysing the contribution of uncertainty by sampling, and how this affects the overall measurement uncertainty. The third section investigates the methods for determining the uncertainty of the online methods and how they can be related to current practices. Chapter 7 summarises the work undertaken as part of this thesis and Chapter 8 proposes future work that can be undertaken in this area.

2 Theory and Literature Review

2.1 Produced Water Production

Produced water is a name given to all water that is extracted as part of the production of oil and gas. Produced water is typically split and referred to as formation and injected waters, depending on where they originate. During the exploration and production of oil and gas, produced water is considered the main waste stream (Veil, 2004), with the management and handling of the fluid being of critical importance to ensuring environmental guidelines are being met.

During production of the oil, gas and water, the multiphase flow needs to be separated into the individual phases. The separation process is generally broken down into multiple stages to improve purification of each phase. Figure 2.1 shows a simplified treatment process (Yang, 2019), however the number and type of stages are dependent on the production fluid characteristics type of field, such as oil type, droplet size and solid content.

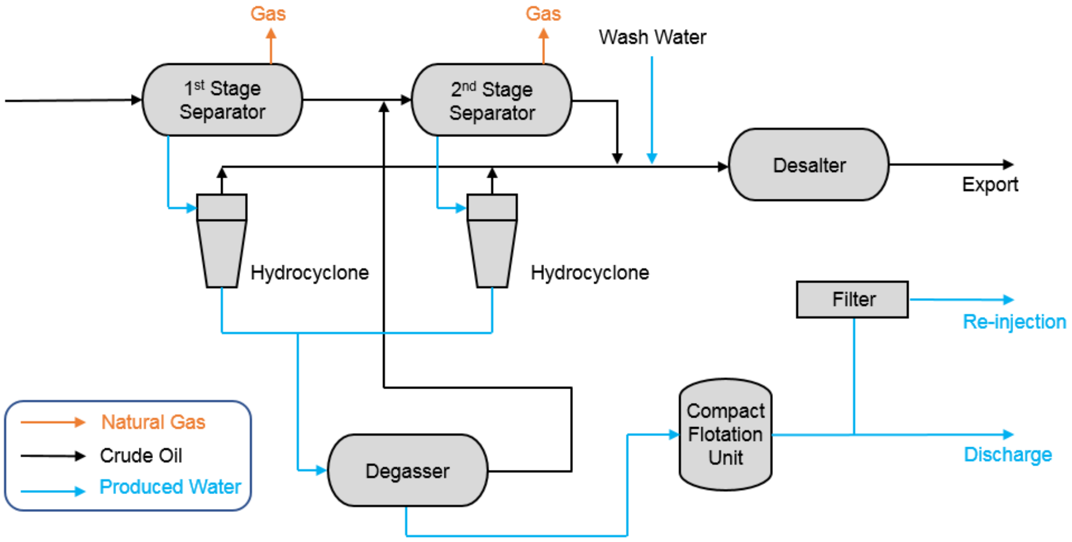

Figure 2.1 – Example Oil and Gas Produced Water Treatment Process in the North Sea

The treatment process is a critical part of the process in handling produced water in the oil and gas industry, as this can dictate the residual oil-in-water concentration. There are many types of treatment options, which can be split into the following categories (Igunnu & Chen, 2014):

- Mechanical
- Absorption / Adsorption / Extraction
- Advanced Oxidation Process
- Biological
- Combination of above

Depending on the type of treatment options utilised, several conditions of the treated produced water may need to be taken into consideration. However, the characteristics of produced water can vary from field to field, depending on several factors such as age and type of reservoir. Example representative produced water characteristics are summarised in Table 2.1.

Table 2.1 – Characteristics of Typical Produced Water (Tibbetts, et al., 1992)

Parameter	Value
Density	1014 – 1140 Kg/m^3
Surface Tension	43 – 78 dynes/cm
Total Hydrocarbon	2.0 –565 mg/l
Volatiles	0.39 –35 mg/l
Chemical Oxygen Demand (COD)	1220 mg/l
Total Organic Carbon (TOC)	0 – 1500 mg/l
Total Suspended Solids (TSS)	1.2 –1000 mg/l
pH	4.3 –10

The current ratio of produced water to production crude oil has reached over 4:1 globally, with an estimated production in 2014 of over 250 million barrels of water being extracted every day (Ahmadun, et al., 2009).

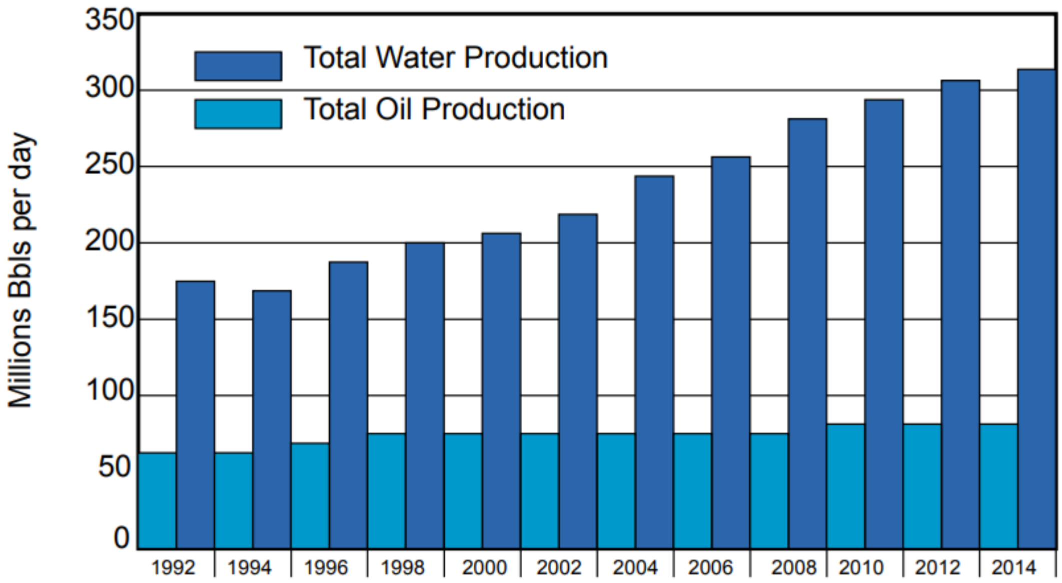

Figure 2.2 – Ratio of Global Water to Oil Production (Robertson & Jahsen, 2006)

The ratio of production water to oil changes depending on location, from 3:1 in the UK (O&G UK, 2018), increasing up to 10:1 in the Gulf of Mexico (Veil, 2015). As oil reservoirs age, the water cut of produced fluids increases, with production occurring with up to 98% water cut seen (Stephenson, 1992). Table 2.2, Table 2.3 and Table 2.4 summarises the discharge of produced water in OSPAR nations for 2014 (OSPAR, 2016).

Table 2.2 – Discharge of Produced Water in the OSPAR Nations in 2014 (OSPAR, 2016)

Country	Total number of installations	Annual quantity of PW discharged (m^3)
Denmark	16	24,109,367
Germany	1	9,595
Ireland	1	1,126
Netherlands	77	2,277,430
Norway	42	141,006,271
Spain	0	0
UK	108	156,247,100
Total	**245**	**323,650,889**

Table 2.3 – Dispersed Oil Discharged in the OSPAR Nations in 2014 (OSPAR, 2016)

Country	Annual average dispersed oil concentration (mg/l)	Total dispersed oil discharged (tonnes)
Denmark	6.7	161
Germany	18.1	0.1
Ireland	27.5	0.03
Netherlands	16	36.44
Norway	12.5	1,761
Spain	0	0
UK	12.8	1997
Total	**12.2**	**3,956**

Table 2.4 – Benzene, Toluene, Ethylbenzene and Xylene (BTEX) Discharged in the OSPAR Nations in 2014 (OSPAR, 2016)

Country	Annual average BTEX concentration (mg/l)	Total amount of BTEX discharged (tonnes)
Denmark	3.9	93
Germany	99.3	0.6
Ireland	60.5	0.1
Netherlands	21.1	48
Norway	13.5	1,190
Spain	0	0
UK	15.6	2,430
Total	**13.8**	**4,481**

The data shows that nearly 8500 combined tonnes of dispersed and dissolved oil respectively were discharged into the environment from the OSPAR nations in 2014. The potential environmental impact shows why the measurement of oil-in-water is a key part of the produced water management process. To overcome this challenge, produced water is often re-injected back into the reservoir for enhanced oil recovery. Care still needs to be taken however, as contaminants in the produced water can plug or fracture the well (Oort, et al., 1993), and thus produced water still needs to be sampled and analysed. This method however, decreases the environmental impact from the field by negating oil-in-water discharge completely.

2.2 Produced Water Composition

This section will provide background information on the basic chemistry principles in produced water. These principles lay the foundation on the measurement principles discussed in later sections of the thesis.

Oil-in-water is referred to as any hydrocarbon compound that can be determined in the produced water. The main contaminants of produced water (Ahmadun, et al., 2009):

- Dissolved and dispersed hydrocarbons
- Production chemicals
- Total Suspended Solids
- Entrained gases

The dissolved and dispersed components of the crude oil can be further broken down into individual compounds (Yang, 2019), as graphically depicted in Figure 2.3.

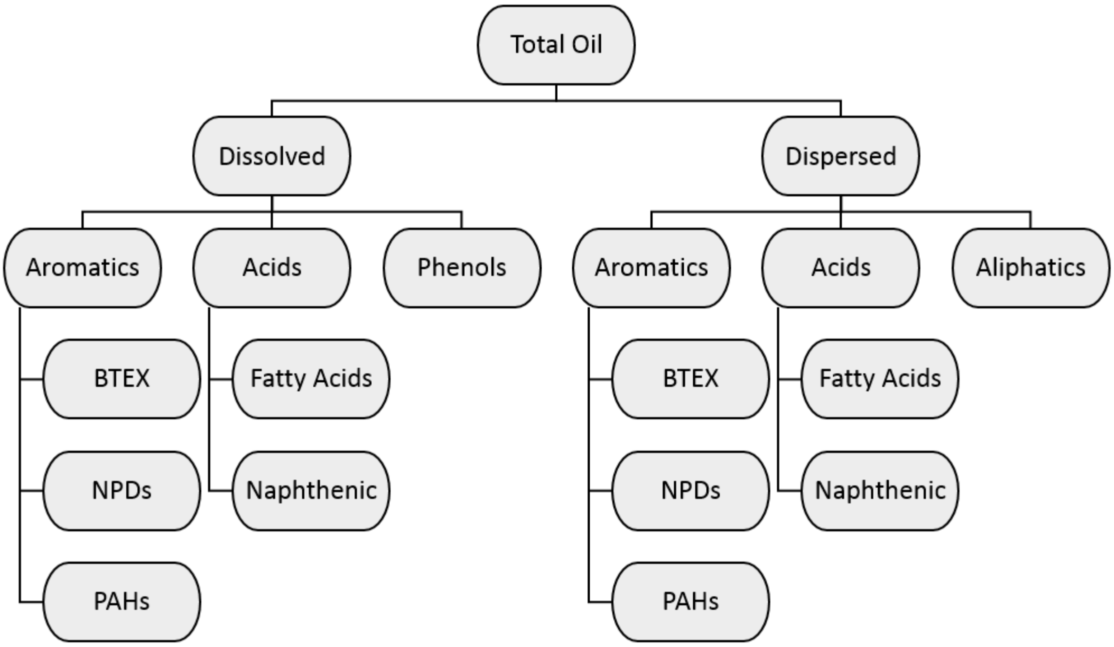

Figure 2.3 – Breakdown of Components in Crude Oil in Produced Water (Yang, 2019)

It is important to note that results of measured oil in water concentration are method dependent. Without specifying the technique used, the measurement of oil-in-water concentration cannot be related, as depending on the technique used, the results can vary significantly. One of the main reasons for this is that different techniques can measure different carbon chain ranges of crude oil, and due to dispersed vs dissolved crude oil. The different ranges for the reference methods are discussed further in Section 2.4. Similarly, online techniques will also measure different components of the crude oil-in-water mixture. Optical based devices such as, light scattering and image analysis, can only measure dispersed oil, and thus any component of the crude oil that is dissolved is not accounted for. Other techniques, such as fluorescence-based devices, can measure both dissolved and dispersed oil, however primary only polyaromatic hydrocarbons (PAHs). Due to these differences, as previously mentioned, it is crucial to state the method used whilst reporting an oil-in-water concentration measurement.

The amount of dissolved and dispersed crude oil in water is related to several factors, such as:

- Type of crude oil
- Ratio of oil and water
- Fluid properties such as; pH, salinity, total dissolved solids (TDS) and temperature
- Stabilising compounds such as; chemicals, waxes and total suspended solids (TSS)

Dispersed oil is referred to as the oil-in-water that forms individual crude oil droplets, which can range in diameter from microns to millimetres. Typically, dispersed oil is made up of primary aromatic and aliphatic hydrocarbons. Dissolved oil is referred to as the oil which is soluble in water and has fully dissolved into the produced water. The chemical composition of dissolved oil can vary depending on several parameters.

Typical water-soluble hydrocarbons are polar constituents of the lower carbon chain ranges. It is important to note that the characteristics and physical properties of the fluid, such as oil type, volume ratio and temperature, can affect the solubility level (Stephenson, 1992). Some properties however, such as salinity, do not reportedly affect the amount of dissolved oil (Bostick, et al., 2002). Solubility of several aliphatic hydrocarbons in water is given in Table 2.5.

Table 2.5 – Solubility of Aliphatic Hydrocarbons (Frintrop, 2007)

Hydrocarbon	n- pentane	n- hexane	n- heptane	n- octane	decane
Solubility	39 mg/l	11 mg/l	2 mg/l	1 mg/l	0 mg/l

In comparison to aliphatic hydrocarbons, aromatics contribute to a larger portion of dissolved oil and need to be carefully considered whilst undertaking oil-in-water measurement. Phenols and aromatics have the highest solubility in produced water, as shown in Table 2.6.

Table 2.6 – Solubility of BTEX Compounds (Ekins, et al., 2007)

Compound	**Molecule formula**	**Solubility at 25 °C**
Benzene	C_6H_6	1790 mg/l
Toluene	C_7H_8	526 mg/l
Ethyl Benzene	C_8H_{10}	169 mg/l
p-ethyl toluene	C_9H_{12}	95 mg/l
n-butyl benzene	$C_{10}H_{14}$	12 mg/l

When samples of produced water are collected, steps during the extraction process can often lead to organic acid and phenols transferring from dissolved state to dispersed. Depending on the method used, these need to be taken into consideration in the overall oil-in-water result.

2.3 Produced Water Regulations

This section will describe the regulations surrounding oil-in-water pollution limits for individual countries and regional conventions. This pollution can come from many different sources and strict regulatory guidelines have been put in place in the limit of amount of oil-in-water concentration can be discharged back into the ocean. This limit varies depending on location.

2.3.1 Global Oil Discharge Limits

To prevent marine pollution, a significant number of regional conventions have been established under the Regional Sea Programme of the United National Environment Programme (UNEP). All these conventions are common in that they have a framework convention, which contains procedures to combat different sources of pollution. All these procedures endorse the provision of the MARPOL 73/78, the International Convention for the Prevention of Pollution from Ships (IMO, 2015).

Table 2.7 shows some of the well-known regional conventions with which oil in produced water discharge limits are either stipulated or derived for those countries signed to the individual conventions (Veil, 2004). It should be noted that the limits discussed are for dispersed oil only and does not account for dissolved oil.

Table 2.7 – Discharge Levels of Oil-in-Produced Water applied Regionally (Veil, 2004)

Convention	Discharge Limits (mg/l)
Barcelona Convention, 1976	40; 100 peak
Helsinki Convention, 1992	15; 40 if cannot achieve 15
Kuwait Regional Convention, 1978	40; 100 peak
OSPAR Convention, 1992	30

The Barcelona Convention (UNEP, 1976) was established for the Protection of the Marine Environment of the Coastal Region of the Mediterranean, which came into force in February 1978. The discharge limit is an average oil-in-water concentration of 40 mg/l with max allowed peak of 100 mg/l.

The Helsinki Convention (HELCOM, 1992) was agreed for the Protection of the Marine Environment of the Baltic Sea Area in 1974 and renewed in 1992. The discharge of produced water is forbidden unless the oil content is demonstrated to be less than 15 mg/l. However, if this limit cannot be achieved using the Best Available Technology (BAT) and Best Environmental Practice (BEP), a higher limit of 40 mg/l may be used, if prior agreement has been established with the national authority.

The Kuwait Regional Convention (UNTC, 1978) for Co-operation on the Protection of the Marine Environment from Pollution was agreed in 1978 and came into force in 1979. Like the Barcelona Convention, the average discharge limit is 40 mg/l, with a maximum peak of 100 mg/l allowed. The OSPAR Convention (OSPAR, 1992) for the Protection of the Marine Environment is based in the North East Atlantic. The discharge limit in terms of the dispersed oil in produced has been reduced from 40 mg/l to 30 mg/l at the end of year 2006.

In the OSPAR region, only dispersed oil is counted towards the 30 mg/l discharge limit (OSPAR, 2011). In this region, dispersed oil is measured by the OSPAR defined reference method, which currently is an adapted version of the ISO 9377-2 technique (BSI, 2010). The measured oil in produced water will essentially be the hydrocarbons with carbon number between C_7-C_{40} excluding the TEX. Acids, phenols and those hydrocarbons with carbon number above C_{40} and below C_7 will not be included.

2.3.2 Produced Water Reporting in the UK

Depending upon the type of installation and the quantity of dispersed oil in water that is discharged per year from an offshore oil and gas installation, the requirements for reporting may vary. Table 2.8 and Table 2.9 provides a summary of these requirements under OSPAR regulations (OSPAR, 2011).

Table 2.8 – Produced Water Sampling Requirements in OSPAR Region (OSPAR, 2011)

Manned Installations that discharge continuously	• A minimum of 16 samples per month • Samples taken at equal time intervals • Samples taken after the last item of treatment equipment in a turbulent region • Method of sampling yielding equivalent results approved by the competent authority can be accepted
Unmanned or with batch or small discharges	• The frequency and timing of sampling should make sure that samples are representative of the effluent, considering operational aspects and logistics • Small discharges refer to discharges of no more than 2 tonnes of dispersed oil per annum

In terms of sampling requirements in the UK, specific procedures are detailed in its guidance *‘Methodology for Sampling and Analysis of Produced Water and Other Hydrocarbon Discharges’* (BEIS, 2014).

Table 2.9 – Oil in Produced Water Sampling Requirements in the UK (OSPAR, 2011)

Discharge quantity of dispersed oil per annum	**Types of Installations**	
	Manned	**Unmanned**
Less than 2 tonnes	A set of samples collected and analysed at least once a month	One set of samples taken during each visit and analysed
More than 2 tonnes	At least two samples collected at approximately equal time intervals and analysed per day	Not foreseen and unspecified. Requirements to be agreed on a case by case basis

In terms of compilation and reporting of the monthly dispersed oil in produced water figures, the following is specified in the BEIS Guidance (BEIS, 2014):

- Monthly average of oil-in-water is required to be calculated, which must not exceed the 30 mg/l performance standard, or a lower figure as agreed with BEIS;
- All available oil-in-water data must be included in the calculation of the monthly average;
- The concentration must not exceed 100 mg/l limit at any time;
- In any 12-hour period, the quantity of dispersed oil in produced water discharged must not exceed 1 tonne.

In general, the above requirements are for manned installations where manual samples are taken, analysed and reported using either the OSPAR GC-FID method or an alternative method that will have been correlated to the OSPAR GC-FID method.

2.4 Reference Methods for Oil-in-Water Measurement

There are three main reference methods that are used to measure oil in water concentration for produced water.

- Infrared absorption,
- Gravimetric,
- Gas Chromatography and Frame Ionization Detection (GC-FID).

This section will provide a summary of the operating principles of each reference technique. All current reference methods require samples to be collected and transported to a laboratory for analysis. This is reflected in the regulations, as previously discussed, where a number of samples are stipulated to be collected.

2.4.1 Infrared (Transmission Based)

To conduct an oil-in-water analysis, the infrared (IR) absorption-based technique compares the absorbance values of an extract of the sample to a set of known absorbance values. To get the extract for infrared measurement, several steps need to be undertaken after collection of the oil-in-water sample.

1. Acid is injected to reduce the pH to less than 2,
2. The total crude oil is extracted using a chlorofluorocarbon solvent,
3. Polar compounds are then removed from the extract,
4. The extract is then placed into a quartz cuvette cell for measurement

The set of known values is found during calibration using laboratory prepared samples of known concentration. The absorbance value obtained from the extracted sample can then be compared to the laboratory prepared samples, thus the oil-in-water concentration can be determined.

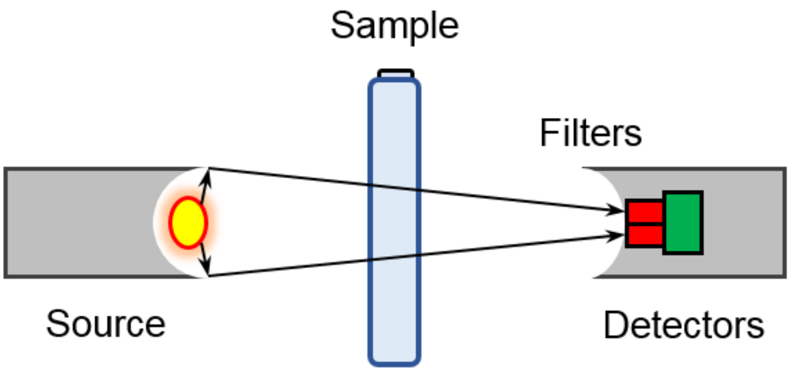

Figure 2.4 – Schematic of Typical Infrared Transmission Unit (Spectro Scientific, 2019)

The fundamental principle behind infrared techniques is based on the Beer-Lambert law. The law is shown by the formula below:

$$A = \log\left(\frac{I_o}{I}\right) = ELc \qquad (1)$$

Where,

A = Absorbance value
E = Constant
L = Path Length
I_o = Intensity of Incident Light
I = Intensity of Transmitted Light
c = Concentration of Hydrocarbons

Table 2.10 summarises the main infrared based standards used in the measurement of oil in water.

Table 2.10 – Infrared Transmission Based Standards

Wavelength	Reference Technique	Solvent	Calibration Method
Single	DECC IR Method (Lava, et al., 2017)	Tetrachloroethylene or S-316	Field Specific oil
	ASTM D 7066 - 04 (ASTM, 2004)	S-316	n-hexadecane + isooctane or target oil
Triple	IP 426/98 (IP, 1998)	Tetrachloroethylene	pristane, n-hexadecane, and toluene
	GB/T 17923 - 1999 (NMEMC, 1999)	Carbon Tetrachloride	pristane, n-hexadecane, and toluene

The IR transmission-based techniques can be utilised either in single or triple wavelength methods. The main difference between the methods is simply the wavelengths used to measure the absorbance in the extract. However, it should be noted that extraction solvents are an important part in infrared reference methods as any hydrocarbon that is not extracted will not be included in the analysis.

2.4.2 Gravimetric

Like the infrared technique, the gravimetric method involves extracting the crude oil from water using a solvent. Depending on the exact method, the extract can be further purified to remove polar compounds. After the extraction, using a pre-weighed flask, the extract is placed into a water bath which is temperature controlled, to allow the solvent to evaporate. The residual crude oil can then be directly measured by re-weighing the flask and calculating the difference in weight. Examples of standards are shown in Table 2.11.

Table 2.11 – Gravimetric Standards

Reference Technique	Location	Solvent	Elevation Temperature (°C)
Method 5520 B (APHA, 1999)	United States	n-hexane	85
EPA 1664 A (EPA, 1999)	United States	n-hexane	85

Due to the evaporation procedure in the gravimetric methods, light components extracted into the solvent may be lost. The methods also can take up to 3 hours to obtain a result.

2.4.3 Gas Chromatography and Flame Ionization Detection (GC-FID)

Gas Chromatography is a method that allows for different types of hydrocarbons to be determined. Similar to the other methods, a procedure was followed to prepare the oil-in-water sample for analysis. After preparation of the extract, it can then be placed into a gas chorography instrument. Using a chromatographic column and carrier gas, different portions of hydrocarbons will be separated and measured at different intervals. In comparison to other techniques, GC-FID methods are generally time consuming, expensive and require a skilled person to do the analysis.

A typical GC-FID schematic is shown in Figure 2.5. The following list summarises the main components used through the process.

- Gaseous carrier stream
- Sample injector
- Separation column
- Detector
- Data Acquisition System

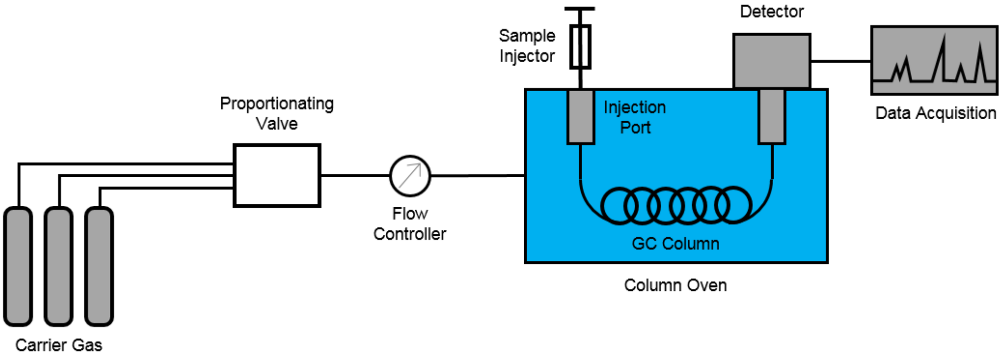

Figure 2.5 – Schematic of Typical GC-FID Unit (Yang, 2011)

The hydrocarbons at each stage are combusted and using a flame ionisation detector (FID), each component can be detected. For oil-in-water measurement, specific carbon ranges are used to specify what hydrocarbons are recorded. An example of these ranges and typical technique standards are shown in Table 2.12.

Table 2.12 – Examples of Reference GC-FID Methods

Technique	Location	Solvent	Hydrocarbon Range
ISO 9377 - 2 (BSI, 2010)	International	Temperature range (36 to 69 °C)	C_{10}-C_{40}
OSPAR GC - FID (OSPAR, 2011)	OSPAR Region	n-pentane	C_7-C_{40} minus TEX
TNRCC Method 1005 (TNRCC, 2001)	United States	n-pentane	C_6-C_{35}

The OSPAR GC-FID method, which is the current reference method for oil in water in the OSPAR region, is an adapted version of the ISO 9377-2. Compared to the ISO 9377-2, the OSPAR GC-FID technique requires a higher resolution gas chromatograph so that the TEX can be separated and excluded from the detection range of C_7-C_{40}.

2.4.4 Uncertainties Associated with Oil-in-Water Reference Measurement

Precision information for some well-established oil-in-water concentration measurement methods are shown in the Table 2.13. It should be noted that the information provided are repeatability and reproducibility information and not actual measurement uncertainties. Repeatability is derived from repeated measurements of a constant quantity, made using the same method on identical test material or under the same conditions (operator, instrument, process and short time interval). The problem is that the results of these measurements are reported in many ways e.g. from simply taking the difference of the maximum and minimum values of a set of results, to reporting the standard deviation as the repeatability. So, when using repeatability figures, it is important to know how it has been derived.

Table 2.13 – Precision Information of Typical Oil-In-Water Reference Methods

Reference Method	Principle	Range	Precision Information
ASTM 3921-85 (ASTM, 2013)	Freon extraction & IR	0.5–100 mg/l	Precision = 0.167*(x + 0.333) mg/l Where x is the mean oil concentration in 0.6 – 66 mg/kg range
ASTM D 7066-04 (ASTM, 2017)	S-316 extraction & IR	5 – 100 mg/l, could be extended with a larger or smaller sample	50.3, 66.3, 49.9, 47.1, 37.2 and 24.7% were found for mean values respectively at 6.4, 6.6, 21.2 30.5, 429.9 and 551.2 mg/l
IP 426/98 (IP, 1998)	Tetrachloroethylene and IR with Florisil cleaning	0.5–150 mg/kg	1 mg/kg over 0.5 to 5 mg/kg range
			Precision = 0.2127*(x + 5) mg/kg Where x is the mean oil concentration in 5 – 150 mg/kg range
ASTM D7678-11 (ASTM, 2011)	Cyclohexane extraction and IR	0.5 – 1000 mg/l	Repeatability is within 13% in the concentration range up to 50 mg/l
EPA 1664 (EPA, 1999)	N-Hexane extraction & gravimetric	5-1000 mg/l (oil and grease) with a minimum detection limit of 0.91mg/l	Initial precision of 11% is acceptable on lab prepared standard.
ISO 9377-2:2000 (BSI, 2010)	Solvent extraction and GC FID (C10 to C40)	0.1 mg/l – 150 mg/l	33.5%, 40.5%, 9.6%, 21.1 were found for mean values respectively at 0.7, 1.04, 2.99 and 3.61 mg/l

The sources of precision data provided in Table 2.13 do not state how the results were determined. Information such as the number of data points, removal of outliers, and actual method to determine the precision results are not available. It should be noted that the precision results discussed for the reference methods are based on data collected solely from lab prepared standard samples, either by injecting oil directly into a solvent or by spiking oil into a water sample and then extracted. In preparing the standard samples, standard procedures are strictly followed to minimise the uncertainty linked to this step.

One key part of the process which can account for a large portion of the uncertainty of the reference techniques, is sampling. The precision information discussed does not consider the act of collecting the samples used. Even though a significant amount of research has been conducted in sampling of multiphase flows, research investigating the effect of sampling on the uncertainty of oil-in-water concentration is very limited. However, studies which are not directly investigating this issue can give insight into the magnitude of uncertainty associated with sampling. Work completed looking at issues with oil-in-water measurements (Lava, et al., 2017) concluded that 75% of the uncertainty of oil-in-water measurements could be due to method of sampling. Other figures have also been stated by different sources, with (Michael, et al., 2007) stating that sampling could be over 90% of the measurement uncertainty. (Paquet, 2009) has also determined sampling could be up to 70% of the total uncertainty.

Comparing the estimated uncertainties associated with sampling to the precision information for standard reference methods, it is clear that sampling can add a large contribution of the total uncertainty of the resulting oil-in-water concentration.

2.5 Review of Online Measurement Techniques

To overcome some of the challenges discussed, industry has been moving towards online methods of measuring oil-in-water concentration. Several key benefits, such as; continuous data measurement; ability to measure other parameters such as droplet size, and negating the requirement of sampling. The move towards continuous measurement feeds into the progression of digitisation, which is seen across the oil and gas industry. Online methods also allow development of unmanned platforms and is seen as a limiting factor in the progression towards subsea development.

This section will discuss the types of online techniques that can be used to measure oil-in water concentration online and review the previous research work that has been completed for these technologies. Some of the main technologies are listed:

- Ultrasonic acoustics;
- Image analysis;
- UV fluorescence
- Light Scattering

2.5.1 Ultrasonic Acoustics

In this technology, an ultrasonic transducer is fitted into the produced water flow stream and acoustic energy is focused into a small volume directly in front of the transducer. As droplets or particles flow through this measurement window, the acoustic waves are reflected or scattered.

The amplitude of the scattered waves can then be correlated to the size of the passing droplets or particles using a known model. Sweeps of ultrasound are sent out, each containing thousands of measurements. Size distribution and particle concentration can then be obtained from the produced curves. Discrimination of oil droplets, solid particles and gas bubbles however is not straightforward, and parameters are required to be updated depending on the application to match the measured curve to ensure discrimination.

Chanamai et al (1998) investigated the use of an ultrasonic technique to measure oil concentration in oil in water emulsions. It was reported that the ultrasonic attenuation coefficient varied with composition and droplet size. The attenuation coefficient is the combination of absorption and scattering of the sound waves and dictates their respective rate of decay. The results from the research demonstrate that the measurement of size distribution and concentration of in emulsions were viable under certain conditions, by correlating this coefficient with known oil-in-water concentration and droplet size models.

Both size and concentration information of dispersed oil can be provided by an ultrasonic acoustic technique (Gulsrud & Aanensen, 2007), however dissolved oil is not accounted for as only free oil droplets can be detected. The technology is also said to cope with fouling relatively well as it is does not use optical windows, thus fouling is thought to take place uniformly on the ultrasonic transducer’s surfaces resulting in a drift occurring in comparison to typical measurement failures. In addition, measurement using the technology is independent of colour and opacity of oil droplets. The technology is less established compared to LIF and image analysis technologies, and only a limited field applications and trials are known to date. However, data has been shown to be an effective method to measure oil-in-water up to 500 mg/l (Aanensen & Volker, 2006).

2.5.2 Image Analysis

Microscopy based systems use the technology of Imaging Analysis to determine characteristics of particles and dispersed oil droplets. Image analysis is utilised in many applications and is not limited to the Oil and Gas Sector. Al-Thyabat & Miles (2006) carried out research work to improve this imaging technique; however, their focus was on mineral processing operations and the characterisation of rocks. Most other technologies are only able to determine a single parameter in particle characterisation; however, image analysis allows multiple parameters to be captured.

Particles such gas bubbles, solid particles and oil droplets are captured on the images, which are then classified based on using a shape factor and the difference in optical properties between gas bubbles and oil droplets. The classified particles are then measured to obtain the content, size and size distribution information. The size information can then be used to determine the concentration of particulates in the process flow. Most of the other technologies that can determine particle size cannot characterise non-spherical particles. In image analysis, there are several key parameters used to determine the characteristics of a particle, called shape factors.

The shape factors comprise of many different parameters such as; circularity, aspect ratio, convexity, elongation and optical density.

Xu & Guida (2003) carried out a comparison of sizing small particles using electrical sensing zone method, laser diffraction and image analysis. The experimental work was done using glass beads as the spherical particulate and water as the medium. All three technologies produced good results for small aspect ratios of oil-in-water.; however, image analysis was the best at measuring non-spherical particles.

Kashdan & Shrimpton (2003) carried out further work on dynamic imaging, stating that the accuracy is dependent on three factors; optical resolution, defocus and the effects of diffraction. The experimental work was carried out to determine the accuracy of imaging using known particulate sizes. The research showed that image analysis is sensitive to the focus of particles, and it is extremely important to ensure correct set-up of threshold settings for calibration.

Gaskin et al (2001) discussed a collaboration undertaken between BP and Jorin to evaluate the performance of an online measurement device. A microscopy-based device, the image analysis technology was used during a short trial for monitoring of BP Andrews overboard discharge. The device was installed upstream and downstream of several separation devices and the trial was used to determine the suitability of the instrument for permanent monitoring. Total oil and total suspended solids were measured during the experimental work and demonstrated that image analysis can measure oil-in-water concentration successfully in comparison to reference samples.

2.5.3 Ultraviolet Fluorescence

Laser Induced Fluorescence (LIF) is another technique that can be used to measure oil-in-water concentration. Here ultraviolet (UV) light is induced onto a produced water stream by a microchip-based laser; aromatic hydrocarbons absorb UV light and then emit fluorescence light which is then picked up by a sensor, as shown in the schematic in Figure 2.6. Assuming the ratio of the number of aromatic hydrocarbons to total amount of hydrocarbons in a produced water stream remains constant and no other influencing parameters are present, the total amount of oil-in-water can be determined through calibration. The LIF technique allows construction of devices that can be installed an inline and by-pass installation configuration, allowing for more applications to be viable. Inline configuration is where the instrument is installed directly into the main pipe, allowing for direct measurement of the target fluid, however leads to several disadvantages such as increasing pressure drop and also potential shut-down of main line for routine maintenance. A bypass configuration is where the instrument is installed in a sample line taken from the main pipe, resulting in easier installation and maintenance, however this brings certain challenges as the measured result is only as representative as the sample line.

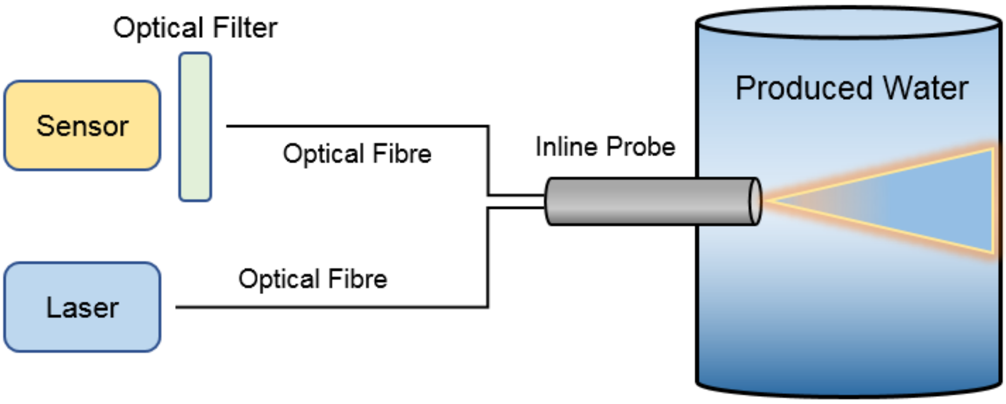

Figure 2.6 – Schematic of Laser Induced Fluorescence Technique (Yang, 2019)

Lambert et al (2003) studied fluorescence as a possibility for oil-in-water monitors as they undertook a laboratory study of a Turner 10AU fluorometer. The experimental work was carried out in a recirculation-based system using slightly saline water and nine different oil types. A recirculation-based laboratory environment allows stable and controllable parameters in comparison to field conditions. The oil was dispersed into the test loop and the fluorometer was used to record the oil concentration. With weathered samples containing high amounts of PAH compounds, a high fluorescence response should be expected however this was not the case with the results. The resulting theory is that volatile organic components may also influence the fluorometer and the fluorescence generated is not limited to PAH as other research has suggested.

Skeidsvoll et al (2007) presented several findings from recent case studies in collaboration with Statoil. The online instrument used LIF technology set to 10 Hz sampling rate and was positioned between two treatment processes. The field trial initially lasted 12 months with the instrument being kept on the platform for further trials after, with sample results showing the comparison between the online device and the reference values. During the trial, production chemical use was optimised, varying the treatment levels and monitoring oil concentration in the discharge stream. Overall, the results of the trial showed that the inclusion of an online device increased overall performance of the treatment process by collecting data continuously, in comparison to periodic sampling.

Steffens (2010) discusses important theory behind the principle of crude oil fluorescence detection. The wavelengths utilised during the research were 350, 450 and 532nm, which were shown to be effective in the measurement of the crude oil as previously found (Karpicz, et al., 2005). A total of six samples were created with a concentration range from 0.005-0.05% of oil-in-solvent. Steffens (2010) stated that the samples were shaken to achieve uniformity, however, this would lead to inconsistent test samples. They concluded stating that the research was able to show an effective means to obtain rapidly distribution of crude oil concentration, however disappointingly the research did not address the concerns previously raised regarding the droplet size.

Standard UV fluorescence monitors are devices which follow the same principle as LIF however use traditional light sources other than lasers. These devices can only typically be installed in bypass lines, which can have challenges such as non-representative sampling.

He et al proposed an oil content meter by undertaking an experimental study that looked at the combination of two technologies; ultraviolet fluorescence and light scattering (He, et al., 2003). The research involved using this technology to test four types of oils each with twelve subtypes of samples. The experimental work was carried out utilising a bench-scale method; with oil-in-water samples being produced manually and mixed using a laboratory blender. Overall, the research successfully demonstrated the differences between oil types and proposed some solutions to counter these issues. However little data was provided for exact oil concentrations utilised in most cases. Also, in the preparation of oil in water samples, information was provided in the tools used to ensure a low uncertainty in the generation stage.

2.5.4 Light Scattering

Light Scattering technology is based on the phenomenon whereby light, passing through a medium with suspended particles, is attenuated in intensity by scattering as shown in Figure 2.7. The intensity of the scattered light is detected using detectors. By placing the detectors at multiple angles and measuring the intensity of the scattered lights at these angles, oil-in-water concentration can be measured with the other components such as solid particles and gas bubbles present. Oil droplet size as well as the refractive index of the particles and oil droplets play an important part in deciding at what angles the detectors need to be placed. Only oil droplets that scatter light will be included in the measurement. Thus, it is only dispersed oil that will be measured.

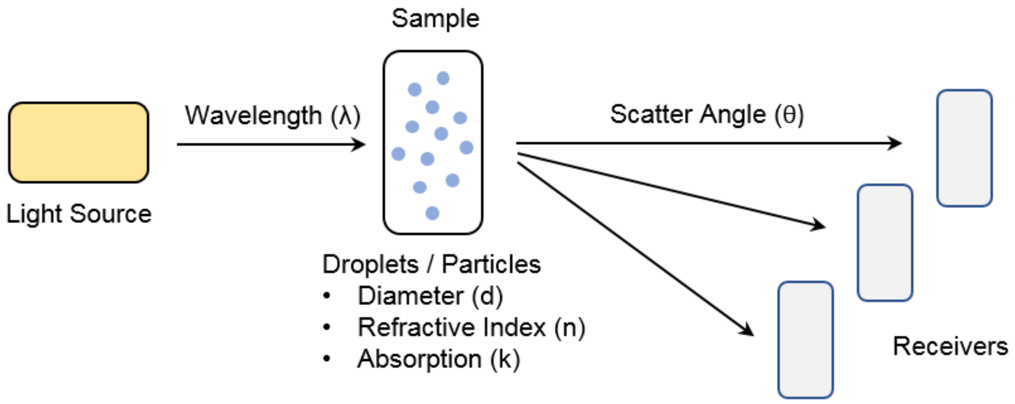

Figure 2.7 – Schematic of Light Scattering Technique (Schmidt, 2013)

Friedmen (1977) discusses a potential theoretical method for distinguishing between oil droplets and particles during the process of using light scattering as a technology for the measurement of oil-in-water. The research investigates the intensity of the scattered light to determine the oil concentration, focusing on previous influential work for plane light reflection for particles based on Mie Theory (Mie, 1908). The initial work summarises the previous theoretical equations discovered by Hodkinson (Hodkinson, 1963). These equations are focussed on determining the angular intensity distribution of light scattered from droplets or particles, which is a crucial step in determining the droplet size for light scattering devices. These equations are based on the ratio of indices of refraction between the target crude oil and water. No experimental data was presented; however, the paper draws upon the importance of considering the weaknesses of light scattering technique as a potential oil-in-water monitoring device.

Schmidt (2013) demonstrates several findings as part of a case study undertaken, using light scattering as an oil-in-water monitor. The light scattering instrument, OMD-7 from Deckma was set-up to measure oil-in-water concentration up to 200 mg/l. During the trial, the light scattering device was compared to typical offline reference methods. No statistical parameters were presented, however close trends between the online device and the reference method were noted. Increased response rate allowed spikes in oil concentration to also be found, which were not seen by conventional sampling and analysis methods.

2.5.5 Other Technologies

Other than the four techniques described, there are a number of other technologies that are capable or have the potential to measure oil-in-water concentration in an online capacity. A summary of some of these other technologies is given here.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) works by using magnetic fields and radio waves to determine the atomic structure of the sample under test and is typically conducted within a laboratory. Wagner at al (2016) presented the use of nuclear magnetic resonance with solid phase extraction to measure oil in water concentration in the range of 1 to 30 mg/l, with the results of the trial compared with infrared analysis and gas chromatography. The NMR instrument was trialled in a semi-automated capacity, therefore not fully online. However, the research described several steps planned to be undertaken to develop the device to a fully automated system. The main challenges to overcome involve extending the range of the measurements and by replacing several mechanical processes to optimise the operating procedure. Other challenges will include external validation, increased speed of response, and installation configuration requirements.

Photoacoustic

A pulsating laser light is focused on to a portion of the target water through a sapphire window. Any hydrocarbon component found within the sample absorbs the optical energy causing local heating to occur which generates a high frequency pressure wave due to thermal expansion. Acoustic detectors are then utilised to detect the pressure waves, and the frequency can then be correlated to the oil concentration. Foster et al (2001) used the photoacoustic principle to characterise five different types of oil in water. The main results showed however that the lowest detection limit that can be achieved was 45 mg/l. With further development into an improved detection limits, the technique shows potential as an online method.

Confocal Laser Fluorescence Microscopy

Confocal Laser Fluorescence Microscopy is a technique based on the principles of LIF and microscopy (Wickramaratne, et al., 2018). In this technique, the microscope illuminates a volume of target fluid with a laser beam in a scanning manner. The fluorescence generated by the oil droplets in the water sample is captured by a charge-coupled device (CCD). The digital signals from the CCD are then sent to an image processing computer which utilizes deconvolution to remove the noise caused by light contributions from out-of-focal plane locations. The processed signals are then analysed to determine the location and size of the oil droplets in the sample. A prototype online device was trialled and was able to trend closely with the reference method, however further work is required for further development (Zhang, 2016).

2.5.6 Application of Online Measurement Techniques

As discussed, there has been a growing trend towards the use of online measurement techniques in the oil and gas industry. Current applications however have focussed on using these devices at higher oil-in-water concentrations, such as before and after separation stages, and have typically been used for trending purposes (Yang, 2011). Research work has also been undertaken to investigate the use of online oil-in-water techniques for improving process control of produced water treatment systems (Durdevic, et al., 2016).

Due to the current regulations, the use of alternative reporting methods needs to be discussed with the regulator and are approved on a case by case basis. If an online oil-in-water analyser is to be used for reporting in the UK, the following is detailed in the BEIS guidance document (BEIS, 2014).

- Monthly averages are calculated and reported;
- Reported monthly averages must be OSPAR GC-FID equivalent;
- BEIS recognises that online analysers may record many values above 100 mg/l OIW results, in particular during a plant upset condition. An agreement with BEIS should be reached with regard to reporting OIW values above 100 mg/l.

The current online guidance does not cover key principles such as: calibration methodology, instrument type, data collection frequency and reporting procedures. There is a significant gap in the current guidance for use of online techniques.

In the use of online techniques for regulatory reporting, there are only a very limited number of cases. At present, only two cases globally of using online methods for regulatory reporting have been confirmed; located in the Norwegian fields, Alvheim and Stafjord B, controlled by the operators, Aker BP (Olasen, 2019) and Equinor (Knudsen, 2019), respectively. Details of these cases are discussed below.

In the Aker BP (Alvheim) case, the details of the reporting arrangement can be summarised as follows:

- Laser Induced Fluorescence correlated to IR method
- Acceptance criteria of online measurement: of ± 4 mg/l oil-in-water
- One sample per week (Two additional samples taken if outside acceptance range)
- New correlation curve required if all three samples not outside acceptance criteria
- 24 hour average for reporting of data
- Agreed with Norwegian Authority

A similar summary is described for Equinor (Statfjord B):

- Laser Induced Fluorescence correlated to OSPAR GC-FID method
- Acceptance criteria of online measurement: of ± 4 mg/l oil-in-water
- One sample per week (If outside acceptance range, additional samples collected for troubleshooting)
- New correlation curve required every six month period
- 24 hour average for reporting of data
- Agreed with Norwegian Authority

Both cases are very similar, and several conclusions can be drawn from these applications:

- Online monitors have now been allowed for reporting in Norway; however, acceptance is still on approved on a case by case basis.
- OSPAR guidance is not strictly followed regarding validation and acceptance.
- Only a single sample validation is carried out with an acceptance based on the deviation between the online monitor and reference method within ± 4 mg/l.

Even with this progress towards online methods for reporting, it shows significant gaps, especially for regulations within the UK. Important items, such as correlation methodology and acceptance criteria need to be considered to make applicable to generalised guidelines. Laser induced fluorescence was used in both fields, and other techniques will require different validation and reporting procedures. However, the acceptance within Norway shows positive progress being made towards online oil-in-water measurement reporting.

2.6 Summary of Literature Review

This chapter focussed on providing background surrounding the measurement of oil-in-water concentration whilst highlighting key gaps within industry and current research.

The first gap is the lack of uncertainty analysis in the measurements of produced water, specifically the reference measurements and regulations. Uncertainty is very important when stating any measurement, as without it, the closeness to the true value cannot be determined. A small portion of repeatability data is supplied within literature for some reference techniques, however details on how these were calculated are not clear.

The second gap is a key part of the process which can account for a large portion of the uncertainty of the reference techniques, which is sampling. The precision information discussed previously does not consider the act of collecting the samples used. The data collected solely from lab prepared standard samples, either by injecting oil directly into a solvent or by spiking oil into a water sample and then extracted. Some research work has been undertaken to determine the representativeness of sampling, however not in the application of produced water. Comparing the estimated uncertainties likely associated with sampling to the precision information for standard reference methods, it is projected that sampling can add a large contribution of the total uncertainty of the resulting oil-in-water concentration.

Another gap is surrounding the use of online oil-in-water measurement methods. To overcome some of the challenges discussed, industry has been moving towards online methods of measuring oil-in-water concentration. This provides several key benefits, such as: continuous data measurement; ability to measure other parameters such as droplet size and negating the requirement of sampling. However, there is a clear lack of data in the public domain for these methods. There is also little information on their performance under varying typical produced water conditions.

In general, the existing requirements for oil-in-water measurement within the UK are formulated for standard manned installations, where manual samples are taken, analysed and reported using either the OSPAR GC-FID method or an alternative method that will have been correlated to the OSPAR GC-FID method. There are several gaps within the current guidance, the main being the use of online methods for reporting. Currently, alternative methods are accepted on a case by case basis, and the requirements to demonstrate that the alternative method qualifies are not stipulated. Even with this progress towards online methods for reporting, there are other gaps with this progression. Important items, such as correlation methodology, acceptance criteria and reporting requirements need to be considered to make applicable to generalised guidelines to allow full acceptance of online methods for oil-in-water measurement reporting.

Overall, to move away from conventional sampling and laboratory analysis to online methods of measuring oil-in-water concentration, current regulations need to be updated to allow for this change. To achieve this goal, the gaps previously described first need to be filled, with the aim of the thesis to investigate these challenges to allow the use of online techniques for regulatory reporting.

3 Produced Water Facility Development

This section will describe the design and construction of the produced water facility at the National Engineering Labroatory (NEL). It will be used as the foundation for all experimental tests carried out in the project. As discussed in Chapter 1, the use of online techniques for measuring oil-in-water comes with many challenges, with the first being able to demonstrate that an online technique is capable of measuring oil-in-water concentration which is statistically equivalent or better than currently accepted reference methods. Without being able to demonstrate the performance of an online oil-in-water measurement device, the ability to use techniques for the regulatory reporting cannot be achieved.

To overcome this challenge, a series of experiments need to be undertaken. However, to undertake any experiments, a facility capable of simulating produced water conditions needs to be found. There are several test facilities across the world that claim to be able to achieve the conditions, however most of these facilities are in-house facilities for internal research and development with very little or no publications or access allowed. The specifications of these facilities are also unknown. There is one test facility in the UK that can achieve some of the conditions required (Fjords, 2019), which was used as part of this research for some initial experiments, as discussed in Appendix I. However, due to the design of this facility, there were several issues regarding flexibility, stability and range of achievable test conditions.

Therefore, this chapter aims to answer the first research question of the thesis:

- Can you simulate stable and realistic produced water conditions in a full-scale experimental facility? Can the droplet size be controlled to be within specified diameter ranges?

As previously mentioned, there are several facilities which have attempted to achieve this goal, however all have several limitations either in terms of availability, stability or ranges of conditions that can be achieved. The key factors in oil-in-water measurement for simulation purposes can be simplified to oil-in-water concentration and oil droplet size. To effectively simulate produced water conditions, the ability to control oil concentration and droplet size, along with the ability to generate stable mixtures is critical. Unlike other multiphase flows, the main constituent of produced water is mainly below 100 mg/l oil-in-water concentration, which can lead to challenges in how to produce stable and controllable conditions at these concentrations, due to the small quantities of crude oil present.

To answer this research question, it was decided to design and construct a facility capable of simulating produced water conditions. The facility was designed to be nominally 80 mm bore stainless steel pipe size, capable of testing actual oil-in-water online measurement devices that are currently commercially available, as discussed in Chapter 2.

To design a facility capable of simulating produced water conditions, the actual conditions required to be met need to be first established. The following table summarises typical ranges of components in produced water discharges (Zhang, 2016).

Table 3.1 – Target Produced Water Conditions

Parameters	Range
Oil concentration	5 – 5000 mg/l
Oil Droplet size	1 – 100 µm
Solid concentration	0 – 300 mg/l
Solid particle size	1 – 200 µm
Process temperature	4 – 100 °C
Flow velocity	1 – 10 m/s

3.1 Test Facility Schematic and Components

Figure 3.1 shows the process diagram of the produced water facility. The basic operation of the facility can be summarised into the following steps: a clean water tank is filled using mains water, and then used to fill the test loop with fresh water as required. A main 37 kW centrifugal pump is then utilised to circulate the fluids inside the loop and to increase the pressure up to a maximum of 5 bar(g) through the test section. Main flow direction marked on the diagram via arrows. A jet mixing system is also connected around the main centrifugal pump, to increase mixing.

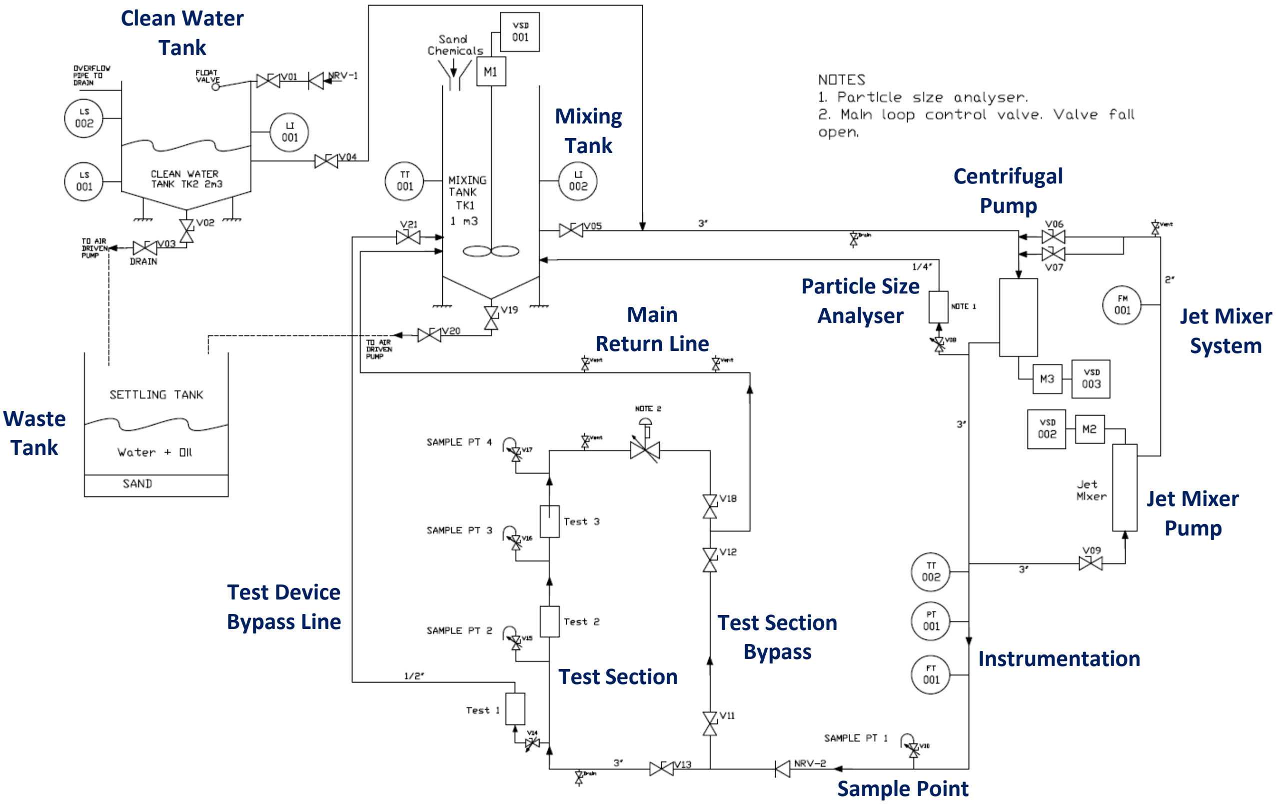

Figure 3.1 – Test Facility Schematic

3.2 Reference Measurements

A data acquisition system (DAQ) was setup to measure and record all the data being collected by the instrumentation on the facility. The control panel is connected to a main desktop computer, which is used to collect and process the data from the facility. Controlling the facility is done via the control panel and local variable speed drives.

Table 3.2 summarises the main instrumentation and associated uncertainties used in the Produced Water facility. All reference instruments were calibrated prior to any test using NEL's calibration facilities.

Table 3.2 – Reference Instruments for Flow Loop Tests

Parameter	Measurement Instrument	Uncertainty
Flow rate	E&H Promass Coriolis	±0.25%
Temperature	PT100 Probe	±0.1°C
Pressure	SICK PBT Transducer	±1%

Table 3.3 provides a summary of the reference measurements added to the facility. Each of these measurements are critical to the control and operation of the facility and for all experimental testing, as the results from these measurements will form the reference data in which all experimental test data will be compared to.

Table 3.3 – Reference Methods for Flow Loop Tests

Parameter	Measurement Principle	Measurement Instrument	Comments
Oil in Water Concentation	IR	Wilks Infracal 2	Calibrated and correlated to the OSPAR GC-FID
	OSPAR GC-FID	Varian	By RUM consultancy, used for correlations
Solids in water	Filtration	SM 2540 D	With sampling
Solids particle and oil droplet size	Light Scattering	Malvern Insitec	Used for measuring both oil droplet and solids particles

Two types of oil are used throughout the experimental work, a standard crude oil and a lighter condensate oil. Density and viscosity fluid properties of each oil were measured using the Anton-Paar DMA 5000 and SVM 3000 respectively. The fluid properties measurements have an uncertainty of ±0.02% for density, and ±2% for viscosity, within a temperature range of 10 to 40°C.

