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Laboratory and Field Experience Using a New Tool for Finding Crude Oil Contamination in Synthetic-Based Drilling Fluids

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Abstract

On-site monitoring of crude oil contamination in synthetic-based drilling fluids was a key compliance concern of the EPA during the introduction of synthetic-based fluids. The limitations of the traditional Static Sheen Test resulted in the need for a new test that could detect low levels of formation oil in the synthetic fluids. An industry work group developed a new practical field test to meet the EPA requirements. The new test was accepted by the EPA and included in EPA guidelines for synthetic-based fluids and the offshore permit for the Western Gulf of Mexico as a supplement to the Static Sheen Test. The new monitoring method is based on the same operating principles used to detect crude oil in cuttings for many years. A black light shines on the sample and the sample fluoresces (glows) when crude oil is present. In order to minimize the interferences from drilling fluid emulsifiers, the synthetic fluid goes through a Reverse Phase Extraction (RPE) as part of the test process. The new method was named RPE after this process. This paper reflects the field experience with the RPE method on over 100 wells. The paper reviews the development and performance of the method, as well as a quality assurance/quality control and associate training program. Practical experiences with the limitations of the method and resolutions of failing results are also discussed.

Introduction

In December 2001, EPA published a final modification of the general permit of the National Pollutant Discharge Elimination System for the Western Gulf of Mexico.[1] The effective date of the permit was February 1, 2002. Clear authorization for discharge of cuttings from synthetic-based mud (SBM) was the major change in the permit from previous versions. Along with the specific permission to discharge SBM cuttings, the EPA included new requirements in the permit to control SBM discharges. One of the new compliance tests added to this modified permit is the Reverse Phase Extraction (RPE) Test.

Background

Crude oil, some times called formation oil, is a liquid form of petroleum hydrocarbons. It is mainly composed of paraffins, aromatics and sulfur/nitrogen compounds. The aromatics have adverse effects to human beings and ocean animals. The Agency has identified some of these aromatic compounds as priority pollutants and uses the detection of crude as an indicator of the presence of priority pollutants.

During petroleum drilling, crude oil sometimes invades the drilling mud and cuttings. On-site monitoring of crude oil contamination has been a key compliance concern of EPA. In the early 1990s, the Agency selected the Static Sheen Test in the offshore guidelines for drilling fluids as the primary tool for detection of crude oil in drilling fluids.

Just as the offshore guidelines were being finalized, SBM technology was introduced to drilling operations in the Gulf of Mexico. SBMs emerged as a pollution-prevention technology with enhanced drilling performance. SBMs are non-aqueous drilling fluids (NAFs). The base fluids of SBMs use manufactured organic compounds that are selected on the basis of physical properties that enhance drilling performance and environmental properties that lower toxicity, improve biodegradation, and minimize bioaccumulation. The most commonly used base fluids today that meet the requirements issued in February 2002 include olefins and esters.

During their initial use, the EPA recognized the significant pollution-prevention opportunities associated with SBM use and required that SBMs meet the discharge requirements for water-based muds (WBM). Consequently, SBM cuttings were required to pass the Static Sheen Test compliance test.

As the Agency moved forward in the regulatory process, it continued to recognize the pollution-prevention aspects of SBMs in its coastal Effluent Limitation Guidelines. However, the Agency recognized the physical characteristics of SBMs and SBM cuttings had generated the need for an additional compliance tests to supplement WBM testing requirements. Based on information supplied by industry representatives, the Agency initially recommended Gas Chromatography (GC) techniques to supplement the Static Sheen Test for detection of formation oil.

Shortly after the Coastal Effluent Limitation Guidelines were issued, the Agency recognize the testing issues surrounding SBM use and discharge would require a separate Effluent Limitation Guideline and initiated a new presumptive rulemaking process. This new process was designed to reduce the time to write guidelines while increasing the level of cooperation between interested parties. The industry formed a Work Group of interested parties to develop a tool that would meet the needs identified by the Agency to supplement the Static Sheen Test for SBMs.

The Development of RPE Test Method

An Analytical Work Group was formed in 1997. The group members were from major oil production companies, oil field service companies and EPA. The API was contracted to assist with the work group. The mission of the work group was to find a test method for detecting crude oil in SBM and EMO (enhanced mineral oil) muds as a supplement for the Static Sheen Test.

