Oil-in-Water Fluorescence Sensor in Wastewater and Other Industrial Applications

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ABSTRACT

In order to simplify and accelerate the analyses of oil and grease in industrial wastewaters, particularly those discharged from various parts of the oil-refining process, an ultraviolet fluorescent sensor sensitive to polycyclic aromatic hydrocarbons (PAH) was tested. The correlation between total oil-in-water concentration and the concentration of the model PAH compound was found to be attainable in samples containing stable contents of oils.

INTRODUCTION

The analysis of oil and grease in industrial process waters, wastewater in general, and then particulary in the oil refining industry presents a real challenge due to the variability in the analytes and the matrix. This variability depends largely on the applications where the water is used; the challenge rises most sharply in areas where on-line analysis is implemented. One major task in applying methods other than direct oil-in-water (OIW) laboratory analysis is to prove the correlation between the oil concentration and the instrument readings. A general description of existing methods for measuring OIW along with their respective advantages and drawbacks is presented in Table 1.

The challenge of establishing the correct correlation becomes particularly important when a method is based on the response of a specific model compound found in the oils and not in the water matrix. Ideally, this model compound should be present in all kinds of oil so that it is not necessary to restrict the type of product to be analyzed. Furthermore, it should generate a strong enough signal, free of interference, to be detected and correctly interpreted by the measuring instruments.

There are several compounds regularly found in crude oil and refined oil products that can serve as a model for optical methods; these are aromatic hydrocarbons represented by two major groups of substances – monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes a.k.a. BTEX), and polycyclic aromatic hydrocarbons (PAH).

Polycyclic aromatic compounds present in oils are mostly derivatives of naphthalene, anthracene, and phenanthrene; their common structural feature is a system of conjugate bonds (Figure 1) allowing for the fluorescent properties of these substances.

The subject of this testing – an ultraviolet (UV) fluorescence probe – was chosen based on the potential applicability to all refined and crude oils which is due to the fact that the method is sensitive and quite specific to PAH, which are considered to be constituents of all such products.

Since the BTEX and PAH are both detectable with spectrophotometry, it was interesting to compare this method with fluorometry.
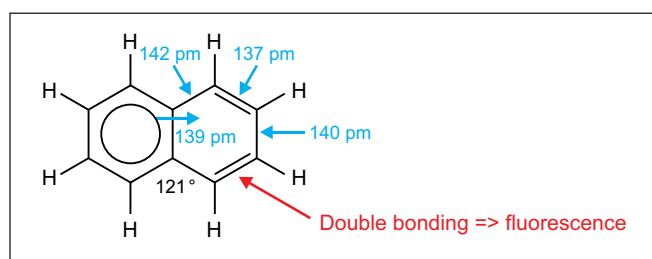

Figure 1:
Structural formula of naphthalene as an example of PAH.

EXPERIMENTAL PART

Based on data compiled in Table 1, UV and Vis fluorescence techniques were selected for our experiments. Probes tested needed to be medium-priced, compact-sized sensors able to provide reagentless measurements

Method	Advantages	Disadvantages
Lab analysis of a grab sample	Ultimate method for direct determination of oil and grease in water	Long and complex analysis, special equipment required, representative sample required
Nephelometry (light surface scattering)	Cost effective on-line instrumentation	Difficult to distinguish between turbidity caused by oil and other particulate matter
UV absorbance	Robust, well-known technology	Interference from compounds other than oil, biological matter, and suspended solids
Vis fluorescence	LPP on-line analyzers and submersible probes	Low sensitivity to PAH, interference from natural organic matter
UV fluorescence	High sensitivity and selectivity toward PAH, wide range of measurements, online analyzers and submersible probes available	Relatively high price, necessary to calibrate per matrix/application

Table 1:
Comparison of different methods for OIW measurements.

specific to oil content. Physical dimensions of the sensors varied based on what light source was implemented, which also resulted in different ranges of light spectrum analyzed by the probe. Our main interest was placed on a UV fluorescence probe pictured in Figure 2 (left), where the light source was a standard xenon flash lamp with an interference filter producing light at 254 nm (excitation) and collecting feedback at 360 nm (emission).

An alternative to the UV fluorescence sensor was a visible light-based fluorescence probe (Vis fluorescence), where the light source was a light-emitting diode (LED) whose major characteristics are normally within the following range: excitation = 370–460 nm / emission = 520–715 nm depending on the intended analyte. Such sensors are less expensive and have a smaller physical size; therefore, a Vis fluorescence probe designed for crude oil detection was also tried in this study. The testing conducted for the Vis fluorescence sensor was minimal; the main focus was on the UV probe. Therefore, most of the information found below is related to the latter instrument. General schematic for both UV and Vis probes is presented in Figure 2 (right).

Both types of sensors can be purchased with either a stainless steel or titanium body, and they produce an ana-
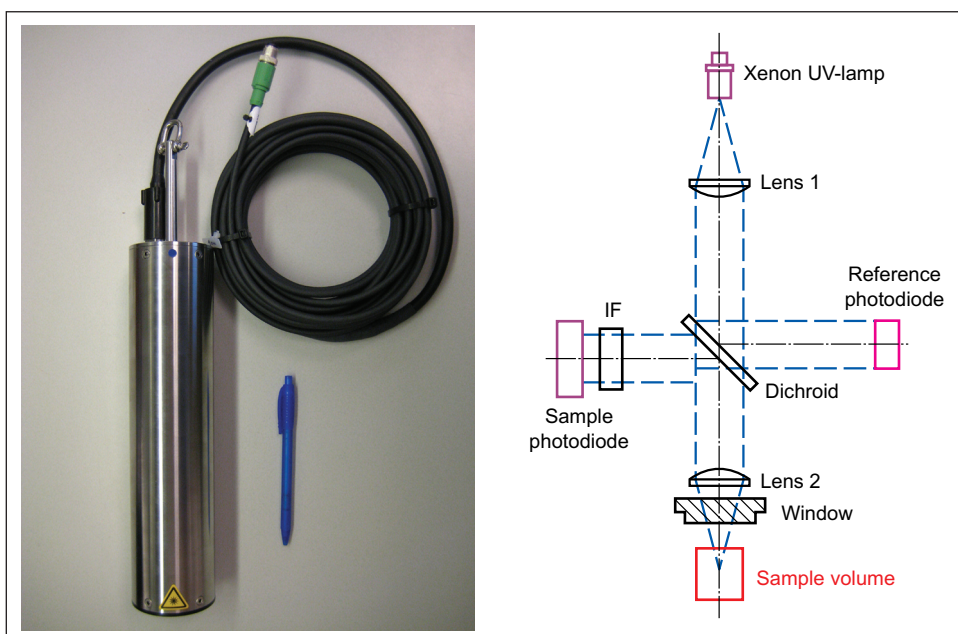

Figure 2:
UV fluorescence OIW sensor and principle of its operation.

