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OPERATIONAL PERSPECTIVE, OF 0IL-IN-WATER MONITORING OFFSHORE

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Abstract

Petrobras has been testing on-line oil-in-water monitors in offshore Campos Basin, Brazil, aimed at establishing cost effective, accurate and reliable operational procedures and at the same time complying with the legislation for the discharge of produced water Into the marine environment. There are many available technologies and some were chosen according to their adequacy to measure oil and grease (O&G) in produced water and re-injection water offshore. The need of Freon replacements and alternative laboratory analysis methods are evident. Systems based on ultraviolet fluorescence (UVF), infrared absorption, infrared scattering and Laser scattering techniques are among the targets of these field tests which seek simplicity, easiness of sample conditioning and low sensitivity to variations due to processed oil blending. This paper intends to present the status of the first results and the operational perspectives from the use of on-line oil-in-water monitoring systems.

1. INTRODUCTION

One production unit always generates what is known as produced water, typically a blend of formation water and injection water. It may contain oil, salts, chemical compounds, solids and metals. Produced water is the primary product for discharge resulting from the separation of oil, gas and water of one production unit and its quality is normally monitored through a daily analysis of oil and grease concentration measured in ppm (parts per million) (mg/l). The technologies for O&G measurement instruments are substantially different from those used in BS&W meters.

Environmental restrictions and the need for a better control over the process, associated with water treatment plant operation, have taken the oil industries to a growing interest for oil-in-water content real time monitoring. TOP analysis methods approved by environment control agencies are as follows. Gravimetric Method USEPA 1664 and Infrared Spectrophotometry – ASTM 3921, Standard Methods 5520C or 5520F. The first method uses hexane extraction, solvent evaporation followed by oil residue weighting. Measurement through the Infrared Spectrophotometry Standard Methods 5520C is performed by mean of oil and grease extraction from the water sample using organohalogenated solvent (carbon tetrachloride or dichlordifluoretane).

The main reasons for the petroleum industry choice by on-line monitoring of oil-in-water content are, as follows:

- Real time response, providing better control for oil processing;
- Cost reduction related to routine laboratory analysis;
- Database generation extremely useful at the process plant control and modifications to design new plants;
- Effective monitoring of discharged water.

In Brazil the discharge of the produced water into the environment is regulated by IBAMA/CONAMA 20/86, Article 21, which imposes contaminant level limits in efluents by gravimetric method. For oil and greases this limit is 20 ppm (mg/l). The same legislation establishes on Article 24 that sample collect and analysis methods should be either those specified by INMETRO approved standards, or if they are not available, by Standard Methods for Examination of Water and Waste Water, last edition. IMO – International Marine Organization requires for international waters or floating systems connected to a riser one maximum per month of 29 ppm for O&G, with acceptable daily peaks of 42 ppm. IMO still requires for floating systems not connected to riser the use of on-line O&G analyzer for control of this parameter in real time.

On-line Oil and Gas Content Analyzers with different working principles such as scattering of infrared light (IR), scattering of IR/laser/visible light, IR spectrophotometry or absorption and ultraviolet fluorescence (UV) are available on the market to provide reasonably uncertain real time analysis.

The continuous and on-line water quality monitoring through Oil an Grease Content monitors provides one better operational control of the process, in real time, specially in the case of unattended installations, or if there is a need for water purification to be re-injected in the reservoir.

The Oil and Grease Content meter selection should be done through a previous characterization of oil and water of the related production unit. In addition, it must be set:

- concentration range to be measured (ppm);
- detection technique compatibility with the kind of oil to be measured;
- sample preconditioning procedure and periodic cleaning of the measurement system;
- simplicity and strength for severe operational conditions such as explosibility, corrodibility and unattended installations.

Meters that employ extraction before solid removal are those with lower uncertainties. Meters operating by light scattering have been mostly used in oil ships with reasonable results in the O&G range, 100 – 1000 ppm. Meters without sample contact with the measurement cell are those presenting the lowest complexity and minimum failure occurrence. Those meters constitute a promising technological innovation of the last years, with good possibilities of expansion and development.