The Static Sheen Test was originally designed to detect approximately 1% diesel or crude oil in a water-based mud. During the initial regulatory use of the Static Sheen Test, several formal and informal studies were conducted by industry and the Agency. Significant concerns were raised by industry about the subjective nature of the test and the occurrence of false positives. However, in spite of its limitations, the Static Sheen Test was incorporated into permits for routine compliance limitations for WBMs.

Phase One of the Analytical Work Group effort was to design and conduct a study to confirm the concerns regarding false negatives for crude oil contamination in the Static Sheen Test when it was applied to SBMs. The study followed the same design and analysis of previous static sheen studies conducted on WBMs. The study concluded that when applied to SBMs, the test could result in false negatives. Therefore, the Analytical Work Group moved to identify a new test to meet the needs of SBMs.

In order to focus the effort on identification of the best test for meeting the regulatory need, the Work Group identified the following list of nine characteristics that the test method should possess:

- **Works well at rig site –** Recognizing that the method needed to be adapted to the conditions that exist at offshore locations, the method would need to operate under vibration, lighting, and power conditions typically found at the rig site.
- **Comparable to Static Sheen Test** – In order to supplement the Static Sheen Test, the new test should have the same characteristics in terms of equipment, training requirements and effectiveness.
- **Reasonable cost** – The test should not significantly increase daily operating costs or require major modifications of the drilling rig.
- **Repeatable** – Within the scope of a field test, the analytical variability between test runs should be low.
- **Easily operable-minimum expertise** – The nature of the test should be within the analytical capabilities of personnel typically employed to conduct mud checks.
- **Easily maintainable** – The equipment used in the test should not require extensive maintenance or calibration beyond what is typically available at offshore locations.
- **Works well with a variety of crudes and SBMs** – The test should provide similar results for the wide variety of crude oil and the variety of SBM base fluids and emulsifier packages.
- **Minimum false positive** – The test should not indicate crude oil contamination when crude oil was not present in the sample.
- **Single pass/fail limit** – Within the wide range of crude oils, base fluids, and emulsifier packages, the test should provide an universal pass/fail limit that would be consistent across the industry.

Phase Two of the work group efforts focused on identifying and evaluating a wide variety of available analytical methods in order to select the method that best met the desired characteristics. In order to move forward quickly, work group members familiar with specific techniques volunteered to modify and evaluate the effectiveness of candidate techniques. Split samples of SBM samples spike with increasing concentrations of crude oil were supplied to work group members who conducted tests in their laboratories and reported summary data back to the work group for discussion.

The work group held meetings regularly to discuss results from the test methods submitted by group members. The candidate methods included GC/MS, GC/FID, HPLC, TLC, IR, QFT, black light spot test, retort, PID, ELISA and RPE. Each method was intensively reviewed by the experts in the work group. The main difficulty from an analytical chemistry perspective was finding chemical characteristics in crude oil that were consistently different than the synthetic base fluids. As the range of available test methods was reviewed, the key target identified was aromatic compounds that are typically present in crude oils and not present in synthetic fluids. As the test results from various methods were evaluated the impact of the variability of crude oil played a major role in variability of test results.

One of the basic approaches identified by the Agency was the potential use of GC. These instruments are typically used in a laboratory setting and the practical limitations in field applications became quickly apparent. In addition to practical limitations, the GC technique was subject to matrix interferences from some synthetic base fluids. In order to resolve matrix interference problems, the GC technique was modified to a GC/MS technique. This modification resulted in excellent analytical results but pushed the cost, complexity and practicality beyond a rig-site application.

The focus of the search for an onsite method moved away from GC instrumentation and toward UV methods. Using UV light, *i.e.*, black light, to detect crude oil is a traditional technique that field engineers are familiar with. The aromatic compounds fluoresce under a UV light. The brightness of the fluorescence is related to the amount of crude oil in mud. However, some non-aromatics, such as some emulsifiers and wetting agents, also fluoresce under UV. These matrix interferences result in false positives. In development of potential UV techniques, the testing techniques ranged from portable instrument capable of determining a specific UV response to a simple test of observing a drop of SBM under a black light to identify a response. As test methods were conducted and evaluated, it became apparent that false positives due to matrix interferences from emulsifying packages needed to be resolved. By combining the Work Group's ingenuity with traditional UV techniques, a simple extraction step that helped minimize the matrix interference caused by emulsifiers was developed.

After several rounds of testing, the work group elected to use visual observations instead of an instrument to detect a UV response. While the instrument offered more precise measurement of UV response, the visual observations were more practical.

