

## **ATTACHMENT 7**

### **APPENDIX 6 TO SUBPART A OF PART 435—REVERSE PHASE EXTRACTION (RPE) METHOD FOR DETECTION OF OIL CONTAMINATION IN NON-AQUEOUS DRILLING FLUIDS (NAF)**

#### **1.0 SCOPE AND APPLICATION**

- 1.1 This method is used for determination of crude or formation oil, or other petroleum oil contamination, in non-aqueous drilling fluids (NAFs).
- 1.2 This method is intended as a positive/negative test to determine a presence of crude oil in NAF prior to discharging drill cuttings from offshore production platforms.
- 1.3 This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act, including monitoring of compliance with the Gulf of Mexico NPDES General Permit for monitoring of oil contamination in drilling fluids.
- 1.4 This method has been designed to show positive contamination for 5% of representative crude oils at a concentration of 0.1% in drilling fluid (vol/vol), 50% of representative crude oils at a concentration of 0.5%, and 95% of representative crude oils at a concentration of 1%.
- 1.5 Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR Parts 136.4 and 136.5.
- 1.6 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2 of this appendix.

#### **2.0 SUMMARY OF METHOD**

- 2.1 An aliquot of drilling fluid is extracted using isopropyl alcohol.
- 2.2 The mixture is allowed to settle and then filtered to separate out residual solids.
- 2.3 An aliquot of the filtered extract is charged onto a reverse phase extraction (RPE) cartridge.
- 2.4 The cartridge is eluted with isopropyl alcohol.
- 2.5 Crude oil contaminants are retained on the cartridge and their presence (or absence) is detected based on observed fluorescence using a black light.

#### **3.0 DEFINITIONS**

- 3.1 A NAF is one in which the continuous phase is a water immiscible fluid such as an oleaginous material (e.g., mineral oil, enhance mineral oil, paraffinic oil, or synthetic material such as olefins and vegetable esters).

#### **4.0 INTERFERENCES**

- 4.1 Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts that affect results. Specific selection of reagents and purification of solvents may be required.
- 4.2 All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running laboratory reagent blanks as described in Section 9.5 of this appendix.

## 5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical shall be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Material Safety Data Sheets (MSDSs) shall be available for all reagents.

5.2 Isopropyl alcohol is flammable and should be used in a well-ventilated area.

5.3 Unknown samples may contain high concentration of volatile toxic compounds.

Sample containers should be opened in a hood and handled with gloves to prevent exposure. In addition, all sample preparation should be conducted in a well-ventilated area to limit the potential exposure to harmful contaminants. Drilling fluid samples should be handled with the same precautions used in the drilling fluid handling areas of the drilling rig.

5.4 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) shall be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 16.1–16.2.

## 6.0 EQUIPMENT AND SUPPLIES

NOTE: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

### 6.1 Sampling equipment.

6.1.1 Sample collection bottles/jars—New, pre-cleaned bottles/jars, lot-ertified to be free of artifacts. Glass preferable, plastic acceptable, wide mouth approximately 1–L, with Teflon-lined screw cap.

### 6.2 Equipment for glassware cleaning.

#### 6.2.1 Laboratory sink.

6.2.2 Oven—Capable of maintaining a temperature within  $\pm 5$  °C in the range of 100–250 °C.

### 6.3 Equipment for sample extraction.

6.3.1 Vials—Glass, 25 mL and 4 mL, with Teflon-lined screw caps, baked at 200–250 °C for 1–h minimum prior to use.

6.3.2 Gas-tight syringes—Glass, various sizes, 0.5 mL to 2.5 mL (if spiking of drilling fluids with oils is to occur).

6.3.3 Auto pipetters—various sizes, 0.1 mL, 0.5 mL, 1 to 5 mL delivery, and 10 mL delivery, with appropriate size disposable pipette tips, calibrated to within  $\pm 0.5\%$ .

#### 6.3.4 Glass stirring rod.

#### 6.3.5 Vortex mixer.

6.3.6 Disposable syringes—Plastic, 5 mL.

6.3.7 Teflon syringe filter, 25-mm, 0.45 $\mu$ m pore size—Acrodisc<sup>®</sup>CR Teflon (or equivalent).

6.3.8 Reverse Phase Extraction C18 Cartridge—Waters Sep-Pak<sup>®</sup>Plus, C18 Cartridge, 360 mg of sorbent (or equivalent).

6.3.9 SPE vacuum manifold—Supelco Brand, 12 unit (or equivalent). Used as support for cartridge/syringe assembly only. Vacuum apparatus not required.

6.4 Equipment for fluorescence detection.

6.4.1 Black light—UV Lamp, Model UVG 11, Mineral Light Lamp, Shortwave 254 nm, or Longwave 365 nm, 15 volts, 60 Hz, 0.16 amps (or equivalent).