Parameter	Specification
Detection parameter (PAH)	Phenanthrene (model compound)
Measuring principle	UV fluorescence (excitation 254 nm / emission 360 nm)
Measuring range	Related to PAH calibration standard
Low-range probe	0–50 µg · L^{-1} & 0–500 µg · L^{-1}, corresponding to 0–1.5 mg · L^{-1} and 0–15 mg · L^{-1} oil calibration standards
High-range probe	0–500 µg · L^{-1} and 0–5000 µg · L^{-1}, corresponding to 0–15 mg · L^{-1} and 0–150 mg · L^{-1} oil calibration standards
Limit of detection	1 µg · L^{-1} (phenanthrene)
Probe housing material	Stainless steel, titanium
Mounting options	– chain (submersible) – in-line (in-pipe mounting hardware) – bypass (flow cell)

Table 2:
UV fluorescence sensor technical specifications.

log signal that can be registered by a standard controller. The UV-probe used in this study generated a 4–20 mA signal that was processed by an sc1000 controller. The readings were displayed in either raw format (mA) or in relative (% of scale) or absolute concentration of oil in water.

The main technical specifications for the tested UV fluorescence sensor are presented in Table 2. The measurement range limits are set to the factory settings and the calibration standards are also available for both low and high range sensors (Table 2).

Currently, there is also some optional equipment available, such as an automated cleaning system that would also prove to be very helpful during this study.

RESULTS AND DISCUSSION

Laboratory Testing

Laboratory performance evaluation was conducted prior to moving onto field testing. The main goal of the laboratory testing was to establish correlations between the concentrations of the model compound (phenanthrene) and the total oil concentration in order to confirm the probe's suitability for determination of such oils in water. Thus, the calibration coefficients and measurement ranges were derived for readily available oil products. The

matrix effect analysis was also conducted on a few of the representative oils.

The results of the laboratory calibrations are presented in Figures 3 and 4.

Figure 3 shows linear response of the sensor calibrated to phenanthrene concentration (y-axis) to the prepared oil concentration in deionized water (x-axis). The calibration coefficients (slope and offset) can be easily established based on the linear regression for several of the oil products such as diesel fuel, gasoline, gear oil and motor oil. At the same time, the chainsaw oil, being a natural product derived from a biological raw material, does not show any presence of the model compound.

In Figure 4, the results for simultaneous testing of both UV and Vis fluorescence sensors are shown. As shown in the charts, the Vis sensor did not indicate any response to diesel fuel, which was found to be the most indicative oil for the UV-based probe. The readings from both sensors were registered in raw mA format and scaled to the same 4–20 mA range. Also confirmed by the experiment, the linearity of the response of the UV-based probe does not change much for the wide range of the analyte concentration. Based on the correlation coefficients (R^2), the relationship may be considered linear throughout the entire range of tested diesel fuel concentrations.
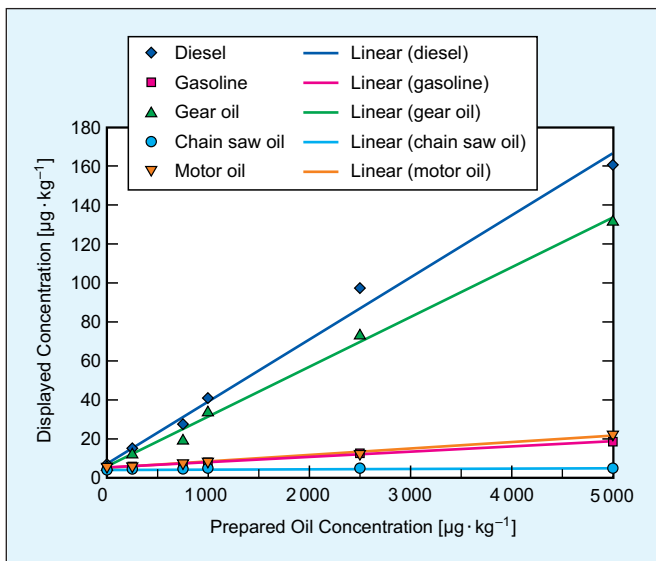
Figure 3:
Calibration curves for series of available oil products in water.

Figure 4:
UV fluorescence: diesel fuel (DF) calibration test results.

The UV sensor comes with daylight automatic compensation; therefore, it was not necessary to take any precautions to avoid ambient light.

A set of experiments was conducted to define the matrix effect on the measurement of OIW concentration with the UV-based sensor (Figure 5). The test results presented here were performed in deionized water, tap water, river water and wastewater. A significant influence of the water matrix requires in-process calibration of the sensor (grab sample analysis) or in the process sample (standard additions method) as preferred calibration procedures. As seen in Figure 5, the signal of 500 $\mu g \cdot L^{-1}$ (ppb) of diesel fuel in wastewater was very small due to the matrix effect;

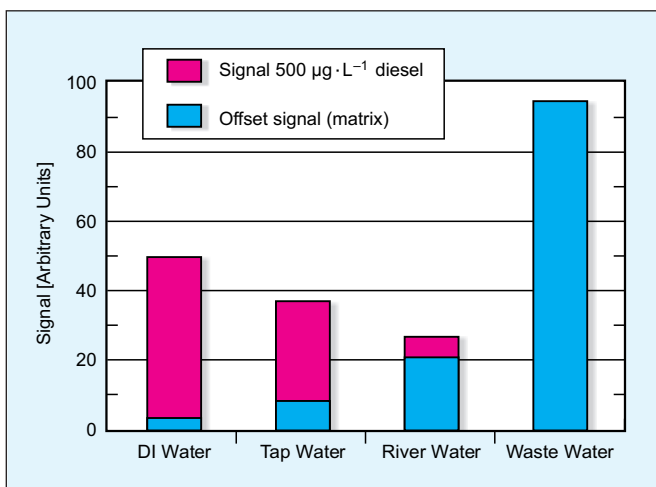however, multiplying the analyte concentration by 10 provided a clear response, even in this type of matrix (Figure 6).