The identification of a universal pass/fail criteria was one of the most difficult characteristics to meet. Because of the variability of crude oils, wherever the pass/fail fluorescence limit was set, it would identify higher concentrations of some crude oil and lower concentrations of other crude oils. By going back to the original design parameters of the Static Sheet Test, the Work Group identified the specific target of consistently identifying a 1% spike of crude oil in a mud sample. As a performance criteria for the universal pass/ fail limit the Work Group targeted the test to pass 95% of the samples containing 0.1% crude oil and fail 95% of the sample containing 1.0% crude oil.

Based on the performance, the RPE test method was selected by the work group to be the best method meeting the nine characteristic criteria.

The Evaluation of RPE Test Method

In Phase Three, the Analytical Work Group provided the draft test procedure to a nationally recognized testing lab and contracted them to document the method detection limit and to formalize the procedures using approved EPA protocol guidelines.

The sample matrix was composed of five crude oils in five concentration levels, four different SBMs and one EMO. Since the test was required to work on a variety of crude oils, the test design selected a range of crude oils that could reasonably be expected to be encountered in offshore drilling. Crude oil varies in aromatic content in different locations. The work group selected crude oil samples based on GC/MS and HPLC analysis. They were labeled as A, B, C, E and F with API gravities ranging from 23-40.

A total of 250 RPE analyses were conducted on spiked samples of SBM using three observers. The results showed crude oil A and F have the lowest false positive/negative rate[2] and provided a "representative" response compared to the range of crude oils that were tested. Crude oil A and F have API gravities of 29 and 35 respectively. They were in the middle of all crude oils. The test met the basic design targets but the unacceptably high occurrence of false positives indicated that additional test development was needed.

Additional review indicated that the false positives were caused by the background matrix interference from the trace emulsifiers left in the cartridge. In order to clearly distinguish positive results from background response, the test needed a pass/fail standard in addition to the blank control. Phase Three of the project was extended and the search of a pass/fail brightness standard reviewed a wide variety of potential options. Unfortunately, the simple options were not effective and the work group concluded that the pass/fail brightness standard would have to be based on spiking a crude oil into the cartridge.

Although crude oils A and F were found to be "representative" for this objective, they did not come from a stable source. Later, the work group found out NIST supplied a commercial crude oil product with consistent aromatic content. However, NIST crude oil has a different amount of aromatic than crude oil A or F and is not a representative sample of crude oils that may be encountered in the field. The concentration of NIST crude oil was then adjusted to meet the performance criteria targeted for the test. Specifically, the concentration of NIST oil was targeted to pass 95% of the samples containing 0.1% crude oil and fail 95% of the samples containing 1.0% crude oil.

After Phase Three was completed, the Work Group moved to Phase Four of the project which included training industry representatives how to conduct the test at the field level.

Laboratory Experience

In order to confirm that the test procedure would work before the guidelines were finalized, a comparative test of NIST crude oil against crude oil A and F was conducted in a field services laboratory. Ten mud samples were prepared by spiking in 0%, 0.25%, 0.5%, 1.0% and 2.0% crude oils A and F respectively. A positive-control cartridge prepared from NIST crude oil solution was used for comparison. Five viewers participated in the tests to give a pass or fail report for the samples. Results are shown in Table 1. The results are compiled into percentages in Table 2. Table 2 showed that 100% of the mud sample containing less than 1.0% crude oil A or F passed the test. 100% of the mud sample containing 1.0% or above failed the test. The tests showed using NIST crude oil to replace Crude oil A or F was acceptable.

The RPE method was also tested on field muds. Four field mud samples from different wells were sent in for RPE tests. The results were then confirmed by GC/MS analysis.[3] The results are showed in Table 3. For the mud that passed the RPE, or showed negative result, the GC/MS showed crude oil content was below 1%. For the mud that failed the RPE, or showed positive results, the GC/MS confirmed the crude oil content was above 1%.

RPE test procedure

The RPE method utilizes a C18 reversed-phase extraction cartridge to retain the aromatics. The more polar emulsifiers and wetting agents are rinsed out of RPE cartridge by isopropyl alcohol (IPA). IPA was chosen because it has the appropriate polarity and low toxicity. The cartridge is examined under a UV light and the brightness of the response is compared against a pass/fail standard.

The RPE test is composed of two parts. First part is the preparation of a positive-control cartridge (pass/fail standard cartridge). This part is usually done in a laboratory. The positive-control cartridge is then sealed in a amber glass vial and sent to the drilling rig. The second part is the preparation of mud sample cartridges, which is conducted onsite at the drilling rig.