The presence of solids or free gas in the oil-in-water to be monitored are factors with a substantial influence on the performance of O&G meters.

2 O&G MONITOR TECHNOLOGIES

A number of different technologies for measurement of oil and Grease-in-water content are presented, as follows, with the related detection techniques. The measurement uncertainties are affected by the quality variations of the oil-in-water and of the produced or processed oil. The presence of solids and free gas is the main source of variations affecting the performance of the O&G meters.

2.1 IR scattering and IR/Laser/Visible Light Scattering

One monochromatic light beam of a certain wavelength is directed to the circulating flow of a small cell with optical glass walls. The scattered beam from the sample passes through transformation lens that produce one scattering pattern over one detector.

The transformation lens receive the scattered light in a broad angle range, producing an image in which each scattered angle has a corresponding ring in the detector plane. Consequently, the signal for each detector angular position corresponds to a light scattered by the sample in a certain angle. There is a correspondence among scattered angle, intensity and particle size: larger scattering angles are produced by smaller particles, while lower angles are associated to larger particles. Scattering intensity and incident light beam attenuation are then related to substances in suspension on the sample.

2.2 IR Spectrophotometry

The technique of oil and grease detection in the water by the spectrophotometry measurement or infrared absorption is based on the difference between the absorption coefficients of oil and water at 3.4 micron. Additional analysis at 3.6 micra wavelength (where hydrocarbons don’t have an intensive absorption) allow the compensation of disturbances caused by the presence of solids or air in the oil-in-water.

To remove all oil and solids in suspension, one oil-in-water sample (reference sample) can be collected and passed though an ultra filtration system. This sample is analyzed at 3.4 micron and the same oil-in-water cell to compensate for any background reading. Only oil components are measured, since the effect of any dissolved oil (present in the reference sample) is discounted as a background reading. Facilities required for background compensation (solids in suspension and air) by this technique can lead to a complex measurement system and to an increase in investment and operation / maintenance costs of the analyzer.

Another potential problem is the small length interval to differentiate oil from water at 3.4 micron, forcing cell use with narrow optical path, which defines the volume of the radiated sample. As a result, the sampling cell is highly influenced by the sample incrustation and automatic cell washing. One typical sample pre-conditioning includes a pump to dissolve solids and oil, to prevent system clogging and to generate a constant and uniform distribution in the oil drop size. If it is required a distinction between hydrocarbons and aromatics, an additional analysis in the UV wavelength is made to detect the aromatic hydrocarbons.

Another analysis through IR spectrophotometry consists of a hydrocarbon pre-extraction with organic solvent, free of carbon-hydrogen bindings such as dichlorodifluoretane, carbon tetrachloride and others. The extract is then submitted to an infrared source, and measured the absorbance corresponding to the vibration of CH3, CH2 and CH groups. Then, this absorbance is converted in oil and grease concentration in the water. The O&G measurement by IR spectrophotometry in comparison with the other monitors, has as main advantage, the independence of the water source being analyzed, allowing its use in systems where the bend of processed oil has frequent time variations.

2.2 UV Fluorescence (UVF)

When aromatic hydrocarbons are radiated with UV light, they emit light at the visible wavelength and the intensity of its fluorescence is proportional to the oil concentration. In case of interference problems due to solids in suspension in the sample, there is a light emission in the visible wavelength band to compensate for the turbidity. This technique has a good level of uncertainty and a high sensitivity to oil detection at low concentrations (ppm).

The method is specific for a certain type of oil, and not sensitive to oils with low aromatic compounds concentration. Furthermore, there is an always concern with oil drop size, because there is one sole light emission by the drops in the radiated surface, in view of light emission neutralization of one drop by another one located in the liquid medium in which oil is being measured.

