

# Online Oil-in-Water Monitoring Experience

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## Controlling and reporting oil discharge to sea, what is best?



**At-line sampling for Lab analysis**



**BRAGE monitor**

**On-line sampling and analysis**

## Introduction

*OSPAR CONVENTION FOR THE PROTECTION OF THE MARINE ENVIRONMENT OF THE NORTH-EAST ATLANTIC  
MEETING OF THE OFFSHORE INDUSTRY COMMITTEE (OIC)  
EDINBURGH: 14-18 MARCH 2005*

Proposals for new methods of analysis and harmonised methods for sampling of oil in produced water  
Presented by the United Kingdom

This document invites OIC to prepare an OSPAR Agreement on alternative method acceptance criteria  
and harmonised methods for sampling of oil in produced water based on the attached report.

**OIL IN PRODUCED WATER ANALYSIS**  
**– ALTERNATIVE METHOD ACCEPTANCE AND GENERAL GUIDELINES ON SAMPLE TAKING AND HANDLING**

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## Implementing the ISO Mod Method using an online Monitor (OSPAR doc.)

### [3.1] General Approach/Steps

1. **Select and procure an suitable online monitor**
2. **Properly install the online monitor**
3. Select an onshore laboratory where the ISO Mod method will have been established and acceptable to the regulators
4. **Establish an initial calibration / correlation over a period of time by taking replicate samples which are analysed by both the online monitor and the ISO Mod method**
5. **On-going validation of the correlation**
6. **On-going routine calibration checks using a control chart**
7. **Data for reporting**

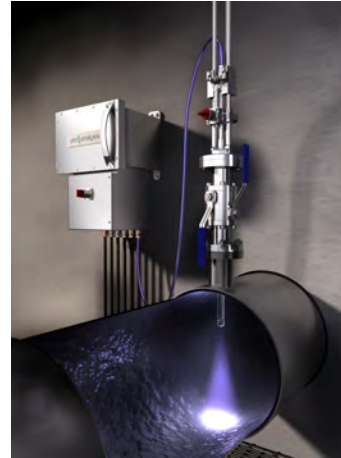
## [1.] Select and procure an suitable online monitor



Roxar, OiW monitor



Jorin, ViPA model MZ-3



ProAnalysis, Argus 100



Optek, model TF16



Advanced Sensors,  
OiW-EX100/1000 monitor



Teledyne Analytical instruments,  
6650 OiW monitor



Sigrist Process-Photometer,  
OilGuard EX



Turner Designs Hydrocarbon Instruments,  
TD-4100 XD

## [1.] Test Rig at StatoilHydro Research Centre in Porsgrunn

### Water Test Rig:

Direct seawater input

Heater

Pump

Oil reservoir

Injection pumps

Choke

Test section

Valves

Drain with separator

Pressure measurements

Flow measurement

Temperature measurements



## [1.] Online Monitors Test 2007 in Porsgrunn



## [2.] Properly install the online monitor [4.2 [Specific Guidelines for Sampling](#)]

### **Guideline 1: Sample Point Location**

**The sample point for the collection of samples used for legislative monitoring, should conform to the following criteria:**

1. The sampling point shall be immediately downstream of the final oil-water separation, and from, or just downstream of, a turbulent region.
2. The siting of the sample point should be approved by the regulator and should not be moved subsequently without permission.

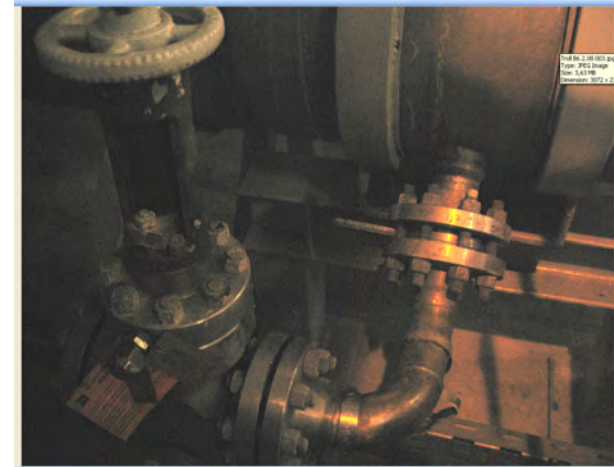
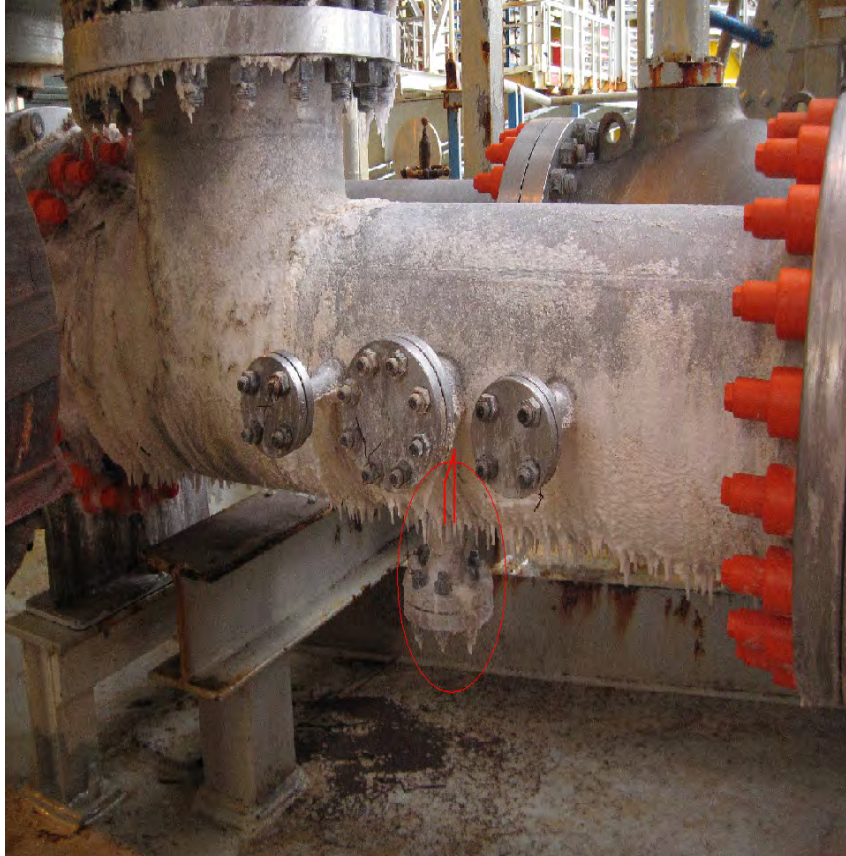
### **Guideline 2: Design of Sample Point**

