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integer. Let S be the sum of the squares of the ranks or average ranks of all N observations. Let N = n + m.

$$\text{CriticalValue} = 0.5 * n * (N+1) - 3.0902 * \sqrt{V}$$

In the preceding formula, calculate V using

$$V = \frac{n * m * S}{N * (N-1)} - \frac{n * m * (N+1)^2}{4 * (N-1)}$$

[67 FR 3408, Jan. 23, 2002]

PART 435—OIL AND GAS EXTRACTION POINT SOURCE CATEGORY

Subpart A—Offshore Subcategory

Sec.

Subpart B [Reserved]

Subpart C—Onshore Subcategory

Subpart D—Coastal Subcategory

AUTHORITY: 33 U.S.C. 1251, 1311, 1314, 1316, 1317, 1318, 1342 and 1361.

SOURCE: 44 FR 22075, Apr. 13, 1979, unless otherwise noted.

Subpart A—Offshore Subcategory

SOURCE: 58 FR 12504, Mar. 4, 1993, unless otherwise noted.

§ 435.10 Applicability; description of the offshore subcategory.

The provisions of this subpart are applicable to those facilities engaged in field exploration, drilling, well production, and well treatment in the oil and gas industry which are located in waters that are seaward of the inner boundary of the territorial seas (''offshore'') as defined in section 502(g) of the Clean Water Act.

[61 FR 66123, Dec. 16, 1996]

§ 435.11 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

(b) *Average of daily values for 30 consecutive days* means the average of the daily values obtained during any 30 consecutive day period.

(c) *Base fluid* means the continuous phase or suspending medium of a drilling fluid formulation.

(d) *Base fluid retained on cuttings* as applied to BAT effluent limitations and NSPS refers to the ''Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings by a Retort Chamber (Derived from API Recommended Practice 13B–2)'', EPA Method 1674, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(e) *Biodegradation rate* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the ''Protocol for the Determination of Degradation of Non Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995,'' EPA Method 1647, supplemented with ''Procedure for Mixing Base Fluids With Sediments,'' EPA Method 1646. Both EPA Method 1646 and 1647 are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(f) *Daily values* as applied to produced water effluent limitations and NSPS means the daily measurements used to assess compliance with the maximum for any one day.

(g) *Deck drainage* means any waste resulting from deck washings, spillage, rainwater, and runoff from gutters and drains including drip pans and work areas within facilities subject to this subpart.

(h) *Development facility* means any fixed or mobile structure subject to this subpart that is engaged in the drilling of productive wells.

(i) *Diesel oil* refers to the grade of distillate fuel oil, as specified in the American Society for Testing and Materials Standard Specification for Diesel Fuel Oils D975–91, that is typically

used as the continuous phase in conventional oil-based drilling fluids. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA, 19428. Copies may be inspected at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*. A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave., NW., Washington, DC 20460.

(j) *Domestic waste* means materials discharged from sinks, showers, laundries, safety showers, eye-wash stations, hand-wash stations, fish cleaning stations, and galleys located within facilities subject to this subpart.

(k) *Drill cuttings* means the particles generated by drilling into subsurface geologic formations and carried out from the wellbore with the drilling fluid. Examples of drill cuttings include small pieces of rock varying in size and texture from fine silt to gravel. Drill cuttings are generally generated from solids control equipment and settle out and accumulate in quiescent areas in the solids control equipment or other equipment processing drilling fluid (*i.e.*, accumulated solids).

(1) *Wet drill cuttings* means the unaltered drill cuttings and adhering drilling fluid and formation oil carried out from the wellbore with the drilling fluid.

(2) *Dry drill cuttings* means the residue remaining in the retort vessel after completing the retort procedure specified in EPA Method 1674, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(l) *Drilling fluid* means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. Classes of drilling fluids are:

(1) *Water-based drilling fluid* means the continuous phase and suspending medium for solids is a water-miscible fluid, regardless of the presence of oil.

(2) *Non-aqueous drilling fluid* means the continuous phase and suspending medium for solids is a water-immiscible fluid, such as oleaginous materials (e.g., mineral oil, enhanced mineral oil, paraffinic oil, C_{16}–C_{18} internal olefins, and C_8–C_{16} fatty acid/2-ethylhexyl esters).

(i) *Oil-based* means the continuous phase of the drilling fluid consists of diesel oil, mineral oil, or some other oil, but contains no synthetic material or enhanced mineral oil.

(ii) *Enhanced mineral oil-based* means the continuous phase of the drilling fluid is enhanced mineral oil.

(iii) *Synthetic-based* means the continuous phase of the drilling fluid is a synthetic material or a combination of synthetic materials.

(m) *Enhanced mineral oil* as applied to enhanced mineral oil-based drilling fluid means a petroleum distillate which has been highly purified and is distinguished from diesel oil and conventional mineral oil in having a lower polycyclic aromatic hydrocarbon (PAH) content. Typically, conventional mineral oils have a PAH content on the order of 0.35 weight percent expressed as phenanthrene, whereas enhanced mineral oils typically have a PAH content of 0.001 or lower weight percent PAH expressed as phenanthrene.

(n) *Exploratory facility* means any fixed or mobile structure subject to this subpart that is engaged in the drilling of wells to determine the nature of potential hydrocarbon reservoirs.

(o) *Formation oil* means the oil from a producing formation which is detected in the drilling fluid, as determined by the GC/MS compliance assurance method, EPA Method 1655, when the drilling fluid is analyzed before being shipped offshore, and as determined by the RPE method, EPA Method 1670, when the drilling fluid is analyzed at the offshore point of discharge. The GC/MS compliance assurance method and the RPE method approved for use with this part are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction

Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section. Detection of formation oil by the RPE method may be confirmed by the GC/MS compliance assurance method, and the results of the GC/MS compliance assurance method shall apply instead of those of the RPE method.

(p) *M9IM* means those offshore facilities continuously manned by nine (9) or fewer persons or only intermittently manned by any number of persons.

(q) *M10* means those offshore facilities continuously manned by ten (10) or more persons.

(r) *Maximum* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the maximum concentration allowed as measured in any single sample of the barite for determination of cadmium and mercury content.

(s) *Maximum for any one day* as applied to BPT, BCT and BAT effluent limitations and NSPS for oil and grease in produced water means the maximum concentration allowed as measured by the average of four grab samples collected over a 24-hour period that are analyzed separately. Alternatively, for BAT and NSPS the maximum concentration allowed may be determined on the basis of physical composition of the four grab samples prior to a single analysis.

(t) *Maximum weighted mass ratio averaged over all NAF well sections* for BAT effluent limitations and NSPS for base fluid retained on cuttings means the weighted average base fluid retention for all NAF well sections as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(u) *Method 1654A* refers to EPA Method 1654, Revision A, entitled ''PAH Content of Oil by HPLC/UV,'' December 1992, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(v) *Minimum* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the minimum 96-hour LC_5. value allowed as measured in any single sample of the discharged waste stream. *Minimum* as applied to BPT and BCT effluent limitations and NSPS for sanitary wastes means the minimum concentration value allowed as measured in any single sample of the discharged waste stream.

(w)(1) *New source* means any facility or activity of this subcategory that meets the definition of ''new source'' under 40 CFR 122.2 and meets the criteria for determination of new sources under 40 CFR 122.29(b) applied consistently with all of the following definitions:

(i) *Water area* as used in ''site'' in 40 CFR 122.29 and 122.2 means the water area and water body floor beneath any exploratory, development, or production facility where such facility is conducting its exploratory, development or production activities.

(ii) *Significant site preparation work* as used in 40 CFR 122.29 means the process of surveying, clearing or preparing an area of the water body floor for the purpose of constructing or placing a development or production facility on or over the site.

(2) ''New Source'' does not include facilities covered by an existing NPDES permit immediately prior to the effective date of these guidelines pending EPA issuance of a new source NPDES permit.

(x) *No discharge of free oil* means that waste streams may not be discharged that contain free oil as evidenced by the monitoring method specified for that particular stream, e.g., deck drainage or miscellaneous discharges cannot be discharged when they would cause a film or sheen upon or discoloration of the surface of the receiving water; drilling fluids or cuttings may not be discharged when they fail EPA Method 1617 (Static Sheen Test), which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(y) Parameters that are regulated in this subpart and listed with approved methods of analysis in Table 1B at 40 CFR 136.3 are defined as follows:

(1) *Cadmium* means total cadmium.

(2) *Chlorine* means total residual chlorine.

(3) *Mercury* means total mercury.

(4) *Oil and Grease* means total recoverable oil and grease.

(z) *PAH (as phenanthrene)* means polynuclear aromatic hydrocarbons reported as phenanthrene.

(aa) *Produced sand* means the slurried particles used in hydraulic fracturing, the accumulated formation sands and scales particles generated during production. Produced sand also includes desander discharge from the produced water waste stream, and blowdown of the water phase from the produced water treating system.

(bb) *Produced water* means the water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

(cc) *Production facility* means any fixed or mobile structure subject to this subpart that is either engaged in well completion or used for active recovery of hydrocarbons from producing formations.

(dd) *Sanitary waste* means the human body waste discharged from toilets and urinals located within facilities subject to this subpart.

(ee) *Sediment toxicity* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' and sediment preparation procedures specified in EPA Method 1646. EPA Method 1644 is published in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' (see paragraph (uu) of this section) and EPA Method 1646 is published as an appendix to subpart A of this part.

(ff) *Solids control equipment* means shale shakers, centrifuges, mud cleaners, and other equipment used to separate drill cuttings and/or stock barite solids from drilling fluid recovered from the wellbore.

(gg) *SPP toxicity* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the bioassay test procedure, ''Suspended Particulate Phase (SPP) Toxicity Test,'' presented in EPA Method 1619, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(hh) *Static sheen test* means the standard test procedure that has been developed for this industrial subcategory for the purpose of demonstrating compliance with the requirement of no discharge of free oil. The methodology for performing the static sheen test is presented in EPA Method 1617, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (uu) of this section.

(ii) *Stock barite* means the barite that was used to formulate a drilling fluid.

(jj) *Stock base fluid* means the base fluid that was used to formulate a drilling fluid.

(kk) *Synthetic material* as applied to synthetic-based drilling fluid means material produced by the reaction of specific purified chemical feedstock, as opposed to the traditional base fluids such as diesel and mineral oil which are derived from crude oil solely through physical separation processes. Physical separation processes include fractionation and distillation and/or minor chemical reactions such as cracking and hydro processing. Since they are synthesized by the reaction of purified compounds, synthetic materials suitable for use in drilling fluids are typically free of polycyclic aromatic hydrocarbons (PAH's) but are sometimes found to contain levels of PAH up to 0.001 weight percent PAH expressed as phenanthrene. Internal olefins and vegetable esters are two examples of synthetic materials suitable for use by the oil and gas extraction industry in formulating drilling fluids. Internal olefins are synthesized from the isomerization of purified straight-chain (linear) hydrocarbons such as C_{16}–C_{18} linear alpha olefins. C_{16}–C_{18} linear alpha olefins are unsaturated hydrocarbons with the carbon to carbon double bond in the terminal position.

Internal olefins are typically formed from heating linear alpha olefins with a catalyst. The feed material for synthetic linear alpha olefins is typically purified ethylene. Vegetable esters are synthesized from the acid-catalyzed esterification of vegetable fatty acids with various alcohols. EPA listed these two branches of synthetic fluid base materials to provide examples, and EPA does not mean to exclude other synthetic materials that are either in current use or may be used in the future. A synthetic-based drilling fluid may include a combination of synthetic materials.

(ll) *Well completion fluids* means salt solutions, weighted brines, polymers, and various additives used to prevent damage to the well bore during operations which prepare the drilled well for hydrocarbon production.

(mm) *Well treatment fluids* means any fluid used to restore or improve productivity by chemically or physically altering hydrocarbon-bearing strata after a well has been drilled.

(nn) *Workover fluids* means salt solutions, weighted brines, polymers, or other specialty additives used in a producing well to allow for maintenance, repair or abandonment procedures.

(oo) *4-day LC_5*. as applied to the sediment toxicity BAT effluent limitations and NSPS means the concentration (milligrams/kilogram dry sediment) of the drilling fluid in sediment that is lethal to 50 percent of the Leptocheirus plumulosus test organisms exposed to that concentration of the drilling fluids after four days of constant exposure.

(pp) *10-day LC_5*. as applied to the sediment toxicity BAT effluent limitations and NSPS means the concentration (milligrams/kilogram dry sediment) of the base fluid in sediment that is lethal to 50 percent of the Leptocheirus plumulosus test organisms exposed to that concentration of the base fluids after ten days of constant exposure.

(qq) *96-hour LC_5*. means the concentration (parts per million) or percent of the suspended particulate phase (SPP) from a sample that is lethal to 50 percent of the test organisms exposed to that concentration of the SPP after 96 hours of constant exposure.

(rr) *C_{16}–C_{18} internal olefin* means a 65/35 blend, proportioned by mass, of hexadecene and octadecene, respectively. Hexadecene is an unsaturated hydrocarbon with a carbon chain length of 16, an internal double carbon bond, and is represented by the Chemical Abstracts Service (CAS) No. 26952–14–7. Octadecene is an unsaturated hydrocarbon with a carbon chain length of 18, an internal double carbon bond, and is represented by the Chemical Abstracts Service (CAS) No. 27070–58–2. (Properties available from the Chemical Abstracts Service, 2540 Olentangy River Road, PO Box 3012, Columbus, OH, 43210).

(ss) *C_{16}-C_{18} internal olefin drilling fluid* means a C_{16}-C_{18} internal olefin drilling fluid formulated as specified in appendix 1 of subpart A of this part.

(tt) *C_{12}–C_{14} ester* and *C_8 ester* means the fatty acid/2-ethylhexyl esters with carbon chain lengths ranging from 8 to 16 and represented by the Chemical Abstracts Service (CAS) No. 135800–37–2. (Properties available from the Chemical Abstracts Service, 2540 Olentangy River Road, PO Box 3012, Columbus, OH, 43210)

(uu) *Analytic Methods for the Oil and Gas Extraction Point Source Category* is the EPA document, ''Analytic Methods for the Oil and Gas Point Source Category,'' December 2011, EPA–821–R–11–004, that compiles analytic methods for this category. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be inspected at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*. A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460. This method may be obtained at *http://water.epa.gov/scitech/methods/cwa/index.cfm*.

[61 FR 66124, Dec. 16, 1996, as amended at 66 FR 6895, Jan. 22, 2001; 69 FR 18803, Apr. 9, 2004; 77 FR 29834, May 18, 2012]

§ 435.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

Except as provided in 40 CFR 125.30–32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available:

BPT EFFLUENT LIMITATIONS—OIL AND GREASE

[In milligrams per liter]

Pollutant parameter waste source	Maximum for any 1 day	Average of values for 30 consecutive days shall not exceed	Residual chlorine minimum for any 1 day
Produced water	72	48	NA
Deck drainage	(1)	(1)	NA
Water-based:			
Drilling fluids	(1)	(1)	NA
Drill Cuttings	(1)	(1)	NA
Non-aqueous:			
Drilling fluids	No discharge	No discharge	NA
Drill Cuttings	(1)	(1)	NA
Well treatment fluids	(1)	(1)	NA
Sanitary:			
M10	NA	NA	2 1
M9IM 3	NA	NA	NA
Domestic	NA	NA	NA

1 No discharge of free oil. See § 435.11(x).
2 Minimum of 1 mg/l and maintained as close to this concentration as possible.
3 There shall be no floating solids as a result of the discharge of these wastes.

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6897, Jan. 22, 2001; 77 FR 29836, May 18, 2012]

§ 435.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT).

Except as provided in 40 CFR 125.30–32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT):

BAT EFFLUENT LIMITATIONS

Waste source	Pollutant parameter	BAT effluent limitation
Produced water	Oil & grease	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Drilling fluids and drill cuttings:		
(A) For facilities located within 3 miles from shore.		No discharge. 1
(B) For facilities located beyond 3 miles from shore:.		
Water-based drilling fluids and associated drill cuttings.	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test 2 shall be 3% by volume.
	Free oil	No discharge. 3
	Diesel oil	No discharge.
	Mercury	1 mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
Non-aqueous drilling fluids (NAFs).		No discharge.
Drill cuttings associated with non-aqueous drilling fluids:		
Stock Limitations (C_{16}–C_{18} internal olefin).	Mercury	1 mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
	Polynuclear Aromatic Hydrocarbons (PAH).	PAH mass ratio 5 shall not exceed 1×10^{-5}.
	Sediment toxicity.	Base fluid sediment toxicity ratio 6 shall not exceed 1.0.
	Biodegradation rate.	Biodegradation rate ratio 7 shall not exceed 1.0.
Discharge Limitations.	Diesel oil	No discharge.
	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test 2 shall be 3% by volume.
	Sediment toxicity.	Drilling fluid sediment toxicity ratio 8 shall not exceed 1.0.
	Formation Oil	No discharge. 9

BAT EFFLUENT LIMITATIONS—Continued

Waste source	Pollutant parameter	BAT effluent limitation
	Base fluid retained on cuttings.	For NAFs that meet the stock limitations (C_{16}–C_{18} internal olefin) in this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 6.9 g-NAF base fluid/100 g-wet drill cuttings.[10] For NAFs that meet the C_{12}–C_{14} ester or C_8 ester stock limitations in footnote 11 of this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 9.4 g-NAF base fluid/100 g-wet drill cuttings.
Well treatment, completion, and workover fluids.	Oil and grease.	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Deck drainage	Free oil	No discharge.[4]
Produced sand	.....	No discharge.
Domestic Waste	Foam	No discharge.

[1] All Alaskan facilities are subject to the drilling fluids and drill cuttings discharge limitations for facilities located beyond 3 miles offshore.

[2] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.11(gg).

[3] As determined by the static sheen test. See § 435.11(hh).

[4] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[5] PAH mass ratio = Mass (g) of PAH (as phenanthrene)/Mass (g) of stock base fluid as determined by EPA Method 1654, Revision A, [specified at § 435.11(u)] entitled ''PAH Content of Oil by HPLC/UV,'' December 1992, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[6] Base fluid sediment toxicity ratio = 10-day LC_5. of C_{16}-C_{18} internal olefin/10-day LC_5. of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after preparing the sediment according to the procedure specified in EPA Method 1646, which are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[7] Biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{16}-C_{18} internal olefin/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu).

[8] Drilling fluid sediment toxicity ratio = 4-day LC_5. of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_5. of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[9] As determined before drilling fluids are shipped offshore by the GC/MS compliance assurance method (EPA Method 1655), and as determined prior to discharge by the RPE method (EPA Method 1670) applied to drilling fluid removed from drill cuttings. If the operator wishes to confirm the results of the RPE method (EPA Method 1670), the operator may use the GC/MS compliance assurance method (EPA Method 1655). Results from the GC/MS compliance assurance method (EPA Method 1655) shall supersede the results of the RPE method (EPA Method 1670). EPA Method 1655 and 1670 are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[10] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings averaged over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the base fluid sediment toxicity ratio (Footnote 6), biodegradation rate ratio (Footnote 7), PAH, mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[11] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings average over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the ester base fluid sediment toxicity ratio and ester biodegradation rate ratio stock limitations defined as:

(a) ester base fluid sediment toxicity ratio = 10-day LC_5. of C_{12}-C_{14} ester or C_8 ester/10-day LC_5. of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu);

(b) ester biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{12}-C_{14} ester or C_8 ester/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu); and

(c) PAH mass ratio (Footnote 5), mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6898, Jan. 22, 2001; 69 FR 18803, Apr. 9, 2004; 77 FR 29836, May 18, 2012]

§ 435.14 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT).

Except as provided in 40 CFR 125.30–32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT):

BCT EFFLUENT LIMITATIONS

Waste source	Pollutant parameter	BCT effluent limitation
Produced water	Oil & grease	The maximum for any one day shall not exceed 72 mg/l; the average of values for 30 consecutive days shall not exceed 48 mg/l.
Drilling fluids and drill cuttings:		
(A) For facilities located within 3 miles from shore.	.....	No discharge.[1]
(B) For facilities located beyond 3 miles from shore:.		
Water-based drilling fluids and associated drill cuttings.	Free Oil	No discharge.[2]
Non-aqueous drilling fluids.	.....	No discharge.
Drill cuttings associated with non-aqueous drilling fluids.	Free Oil	No discharge.[2]
Well treatment, completion and workover fluids.	Free oil	No discharge.[2]
Deck drainage	Free oil	No discharge.[3]
Produced sand	.....	No discharge.
Sanitary M10	Residual chlorine.	Minimum of 1 mg/l and maintained as close to this concentration as possible.
Sanitary M91M	Floating solids.	No discharge.
Domestic Waste	Floating solids.	No discharge.
	All other domestic waste.	See 33 CFR part 151.

[1] All Alaskan facilities are subject to the drilling fluids and drill cuttings discharge limitations for facilities located more than 3 miles offshore.