Therefore, the UV fluorescence probe may be considered suitable for wastewater applications, since the limit of detection for diesel fuel was found to be significantly lower than 1 $mg \cdot L^{-1}$ (ppm), which is considered satisfactory.

The comparison of performance of the UV fluorescence and UV spectrophotometric (Hach UVAS instrument, 254 nm) sensors was conducted to identify key differences between these technologies. Test for sensitivity to pure phenanthrene in water revealed that monitoring

Figure 5:
Water matrix influence at 500 $\mu g \cdot L^{-1}$ of diesel fuel.
DI deionized

Figure 6:
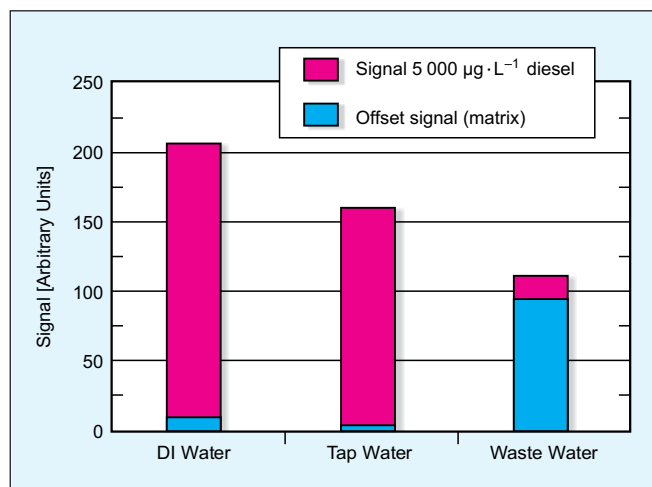Water matrix influence at 5 000 $\mu g \cdot L^{-1}$ of diesel fuel.

Industry	Application
Drinking Water	– Environmental – early detection in natural sources – Detection of oil in artificial reservoirs, as well as in raw water (water treatment plant inlet) – Monitoring desalination plants water intake
Wastewater	– WWTP inlet – Monitoring direct and indirect discharge – Storm water runoff – Membrane plants (water reuse) – Ground water reclamation sites
Industrial Water	– Fuel storage tank area drainage systems – Cooling water – Condensate return – Leaks from heat exchangers – Turbine oil in power plants' process water – Effluent monitoring after oil-water separators (refineries) – Aircraft and truck wash-down facilities – Petrochemical: detection of oil in water separated from crude oil – Maritime applications (holding tanks washdown: < 15 mg $\cdot$ L^{-1} OIW discharge limit)

Table 3:
Potential applications for OIW sensor.

based on UV absorbance was approximately 10 times less sensitive to this model compound than monitoring based on the UV fluorescence. Also the slope of linear correlation was approximately 100 times lower for the spectrophotometric method vs. the fluorescence (0.0443 vs. 3.945).

Test for sensitivity to the same set of oils (Figure 4) showed the expected lower sensitivity of light absorbance to all oils except the chainsaw oil which is a natural product that does not contain PAH. This observation confirmed that UV absorbance is not specific to the presence of PAH and will therefore be affected by interference.

After finishing the series of laboratory tests discussed above, several field test opportunities were identified; some of them have been conducted. Our main focus was on testing the sensor in municipal wastewater applications and also at different applications involving industrial process water. Major interest lies in refinery applications, which are the most challenging due to their harsh environment and demands.

By analysis of the literature and through our own extensive experience, we identified a list of potential applications for the OIW sensors in municipal waters (drinking water and wastewater) as well as numerous opportunities in industrial waters (Table 3).

Field Testing

Testing in a Municipal Wastewater Treatment Plant
A UV fluorescence high-range sensor (0–5 000 µg $\cdot$ L^{-1}) was installed at the inlet of a municipal wastewater treatment plant (WWTP) in Germany. The possible sources of oil contamination were some small manufacturing plants together with a small town and several villages in the surrounding area, thus representing the typical structure of a mid-sized municipal WWTP.

The probe was installed in the tail water at the bottom of a weir, located between the screen and sand trap and allowing strong mixing of the sample with a more or less even distribution of oil contamination. To test the performance of the probe, a mixture of 2 L of diesel fuel in 20 L of water was spilled into the wastewater several meters upstream of the weir. An immediate response could be observed as shown in Figure 7.

After several days of normal operation with readings close to zero, an oil spill accident led to a severe contamination of the first stage of the plant (Figure 8). The contamination was described by the plant operator as a fuel oil-based emulsion.