#### **Online Sampling (with an Oil-in-Water monitor)**

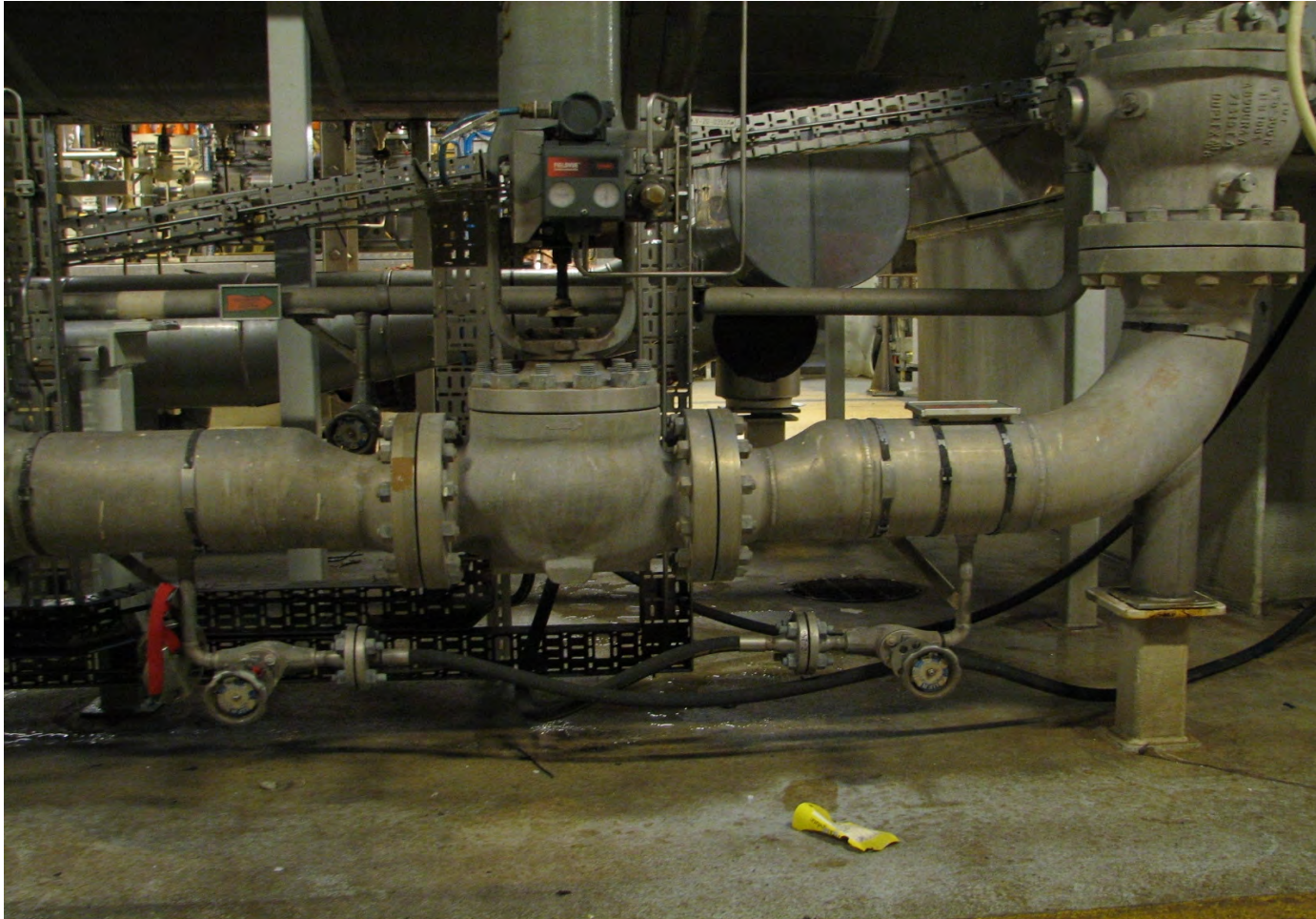
1. Where online systems require a side stream feed to the monitor, the feed should be provided by way of a dedicated sample connection. A centre line pitot should be used to ensure that the sample is representative. Depending on the available head and the monitor flow requirements, the sample may need to be pumped to the monitor.
2. Where online systems require the installation of a probe in to the main pipe, the location should be such that there is confidence that the probe is exposed to representative flow conditions.
3. The distance between the sample point and any external online monitor, should be minimised as far as practically possible.



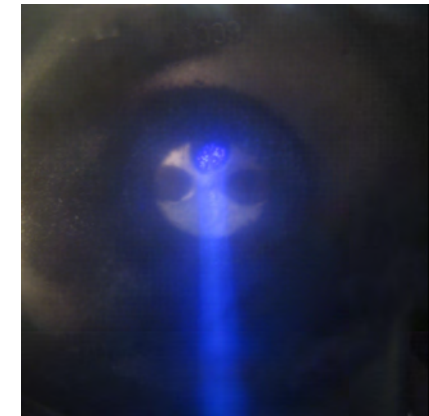
## [2.] Sampling challenges for online OiW monitoring



## [2.] Sampling challenge for online OiW monitoring



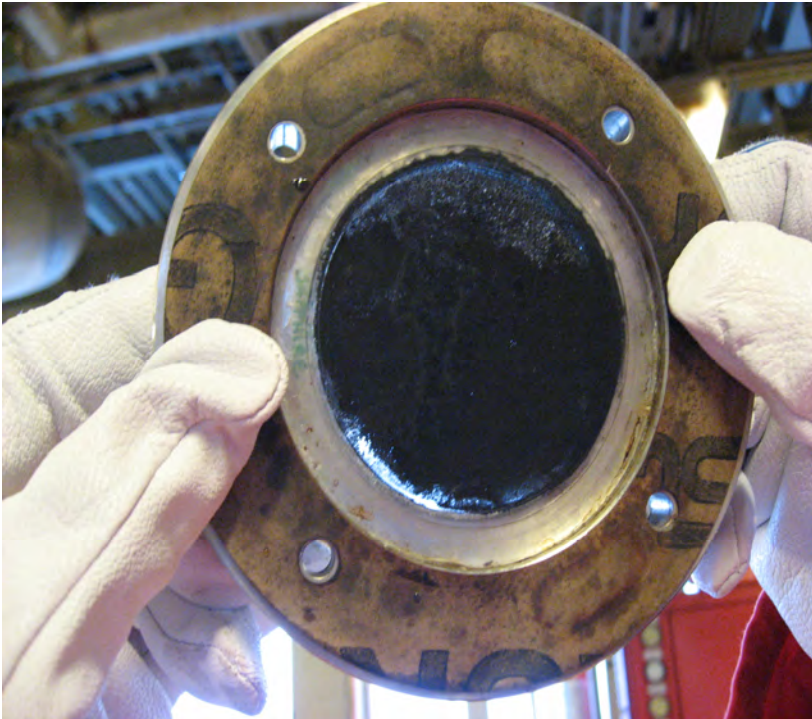
## [2.] Online OiW monitor after the degassing tank at Brage platform



Light from the UV laser  
in the sample chamber

Advanced Sensors OiW-EX1000 monitor

## [2.] Reliable Automatic Cleaning System



**Automatic cleaning system of the sapphire glass in front of the light probes based on ultrasonic wave generated by the transducer. Result after 30 days continuing measurements.**

## **[4.] Establish an initial calibration / correlation over a period of time by taking replicate samples which are analysed by both the online monitor and the ISO Mod method**

### **Initial calibration / correlation:**

In order to calibrate an online monitor against the ISO Mod method, a three-calibration points approach is suggested. These three calibration points shall ideally correspond to high, mid-scale and low readings within the monitor measurement range, which should at least cover 0 to 100 mg/l. As guidance, “low” means a reading in the 10-25% of the measurement range, “mid-scale” in the 40-60% and high in the 75-90% respectively. For each calibration point, at least 3 parallel analyses / readings should be respectively taken by the online monitor and also by the ISO Mod method.

Correlation should be obtained by plotting the average reading from the monitor at a time when samples are withdrawn against the average reference value and then fit the points using linear regression. One must realise that establishing this initial calibration/correlation may take weeks instead of days. Such a calibration may also include drifting which may occur during the time period when this initial calibration is established.

During the initial calibration / correlation period, for the purpose of reporting daily samples should be taken and sent onshore to be analysed. Alternatively another bench top analyser which has already been calibrated against the ISO Mod method can be used.

