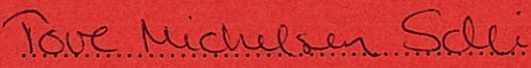




University of  
Stavanger

Faculty of Science and Technology

## MASTER'S THESIS

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# Evaluation of UV fluorescence for oil in water analysis.



**By Tove Michelsen Solli**

**June 2011**

## Summary

Slop water is a mixture of various fluids that is generated during drilling and well operations offshore and it can also be water from operations such as pit and rig cleaning and rainwater from drilling area or areas on the rig adjacent to drilling area. Due to government regulations and environmental concerns the slop water must be treated before it can be discharged. According to the activities regulations Chapter XI, § 60 *Discharge of oily water*; “the requirement is that the oil content shall not exceed 30 mg oil per liter of water as a weighted average for one calendar month”.

Treatment of slop water has mostly been done by transporting it to an onshore treatment facility. Halliburton has newly launched a mobile offshore treatment plant for slop water where the basic principle is chemical flocculation with dissolved air flotation (DAF).

In Chapter XI, of the activities regulations § 70 *Measuring the discharged quantity of oil, other substances and water* it states that; “the content of oil and other substances in the discharges shall be measured”. “The test results shall be used to verify the treatment plant's performance.” To verify that the discharge of oily water is according to § 60 Halliburton uses an instrument called OIW EX 1000. This analyzer is based on molecular fluorescence spectroscopy. The oil content is then determined by applying UV radiation at a specific wavelength to a sample and measuring the amount of energy that is emitted by the oil. The instrument has normally been used for produced water and Halliburton is the first company to use the instrument to analyze treated slop water. Produced water contains crude oil that has a high content of aromatics and according to theory aromatics has the most intense fluorescence. Slop water on the other hand does not contain aromatics, the oil based muds are normally mineral oils or linear paraffin. These oil types have aliphatic carbonyl structures and according to theory only a small number of these compounds may exhibit fluorescence.

In this thesis different tests were performed to evaluate if this instrument is a valid method to measure oil in treated slop water and find out which operating parameters can influence the measurements and whether or not they can be neglected.

After evaluating all the data it was concluded that the advanced sensor EX OIW 1000 is a valid method for measuring oil content in slop water but only if it is calibrated and adjusted correctly. The instrument should be adjusted so the spectra of the base oils are read at 510 nm to achieve the best measurements, and a mask should be applied to the spectra to eliminate any uncertainties in the intensity. Two parameters can have a profound effect on the measurements; droplet oil size and concentration. A procedure was developed to verify the instrument according to ISO 9377-2.

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## Nomenclatures

$v$  = Velocity

$g$  = Gravitational acceleration

$p$  = Pressure

$\rho$  = Density

$\mu$  = Viscosity

$R$  = The radius of the particle

$\lambda$  = Wavelength

$n$  = Frequency or refractive index

$\tilde{\nu}$  = Wavenumber

$\tilde{\nu}_A$  = wavenumber of absorption (cm-1)

$\tilde{\nu}_F$  = wavenumber of emission (cm-1)

$c'$  = Speed of light

$c$  = Concentration

$h$  = Planck's constant

$P$  = Radiant power

$P_0$  = The power of the beam before it goes through sample

$P$  = The power after the beam has gone through the sample

$T$  = Transmittance

$A$  = Absorbance

$b$  = Length

$k_f$  = Fluorescence

$k_i$  = Intersystem crossing

$k_{ec}$  = External conversion

$k_{ic}$  = Internal conversion

$k_{pd}$  = Predissociation

$k_d$  = Dissociation

$\Gamma = k_f$  = Emissive rate of the fluorophore

$k_{nr}$  = The nonradiative decay to  $S_0$ .

$a$  = The cavity where the fluorophore resides

$\epsilon$  = Dielectric constant of the solvent

$F$  = Fluorescent radiation

$K'$  = A constant that depends upon the quantum efficiency of the fluorescence.

$\pi \rightarrow n$  = excited state

$\pi \rightarrow \pi^*$  = excited singlet state

$\mu_E$  = the dipole moment in excited state

$\mu_G$  = the dipole moment in ground state



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Stavanger, June 2011

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Tove Michelsen Solli

## 1. Introduction

Treatment and disposal of slop water from the offshore industry is traditionally done onshore. However, Halliburton has newly launched a mobile offshore treatment plant for slop water that is based on Nijhuis Water Technology's flocculant- and flotation units. The treated water is then discharged to sea, thereby reducing the volume of waste that must be transported onshore. The oil content in the discharged water shall according to the activities regulations Chapter XI, § 60 *Discharge of oily water*, not exceed 30 mg oil per liter of water as a weighted average for one calendar month. The activities regulations § 70 *Measuring the discharged quantity of oil*, states that the content of oil in discharged water shall be measured to verify the treatment unit performance. Halliburton uses an UV fluorescence instrument from Advanced Sensors to measure the concentration of oil in water. [3]

The objective of this thesis is to evaluate if this instrument is a valid method for measuring oil in discharged water. Different test were performed to identify which operating parameters can influence the reading and see if different problems that may or have occurred during operation can be resolved:

1. Do the base oils fluoresce?
2. The instrument has displayed "out of range" when the concentration is expected to be low. Why?
3. Will different chemicals and compounds that are normally in the slop influence the readings of the oil content?
4. Which operational conditions may influence the measurement?
5. When a sample of untreated slop water is analyzed the readings show low fluorescence intensity values when they should have been high. Why?

If the instrument can be verified for this type of measurements the goal is to develop a procedure to verify the instrument according to ISO 9377-2.

## 2. Definition of slop water

Slop is an expression that is used for all oil-containing waste fluids that has been generated during drilling and well operations offshore and has an oil concentration higher than 30 mg/l. It can also be water from operations such as pit and rig cleaning where storage tanks, rig floors and shale shakers are hosed with water between operations. North for the Polar circle rainwater is also considered as slop water. Slop will therefore cover a wide specter of fluids, all from cleaning water and produced water to used drilling- or well fluids and waste oil that are all mixed together and form a slop emulsion. [3, 4]

## 3. Drilling- and well fluid characteristic

### 3.1 Well fluids

Well fluid is a common name for three different fluids that is used during drilling and production of oil and gas;

- 1) Drilling fluid is defined as a circulating wellbore fluid that is used during drilling operations. A name that is much used in connection with drilling fluid is mud.
- 2) Service fluids are used in workover and completion operations. The fluid can be composed in many different ways but the basis is normally a solution of salt.
- 3) Cement is cement slurry fluid that is used in several operations, most importantly in primary cementation.

The composition of the fluid depends on where and how it will be used and which conditions are present in the well. [13]

### 3.2 Drilling fluids.

The well fluid technology is an important part of the total drilling process, commissioning of the well for production and completion. The development in the petroleum industry requires that the drilling fluids must function satisfying under both low and high pressures and temperatures. The drilling fluid should also maintain high drilling velocity, have low affect on the equipment and ensure pressure control in the well. [13]

The primary functions of the drilling fluid are: [4]

- Controlling the hydrostatic pressure in the well and stabilizing the well by preventing penetration of formation fluid and collapse of well.
- Cleaning the well by circulating and removing cutting from the bottom of the well and transporting it to the surface.
- Inhibit corrosion of drilling string and casing.
- Lubricate and cool down the bit.

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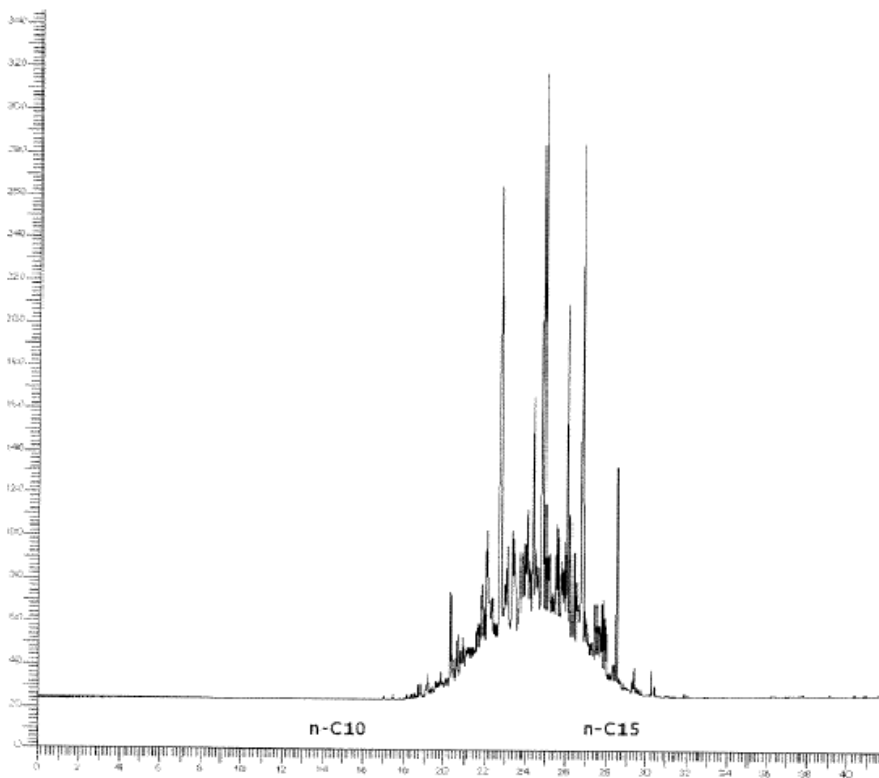
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- Hole stability and prevent that it react adversely with the formation.
- Deposit a thin, solid and impermeable mud cake on the wall in the well to prevent that fluids and particles penetrates the formation.

The base fluid in a drilling fluid is based on water, oil or synthetic oil. From an environmental point of view it is best to use water based drilling fluid because they contain chemicals that are in the natural marine environment or have low toxicity. The fluid also contains weight material, viscosity products and other chemicals. [13]

### 3.2.1 Oil based drilling mud.

Oil based drilling fluid has oil as the continuous phase and water as the dispersed phase. The oil phase consisted mostly of diesel until 1980 but has been replaced by mineral oil or linear paraffin due to toxicity. These oils are a by-product of the distillation of petroleum to produce gasoline and other petroleum based products from crude oil. Halliburton uses a mineral oil that is called EDC 95-11 or linear paraffin called Sipdrill 2.0. The base oils are transparent and colorless and consists mainly of alkanes. The gas chromatography in *Figure 1* shows that the main alkanes in EDC 95-11 are C10-C15. The base oils also contain sulphur, nitrogen, oxygen, trace elements of metals and water. [4, 6]



*Figure 1: Gas chromatography of EDC 95-11. [31]*



The main composition of oil based drilling fluids [4, 14]

- 50-95 vol% base oil or linear paraffin.
- 5-50 vol% water.
- Emulsifiers lower the interfacial tension between oil and water, which allows stable emulsions with small drops to be formed.
- Polymer can be added to increase viscosity, reduce fluid loss or avoid clay swelling.
- Weight material (mainly BaSO<sub>4</sub> and FeTiO<sub>3</sub>).
- Salts (mainly CaCl<sub>2</sub>).
- Lime (Ca(OH)<sub>2</sub>) for activation of emulsifiers.
- Organophilic clay, where the surfaces of the clay have been coated with a chemical to make it oil-dispersible.

Other additives [4]

- Defoamers lower the interfacial tension so that trapped gas will readily escape from the mud.
- Corrosion inhibitor.
- Scale inhibitor.
- Lubricants.
- Dispersing agents.
- Biocides.
- Fluid-loss-control materials lower the volume of filtrate that passes through a filter medium.

The oil based drilling fluid has many positive and operational qualities compared to the other drilling fluids. [7]

Benefits by using oil based drilling fluids [7]

- It will not react with swelling clay.
- Less friction when drilling in horizontal wells.
- Reduces the chance of corrosion on the equipment.
- Higher rate of penetration.
- Tolerates higher temperatures.
- The formation has little influence on the drilling fluid.
- Less damage when drilling into the reservoir.

### 3.2.2 Water based drilling mud

The simplest form of mud is composed of water and clay (usually bentonite) that is applied to enhance the viscosity. Different additives are also added to modify the properties of the mud. [4]

#### The main composition of water based drilling mud [4]

- Water.
- Clay (mainly bentonite).
- $\text{CaCO}_3$ .
- KCl (for stabilization of clay).
- Viscosity modifier/polymers (Carboxymethyl cellulose (CMC), Polyanionic cellulose (PAC)).
- Glycol (for stabilization of clay and lower the freezing point).
- Weight material (mainly  $\text{BaSO}_4$  and  $\text{FeTiO}_3$ )

#### Other additives [4]

- Defoamer.
- Corrosion inhibitor.
- Scale inhibitor.
- Lubricants.
- Dispersing agents
- Emulsifiers.
- Fluid-loss-control material.

### 3.2.3 Synthetic based mud (SBM)

Synthetic based mud were developed to produce a more environmental friendly alternative to oil based drilling mud and to comply with government regulations. It has also reduced the risk of severe downhole losses and overall well costs on many deepwater projects. In SBM the continuous phase consists of oliogenous fluids; internal olefins (IO), linear alpha olefins (LAO), linear paraffin (LP) etc. The aqueous phase is normally made up of calcium chloride,  $\text{CaCl}_2$ . The physical properties of the synthetic-based fluids depend on the chemical composition, structure, and molecular weight and are important when used in the field. For instance it is desired lower pour points in cold weather applications and high flash points are important for fire and safety hazards. The polarity and solvency are also important when choosing the type of elastomers that can be used in the drilling equipment.

Most synthetic-based mud is formulated very similarly to oil based drilling mud. SBM contain emulsifiers, wetting agents, viscosifiers, fluid-loss agents and weight material (barite is most common). Because the chemical and physical properties of various synthetic-based fluids may differ the surfactant package modifications or totally new surfactants may sometimes be required to formulate stable invert-emulsion drilling fluids. Synthetic based drilling fluids has normally higher viscosity than oil used in conventional OBM and are therefore normally limited to either lower mud weights or higher synthetic-based fluid to water (S/W) ratios. [5]

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### 3.2.4 “Pills”

A “pill” is a small quantity of a special blend of drilling fluid that is pumped down in the well to accomplish a specific task that the regular drilling fluid cannot perform. A standard pill has the same composition as oil and water based drilling fluid but with a much larger content of viscosifiers. It can also contain high amounts of salt depending on the composition and usage.

There are different types of pills for various purposes, for instance:

- To help lift cuttings out of a wellbore.
- Freshwater pills to dissolve encroaching salt formations.
- Pipe-freeing pills to destroy filter cake and relieve differential sticking forces.
- Material pills to plug a thief zone.
- Cleaning pills that is a part of the completion phase. [4, 14]

### 3.3 Service fluids; workover and completions fluids.

The fluids that are used in penetration of the reservoir and in workover and completion operations must be chemically compatible with the reservoir fluids and the formation matrix. The basis of the fluids is brine where a type of salt is dissolved in water. The brine is solid free without particles that might plug or damage a producing formation. The salts in the brine may also inhibit undesirable formation reactions such as clay swelling. Brines are typically formulated and prepared for specific conditions, with a range of salts available to achieve a preferred density. The most common brines are K, Ca and Na in combination with Cl, Br and COOH (formate).

The requirement for these fluids includes purity, low turbidity, density, crystallization temperature and compatibility with the other reservoir fluids. [13]

Classification of workover and completion fluids:

1. **Packer fluid:** Fluid that is placed above a packer in the annular region of a well between tubing and outer casing.  
The main functions of a packer fluid are:
  - Provide hydrostatic pressure in order to lower differential pressure across the sealing element.
  - Lower differential pressure on the wellbore and casing to avoid collapse.
  - Protect the metals and elastomers from corrosion.
2. **Workover fluid:** Fluid that is used during certain operations in the well such as replacement of downhole equipment, primary completion and various repair work.
3. **Perforation fluid:** Fluid that is used during perforation; a tunnel that is created from the casing or liner into the reservoir formation where oil and gas are produced.

4. Spacer fluid: It is used to physically separate to different fluids. The most common spacer is simply water but chemicals are usually added to enhance its performance for the particular operation. It can be used in cementation to divide cement from the drilling mud or to divide a salt solution from the drilling fluid.
5. Gravel pack fluid: Gravel pack is a sand control method used to prevent production of formation sand. Sand is then pumped down and fills up the annulus between the production string and casing. The gravel pack fluid is used to transport the sand.
6. Perforating fluid: Fluid that is placed in the wellbore over the interval that will be perforated. The ideal fluid is clean and free of solids and will not react to or produce damaging by-products in contact with the reservoir formation. Saturated salt solutions and oil based solutions can be used. [13,14]

### 3.4 Cement

Cement is a mixture of water and cement, where Portland cement is the main component. The cement is used in several operations most importantly primary cementation. The casing is then cemented to the formation wall. The cement will hinder flow of fluid/gas between the formation and surface, anchor and support the casing string and support the casing against corrosion. Different additives can be added to achieve wanted properties. The additives can influence rheology, fluid loss and setting time of the cement slurry. It can also affect the compressive strength and the strength of the dried cement. [13]

#### Additives in the cement [13, 14]

- Cement accelerator is added to the cement slurry to reduce the time required for the set cement to develop sufficient compressive strength to enable drilling operations to continue.
- Retarder is added to the cement to increase the thickening time.
- Extenders reduce the density of the cement slurry and stabilize the secretion of water.
- Weight materials increase the density and thereby controlling unstable formation with high hydrostatic pressure.
- Thinners reduce the viscosity.
- Fluid-loss-control material. When the cement slurry is added to a permeable formation under pressure the water phase penetrates the formation. Fluid-loss-control material is added to maintain the solid and water ratio in the cement.
- Loss circulation material (LCM) is granulated material that is inert to the cement and will stop the loss of cement slurry to the formation.
- Special additives.



## **4. Discharge of oil to the environment**

### **4.1 Effects of oil discharge to the environment.**

The oil and gas industry has an impact on large areas at sea, seabed and land. Discharges to sea and air when building installations, drilling and during operations can affect the surrounding environment and lead to changes in animal life. Even though the discharges today are less toxic to the environment than before the decomposition of the drill cutting still takes a long time. [11]

Until 1980 diesel were used as base oil in drilling fluid. Diesel oil is a refined form of crude oil and has a high aromatic content (18-24%). Many aromatic compounds such as benzene and toluene are harmful to aquatic organisms. This is with regard to their inherent properties; acute toxicity, bioaccumulation and biodegradation. Mineral oil with low content of aromatics has therefore replaced diesel oil as base oil. [3]

In areas in deep water further north and closer to the shore the ecosystems are more sensitive to change. Due to lower temperatures and lack of sunlight at wintertime the decomposition of the pollutions are much slower. In the areas from Lofoten and further north it is therefore stricter regulations to discharge from drilling and produced water. [11]

Pollution of the North Sea has many sources and it is not only from the oil and gas industry. It is therefore difficult to prove the chronic effects the industry will have and there are few approved methods of monitoring the effects in the maritime zones. [11]

According to OSPAR ‘s “Quality report 2010” oil discharges from produced water are reduced by an average of 20% in the OSPAR area. The majority of countries have met the OSPAR 15% reduction target, but volumes of produced water are expected to increase. Pollution from drilling fluids and cuttings piles has also been considerably reduced. The impact of offshore activities is reduced around some installations, but the evidence base for environmental impact is limited. *Figure 2* shows the OSPAR strategy objectives for the offshore oil and gas industry. Norway belongs to region I (Arctic waters) and II (Greater North Sea’s). [12]

Delivering OSPAR Strategy objectives for the offshore oil and gas industry					
OSPAR Region	Prevent/eliminate pollution	Environmental status 1998-2006	Key factors and pressures	Outlook for pressures	Action needed
Region I	Partly achieved ***	Improved *	Oil discharges and spills Input of contaminants Air emissions	↑	OSPAR OSPAR
Region II	Partly achieved ***	Improved *	Oil discharges and spills Input of contaminants Air emissions	↓	OSPAR OSPAR
Region III	Partly achieved ***	Improved *	Minor activity: Oil discharges and spills Input of contaminants Air emissions	↔	OSPAR OSPAR
Region IV	Mostly achieved ***	?	One non-discharging installation: Air emissions	↔	OSPAR
Region V	Not applicable	Not applicable	Exploration activities: Oil spills Air emissions	?	OSPAR

Status in delivering Strategy objectives	Changes and outlook for pressure	Confidence	Action needed
■ Many problems	↑ Increase	* Low: assessment is mainly based on expert judgement	Management and measures
■ Some problems	↔ No change		Monitoring and assessment
■ No problems	↓ Decrease	** Moderate: assessment is based on monitoring and expert judgement	Keep under review
■ Not known	? Not known		Research and information collection
		*** High: assessment is mainly based on monitoring	

Figure 2: OSPAR strategy objectives for the offshore oil and gas industry. [12]

## 4.2 Regulations.

### 4.2.1 Regulations regarding treatment of slop water.

Companies that perform any activity that may lead to pollution must have a permit from the pollution control authority according to the law “Act of 13 March 1981 No.6 Concerning Protection Against Pollution and Concerning Waste”. The law says that no person may possess, do, or initiate anything that may entail a risk of pollution unless this is lawful pursuant to section 8 or 9 or permitted by a decision made pursuant to section 11. The Act shall ensure that the quality of the environment is satisfactory, so that pollution and waste do not result in damage to human health or adversely affect welfare, or damage the productivity of the natural environment and its capacity for self-renewal. [8]

#### **Definition – what is pollution?**

##### **§ 9**

1. *the introduction of solids, liquids or gases to air, water or ground,*
2. *noise and vibrations,*
3. *light and other radiation to the extent decided by the pollution control authority,*
4. *effects on temperature*

*which cause or may cause damage or nuisance to the environment.*

*The term pollution also means anything that may aggravate the damage or nuisance caused by earlier pollution, or that together with environmental impacts such as are mentioned in items 1 to 4 causes or may cause damage or nuisance to the environment.*

#### **§ 4. Application of the Act to activity on the continental shelf**

*The provisions of this Act also apply, subject to any restrictions deriving from international law and from the Act itself (cf. Chapter 8), to exploration for and production and utilization of natural subsea resources on the Norwegian part of the continental shelf, including decommissioning of facilities. The provisions of section 7, first paragraph, cf. Chapter 3, on the duty to obtain a permit and of section 9 on regulations nevertheless apply only to those aspects of such activity that regularly result in pollution. Nor do the provisions of section 7, second paragraph, cf. fourth paragraph, apply to measures to prevent or stop acute pollution.*

**Discharge permit from the pollution control authority is needed when:**

*§ 13. Any person that is planning any activity which may involve serious pollution at a new site or significant developments of a new character at a site where there is existing activity shall at an early stage of the planning process send notification to the pollution control authority.*

*§ 12. An application for a permit pursuant to section 11 shall contain any information necessary to evaluate whether a permit should be granted and which conditions should be laid down. The pollution control authority may by regulations or in individual cases lay down which information or investigations must be provided by the applicant.*

**The pollution control authority may issue regulation laying down:**

**§9**

- 1. emission limit values for types of pollution that shall be permitted or laying down that pollution shall be prohibited completely or at certain times,*
- 2. threshold limit values for the occurrence of certain substances, noise, vibrations, light and other radiation in the environment, and the measures that shall be taken if these values are exceeded,*
- 3. how permanent and temporary installations shall be set up and how an enterprise shall be managed to prevent pollution,*
- 4. quality requirements for pollution control equipment and a requirement that such equipment must not be sold without being approved by the pollution control authority,*
- 5. that personnel operating an enterprise that may involve pollution shall have specific qualifications.*

*The pollution control authority may in individual cases grant exemptions from regulations that permit pollution if the conditions mentioned in section 18, first paragraph, are fulfilled or if the regulations provide the authority for this.*

**§ 18. Alteration and withdrawal of a permit**

*The pollution control authority may rescind or alter the conditions attached to a permit issued in accordance with this Act or regulations pursuant thereto, or impose new conditions, and if necessary withdraw the permit, if*

- 1. the damage or nuisance caused by the pollution proves to be significantly greater than or different from that anticipated when the permit was issued,*
- 2. the damage or nuisance can be reduced without unreasonable cost to the polluter,*
- 3. new technology makes substantial reduction of the pollution possible,*
- 4. the conditions laid down in the permit are not necessary for the purpose of counteracting pollution,*

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5. *the advantages to the polluter or others of relaxing or rescinding conditions will be substantially greater than the damage or nuisance to the environment that will result, or*
6. *this otherwise follows from the rules for reversing decisions that are currently in force.*

*A permit may in any case be withdrawn or altered if it is more than 10 years since it was issued. [8]*

#### **4.2.2 Regulations regarding discharge of oil.**

OSPAR is a cooperation of fifteen countries in the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic. It started in 1972 with the Oslo Convention against dumping. Decisions and recommendations made by the OSPAR convention are legally binding on the Contracting Parties.

OSPAR Strategy objectives for the offshore oil and gas industry:

- Prevent and eliminate pollution and take the necessary measures to protect the maritime area against the adverse effects of offshore activities.
- Safeguard human health and conserve marine ecosystems and, when practicable, restore marine areas which have been adversely affected.