This type of systems can have automatic washing subsystems or subsystems without sample direct contact with the measuring optical system, in order to prevent and control incrustations, corrosion and dirtiness in the measurement cell, and also sample preconditioned systems to control the oil drop size.

2.4 UV Absorption

When a beam of UV light in the 254 nm wavelength band is directed to an oil-in-water flow, aromatic hydrocarbons in this flow absorb this light, with an intensity proportional to their concentration. Taking as constant the aromatic hydrocarbon fraction, the total oil concentration in the water can be determined. To eliminate the effects of cell incrustation and sample turbidity, it is normally used a dual system in the visible wavelength band.

2.5 Ultra-sonic

This technique uses an ultra-sonic beam for measurement of material in suspension on oil-in-water. An energy pulse is converted to an acoustic wave, directed toward the sample. The reflexes of the dispersed phase are then converted to an electric signal which is processed, providing the sample oil content. This type of monitors have sampling units directly inserted in the oil flow, through which the measurements can be made, therefore eliminating the problems concerning to collect of representative samples and oil losses in the line. The ultra-sound detection technique is effective for the dispersed phases under 1 micron of diameter, and has a fast response. The main problem is that the measured oil content will always be overestimated when gas bubbles and solid particles are present in the sample, a normal occurrence in the oil-in-water effluents of the oil industry. Whenever possible, an efficient treatment of the oil-in-water sample should anticipate the ultra-sound analysis. Such a treatment should remove free gas, solids in suspension and will allow a control of the oil drop distribution.

3 TESTS PERFORMED

O&G monitors are instruments under implementation phase by PETROBRAS, so, are considered a new technology. The Campos Basin E&P segment has performed field tests with equipment available in the international market and using different measurement principles, in order to evaluate its technical performance. Other long duration test are now foreseen with those analyzers.

3.1 O&G Analysis by UV Fluorescence

One O&G analyzer by UV fluorescence has been tested at the production rig P-08. This on-line analyzer uses UV radiation. This radiation, reaching the flow sample produces fluorescence whose intensity is proportional to the aromatic concentration which, in turn, is proportional to oil-in-water coming from the same oil field and under the same treatment system. For water coming from the same oil field, residual oil in water keeps the same proportion between aromatic and aliphatic compounds. Therefore, by measuring the aromatic concentration it can be calculated the total oil concentration through correlation by laboratory analysis, following methods accepted by environmental control agencies. The test purpose aimed at checking the technical performance of the on-line O&G meter in the range of concern, by comparing results through a simultaneous laboratory analysis following the gravimetric method and IR absorption.

During the test performed at the rig P-08 the analyzer was connected to a degasser output line and to a floating auxiliary tank, in order to get samples of residual oil with different concentrations, covering the whole instrument working range.

The results have not been satisfactory in this first program step, due to the large amount of gas in the water, causing drop accumulation on the windows of the measuring cell, therefore, polluting with oil, salt and iron oxide, and producing erroneous results. To solve this problem, the gas bubble remover, installed at the analyzer upstream, has been changed by another one with better efficiency and installed in a higher point. In addition, a periodic check of the measurement cell conditions has become a routine procedure, through a steady standard of UV fluorescence emission for the UV source in use. With the new sampling condition, results have been more significant. This can be seen on Table 1 that shows the results of O&G meter evaluation by UV fluorescence, after adjustment in the sample conditioner system bubble trap in comparison with the IR method.

Table 1. O&G Test Results by UV Fluorescence

O&G by IR Standard Methods 5520C (ppm)	O&G by on-line Analyser UV Fluorescence (ppm)	Fluorescence Units Reading (FSU)	Sample Number
104	121	964	01
107	123	970	02
102	116	846	03
112	112	935	04
113	99	890	05
115	101	898	06
114	110	923	07
108	107	918	08
114	99	890	09
109	97	885	10
108	98	888	11
108	97	884	12
100	94	875	13
101	92	870	14
67	82	838	15
69	83	840	16
58	73	808	17
28	30	670	18
29	30	670	19
27	28	664	20