6.4.2 Black box—cartridge viewing area. A commercially available ultraviolet viewing cabinet with viewing lamp, or alternatively, a cardboard box or equivalent, approximately 14×7.5×7.5in size and painted flat black inside. Lamp positioned in fitted and sealed slot in center on top of box. Sample cartridges sit in a tray, ca. 6from lamp. Cardboard flaps cut on top panel and side of front panel for sample viewing and sample cartridge introduction, respectively.

6.4.3 Viewing platform for cartridges. Simple support (hand made vial tray—black in color) for cartridges so that they do not move during the fluorescence testing.

## 7.0 REAGENTS AND STANDARDS

7.1 Isopropyl alcohol—99% purity.

7.2 NAF—Appropriate NAF as sent from the supplier (has not been circulated downhole). Use the clean NAF corresponding to the NAF being used in the current drilling operation.

7.3 Standard crude oil—NIST SRM 1582 petroleum crude oil.

## 8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collect approximately one liter of representative sample (NAF, which has been circulated downhole) in a glass bottle or jar. Cover with a Teflon lined cap. To allow for a potential need to re-analyze and/or re-process the sample, it is recommended that a second sample aliquot be collected.

8.2 Label the sample appropriately.

8.3 All samples must be refrigerated at 0–4 °C from the time of collection until extraction (40 CFR Part 136, Table II).

8.4 All samples must be analyzed within 28 days of the date and time of collection (40 CFR Part 136, Table II).

## 9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.3). The minimum requirements of this program consist of an initial demonstration of laboratory capability, and ongoing analyses of blanks and spiked duplicates to assess accuracy and precision and to demonstrate continued performance. Each field sample is analyzed in duplicate to demonstrate representativeness.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2 of this appendix.

9.1.2 Preparation and analysis of a set of spiked duplicate samples to document accuracy and precision. The procedure for the preparation and analysis of these samples is described in Section 9.4 of this appendix.

9.1.3 Analyses of laboratory reagent blanks are required to demonstrate freedom

from contamination. The procedure and criteria for preparation and analysis of a reagent blank are described in Section 9.5 of this appendix.

9.1.4 The laboratory shall maintain records to define the quality of the data that is generated.

9.1.5 Accompanying QC for the determination of oil in NAF is required per analytical batch. An analytical batch is a set of samples extracted at the same time, to a maximum of 10 samples. Each analytical batch of 10 or fewer samples must be accompanied by a laboratory reagent blank (Section 9.5 of this appendix), corresponding NAF reference blanks (Section 9.6 of this appendix), a set of spiked duplicate samples blank (Section 9.4 of this appendix), and duplicate analysis of each field sample. If greater than 10 samples are to be extracted at one time, the samples must be separated into analytical batches of 10 or fewer samples.

9.2 Initial demonstration of laboratory capability. To demonstrate the capability to perform the test, the analyst shall analyze two representative unused drilling fluids (e.g., internal olefin-based drilling fluid, vegetable

ester-based drilling fluid), each prepared separately containing 0.1%, 1%, and 2% or a representative oil. Each drilling fluid/concentration combination shall be analyzed 10 times, and successful demonstration will yield the following average results for the data set:

0.1% oil—Detected in <20% of samples

1% oil—Detected in >75% of samples

2% oil—Detected in >90% of samples

9.3 Sample duplicates.

9.3.1 The laboratory shall prepare and analyze (Section 11.2 and 11.4 of this appendix) each authentic sample in duplicate, from a given sampling site or, if for compliance monitoring, from a given discharge.

9.3.2 The duplicate samples must be compared versus the prepared corresponding NAF blank.

9.3.3 Prepare and analyze the duplicate samples according to procedures outlined in Section 11 of this appendix.

9.3.4 The results of the duplicate analyses are acceptable if each of the results give the same response (fluorescence or no fluorescence).

If the results are different, sample non-homogeneity issues may be a concern.

Prepare the samples again, ensuring a well mixed sample prior to extraction. Analyze the samples once again.

9.3.5 If different results are obtained for the duplicate a second time, the analytical system is judged to be out of control and the problem shall be identified and corrected, and the samples re-analyzed.

9.4 Spiked duplicates—Laboratory prepared spiked duplicates are analyzed to demonstrate acceptable accuracy and precision.

9.4.1 Preparation and analysis of a set of spiked duplicate samples with each set of no more than 10 field samples is required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). A field NAF sample expected to contain less than 0.5% crude oil (and documented to not fluoresce as part of the sample batch analysis) shall be spiked with 1% (by volume) of suitable reference crude oil and analyzed as field samples, as described in Section 11 of this appendix. If no low-level drilling fluid is available, then the unused NAF can be used as the drilling fluid sample.