OSPAR has a target of 15% reduction in the total amount of oil in produced water discharged and the performance standard of dispersed oil of 30mg/l (as in OSPAR Recommendation 2001/1). [10]

Norway is a member of OSPAR and has implemented this decision in “the activities regulations”

#### Chapter XI, § 60 Discharge of oily water

*Oily water shall be cleaned prior to discharge to sea. This does not apply to displacement water.*

*A treatment plant shall be operated with environmentally optimal effect regardless of whether the discharge limitations, cf. the third subsection, can also be met with reduced treatment effect. When evaluating what is the environmentally optimal effect, the degree of treatment shall be evaluated in relation to e.g. use of chemicals.*

*The oil content in water discharged to sea, shall be as low as possible, cf. Chapter II of the Framework Regulations and Sections 7 and 8 of the Management Regulations. The oil content shall not exceed 30 mg oil per litre of water as a weighted average for one calendar month.*

*The operator shall obtain permission according to Chapter 3 of the Pollution Control Act (in Norwegian only) for injection of oily water. [9]*

Chapter XI, § 70 Measuring the discharged quantity of oil, other substances and water

*The content of oil and other substances in the discharges shall be measured. Other substances means substances for which reporting requirements are set, cf. the Climate and Pollution Agency's Guidelines for reporting from offshore petroleum activities. The test results shall be used to verify the treatment plant's performance.*

*The measurement frequency, discharge parameters and measurement methods shall be described in a measurement programme.*

*The measurement programme shall be established such that the scope of measurements is sufficient for the purpose, to ensure representative and comparable measurements.*

*Analyses shall be carried out in a systematic and standardised manner. The oil content of water shall be analysed according to OSPAR's reference method for determining dispersed oil in water (OSPAR ref. No. 2005-15, which is a modification of ISO 9377-2) or analysis methods calibrated towards this.*

*For drainage water, displacement water and injected oily water, the amount of water and content of oil shall be measured, calculated or estimated .[9]*

To comply with “Act of 13 March 1981 No.6 Concerning Protection Against Pollution and Concerning Waste”, “the activities regulations” §60 and the Norwegian governments ambitions of treating waste at point of origin Halliburton has developed an offshore slop treatment unit to treat slop water and oily waste water offshore.

## 5. Halliburton's offshore slop treatment unit

### 5.1 Description of the slop unit

The basic treatment principle in Halliburton's offshore slop treatment unit, *Figure 3*, is chemical flocculation combined with dissolved air flotation (DAF). Chemicals are added to enhance the flotation process. The process can also be run without chemicals on light contaminated water or a mixture can be used on more heavily contaminated slop water. A filtration package (parallel or serial) can also be applied to the process as a safety stage or for light contaminated water treatment.

The slop unit consists of two inlet mixing tanks, a pipe mixer/flocculator with three chemical mixing lines and a dissolved air flotation unit. The entire treatment process is run from a Programmable Logic Controller (PLC), making the process fully automatic with the option of manual operation if preferred. [4]



*Figure 3: Halliburton's offshore slop treatment unit.*

## 5.2 Description of the treatment process

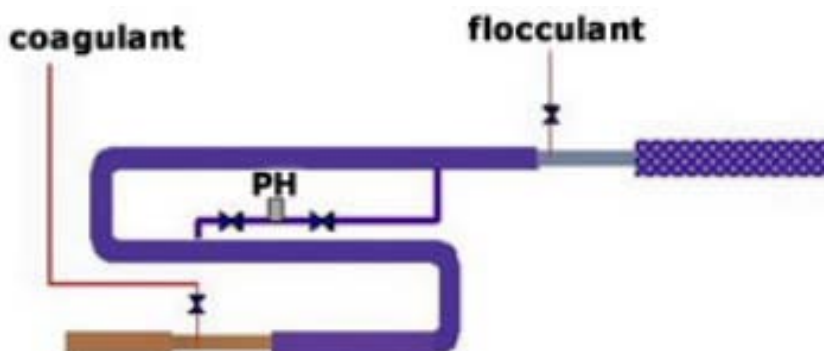
The process starts with settling the slop water in the first inlet tank and then transferring it to a second inlet tank. After the fluid level in the second influent tank has reached a preset level an eccentric screw pump starts to transfer the fluid through the flocculator. In the flocculator chemicals are applied to promote the aggregation of small particles into larger particles to enhance their removal.

The flocculator is a pipe mixer that is specially designed for the type of fluid treated in Halliburton's slop unit, *Figure 4*.



*Figure 4: Pipe Flocculator with chemical dosing lines and pumps. [4]*

The flocculator consists of a series of pipes with two different diameters as shown in *Figure 5*. The mixing point is where the pipes have the smallest diameter. The decrease in diameter ensures turbulent flow in the mixing points which gives an ideal mixing of chemicals into the fluid.



*Figure 5: Principle drawing of the pipe flocculator.[4]*

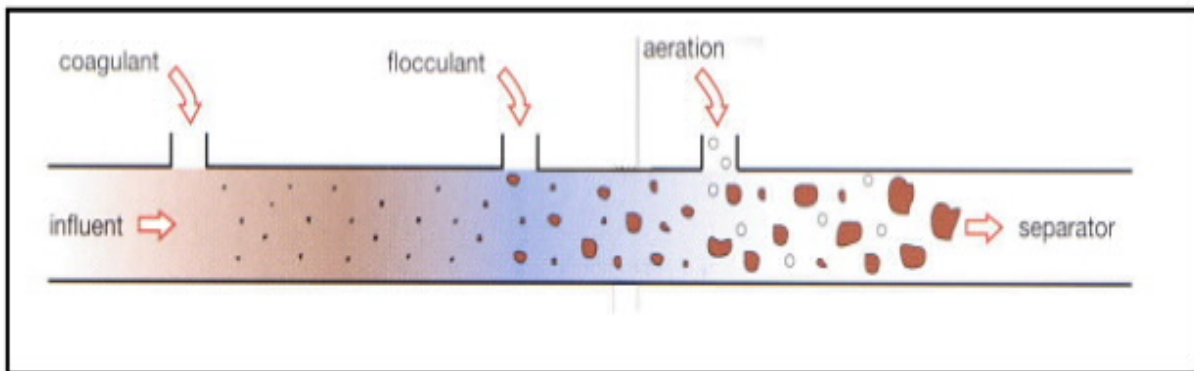


The Slop Treatment Unit has three chemical dosing lines:

1. A pH adjustment dosing line.
2. A flocculent dosing line.
3. Coagulant line if the treatment process requires emulsion breaker and/or coagulant added.

Each of the chemical dosing lines is connected to a mixing point. Chemical dosing pumps located above the flocculator ensures a constant and accurate amount of chemical added to the fluid.

A principal drawing of the build-up of flock's through the pipe flocculator is given in *Figure 6*.



*Figure 6: Principle drawing of flock's build-up. [4]*

The physical properties of the fluid flow in the flocculator can be determined by the Bernoulli's equation:

$$(1) \quad \frac{v^2}{2} + gz + \frac{p}{\rho} = \text{constant}$$

$v$  = The fluid flow speed at a point on a streamline.

$g$  = The gravitational acceleration ( $\text{m/s}^2$ ).

$z$  = The elevation of the point above a reference plane, with the positive  $z$ -direction pointing upward – so in the direction opposite to the gravitational acceleration.

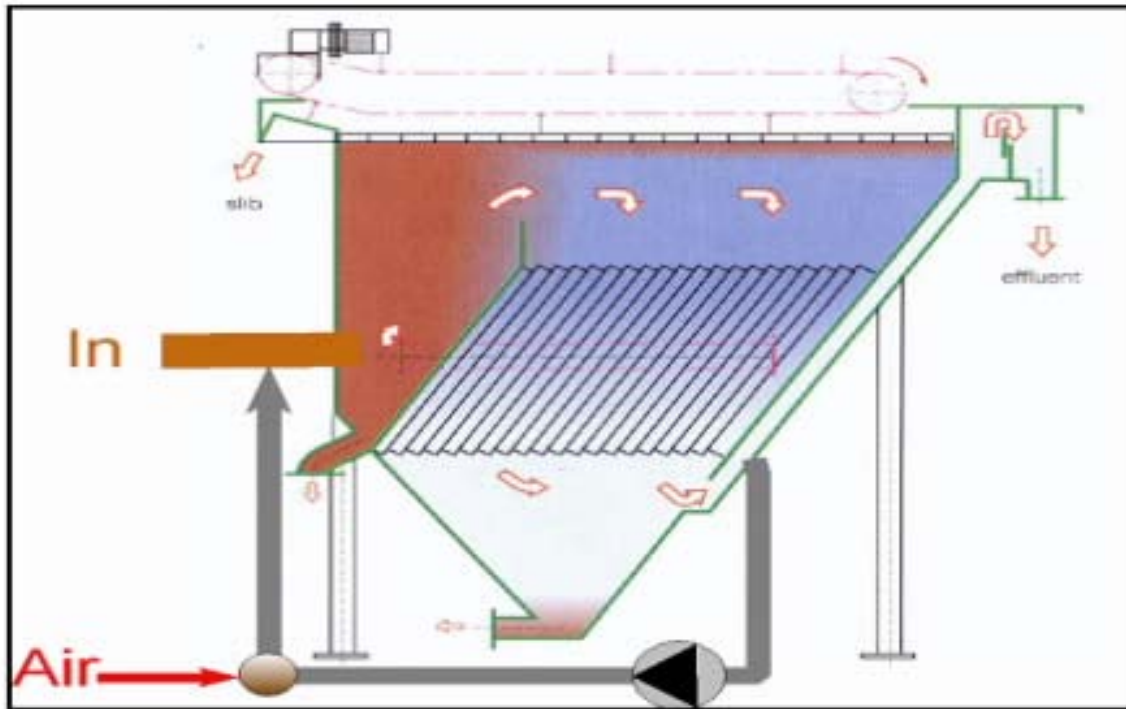
$p$  = The pressure at a specific point.

$\rho$  = The density of the fluid at all points in the fluid.

From the flocculator the slop water is transferred to the dissolved air flotation tank, where light particles, flocks and oil are separated. [4]

Detailed description of the DAF process

The system operates on the principle of counter current separation. Slower rising particles are being separated in the corrugated plate assembly, *Figure 7*. Due to the distance between the plates and the flow regime a laminar flow is maintained between the plates. Particles can travel without interference to the nearest plate. When the particle reaches the plate it will start moving upward against the direction of the flow. This is possible because of the velocity distribution of laminar flow pattern. The flow velocity at the wall (plate) is zero. The particles can therefore move upwards without being restrained.



*Figure 7: Principle drawing of DAF with fluid movement. [4]*

Due to the corrugations, particles will all tend to move through the top of the corrugation. This will result in coalescing with oil and grease and give faster rising velocities. The heavy particles like sand, grains etc. will settle at the bottom of the tank and will be removed from the plate pack concurrently. Whether the particles will rise or settle at the bottom, are determined by Stoke's law:

$$(2) \quad V_s = \frac{2(\rho_p - \rho_f)}{9\mu} g R^2$$

$V_s$  = The particles' settling velocity (m/s) (vertically downwards if  $\rho_p > \rho_f$ , upwards if  $\rho_p < \rho_f$ )

$g$  = The gravitational acceleration ( $m/s^2$ )

$\rho_p$  = The mass density of the particles ( $kg/m^3$ )

$\rho_f$  = The mass density of the fluid ( $kg/m^3$ )

$\mu$  = The fluids viscosity ( $kg\ m^{-1}\ s^{-1}$ )

$R$  = The radius of the particle (m)

Clean water is withdrawn from a middle section in the flotation tank. The treated water can then either go directly to discharge or through a second polishing stage by using filters. The clarified water leaves the plate assembly at the bottom side and is discharged via effluent channels and an adjustable overflow weir. This weir is adjusted to the actual conditions of flow and sludge characteristics. The sludge that is floating at the top is scraped of the water with a skimmer and transported to the sludge tank, *Figure 8*.



*Figure 8: Sludge tank. [4]*

A fraction of the clean water is recycled and saturated with air at pressures above atmospheric pressure. The air will leave the liquid state as small air bubbles upon pressure relief. The bubbles will attach to the particles and the particles will rise upwards to the surface. This recycling process is done by dosing air into a saturation pipe right after the recirculation pump. This is a specially designed pipe, which saturates the water with air at a pressure between 4 and 7 bar.

Most of the air is dissolved in the water by the mixing action in the inlet section of the pipe. In the aeration pipe the air is further dissolved. At a specific point in the pipe a de-aeration valve is installed to release air that is not dissolved.

The depressurization takes place just before the aerated water is mixed with the influent. The entire treatment process is run automatically by a PLC in the electrical cabinet. [4]

According to the “activities regulations” § 70 the content of oil and other substances in the discharges shall be measured to verify the treatment plant performance. To verify that the discharge of oily water is according to § 60 Halliburton uses an online oil in water analyzer called Advanced Sensors OIW EX 1000. This instrument is based on molecular fluorescence spectroscopy.

## 6. Spectroscopy

The ability to analyse compounds and finding the properties of different chemicals are important in many fields; for instance the development of materials and medicine, environmental monitoring and research. Some effective and widely used analytic methods are measurements that are based on light and other forms of electromagnetic radiation.

Common for all spectrometric methods is that the analysis results in a specter that will give information about the sample. The specter can show how molecules behave when they are exposed to electromagnetic radiation at a certain wavelength and energy. Depending on the wavelength the electromagnetic radiation can result in a change in how the electrons are distributed around the nucleus of the atom, how the electrons or nucleoside orient them self according to each other, or how the molecules rotate, vibrate or moves. [16]

### 6.1 Electromagnetic radiation

Electromagnetic radiation is a form of energy transmitted through space at very fast velocities. It can be described as a wave with properties of wavelength, frequency, velocity and amplitude. In order of increasing frequency and decreasing wavelength the electromagnetic spectrum consist of gamma rays, x-rays, ultraviolet radiation, visible light, infrared radiation, microwaves and radio waves,. Radiation with wavelengths between 400 - 750 nm can be detected by the human eye and are perceived as visible light as seen in *Figure 9*. [17]

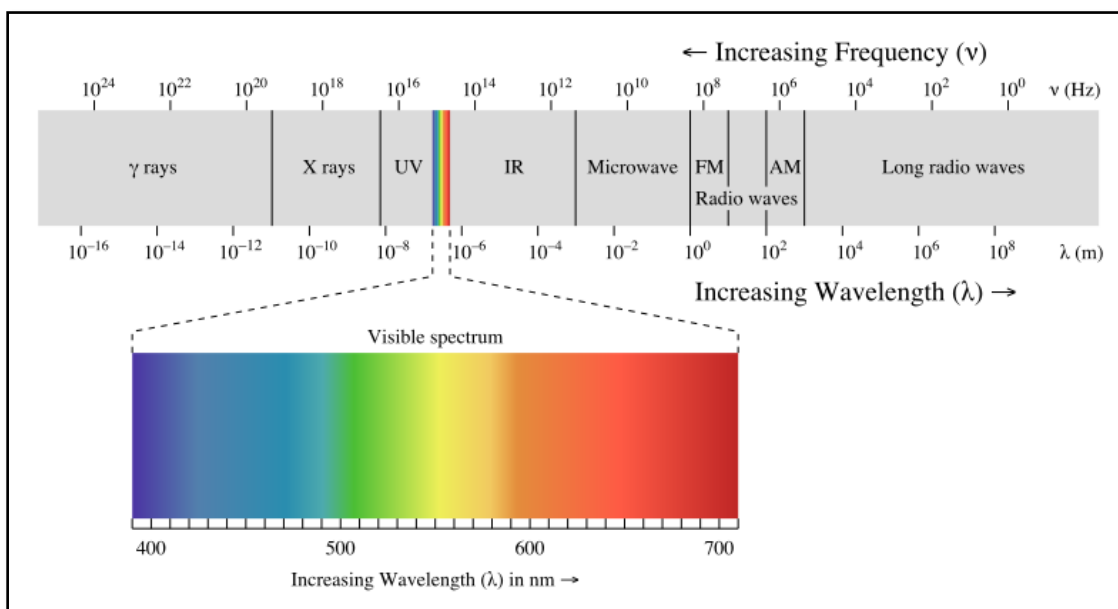


Figure 9: Electromagnetic radiation. [20]

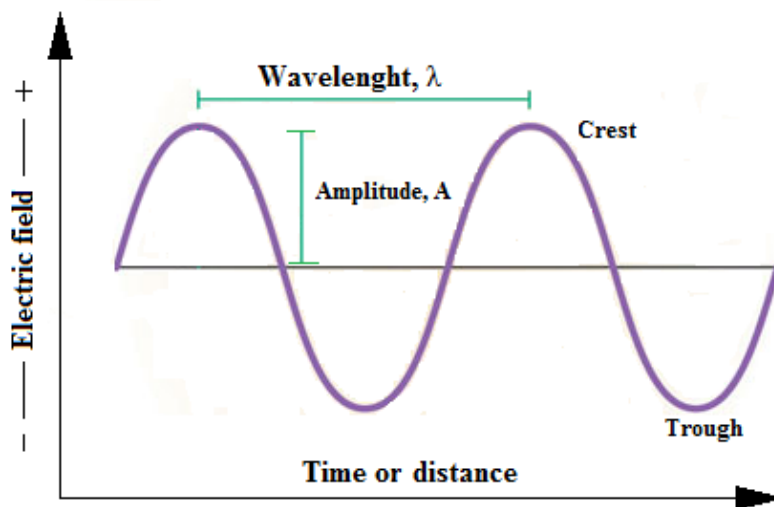
### 6.1.1 Wave properties

As explained at previous page, a wave has different properties, *Figure 10*.

1. Amplitude: A wave's intensity is measured at its amplitude, which is the maximum height of the wave's peak.
2. Wavelength: A wave's wavelength ( $\lambda$ ) is the distance between two following wave crests or trough.
3. Frequency: A wave's frequency ( $n$ ) is the number of oscillations that occur in one second. The unit of frequency is Hertz which correspond to one cycle per second.  $1\text{Hz} = 1\text{s}^{-1}$ .
4. Wavenumber: ( $\tilde{\nu}$ ) is the reciprocal of its wavelength in centimetre, the number of wavelengths per unit distance where  $\tilde{\nu} = 1 / \lambda$ .
5. Period: It is the time in seconds for the passage of successive maxima or minima to pass a point in space.

For each wave there is a connection between its wavelength and frequency. Multiplication of the frequency (in wave per unit per time) by the wavelength (in distance per wave) equals the velocity of the wave. [17]

$$(3) \quad (\text{wavelength}) \times (\text{frequency}) = \text{velocity} \rightarrow \lambda * \nu = c$$



*Figure 10: wave properties [17]*

A German scientist named Max Planck studied in 1900 the light that was emitted from heated objects. He concluded that light sometimes behave as it was composed of small particles or quanta of energy, later called photons. He also discovered that the energy to a photon was proportional to the frequency of the light. The energy per photon can be calculated from the Planck–Einstein equation,

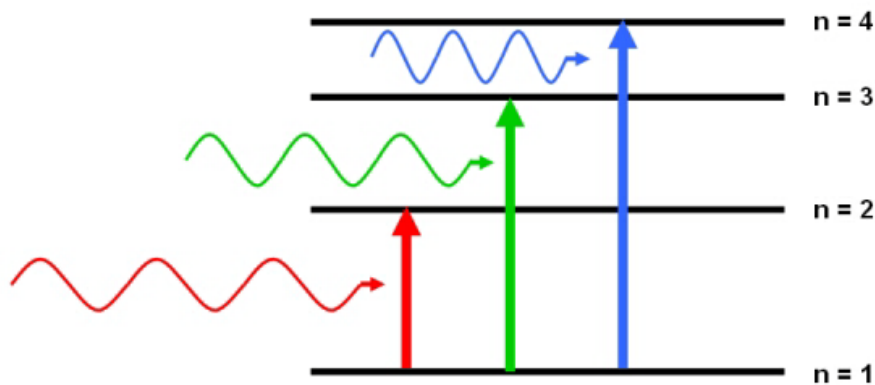
$$(4) \quad E_{\text{photon}} = h * \nu$$

where  $h$  is a Planck's constant ( $6.63 * 10^{-34}$  J s). [17]



## 6.2 Absorption and emission of electromagnetic radiation

In spectroscopy absorption is a process in where chemical species in a transparent medium decreases the intensity of certain frequencies of electromagnetic radiation. Every elementary particle has according to the quantum theory a unique set of energy states. Most particles are at room temperature at the lowest level, called ground state. When a photon of electromagnetic radiation passes an elementary particle absorption is possible if the energy difference of the ground state and a higher energy level of the particle matches exactly the photons energy. If the photon is absorbed the photons energy is transferred to the atom, ion or molecule and promoted to a higher energy state. This process is called excitation and can be shown in *Figure 11* where  $n=1$  equals ground state. [18]



*Figure 11: Excitation.*

Excitation can be described by the equation:



Where  $M^*$  is the species in the excited state.

After a short time ( $10^{-6}$  to  $10^{-9}$ s) the excited species will give up their excess energy and relax back to ground state. In this process there is a small increase in temperature of the surroundings that can be described by the following equation:



Relaxation can also occur by photochemical decomposition of  $M^*$  to create new species or by the fluorescent or phosphorescent reemission of radiation. [18]

### 6.3 Spectroscopy methods.

Spectrometry and spectrometric methods are based on atomic and molecular spectroscopy, where the intensity of radiation is measured with a photoelectric transducer or another type of electronic device. Spectroscopy has played an important role in the atomic theory. It has been used to explain the molecular structure as well as the quantitative and qualitative determination of organic and inorganic compounds. [17]

In spectrometric methods the interactions of radiation with matter is used to obtain information about the sample. The sample is usually stimulated by applying energy in the form of heat, electric energy, light, particles or a chemical reaction. Before applying the stimulus, the species in the sample is mainly in its lowest energy state, ground state. Then after the sample is stimulated with energy the species undergo transition to a higher energy or excited state. To get information about the sample the electromagnetic radiation that is emitted is measured as it returns to ground state or by measuring the quantity of electromagnetic radiation absorbed as a result of excitation. [15, 18]

There are four major classes of spectrochemical methods; Absorption, emission, luminescence and scattering. They all require energy from a beam of radiation, a radiant power  $P$ , which reaches a given area per second. The difference between them is which radiant power is measured, Table 1.

Table 1: Major classes of spectrochemical methods. [15]

Class	Radiant Power Measured	Type of methods
Emission	Emitted, $P_e$	Atomic emission
Luminescence	Luminescent, $P_l$	Photoluminescence and chemiluminescence
Scattering	Scattered, $P_{SC}$	Raman scattering, turbidimetry and particle sizing
Absorption	Insident, $P_0$ and transmitted, $P$	Atomic and molecular absorption

In absorption spectroscopy the amount of light absorbed as a function of wavelength is measured. Two different measurements will be performed; one before the beam has passed through the sample ( $P_0$ ) and one after ( $P$ ). There are two terms that are used in absorption spectroscopy that relate to the ratio between  $P_0$  and  $P$ ; transmittance and absorbance. [15, 18]

Transmittance:

Transmittance,  $T$ , of the medium is the fraction of incident radiation transmitted by the medium.

$$(7) \quad T = \frac{P_{\text{solution}}}{P_{\text{solvent}}}$$

Transmittance is often expressed in percentage.

Absorbance:

The absorbance of a medium is the logarithm of  $1/T$

$$(8) \quad T = \frac{P_{\text{solvent}}}{P_{\text{solution}}} \approx \log \frac{P_0}{P}$$

In emission, luminescence and scattering methods the measurement are performed of the radiant power emitted of the sample as it relax back to ground state. These measurements can give information about the identities of the species in the sample or the concentration. [15]

## 7. Fluorescence Spectroscopy

In photoluminescence spectroscopy the emission of photons are measured after absorption. Two of the most important types of photoluminescence are fluorescence and phosphorescence spectroscopy. The difference between them is that the transitions responsible for fluorescence do not involve a change in electron spin. Fluorescence is therefore much faster than phosphorescence and is generally complete in about  $10^{-5}$  s from the time of excitation. A fluorophore is a substance which causes a molecule to be fluorescent.

One of the best features of luminescence methods is their inherent sensitivity with detection limits that are often one to three orders of magnitude lower than those encountered in absorption spectroscopy. In some selective species it is possible to detect single molecules with fluorescence spectroscopy. [15, 18]

### 7.1 Electron Spin

According to the Pauli Exclusion Principle; two electrons cannot have the same four quantum numbers ( $n, l, m_l, m_s$ ). This limits the number of electrons to two in each orbital and requires that they have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing these molecules are diamagnetic; the electrons are not attracted or repelled by the static electric field. Free radicals are however said to be paramagnetic because they contain unpaired electrons and have magnetic moments that are attracted to the magnetic field. [15]

#### 7.1.1 Singlet and triplet excited states.

In *singlet state* all the electrons are paired and there is no splitting of the electronic energy levels if the molecule is exposed to a magnetic field. The ground state of a free radical can have two possible orientations for the odd electron in the magnetic field and is therefore called *doublet state*. A singlet or *triplet state* is formed when one of the electrons in a pair is excited to a higher energy level. In the excited singlet state, the spin of the electron in excited and ground state are still paired. In triplet state on the other hand the spins in the excited and ground state are not paired. This phenomenon is illustrated in *Figure 12*. The properties of a molecule in triplet excited state differ and are less energetic than a molecule in corresponding excited singlet state. [15]

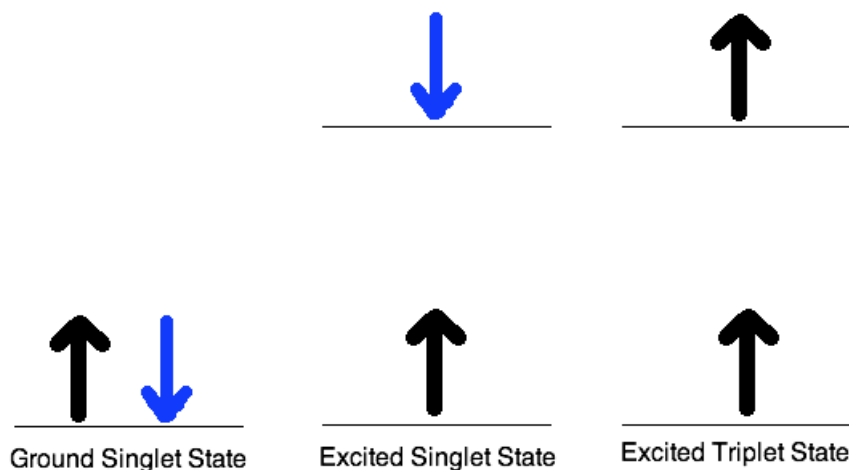


Figure 12: Electron spin states of a molecule.