Another example of data collected at a WWTP is presented in Figures 9 and 10. The instrument (UV fluores-
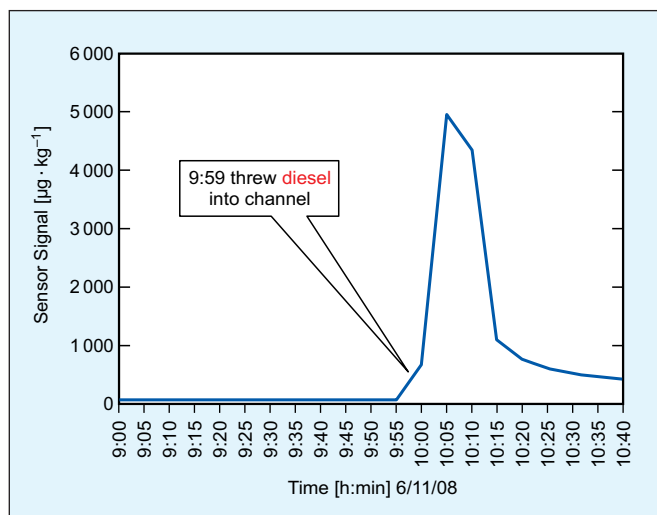
Figure 7:
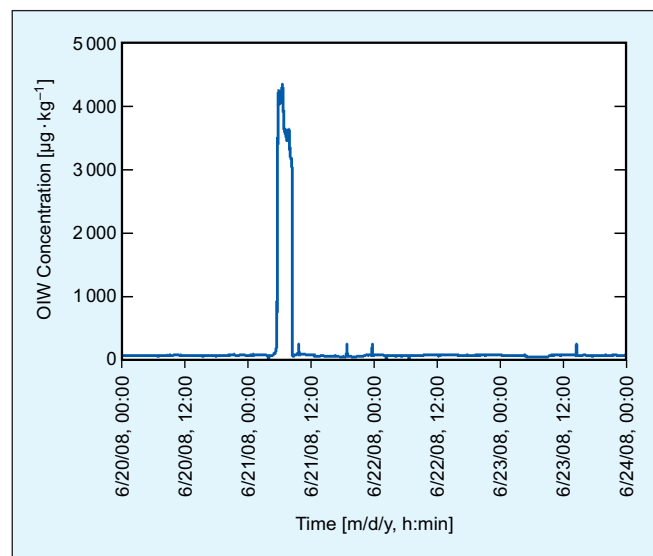Experiment at a wastewater treatment plant, high-range sensor.

Figure 8:
Real-life oil accident at a wastewater treatment plant, high-range sensor.

cence low-range sensor, 0–500 µg · L^{-1}) was installed at the inlet collector in front of the central aeration station of a large water reclamation facility in Saint Petersburg, Russia. The water was coming from a commercial marine port area and the customer was legitimately concerned with possible excessive discharge of oil products from the ships and other port infrastructure. The installation was performed in the open well (chain-mounted sensor) and the test lasted for several months.

A grab sample analysis was conducted in a laboratory at the beginning of the test to establish a baseline for normal OIW background (see pink dot on chart, Figure 9) and shortly after this, an event was registered by the instrument (Figure 9).

Because the event happened right before the weekend, the incident could have gone unnoticed; however, the OIW monitor registered it. Therefore, based on this finding, a decision was made to equip the monitoring point with an autosampler connected to the same controller and driven by the OIW monitor.

Thus, in further testing, the automatic grab sampling routine was triggered when the OIW concentration exceeded the pre-programmed threshold, which was set at the level of 3.5 mg · L^{-1} OIW that corresponded to ~25 % of the scale (Figure 10).

The autosampler provided the customer with an opportunity to analyze the stored water samples later in a laboratory (within 4 h from the sampling) to determine the absolute concentration of oil products at the time of event. This would also help to pinpoint the source of contamination. Unfortunately, the customer considered the labora-
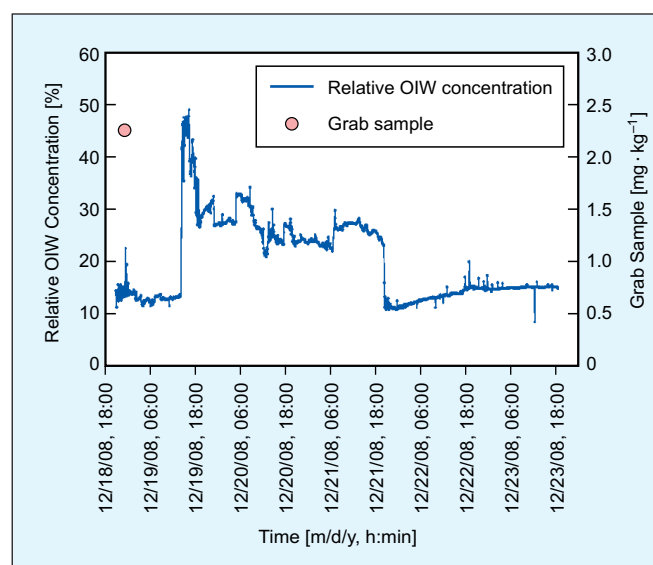

Figure 9:
Wastewater treatment plant test in Russia – initial results.

tory analysis too expensive and did not make use of the opportunity; however, merely combining the autosampler with the OIW monitor can certainly be very effective.

Refinery Testing (Wastewater)   In conversations with petrochemical customers, three potential applications were identified as most valuable for refineries: wastewater (after API separators but prior to the bioreactor), desalters, and cokers. The desalter and coker applications normally involve high sample temperatures and high concentrations of chloride (desalter), and therefore require special

body materials, i.e., titanium. The wastewater (WW) application does not require special precautions, such as titanium body material or intrinsically safe electronics; for this reason, it was chosen as the most appropriate for field testing at a refinery.
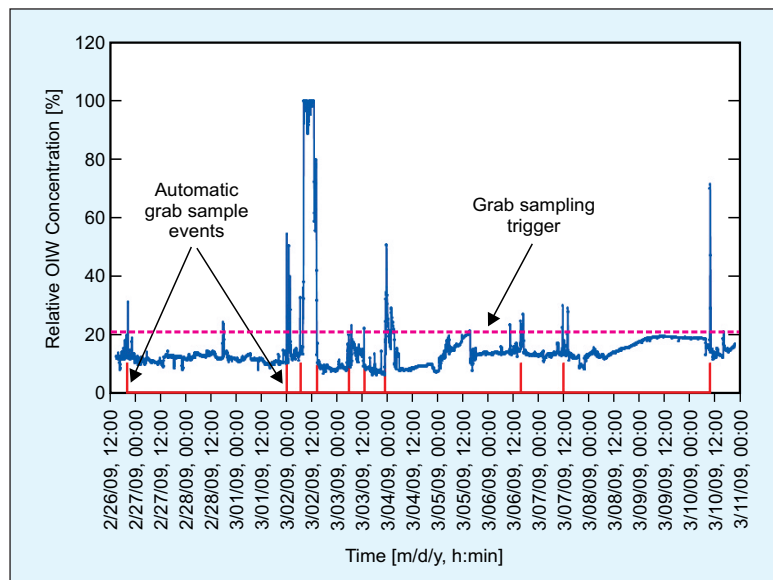

Figure 10:
Russian wastewater treatment plant – long-term trial with autosampler.