Final test results have shown a good correlation with Standard Method 5520C, IR spectrophotometry, for O&G range 0-150 ppm. The initial correlation between the reading in fluorescence units and oil and grease concentration is given by:

$$Y = aX + b \tag{1}$$

where

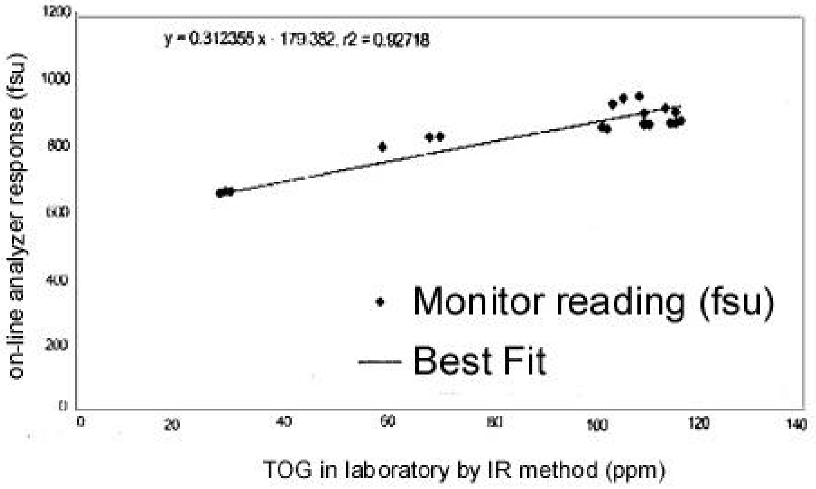
Y = O&G, in ppm
X = Reading in fluorescence units provided by the monitor
a = 0.31236
b = 179.38
R2 = 0.927 (results correlation equal to 93%)

Note: Values of constants “a” and “b” should be recalculated for each equipment adjustment.

Table 2 and Figure 1 show a good result correlation between laboratory analysis through gravimetric method US EPA 1664 and the on-line UV fluorescence analyzer.

Table 2 O&G Test Results by UV Fluorecence

Sample Number	Monitor Reading (ufs)	O&G by the Monitor (ppm)	O&G by Gravimetric Method (ppm)
1	665	13	11
2	666	13	11
3	1104	66	57
4	1100	65	55
5	910	42	44
6	915	43	55
7	880	39	42
8	880	39	44



O&G on line by UV Fluorescence

Figure 1. TOG test results by UV Fluorescence

3.2 On-line O&G Analyzers by IR/laser/visible light scattering

O&G on-line Analyzers by IR/laser/visible light scattering are being tested on Campos Basin. Those analyzers employ one sample conditioner in which oil is dispersed in small drops, by agitation or passage through one small hole and a deflecting plate. Then, the sample goes through the measurement cell, where the oil drops scatter part of the incident radiation. Light scattering is proportional to the oil drop number and, consequently, to their concentration. Sensors around the measurement cell measure the transmitted, scattered and reflected radiation intensity. Scattered light intensity is proportional to oil concentration. The reflected fraction corresponds to solids present in the sample. The sensor response is taken to the processing unit, where is calculated the oil and grease concentration in parts per million (ppm). Table 3 shows short duration test results obtained with an IR/laser/visible light scattering analyzer.

Table 3. O&G test Results by IR/laser/Visible Light Scattering

Sample Number	O&G in Lab by IR (ppm)	O&G by On-line IR/Laser/Visible Light Scattering Analyzer (ppm)
1	129	140
2	130	135
3	123	128
4	125	124
5	101	116
6	177	110
7	104	103
8	99	96
9	89	92
10	90	84
11	87	78
12	79	74
13	87	38
14	77	61
15	78	56
16	71	51
17	65	45
18	75	42
19	69	37
20	86	32
21	44	29
22	52	28
23	34	25
24	58	24
25	48	21
26	44	17
27	15	13
28	6	69
29	7	0
30	129	155
31	143	164
32	150	172
33	165	181
34	154	187
35	157	195
36	163	220
37	163	203
38	214	207
39	213	217
40	181	226
41	186	229
42	178	234
43	184	220