In fluorescence the emission of light is from singlet excited states and in phosphorescence the emission of light is from the triplet excited state. Since the transitions to ground state in phosphorescence is “forbidden” (two electrons with same spin configuration) the emission rates are slow. [22]

## 7.2 Jablonski diagram

The overall energy  $E$  that can be associated with the bands of a molecule consists of three components;

$$(9) \quad E = E_{\text{electronic}} + E_{\text{rotational}} + E_{\text{vibrational}}$$

- Electronic energy is the energy associated with the electrons in the different outer orbitals.
- Rotational energy is the energy associated with the center of gravity of a molecule.
- Vibrational energy is the energy associated with the molecule as a whole due to interatomic vibrations.

A Jablonski diagram is graphical representation of a molecule’s energy levels with a few of the numerous electronic and vibrational states. The diagram can be used to describe the process that occur when a fluorophore absorb and emit light, *Figure 13*. In the diagram the lines depicted as  $S_0$ ,  $S_1$  and  $S_2$  represent the electronic ground, first and second electronic ground states and the line depicted as  $T_1$  is the first electronic triplet state. The energy of the first excited triplet state is lower than the energy for the corresponding singlet state. The thinner horizontal lines at each electronic level represent some of the numerous vibrational levels. The upper thick lines are the ground vibrational state of the three excited electronic state. [15, 22]

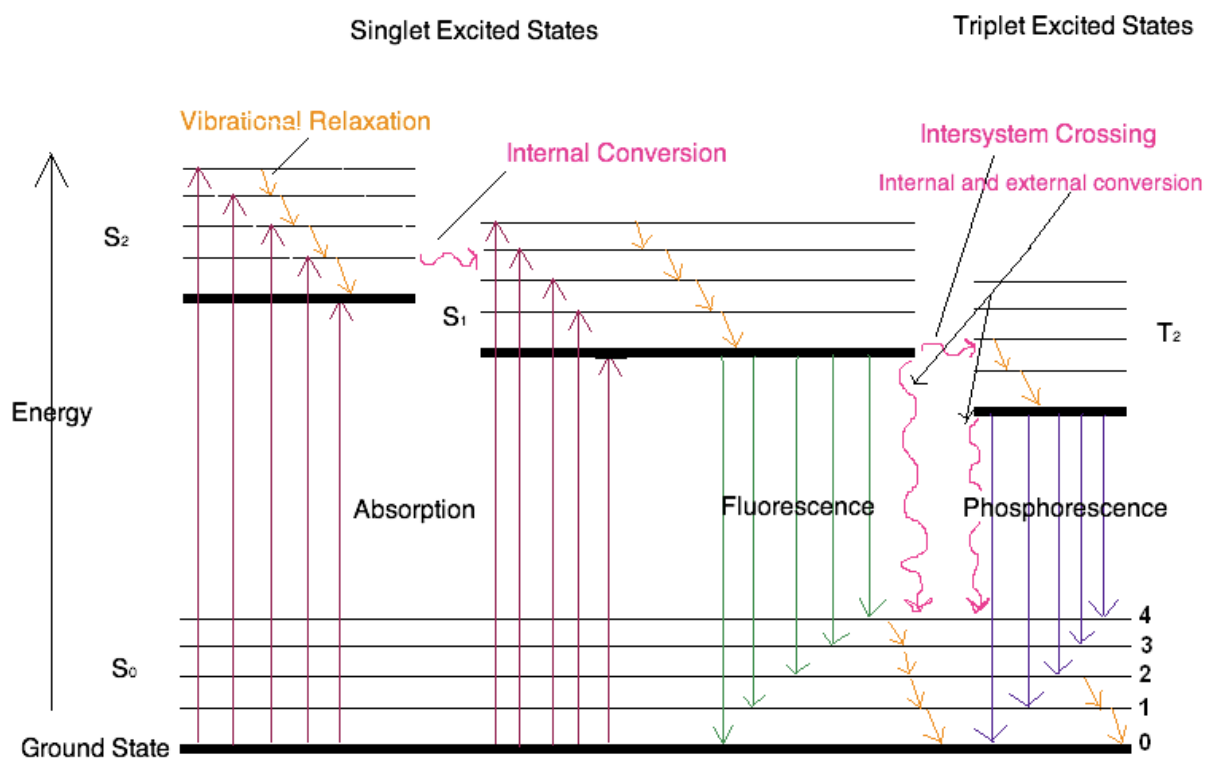


Figure 13: Jablonski diagram.[28]

## 7.3 Characteristics of fluorescence emission.

### 7.3.1 Atomic fluorescence

Fluorescence spectrometry is based on atomic and molecular spectrometry. In atomic fluorescence spectrometry (AFS) gaseous atoms fluoresce when they are exposed to radiation that has the same wavelength as one of their absorption or emission lines. When the excitation and emission wavelengths are the same it results in an emission that is called resonance fluorescence. AFS is useful to study the electronic structure of atoms and to perform quantitative measurements of sample concentrations. In AFS the sample is nebulized by a flow of gaseous oxidant and blended with a gaseous fuel before it is transported into a flame where atomization occurs. The emission resulting from the decay of the atoms excited by the source light is measured and the intensity of fluorescence will increase with increasing atom concentration. [15, 18, 24]



### 7.3.2 Molecular fluorescence

Molecular fluorescence spectrometry is much more complex than AFS and a relative small number will fluoresce because fluorescence requires structural features that will reduce the rate of other deactivation processes. In the Jablonski diagram, *Figure 13*, the fluorescence lines normally consists of only one band with many closely spaced lines that represent radiation from relaxation; this is because the internal conversion and vibrational relaxations are very fast compared to fluorescence. Due to vibrational relaxation, fluorescence will always involve a transition from the lowest vibrational level of an excited electronic state to one of the vibrational levels in ground state. The fluorescence band will then be displaced towards lower frequency or wavelengths than the band of absorbed radiation responsible for their excitation. This phenomenon was first discovered by Sir. George Gabriel Stokes and is called the Stokes shift. Transition from  $E_1$  to the lowest lying vibrational state in  $E_0$ ,  $\lambda_1$ , has the highest energy and produce fluorescence emission with the shortest wavelength. [15, 22]

## 7.4 Deactivation Processes

As seen from *Figure 13*, a fluorophore can return to its ground state by a combination of several mechanistic steps. The deactivation process of fluorescence and phosphorescence involve an emission of a photon radiation as shown in *Figure 13* by the straight downward pointing arrows. The wavy arrows in *Figure 13* are other deactivation processes without the use of radiation. The deactivation process that is favored is the one with the route that is most rapid and spends less time in the excited state. If and how intense a compound will fluoresce, is therefore depended on which path is most favorable. [15, 22]

### 7.4.1 Vibrational deactivation/ relaxation

Vibrational deactivation takes place during collision between excited molecules and molecules of the solvent. Under the collisions, the excess vibrational energy is transferred to the solvent molecules in a series of steps, as described with orange arrows in *Figure 13*. Vibrational excitation is a so rapid and efficient process that the average lifetime is much shorter than the average lifetime of any electronic state. [15, 18]

### 7.4.2 Internal conversion

Internal conversion is relaxation between the lowest vibrational level of an excited electronic state and the upper vibrational level of another electronic state. It is described in *Figure 13* with pink wavy arrows. The probability for it to occur is much higher if two electronic energy levels are close enough for an overlap in the vibrational levels. If the vibrational levels overlap, internal conversion is more likely to happen than fluorescence. [15, 18]

### 7.4.3 External Conversion

External conversion is interactions and energy transfer between the excited molecule and the solvent or other solute. This process can have an effect on the fluorescence intensity. [15]

### 7.4.4 Intersystem crossing

Intersystem crossing is transition between two electronic states with different multiplicity. The process that is most common is from the first singlet state ( $S_1$ ) to the first triplet excited state ( $T_1$ ). The process is more likely to occur if the vibrational levels of the two states overlap and is most common in heavy atoms. [15, 22]

### 7.4.5 Phosphorescence

Phosphorescence is emission from triplet state and can occur after intersystem crossing. It is normally shifted to longer wavelengths relative to fluorescence. Transition from triplet to singlet ground state are forbidden and it is therefore a much slower process than fluorescence. External and internal conversion from triplet state are often much more favorable than phosphorescence and it is therefore generally just seen at low temperatures in highly viscous media. [15, 22]

## 7.5 Variables affecting fluorescence

### 7.5.1 Fluorescence lifetime and quantum yield ( $\Phi$ )

Fluorescence lifetime and quantum yield are one of the most important characteristics of a fluorophore. Quantum yield is the total number of emitted photons relative to the total number of absorbed photons. For highly fluorescent molecules the quantum efficiency approaches unity under some conditions. Compounds that don't fluoresce appreciably have efficiencies near zero, therefore the higher quantum yield value the brighter emission.

It can be determined by the following equation:

$$(10) \quad \Phi = \frac{k_f}{k_f + k_i + k_{ec} + k_{ic} + k_{pd} + k_d}$$

$k_f$  = fluorescence  
 $k_i$  = intersystem crossing  
 $k_{ec}$  = external conversion  
 $k_{ic}$  = internal conversion  
 $k_{pd}$  = predissociation  
 $k_d$  = dissociation

To only focus on the processes that are responsible for the return to ground state the equation can be simplified;

$$(11) \quad \Phi = \frac{\Gamma}{\Gamma + k_{nr}}$$

$\Gamma = k_f =$  emissive rate of the fluorophore  
 $k_{nr}$  = is the nonradiative decay to  $S_0$ .

The fluorescence lifetime is the average time the molecule stays in its excited state before emitting a photon. Generally fluorescence lifetimes are near 10 ns. It can be determined by the following equation:

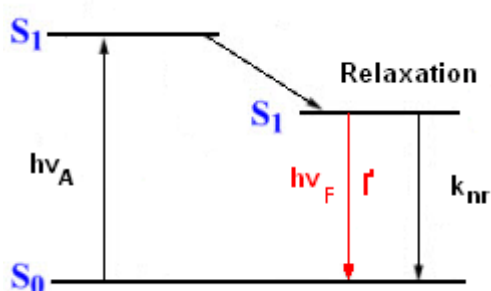
$$(12) \quad \tau = \frac{1}{\Gamma + k_{nr}} \quad \tau = \text{fluorescence lifetime}$$

Fluorescence is a random process and there are only a few molecules that will emit photons at exactly  $t = \tau$ , the fluorescence lifetime is therefore an average value.

The lifetime of a fluorophore in the absence of nonradiative processes is named intrinsic or natural lifetime ( $\tau_n$ ) and can be determined by the following equation:

$$(13) \quad \tau_n = \frac{1}{\Gamma}$$

Quantum yield and lifetime can be illustrated by *Figure 14*.



*Figure 14: Illustration of quantum yield and lifetime.*

Fluorescence lifetime can provide information about the collisional deactivation processes, energy transfers rates and excited-state reactions. It can also be used analytically to give additional selectivity in the analysis of a sample with a mixture of fluorophores. [15, 22]

### 7.5.2 Transition types in fluorescence

Fluorescence seldom results from absorption of ultraviolet radiation shorter than 250 nm. Radiation below this is sufficiently energetic to cause deactivation of the excited states by predissociation or dissociation. Fluorescence usually arises from a transition from the lowest vibrational levels of the first excited electronic state to one of the vibrational levels of the electronic ground state. Therefore the radiation from the most fluorescent compounds are produced by either a  $\pi \rightarrow n$  (excited state) or a  $\pi \rightarrow \pi^*$  (excited singlet state), depending on which is less energetic.  $\pi \rightarrow \pi^*$  transitions are

most common because these excited states exhibit relatively short average lifetimes and the other deactivation processes are less likely to occur. [15]

### 7.5.3 Fluorescence and structure

Fluorophores can be divided into two major groups intrinsic and extrinsic. Intrinsic fluorophores are those who occur naturally. Extrinsic fluorophores can be added to a sample that doesn't contain a fluorophore to provide fluorescence or to change a sample's spectral properties. [22]

Fluorophores that have the most intense and useful fluorescence contain aromatic functional groups with low energy  $\pi \rightarrow \pi^*$  transitions. A small number of compounds containing alicyclic and aliphatic carbonyl structures or highly conjugated double-bonds structures may also exhibit fluorescence. Most simple heterocyclic compounds will not exhibit fluorescence but if they have fused-ring structures they can emit fluorescence. Most unsubstituted aromatic hydrocarbons fluoresce in solution and the efficiency increases with number of number of rings and their degree of condensation, Table 2. [15]

Table 2: Effect of substitution on the fluorescence of Benzene derivates. [15]

Effect of Substitution on the Fluorescence of Benzene Derivatives*	
Compound	Relative Intensity of Fluorescence
Benzene	10
Toluene	17
Propylbenzene	17
Fluorobenzene	10
Chlorobenzene	7
Bromobenzene	5
Iodobenzene	0
Phenol	18
Phenolate ion	10
Anisole	20
Aniline	20
Anilinium ion	0
Benzoic acid	3
Benzonitrile	20
Nitrobenzene	0

The relative intensity of fluorescence increases as oxygenated compounds increases in substitution.

In halogen substitution the fluorescence intensity will decrease as the molar mass of the halogen increases. This is called the "heavy atom effect" and the probability of intersystem crossing will therefore increases as the size of the molecule increases. For instance in substitution of a heavy halogen such as iodobenzene, the compounds are subject to predissociation. The bonds in these compounds will easily rupture and will absorb excitation energy and go through internal conversion. Therefore, the relative intensity of fluorescence and fluorescent wavelength will not be observed.

An aromatic ring containing an carboxylic acid or carbonyl group will most likely inhibit fluorescence since the energy of the  $n \rightarrow \pi^*$  transition is less than  $\pi \rightarrow \pi^*$  transition. Therefore, the fluorescence yield from  $n \rightarrow \pi^*$  transition is low. [15, 22]

#### 7.5.4 Effect of structural rigidity

Fluorescence is particularly favored in molecules with rigid structures. The rigidity lowers the rate of nonradiative relaxation so that fluorescence may occur. The lack of rigidity will most likely be due to the enhanced internal conversion rate ( $k_{ic}$ ) which increases the probability that there will be radiationless deactivation. Molecules that are not rigid can also undergo low-frequency vibration which accounts for small energy loss. [15, 22]

#### 7.5.5 Solvent and environmental effects

The solvents polarity and the local environment have a profound effect on the emission spectral properties of a sample. The effect is complex and due to several factors in addition to solvent polarity.

The factors that affect fluorescence emission spectra and quantum yield are:

- Solvent polarity and viscosity.
- Rate of solvent relaxation.
- Probe conformational changes.
- Rigidity of the local environment.
- Internal charge transfer.
- Proton transfer and excited state reactions.
- Probe-probe interactions.
- Changes in radiative and non-radiative decay rates.

When considering environmental effects the solvents polarity is the most important. Environmental effects are complex and polarity can't be described with only one theory. The Lippert equation (14) can be used to describe polarity but it doesn't take into account other affects such as hydrogen bonding and internal charge transfer.

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc} \left( \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \frac{(\mu_E - \mu_G)^2}{a^3} + \text{constant}$$

(14)

$h$  = Planck's constant ( $6.6256 \cdot 10^{-27}$  ergs)

$\epsilon$  = dielectric constant of the solvent

$n$  = refractive index

$\bar{\nu}_A$  = wavenumber of absorption (cm<sup>-1</sup>)

$\bar{\nu}_F$  = wavenumber of emission (cm<sup>-1</sup>)

$\mu_E$  = the dipole moment in excited state

$\mu_G$  = the dipole moment in ground state

$c$  = speed of light ( $2.9979 \cdot 10^{10}$  cm/s)

$a$  = the cavity where the fluorophore resides.

*Constant* = reflects to the Stokes shift that results from the vibrational relaxation and internal conversion effects.

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The fluorophore will typically have a larger dipole moment in the excited state ( $\mu_E$ ) than in ground state ( $\mu_G$ ). Following excitation the solvents dipoles can reorient or relax around  $\mu_E$ , this will decrease the energy of the excited state. When the polarity of the solvent increases this effect becomes larger and leads to emission at lower energies or longer wavelengths. Fluorophores that are polar will generally have a large sensitivity to solvent polarity. Nonpolar species such as unsubstituted aromatic hydrocarbons are less sensitive to the solvents' polarity. The lifetime of the fluorophore is much longer than the time for the solvent relaxation. The solvent polarity can therefore have a profound effect on the emission spectra since the emitting fluorophore is exposed to the relaxed environment that contains solvent molecules that are oriented around the dipole moment of excited state.

With increasing temperature the quantum efficiency of fluorescence in most molecules decreases. This is because the increased frequency of collisions at high temperatures increases the probability for deactivation by external conversion. This also happens with a decrease in a solvents viscosity.

The fluorescence of a molecule is decreased by solvents containing heavy atoms. This is a result of orbital spin interactions that lead to an increase in the rate of triplet formation and a corresponding decrease in fluorescence. [15, 22]

#### **7.5.6 Effect of pH on fluorescence**

The fluorescence of an aromatic compound is usually pH depended if they have a acidic or alkaline ring substituent. Both the emission intensity and the wavelength are likely to be different for the protonated and unprotonated forms of the compounds. An example is fluorescence of the phenolic form of 1-naphtol-4-sulfonic acid. This compound is not detectable by the human eye because it occurs in the ultraviolet region. If the compound is added base and converted to the phenolate ion, the emission band shift to visible wavelength and can be seen. [15]

#### **7.5.7 Fluorescence quenching**

Fluorescence quenching refers to any process that will decrease the intensity of a sample. Many molecular interactions can result in quenching; excited state reactions, molecular arrangement, energy transfer, ground-state complex formation and collision quenching. For instance in dynamic quenching, there is a nonradiative energy transfer in collisions between the excited and quenching agent species. Dynamic quenching will reduce the fluorescence quantum yield and the fluorescence lifetime.

In *Static quenching* the quencher and a fluorophore in ground state creates a complex called the dark complex. Fluorescence is normally only observed from unbound fluorophores. Static quenching differs from dynamic quenching in that the lifetime is not affected. [15, 22]



### 7.5.8 Effect of concentration on fluorescence intensity

The power of fluorescent radiation  $F$  is proportional to the radiant power of the excitation beam that is absorbed by the system:

$$(15) \quad F = K'(P_0 - P)$$

Here  $P_0$  represent the power of the beam before it goes through the sample.  $P$  is the power after the beam traverses a length  $b$  through the sample.  $K'$  is a constant that depends upon the quantum efficiency of the fluorescence.

From equation (8) absorbance can be found by the equation Beer's law;

$$(16) \quad \text{Log} \frac{P_0}{P} = \epsilon bc$$

Where  $\epsilon$  is the molar absorptivity of the fluorophores and  $c$  is the concentration. To relate  $F$  to the concentration Beer's law is expressed in exponential form:

$$(17) \quad \frac{P_0}{P} = 10^{-\epsilon bc}$$

By combining equation (16) and (17);

$$(18) \quad F = K' P_0 (1 - 10^{-\epsilon bc})$$

Expansion of the equation (18)

$$(19) \quad F = K' P_0 [2.3\epsilon bc - \frac{(-2.3\epsilon bc)^2}{2!} - \frac{(-2.3\epsilon bc)^3}{3!} - \dots ]$$

If the absorbance ( $\epsilon bc$ ) is less than 0.05 the subsequent terms in the bracket are insignificant compared to the first;

$$(20) \quad F = 2.3K' \epsilon bc P_0$$

Or at a constant  $P_0$ ;

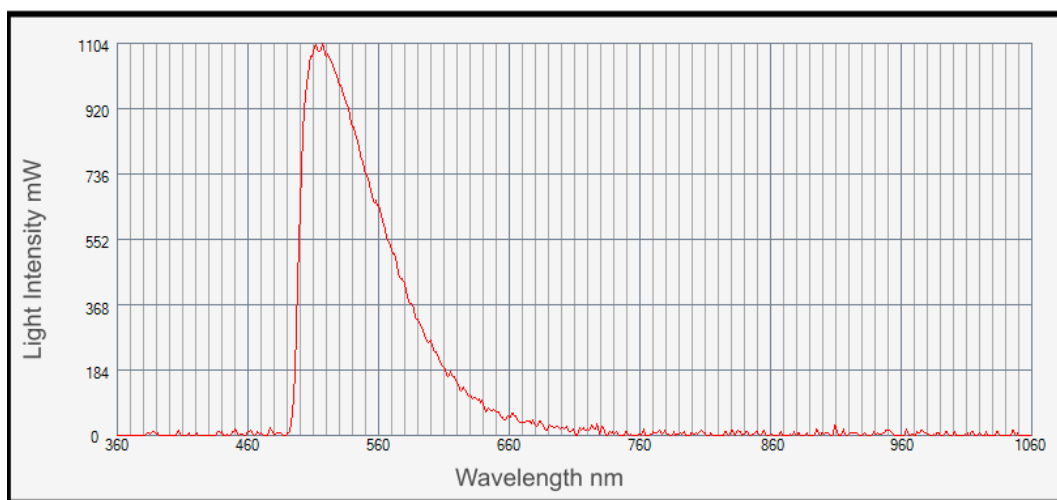
$$(21) \quad F = Kc$$

If the fluorescence power of a sample is plotted against the concentration of the fluorophores, the curve should be linear at low concentrations. When the concentration is high enough so that the absorbance is more than 0.05, the curve will no longer be linear. This excessive absorption is the primary absorption. Another reason of this loss of linearity is the secondary absorption when the wavelength of emission overlaps the

absorption band. This happens when the emission transverse the solution and gets reabsorbed by other analyte molecules in the sample, which leads to a decrease in fluorescence. [18]

## 7.6 Emission spectra

Emission spectra are usually used to present fluorescence spectral data. The spectrum is a plot of fluorescence intensity versus wavelength (nanometers) or wavenumber ( $\text{cm}^{-1}$ ). The spectra may vary widely and are depended on the chemical structure of the compound and on the solvent. *Figure 15* illustrates an emission spectrum of one of Halliburton's emulsifiers. The spectrum shows that at wavelength 515 nm the curve has its peaks with a light intensity of 1104 mW.



*Figure 15: Emission spectra.*

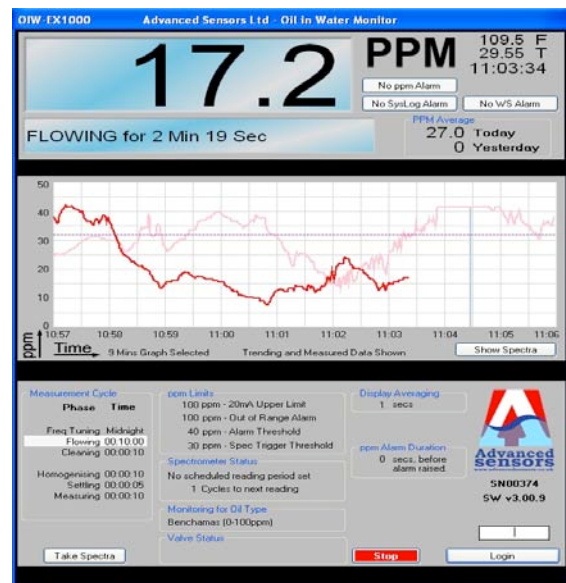
Emission spectra are generally independent of the excitation wavelength; the Kasha's rule. Before excitation into higher electronic and vibrational levels, the excess energy is rapidly dissipated and the fluorophore will be left in the lowest vibrational level of  $S_1$ , *Figure 13*. The relaxation to ground state will happen in about  $10^{-12}$  s and are most likely a result of strong overlap among numerous states of nearly equal energy. Because this relaxation is very fast, emission spectra are usually independent of the excitation wavelength. [22]

## 8. Advanced Sensors OIW EX 1000

The Advanced Sensors OIW EX 1000 is a UV fluorescence instrument that can measure the content of oil in discharged water, *Figure 16*. The device can be applied to the process on-line, in-line or at-line. Halliburton operates the instrument on-line, it is then installed downstream of the slop treatment unit as illustrated in *Figure 18*. A small fraction of the slop water will then bypass through the analyzer. Measurements are performed at a set time and the average oil content for each 24 hour is reported. The standard for these analyses is ISO 9377-2. [2]



*Figure 16: OIW EX 1000. [2]*



*Figure 17: Operating system. [2]*

The OIW EX 1000 is based on a standard Windows XP Pro interface and all measurement is stored on the hard drive, *Figure 17*. The instrument can both measure oil in water in mg/l /ppm/ppb and display a spectrum of the oil type that is measured.