[2] As determined by the static sheen test. See § 435.11(hh).

[3] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

NEW SOURCE PERFORMANCE STANDARDS

Waste source	Pollutant parameter	NSPS
Produced water	Oil and grease.	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Drilling fluids and drill cuttings:		
(A) For facilities located within 3 miles from shore.	.....	No discharge.[1]
(B) For facilities located beyond 3 miles from shore:		
Water-based drilling fluids and associated drill cuttings.	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test[2] shall be 3% by volume.
	Free oil	No discharge.[3]
	Diesel oil	No discharge.
	Mercury	1mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
Non-aqueous drilling fluids.	.....	No charge.
Drill cuttings associated with non-aqueous drilling fluids:		
Stock Limitations (C_{16}–C_{18} internal olefin.	Mercury	1mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
	Polynuclear Aromatic Hydrocarbons (PAH).	PAH mass ratio[5] shall not exceed 1×10^{-5}.
	Sediment toxicity.	Base fluid sediment toxicity ratio[6] shall not exceed 1.0.
	Biodegradation rate.	Biodegradation rate ratio[7] shall not exceed 1.0.
Discharge Limitations.	Diesel oil	No discharge.
	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test[2] shall be 3% by volume.
	Sediment toxicity.	Drilling fluid sediment toxicity ratio[8] shall not exceed 1.0.
	Formation Oil	No discharge.[9]

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6899, Jan. 22, 2001; 77 FR 29836, May 18, 2012]

§ 435.15 Standards of performance for new sources (NSPS).

Any new source subject to this subpart must achieve the following new source performance standards (NSPS):

NEW SOURCE PERFORMANCE STANDARDS—Continued

Waste source	Pollutant parameter	NSPS
	Base fluid retained on cuttings.	For NAFs that meet the stock limitations (C_{16}–C_{18} internal olefin) in this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 6.9 g-NAF base fluid/100 g-wet drill cuttings.[10] For NAFs that meet the C_{12}–C_{14} ester or C_8 ester stock limitations in footnote 11 of this table, the maximum weighted mass ratio averaged over all NAF well sections shall be 9.4 g-NAF base fluid/100 g-wet drill cuttings.
Well treatment, completion, and workover fluids.	Oil and grease.	The maximum for any one day shall not exceed 42 mg/l; the average of daily values for 30 consecutive days shall not exceed 29 mg/l.
Deck drainage	Free oil	No discharge.[4]
Produced sand	.....	No discharge.
Sanitary M10	Residual chlorine.	Minimum of 1 mg/l and maintained as close to this as possible.
Sanitary M9IM	Floating solids.	No discharge.
Domestic Waste	Floating solids.	No discharge.
	Foam	No discharge.
	All other domestic wastes.	See 33 CFR part 151.

[1] All Alaskan facilities are subject to the drilling fluids and drill cuttings discharge standards for facilities located more than three miles offshore.

[2] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.11(gg).

[3] As determined by the static sheen test. See § 435.11(hh).

[4] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[5] PAH mass ratio = Mass (g) of PAH (as phenanthrene)/Mass (g) of stock base fluid as determined by EPA Method 1654, Revision A, [specified at § 435.11(u)] entitled ''PAH Content of Oil by HPLC/UV,'' December 1992, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[6] Base fluid sediment toxicity ratio = 10-day LC_5. of C_{16}-C_{18} internal olefin/10-day LC_5. of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after preparing the sediment according to the procedure specified in EPA Method 1646, which are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[7] Biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{16}-C_{18} internal olefin/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu).

[8] Drilling fluid sediment toxicity ratio = 4-day LC_5. of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_5. of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

[9] As determined before drilling fluids are shipped offshore by the GC/MS compliance assurance method (EPA Method 1655), and as determined prior to discharge by the RPE method (EPA Method 1670) applied to drilling fluid removed from drill cuttings. If the operator wishes to confirm the results of the RPE method (EPA Method 1670), the operator may use the GC/MS compliance assurance method (EPA Method 1655). Results from the GC/MS compliance assurance method (EPA Method 1655) shall supersede the results of the RPE method (EPA Method 1670). EPA Method 1655 and 1670 are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu).

[10] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings averaged over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the base fluid sediment toxicity ratio (Footnote 6), biodegradation rate ratio (Footnote 7), PAH, mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[11] Maximum permissible retention of non-aqueous drilling fluid (NAF) base fluid on wet drill cuttings average over drilling intervals using NAFs as determined by EPA Method 1674, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(uu). This limitation is applicable for NAF base fluids that meet the ester base fluid sediment toxicity ratio and ester biodegradation rate ratio stock limitations defined as:

(a) ester base fluid sediment toxicity ratio = 10-day LC_5. of C_{12}-C_{14} ester or C_8 ester/10-day LC_5. of stock base fluid as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu);

(b) ester biodegradation rate ratio = Cumulative headspace gas production (ml) of C_{12}-C_{14} ester or C_8 ester/Cumulative headspace gas production (ml) of stock base fluid, both at 275 days as determined by EPA Method 1647, which is published as an appendix to subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(e) and (uu); and (c) PAH mass ratio (Footnote 5), mercury, and cadmium stock limitations (C_{16}-C_{18} internal olefin) defined above in this table.

[58 FR 12504, Apr. 13, 1979, as amended at 66 FR 6900, Jan. 22, 2001; 66 FR 33134, June 20, 2001; 69 FR 18803, Apr. 9, 2004; 77 FR 29836, May 16, 2012]

APPENDIX 1 TO SUBPART A OF PART 435—STATIC SHEEN TEST (EPA METHOD 1617)

1. Scope and Application

This method is to be used as a compliance test for the ''no discharge of free oil'' requirement for discharges of drilling fluids, drill cuttings, produced sand, and well treatment, completion and workover fluids. ''Free oil'' refers to any oil contained in a waste stream that when discharged will cause a film or sheen upon or a discoloration of the surface of the receiving water.

2. Summary of Method

15-mL samples of drilling fluids or well treatment, completion, and workover fluids, and 15-g samples (wet weight basis) of drill cuttings or produced sand are introduced into ambient seawater in a container having an air-to-liquid interface area of 1000 cm^2 (155.5 in^2). Samples are dispersed within the container and observations made no more than one hour later to ascertain if these materials cause a sheen, iridescence, gloss, or increased reflectance on the surface of the test seawater. The occurrence of any of these visual observations will constitute a demonstration that the tested material contains ''free oil,'' and therefore results in a prohibition of its discharge into receiving waters.

3. Interferences

Residual ''free oil'' adhering to sampling containers, the magnetic stirring bar used to mix the sample, and the stainless steel spatula used to mix the sample will be the principal sources of contamination problems. These problems should only occur if improperly washed and cleaned equipment are used for the test. The use of disposable equipment minimizes the potential for similar contamination from pipettes and the test container.

4. Apparatus, Materials, and Reagents

4.1 Apparatus

4.1.1 Sampling Containers: 1-liter polyethylene beakers and 1-liter glass beakers.

4.1.2 Graduated cylinder: 100-mL graduated cylinder required only for operations where predilution of mud discharges is required.

4.1.3 Plastic disposable weighing boats.

4.1.4 Triple-beam scale.

4.1.5 Disposable pipettes: 25-mL disposable pipettes.

4.1.6 Magnetic stirrer and stirring bar.

4.1.7 Stainless steel spatula.

4.1.8 Test container: Open plastic container whose internal cross-section parallel to its opening has an area of 1000 $cm^2 \pm 50$ cm^2 (155.5 ± 7.75 in^2), and a depth of at least 13 cm (5 inches) and no more than 30 cm (11.8 inches).

4.2 Materials and Reagents.

4.2.1 Plastic liners for the test container: Oil-free, heavy-duty plastic trash can liners that do not inhibit the spreading of an oil film. Liners must be of sufficient size to completely cover the interior surface of the test container. Permittees must determine an appropriate local source of liners that do not inhibit the spreading of 0.05 mL of diesel fuel added to the lined test container under the test conditions and protocol described below.

4.2.2 Ambient receiving water.

5. Calibration

None currently specified.

6. Quality Control Procedures

None currently specified.

7. Sample Collection and Handling

7.1 Sampling containers must be thoroughly washed with detergent, rinsed a minimum of three times with fresh water, and allowed to air dry before samples are collected.

7.2 Samples of drilling fluid to be tested shall be taken at the shale shaker after cuttings have been removed. The sample volume should range between 200 mL and 500 mL.

7.3 Samples of drill cuttings will be taken from the shale shaker screens with a clean spatula or similar instrument and placed in a glass beaker. Cuttings samples shall be collected prior to the addition of any washdown water and should range between 200 g and 500 g.

7.4 Samples of produced sand must be obtained from the solids control equipment from which the discharge occurs on any given day and shall be collected prior to the addition of any washdown water; samples should range between 200 g and 500 g.

7.5 Samples of well treatment, completion, and workover fluids must be obtained from the holding facility prior to discharge; the sample volume should range between 200 mL and 500 mL.

7.6 Samples must be tested no later than 1 hour after collection.

7.7 Drilling fluid samples must be mixed in their sampling containers for 5 minutes prior to the test using a magnetic bar stirrer. If predilution is imposed as a permit condition, the sample must be mixed at the same ratio with the same prediluting water as the discharged muds and stirred for 5 minutes.

7.8 Drill cuttings must be stirred and well mixed by hand in their sampling containers prior to testing, using a stainless steel spatula.

8. Procedure

8.1 Ambient receiving water must be used as the ''receiving water'' in the test. The temperature of the test water shall be as close as practicable to the ambient conditions in the receiving water, not the room temperature of the observation facility. The test container must have an air-to-liquid interface area of 1000 ±50 cm^2. The surface of the water should be no more than 1.27 cm (.5 inch) below the top of the test container.

8.2 Plastic liners shall be used, one per test container, and discarded afterwards. Some liners may inhibit spreading of added oil; operators shall determine an appropriate local source of liners that do not inhibit the spreading of the oil film.

8.3 A 15-mL sample of drilling fluid or well treatment, completion, and workover fluids must be introduced by pipette into the test container 1 cm below the water surface. Pipettes must be filled and discharged with test material prior to the transfer of test material and its introduction into test containers. The test water/test material mixture must be stirred using the pipette to distribute the test material homogeneously throughout the test water. The pipette must be used only once for a test and then discarded.

8.4 Drill cuttings or produced sand should be weighed on plastic weighing boats; 15-g samples must be transferred by scraping test material into the test water with a stainless steel spatula. Drill cuttings shall not be prediluted prior to testing. Also, drilling fluids and cuttings will be tested separately. The weighing boat must be immersed in the test water and scraped with the spatula to transfer any residual material to the test container. The drill cuttings or produced sand must be stirred with the spatula to an even distribution of solids on the bottom of the test container.

8.5 Observations must be made no later than 1 hour after the test material is transferred to the test container. Viewing points above the test container should be made from at least three sides of the test container, at viewing angles of approximately 60° and 30° from the horizontal. Illumination of the test container must be representative of adequate lighting for a working environment to conduct routine laboratory procedures. It is recommended that the water surface of the test container be observed under a fluorescent light source such as a dissecting microscope light. The light source shall be positioned above and directed over the entire surface of the pan.

8.6 Detection of a ''silvery'' or ''metallic'' sheen or gloss, increased reflectivity, visual color, iridescence, or an oil slick on the water surface of the test container surface shall constitute a demonstration of ''free oil.'' These visual observations include patches, streaks, or sheets of such altered surface characteristics. If the free oil content of the sample approaches or exceeds 10%, the water surface of the test container may lack color, a sheen, or iridescence, due to the increased thickness of the film; thus, the observation for an oil slick is required. The surface of the test container shall not be disturbed in any manner that reduces the size of any sheen or slick that may be present.

If an oil sheen or slick occurs on less than one-half of the surface area after the sample is introduced to the test container, observations will continue for up to 1 hour. If the sheen or slick increases in size and covers greater than one-half of the surface area of the test container during the observation period, the discharge of the material shall cease. If the sheen or slick does not increase in size to cover greater than one-half of the test container surface area after one hour of observation, discharge may continue and additional sampling is not required.

If a sheen or slick occurs on greater than one-half of the surface area of the test container after the test material is introduced, discharge of the tested material shall cease. The permittee may retest the material causing the sheen or slick. If subsequent tests do not result in a sheen or slick covering greater than one-half of the surface area of the test container, discharge may continue.

APPENDIX 2 TO SUBPART A OF PART 435—DRILLING FLUIDS TOXICITY TEST (EPA METHOD 1619)

I. Sample Collection

The collection and preservation methods for drilling fluids (muds) and water samples presented here are designed to minimize sample contamination and alteration of the physical or chemical properties of the samples due to freezing, air oxidation, or drying.

I-A. Apparatus

(1) The following items are required for water and drilling mud sampling and storage:

a. Acid-rinsed linear-polyethylene bottles or other appropriate noncontaminating drilling mud sampler.

b. Acid-rinsed linear-polyethylene bottles or other appropriate noncontaminating water sampler.

c. Acid-rinsed linear-polyethylene bottles or other appropriate noncontaminated vessels for water and mud samples.

d. Ice chests for preservation and shipping of mud and water samples.

I-B. Water Sampling

(1) Collection of water samples shall be made with appropriate acid-rinsed linear-polyethylene bottles or other appropriate

non-contaminating water sampling devices. Special care shall be taken to avoid the introduction of contaminants from the sampling devices and containers. Prior to use, the sampling devices and containers should be thoroughly cleaned with a detergent solution, rinsed with tap water, soaked in 10 percent hydrochloric acid (HCl) for 4 hours, and then thoroughly rinsed with glass-distilled water.

I-C. Drilling Mud Sampling

(1) Drilling mud formulations to be tested shall be collected from active field systems. Obtain a well-mixed sample from beneath the shale shaker after the mud has passed through the screens. Samples shall be stored in polyethylene containers or in other appropriate uncontaminated vessels. Prior to sealing the sample containers on the platform, flush as much air out of the container by filling it with drilling fluid sample, leaving a one inch space at the top.

(2) Mud samples shall be immediately shipped to the testing facility on blue or wet ice (do not use dry ice) and continuously maintained at 0–4 °C until the time of testing.

(3) Bulk mud samples shall be thoroughly mixed in the laboratory using a 1000 rpm high shear mixer and then subdivided into individual, small wide-mouthed (e.g., one or two liter) non-contaminating containers for storage.

(4) The drilling muds stored in the laboratory shall have any excess air removed by flushing the storage containers with nitrogen under pressure anytime the containers are opened. Moreover, the sample in any container opened for testing must be thoroughly stirred using a 1000 rpm high shear mixer prior to use.

(5) Most drilling mud samples may be stored for periods of time longer than 2 weeks prior to toxicity testing provided that proper containers are used and proper condition are maintained.

II. Suspended Particulate Phase Sample Preparation

(1) Mud samples that have been stored under specified conditions in this protocol shall be prepared for tests within three months after collection. The SPP shall be prepared as detailed below.

II-A. Apparatus

(1) The following items are required:

a. Magnetic stir plates and bars.

b. Several graduated cylinders, ranging in volume from 10 mL to 1 L

c. Large (15 cm) powder funnels.

d. Several 2-liter graduated cylinders.

e. Several 2-liter large mouth graduated Erlenmeyer flasks.

(2) Prior to use, all glassware shall be thoroughly cleaned. Wash all glassware with detergent, rinse five times with tap water, rinse once with acetone, rinse several times with distilled or deionized water, place in a clean 10-percent (or stronger) HCl acid bath for a minimum of 4 hours, rinse five times with tap water, and then rinse five times with distilled or deionized water. For test samples containing mineral oil or diesel oil, glassware should be washed with petroleum ether to assure removal of all residual oil.

NOTE: If the glassware with nytex cups soaks in the acid solution longer than 24 hours, then an equally long deionized water soak should be performed.

II-B. Test Seawater Sample Preparation

(1) Diluent seawater and exposure seawater samples are prepared by filtration through a 1.0 micrometer filter prior to analysis.

(2) Artificial seawater may be used as long as the seawater has been prepared by standard methods or ASTM methods, has been properly ''seasoned,'' filtered, and has been diluted with distilled water to the same specified 20±2 ppt salinity and 20±2 °C temperature as the ''natural'' seawater.

II-C. Sample Preparation

(1) The pH of the mud shall be tested prior to its use. If the pH is less than 9, if black spots have appeared on the walls of the sample container, or if the mud sample has a foul odor, that sample shall be discarded. Subsample a manageable aliquot of mud from the well-mixed original sample. Mix the mud and filtered test seawater in a volumetric mud-to-water ratio of 1 to 9. This is best done by the method of volumetric displacement in a 2–L, large mouth, graduated Erlenmeyer flask. Place 1000 mL of seawater into the graduated Erlenmeyer flask. The mud subsample is then carefully added via a powder funnel to obtain a total volume of 1200 mL. (A 200 mL volume of the mud will now be in the flask).

The 2–L, large mouth, graduated Erlenmeyer flask is then filled to the 2000 mL mark with 800 mL of seawater, which produces a slurry with a final ratio of one volume drilling mud to nine volumes water. If the volume of SPP required for testing or analysis exceeds 1500 to 1600 mL, the initial volumes should be proportionately increased. Alternatively, several 2–L drill mud/water slurries may be prepared as outlined above and combined to provide sufficient SPP.

(2) Mix this mud/water slurry with magnetic stirrers for 5 minutes. Measure the pH and, if necessary, adjust (decrease) the pH of the slurry to within 0.2 units of the seawater by adding 6N HCl while stirring the slurry. Then, allow the slurry to settle for 1 hour. Record the amount of HCl added.

(3) At the end of the settling period, carefully decant (do not siphon) the Suspended Particulate Phase (SPP) into an appropriate container. Decanting the SPP is one continuous action. In some cases no clear interface will be present; that is, there will be no solid phase that has settled to the bottom. For those samples the entire SPP solution should be used when preparing test concentrations. However, in those cases when no clear interface is present, the sample must be remixed for five minutes. This insures the homogeneity of the mixture prior to the preparation of the test concentrations. In other cases, there will be samples with two or more phases, including a solid phase. For those samples, carefully and continuously decant the supernatant until the solid phase on the bottom of the flask is reached. The decanted solution is defined to be 100 percent SPP. Any other concentration of SPP refers to a percentage of SPP that is obtained by volumetrically mixing 100 percent SPP with seawater.

(4) SPP samples to be used in toxicity tests shall be mixed for 5 minutes and must not be preserved or stored.

(5) Measure the filterable and unfilterable residue of each SPP prepared for testing. Measure the dissolved oxygen (DO) and pH of the SPP. If the DO is less than 4.9 ppm, aerate the SPP to at least 4.9 ppm which is 65 percent of saturation. Maximum allowable aeration time is 5 minutes using a generic commercial air pump and air stone. Neutralize the pH of the SPP to a pH 7.8 ±.1 using a dilute HCl solution. If too much acid is added to lower the pH saturated NaOH may be used to raise the pH to 7.8 ±.1 units. Record the amount of acid or NaOH needed to lower/raise to the appropriate pH. Three repeated DO and pH measurements are needed to insure homogeneity and stability of the SPP. Preparation of test concentrations may begin after this step is complete.

(6) Add the appropriate volume of 100 percent SPP to the appropriate volume of seawater to obtain the desired SPP concentration. The control is seawater only. Mix all concentrations and the control for 5 minutes by using magnetic stirrers. Then, the animals shall be randomly selected and placed in the dishes in order to begin the 96-hour toxicity test.

III. Guidance for Performing Suspended Particulate Phase Toxicity Tests Using Mysidopsis bahia

III-A. Apparatus

(1) Each definitive test consists of 18 test containers: 3 replicates of a control and 5 SPP dilutions. Test containers should be Pyrex or equivalent glass. For definitive tests, 5 SPP dilutions with 3 replicates of at least 500 ml each are required. Twenty mysids per replicate, 360 per definitive test are required.

III-B. Sample Collection Preservation

(1) Drilling muds and water samples are collected and stored, and the suspended particulate phase prepared as described in section 1–C.

III-C. Species Selection

(1) The Suspended Particulate Phase (SPP) tests on drilling muds shall utilize the test species *Mysidopsis bahia*. Test animals shall be 3 to 6 days old on the first day of exposure. Whatever the source of the animals, collection and handling should be as gentle as possible. Transportation to the laboratory should be in well-aerated water from the animal culture site at the temperature and salinity from which they were cultured. Methods for handling, acclimating, and sizing bioassay organisms given by Borthwick [1] and Nimmo [2] shall be followed in matters for which no guidance is given here.

III-D. Experimental Conditions

(1) Suspended particulate phase (SPP) tests should be conducted at a salinity of 20 ±2 ppt. Experimental temperature should be 20 ±2 °C. Dissolved oxygen in the SPP shall be raised to or maintained above 65 percent of saturation prior to preparation of the test concentrations. Under these conditions of temperature and salinity, 65 percent saturation is a DO of 5.3 ppm. Beginning at Day 0-before the animals are placed in the test containers DO, temperature, salinity, and pH shall be measured every 24 hours. DO should be reported in milligrams per liter.