(1) Preparation of <u>positive-control cartridge</u>:

1.1 Obtain a crude oil standard from NIST. The commercial name for the standard is SRM 1582 petroleum crude oil.[4]

1.2 Weight 87 mg of the crude oil standard into a 10-mL volumetric flask. Fill to mark with dichloromethane.

1.3 Draw 40 µL of the above crude oil solution into a 10-mL volumetric flask. Fill to mark with IPA.

1.4 Obtain a RPE C18 cartridge[5]. Precondition the cartridge by passing 20-mL IPA through it with a syringe.

1.5 Draw 0.5 mL of the crude oil/IPA solution from Step 1.3 and inject it into the preconditioned cartridge.

1.6 Inject 2 mL of IPA through the above cartridge. This cartridge is now the positive-control cartridge.

(2) Preparation of the <u>mud-sample cartridge</u>:

2.1 Collect a representative synthetic-based mud sample. Place 0.2 mL of mud into a 20-mL glass vial.

2.2 Add 20-mL IPA to vial, cap the vial and shake it for 1 minute.

2.3 Draw 4 mL of the above solution and filter it through a 0.45-µm Teflon syringe filter disc. Store filtrate in a clean vial.

2.4 Precondition a C18 cartridge as in 1.4.

2.5 Inject 0.5 mL of the filtrate from Step 2.3 into the precondition C18 cartridge.

2.6 Inject 2 mL of IPA through the above cartridge. This cartridge is the mud-sample cartridge.

Place the mud-sample cartridge alongside the positive-control cartridge under a UV light (wavelength 365 nm) in a black box. Compare the brightness. If the fluorescence of the sample cartridge is dimmer than the positive-control cartridge, the mud passes the test, or the test result is negative. Otherwise, if the fluorescence of the sample cartridge is equal to or brighter than the positive control, the mud fails the test. The test result is positive and the mud is considered to be contaminated with crude oil. A demonstration of pass/fail cartridges are shown in Fig. 1.

Field Engineer Training on Quality Control/Quality Assurance

Although the RPE test is easy to operate, it is a subjective test. To reduce the subjectivity, an intensive training program and QA/QC requirements were incorporated into the test method. In this particular way the RPE test is significantly different from the Static Sheen Test. The Static Sheen Test has limited training and QA/QC requirements. The RPE training program can be incorporated into a one-day lecture and lab experiment course. The lecture reviews the EPA regulation and RPE test standard operating procedures. A videotape demonstration of the RPE operation is also included. The training described in the permit requires 70 hands-on RPE tests in order to qualify personnel to conduct the test for compliance purposes. 70 samples are prepared by spiking 0%, 0.1%, 1% and 2% of a representative crude oil (such as crude oil F or equivalent) into a clean IO mud and a clean ester mud. Each sample is to be run 10 times. To be qualified to conduct the test for compliance purposes, a trainee has to prepare all 70 RPE test cartridges and demonstrate a capability of passing a minimum of 80% of mud containing 0.1% of a representative crude oil and failing at least 75% of mud containing 1% of a representative crude oil and at least 90% of mud containing 2% of a representative crude oil. Detail criteria are shown in Table 4 and Table 5. If the result is not achieved at this rate, the source of the problem will be identified and corrected. It is important to recognize that the representative crude oil is different than the Standard Crude oil from NIST.

Field Experience

Since January 1, 2002, a major drilling fluid company has run 505 RPE test on 135 wells in the Gulf of Mexico. Three failing test results were reported. Further GC/MS analysis showed that these three failing results were false positives. Investigations found these false positives were due to improper handling of the RPE cartridges. The RPE tests were re-run and returned with negative results.

During the past year, practical experience with the RPE test has indicated that proper storage of the positive-control cartridge is vital to a successful test. Offshore drilling rigs often experience dry and hot conditions that deteriorate the positive-control cartridge. The positive-control cartridge needs to be kept in a cool place and in its amber container when it is not in use. In addition, the cartridge should be saturated with IPA at all times. It is a good practice to put a few drops of IPA into the positive-control cartridge before using it.

Conclusions

Detecting crude oil contamination in synthetic-based drilling mud will continue to be an analytical challenge. The Analytical Work Group made a significant effort to review all available analytical techniques and select the technique that provided the best possible solution. The RPE test still has limitations that are related to the variability of crude oils and matrix interferences from the drilling muds. However, the laboratory and field experience have proved the RPE application can be strengthened with a training program and QA/QC requirements. As experience with the RPE test continues, it is anticipated that additional refinements will continue to address and resolve the limitations of this test.