The installation was conducted at a refinery in Wyoming where customers have already tried several methods to monitor the OIW concentration in WW discharge into the biotreatment. During biotreatment, excess of oil can wear out the bacteria, which is costly to replace. The customer implemented an induced-air flotation (IAF) procedure right after the API separator to reduce the amount of oil in WW going into the bioreactor. This refinery tried a full-scale on-line OIW analyzer based on a chemical method several years ago. However, due to its high maintenance requirements and unreliable results, the instrument was abandoned. The refinery currently conducts several different lab analyses of the sample along with on-line turbidity monitoring (surface scattering) in order to evaluate the OIW content and keep it under control.

The two sensors, UV (low-range, 0–500 $\mu g \cdot L^{-1}$) and Vis fluorescence (crude oil), were installed on the same sample line with the surface scatterer after the IAF device and the data were collected with a single multiparameter controller (Hach sc1000) – Figure 11, left. The sensors and controller were mounted on a panel along with a flow chamber made out of available materials.
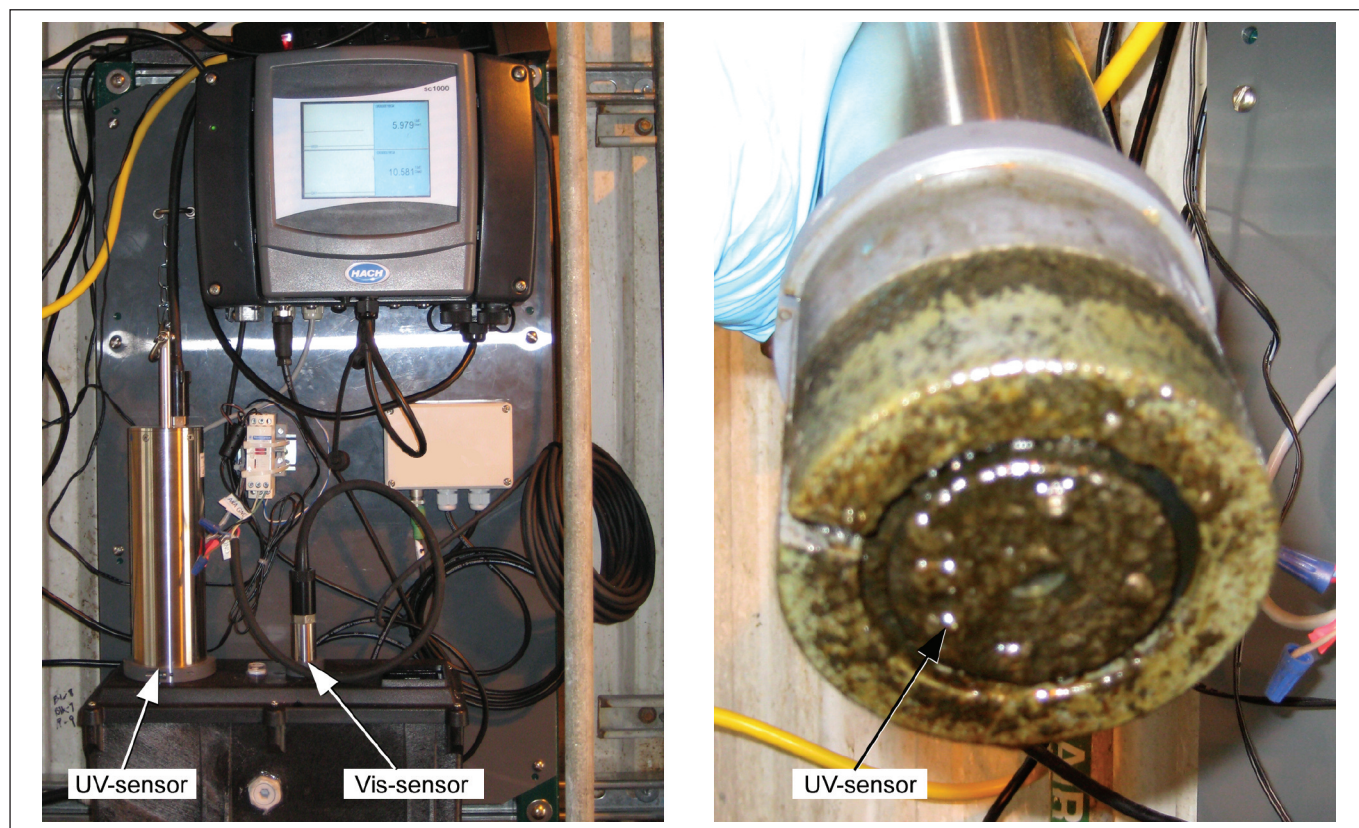

Figure 11:
Refinery installation – wastewater stream after induced-air flotation and before the bioreactor.

There were several challenges met in this application. First, fast sensor window fouling (Figure 11, right) due to slow sample flow through the chamber was encountered. Unfortunately, the flow could not be increased without interfering with the surface scatterer, and hence were the results provided by that instrument. Also, the automated air-blast cleaning system was not available at the time of testing.

Another challenge was with the nature of the oils in the sample – according to the customer, there was never only a single type of crude oil being treated at the refinery at a time. Therefore, the sample content was never consistent in terms of the type of oil and consequently also with the PAH content in the sample. This resulted in inconsistency of the readings received from both sensors with the grab sample analyses (Figure 12). All attempts to calibrate the sensors using the grab sample data failed due to the abovementioned limitations.