## [4.] Initial Calibration can be done in the Water Test Rig

### Water Test Rig:

Direct seawater input

Heater (max 60 °C)

Pump

Oil reservoir

Injection pumps (oil, chemicals, solid)

Choke (oil droplet size, gas bubbles size)

Test section

Valves

Drain with separator

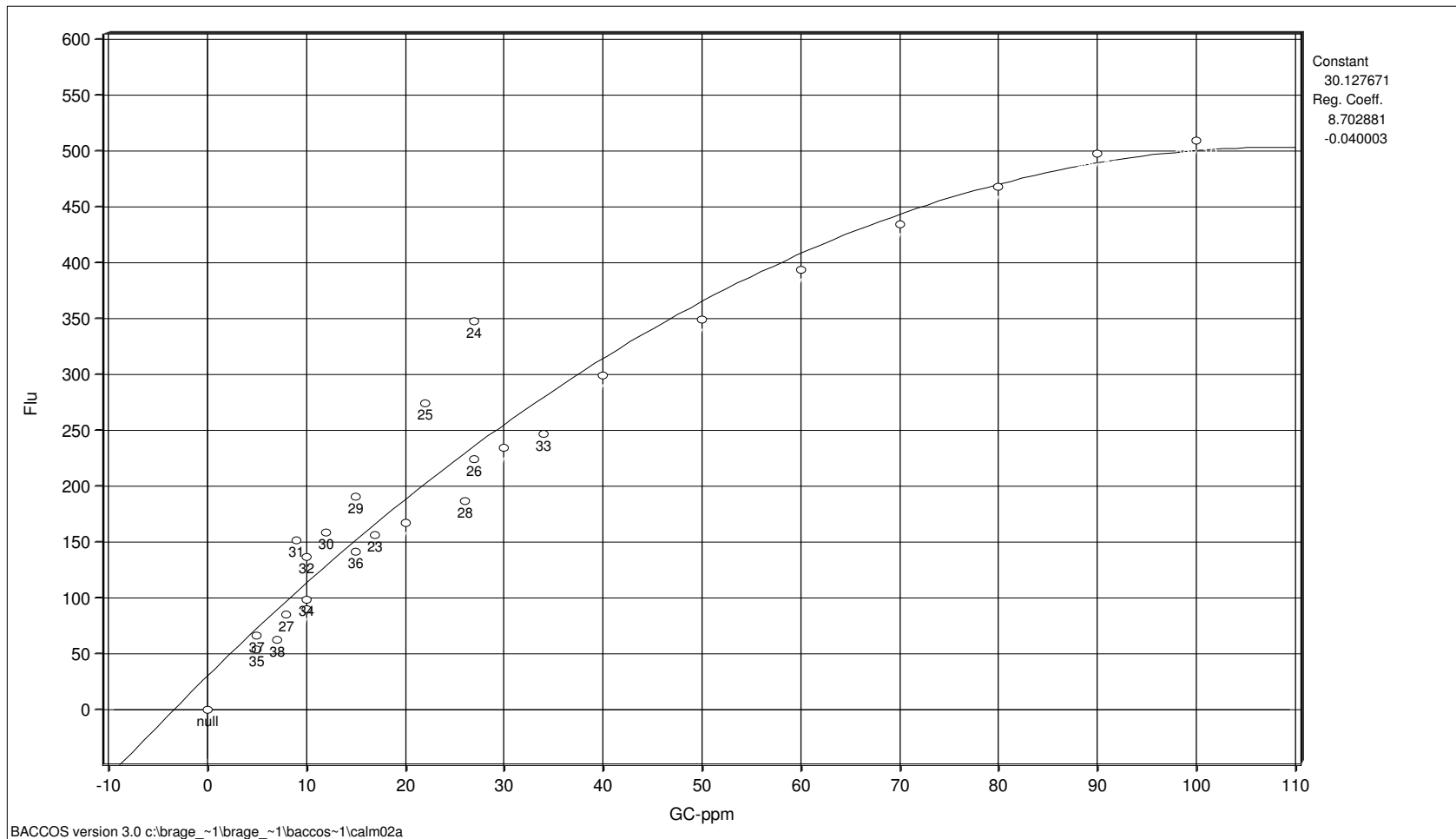
Pressure measurements (max 25 bar)