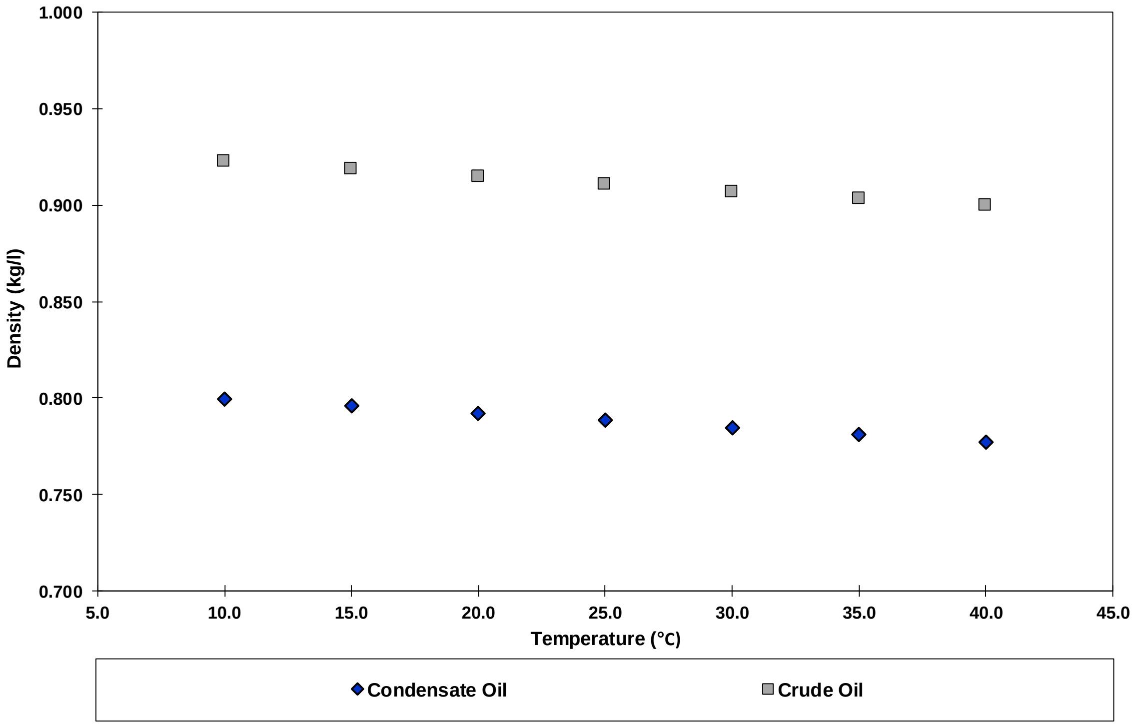

Figure 3.2 – Density Fluid Properties for Crude and Condensate Oil [10 to 40°C]

At 20°C, the API gravity of the oils are determined to be 23.2 and 47.1 for the crude and condensate oil respectively. Figure 3.3 shows the viscosity measurements determined:

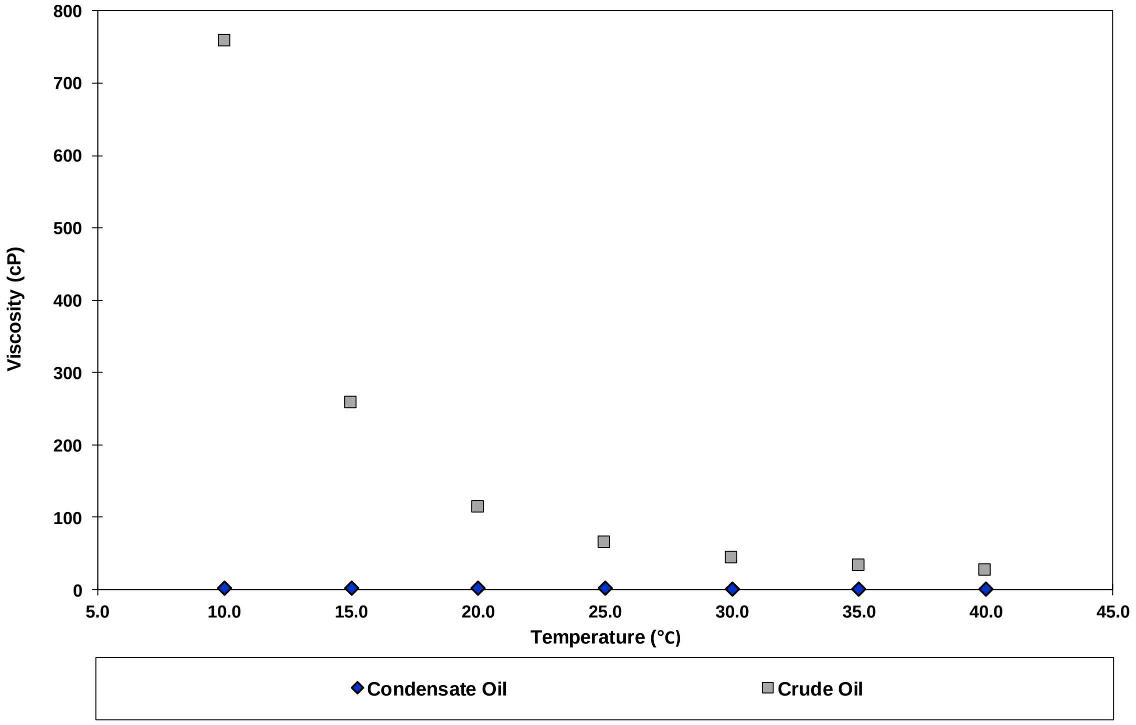

Figure 3.3 – Viscosity Fluid Properties for Crude and Condensate Oil [10 to 40°C]

At 20°C the dynamic viscosity is measured at 113.430 and 1.499 centipoise for the crude and condensate oil respectively.

For total suspended solids, two different solid particle sizes are used, 6.47 and 17.03 µm. These two sizes were selected to simulate solids found after final stage produced water treatment processes, which typically have a diameter below 20 µm, and due to their availability. To ensure full insolubility within water, the solid type used is silicone dioxide. Prior to use in the produced water facility, both types of solids were analysed using a Malvern Mastersizer. The results are shown in Figure 3.4.

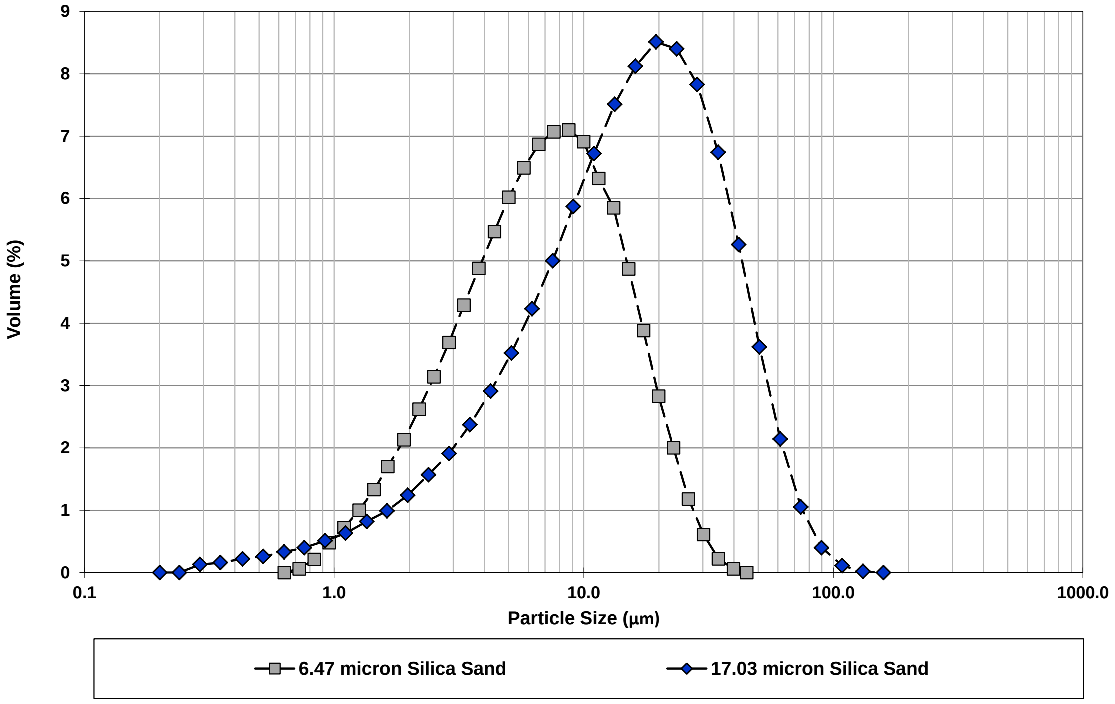

Figure 3.4 – Particle Size Analysis using Malvern Mastersizer

The main reference required was for oil-in-water measurement. Two methods were included.

- Infrared method: Wilk's InfraCal 2 Trans SP as shown in Figure 3.5 (a)
- GC-FID method: Varian 3800 GC as shown in Figure 3.5 (b)

A relationship was also established between the IR instrument and the OSPAR GC-FID method by RUM Consultancy (RUM Consultancy, 2019). By creating this relationship, it means that all IR results obtained at NEL can be converted to the OSPAR GC-FID equivalent if required. The IR method was used for day to day operations during the test program at NEL whilst the GC-FID results was used as an external validation if required.

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Figure 3.5 – (a) InfraCal 2 Trans SP; (b) Varian 3800 GC (Spectro Scientific, 2019)

Prior to use as a reference method, the infrared instrument needs to be calibrated. To undertake this calibration, an oil-in-water stock sample is required to be created. Table 3.4 shows the calibration data for the infrared instrument using the prepared stock sample.

Table 3.4 – Infrared Calibration Standard Data

Volume of IR Stock standard used (ml)	Concentration of IR Stock standard used (mg/l)	Total volume of calibration standard (ml)	Concentration of Calibration Standard (mg/l)	IR absorbance
1	203.2	200	1.016	0.013
2	203.2	200	2.032	0.026
4	203.2	200	4.064	0.049
10	203.2	200	10.16	0.11
20	203.2	200	20.32	0.202
40	203.2	200	40.64	0.36
50	203.2	200	50.8	0.425

The IR calibration data is graphed with 95% confidence limits as shown in Figure 3.6:

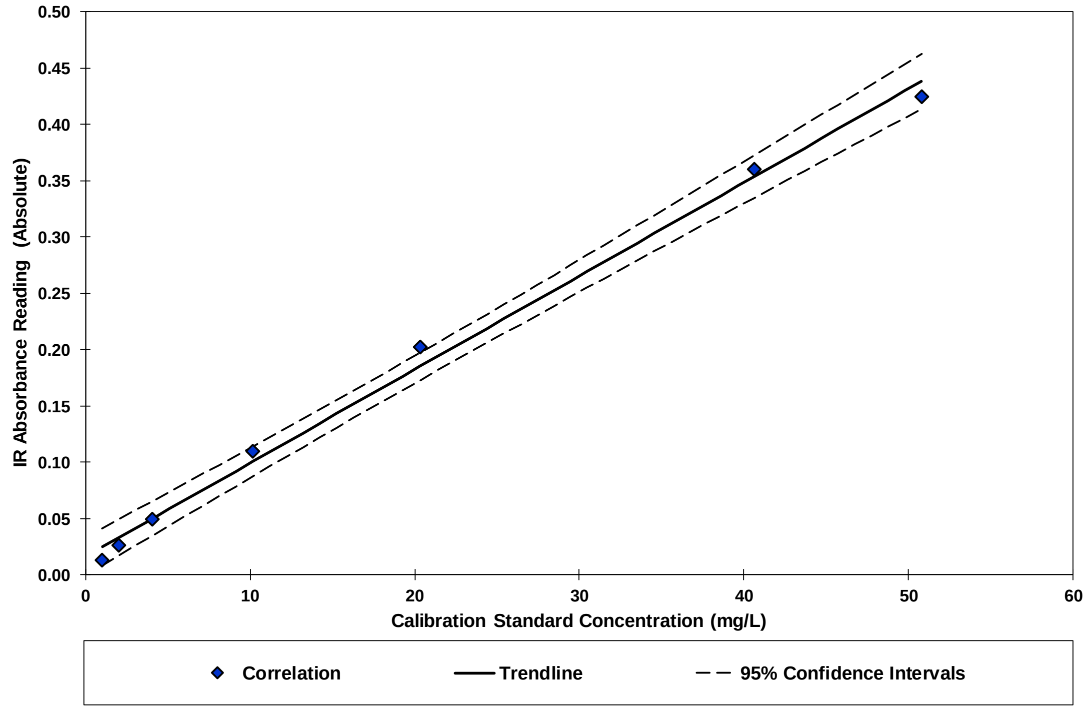


Figure 3.6 – Calibration of Infracal IR Instrument with 95% Confidence Limits

A correlation was established between IR method and GC-FID completed by RUM consultancy shown in Figure 3.7.

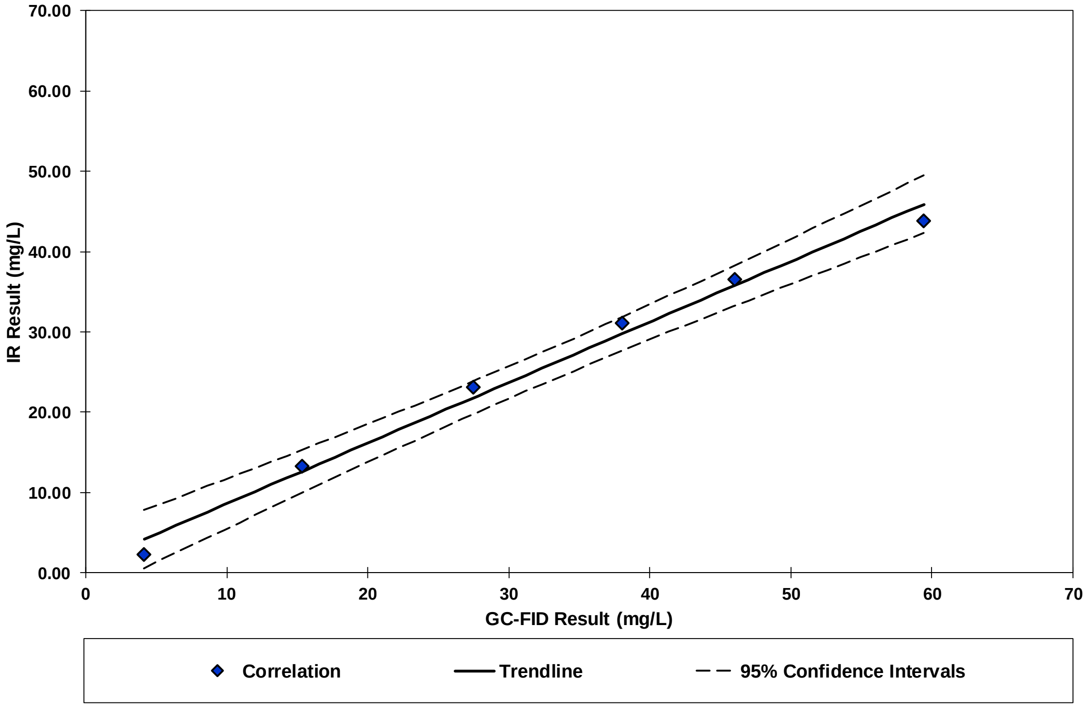


Figure 3.7 – Relationship between OSPAR GC-FID Method and DECC IR Method

As discussed in Chapter 2, due to differences in techniques, the results from different methods can produce slightly different results. Thus, it is important to state the oil-in-water measurement method along with the result.

Two reference methods are related to the total suspended solids in the test facility. The two conditions measured are:

- Solids in water concentration;
- Solid particle and oil droplet size.

For oil droplet size and solid particle size measurement, a Malvern Insitec device was installed in the bypass configuration, as a pictured shown in Figure 3.8 (b). The Malvern Insitec uses light scattering as the measurement principle. The solid particle sizes were also measured offline via a Malvern Mastersizer as previously shown in Figure 3.4.

For solids in water concentration measurement, a filtration based standard method, SM 2540 D, was used. Here a fixed volume sample was filtered through a weighed standard filter (as shown in Figure 3.8(a)) and the remaining solids on the filter dried at 103 to 105 °C until no change of mass is noted. The difference in weight of the filter, before and after filtration, can then be used to determine the total suspended solids in water. If oil was initially present, then the filter was solvent washed before drying.

(a) **(b)**

Figure 3.8 – (a) Filtration Based Solids in Water Analysis (b) Malvern Insitec Particle Size Analyser

The total suspended solid analysis is summarised into the following main steps:

- Weigh 0.45-micron filter paper before use
- Discharge sample into filter paper holder
- Wash bottle with solvent as appropriate and pour into filter paper holder
- Wash filter paper with solvent as appropriate
- Remove filter paper and place in oven for evaporation.
- Re-weigh filter paper

The difference in weight can then be used to calculate the concentration of solids in the collected sample. This is the typical methodology utilised in the North Sea for the measurement of total suspended solids (ASTM, 2018).

3.3 Test Section

In the design of the test section spool piece, a T-piece was used at the start of the test spool, as shown in Figure 3.9. This increases turbulence to aid the mixing of the oil, solid particles and water, and avoided inconsistent distribution of the dispersed phase, e.g. solid particles and oil droplets. T-pieces are commonly used upstream of multiphase meters in the oil and gas industry to increase turbulence and aid in mixing.

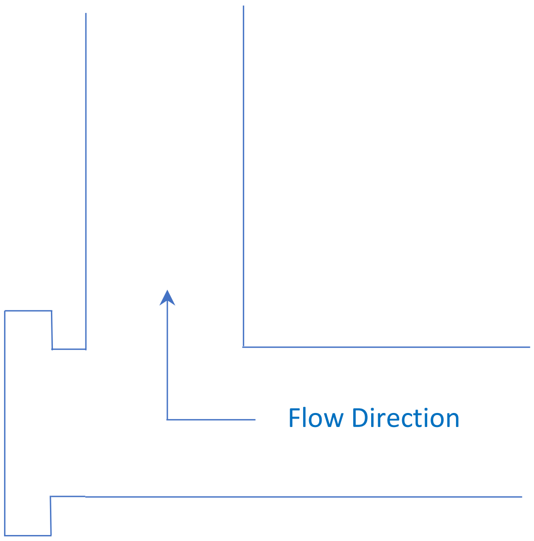


Figure 3.9 –Test Section with T-Piece Upstream

To confirm the droplet size consistency throughout the test section, two trials were conducted during the commissioning period. The first trial was based on an issue that occurred at previously used test facilities, with the distribution of solids across the cross-section area of the test spool piece being uneven, i.e. the larger solid particles were closer to the pipe wall due to the centrifugal force created as fluids containing solids pass through an elbow fitted at the bottom of the test spool piece. This trial was carried out by moving the sample probe from the front to middle to the back of the pipe and using the Malvern Insitec to detect any changes in average particle size. The results from this trial are shown in Figure 3.10.

Figure 3.10 shows that there is little variation in particle size measured between front, middle and back positions of the test spool piece. The trial was conducted using a concentration of 100 mg/L of solids, with a particle size of 17.03µm. This demonstrates that the inclusion of the blank T-piece effectively aided in keeping the TSS and water mixed in the test section.

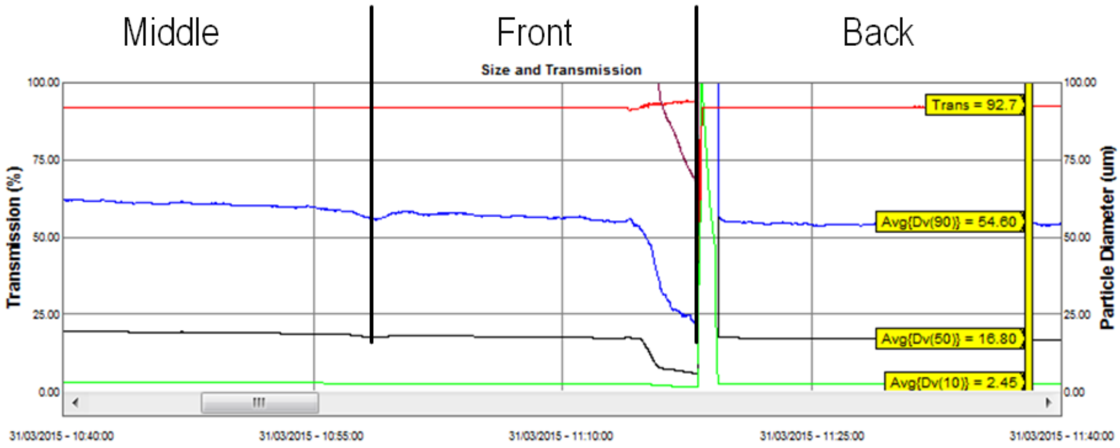


Figure 3.10 – Test Spool Piece Front / Middle / Back Trial Using Malvern Insitec

The second trial carried out was to see if there was consistency in the test fluid along the test spool piece. This was done by taking samples at the three sample port locations along the spool and comparing results. Figure 3.11 shows oil-in-water droplet size results obtained from this trial with three samples taken at for each sample port location, with an oil-in-water concentration of 49.8 mg/l. They are comparable, which means that there is consistency in the test fluid along the spool.

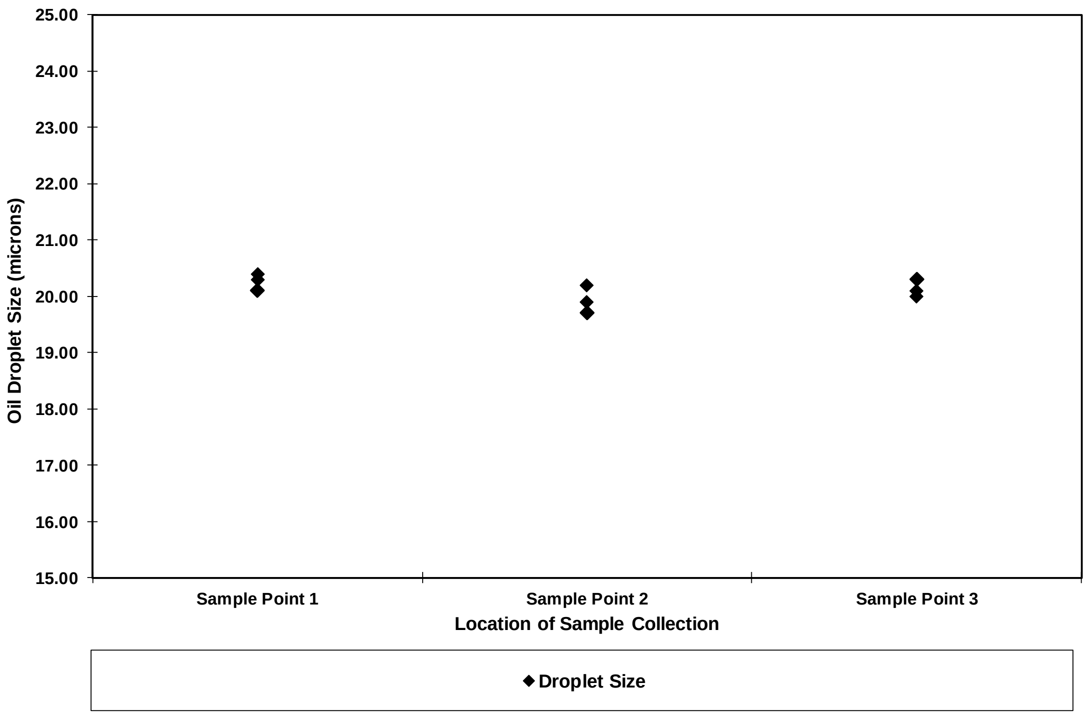


Figure 3.11 – Oil Droplet Size Trial along the Test Spool Piece

Results from the two trials demonstrate that there is consistency in test fluids along the test spool piece, which gives confidence in the test section and instruments setup.

3.4 Droplet Control

The test loop was designed to ensure a consistent mixture of the test fluid whilst also being able to control the oil droplet size. This is achieved by three mechanisms: the jet mixer system, the stirrer in the mixing tank and the velocity within the loop itself.

Figure 3.12 shows the Produced Water Facility jet mixer system. It consists of an oil injection port, a centrifugal pump, a coriolis flow meter, two injection pipes and a jet mixer. The jet mixer is an acrylic block with two 6mm injection ports perpendicular to the 80mm main bore. The jet mixer block was designed to increase turbulence and to shear the crude oil droplets. Fluid drawn from the exit of the main line centrifugal pump feeds the jet mixing line centrifugal pump. The flow through the jet mixer is monitored by a coriolis flow meter which determines the jet velocity and therefore the level of jet mixing. The flow rate in the mixing system is controlled by the motor speed of the centrifugal pump. Oil injected into the feed of the mixer line centrifugal pump, allows the oil to be initially sheared before further mixing at the jet mixer. The jet mixing system was constructed based on typical dynamic mixing systems found in the oil and gas industry, using a higher-pressure bypass line to re-inject fluid back into the main process line through a restriction.

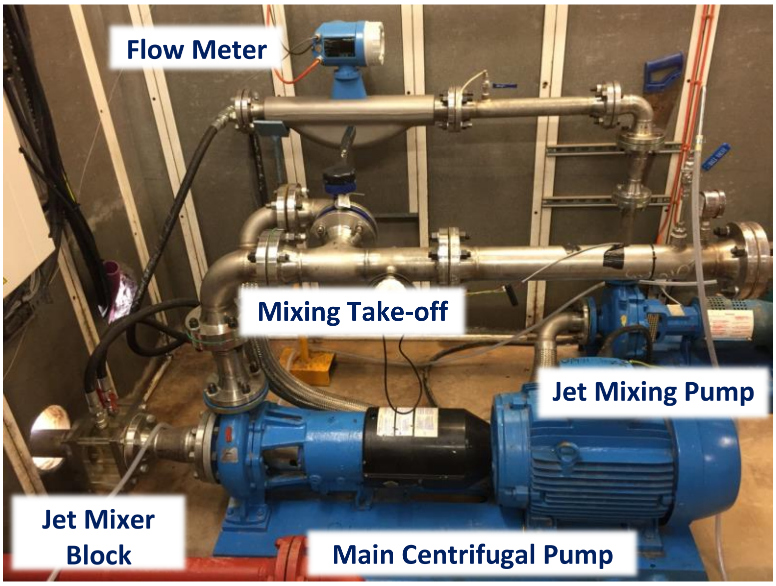


Figure 3.12 – Jet Mixer System Set-up

Once the oil is injected and mixed with water using the jet mixer system, the jet mixer system can be switched off and isolated. The velocity within the flow loop and the stirrer in the mixing tank ensures the dispersion created remains stable and suitable for testing.

Figure 3.13 shows the final design of the jet mixer constructed, with dimensions shown in millimetres.

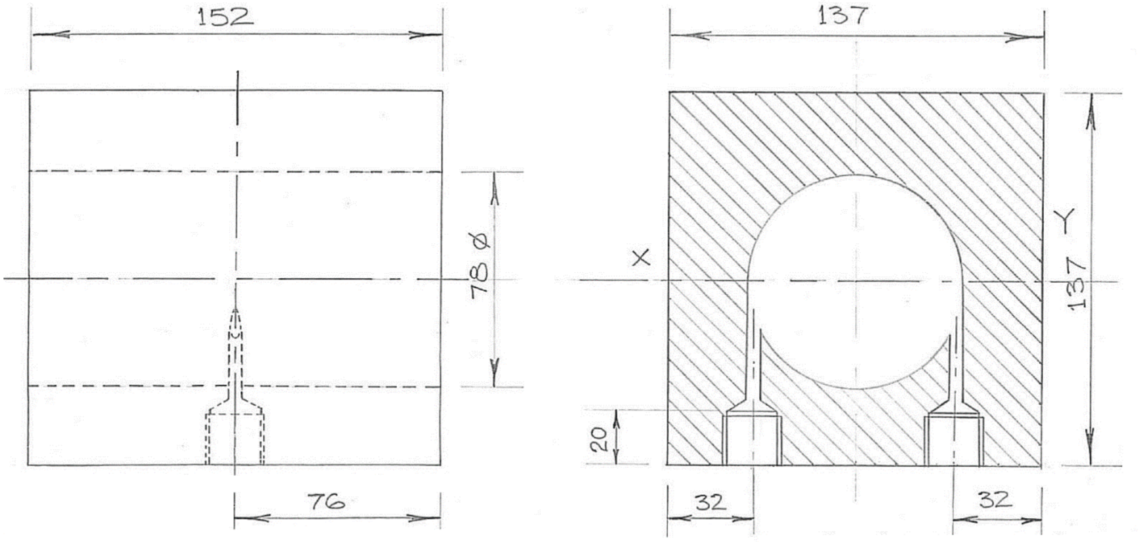


Figure 3.13 – Jet Mixer Design

During the design of the jet mixer, a series of exploratory computation fluid dynamic simulations were untaken to investigate the mixing profile after the injection ports. Figure 3.14 shows an example graphical outputs from one of the simulations, demonstrating the velocity profile of the jet mixing system. To verify the jet mixing system, an experimental analysis was completed with the results from the droplet size trial being shown in Figure 3.14.

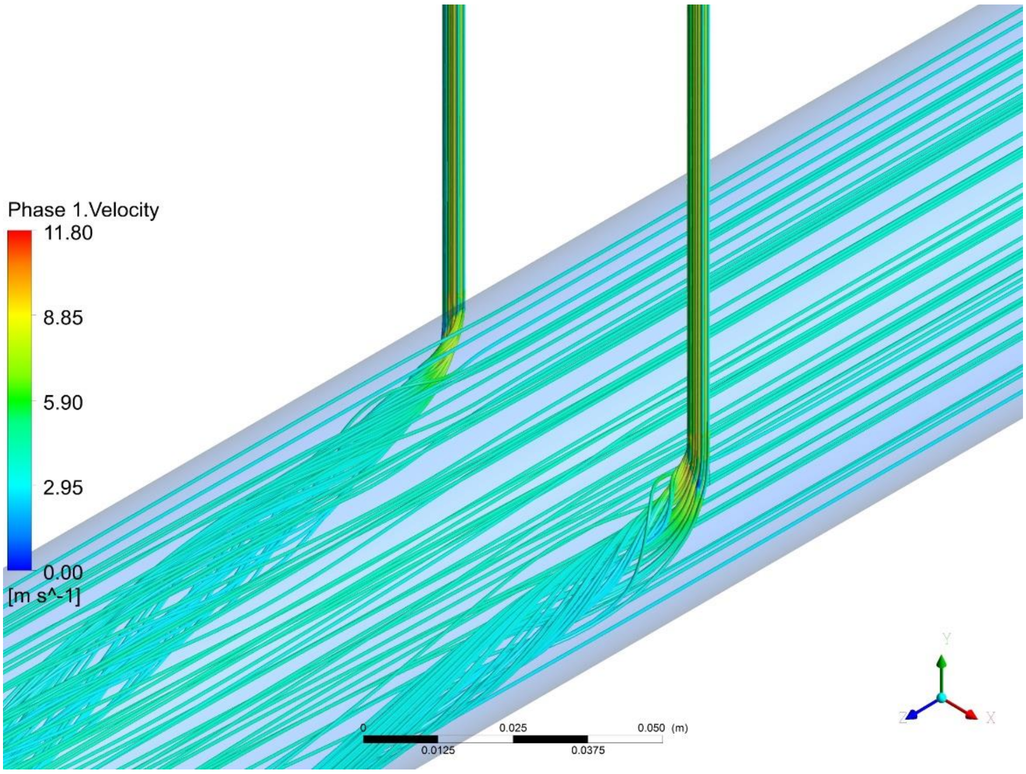


Figure 3.14 – Jet Mixer Velocity Profile

The two-phase simulation was carried out on ANSYS Fluent using the turbulence model, k-epsilon. The conditions were set-up as steady-state under the assumption of incompressible and isothermal conditions. As an output from a mesh sensitivity study, a standard unstructured tetrahedral mesh of size 2.5 mm was utilised throughout the model, with 0.25 mm used in the 6mm jet mixing lines. Three inlet velocity boundary conditions were assumed, one for the main line and each of the injection points.

Using an oil-in-water concentration of 30mg/l, a trial was conducted varying the jet mixer speed to demonstrate the ability to control oil droplet size in the facility, as shown in Figure 3.15. As discussed previously, other mechanisms such as mixing tank speed and main line velocity can also be used to further tweak the droplet size to the desired value.

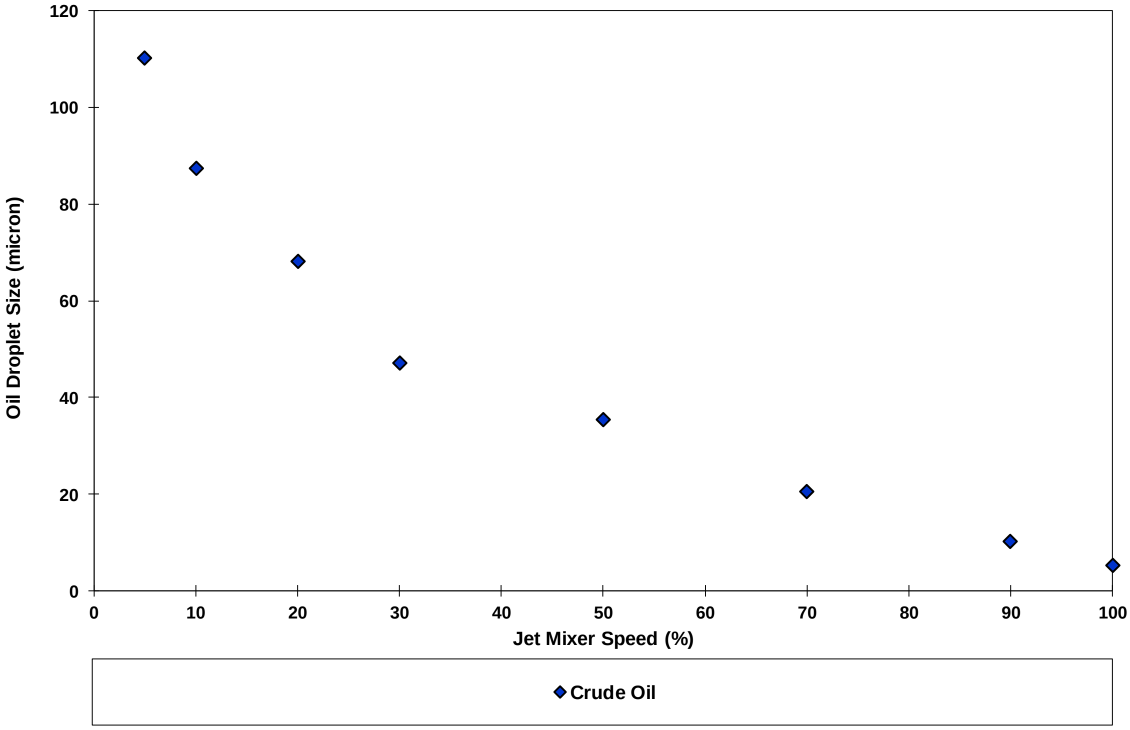


Figure 3.15 – Crude Oil Droplet Size vs. Jet Mixer Speed

By knowing the density of the test oils and the volume injected together with the known amount of water volume within the loop, oil concentration can be estimated. The actual oil concentration of the test fluid was determined using the infrared based reference method, as discussed in Chapter 2. By varying the jet mixing flow rate, the speed of stirrer in the mixing tank and the velocity in the main flow loop, the oil droplet size can be altered for a specific concentration.

Figure 3.16 – Mixing Tank and Clean Water Storage Tank

Figure 3.16 shows a picture of the mixing tank and clean water supply tank for the test loop. The mixing tank, which is part of the circulation loop, has a cooling jacket and is equipped with a 375 mm four blade 45° pitched turbine mixer controlled via a 1.1kW motor. With water circulated at speed set by the main line 37 kW centrifugal pump, the temperature of the water can rise with energy input by the pump. The clean water tank is used to initially fill the loop and used for cleaning/flushing cycles. This tank is lagged and is also temperature controlled using an immersion heater. This provides an enhanced cleaning process as water at an elevated temperature can be utilised.

All sample probes used in the test facility are designed to ensure representative samples. The design of the probe is a pitot tube, inserted directly into the centre of the pipe, facing against the flow direction. An example sample probe is shown in Figure 3.17.

Figure 3.17 – Sample Point No.1

3.5 Operating Procedures

To prepare the loop for a test condition, the following start-up procedures were followed:

1. Fill the test loop with fresh water from the water supply tank
2. Start the main line circulation pump
3. Take samples for oil-in-water concentration analysis
4. If it is deemed clean (below 1 mg/l oil-in-water concentration), move to next step. If not, repeat the cleaning cycle (see below)

However, to set up a test condition further steps were required to be followed. To set up an oil-in-water condition, the following steps are required:

1. Set the jet mixer pump and mixing impeller speed for target particle size. Jet mixer and impeller speed is based off main line velocity, trials ran during commissioning and target droplet size.
2. Enable the Malvern Insitec device for oil droplet size analysis
3. Inject oil via jet mixer stream using a manual dosing system. Amount of oil injected based upon final oil-in-water concentration required.
4. Allow the flow in the test loop to reach a steady-state
5. Take samples for oil-in-water concentration analysis
6. Check oil droplet size measurement via the Malvern Insitec and alter the jet mixer speed accordingly. Jet mixer and impeller speed is based off main line velocity, trials ran during commissioning and target droplet size.
7. Start recording test facility parameters (i.e. Pressure, Temperature, Flow)

8. Enable test instrument measurements
9. Collect samples for oil-in-water concentration analysis via test section sample points.
10. Stop test instrument measurement
11. Analyse oil-in-water concentration samples
12. Record results along with test facility conditions and all test instrument data
13. Drain the test loop
14. Start the cleaning cycle

To increase the oil concentration in the loop, steps 1 – 11 were repeated. After the final oil concentration test point was completed, steps 12 and 13 were carried out. The cleaning cycle was done to prepare the test loop for the next test condition.

The cleaning cycle, which needs to be performed at the end of each test, is an important step to ensure that any oil, solids or other contaminants in the flow loop are removed before setting up the next condition. The steps involved in the cleaning cycle include:

1. Fully drain the test loop
2. Fill the test loop with fresh water at an elevated temperature (minimum 50ºC)
3. Start the main line circulation pump (30 minutes minimum)
4. Take samples for oil-in-water concentration analysis.
5. Drain the test loop

The cleaning cycle is repeated until the level of contamination in the loop is below 1 mg/L as measured by the reference method.

3.6 Initial Commissioning

A range of flow conditions were trialled during the commissioning period of the test facility. The commissioning focused on the following aspects:

- Generation of oil-in-water with different oil droplet size and concentration
- Generation of consistent solid in water dispersion
- Creation of consistent and stable test conditions
- Demonstration of the reference methods

To ensure full confidence in the particle size measurement, certified latex spheres with a Dv50 of 9.45 microns were purchased and used. The Malvern was disconnected from the test loop and a sample mixture of the latex particles and water were added to the Malvern's measurement cell. Two runs were carried out with the results shown in Figure 3.18 and Figure 3.19.

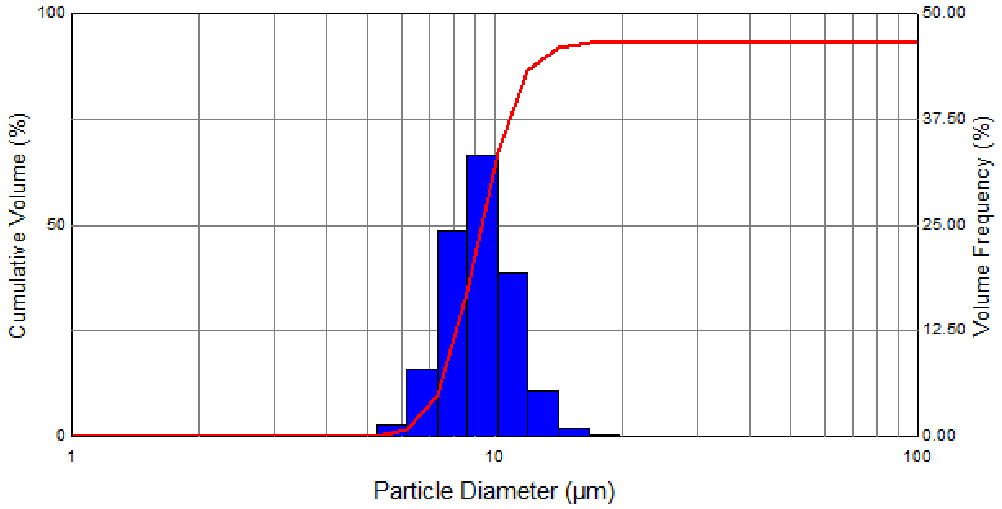


Figure 3.18 – Particle Size Reference with Latex Spheres Run 1

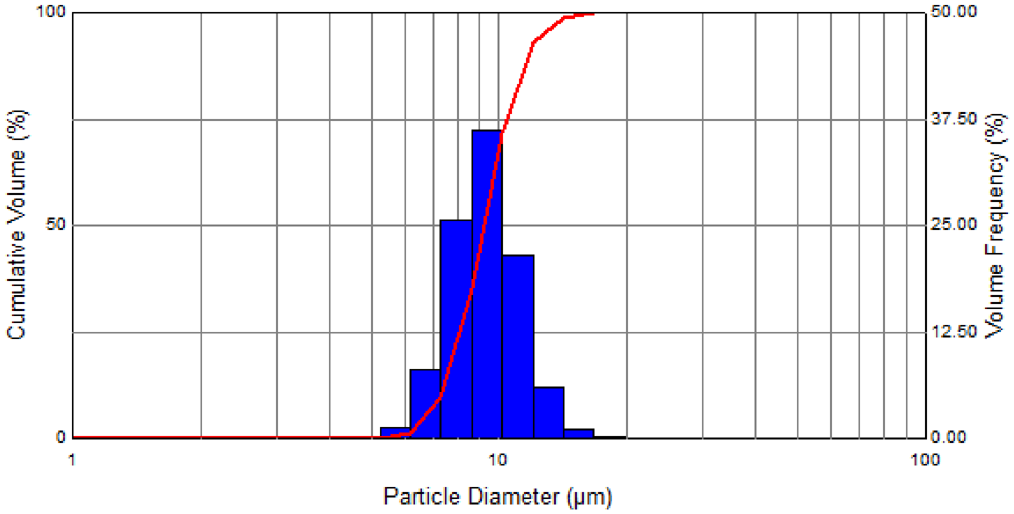


Figure 3.19 – Particle Size Reference with Latex Spheres Run 2

The results from both trials with the latex spheres were very close and show repeatable results, with a Dv50 of 9.37 and 9.25 microns respectively.

The generation of consistent oil-in-water with the ability to manipulate oil droplet size is very important in the simulation of produced water conditions. Summary results are given below to show different oil droplet sizes that have been achieved from the test loop as measured by the Malvern Insitec instrument. Two oils were used in the trials, a crude oil and a condensate oil.

In this case, oil was injected into the loop at a concentration of 1000 mg/l and allowed to reach steady state at 3 m/s mainline velocity. Figure 3.20 shows a typical droplet size distribution as measured by the Malvern Insitec instrument with a Dv50 of 45 µm.

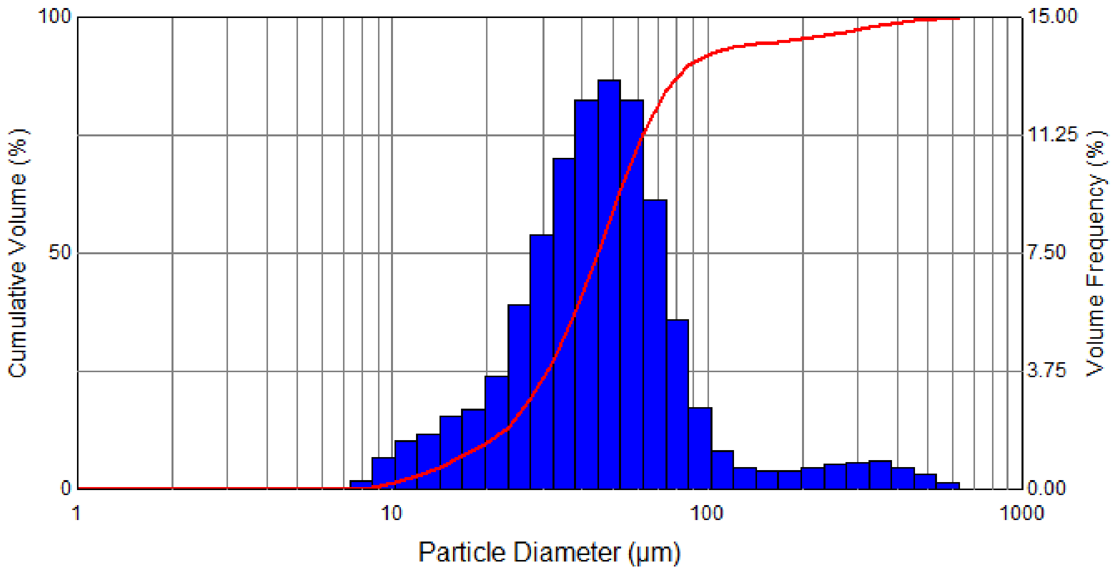


Figure 3.20 – Mean Particle Size of 45 µm using Crude Oil at 1000 mg/l, 3 m/s

Oil was injected into the loop at a concentration of 300 mg/l and allowed to reach steady state at 3 m/s mainline velocity. Figure 3.21 shows a typical droplet size distribution as measured by the Malvern Insitec instrument with a Dv50 of 20 µm.

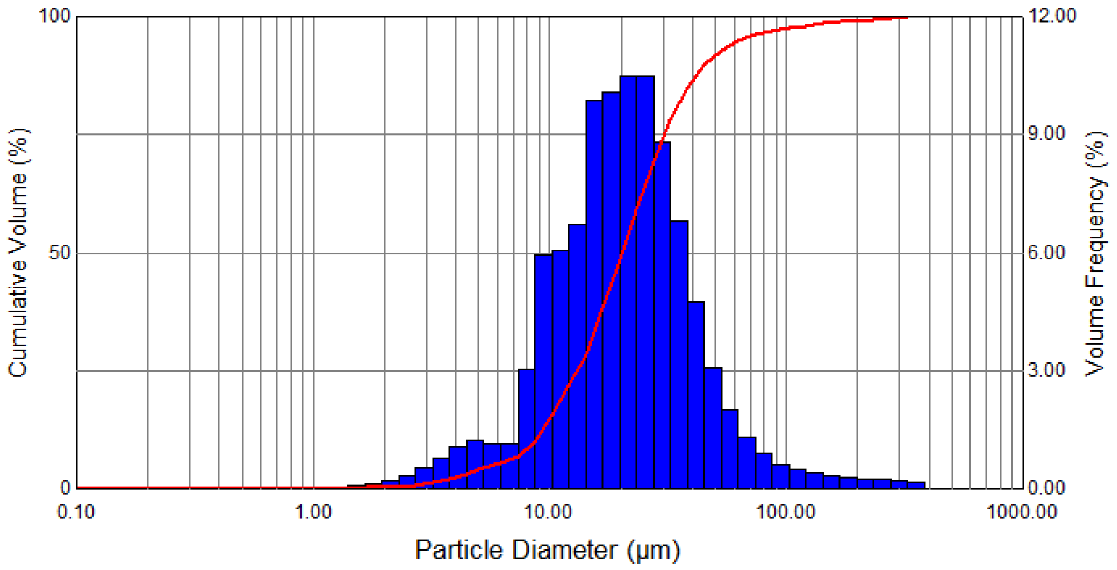


Figure 3.21 – Mean Particle Size of 20 µm using Crude Oil at 300 mg/l, 3 m/s

Under the same conditions as in the previous test but this time at a reduced mainline velocity of 2 m/s, as anticipated an increase in the oil droplet size was detected. Typical oil-in-water droplet size distribution with a Dv50 of 35 µm is shown in Figure 3.22.

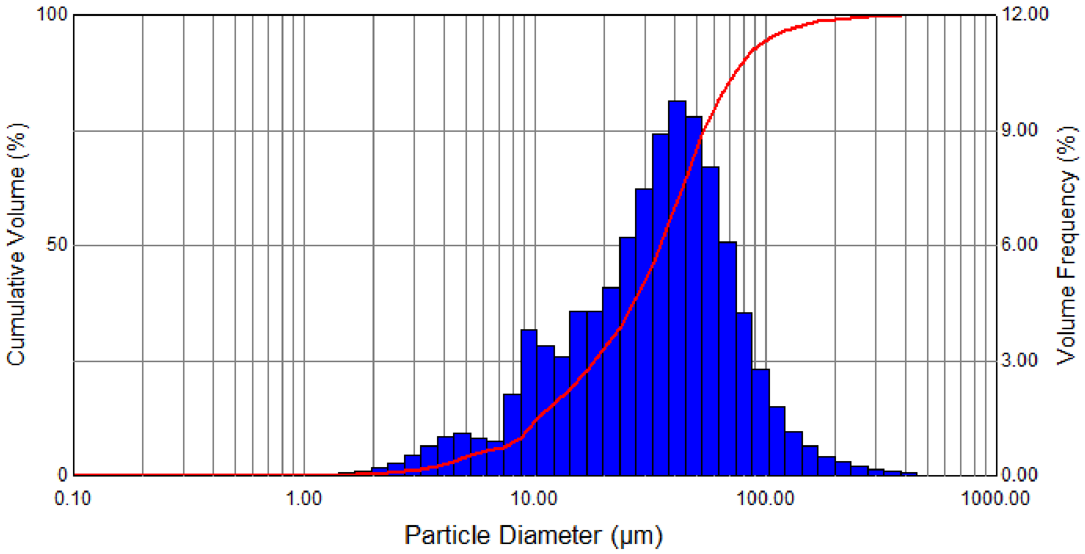


Figure 3.22 – Mean Particle Size of 35 µm using Crude Oil at 300 mg/l, 2 m/s

Figure 3.23 shows the particle size distribution achieved when a concentration of 30 mg/l of condensate oil was injected with the main pipeline velocity of 3 m/s. A mean droplet size of 5 µm was achieved and the droplet size distribution remained stable for a long period of time.

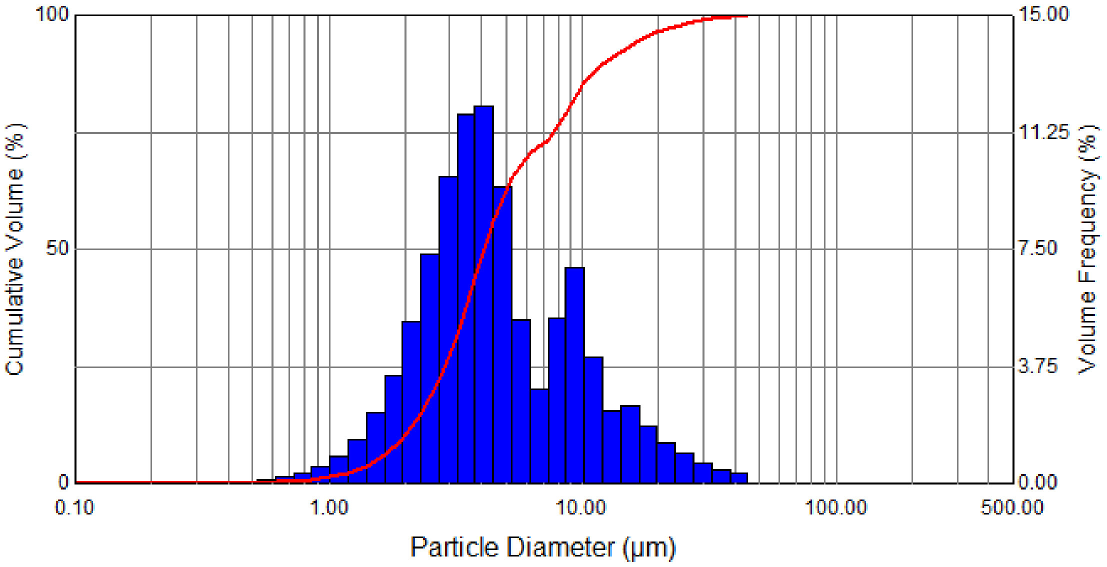


Figure 3.23 – Mean Particle Size of 5 µm using Condensate Oil at 30 mg/l, 3 m/s

To further verify the stability of oil-in-water concentration, a trial was completed with a target concentration of 10 mg/L set-up in the facility. During a period of four hours, three samples were collected at 30-minute intervals and analysed using the infrared reference method to determine any changes to oil concentration over time. This trial was undertaken to ensure oil is not being lost or trapped within parts of the recirculation facility, which would lead to a loss of oil overtime. It should be noted however, as the overall system is open to atmosphere, external conditions such as temperature could lead to a small amount of oil evaporation over time, which would also be determined as part of this experiment.

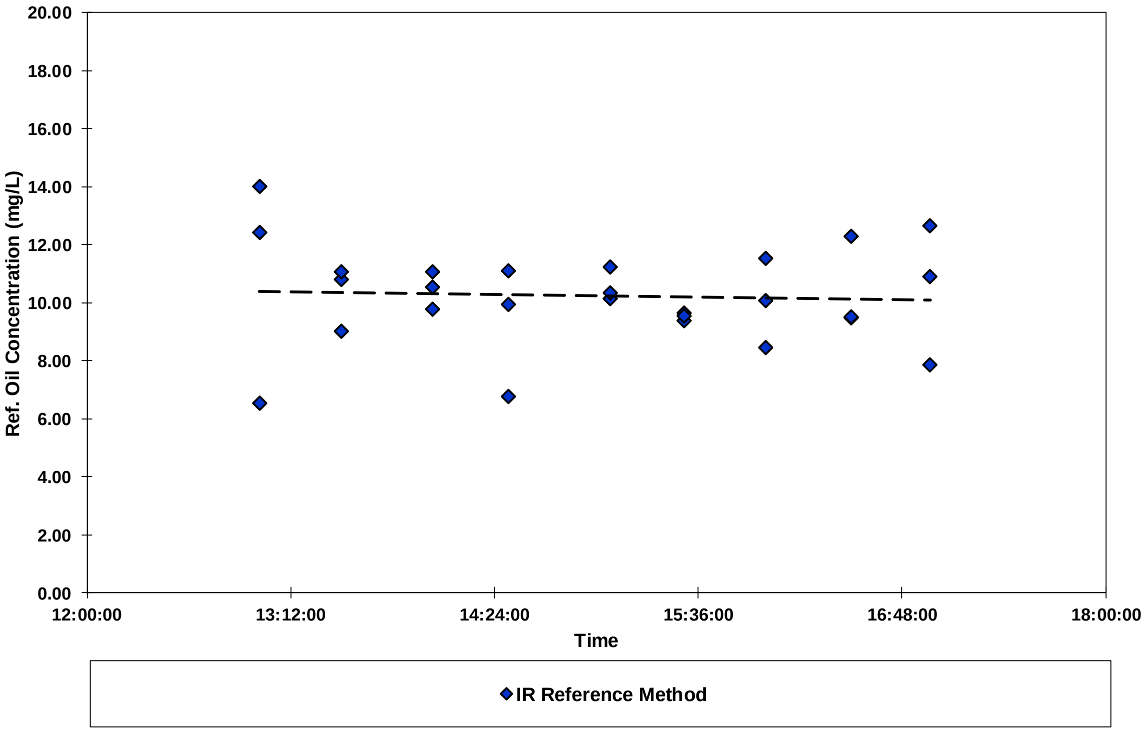


Figure 3.24 – Oil-in-Water Concentration Stability over 4 hours

The results from Figure 3.24 demonstrate that the concentration remained stable of the testing period and no major fluctuations were observed.

3.7 Facility Specification Overview

The produced water facility at NEL was designed to simulate produced water conditions. To verify the range of oil-in-water concentration, a trial was conducted to incrementally increase the dosage of crude oil into the facility to increase the oil-in-water concentration up to 5000 mg/l. Figure 3.25 shows the results of this trial. The results are an average of five samples at each oil-in-water concentration.

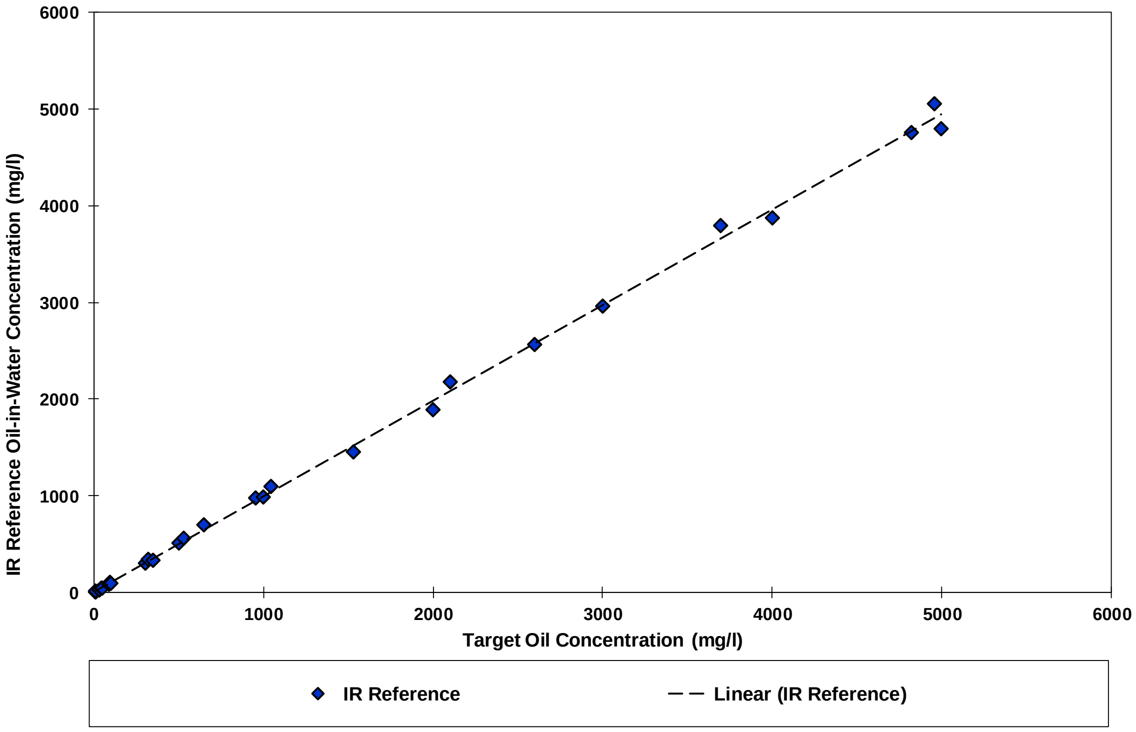


Figure 3.25 – Oil-in-Water Concentration Range in Produced Water Facility

A similar trial was also conducted for solid particles up to 1000 mg/l, as shown in Figure 3.26. The solids used in this trial had a DV50 particle size of 17µm.