On the positive side, it should be noted that there was a similar trend found between the results collected from both sensors; however, the Vis fluorescence provided a significantly narrower range and therefore was excluded from later experiments (Figure 12).

Given the discovered limitations, the next test was conducted in an industrial application with lower-to-no variation in oil types found in the wastewater discharge.
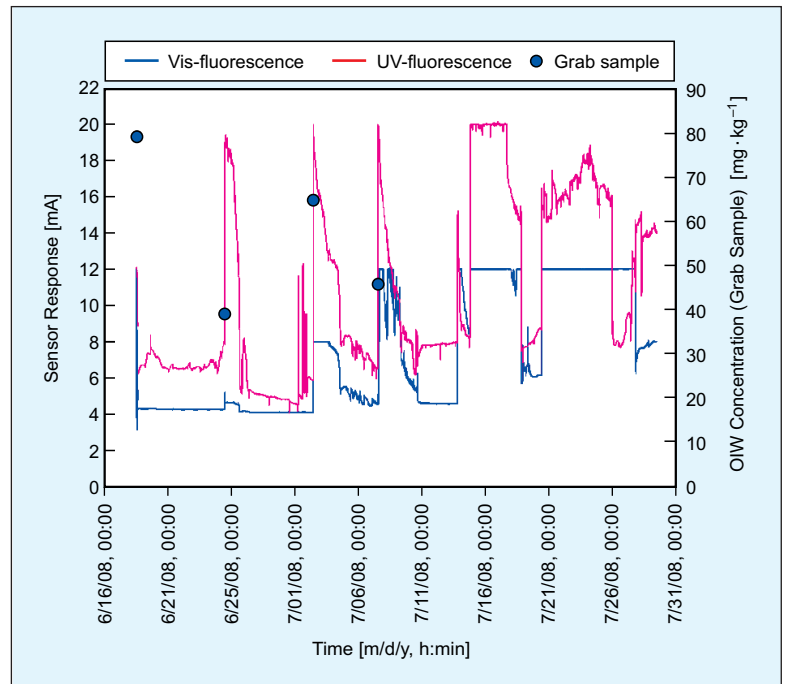

Figure 12:
Refinery wastewater application test results.

Auto Parts Plant (Industrial Wastewater) This test only involved the same UV fluorescence probe (low-range, $0–500 \ \mu g \cdot L^{-1}$) that demonstrated a wider range of response to the OIW concentrations in previous trials. The sensor was installed in an open channel (chain-mounted) at the inlet to the wastewater treatment facility of an auto parts plant in Michigan (Figure 13).
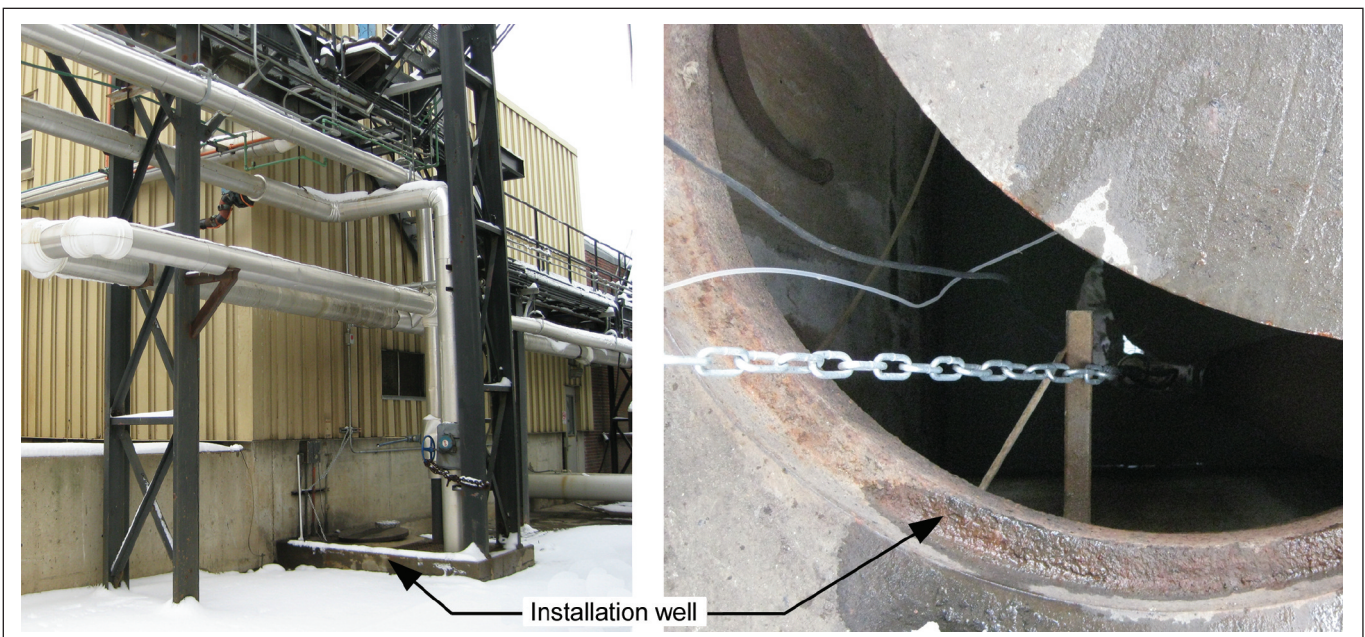

Installation well

Figure 13:
Installation.

During this process, the wastewater from all plant operations was collected in a tank and then underwent chemical treatment prior to discharging to the municipal collector. The major constituents of the analyzed sample in terms of oils were identified as various lubricants from the metal works.

The entire test continued for approximately two months and the data were logged by the controller, which also allowed for remote wireless access to all data and the controller's functions. The process calibration, described below, was performed in the middle of the test using the grab sample technique presented in Figures 14 and 15.

Grab sample was taken at a stamped time (Figure 14) and after laboratory analysis; the obtained OIW concentration was entered in a simple linear relationship, which yielded the calibration equation (Figure 15).