9.5 Laboratory reagent blanks—Laboratory reagent blanks are analyzed to demonstrate freedom from contamination.

9.5.1 A reagent blank is prepared by passing 4 mL of the isopropyl alcohol through a Teflon syringe filter and collecting the filtrate in a 4-mL glass vial. A Sep PaqC18 cartridge is then preconditioned with 3 mL of isopropyl alcohol. A 0.5-mL aliquot of the filtered isopropyl alcohol is added to the syringe barrel along with 3.0 mL of isopropyl alcohol. The solvent is passed through the preconditioned Sep Paq cartridge. An additional 2-mL of isopropyl alcohol is eluted through the cartridge. The cartridge is now considered the “reagent blank” cartridge and is ready for viewing (analysis). Check the reagent blank cartridge under the black light for fluorescence. If the isopropyl alcohol and filter are clean, no fluorescence will be observed.

9.5.2 If fluorescence is detected in the reagent blank cartridge, analysis of the samples is halted until the source of contamination is eliminated and a prepared reagent blank shows no fluorescence under a black light. All samples shall be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.6 NAF reference blanks—NAF reference blanks are prepared from the NAFs sent from the supplier (NAF that has not been circulated downhole) and used as the reference when viewing the fluorescence of the test samples.

9.6.1 A NAF reference blank is prepared identically to the authentic samples. Place a 0.1 mL aliquot of the “clean” NAF into a 25-mL glass vial. Add 10 mL of isopropyl alcohol to the vial. Cap the vial. Vortex the vial for approximately 10 sec. Allow the solids to settle for approximately 15 minutes. Using a 5-mL syringe, draw up 4 mL of the extract and filter it through a PTFE syringe filter, collecting the filtrate in a 4-mL glass vial. Precondition a Sep PaqC18 cartridge with 3 mL of isopropyl alcohol. Add a 0.5-mL aliquot of the filtered extract to the syringe barrel along with 3.0 mL of isopropyl alcohol. Pass the extract and solvent through the preconditioned Sep Paq cartridge. Pass an additional 2-mL of isopropyl alcohol through the cartridge. The cartridge is now considered the NAF blank cartridge and is ready for viewing (analysis). This cartridge is used as the reference cartridge for determining the absence or presence of fluorescence in all authentic drilling fluid samples that originate from the same NAF. That is, the specific NAF reference blank cartridge is put under the black light along with a prepared cartridge of an authentic sample originating from the same NAF material. The fluorescence or absence of fluorescence in the authentic sample cartridge is determined relative to the NAF reference cartridge.

9.6.2 Positive control solution, equivalent to 1% crude oil contaminated mud extract, is prepared by dissolving 87 mg of standard crude oil into 10.00 mL of methylene chloride. Then mix 40 µL of this solution into 10.00 mL of IPA. Transfer 0.5 mL of this solution into a preconditioned C18 cartridge, followed by 2 ml of IPA.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibration and standardization methods are not employed for this procedure.

## 11.0 PROCEDURE

This method is a screening-level test. Precise and accurate results can be obtained only by strict adherence to all details.

11.1 Preparation of the analytical batch.

11.1.1 Bring the analytical batch of samples to room temperature.

11.1.2 Using a large glass stirring rod, mix the authentic sample thoroughly.

11.1.3 Using a large glass stirring rod, mix the clean NAF (sent from the supplier) thoroughly.

11.2 Extraction.

11.2.1 Using an automatic positive displacement pipetter and a disposable pipette tip transfer 0.1-mL of the authentic sample into a 25-mL vial.

11.2.2 Using an automatic pipetter and a disposable pipette tip dispense a 10-mL aliquot of solvent grade isopropyl alcohol (IPA) into the 25 mL vial.

11.2.3 Cap the vial and vortex the vial for ca. 10–15 seconds.

11.2.4 Let the sample extract stand for approximately 5 minutes, allowing the solids to separate.

11.2.5 Using a 5-mL disposable plastic syringe remove 4 mL of the extract from the 25-mL vial.

11.2.6 Filter 4 mL of extract through a Teflon syringe filter (25-mm diameter, 0.45  $\mu\text{m}$  pore size), collecting the filtrate in a labeled 4-mL vial.

11.2.7 Dispose of the PFTE syringe filter.

11.2.8 Using a black permanent marker, label a Sep Pa $\checkmark$ C18 cartridge with the sample identification.

11.2.9 Place the labeled Sep Pa $\checkmark$ C18 cartridge onto the head of a SPE vacuum manifold.

11.2.10 Using a 5-mL disposable plastic syringe, draw up exactly 3-mL (air free) of isopropyl alcohol.

11.2.11 Attach the syringe tip to the top of the C18 cartridge.

11.2.12 Condition the C18 cartridge with the 3-mL of isopropyl alcohol by depressing the plunger slowly.

NOTE: Depress the plunger just to the point when no liquid remains in the syringe barrel. Do not force air through the cartridge. Collect the eluate in a waste vial.