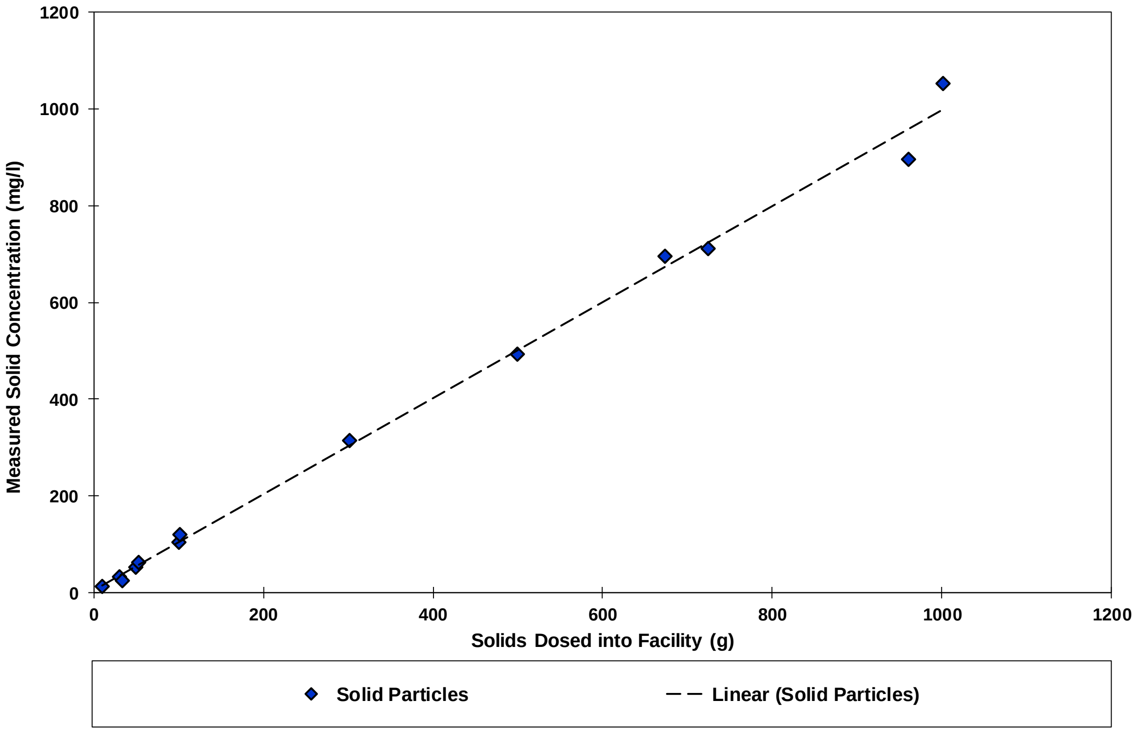


Figure 3.26 – Solid Concentration Range in Produced Water Facility

Two different solid particles sizes are used during this research with a DV50 of 6.47 and 17.03µm. These solids are pre-measured before injecting into the facility. To demonstrate the stability of the solid particles, a trial was also conducted for 3 hours, measuring the droplet size every 30 minutes. The results are shown in Figure 3.27.

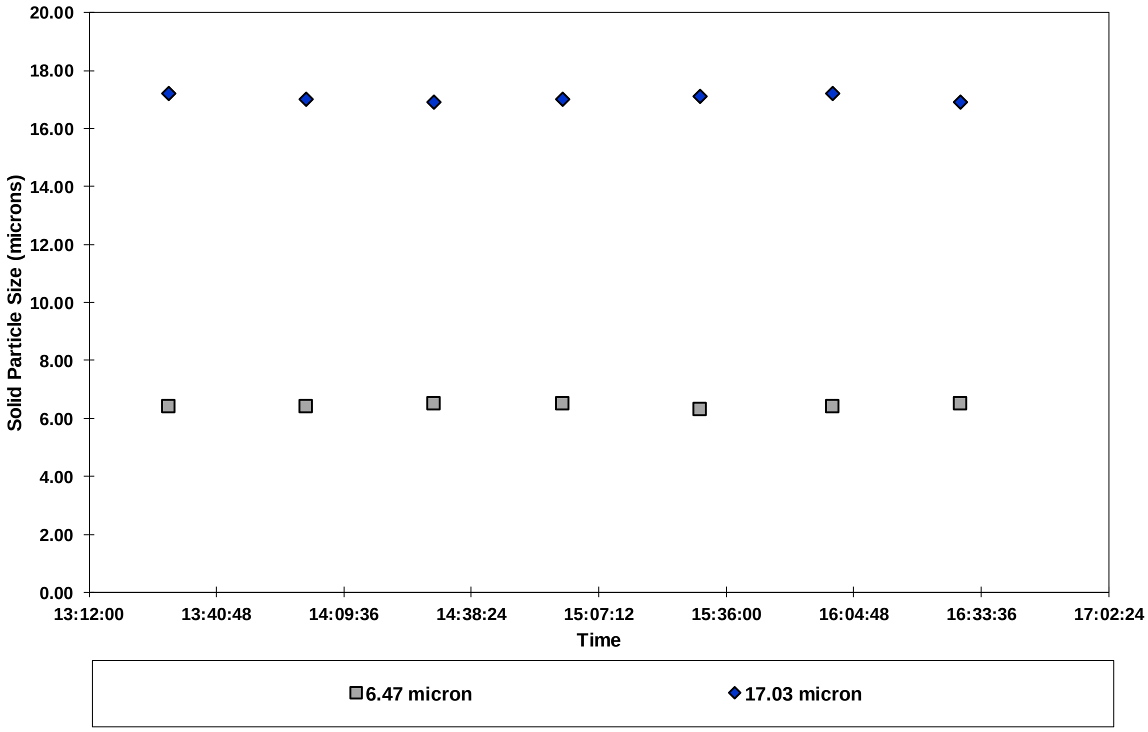


Figure 3.27 – Solid Particle Size Stability in Produced Water Facility

This trial demonstrates that the particle size is stable and does not change throughout typical testing periods.

3.8 Summary

This chapter aimed to solve this challenge by answering the first research question of the thesis:

- Can we simulate stable produced water conditions in an experimental facility? Can the droplet size be controlled to be within specified diameter ranges?

This chapter discusses the development of a produced water facility that was able to demonstrate effective simulation of stable produced water conditions with controllable droplet size, thus successfully answering the research question posed. This development allows the experimental work required to answer the remaining research questions, to be undertaken. To summarise the key aspects of the design of the test facility, the facility can be broken down into three main parts: the jet mixing system, the test section and the holding tanks.

. The jet mixing system was configured to add a shear force to oil droplets through two small bore pipes angled 90^o into an acrylic 80mm diameter pipe section. By varying the velocity of the jet mixer stream, the velocity at the jet mixer could be altered and therefore the magnitude of shear and resulting oil droplet size could also be controlled. During commissioning droplet size range from 5 to 110 microns were successfully established.

The test section was designed in the vertical orientation with a blind t-piece situated at the start. The test section was configured in this way to try to maintain as stable and consistent fluid conditions throughout the whole test section. Several trials during commissioning were completed to confirm consistent results. On the test section, five sample locations are located, to allow for up to five online analysers to be installed in series.

The holding tanks are where the bulk fluids are held. At typical flow rates, the retention time in the facility is less than one minute. However, to ensure droplets and particles remain in suspension within the holding tank, especially at lower fluid velocities, a four blade 45° pitched turbine impeller was designed and installed into the main tank.

Table 3.5 summarises the range of specifications that were achieved in the produced water facility during commissioning.

Table 3.5 – NEL's Produced Water Facility Specifications

Oil concentration	0 – 5000 mg/l
Oil Droplet size	5 – 110 µm
Solid concentration	0 – 1000 mg/l
Solid particle size	0 – 130 µm
Process temperature	15 – 80 °C
Flow velocity	0.5 – 7 m/s

There are several test facilities across the world that claim to be able to achieve the conditions, however most of these facilities are in-house facilities for internal research and development with very little or no publications or access allowed. The design of a new facility capable of simulating produced water conditions, allows research, development and evaluation of oil-in-water measurement techniques to be undertaken. As the facility has been designed in a recirculation-based design, it allows enhanced stability compared to other typical once-through system, as the same fluid recirculates leading to higher repeatability.

4 Produced Water Parameter Characterisation

As produced water streams contain many different contaminants and can vary greatly depending on the application and location, the use of technologies to measure oil-in-water concentration in real time, requires the knowledge of how certain key parameters can affect measurement performance. The second research question, as discussed further in Chapter 1, poses the following challenges:

- What techniques are available that can detect oil-in-water at concentrations below 30 mg/L? In addition, can the impact of typical parameters found in produced water applications be quantified for individual techniques?

The first of these challenges is to determine which technologies are currently available that can detect typical produced water discharge concentrations. The second question poses a more difficult challenge of quantifying the effects of varying parameters. Due to most of experimental work being carried out during development by instrument manufacturers, very little data of how the technologies are impacted by various parameters are published or made publicly available. Due to this, and the fact that most of research that has been published has not focussed on a specific technique, comparisons between techniques cannot be easily achieved. For regulators to allow the use of online measurements instead of currently accepted offline methods, it is understood that the operator will be required to prove that the online technique used is statistically equivalent.

To answer the research questioned posed, experimental work was undertaken to evaluate the performance and uncertainty of each selected technology.

4.1 Preliminary Experimental Work

The purpose of the initial testing described in this section is to determine the measurement issues associated with three well established oil-in-water measurement technologies. The research focussed on generic technology principles and not specific manufacturers or instrument models. Image Analysis, Laser Induced Fluorescence and Ultrasonic technologies are used extensively throughout many industries for the measurement of liquid-liquid, solid-liquid and many other multiphase flow conditions. The experiments replicated conditions often found in real produced water discharge and re-injection streams, however with variables controlled to determine the effects of each parameter.

The preliminary experimental work was completed using a single pass flow facility situated in Orkney, UK. Full details of the facility and test procedure is described in Appendix I.

Table 4.1 – Preliminary Test Matrix

Test Types	Oil		Added Solid		Presence of Gas	Chemical	Temperature (°C)	Flow Velocity (m/s)
	Conc (mg/l)	Size (µm)	Conc (mg/l)	Size (µm)				
Crude Oil	0, 30, 50, 100, 300, 1000	20, 50, 100	-	-	-	-	20	3
Solids Only	-	-	0, 10, 50, 100, 300	5, 22, 110	-	-	20	3
Oil & Solids	10, 30, 50, 100, 300	20	10	5	-	-	20	3
Gas Bubbles	10, 100	20	20	5	Yes	-	20	3
Chemicals	10, 100	20	20	5	-	C. Inhibitor	20	3
Temperature	30	20	20	5	-	-	20, 35, 50, 65	3
Flow Velocity	50	20	20	5	-	-	20	0.5, 1, 3
Dynamic Response	100, 2000, 100	-	20	5	-	-	20	3
Fouling	50	20	20	5	-	-	20	3

The purpose of the tests performed was to determine the effect of individual parameters on the respective measurement of oil in water concentration and total suspended solid concentration. To achieve this, baseline measurements were taken for oil only and for solid only, which were used to compare with the parameter tests to determine any impact. The full test matrix completed in this preliminary work is shown in Table 4.1 to be able to determine individual parameter effects, it is key that all other variables not being tested remain constant to ensure errors are not incorporated in the results. The following parameters are controlled throughout each test:

- Oil type – 36^{o} API oil
- Oil concentration – Injected rate via oil metering pump
- Solid concentration – Injected rate via slurry dosing pump
- Oil droplet size – Choke valve position and pressure drop
- Solid particle size – Silica sand of Dv50 length 5, 22 and 110 µm
- Gas – Gas injector system
- Chemical – Corrosion Inhibitor (Nalco EC1231A) via chemical metering pump
- Temperature – Heat exchanger in main process line
- Flow rate – Main process pumps
- Fouling – Inspections in-between test conditions

The purpose of this preliminary experiment was to identify the impact on individual parameters on the primary measurements of each technology. Several operational and hardware issues were encountered during the experimental, however most tests planned were able to be completed. Some of the issues and problems encountered by the tested instruments included:

- Light source failures (Image Analysis)
- Condensation (Image Analysis)
- Ineffective fouling mitigation mechanism (Image analysis and Ultrasonic)
- Slow response to a change in test condition (Ultrasonic)
- Sensitivity to oil droplet size (LIF)

Overall image analysis and LIF performed better in comparison with the ultrasonic device, however the full test results and outcomes are discussed further in Appendix I.

4.2 Characterising Parameter Effects

The preliminary work found that there are several parameters which can impact the oil concentration measurement for the evaluated techniques. To gain a better understanding of these effects, a second experimental study was carried out using the Produced Water test facility at NEL.

As discussed previously in Chapter 3, the facility was designed to specifically simulate produced water under stable and controllable conditions for this research. Two technologies, Laser Induced Fluorescence and Image Analysis were selected to be included in this experiment due to their performance in the preliminary trial. Like the preliminary trial, all parameters were held constant with a single variable controlled to determine the influence of a specific parameter. The purpose of this experiment is to determine the limitations of the online techniques, and what challenges are required to be overcome.

4.2.1 Test Instrument Configuration

Even though two technologies were selected as part of this research, four instruments in total were evaluated for this experiment. Each instrument was installed in an inline and in a bypass configuration. The additional configuration will increase the total number of data points captured for each technology and allow comparisons to be made between the different installation configurations. Table 4.2 summarises the configuration for each test instrument:

Table 4.2 – Test Instrument Configuration

Configuration	Laser Induced Fluorescence	Image Analysis
Inline	2-inch branched T	3-inch direct inline
Bypass	1-inch sample line	1/2-inch sample line

The two instruments on bypass lines are installed using modified sample points. These bypass lines use bypass take-off points shown in Figure 4.1 and Figure 4.2.

Figure 4.1 – Example Bypass Take-Off Point (Facility view)

Figure 4.2 – Example ½” Bypass Take-Off Point (Inside View)

The other two instruments are installed in the inline configuration. The inline configuration means the devices are exposed directly to the main flow, and no sampling or alternate method of extracting part of the flow is required. There are many advantages and disadvantages to both inline and bypass configurations. The best configuration to use is typically situational and depend on the desired application. Some of these advantages and disadvantages are summarised in Table 4.3.

Table 4.3 – Inline vs. Bypass Configuration

Configuration	Advantages	Disadvantages
Inline	• Will typically see a higher portion of conditions. • Configuration can still allow device to be extracted.	• More intrusive compared to bypass • Portion of flow ‘captured’ dependent on inline design • Removal of instrument may require main line to be shut off.
Bypass	• Installation of devices is straightforward. • Several instruments can be connected to the same bypass line. • Removal and maintenance of instruments do not interrupt main line.	• Requires a sample line which may not be representative of the main flow conditions. • Velocity of sample lines may cause fouling to occur.

For each test point completed, data was collected for a minimum of 1 hour. The raw data from each of the techniques was then averaged to get their output for that test condition. Similarly, the results from the three reference samples collected throughout the test point was also averaged into a single oil-in-water concentration reference value.

4.2.2 Laser Induced Fluorescence

Figure 4.3 shows the processing units that control both Laser Induced Fluorescence devices. These units are processing computers with internal data acquisition systems, allowing full local operator control via a USB point.

Figure 4.3 – Laser Induced Fluorescence Processing Units

The LIF inline analyser was installed perpendicular to the flow with the probe being inserted directly into the process stream. The unit supplied consisted of a processing unit and a probe, shown in Figure 4.3 and Figure 4.4 respectively. The probe was connected to the processing unit via a fibre optical cable encased in an umbilical. The unit had recently been upgraded to allow the probe to allow extract from the process without having to stop the process, by incorporating two isolation valves in the instrument design. The instrument is fully controllable via the processing unit, however can also be manually controlled by an operating laptop.

Figure 4.4 – Inline Laser Induced Fluorescence Analyser

The LIF probe comes equipped with an automatic ultrasonic cleaning mechanism. The unit is set up on a cleaning cycle, turning on the ultrasonic cleaning every 15 minutes. The cleaning mechanism works by generating ultrasonic waves through the optical window, creating cavitation. The cavitation results in the removal of any fouling that may have occurred. The unit can only measure oil-in-water concentration and cannot measure particle size.

The LIF bypass unit was set up on a one-inch sample line, with the flow cell being connected to the processing unit. An isolation valve is also present downstream of the flow cell, allowing the flow to be stopped through the unit at any time. The bypass arrangement is shown in Figure 4.5.

Figure 4.5 – Laser Induced Fluorescence Bypass Analyser

The LIF bypass unit also comes equipped with an automatic ultrasonic cleaning mechanism, which works in the same way as the probe. Ultrasonic waves are generated through the optical window which creates cavitation. The unit is set up on a 15-minute cleaning cycle. Every 15 minutes, the flow is stopped automatically via the isolation valve and homogenising takes place. The unit uses the ultrasonic waves to homogenise and create smaller and more uniform oil droplets, and therefore leads to more accurate oil-in-water measurements. After this cycle has occurred, cleaning then takes place.

4.2.3 Image Analysis

The first image analysis instrument is a 3" device fitted inline as shown in Figure 4.6. The supplied unit was an upgraded version of what was tested previously in the preliminary experimental program, as described in Section 4.1. The encased unit encompasses the light source, camera, on-board processer and electronics, with only an ethernet connection to a desktop computer and a power supply required to be connected. For faster processing speeds, the unit is set up to process the data using the on-board processer, controllable using remote access via the desktop computer. The housing has also been upgraded to a design pressure of 3000 psi.

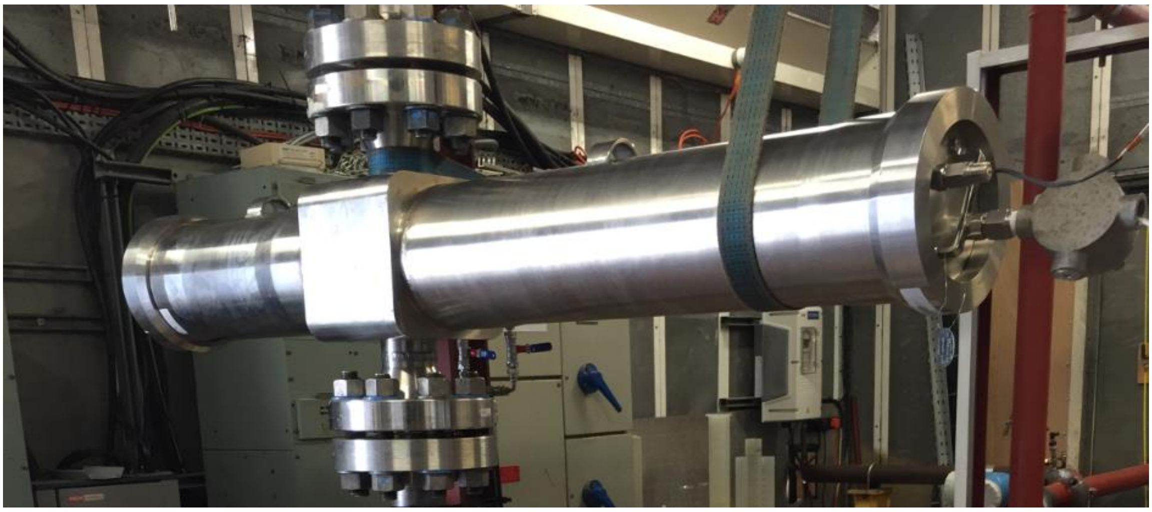


Figure 4.6 – Inline Image Analysis Analyser

The light source of the device had been upgraded to LED which reduces its failure rate and increases the instruments reliability. The image analysis device also had an upgraded cleaning mechanism, consisting of two jet spray rings located at the optical windows.

Figure 4.7 – Inline Image Analysis: Cleaning Mechanism Arrangement

Two ½" Swagelok pipe fitting ports at the side of device shown in Figure 4.7, allow for high pressure cleaning fluids to enter. The cleaning mechanism as shown requires up to a 1000 psi fresh water supply and jetting at a rate of around 6 litres per minute at a frequency of 1 minute per side per hour.

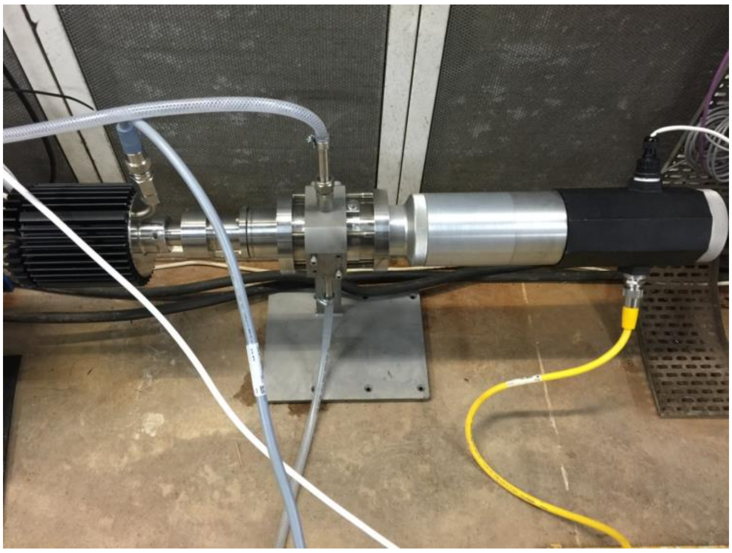


Figure 4.8 – Image Analysis Bypass Device

The second image analysis instrument is a bypass-based device. The unit was set up in an arrangement as shown in Figure 4.8. The unit supplied is connected such that sample fluids from the test spool enter at the bottom of the instrument and flow upward through the instrument flow cell before returning to the flow loop. The instrument has no automatic cleaning capability and thus is required to be cleaned manually. This is carried out by disconnecting the return flow line and then removing the flow cell revealing the optical windows, which can then be cleaned using a solvent.

Image analysis devices can discriminate between oil droplets, solid particles and gas bubbles and can measure each in terms of concentration and particle size independently.

4.2.4 Test Device Calibration

Prior to the start of the tests, several steps were required to be undertaken to set-up and calibrate the test instruments. As the purpose of the test program is to quantify the impact different parameters have on the oil-in-water concentration measurement of the test devices, the first test focusses on creating a baseline for the remaining tests to be compared against. With this baseline, the initial calibration is not as critical as in other parts of the research work. However, to obtain realistic results, all instruments underwent a calibration procedure prior to commencement of the tests. It should also be noted that after this calibration step, all settings and correlations were fixed and remained unchanged throughout this work. This was necessary to get representative test results, as changing settings would add another variable which may skew results.

Several steps were required to set-up the image analysis units. These steps were carried out for both devices. The first step involved using a mesh grid to set-up the camera zoom function, as shown in Figure 4.9. The grid is designed for each individual square to measure exactly 10µm, thus the zoom and particle size settings were altered based on the grid.

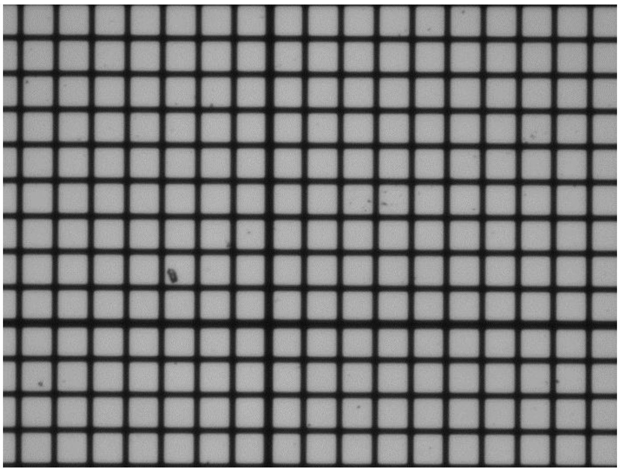


Figure 4.9 – Image Analysis Particle Size Grid Calibration

After setting up the particle sizing element of the devices, the next step is to determine the threshold settings. The threshold settings are based upon two factors; intensity and colour. By varying these parameters, the detection limits of the devices can be altered. If these settings are too high, then background noise and fouling may be detected as oil droplets, if too low, most of the target oil may not be distinguished. Figure 4.10 shows an image of oil droplets when threshold settings have been set-up and applied.

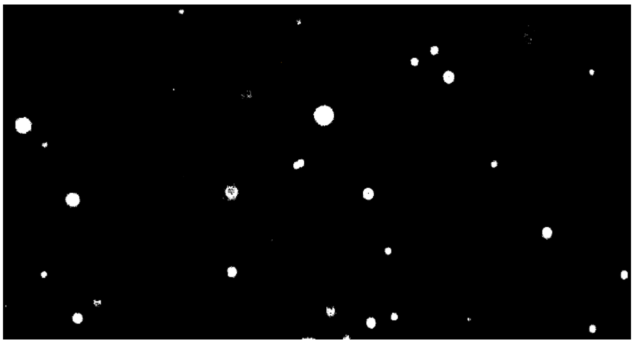


Figure 4.10 – Image Analysis Threshold Set-Up

The last step for the image analysis units is to set-up the particle filter settings. These settings determine what is detected as an oil droplet, solid particle, gas bubble or not counted. The particle filter settings are very important as skewed results can occur if not set-up correctly. The following parameters are controlled in these settings:

1. Particle Area
2. Perimeter
3. Major and Minor Axis
4. Circularity
5. Fill percent (Opacity)
6. Rotation
7. Aspect Ratio

The calibration of both LIF devices required a different procedure. The procedure is split into two steps, an offline calibration and then validation on the test facility. The offline calibration involves creating an oil-in-water sample of 1000 mg/l, by spiking a known weight of 1000 mg crude oil into 1000ml measured volume of water. Half of the prepared sample was then added to a container designed for the LIF devices to measure the oil-in-water concentration. The remaining portion of the prepared sample was then diluted by topping up the volume with water to reach 1000 ml. By repeating these steps, the oil-in-water concentration is reduced by half each time, creating known reference oil-in-water concentration steps.

After the offline calibration was completed, the LIF devices were then installed into the test facility and validated by trialling several oil-in-water concentrations.

4.2.5 Test Matrices and Methodology

Table 4.4 summarises the test matrix covered during this research. The parameters chosen to be evaluated were based upon the data of the preliminary experimental evaluation.

Table 4.4 – Summary Test Matrix

Test Types	Oil		Added Solid		Presence of Gas (%)	Chemical (mg/l)	Salinity (g/l)	Temperature (°C)	Flow Velocity (m/s)
	Conc (mg/l)	Size (µm)	Conc (mg/l)	Size (µm)					
Crude Oil	0, 30, 100, 300, 500, 1000	20, 50, 100	-	-	-	-	-	20	3
Condensate Oil	0, 30, 100, 300, 500, 1000	20, 50, 100	-	-	-	-	-	20	3
Solids	30	20	10, 50, 100, 300	6.5	-	-	-	20	3
Gas Bubbles	30, 50, 100	20	-	-	1	-	-	20	3
Chemicals	30, 50, 100	20	-	-	-	50	-	20	3
Salinity	30	20	-	-	-	-	10, 20, 30	20	3
Temperature	30	20	-	-	-	-	-	20, 35, 50, 65	3
Flow Velocity	30	20	-	-	-	-	-	20	0.5, 1, 3, 5
Dynamic Response	5000, 1000, 30	-	-	-	-	-	-	20	3
Fouling	-	-	-	-	-	-	-	20	3

A picture of the overall installation is shown in Figure 4.11.

Figure 4.11 – NEL Produced Water Facility Test Set-up

The main operating procedures of the facility are described in Chapter 3. This section will summarise the additional procedures undertaken as part of this experimental work. The effect of solids test procedure is split into several sections; however, they need to be carried out in a particular order.

Addition of solids procedure:

1. Set the mixing tank impeller speed as required for sufficient solids mixing
2. Enable the Malvern Insitec for particle size measurement
3. Weigh the required quantity of sand using a calibrated scale
4. Inject the solids into the mixing tank
5. Allow the flow in the test loop to come to a steady-state. Steady-state is achieved after a minimum of 15 minutes and no trending of particle size seen during this time period.
6. Take samples for solid in water concentration analysis
7. Check solid particle size measurement via the Malvern Insitec device

Addition of crude oil procedure:

1. Set jet mixer pump and mixing impeller speed for target particle size
2. Enable the Malvern Insitec device for droplet size analysis
3. Inject oil via jet mixer stream using a manual dosing system
4. Allow the flow in the test loop to reach a steady-state. Steady-state is achieved after a minimum of 15 minutes and no trending of droplet size seen during this time period.
5. Take samples for oil-in-water concentration analysis
6. Check oil droplet size measurement via the Malvern Insitec and alter the jet mixer speed accordingly

Combined test procedure:

1. Start recording test facility parameters (i.e. Pressure, Temperature, Flow)
2. Enable test instrument measurements
3. Take samples for oil/solid in water concentration analysis
4. Stop test instrument measurement
5. Analyse oil/solid in water concentration sample
6. Record results along with test facility conditions and all test instrument data
7. Drain test loop to settling tanks
8. Start the cleaning cycle

Once the first test condition had been complete, the addition of crude oil procedure was repeated to increase the oil concentration to the next target test point. After completion of the test, the standard cleaning procedures, described in Chapter 3, were carried out.

Three tests were carried out with the addition of chemicals, each using a corrosion inhibitor (Nalco EC1544A) to determine the impact of production chemicals. The chemical tests were set up and operated in a similar manner to the Oil Only test procedure. After the crude oil has been added, the required dosage of corrosion inhibitor was injected. The chemical was injected via the jet mixer stream with a syringe. The concentration of the corrosion inhibitor was estimated based upon the volumes of chemical added and the volume of the test fluid in the loop.

The Effect of Temperature test was carried out initially using the Oil Only procedures. Fresh water in the fresh water tank was initially heated to above 80ºC using the immersion heater. This fresh water was then added to the test loop to allow for testing to be conducted at an elevated temperature. By controlling the cooling water flow rate through the cooling jacket on the mixing tank, specific temperatures were set and maintained within ±0.5ºC.

The Effect of Gas Bubbles test followed the same steps as the Oil Only procedure. Once the correct oil concentration and solid concentration were achieved, gas was then induced into the test loop system via the mixing tank. The type of impeller used in the mixing tank created a vortex, and by increasing the speed of the impeller, air was entrained into the test fluid.

The Effect of Flow Velocity test was carried out using the Oil Only procedure. The only difference was that the speed of the main line centrifugal pump and control valve position were altered to change the velocity in the test spool piece to the target test conditions.

The Salinity Test was carried out using a similar procedure to the Oil Only test. However, prior to the start of the Oil Only procedure, a fixed amount of Sodium Chloride was weighed and added into the mixing tank to create a saline water solution containing the desired concentration of sodium chloride. To make sure that all sodium chloride was dissolved before the oil was injected; the mixture of water and sodium chloride in the test loop was allowed to circulate. Samples were taken every 15 minutes to check if the sodium chloride had fully dissolved.

The dynamic response test was carried out in several stages. First, a very high oil concentration test is completed, subjecting the instruments to abnormally high amounts of oil-in-water. The oil concentration is then reduced in several steps, with a test point taken each time, until a typical oil-in-water concentration is reached. The results from this test will determine if exposing the devices to high concentrations of oil will leave any residual memory effect on their results. To further investigate this effect, a fouling test was completed. All instruments were manually fouled using the test crude oil and left exposed to the oil for 24 hours. The instruments were then re-installed into the facility and a test condition was undertaken to determine if the manual fouling had resulted in any errors.

4.2.6 Results

For each test run during this experimental work, the results in terms of oil concentration, solid concentration, oil droplet size and solid particle size were obtained from the respective instruments together with reference values of oil and solid concentration, and size information from the particle size analyser. For the purposes of this research work, the focus is primarily on oil concentration, with the oil droplet size, temperature, pressure and flow velocity data measured and used to ensure stability and repeatable test conditions.

To determine impact of specific parameters and trends for each technology over a range of conditions, the data was mainly assessed according to the percentage deviation between the averaged outputs of each device versus the average reference value. Using this methodology allows the results from several tests points to be compared directly, even with varying oil reference concentrations.

The full results for each of the tests are tabulated and shown in Appendix II.

4.2.6.1 Baseline Crude Oil

Instruments were initially tested with different oil concentrations ranging from 0 to 1000 mg/l. Figure 4.12 shows a summary of the results from this baseline test.

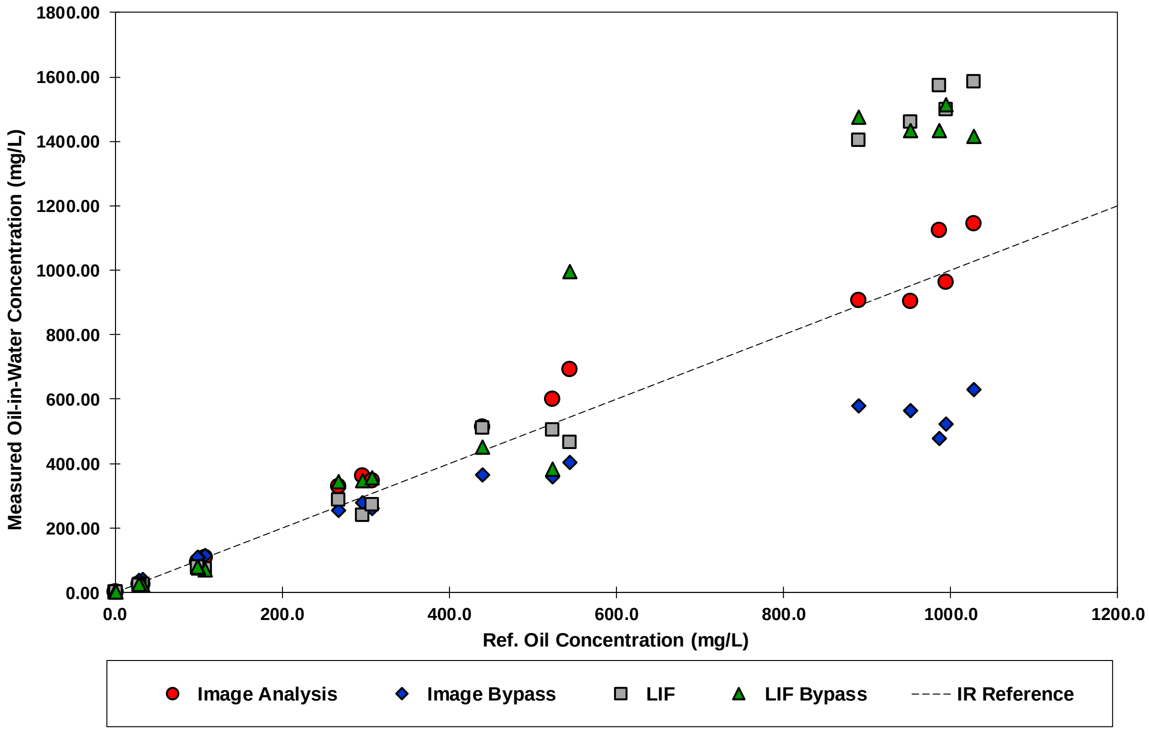


Figure 4.12 – Baseline Oil Results

Due to the scaling on the x-axis on the graph that the data plotted below the 100 mg/l cannot be easily seen. To rectify this, Figure 4.13, shows the 0 to 100 mg/l results with better resolution.

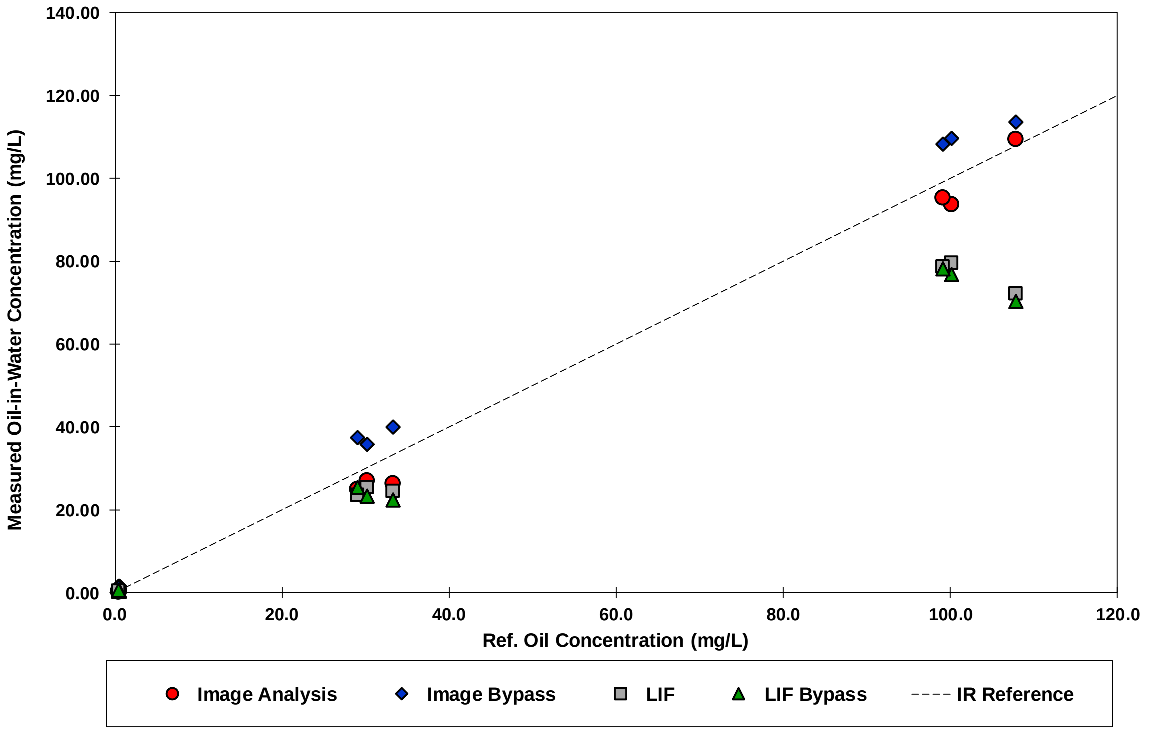


Figure 4.13 – Baseline Oil Results (Scaled)

Figure 4.14 shows the oil concentration measurement of each device plotted against percentage error determined using the infrared reference method.

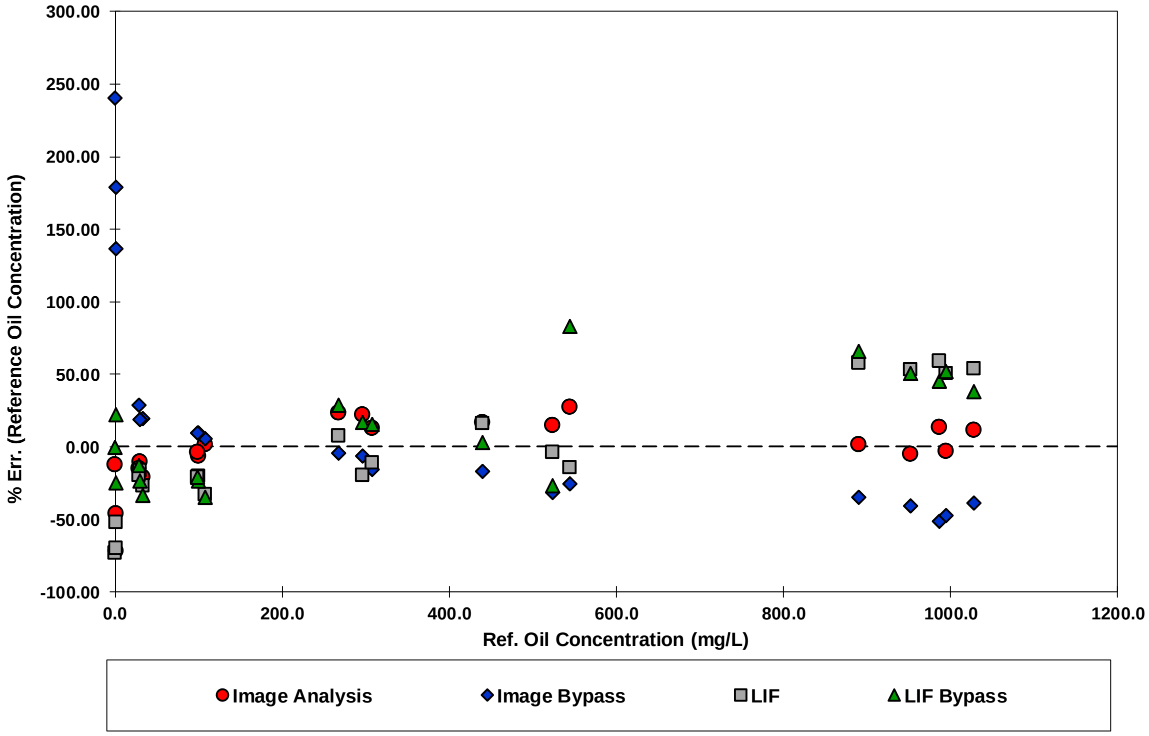


Figure 4.14 – Baseline Oil Results (Percentage Deviation)

At lower oil concentrations, between 30 and 300 mg/L, all the instruments were able to remain within ±30% of the reference value. A high initial reading by the image analysis bypass device at the zero condition was caused by residual fouling, which was rectified by manual cleaning prior to restarting the test program.

At the 0mg/l test condition, deviations from the reference are seen up to ±75%. At this condition, there is a small quantity of residual oil in the system, typically measured less than 1 mg/l. As the oil concentration is very low, when comparing measurements by the devices, deviations of ±75% only equate to 0.75 mg/l differences. This impact of viewing the results in as a percentage deviation need to be carefully considered, as interpretation of results may be skewed. This can be demonstrated by viewing Figure 4.13; all test instruments at the 0mg/l test condition are close to the reference value, however high percentage deviation results can be seen. For the majority of the tests completed during this part of the research, the purpose is to determine influences on specific parameters and therefore percentage deviation allows trends to be noticed and quantified.

Increasing the oil concentration up to 500 mg/L, again most of the devices remain within ±30% of the reference, however a single high reading of +90% is seen by the LIF bypass unit. After investigating this measurement, it was noted that the optical window had significant fouling, however the device was able to recover by increasing the cleaning frequency of its ultrasonic cleaning system. At the highest concentration, nominal 1000 mg/l, the inline image analysis unit remained within the ±30% deviation from reference value. The bypass image analysis technique however was lower than previous, down to -50%, leading to a downward trend with increasing oil concentration. Both LIF instruments significantly over measured up to 60% higher than the reference.

As both Laser Induced Fluorescence devices use the same core equipment, their measurements remain close to each other throughout all test points. This demonstrates that for the baseline oil condition, the installation configuration of inline versus bypass makes little impact on the measurement performance. However, looking at the image analysis results, the measurements between inline and bypass are quite different. This is thought to be down to the fact that the two image analysis devices are using different equipment, such as, light source, camera, optical window dimensions, and thus have different performances.

As discussed previously, for produced water discharge, typically oil concentrations under 100 mg/l are seen, however in upset conditions or in reinjection for enhanced oil recovery situations, higher concentrations are encountered. As this test is the baseline which all other tests are compared against, due to the high errors associated with the upper oil concentrations range, it was decided that extra points were taken at oil concentrations at 1000 mg/l. With these additional test points, it was demonstrated that the inline image analysis was the most repeatable. It should be noted however that the majority other parameter tests focus on lower oil concentrations, typically 30 to 100 mg/l, so direct comparisons can be easily established.

4.2.6.2 Condensate Oil

Instruments were tested under Condensate Oil Only conditions from a concentration of 0 mg/L to 1000 mg/L. All instruments had difficulty measuring the condensate oil concentration correctly.

Figure 4.15 shows the results of this test with all the test instruments measured oil-in-water concentration plotted against the infrared reference method.

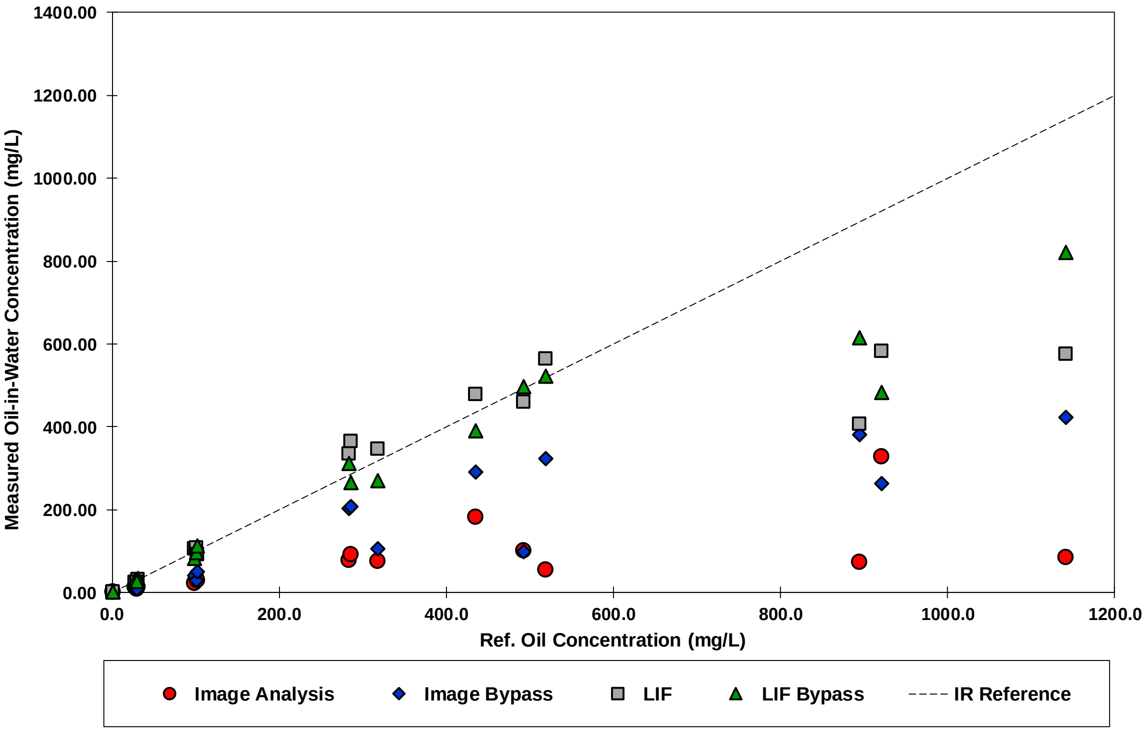


Figure 4.15 – Condensate Oil Results

Figure 4.16 displays the test instruments measured oil-in-water concentration as a percentage deviation from the infrared reference method.

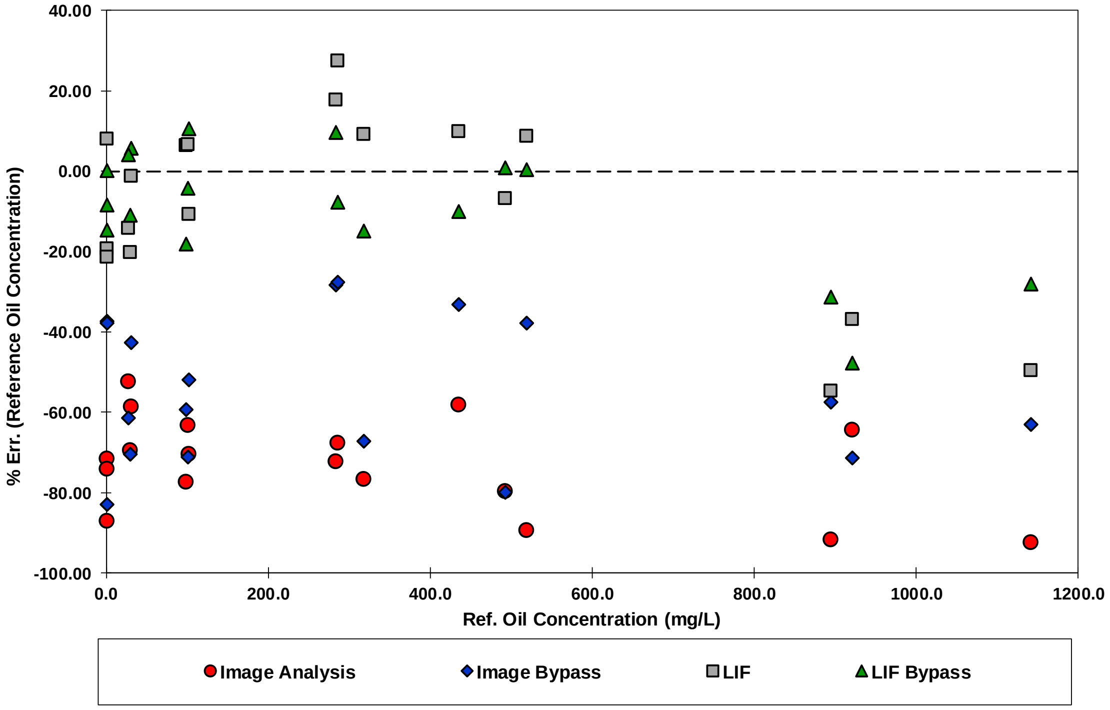


Figure 4.16 – Condensate Oil Results (Percentage Deviation)

The LIF devices remained within ±25% to the reference value up to 500 mg/l oil-in-water concentration. Above this, towards 1000 mg/l, both instruments started to undermeasure leading to deviations down to -50%, with the inline unit having a larger deviation compared to the bypass device. A similar increase in measurement error is noted for the image analysis devices, however both instruments had significantly higher errors. At all concentrations evaluated, the inline image analysis unit was not capable of measuring the condensate oil concentration leading to errors down to -90%. The bypass device performed in a similar manner, however only slightly better with errors averaging towards -60%.

These results were expected as all the instruments were initially calibrated using crude oil, with significantly different properties. Some of these fluid properties were characterised previously in Chapter 3. LIF techniques require a constant ratio of aromatic to non-aromatic compounds, thus a change of oil without prior calibration would also affect the measurement results for both devices. As the image analysis technology relies on properties such as opacity and optical density, the large change in optical properties between standard crude oil and condensate oil would result in large errors in measurement. Essentially the image analysis devices would not be able to discriminate between near transparent condensate oil and the background water flow.

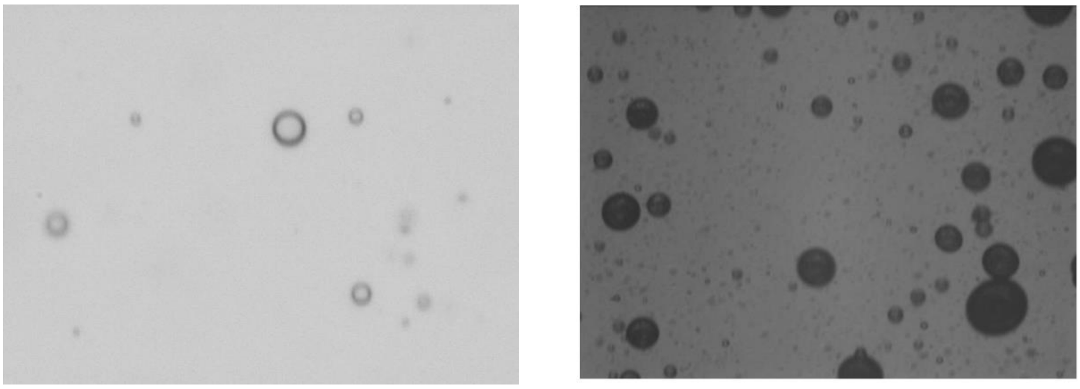


Figure 4.17 – Example Images of Condensate Oil (left) and Crude Oil (right)

Figure 4.17 shows the optical difference between the condensate oil versus standard crude oil. It is clear from the figure that the condensate oil is near transparent whereas the crude oil is typically solid opaque. Other than not being able to detect the condensate oil due to the low colour difference between the droplet and background water, some droplets may also be falsely recorded as gas bubbles due to their low opacity.

Another issue that can be found with condensate oil detection can occur during setting up the threshold conditions for the image analysis systems. Figure 4.18 shows an image taken during one of the 100 mg/l test conditions. As shown in the thresholding image, it can be difficult to set the threshold to capture a representative sample of the droplets without capturing background noise, as demonstrated in the corners of the image.

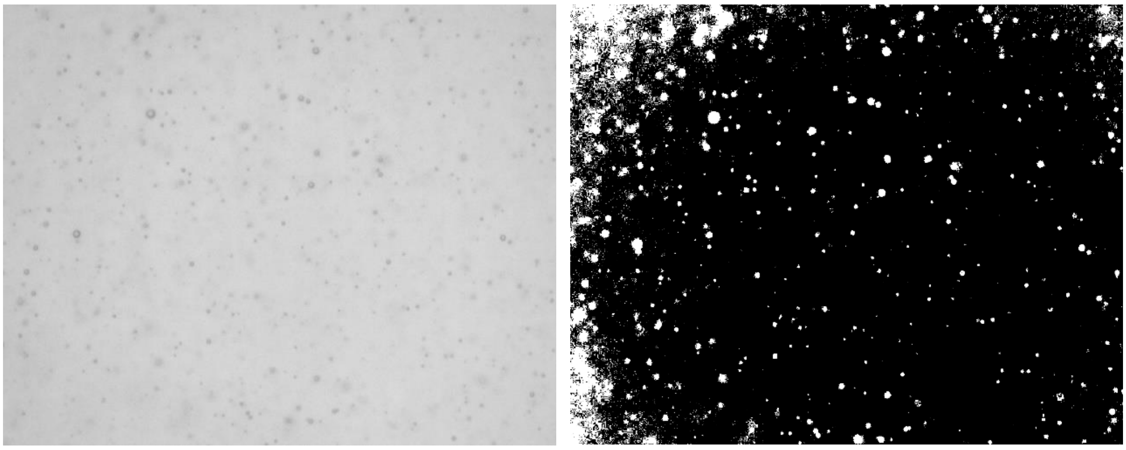


Figure 4.18 – Condensate Oil during Thresholding Process

To overcome these problems, the threshold settings need to be carefully adjusted for specific oil types, especially in lighter oils such as condensates.

4.2.6.3 Effect of Solids

The effect of solids test was carried by increasing the total suspended solid concentration between 10 and 300 mg/l whilst maintaining a constant oil-in-water concentration of 30 mg/l. The solid type chosen was a silica sand with a D50 diameter of 6.47 microns, with further details of the sand described in Chapter 3.

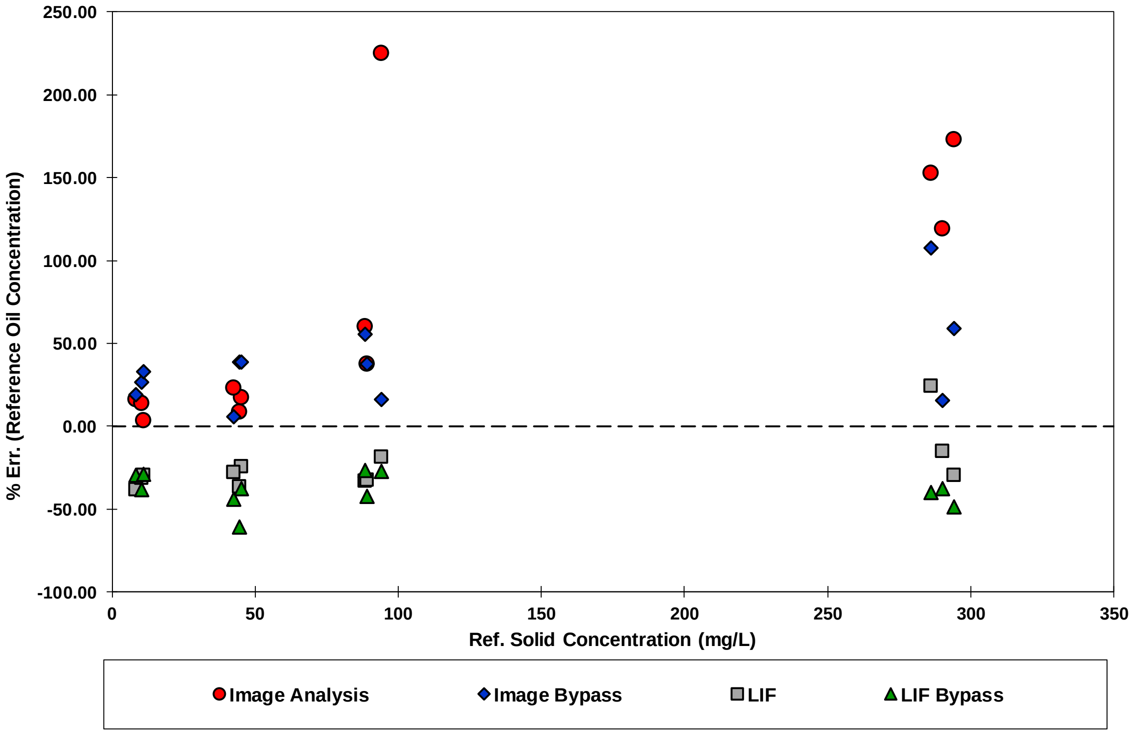


Figure 4.19 – Effect of Solids (Percentage Deviation)

For both LIF devices, the oil-in-water concentration measurements remained constant at close to -40%, however at the higher solid concentration of 300 mg/l, the inline LIF instrument had a higher reading of +20% deviation from reference. This measurement could be an error in the results or could be due to the presence of solids, however further testing would be required to verify this relationship, which is out with the scope of this research. For the inline image analysis unit, increasing solid concentration leads to higher deviations from the reference value, from +20% at 10mg/l and up to +150% at 300 mg/l solid concentration. A smaller but similar trend is seen for the bypass image analysis device.