(2) Aeration of test media is required during the entire test with a rate estimated to be 50–140 cubic centimeters/minute. This air flow to each test dish may be achieved through polyethylene tubing (0.045-inch inner diameter and 0.062-inch outer diameter) by a small generic aquarium pump. The delivery method, surface area of the aeration stone, and flow characteristics shall be documented. All treatments, including control, shall be the same.

(3) Light intensity shall be 1200 microwatts/cm^2 using cool white fluorescent bulbs with a 14-hr light and 10-hr dark cycle. This light/dark cycle shall also be maintained during the acclimation period and the test.

III-E. Experimental Procedure

(1) Wash all glassware with detergent, rinse five times with tap water, rinse once with acetone, rinse several times with distilled or deionized water, place in a clean 10 percent HCl acid bath for a minimum of 4 hours, rinse five times with tap water, and then rinse five times with distilled water.

(2) Establish the definitive test concentrations based on results of a range finding test or based on prior experience and knowledge of the mud system.

(3) Twenty organisms are exposed in each test dish. Nytex® cups shall be inserted into every test dish prior to adding the animals. These ''nylon mesh screen'' nytex holding cups are fabricated by gluing a collar of 363-micrometer mesh nylon screen to a 15-centimeter wide Petri dish with silicone sealant. The nylon screen collar is approximately 5 centimeters high. The animals are then placed into the test concentration within the confines of the Nytex cups.

(4) Individual organisms shall be randomly assigned to treatment. A randomization procedure is presented in section V of this protocol. Make every attempt to expose animals of approximately equal size. The technique described by Borthwick [1], or other suitable substitutes, should be used for transferring specimens. Throughout the test period, mysids shall be fed daily with approximately 50 *Artemia* (brine shrimp) nauplii per mysid. This will reduce stress and decrease cannibalism.

(5) Cover the dishes, aerate, and incubate the test containers in an appropriate test chamber. Positioning of the test containers holding various concentrations of test solution should be randomized if incubator arrangement indicates potential position difference. The test medium is not replaced during the 96-hour test.

(6) Observations may be attempted at 4, 6 and 8 hours; they must be attempted at 0, 24, 48, and 72 hours and must be made at 96 hours. Attempts at observations refers to placing a test dish on a light table and visually counting the animals. Do not lift the ''nylon mesh screen'' cup out of the test dish to make the observation. No unnecessary handling of the animals should occur during the 96 hour test period. DO and pH measurements must also be made at 0, 24, 48, 72, and 96 hours. Take and replace the test medium necessary for the DO and pH measurements outside of the nytex cups to minimize stresses on the animals.

(7) At the end of 96 hours, all live animals must be counted. Death is the end point, so the number of living organisms is recorded. Death is determined by lack of spontaneous movement. All crustaceans molt at regular intervals, shedding a complete exoskeleton. Care should be taken not to count an exoskeleton. Dead animals might decompose or be eaten between observations. Therefore, always count living, not dead animals. If daily observations are made, remove dead organisms and molted exoskeletons with a pipette or forceps. Care must be taken not to disturb living organisms and to minimize the amount of liquid withdrawn.

IV. Methods for Positive Control Tests (Reference Toxicant)

(1) Sodium lauryl sulfate (dodecyl sodium sulfate) is used as a reference toxicant for the positive control. The chemical used should be approximately 95 percent pure. The source, lot number, and percent purity shall be reported.

(2) Test methods are those used for the drilling fluid tests, except that the test material was prepared by weighing one gram sodium lauryl sulfate on an analytical balance, adding the chemical to a 100-milliliter volumetric flask, and bringing the flask to volume with deionized water. After mixing this stock solution, the test mixtures are prepared by adding 0.1 milliliter of the stock solution for each part per million desired to one liter of seawater.

(3) The mixtures are stirred briefly, water quality is measured, animals are added to holding cups, and the test begins. Incubation and monitoring procedures are the same as those for the drilling fluids.

V. Randomization Procedure

V-A. Purpose and Procedure

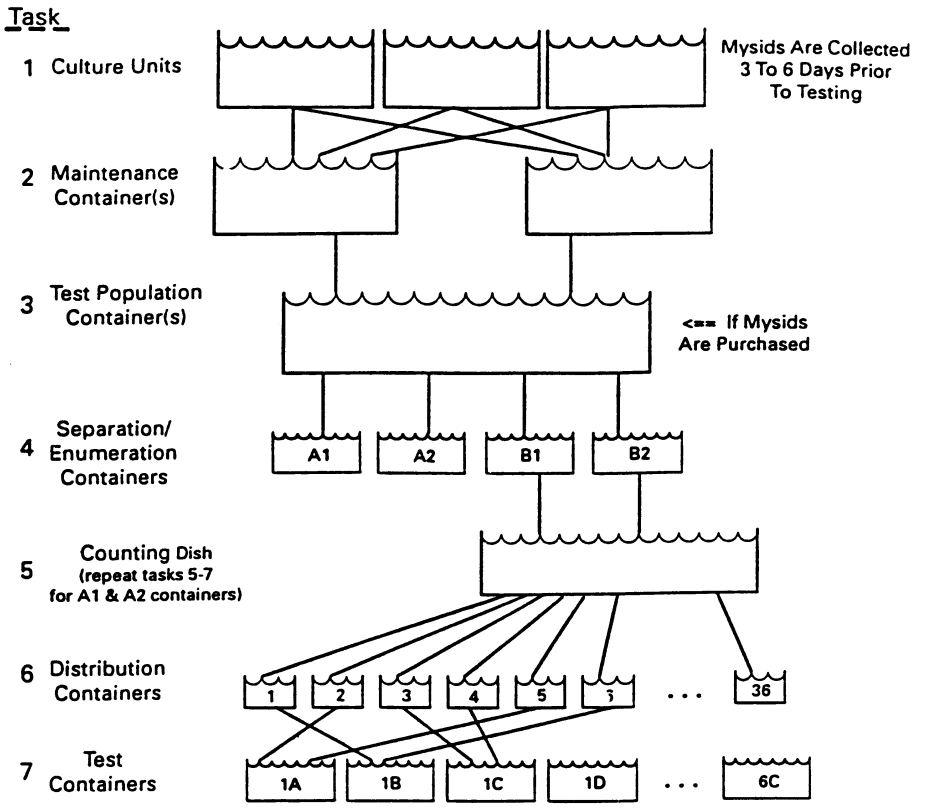
(1) The purpose of this procedure is to assure that mysids are impartially selected and randomly assigned to six test treatments (five drilling fluid or reference toxicant concentrations and a control) and impartially counted at the end of the 96-hour test. Thus, each test setup, as specified in the randomization procedure, consists of 3 replicates of 20 animals for each of the six treatments, *i.e.*, 360 animals per test. Figure 1 is a flow diagram that depicts the procedure schematically and should be reviewed to understand the over-all operation. The following tasks shall be performed in the order listed.

(2) Mysids are cultured in the laboratory in appropriate units. If mysids are purchased, go to Task 3.

(3) Remove mysids from culture tanks (6, 5, 4, and 3 days before the test will begin, *i.e.*, Tuesday, Wednesday, Thursday, and Friday if the test will begin on Monday) and place them in suitably large maintenance containers so that they can swim about freely and be fed.

NOTE: Not every detail (the definition of suitably large containers, for example) is provided here. Training and experience in aquatic animal culture and testing will be required to successfully complete these tests.

Figure 1
Mysid Randomization Procedure



(4) Remove mysids from maintenance containers and place all animals in a single container. The intent is to have homogeneous test population of mysids of a known age (3–6 days old).

(5) For each toxicity test, assign two suitable containers (500-milliliter (mL) beakers are recommended) for mysid separation/enumeration. Label each container (A1, A2, B1, B2, and C1, C2, for example, if two drilling fluid tests and a reference toxicant test are to be set up on one day). The purpose of this task is to allow the investigator to obtain a close estimate of the number of animals available for testing and to prevent unnecessary crowding of the mysids while they are being counted and assigned to test containers. Transfer the mysids from the large test population container to the labeled separation and enumeration containers but do not place more than 200 mysids in a 500-mL beaker. Be impartial in transferring the mysids; place approximately equal numbers of animals (10–15 mysids is convenient) in each container in a cyclic manner rather than placing the maximum number each container at one time.

NOTE: It is important that the animals not be unduly stressed during this selection and assignment procedure. Therefore, it will probably be necessary to place all animals (except the batch immediately being assigned to test containers) in mesh cups with flowing seawater or in large volume containers with aeration. The idea is to provide the animals with near optimal conditions to avoid additional stress.

(6) Place the mysids from the two labeled enumeration containers assigned to a specific test into one or more suitable containers to be used as counting dishes (2-liter Carolina dishes are suggested). Because of the time required to separate, count, and assign mysids, two or more people may be involved in completing this task. If this is done, two or more counting dishes may be used, but the investigator must make sure that approximately equal numbers of mysids from each labeled container are placed in each counting dish.

(7) By using a large-bore, smooth-tip glass pipette, select mysids from the counting dish(es) and place them in the 36 individually numbered distribution containers (10-ml beakers are suggested). The mysids are assigned two at a time to the 36 containers by using a randomization schedule similar to the one presented below. At the end of selection/assignment round 1, each container will contain two mysids; at the end of round 2, they will contain four mysids; and so on until each contains ten mysids.

EXAMPLE OF A RANDOMIZATION SCHEDULE

Selection/assignment round (2 mysids each)	Place mysid in the numbered distribution containers in the random order shown
1	8, 21, 6, 28, 33, 32, 1, 3, 10, 9, 4, 14, 23, 2, 34, 22, 36, 27, 5, 30, 35, 24, 12, 25, 11, 17, 19, 26, 31, 7, 20, 15, 18, 13, 16, 29.
2	35, 18, 5, 12, 32, 34, 22, 3, 9, 16, 26, 13, 20, 28, 6, 21, 24, 30, 8, 31, 7, 23, 2, 15, 25, 17, 1, 11, 27, 4, 19, 36, 10, 33, 14, 29.
3	7, 19, 14, 11, 34, 21, 25, 27, 17, 18, 6, 16, 29, 2, 32, 10, 4, 20, 3, 9, 1, 5, 28, 24, 31, 15, 22, 13, 33, 26, 36, 12, 8, 30, 35, 23.
4	30, 2, 18, 5, 8, 27, 10, 25, 4, 20, 26, 15, 31, 36, 35, 23, 11, 29, 16, 17, 28, 1, 33, 14, 9, 34, 7, 3, 12, 22, 21, 6, 19, 24, 32, 13.
5	34, 28, 16, 17, 10, 12, 1, 36, 20, 18, 15, 22, 2, 4, 19, 23, 27, 29, 25, 21, 30, 3, 9, 33, 32, 6, 14, 11, 35, 24, 26, 7, 31, 5, 13, 8.

(8) Transfer mysids from the 36 distribution containers to 18 labeled test containers in random order. A label is assigned to each of the three replicates (A, B, C) of the six test concentrations. Count and record the 96 hour response in an impartial order.

(9) Repeat tasks 5–7 for each toxicity test. A new random schedule should be followed in Tasks 6 and 7 for each test.

NOTE: If a partial toxicity test is conducted, the procedures described above are appropriate and should be used to prepare the single test concentration and control, along with the reference toxicant test.

V-B. Data Analysis and Interpretation

(1) Complete survival data in all test containers at each observation time shall be presented in tabular form. If greater than 10 percent mortality occurs in the controls, all data shall be discarded and the experiment repeated. Unacceptably high control mortality indicates the presence of important stresses on the organisms other than the material being tested, such as injury or disease, stressful physical or chemical conditions in the containers, or improper handling, acclimation, or feeding. If 10 percent mortality or less occurs in the controls, the data may be evaluated and reported.

(2) A definitive, full bioassay conducted according to the EPA protocol is used to estimate the concentration that is lethal to 50 percent of the test organisms that do not die naturally. This toxicity measure is known as the median lethal concentration, or LC–50. The LC–50 is adjusted for natural mortality or natural responsiveness. The maximum likelihood estimation procedure with the adjustments for natural responsiveness as given by D.J. Finney, in *Probit Analysis* 3rd edition, 1971, Cambridge University Press, chapter 7, can be used to obtain the probit model estimate of the LC–50 and the 95 percent fiducial (confidence) limits for the LC–50. These estimates are obtained using the logarithmic transform of the concentration. The heterogeneity factor (Finney 1971, pages 70–72) is not used. For a test material to pass the toxicity test, according to the requirements stated in the offshore oil and gas extraction industry BAT effluent limitations and NSPS, the LC–50, adjusted for natural responsiveness, must be greater than 3 percent suspended particulate phase (SPP) concentration by volume unadjusted for the 1 to 9 dilution. Other toxicity test models may be used to obtain toxicity estimates provided the modeled mathematical expression for the lethality rate must increase continuously with concentration. The lethality rate is modeled to increase with concentration to reflect an assumed increase in toxicity with concentration even though the observed lethality may not increase uniformly because of the unpredictable animal response fluctuations.

(3) The range finding test is used to establish a reasonable set of test concentrations in order to run the definitive test. However, if the lethality rate changes rapidly over a narrow range of concentrations, the range finding assay may be too coarse to establish

an adequate set of test concentrations for a definitive test.

(4) The EPA Environmental Research Laboratory in Gulf Breeze, Florida prepared a Research and Development Report entitled Acute Toxicity of Eight Drilling Fluids to Mysid Shrimp (*Mysidopsis bahia*), May 1984 EPA–600/3–84–067. The Gulf Breeze data for drilling fluid number 1 are displayed in Table 1 for purposes of an example of the probit analysis described above. The SAS Probit Procedure (SAS Institute, Statistical Analysis System, Cary, North Carolina, 1982) was used to analyze these data. The 96-hour LC50 adjusted for the estimated spontaneous mortality rate is 3.3 percent SPP with 95 percent limits of 3.0 and 3.5 percent SPP with the 1 to 9 dilution. The estimated spontaneous mortality rate based on all of the data is 9.6 percent.

TABLE 1—LISTING OF ACUTE TOXICITY TEST DATA (AUGUST 1983 TO SEPTEMBER 1983) WITH EIGHT GENERIC DRILLING FLUIDS AND MYSID SHRIMP

[fluid N2 = 1]

Percent concentration	Number exposed	Number dead (96 hours)	Number alive (96 hours)
0	60	3	57
1	60	11	49
2	60	11	49
3	60	25	35
4	60	48	12
5	60	60	0

V-C. The Partial Toxicity Test for Evaluation of Test Material

(1) A partial test conducted according to EPA protocol can be used economically to demonstrate that a test material passes the toxicity test. The partial test cannot be used to estimate the LC–50 adjusted for natural response.

(2) To conduct a partial test follow the test protocol for preparation of the test material and organisms. Prepare the control (zero concentration), one test concentration (3 percent suspended particulate phase) and the reference toxicant according to the methods of the full test. A range finding test is not used for the partial test.

(3) Sixty test organisms are used for each test concentration. Find the number of test organisms killed in the control (zero percent SPP) concentration in the column labeled X_0 of Table 2. If the number of organisms in the control (zero percent SPP) exceeds the table values, then the test is unacceptable and must be repeated. If the number of organisms killed in the 3 percent test concentration is less than or equal to corresponding number in the column labeled X_1 then the test material passes the partial toxicity test. Otherwise the test material fails the toxicity test.

(4) Data shall be reported as percent suspended particulate phase.

TABLE 2

X_0	X_1
0	22
1	22
2	23
3	23
4	24
5	24
6	25

VI. References

1. Borthwick, Patrick W. 1978. Methods for acute static toxicity tests with mysid shrimp (*Mysidopsis bahia*). Bioassay Procedures for the Ocean Disposal Permit Program, [EPA–600/9–78–010:] March.

2. Nimmo, D.R., T.L. Hamaker, and C.A. Somers. 1978. Culturing the mysid (*Mysidopsis bahia*) in flowing seawater or a static system. Bioassay Procedures for the Ocean Disposal Permit Program, [EPA–600/9–78–010]: March.

3. American Public Health Association et al. 1980. Standard Methods for the Examination of Water and Wastewater. Washington, DC, 15th Edition: 90–99.

4. U.S. Environmental Protection Agency, September 1991. Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. EPA/600/4–90/027. Washington, DC, 4th Edition.

5. Finney, D.J. Probit Analysis. Cambridge University Press; 1971.

6. U.S. Environmental Protection Agency, May 1984. Acute Toxicity of Eight Drilling Fluids to Mysid Shrimp (*Mysidopsis bahia*). EPA–600/3–84–067.

[58 FR 12504, Mar. 4, 1993, as amended at 77 FR 29837, May 18, 2012]

APPENDIX 3 TO SUBPART A OF PART 435—PROCEDURE FOR MIXING BASE FLUIDS WITH SEDIMENTS (EPA METHOD 1646)

This procedure describes a method for amending uncontaminated and nontoxic (control) sediments with the base fluids that are used to formulate synthetic-based drilling fluids and other non-aqueous drilling fluids. Initially, control sediments shall be press-sieved through a 2000 micron mesh sieve to remove large debris. Then press-sieve the sediment through a 500 micron sieve to remove indigenous organisms that may prey on the test species or otherwise confound test results. Homogenize control sediment to limit the effects of settling that

may have occurred during storage. Sediments should be homogenized before density determinations and addition of base fluid to control sediment. Because base fluids are strongly hydrophobic and do not readily mix with sediment, care must be taken to ensure base fluids are thoroughly homogenized within the sediment. All concentrations are weight-to-weight (mg of base fluid to kg of dry control sediment). Sediment and base fluid mixing shall be accomplished by using the following method.

1. Determine the wet to dry ratio for the control sediment by weighing approximately 10 g subsamples of the screened and homogenized wet sediment into tared aluminum weigh pans. Dry sediment at 105 °C for 18–24 h. Remove sediment and cool in a desiccator until a constant weight is achieved. Reweigh the samples to determine the dry weight. Determine the wet/dry ratio by dividing the net wet weight by the net dry weight:

[Wet Sediment Weight (g)]/[Dry Sediment Weight (g)] = Wet to Dry Ratio [1]

2. Determine the density (g/mL) of the wet control or dilution sediment. This shall be used to determine total volume of wet sediment needed for the various test treatments.

[Mean Wet Sediment Weight (g)]/[Mean Wet Sediment Volume (mL)] = Wet Sediment Density (g/mL) [2]

3. To determine the amount of base fluid needed to obtain a test concentration of 500 mg base fluid per kg dry sediment use the following formulas:

Determine the amount of wet sediment required:

[Wet Sediment Density (g/mL)] × [Volume of Sediment Required per Concentration (mL)] = Weight Wet Sediment Required per Conc. (g) [3]

Determine the amount of dry sediment in kilograms (kg) required for each concentration:

{[Wet Sediment per Concentration (g)]/[Mean Wet to Dry Ratio]} × (1kg/1000g) = Dry Weight Sediment (kg) [4]

Finally, determine the amount of base fluid required to spike the control sediment at each concentration:

[Conc. Desired (mg/kg)] × [Dry Weight Sediment (kg)] = Base Fluid Required (mg) [5]

For spiking test substances other than pure base fluids (e.g., whole mud formulations), determine the spike amount as follows:

[Conc. Desired (mL/kg)] × [Dry Weight Sediment (kg)] × [Test Substance Density (g/mL)] = Test Substance Required (g) [6]

4. For primary mixing, place appropriate amounts of weighed base fluid into stainless mixing bowls, tare the vessel weight, then add sediment and mix with a high-shear dispersing impeller for 9 minutes. The concentration of base fluid in sediment from this mix, rather than the nominal concentration, shall be used in calculating LC_5. values.

5. Tests for homogeneity of base fluid in sediment are to be performed during the procedure development phase. Because of difficulty of homogeneously mixing base fluid with sediment, it is important to demonstrate that the base fluid is evenly mixed with sediment. The sediment shall be analyzed for total petroleum hydrocarbons (TPH) using EPA Methods 3550A and 8015M, with samples taken both prior to and after distribution to replicate test containers. Base-fluid content is measured as TPH. After mixing the sediment, a minimum of three replicate sediment samples shall be taken prior to distribution into test containers. After the test sediment is distributed to test containers, an additional three sediment samples shall be taken from three test containers to ensure proper distribution of base fluid within test containers. Base-fluid content results shall be reported within 48 hours of mixing. The coefficient of variation (CV) for the replicate samples must be less than 20%. If base-fluid content results are not within the 20% CV limit, the test sediment shall be remixed. Tests shall not begin until the CV is determined to be below the maximum limit of 20%. During the test, a minimum of three replicate containers shall be sampled to determine base-fluid content during each sampling period.