The calibration coefficients (slope and offset, Figure 15) generated by the equation were used to calculate the concentration range in units of OIW, which was followed by the calibration of the probe in order to display the concentration. After this, the customer was able to make adjustments to their process to optimize the chemical treatment (Figure 16). In communicating with the customer, the nature of the positive spikes was discussed and there was always an explanation providing legitimacy of the probe's response.

As seen from Figure 16 and according to the customer, the process optimization resulted in smoother wastewater treatment operation.
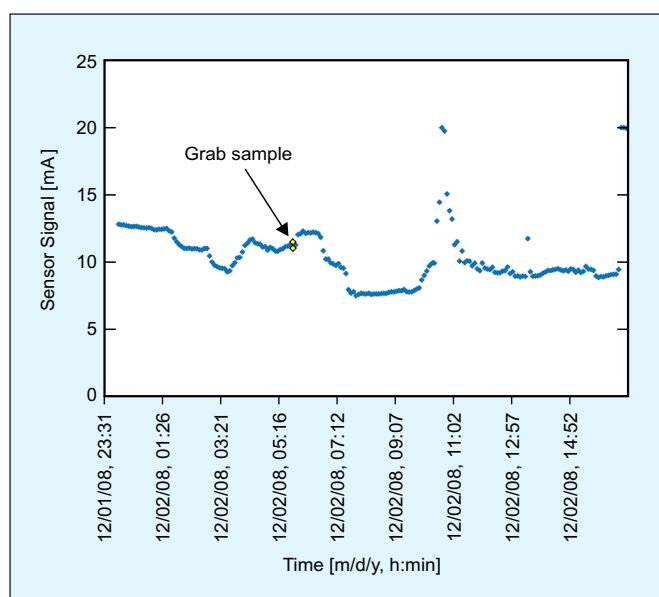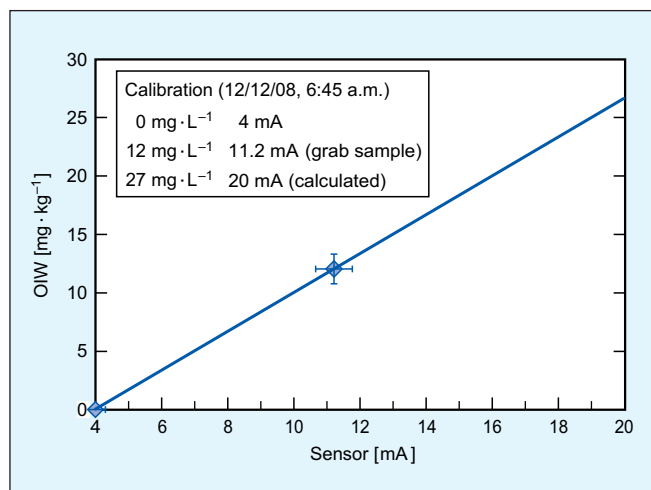

Figure 14:
Process calibration procedure.

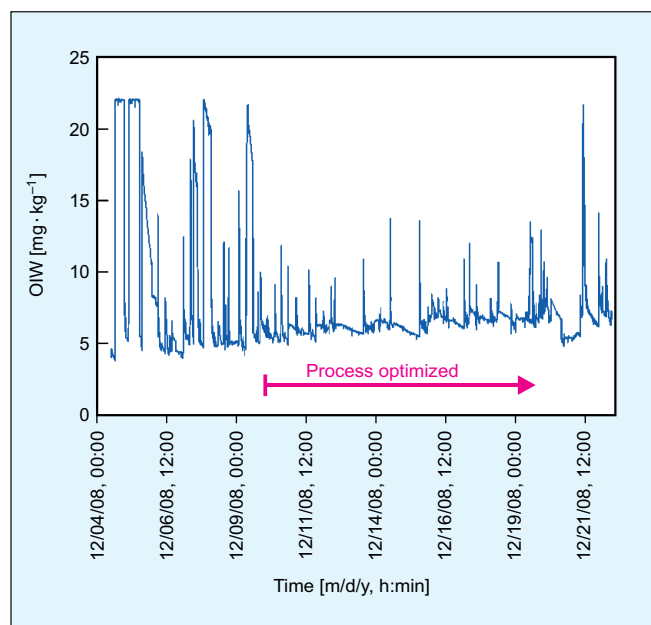Figure 15:
Process calibration procedure.

Figure 16:
Auto parts plant in Michigan (industrial wastewater) – test results.

Cooling Water (Heat Exchanger)   A UV fluorescence high-range sensor (0–5 000 µg·L^{-1}, titanium) was installed at a cooling tower of the gas production facility in Southwestern Colorado. The customer's major concern was repeated oil leakage from the heat exchanger serving the compressors to produce liquid carbon dioxide. The system was installed in a shed harboring the chemical feed system for corrosion control near the cooling tower and the sample feed was provided with the flow cell as shown in Figure 17.

Figure 17:
Cooling tower installation.

Figure 18:
Real-life oil leak from heat exchanger.

After several days of normal operation with readings close to zero, an oil leak from the heat exchanger was detected (Figure 18). The contamination cost the customer more than $1,000 in loss of oil. Besides the direct oil loss, the company had to complete a series of procedures to clean up the cooling water which involved the use of a biocide, oil absorbing mats, higher chlorine injection, followed by draining the entire cooling tower water to re-establish its chlorine and polymer levels. All these actions required approximately 8 hours of work time and an additional material cost of $1,000.

The accident cost was high enough; however, it could have been even more costly if there had been no sensor installed at the time. According to the customer, without such early detection, the leak would have been discovered only after the shutdown of the compressor on low oil level. This could have led to a possible plant shutdown or damage to the compressor necessitating an extensive cleanup of the cooling tower, which would have resulted in the loss of many thousands of dollars for the company.