The addition of solids adds several properties which need to be considered. For the image-based systems, solids can be mistakenly measured as oil droplets. Figure 4.20 shows images taken by the inline image analysis system, showing some example images of the 6.47µm solid particles. As can be seen, the properties of the solid particles differ substantially from oil droplets, mainly in regard to their sphericity.

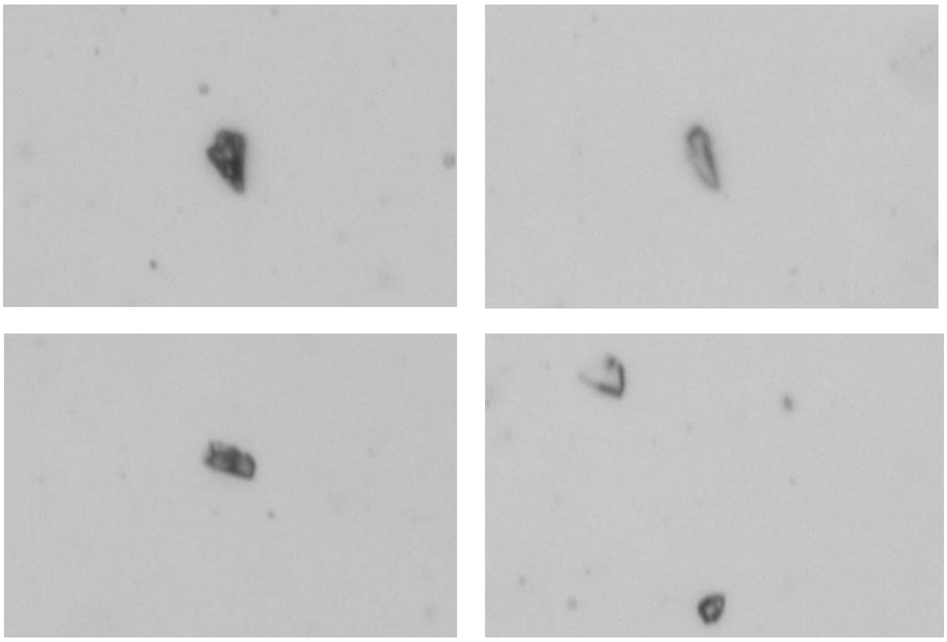


Figure 4.20 – Image of 6.47µm Solid Particles in Water

Also, cases of oil-coated solids and solid-coated oil needs to be included. Oil and solid agglomerations can lead to skewed results due to the optical properties measuring as just oil. Further research into this area would need to be completed to fully understand this effect.

4.2.6.4 Gas Bubbles

To determine the impact of gas bubbles on the measurements of the online measurement techniques, three oil concentrations 30, 50 and 100 mg/l were selected to be evaluated. At each of these conditions, an estimated rate of 1% gas by volume was injected into the facility using the method stated in Chapter 3.

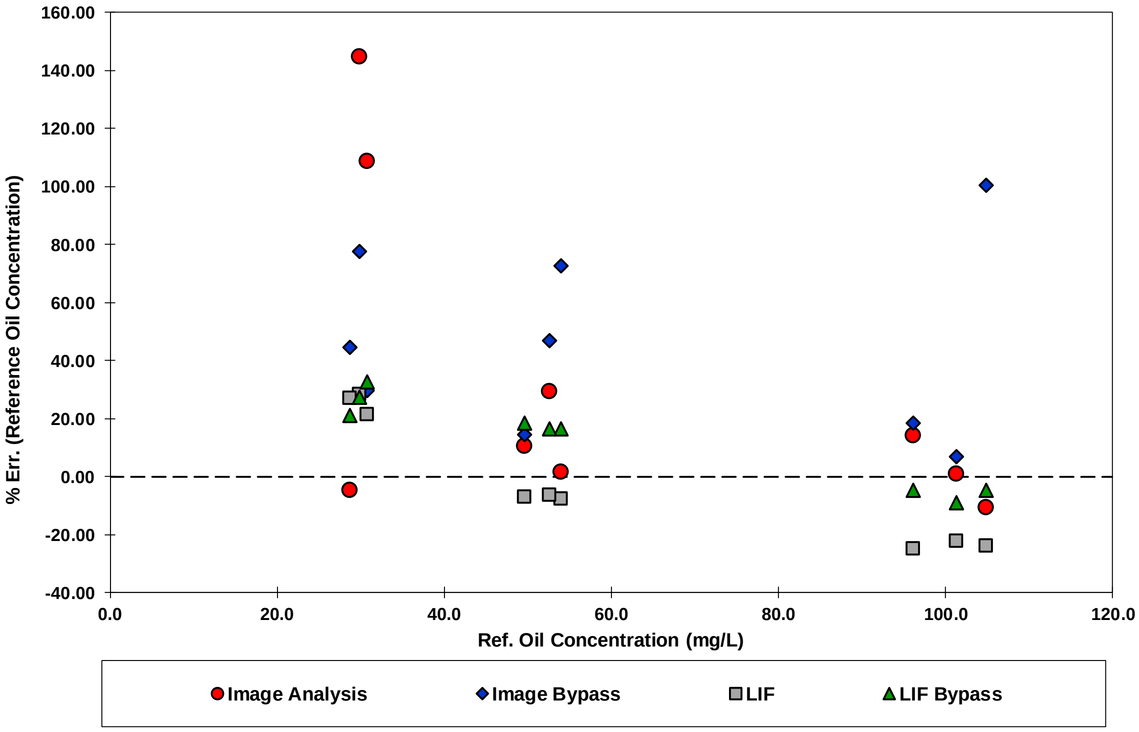


Figure 4.21 – Effect of Gas Bubbles (Percentage Deviation)

Figure 4.21 shows the results obtained during the effect of gas addition test. The baseline results for all instruments at 30 to 100 mg/l was within ±30% of the reference. For both LIF units, the measurements stay within this range and thus are unaffected by the introduction of gas bubbles. When compared with the baseline, the addition of gas bubbles has drastically increased the measurement error for both image analysis devices. However, at higher concentrations, this effect occurs much less.

This discrepancy is due to the devices incorrectly detecting the gas bubbles as oil droplets, similar to the effect of solid particles, and thus at lower concentrations of oil, this effect is much larger, as the total number of oil droplets versus bubbles are much lower. Figure 4.22 shows an image captured on the image analysis bypass device. This image shows an example of a single gas bubble, with a diameter of 21µm.

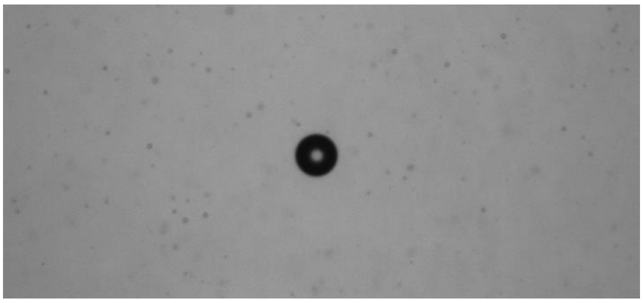


Figure 4.22 – Single Gas Bubble from Image Analysis Device

A variety of factors, such as: the initial threshold settings, fouling and agglomeration of oil droplets and bubbles, can lead to the image analysis devices detecting a portion of the gas bubbles as oil droplets. As LIF's technology does not rely on using droplet size to determine concentration, the addition of gas bubbles did not appear to have any effect. It is important to note that due to changes in pressure and because of produced water treatment techniques, gas bubbles are typically found in produced water conditions.

4.2.6.5 Effect of Chemicals

All instruments were tested with oil at 30, 50 and 100 mg/l in the presence of a corrosion inhibitor (Nalco EC1544A). The purpose of the tests was to see if the presence of a corrosion inhibitor dosed at a concentration of 50 mg/l would affect the ability of each instrument in correctly measuring oil-in-water concentration. Corrosion inhibitors are well known for causing emulsion and separation issues.

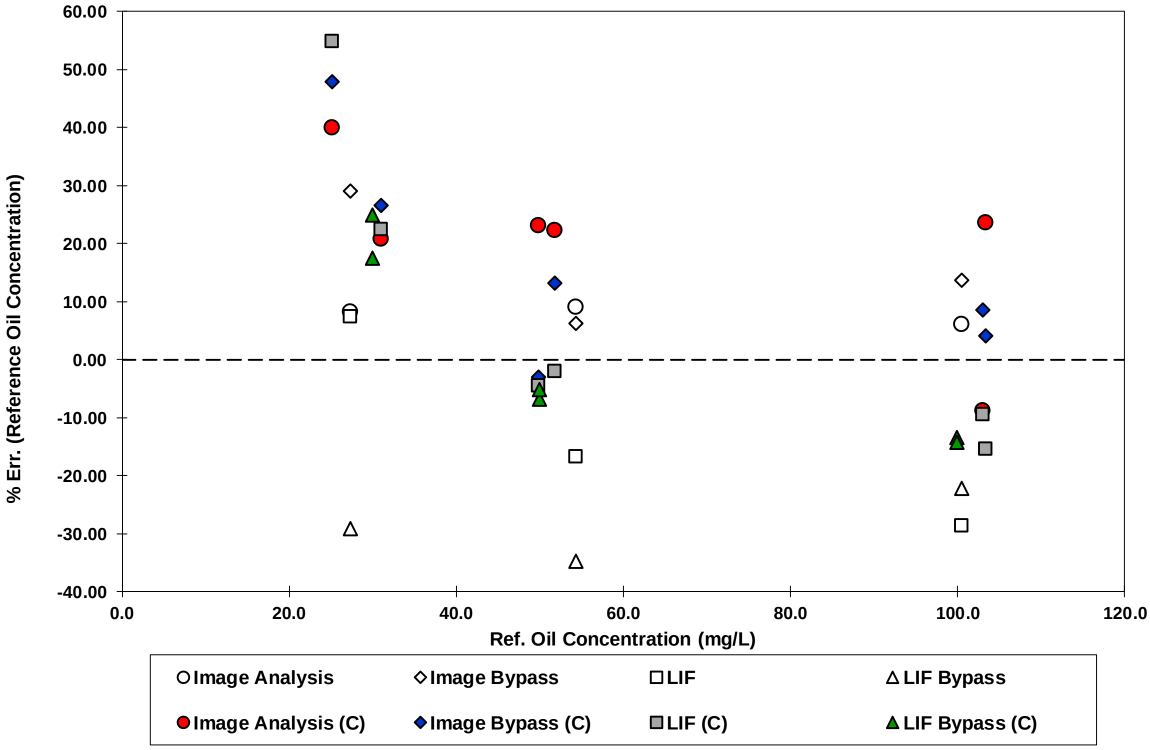


Figure 4.23 – Effect of Chemicals (Percentage Deviation)

Figure 4.23 shows the results found during with the addition of 50 mg/L of corrosion inhibitor. Similar to the addition of gas bubbles test, at lower concentrations, the addition of chemical did have an impact on the measurements on the image analysis devices, however did not seem to have a large effect at higher oil concentrations. For all concentrations, the measurements of the LIF units increased in the presence of the corrosion inhibitor, showing a direct influence due to the added 50 mg/l chemical.

It should be noted however that even though corrosion inhibitor is very commonly found in produced water streams, there are many other production chemicals which can also be found which may have different impacts. Chemicals which contain organic compounds would inadvertently cause the LIF readings to increase as they would also fluorescence and could significantly increase readings. During this test, every parameter except from the addition of the chemical was made to be the same as the baseline results. This is however not fully representative of the effect of the chemical. The addition of corrosion inhibitor would affect the fluid properties of the oil and may skew the droplet distribution which may impact the technologies results. Due to this, the effect of chemical is not easily characterised in this method of testing.

4.2.6.6 Salinity

Most of the tests carried out in the test program were done using fresh water. The properties of the water are characterised in Chapter 3. To see the effect of varying salinity, a set of tests were carried out using different concentrations of sodium chloride in water. The sodium chloride used was a 99% analytical grade salt, from Sigma-Aldrich (Sigma-Aldrich, 2019). The concentration of sodium chloride in water was increased from 10,000 mg/l to 30,000 mg/l while maintaining the oil in water concentration to a target of 30 mg/l.

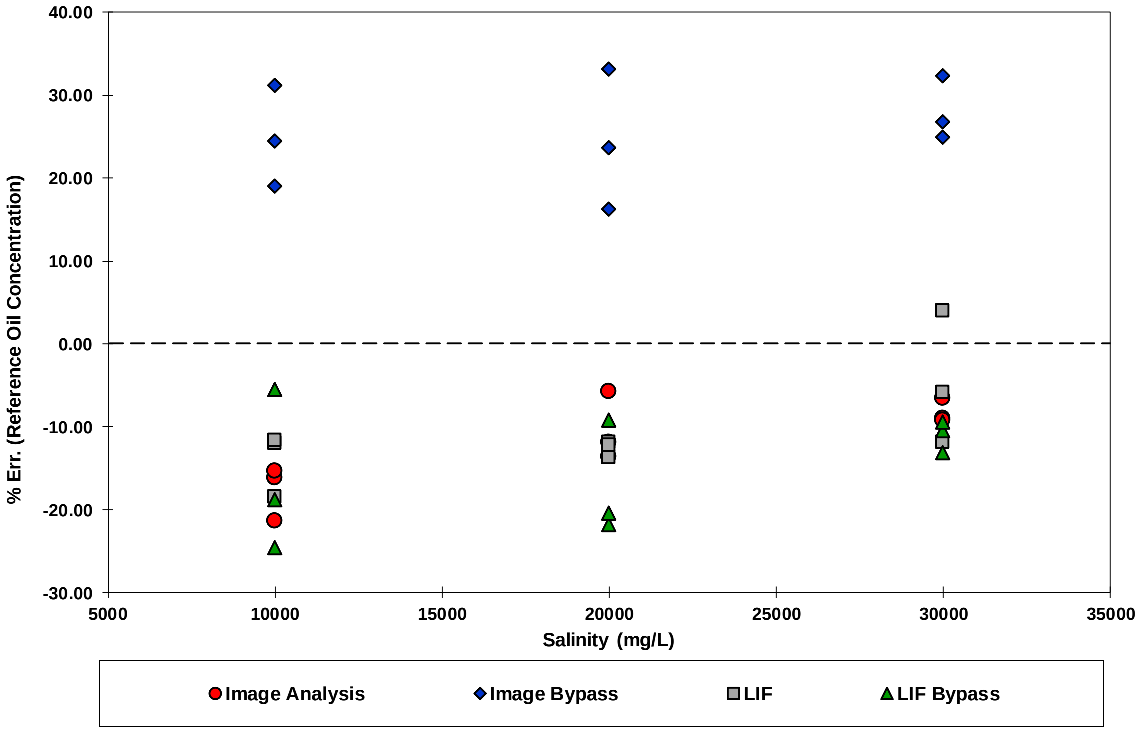


Figure 4.24 – Effect of Salinity (Percentage Deviation)

Results from the tests, displayed in Figure 4.24, were similar to the baseline results. All measurements remained consistent throughout, however at a salinity of 30,000 mg/l, a very slight increase of measurements could be noted, specifically for the inline LIF device. Prior to the start of each test, the test facility was dosed with sodium chloride and mixed for 2 hours to ensure all solids were dissolved. Even with this time, small quantities of solids may have remained as suspended solids and not dissolved yet. Other impurities are unlikely due to specification of sodium chloride used, with <0.005% insoluble purity stated (Sigma-Aldrich, 2019).

This effect would be more prevalent at the higher salinity of 30,000 mg/l and therefore may be the cause for the slight increase of measurements. As noted in the Effect of Solids section, one of the LIF measurements was increased by over 20% at the 300 mg/l solid concentration.

4.2.6.7 Effect of Temperature

All instruments were tested with oil and solids at elevated temperatures of 20, 34, 51 and 66°C with target oil concentration set at 30 mg/l. The purpose of the tests was to determine what influence changing temperature had on the oil-in-water measurement of the devices.

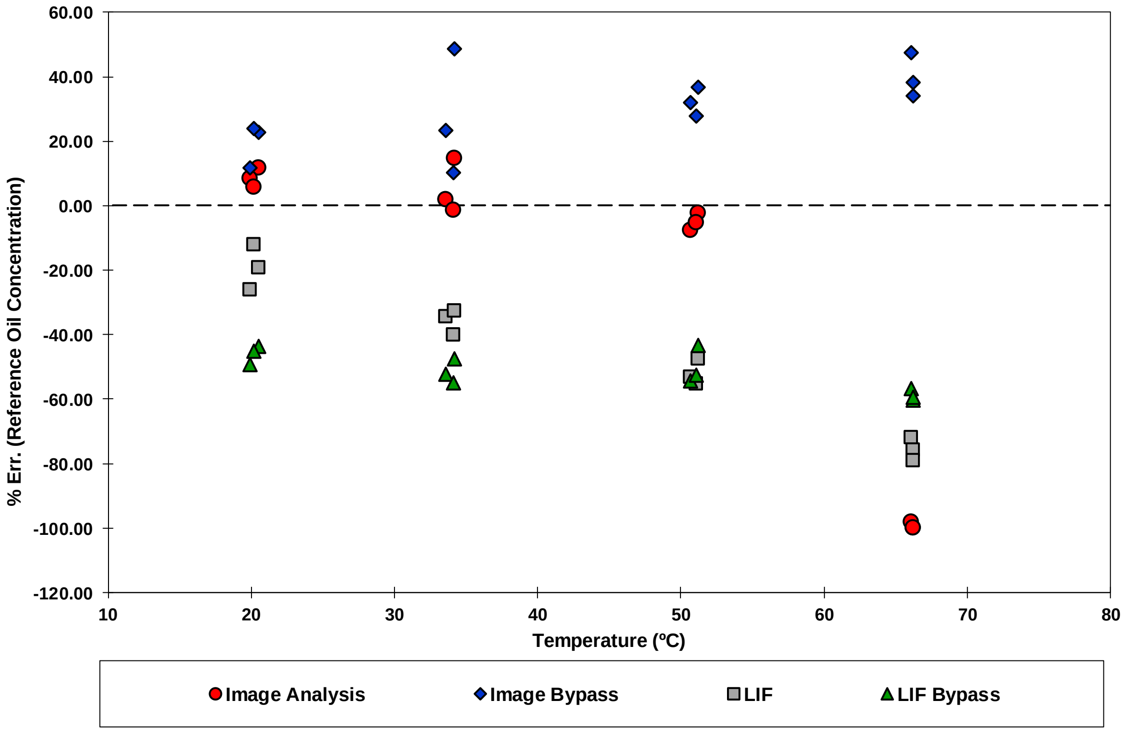


Figure 4.25 – Effect of Temperature (Percentage Deviation)

At an elevated temperature, all instruments deviate further from the reference value. The inline Image analysis unit was not able to measure concentration at all at higher temperatures. An issue that was previously found with the inline image analysis unit was that condensation was occurring behind the optical window, causing the view to become obstructed. This flaw was rectified by incorporating absorption packs into the housing of the instrument, however these packs needed to be replaced as they became statured during the higher temperature conditions. The inline LIF device remained constant throughout, however a downward trend between -20% and -70% is noted for the bypass LIF unit between 20 and 66°C. Similar to the inline LIF unit, the bypass image analysis device remained constant.

Effect of temperature is an important parameter as produced water process streams can vary in temperature widely depending on the application and location of measurement. Solubility of oil in water also becomes an additional variable in temperature dependant tests. LIF measures both dispersed and dissolved oil whereas image analysis can only measure dispersed oil. This is important as the infrared reference method used for oil concentration considers both dissolved and dispersed oil. As temperature increases, the solubility increases, thus the proportion of dissolved oil increases, which can affect measurement results for the image analysis devices. However, as seen in Figure 4.25, the bypass LIF measurement decreases by 60% overall, showing that this is not the only factor that affects the measurement performance. As the temperature increases, fluid properties such as density will decrease which may impact unit measurement.

Effect of Flow Velocity

To determine if flow velocity had any impact on the measurement performance of the devices, the main line velocity was varied from 0.5 to 5 m/s, while maintaining the oil concentration at 30 mg/. As two of the devices are connected in a bypass configuration, the velocity of the sample line where each of the bypass units were configured was varied to match the flow rate of the main line for each of the tests.

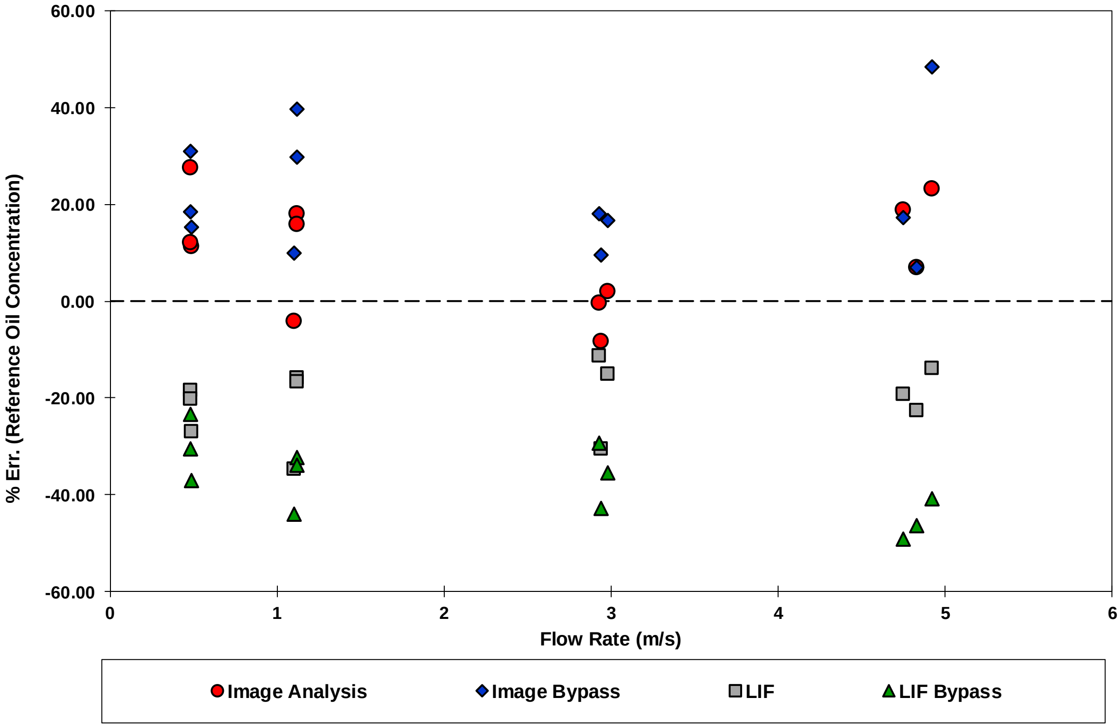


Figure 4.26 – Effect of Flow Rate (Percentage Deviation)

Both image analysis and LIF remained consistent throughout all flow rates, demonstrating that flow velocity did not cause any effect on their measurement ability. It should be noted however that the droplet size was controlled to be constant throughout all flow rates, as typically higher flow rates would lead to smaller droplets due to an increase in shear rate on the oil. The ability of the instruments to measure oil concentration in varying velocities is down to the response rate of the individual techniques. As long as the response rate is sufficient for the flow condition and changing flow rate does not impact other properties, the effect of flow rate should be negligible.

4.2.6.8 Dynamic Response and Fouling Effect

The dynamic response tests were used to determine the instrument's ability to recover from high concentration conditions. The test was split into three sections; initially the instruments were tested at a starting oil concentration of 5000 mg/l. The concentration was then decreased to 1000 mg/l, before finally, an end concentration of 30 mg/l was reached to see if there was any memory effect on the instrument's measurements. The test was carried out following the procedures in Section 4.2.5.

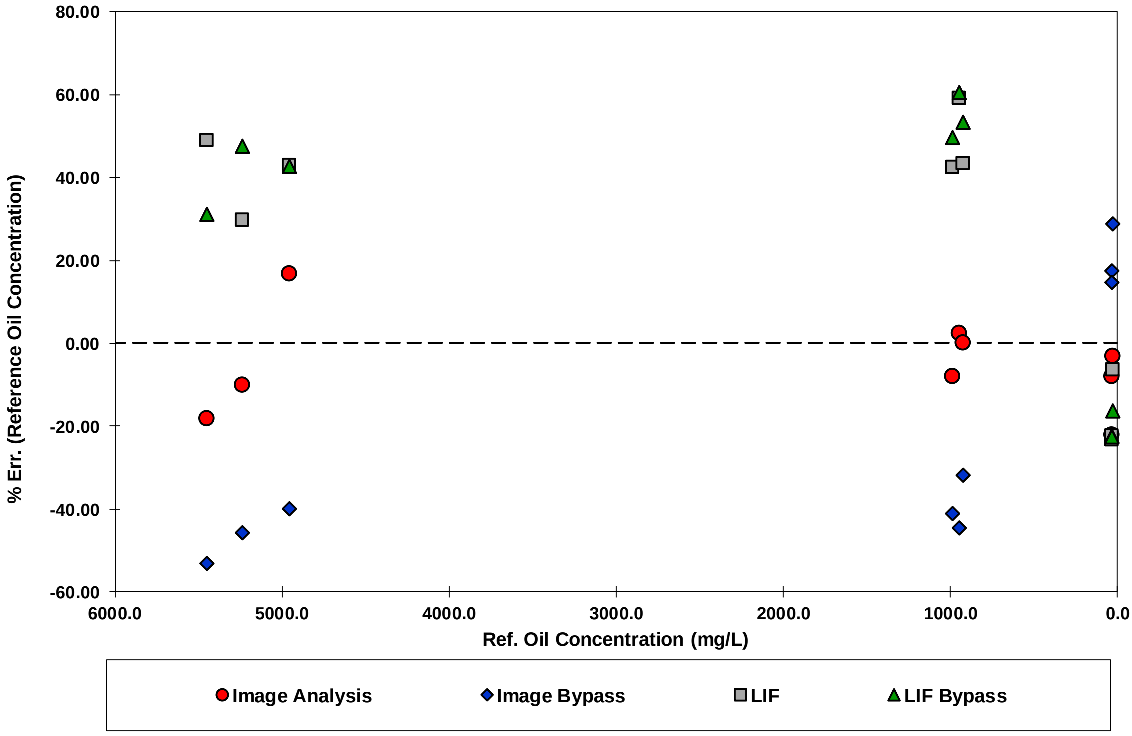


Figure 4.27 – Dynamic Response (Percentage Deviation)

Figure 4.27 shows the results from the dynamic response test. The x-axis for this graph has been reversed to be in line with the order of test completion. The inline image analysis remained within the 30% deviation as seen in the baseline tests. The image analysis bypass device however did see an effect, with a -50% error noticed at the higher concentrations before increasing to normal levels at the 30 mg/l condition. As discussed previously, the image analysis bypass unit does not have any automatic cleaning capabilities and during the 5000 mg/l test condition, oil droplets being stuck on the optical window caused the bypass unit to foul. At 1000 mg/l, the fouling was reduced however a full manual clean was required to rectify the fouling prior to the final test of 30 mg/l. A similar but opposite trend is seen for both LIF devices. Overall, all instruments were able to successfully recover and measure the 30mg/l condition within baseline deviation.

To further investigate these effects, a fouling test was completed. After the manual fouling, all instruments were re-tested at a low oil concentration of 30 mg/l. To undertake this fouling test, crude oil was manually applied to the optical windows of each device and left to dry for 24 hours prior to restarting the test. Figure 4.28 shows an image captured by the inline image analysis unit. As can be seen, after manually fouling the optical window, the image is nearly fully black. The same is also seen in the bypass unit.

Figure 4.28 – Manual Fouling on Image Analysis Devices

Figure 4.29 shows the optical window of the inline LIF unit covered in crude oil.

Figure 4.29 – Manual Fouling on Inline LIF

Similar to the inline LIF unit, the manually fouled optical window for the LIF bypass can also be seen in Figure 4.30.

Figure 4.30 – Manual Fouling on LIF Bypass Device

The devices were then re-installed back into the facility and allowed to run for 1 hour prior to the start of the 30mg/l test condition. Results from this test is shown in Figure 4.31.

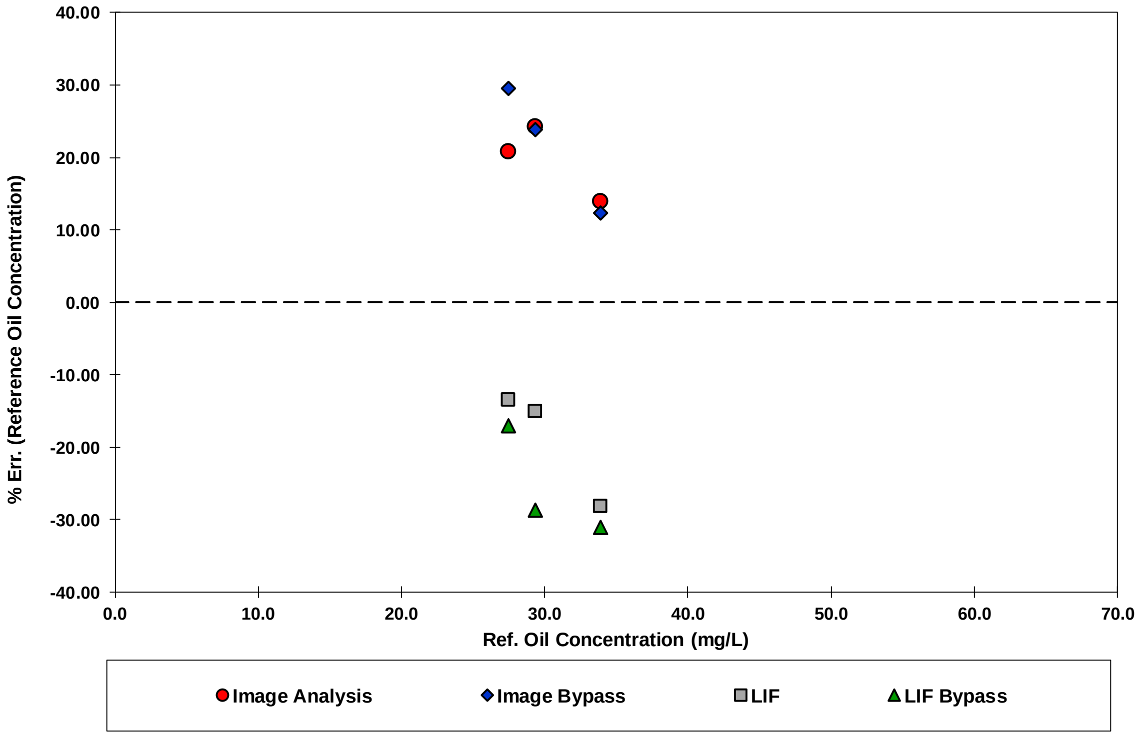


Figure 4.31 – Fouling Effect (Percentage Deviation)

Again, it should be noted that the bypass image analysis unit was also included in this test even though it has no automatic cleaning capabilities. Results obtained were similar to those seen in the baseline tests, which indicates that all instruments were able to recover from the fouling.

4.3 Summary

As produced water streams contain many different contaminants and can vary greatly depending on the application and location, the use of technologies to measure oil-in-water concentration in real time, requires the knowledge of how certain key parameters can affect measurement performance.

The second research question, as discussed further in Chapter 1, poses the following challenges:

- What techniques are available that can detect oil-in-water at concentrations below 30 mg/L? In addition, can the impact of typical parameters found in produced water applications be quantified for individual techniques?

A preliminary experiment was carried out to identify the impact on individual parameters on the primary measurements of each technology. The outcome of the initial research work demonstrated that several factors can influence the measurement performance of the three technologies tested. Image Analysis and Laser Induced Fluorescence both were ranked higher than other techniques and therefore were selected to continue as part of this research.

To gain a better understanding of these effects, a second experimental study was carried out using the Produced Water test facility at NEL with four total instruments evaluated for this experiment. Both image analysis and LIF techniques were installed in an inline and bypass configuration allowing for direct comparisons to be made between configurations.

During this experimental program, several challenges were encountered. Table 4.5 summarises the key operational experiences found with each technique.

Table 4.5 – Summary of Experience with Each Test Instrument

Instrument	Installation/commissioning	Operability	Challenges
Image Analysis	• Simple inline installation • Oil only, solid only and oil and solids commissioning verification required • Fully enclosed system, simple Ethernet and power connection	• Typical settings were pre-set, however changing thresholds was user friendly • Live view to check process conditions • Record / reprocess videos very helpful	• Data reprocessing required • Minor fouling issues
Image Analysis Bypass	• Installed on a ½” bypass line • Commissioning required only minor settings changes • Controlled via laptop	• Typical settings were pre-set, however easy to change thresholds • Live view to check process conditions • Record / reprocess videos very helpful	• No automatic cleaning which resulted in frequent manual cleaning • Data reprocessing required
LIF Inline	• Installed via a 2” branched flange on the test spool piece • Self-supported unit, no additional supports required. • Commissioning carried out offsite and only validation required	• Software came preinstalled onto the unit • User friendly interface controllable by laptop/keyboard • Unit can either be on or off	• Connectivity issues between the probe and laptop
LIF Bypass	• Unit installed onto bypass line • Self-supported unit, easy to install • Commissioning carried out offsite and only validation required Controlled via laptop or USB keyboard	• Software came preinstalled on unit • User friendly interface controllable by laptop/keyboard • Unit set up on Flow, Homogenise, Clean cycle	• Some connectivity issues between unit and laptop • Fouling issue with oil being trapped in flow cell. Required full manual clean

For each test point ran, data was collected for a minimum of 1 hour. The raw data from each of the technologies was then averaged to get their output for that test condition. To create a baseline, instruments were initially tested with different oil concentrations ranging from 0 to 1000 mg/l. At the key lower oil concentrations, where the majority of the tests will be undertaken, up to 100 mg/L, all of the instruments measured were able to remain within ±30% of the reference value.

Out of all the tests, four key parameters were found to have the most significant impact:

- Condensate Oil – Ability for both image analysis and LIF to detect condensate oil.
- Effect of Gas Bubbles - Discrimination and ability to detect gas bubbles using image analysis.
- Addition of Chemicals - Fluorescence properties of chemicals and their impact on LIF.
- Temperature Effect - Effect of solubility on dissolved / dispersed ratio.

5 Overcoming Challenges in Online Measurements

This chapter looks to answer the third question of this research:

- Can improvements be made to current online techniques or methods, to improve performance of measuring oil-in-water concentration?

The first section investigates the development of a correction factor for oil droplet size on Laser Induced Fluorescence techniques. It was noted during the experiments in Chapter 4 that changing droplet size had an impact on the measurement of both LIF techniques, even though this was not a specific variable tested. To explore this further, a series of experimental and theoretical studies are undertaken to determine the extent of this relationship, and how it can be corrected.

The second section looks at developing a method for in-situ verification of Laser Induced fluorescence. A challenge that occurs with all online techniques is their ability to be verified after installation. Depending on the application, the installation of the devices may be in difficult environments that are not easy to access. Typical methods for verification and calibration involve sampling the process stream and analysed using an offline method. However, even though this method allows for spot checking, full ranges of oil concentrations cannot often be achieved by the process stream, which is required for proper calibration. Also, sampling can be costly and brings additional uncertainty into the process. To overcome this, this section looks at using tracers as a method of verifying and calibrating LIF techniques in-situ, without the need for sampling or changing process conditions.

The third section explores the use of image analysis to measure condensate oil and enhance the technique using tracers. As seen in Chapter 4, the measurement of condensate oil demonstrated several challenges for the image analysis devices. This section looks at how we can reduce the impact of this variable, by undertaking several approaches to improve their performance.

As discussed in the previous chapter, there are several parameters that can impact the measurement of oil in water concentration. To investigate improvement to current online methods, the research looks at three different issues:

1. Effect of droplet size on Laser Induced Fluorescence techniques
2. Verification / calibration methodology for online methods
3. Image Analysis of condensate oil

To investigate each of these, this chapter is broken down into three sections which describe methods for improving the oil-in-water concentration measurement for Laser Induced Fluorescence and Image Analysis technologies.

5.1 Droplet Size Correction

5.1.1 Initial Correction Factor Development

It has been known that oil droplet size can affect fluorescence measurements from LIF devices, as demonstrated in Chapter 4. To determine these effects, a series of experiments were set-up with varying droplet sizes whilst ensuring all other variables were maintained to be constant. Table 5.1 summarises the tests carried out, six different droplet sizes ranging from 5 to 60 microns with the standard crude oil described in Chapter 3 being used. All tests were completed using the test facility set at a constant target concentration, measured using the infrared reference technique, with droplet size being determined using Image Analysis. By undertaking this study, a relationship between droplet size and LIF measurement accuracy could be established, allowing corrections to be made to improve current measurement performance. As data in the public domain for droplet size and oil concentration using online techniques are very limited, effects with different conditions, such as different oil types or LIF techniques, may need to be further considered.

Table 5.1 – Droplet Size Test Matrix

Test Number	Crude Oil		Temperature (°C)	Flow Rate (m/s)
	Conc. (mg/l)	Size (μm)		
1	28.1	4.9	20.1	2.97
2	27.6	7.8	20.1	2.99
3	28.5	12.7	20.0	3.01
4	28.0	28.2	20.1	2.98
5	27.9	45.0	19.8	2.98
6	28.4	63.3	19.9	2.99

To determine the effect of varying droplet size, Figure 5.1 summarises the results obtained at average oil-in-water concentration of 28.1 mg/L, at a droplet size diameter of 4.9 to 63.3 microns. After the injection of oil to set the oil-in-water concentration, the facility was allowed to reach steady-state prior to the commencement of testing. Droplet size was altered by varying jet mixer speed, from largest to smallest droplet size to ensure stability. After achieving the desired droplet size, the facility could stabilise for a minimum of one-hour prior starting the test points. Each test point displayed shows an average of data collected by the LIF device over a 15-minute period.

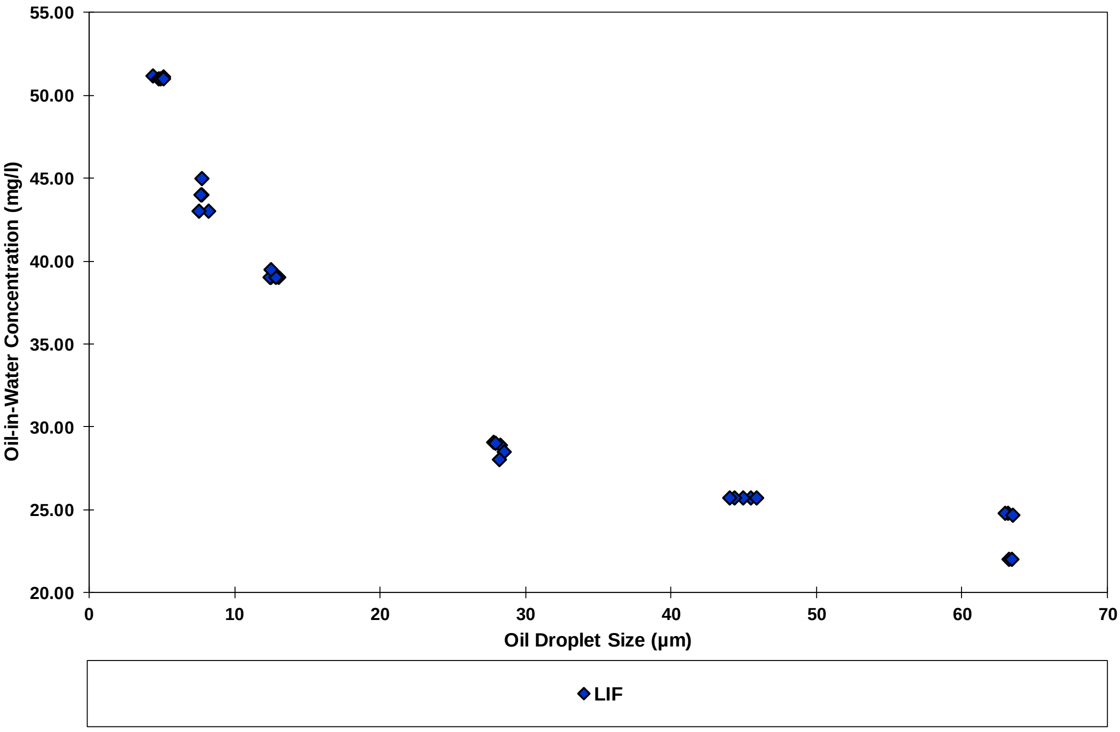


Figure 5.1 – Effect of Droplet Size on LIF and Reference Measurements

From the results, there is a clear relationship between droplet size and measured oil-in-water concentration from the LIF technique. From the droplet size of 4.9 to 63.3 µm, the mean measured oil-in-water concentration changes from 51.1 to 23.6 mg/l. It should be noted that the oil-in-water concentration, measured via the reference method, had a mean value of 28.1 mg/l throughout all droplet sizes.

Using the data from Figure 5.1, the measured oil-in-water concentration was concluded to be inversely proportional to the droplet size, thus the functional form of an inverse power relationship was selected to be the best fit to the points, as shown in Figure 5.2.

The functional form of the inverse power relationship is shown in the following formula.

$$y = ax^b \qquad (2)$$

Using the power equation shown in equation 2, the coefficients of this relationship can be shown in Table 5.2:

Table 5.2 – Droplet Size Coefficients

Curve Variable	Coefficients
a	82.855
b	-0.307

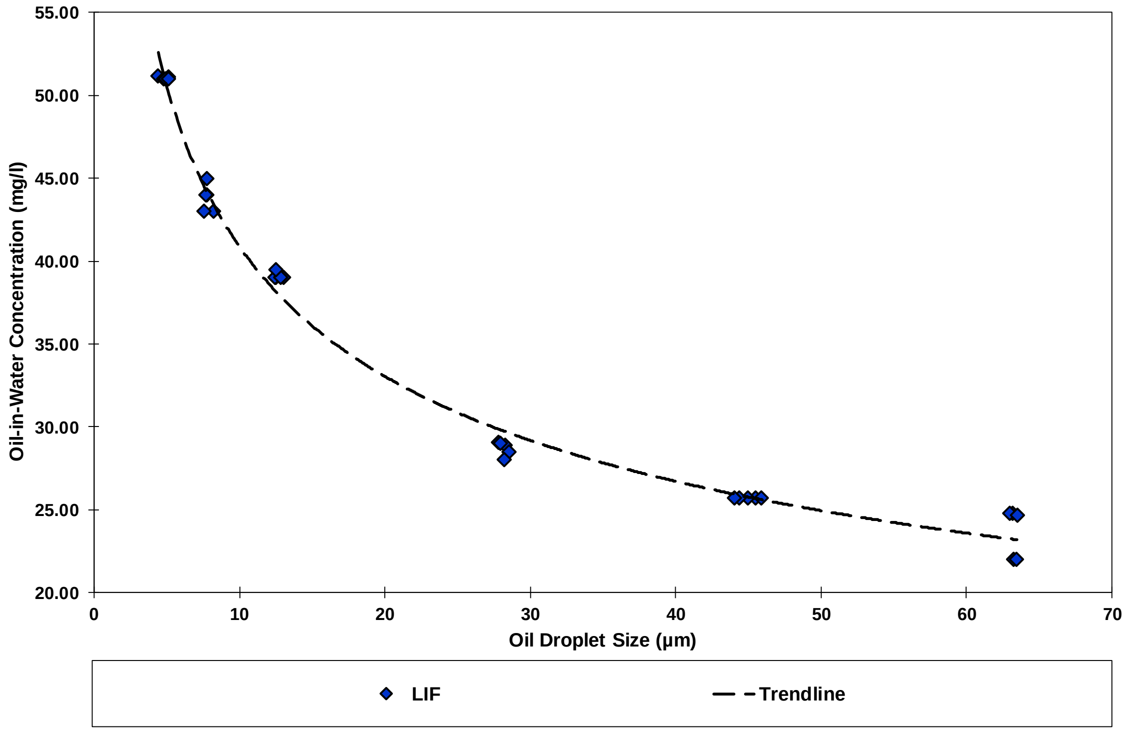


Figure 5.2 – Power Relationship between LIF Measurement and Droplet Size

Using these coefficients, the data shown in Figure 5.1 can be corrected, as shown in Figure 5.3.

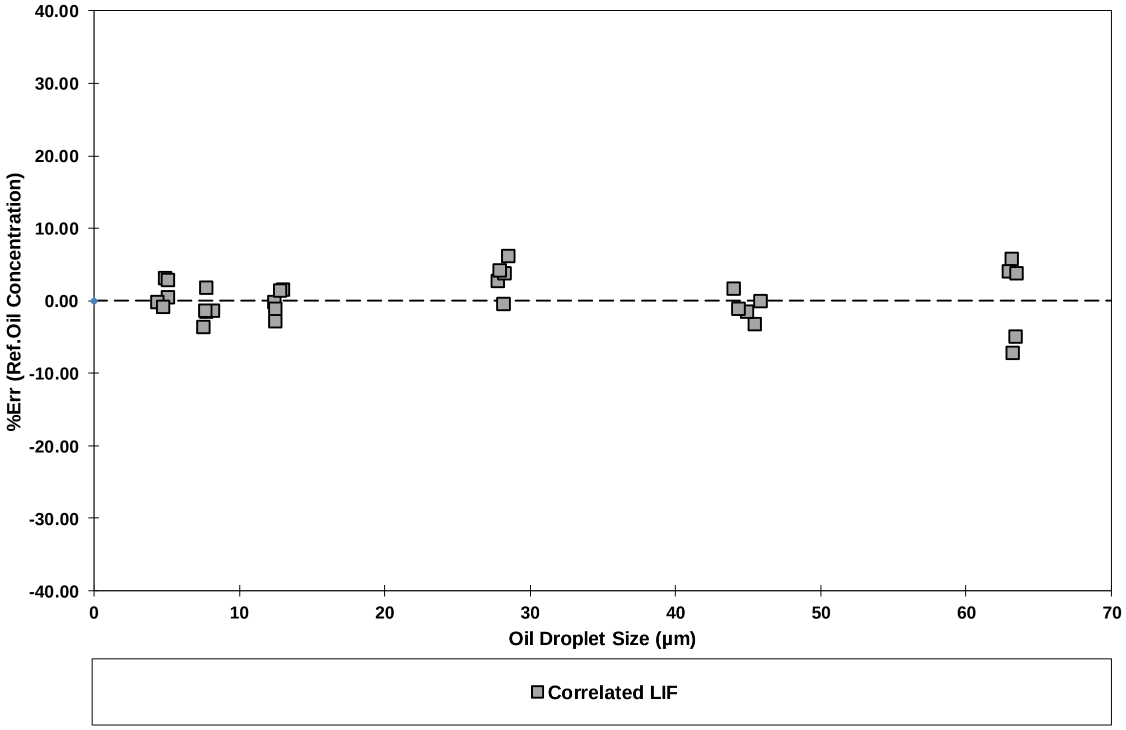


Figure 5.3 – LIF Measurements using Droplet Size Coefficients

Using the coefficients established, percentage deviation results seen in Figure 5.2 can be significantly reduced to ±7.2% using this correction. However, to further improve the coefficients to become applicable to other situations, further data points would be required. The current relationship is only based upon a single set of data points and therefore may contain system bias or other errors which may skew results.

To determine if the developed coefficients are able to improve measurement performance in a general basis, the relationship was applied to data found in literature (Yang, 2016), demonstrated in Figure 5.4. As discussed previously, there is very little data in the public domain for online oil-in-water measuring devices, with the data shown in Figure 5.4 being the only relevant data for this experiment found.

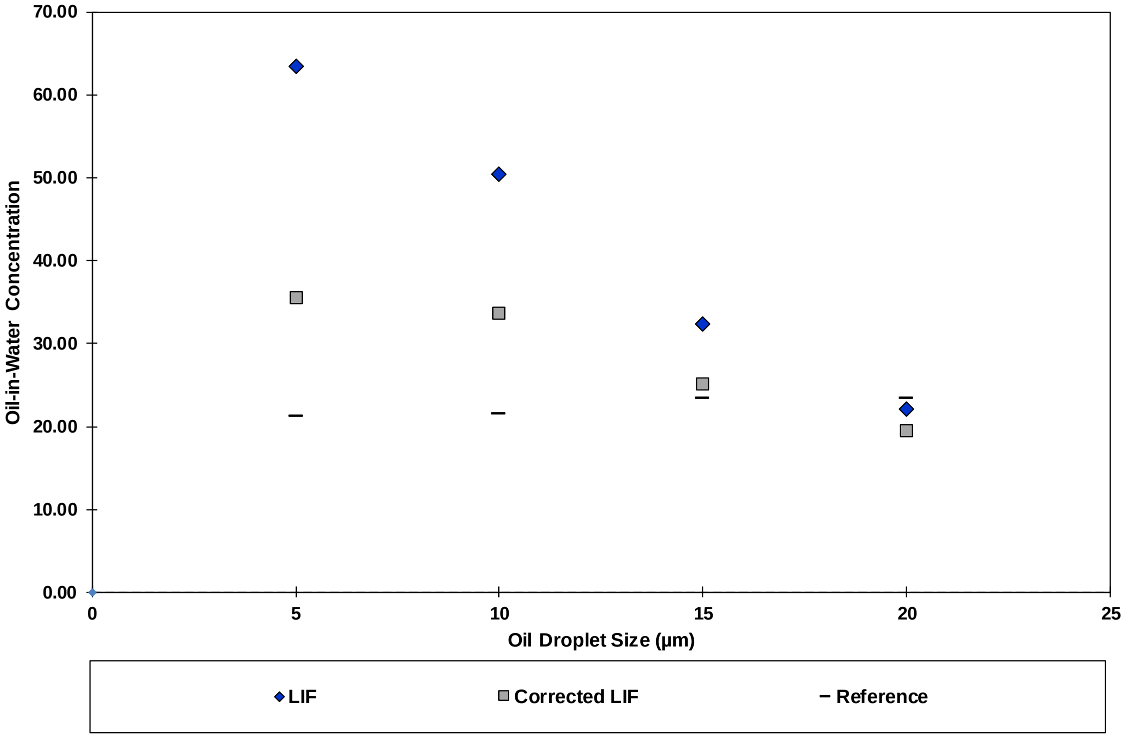


Figure 5.4 – Correction Factor Applied to External Data

It should be noted that the collection of data presented in Figure 5.4 was measured using the EPA 1664A technique as the reference method, and as oil-in-water concentration is a method defined parameter, variances in the reference value are expected. After applying the coefficients, the results show an improvement at all droplet sizes as summarised in Table 5.3.

Table 5.3 – Corrected Data from External Literature

	Oil in Water Concentration		
Droplet Size (µm)	**Reference [EPA 1664A] (mg/l)**	**LIF from Literature (mg/l)**	**Corrected LIF (mg/l)**
5	21.30	63.5	35.5
10	21.55	50.5	33.6
15	23.39	32.3	25.1
20	23.36	22.0	19.4

Due to this significant gap in literature, it is not possible to further modify the coefficients based upon data solely from other research. To improve the coefficients, further investigation was required.

5.1.2 Relationship with Surface Area to Volume Ratio

This current relationship described is very simple and other parameters need to be considered to allow the coefficients to be used in other applications. Due to how LIF operates, it was hypothesised that the ratio of total surface area of the droplets versus the total volume can impact the total amount of fluorescence generated. Essentially, as the average size of oil droplets decrease, their surface to volume ratio increases, which can lead to an overall increase of fluorescence being generated and therefore an increase in measured oil-in-water concentration.

Equation 3 shows the formula for determining surface area to volume ratio for a perfect sphere. Typically, oil droplets will conform to spherical shape while surrounded by another medium (Marchand, et al., 2011).

$$Ratio = \frac{Surface\ Area}{Volume} = \frac{3}{r} \tag{3}$$

Using this equation, an inversely proportional relationship can therefore be found between droplet size and the surface to volume ratio, as shown in Figure 5.5.

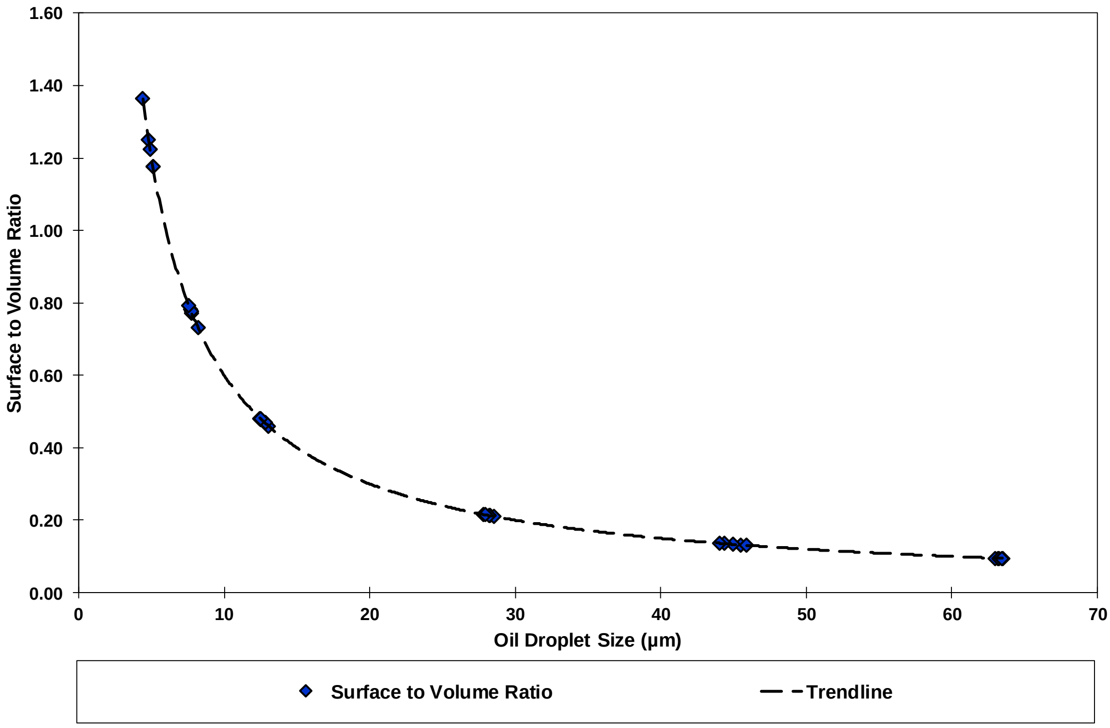


Figure 5.5 – Surface to Volume Ratio for Increasing Oil Droplet Size

From the data collected, it is thought that the relationship between fluorescence measurement and droplet size is mainly due to the surface to volume ratio. It is clear that very similar trends are seen between the surface to volume relationship and the data previously collected in Figure 5.1.

Frackowiak et al (2008) investigated fluorescence measurements of a single oil droplet, n-heptane in water. Even though this work was focussed for the application in spray systems, the LIF analysis of a single droplet can be used to verify the surface to volume relationship shown in Figure 5.5. Several significant findings can be drawn from this data found in literature. The findings show that the amount of fluorescence generated for a single droplet scales linearly with droplet size. A 100µm droplet produces 10 times more fluorescence than a 10µm droplet. However, if fluorescence was generated solely on oil volume, the expected increase from 10 to 100µm would be 100 times greater than recorded. This relationship demonstrates that the surface to volume ratio is critical in fluorescence measurements. As the droplet size increases, the surface to volume ratio decreases, leading to a significant reduction in the total fluorescence produced, in comparison to volume ratio alone.

Even though this relationship between droplet size and measured oil-in-water concentration can be explained by this power relationship, other factors would also need to be considered to fully establish the relationship, such as, type of oil, different online devices and additional operating ranges.