6. Mix enough sediment in this way to allow for its use in the preparation of all test concentrations and as a negative control. When commencing the sediment toxicity test, range-finding tests may be required to determine the concentrations that produce a toxic effect if these data are otherwise unavailable. The definitive test shall bracket the LC_5., which is the desired endpoint. The results for the base fluids shall be reported in mg of base fluid per kg of dry sediment.

References

American Society for Testing and Materials (ASTM). 1996. Standard Guide for Collection, Storage, Characterization, and Manipulation of Sediments for Toxicological Testing. ASTM E 1391–94. Annual Book of ASTM Standards, Volume 11.05, pp. 805–825.

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U.S. EPA. 1994. Methods for Assessing the Toxicity of Sediment-associated Contaminants with Estuarine and Marine

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[66 FR 6901, Jan. 22, 2001]

APPENDIX 4 TO SUBPART A OF PART 435—PROTOCOL FOR THE DETERMINATION OF DEGRADATION OF NON-AQUEOUS BASE FLUIDS IN A MARINE CLOSED BOTTLE BIODEGRADATION TEST SYSTEM: MODIFIED ISO 11734:1995 (EPA METHOD 1647)

1.0. SUMMARY OF EPA METHOD 1647

a. This method determines the anaerobic degradation potential of mineral oils, paraffin oils and non-aqueous fluids (NAF) in sediments. These substrates are base fluids for formulating offshore drilling fluids. The test evaluates base fluid biodegradation rates by monitoring gas production due to microbial degradation of the test fluid in natural marine sediment.

b. The test procedure places a mixture of marine/estuarine sediment, test substrate (hydrocarbon or controls) and seawater into clean 120 mL (150 mL actual volume) Wheaton serum bottles. The test is run using four replicate serum bottles containing 2,000 mg carbon/kg dry weight concentration of test substrate in sediment. The use of resazurin dye solution (1 ppm) evaluates the anaerobic (redox) condition of the bottles (dye is blue when oxygen is present, reddish in low oxygen conditions and colorless if oxygen free). After capping the bottles, a nitrogen sparge removes air in the headspace before incubation begins. During the incubation period, the sample should be kept at a constant temperature of 29 ±1 °C. Gas production and composition is measured approximately every two weeks. The samples need to be brought to ambient temperature before making the measurements. Measure gas production using a pressure gauge. Barometric pressure is measured at the time of testing to make necessary volume adjustments.

c. ISO 11734:1995 specifies that total gas is the standard measure of biodegradation. While modifying this test for evaluating biodegradation of NAFs, methane was also monitored and found to be an acceptable method of evaluating biodegradation. Section 7 contains the procedures used to follow biodegradation by methane production. Measurement of either total gas or methane production is permitted. If methane is followed, determine the composition of the gas by using gas chromatography (GC) analysis at each sampling. At the end of the test when gas production stops, or at around 275 days, an analysis of sediment for substrate content is possible. Common methods which have been successfully used for analyzing NAFs from sediments are listed in Section 8.

2.0 SYSTEM REQUIREMENTS

This environmental test system has three phases, spiked sediment, overlying seawater, and a gas headspace. The sediment/test compound mixture is combined with synthetic sea water and transferred into 120-mL serum bottles. The total volume of sediment/sea water mixture in the bottles is 75 mL. The volume of the sediment layer will be approximately 50 mL, but the exact volume of the sediment will depend on sediment characteristics (wet:dry ratio and density). The amount of synthetic sea water will be calculated to bring the total volume in the bottles to 75 mL. The test systems are maintained at a temperature of 29 ±1 °C during incubation. The test systems are brought to ambient temperatures prior to measuring pressure or gas volume.

2.1 SAMPLE REQUIREMENTS

a. The concentration of base fluids are at least 2,000 mg carbon test material/kg dry sediment. Carbon concentration is determined by theoretical composition based on the chemical formula or by chemical analysis by ASTM D5291–96. Sediments with positive, intermediate and negative control substances as well as a C_{16}-C_{18} internal olefin type base fluid will be run in conjunction with test materials under the same conditions. The positive control is ethyl oleate (CAS 111–62–6), the intermediate control is 1-hexadecene (CAS 629–73–2), and the negative control is squalane (CAS 111–01–3). Controls must be of analytical grade or the highest grade available. Each test control concentration should be prepared according to the mixing procedure described in Section 3.1.

b. Product names will be used for examples or clarification in the following text. Any use of trade or product names in this publication is for descriptive use only, and does not constitute endorsement by EPA or the authors.

2.2. SEAWATER REQUIREMENTS

Synthetic seawater at a salinity of 25 ±1 ppt should be used for the test. The synthetic seawater should be prepared by mixing a commercially available artificial seawater mix, into high purity distilled or de-ionized water. The seawater should be aerated and allowed to age for approximately one month prior to use.

2.3. SEDIMENT REQUIREMENTS

a. The dilution sediment must be from a natural estuarine or marine environment and be free of the compounds of interest. The collection location, date and time will be documented and reported. The sediment is prepared by press-sieving through a 2,000-micron mesh sieve to remove large debris, then press-sieving through a 500-micron sieve to

remove indigenous organisms that may confound test results. The water content of the sediment should be less than 60% (w/w) or a wet to dry ratio of 2.5. The sediment should have a minimum organic matter content of 3% (w/w) as determined by ASTM D2974–07a (Method A and D and calculate organic matter as in Section 8.3 of method ASTM D2974–07a).

b. To reduce the osmotic shock to the microorganisms in the sediment the salinity of the sediment's pore water should be between 20–30 ppt. Sediment should be used for testing as soon as possible after field collection. If required, sediment can be stored in the dark at 4 °C with 3–6 inches of overlying water in a sealed container for a maximum period of 2 months prior to use.

3.0 TEST SET UP

The test is set up by first mixing the test or control substrates into the sediment inoculum, then mixing in seawater to make a pourable slurry. The slurry is then poured into serum bottles, which are then flushed with nitrogen and sealed.

3.1. MIXING PROCEDURE

Because base fluids are strongly hydrophobic and do not readily mix with sediments, care must be taken to ensure base fluids are thoroughly homogenized within the sediment. All concentrations are weight-to-weight comparisons (mg of base fluid to kg of dry control sediment). Sediment and base fluid mixing will be accomplished by using the following method.

3.1.1. Determine the wet to dry weight ratio for the control sediment by weighing approximately 10 sub-samples of approximately 1 g each of the screened and homogenized wet sediment into tared aluminum weigh pans. Dry sediment at 105 °C for 18–24 h. Remove the dried sediments and cool in a desiccator. Repeat the drying, cooling, and weighing cycle until a constant weight is achieved (within 4% of previous weight). Reweigh the samples to determine the dry weight. Calculate the mean wet and dry weights of the 10 sub samples and determine the wet/dry ratio by dividing the mean wet weight by the mean dry weight using Equation 5–1. This is required to determine the weight of wet sediment needed to prepare the test samples.

$$\frac{\text{Mean Wet Sediment Weight (g)}}{\text{Mean Dry Sediment Weight (g)}} = \text{Wet to Dry Ratio} \qquad \text{[Eq.1]}$$

3.1.2. Determine the density (g/ml) of the wet sediment. This will be used to determine total volume of wet sediment needed for the various test treatments. One method is to tare a 5 ml graduated cylinder and add about 5 ml of homogenized sediment. Carefully record the volume then weigh this volume of sediment. Repeat this a total of three times. To determine the wet sediment density, divide the weight by volume per the following formula:

$$\frac{\text{Mean Wet Sediment Weight (g)}}{\text{Mean Wet Sediment Volume (mL)}} = \text{Wet Sediment Density (g/mL)} \qquad \text{[Eq. 2]}$$

3.1.3. Determine the amount of base fluid to be spiked into wet sediment in order to obtain the desired initial base fluid concentration of 2,000 mg carbon/kg dry weight. An amount of wet sediment that is the equivalent of 30 g of dry sediment will be added to each bottle. A typical procedure is to prepare enough sediment for 8 serum bottles (3 bottles to be sacrificed at the start of the test, 4 bottles incubated for headspace analysis, and enough extra sediment for 2 extra bottles). Extra sediment is needed because some of the sediment will remain coated onto the mixing bowl and utensils. Experience with this test may indicate that preparing larger volumes of spiked sediment is a useful practice, then the following calculations should be adjusted accordingly.

a. Determine the total weight of dry sediment needed to add 30 g dry sediment to 8 bottles. If more bottles are used then the calculations should be modified accordingly. For example:

$$30 \text{ g dry sediment per bottle} \times 8 = 240 \text{ g dry sediment} \quad \text{[Eq.3]}$$

b. Determine the weight of base fluid, in terms of carbon, needed to obtain a final base fluid concentration of 2,000 mg carbon/kg dry weight. For example:

$$\frac{2{,}000 \text{ mg carbon}}{\text{Per kg dry sediment}} \times \frac{240 \text{ g}}{1{,}000} = 480 \text{ mg carbon} \quad \text{[Eq. 4]}$$

c. i. Convert from mg of carbon to mg of base fluid. This calculation will depend on the % fraction of carbon present in the molecular structure of each base fluid. For the control fluids, ethyl oleate is composed of 77.3% carbon, hexadecene is composed of 85.7% carbon, and squalane is composed of 85.3% carbon. The carbon fraction of each base fluid should be supplied by the manufacturer or determined before use. ASTM D5291–96 or equivalent will be used to determine composition of fluid.

ii. To calculate the amount of base fluid to add to the sediment, divide the amount of carbon (480 mg) by the percent fraction of carbon in the fluid.

iii. For example, the amount of ethyl oleate added to 240 g dry weight sediment can be calculated from the following equation:

$$\frac{480 \text{ mg carbon}}{(77.3 \div 100)} = 621 \text{ mg ethyl oleate} \quad \text{[Eq. 5]}$$

iv. Therefore, add 621 mg of ethyl oleate to 240 g dry weight sediment for a final concentration of 2,000 mg carbon/kg sediment dry weight.

3.1.4. Mix the calculated amount of base fluid with the appropriate weight of wet sediment.

a. Use the wet:dry ratio to convert from g sediment dry weight to g sediment wet weight, as follows:

$$240 \text{ g dry sediment} \times \text{wet:dry ratio} = \text{g wet sediment needed} \quad \text{[Eq. 6]}$$

b. i. Weigh the appropriate amount of base fluid (calculated in Section 3.1.3.c) into stainless mixing bowls, tare the vessel weight, then add the wet sediment calculated in Equation 5, and mix with a high shear dispersing impeller for 9 minutes.

ii. The sediment is now mixed with synthetic sea water to form a slurry that will be transferred into the bottles.

3.2. Creating Seawater/Sediment Slurry

Given that the total volume of sediment/sea water slurry in each bottle is to be 75 mL, determine the volume of sea water to add to the wet sediment.

3.2.1. If each bottle is to contain 30 g dry sediment, calculate the weight, and then the volume, of wet sediment to be added to each bottle.

30 g dry sediment × wet:dry ratio = g wet sediment added to each bottle [Eq. 7]

$$\frac{\text{g wet sediment}}{\text{Density (g/mL) of wet sediment}} = \text{mL wet sediment} \quad \text{[Eq. 8]}$$

3.2.2. Calculate volume of sea water to be added to each bottle.

75 mL total volume – mL wet sediment (from Eq. 8) = mL of sea water [Eq. 9]

3.2.3. Determine the ratio of sea water to wet sediment (volume:volume) in each bottle.

$$\frac{\text{Volume sea water per bottle (Eq. 9)}}{\text{Volume sediment water per bottle (Eq. 8)}} = \text{Ratio of sea water:wet sediment} \quad \text{[Eq. 10]}$$

3.2.4. Convert the wet sediment weight from Equation 6 into a volume using the sediment density.

g wet sediment (Eq. 6) density = volume (mL) of sediment [Eq. 11]

3.2.5. Determine the amount of sea water to mix with the wet sediment.

$$\underset{\text{(Eq. 11)}}{\text{mL wet sediment}} \times \underset{\text{(Eq. 10)}}{\text{Sea water:sediment ratio}} = \text{mL sea water to add to wet sediment} \quad \text{[Eq. 12]}$$

Mix sea water thoroughly with wet sediment to form a sediment/sea water slurry.

3.3. Bottling the Sediment Seawater Slurry

The total volume of sediment/sea water slurry in each bottle is to be 75 mL. Convert the volume (mL) of sediment/sea water slurry into a weight (g) using the density of the sediment and the seawater.

3.3.1. Determine the weight of sediment to be added to each bottle.

mL sediment (Eq. 8) × density of wet sediment (g/mL) = g wet sediment [Eq. 13]

3.3.2. Determine the weight of sea water to be added to each bottle.

mL sea water (Eq. 9) × density of sea water (1.01 g/mL) = g sea water [Eq. 14]

3.3.3. Determine weight of sediment/sea water slurry to be added to each bottle.

g wet sediment (Eq. 13) + g sea water (Eq. 14) = g sediment/sea water slurry [Eq. 15]

This should provide each bottle with 30 g dry sediment in a total volume of 75 mL.

3.3.4. Putting the sediment:seawater slurry in the serum bottles.

a. NOTE: The slurry will need to be constantly stirred to keep the sediment suspended.

b. Place a tared serum bottle on a balance and add the appropriate amount of slurry to the bottle using a funnel. Once the required slurry is in the bottle remove the funnel, add 2–3 drops (25 μL) of a 1 gram/L resazurin dye stock solution. Cap the bottle with a butyl rubber stopper (Bellco Glass, Part #2048–11800) and crimp with an aluminum seal (Bellco Glass Part #2048–11020).

c. Using a plastic tube with a (23-gauge, 1-inch long) needle attached to one side and a nitrogen source to the other, puncture the serum cap with the needle. Puncture the serum cap again with a second needle to sparge the bottle's headspace of residual air for two minutes. The nitrogen should be flowing at no more than 100 mL/min to encourage gentle displacement of oxygenated air with nitrogen. Faster nitrogen flow rates would cause mixing and complete oxygen removal would take much longer. Remove the nitrogen needle first to avoid any initial pressure problems. The second (vent) needle should be removed within 30 seconds of removing the nitrogen needle.

d. Triplicate blank test systems are prepared, with similar quantities of sediment and seawater without any base fluid. Incubate in the dark at a constant temperature of 29 ±1 °C.

e. Record the test temperature. The test duration is dependent on base fluid performance, but at a maximum should be no more than 275 days. Stop the test after all base fluids have achieved a plateau of gas production. At termination, base fluid concentrations can be verified in the terminated samples by extraction and GC analysis according to Section 8.

4.0. CONCENTRATION VERIFICATION CHEMICAL ANALYSES

a. Because of the difficulty of homogeneously mixing base fluid with sediment, it is important to demonstrate that the base fluid is evenly mixed within the sediment sea water slurry that was added to each bottle. Of the seven serum bottles set up for each test or control condition, three are randomly selected for concentration verification analyses. These should be immediately placed at 4 °C and a sample of sediment from each bottle should be analyzed for base fluid content as soon as possible. The coefficient of variation (CV) for the replicate samples must be less than 20%. The results should show recovery of at least 70% of the spiked base fluid. Use an appropriate analytical procedure described in Section 8 to perform the extractions and analyses. If any set of sediments fail the criteria for concentration verification, then the corrective action for that set of sediments is also outlined in Section 8.

b. The nominal concentrations and the measured concentrations from the three bottles selected for concentration verification should be reported for the initial test concentrations. The coefficient of variation (CV) for the replicate samples must be less than 20%. If base fluid content results are not within the 20% CV limit, the test must be stopped and restarted with adequately mixed sediment.

5.0. GAS MONITORING PROCEDURES

Biodegradation is measured by total gas as specified in ISO 11734:1995. Methane production can also be tracked and is described in Section 7.

5.1. TOTAL GAS MONITORING PROCEDURES

Bottles should be brought to room temperature before readings are taken. a. The bottles are observed to confirm that the resazurin has not oxidized to pink or blue. Total gas production in the culture bottles should be measured using a pressure transducer (one source is Biotech International). The pressure readings from test and control cultures are evaluated against a calibration curve created by analyzing the pressure created by known additions of gas to bottles established identically to the culture bottles. Bottles used for the standard curve contain 75 mL of water, and are sealed with the same rubber septa and crimp cap seals used for the bottles containing sediment. After the bottles used in the standard curve have been sealed, a syringe needle inserted through the septa is used to equilibrate the pressure inside the bottles to the outside atmosphere. The syringe needle is removed and known volumes of air are injected into the headspace of the bottles. Pressure readings provide a standard curve relating the volume of gas injected into the bottles and headspace pressure. No less than three points may be used to generate the standard curve. A typical standard curve may use 0, 1, 5, 10, 20 and 40 mL of gas added to the standard curve bottles.

b. The room temperature and barometric pressure (to two digits) should be recorded at the time of sampling. One option for the barometer is Fisher Part #02–400 or 02–401. Gas production by the sediment is expressed in terms of the volume (mL) of gas at standard temperature (0 °C = 273 °K) and pressure (1 atm = 30 inches of Hg) using Eq. 16.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{T_1 \times P_2} \quad [Eq.16]$$

Where:

V_2 = Volume of gas production at standard temperature and pressure

P_1 = Barometric pressure on day of sampling (inches of Hg)

V_1 = Volume of gas measured on day of sampling (mL)

T_2 = Standard temperature = 273 °K

T_1 = Temperature on day of sampling (°C + 273 = °K)

P_2 = Standard pressure = 30 inches Hg

c. An estimate can be made of the total volume of anaerobic gas that will be produced in the bottles. The gas production measured for each base fluid can be expressed as a percent of predicted total anaerobic gas production.

5.1.1. Calculate the total amount of carbon in the form of the base fluid present in each bottle.

a. Each bottle is to contain 30 g dry weight sediment. The base fluid concentration is 2,000 mg carbon/kg dry weight sediment. Therefore:

$$2{,}000 \text{ mg carbon/kg sediment} \times (30 \text{ g} \div 1{,}000) = 60 \text{ mg carbon per bottle} \quad [Eq.\ 17]$$

5.1.2. Theory states that anaerobic microorganisms will convert 1 mole of carbon substrate into 1 mole of total anaerobic gas production.

a. Calculate the number of moles of carbon in each bottle.

b. The molecular weight of carbon is 12 (*i.e.*, 1 mole of carbon = 12 g). Therefore, the number of moles of carbon in each bottle can be calculated.

$$\frac{60 \text{ mg carbon per bottle}/1{,}000}{12 \text{ g/mole}} = 0.005 \text{ moles carbon} \quad [Eq.\ 18]$$

5.1.3. Calculate the predicted volume of anaerobic gas.

One mole of gas equals 22.4 L (at standard temperature and pressure), therefore,

$$0.005 \text{ moles} \times 22.4 \text{ L} = 0.112\text{L (or 112 mL total gas production)} \quad [Eq.\ 19]$$

5.2. GAS VENTING

a. If the pressure in the serum bottle is too great for the pressure transducer or syringe, some of the excess gas must be wasted. The best method to do this is to vent the excess gas right after measurement. To do this, remove the barrel from a 10-mL syringe and fill it ⅓ full with water. This is then inserted into the bottle through the stopper using a small diameter (high gauge) needle. The excess pressure is allowed to vent through the water until the bubbles stop. This allows equalization of the pressure inside the bottle to atmospheric without introducing oxygen. The amount of gas vented (which is equal to the volume determined that day) must be kept track of each time the bottles are vented. A simple way to do this in a spreadsheet format is to have a separate column in which cumulative vented gas is tabulated. Each time the volume of gas in the cultures is analyzed, the total gas produced is equal to the gas in the culture at that time plus the total of the vented gas.

b. To keep track of the methane lost in the venting procedure, multiply the amount of gas vented each time by the corrected % methane determined on that day. The answer gives the volume of methane wasted. This must be added into the cumulative totals similarly to the total gas additions.

6.0. TEST ACCEPTABILITY AND INTERPRETATION

6.1. TEST ACCEPTABILITY

At day 275 or when gas production has plateaued, whichever is first, the controls are evaluated to confirm that the test has been performed appropriately. In order for

this modification of the closed bottle biodegradation test to be considered acceptable, all the controls must meet the biodegradation levels indicated in Table 1. The intermediate control hexadecene must produce at least 30% of the theoretical gas production. This level may be reexamined after two years and more data has been generated.

TABLE 1—TEST ACCEPTABILITY CRITERIA

Concentration	Percent biodegradability as a function of gas measurement		
	Positive control	Squalane negative control	Hexadecene intermediate control
2,000 mg carbon/kg	≥60% theoretical	≤5% theoretical	≥30% theoretical.