Flow measurement

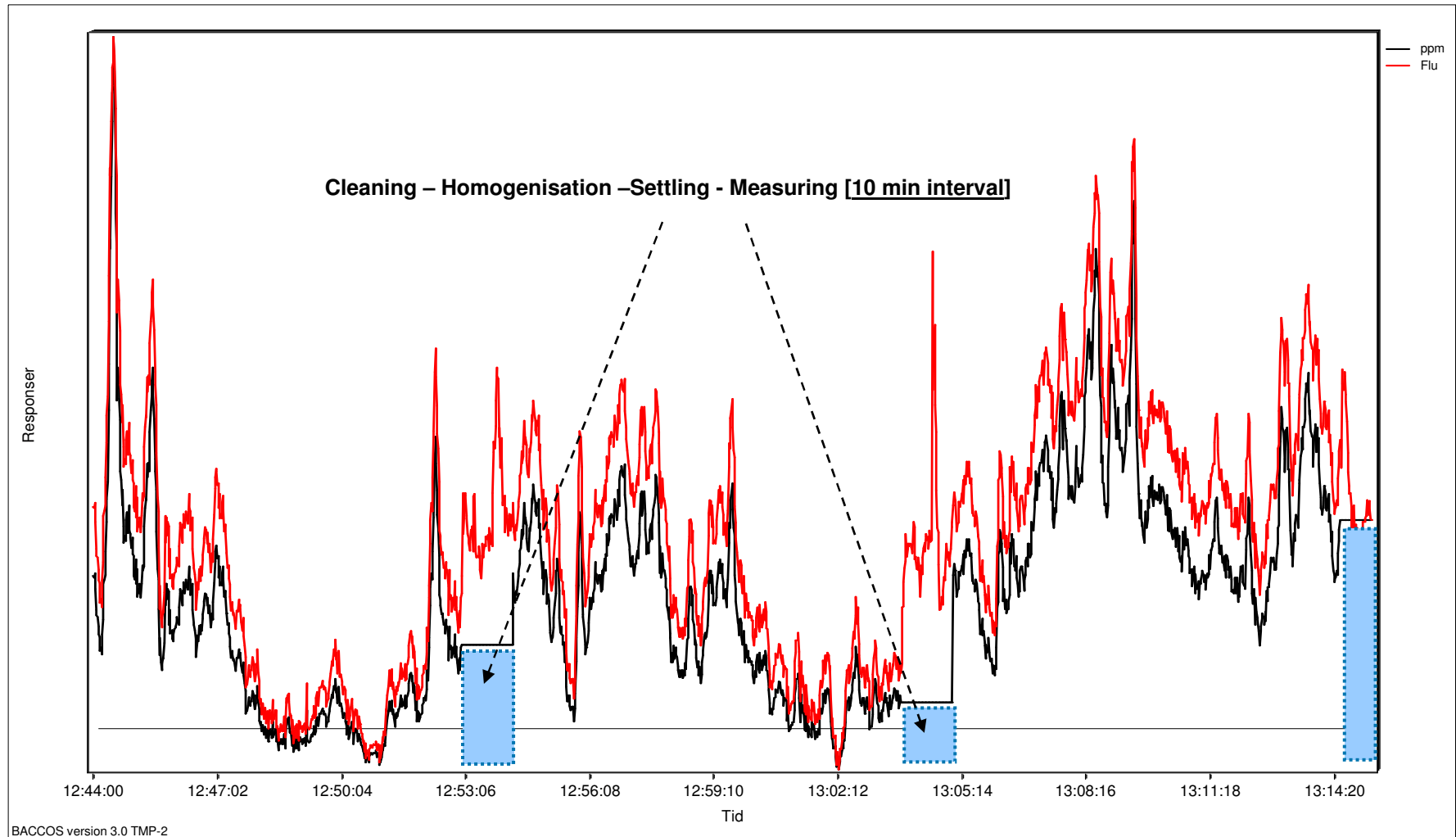
Temperature measurements



## [4.] Example of Calibration curve (mix of lab and offshore)

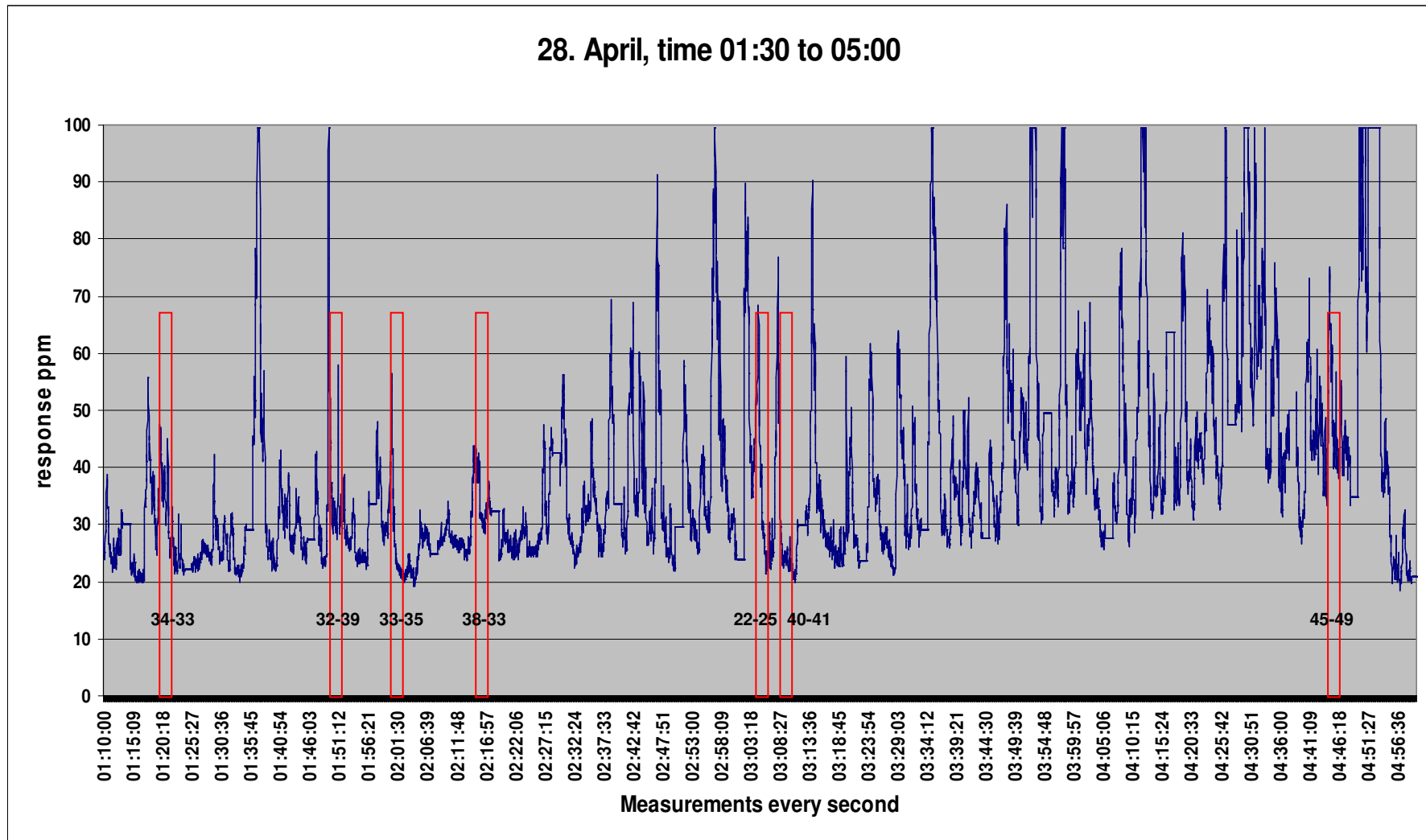


#### [4.] Sample cycles for Advanced Sensors OIW-EX1000 monitor





## [4.] Results from spot samples, initial calibration / correlation



## **[5.] On-going validation of the correlation**

## **[6.] On-going routine calibration checks using a control chart**

Once an initial calibration/correlation is established, the online monitor's performance should be continuously monitored to confirm satisfactory operation and to detect any drift from the initial calibration.

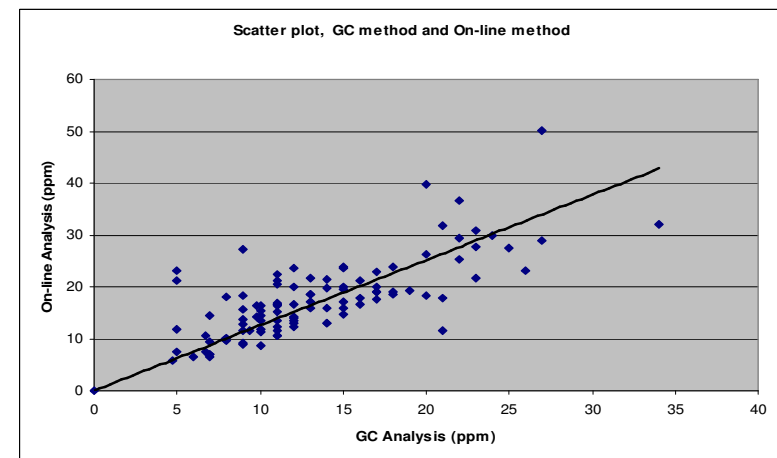
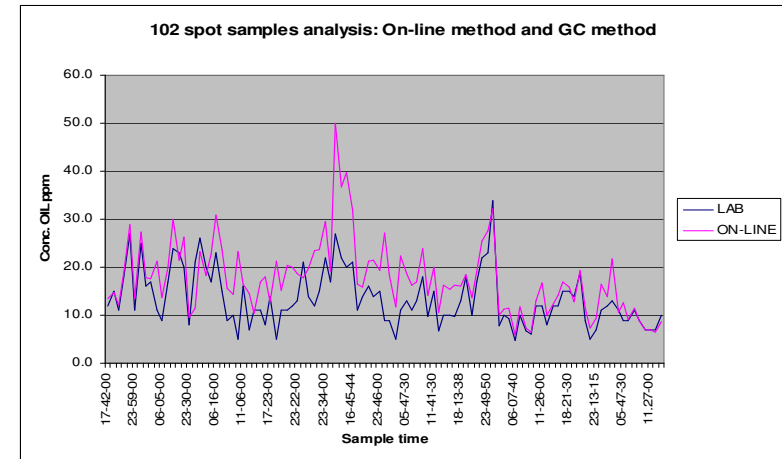
It is suggested that routine calibration checks are carried out, initially once a week. Also validation should be done from time to time to confirm that the initial calibration is still valid. Procedures involved in validation and routine calibration checks are similar. Calibration curve / correlation shall consider to be valid if the difference between its readings (after converting to the reference equivalent using the calibration curve / correlation) and the ISO Mod reference method does not exceed the reproducibility of the ISO Mod method.

Routine calibration checks are carried out by analysing parallel samples as in establishing the initial calibration, i.e. taking three samples during which readings from the online monitor are recorded. Then the difference in average between the reference equivalent from the online monitor and the reference method is plotted on a control chart.

## [5, 6] Validation results from Brage

- Test period 12. March to 15. April
  - Mean deviation between GC method and on-line method: - 4.2 mg/l (std dev. 5.0 mg/l) for 102 spot samples
- ” Monthly reporting” 12. March – 15. April
  - Spot samples and same time period on-line
  - GC method (average of 4 spot samples/day): 13.5 mg/l
  - On-line method (average of 4 spot sampling time/day): 17.7 mg/l
  - On-line analysis (mean value over 24 hours): 17.8 mg/l

### Spot samples



## [7.] Data for reporting

Online monitors gather data continuously. However for regulatory compliance monitoring, only two grab samples per day currently require to be analysed. Therefore in theory not all the information generated by the on-line monitor needs to be reported. There are a number of possible ways which may be considered for reporting:

- (i) select two specific time of the day, and take the two oil-in-water results closest to that time for reporting;
- (ii) select two specific short periods of time (say 5 minutes or a time duration which allows to take 3 consecutive measurements) each day and then take the average of the online monitor readings for reporting;
- (iii) average all the results obtained daily and then report the average result.