5.1.3 Effect of Oil Solubility in Water on Droplet Size Effect

As discussed in Chapter 2, the solubility of crude oil in water will determine the ratio of dissolved to dispersed crude oil-in-water. To determine if changing the solubility will affect the relationship between droplet size and measured oil-in-water concentration, a series of tests was carried out at three different temperatures, 20, 40 and 60ºC. This temperature test is shown in Figure 5.6:

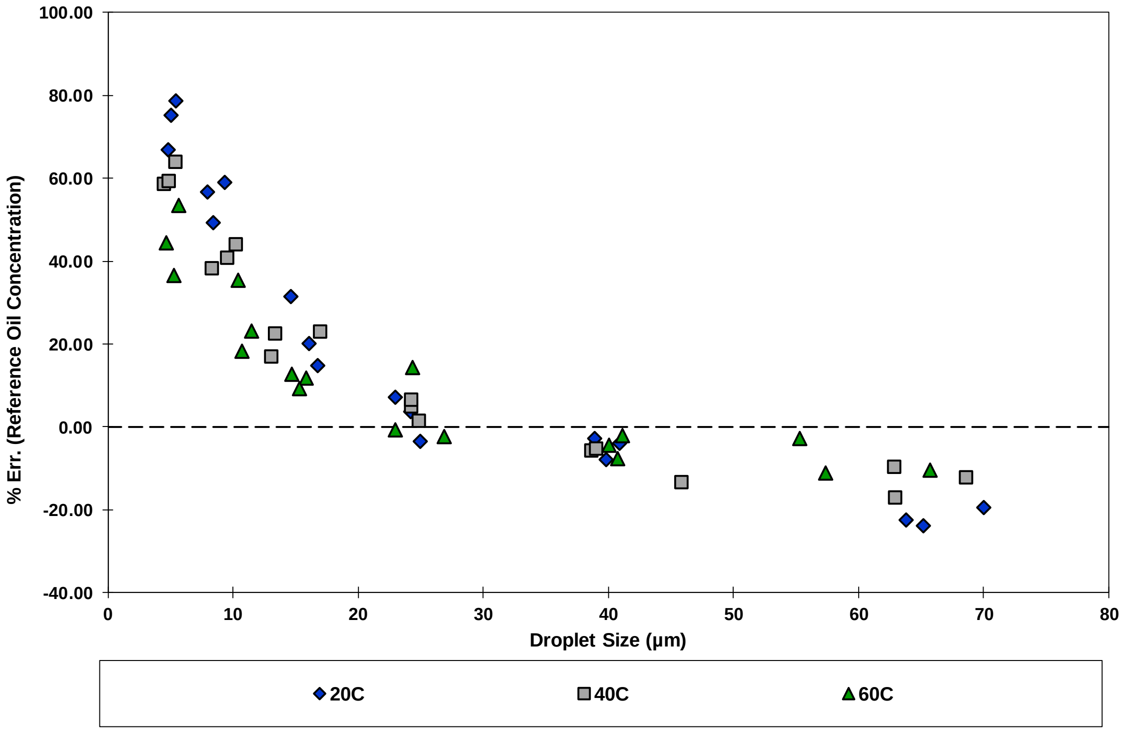


Figure 5.6 – Temperature Effect for Different Droplet Sizes [30 mg/L, 3 m/s, 20 to 60°C]

A similar trend is seen in the data as previously discussed in Chapter 4 where the oil-in-water concentration measurements from the LIF devices decreased with increasing temperature. Again, this effect is thought to be caused by the ratio of dissolved to dispersed oil droplets.

A similar effect has been observed by Chandio et al, who investigated the effect of temperature on the solubility of asphaltenes in crude oils (Chandio, et al., 2015). Even though a solubility parameter was used rather than direct oil-in-water concentration, the results demonstrate that with increasing temperature, the solubility of crude oil components in water increase.

The solubility of a crude oil mixture depends on the solubility of the individual components in the crude oil. A number of studies has been carried out in this area (Burris & Macintyre, 1985), (Leinonen, et al., 1971). Equation 4 describes the formula to determine the solubility of individual components:

$$C_W = x_H C_W^* \gamma_{\mathrm{H}} \tag{4}$$

Where,

C_W = Aqueous concentration of any component of the mixture
C_W^* = Pure compound solubility
x_H = Mole fraction of component in hydrocarbon mixture
γ_{H} = Activity coefficient in the hydrocarbon phase

Using the initial inversely proportional droplet size relationship developed previously, the effect of crude oil solubility can be demonstrated. By changing the ratio of dispersed to dissolved oil, the initial relationship can be adjusted to simulate the effect of increasing temperature. Figure 5.7 shows an example of this solubility effect, with increasing dissolved oil-in-water solubility percentages. Each line represents a different percentage of dissolved components in the mixture, based on Equation 4, thus 100% represents a fully dissolved mixture and 0% represents a fully dispersed mixture.

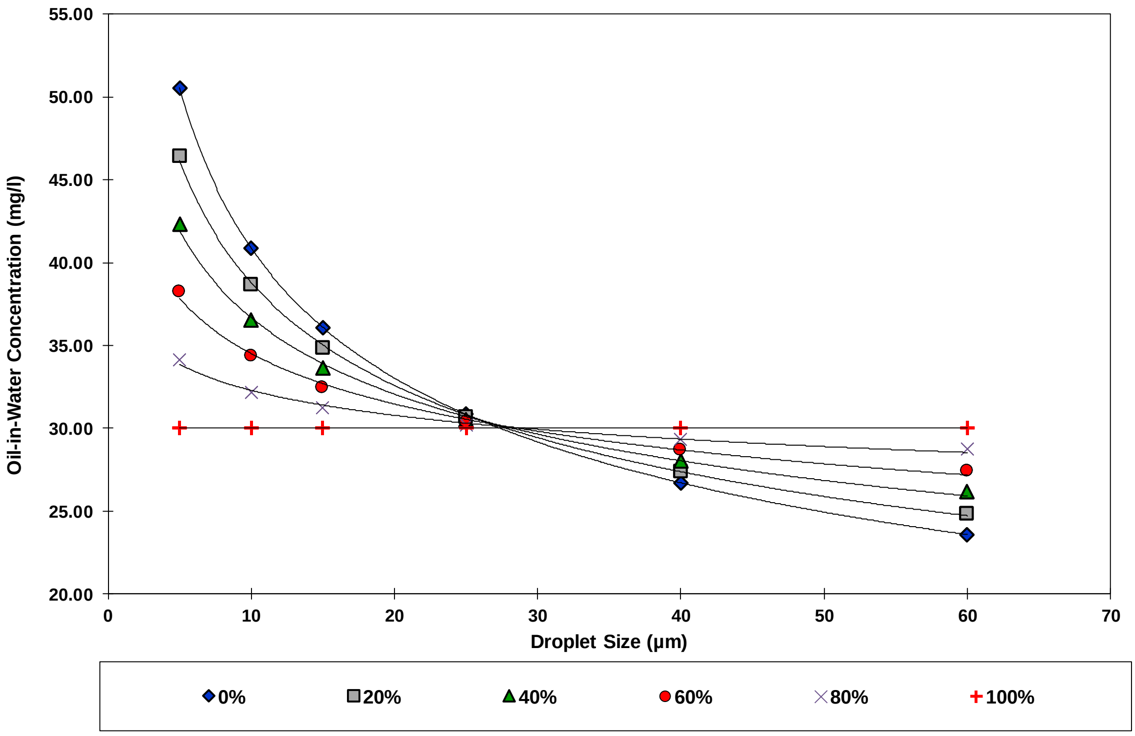


Figure 5.7 – Example of Solubility Effect on Droplet Size Relationship [30 mg/L]

It is clear from the graph that changing the percentage of dissolved oil can have a significant impact on the relationship between droplet size and measured oil-in-water concentration. As what would be expected, at 0% dissolved oil, all the oil is in the dispersed phase leading to the greatest impact due to droplet size. Increasing to 100%, where all the crude oil is dissolved, there is no droplet size effect. Going from 0% dissolved oil up to 100%, leads to a 60% measurement difference at the lower oil droplet sizes. The data also shows that with a higher dissolved to dispersed ratio, the relationship trends closer to the reference value throughout all droplet sizes. This is due to the droplet size only effecting a smaller portion of the total crude oil-in-water, as the dissolved phase remains constant in terms of droplet size effect.

5.1.4 Effect of Oil Concentration at Different Droplet Sizes

An experiment was also carried out to determine the impact on oil concentration on the droplet size coefficients. These results are shown in Figure 5.8.

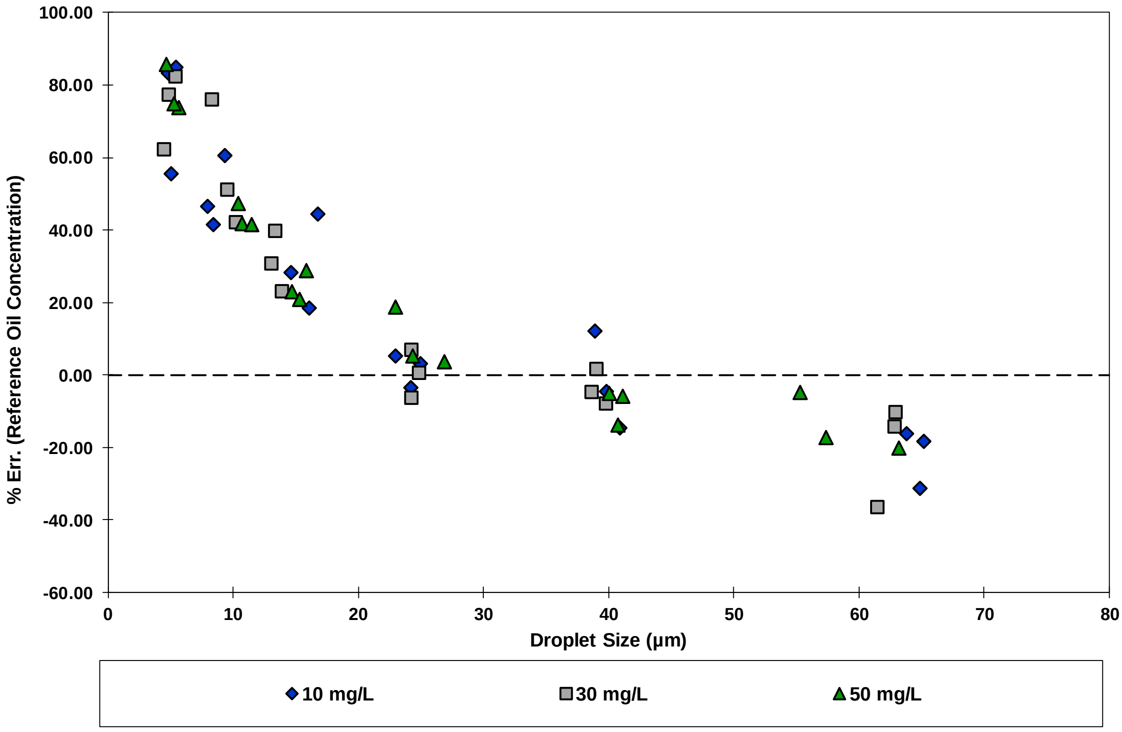


Figure 5.8 – Oil-in-Water Concentration Effect on Droplet Size Coefficient [10 to 50 mg/L, 3 m/s, 20°C]

The results from this test do not show any discerning influence by varying the oil concentration. However, it should be noted that similar to the oil solubility effect, a similar principle is expected to be noted with increasing oil concentration.

Shiu et al (1990) studied the effects of crude oil solubility in water by undertaking experimental analysis of how water to oil ratio affected the solubility of key components found in crude oil. The results from this study demonstrate that with decreasing oil concentration, the solubility of the individual parameters also decrease, relative to the volume of water. Even though the data shown in Figure 5.7 show large differences in oil solubility, with typical produced water concentrations ranging from 10 to 100 mg/l, solubility changes would be small.

Other than the impact on solubility itself, at a specific temperature, the greater the concentration, the lower the expected dissolved to dispersed ratio therefore, the effect of droplet size should be more pronounced. Further work in would need to be completed to fully quantify this effect.

5.1.5 Development of Updated Coefficients

Using all the influences on LIF measurement discussed, an updated relationship based on a function of oil droplet size, temperature and concentration can be developed. This function is shown in the following equations.

$$\%\,Error = f(Droplet\ Size, Concentration, Temperature) = f(r,t,c) \tag{5}$$

$$\%\,Error = a \cdot r^{n1} \cdot c^{n2} \cdot t^{n3} + b \tag{6}$$

Where K is a constant, n1, n2 and n2 are power indices.

Using the data collected throughout the research, these indices can be determined:

$$\%\,Error = 293.42 \cdot r^{-0.376} \cdot c^{0.01} \cdot t^{0.121} - 72.39 \qquad (7)$$

The limits of the data used to develop the coefficients are shown in Table 5.4.

Table 5.4 – Application Range of Empirical Coefficients

Condition	Range
Droplet Size	5 to 65 µm
Temperature	20 to 60°C
Oil-in-Water Concentration	10 to 50 mg/l

Several findings can be derived from analysing the power indices of the updated relationship. A small relationship is seen between concentration and measurement error, which is what was found in the initial experiment. The most prominent relationship is found with droplet size, as what would be expected. As droplet size increases, measurement error is determined to decrease. However, the limits of the data used to develop the relationship should be carefully considered.

To demonstrate the updated coefficients, Figure 5.9 shows the corrected data based upon the initial droplet size effect data collected.

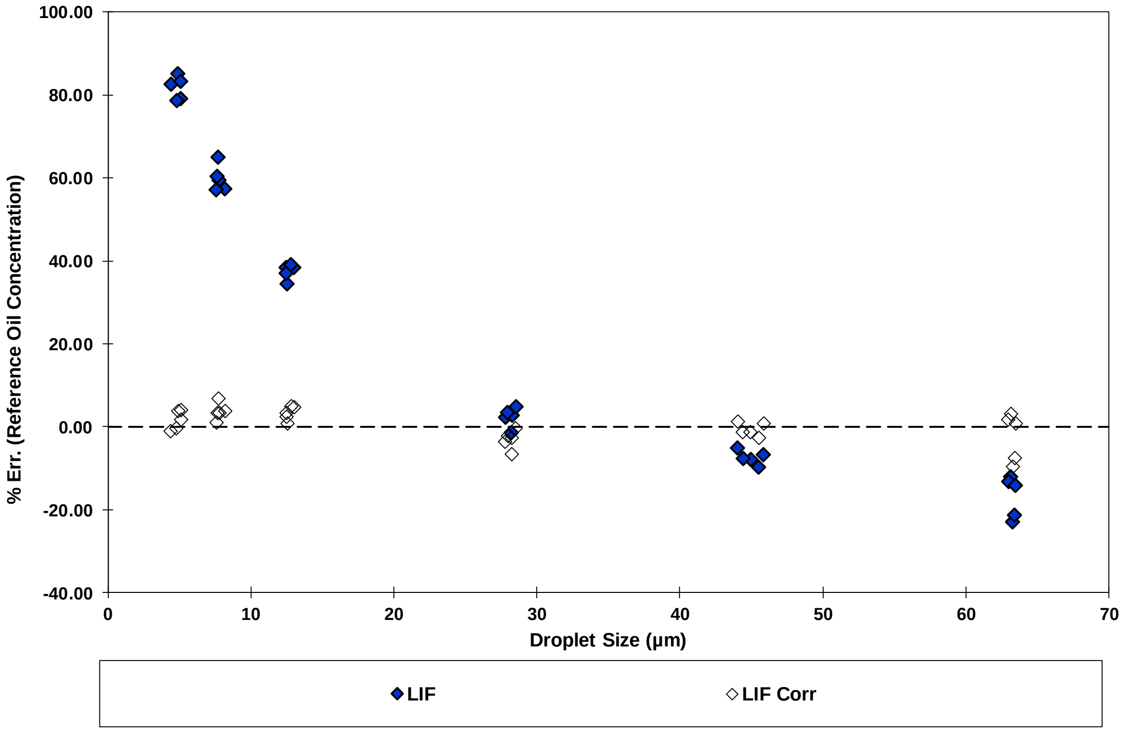


Figure 5.9 – Updated Coefficients Applied to Figure 5.1

Similarly, Figure 5.10 shows the corrected data versus the original data collected during the effect of temperature on droplet size effect trial.

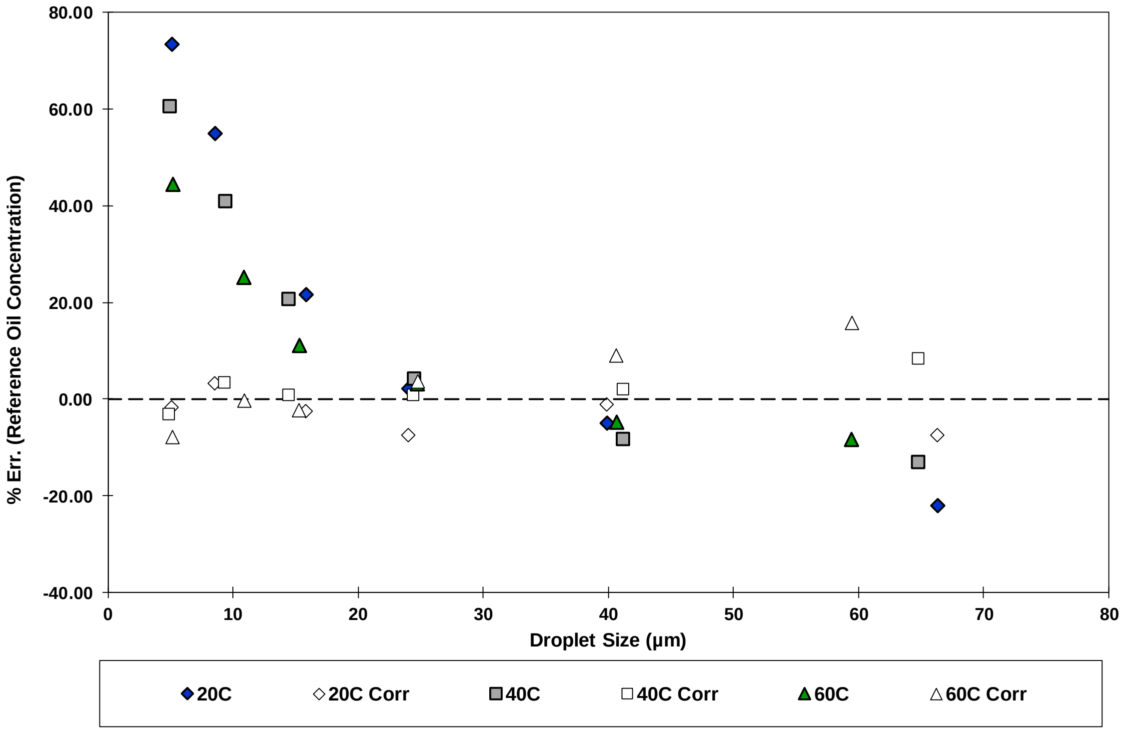


Figure 5.10 – Updated Coefficients applied to Averaged Data from Figure 5.6

Using the relationship, the data collected during the change of oil concentration trial can also be corrected.

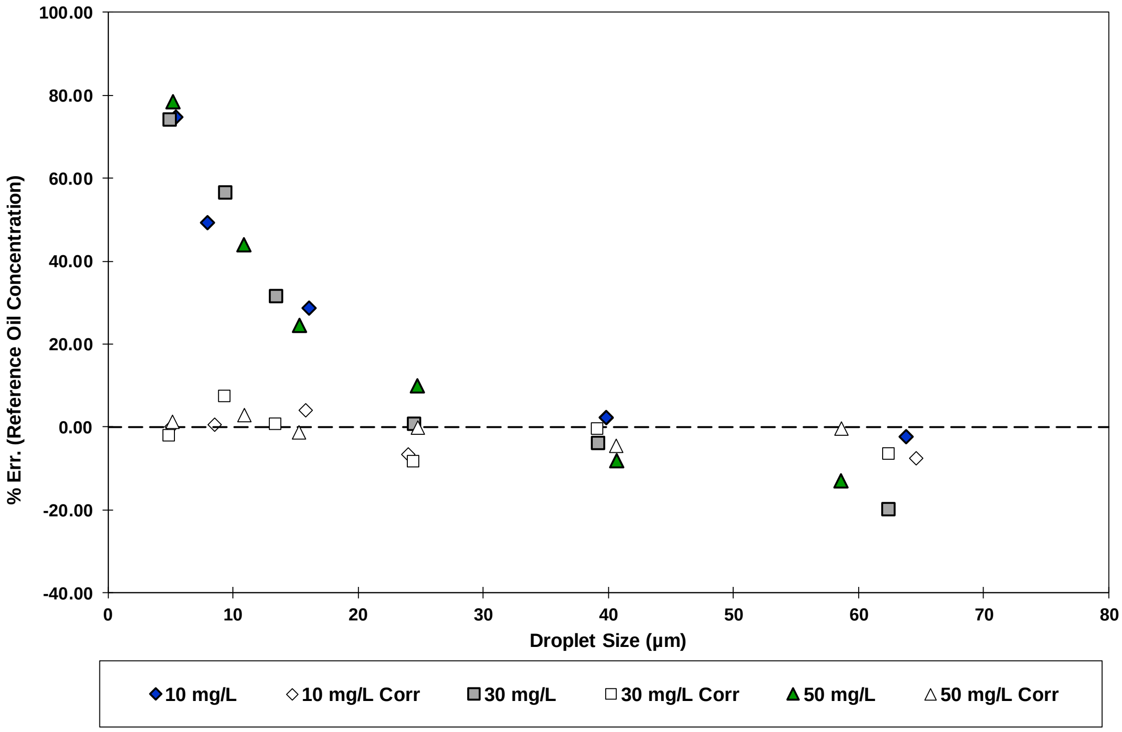


Figure 5.11 – Coefficients applied to Averaged Data from Figure 5.8

As demonstrated in the above figures, the relationship can reduce the percentage error of the majority of data points to within ±8.5% of the reference.

These updated coefficients shown in Table 5.4 aimed to correct for a droplet size effect found in this research, however the developed relationship is based upon limited sets of data. To fully establish the relationship, further research work would be required, to increase the limits and to include other variables not considered. Other variables such as type of crude oil and different laser induced fluorescence instruments can have an impact on the relationship.

5.2 In-situ Oil-in-Water Measurement Verification using Tracers

The method of sampling and laboratory analysis with current reference methods can be very costly, especially in remote or challenging conditions, such as in subsea environments. To overcome this, the research has focussed on online methods to measure oil-in-water continuously, however significant challenges remain before this can be utilised for regulatory monitoring. One of the challenges is calibration and validation of deployed online techniques, as under current methods, samples would still be required to be collected and analysed. Conditions during discharge also do not allow validation as only a small region of oil-in-water concentration will be seen, and thus the full range cannot be verified. Other challenges such as varying parameter effects have been noted to influence online measurement of oil-in-water.

This research describes a new method for calibrating and validating Laser Induced Fluorescence devices without the need for sampling by using fluorescent tracers with an established relationship to a reference oil-in-water concentration.

5.2.1 Tracer Technique

A tracer is essentially any property that can be used to track fluid parameters. Fluid characteristics such as temperature are considered physical tracers, whereas the properties of chemical compounds within the fluid are considered chemical tracers. Tracers may occur naturally, such as radioactive materials (Biswal, et al., 2018) or injected into the flow, such as dyes (Magal, et al., 2008). Tracers have typically been used as flow measurement validation or used to fingerprint fluids such as co-mingled crude oil streams (Yusoff, et al., 2015). This section describes a methodology for using tracers as method to measure the flow rate of a fluid using a fluorescence-based tracer, using a tracer dilution technique (Smart & Laidlaw, 1977).

Tracer dilution is a technique where a tracer is injected into the flow at a known rate and after a period, the concentration at a downstream position becomes constant and can be measured. This measured concentration can then be used along with the injection rate to determine the overall flow rate of fluid between the injection and downstream positions.

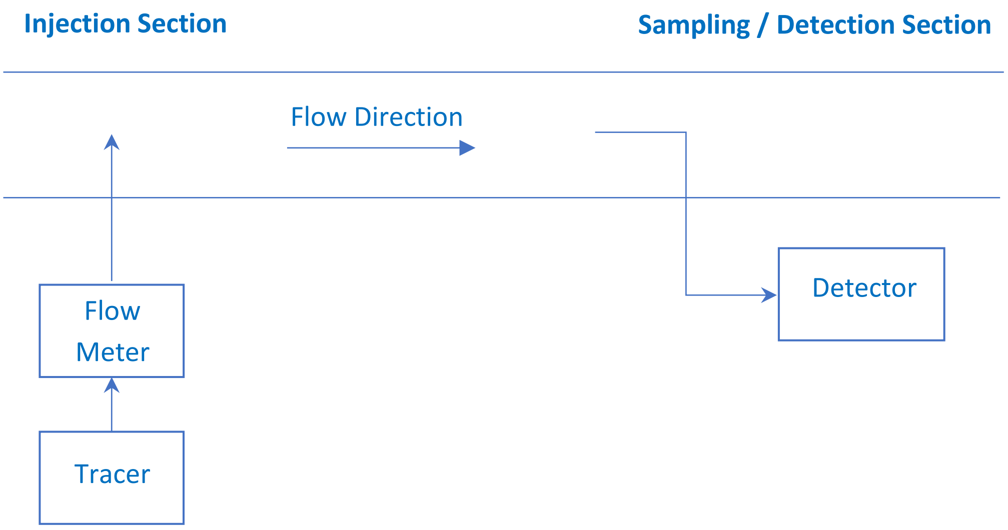


Figure 5.12 – Schematic of simple Tracer Dilution System

Once injected and after sufficient mixing, a sample can be taken and analysed or use of an online instrument to determine the dilution ratio and therefore the liquid flow rates using the following calculation (Shell, 2008):

$$Q_c = \left(\frac{c_i}{c_c} \cdot Q_t\right) - Q_t \approx \frac{c_i}{c_c} Q_t \qquad c_c \ll c_i \tag{8}$$

Where:

Q_c = Volume flow rate of target fluid
Q_t = Injection flow rate of tracer
c_i = Concentration of injected tracer
c_c = Concentration of tracer under line conditions

Using this method, the target flow rate of the process fluid can be determined. In the case of produced water measurement, the flow rates of oil are too small to use this this technique to determine oil-in-water concentration. The proposed technique uses a variation of this method, using fluorescent tracers to validate or calibrate laser induced fluorescence devices in inaccessible or challenging conditions. After an online measurement device has been deployed, it is difficult to check the performance of the device, and often samples are required to be taken and analysed using a reference method for comparison. The requirement for sampling for validation can prove challenging as online devices for remote or unmanned locations are trying to remove samples being required, and solely using the online measurement as for regulatory compliance. Thus, a method that can validate the performance of an online technique without sampling could be used much more frequently and increase confidence in the online measurement. This method also moves away from requiring an offline method as a reference, which can bring sampling errors into the oil-in-water concentration if calibrated due to incorrect reference measurement.

5.2.2 Tracer Verification of Laser Induced Fluorescence Techniques

To demonstrate this method of calibration, a series of tests were set-up to calibrate a LIF device for measurement of oil in water. Any fluorescent tracer can be used for this method; however, a Rhodamine B solution was selected due to its availability and previous use in the oil and gas industry.

To establish the relationship, 8 samples of varying concentration of tracer solution was created. A measuring cylinder was used to measure out 1000ml of distilled water into a 1000 ml sample bottle. Using a 25 µl syringe, a known volume of the tracer solution is then spiked into the sample of water. The syringe is weighed using a high accuracy measuring scale before and after injection to determine the actual mass of tracer injected. It is important that the tip of the syringe does not enter the water as this will increase the error in the mass measurement. Table 5.5 shows a summary of the verification samples created.

Table 5.5 – Prepared Samples Injected with Tracer Mixture

Sample Number	Target Water Volume (mL)	Mass of Tracer Solution Injected (mg)
1	1000	1.55
2	1000	3.17
3	1000	4.53
4	1000	6.12
5	1000	7.47
6	1000	9.05
7	1000	10.38
8	1000	11.91

After preparation, all of the samples were stored in the fridge until required. This is to ensure their stability and reduce any evaporation of volatile components. Each sample was thoroughly mixed using an ultra-turrax mixer for two minutes, to try to achieve as close to homogenous conditions as possible. An image of the mixer used is shown in Figure 5.13:

Figure 5.13 – High-Speed Ultra-Turrax Mixer

Figure 5.14 – Ultra-Turrax Mixer Tip

After mixing, the LIF device was positioned into the sample bottle and resulting oil-in-water concentrations noted. By knowing the tracer concentration and measured oil-in-water concentration, a relationship was then established. As the properties of typical fluorescent tracers are stable, the coefficients can then be utilised whenever validation and/or calibration is required.

Figure 5.15 shows the established relationship between tracer concentration and oil-in-water concentration measured by the LIF technique.

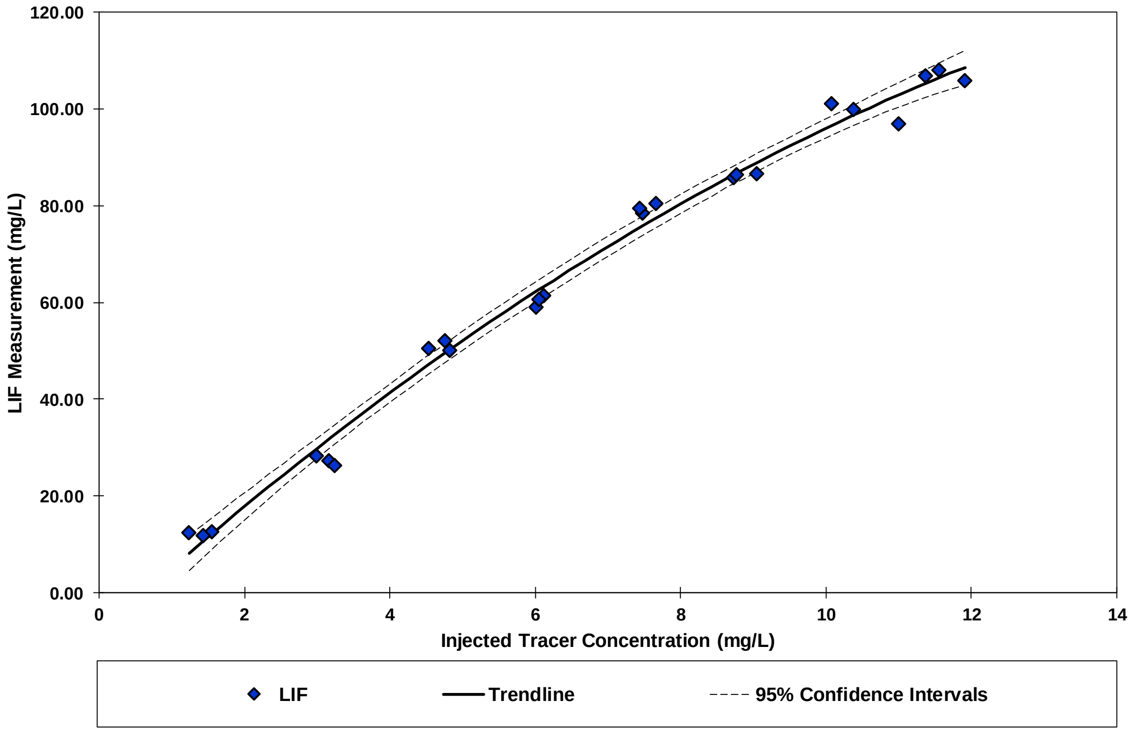


Figure 5.15 – Relationship between tracer and LIF oil-in-water concentration

To prove the effectiveness of this method, a series of trials were conducted using the Produced Water test facility, as shown in Table 5.6. This initial test is conducted with an uncalibrated LIF device, which is then calibrated using the relationship established in Figure 5.15.

Table 5.6 – Initial Matrix for Tracer Validation

Test Number	Ave. Tracer Conc. (mg/l)	Temperature (˚C)	Flow Rate (m/s)
1	1.96	20	3
2	3.92	20	3
3	6.06	20	3
4	8.27	20	3
5	9.66	20	3
6	12.27	20	3

As a recirculation facility is used for the testing, the required amount of tracer is added in a batch, however for typical applications, the flow rate of the process stream needs to be accounted for to determine the tracer injection rate. Figure 5.16 shows the initial data collected from this trial.

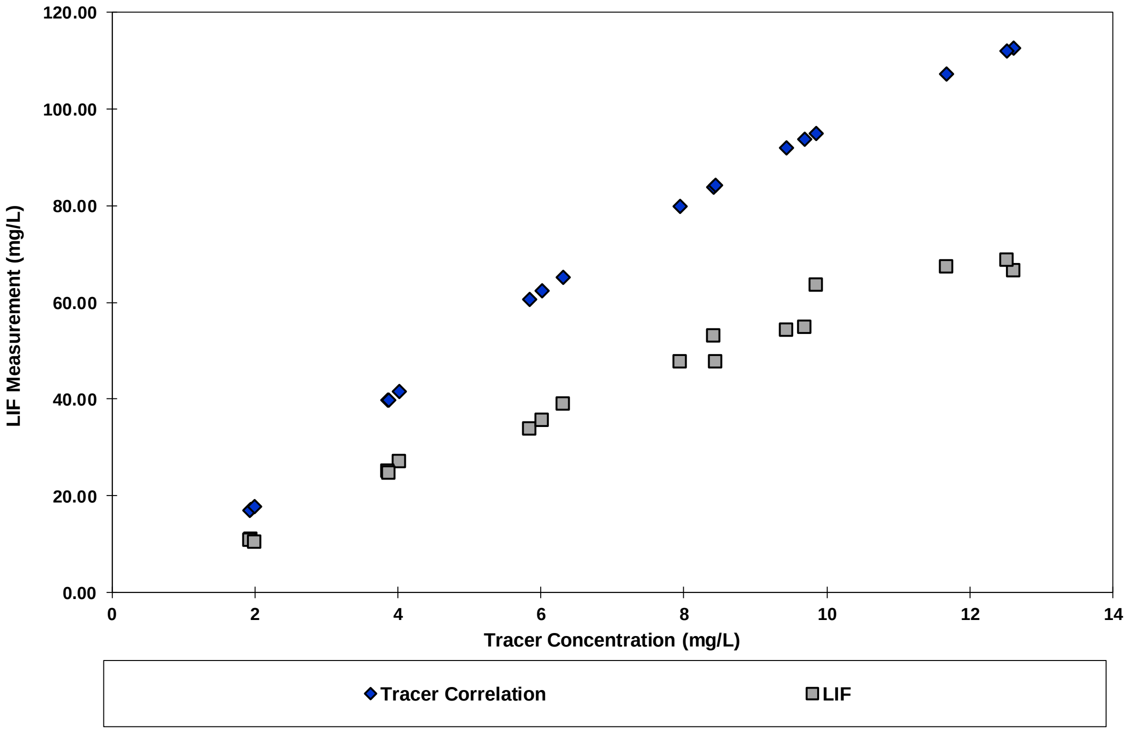


Figure 5.16 – Calibration of LIF device using Tracer Relationship [3 m/s, 20°C]

Assuming the initial tracer correlation is correct, a calibration can then be determined between these two data sets. This calibration is shown in Figure 5.17.

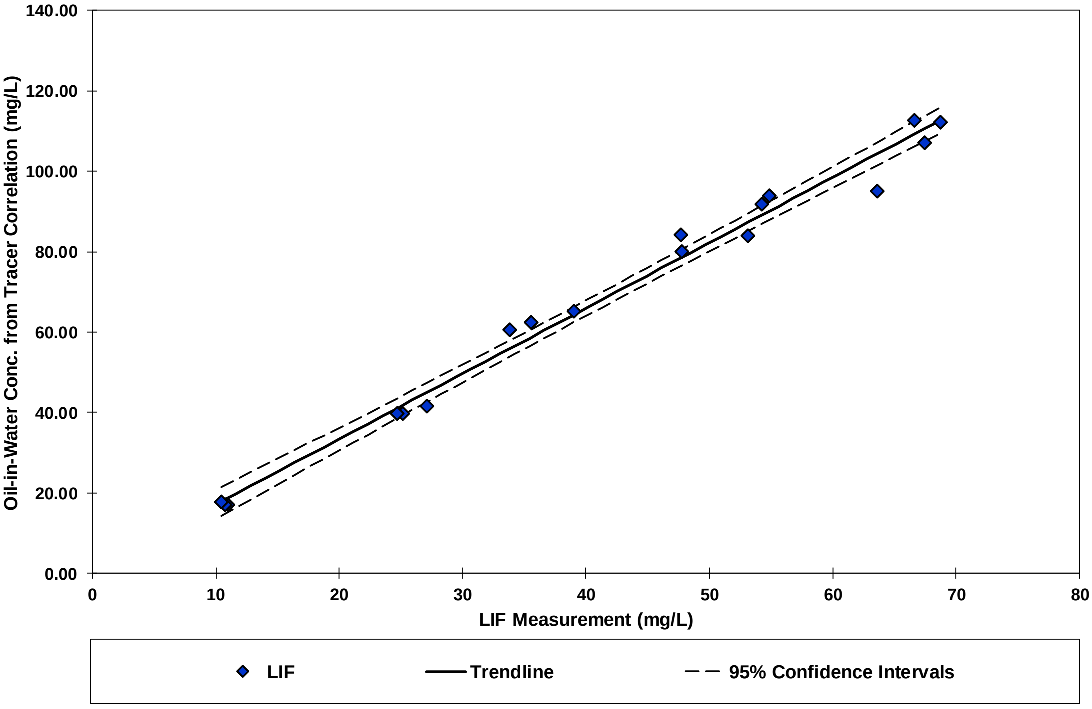


Figure 5.17 – LIF Measurement vs. Predicted Tracer Measurement [3 m/s, 20°C]

The relationship is linear with narrow 95% confidence intervals which demonstrate a good correlation between the LIF results and the tracer relationship. Application of the calibration to the LIF results reduces the -40% offset error in Figure 5.16 significantly as shown in Figure 5.18.

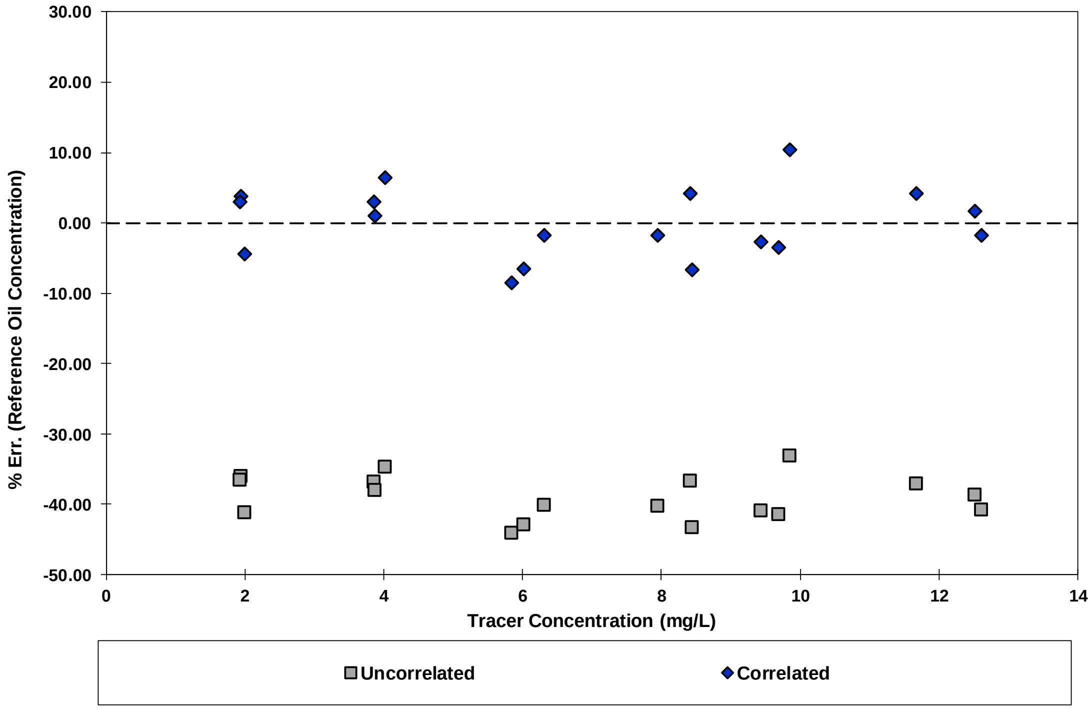


Figure 5.18 – Percentage Deviation of Calibration using Tracers [3 m/s, 20°C]

To further verify this calibration, another set of tests was completed, ranging from 10 to 100 mg/L of oil in water. The graph in Figure 5.19 show the results from LIF device before and after applying the new calibration against the infrared reference method.

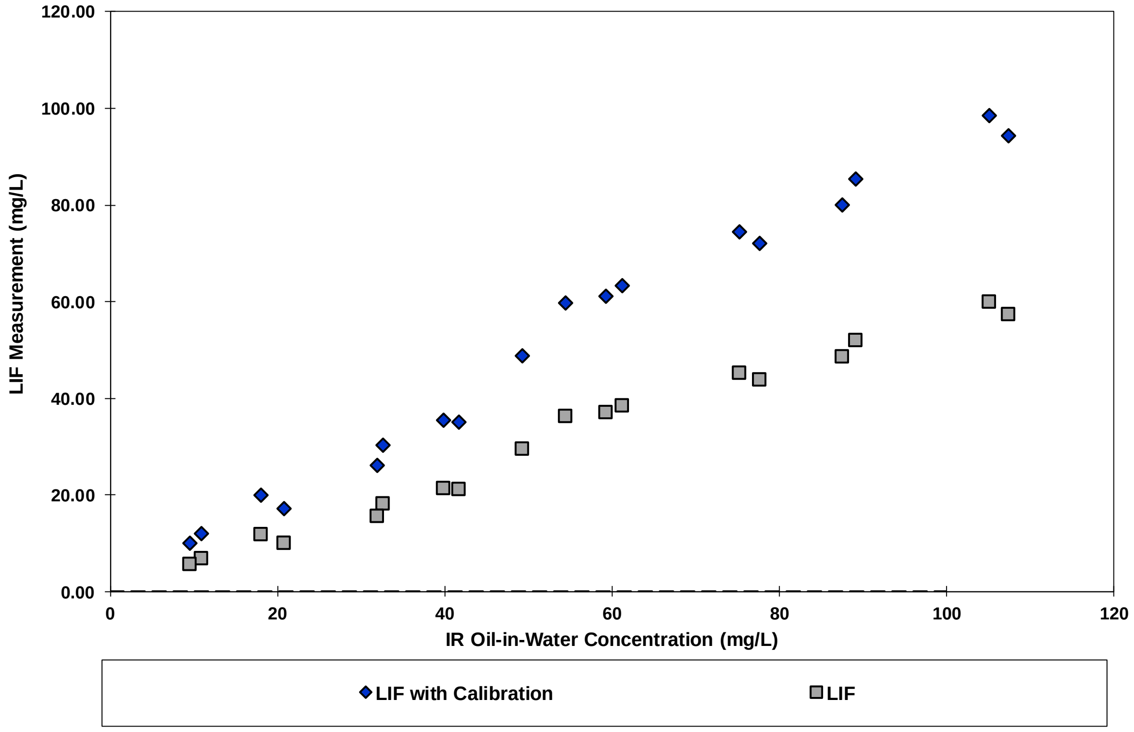


Figure 5.19 – Calibration of LIF using Tracer Technique [10 to 100 mg/L, 3 m/s, 20°C]

it is clear from the results that the method used to calibrate the LIF technique was successful using the newly developed technique with tracers. The results can also be shown as the percentage deviation from the reference measurement, as shown in Figure 5.20, to further highlight the results. The results shown in Figure 5.20 demonstrate that the corrected measurements are closer to the reference measurement. However, further refinement in the tracer relationship may be required with greater focus at lower concentrations.

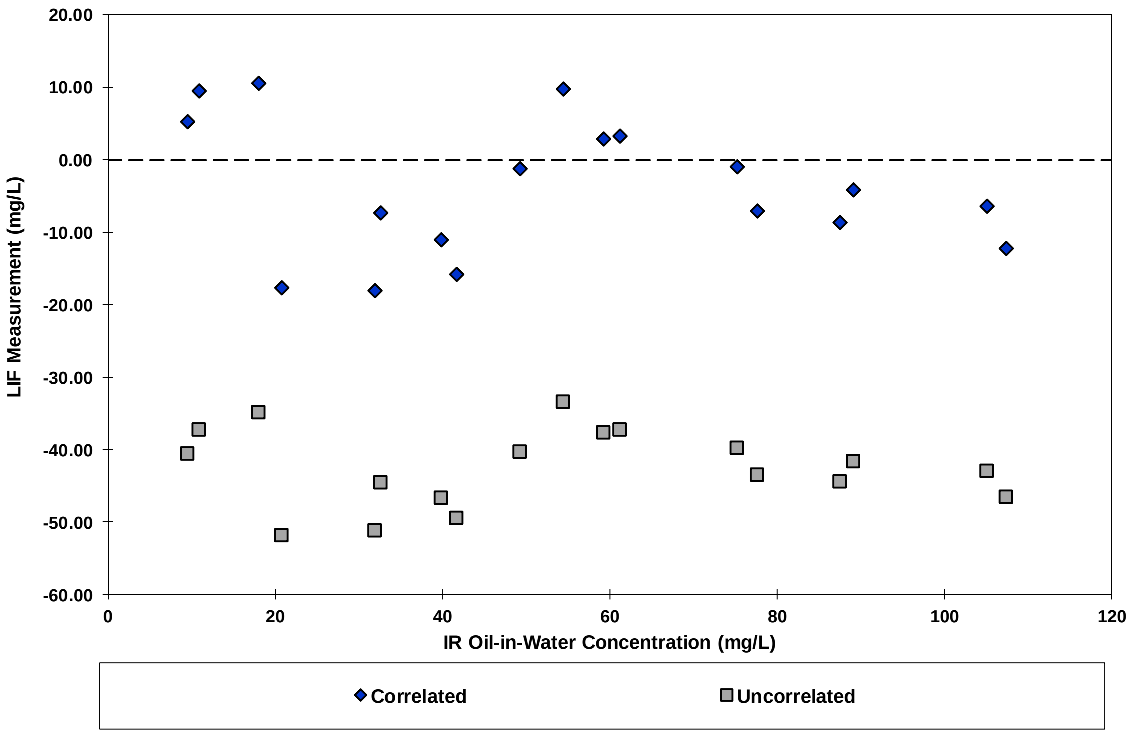


Figure 5.20 – Percentage Deviation of Tracer Technique [0 to 100 mg/L, 3 m/s, 20°C]

5.2.3 Summary

A summary of the main steps for the in-situ tracer verification method are shown in Figure 5.21.

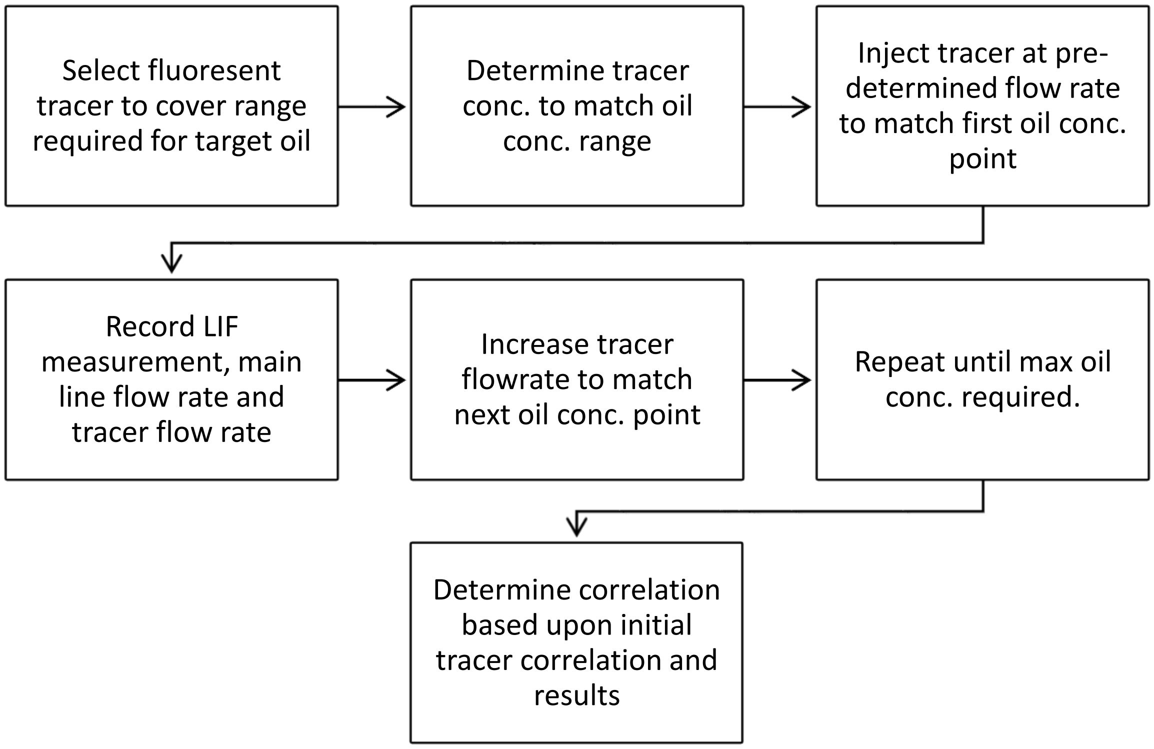


Figure 5.21 – Flowchart Summary of Tracer Verification Method for LIF devices

The objective of this experimental work was to evaluate the effectiveness of a novel method with use of fluorescent tracers to validate and calibrate LIF devices without the need for sampling or conventional reference methods. A review of the data has shown that the use of tracers as an alternative calibration method is viable with consistent results that can be expanded to fit many applications. Negating the requirement of sampling can be vital in the deployment and update of online measurement devices used for measuring oil-in-water in produced water discharge and re-injection applications, which can increase viability of fully unmanned or subsea situations. Overall, the method is demonstrated to be an effective method of calibration and verification.

5.3 Image Analysis of Condensate Oil

As Image Analysis is known to be one of the better methods for determining droplet size, due to its ability to discriminate between oil droplets, solid particles and gas bubbles, a method to improve the measurement in challenging conditions is demonstrated.

The use of tracers to enhance the measurement of Image Analysis devices was also undertaken. As Image Analysis is based upon optical detection of individual oil droplets, the technology is known to be susceptible to high errors in measurement due to changing optical properties. Tracers have commonly been used to improve image capture in a variety of applications, such as in the medical field where radioisotope tracers are typically used to gather detailed images of patients, such as in Positron Emission Tomography (PET) scans. (A.Berson & S.Yalow, 1959).

Image Analysis based systems rely on the optical properties of the target oil to determine droplet size, which can be correlated to oil concentration. The issue with this however is certain oils, typically lighter condensate oils, are less opaque and thus the concentration can be challenging to measure correctly using this technique..

An initial experimental trial was undertaken using Image Analysis to measure oil concentration with condensate oil ranging from 10 to 100 mg/L in the test facility. The results from this test are used as a baseline to determine the improvement of performance of tracer dye injection method. The tracer used in this experiment was a black oil soluble dye, which was pre-dissolved into the condensate oil, in a ratio of 1:50 of dye tracer to condensate oil by volume. The test was then repeated, with the condensate and tracer injected to simulate conditions of 10 to 100 mg/L and results compared. The oil-in-water concentration at each test point was verified using the infrared reference method described previously. It should be noted that the image analysis thresholds were initially altered to account for the increased opacity of the condensate oil, to improve detection.

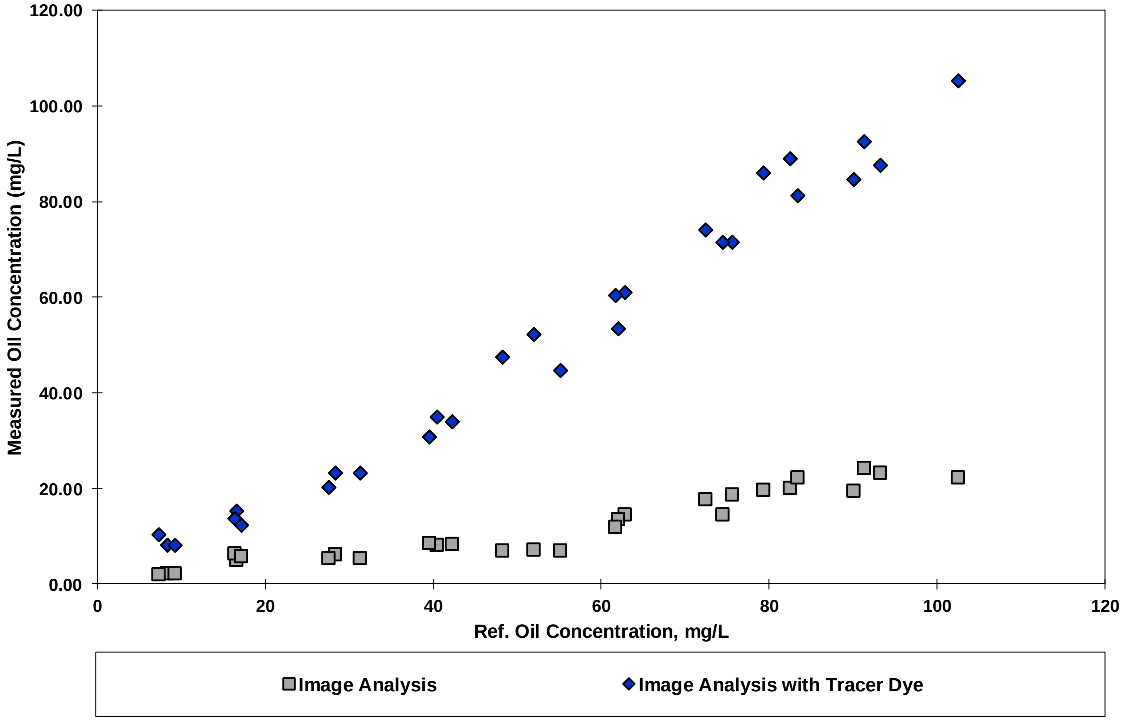


Figure 5.22 – Use of Dye Tracer with Image Analysis [0 to 100 mg/L, 3 m/s, 20°C]

The results from Figure 5.22 demonstrate an increase in performance with the addition of tracer. These results can also be shown as a percentage deviation from reference measurement, as shown in Figure 5.23.

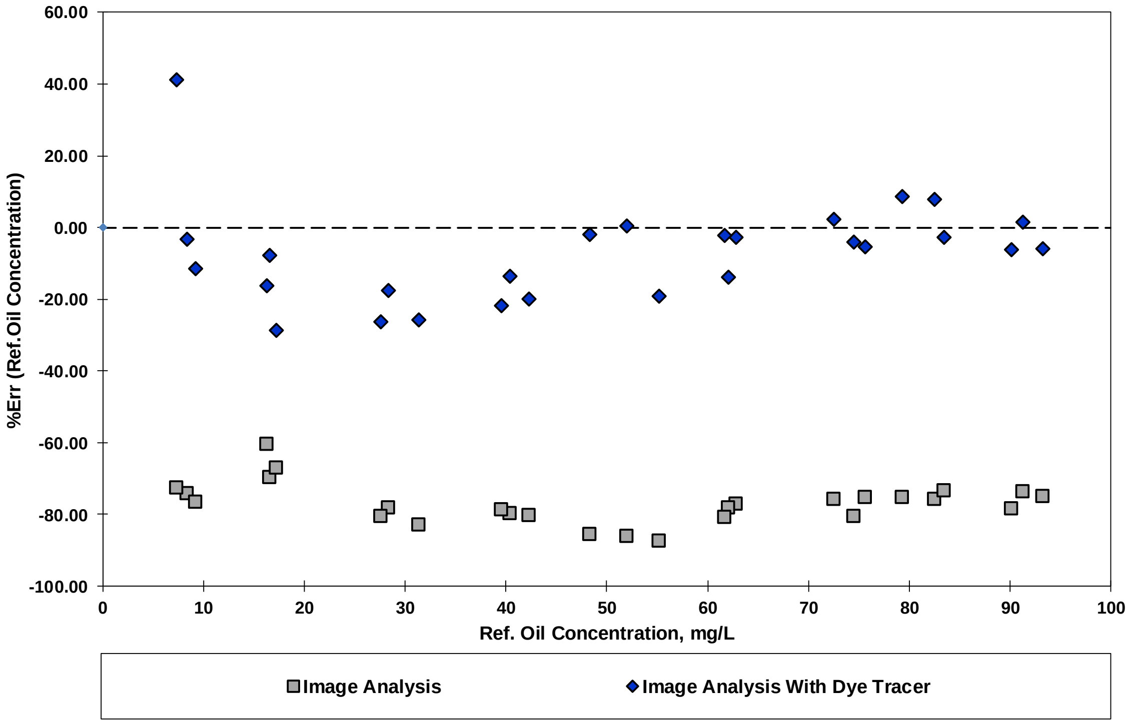


Figure 5.23 – Percentage Deviation with Dye Tracers [0 to 100 mg/L, 3 m/s, 20°C]

A clear improvement is noted, reducing the associated errors from ±80% down to mostly within ±30%. As discussed in the literature review, the principle of image analysis is based upon discrimination of oil droplets and background water via thresholding. As discussed in Chapter 4, the threshold conditions of the image analysis can be split into several parts:

1. Particle Area
2. Perimeter
3. Major and Minor Axis
4. Circularity
5. Fill percent (Opacity)
6. Rotation
7. Aspect Ratio

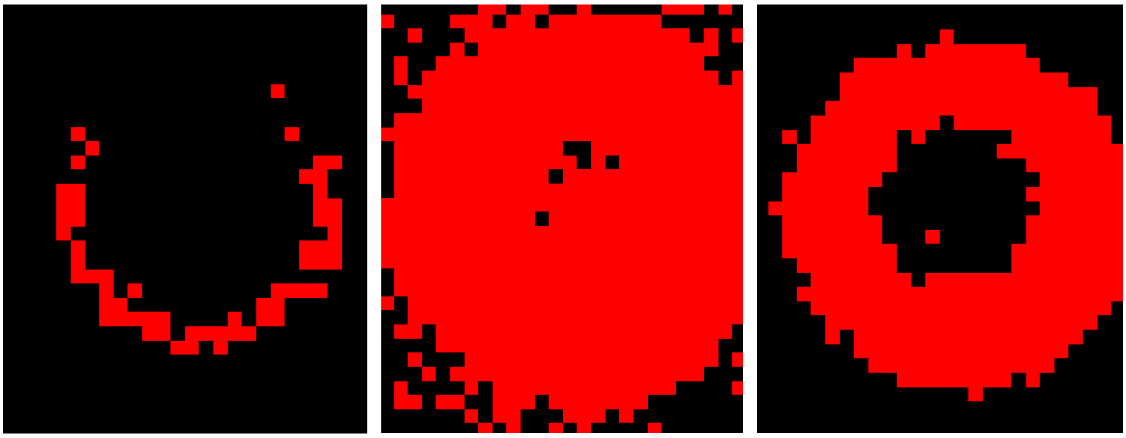
A study was also undertaken to determine if image analysis could better detect condensate oil without the requirement for tracers. In certain applications, such as in the production of natural gas, condensate oil is formed without the presence of any other crude oils. To determine whether image analysis technique could be set-up to measure only condensate oil in water, an experimental study was undertaken.