6.2 INTERPRETATION

a. In order for a fluid to pass the closed bottle test, the biodegradation of the base fluid as indicated by the total amount of total gas (or methane) generated once gas production has plateaued (or at the end of 275 days, which ever is first) must be greater than or equal to the volume of gas (or methane) produced by the reference standard (internal elefin or ester).

b. The method for evaluating the data to determine whether a fluid has passed the biodegradation test must use the equations:

$$\frac{\%\ \text{Theoretical gas production of reference fluid}}{\%\ \text{Theoretical gas production of NAF}} \leq 1.0 \qquad \text{[Eq. 20]}$$

Where:

NAF = Stock base fluid being tested for compliance

Reference fluid = C_{16}-C_{18} internal olefin or C_{12} –C_{14} or C_8 ester reference fluid

7.0. METHANE MEASUREMENT

7.1. METHANE MONITORING PROCEDURES

a. The use of total gas production alone may result in an underestimation of the actual metabolism occurring since CO_2 is slightly soluble in water. An acceptable alternative method is to monitor methane production and total gas production. This is easily done using GC analysis. A direct injection of headspace gases can be made into a GC using almost any packed or capillary column with an FID detector. Unless volatile fuels or solvents are present in the test material or the inocula, the only component of the headspace gas that can be detected using an FID detector is methane. The percent methane in the headspace gas is determined by comparing the response of the sample injections to the response from injections of known percent methane standards. The percent methane is corrected for water vapor saturation using Eq. 21 and then converted to a volume of dry methane using Eq. 22.

$$\text{Corrected \% } CH_4 = \frac{\%\ CH_4}{1 - \dfrac{D \times 22.4\ \text{L/mol}}{18\ \text{g/mol} \times 1{,}000}} \qquad \text{[Eq. 21]}$$

Where:

D = The density of water vapor at saturation (g/m^3, can be found in CRC Handbook of Chemistry and Physics) for the temperature of sampling.

$$V_{CH4}\ (\text{ml}) = (S + V) \times \frac{P - P_W}{T + 273} \times \frac{CH_4}{100} \times \frac{273}{760} \qquad \text{[Eq. 22]}$$

Where:

V_{CH4} = Volume of methane in the bottle

S = Volume of excess gas production (measured with a pressure transducer)
V = Volume of the headspace in the culture bottle (total volume—liquid phase)
P = Barometric pressure (mm Hg, measured with barometer)
T = Temperature (°C)
P_w = Vapor pressure of water at T (mm Hg, can be found in CRC Handbook of Chemistry and Physics)
CH_4 = % methane in headspace gas (after correction for water vapor)

b. The total volume of serum bottles sold as 125 mL bottles (Wheaton) is 154.8 mL.

c. The volumes of methane produced are then compared to the volumes of methane in the controls to determine if a significant inhibition of methane production or a significant increase of methane production has been observed. Effective statistical analyses are important, as variability in the results is common due to the heterogeneity of the inoculum's source. It is also common to observe that the timing of the initiation of culture activity is not equal in all of the cultures. Expect a great variability over the period when the cultures are active, some replicates will start sooner than others, but all of the replicates should eventually reach similar levels of base fluid degradation and methane production.

7.2. Expected Methane Production Calculations

a. The amount of methane expected can be calculated using the equation of Symons and Buswell (Eq. 23). In the case of complete mineralization, all of the carbon will appear as wither CO_2 or CH_4, thus the total moles of gas produced will be equal to the total moles of carbon in the parent molecule. The use of the Buswell equation allows you to calculate the effects the redox potential will have on the distribution of the products in methanogenic cultures. More reduced electron donors will allow the production of more methane, while more oxidized electron donors will cause a production of more carbon dioxide.

$$\frac{12 \text{ mole } CH_4}{\text{mole hexadecene}} \times \frac{22.4 \text{ L}}{\text{mole } CH_4} \times \frac{1{,}000 \text{ ml}}{\text{L}} \times \frac{1 \text{ mole hexadecene}}{224.4 \text{ g hexadecene}} \times \frac{23 \text{ g hexadecene}}{\text{kg dry soil}} \times \frac{0.03 \text{ kg}}{\text{culture}} = 84 \text{ (ml)} \quad \text{[Eq. 24]}$$

b. An example calculation of the expected methane volume in a culture fed 2,000 mg/kg hexadecene is as follows. The application of Symons and Buswell's equation reveals that hexadecene ($C_{16}H_{32}$) will yield 4 moles of CO_2 and 12 moles of CH_4. Assuming 30 g of dry sediment are added to the bottles with 2,334 mg hexadecene/kg dry sediment (*i.e.*, equivalent to 2,000 mg carbon/kg dry sediment) the calculation is as follows.

$$\frac{12 \text{ mole } CH_4}{\text{mole hexadecene}} \times \frac{22.4 \text{ L}}{\text{mole } CH_4} \times \frac{1{,}000 \text{ ml}}{\text{L}} \times \frac{1 \text{ mole hexadecene}}{224.4 \text{ g hexadecene}} \times \frac{23 \text{ g hexadecene}}{\text{kg dry soil}} \times \frac{0.03 \text{ kg}}{\text{culture}} = 84 \text{ (ml)} \quad \text{[Eq. 24]}$$

c. By subtracting the average amount of methane in control bottles from the test bottles and then dividing by the expected volume an evaluation of the completion of the process may be conducted.

8.0. Concentration Verification Analysis

The Concentration Verification analysis is required at the beginning of the test to ensure homogeneity and confirm that the required amount of fluid was delivered to the sediments at the start of the test.

8.1. Three samples per fluid need to be analyzed and achieve ≤20% Coefficient of Variability and an average of ≥70% to ≤120% of fluid delivered to sediment.

8.2. If a third party performs the analysis, then the laboratory should be capable of delivering the homogeneity data within seven days, in order to identify any samples that do not meet the homogeneity requirement as quickly as possible.

8.3. If one sediment/fluid set, out a multiple set batch of samples, fails these criteria, then that one set of samples must be discarded and a fresh set of spiked sediment prepared, started, and analyzed to ensure homogeneity. The same stock sediment is used to prepare the replacement set(s). The remaining sets do not need to be re-mixed or restarted.

8.4. The re-mixed set(s) will need to be run the additional days as appropriate to ensure that the total number of days is the same for all sets of bottles, even though the specific days are not aligned.

8.5. Re-mixing of bottle sets can be performed multiple times as a result of a failure of the analytical criteria, until the holding time for the stock sediment has expired (60 days). If the problem set(s) has not fallen within the acceptable analytical criteria by then, it must not be part of the batch of bottles run. If the problem batch is one of the controls, and those controls were not successfully prepared when the sediment holding time expired, then the entire test must be restarted.

9.0 Program Quality Assurance and Quality Control

9.1 Calibration

9.1.1. All equipment/instrumentation will be calibrated in accordance with the test method or the manufacturer's instructions and may be scheduled or triggered.

9.1.2. Where possible, standards used in calibration will be traceable to a nationally recognized standard (e.g., certified standard by NIST).

9.1.3. All calibration activities will be documented and the records retained.

9.1.4. The source, lot, batch number, and expiration date of all reagents used with be documented and retained.

9.2. Maintenance

9.2.1. All equipment/instrumentation will be maintained in accordance with the test method or the manufacturer's instructions and may be scheduled or triggered.

9.2.2. All maintenance activities will be documented and the records retained.

9.3. Data Management and Handling

9.3.1. All primary (raw) data will be correct, complete, without selective reporting, and will be maintained.

9.3.2. Hand-written data will be recorded in lab notebooks or electronically at the time of observation.

9.3.3. All hand-written records will be legible and amenable to reproduction by electrostatic copiers.

9.3.4. All changes to data or other records will be made by:

a. Using a single line to mark-through the erroneous entry (maintaining original data legibility).

b. Write the revision.

c. Initial, date, and provide revision code (*see* attached or laboratory's equivalent).

9.3.5. All data entry, transcriptions, and calculations will be verified by a qualified person.

a. Verification will be documented by initials of verifier and date.

9.3.6. Procedures will be in place to address data management procedures used (at minimum):

a. Significant figures.

b. Rounding practices.

c. Identification of outliers in data series.

d. Required statistics.

9.4. Document Control

9.4.1. All technical procedures, methods, work instructions, standard operating procedures must be documented and approved by laboratory management prior to the implementation.

9.4.2. All primary data will be maintained by the contractor for a minimum of five (5) years.

9.5. Personnel and Training

9.5.1. Only qualified personnel shall perform laboratory activities.

9.5.2. Records of staff training and experience will be available. This will include initial and refresher training (as appropriate).

9.6. Test Performance

9.6.1. All testing will done in accordance with the specified test methods.

9.6.2. Receipt, arrival condition, storage conditions, dispersal, and accountability of the test article will be documented and maintained.

9.6.3. Receipt or production, arrival or initial condition, storage conditions, dispersal, and accountability of the test matrix (e.g., sediment or artificial seawater) will be documented and maintained.

9.6.4. Source, receipt, arrival condition, storage conditions, dispersal, and accountability of the test organisms (including inoculum) will be documented and maintained.

9.6.5. Actual concentrations administered at each treatment level will be verified by appropriate methodologies.

9.6.6. Any data originating at a different laboratory will be identified and the laboratory fully referenced in the final report.

9.7. The following references identify analytical methods that have historically been successful for achieving the analytical quality criteria.

9.7.1. Continental Shelf Associates Report 1998. Joint EPA/Industry Screening Survey to Assess the Deposition of Drill Cuttings and Associated Synthetic Based Mud on the Seabed of the Louisiana Continental Shelf, Gulf of Mexico. Analysis by Charlie Henry Report Number IES/RCAT97–36 GC–FID and GC/MS.

9.7.2. EPA Method 3550 for extraction with EPA Method 8015 for GC–FID. EPA Method 3550C, Revision 3. February 2007. Ultrasonic Extraction. EPA Method 8015C, Revision 3. February 2007. Nonhalogenated Organics by Gas Chromatography.

9.7.3. Chandler, J.E., S.P. Rabke, and A.J.J. Leuterman. 1999. Predicting the Potential Impact of Synthetic-Based Muds With the

Use of Biodegradation Studies. Society of Petroleum Engineers SPE 52742.

9.7.4. Chandler, J.E., B. Lee, S.P. Rabke, J.M. Geliff, R. Stauffer, and J. Hein. 2000. Modification of a Standardized Anaerobic Biodegradation Test to Discriminate Performance of Various Non-Aqueous Base Fluids. Society of Petroleum Engineers SPE 61203.

9.7.5. Munro, P.D., B Croce, C.F. Moffet, N.A Brown, A.D. McIntosh, S.J. Hird, and R.M. Stagg. 1998. Solid-Phase Test for Comparison for Degradation Rates of Synthetic Mud Base Fluids Used in the Off-shore Drilling Industry. *Environ. Toxicol. Chem.* 17:1951–1959.

9.7.6. Webster, L., P.R. Mackie, S.J. Hird, P.D. Munro, N.A. Brown, and C.F. Moffat. 1997. Development of Analytical Methods for the Determination of Synthetic Mud Base Fluids in Marine Sediments. *The Analyst* 122:1485–1490.

9.8 The following standards are approved for incorporation by reference by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460 and at at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*.

9.8.1 ASTM International. Available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428–2959, or online at *http://www.astm.org*.

9.8.1.1 ASTM D5291–96, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, approved April 10, 1996.

9.8.1.2 ASTM D2974–07a, Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, approved March 15, 2007.

[77 FR 29837, May 18, 2012]

APPENDIX 5 TO SUBPART A OF PART 435—DETERMINATION OF CRUDE OIL CONTAMINATION IN NON-AQUEOUS DRILLING FLUIDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) (EPA METHOD 1655)

1.0 SCOPE AND APPLICATION

1.1 This method determines crude (formation) oil contamination, or other petroleum oil contamination, in non-aqueous drilling fluids (NAFs) by comparing the gas chromatography/mass spectrometry (GC/MS) fingerprint scan and extracted ion scans of the test sample to that of an uncontaminated sample.

1.2 This method can be used for monitoring oil contamination of NAFs or monitoring oil contamination of the base fluid used in the NAF formulations.

1.3 Any modification of this method beyond those expressly permitted shall be considered as a major modification subject to application and approval of alternative test procedures under 40 CFR 136.4 and 136.5.

1.4 The gas chromatography/mass spectrometry portions of this method are restricted to use by, or under the supervision of analysts experienced in the use of GC/MS and in the interpretation of gas chromatograms and extracted ion scans. Each laboratory that uses this method must generate acceptable results using the procedures described in Sections 7, 9.2, and 12 of this appendix.

2.0 SUMMARY OF METHOD

2.1 Analysis of NAF for crude oil contamination is a step-wise process. The analyst first performs a qualitative assessment of the presence or absence of crude oil in the sample. If crude oil is detected during this qualitative assessment, the analyst must perform a quantitative analysis of the crude oil concentration.

2.2 A sample of NAF is centrifuged to obtain a solids free supernate.

2.3 The test sample is prepared by removing an aliquot of the solids free supernate, spiking it with internal standard, and analyzing it using GC/MS techniques. The components are separated by the gas chromatograph and detected by the mass spectrometer.

2.4 Qualitative identification of crude oil contamination is performed by comparing the Total Ion Chromatograph (TIC) scans and Extracted Ion Profile (EIP) scans of test sample to that of uncontaminated base fluids, and examining the profiles for chromatographic signatures diagnostic of oil contamination.

2.5 The presence or absence of crude oil contamination observed in the full scan profiles and selected extracted ion profiles determines further sample quantitation and reporting requirements.

2.6 If crude oil is detected in the qualitative analysis, quantitative analysis must be performed by calibrating the GC/MS using a designated NAF spiked with known concentrations of a designated oil.

2.7 Quality is assured through reproducible calibration and testing of GC/MS system and through analysis of quality control samples.

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).

3.2 TIC—Total Ion Chromatograph.

3.3 EIP—Extracted Ion Profile.

3.4 TCB—1,3,5-trichlorobenzene is used as the internal standard in this method.

3.5 SPTM—System Performance Test Mix standards are used to establish retention times and monitor detection levels.

4.0 Interferences and Limitations

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms.

4.2 All Materials used in the analysis shall be demonstrated to be free from interferences by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

4.3 Glassware shall be cleaned by rinsing with solvent and baking at 400 °C for a minimum of 1 hour.

4.4 Interferences may vary from source to source, depending on the diversity of the samples being tested.

4.5 Variations in and additions of base fluids and/or drilling fluid additives (emulsifiers, dispersants, fluid loss control agents, etc.) might also cause interferences and misinterpretation of chromatograms.

4.6 Difference in light crude oils, medium crude oils, and heavy crude oils will result in different responses and thus different interpretation of scans and calculated percentages.

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.

5.2 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 fume hood to limit the potential exposure to harmful contaminates.

5.3 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 references to laboratory safety can be found in References 16.1 through 16.3.

5.4 NAF base fluids may cause skin irritation, protective gloves are recommended while handling these samples.

6.0 Apparatus and Materials

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 meeting the requirements of this method is the responsibility of the laboratory.

6.1 Equipment for glassware cleaning.

6.1.1 Laboratory sink with overhead fume hood.

6.1.2 Kiln—Capable of reaching 450 °C within 2 hours and holding 450 °C within ±10 °C, with temperature controller and safety switch (Cress Manufacturing Co., Santa Fe Springs, CA B31H or X31TS or equivalent).

6.2 Equipment for sample preparation.

6.2.1 Laboratory fume hood.

6.2.2 Analytical balance—Capable of weighing 0.1 mg.

6.2.3 Glassware.

6.2.3.1 Disposable pipettes—Pasteur, 150 mm long by 5 mm ID (Fisher Scientific 13–678–6A, or equivalent) baked at 400 °C for a minimum of 1 hour.

6.2.3.2 Glass volumetric pipettes or gas tight syringes—1.0-mL ±1% and 0.5-mL ±1%.

6.2.3.3 Volumetric flasks—Glass, class A, 10-mL, 50-mL and 100-mL.

6.2.3.4—Sample vials—Glass, 1- to 3-mL (baked at 400 °C for a minimum of 1 hour) with PTFE-lined screw or crimp cap.

6.2.3.5 Centrifuge and centrifuge tubes—Centrifuge capable of 10,000 rpm, or better, (International Equipment Co., IEC Centra MP4 or equivalent) and 50-mL centrifuge tubes (Nalgene, Ultratube, Thin Wall 25 × 89 mm, #3410–2539).

6.3 Gas Chromatograph/Mass Spectrometer (GC/MS):

6.3.1 Gas Chromatograph—An analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, analytical columns, and gases.

6.3.1.1 Column—30 m (or 60 m) × 0.32 mm ID (or 0.25 mm ID) 1 µm film thickness (or 0.25 µm film thickness) silicone-coated fused-silica capillary column (J&W Scientific DB–5 or equivalent).

6.3.2 Mass Spectrometer—Capable of scanning from 35 to 600 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode (Hewlett Packard 5970MS or comparable).

6.3.3 GC/MS interface—the interface is a capillary-direct interface from the GC to the MS.

6.3.4—Data system—A computer system must be interfaced to the mass spectrometer.

The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundance versus retention time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EIP). Software must also be available that allows integrating the abundance in any total ion chromatogram (TIC) or EIP between specified retention time or scan-number limits. It is advisable that the most recent version of the EPA/NIST Mass Spectral Library be available.

7.0 REAGENTS AND STANDARDS

7.1 Methylene chloride—Pesticide grade or equivalent. Use when necessary for sample dilution.

7.2 Standards—Prepare from pure individual standard materials or purchase as certified solutions. If compound purity is 96% or greater, the weight may be used without correction to compute the concentration of the standard.

7.2.1 Crude Oil Reference—Obtain a sample of a crude oil with a known API gravity. This oil shall be used in the calibration procedures.

7.2.2 Synthetic Base Fluid—Obtain a sample of clean internal olefin (IO) Lab drilling fluid (as sent from the supplier—has not been circulated downhole). This drilling fluid shall be used in the calibration procedures.

7.2.3 Internal standard—Prepare a 0.01 g/mL solution of 1,3,5-trichlorobenzene (TCB). Dissolve 1.0 g of TCB in methylene chloride and dilute to volume in a 100-mL volumetric flask. Stopper, vortex, and transfer the solution to a 150-mL bottle with PTFE-lined cap. Label appropriately, and store at −5 °C to 20 °C. Mark the level of the meniscus on the bottle to detect solvent loss.

7.2.4 GC/MS system performance test mix (SPTM) standards—The SPTM standards shall contain octane, decane, dodecane, tetradecane, tetradecene, toluene, ethylbenzene, 1,2,4-trimethylbenzene, 1-methylnaphthalene and 1,3-dimethylnaphthalene. These compounds can be purchased individually or obtained as a mixture (*i.e.*, Supelco, Catalog No. 4–7300). Prepare a high concentration of the SPTM standard at 62.5 mg/mL in methylene chloride. Prepare a medium concentration SPTM standard at 1.25 mg/mL by transferring 1.0 mL of the 62.5 mg/mL solution into a 50 mL volumetric flask and diluting to the mark with methylene chloride. Finally, prepare a low concentration SPTM standard at 0.125 mg/mL by transferring 1.0 mL of the 1.25 mg/mL solution into a 10-mL volumetric flask and diluting to the mark with methylene chloride.

7.2.5 Crude oil/drilling fluid calibration standards—Prepare a 4-point crude oil/drilling fluid calibration at concentrations of 0% (no spike—clean drilling fluid), 0.5%, 1.0%, and 2.0% by weight according to the procedures outlined in this appendix using the Reference Crude Oil:

7.2.5.1 Label 4 jars with the following identification: Jar 1—0%Ref-IOLab, Jar 2—0.5%Ref-IOLab, Jar 3—1%Ref-IOLab, and Jar 4—2%Ref-IOLab.

7.2.5.2 Weigh 4, 50-g aliquots of well mixed IO Lab drilling fluid into each of the 4 jars.

7.2.5.3 Add Reference Oil at 0.5%, 1.0%, and 2.0% by weight to jars 2, 3, and 4 respectively. Jar 1 shall not be spiked with Reference Oil in order to retain a ''0%'' oil concentration.

7.2.5.4 Thoroughly mix the contents of each of the 4 jars, using clean glass stirring rods.

7.2.5.5 Transfer (weigh) a 30-g aliquot from Jar 1 to a labeled centrifuge tube. Centrifuge the aliquot for a minimum of 15 min at approximately 15,000 rpm, in order to obtain a solids free supernate. Weigh 0.5 g of the supernate directly into a tared and appropriately labeled GC straight vial. Spike the 0.5-g supernate with 500 µL of the 0.01g/mL 1,3,5-trichlorobenzene internal standard solution (*see* Section 7.2.3 of this appendix), cap with a Teflon lined crimp cap, and vortex for ca. 10 sec.

7.2.5.6 Repeat step 7.2.5.5 except use an aliquot from Jar 2.

7.2.5.7 Repeat step 7.2.5.5 except use an aliquot from Jar 3.

7.2.5.8 Repeat step 7.2.5.5 except use an aliquot from Jar 4.

7.2.5.9 These 4 crude/oil drilling fluid calibration standards are now used for qualitative and quantitative GC/MS analysis.