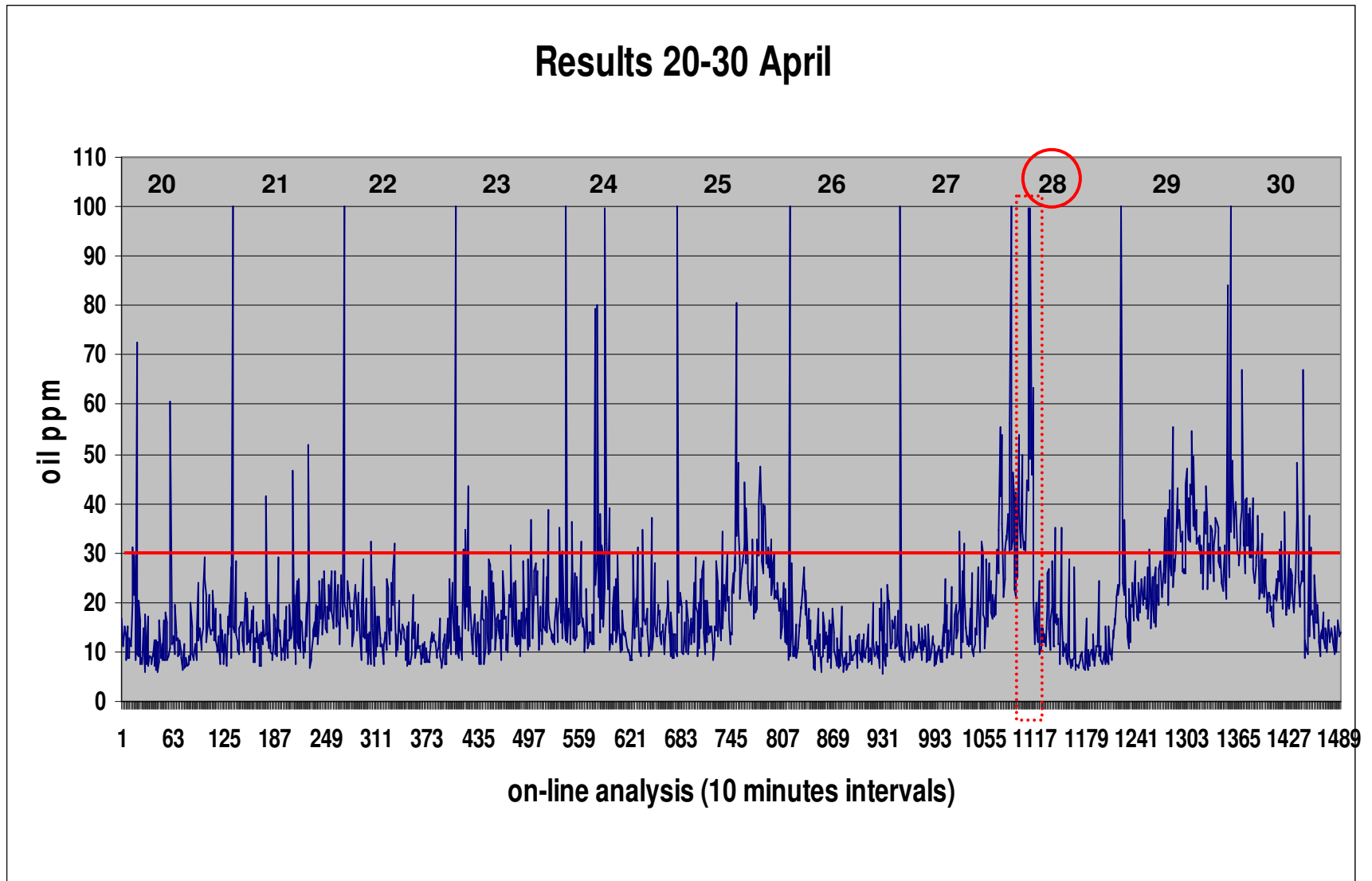
Of the three options, option (ii) is probably better than the other two as it will smooth out the readings and at the same time allow plenty of time for the instrument to be maintained daily if required.