This trial repeated the set-up described in the previous tests with tracer dye, however the focus was on improving the threshold conditions to allow the image analysis device to detect the condensate oil droplets without the need for tracers.

The main issue with image analysis of condensate oil in comparison to standard crude oil is the low opacity which causes the contrast between the droplet and the background to be very low. Figure 5.24 shows an image of a single condensate droplet that was taken by the image analysis technique.

Figure 5.24 – Single Condensate Droplet Captured by Image Analysis Unit

The image of the condensate droplet shows the low contrast that was discussed. A standard crude oil would be fully opaque and much darker in colour, allowing for easier detection. However, even with this limitation, altering the threshold condition to detect these droplets is still possible. Figure 5.25 shows the process of manually changing the threshold condition with this single condensate droplet.



(a) **(b)** **(c)**

Figure 5.25 – Threshold of Single Condensate Oil Droplet

The series of images shows the different stages of thresholding for a single condensate oil droplet. With typical settings for crude oil, Figure 5.25 (a) shows an example of how the image analysis device detects condensate oil.

By significantly increasing the threshold range, the image shown in Figure 5.25 (b). As can be seen, the device can fully detect the droplet, however at the expense of also detecting significant background noise. This leads to several issues; any fouling or oil residue is detected; any changes in lighting can skew results, and due to the much larger portion of 'detected' area, the processing power of the computer required to interpret the results increases substantially, which can slow down response time. This decrease of response time can be significant, reducing the number of frames that can be analysed, which can lead to skewed results.

After carefully altering the settings to match the specific condition, Figure 5.25 (c), demonstrates the best threshold settings for this condensate oil droplet. The selected settings also have limitations however, the largest being that the image analysis device can no longer discriminate between the condensate droplets and air bubbles. As air bubbles are discriminated due to their fill percentage, air bubbles and condensate droplets in this manner are very similar.

The process of manually changing the threshold settings is very tedious and is also very specific to a single case. Taking the previous example, an assumption is made that the threshold settings will apply to all droplets which may not be the case. To overcome this challenge, a method for automatically setting the threshold conditions was utilised, based on a classification principle. Figure 5.26 shows a series of condensate droplets captured by the image analysis device.

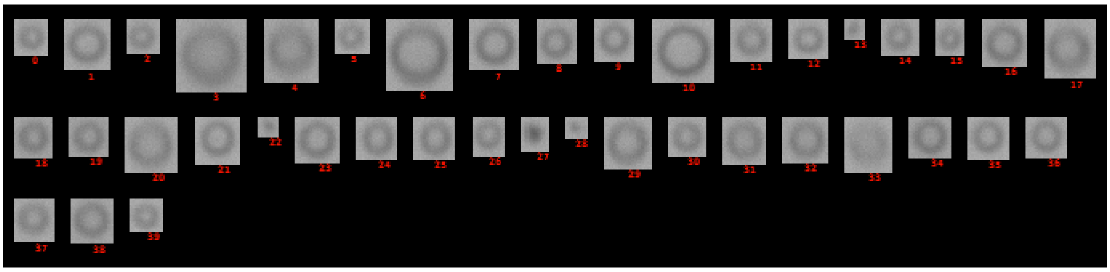


Figure 5.26 – Set of Condensate Oil Droplets

A series of snapshot images can be taken of the target fluid and the properties of the single droplets stored in a particle list. Using this particle list, classification of the particles can be undertaken. Classification is the process in which each droplet can be assigned to a group, such as, oil droplets, sand particles and air bubbles. After completion of this process, re-running the classification allows the software to best determine the threshold settings for each group based on the selection of particles manually assigned to get the best rate of detection. Like before, this also has limitations regarding ensuring a representative sample of each group is collected, however the overall process is much quicker in comparison to manual thresholding.

After undertaking the work to improve the threshold conditions in respect to condensate oil, an experimental trial was completed with condensate oil ranging from 0 to 100 mg/l. Even with the limitations discussed, the method was able to still measure the oil concentration within ±32.8% as demonstrated in Figure 5.27, which is comparable to the results seen during the tracer trial, shown in Figure 5.23.

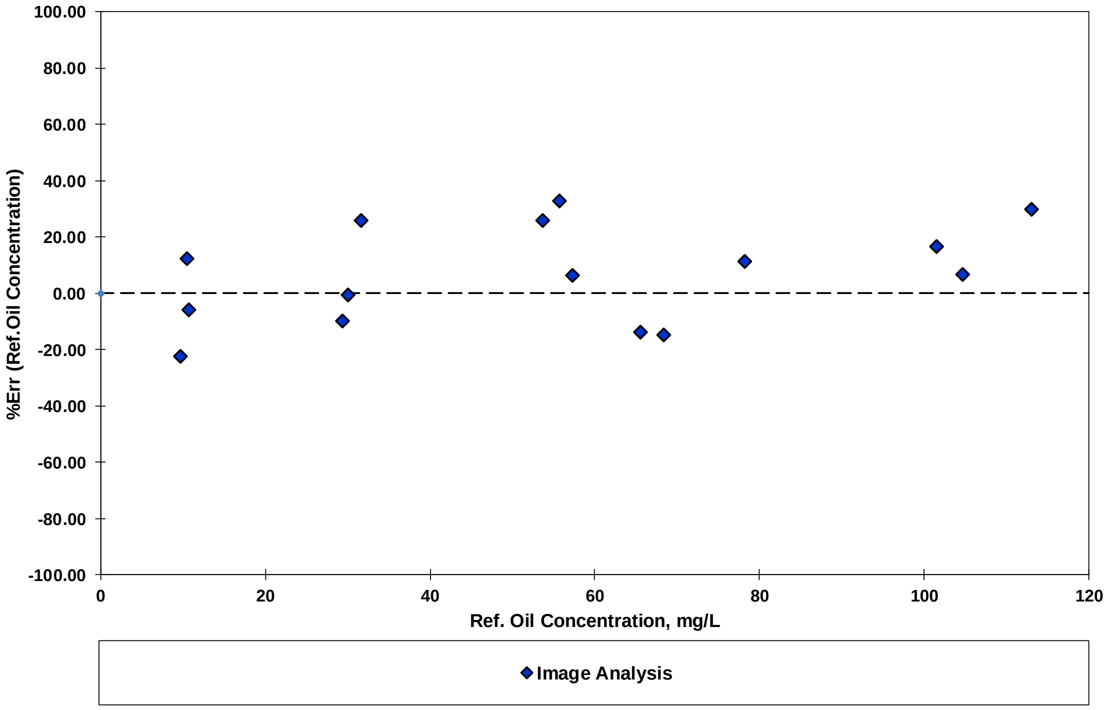


Figure 5.27 – Condensate Oil Droplet Thresholding [0 to 100 mg/L, 3 m/s, 20°C]

5.4 Summary

This chapter aimed to answer the third research question of this research:

- Can improvements be made to current online techniques or methods, to improve performance of measuring oil-in-water concentration?

To answer this question, three different methods to improve current techniques were investigated.

The first method described the use of droplet size measurement to improve the oil concentration measurement of LIF devices. Depending on the produced water treatment option deployed, the droplet size can vary from <1 micron up to 100 microns. The research demonstrated that this change of droplet size can impact the measurement significantly and can also cause the initial calibration to become invalid if completed under the wrong droplet size. The experimental work carried out found the dependency between droplet size and oil-in-water measurement to be related to the surface area of the oil droplet. This finding conveys the theory found in literature that fluorescence produced by light excitement is dependent on the total surface area of the oil. Additionally, the work, following on from Chapter 4 results, found that temperature also needs to be considered as temperature plays an important part as the solubility of crude oil in water needs to also be considered. As discussed, as temperature increases, the proportion of free oil decreases, causing the amount of correction required to decrease due to fact that the influence of droplet size with the inverse is true also for reduction of temperature. The impact of this improvements is that it allows the use of LIF based devices in situations with a varying known droplet size.

Typical methods for verification and calibration involve sampling the process stream and analysed using an offline method. However, even though this method allows for spot checking, full ranges of oil concentrations cannot often be achieved by the process stream, which is required for proper calibration. Also, sampling can be costly and brings additional uncertainty into the process. The second part of this chapter focussed on the development of a method for calibrating and verifying LIF techniques using tracers. Tracers have been previously utilised for flow measurement purposes and depending on the fluid medium and application, the type of tracer used can vary. For this research, a variation on the tracer dilution technique was proposed, using a fluorescent tracer compound to match the concentration profile of the crude oil and therefore using the tracer in known quantities to verify the result of the device.

The use of tracers to validate image analysis of condensate oil was also investigated. As discussed in Chapter 4 results, the image analysis technique had challenges relating to the contrast between the lighter condensate oil and the background water. By using the tracer technique, the image analysis device was also to successfully detect the condensate oil. Another method was also undertaken, by adapting the threshold settings to improve the contrast ratio between the condensate oil and the background, measurements from the image analysis device was significantly improved. This however has limitations as it would only work in very specific applications, however it demonstrates the unit’s ability to measure the condensate oil without the requirement for external chemicals. The ability to measurement condensate oil using an image analysis device cannot be understated. In comparison to other techniques, image analysis also measures droplet size and can differentiate between solid particles, gas bubbles and oil droplets. Using tracers or by changing threshold settings, this allows the use of this technique in an area which has primarily been challenging, allowing for more suitable applications and also negating the need of multiple devices in varying process conditions.

The impact of these improvements brings the measurements from online oil-in-water measurement techniques closer to the ideal reference results and allow the use of online techniques for regulatory reporting to be more viable, in terms of measurement performance.

6 Measurement Uncertainty of Sampling and Online Methodology

Whenever a measurement is made, the result is only an estimate of the true value. The margin of doubt between the estimate of the measurement and the true value is referred to as the uncertainty. To appropriately express measurement results fully, three items are required:

- The measured value from a method or a device
- The measurement uncertainty which is the limits around the measured value where the true value is expected to be.
- The level of confidence, which expresses how often the true value is likely to be within the uncertainty limits.

No measurement is ever fully absolute; there is always a margin of doubt about the result, even in the most accurate cases. However, the uncertainty gives an indication of the quality or reliability of a measurement.

Uncertainty is considered an extremely important parameter throughout many industries; however, it is not commonly quoted in the measurement of oil-in-water for produced water discharge and/or reinjection. The importance of uncertainty can be demonstrated by examining regulatory compliance limits of oil-in-water concentrations around the globe.

This chapter aims to answer the following two research questions:

1. Can we determine the uncertainty of reference techniques typically used to measure oil-in-water concentration? In addition, can we predict the impact of uncertainty due to sampling? If so, what sampling parameters have the largest contribution?
2. Can online techniques be used for produced water regulatory compliance monitoring? What methods of correlation are required to demonstrate this ability?

As previously mentioned, the average UK limit for oil-in-water concentration is 30 mg/L, however as no uncertainty value is attached, any value above this concentration would effectively not meet specifications. However, if the uncertainty of the result was considered, the true value may still be within regulations. As there is a lack of information on this subject, especially in relation to produced water, the output from this research becomes important for ensuring correct interpretation of results in terms of filling the knowledge gap and for regulatory compliance monitoring.

To determine the uncertainty of a measurement, a series of steps can be taken. These are illustrated in Figure 6.1 (NEL, 2015).

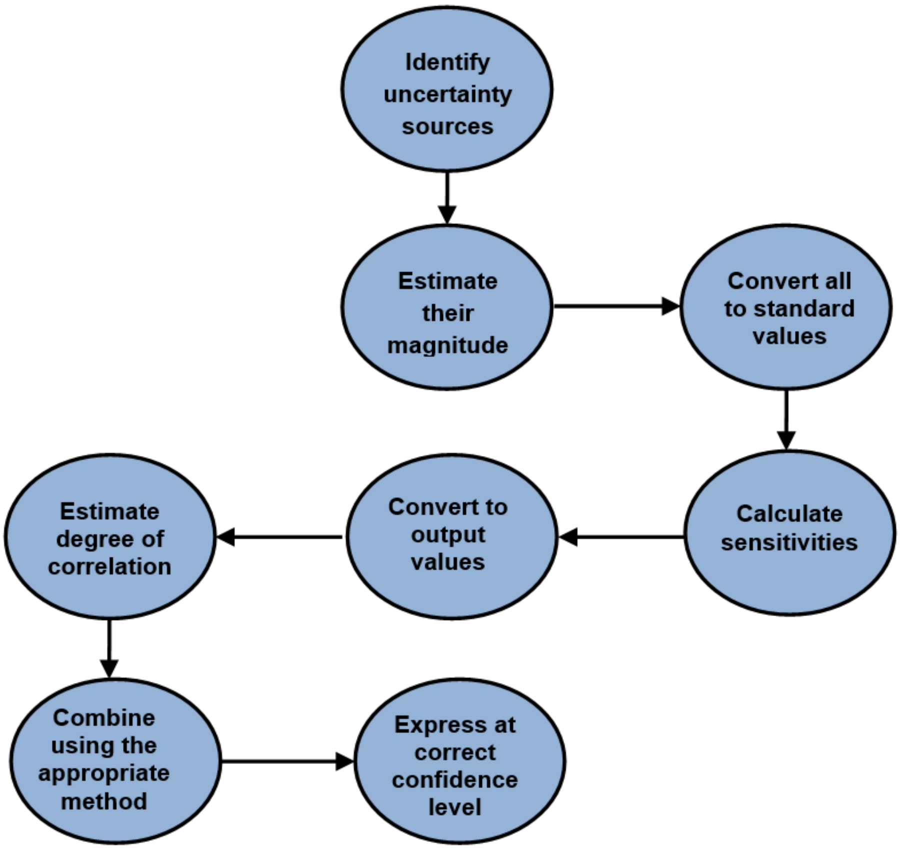


Figure 6.1 – Summary of Standard Uncertainty Calculation Steps (NEL, 2015)

Due to the widely varying nature of the sources that can be identified, there is not a single method of assessing the magnitude of uncertainties. The definitive document on the assessment of measurement uncertainty is the ISO Guide to the Expression of Uncertainties in Measurement (BSI, 2004), which recognizes two basic approaches:

- The analysis of statistical data – referred to as a Type A assessment. In this approach, a numerical value is assigned to the uncertainty, by analysing the results of a series of readings.
- Non-statistical assessments – referred to as Type B. In this method, previous experience and professional judgement are used to place numerical limits on the uncertainty of a measurement.

As part of this research, a Type A assessment is used to conduct an uncertainty analysis on oil-in-water measurement.

When a series of measurements has been taken to determine a parameter, the best estimate of the parameter is calculated to be the arithmetic mean of the values.

$$\bar{x} = \frac{(x_1 + x_2 + \ldots\ldots + x_n)}{n} = \frac{1}{n}\sum_{i=1}^{n} x_i \tag{9}$$

What is needed for the assessment of uncertainty is to define the interval, either side of this estimate, within which the true value expected to be between. The best approach is to consider the deviation of each reading from the calculated mean and calculate a statistical parameter known as the estimated standard deviation.

$$s(x) = \sqrt{\frac{\sum_{i=1}^{n}(d_i)^2}{n-1}} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{\boldsymbol{x}})^2}{n-1}} \tag{10}$$

The standard deviation is often expressed as a proportion of the mean. This is called coefficient of variance CV and is defined as:

$$CV = \frac{s(x)}{\bar{x}} \tag{11}$$

It can also be expressed as the percentage deviation or relative standard deviation:

$$RSD = 100\ \frac{s(x)}{\bar{x}}\ \% \tag{12}$$

Having obtained the estimated standard deviation of a single value, the estimated standard deviation of the mean is obtained from:

$$s(\bar{x}) = \frac{s(x)}{\sqrt{n}} \tag{13}$$

The standard uncertainty of the mean is then given by:

$$u(\bar{x}) = s(\bar{x}) \tag{14}$$

The standard uncertainty defines a narrow band on either side of the mean value which the true value is estimated to be within. The confidence level depends on the degrees of freedom in deriving the standard deviation, thus with three readings, there is a greater than 40% chance that the true value lies outside the defined range. Increasing this to 100 readings there is still a 32% chance.

To increase the chances of the true value lying within the quoted band, the confidence level is often extended by multiplying the standard uncertainty by a coverage factor, k. This factor reflects the confidence in the standard uncertainty, as defined by the degrees of freedom, and the confidence required in the expanded uncertainty (U(x)), thus:

$$U(x) = k \cdot u(x) \tag{15}$$

$$U(\bar{x}) = k \cdot u(\bar{x}) \tag{16}$$

The value of k is taken for the appropriate degrees of freedom and required confidence level. The coverage factor is also known as Student's t from the original publication by W. Gosset (Lehmann, 2011). The uncertainty obtained from a Type A assessment is called a standard uncertainty, and a plot of the data would, with a sufficiently large set of measurements, would trend towards a normal distribution as shown in Figure 6.2.

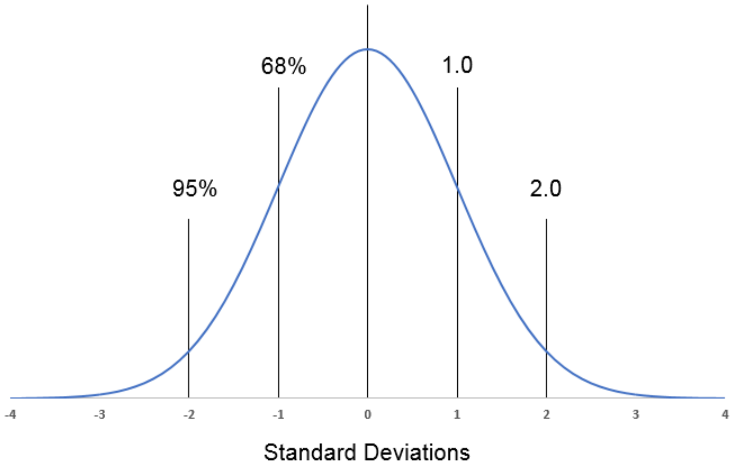


Figure 6.2 – Normal (Gaussian) Distribution

This distribution is common to many measurements and is known as the normal distribution or the Gaussian distribution (TUV NEL, 2010). In the normal distribution roughly 68% of the values will fall within one standard deviation of the mean and roughly 95% within two standard deviations of the mean.

6.1 Initial Experimental Work

In this initial experimental work, the subject of uncertainty within oil-in-water sampling and measurement is explored. To initially estimate the uncertainties related to current reference measurements and the effect of sampling, two series of experiments were carried out. This section will summarise the oil-in-water measurement results collected by undertaking analysis of laboratory prepared standard samples and samples collected from the produced water test facility using an infrared based measurement method. Other than determining the uncertainty of the reference technique, by comparing these results, the additional uncertainty from sampling can also be determined, something that is not accounted for in the precision information discussed in Chapter 2.

Figure 6.3 summarises the results measured from the 30 mg/L oil-in-water laboratory prepared samples using the infrared analysis technique described in prior sections.

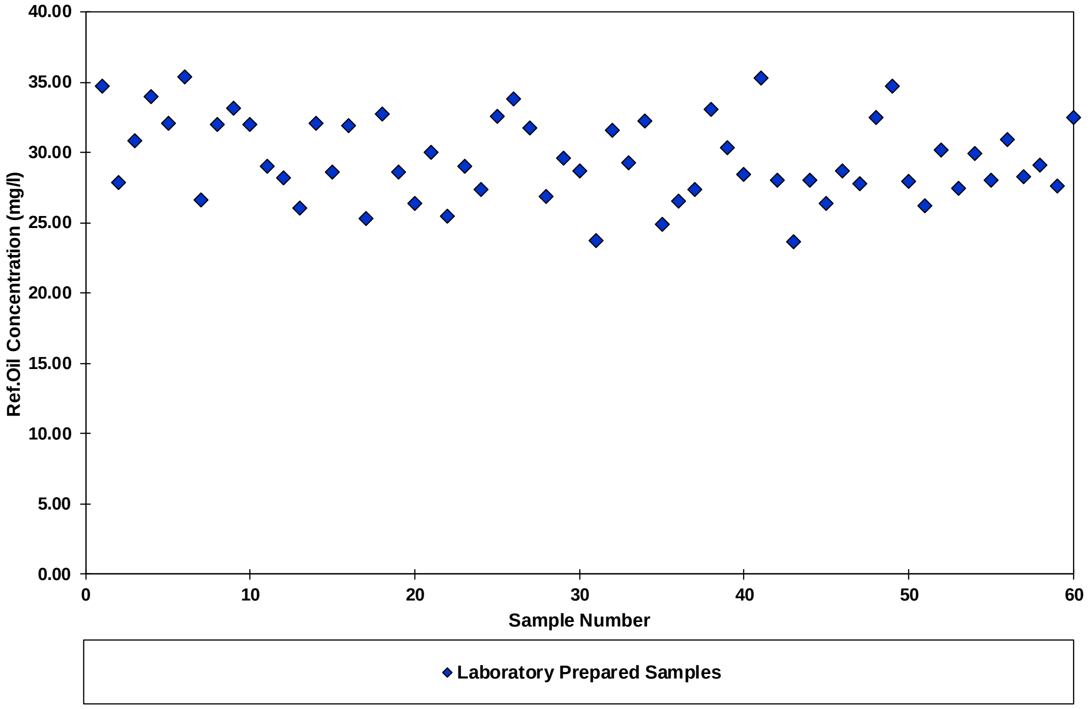


Figure 6.3 – Oil-in-Water Results from Laboratory Prepared Samples [30mg/L]

The uncertainty, using Equation 10, for individual points is determined to be 19.29% at a 95% confidence interval with a mean of 29.6 mg/L. In the UK, it is required that samples are taken twice per day and the monthly average reported for regulatory compliance. Considering the 60-sample population, the uncertainty of the mean, using equation 14, was determined to be 2.51% at a 95% confidence interval. However, it should be noted that the samples collected from operators will not be at the same oil-in-water concentration each time the sample is collected; thus, the uncertainty of the mean will not be fully representative. With regards to the precision information given for the other techniques, the 19.29% at 95% confidence interval seems to be comparable.

Looking at the precision information from literature, previously discussed in Chapter 2, at lower oil-in-water concentrations, the uncertainty increases as expected. To determine this effect, Figure 6.4 summarises the results obtained from 5 to 25 mg/L oil-in-water concentration laboratory prepared samples, with 12 samples being processed at each concentration.

For 5, 10, 15, 20 and 25 mg/L, the uncertainties determined for individual points are given respectively: 28.18%, 27.29%, 22.33%, 22.69% and 19.72% at a 95% confidence level. These results show a clear trend of decreasing uncertainty of the individual measurements at increasing oil-in-water concentrations.

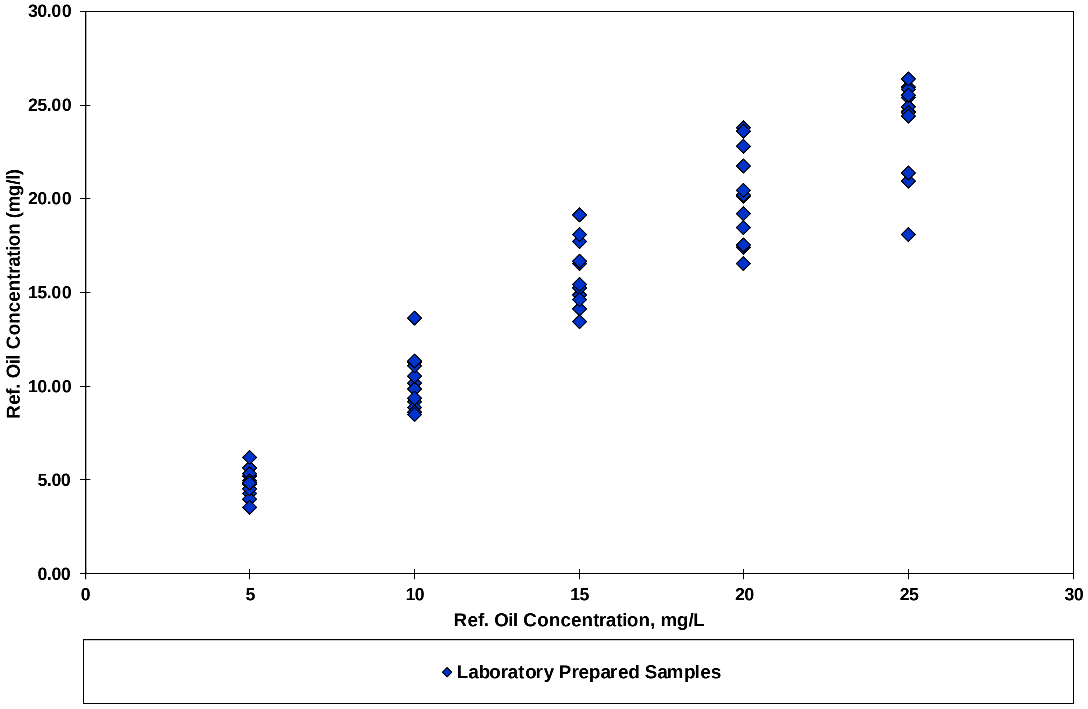


Figure 6.4 – Results from Laboratory Prepared Samples [5 To 25 Mg/L].

To undertake the tests on the produced water facility, a sampling device was designed to remove a fraction of the main flow for subsequent analysis. A sampling device similar to that shown in Figure 6.5 was used (IMO, 2003). For this test, 8 mm stainless steel tubes were used within a 12.7mm sample point.

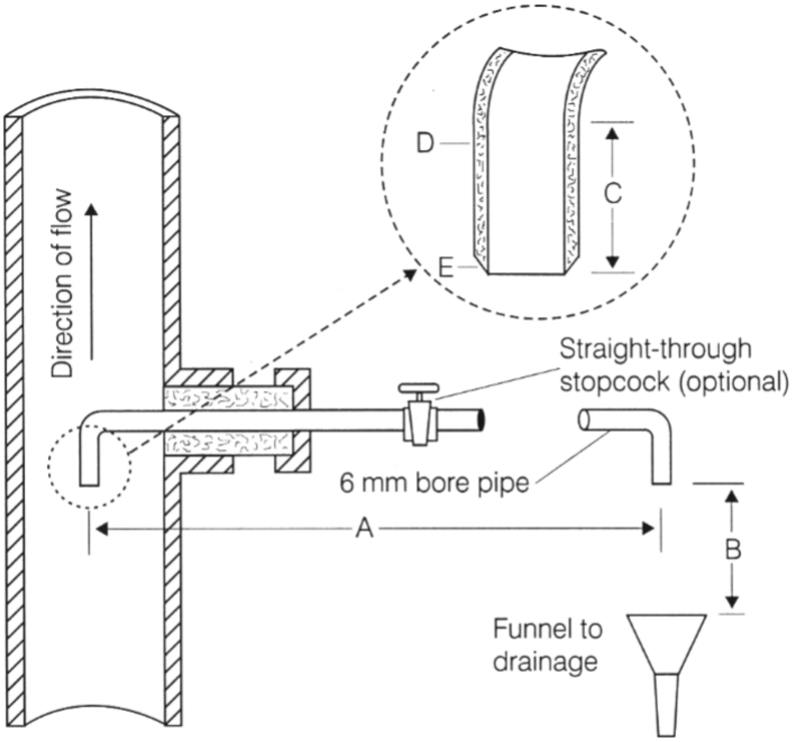


Figure 6.5 – Schematic of Sampling Point (IMO, 2003)

The test section had five different sample points fitted strategically along the length of the pipe, which allowed for checking the consistency of the test fluid conditions. The test section was deliberately set in the vertical orientation so that there is a better chance of having a more uniform dispersion of oil-in-water. The main flow was also upwards, again to ensure consistent samples. At the base of the test section, a T-piece was fitted to aid in mixing and to increase turbulence downstream, as discussed in Section 3.3. If a standard 90º bend is used, a skewed velocity profile of oil droplets would occur due to the centrifugal force effect which can impact on the oil-in-water droplet profile and therefore sampling repeatability.

To further ensure representative results, the samples were collected under isokinetic conditions. Isokinetic sampling means that the velocity of the sample line matches the velocity in the main pipe flow. As the flow in the main line is controlled to a constant velocity, the velocity of the sample point valve positions set to ensure iso-kinetic conditions. The test fluid was allowed to flow through the sample point for 1 minute prior to sample collection to reduce contamination.

After collection of the samples, they were analysed using the infrared method. It should be noted that due to the process of sample collection, the volume of sample collected may differ slightly, and thus the water volume after extraction is measured using a volumetric cylinder and accounted for in the calculations to obtain the final oil-in-water concentrations. Samples were collected in batches of 12 using a duplicate sampling technique. This technique involves collecting all 12 samples at the same time by filling up each sample bottle to a third of the total volume required, and then repeating twice until all bottles have the required volume. Collecting the samples using this method ensures that any discrepancies are consistent throughout the samples and effectively averages out any potential fluctuations in oil-in-water concentration that may be present with in the test facility.

Figure 6.6 summarises the measurement results determined by collecting 60 samples at a concentration of 30 mg/L from the test facility. Several modifications were made to ensure the sample point used was in optimal location regarding surrounding pipework and turbulent regions, again to ensure consistent samples.

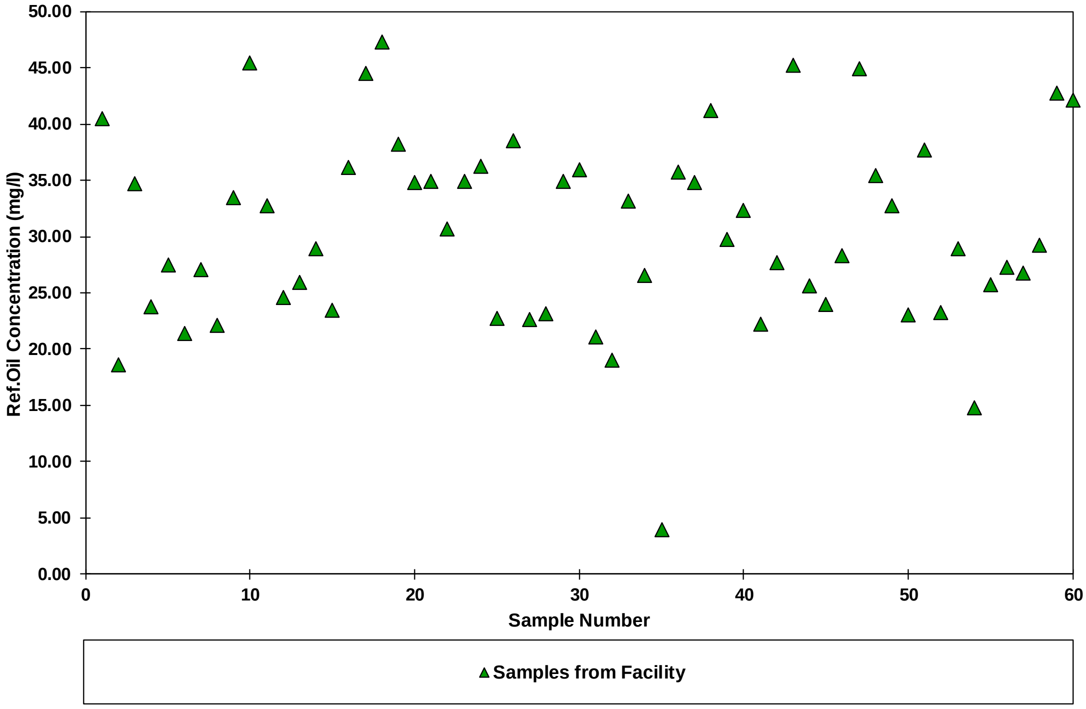


Figure 6.6 – Oil-in-Water Concentration Results from Samples Collected from Test Facility [30 mg/L, 3 m/s, 20°C]

From the data in Figure 6.6, the uncertainty for individual points is 52.1% at a 95% confidence interval with a mean of 30.6 mg/L. Considering the 60-sample population, the uncertainty of the mean was determined to be 6.78% at a 95% confidence interval.

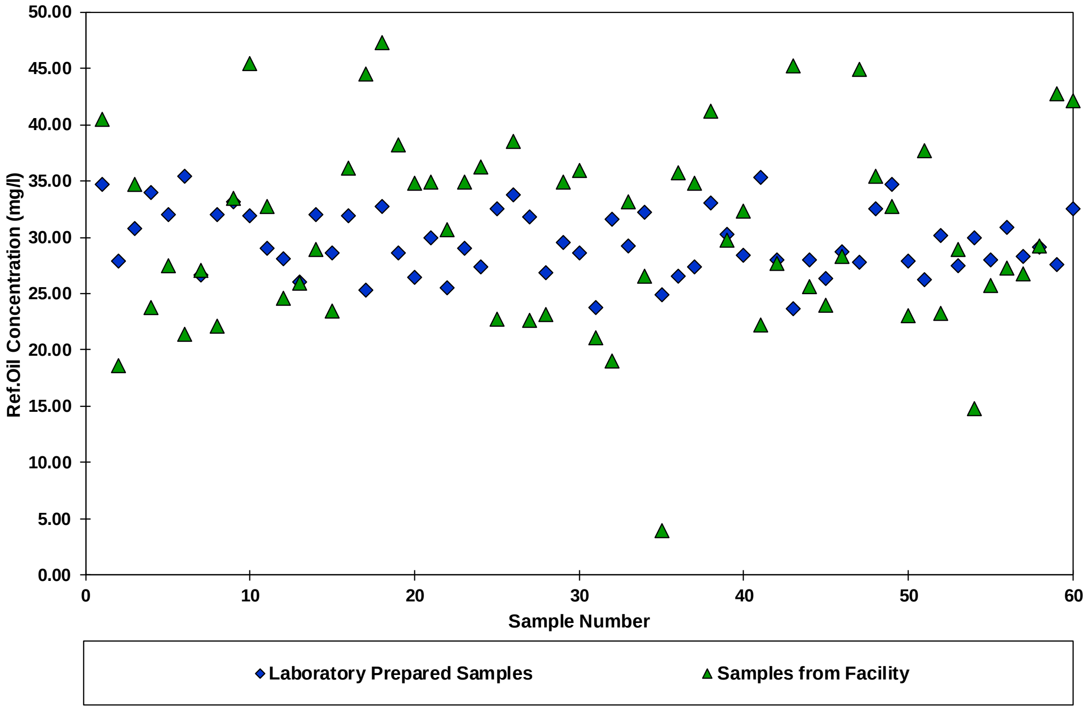


Figure 6.7 – Combined Laboratory Prepared Samples and Facility Results [30 mg/L]

Comparison of the sampling technique results and results from the reference method are shown in Figure 6.7. The graph shows that sampling method affects increases the overall uncertainty of oil-in-water measurement quite substantially. By simply subtracting the uncertainty related to the reference method from that associated with the sampling technique, an uncertainty of 32.81% at 95% confidence level is found, which is over 1.5 times higher than the uncertainty of the reference method alone, making up 63% of the total uncertainty.

As flow regime, droplet size, temperature, pressure and other parameters will differ for each field or application, the uncertainty associated with sampling can vary. As test conditions for this experiment were set up under as close to optimal conditions as possible, it is likely that the uncertainties achieved with sampling in real life will be even greater.

6.2 The Effect of Sampling on Oil-in-Water Measurement

As all current reference methods require samples to be collected prior to analysis, the importance of obtaining a representative sample from the produced water process stream cannot be understated. For regulatory compliance, sample collecting locations are often pre-determined and approval from the regulator is often required to move to other locations. Depending on where the sample is being analysed, several considerations such as: temperature control, pH level, transportation and storage techniques need to be accounted for. All these factors can influence measurement results and thus these factors need to be considered to determine how the final measurement result could be affected.

As demonstrated in the previous section, the uncertainty associated with sampling can be seen to contribute to more than half of the uncertainty of the infrared reference method typically used in the UK. This initial research work, however, only investigated a single sampling methodology and did not account for a number of other parameters which are commonly seen in sample collection throughout the industry. There is a significant gap in research involving sampling methodology of oil-in-water flows, and how differing methods can affect the overall representativeness and uncertainty contribution to the oil-in-water measurement.

To fill this gap in knowledge, this section builds upon the initial experimental research carried out in the previous section. By calculating the total uncertainty of the oil-in-water measurement from sampling to final laboratory measurement, and using the previously determined uncertainty information, the contribution of sampling on the overall measurement can be determined. By varying individual key sampling methodology parameters, the impacts on sampling uncertainty can be determined.

6.2.1 Test Methodology

The following list summarises the tests that were undertaken:

- Sample Point Velocity
- Installation Effect

- Horizontal vs. Vertical Orientation
- Droplet Size Distribution
- Main Line Velocity
- Oil Concentration

Prior to the collection of samples, the facility was allowed to fully stabilise for a minimum of one hour to ensure consistent results. Sample points were drained for a minimum of one minute prior to collection of samples, to ensure the sample points are fully flushed and residual oil does not cause contamination effects. After collection of the samples, they are analysed using the Infrared method previously discussed in Section 2.3.1.

Unless specified otherwise, all samples were collected via one of the 4 sample points situated on the vertical test section, with the intake of the sample point taken from the midpoint of the pipe. An example vertical sample point is shown in the schematic in Figure 6.8.

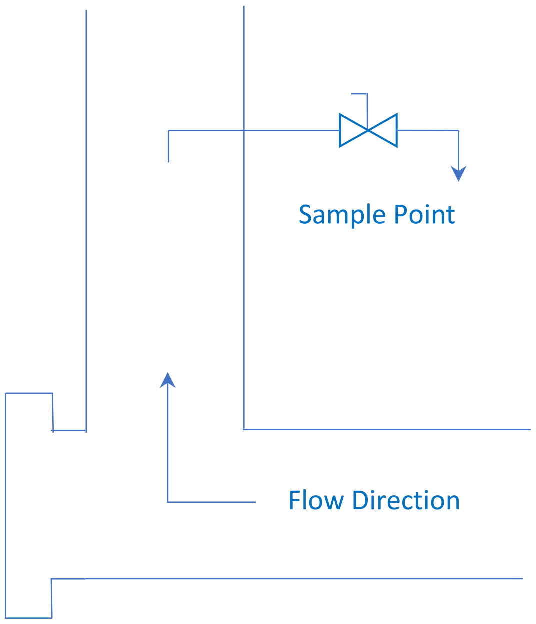


Figure 6.8 – Vertical Test Section Schematic

6.2.2 Sample Point Velocity

Five different velocities were investigated at a main line velocity of 3 m/s to determine the impact of sub-isokinetic, isokinetic and super-isokinetic sampling regimes. The sample line velocities chosen were 1, 2, 3, 4 and 5 m/s to cover several sampling conditions. As the main line velocity is set to 3 m/s, sample line velocities of 1 and 2 m/s conditions are sub-isokinetic, 3 m/s is isokinetic, and 4 and 5 m/s are super-isokinetic.

Sample Line velocity was determined by using a gravimetric system to calculate the flow rate and therefore the velocity within the 8 mm sample tube. The gravimetric system comprised of a small tank, weighing scales and a timer system, connecting to the test facility data acquisition system. To determine the flow rate, the weight of the tank was measured before and after a specified period of time. Knowing the difference in mass and the time elapsed; the mass flow rate can be calculated. The mass flow rate can then be converted to a volume flow rate using the density of water and then the final velocity can be deduced. Figure 6.9 shows a picture of the gravimetric system used.

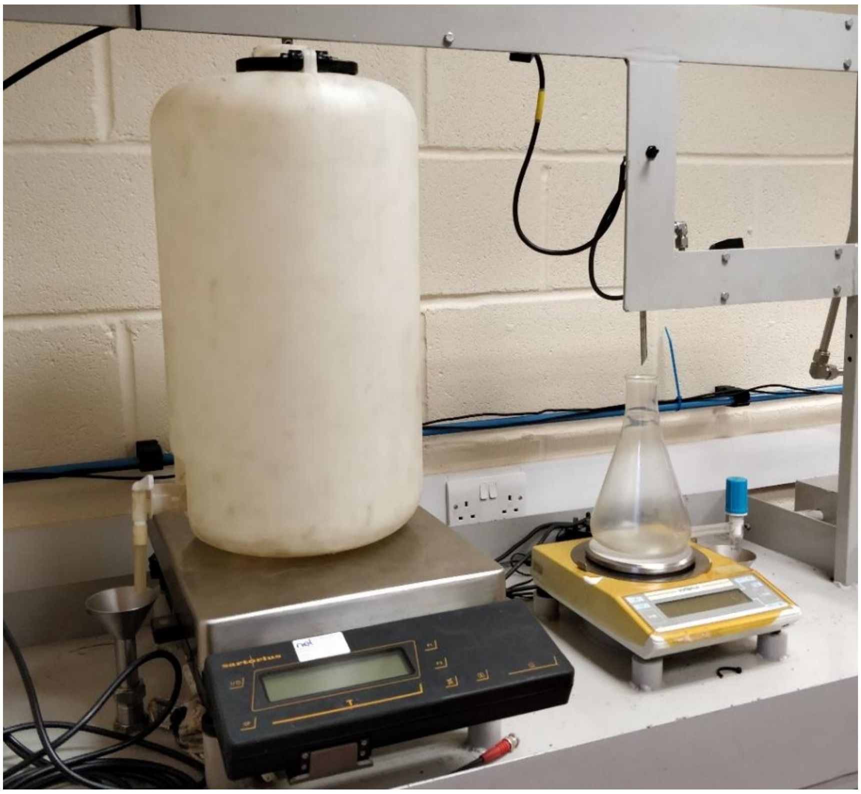


Figure 6.9 – Sample Point Gravimetric System

For each sample line velocity, 12 samples were collected and analysed using the infrared based reference methodology. Figure 6.10 graphically summarises the effect of how the velocity profile of the sample line can affect the proportion of fluid sampled.

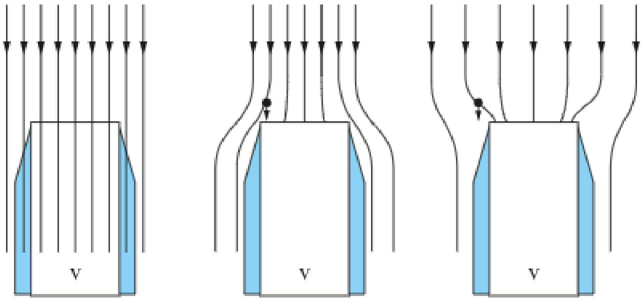


Figure 6.10 – Isokinetic and Anisokinetic Sampling Velocity Profiles (SIGRIST, 2019)

From left to right, as shown in Figure 6.10, the diagram shoes: isokinetic, sub-isokinetic and super-isokinetic. As depicted, Isokinetic sampling minimizes the momentum effects between the phases, therefore the sample contains the same proportion of the individual phases as the main flow. In sub-isokinetic and super-isokinetic conditions, the velocity in the sample line varies in comparison to the main line, representativeness of the sample will reduce. Figure 6.11 shows the results of the sample line velocity measurements.

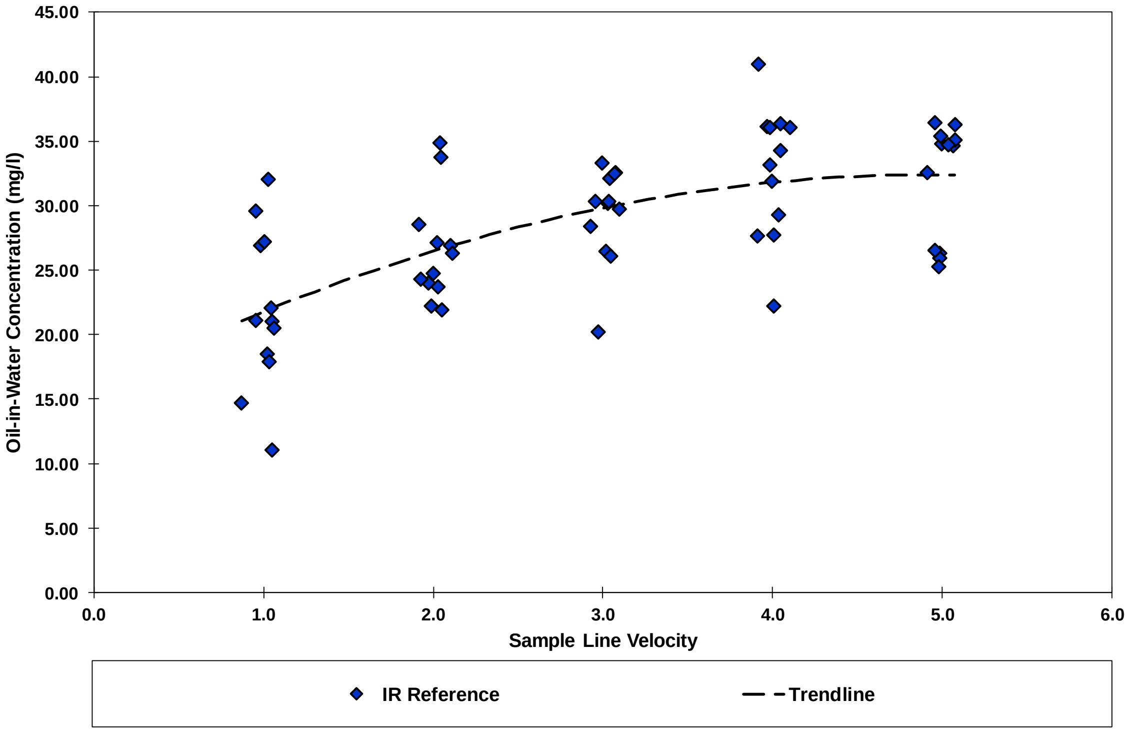


Figure 6.11 – Effect of Sample Line Velocity [30 mg/L, 3 m/s, 20°C]

The mean oil-in-water concentration measured between 1 to 5 m/s changed from 21.9 to 32.0 mg/l. The results for each test condition are summarised in Table 6.1.

Table 6.1 – Effect of Sample Line Velocity Results

Sample Line Velocity (m/s)	Mean Oil-in-Water Conc. (mg/l)	Standard Deviation (mg/l)
1	21.9	5.9
2	26.5	4.0
3	29.3	3.5
4	32.7	4.9
5	32.0	4.3

Taking the mean concentration measured at the isokinetic sample line velocity of 3 m/s as the true measured oil-in-water concentration, the graph can be changed to percentage deviation from this mean value can be calculated, as shown in Figure 6.12.

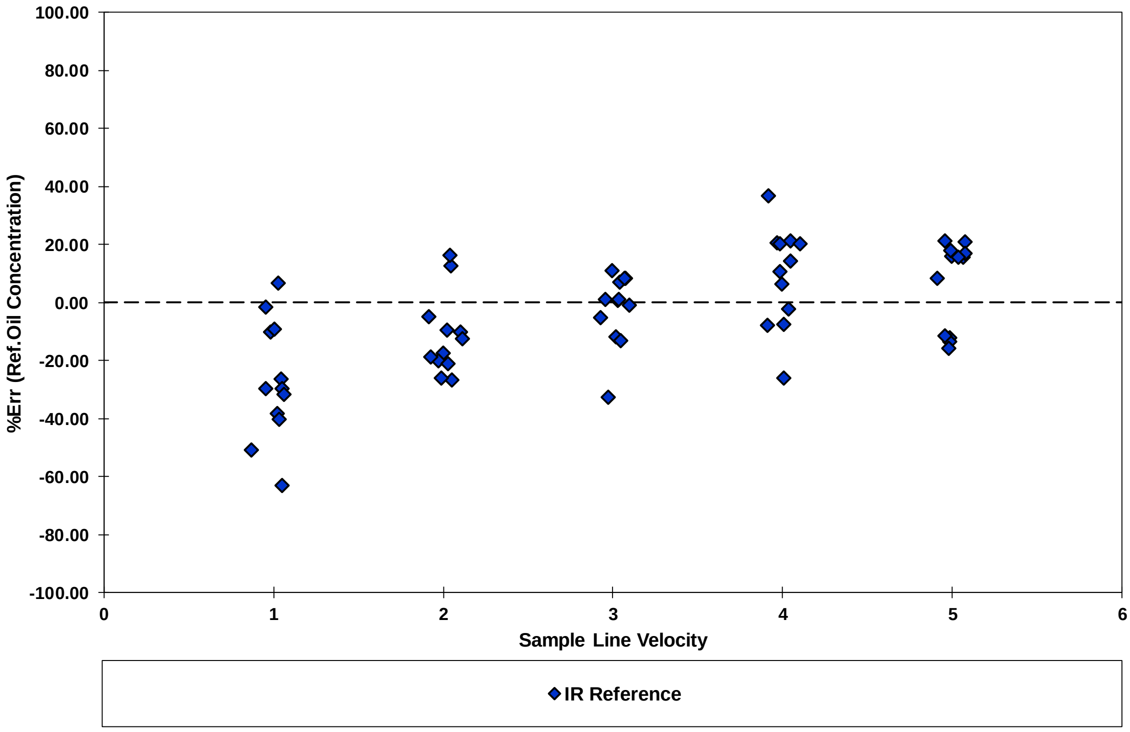


Figure 6.12 – Effect of Sample Line Velocity on Oil-in-Water Concentration Measurement [30 mg/L, 3 m/s] (Percentage Deviation)

The effect demonstrated from the experiment can be supported by research work which was carried out in this subject by Rader and Marple. The work looked at a numerical investigation on the effect of sampling representativeness through sample probes under anisokinetic conditions (Rader & Marple, 1988). The research focussed on the velocity ratio and aspiration coefficient of aerosols, as described in Equation 17 and 18 respectively.

$$Velocity\ Ratio = \frac{\bar{U}}{U_0} \tag{17}$$

$$A_i = \frac{\bar{C}}{C_0} \tag{18}$$

Where,

A_i	= Aspiration coefficient
$\bar{C}$	= Particle concentration in sample probe
C_0	= Particle concentration in main line
$\bar{U}$	= Velocity of sample probe
U_0	= Velocity in main line

Results from the numerical model was compared with experimental data collected by Belyaev and Levin (Belyaev & Levin, 1974). A relationship was determined between the velocity ratio of sample probe to main line and the resulting concentration of collected sample. Even though this work was investigating aerosols, the principles can also be seen in oil-in-water measurement.

Similar work has also been undertaken in other areas, such as wet gas sampling (Yanfeng, et al., 2002).

6.2.3 Installation Effect

To determine the impact of installation effects on sample collection, a series of tests was undertaken. Like the previous experiments, the test section is orientated in the vertical configuration. To simulate differing installation effects and to determine their impact, two upstream arrangements were used; a T-piece and a 90^o bend. Throughout industry, it is common knowledge that a T-piece should be placed at the start of a vertical section for enhanced measurement. This is due to the mixing effect through the T-piece, creating a more homogenous flow pattern at the output. Typical 90^o bends however, have been known to create skewed flow profiles, leading to issues for typical measurement devices.

This section plans to evaluate this theory in oil-in-water measurement by using a traversing sample probe along the cross section of the pipe to determine the impact of such installations. The three points at which the samples are taken along the cross section are shown in the figure below.

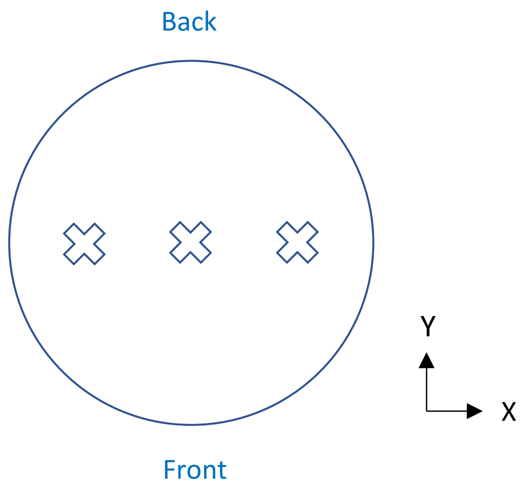


Figure 6.13 – Sample Point Locations Across Pipe Cross Section

To further investigate the effects of installation, the sample point distance from start of vertical section was also controlled. Four different upstream lengths from 5 diameters to 20 diameters were utilised. By traversing the sample probes along the cross-sectional area and combining this with different upstream length, the overall installation effect can be modelled throughout the test section.

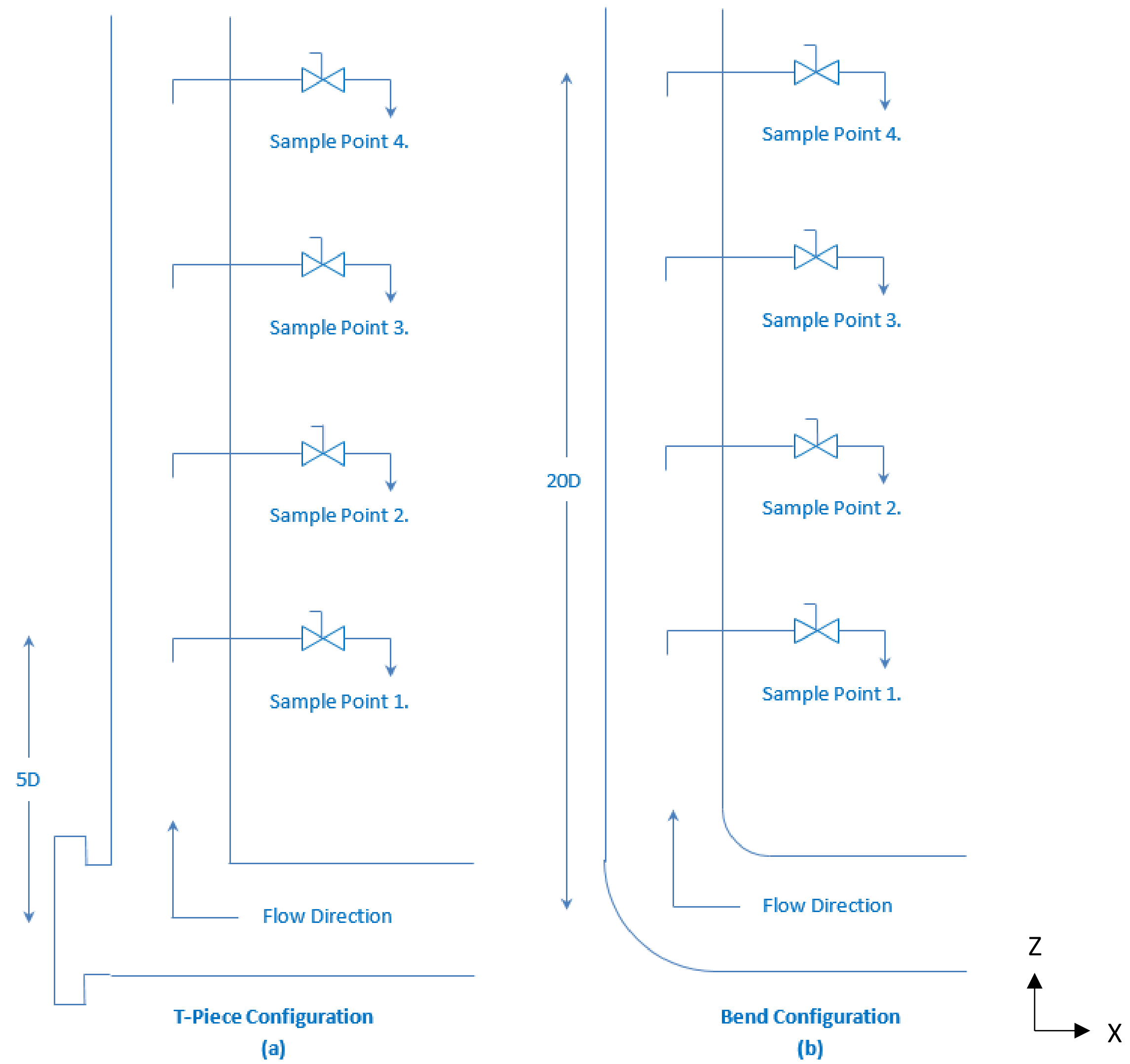


Figure 6.14 – Sample Location Schematic for T-Piece (a) and Bend (b) Configuration

For each sample position, three samples were collected and analysed. The results from the samples at each sample point are averaged and shown for the 90° bend and T-piece in Figure 6.15 and Figure 6.16 respectively.