7.2.6 Precision and recovery standard (mid level crude oil/drilling fluid calibration standard)—Prepare a mid point crude oil/drilling fluid calibration using IO Lab drilling fluid and Reference Oil at a concentration of 1.0% by weight. Prepare this standard according to the procedures outlined in Section 7.2.5.1 through 7.2.5.5 of this appendix, with the exception that only ''Jar 3'' needs to be prepared. Remove and spike with internal standard, as many 0.5-g aliquots as needed to complete the GC/MS analysis (*see* Section 11.6 of this appendix—bracketing authentic samples every 12 hours with precision and recovery standard) and the initial demonstration exercise described in Section 9.2 of this appendix.

7.2.7 Stability of standards

7.2.7.1 When not used, standards shall be stored in the dark, at −5 to −20 °C in screw-capped vials with PTFE-lined lids. Place a mark on the vial at the level of the solution so that solvent loss by evaporation can be detected. Bring the vial to room temperature prior to use.

7.2.7.2 Solutions used for quantitative purposes shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. A standard shall remain acceptable if the peak area remains within ±15% of the area obtained in the initial analysis of the standard.

8.0 Sample Collection Preservation and Storage

8.1 Collect NAF and base fluid samples in 100- to 200-mL glass bottles with PTFE- or aluminum foil lined caps.

8.2 Samples collected in the field shall be stored refrigerated until time of preparation.

8.3 Sample and extract holding times for this method have not yet been established. However, based on initial experience with the method, samples should be analyzed within seven to ten days of collection and extracts should be analyzed within seven days of preparation.

8.4 After completion of GC/MS analysis, extracts shall be refrigerated at 4 °C until further notification of sample disposal.

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.4). The minimum requirements of this program shall consist of an initial demonstration of laboratory capability, and ongoing analysis of standards, and blanks as a test of continued performance, analyses of spiked samples to assess accuracy and analysis of duplicates to assess precision. Laboratory performance shall be compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

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

9.1.2 The analyst is permitted to modify this method to improve separations or lower the cost of measurements, provided all performance requirements are met. Each time a modification is made to the method, the analyst is required to repeat the calibration (Section 10.4 of this appendix) and to repeat the initial demonstration procedure described in Section 9.2 of this appendix.

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in Section 9.3 of this appendix.

9.1.4 Analysis of a matrix spike sample is required to demonstrate method accuracy. The procedure and QC criteria for spiking are described in Section 9.4 of this appendix.

9.1.5 Analysis of a duplicate field sample is required to demonstrate method precision. The procedure and QC criteria for duplicates are described in Section 9.5 of this appendix.

9.1.6 Analysis of a sample of the clean NAF(s) (as sent from the supplier—*i.e.*, has not been circulated downhole) used in the drilling operations is required.

9.1.7 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (Section 7.2.6 of this appendix) that the analysis system is in control. These procedures are described in Section 11.6 of this appendix.

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

9.2 Initial precision and accuracy—The initial precision and recovery test shall be performed using the precision and recovery standard (1% by weight Reference Oil in IO Lab drilling fluid). The laboratory shall generate acceptable precision and recovery by performing the following operations.

9.2.1 Prepare four separate aliquots of the precision and recovery standard using the procedure outlined in Section 7.2.6 of this appendix. Analyze these aliquots using the procedures outlined in Section 11 of this appendix.

9.2.2 Using the results of the set of four analyses, compute the average recovery (X) in weight percent and the standard deviation of the recovery(s) for each sample.

9.2.3 If s and X meet the acceptance criteria of 80% to 110%, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for accuracy, system performance is unacceptable. In this event, review this method, correct the problem, and repeat the test.

9.2.4 Accuracy and precision—The average percent recovery (P) and the standard deviation of the percent recovery (Sp) Express the accuracy assessment as a percent recovery interval from $P–2S_p$ to $P + 2S_p$. For example, if P = 90% and S_p = 10% for four analyses of crude oil in NAF, the accuracy interval is expressed as 70% to 110%. Update the accuracy assessment on a regular basis.

9.3 Blanks—Rinse glassware and centrifuge tubes used in the method with 30 mL of methylene chloride, remove a 0.5-g aliquot of the solvent, spike it with the 500 µL of the internal standard solution (Section 7.2.3 of this appendix) and analyze a 1-µL aliquot of the blank sample using the procedure in Section 11 of this appendix. Compute results per Section 12 of this appendix.

9.4 Matrix spike sample—Prepare a matrix spike sample according to procedure outlined in Section 7.2.6 of this appendix. Analyze the sample and calculate the concentration (% oil) in the drilling fluid and % recovery of oil from the spiked drilling fluid using the methods described in Sections 11 and 12 of this appendix.

9.5 Duplicates—A duplicate field sample shall be prepared and analyzed according to Section 11. The relative percent difference (RPD) of the calculated concentrations shall be less than 15%.

9.5.1 Analyze each of the duplicates per the procedure in Section 11 of this appendix and compute the results per Section 12 of this appendix.

9.5.2 Calculate the relative percent difference (RPD) between the two results per the following equation:

$$RPD = \frac{|D_1 - D_2|}{[(D_1 + D_2)/2]} \times 100$$

where:

D_1 = Concentration of crude oil in the sample; and

D_2 = Concentration of crude oil in the duplicate sample.

9.5.3 If the RPD criteria are not met, the analytical system shall be judged to be out of control, and the problem must be immediately identified and corrected, and the sample batch re-analyzed.

9.6 A clean NAF sample shall be prepared and analyzed according to Section 11. Ultimately the oil-equivalent concentration from the TIC or EIP signal measured in the clean NAF sample shall be subtracted from the corresponding authentic field samples in order to calculate the true contaminant concentration (% oil) in the field samples (*see* Section 12).

9.7 The specifications contained in this method can be met if the apparatus used is calibrated properly, and maintained in a calibrated state. The standards used for initial precision and recovery (Section 9.2 of this appendix) and ongoing precision and recovery (Section 11.6 of this appendix) shall be identical, so that the most precise results will be obtained. The GC/MS instrument will provide the most reproducible results if dedicated to the setting and conditions required for the analyses given in this method.

9.8 Depending on specific program requirements, field replicates and field spikes of crude oil into samples may be required when this method is used to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration

10.1 Establish gas chromatographic/mass spectrometer operating conditions given in Table 1 of this appendix. Perform the GC/MS system hardware-tune as outlined by the manufacture. The gas chromatograph shall be calibrated using the internal standard technique.

NOTE: Because each GC is slightly different, it may be necessary to adjust the operating conditions (carrier gas flow rate and column temperature and temperature program) slightly until the retention times in Table 2 of this appendix are met.

TABLE 1—GAS CHROMATOGRAPH/MASS SPECTROMETER (GC/MS) OPERATION CONDITIONS

Parameter	Setting
Injection pot	280 °C
Transfer line	280 °C
Detector	280 °C
Initial Temperature	50 °C
Initial Time	5 minutes
Ramp	50 to 300 °C @ 5 °C per minute
Final Temperature	300 °C
Final Hold	20 minutes or until all peaks have eluted
Carrier Gas	Helium
Flow rate	As required for standard operation
Split ratio	As required to meet performance criteria (~1:100)
Mass range	35 to 600 amu

TABLE 2—APPROXIMATE RETENTION TIME FOR COMPOUNDS

Compound	Approximate retention time (minutes)
Toluene	5.6
Octane, n−C_8	7.2
Ethylbenzene	10.3
1,2,4-Trimethylbenzene	16.0
Decane, −C_{10}	16.1
TCB (Internal Standard)	21.3
Dodecane, −C_{12}	22.9
1-Methylnaphthalene	26.7
1-Tetradecene	28.4
Tetradecane, −C_{14}	28.7
1,3-Dimethylnaphthalene	29.7

10.2 Internal standard calibration procedure—1,3,5-trichlorobenzene (TCB) has been shown to be free of interferences from diesel and crude oils and is a suitable internal standard.

10.3 The system performance test mix standards prepared in Section 7.2.4 of this appendix shall be used to establish retention times and establish qualitative detection limits.

10.3.1 Spike a 500-mL aliquot of the 1.25 mg/mL SPTM standard with 500 µL of the TCB internal standard solution.

10.3.2 Inject 1.0 µL of this spiked SPTM standard onto the GC/MS in order to demonstrate proper retention times. For the GC/MS used in the development of this method, the ten compounds in the mixture had typical retention times shown in Table 2 of this appendix. Extracted ion scans for m/z 91 and 105 showed a maximum abundance of 400,000.

10.3.3 Spike a 500-mL aliquot of the 0.125 mg/mL SPTM standard with 500 µL of the TCB internal standard solution.

10.3.4 Inject 1.0 μL of this spiked SPTM standard onto the GC/MS to monitor detectable levels. For the GC/MS used in the development of this test, all ten compounds showed a minimum peak height of three times signal to noise. Extracted ion scans for m/z 91 and 105 showed a maximum abundance of 40,000.

10.4 GC/MS crude oil/drilling fluid calibration—There are two methods of quantification: Total Area Integration (C_8–C_{13}) and EIP Area Integration using m/z's 91 and 105. The Total Area Integration method should be used as the primary technique for quantifying crude oil in NAFs. The EIP Area Integration method should be used as a confirmatory technique for NAFs. However, the EIP Area Integration method shall be used as the primary method for quantifying oil in enhanced mineral oil (EMO) based drilling fluid. Inject 1.0 μL of each of the four crude oil/drilling fluid calibration standards prepared in Section 7.2.5 of this appendix into the GC/MS. The internal standard should elute approximately 21–22 minutes after injection. For the GC/MS used in the development of this method, the internal standard peak was (35 to 40)% of full scale at an abundance of about 3.5e + 07.

10.4.1 Total Area Integration Method—For each of the four calibration standards obtain the following: Using a straight baseline integration technique, obtain the total ion chromatogram (TIC) area from C_8 to C_{13}. Obtain the TIC area of the internal standard (TCB). Subtract the TCB area from the C_8–C_{13} area to obtain the true C_8–C_{13} area. Using the C_8–C_{13} and TCB areas, and known internal standard concentration, generate a linear regression calibration using the internal standard method. The r^2 value for the linear regression curve shall be greater than or equal to 0.998. Some synthetic fluids might have peaks that elute in the window and would interfere with the analysis. In this case the integration window can be shifted to other areas of scan where there are no interfering peaks from the synthetic base fluid.

10.4.2 EIP Area Integration—For each of the four calibration standards generate Extracted Ion Profiles (EIPs) for m/z 91 and 105. Using straight baseline integration techniques, obtain the following EIP areas:

10.4.2.1 For m/z 91 integrate the area under the curve from approximately 9 minutes to 21–22 minutes, just prior to but not including the internal standard.

10.4.2.2 For m/z 105 integrate the area under the curve from approximately 10.5 minutes to 26.5 minutes.

10.4.2.3 Obtain the internal standard area from the TCB in each of the four calibration standards, using m/z 180.

10.4.2.4 Using the EIP areas for TCB, m/z 91 and m/z105, and the known concentration of internal standard, generate linear regression calibration curves for the target ions 91 and 105 using the internal standard method. The r^2 value for each of the EIP linear regression curves shall be greater than or equal to 0.998.

10.4.2.5 Some base fluids might produce a background level that would show up on the extracted ion profiles, but there should not be any real peaks (signal to noise ratio of 1:3) from the clean base fluids.

11.0 Procedure

11.1 Sample Preparation—

11.1.1 Mix the authentic field sample (drilling fluid) well. Transfer (weigh) a 30-g aliquot of the sample to a labeled centrifuge tube.

11.1.2 Centrifuge the aliquot for a minimum of 15 min at approximately 15,000 rpm, in order to obtain a solids free supernate.

11.1.3 Weigh 0.5 g of the supernate directly into a tared and appropriately labeled GC straight vial.

11.1.4 Spike the 0.5-g supernate with 500 μL of the 0.01g/mL 1,3,5-trichlorobenzene internal standard solution (*see* Section 7.2.3 of this appendix), cap with a Teflon lined crimp cap, and vortex for ca. 10 sec.

11.1.5 The sample is ready for GC/MS analysis.

11.2 Gas Chromatography.

Table 1 of this appendix summarizes the recommended operating conditions for the GC/MS. Retention times for the n-alkanes obtained under these conditions are given in Table 2 of this appendix. Other columns, chromatographic conditions, or detectors may be used if initial precision and accuracy requirements (Section 9.2 of this appendix) are met. The system shall be calibrated according to the procedures outlined in Section 10 of this appendix, and verified every 12 hours according to Section 11.6 of this appendix.

11.2.1 Samples shall be prepared (extracted) in a batch of no more than 20 samples. The batch shall consist of 20 authentic samples, 1 blank (Section 9.3 of this appendix), 1 matrix spike sample (9.4), and 1 duplicate field sample (9.5), and a prepared sample of the corresponding clean NAF used in the drilling process.

11.2.2 An analytical sequence shall be analyzed on the GC/MS where the 3 SPTM standards (Section 7.2.4 of this appendix) containing internal standard are analyzed first, followed by analysis of the four GC/MS crude oil/drilling fluid calibration standards (Section 7.2.5 of this appendix), analysis of the blank, matrix spike sample, the duplicate sample, the clean NAF sample, followed by the authentic samples.

11.2.3 Samples requiring dilution due to excessive signal shall be diluted using methylene chloride.

11.2.4 Inject 1.0 μL of the test sample or standard into the GC, using the conditions in Table 1 of this appendix.

11.2.5 Begin data collection and the temperature program at the time of injection.

11.2.6 Obtain a TIC and EIP fingerprint scans of the sample (Table 3 of this appendix).

11.2.7 If the area of the C_8 to C_{13} peaks exceeds the calibration range of the system, dilute a fresh aliquot of the test sample weighing 0.50-g and re-analyze.

11.2.8 Determine the C_8 to C_{13} TIC area, the TCB internal standard area, and the areas for the m/z 91 and 105 EIPs. These shall be used in the calculation of oil concentration in the samples (see Section 12 of this appendix).

TABLE 3—RECOMMENDED ION MASS NUMBERS

Selected ion mass numbers	Corresponding aromatic compounds	Typical rentention time (minutes)
91	Methylbenzene	6.0
	Ethylbenzene	10.3
	1,4-Dimethylbenzene	10.9
	1,3-Dimethylbenzene	10.9
	1,2-Dimethylbenzene	11.9
105	1,3,5-Trimethylbenzene	15.1
	1,2,4-Trimethylbenzene	16.0
	1,2,3-Trimethylbenzene	17.4
156	2,6-Dimethylnaphthalene	28.9
	1,2-Dimethylnaphthalene	29.4
	1,3-Dimethylnaphthalene	29.7

11.2.9 Observe the presence of peaks in the EIPs that would confirm the presence of any target aromatic compounds. Using the EIP areas and EIP linear regression calibrations compare the abundance of the aromatic peaks, and if appropriate, determine approximate crude oil contamination in the sample for each of the target ions.

11.3 Qualitative Identification—See Section 17 of this method for schematic flowchart.

11.3.1 Qualitative identification shall be accomplished by comparison of the TIC and EIP area data from an authentic sample to the TIC and EIP area data from the calibration standards (*see* Section 10.4). Crude oil shall be identified by the presence of C_{10} to C_{13} n-alkanes and corresponding target aromatics.

11.3.2 Using the calibration data, establish the identity of the C_8 to C_{13} peaks in the chromatogram of the sample. Using the calibration data, establish the identity of any target aromatics present on the extracted ion scans.

11.3.3 Crude oil is not present in a detectable amount in the sample if there are no target aromatics seen on the extracted ion scans. The experience of the analyst shall weigh heavily in the determination of the presence of peaks at a signal-to-noise ratio of 3 or greater.

11.3.4 If the chromatogram shows n-alkanes from C_8 to C_{13} and target aromatics to be present, contamination by crude oil or diesel shall be suspected and quantitative analysis shall be determined. If there are no n-alkanes present that are not seen on the blank, and no target aromatics are seen, the sample can be considered to be free of contamination.

11.4 Quantitative Identification—

11.4.1 Determine the area of the peaks from C_8 to C_{13} as outlined in the calibration section (10.4.1 of this appendix). If the area of the peaks for the sample is greater than that for the clean NAF (base fluid) use the crude oil/drilling fluid calibration TIC linear regression curve to determine approximate crude oil contamination.

11.4.2 Using the EIPs outlined in Section 10.4.2 of this appendix, determine the presence of any target aromatics. Using the integration techniques outlined in Section 10.4.2 of this appendix, obtain the EIP areas for m/z 91 and 105. Use the crude oil/drilling fluid calibration EIP linear regression curves to determine approximate crude oil contamination.

11.5 Complex Samples—

11.5.1 The most common interferences in the determination of crude oil can be from mineral oil, diesel oil, and proprietary additives in drilling fluids.

11.5.2 Mineral oil can typically be identified by its lower target aromatic content, and narrow range of strong peaks.

11.5.3 Diesel oil can typically be identified by low amounts of n-alkanes from C_7 to C_9, and the absence of n-alkanes greater than C_{25}.

11.5.4 Crude oils can usually be distinguished by the presence of high aromatics, increased intensities of C_8 to C_{13} peaks, and/or the presence of higher hydrocarbons of C_{25} and greater (which may be difficult to see in some synthetic fluids at low contamination levels).

11.5.4.1 Oil condensates from gas wells are low in molecular weight and will normally produce strong chromatographic peaks in the C_8–C_{13} range. If a sample of the gas condensate crude oil from the formation is available, the oil can be distinguished from other potential sources of contamination by using it to prepare a calibration standard.

11.5.4.2 Asphaltene crude oils with API gravity <20 may not produce chromatographic peaks strong enough to show contamination at levels of the calibration. Extracted ion peaks should be easier to see than increased intensities for the C8 to C13 peaks. If a sample of asphaltene crude from the formation is available, a calibration standard shall be prepared.

11.6 System and Laboratory Performance—

11.6.1 At the beginning of each 8-hour shift during which analyses are performed,

GC crude oil/drilling fluid calibration and system performance test mixes shall be verified. For these tests, analysis of the medium-level calibration standard (1-% Reference Oil in IO Lab drilling fluid, and 1.25 mg/mL SPTM with internal standard) shall be used to verify all performance criteria. Adjustments and/or re-calibration (per Section 10 of this appendix) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples and blanks be analyzed.

11.6.2 Inject 1.0 μL of the medium-level GC/MS crude oil/drilling fluid calibration standard into the GC instrument according to the procedures in Section 11.2 of this appendix. Verify that the linear regression curves for both TIC area and EIP areas are still valid using this continuing calibration standard.

11.6.3 After this analysis is complete, inject 1.0 μL of the 1.25 mg/mL SPTM (containing internal standard) into the GC instrument and verify the proper retention times are met (*see* Table 2 of this appendix).

11.6.4 Retention times—Retention time of the internal standard. The absolute retention time of the TCB internal standard shall be within the range 21.0 ±0.5 minutes. Relative retention times of the n-alkanes: The retention times of the n-alkanes relative to the TCB internal standard shall be similar to those given in Table 2 of this appendix.