11.2.13 Remove the syringe temporarily from the top of the cartridge, then remove the plunger, and finally reattach the syringe barrel to the top of the C18 cartridge.

11.2.14 Using automatic pipettors and disposable pipette tips, transfer 0.5 mL of the filtered extract into the syringe barrel, followed by a 3.0-mL transfer of isopropyl alcohol to the syringe barrel.

11.2.15 Insert the plunger and slowly depress it to pass only the extract and solvent through the preconditioned C18 cartridge.

NOTE: Depress the plunger just to the point when no liquid remains in the syringe barrel. Do not force air through the cartridge. Collect the eluate in a waste vial.

11.2.16 Remove the syringe temporarily from the top of the cartridge, then remove the plunger, and finally reattach the syringe barrel to the top of the C18 cartridge.

11.2.17 Using an automatic pipetter and disposable pipette tip, transfer 2.0 mL of isopropyl alcohol to the syringe barrel.

11.2.18 Insert the plunger and slowly depress it to pass the solvent through the C18 cartridge.

NOTE: Depress the plunger just to the point when no liquid remains in the syringe barrel. Do not force air through the cartridge. Collect the eluate in a waste vial.

11.2.19 Remove the syringe and labeled C18 cartridge from the top of the SPE vacuum manifold.

11.2.20 Prepare a reagent blank according to the procedures outlined in Section 9.5 of this appendix.

11.2.21 Prepare the necessary NAF reference blanks for each type of NAF encountered in the field samples according to the procedures outlined in Section 9.6 of this appendix.

11.2.22 Prepare the positive control (1% crude oil equivalent) according to Section 9.6.2 of this appendix.

11.3 Reagent blank fluorescence testing.

11.3.1 Place the reagent blank cartridge in a black box, under a black light.

11.3.2 Determine the presence or absence of fluorescence for the reagent blank cartridge. If fluorescence is detected in the blank, analysis of the samples is halted until the source of contamination is eliminated and a prepared reagent blank shows no fluorescence under a black light. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

11.4 Sample fluorescence testing.

11.4.1 Place the respective NAF reference blank (Section 9.6 of this appendix) onto the tray inside the black box.

11.4.2 Place the authentic field sample cartridge (derived from the same NAF as the NAF reference blank) onto the tray, adjacent and to the right of the NAF reference blank.

11.4.3 Turn on the black light.

11.4.4 Compare the fluorescence of the sample cartridge with that of the negative control cartridge (NAF blank, Section 9.6.1 of this appendix) and positive control cartridge (1% crude oil equivalent, Section 9.6.2 of this appendix).

11.4.5 If the fluorescence of the sample cartridge is equal to or brighter than the positive control cartridge (1% crude oil equivalent, Section 9.6.2 of this appendix), the sample is considered contaminated. Otherwise, the sample is clean.

## 12.0 DATA ANALYSIS AND CALCULATIONS

Specific data analysis techniques and calculations are not performed in this SOP.

## 13.0 METHOD PERFORMANCE

This method was validated through a single laboratory study, conducted with rigorous statistical experimental design and interpretation (Reference 16.4).

## 14.0 POLLUTION PREVENTION

14.1 The solvent used in this method poses little threat to the environment when recycled and managed properly.

## 15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal

restriction, and to protect the air, water, and land by minimizing and controlling all releases from bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 All authentic samples (drilling fluids) failing the fluorescence test (indicated by the presence of fluorescence) shall be retained and classified as contaminated samples. Treatment and ultimate fate of these samples is not outlined in this SOP.

15.3 For further information on waste management, consult “The Waste Management Manual for Laboratory Personnel,” and “Less is Better: Laboratory Chemical Management for Waste Reduction,” both available from the American Chemical Society’s Department of Government Relations and Science Policy, 1155 16th Street, NW, Washington, DC 20036.

## 16.0 REFERENCES

16.1 “Carcinogen—Working with Carcinogens,” Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

16.2 “OSHA Safety and Health Standards, General Industry,” (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

16.3 “Handbook of Analytical Quality Control in Water and Wastewater Laboratories,” USEPA, EMSL-Ci, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.

16.4 Report of the Laboratory Evaluation of Static Sheen Test Replacements—Reverse Phase Extraction (RPE) Method for Detecting Oil Contamination in Synthetic Based Mud (SBM). October 1998. Available from API, 1220 L Street, NW, Washington, DC 20005-4070, 202-682-8000.

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