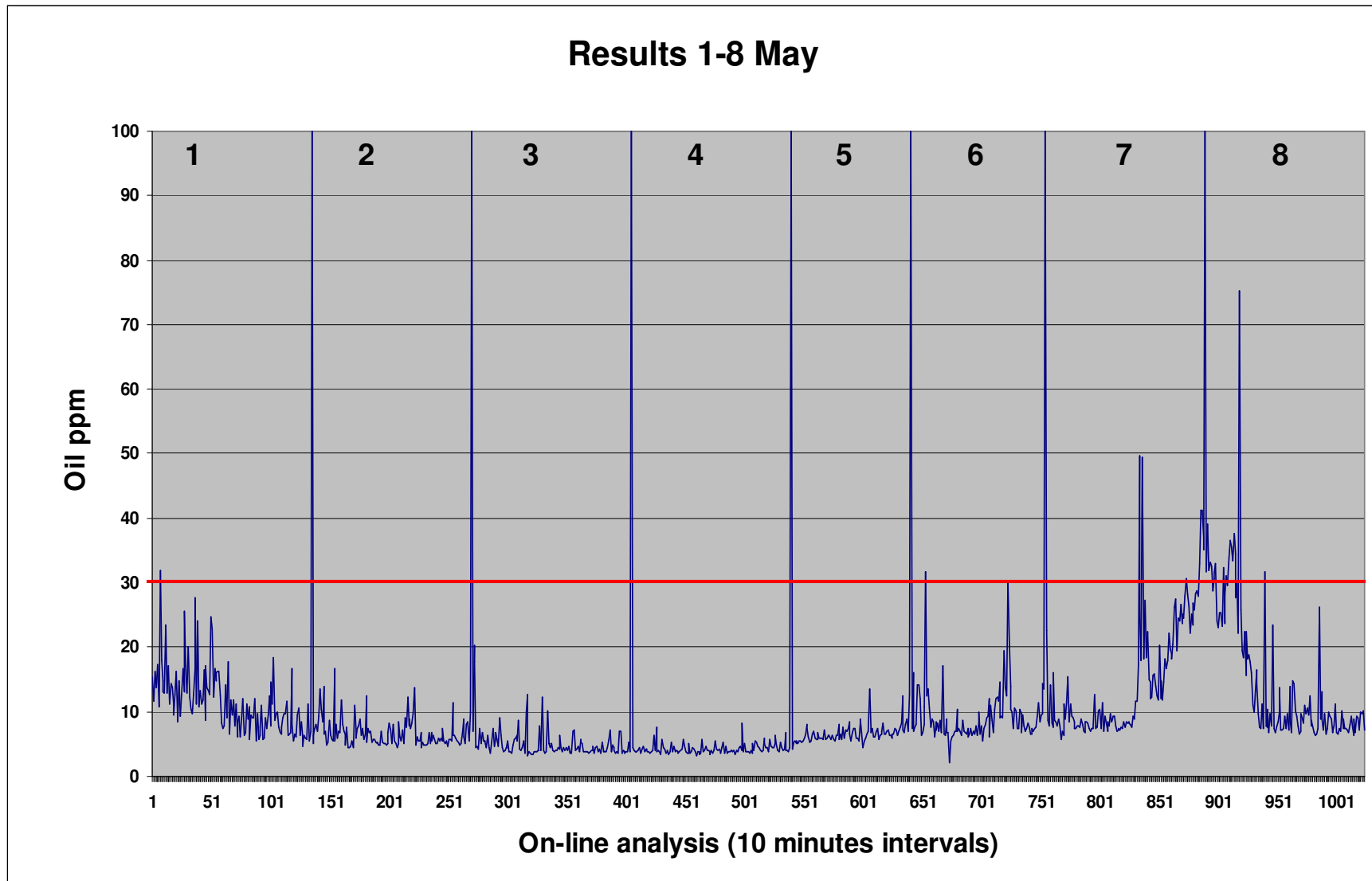
## [7.] Data for reporting

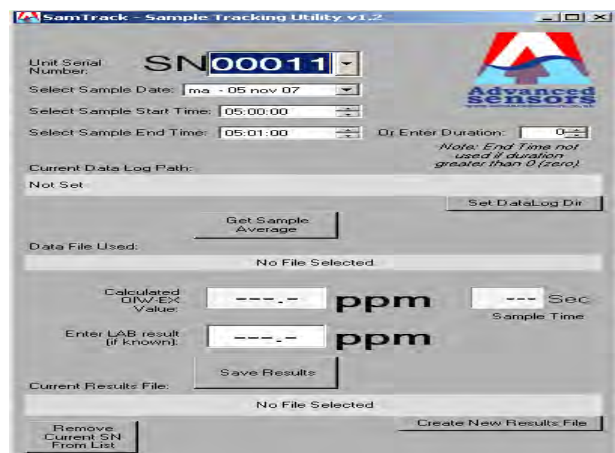
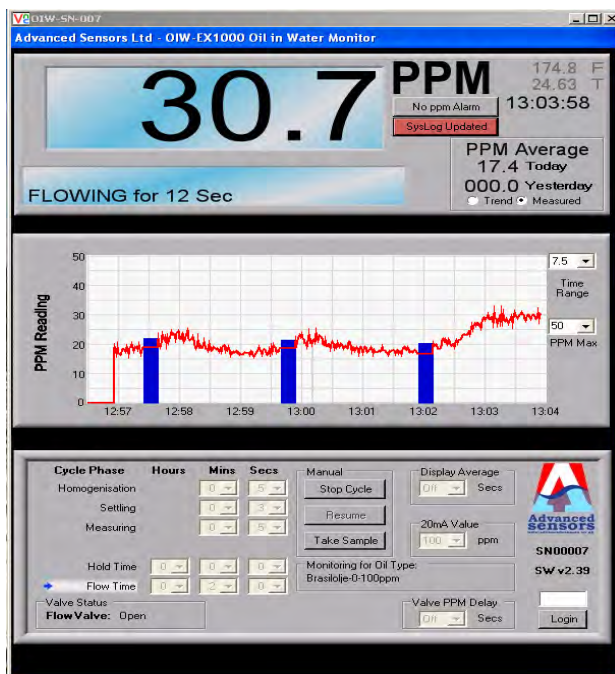
Further checks on the equivalence of the results obtained from the online monitor and the reference method using statistical significance tests (F tests and Student-t tests) can be carried out.

Dealing with online monitor break-down: if an online monitor is used for compliance monitoring / reporting, it is suggested that at least a laboratory bench top analyser which has been calibrated against the ISO Mod method should be available as a back-up.

Responsibility: for online monitors, it is thought that it is better that the operator using the monitor takes the full responsibility in establishing and validating the correlation between the alternative method and the ISO Mod method, and also the running of the control chart.







## 24 hours report (automatic)

Daily online Oil-in-Water Monitor Report

Date: 2007-09-19.

RESULT for DEGLASSING TANK and OIW-EX1000 Monitor (SN0011)

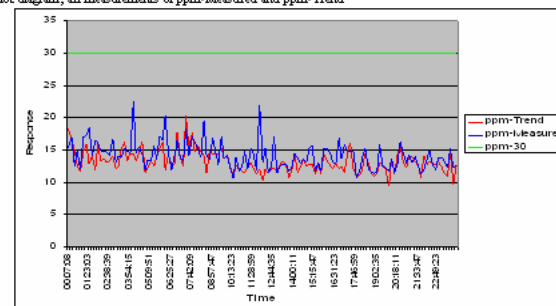
All data are collected from Data file: [SN0011-19\_Sep\_07-00\_00\_Wed\_OIW\_Data.csv]

Oil concentration for reporting: 14 ppm

Statistical data

Parameter	ppm-Measured	ppm-Trend	Difference [M-T]	ppm-All (sec)	Difference [M-All]	Water-Temp. °C (sec)
Average	14.2	12.2	2.0	13.4	0.8	73.2
Standard Deviation	2.1	1.7	0.4	2.5	-0.7	1.2
Measurement	12.5	12.5	0	51341	-	8331
Maximum	22.5	20.2	2.3	28.5	+4.0	74.4
Minimum	10.4	9.5	1.1	7.5	2.9	70.3
% > 30 ppm	0	0	0	0	-	-
% > 25 ppm	0	0	0	0	-	-

Plot diagram, all measurements of ppm-Measured and ppm-Trend



Spot samples analysed

Time sampling	Monitor result in ppm	Est. Method result in ppm	Diff (Monitor - Est-method)
20:20:30 - 20:21:30	12	9.5	2.5
22:21:30 - 22:22:30	11	11	0

COMMENTS:

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 \_\_\_\_\_  
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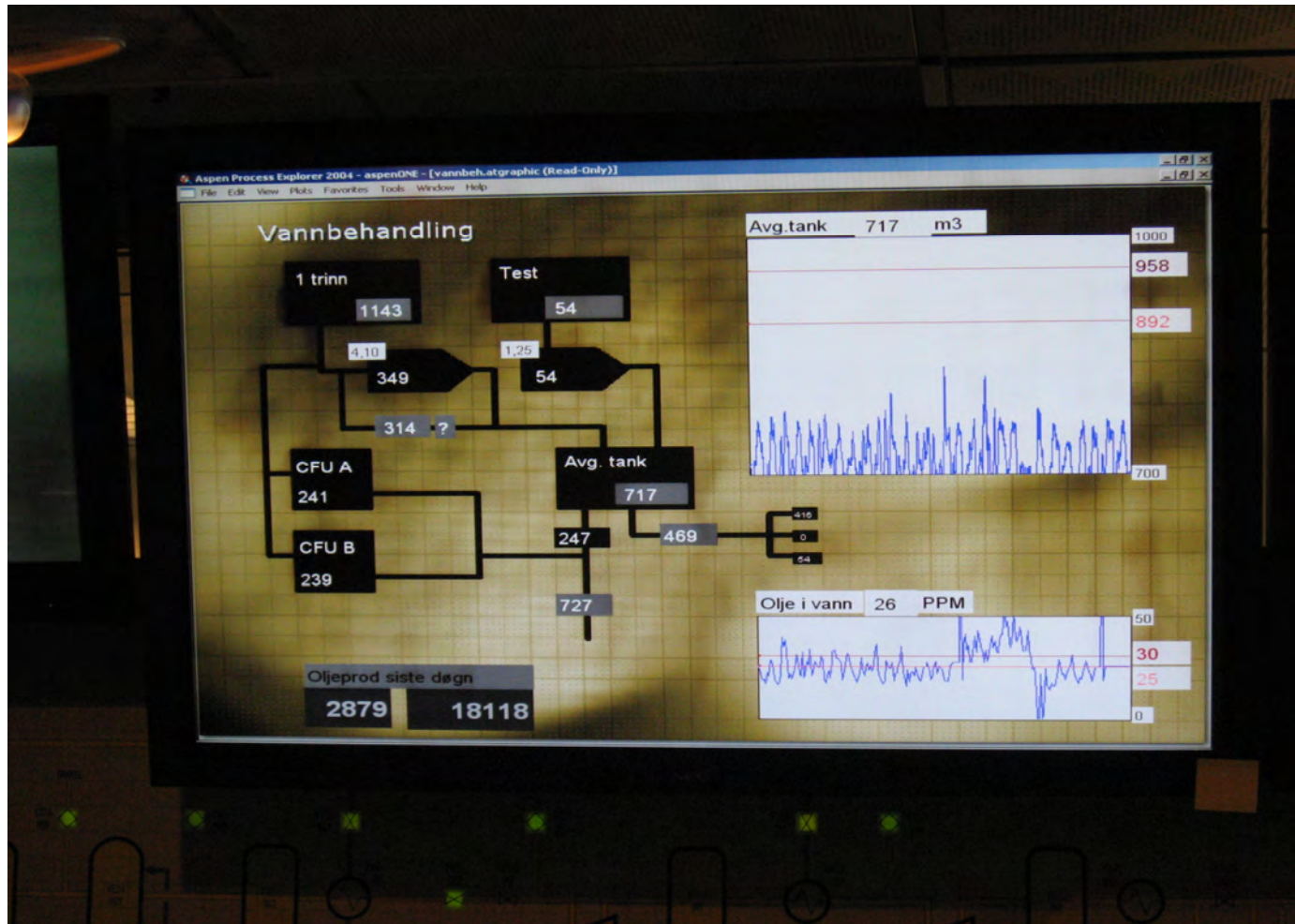
APPROVED: (Yes/No): \_\_\_\_\_