11.6.17 Schematic Flowchart for Qualitative Identification

6.17 Schematic Flowchart for Qualitative Identification

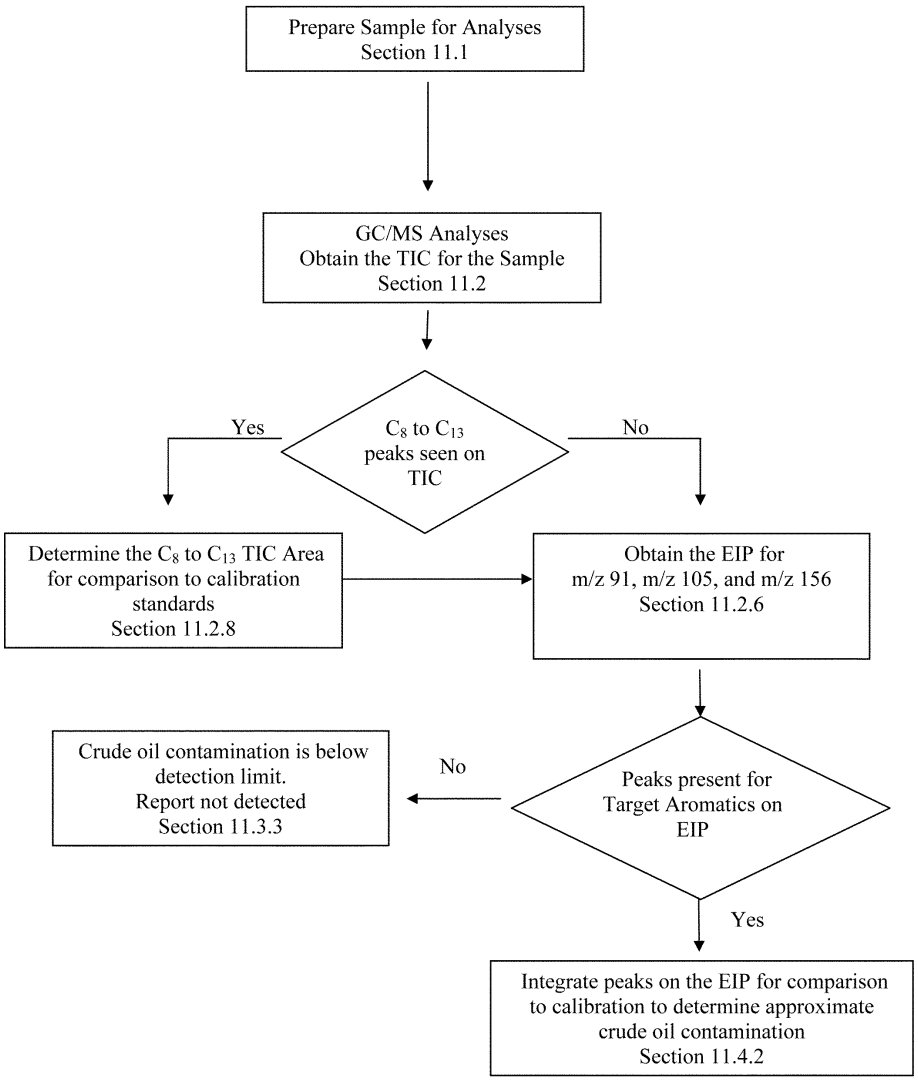

Figure 1. Schematic Flowchart for Qualitative Identification

12.0 CALCULATIONS

The concentration of oil in NAFs drilling fluids shall be computed relative to peak areas between C_8 and C_{13} (using the Total Area Integration method) or total peak areas from extracted ion profiles (using the Extracted Ion Profile Method). In either case, there is a measurable amount of peak area, even in clean drilling fluid samples, due to spurious peaks and electrometer ''noise'' that contributes to the total signal measured using either of the quantification methods. In this procedure, a correction for this signal is applied, using the blank or clean sample correction technique described in American Society for Testing Materials (ASTM) Method D–3328–90, Comparison of Waterborne Oil by Gas Chromatography. In

this method, the ''oil equivalents'' measured in a blank sample by total area gas chromatography are subtracted from that determined for a field sample to arrive at the most accurate measure of oil residue in the authentic sample.

12.1 Total Area Integration Method

12.1.1 Using C_8 to C_{13} TIC area, the TCB area in the clean NAF sample and the TIC linear regression curve, compute the oil equivalent concentration of the C_8 to C_{13} retention time range in the clean NAF.

NOTE: The actual TIC area of the C_8 to C_{13} is equal to the C_8 to C_{13} area minus the area of the TCB.

12.1.2 Using the corresponding information for the authentic sample, compute the oil equivalent concentration of the C_8 to C_{13} retention time range in the authentic sample.

12.1.3 Calculate the concentration (% oil) of oil in the sample by subtracting the oil equivalent concentration (% oil) found in the clean NAF from the oil equivalent concentration (% oil) found in the authentic sample.

12.2 EIP Area Integration Method

12.2.1 Using either m/z 91 or 105 EIP areas, the TCB area in the clean NAF sample, and the appropriate EIP linear regression curve, compute the oil equivalent concentration of the in the clean NAF.

12.2.2 Using the corresponding information for the authentic sample, compute its oil equivalent concentration.

12.2.3 Calculate the concentration (% oil) of oil in the sample by subtracting the oil equivalent concentration (% oil) found in the clean NAF from the oil equivalent concentration (% oil) found in the authentic sample.

13.0 METHOD PERFORMANCE

13.1 Specification in this method are adopted from EPA Method 1663, Differentiation of Diesel and Crude Oil by GC/FID (Reference 16.5).

13.2 Single laboratory method performance using an Internal Olefin (IO) drilling fluid fortified at 0.5% oil using a 35 API gravity oil was:

Precision and accuracy 94 ±4%
Accuracy interval—86.3% to 102%
Relative percent difference in duplicate analysis—6.2%

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 fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 All authentic samples (drilling fluids) failing the RPE (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 Carcinogens—''Working With Carcinogens.'' Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control (available through National Technical Information Systems, 5285 Port Royal Road, Springfield, VA 22161, document no. PB–277256): August 1977.

16.2 ''OSHA Safety and Health Standards, General Industry [29 CFR 1910], Revised.'' Occupational Safety and Health Administration, OSHA 2206. Washington, DC: January 1976.

16.3 ''Handbook of Analytical Quality Control in Water and Wastewater Laboratories.'' USEPA, EMSSL-CI, EPA–600/4–79–019. Cincinnati, OH: March 1979.

16.4 ''Method 1663, Differentiation of Diesel and Crude Oil by GC/FID, Methods for the Determination of Diesel, Mineral, and Crude Oils in Offshore Oil and Gas Industry Discharges, EPA 821–R–92–008, Office of Water Engineering and Analysis Division, Washington, DC: December 1992.

[66 FR 6901, Jan. 22, 2001, as amended at 77 FR 29843, May 18, 2012]

APPENDIX 6 TO SUBPART A OF PART 435—REVERSE PHASE EXTRACTION (RPE) METHOD FOR DETECTION OF OIL CONTAMINATION IN NON-AQUEOUS DRILLING FLUIDS (NAF) (GC/MS) (EPA METHOD 1670)

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 contaminates 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-certified 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 ±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 ±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 μm pore size—Acrodisc® CR Teflon (or equivalent).

6.3.8 Reverse Phase Extraction C_{18} Cartridge—Waters Sep-Pak®Plus, C_{18} 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″ × 7.5″ in 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. 6″ from 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-homogenicity 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 Pak® C_{18} 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 Pak® 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 Pak® C_{18} 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 Pak® 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 μm 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 Pak® C_{18} cartridge with the sample identification.

11.2.9 Place the labeled Sep Pak® C_{18} 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 C_{18} cartridge.

11.2.12 Condition the C_{18} 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 C_{18} cartridge.

11.2.14 Using automatic pipetters 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 C_{18} 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 C_{18} 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 C_{18} 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 C_{18} 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.

[66 FR 6901, Jan. 22, 2001; 66 FR 30811, June 8, 2001]

Appendix 7 to Subpart A of Part 435—Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid From Drill Cuttings by a Retort Chamber (Derived From API Recommended Practice 13B–2) (EPA Method 1674)

1. Description

a. This procedure is specifically intended to measure the amount of non-aqueous drilling fluid (NAF) base fluid from cuttings generated during a drilling operation. This procedure is a retort test which measures all oily material (NAF base fluid) and water released from a cuttings sample when heated in a calibrated and properly operating ''Retort'' instrument.

b. In this retort test a known mass of cuttings is heated in the retort chamber to vaporize the liquids associated with the sample. The NAF base fluid and water vapors are then condensed, collected, and measured in a precision graduated receiver.

NOTE: Obtaining a representative sample requires special attention to the details of sample handling (e.g., location, method, frequency). See Addendum A and B for minimum requirements for collecting representative samples. Additional sampling procedures in a given area may be specified by the NPDES permit controlling authority.

2. Equipment

a. Retort instrument—The recommended retort instrument has a 50-cm^3 volume with an external heating jacket.

Retort Specifications:

1. Retort assembly—retort body, cup and lid.

(a) Material: 303 stainless steel or equivalent.

(b) Volume: Retort cup with lid.

Cup Volume: 50-cm^3.

Precision: ±0.25-cm^3.

2. Condenser—capable of cooling the oil and water vapors below their liquification temperature.

3. Heating jacket—nominal 350 watts.

4. Temperature control—capable of limiting temperature of retort to at least 930 °F (500 °C) and enough to boil off all NAFs.

b. Liquid receiver (10-cm^3, 20-cm^3)—the 10-cm^3 and 20-cm^3 receivers are specially designed cylindrical glassware with rounded bottom to facilitate cleaning and funnel-shaped top to catch falling drops. For compliance monitoring under the NPDES program, the analyst shall use the 10-cm^3 liquid receiver with 0.1 ml graduations to achieve greater accuracy.

1. Receiver specifications:

Total volume: 10-cm^3, 20-cm^3.

Precision (0 to 100%): ±0.05 cm^3, ±0.05 cm^3.

Outside diameter: 10-mm, 13-mm.

Wall thickness: 1.5 ±0.1mm, 1.2 ±0.1mm.

Frequency of graduation marks (0 to 100%): 0.10-cm^3, 0.10-cm^3.

Calibration: To contain ''TC'' @ 20 °C.

Scale: cm^3, cm^3

2. Material—Pyrex® or equivalent glass.

c. Toploading balance—capable of weighing 2000 g and precision of at least 0.1 g. Unless motion is a problem, the analyst shall use an electronic balance. Where motion is a problem, the analyst may use a triple beam balance.

d. Fine steel wool (No. 000)—for packing retort body.

e. Thread sealant lubricant: high temperature lubricant, e.g. Never-Seez® or equivalent.

f. Pipe cleaners—to clean condenser and retort stem.

g. Brush—to clean receivers.

h. Retort spatula—to clean retort cup.

i. Corkscrew—to remove spent steel wool.

3. Procedure

a. Clean and dry the retort assembly and condenser.

b. Pack the retort body with steel wool.

c. Apply lubricant/sealant to threads of retort cup and retort stem.

d. Weigh and record the total mass of the retort cup, lid, and retort body with steel wool. This is mass (A), grams.

e. Collect a representative cuttings sample (*see* note in section 1 of this appendix).

f. Partially fill the retort cup with cuttings and place the lid on the cup.

g. Screw the retort cup (with lid) onto the retort body, weigh and record the total mass. This is mass (B), grams.

h. Attach the condenser. Place the retort assembly into the heating jacket.

i. Weigh and record the mass of the clean and dry liquid receiver. This is mass (C), grams. Place the receiver below condenser outlet.

j. Turn on the retort. Allow it to run a minimum of 1 hour.

NOTE: If solids boil over into receiver, the test shall be rerun. Pack the retort body with a greater amount of steel wool and repeat the test.

k. Remove the liquid receiver. Allow it to cool. Record the volume of water recovered. This is (V), cm^3.

NOTE: If an emulsion interface is present between the oil and water phases, heating the interface may break the emulsion. As a suggestion, remove the retort assembly from the heating jacket by grasping the condenser. Carefully heat the receiver along the emulsion band by gently touching the receiver for short intervals with the hot retort assembly. Avoid boiling the liquids. After the emulsion interface is broken, allow the liquid receiver to cool. Read the water volume at the lowest point of the meniscus.

l. Weigh and record the mass of the receiver and its liquid contents (oil plus water). This is mass (D), grams.

m. Turn off the retort. Remove the retort assembly and condenser from the heating jacket and allow them to cool. Remove the condenser.

n. Weigh and record the mass of the cooled retort assembly without the condenser. This is mass (E), grams.

o. Clean the retort assembly and condenser.

4. CALCULATIONS

a. Calculate the mass of oil (NAF base fluid) from the cuttings as follows:

1. Mass of the wet cuttings sample (M_w) equals the mass of the retort assembly with the wet cuttings sample (B) minus the mass of the empty retort assembly (A).

$$M_w = B - A \quad [1]$$

2. Mass of the dry retorted cuttings (M_D) equals the mass of the cooled retort assembly (E) minus the mass of the empty retort assembly (A).

$$M_D = E - A \quad [2]$$

3. Mass of the NAF base fluid (M_{BF}) equals the mass of the liquid receiver with its contents (D) minus the sum of the mass of the dry receiver (C) and the mass of the water (V).

$$M_{BF} = D - (C + V) \quad [3]$$

NOTE: Assuming the density of water is 1 g/cm^3, the volume of water is equivalent to the mass of the water.

b. Mass balance requirement:

The sum of M_D, M_{BF}, and V shall be within 5% of the mass of the wet sample.

$$(M_D + M_{BF} + V)/M_w = 0.95 \text{ to } 1.05 \quad [4]$$

The procedure shall be repeated if this requirement is not met.

c. Reporting oil from cuttings:

1. Assume that all oil recovered is NAF base fluid.

2. The mass percent NAF base fluid retained on the cuttings ($\%BF_i$) for the sampled discharge ''i'' is equal to 100 times the mass of the NAF base fluid (M_{BF}) divided by the mass of the wet cuttings sample (M_w).

$$\%BF_i = (M_{BF}/M_w) \times 100 \quad [5]$$

Operators discharging small volume NAF-cuttings discharges which do not occur during a NAF-cuttings discharge sampling interval (*i.e.*, displaced interfaces, accumulated solids in sand traps, pit clean-out solids, or centrifuge discharges while cutting mud weight) shall either: (a) Measure the mass percent NAF base fluid retained on the cuttings ($\%BF_{SVD}$) for each small volume NAF-cuttings discharges; or (b) use a default value of 25% NAF base fluid retained on the cuttings.

3. The mass percent NAF base fluid retained on the cuttings is determined for all cuttings wastestreams and includes fines discharges and any accumulated solids discharged [*see* Section 4.c.6 of this appendix for procedures on measuring or estimating the mass percent NAF base fluid retained on the cuttings (%BF) for dual gradient drilling seafloor discharges performed to ensure proper operation of subsea pumps].

4. A mass NAF-cuttings discharge fraction (X, unitless) is calculated for all NAF-cuttings, fines, or accumulated solids discharges every time a set of retorts is performed (*see* Section 4.c.6 of this appendix for procedures on measuring or estimating the mass NAF-cuttings discharge fraction (X) for dual gradient drilling seafloor discharges performed to ensure proper operation of subsea pumps). The mass NAF-cuttings discharge fraction (X) combines the mass of NAF-cuttings, fines, or accumulated solids discharged from a particular discharge over a set period of time with the total mass of NAF-cuttings, fines, or accumulated solids discharged into the ocean during the same period of time (*see* Addendum A and B of this appendix). The mass NAF-cuttings discharge

fraction (X) for each discharge is calculated by direct measurement as:

$X_i = (F_i)/(G)$ [6]

where:

X_i = Mass NAF-cuttings discharge fraction for NAF-cuttings, fines, or accumulated solids discharge ''i'', (unitless)

F_i = Mass of NAF-cuttings discharged from NAF-cuttings, fines, or accumulated solids discharge ''i'' over a specified period of time (*see* Addendum A and B of this appendix), (kg)

G = Mass of all NAF-cuttings discharges into the ocean during the same period of time as used to calculate F_i, (kg)

If an operator has more than one point of NAF-cuttings discharge, the mass faction (X_i) must be determined by: (a) Direct measurement (*see* Equation 6 of this appendix); (b) using the following default values of 0.85 and 0.15 for the cuttings dryer (e.g., horizontal centrifuge, vertical centrifuge, squeeze press, High-G linear shakers) and fines removal unit (e.g., decanting centrifuges, mud cleaners), respectively, when the operator is only discharging from the cuttings dryer and the fines removal unit; or (c) using direct measurement of ''F_i'' (*see* Equation 6 of this appendix) for fines and accumulated solids, using Equation 6A of this appendix to calculate ''G_{EST}'' for use as ''G'' in Equation 6 of this Appendix, and calculating the mass (kg) of NAF-cuttings discharged from the cuttings dryer (F_i) as the difference between the mass of ''G_{EST}'' calculated in Equation 6A of this appendix (kg) and the sum of all fines and accumulated solids mass directly measured (kg) (*see* Equation 6 of this appendix).

G_{EST} = Estimated mass of all NAF-cuttings discharges into the ocean during the same period of time as used to calculate F_i (*see* Equation 6 of this appendix), (kg) [6A]

where:

G_{EST} = Hole Volume (bbl) × (396.9 kg/bbl) × (1 + Z/100)

Z = The base fluid retained on cuttings limitation or standard (%) which apply to the NAF being discharge (*see* §§435.13. and 435.15).

Hole Volume (bbl) = [Cross-Section Area of NAF interval (in^2)] × Average Rate of Penetration (feet/hr) × period of time (min) used to calculate F_i (*see* Equation 6 of this appendix) × (1 hr/60 min) × (1 bbl/5.61 ft^3) × (1 ft/12 in)^2

Cross-Section Area of NAF interval (in^2) = (3.14 × [Bit Diameter (in)]^2)/4

Bit Diameter (in) = Diameter of drilling bit for the NAF interval producing drilling cuttings during the same period of time as used to calculate F_i (*see* Equation 6 of this appendix)

Average Rate of Penetration (feet/hr) = Arithmetic average of rate of penetration into the formation during the same period of time as used to calculate F_i (*see* Equation 6 of this appendix)

NOTE: Operators with one NAF-cuttings discharge may set the mass NAF-cuttings discharge fraction (X_i) equal to 1.0.

5. Each NAF-cuttings, fines, or accumulated solids discharge has an associated mass percent NAF base fluid retained on cuttings value (%BF) and mass NAF-cuttings discharge fraction (X) each time a set of retorts is performed. A single total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) is calculated every time a set of retorts is performed. The single total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) is calculated as:

$\%BF_{T,j} = \Sigma(X_i) \times (\%BF_i)$ [7]

where:

$\%BF_{T,j}$ = Total mass percent NAF base fluid retained on cuttings value for retort set ''j'' (unitless as percentage, %)

X_i = Mass NAF-cuttings discharge fraction for NAF-cuttings, fines, or accumulated solids discharge ''i'', (unitless)

$\%BF_i$ = Mass percent NAF base fluid retained on the cuttings for NAF-cuttings, fines, or accumulated solids discharge ''i'' , (unitless as percentage, %)

NOTE: $\Sigma X_i = 1$.

Operators with one NAF-cuttings discharge may set $\%BF_{T,j}$ equal to $\%BF_i$.

6. Operators performing dual gradient drilling operations may require seafloor discharges of large cuttings (>¼′) to ensure the proper operation of subsea pumps (e.g., electrical submersible pumps). Operators performing dual gradient drilling operations which lead to seafloor discharges of large cuttings for the proper operation of subsea pumps shall either: (a) Measure the mass percent NAF base fluid retained on cuttings value (%BF) and mass NAF-cuttings discharge fraction (X) for seafloor discharges each time a set of retorts is performed; (b) use the following set of default values, (%BF = 14%; X = 0.15); or (c) use a combination of (a) and (b) (e.g., use a default value for %BF and measure X).

Additionally, operators performing dual gradient drilling operations which lead to seafloor discharges of large cuttings for the proper operation of subsea pumps shall also perform the following tasks:

(a) Use side scan sonar or shallow seismic to determine the presence of high density chemosynthetic communities. Chemosynthetic communities are assemblages of tube worms, clams, mussels, and bacterial mats that occur at natural hydrocarbon seeps or vents, generally in water depths of 500 meters or deeper. Seafloor discharges of large cuttings for the proper operation of subsea pumps shall not be permitted

within 1000 feet of a high density chemosynthetic community.

(b) Seafloor discharges of large cuttings for the proper operation of subsea pumps shall be visually monitored and documented by a Remotely Operated Vehicle (ROV) within the tether limit (approximately 300 feet). The visual monitoring shall be conducted prior to each time the discharge point is relocated (cuttings discharge hose) and conducted along the same direction as the discharge hose position. Near-seabed currents shall be obtained at the time of the visual monitoring.

(c) Seafloor discharges of large cuttings for the proper operation of subsea pumps shall be directed within a 150 foot radius of the wellbore.

7. The weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) is the compliance value that is compared with the ''maximum weighted mass ratio averaged over all NAF well sections'' BAT discharge limitations (*see* the table in §435.13 and footnote 5 of the table in §435.43) or the ''maximum weighted mass ratio averaged over all NAF well sections'' NSPS discharge limitations (*see* the table in §435.15 and footnote 5 of the table in §435.45). The weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) is calculated as the arithmetic average of all total mass percent NAF base fluid retained on cuttings values ($\%BF_T$) and is given by the following expression:

$\%BF_{well} = [j = 1 \text{ to } j = n\ \Sigma\ (\%BF_{T,j})]/n$ [8]

where:

$\%BF_{well}$ = Weighted mass ratio averaged over all NAF well sections (unitless as percentage, %)

$\%BF_{T,j}$ = Total mass percent NAF base fluid retained on cuttings value for retort set ''j'' (unitless as percentage, %)

n = Total number of retort sets performed over all NAF well sections (unitless)

Small volume NAF-cuttings discharges which do not occur during a NAF-cuttings discharge sampling interval (*i.e.*, displaced interfaces, accumulated solids in sand traps, pit clean-out solids, or centrifuge discharges while cutting mud weight) shall be mass averaged with the arithmetic average of all total mass percent NAF base fluid retained on cuttings values (see Equation 8 of this appendix). An additional sampling interval shall be added to the calculation of the weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$). The mass fraction of the small volume NAF-cuttings discharges (X_{SVD}) will be determined by dividing the mass of the small volume NAF-cuttings discharges (F_{SVD}) by the total mass of NAF-cuttings discharges for the well drilling operation ($G_{WELL} + F_{SVD}$).