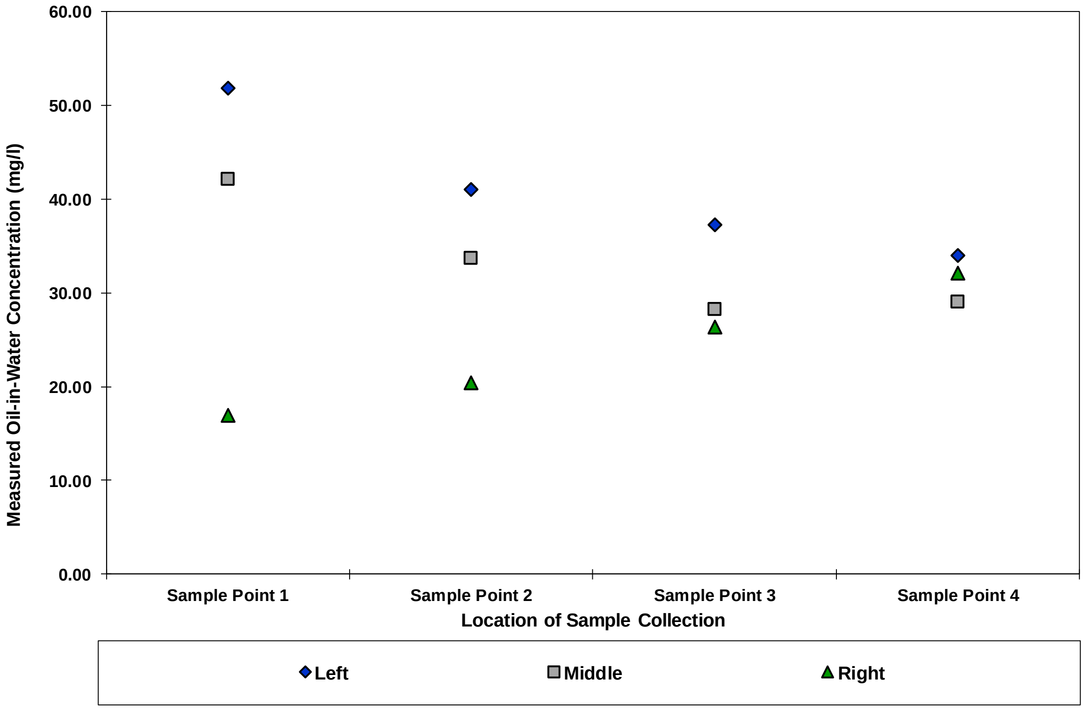


Figure 6.15 – Effect of 90° Bend on Sample Measurement [30mg/l, 3m/s, 20°C]

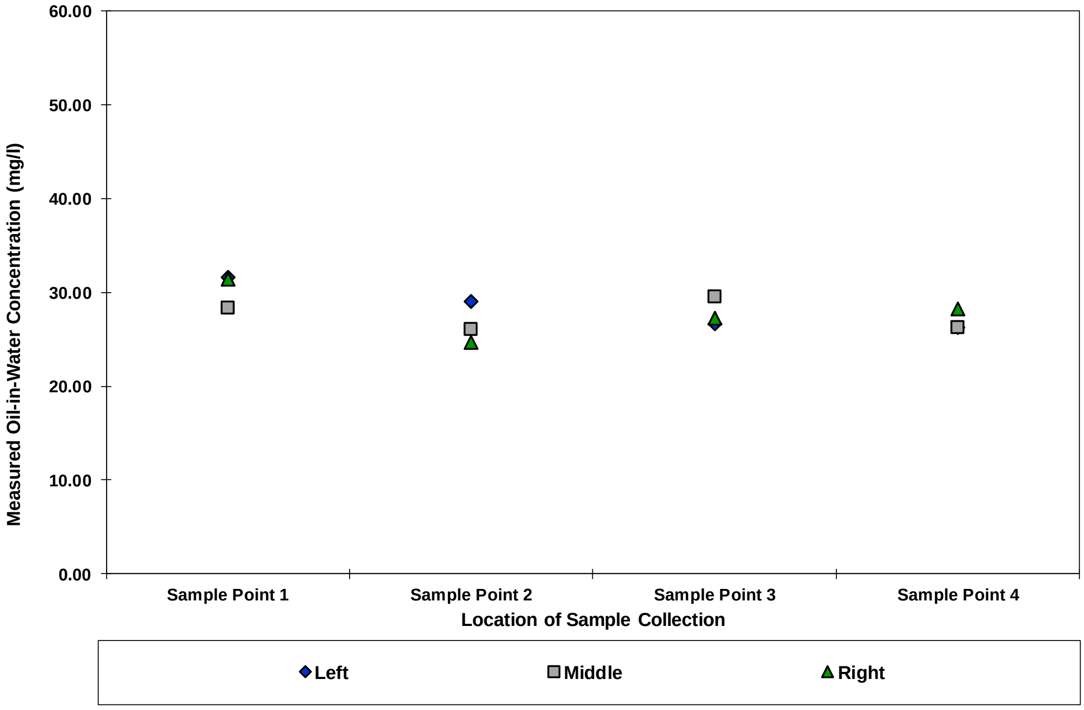


Figure 6.16 – Effect of T-Piece on Sample Measurement [30mg/l, 3m/s, 20°C]

As the flow from upstream is entering the vertical section perpendicular, this skew is noticed from the left to right side of the pipe. This skew affects the concentration profile across the pipe which can be seen in Figure 6.15, however this can also be demonstrated by looking at the droplet size distributions.

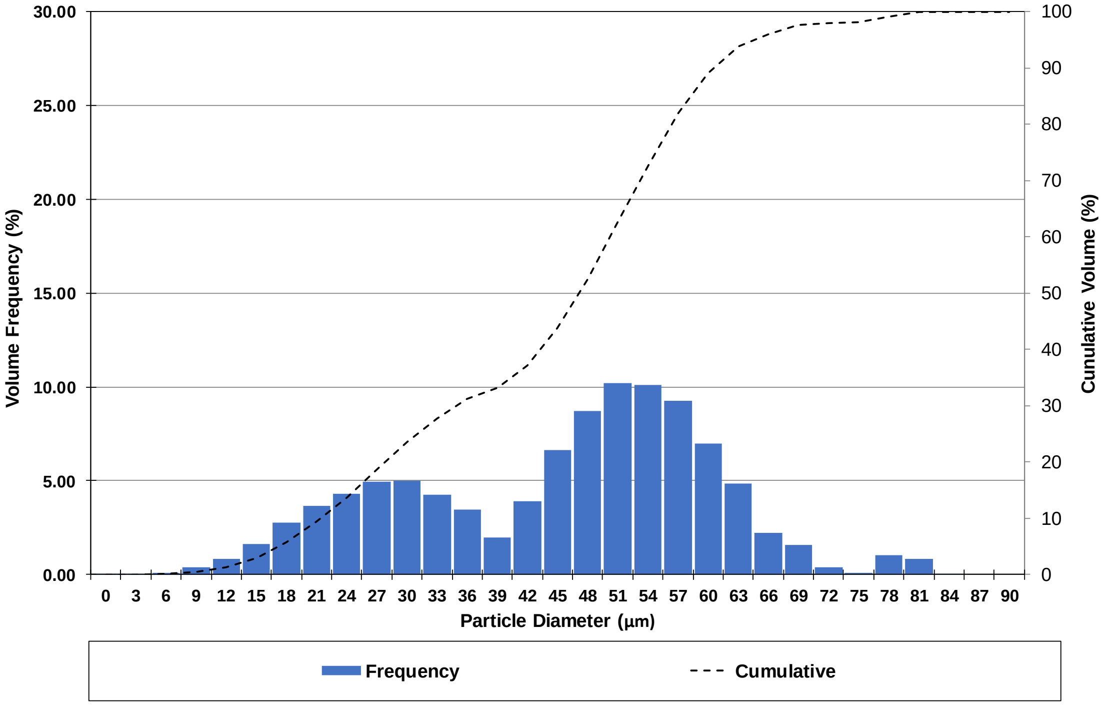


Figure 6.17 – (Left) Droplet Size Distribution at Sample Point 1 in 90° Bend

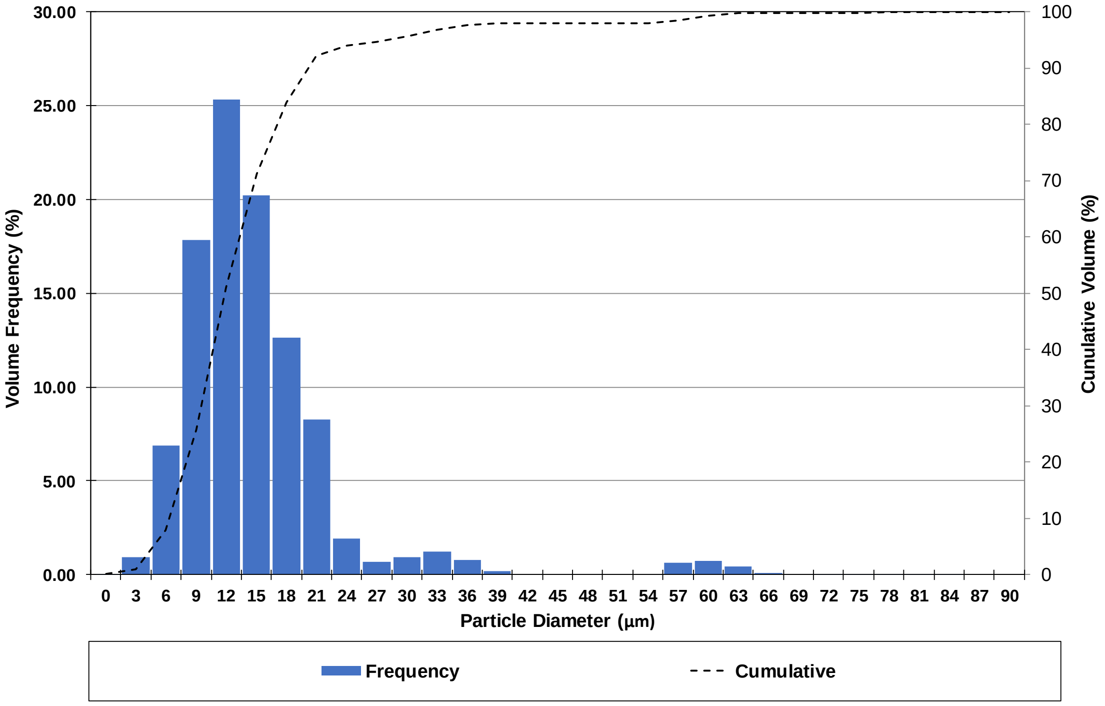


Figure 6.18 – (Right) Droplet Size Distribution at Sample Point 1 in 90° Bend

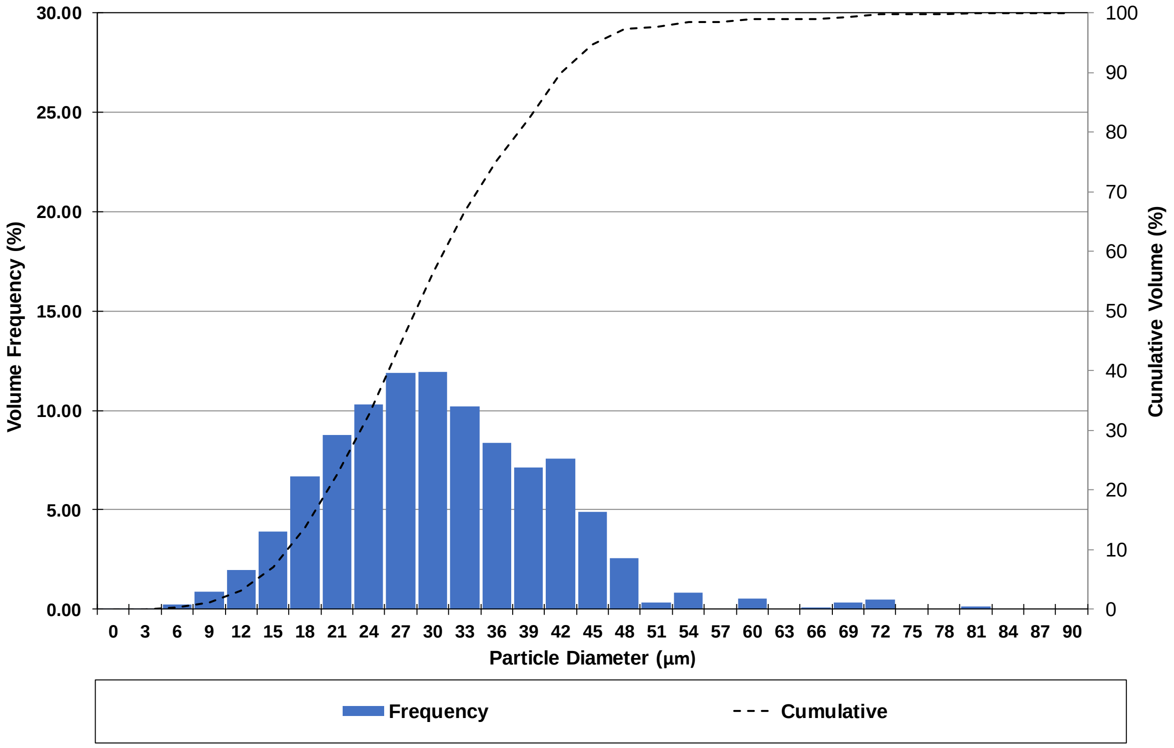


Figure 6.19 – (Middle) Droplet Size Distribution at Sample Point 1 in 90° Bend

As shown in Figure 6.17, Figure 6.18 and Figure 6.19 the droplet size distribution varies across the pipe for the 90° bend. In comparison to the T-piece, where the droplet size is more uniform as further demonstrated in the DV50 measurement shown in Table 6.2.

Table 6.2 – Droplet size DV50 for Sample Point 1

	Left	**Middle**	**Right**
90° Bend	47.2 µm	30.5 µm	14.4 µm
T-piece	27.9 µm	29.5 µm	28.3 µm

6.2.4 Horizontal vs. Vertical Orientation

Throughout industry, it is common practice to always collect samples in the vertical orientation with the fluid flowing upwards to reduce the gravitational effect on the target fluid. The effect of horizontal versus vertical orientations has been studied previously for flow pattern mapping of multiphase flows. Thus by undertaking this method, it is expected that stratified flow regimes are avoided, leading to better sampling results. To prove this theory, a small set of experiments are also carried out to determine the effect of horizontal vs. vertical sampling, and the magnitude on oil-in-water sampling. Depending on the specific installation, sometimes it is not possible for samples to be collected in the most optimal location and therefore effects such as this can play a large role in the overall representativeness of the samples.

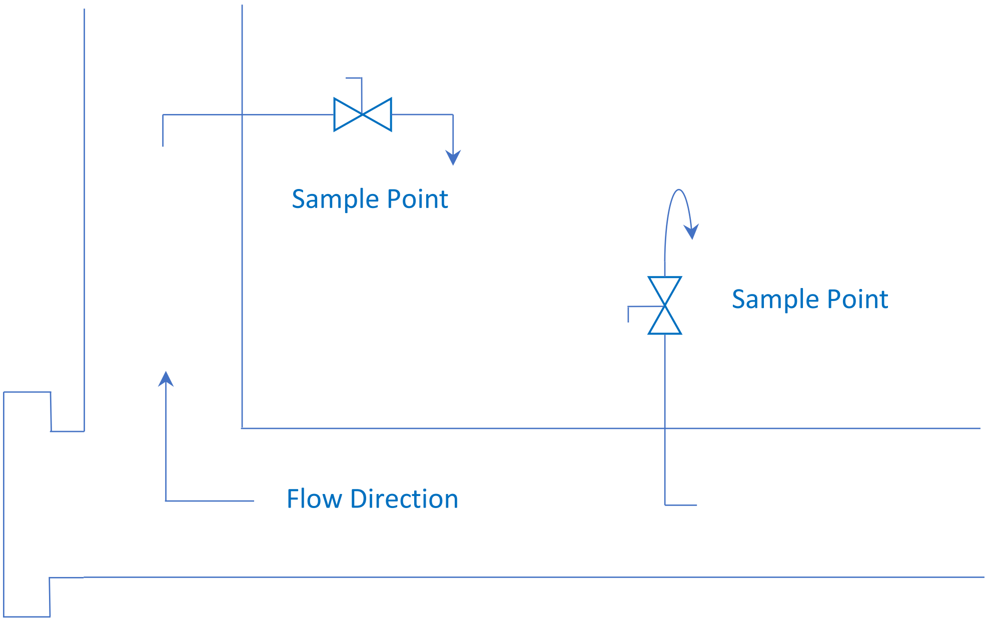


Figure 6.20 – Horizontal vs. Vertical Sample Point Schematic

The sample probe installed in the horizontal pipe was traversed through different vertical positions in the pipe as shown in Figure 6.21. The sample probe on the vertical section remained stationary positioned in the centre of the pipe which was used as the reference.

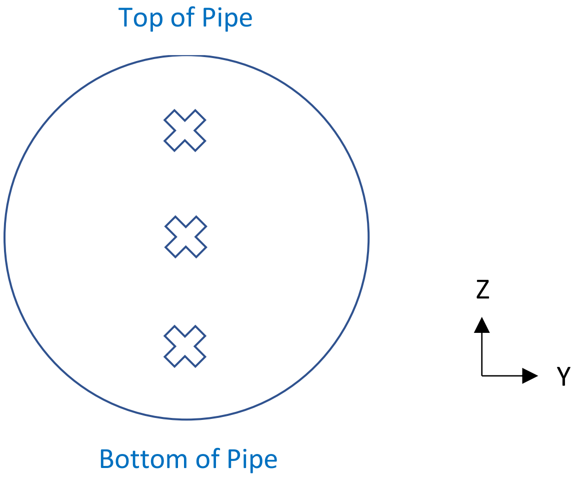


Figure 6.21 – Sample Point Locations Across Horizontal Pipe Section

For each sample position, three samples were collected and analysed using the infrared based reference methodology. The results are shown, with a target oil-in-water concentration of 10 to 100 mg/L.

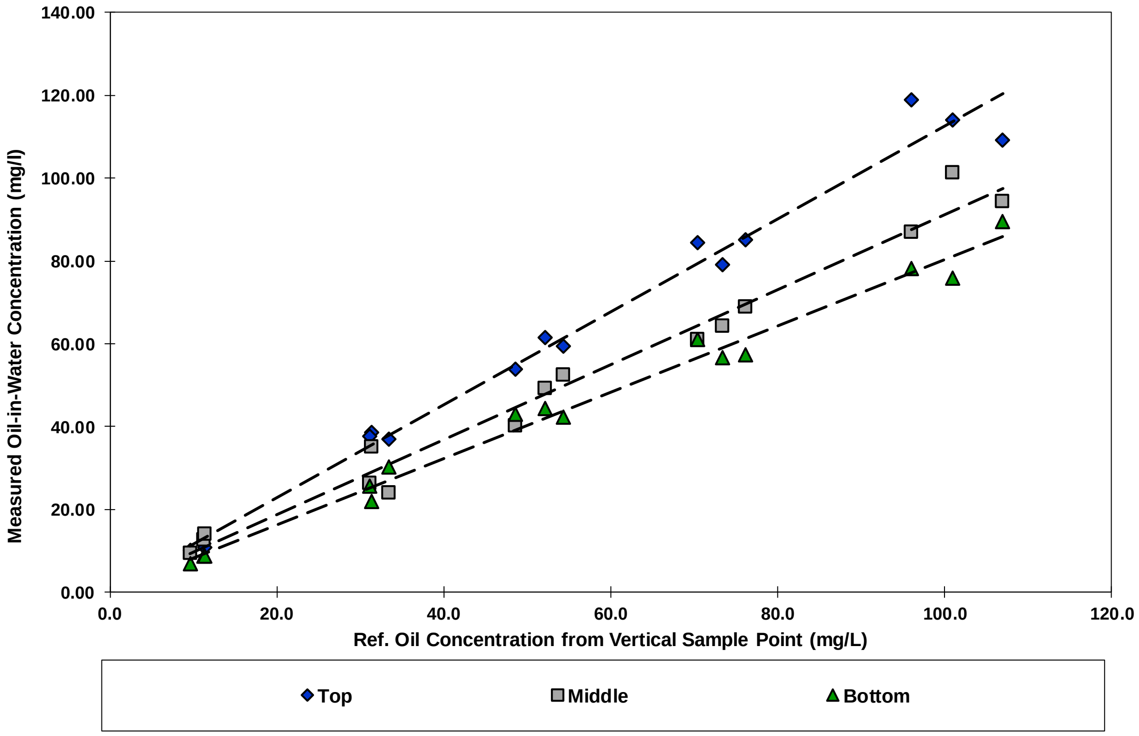


Figure 6.22 – Vertical vs. Horizontal Sample Collection [10 to 100mg/L, 3 m/s, 20°C]

A noticeable decrease in oil-in-water concentration is measured from the top to the bottom of the horizontal pipe. This decrease is expected due to stratification occurring due to the density different of the crude oil and water. Typically, multiphase flow measurements have required vertical installation to remove the challenges associated with horizontal flow patterns. To quantify the effect of horizontal in comparison to vertical installations, the data from Figure 6.22 can be shown as a percentage deviation of the horizontal samples vs. the ideal vertical position. This is shown in Figure 6.23.

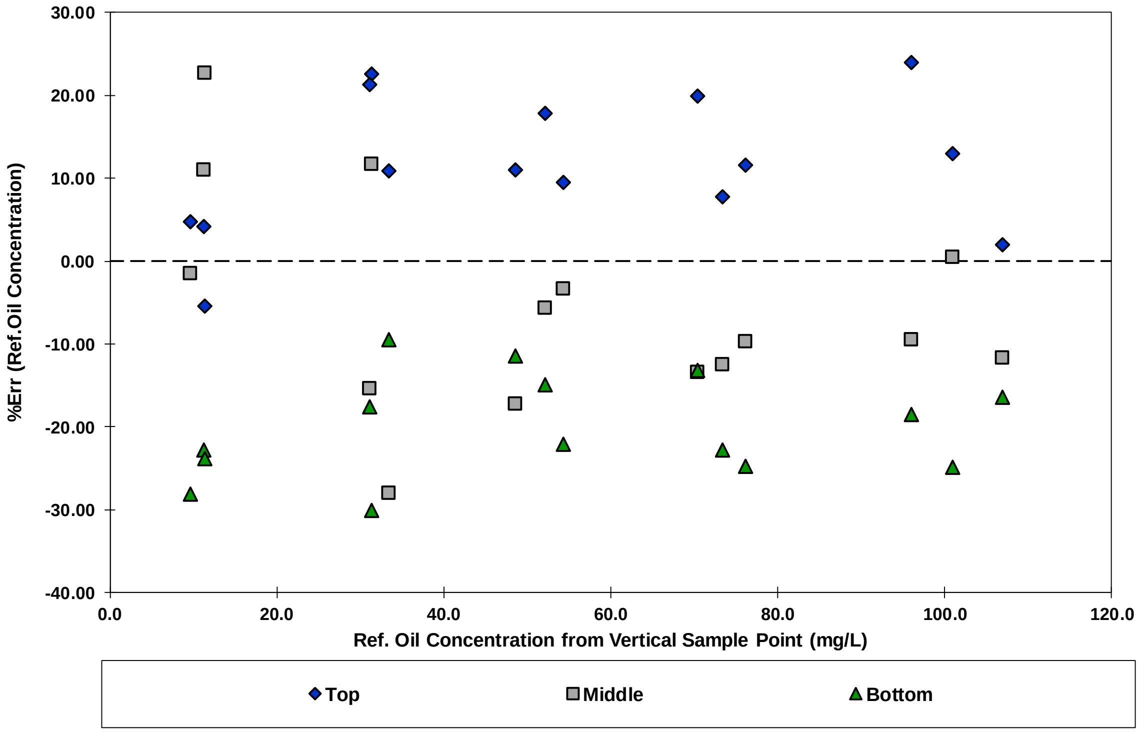


Figure 6.23 – Vertical vs. Horizontal Sample Collection (Percentage Deviation)

As shown in the figure, the top sample point in the horizontal section leads to an average over measurement of +11.6% in comparison to the vertical measurement. As the sample point is moved lower to the middle and bottom, a decrease is noted instead. An average error of -5.5% and -20.1% is seen for the middle and bottom point respectively.

This experiment demonstrates that the current method of vertical sampling to reduce errors associated with stratification can reduce errors by ±20%. Often however, installation limitations may reduce optimal sample locations and therefore consideration to this effect needs be accounted for.

6.2.5 Droplet Size and Distribution

A series of experiments of varying droplet size distributions was also undertaken. The purpose of this investigation was to determine the effect of droplet size on sampling representativeness. Theoretically, the smaller the average droplets size by volume, the more homogenous the overall mixture, therefore leading to better sampling conditions. As droplet size increases, there is a larger variance expected due to the smaller number of larger droplets to create the same oil-in-water concentration.

To undertake this study, a target concentration of 30 mg/L was set in the produced water facility. Oil droplet size was then controlled to seven different droplet sizes between 5 and 100 µm, using the jet mixing system described in Chapter 3. For each droplet size condition, five samples were collected and analysed using the infrared based reference methodology.

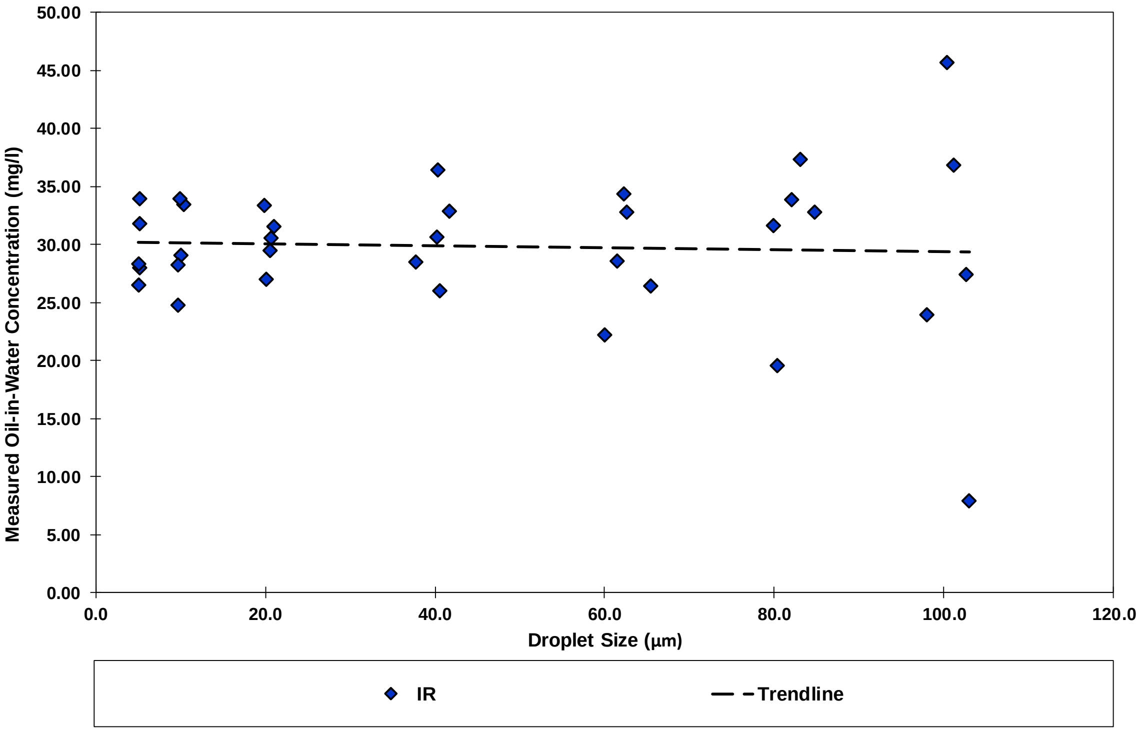


Figure 6.24 – Effect of Droplet Size on Sample Measurement [30mg/L, 3 m/s, 20°C]

The results shown in Figure 6.24 show a trend between increasing droplet size and the scatter of results. This increased scatter of measurements is expected as with higher droplet sizes, the chance of getting a representative single sample is reduced. Overall however, the results show that the mean concentration at each droplet size remains consistent, meaning that at higher droplet size conditions, more samples are required to get a representative mean measurement. This can be demonstrated by looking at the increase of standard deviation at increased droplet sizes, as demonstrated in Table 6.3.

Table 6.3 – Effect of Droplet Size Standard Deviation Results

Target Droplet Size (μm)	Mean Droplet Size (μm)	Standard Deviation (mg/l)
5	5.1	2.7
10	9.9	3.4
20	20.4	2.1
40	40.1	3.6
60	62.3	4.4
80	82.0	6.0
100	101.0	12.7

An aspect of the droplet size parameter that has not been taken into consideration however is the droplet size distribution. In the creation of the test conditions in Figure 6.24, care was taken to ensure that all the droplet sizes were of similar normal distributions. An example droplet size distribution for the previous test condition of 42.1μm is shown in Figure 6.25.

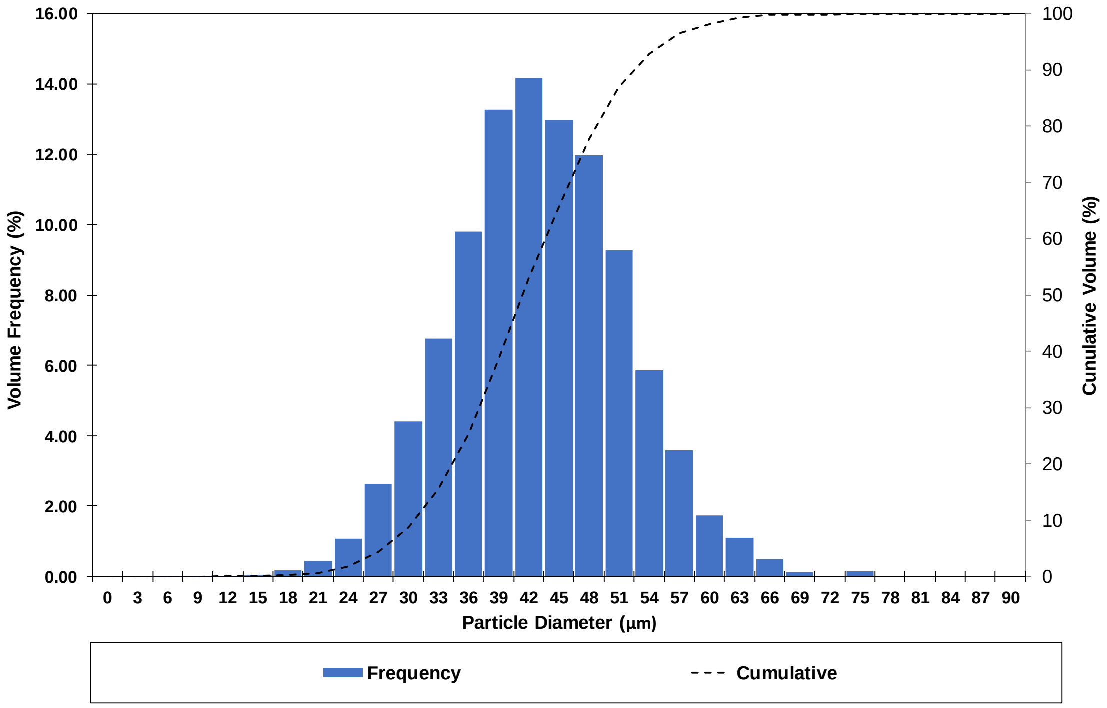


Figure 6.25 – Example Oil Droplet Size Distribution [30mg/l, 42.1μm]

To determine if the distribution of droplet size influences the measurement from sampling, another experiment was conducted. With an oil-in-water concentration of 50 mg/l, four different droplet size distributions were created, all with a target droplet size DV50 of 35μm. This was achieved by varying the jet mixing and mixing tank speeds as described in Chapter 3. By undertaking this test, the results would show whether different droplet size distributions with the same average droplet size can affect the representativeness of sampling. At each droplet size distribution, five samples were collected and analysed.

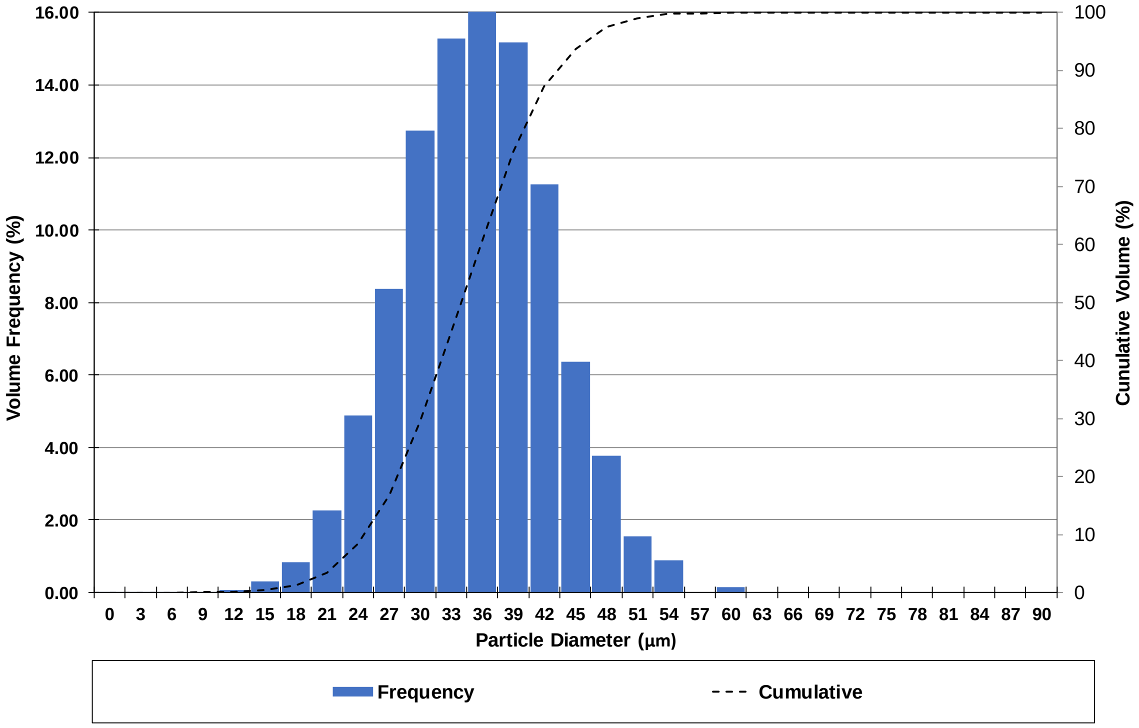


Figure 6.26 – (a) Different Droplet Size Distributions [50mg/l, 35µm]

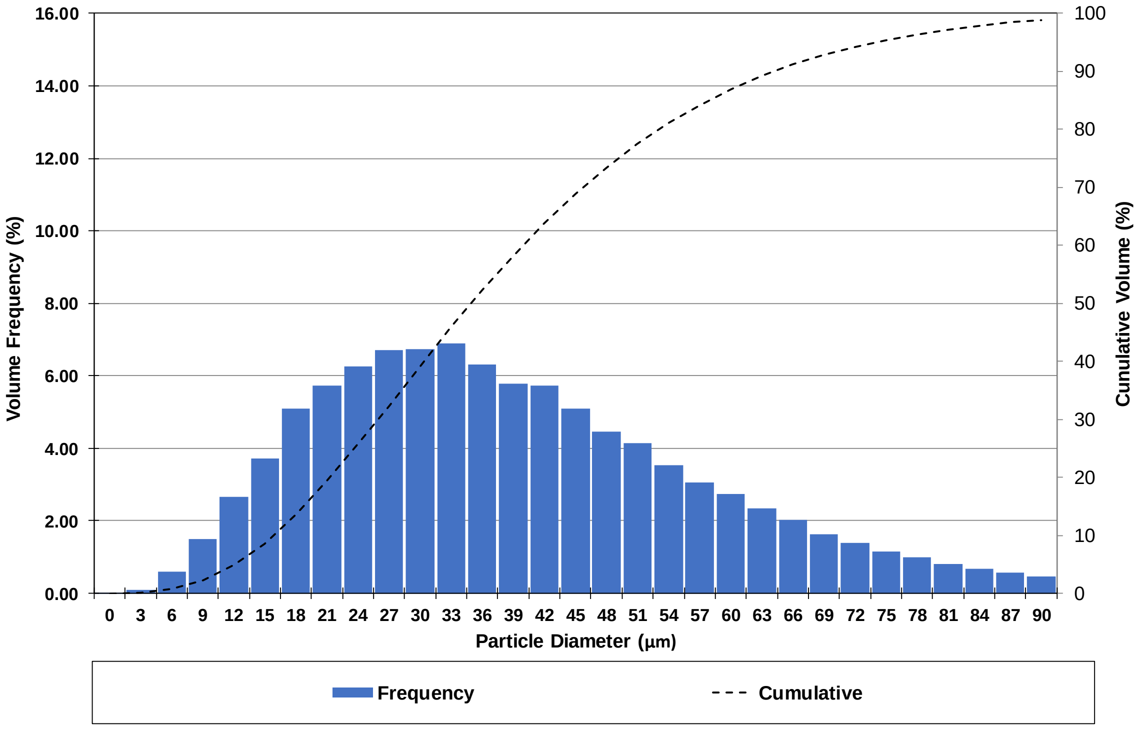


Figure 6.27 – (b) Different Droplet Size Distributions [50mg/l, 35µm]

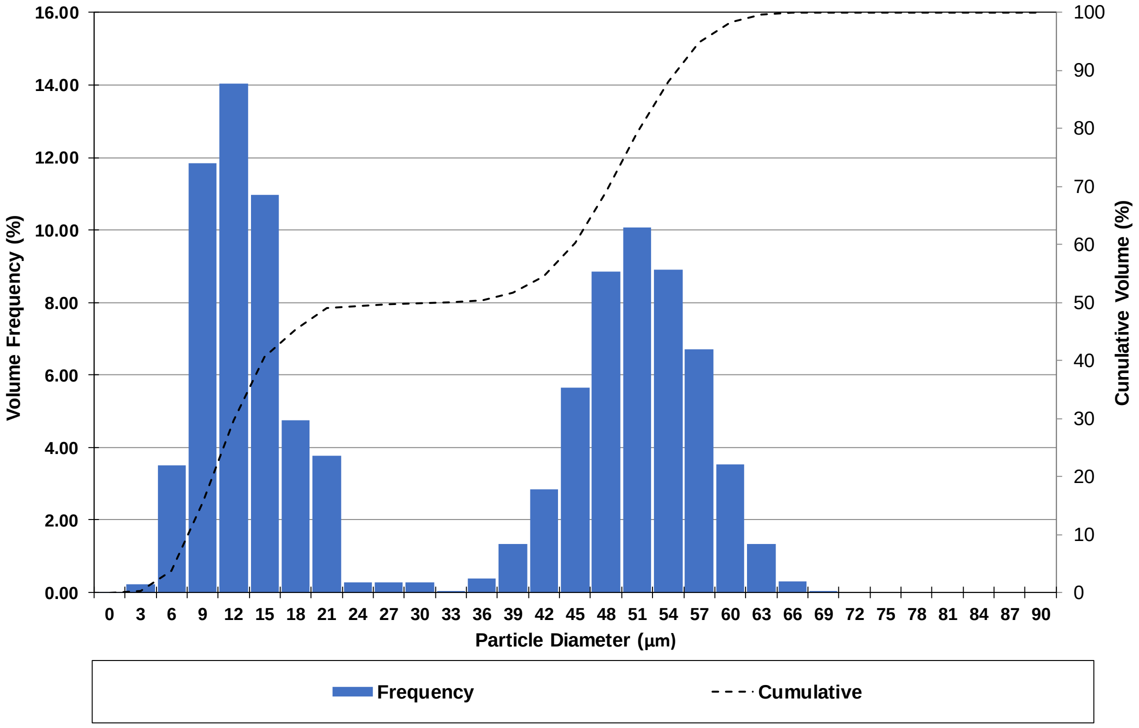


Figure 6.28 – (c) Different Droplet Size Distributions [50mg/l, 35µm]

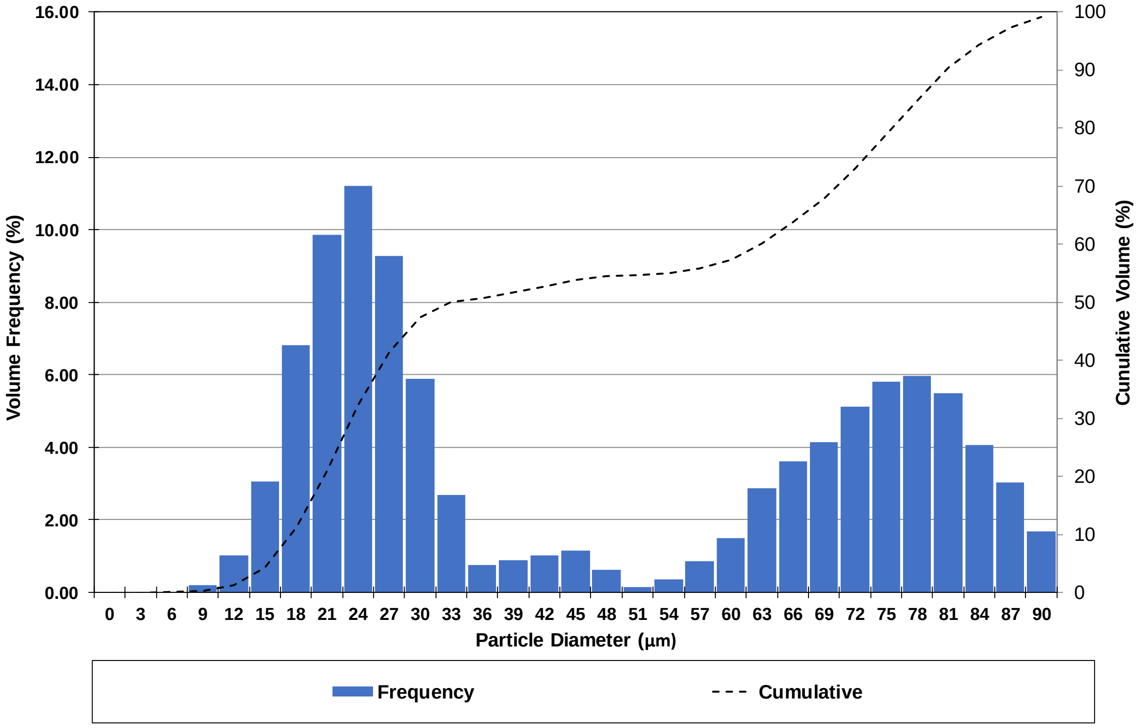


Figure 6.29 – (d) Different Droplet Size Distributions [50mg/l, 35µm]

The results for each of the droplet size distributions is shown in Figure 6.30.

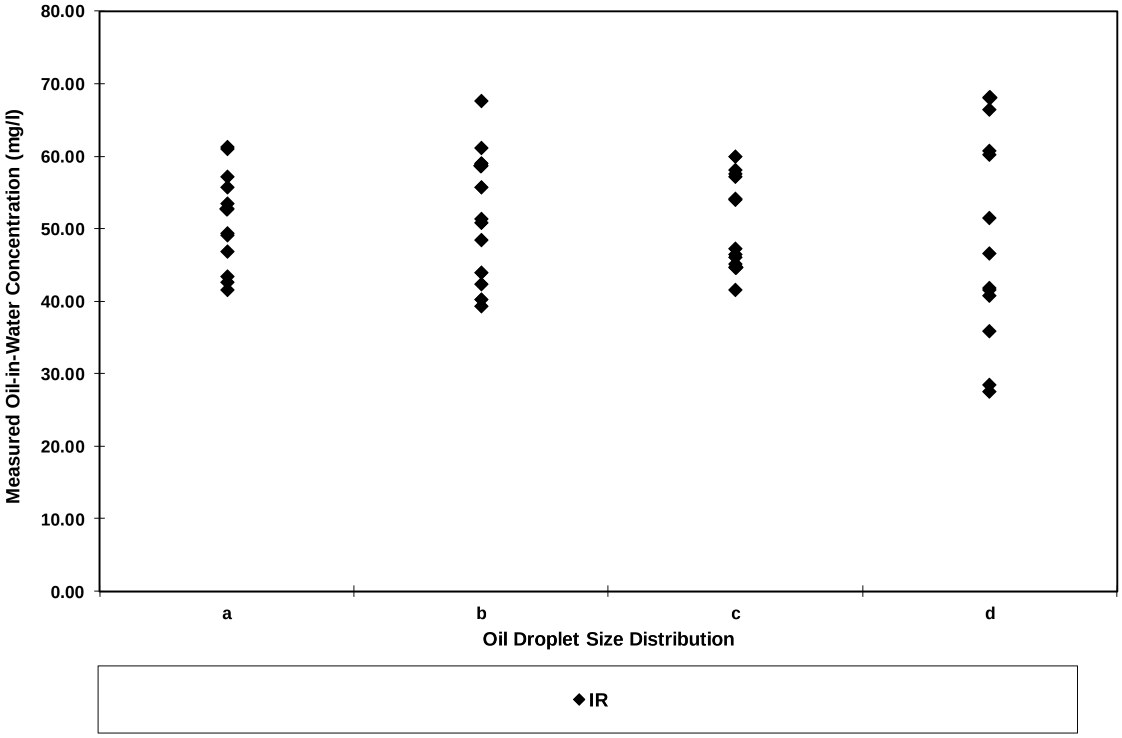


Figure 6.30 – Effect of Droplet Size Distribution [50mg/l, 35µm]

Using Figure 6.26 (a) as the ideal distribution, several comparisons can be made between the different droplet size distributions. The distribution in Figure 6.27 (b) has a left skew profile with a portion of droplets larger than 60µm which is not seen in Figure 6.28 (c). Due to the percentage of higher droplets, like what was measured in previous section in Figure 6.24, a larger scatter of results is noted. A similar effect is seen in Figure 6.29 (d) which has a larger left skew leading to an increased scatter. An opposite trend is demonstrated in Figure 6.28 (c), as a larger portion of the oil droplets are less than 20µm.

The results show that even at a single DV50 droplet size, the distribution of droplets can increase the scatter of measurements, as shown in Figure 6.30, like what is seen with an increase of droplet size. A variation of ±21mg/l scatter is noted throughout all four droplet distributions. This means that an increased number of samples are required to ensure the mean oil-in-water concertation measurement remains correct.

6.2.6 Main Line Flowrate

To investigate the effect of main line velocity on sampling, five conditions were set-up at velocities of 1, 2, 3, 4 and 5 m/s. Unlike the sample point velocity tests discussed previously, all samples were collected under isokinetic conditions. The purpose of this test is to determine if samples are affected by the main line velocity they are trying to capture. With the samples being collected in isokinetic conditions, it is expected that no effect is seen, however other forces may come into effect.

For each main line velocity, 12 samples were collected and analysed using the infrared based reference methodology. The droplet size throughout these tests were controlled to a target DV50 of 20µm.

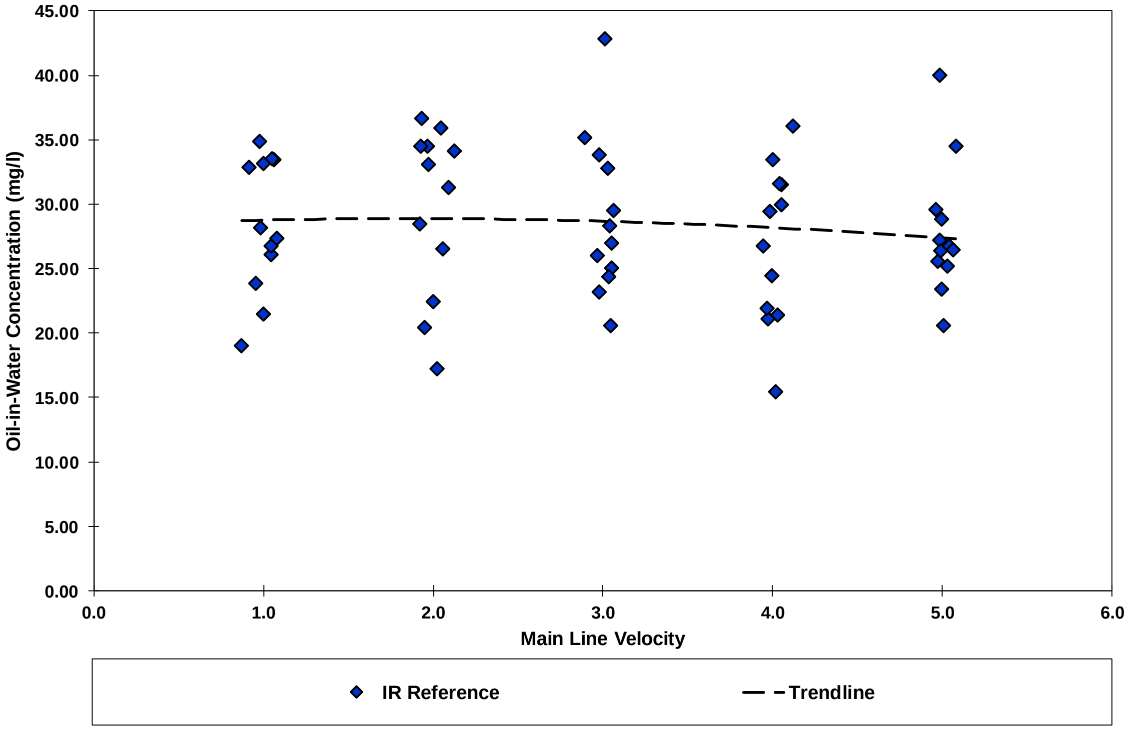


Figure 6.31 – Effect of Main Line Velocity on Sample Measurement on Oil-in-Water Concentration [30 mg/L, 1 to 5 m/s, 20°C]

The results shown in Figure 6.31 demonstrate that changing main line velocity does not affect the oil-in-water concentration measurement whilst maintaining isokinetic sampling throughout. This can be further demonstrated by analysing the standard deviation of the measured oil-in-water concentration at each main line velocity, as summarised in Table 6.4.

Table 6.4 – Effect of Main Line Velocity Standard Deviation Results

Target Main Line Velocity (m/s)	Mean Main Line Velocity (m/s)	Standard Deviation (mg/l)
1	0.99	5.0
2	2.02	6.2
3	3.06	5.9
4	4.01	5.8
5	5.04	4.8

No trend is noticed from increasing main line velocity from 1 to 5 m/s on the standard deviation of results. This result is expected as maintaining isokinetic sampling ensures the velocity profile between the main line fluid and the sample port remains constant at each velocity change.

6.2.7 Oil Concentration

To build upon the work undertaken in the initial experiment section, several different oil concentrations are trialled. As seen in the initial results, as oil concentration increases, the uncertainty decreases, however this is only shown for a small range of concentrations. To determine if this effect continues, a large range of concentrations is investigated. The concentrations to be included range from 5 to 100 mg/l, the typical range of oil-in-water concentrations that are seen in produced water. Even though the discharge limits are typically in the region of 30 mg/l, concentrations up to 100 mg/l can often be noted in certain situations.

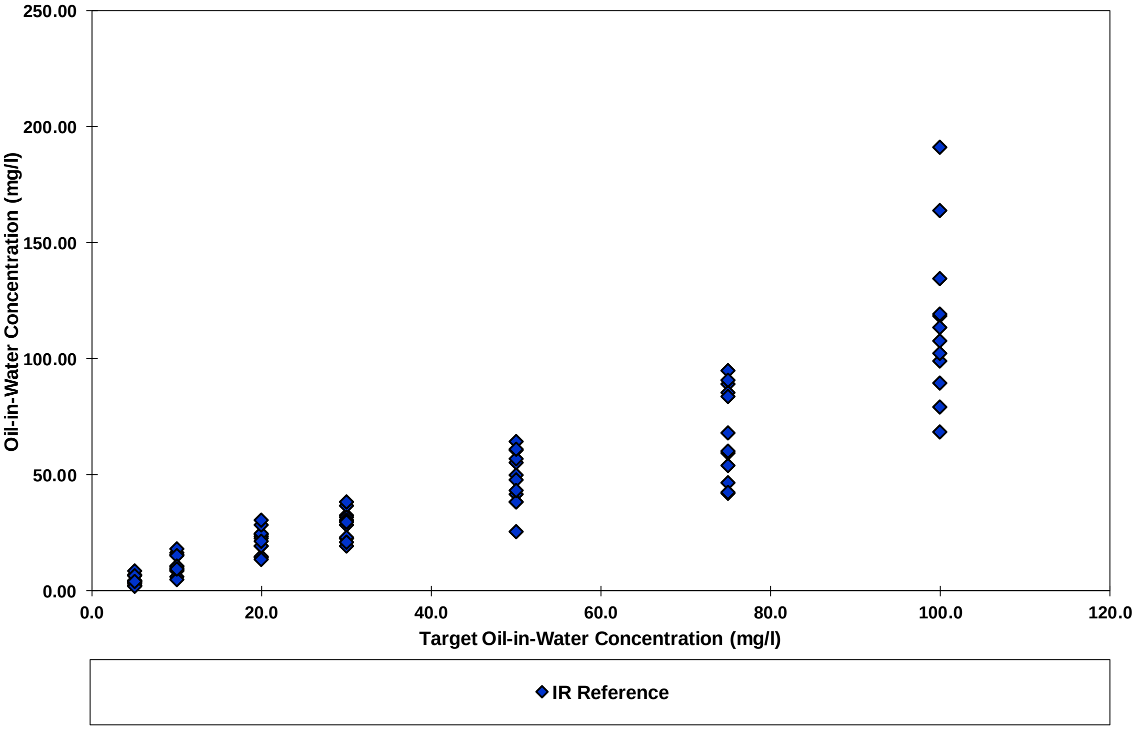


Figure 6.32 – Effect of Oil Concentration on Total Uncertainty of Oil-in-Water Concentration [3 m/s, 20°C, 0 to 100 mg/L]

The results from Figure 6.32 are tabulated to show uncertainty information as shown in Table 6.5. Increasing oil-in-water concentration from 5 mg/l to 30 mg/l leads to an overall decrease of uncertainty, from ±85.81% to ±45.13% at a 95% confidence interval. It should be noted that larger uncertainties are expected at lower concentrations due to the proportional difference that a small variation has, for example, the ±85.81% expanded uncertainty at 4.40 mg/l is only a standard deviation of ±1.93 mg/l. A slight increase in uncertainty of 3.1% is seen increasing oil-in-water concentration from 30 to 50 mg/l, however this is expected to be down to natural variation in the sampling results.

Table 6.5 – Effect of Oil Concentration Tabulated Results

Target Concentration (mg/l)	Mean Concentration (mg/l)	Standard Deviation (mg/l)	Expanded Uncertainty at 95% Confidence (%)
5	4.40	1.93	±85.81
10	11.14	4.01	±70.49
20	21.42	5.17	±47.28
30	28.05	6.02	±42.03
50	48.58	11.19	±45.13
75	68.06	19.09	±54.98
100	115.66	33.11	±56.10

Increasing the oil-in-water concentration further to 75 and 100 mg/l, an overall increase is uncertainty is demonstrated to ±56.10% at a 95% confidence interval. This is thought to be due to the calibration methodology of the infrared reference method. As shown in Chapter 3, the infrared technique is calibrated up to 60 mg/l using stock samples. Due to this upper range, any oil-in-water concentration measurements above 60 mg/l require an additional dilution step after extraction prior to measurement. This additional step is thought to add to the uncertainty of the method, leading to this increased measurement uncertainty.

6.3 Uncertainty Associated with Online Techniques

The importance of knowing the uncertainty associated with an online oil-in-water technique cannot be understated. At present, the only way to use an online technique is to correlate the device with an approved reference method. As demonstrated in the previous section, the uncertainty of the reference techniques can be estimated, and are mostly above ±40% uncertainty at a 95% confidence interval with the inclusion of sampling. Due to these high uncertainties, requiring the online techniques to be correlated to reference methods can pose significant issues. To overcome this challenge, this section discusses the possibilities of creating a correlation without the requirement of being related to a reference method.

6.3.1 Correlation Methodology

Oil-in-water concentration is a method defined parameter, as discussed in Chapter 2. This means that typically, the true oil-in-water concentration value is based upon the method used to measure the concentration. Due to this, continuous online methods have been required to be correlated to a specific reference method before use. As previously discussed, the current reference techniques have high levels of uncertainty associated with their method and therefore, correlating to the reference method can significantly impact on the achieved correlation.

To overcome this, a method is proposed to correlate online techniques to a dosage based system rather than the conventional reference method. As described in Chapter 2, current reference methods are calibrated using standard samples, created by measuring out a volume of water which has been spiked with a specific mass of crude oil. By varying the oil injected, different known concentrations are created and therefore can be used to calibrate the reference device. The method proposed to correlate online techniques uses a similar method to this, however instead of correlating the online technique to the reference method, correlating the technique directly to a standard sample. Unlike the reference methods however, online techniques require a bulk fluid flow.

The concept of the method uses the produced water facility, by knowing the volume of water in the facility, a known quantity of oil can be added to create a flow stream with known oil-in-water concentration. Using the commissioning experience in Chapter 3, it can be assumed that all the injected oil mixes with the water, essentially creating a standard flow condition. Using this technique, an online device can be correlated directly to an oil-in-water concentration without the requirement of a reference method with sampling.

To demonstrate this method, an experimental study was set-up to replicate both methods; the current procedure of correlating to a reference method and the proposed method described. To carry out this experiment, the initial calibration was completed using the method described in the Chapter 2, following the UK guidelines (OSPAR, 2011). Figure 6.33 shows the results of the completed calibration between the LIF device and the infrared reference method.

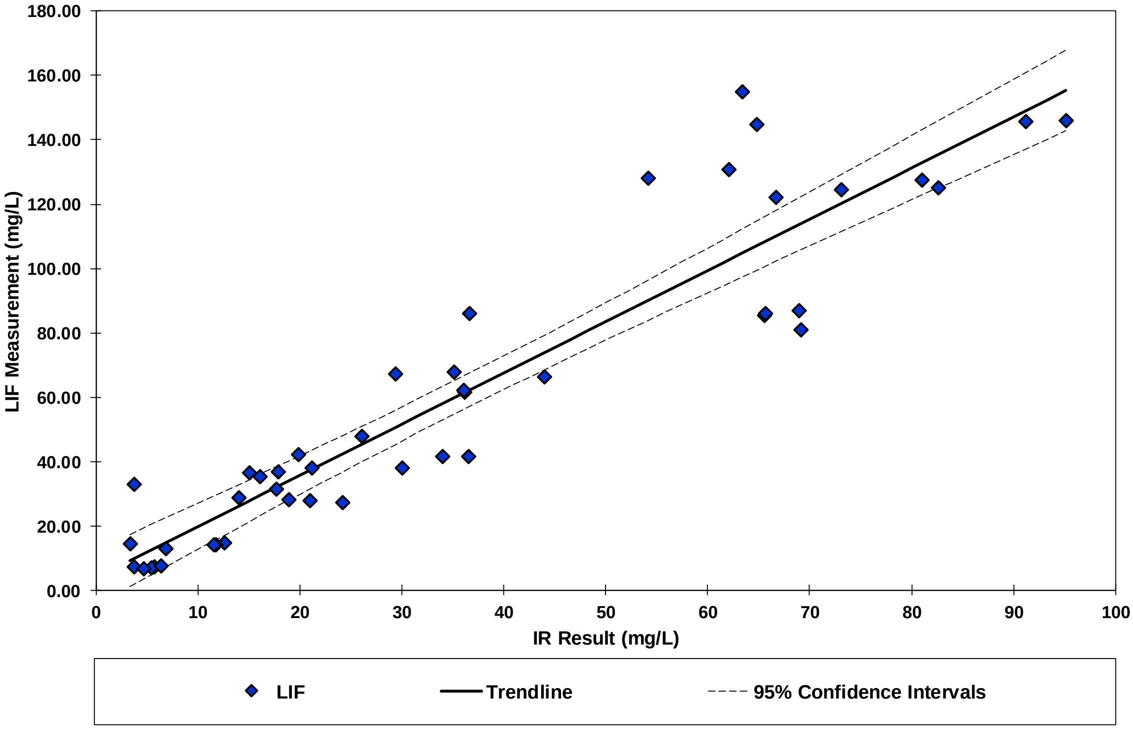


Figure 6.33 – LIF and IR Calibration [3 m/s, 20°C, 0 to 100 mg/L]

A similar calibration was also undertaken using the true value of the oil-in-water concentration determined by dosage ratio. Figure 6.34 shows the results of the calibration.