Sample Number	O&G in Lab by IR (ppm)	O&G by On-line IR/Laser/Visible Light Scattering Analyzer (ppm)
44	101	115
45	155	189
46	137	150
47	68	54
48	25	23
49	53	43
50	80	77
51	250	342
52	210	313
53	130	163
54	139	157
55	122	139
56	127	242
57	119	129
58	109	108
59	87	85
60	77	63
61	82	77
62	73	63
63	70	59
64	66	53
65	60	48
66	57	43
67	45	31
68	35	28
69	54	35

Another analyzer using only IR scattering has been tested and results are presented on Table 4 with a good correlation. However, it presents some problems of operational continuity. The equipment is still under observation in PSO S-32, with constant shutdowns due to sample flow problems through the O&G measuring system. One of monitor setbacks is the iron sulphide interference with the measurement. In waters with sulphides, it requires an upstream acid continuos injection either to convert iron sulphide in H2S, or to guarantee that all sulphide comes under acid form.

Table 4. O&G test Results by IR Scattering

Sample Number	O&G in Laboratory by IR (ppm)	O&G by On-line Monitor IR Scattering
1	39,6	31
2	39,3	32
3	36,6	31
4	10,4	13
5	6,5	8
6	38,1	27

3.3 On-line O&G Analyzer by IR Spectrophotometry

One on-line O&G Analyzer by IR Spectrophotometry has been pre-tested in P-18 production rig, to evaluate technical performance and feasibility for its use in other operational units.

The analyzer carries out a hydrocarbon extraction with organic solvent, free of carbon hydrogen bindings such as dichlordifluoretane or carbon tetrachloride. The extract is then submitted to an infrared source, being measured the absorbance corresponding to the frequencies of CH3, Ch2 and CH groups. This absorbance is further converted to oil and grease concentration in the water.

The main advantage of the O&G measurement by IR spectrophotometry over the other monitors is its independence on the water source origin, so, allowing its use in cases where the processed oil blend has frequent time variations. On the other hand, it requires a sample temperature under 30ºC, has a monthly consumption of 1 liter of halogen solvent and the highest acquisition cost.

During the pre-operation phase performed on 16th and 17th, May 1999, on P-18 rig, the equipment has been tested with the rig discharge water. During the test, O&G kept a 75 ppm level, and the test with samples with different oil and grease concentration was not possible, precluding the verification in all the equipment range, 0 to 100 ppm. So, the test will have to be complemented after the cooler installation for sample cooling.

A good result correlation has been observed in the test range, and the results are presented on Table 5.

Table 5 O&G Test Results by IR Spectrophotometry

Date	Time	On-line Monitor Reading Times 2.5 (ppm)	O&G in Laboratory by IR (ppm)
16/05/99	08:45	70	79
16/05/99	08:45	75	79
16/05/99	15:10	80	71
16/05/99	19:00	80	78
16/05/99	20:30	70	82
16/05/99	21:15	85	82
17/05/99	11:00	83	81

CONCLUSIONS

- Monitors by IR spectrophotometry, Laser/IR/visible light scattering, IR scattering and UV fluorescence have shown a satisfactory result correlation when compared with laboratory analysis by IR spectrophotometry and gravimetric analysis.
- The analyzer by UV fluorescence presents the best operational simplicity among all tested.
- Analyzers by Laser/IR/visible light scattering, UV fluorescence and IR scattering require a careful sample conditioning and recalibration whenever exist blend variations of the processed oil.
- The analyzer by IR spectrophotometry can be used in systems with frequent blend variations of the processed oil. However, it presents the highest cost and complexity among all tested.
- Investments in a test program of O&G monitor technologies are fundamental to meet the goals of productivity and compliance with environmental regulations.

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