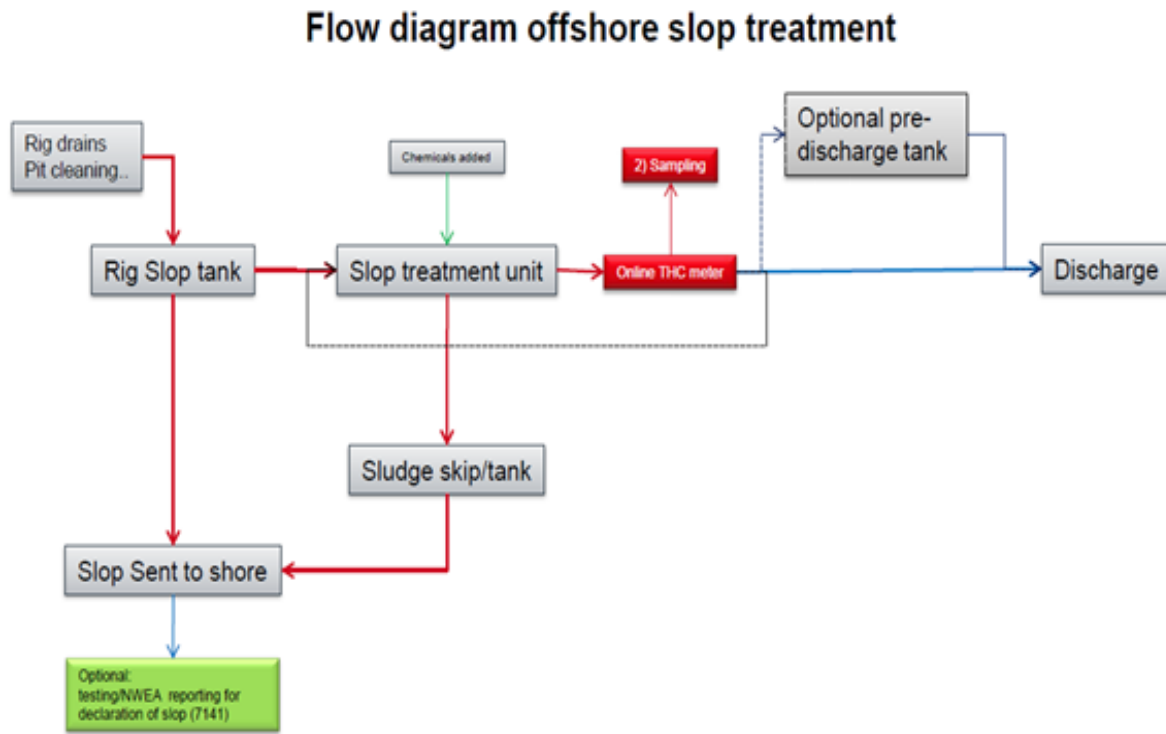


Figure 18: Flow diagram of offshore slop treatment. [4]

## 8.1 Analysis principle

The analyzer will send UV radiation with a specific wavelength through the sample in the sample chamber. The fluorophores in the samples will be excited from ground state to a higher electronic state. When the fluorophores relax back to ground state they will give up their excess energy, this energy is measured by the analyzer. The analyzer will read the fluorescence intensity at a specific wavelength and convert this intensity to concentration (ppm/ppb/mg/l) by using the oil type's calibration curve. The fluorescence band will be displaced at a lower frequency or wavelength than the band of absorbed radiation responsible for their excitation due to Stokes shift, see section 7.3.2. If and how much a compound will fluoresce is depended on its structure and composition. [15, 19, 22]

The instrument has two main functions:

- Measure the oil concentration (ppm/ppb/mg/l) by the help of a photomultiplier tube.
- Compose spectra of the readings by the help of a charge-coupled device.

Each compound has a unique spectrum, a “fingerprint” that is used to either identify the correct compound or differentiate between them. A mask may be applied to the curve to increase the area of the “fingerprint” and to rule out any uncertainties in the readings of the relative intensity and ensure correct readings, *Figure 19*. [19]

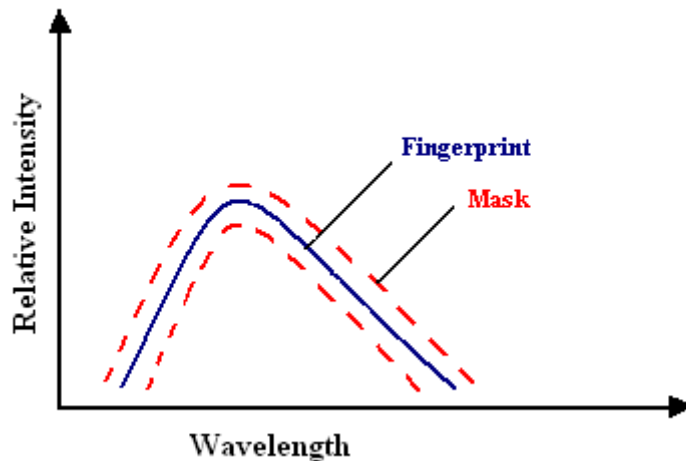


Figure 19: Identifying a compound with the OIW EX 1000.

If the compounds in the sample fluoresce at different wavelengths the mask may not be applied. But if the compounds fluoresce at the same wavelength the mask can be applied to ensure that the instrument will measure the correct oil type. The width of the mask depends on how similar the fingerprints of the compounds are. When a sample is analyzed, the device will take spectra of the oil and compare it with different oil types in the library. The analyzer will then find the oil type that is the best match and upload it. If a mask is applied to the oil type, it will ensure that a new oil type file is not loaded because of local uncertainties in the fingerprint. A new oil type will then only be uploaded when a different oil type with a different fingerprint is present.

The instrument can also calibrate the concentration of chemicals, fluids and particles.

The instrument has two important configuration tabs when calibrating the system:

- Gain control: It is a multiplication factor that will enhance the signal. If a compound has low fluorescence the gain can be set high to get a higher fluorescence value and more accurate reading. Each oil type has a fixed gain value that is set during calibration.
- Offset control: It is an addition or subtraction factor that is used to adjust the neutral point. [1, 2, 19]

## 8.2 The different components in the instrument.

Typical instruments for molecular fluorescence spectroscopy contain five different components;

1. An external source of radiant energy.
2. A container holding the sample.
3. A wavelength selector (not required if it is a Fourier transform instrument, then a frequency modulator is used instead).
4. A radiant detector that converts radiant energy to usable electrical signal.
5. A signal processor and readout.

Figure 20 shows a typical configuration of the components. Here there are two wavelength selectors, one for excitation and one for emission. [15]

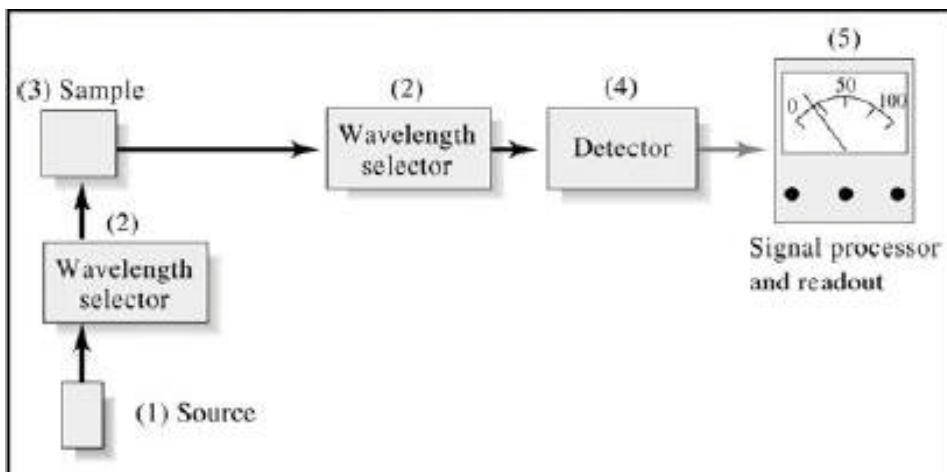
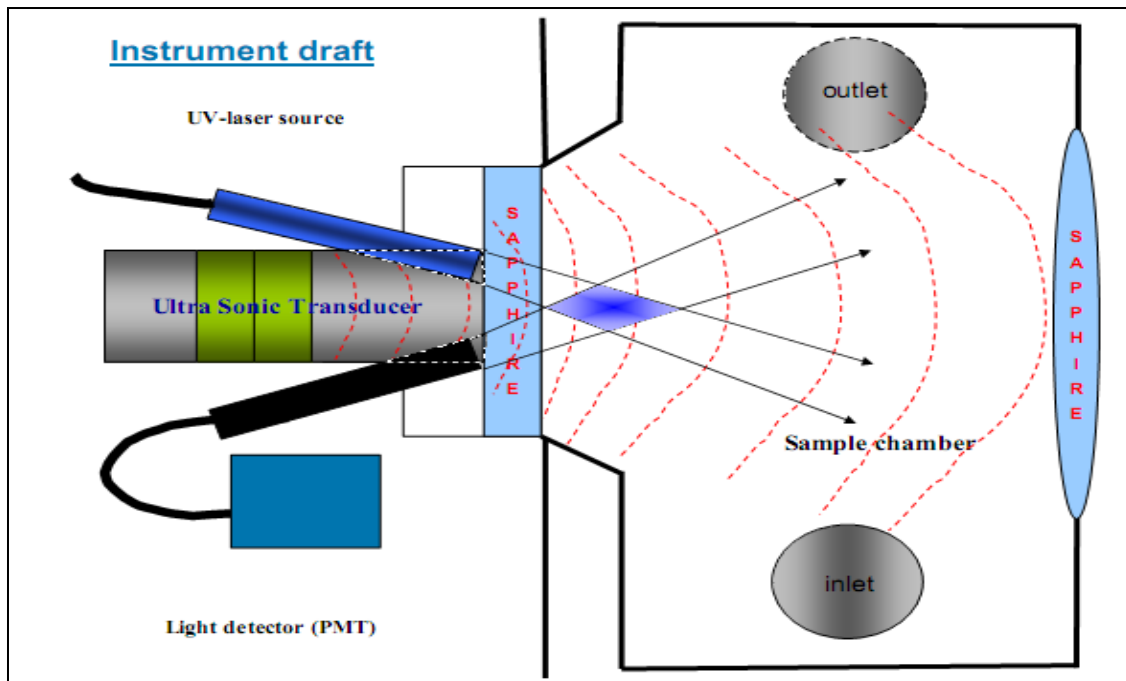


Figure 20: Configuration of a typical fluorescence spectroscopy instrument. [15]



The OIW EX 100 is based on this principle and *Figure 21* illustrates the instrument set up.



*Figure 21: Instrument draft. [2]*

➤ **Light source**

The instrument uses a 3R laser as light source to send UV radiation through the sample. Benefits by using laser are their high intensities, narrow bandwidths and the coherent nature of their output. [1, 15]

➤ **Sample chamber**

The sample chamber is placed on the back of the instrument and has one inlet upstream of the chamber and an outlet downstream. At the inlet there is a flow valve that controls the flow of water entering the chamber, *Figure 22a and b*. The valve will close when a sample is maintained in the chamber for measurements. The valve can be electrically or pneumatic. The chamber also has a lid that can open and show the inside of the chamber. The lid must be closed during measurement or incident light will affect the reading. [1, 15]

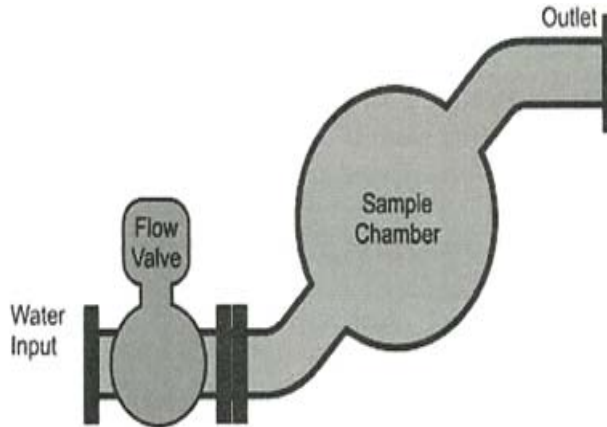


Figure 22a: Sample chamber. [1]



Figure 22b: Sample chamber. [1]

➤ **Wavelength selector**

The OIW EX1000 models use a fixed wavelength laser light source to provide the fluorescence excitation. For fluorescence detection the instrument use a fixed wavelength bandpass emission filter. However, because the OIW EX 1000 also has the full scan spectrometer, it can measure the fluorescence at any emission wavelength (like a tunable filter). This is very important when measuring hydrocarbons in the presence of process chemicals which could interfere with the measurement. [19]

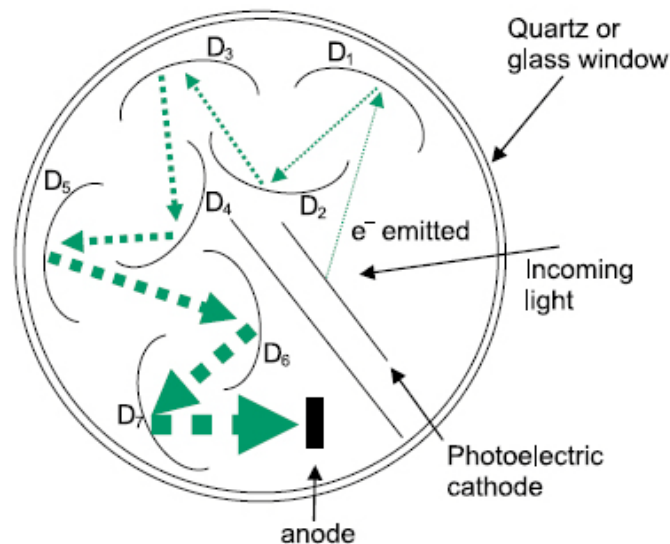
➤ **Detectors**

The instrument has two detectors; a photomultiplier tube to measure the oil content and charged coupled device to display a spectra of the readings. [19]

### Photomultiplier tube (PMT)

In the analyzer a photomultiplier tube is used as a light detector. It will detect how much is absorbed of the photons energy. This is done by measuring the wavelength and the energy level to light that reaches the detector. The measurement will be displayed on the instrument in ppm, ppb or mg/l. [1, 15]

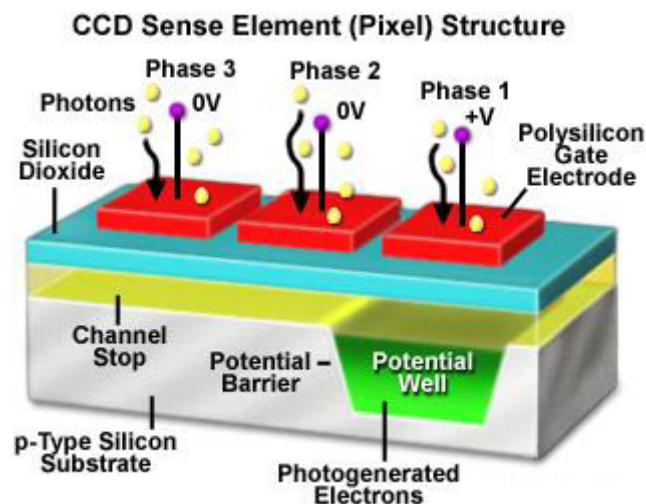
The device consists of a glass envelope with high vacuum inside, which houses a photocathode, an anode and several additional electrodes called dynodes. In *Figure 23* there is 7 dynodes, D1-D7, but the amount of dynodes may vary. A beam of photons will strike the photocathode material and electrons are produced as a consequence of the photoelectric effect. D1 has a voltage that is more positive than the cathode and the electrons will therefore accelerate towards the dynode and cause emission of several additional electrons. All these electrons will then accelerate to the D2 that has a higher voltage than D1. This process will be repeated seven times from D1 to D7 and every electron that is emitted from the cathode can produce  $10^6$ - $10^7$  electrons. The cascade of electrons that is formed will be collected at the anode and produce a current that is converted to voltage and then measured. The photomultiplier tube is highly sensitive to ultraviolet and visible radiation and has a very fast response time. Photomultiplier tubes can only measure low-power radiation because intense light can cause irreversible damage to the photoelectric surface. The device must therefore be placed in a light-tight compartment. [15]



*Figure 23: Photomultiplier tube. [26]*

## Charged coupled device CCD

The charged coupled device is an imaging detector that is used to make a spectrum of the instrument's readings. A CCD consists of an array of small photosensitive elements that are arranged in a two dimensionally way on a metal oxide semiconductor chip that is formed from *p*-type silicon, *Figure 24*. The chip also contains electronic circuitry to give an output signal from each of the elements either sequentially or simultaneously. The elements, also called pixels, act as an accumulating detector where charge accumulates in proportion to total light exposure. Every pixel has 3 electrodes marked as phase 1, 2 and 3 in *Figure 24*. The pixels overlie an insulating layer of silica dioxide that separates it from a layer of *p*-silicon. This assembly constitutes a light-sensing metal oxide semiconductor that acts as a photodiode and storage device. When a negative voltage is applied to the electrodes, there are created a charge inversion region under the electrodes that is energetically favorable for the storage of holes. The mobile holes that are created by the absorption of photons then migrate and is collected in this storage hole, also called potential well. As seen from *Figure 24*, electrode 1 is more negative than the others and therefore the accumulation of charge is favored under this electrode. The charge is moved by a charge-sensing amplifier. CCD can be used in many applications such as cameras, television astronomy and spectroscopy. [15, 22]



*Figure 24: CCD structure. [27]*

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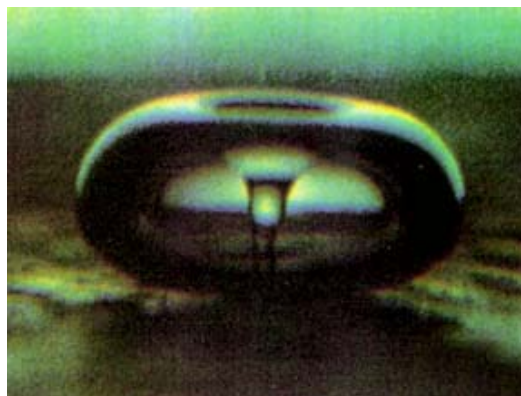
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➤ **Ultrasonic transducer**

The instrument also contains another component called ultrasonic transducer. A transducer is defined as a device that converts information in nonelectrical domains to information in electrical domains and the converse. The method of measuring oil in water is depended on the oil droplet size. If there are variations in the droplet size, it may significantly affect the PPM reading even if the oil content remains unchanged. An ultrasonic transducer is added to homogenize the sample or provide cleaning of the instrument by removing any oil, grease or any deposits from the sensor head and chamber. This is done by creating cavitations in the fluid by applying ultrasonic waves with high intensities. It is called a transducer because it transforms electrical energy to mechanical energy. This mechanical energy causes mechanical vibrations which results in the cavitations in the liquid. [1, 19, 23]

The sound waves that propagate into the liquid result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles, where the velocity is depending on the frequency. During the low-pressure cycle, high-intensity ultrasonic waves will form small vacuum bubbles or voids in the liquid. When the bubbles attain such a volume that they can no longer absorb energy, they collapse intensively during a high-pressure cycle. During the implosion very high pressures and temperatures are created locally. It can also result in liquid jets with a velocity up to 280 m/s. [21]

*Figure 25* illustrates an imploding cavity, where the top of the cavity is folding inward and producing a jet of liquid down in the center of the cavity. These cavities are created tens of thousands of times each second to gently remove contaminants or homogenize a sample without inflicting the instrument any damage. [23]



*Figure 25: An imploding cavity. [23]*

The ultrasonic cleaning and homogenization are the same. The only difference is that the ultrasonic cleaning is done while the process flow control valve open whereas the homogenization is done when the valve is closed. This allows a sample of the liquid to be mixed (homogenized) and measured with the process flow stopped. [19]

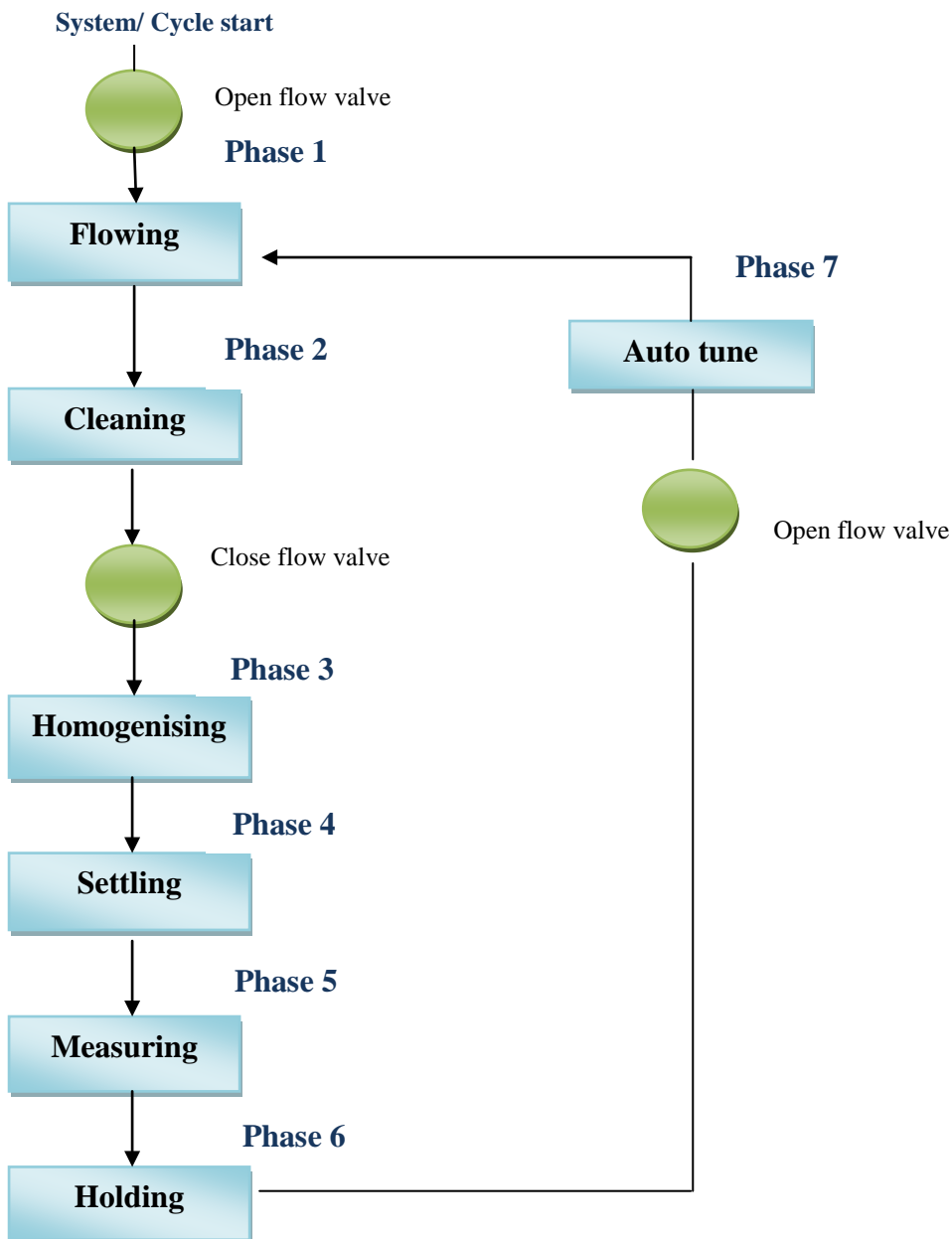
## The measurement cycle to the OIW-EX 1000

The OIW –EX 1000 have two methods of measurements:

1. Trending selected: Continuous flow (but un-calibrated) measurement and scheduled calibrated measurement.
2. Trending Unselected: scheduled calibrated only.

Method one is required with continuously monitoring.

### The measurement cycle of the instrument, *Figure 26* [1]



*Figure 26: Measurement cycle. [1]*



- Phase 1: Flowing

The treated slop water will flow freely through the sample chamber for a selected period.

When trending is selected, the PPM reading will be latched at the last trended reading in the last flowing phase.

When trending is not selected, the PPM valve will be latched at the last reading taken at the end of the last measurement phase.
- Phase 2: Cleaning and flow valve closing
  - I. Cleaning

The measuring window will be cleaned for a selected period.
  - II. Flow valve closing:

The flow valve will start to close. There are two types of valve: an electrically operated valve or a pneumatic valve. The pneumatic valve can close at a much shorter time.
- Phase 3: Homogenisation

After the valve has closed the slop water in the sample chamber will be homogenized for a selected period.
- Phase 4: Settling

After the homogenization is finished the sample in the chamber will settle for a selected period of time so particles will sink at the bottom to prevent influence of the measurement.
- Phase 5: Measuring

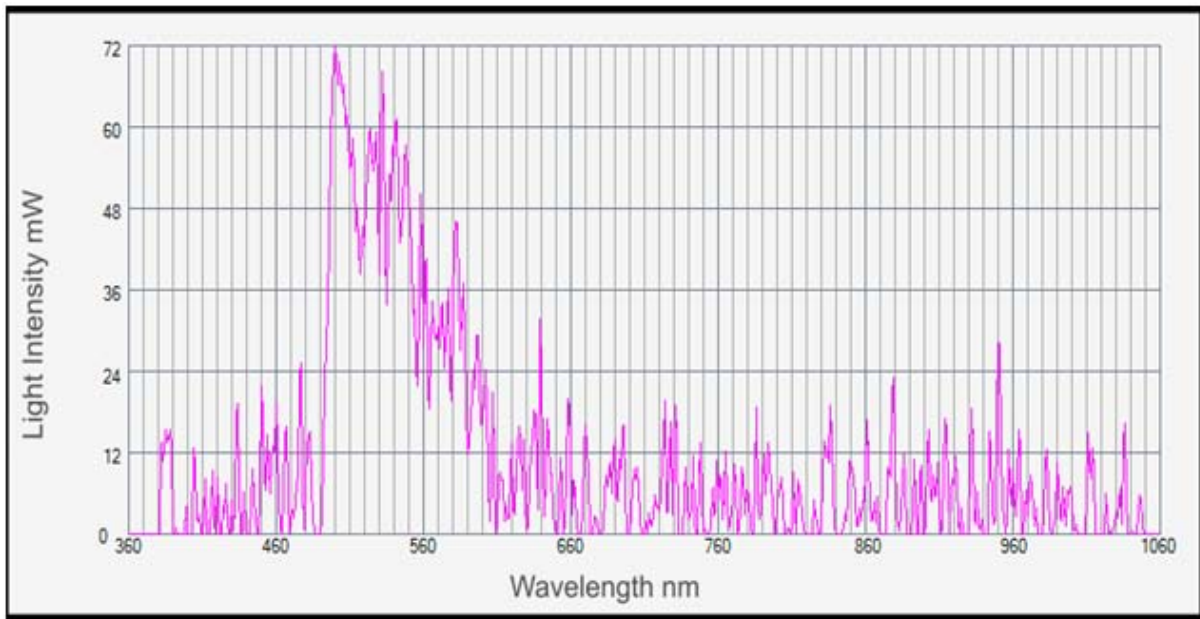
The instrument will measure the oil content of the sample after the principle mentioned above.
- Phase 6: Holding
  - I. Holding: When flushing has finished, the content in the sample chamber will be held for a selected period.
  - II. End of Holding: At the end of the hold time the flow will start to open.
- Phase 7: Auto tuning

Auto tuning can be set if there are significant temperature changes

## 9. Results

### 9.1 Spectra of the different base oils, crude oil and hydraulic oil.

Different measurements were performed with the OIW EX 1000 analyzer to find out if the selected base oils fluoresce and see which operating parameters and conditions that may influence the instrument readings. The instrument has two functions; it can read oil in water and make a spectrum of the sample analyzed (fluorescence intensity vs. wavelength). First a sample of water were taken, this is consider as noise and will be used to compare with the other measurement, *Figure 27*.