Date/Name: \_\_\_\_\_

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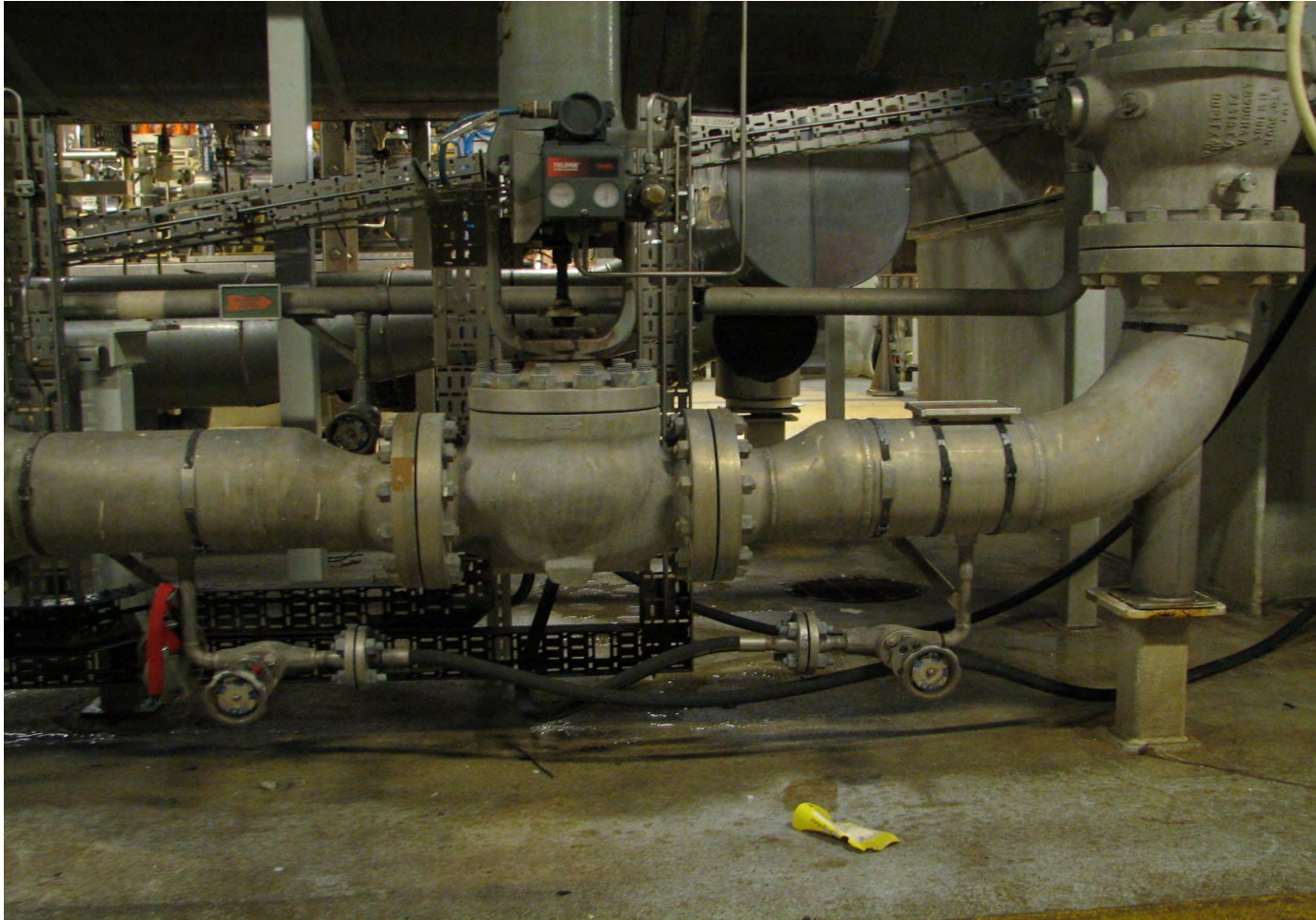