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Nomenclature

RPE = *reverse phase extraction*
GC/MS = *gas chromatography/mass spectroscopy*
GC/FID = *gas chromatography/flame ionization detector*
HPLC = *high performance liquid chromatography*
TLC = *thin layer chromatography*
IR = *infrared spectroscopy*
QFT = *quantitative fluorescence test*
PID = *photoionization detector*
ELISA = *enzyme-linked immuno assay*
NIST = *National Institute of Standards and Technology*

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4. NIST Petroleum Crude Oil Standard, Standard Reference Material (SRM) 1582. For ordering information, visit http://nist.gov.
5. C18 Reversed-Phase Extraction Cartridge, Sep-Pak Plus C18 cartridge from Waters (WAT020515) or equivalent. www.waters.com.

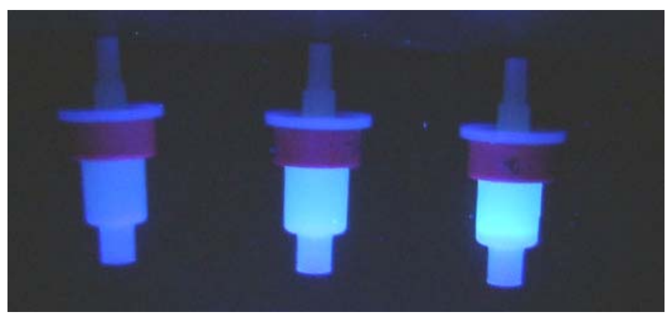

Fig. 1 – RPE cartridges that show no crude oil contamination (left) and crude oil contamination (right) are set alongside with a positive-control cartridge (middle).

Table 1 - RPE Test Results* of Lab-Prepared Mud Samples Containing Crude Oil A and F

Sample Label	Viewer No.1	Viewer No.2	Viewer No.3	Viewer No.4	Viewer No.5
A-1	-	-	-	-	-
A-2	-	-	-	-	-
A-3	-	-	-	-	-
A-4	+	+	+	+	+
A-5	+	+	+	+	+
F-1	-	-	-	-	-
F-2	-	-	-	-	-
F-3	+	+	+	+	+
F-4	+	+	+	+	+
F-5	+	+	+	+	+

* In this table, “ - “ represents negative result. “+” represents positive result.

Table 2 - RPE Test Results from Table 1
Pass/Fail Rate vs. Crude Oil Content

Sample Label	Crude Oil Content in Mud	Percent Passed	Percent Failed
A-1	0% A	100%	0
A-2	0.25% A	100%	0
A-3	0.5% A	100%	0
A-4	1.0% A	0	100%
A-5	2.0% A	0	100%
F-1	0% F	100%	0
F-2	0.25% F	100%	0
F-3	0.5% F	0	100%
F-4	1.0% F	0	100%
F-5	2.0% F	0	100%

Table 3 - RPE Test Results Field Mud with Comparison Data from GC/MS Analysis		
Sample Label	**Result from RPE test**	**Confirmed Result from GC/MS**
Field Mud Sample A	-	0.5% crude oil
Field Mud Sample B	+	1 – 1.2% crude oil
Field Mud Sample C	+	1.2 – 1.5% crude oil
Field Mud Sample D	+	1.2 – 1.5% crude oil
*** In this table, "-" represents negative result. "+" represents positive result.**		

Table 4 - QA/QC training requirement		
Cartridge content	Number of test runs	Number of pass/fail required
Reagent blank	2	2 pass
Clean IO mud (Blank)	2	2 pass
Clean ester mud (blank)	2	2 pass
IO mud spiked with 1% crude oil	2	2 fail
Ester mud spiked with 1% crude oil	2	2 fail

Table 5 - Initial demonstration of acceptable performance			
Cartridge content	Number of test run	Number of pass/fail required	Percent of pass/fail required
IO mud containing 0.1% crude oil	10	< 4 fails	< 20% fails
Ester mud containing 0.1% crude oil	10		
IO mud containing 1% crude oil	10	> 15 fails	> 75% fails
Ester mud containing 1% crude oil	10		
IO mud containing 2% crude oil	10	> 18 fails	> 90% fails
Ester mud containing 2% crude oil	10		