*Figure 27: Spectra of pure water.*

Spectra were taken of selected base oils to see if they fluoresce. Previously Halliburton used the paraffin XP-07 but it has now been replaced by Sipdrill 2.0. Also the mineral oil Clarisol NS has been replaced by EDC 95-11. These new oils are almost identical to the previous one; it was therefore performed measurements to view if they had equal or nearly identical fluorescence spectra, *Figures 28 -31*.

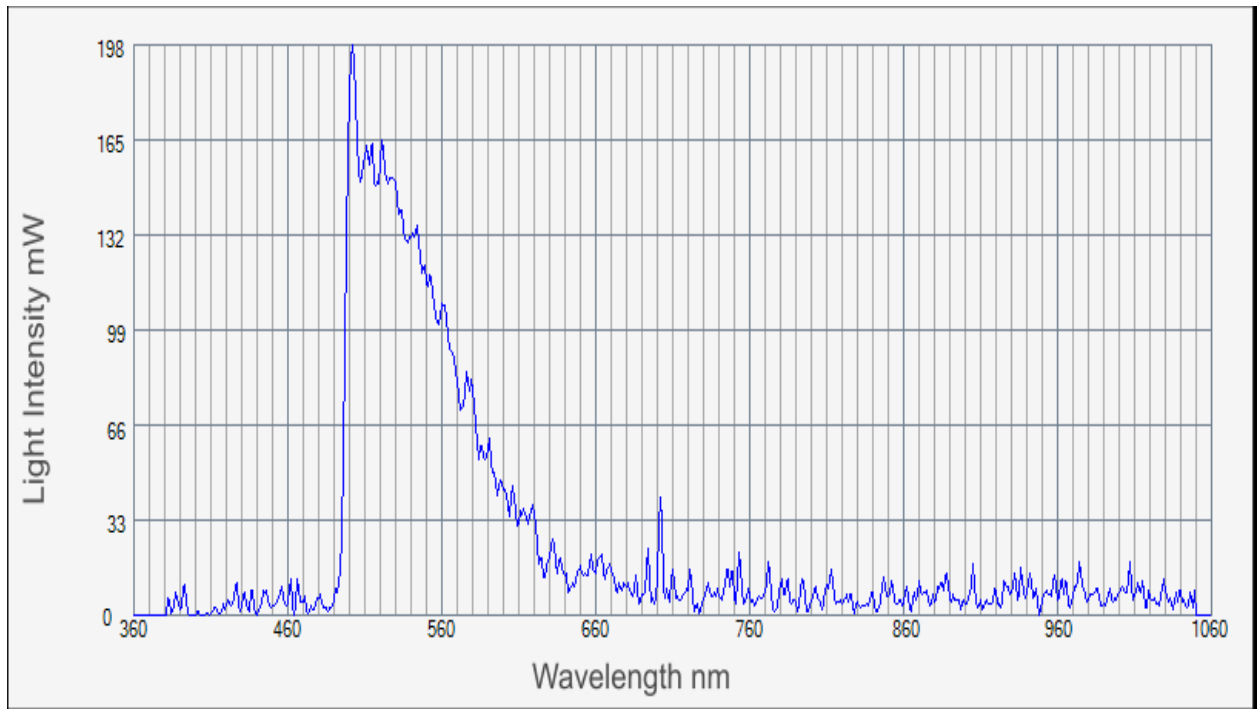


Figure 28: Spectrum of EDC95-11, 100ppm.

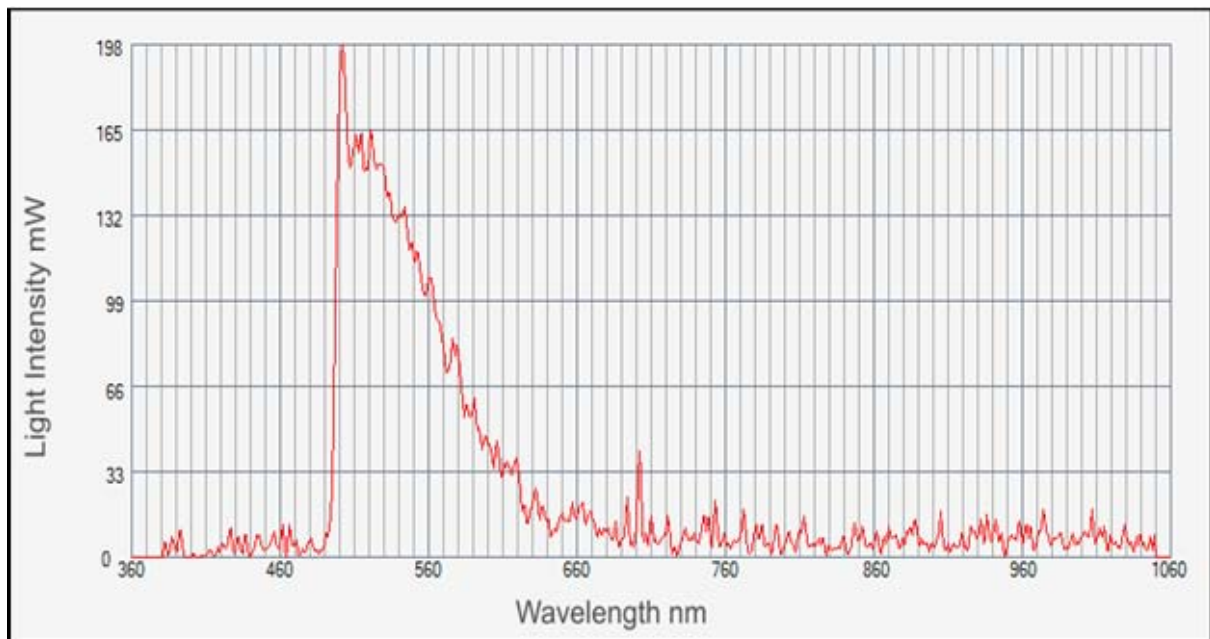


Figure 29: Spectrum of Clarisol NS, 100 ppm.

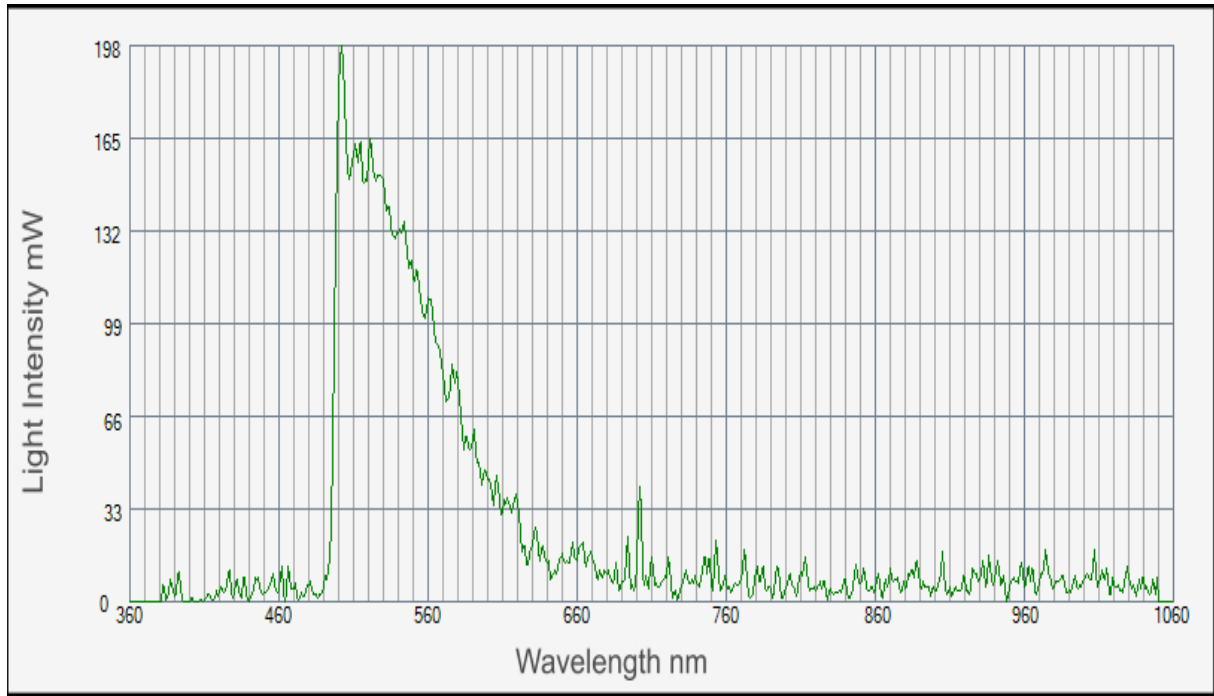


Figure 30: Spectrum of Sipdrill 2.0, 100ppm.

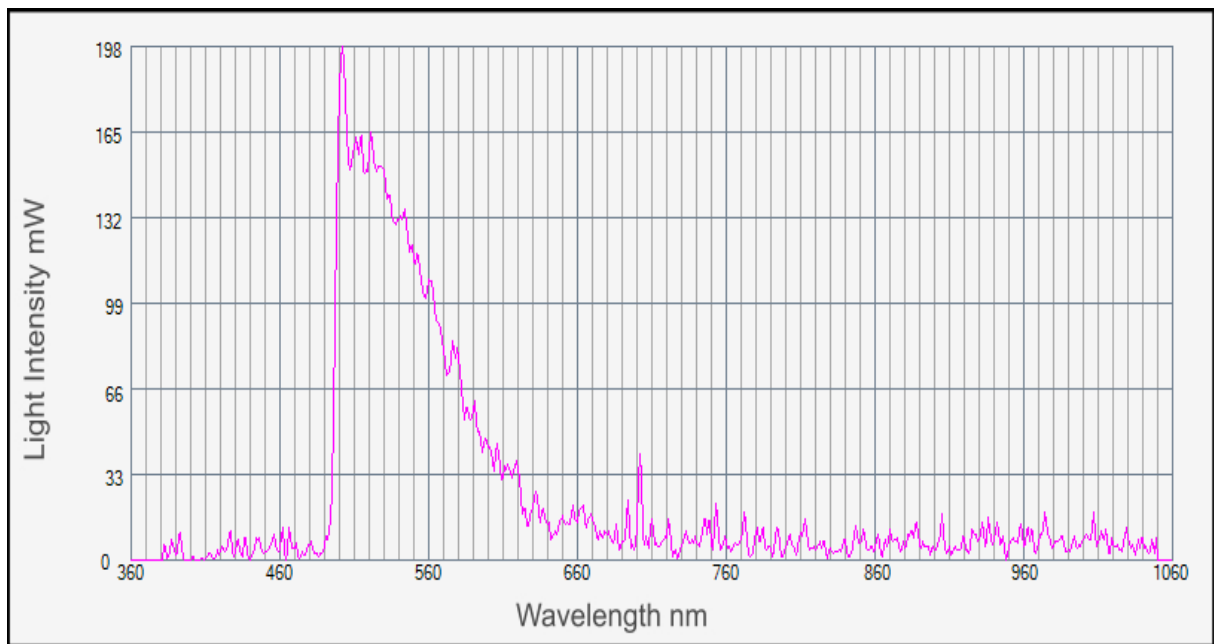


Figure 31: Spectrum of XP-07, 100ppm.

The spectra of the base oils will be used as fingerprints for identification and stored in the analyzer's oil type library. To achieve the correct ppm measurement a calibration curve was made of each of the base oils. The calibration curves can be seen in Appendix I. The

calibration curve was made by preparing a sample of 100 ppm base oil and diluting it to 10 different samples from 100-0ppm. A 200 ml sample was added to the analyzers sample chamber and the measured value was recorded. The calibration curve were created from these values with 2<sup>nd</sup> order regression ( $y = a x + b x^2 + \text{constant}$ ).

To verify that the calibration curves were accurate and measured correctly test samples with known concentration were performed. The calibration verification can be seen in Table 3.

Table 3: Verification of the calibration curves

Base Oil Concentration (PPM)	OIW Analyser Reading (Clairsol NS)	OIW Analyser Reading (EDC 95-11)	OIW Analyser Reading (XP-07)	OIW Analyser Reading (Sipdrill 2.0)
100	97	98	98	96
50	48	52	51	47
25	23.5	26	25.7	24
12.5	11.8	12.8	11.9	11.5
6.25	5.9	6.0	6.1	5.7

The spectra of the different base oils are very similar at low concentration so measurement were performed of each base oil at 1000 ppm to see the difference between them, *Figure 32*.

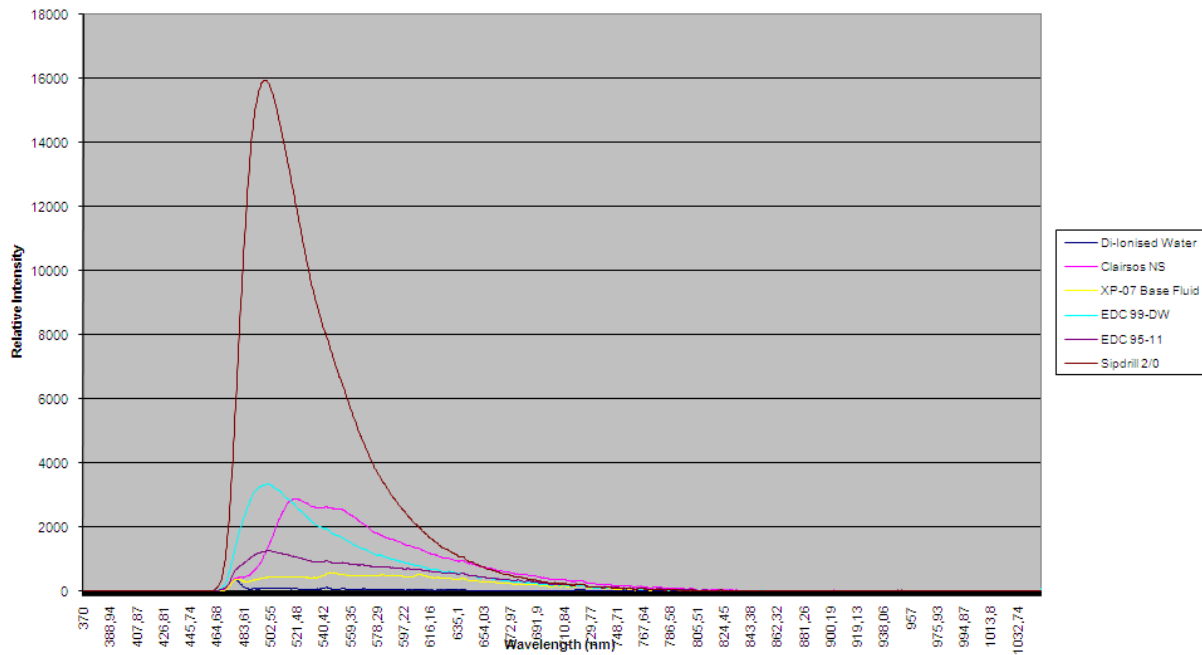
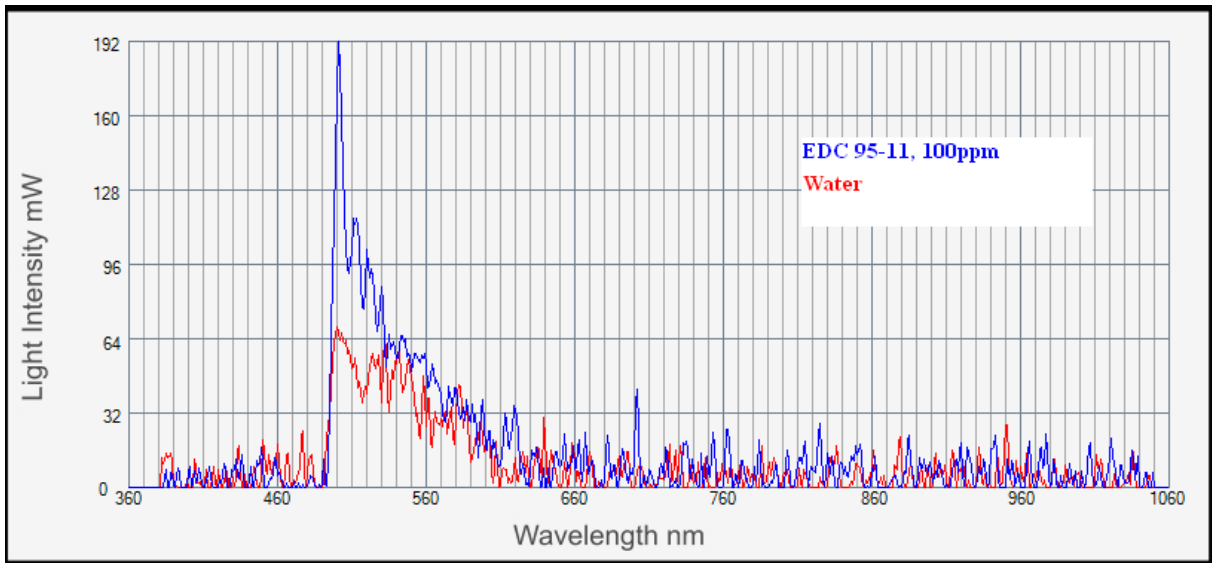


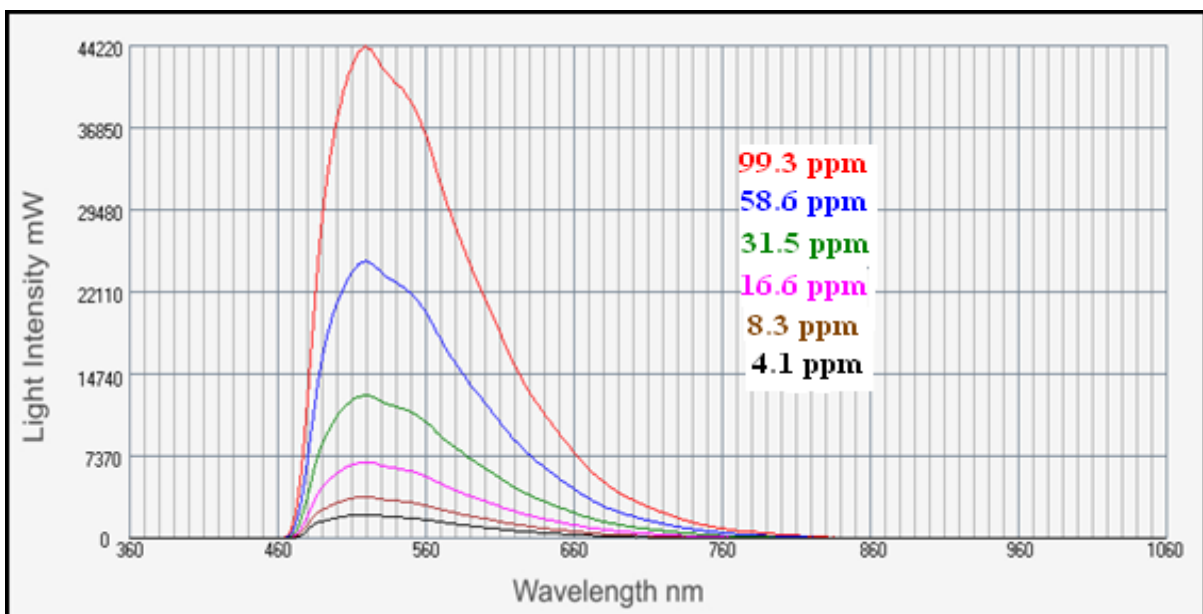
Figure 32: Spectrum of the base oils, 1000 ppm.

To confirm that the base oils fluoresce their spectrum were compared with water. *Figure 33* shows a comparison of the spectra of water and EDC 95-11.



*Figure 33: Spectra of water and EDC 95-1, 100 ppm.*

Measurements were also performed of crude oil and hydraulic oil, the spectra can be seen in *Figure 34 and 35* and the calibration curves are in Appendix I. The spectra were used to compare the fluorescence intensity with the base oils and to see how similar the fingerprints were. *Figure 36* illustrates the comparison of EDC 95-11 and crude oil and *Figure 37* the comparison of EDC 95-11 and hydraulic oil. *Figure 38* also displays a comparison of EDC 95-11, hydraulic oil and crude oil. The spectra and calibration curves were stored on the analyzer for identification.



*Figure 34: Spectra of Crude Oil.*

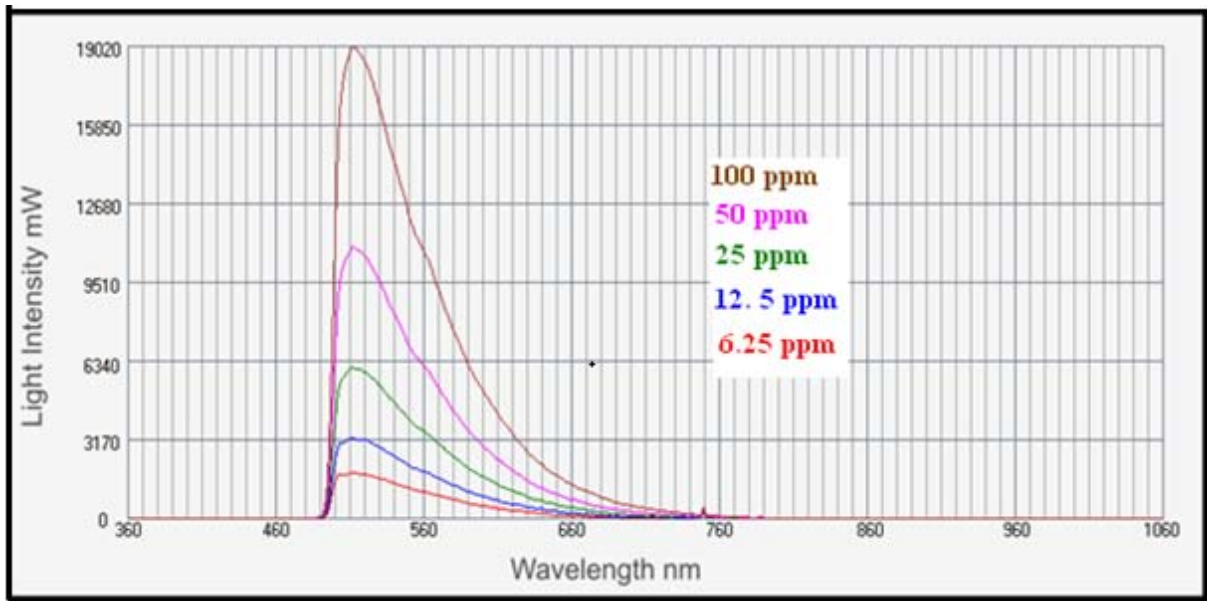


Figure 35: Spectra of Hydraulic Oil.

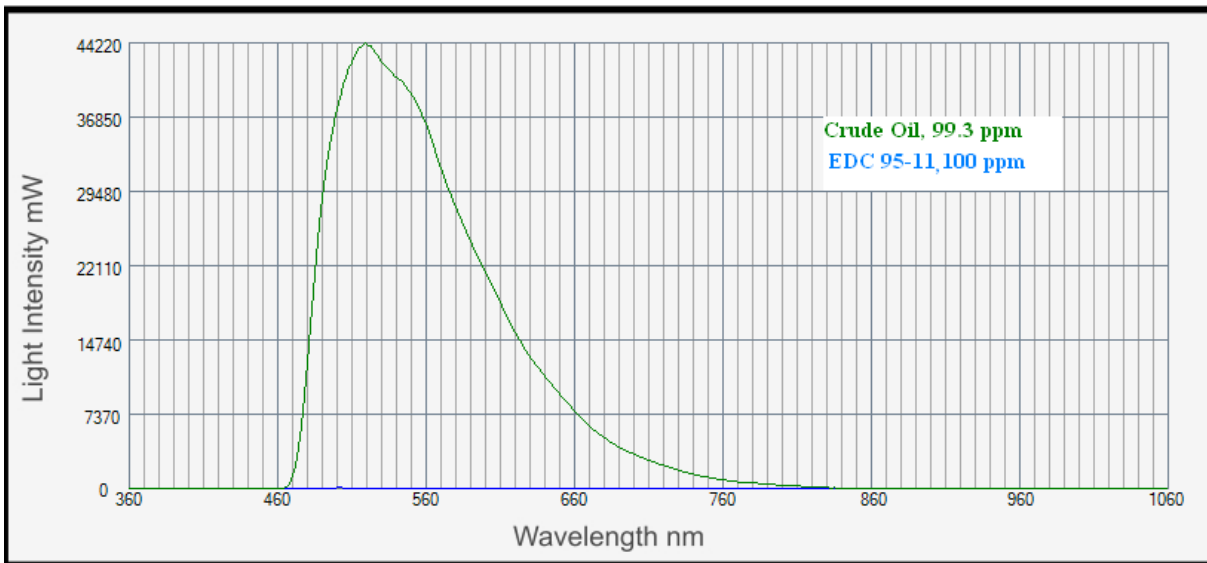


Figure 36: EDC 95-11 and Crude Oil.