## Online oil in water measurements for real time process control

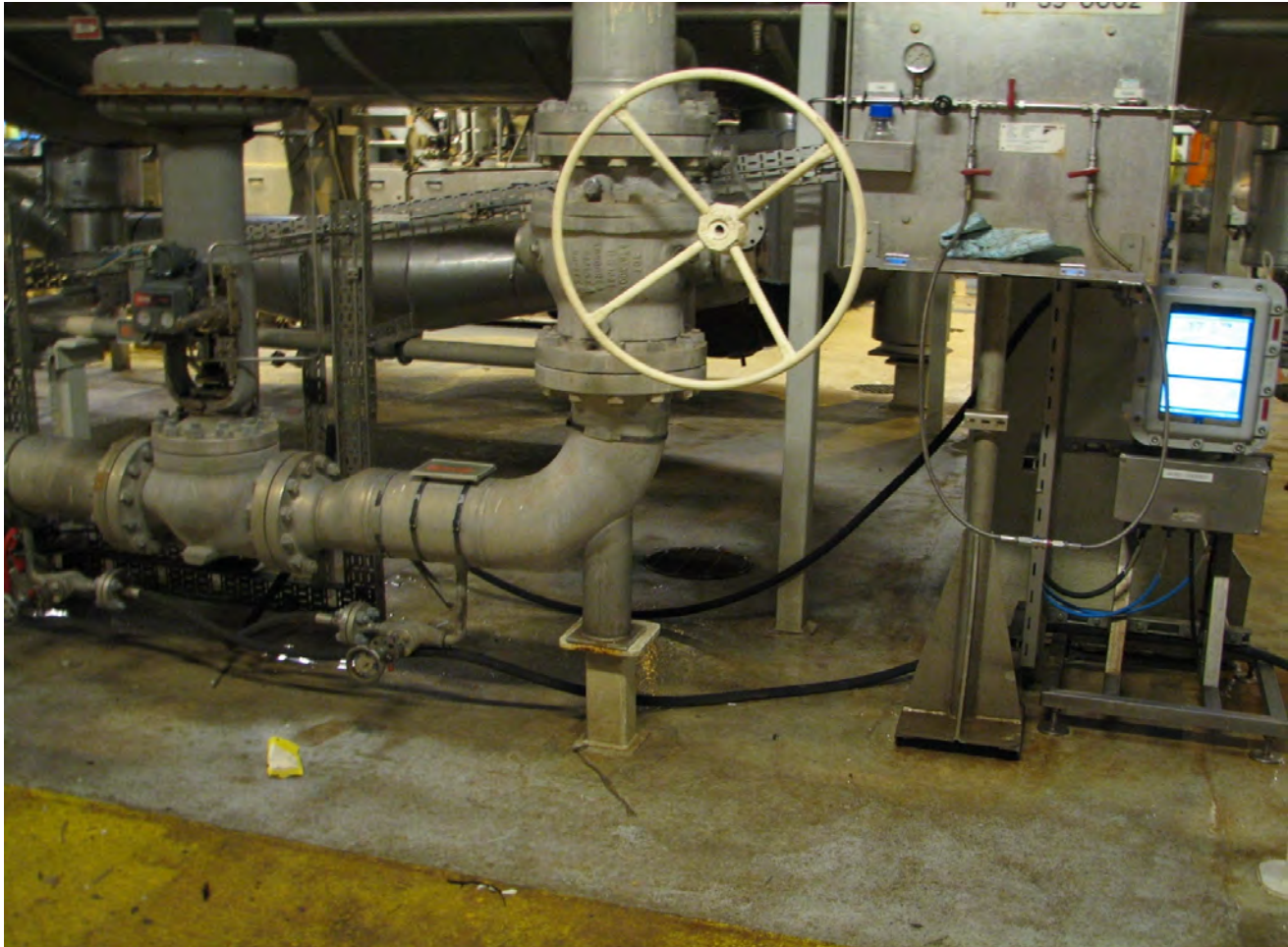


Monitor Screen at BRAGE Control Room

## Online OiW monitoring at TROLL C platform (2007)

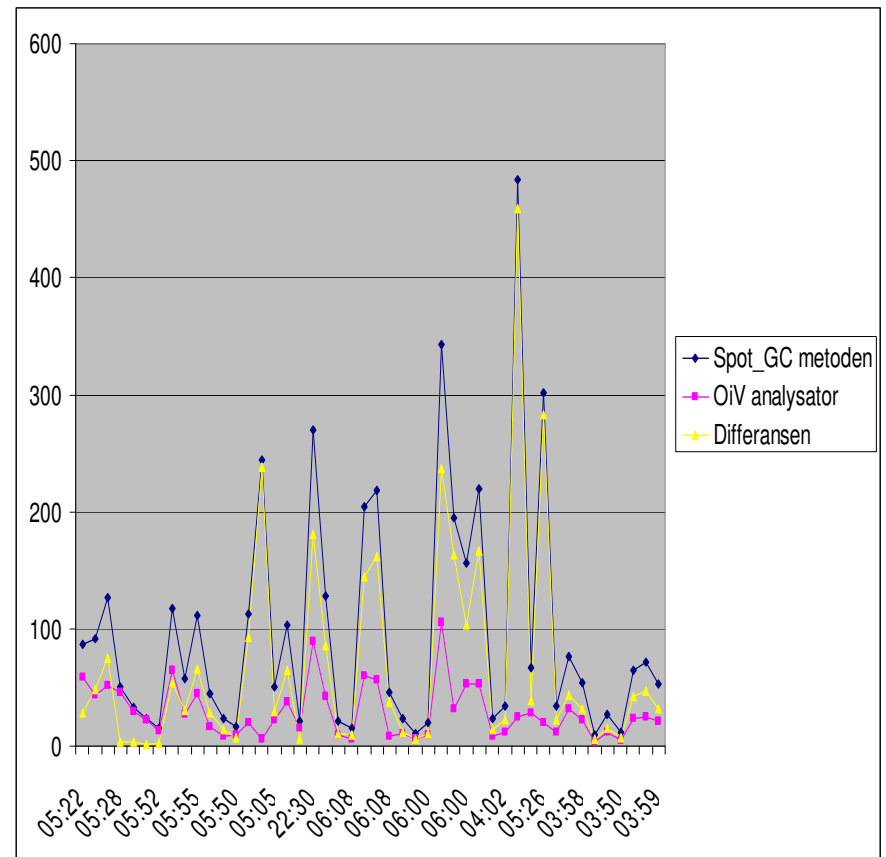


## Online OiW monitoring at TROLL C platform (2007)

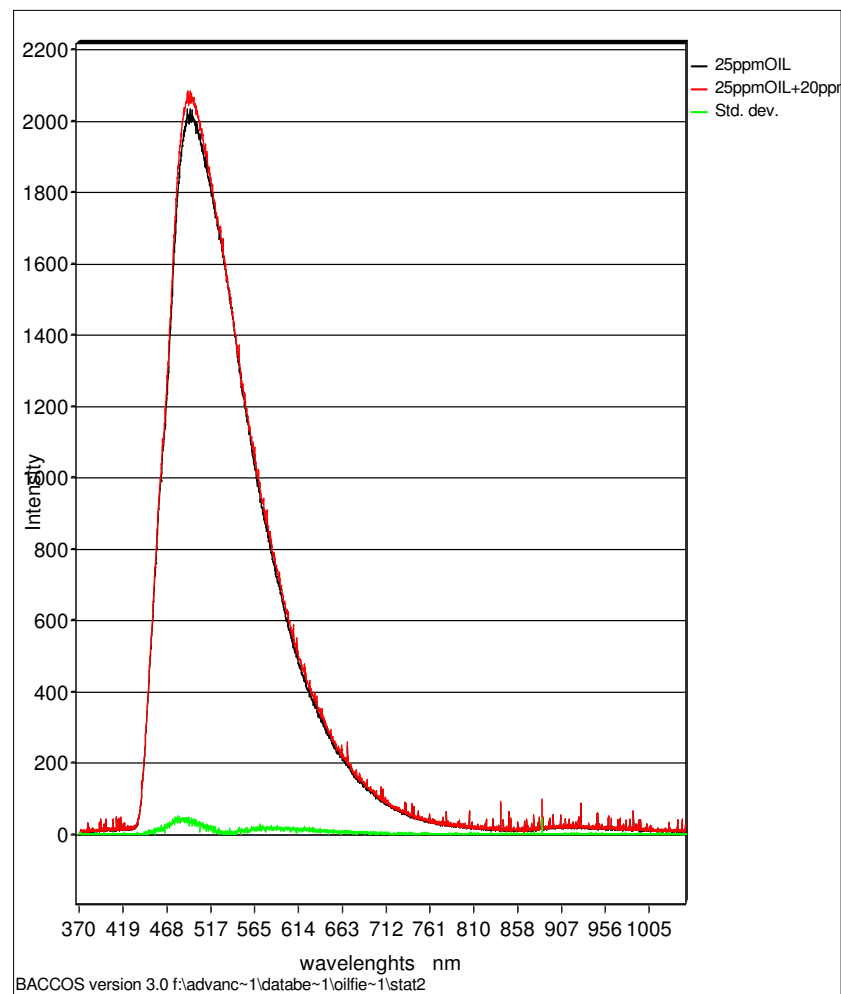
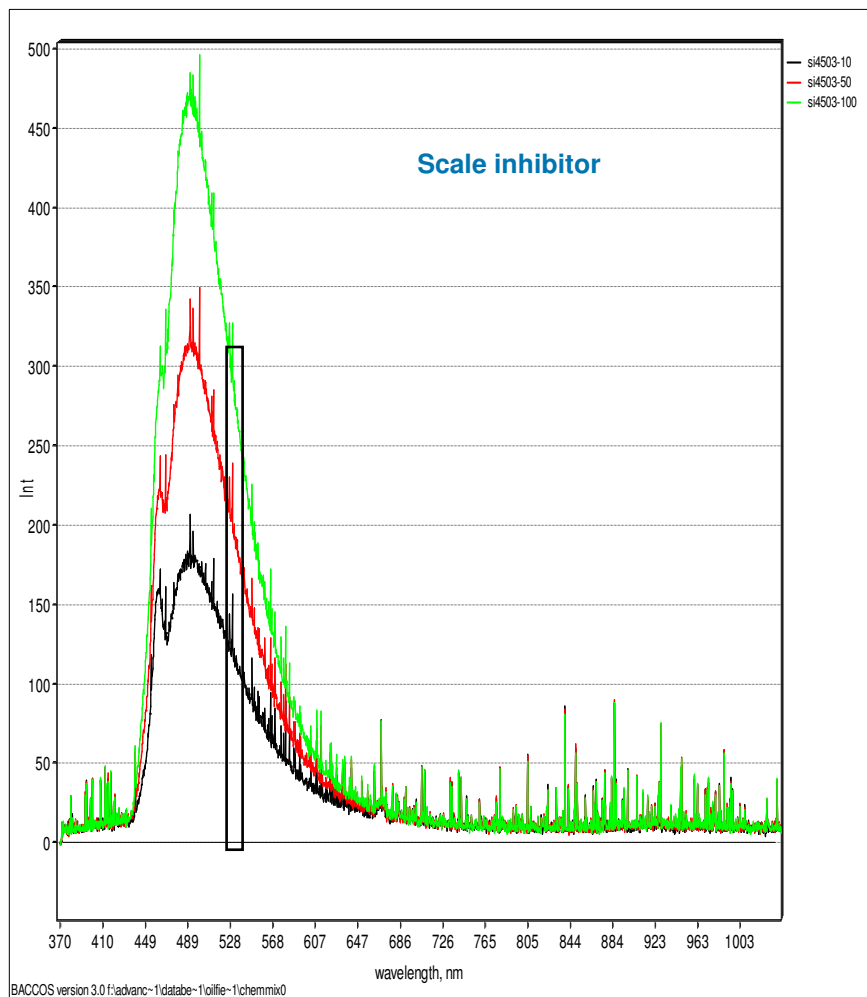


## TROLL C trend measurements for 35 days after the start up (July – August)

- The installation was a test application June 2007
- OiW monitor measuring the inlet water stream to the degassing tank
- The calibration is not optimised (0 to 600 ppm)
- The platform used the 4-20 mA signal (ppm) today for process responding when the oil concentration rapidly increase
- Need a better calibration (in progress)
- Instrument has been running for 9 months without any maintenance



## Production chemical in produced water (Full Scan Spectrometer)



## Conclusion: Online Oil-in-Water Monitoring Advantages

### ENVIRONMENT (real-time analysis)

- Oil discharge analysis for 24 hours
- Operator can handle quickly to process disturbance and minimise oil to sea discharge
- Platform can use the analysis for SFT reporting
- Reduction in Lab work at the platform

### PRODUCTION (real-time analysis)

- Better process control
- Process optimization for achieving
  - higher oil production
  - without increased oil discharges
- Potential for analysis of
  - higher oil concentration
  - production chemicals
  - Subsea application