As seen from Figure 18, the accident apparently went unnoticed for about two days, because the communication between the controller and the plant's monitoring system had not yet been established. The controller was equipped with a relay card allowing it to send an analog signal to either the central monitoring post or to display an alarm locally in case the prescribed oil-in-water level was exceeded. The other possibility for remote access and control was the wireless communication option enabled through GPRS (Global Packet Radio Service) and provided by most cell phone companies. Unfortunately, due
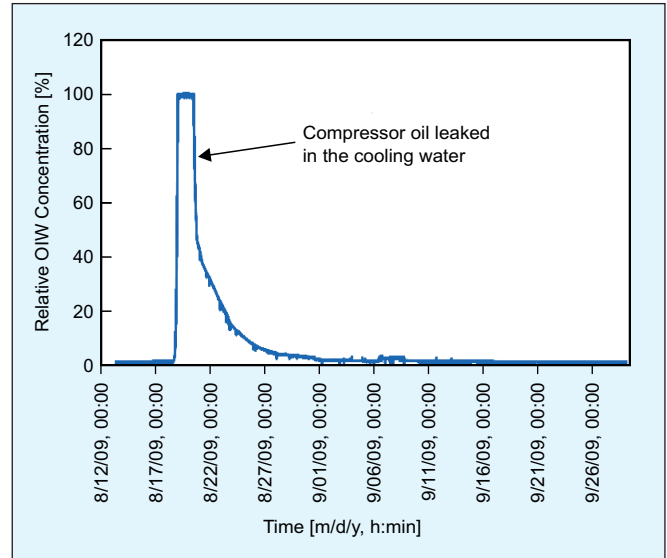
to the extremely remote location of the test site, no such service could be provided by the major US wireless carriers in the area.

Nevertheless, the sensor proved itself very useful by saving the customer a significant amount of money at a nominal cost which was not exacerbated by maintenance requirements. Regular maintenance of the system involves the cleaning of the sensor window; the frequency of cleaning depends on the respective application. For example, when the sensor is submersed in a slow moving dirty sample, the cleaning may occur daily depending on the sample conditions and its origin (application). The cleaning frequency can be significantly minimized either by using an air-blast auto cleaning system (for submersible installations) manageable from the same controller or by employing the flow-through cell. In the latter case, the maintenance can be nothing more than an occasional cleaning of the strainer installed in the sample line feeding the flow cell.

As a matter of fact, in the presented case study, after more than 45 days of testing, there was no maintenance conducted on the sensor. There was some expected fouling found in the flow cell and on the sensor window during the post-test inspection (Figure 19); however, it obviously did not prevent the probe from producing correct readings. As seen from Figure 18, the sensor was operating well during the entire test.
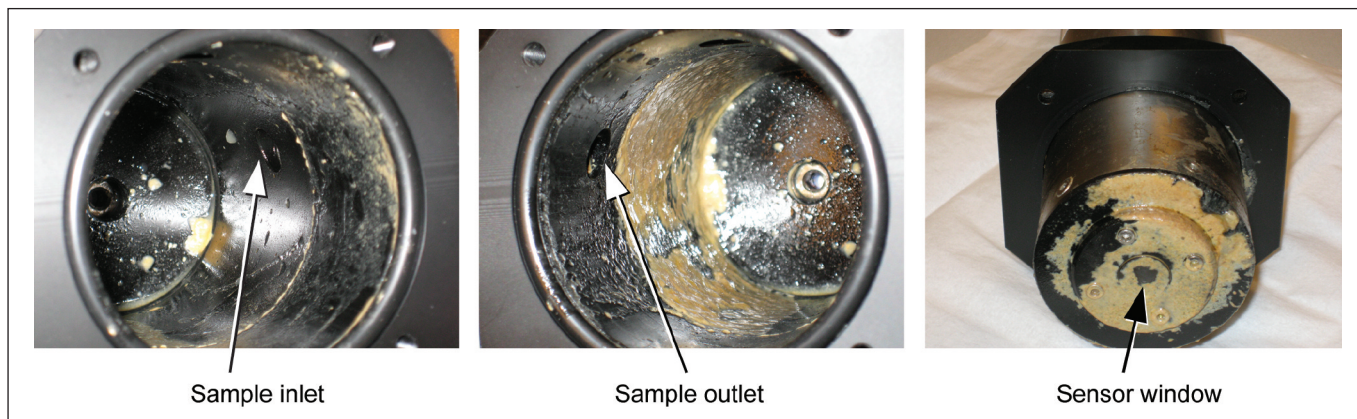
Sample inlet   Sample outlet   Sensor window

Figure 19:
Post-test inspection of the flow cell and sensor window.

CONCLUSIONS

Main conclusions are expressed in the following statements:

– Signals produced by the UV fluorescence sensor were found to be proportional to the oil-in-water concentration;

– The tested UV fluorescence sensor adequately and specifically responds to oil products containing PAH, including crude oil;

– The UV fluorescence sensor provides better sensitivity and selectivity in OIW analysis than UV-absorbance;

– The sensor performance can be improved by implementing a specially designed flow cell providing faster flow and/or an automated cleaning system for open-channel mounting;

– The sensor response can be calibrated by using either commercially available standards or based on the grab sample analysis; however, inconsistent oil content may prohibit quantification of the results.

ACKNOWLEDGMENT

THE AUTHORS

Vadim Malkov (Ph.D., Organic Chemistry, Kazán State University, Russia) joined the Research and Development Division of Hach Company (Loveland, CO) in 2002. His work includes experimental studies in the area of process analysis of water quality in the industrial and municipal applications and he has over 20 years of experience in various fields of chemistry. He has led and participated in the development of several new process analyzers and applications in the field of water disinfection and corrosion control. A holder of one US patent, he has also published more than fifteen papers in scientific and professional journals. Vadim Malkov has presented the results of his work at numerous conferences in the United States and abroad. His current position is a Product Applications Manager for the Process Instrumentation Business Unit (Hach Company).

Dietmar Sievert (Ph.D., Physical Chemistry, University of Essen, Germany) has more than 18 years of experience working for international companies in the development and product management of process analyzers and field instruments. He has published several papers on process instrumentation and analyzers in European journals. Dietmar Sievert is currently working on the development of water quality analyzers for industrial and municipal applications in the Product Application Management Group of the Process Instrumentation Business Department of Hach Lange GmbH (Düsseldorf, Germany).

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