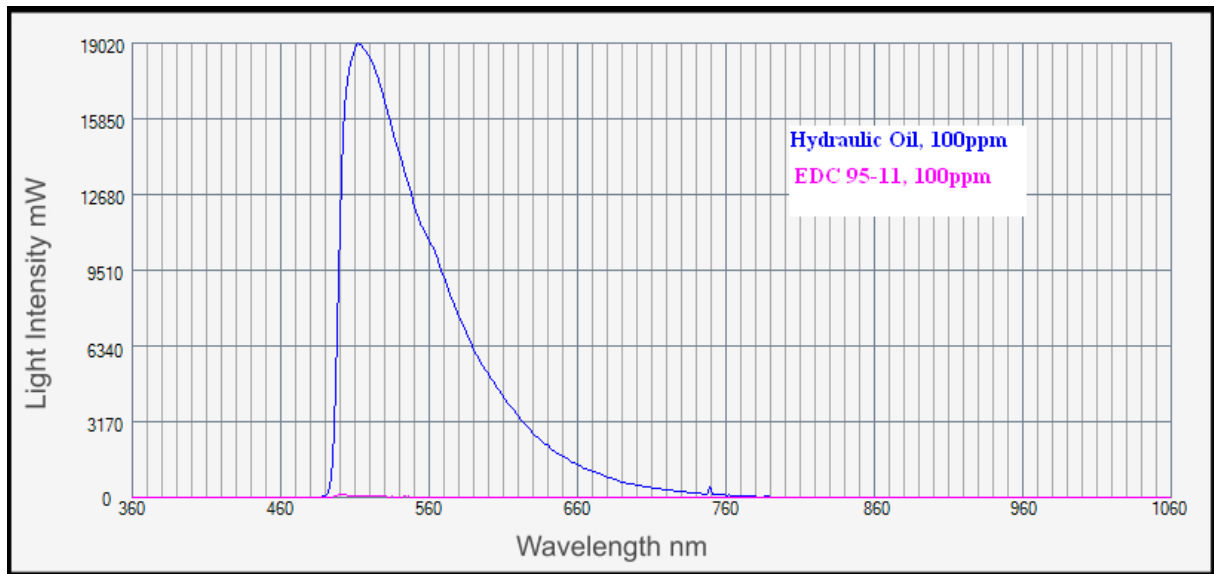


Figure 37: EDC 95-11 and Hydraulic Oil.

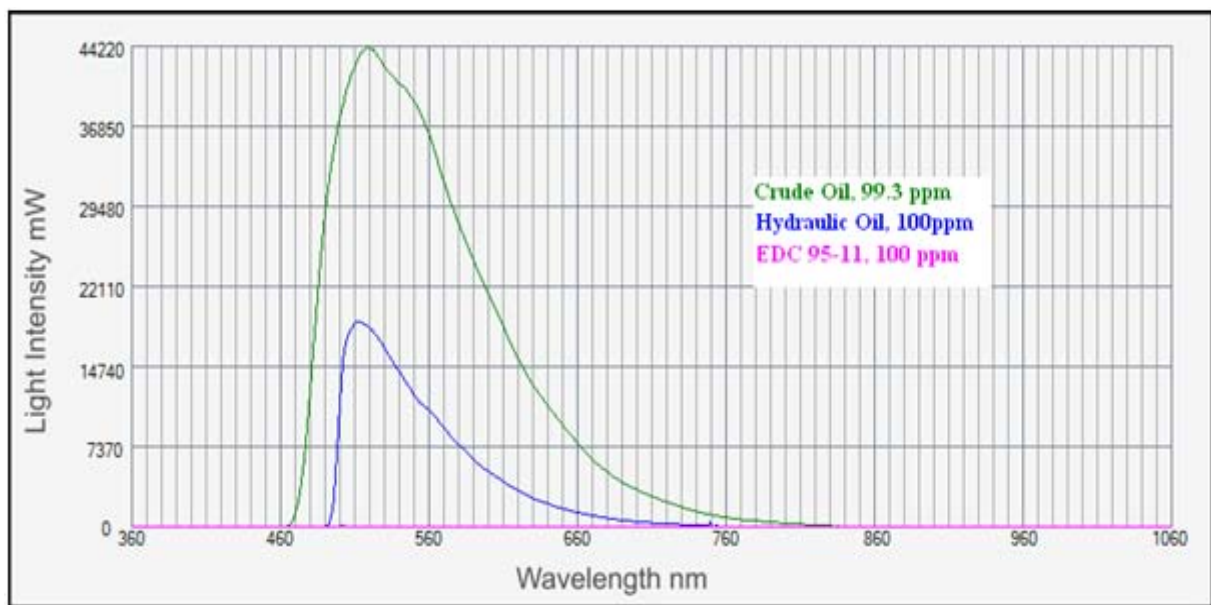


Figure 38: EDC 95-11, Hydraulic Oil and Crude Oil, 100 ppm.

## 9.2 Measurement of different additives.

To evaluate if different additives that are used in mud can interact with the readings of the oil spectra of 6 additives were performed. These additives are:  $\text{CHKO}_2$  (potassium formate),  $\text{KCl}$ ,  $\text{CaCl}_2$ , EZ mul NS, Glycol, GEM-GP. EZ mul NS is an emulsifier and GEM-GP is polyalkylenglycol, both are proprietary chemicals for Halliburton. All the samples were made by diluting a sample in pure form i.e. the concentration that is used when it is added in the mud. The sample is made with a volume of 200 ml and added to the sample chamber where it was measured and recorded. The measurements and spectra can be seen in Table 4-9 and Figures 39-46.

Table 4: Measurements of potassium formate:

Concentration in sample (ppm)	Reading of instrument (ppm)
10 000	No reading
20 000	No reading
50 000	No reading
Pure form: 1.58 s.g	0.5

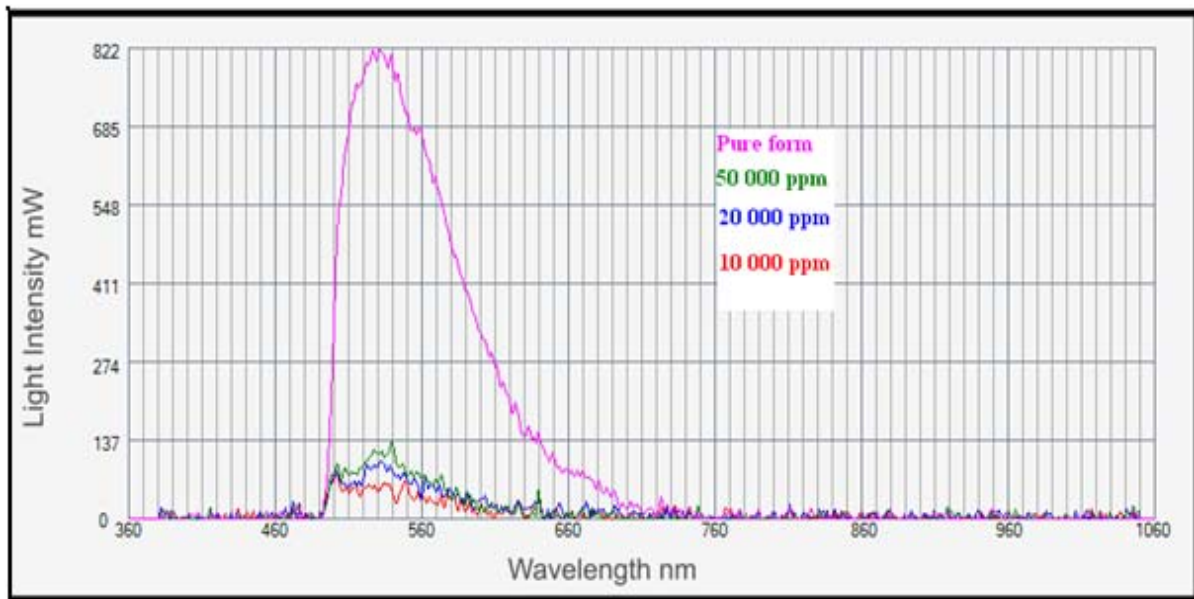


Figure 39: Spectra of potassium formate.

Table 5: Measurements of KCl

Concentration in sample (ppm)	Reading of instrument (ppm)
Pure form: 1.138 s.g	2.05

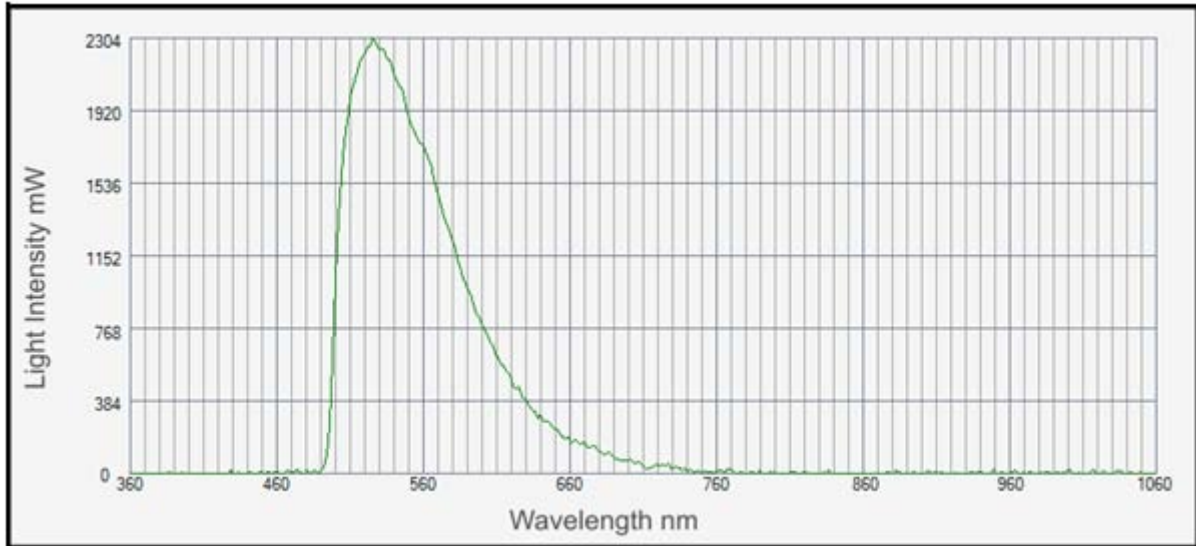


Figure 40: Spectrum of KCl.

Table 6: Measurements of CaCl<sub>2</sub>

Concentration in sample (ppm)	Reading of instrument (ppm)
Pure form: 1.184 s.g	11.5

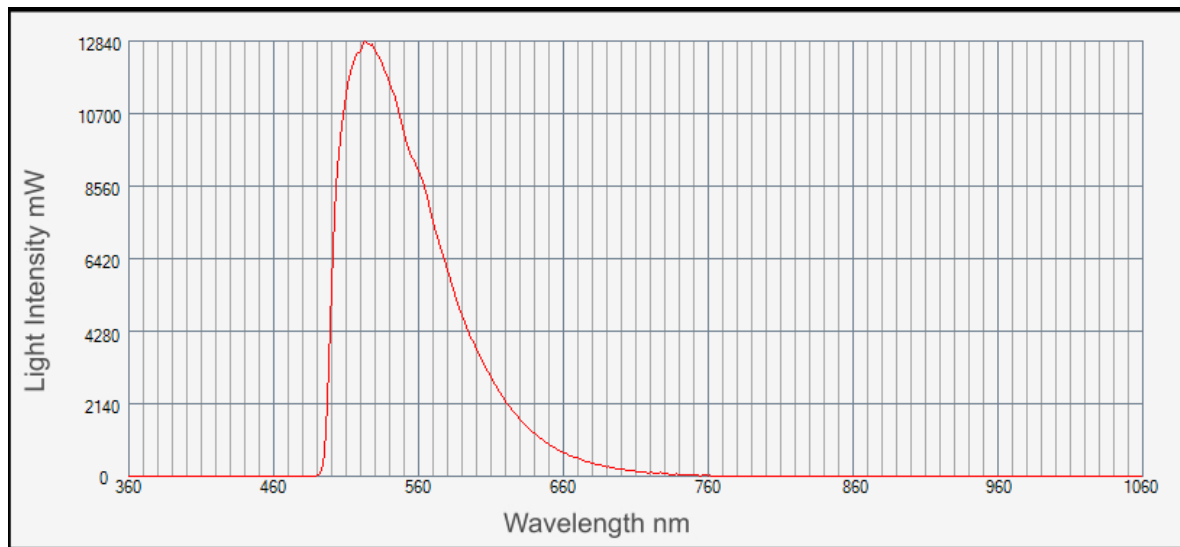


Figure 41: Spectrum of CaCl<sub>2</sub>.

Table 7: Measurements of EZ mul NS

Concentration in sample (ppm)	Reading of instrument (ppm)
100	0.27
500	2.74

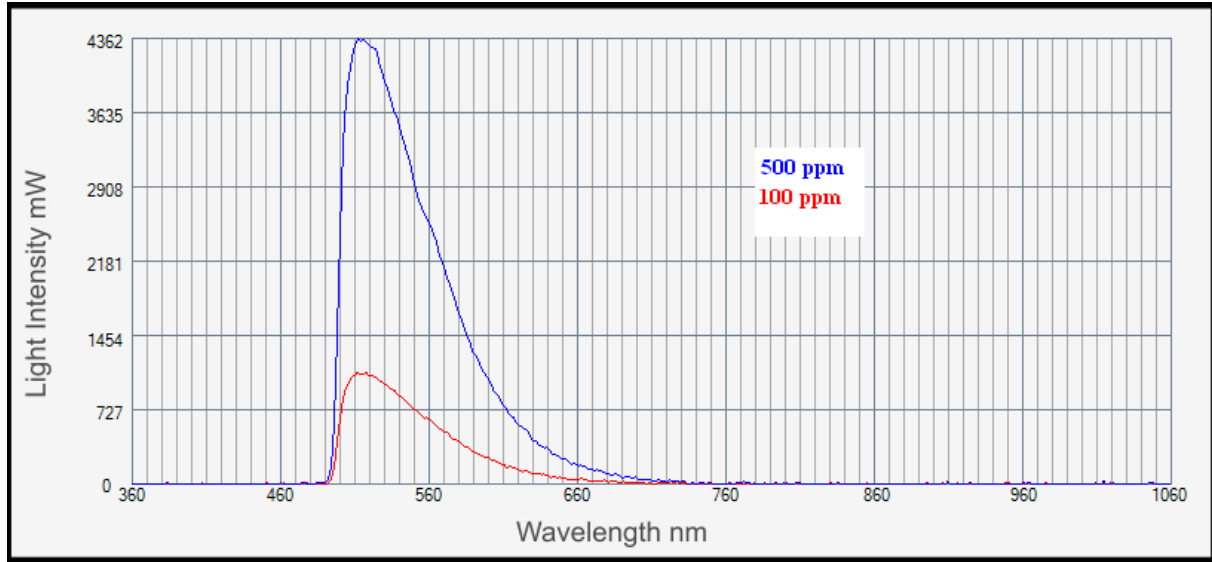


Figure 42: Spectra of EZ mul NS.

Table 8: Measurements of Glycol

Concentration in sample (ppm)	Reading of instrument (ppm)
100	No reading
500	No reading
50 000	No reading
Pure form, 100% Glycol	No reading

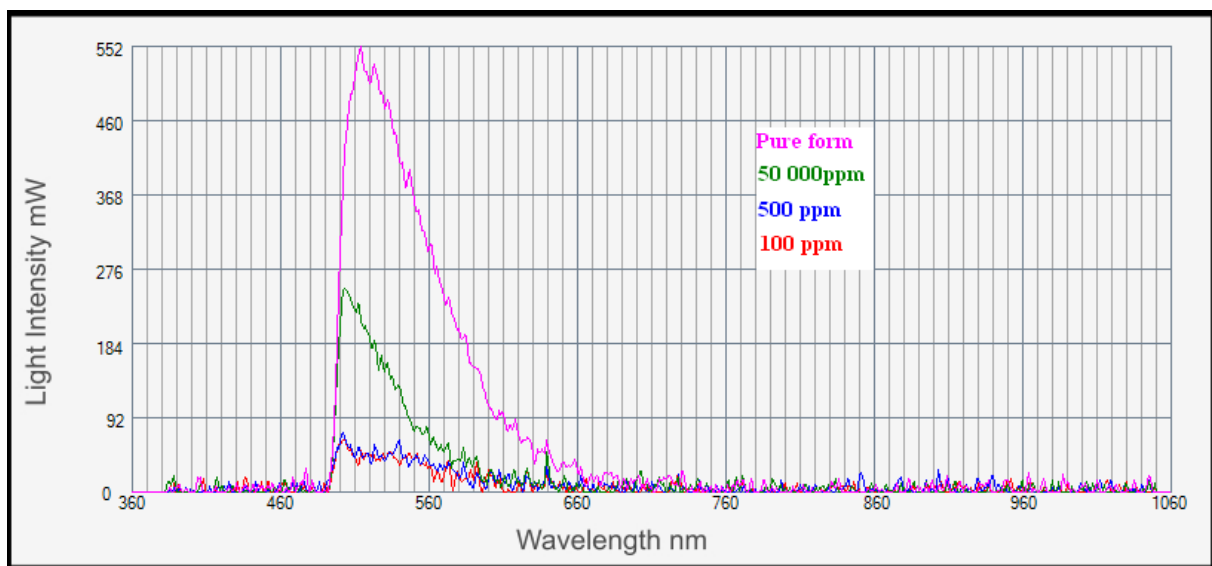


Figure 43: Spectra of Glycol.

Table 9: Measurements of GEM –GP

Concentration in sample (ppm)	Reading of instrument (ppm)
100	No reading
500	No reading
5000	0.76
10 000	2.17
20 000	4.93
Pure form: 100%	92.7

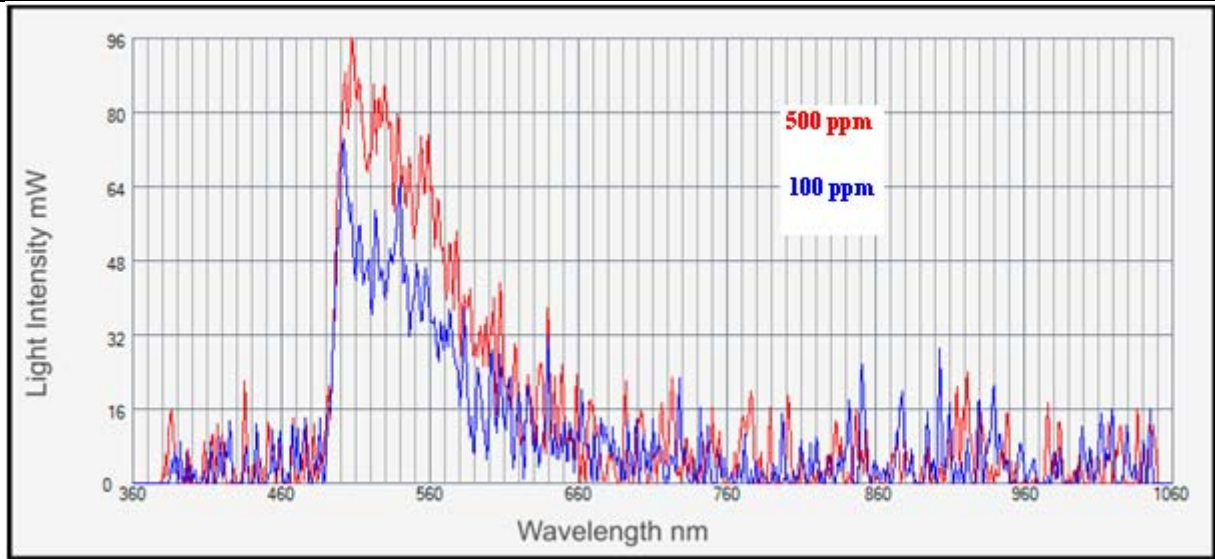


Figure 44: Spectra of GEM-GP, 100 and 500 ppm.

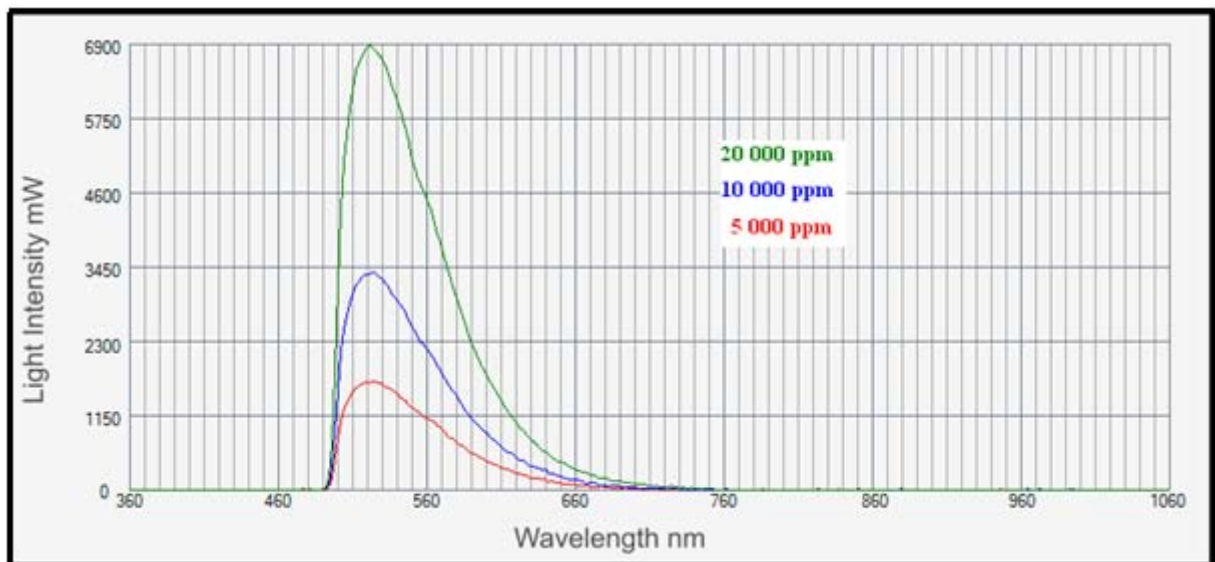


Figure 45: Spectra of GEM-GP, 5000, 10 000 and 20 000 ppm.

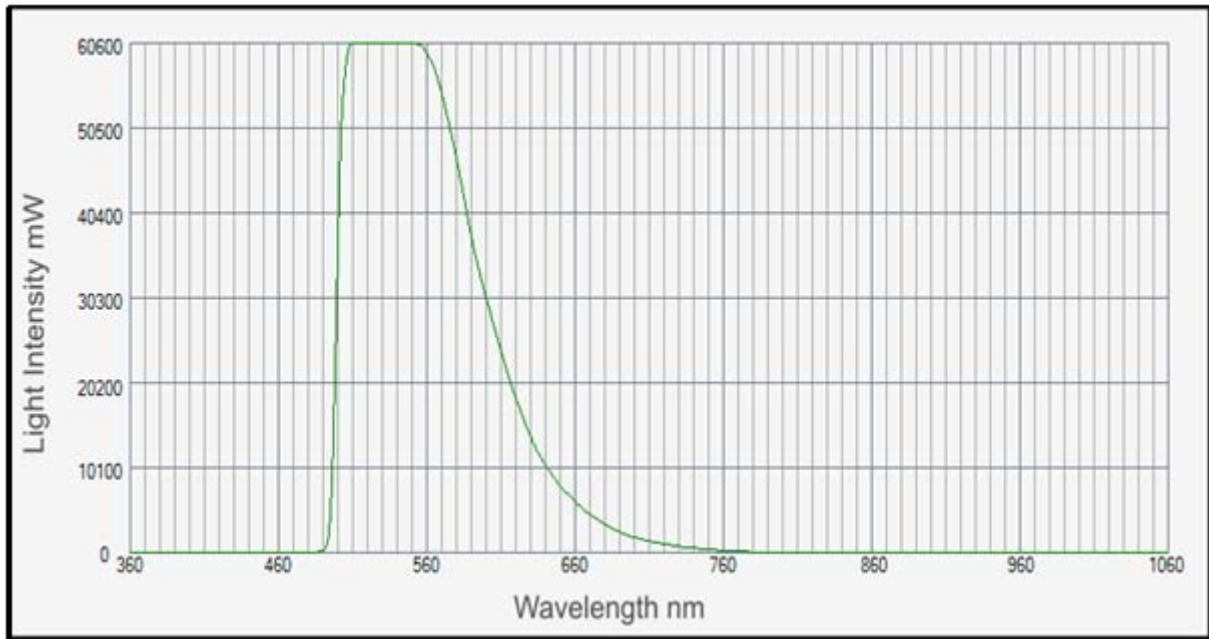


Figure 46: Spectra of Pure GEM- GP.

### 9.3 Measurement with different pH values

Three oil in water samples with the same concentration (50 ppm) but different pH values were measured, Table 10. All the samples had a constant temperature of 20 degrees centigrade.

Table 10: The effect of pH on oil in water samples

Reading (pH 3.0)	Reading (pH 7.0)	Reading (pH 10.0)
50.92ppm	50.26ppm	49.65ppm

## 10. Discussion

Halliburton uses the analyzer OIW EX 1000 to verify that the oil content of the treated slop water don't exceed 30 mg oil per liter as a weighted average for one calendar month. The instrument has normally been used for produced water and Halliburton is the first company to use the instrument to analyze slop water. Produced water contains crude oil that has a high content of aromatics and according to theory aromatics has the most intense fluorescence. Slop water on the other hand have a low content of aromatics and the oil based mud are normally mineral oils or linear paraffin. These oil types have aliphatic carbonyl structures and according to theory only a small number of these compounds may exhibit fluorescence. The goal of this thesis is therefore to evaluate if UV fluorescence is a valid method to verify the oil content, find out which operating parameters can influence the reading and see if different problems that may or have occurred during operation can be resolved:

1. Do the base oils fluoresce?
2. The instrument has displayed "out of range" when the concentration is expected to be low. Why?
3. Will different chemicals and compounds that are normally in the slop influence the readings of the oil content?
4. Which operational conditions may influence the measurement?
5. When a sample of untreated slop water is analyzed the readings show low fluorescence intensity values when they should have been high. Why?