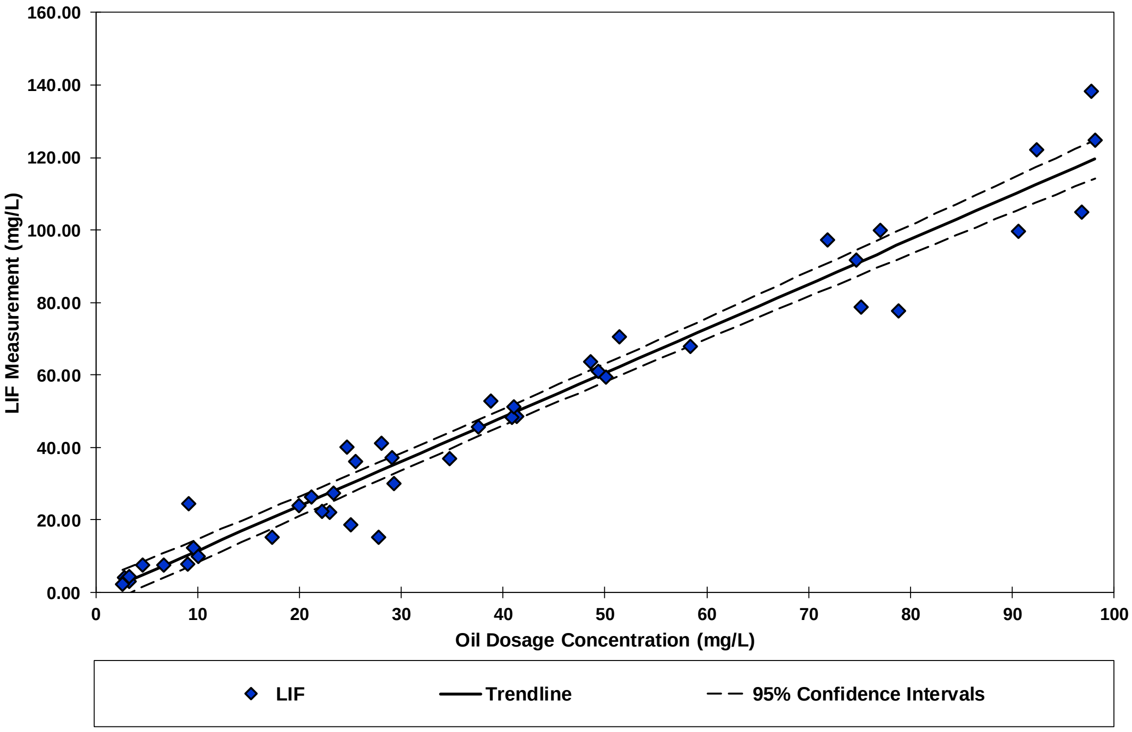


Figure 6.34 – LIF and Oil Dosing Method Calibration [3 m/s, 20°C, 0 to 100 mg/L]

In both cases, a straight line fits both sets of correlation data, however the coefficients of each correlation differ significantly. The 95% uncertainty bands around the IR correlation is much larger than the dosing correlation. As the initial calibration is extremely important to ensure the online instrument is set-up correctly prior to deployment, an incorrect correlation would skew results until a verification procedure was carried out. However, if the verification uses the same method as the initial correlation, then the verification may not remove the error, which is inherent in the approach.

To further demonstrate the methodology, another experiment was completed using the new calibration profiles. The trial was conducted using oil in water, ranging from 0 to 100 mg/l in steps of 10 mg/l. The facility was set-up using to the target concentration and then measured using the LIF instrument. The trial was repeated three times for each concentration. The test was initially carried out using the IR calibration shown in Figure 6.33 and then repeated for the dosing calibration shown in Figure 6.34.

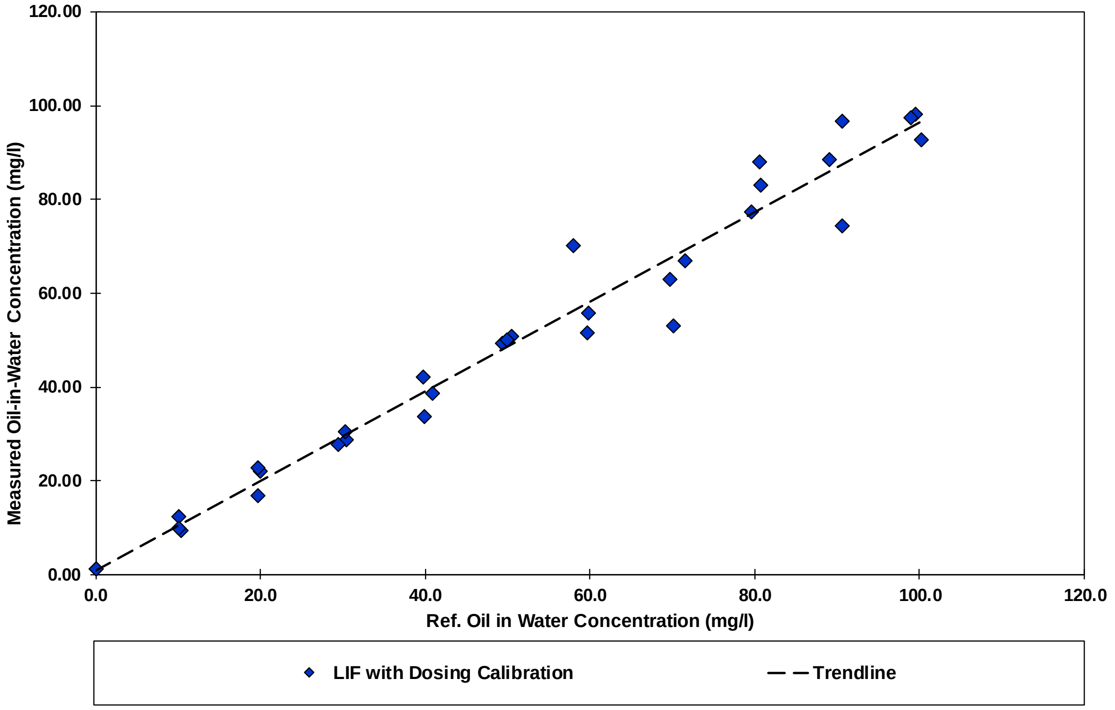


Figure 6.35 – LIF Trial using Dosing Calibration [3 m/s, 20°C, 0 to 100 mg/L]

The results can also be shown in percentage deviation from the reference value, in this case, the calculated dosing concentration.

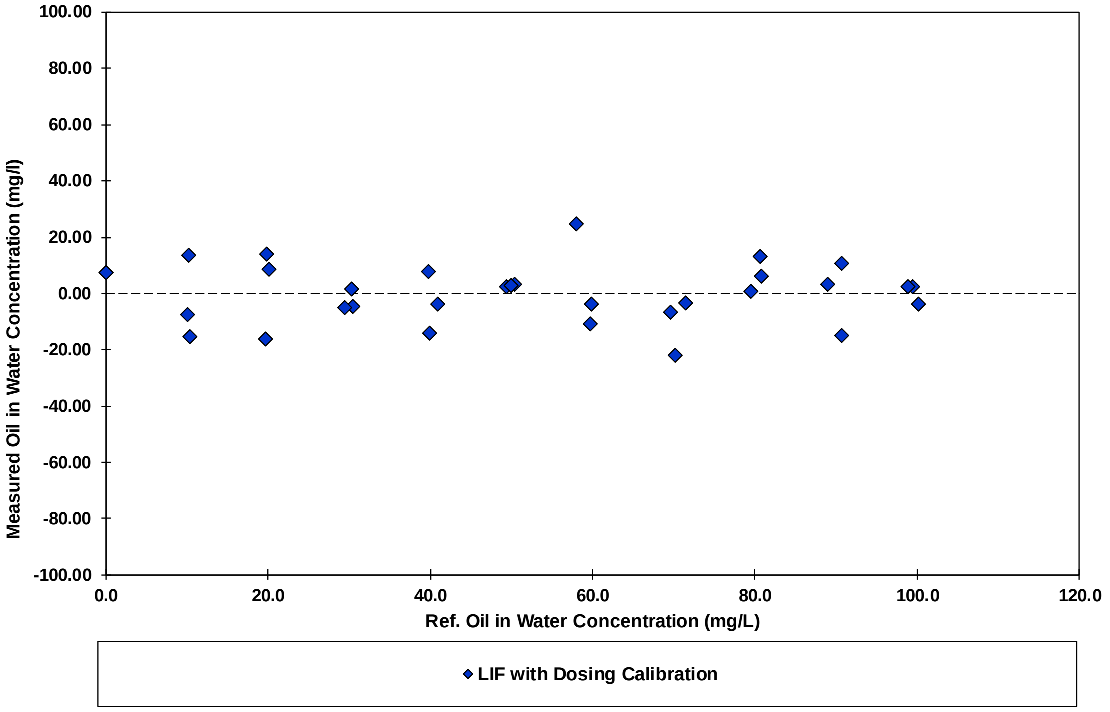


Figure 6.36 – LIF Trial using Dosing Calibration (Percentage Deviation)

The standard deviation of the dosing method was determined to be ±10.02% with an expanded uncertainty of ±19.64% at 95% confidence interval.

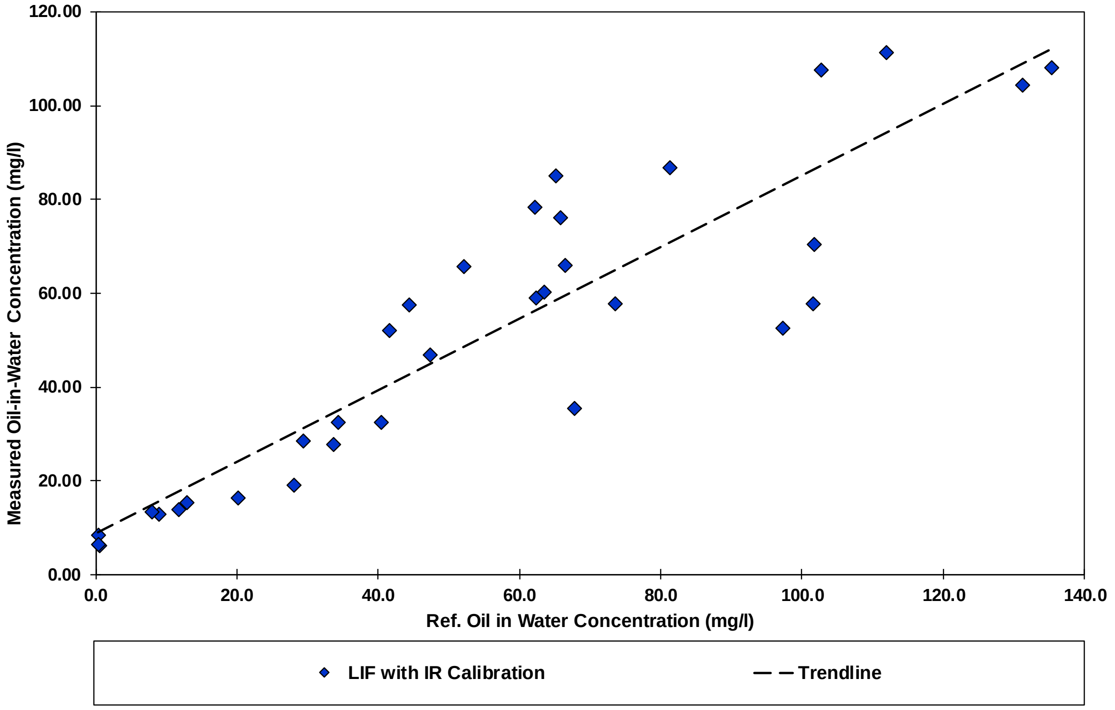


Figure 6.37 – LIF Trial using IR Calibration [3 m/s, 20°C, 0 to 100 mg/L]

The results can also be shown in percentage deviation from the reference method.

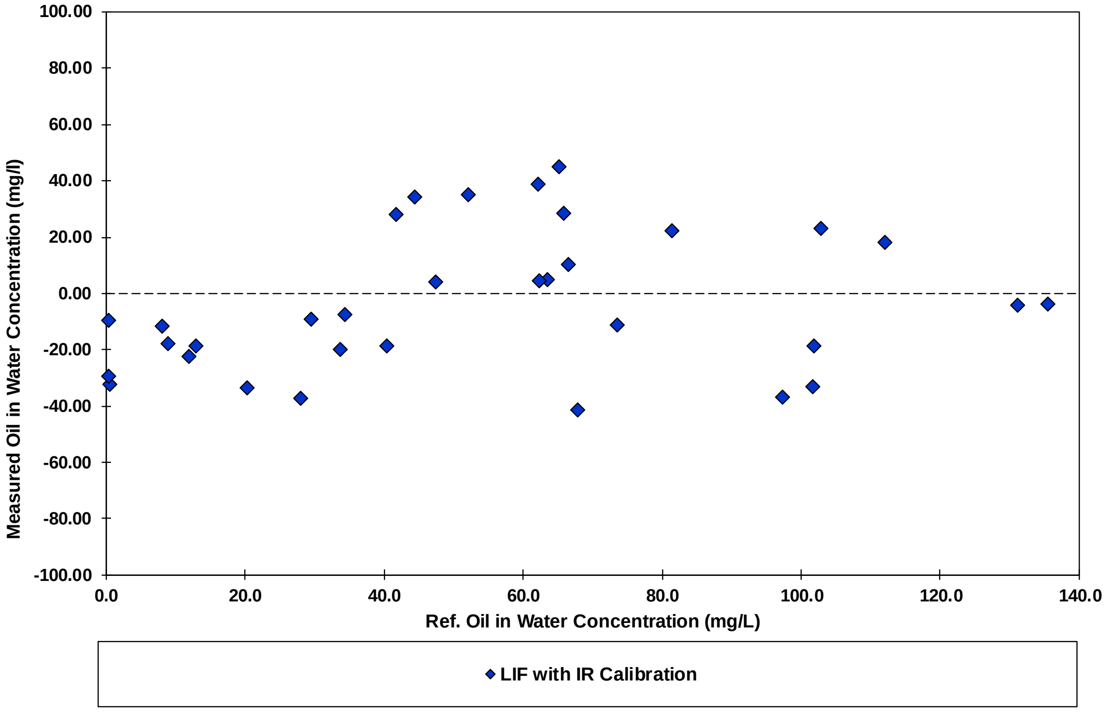


Figure 6.38 – LIF Trial using IR Calibration (Percentage Deviation)

The standard deviation of the IR method was determined to be ±24.63% with an expanded uncertainty of ±48.27% at 95% confidence interval.

As demonstrated, using the dosing method leads to a reduction in the uncertainty of the online method as the uncertainty of the reference method is negated. As discussed in previous chapter, the uncertainty of the IR method with sampling can be over ±50%, which can cause skewed results when calibrating and verifying an online technique.

6.4 Summary

All measurements have an uncertainty associated with it; there is no exception, including oil-in-water concentration measurements. For compliance monitoring, oil-in-water concentration is defined by a reference method, such as infrared absorption, GC-FID or gravimetric method. Measurement uncertainty can be estimated by first identifying the sources of uncertainties related to the measurement; making an estimate of uncertainties associated with each of the separate sources; and then combining the individual uncertainties into an overall uncertainty using a specially developed uncertainty calculation method. For oil-in-water concentration measurement, the main uncertainties are associated with sampling and the reference procedure. Sampling can potentially contribute more towards the overall uncertainty of an oil-in-water measurement compared to the procedure. For a standard oil-in-water measurement method, the uncertainty can be estimated from precision information which is often included in the method published. Literature shows that for a standard method, the repeatability standard deviation (or standard uncertainty), is often larger than ±10%.

The first part of this chapter aimed to answer the fourth research question:

- Can we determine the uncertainty of reference techniques typically used to measure oil-in-water concentration? In addition, can we predict the impact of uncertainty due to sampling? If so, what sampling parameters have the largest contribution?

To fill this gap in knowledge, a series of experimental research was undertaken to build upon the initial experimental research. By calculating the total uncertainty of the oil-in-water measurement from sampling to final laboratory measurement, and using the previously determined uncertainty information, the contribution of uncertainty associated with sampling on the overall measurement can be determined. Varying individual key sampling methodology parameters, the individual impacts on sampling uncertainty can be determined.

The results of the experimental work show an uncertainty of ±19.29% at a 95% confidence interval for the infrared oil-in-water reference method alone, and an overall uncertainty of ±52.1% at a 95% confidence interval with the inclusion of sampling. This uncertainty of oil-in-water measurement can have several practical implications. These may include compliance monitoring, testing and assessing the performance of alternative oil-in-water measurement methods, including online monitors, as well as accepting such methods for the purposes of discharge reporting.

Several experiments were also conducted to determine the impact of various parameters on the overall uncertainty of offline oil-in-water concentration measurement due to sampling. The main outputs of these experiments are shown in Table 6.6.

Table 6.6 – Summary of Sampling Uncertainty Results

Test Parameter	Results Summary
Sample Point Velocity	Results demonstrate that isokinetic sampling leads to the closest to the reference oil-in-water concentration. Sub-isokinetic leads to a reduced measurement of -30% and super-isokinetic leads to an overmeasurement of up to 10% in comparison to the isokinetic condition.
Installation Effect	At 5D downstream of the 90° bend, an oil-in-water concentration deviation of greater than 30mg/l is seen between the left and right sample positions. In comparison, the results from the t-piece shows no differences.
Horizontal vs. Vertical Orientation	In comparison to the vertical sample point, the results from the three horizontal sections vary with an average deviation of ±20% depending on which location used.
Droplet Size Distribution	Increasing the average droplet size from 5 to 80µm leads to a significant increase in standard deviation of results, with a ±25mg/l scatter noted at the highest droplet size. A similar result is seen whilst maintain the average droplet size but altering the droplet size distribution.
Main Line Velocity	No effect is noted varying the main line velocity from 0.5 to 5 m/s whilst maintain isokinetic sampling. Standard deviations remain consistent throughout velocity range.
Oil Concentration	Varying the oil concentration from 5 to 30 mg/l leads to a reduction of uncertainty from ±85.81% to ±45.13%. Further increase to 100 mg/l increases the uncertainty to ±56.10%.

From the summary of results from the research work completed, a best practice of sampling can be determined to minimise uncertainties. Capturing a representative oil-in-water sample should be carried out in the vertical orientation with upward directional flow, using a T-piece upstream to promote mixing and a minimum of 5 diameter upstream straight pipework prior to the sample point. Oil droplet size should be minimised by enhanced mixing, whilst not skewing droplet size distribution. Main line velocity has little effect, however critically, samples should be captured under isokinetic conditions.

The last part of the chapter aimed to answer the fifth research question:

- Can online techniques be used for produced water regulatory compliance monitoring? What methods of correlation are required to demonstrate this ability?

Oil-in-water concentration is a method defined parameter, as discussed in Chapter 2 in the literature review. This means that typically, the true oil-in-water concentration value is based upon the method used to measure the concentration. Due to this, continuous online methods have typically been correlated to a specific reference method before use, which can lead a range of issues. To overcome this, a method is proposed to correlate online techniques to a dosage based system rather than the conventional reference method.

To demonstrate the methodology, another experiment was completed using the new calibration profiles. The trial was conducted using oil in water, ranging from 0 to 100 mg/l in steps of 10 mg/l. The facility was set-up using the dosage method, and then measured using the LIF instrument. The trial was repeated three times for each concentration. The standard deviation of the dosing method was determined to be ±10.02% with an expanded uncertainty of ±19.64% at 95% confidence interval. The standard deviation of the IR method was determined to be ±24.63% with an expanded uncertainty of ±48.27% at 95% confidence interval.

The uncertainties determined during this trial show the advantages of online techniques over the current reference methods, with a significant reduction in uncertainty. It should be noted however that these experiments were carried out under ideal conditions and therefore as described previously in Chapter 4, certain parameters can affect the measurement of online measurements and need to also be considered.

7 Conclusions

This chapter will be used to give final discussion and conclusions on the research work undertaken.

7.1 Research Questions

This thesis aims to explore the use of online techniques for regulatory compliance monitoring of produced water, where current practice decrees only offline laboratory techniques suitable. This overall research goal is broken down into five research questions:

1. Can we simulate stable produced water conditions in an experimental facility? Can the droplet size be controlled to be within specified diameter ranges?
2. What techniques are available that can detect oil-in-water at concentrations below 30 mg/L? In addition, can the impact of typical parameters found in produced water applications be quantified for individual techniques?
3. Can improvements be made to current online techniques or methods, to improve performance of measuring oil-in-water concentration?
4. Can we determine the uncertainty of reference techniques typically used to measurement oil-in-water concentration? In addition, can we predict the impact of uncertainty due to sampling? If so, what sampling parameters have the largest contribution?
5. Can online techniques be used for produced water regulatory compliance monitoring? What methods of correlation are required to demonstrate this ability?

7.1.1 Can we simulate stable produced water conditions in an experimental facility? Can the droplet size be controlled to be within specified diameter ranges?

To be able to demonstrate that an online technique is capable of measuring oil-in-water concentration, a series of experimental trials has been completed. To undertake these experiments, a suitable test facility is required. This chapter aimed to solve this challenge by answering the first research question of the thesis. The research question can be split into two sections, with the first being the ability to simulate stable and realistic produced water conditions in a full-scale experimental facility and the second part being if the droplet size be controlled.

The development of a produced water facility demonstrated effective simulation of stable produced water conditions with controllable droplet size, thus successfully answering the research question posed. This development allows the experimental work required to answer the remaining research questions, to be undertaken. To summarise the key aspects of the design of the test facility, the facility can be broken down into three main parts; the jet mixing system, the test section and the holding tanks.

Table 7.1 summarises the range of specifications that were achieved in the produced water facility during commissioning.

Table 7.1 – NEL's Produced Water Facility Specifications

Oil concentration	0 – 5000 mg/l
Oil Droplet size	5 – 110 µm
Solid concentration	0 – 1000 mg/l
Solid particle size	0 – 130 µm
Process temperature	15 – 80 °C
Flow velocity	0.5 – 7 m/s

There are several test facilities across the world that claim to be able to achieve the conditions, however most of these facilities are in-house facilities for internal research and development with very little or no publications or access allowed. The design of a new facility capable of simulating produced water conditions, allows research, development and evaluation of oil-in-water measurement techniques to be undertaken. As the facility was designed in a recirculation-based design, it allows enhanced stability compared to other typical once-through system, as the same fluid recirculates leading to higher repeatability.

7.1.2 What techniques are available that can detect oil-in-water at concentrations below 30 mg/L? In addition, can the impact of typical parameters found in produced water applications be quantified for individual techniques?

As a significant amount of research exploring continuous measurement techniques for oil-in-water concentration has not been completed, there is very little data in the public domain in this area. However, it is known from previous work in this field that certain parameters found in produced water streams can affect the measurement performance of the online methods. Part of the research in this thesis investigated key parameters to determine which parameters are critical for these measurements. The experimental work found that the following parameters; crude oil type, droplet size and temperature all were critical in impacting the oil-in-water measurement. Knowledge of these parameters is crucial in creating proper correlation and calibration techniques and in the day-to-day operation of online measurement.

Out of all the tests completed, four parameters were found to have the most significant impact:

- Condensate Oil – Ability for both image analysis and LIF to detect condensate oil droplets in water
- Effect of Gas Bubbles - Discrimination and ability to detect gas bubbles using image analysis
- Addition of Chemicals - Fluorescence properties of chemicals and their impact on LIF
- Temperature Effect - Effect of solubility on dissolved / dispersed ratio

During the condensate trial, the LIF devices remained within ±25% to the reference value up to 500 mg/l oil-in-water concentration. Above this, towards 1000 mg/l, both instruments started to undermeasure leading to deviations down to -50%. At all concentrations evaluated, the inline image analysis unit was not capable of measuring the condensate oil concentration leading to errors down to -90%.

In the effect of gas bubbles test, the baseline results for all instruments at 30 to 100 mg/l was within ±30% of the reference. When compared with the baseline, the addition of gas bubbles has drastically increased the measurement error for both image analysis devices. However, at higher concentrations, this effect occurs much less.

During the chemical trial, for all concentrations, the measurements of the LIF units increased in the presence of the corrosion inhibitor, showing a direct influence due to the added 50 mg/l chemical.

In the effect of temperature test, the inline Image analysis unit was not able to measure concentration at all at higher temperatures. The inline LIF device remained constant throughout, however a downward trend between -20% and -70% is noted for the bypass LIF unit between 20 and 66^{o}C. Similar to the inline LIF unit, the bypass image analysis device remained constant.

7.1.3 Can improvements be made to current online techniques or methods, to improve performance of measuring oil-in-water concentration?

Droplet size was discovered to be one of the main parameters which can affect the oil-in-water measurement of Laser Induced fluorescence techniques. To overcome this, the research investigated the correlation between droplet size and oil concentration measurement in a series of experimental tests. The outcome of this was that a correlation was developed based on temperature and droplet size. It was discovered that temperature needed to be considered as the solubility of crude oil in water varies, which in turn, effects the droplet size correlation. This is seen if most of the crude oil is in the dissolved phase, then the impact of droplet size is significantly reduced. This developed correction factor allows for image analysis and laser induced fluorescence to be combined into a single technique for enhanced oil-in-water measurement performance.

One of the main goals of continuous oil-in-water measurement is negating the requirement of collecting samples, which depending on the application, can be very costly and take a significant amount of time. However, like other flow measurement devices; online oil-in-water devices will require periodic calibration and verification, and therefore still require periodic samples to be collected. In unmanned situations, such as in subsea deployment, this is known to be a limiting factor in full scale subsea processing. To overcome this, a method for verifying and calibrating laser induced fluorescence devices *in-situ* using tracers is described. The method works using any fluorescence substance and requires an initial correlation between uncalibrated fluorescence measurement and tracer concentration to be established. After establishing this correlation, the tracer can then be utilised to calibrate or verify the measurement of the laser induced fluorescence device as required. As the fluorescent properties of the selected tracer will not change over time, the correlation would only have to be completed once prior to deployment. To carry out the verification, first a background fluorescence reading would be taken, before injecting the pre-specified concentration of tracer. The new fluorescence reading could then be verified using the initial correlation, and if different, the device could be re-calibrated. This novel verification method allows for no samples to be required and there for allowing a greater number of applications to use continuous measurements. The impact of this improvements is that it allows the use of LIF based devices in situations with a varying known droplet size.

The use of tracers to validate image analysis of condensate oil was also investigated. As discussed in Chapter 4 results, the image analysis technique had challenges relating to the contrast between the lighter condensate oil and the background water. By using the tracer technique, the image analysis device was also to successfully detect the condensate oil. The tracer used in this experiment was a black oil soluble dye, which was pre-dissolved into the condensate oil, in a ratio of 1:50 of dye tracer to condensate oil by volume. The test was then repeated, with the condensate and tracer injected to simulate conditions of 10 to 100 mg/L and results compared. A clear improvement is noted, reducing the associated errors from ±80% down to mostly within ±30%.

Another method was undertaken, by adapting the threshold settings to improve the contrast ratio between the condensate oil and the background, measurements from the image analysis device was significantly improved. However, this method would only work in very specific applications, but the results demonstrate the techniques ability to measure condensate oil without additional chemicals. After undertaking the work to improve the threshold conditions in respect to condensate oil, an experimental trial was completed with condensate oil ranging from 0 to 100 mg/l. Even with the limitations discussed, the method was able to still measure the oil concentration within ±32.8%, which is comparable to the results seen during the tracer trial. The ability to measurement condensate oil using an image analysis device cannot be understated. In comparison to other techniques, image analysis also measures droplet size and can differentiate between solid particles, gas bubbles and oil droplets. Using tracers or by changing threshold settings, this allows the use of this technique in an area which has primarily been challenging, allowing for more suitable applications and also negating the need of multiple devices in varying process conditions.

The impact of these improvements brings the measurements from online oil-in-water measurement techniques closer to the ideal reference results and allow the use of online techniques for regulatory reporting to be more viable, in terms of measurement performance.

7.2.1 Can we determine the uncertainty of reference techniques typically used to measurement oil-in-water concentration? In addition, can we predict the impact of uncertainty due to sampling? If so, what sampling parameters have the largest contribution?

All current reference methods for oil-in-water measurement require samples to be collected before undergoing an extraction step and finally analysis via a laboratory instrument. The precision information found in literature for the reference techniques is very limited, and uncertainty is rarely accounted for in oil-in-water measurement. In the UK, the monthly average discharge limit is 30 mg/l of oil-in-water; however, no uncertainty level is stated. The research in this thesis fills this gap in knowledge, by undertaking a series of studies to determine the uncertainties associated with oil-in-water measurement.

The research found that the largest source of uncertainty was the act of sampling, contributing to more than half the total uncertainty of the method. Sampling multiphase flows has been previously researched in literature; however, in the case of oil-in-water sampling, the literature is extremely limited. The results of the experimental work show an uncertainty of ±19.29% at a 95% confidence interval for the infrared oil-in-water reference method alone, and an overall uncertainty of ±52.1% at a 95% confidence interval with the inclusion of sampling.

To combat this, a series of experimental studies were carried out to determine how the uncertainty of sampling changes in several different typical configurations. The configurations investigated were; sample point velocities, position across pipe, upstream lengths from bend and T-piece, droplet size distribution and main line flow rate. The outcome of this study shows that how the sample was collected can vary the representativeness of the sample dramatically. The results from these experiments are summarised:

- Results demonstrate that isokinetic sampling leads to the closest to the reference oil-in-water concentration. Sub-isokinetic leads to a reduced measurement of -30% and super-isokinetic leads to an overmeasurement of up to 10% in comparison to the isokinetic condition.
- At 5D downstream of the 90° bend, an oil-in-water concentration deviation of greater than 30mg/l is seen between the left and right sample positions. In comparison, the results from the t-piece shows no differences.
- In comparison to the vertical sample point, the results from the three horizontal sections vary with an average deviation of ±20% depending on which location used.
- Increasing the average droplet size from 5 to 80µm leads to a significant increase in standard deviation of results, with a ±25mg/l scatter noted at the highest droplet size. A similar result is seen whilst maintain the average droplet size but altering the droplet size distribution.

- No effect is noted varying the main line velocity from 0.5 to 5 m/s whilst maintain isokinetic sampling. Standard deviations remain consistent throughout velocity range.
- Varying the oil concentration from 5 to 30 mg/l leads to a reduction of uncertainty from ±85.81% to ±45.13%. Further increase to 100 mg/l increases the uncertainty to ±56.10%.

From the summary of results from the research work completed, a best practice of sampling was determined to minimise uncertainties.

7.2.2 Can online techniques be used for produced water regulatory compliance monitoring? What methods of correlation are required to demonstrate this ability?

To demonstrate that continuous oil-in-water measurement techniques can be used for regulatory compliance monitoring, a method was developed to determine their respective uncertainty. Traditionally, online methods have been correlated to laboratory reference methods; however as demonstrated in this research, the uncertainties associated with the reference techniques can reach over ±50% and therefore significantly reduce the quality of the correlation.

To overcome this challenge, a method was proposed to calibrate the online techniques to a dosing-based procedure rather than directly to an offline reference method. The procedure was carried out similar to typical offline calibrations, however the stock sample was set up as a flow with a known mass of crude oil dosed. To evaluate the benefits of this method, the uncertainty of a Laser Induced Fluorescence device was calculated for standard reference method calibration and for the dosing-based calibration. The standard deviation of the dosing method was determined to be ±10.02% with an expanded uncertainty of ±19.64% at 95% confidence interval. The standard deviation of the IR method was determined to be ±24.63% with an expanded uncertainty of ±48.27% at 95% confidence interval. The experimental work demonstrates a reduction in uncertainty using the proposed dosing technique, due to the uncertainty of the online technique not being linked to the uncertainty of the reference method.

The uncertainties determined during this trial show the advantages of online techniques over the current reference methods, with a significant reduction in uncertainty. It should be noted however that these experiments were carried out under ideal conditions and therefore as described previously in Chapter 4, certain parameters can affect the measurement of online measurements and need to also be considered.

8 Further Work

This section describes areas of interest that could not be undertaken as part of this research project, however can have a key impact on the development of knowledge in this area. As produced water is a waste stream, the amount of research completed in this area is limited; therefore, there are a significant number of challenges which still need to be considered. This section will describe some specific examples relevant to the research discussed.

8.1 Improvements to Produced Water Facility

The majority of the experimental work in this thesis was carried out on the produced water facility, designed and built as part of the research. Even though facility was constructed to meet the needs of the research, there are several improvements which could be made to increase the operating envelope of certain parameters, allowing additional experimental trials to be completed. A number of generic improvements can be made such as expanding the total liquid flow rate or increasing the temperatures or pressure limits of the facility, however the current design incorporates the majority of conditions likely seen at produced water stream conditions. Specific improvements however could be made such as; allowing larger TSS particles, the addition of other chemicals, formation of hydrates and greater gas bubble size and concentration control. These parameters would allow additional research to be undertaken in this area.

An aspect which was discussed in Chapter 6 was sampling from a horizontal versus vertical pipe. The main test section for the facility is situated in the vertical orientation to improve mixing and allowing greater distribution of the produced water components, however, alterations could be made to allow the test section to be situated in different inclines. This would allow the effect of different installations to be determined in both sampling representativeness and also determine the impact on online measurements.

8.2 Effect of Total Suspended Solids

Part of the experimental work discussed in Chapter 4 was to determine the effect of TSS on oil-in-water measurement for different technologies, with the results demonstrating large variations in oil-in-water measurement with increasing TSS concentration. The presence of solids can affect online measurements; however, the specific underlying reasons can be further researched and developed. An interesting topic that was not covered is the impact of solid coated oil and oil coated solids and the presence of agglomerates. As techniques such as image analysis work are based on properties of the droplets, such as circularity, the impact of these agglomerates could be profound. The inclusion of solids would also influence light scatter and absorption which would other optical based systems.

In this research, only a limited sample of potential types of TSS was considered. Two particle sizes of 6.47 and 17.03µm were used throughout the experimental work, with the type of solids selected as silica. Further investigations into different particle sizes, shapes and material type would allow the impact of TSS to be further characterised and allow development of corrections to improve oil-in-water measurements.

8.3 Novel Online Techniques

In the initial part of the thesis, a technology review was undertaken to select several different online oil-in-water measurement techniques to be included as part of the overall research. Two main techniques were selected; Laser Induced Fluorescence and Image Analysis, due to their development progress and performance results from literature.

One of the technologies that were not selected however has been quickly advancing to the point where the technology has the possibility to measure oil-in-water is tomographic based techniques. The main tomography systems are x-ray, electrical capacitance and resistance based. Research work has been carried out in this area (Durdevic, et al., 2015), however these devices were not able to be included as part of this research. Other techniques such as nuclear magnetic resonance, photoacoustic, confocal laser fluorescence microscopy and light scattering are also technologies that have potential for oil-in-water measurement.

8.4 Additional Parameter Effects

Several parameters were evaluated as part of this research, as discussed in Chapter 4; however not all parameters seen in produced water could be included. The composition of produced water varies depending on location and reservoir age and therefore specific parameters typical of a well could also be included. Examples of some other conditions that can be included are:

- Effect of pH
- Different emulsion compositions
- Different production chemicals (Biocides, de-foamers, scale inhibitors, de-oilers)
- Oil type (Density, Viscosity and Composition)

By incorporating additional parameters, the specific effects of each variable can be determined on the online measurement techniques. The more variables included in the analysis allows a greater understanding on exactly how the measurement method is affected under non-ideal conditions. Other than solely varying parameters of the simulated produced water process, variables within the online techniques can also be altered to determine the implication on measurement performance. As an example, varying the excitation laser wavelength within the laser induced fluorescence technique or altering the thresholding limits within image analysis software. Larger changes such as experimental testing of multiple online techniques from different vendors using the same technology, to determine effects from different set-ups, can also be investigated.

8.5 Further Droplet Size Correlation Development

In Chapter 5, the effect of droplet size on the oil-in-water measurement of Laser Induced Fluorescence techniques was investigated. The experimental work allowed the effect of droplet size to be characterised, allowing an empirical correlation, based on droplet size, concentration and temperature to be developed. As previously discussed however, this developed relationship is based upon limited sets of data and therefore the limits empirical correlation needs to be carefully considered.

To fully establish the relationship, further research work would be required to increase these limits and to include other variables not currently incorporated. One of the major variables that was not included is the type of crude oil. Varying the type alters a number of parameters; such as; oil density, viscosity, composition and optical properties. The correlation developed in Chapter 5 was based on a single crude oil type, therefore further experimental analysis is required to improve the correlation to incorporate these additional parameters. In different applications, the software and hardware of the Laser Induced Fluorescence device will also differ, which can influence the droplet size effect. By investigating this further, the correlation can be improved and made valid for more situations.

8.6 Alternative Reference Method and Uncertainty Analysis

Throughout the thesis, the majority of the experimental work has been carried out using the infrared based reference methodology typically used in the North Sea. To further increase knowledge and understanding in this area, portions of the research could also be repeated with difference reference techniques, such as the USA based reference method EPA 1664A, to determine if the outcome differs with different methods. As discussed in Chapter 2, different reference methods measure different portions of the hydrocarbon chain range, therefore leading to different results. Differences in extraction methodology and measurement principle will also lead to additional variations between methods. Quantifying these differences could lead to additional information and trends to be seen in several of the experimental work carried out throughout this research.

In Chapter 6, the uncertainty of the infrared reference method is initially calculated using a Type-A uncertainty analysis. The purpose of this is to determine a baseline uncertainty to estimate the additional uncertainty contribution from sampling. However, this baseline uncertainty could be improved upon by further analysis and could also be applied to additional reference techniques. To fully calculate the uncertainty of the reference method, an in-depth analysis of all contributions of uncertainty would need to be undertaken. This analysis would result in an uncertainty budget for the specific instrument which could be used to verify the uncertainty analysis undertaken in this thesis.

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Appendix I – Characterising Parameters in Produced Water: Preliminary Experiment

Preliminary Experiment Test Facility

This section discusses the test facility used to conduct the preliminary experiment as part of Chapter 4. This preliminary test work was undertaken at a facility in Orkney, UK. This part of the experimental work was completed by OPUS, with set-up, test scope and data analysis completed by the author.

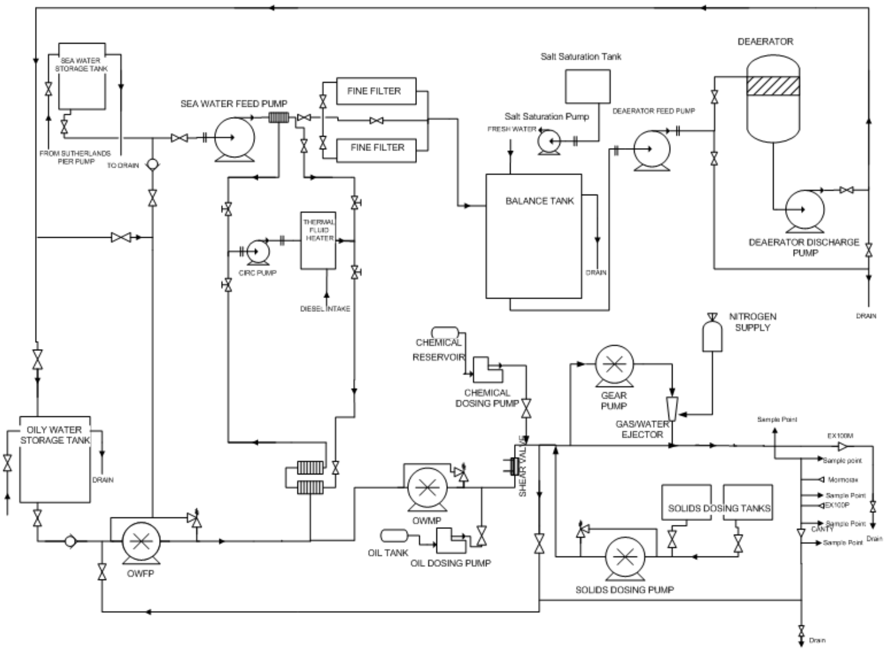

Figure I.1 – Schematic of OPUS Test Facility

Figure I.1 shows a flow chart diagram of the test loop design used throughout the experimental program, which was modified to incorporate testing of three oil-in-water monitors. Basic operation of the facility can be summarised into the following steps: Water is pumped from the surrounding sea into a tank used for bulk storage. The water is passed through a series of filtration vessels to remove any suspended solids or other contaminants and held in a final buffer tank. A combination of centrifugal and positive displacement pumps is then utilised to increase the pressure up to a maximum of 20 bar through the test section.

To create an oil in water mixture, crude oil is injected into the main line through a metering pump at a specific flow rate which can then be related to overall oil concentration via downstream sampling. To vary the oil concentration, the flow of injected crude oil can be simply altered until desired condition is met. To sustain and control oil droplet size, the mixture of oil and water is passed through a choke valve, where the pressure drop created causes the oil droplets to break up. By varying the pressure drop, the droplet size can also be manipulated and sustained throughout a testing period. Oil concentration and droplet size is thus dependant on pressure drop, choke valve position, pump speed and metering injection rate. The combinations of these variables to create specific test conditions are were determined during commissioning and past trials of similar conditions. The final droplet size reported however is measured using a reference method, discussed in the following section.

Test Section

To efficiently test the devices, it was decided that the three meters would be tested in series to ensure each meter under test would be subjected to same test condition for simpler comparison. By testing the meters in series, issues surrounding repeatability of certain variables and external factors can be mitigated. As each meter has differing physical connections, a spool piece was designed specifically to accommodate all of the instruments and equipment. The spool piece was constructed of stainless steel at 3000 mm in length and 80 mm internal diameter to allow sufficient space between each instrument to reduce impact of flow disturbances occurring. Other than the devices under test, there were 3 sample points, one after each device and a temperature and pressure tapping points for the test section. The spool piece ran vertically with an upwards flow, to maintain the most repeatable distribution of oil and solids within the produced water flow.

Several trials were conducted during commissioning to ensure that the installation of each device under test would not impact the oil or solid distribution which could cause errors in downstream measurements. A series of samples was collected at each sample point throughout the test section to verify consistent concentration values. As the test spool piece transitions from horizontal to vertical via a bend prior to the monitors, the effect of this long radius bend on solids distribution was investigated. To do this, a variable length sample pitot; allowing the cross section of the pipeline to be sampled. The initial investigation was conducted at the first sample point, which comes immediately after the bend and the results were as expected. The solids are thrown to the outside of the bend, and therefore that’s where the highest concentration of solids was found. As the pitot was moved closer to the inside of the bend, the concentration decreased. Samples were also taken downstream which show that the solids had dispersed equally throughout the pipeline by the time they reached these sample points thus indicating that all the devices were receiving similar fluids characteristics.

Reference Methods

Four main reference parameters were determined during each test:

- Oil in Water concentration
- Total Suspended Solids (TSS) in water Concentration
- Oil droplet size
- Solids particle size

As oil in produced water is method dependent, it is critical that a reference method is defined and available so that oil in produced water data obtained from different installations can be directly compared. The procedure utilised is in line with the UK regulatory method for determining oil-in-water concentration (BEIS, 2016). The oil droplet size was determined via online measurement during the trial by a ViPA particle size analyser; however, a back-up Malvern Mastersizer Micro Plus was also available for verification purposes.

Two methods for determining the total suspended solids in water concentration were utilised with the first being used to primarily set-up a specific test point and second to determine the actual reference concentration. The first method was determined by adding a known weight of solids to a known volume of water within a mixing tank. The created slurry was then injected into the main process line at a known rate and thus a concentration can be calculated. The actual reference method was found by using a filtration method. Two membrane filter papers are pre-weighed and sealed within a stainless-steel filter holder, and the process fluids flowed through. The sample volume is determined by collecting the fluids that have passed through the filter in a suitable container. Oil and water-soluble salts are washed off the filters and the filters dried. The filters are reweighed, individually, and solids content calculated.

Test Matrices

Table I.1 – Summary Test Matrix

Test Types	Oil		Added Solid		Presence of Gas	Chemical	Temperature (°C)	Flow Velocity (m/s)
	Conc (mg/l)	Size (µm)	Conc (mg/l)	Size (µm)				
Crude Oil	0, 30, 50, 100, 300, 1000	20, 50, 100	-	-	-	-	20	3
Solids Only	-	-	0, 10, 50, 100, 300	5, 22, 110	-	-	20	3
Oil & Solids	10, 30, 50, 100, 300	20	10	5	-	-	20	3
Gas Bubbles	10, 100	20	20	5	Yes	-	20	3
Chemicals	10, 100	20	20	5	-	C. Inhibitor	20	3
Temperature	30	20	20	5	-	-	20, 35, 50, 65	3
Flow Velocity	50	20	20	5	-	-	20	0.5, 1, 3
Dynamic Response	100, 2000, 100	-	20	5	-	-	20	3
Fouling	50	20	20	5	-	-	20	3

The baseline oil concentration tests were conducted from 0 to 1000 mg/L, with the focus of most tests however being under 300 mg/L. As mentioned previously due to regulatory discharge limits, most of produced water discharged will contain crude oil concentrations below 30 mg/L. However up to 1000 mg/L represents upset conditions such as failure in the treatment processes. Total suspended solid concentrations of between 0 to 300 mg/L were selected in a similar way, due to typical rates seen in produced water discharges, and 5, 22 and 110µm particulate size being chosen to cover full range of potential sizes that may be encountered. A main line velocity of 1 m/s was chosen for most of the tests due to facility constraints that meant the maximum velocity achievable in the current configuration was 3 m/s. To allow for a velocity range to be achieved, it was decided that 0.5, 1 and 3 m/s would be selected with the middle velocity utilised as the baseline. It was also decided that the tests would run at a temperature of 20°C and using the main heat exchangers to alter the temperature between 10^{o}C and 80°C for the effect of temperature test. Typically, the temperatures of produced water discharges can vary and due to the solubility of crude oil and water, the amount of dispersed and dissolved oil can also change.

To incorporate a chemical addition test into the experimental program, a corrosion inhibitor (Nalco EC1231A) was selected to be trialled. There are many other production chemicals that are encountered throughout produced water treatment processes, however corrosion inhibitor is typically always used and due to its properties, changes oil and water stability.

To achieve the effect of gas bubbles test, nitrogen gas was utilised. This was done by taking a small portion of the process stream before the test section and using a gas injection system coupled with a rotameter to measure the flow rate injected. To create gas bubbles of similar magnitudes to the oil droplet sizes created, the gas was injected prior to returning to the main process line upstream of the test section.

The dynamic response test was designed to have the test instruments running at a set condition then increase the oil concentration significantly for a length of time then reduce the oil concentration back down to the original set-point, to determine the instrument response to transient and dynamic conditions. To achieve this, an initial oil concentration of 100 mg/l was selected, rising to 2000 mg/l for a set period, before dropping back down to 100 mg/l. By conducting this test, two parameters can be analysed; the technologies reaction time and the technologies ability to measure oil concentration after being subjected to higher concentrations. This is important as upset conditions can occur within the field, causing high oil concentrations to be passed through the produced water process steam. A quick response time aids in the operators' ability to detect upset conditions, and the ability to recover ensures reduced uncertainties after the upset condition has passed.

To effectively simulate the effect of fouling, it was decided that a layer of grease would be manually applied to the working surfaces of each technology. To achieve this, each device was removed from the test section for the manual application. Prior to re-installation, any automatic cleaning systems were switched off to ensure the cleaning systems would not activate prior to the start of the test. After installation, the cleaning systems can be switched back on for the start of the test, which will demonstrate the technologies ability to recover from fouling. It should be noted that manual grease application was chosen due to its ability to effective foul optical surfaces whilst being easy to apply and clean manually if the instruments do not recover. In field conditions, fouling takes many forms such as hard scaling, soft scaling, oil, solids or chemicals. Depending on the application, the fouling that may occur will differ significantly, and in cases where fouling would not normally occur, irregular occurrences such as shut-downs or upset conditions may occur.

Conclusion

Three technologies capable of measuring oil in water online were successfully tested and evaluated using simulated produced water containing both oil droplets and solid particles. The test setup was effective, however if similar tests are to be conducted again, solids injection location and mixing mechanism, as well as concentration measurement method may be improved. Ensuring the exact same produced water characteristics and conditions for all the test instruments proved to be a challenging task. Test experience and results obtained confirmed that all three instruments were relatively easy to install; commission and operate. They were also capable of measuring oil and or solid content as well as size of both oil droplets and solid particles at lower oil concentrations. However, test results have demonstrated that there is room for improvement for all the instruments trialled, some more than others. Some of the issues and problems encountered by the tested instruments include:

- Light source failures (Image Analysis)
- Condensation (Image Analysis)
- Ineffective fouling mitigation mechanism (Image analysis and Ultrasonic)
- Slow response to a change in test condition (Ultrasonic)
- Sensitivity to oil droplet size (LIF)

Overall image analysis and LIF performed better in comparison with the ultrasonic device. They are generally more consistent with results closer to the reference values. However, all instruments have room for improvement, not only in relation to the instrument reliability, but also general performance in terms of accuracy and repeatability. From the test work completed, it is clear that certain parameters can influence the technologies ability to measure oil concentration.

Effect of droplet size had an impact on LIF measurement; however, this was not the focus as part of this test program. High uncertainties found even during baseline tests meant difficulty in determining key trends associated with different parameters. Due to such small quantities of oil present at lower concentrations (less than 30 mg/L), errors up to 100% are seen readily. Uncertainty associated with reference methods also proved difficult to quantify in experiments. Overall however, key parameters which fluctuate during produced water treatment can alter the technologies ability to perform. For regulatory compliance, these would have to be investigated further and be accounted for.

The purpose of this preliminary work was to determine the effects of several parameters on three technologies that have been used to measure oil in water online. The results from the testing show areas where further research is required. As very little data is in the public domain in this subject, the data provided can be used as a starting point to characterise these parameter effects in further detail in future research topics.

Appendix II – Characterising Parameters in Produced Water: Tabulated Results

Table II.1 – Baseline Crude Oil

Target Oil (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
0	0.4	0.4	1.4	0.1	0.4
0	0.6	0.3	1.4	0.2	0.5
0	0.5	0.1	1.4	0.2	0.6
30	33.4	26.4	39.9	24.3	22.2
30	30.2	27.0	35.8	25.4	23.2
30	29.1	24.8	37.3	23.4	25.3
100	107.9	109.5	113.7	72.2	70.3
100	100.2	93.7	109.7	79.6	76.7
100	99.2	95.4	108.3	78.7	78.1
300	296.3	362.6	277.6	238.7	345.6
300	267.2	329.6	254.9	288.1	344.1
300	307.8	346.6	260.4	273.9	354.6
500	544.7	693.7	404.4	467.1	994.7
500	523.4	600.3	358.9	503.2	382.5
500	440.0	514.6	364.2	510.4	452.2
1000	986.7	1122.5	477.1	1573.0	1432.0
1000	952.4	902.5	563.4	1459.6	1432.0
1000	994.6	964.3	522.4	1499.3	1512.4
1000	890.8	905.4	579.8	1403.3	1475.2
1000	1028.5	1145.2	629.3	1584.8	1416.4

Table II.2 – Condensate Oil

Target Oil (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
0	0.9	0.3	0.2	1.0	0.8
0	0.9	0.2	0.5	0.7	0.9
0	0.8	0.1	0.5	0.6	0.7
30	31.2	12.9	17.9	30.8	33.0
30	27.9	13.2	10.8	24.0	29.1
30	30.3	9.2	9.0	24.2	27.0
100	99.2	22.4	40.3	105.5	81.2
100	101.3	37.1	29.3	108.2	97.0
100	102.3	30.1	49.1	91.4	113.2
300	318.1	74.3	104.4	347.2	270.6
300	283.6	78.3	203.0	333.8	310.8
300	286.3	92.3	207.3	365.2	264.4
500	519.0	54.3	322.5	564.5	521.3
500	492.7	100.2	98.4	459.7	497.1
500	435.1	182.3	290.4	477.8	391.1
1000	894.5	73.2	380.7	406.0	614.0
1000	921.8	328.3	263.0	582.5	482.3
1000	1142.0	85.4	422.4	576.3	821.2

Table II.3 – Effect of Solids

Solid Conc. (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
8.4	29.3	33.9	34.8	18.1	20.5
10.3	30.8	35.0	38.9	21.2	19.1
11	30.1	31.1	39.9	21.1	21.4
44.5	28.9	31.3	40.2	18.4	11.3
45.2	25.7	30.2	35.7	19.5	16.0
42.4	30.5	37.5	32.2	21.9	17.1
88.4	26.0	41.6	40.4	17.4	19.0
89.2	28.8	39.5	39.5	19.4	16.6
94.2	27.8	90.2	32.2	22.6	20.1
286.3	27.6	69.8	57.3	34.3	16.6
294.2	23.3	63.7	37.1	16.4	11.9
290.3	27.5	60.2	31.8	23.2	17.1

Table II.4 – Effect of Gas Bubbles

Target Oil (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
30	30.8	64.23	39.89	37.32	40.81
30	29.9	73.20	53.15	38.37	38.02
30	28.7	27.34	41.40	36.43	34.73
50	49.6	54.74	56.84	46.08	58.69
50	54.0	54.85	93.23	49.82	62.87
50	52.6	68.11	77.34	49.33	61.34
100	96.1	109.49	113.68	72.16	91.37
100	104.9	93.65	210.21	79.63	99.74
100	101.3	102.23	108.30	78.65	92.23

Effect of Chemicals:

Target Oil (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
30	27.3	29.53	35.23	29.32	19.33
30	25.2	35.23	37.23	38.98	31.42
30	31.0	37.43	39.23	37.93	36.42
50	54.4	59.27	57.72	45.26	35.43
50	51.8	63.32	58.66	50.76	48.23
50	49.8	61.32	48.32	47.62	47.23
100	100.5	106.60	114.18	71.67	78.23
100	103.0	94.01	111.80	93.32	89.23
100	103.4	127.86	107.67	87.41	88.70

Table II.5 – Effect of Salinity

Salinity (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
10,000	33.5	26.4	39.9	27.3	25.2
10,000	32.2	27.0	40.1	28.4	26.2
10,000	29.9	25.3	39.2	26.4	28.3
20,000	32.3	28.4	39.9	28.4	25.2
20,000	32.9	28.4	38.2	28.4	26.2
20,000	31.1	29.3	41.4	27.3	28.3
30,000	28.2	26.4	37.3	29.3	25.2
30,000	30.1	27.4	38.2	28.4	26.2
30,000	31.2	28.3	39.0	27.5	28.3

Table II.6 – Effect of Temperature

Temperature (°C)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
20.5	32.5	36.4	39.9	26.3	18.3
19.9	34.2	37.0	38.2	25.2	17.3
20.2	33.4	35.3	41.4	29.3	18.3
33.6	32.1	32.7	39.7	21.1	15.3
34.2	28.6	32.7	42.4	19.2	15.0
34.1	33.9	33.5	37.3	20.3	15.3
51.2	28.9	28.2	39.4	15.1	16.3
50.7	32.0	29.5	42.2	14.9	14.6
51.1	30.8	29.2	39.4	13.9	14.6
66.2	30.7	0.0	41.1	7.4	12.2
66.1	25.9	0.5	38.2	7.3	11.2
66.2	30.5	0.0	42.2	6.4	12.4

Table II.7 – Effect of Flow Velocity

Flow Velocity (m/s)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
0.48	28.5	36.4	37.3	23.2	21.9
0.49	33.3	37.0	38.3	24.3	20.9
0.48	31.5	35.3	37.3	25.1	21.9
1.1	34.1	32.7	37.5	22.3	19.1
1.12	27.7	32.7	38.7	23.3	18.8
1.12	28.9	33.5	37.4	24.0	19.1
2.93	28.3	28.2	33.4	25.1	20.0
2.94	32.2	29.5	35.3	22.4	18.4
2.98	28.6	29.2	33.4	24.3	18.5
4.83	30.2	32.3	32.3	23.4	16.2
4.75	30.1	35.8	35.3	24.3	15.3
4.92	27.8	34.2	41.2	23.9	16.4

Table II.8 – Dynamic Response

Target Oil (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
5000	5446.6	4449.8	2553.9	8111.4	7142.1
5000	5233.8	4708.3	2834.6	6784.4	7723.3
5000	4953.2	5778.0	2972.7	7079.5	7069.9
1000	942.3	964.3	522.4	1499.3	1512.4
1000	985.2	905.4	579.8	1403.3	1475.2
1000	923.2	923.1	629.3	1323.2	1416.4
30	29.3	26.9	34.4	22.5	22.7
30	27.6	26.8	35.5	25.8	23.1
30	30.5	23.8	35.0	23.7	23.6

Table II.9 – Effect of Fouling

Target Oil (mg/l)	IR Reference (mg/l)	Image Analysis (mg/l)	Image Bypass (mg/l)	LIF (mg/l)	LIF Bypass (mg/l)
30	27.5	33.2	35.6	23.8	22.8
30	33.9	38.6	38.1	24.3	23.4
30	29.4	36.5	36.4	24.9	20.9