I traveled to Belfast with Halliburton to visit Advanced Sensors who is the manufacturer of the OIW EX 1000. I attended the Advanced Operator Training program for the Advanced Sensors OIW EX-100/1000 series analyzer and performed different tests to verify if the method was valid and to find the answers to the problems listed above.

1. The analyzer has a feature called multispec and can therefore automatic shift between the different oil types if a new oil type is present. In slop water the main oil component is base oil and the primary focus is therefore on base oil. According to theory there are several factors that may influence the fluorescence of a compound, for instance structure; transition type, rigidity and operating conditions (solvent, pH, concentration, etc.). Halliburton now mainly uses two base oils called EDC 95-11 which is a mineral oil and a linear paraffin called Sipdrill 2.0. These oils consist of long flexible chains of carbon with single bonds, alkanes. Since according to theory not all aliphatic compounds will fluoresce and due to lack of rigidity, the first most important question was if Halliburton's base oils even fluoresce at all. Spectra were performed of EDC 95-11 and Sipdrill 2.0, *Figure 28 and 30*. These base oils have just replaced two other base oils, EDC 95-11 has replaced Clarisol NS and Sipdrill 2.0 has replaced XP-07. The difference between them are small so spectra of all four base oils

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were performed to see the similarity between them and to see if one spectra could be used for all 4 of them. All the spectra in *Figures 28-31* look very similar; they have only few variations at 100 ppm. When the concentration were increased to 1000 ppm, *Figure 32*, the difference between them is much more significant. It was therefore concluded that since the concentration of oil in treated slop water that is measured are low only one fingerprint can be used for all four if a mask is added to include any uncertainties. The spectrum of EDC 95-11 was decided to be used for all the base oils. *Figure 33* shows a comparison of the spectra of water and EDC 95-11. The fluorescence signal is very low but there is a signal that has a significant peak at approximately 510 nm. When the analyzer measures an oil type it searches its oil type library and finds the “fingerprint” with the best match. The standard setup of the analyzer is for crude oil where the intensity in the spectrum is read at approximately 600 nm. The instrument uses the oil types’ calibration curve to convert intensity into ppm. *Figure 33* shows that at 600 nm the fluorescence intensity to EDC 95-11 is almost the same as water, it is therefore recommended that the instrument is adjusted to read the intensity at 510 nm were the spectrum has a signal that significantly separates from water.

*Figure 36* displays spectra of EDC 95-11 and crude oil. The spectra clearly illustrate what the theory indicates. Crude oil which contains aromatic compounds has high fluorescence intensity and EDC 95-11 which is an aliphatic compound has a very small signal compared to crude oil. Since the fluorescence is low for EDC 95-11 the gain level was set high during calibration to enhance the signal.

Each oil type has a calibration curve with a set gain value, if the instrument reads the wrong oil type for instance misinterpret another oil type with high intensity as base oil; the ppm measurement will be too high. This clearly illustrates the importance of correct adjustment and calibration of the instrument.

To verify that the calibration curves, Appendix I, to the base oils was accurate and that the analyzer measured correctly, test with known concentration were performed, Table 3. The measurements differ with maximum 3 ppm from the known concentrations. The values also seem to be more accurate with lower concentrations, less than 2 ppm difference. What is important to take into consideration is that ppm and mg/l is not the same units. When dealing with water it will be the same because 1 liter of water at standard conditions weighs approximately 1 kilogram. For oils on the other hand the density is normally between 0,7-1,05 s.g depending on type of oil and refining. Base oil and linear paraffin is the product of a second stage refining of crude oil and their density normally is within 0,75-0,85 s.g. For Sipdrill 2.0 the density is 0.76 s.g and for EDC 95-11 it’s 0,814 s.g. Therefore a factor of approximately 0.8 must be multiplied with the ppm value to achieve the correct mg/l value. So when reporting the values in ppm the concentration in mg/l is less.

For instance 2 ppm of oil equal:

2 ppm = 2 mg/kg

Density oil =  $0.8\text{g/cm}^3 = 0.8\text{kg/dm}^3$

$2\text{ mg/kg} * 0.8\text{kg/dm}^3 = 1.6\text{ mg/dm}^3 = \mathbf{1.6\text{ mg/l}}$

So if the measurements have less than 1.6 mg/l accuracy it is considered as satisfactory for this type of measurements. It must also be taken in consideration any uncertainties in the preparation of the known samples. It was therefore concluded that the instrument were able to measure the correct value of these base oils.

The difference in ppm and mg/l is also important to remember when reporting the value to the authorities, since 30 ppm base oil do not equal 30 mg /l, 30 ppm actually equal 24 mg/l.

2. Sometimes the analyzer has displayed “out of range” when the oil concentration is expected to be lower. The analyzer display “out of range” when the concentration is outside the range of the calibration curve, for base oil the range is normally set to 0-100 ppm. “Out of range” can also be set at a different value if wanted. One assumption for this is if the instrument has misinterpreted another oil type with higher fluorescence intensity to be base oil. All the most common oil types in the slop water are stored in the analyzers oil type library except from hydraulic oil. It was therefore important to evaluate if hydraulic oil may influence the readings and make spectra, *Figure 35*, and a calibration curve, Appendix I. Hydraulic oil can sometimes be in the slop water if there are any spills on the rig and the cleaning water is transported into the slop water tank. When comparing the spectra of EDC 95-11 and hydraulic oil, *Figure 36*, the fluorescence intensity to hydraulic is much higher than EDC 95-11. *Figure 38* illustrates the comparison of the spectra to crude oil, hydraulic oil and EDC 95-11. All the curves have their peak in the same range but all the spectra are very different and will most likely not influence the readings of each other. As long as the instrument has all the oil types’ calibration curves and fingerprints with mask to encounter for any uncertainties in the intensity, the instrument will read the correct oil type. There is a probability that the slop water may contain an oil type that is not encountered for and that is not common in the mud but comes from possible spills on the rig. But the reason the analyzer displayed “out of range” was most likely because the lid on the sample chamber were not closed properly. If the lid is not put tightly on incident light can influence the measurements.

3. 6 different chemicals were tested on the analyzer

- Potassium formate:. The spectrum for 10 000, 20 000 and 50 000 ppm, *Figure 39*, shows intensities below 137 mW. Compared with the spectrum of water, *Figure 27*, the intensities are very low and the ppm readings were zero, Table 4. The spectrum of the compound in pure form on the other hand showed a peak at approximately 550 nm with an intensity of 882mW, *Figure 39*. The intensity is higher than water but the ppm reading were only 0.5. The peak of the base oils is approximately at 510 nm so the spectra are at the same range, but since the ppm readings were so low and potassium formate is added in low concentrations it is evaluated not to influence the readings.

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- KCl: The spectrum of KCl, *Figure 40*, in pure form exhibit fluorescence that is much higher than water and has a low ppm reading, Table 5. According to theory KCl should not fluoresce at all. This may have occurred because the compound was stored in a polyethylene bottle or if there had been any impurities in the sample.
- CaCl<sub>2</sub>: The spectrum of CaCl<sub>2</sub>, *Figure 41*, in pure form exhibit fluorescence that is much higher than water and has a reading of 11.5ppm, Table 6. According to theory CaCl<sub>2</sub> should not fluoresce at all. This may have occurred because the compound was stored in a polyethylene bottle or if there had been any impurities in the sample.
- EZ mul NS: The spectra for 100 ppm and 500 ppm, *Figure 42*, displays peaks that are larger than water, *Figure 27*, and low fluorescence readings, Table 7. EZ mul NS has a peak at the same range as the base oils and high concentrations of the emulsifier can influence the measurements if it is not adjusted correctly, but since the emulsifier is added in low concentrations it is evaluated not to influence the readings.
- Glycol: None of the ppm measurement displayed any readings, Table 8. The spectra, *Figure 43*, of 100 and 500 ppm had a lower intensity than water and are regarded as noise. The spectra for 50 000 ppm and pure form has higher intensity than water, *Figure 43*, but since Table 8 shows that it doesn't exhibit fluorescence it was concluded that it will not influence the readings of the oil.
- GEM-GP: The spectra of 100 and 500 ppm, *Figure 44*, shows low intensities that are very similar to the spectrum of water, *Figure 27*, and there were no ppm reading, Table 9. The spectra of 5000, 10 000 and 20 000 ppm, *Figure 45*, and of pure form, *Figure 46*, had all larger intensity than water. GEM-GP exhibit less fluorescence than the emulsifier but GEM-GP is used in much higher concentrations. It may therefore influence the readings at high concentrations if the instrument is not adjusted correctly. After consulting with Halliburton's business segment manager for Baroid Drilling Fluids it has been estimated that a typical concentration of GEM-GP in water based mud is 0.5 -10 vol%. In the slop water the mud is diluted and the concentration will be so low that any influence of GEM-GP can be neglected.

After evaluating the spectra and ppm readings of the different chemicals it is determined that probably none of the chemicals will influence the readings. This assumption is based on that the concentration of the chemicals are low and that the instrument is adjusted correctly and a mask is applied to the fingerprint. Halliburton has previously also performed tests with soap to evaluate if it can influence the readings. The conclusion was that a concentration higher than 5000 – 6000 ppm of soap can influence the measurements.

4. From theory there are several factors that may influence fluorescence:

- With increasing temperature the quantum efficiency will decrease due to increased probability of deactivation by external conversion. So according to theory changes in temperature may influence the measurements. This subject was discussed with Advanced Sensors and they claimed that they had tested the OIW EX 1000 and concluded that the changes in the measurements were negligible. The analyzer is used Offshore where the water temperature is very stable with only a few degrees in variation. It was therefore concluded that temperature would most likely not influence the readings.
- The solvents polarity and local environmental will have an effect on the emission spectral properties. When dealing with slop water, the solvent is seawater and the fluorophore is oil, mainly base oil. Water is polar and base oil is mineral oil or paraffin which is non-polar. Non-polar species are less sensitive to polarity and the effect on the emission spectrum will most likely be negligible.
- In the slop treatment unit two chemicals are added to the process, sodium hydroxide is added for pH adjustments and polyaluminiumchloride to induce flocculation. Sodium hydroxide is a very strong base and polyaluminiumchloride is an acid, they will therefore have a neutralizing effect on each other. Since sodium hydroxide is a very strong base the pH will normally be around 9 which is an ideal pH for the corrosion inhibitor. pH can affect the fluorescence of aromatic compounds with acidic or alkaline ring substituents. Slop water mainly consists of the base oil used in the mud which has aliphatic carbonyl structures. The base oil also contains sulphur, nitrogen, oxygen, trace elements of metals and water. Based on the structure of the base oil it will most likely not be very pH depended. To ensure that this assumption was correct measurements of samples with same oil concentration but different pH were performed, Table 10. Based on the tests and on theory pH is evaluated not to influence the measurements.
- When measuring oil in water the oil droplet size is very important. Any changes in size may have a significantly affect on the readings even if the oil content remains the same. Smaller droplet results in higher surface area and therefore more intense fluorescence. To get the best and most accurate measurements it is then important to have small droplet size and the sample should be homogeneous. The analyzer has an ultrasonic transducer that will homogenize the sample and produce droplet size of 5  $\mu\text{m}$ . Any smaller droplet size than this will probably not result in very different results. It is therefore very important that this device works properly and is adjusted at the correct frequency.
- The ratio between concentration and fluorescence intensity is linear at low concentration. If the concentration of the sample is high enough so that the absorbance is more than 0.05 the curve will no longer be linear and there is a

decrease in fluorescence. Also if the concentration is high, the light from the UV laser will not be reflected due to the high turbidity. The concentration can therefore have a profound effect on the instruments readings.

5. When performing calibration of an oil type the ppm range of the curve is set, most used range is 0-100 ppm or 0-1000 ppm. For base oil it is normally used 0-100 ppm, and as seen from the calibration curve for EDC 95-11, Appendix I, the curve reaches its maximum fluorescence value at 100 ppm and then the curve straightens out. The fluorescence value will stabilize due to turbidity in the sample.

A sample of untreated slop water has high turbidity and a ppm value of oil much higher than 100 ppm. When the laser sends UV radiation through the sample the light will not be reflected due to the high turbidity and the measurement of the oil content will be wrong. To achieve correct value two different methods can be used.

- Calibrate the oil type with a different ppm range, for instance 0-1000 ppm. The instrument can according to the manufacture read up to 20 000 ppm oil in water.
- Use a correction factor. As explained before a calibration curve of an oil type is created with 2<sup>nd</sup> polynomial equation ( $ax^2 + bx + c$ ) of the measurements . This equation can be used to find the correct value by solving the equation with regard to x.

According to the activities regulation § 70 the content of oil and other substances in the discharges shall be measured to verify the treatment plant's performance. The oil content of water shall be analysed according to OSPAR's reference method for determining dispersed oil in water (OSPAR ref. No. 2005-15, which is a modification of ISO 9377-2) or analysis methods calibrated towards this.

When an alternative online Oil-in-Water (OIW) analyzer is used for a this purpose it must give documented results that statistically provide the same result as measured with OSPAR standard reference method for oil in water . The recommended statistical method to perform and to prove the "similarity" between two analysis methods is correlation and linear regression analysis.

After evaluating all the test data from the OIW EX 1000 it is concluded that the analyzer can be verified for measuring oil in slop water if adjusted and calibrated correctly. To validate that the OIW EX 1000 is according to OSPAR's guidelines a procedure on how to calibrate and validate the OIW EX 1000 analyzer when reporting to the authorities (KLIF) must be made. Section 10.2 illustrates an example of how this can be done.

## **10.2 Procedure on how to calibrate and validate the OIW EX 1000 analyzer, when reporting to the authorities (KLIF).**

This procedure is based on OSPAR agreement 2006-06 [30] and personal communication with Thomas Larsen [31].

### **10.2.1 Documentation requirements for online OIW analysis methods**

The following requirements for documentation must exist when using an online OIW analyzer as an analytical method for reporting discharges of water containing oil to sea to Klif:

- A description of the online OIW analyzer that includes measurement principles, installation, location and how measurement data is saved / applied.
- A description of who owns the online OIW analyzer and what that implies (Owner Responsibility, liability method, follow-up measures / training, maintenance, etc.).
- A description of manual sampling, where the following are described:
  - Location of sample point in relation to OIW analyzer.
  - Withdrawal and treatment of samples (procedure).
- A procedure for alternative handling / reporting method, if the online measurement system is inoperative or if the analyzer is defected. (section 10.2.5.1)
- It should be documented procedures for daily, weekly and monthly inspection / validation of the OIW analyzer. (section 10.2.5.2)
- There must be prepared a qualification report that will ensure that all the requirements for the usage of the OIW analyzer for emission reporting are met.
- Before the OIW analyzer is used all the necessary documentation must be revised to ensure that it is according to authorities regulations.

## 10.2.2 Calibration of the OIW Analyzer

The OSPAR guidance 2006-6 states that the calibration method of an online OIW analyzer shall be described. The recommended method is a regression model for calibration of the OIW analyzer against the reference method.

A water sample taken manually and analyzed in the lab constitutes the y-value. Measurements from the OIW analyzer taken from the same period is the x value in the regression. It is common to use 1 or 2-order regression models (the calibration curve). In the 2 order regression model the coefficient of curvature  $b$  should be small compared to the slope  $a$ .

$$y = a x + \text{constant} \quad [1^{\text{st}} \text{ regression (linear curve)}]$$

$$y = a x + b x^2 + \text{constant} \quad [2^{\text{nd}} \text{ order regression (curve graph)}]$$

$a$  = slope

$b$  = coefficient of curvature

Constant = Intersection with y-axis

The linear regression method gives a calibration curve that can be visualized in a graph with an estimated 90% confidence limit (OSPAR indicates 95%) and regression coefficient.

- Different platforms /rigs may use various types of base oils during drilling operations and it is important that this oil type is stored in the analyzers library for correct reading. When performing calibration the base oil that is used at that specific platform /rig should be used to calibrate the instrument to ensure the best calibration.
- At each calibration point a water sample of approx. 800 ml should be withdrawn in 1-liter sample bottles containing a small amount of hydrochloric acid (water stabilizer). Each water sample shall be analyzed with the current Lab OIW method. This sample will be used to compare (validate) the Lab method and the OIW analyzer.
- There should not be used daily average values based on "regular" oil in water analysis. Exceptions to this are when the installation / platform has an automatic test sampling system where the sample represents the daily value, and can be directly compared with the OIW analyzers' daily value (mean value).



### **10.2.2.1 Initial calibration of the OIW analyzer conducted in a laboratory**

Calibration of the analyzer in a laboratory can be performed by the Advanced Sensors or professional personnel. Base oil from that specific platform/rig should be used and the oil concentration range should be from 0 to 100 mg/L.

The report should contain a description of the execution and all the data and analysis that is relevant to the calibration model of the OIW analyzer.

### **10.2.2.2 Initial calibration of online OIW analyzer performed in a Test Rig**

The calibration can also be done if a test rig is available. Then seawater will represent slop water and base oil is added to the water.

The following important test parameters can be varied in a water rig:

1. The oil concentration from 0 to 100 mg / l or higher.
2. Oil droplet size [mean droplet sizes from 4 to 50 micrometers]
3. The water flow rate and pressure (up to 6 m<sup>3</sup> / h and 60<sup>0</sup> C, and maximum 35 bar water pressure)
4. Determine if the analyzer is affected by chemicals used on the platform.
5. If the analyzer is affected by gas bubbles in the water (gas saturation).
6. If the analyzer is affected by inorganic particles (for instance bentonite).
7. Extraction of water samples similar to samples taken at the platform can be performed and be analyzed according to the current OSPAR reference method (GC-FID method), so that a direct regression model can be established.

### **10.2.3 Establish a calibration model for the OIW analyzer on the installation**

When the initial calibration is finished there should be performed an optimization of the calibration model over a period of time (eg 1 to 2 months) with new water samples from the process. The calibration (regression) analysis can then contain values from both water samples from the platform and samples from the initial calibration data. Experience from qualifying online OIW analyzers have indicated that withdrawal of water samples near the OIW analyzer will most likely be more compatible with the lab analysis performed with an approved OIW reference method.

Requirements for installation / platform calibration model (regression):

1. It is a requirement that the calibration model must contain a minimum of 20 water samples for the entire oil concentration range from 0 to 100 mg / L. The majority of water samples should contain oil concentrations between 5 and 30 mg / L.
2. There is a minimum of 2 water samples in the range from 0 to 10 mg / l, a minimum of 15 water samples in the range 10 to 30 mg / l, and at least 3 water samples in the oil concentration range 30 to 100 mg / L.

3. Requirements for uncertainty in measurements (standard deviation = average deviation):
  - Standard deviation + / - 4 mg / L for the range 0 to 30 mg / L
  - Standard deviation + / - 10 mg / L for the range 30 to 100 mg / L

#### 10.2.3.1 Proposals of how to perform a calibration of the OIW analyzer

- It is recommended that a water sample is withdrawn manually once a day during this period. The timing of withdrawals is noted, and that the sample volume of 800 ml is drained over approx. 60 seconds. If a sample a day is taken over a long period of time it will include the natural variation in oil concentration in the water treatment process.
- Installations that have "approved automatic samplers" for the extraction of oil-in-water samples can also be used. The Lab analysis of the water sample withdrawn over shorter periods, within 24 hours, will then be compared with the estimated average value from all measurement values measured by the OIW analyzer.
- It is recommended that a minimum of 20 new water samples should be included in the optimization of the calibration model from this period.
- It is important to withdraw water samples during process disturbances when the oil flows have "abnormal values" in order to achieve a good dispersion of oil values in the calibration model. A good calibration is dependent on the variations in oil values and good references analysis.

#### 10.2.4 Validation of the calibration model on the installation

When the calibration on the platform is completed, the calibration curve (regression) is validated with new water samples (800 ml) in a test period. There should be used either existing OSPAR method or approved alternative Lab OIW method.

Once the established regression model shall be validated (tested), new analytical results shall not be included in the regression model. It must be developed a validation plan for each installation.

The following requirements for validation must be fulfilled:

1. *Correlation coefficient should be higher than 0.9* for the test samples analyzed with the OIW analyzer and Lab reference method
2. *Requirements for uncertainty in measurements* [standard deviation, Ch. 4 Section 3, page 9]:
  - Average deviation + / - **4** mg / L for the range **0 - 30** mg/L
  - Average deviation + / - **10** mg / L for the range **30 to 100** mg / L

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Comments on a Validation Plan:

- In the validation of new water samples, it is important with a dispersion of the oil values to obtain representative data for the qualification report for the introduction / use of the online method Klif reporting of oil spills at sea.
- During the validation, the personnel must attend necessary training. Procedures and documentation of the OIW analyzer must be established and tested. (Section 10.2.1 "Required Documentation".)
- It is important that the personnel on the platform are involved in developing education plans, procedures, and the implementation plan for validation of the OIW analyzer. The plan must describe the personnel resources and needs, responsibilities, treatment of water samples, capacity, and who is responsible for qualifying the report.

Example of how to report validation data can be seen in Appendix II, Table 12 and *Figure 56*.

### **10.2.5 Procedures that each installation must prepare for daily and continuous monitoring of the OIW analyzer.**

In this section there are listed some suggestions to what a procedure of *how each installation must prepare for daily and continuous monitoring of the OIW analyzer* should contain.

#### **10.2.5.1 Procedures for daily monitoring of the OIW analyzer when it is out of service or any errors in the measurements.**

How will the OIW analyzer be monitored daily and managed if?

- Analyzer problems; instrument alarm (s), probable error in oil measurements, etc.
- Operational problems in the water treatment process on the platform, stop of the water over shorter or longer period of time, very high oil levels, etc.

The procedure must be adapted each installation

Withdrawal of water sample for lab analysis should be carried out as before, but a water sample shall only be analyzed for reporting to Klif if the following criteria are not met:

1. The OIW analyzer has shown 50% of oil readings higher than 30 mg / L
2. The OIW analyzer has shown 10% of oil readings higher than 100 mg / L
3. The OIW analyzer offers instrument alarm (s) that may indicate measurement error or failure of the analyzer. The responsible person for the instrument should be contacted
4. Online OIW analyzer has been out of order in the measurement period (day) for more than 6 hours total, or 4 hours.

5. Added or use of new process chemicals that are not "tested" against online OIW analyzer.

This water sample may not be used in control of the OIW analyzer calibration model.

The OIW analyzer performs continuous measurement of the oil content that is stored on the hard drive throughout the day. From all the measurement that day it is calculated an average value of the oil content in the slop water. All the daily average values over a month period form the basis that is used in the oil spill report to KLIF. Table 11 and *Figure 53* in Appendix illustrate an example of how a 24 hour report may look like.

#### **10.2.5.2 Procedure for monthly monitoring of the OIW analyzer**

A control water sample of 800 ml should be withdrawn each week, a total of four water samples per month. These weekly water samples can be analyzed every week or all four samples analyzed at the end of each month with a lab approved OIW reference analysis method. By performing this lab analysis every week it is easier to monitoring and control the OIW analysis method and detect any problems with the analyzer.

#### Criteria that apply for approved control of the OIW analyzer:

1. Requirements for uncertainty in measurement (standard deviation):  
The average deviation of the 4 control water samples should be:
  - +/- 4 mg / L for oil concentrations in the range 0 to 40 mg / L
  - +/- 10 mg/L for oil concentrations in the range 40 to 100 mg / L
2. Requires that the correlation coefficient should be higher than 0.9 between the control samples that is analyzed with OIW analyzer and the Lab reference method.

#### Measures when the inspection is NOT approved:

- Start using the Lab OIW reference method for reporting of discharges to Klif, acc. 10.2.5.1
- Notify the responsible person for the instrument or Advanced Sensors.

Other measures:

- Verify the online OIW analyzer if possible by comparing the measurements with a standard water sample made from seawater containing known oil concentration according to procedure.
- Perform control analysis of the Lab OIW reference method with a standard water sample with a known quantity of oil.
- Contact professional personnel or supplier of assistance to evaluate the causes and measures that should be performed.

When the reason for that online OIW analyzer does not meet the requirements is resolved, the cause and measures that were performed should be documented in the logbook. This logbook can give valuable information to users and to the person responsible for the instrument.

**10.2.5.3 Update of calibration model (Report - Log)**

Update of calibration model with new analysis results that is based on weekly / monthly inspection samples (Section 10.2.5.2) should be carried out according to the description in the online OIW analysis method. This update must be recorded (when and who) in the log book for the online OIW analysis method.

There should be prepared a report by the person responsible for the instrument every six months that provides an overview of results and experiences with the use of the online OIW analyzer. The report can be a tool for improvement and exchange of experience.

**10.2.5.4 Qualification report of the OIW analyzer**

After the validation plan is implemented, a qualifications report should be written. Based on achieved results the report should contain a conclusion that states if the established procedures and the documentation of the analysis method are "good enough" and if the OIW analyzer meets the authorities' requirement.

## Conclusions

The base oils EDC 95-11 and Sipdrill 2.0 both fluoresce but at low intensities. To ensure correct measurements it is important to have an accurate calibration curve and add a mask to the fingerprint to ensure that correct oil type is read. Oil droplet size and the concentration of the sample are important operating parameters that can have a profound effect on the measurements. The droplet size must be small and homogeneous and the concentration should not be so high that it results in absorbance more than 0.05 or have high turbidity. The spectra of the base oils had a peak at 510 nm that significantly separates from water it is therefore recommended that the instrument reads the intensity at this wavelength.

After evaluating all the data it was concluded that the OIW EX 1000 is a valid method for measuring oil content in treated slop water but only if it is calibrated and adjusted correctly.

The difficulty when dealing with slop water is that the composition will vary and it may contain many other compounds that are not encountered for in this thesis that may influence the measurement.

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## Appendix I

### Calibration curves

The calibrations were performed with 10 samples in the range 0-100ppm. The curves, *Figures 47-52*, are made with 2 order regression ( $y = a x + b x^2 + \text{constant}$ ).

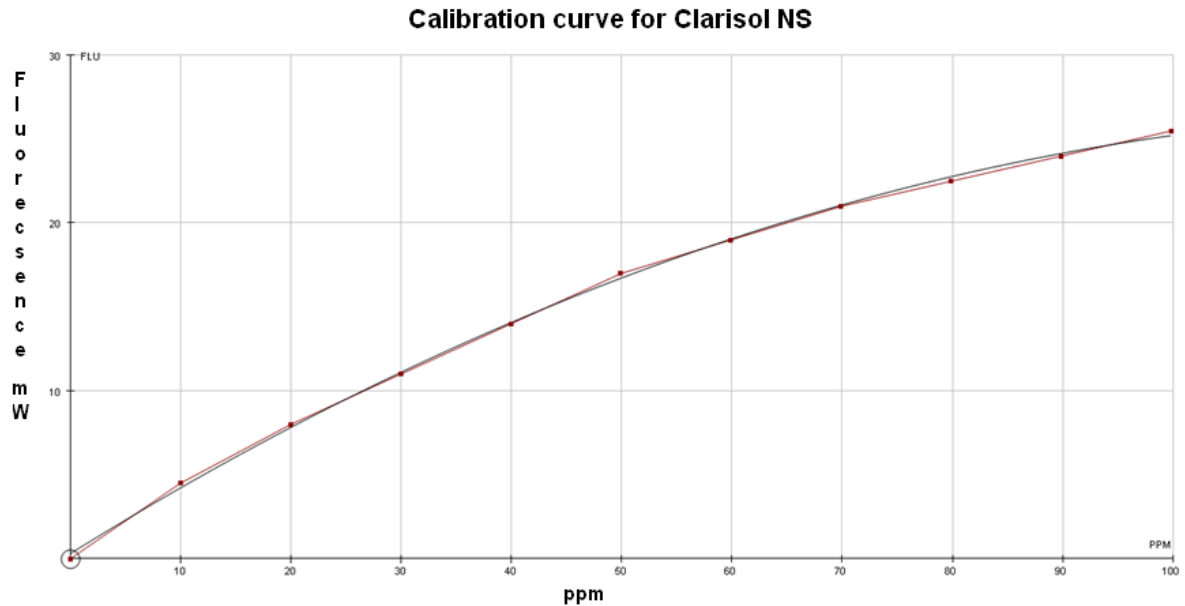


Figure 47: Calibration curve for Clarisol NS

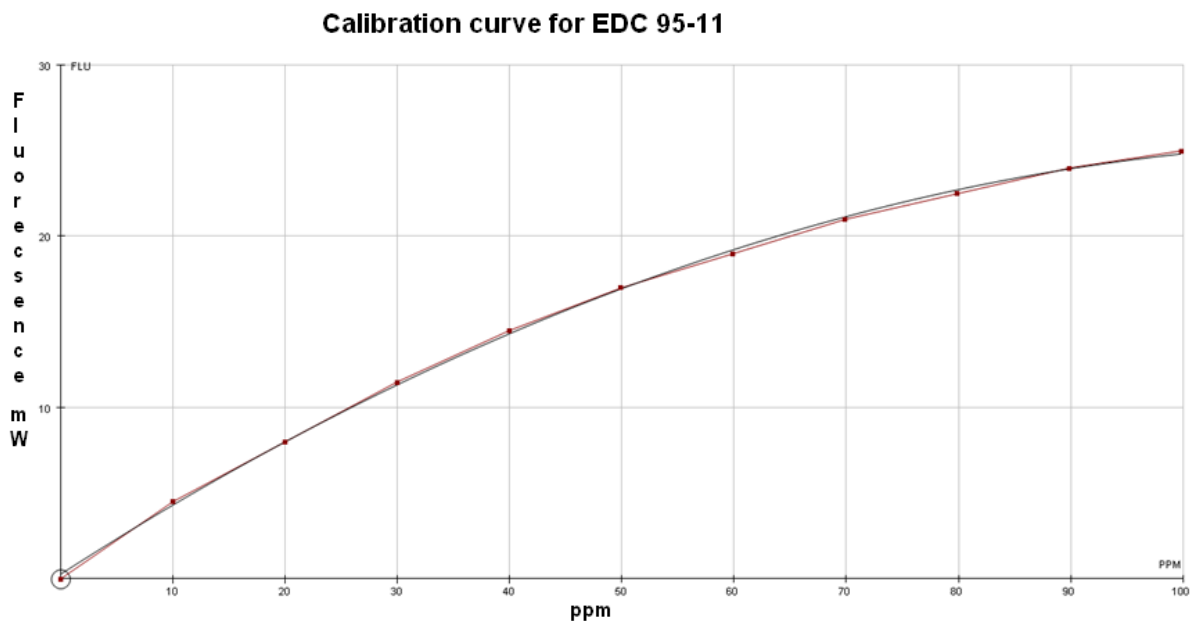


Figure 48: Calibration curve for EDC 95-11

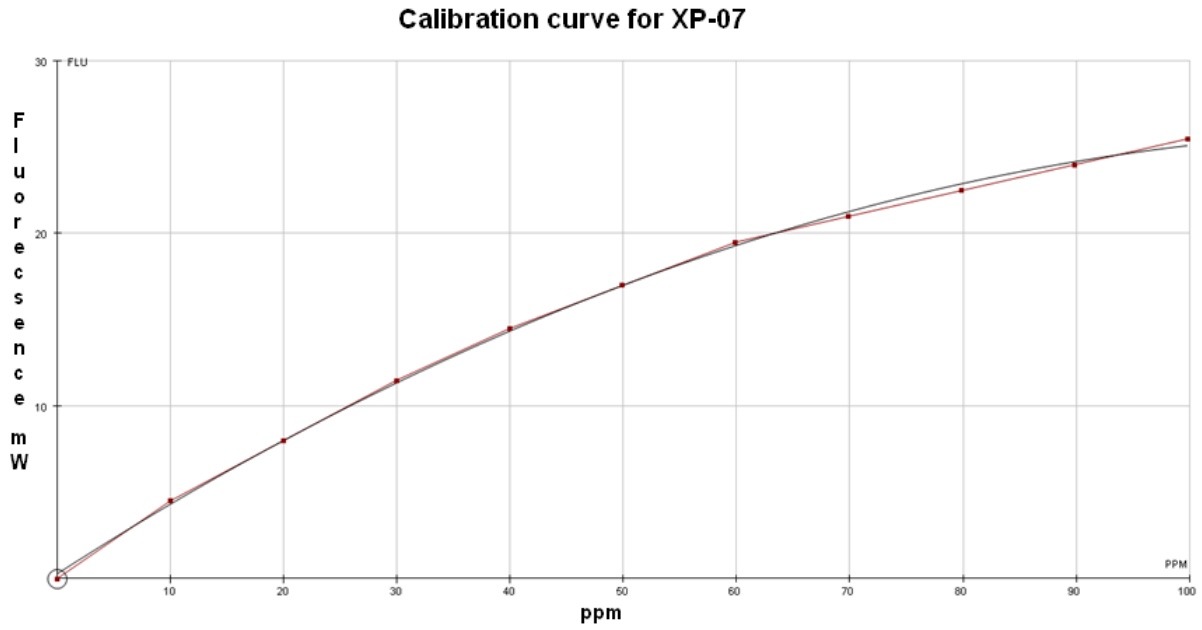


Figure 49: Calibration curve for XP-07

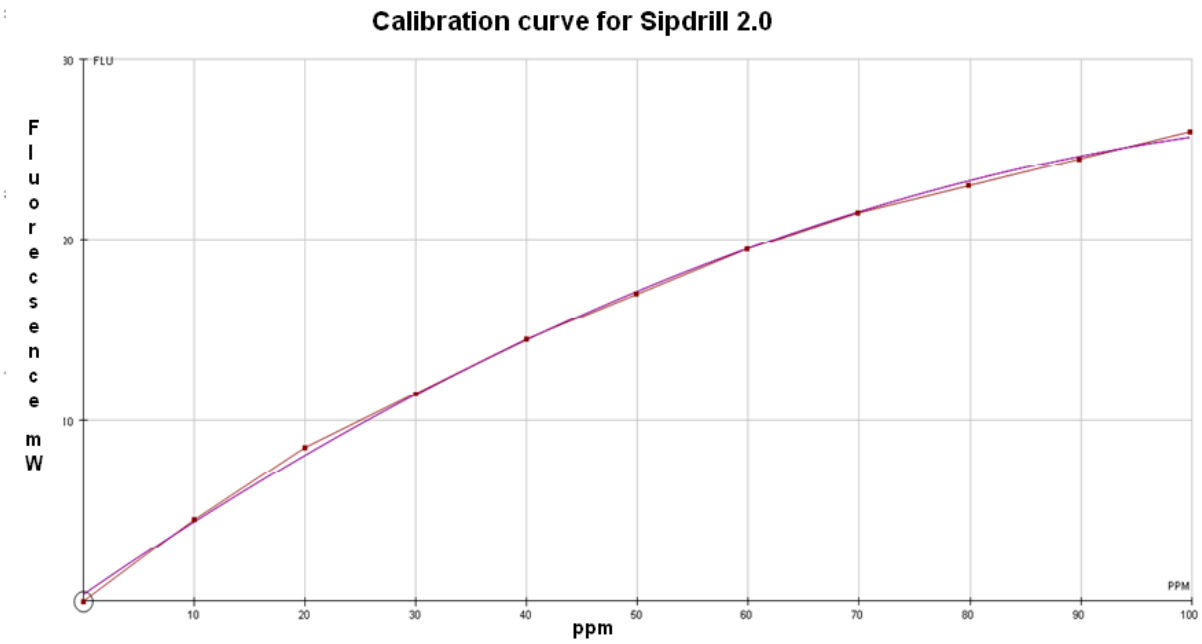


Figure 50: Calibration curve for Sipdrill 2.0

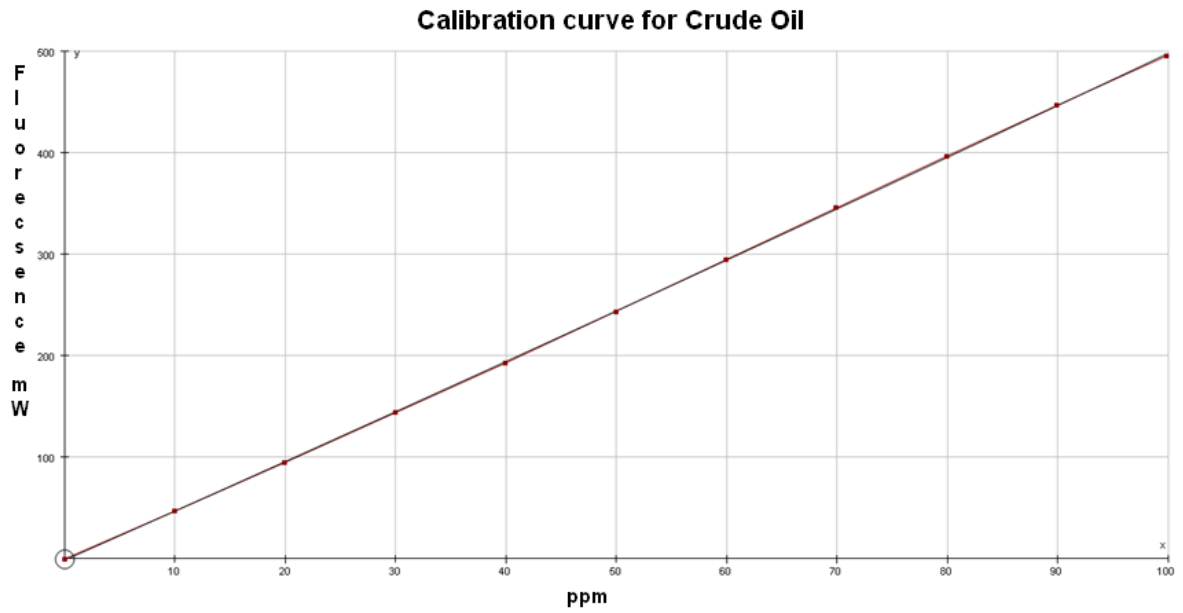


Figure 51: Calibration curve for crude oil

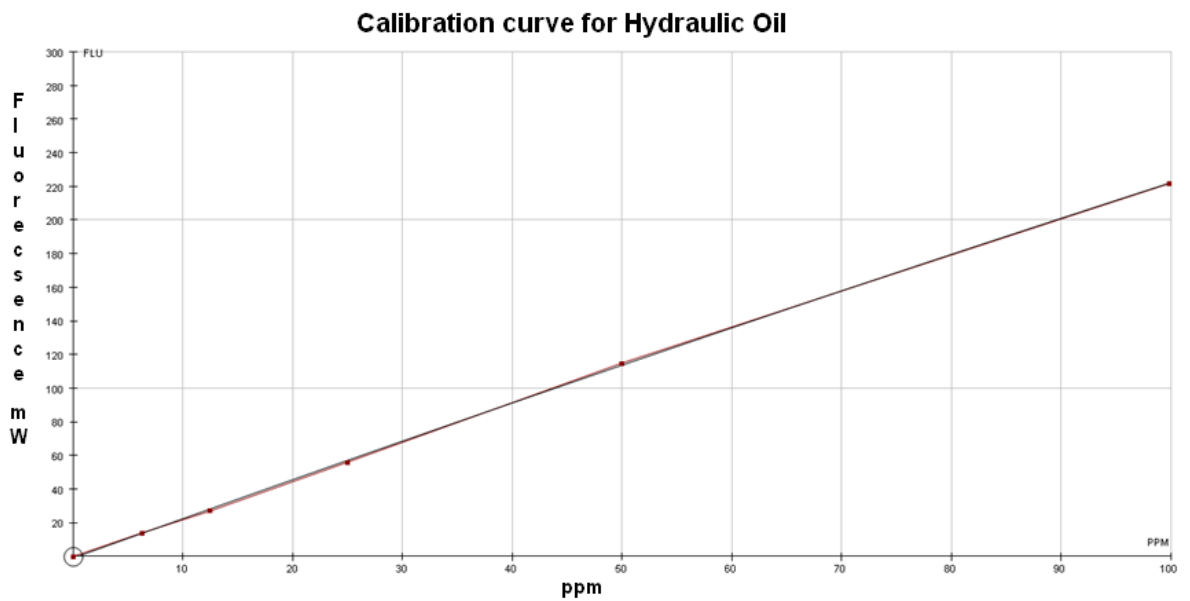


Figure 52: Calibration curve for Hydraulic oil

## Appendix II

### Example of an 24hour report

The data is taken from measurements with an OIW analyzer after a degassing tank. Table 11 contain the statistical data and *Figure 53* a plot of all measurements of mg/L-Measured, mg/L-Trend and 30 mg/L limit

Oil concentration for reporting: 12 mg/L

Table 11: Statistical data in a 24 hour report

Parameter	mg/L-Measured	mg/L-Trend	Difference [M—T]	mg/l-All	Difference [M—All]	Water-Temp. in °C
<b>Average</b>	<b>11.9</b>	11.8	0.1	12.1	-0.3	72.1
<b>Standard Deviation</b>	<b>2.6</b>	2.4	0.3	2.4	0.3	2.1
<b>Measurements</b>	133	133	0	80128	-	80128
<b>Maximum</b>	25.2	24.2	1	34.1	-8.9	75.5
<b>Minimum</b>	6.8	6.6	0.2	6.3	0.5	53.3
<b>% &gt; 30 mg/l</b>	0	0	0	4	-	-
<b>% &gt; 75 mg/l</b>	0	0	0	0	-	-

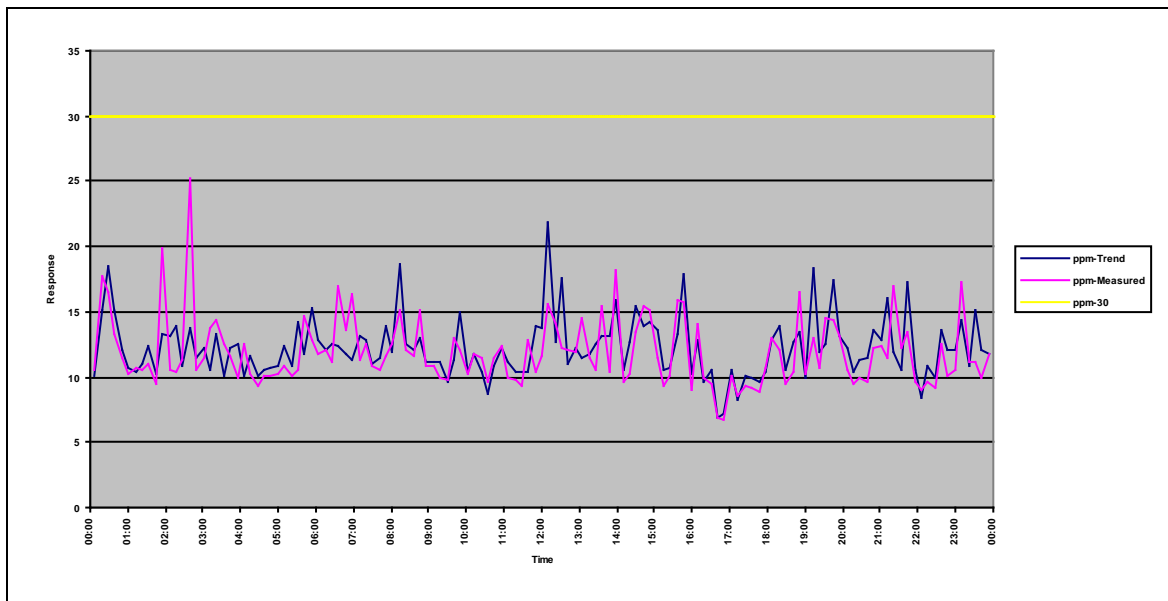


Figure 53: Plot of all the measurements performed with the OIW analyzer.

**Example of 1<sup>st</sup> order calibration curve ( $Y = aX + \text{Constant}$ )**

Figure 54 illustrates a calibration curve for a 1<sup>st</sup> order regression model with confidence limit. The X-axis is the analysis values (mg / L) measured by the OIW reference method. The Y axis is the OIW analyzers response values at the specific time the water samples were withdrawn (bottle samples).

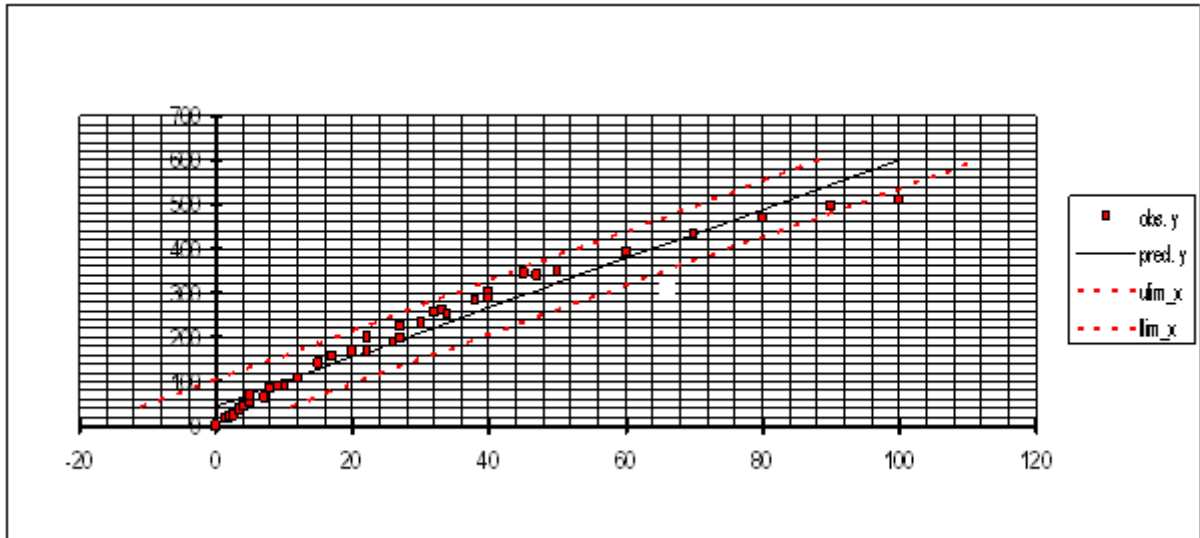


Figure 54: 1<sup>st</sup> order calibration curve

**Example of 2<sup>nd</sup> order calibration curve ( $Y = aX + bX^2 + \text{Constant}$ )**

Figure 55 illustrates a calibration curve for a 2<sup>nd</sup> order regression model. The X-axis is the analysis values (mg / L) measured by the OIW reference method. The Y axis is the OIW analyzers response values at the specific time the water samples were withdrawn (bottle samples) and the constant is zero (the curve goes through origo).

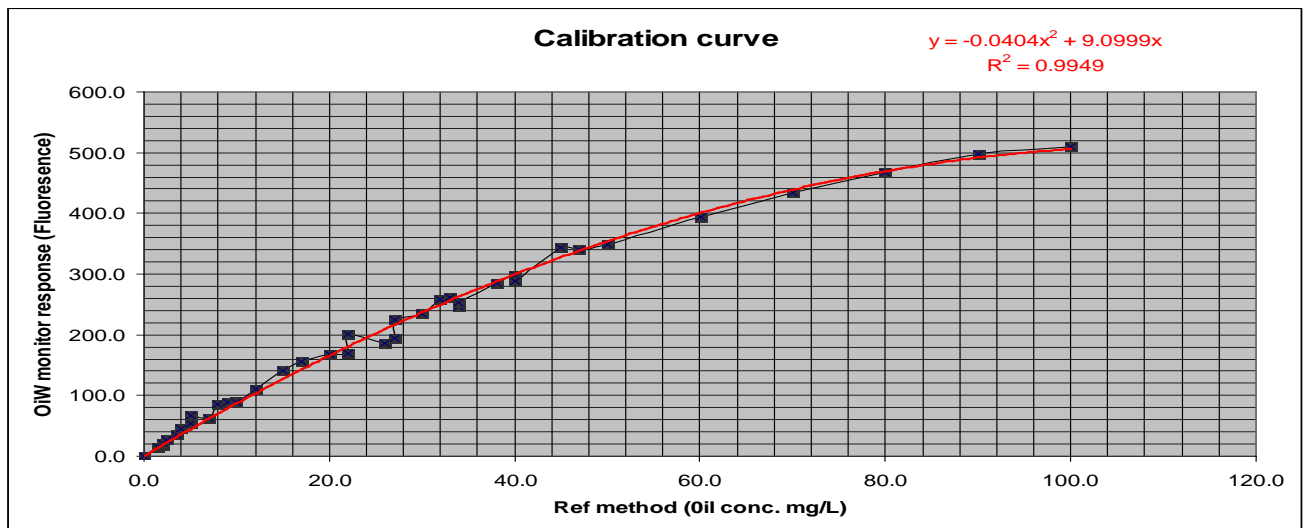


Figure 55: 2<sup>nd</sup> order calibration curve

## Example of how to report Validation data

Validation data are water samples that are not included in the calibration and are analyzed with an infracal method, GC-FID method and online OIW method. The OIW analyzer has an average deviation (std deviation) of  $\pm 7$  (mg / L) against INFRACAL method and  $\pm 8$  (mg / L) against the GC-FID method. The requirement is less or equal to  $\pm 4$  mg / L so the requirements are not met for this OIW analyzer.

Figure 56 illustrates a graphical representation of the validation data.

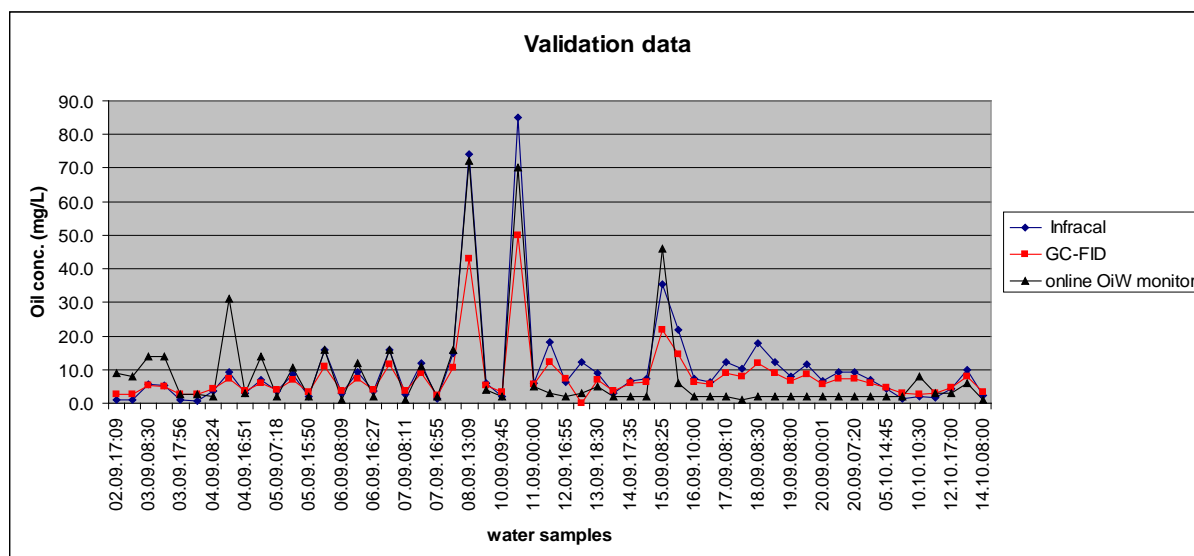


Figure 56: Validation data

Table 12 contains the correlation coefficients for the validation data. The table shows that the OIW analyzer doesn't meet the requirement  $> 0.9$ .

Table 12: Correlation coefficients of the validation data

	Infracal method	GC-FID method	Online OiW method
Infracal method (Platform)	1.0000	0.9843	0.8918
GC-FID method (OSPAR ref. method)	0.9843	1.0000	0.8867
Online OiW monitor method	0.8943	0.8867	1.0000