$X_{SVD} = F_{SVD} / (G_{WELL} + F_{SVD})$ [9]

where:

X_{SVD} = mass fraction of the small volume NAF-cuttings discharges (unitless)

F_{SVD} = mass of the small volume NAF-cuttings discharges (kg)

G_{WELL} = mass of total NAF-cuttings from the well (kg)

The mass of small volume NAF-cuttings discharges (F_{SVD}) shall be determined by multiplying the density of the small volume NAF-cuttings discharges (ρ_{svd}) times the volume of the small volume NAF-cuttings discharges (V_{SVD}).

$F_{SVD} = \rho_{svd} \times V_{SVD}$ [10]

where:

F_{SVD} = mass of small volume NAF-cuttings discharges (kg)

ρ_{svd} = density of the small volume NAF-cuttings discharges (kg/bbl)

V_{SVD} = volume of the small volume NAF-cuttings discharges (bbl)

The density of the small volume NAF-cuttings discharges shall be measured. The volume of small volume discharges (V_{SVD}) shall be either: (a) Be measured or (b) use default values of 10 bbl of SBF for each interface loss and 75 bbl of SBM for pit cleanout per well.

The total mass of NAF-cuttings discharges for the well (G_{WELL}) shall be either: (a) Measured; or (b) calculated by multiplying 1.0 plus the arithmetic average of all total mass percent NAF base fluid retained on cuttings values [see Equation 8 of this appendix] times the total hole volume (V_{WELL}) for all NAF well sections times a default value for the density the formation of 2.5 g/cm^3 (396.9 kg/bbl).

$$G_{WELL} = (1 + (\left[i = 1 \text{ to } j = n \sum (\%BF_{T,j})\right] / n)) \times V_{WELL}(bbl) \times 396.9(kg/bbl) \qquad [11]$$

where:

G_{WELL} = total mass of NAF-cuttings discharges for the well (kg)

[j = 1 to j = n $\Sigma(\%BF_{T,j})$]/n = see Equation 8 of this appendix (unitless as a percentage)

V_{WELL} = total hole volume (V_{WELL}) for all NAF well sections (bbl)

The total hole volume of NAF well sections (V_{WELL}) will be calculated as:

$$V_{WELL}\,(\text{barrels}) = \sum \frac{\text{Bit diameter (in)}^2}{1029} \times \text{change in measured depth (ft)} \qquad [12]$$

For wells where small volume discharges associated with cuttings are made, $\%BF_{WELL}$ becomes:

$$\%BF_{WELL} = ((1 - X_{SVD}) \times \left[i = 1 \text{ to } j = n \sum \left(\%BF_{T,j} \right) \right] / n \ ] \ ) + X_{SVD} \times \%BF_{SVD} \qquad [13]$$

NOTE: See Addendum A and B to determine the sampling frequency to determine the total number of retort sets required for all NAF well sections.

8. The total number of retort sets (n) is increased by 1 for each sampling interval (*see* Section 2.4, Addendum A of this appendix) when all NAF cuttings, fines, or accumulated solids for that sampling interval are retained for no discharge. A zero discharge interval shall be at least 500 feet up to a maximum of three per day. This action has the effect of setting the total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) at zero for that NAF sampling interval when all NAF cuttings, fines, or accumulated solids are retained for no discharge.

9. Operators that elect to use the Best Management Practices (BMPs) for NAF-cuttings shall use the procedures outlined in Addendum B.

ADDENDUM A TO APPENDIX 7 TO SUBPART A OF PART 435—SAMPLING OF CUTTINGS DISCHARGE STREAMS FOR USE WITH API RECOMMENDED PRACTICE 13B–2

1.0 SAMPLING LOCATIONS

1.1 Each NAF-cuttings waste stream that discharges into the ocean shall be sampled and analyzed as detailed in appendix 7. NAF-cuttings discharges to the ocean may include discharges from primary shakers, secondary shakers, cuttings dryer, fines removal unit, accumulated solids, and any other cuttings separation device whose NAF-cuttings waste is discharged to the ocean. NAF-cuttings wastestreams not directly discharged to the ocean (e.g., NAF-cuttings generated from shake shakers and sent to a cuttings dryer for additional processing) do not require sampling and analysis.

1.2 The collected samples shall be representative of each NAF-cuttings discharge. Operators shall conduct sampling to avoid the serious consequences of error (*i.e.*, bias or inaccuracy). Operators shall collect NAF-cuttings samples near the point of origin and before the solids and liquid fractions of the stream have a chance to separate from one another. For example, operators shall collect shale shaker NAF-cuttings samples at the point where NAF-cuttings are coming off the shale shaker and not from a holding container downstream where separation of larger particles from the liquid can take place.

1.3 Operators shall provide a simple schematic diagram of the solids control system and sample locations to the NPDES permit controlling authority.

2.0 TYPE OF SAMPLE AND SAMPLING FREQUENCY

2.1 Each NAF-cuttings, fines, or accumulated solids discharge has an associated mass percent NAF base fluid retained on cuttings value (%BF) and mass NAF-cuttings discharge fraction (X) for each sampling interval (*see* Section 2.4 of this addendum). Operators shall collect a single discrete NAF-cuttings sample for each NAF-cuttings waste stream discharged to the ocean during every sampling interval.

2.2 Operators shall use measured depth in feet from the Kelly bushing when samples are collected.

2.3 The NAF-cuttings samples collected for the mass fraction analysis (*see* Equation 6, appendix 7 of subpart A of this part) shall also be used for the retort analysis (*see* Equations 1–5, appendix 7 of subpart A of this part).

2.4 Operators shall collect and analyze at least one set of NAF-cuttings samples per day while discharging. Operators engaged in fast drilling (*i.e.*, greater than 500 linear NAF feet advancement of drill bit per day) shall collect and analyze one set of NAF-cuttings samples per 500 linear NAF feet of footage drilled. Operators are not required to collect and analyze more than three sets of NAF-cuttings samples per day (*i.e.*, three sampling intervals). Operators performing zero discharge of all NAF-cuttings (*i.e.*, all NAF cuttings, fines, or accumulated solids retained for no discharge) shall use the following periods to count sampling intervals:

(1) One sampling interval per day when drilling is less than 500 linear NAF feet advancement of drill bit per day; and (2) one sampling interval per 500 linear NAF feet of footage drilled with a maximum of three sampling intervals per day.

2.5 The operator shall measure the individual masses (F_i, kg) and sum total mass (G, kg) (*see* Equation 6, appendix 7 of subpart A of this part) over a representative period of time (e.g., <10 minutes) during steady-state conditions for each sampling interval (*see* Section 2.4 of this addendum). The operator shall ensure that all NAF-cuttings are capture for mass analysis during the same sampling time period (e.g., <10 minutes) at approximately the same time (*i.e.,* all individual mass samples collected within one hour of each other).

2.6 Operators using Best Management Practices (BMPs) to control NAF-cuttings discharges shall follow the procedures in Addendum B to appendix 7 of subpart A of 40 CFR 435.

3.0 Sample Size and Handling

3.1 The volume of each sample depends on the volumetric flow rate (cm^3/s) of the NAF-cuttings stream and the sampling time period (e.g., <10 minutes). Consequently, different solids control equipment units producing different NAF-cuttings waste streams at different volumetric flow rates will produce different size samples for the same period of time. Operators shall use appropriately sized sample containers for each NAF-cuttings waste stream to ensure no NAF-cuttings are spilled during sample collection. Operators shall use the same time period (e.g., <10 minutes) to collect NAF-cuttings samples from each NAF-cuttings waste stream. Each NAF-cuttings sample size shall be at least one gallon. Operators shall clearly mark each container to identify each NAF-cuttings sample.

3.2 Operators shall not decant, heat, wash, or towel the NAF-cuttings to remove NAF base fluid before mass and retort analysis.

3.3 Operators shall first calculate the mass of each NAF-cuttings sample and perform the mass ratio analysis (*see* Equation 6, appendix 7 of subpart A of this part). Operators with only one NAF-cuttings discharge may skip this step (*see* Section 4.c.4, appendix 7 of subpart A of this part).

3.4 Operators shall homogenize (e.g., stirring, shaking) each NAF-cuttings sample prior to placing a sub-sample into the retort cup. The bottom of the NAF-cuttings sample container shall be examined to be sure that solids are not sticking to it.

3.5 Operators shall then calculate the NAF base fluid retained on cuttings using the retort procedure (*see* Equations 1–5, appendix 7 of subpart A of this part). Operators shall start the retort analyses no more than two hours after collecting the first individual mass sample for the sampling interval .

3.6 Operators shall not discharge any sample before successfully completing the mass and retort analyses [*i.e.*, mass balance requirements (*see* Section 4.b, appendix 7 of subpart A of this part) are satisfied]. Operators shall immediately re-run the retort analyses if the mass balance requirements (*see* Equation 4, appendix 7 of subpart A of this part) are not within a tolerance of 5% (*see* Section 4.b, Equation 4, appendix 7 of subpart A of this part).

4.0 Calculations

4.1 Operators shall calculate a set of mass percent NAF base fluid retained on cuttings values (%BF) and mass NAF-cuttings discharge fractions (X) for each NAF-cuttings waste stream (*see* Section 1.1 of this addendum) for each sampling interval (*see* Section 2.4 of this addendum) using the procedures outlined in appendix 7 of subpart A of this part.

4.2 Operators shall tabulate the following data for each individual NAF-cuttings sample: (1) Date and time of NAF-cuttings sample collection; (2) time period of NAF-cuttings sample collection (*see* Section 3.1 of this addendum); (3) mass and volume of each NAF-cuttings sample; (4) measured depth (feet) at NAF-cuttings sample collection (*see* Section 2.2 of this addendum); (5) respective linear feet of hole drilled represented by the NAF-cuttings sample (feet); and (6) the drill bit diameter (inches) used to generate the NAF-cuttings sample cuttings.

4.3 Operators shall calculate a single total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) for each sampling interval (*see* Section 2.4 of this addendum) using the procedures outlined in appendix 7 of subpart A of this part.

4.4 Operators shall tabulate the following data for each total mass percent NAF base fluid retained on cuttings value ($\%BF_T$) for each NAF-cuttings sampling interval: (1) Date and starting and stopping times of NAF-cuttings sample collection and retort analyses; (2) measured depth of well (feet) at start of NAF-cuttings sample collection (*see* Section 2.2 of this addendum); (3) respective linear feet of hole drilled represented by the NAF-cuttings sample (feet); (4) the drill bit diameter (inches) used to generate the NAF-cuttings sample cuttings; and (5) annotation when zero discharge of NAF-cuttings is performed.

4.5 Operators shall calculate the weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) using the procedures outlined in appendix 7 of subpart A of this part.

4.6 Operators shall tabulate the following data for each weighted mass ratio averaged over all NAF well sections ($\%BF_{well}$) for each NAF well: (1) Starting and stopping dates of NAF well sections; (2) measured depth (feet)

of all NAF well sections; (3) total number of sampling intervals (*see* Section 2.4 and Section 2.6 of this addendum); (4) number of sampling intervals tabulated during any zero discharge operations; (5) total volume of zero discharged NAF-cuttings over entire NAF well sections; and (6) identification of whether BMPs were employed (*see* Addendum B of appendix 7 of subpart A of this part).

ADDENDUM B TO APPENDIX 7 TO SUBPART A OF PART 435—BEST MANAGEMENT PRACTICES (BMPS) FOR USE WITH API RECOMMENDED PRACTICE 13B–2

1.0 OVERVIEW OF BMPS

1.1 Best Management Practices (BMPs) are inherently pollution prevention practices. BMPs may include the universe of pollution prevention encompassing production modifications, operational changes, material substitution, materials and water conservation, and other such measures. BMPs include methods to prevent toxic and hazardous pollutants from reaching receiving waters. Because BMPs are most effective when organized into a comprehensive facility BMP Plan, operators shall develop a BMP in accordance with the requirements in this addendum.

1.2 The BMP requirements contained in this appendix were compiled from several Regional permits, an EPA guidance document (*i.e.*, Guidance Document for Developing Best Management Practices (BMP)'' (EPA 833–B–93–004, U.S. EPA, 1993)), and draft industry BMPs. These common elements represent the appropriate mix of broad directions needed to complete a BMP Plan along with specific tasks common to all drilling operations.

1.3 Operators are not required to use BMPs if all NAF-cuttings discharges are monitored in accordance with appendix 7 of subpart A of this part.

2.0 BMP PLAN PURPOSE AND OBJECTIVES

2.1 Operators shall design the BMP Plan to prevent or minimize the generation and the potential for the discharge of NAF from the facility to the waters of the United States through normal operations and ancillary activities. The operator shall establish specific objectives for the control of NAF by conducting the following evaluations.

2.2 The operator shall identify and document each NAF well that uses BMPs before starting drilling operations and the anticipated total feet to be drilled with NAF for that particular well.

2.3 Each facility component or system controlled through use of BMPs shall be examined for its NAF-waste minimization opportunities and its potential for causing a discharge of NAF to waters of the United States due to equipment failure, improper operation, natural phenomena (e.g., rain, snowfall).

2.4 For each NAF wastestream controlled through BMPs where experience indicates a reasonable potential for equipment failure (e.g., a tank overflow or leakage), natural condition (e.g., precipitation), or other circumstances to result in NAF reaching surface waters, the BMP Plan shall include a prediction of the total quantity of NAF which could be discharged from the facility as a result of each condition or circumstance.

3.0 BMP PLAN REQUIREMENTS

3.1 The BMP Plan may reflect requirements within the pollution prevention requirements required by the Minerals Management Service (*see* 30 CFR 250.300) or other Federal or State requirements and incorporate any part of such plans into the BMP Plan by reference.

3.2 The operator shall certify that its BMP Plan is complete, on-site, and available upon request to EPA or the NPDES Permit controlling authority. This certification shall identify the NPDES permit number and be signed by an authorized representative of the operator. This certification shall be kept with the BMP Plan. For new or modified NPDES permits, the certification shall be made no later than the effective date of the new or modified permit. For existing NPDES permits, the certification shall be made within one year of permit issuance.

3.3 The BMP Plan shall:

3.3.1 Be documented in narrative form, and shall include any necessary plot plans, drawings or maps, and shall be developed in accordance with good engineering practices. At a minimum, the BMP Plan shall contain the planning, development and implementation, and evaluation/reevaluation components. Examples of these components are contained in ''Guidance Document for Developing Best Management Practices (BMP)'' (EPA 833–B–93–004, U.S. EPA, 1993).

3.3.2 Include the following provisions concerning BMP Plan review.

3.3.2.1 Be reviewed by permittee's drilling engineer and offshore installation manager (OIM) to ensure compliance with the BMP Plan purpose and objectives set forth in Section 2.0.

3.3.2.2 Include a statement that the review has been completed and that the BMP Plan fulfills the BMP Plan purpose and objectives set forth in Section 2.0. This statement shall have dated signatures from the permittee's drilling engineer and offshore installation manager and any other individuals responsible for development and implementation of the BMP Plan.

3.4 Address each component or system capable of generating or causing a release of

significant amounts of NAF and identify specific preventative or remedial measures to be implemented.

4.0 BMP PLAN DOCUMENTATION

4.1 The operator shall maintain a copy of the BMP Plan and related documentation (e.g., training certifications, summary of the monitoring results, records of NAF-equipment spills, repairs, and maintenance) at the facility and shall make the BMP Plan and related documentation available to EPA or the NPDES Permit controlling authority upon request.

5.0 BMP PLAN MODIFICATION

5.1 For those NAF wastestreams controlled through BMPs, the operator shall amend the BMP Plan whenever there is a change in the facility or in the operation of the facility which materially increases the generation of those NAF-wastes or their release or potential release to the receiving waters.

5.2 At a minimum the BMP Plan shall be reviewed once every five years and amended within three months if warranted. Any such changes to the BMP Plan shall be consistent with the objectives and specific requirements listed in this addendum. All changes in the BMP Plan shall be reviewed by the permittee's drilling engineer and offshore installation manager.

5.3 At any time, if the BMP Plan proves to be ineffective in achieving the general objective of preventing and minimizing the generation of NAF-wastes and their release and potential release to the receiving waters and/or the specific requirements in this addendum, the permit and/or the BMP Plan shall be subject to modification to incorporate revised BMP requirements.

6.0 SPECIFIC POLLUTION PREVENTION REQUIREMENTS FOR NAF DISCHARGES ASSOCIATED WITH CUTTINGS

6.1 The following specific pollution prevention activities are required in a BMP Plan when operators elect to control NAF discharges associated with cuttings by a set of BMPs.

6.2 Establishing programs for identifying, documenting, and repairing malfunctioning NAF equipment, tracking NAF equipment repairs, and training personnel to report and evaluate malfunctioning NAF equipment.

6.3 Establishing operating and maintenance procedures for each component in the solids control system in a manner consistent with the manufacturer's design criteria.

6.4 Using the most applicable spacers, flushes, pills, and displacement techniques in order to minimize contamination of drilling fluids when changing from water-based drilling fluids to NAF and vice versa.

6.5 A daily retort analysis shall be performed (in accordance with appendix 7 to subpart A of part 435) during the first 0.33 X feet drilled with NAF where X is the anticipated total feet to be drilled with NAF for that particular well. The retort analyses shall be documented in the well retort log. The operators shall use the calculation procedures detailed in appendix 7 to subpart A of part 435 (*see* Equations 1 through 8) to determine the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.33 X feet drilled with NAF.

6.5.1 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.33 X feet drilled with NAF is less than or equal to the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring of cuttings may cease for that particular well. The same BMPs and drilling fluid used during the first 0.33 X feet shall be used for all remaining NAF sections for that particular well.

6.5.2 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.33 X feet drilled with NAF is greater the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring shall continue for the following (second) 0.33 X feet drilled with NAF where X is the anticipated total feet to be drilled with NAF for that particular well. The retort analyses for the first and second 0.33 X feet shall be documented in the well retort log.

6.5.2.1 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.66 X feet (*i.e.*, retort analyses taken from first and second 0.33 X feet) drilled with NAF is less than or equal to the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring of cuttings may cease for that particular well. The same BMPs and drilling fluid used during the first 0.66 X feet shall be used for all remaining NAF sections for that particular well.

6.5.2.2 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken during the first 0.66 X feet (*i.e.*, retort analyses taken from first and second 0.33 X feet) drilled with NAF is greater than the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), retort monitoring shall continue for all remaining NAF sections for that particular well. The retort analyses for all NAF sections shall be documented in the well retort log.

6.5.3 When the arithmetic average ($\%BF_{well}$) of the retort analyses taken over all NAF sections for the entire well is greater that the base fluid retained on cuttings limitation or standard (*see* §§ 435.13 and 435.15), the operator is in violation of the base fluid retained on cuttings limitation or standard and shall submit notification of these monitoring values in accordance with

NPDES permit requirements. Additionally, the operator shall, as part of the BMP Plan, initiate a reevaluation and modification to the BMP Plan in conjunction with equipment vendors and/or industry specialists.

6.5.4 The operator shall include retort monitoring data and dates of retort-monitored and non-retort-monitored NAF-cuttings discharges managed by BMPs in their NPDES permit reports.

6.6 Establishing mud pit and equipment cleaning methods in such a way as to minimize the potential for building-up drill cuttings (including accumulated solids) in the active mud system and solids control equipment system. These cleaning methods shall include but are not limited to the following procedures.

6.6.1 Ensuring proper operation and efficiency of mud pit agitation equipment.

6.6.2 Using mud gun lines during mixing operations to provide agitation in dead spaces.

6.6.3 Pumping drilling fluids off of drill cuttings (including accumulated solids) for use, recycle, or disposal before using wash water to dislodge solids.

[66 FR 6901, Jan. 22, 2001; 66 FR 30811, June 8, 2001]

APPENDIX 8 TO SUBPART A OF PART 435—REFERENCE C_{16}–C_{18} INTERNAL OLEFIN DRILLING FLUID FORMULATION

The reference C_{16}–C_{18} internal olefin drilling fluid used to determine the drilling fluid sediment toxicity ratio and compliance with the BAT sediment toxicity discharge limitation (*see* § 435.13) and NSPS (*see* § 435.15) shall be formulated to meet the specifications in Table 1 of this appendix.

Drilling fluid sediment toxicity ratio = 4-day LC_5. of C_{16}-C_{18} internal olefin drilling fluid/4-day LC_5. of drilling fluid removed from drill cuttings at the solids control equipment as determined by EPA Method 1644: ''Method for Conducting a Sediment Toxicity Test with *Leptocheirus plumulosus* and Non-Aqueous Drilling Fluids or Synthetic-Based Drilling Muds'' after sediment preparation procedures specified in EPA Method 1646, which are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See § 435.11(ee) and (uu).

TABLE 1—PROPERTIES FOR REFERENCE C_{16}–C_{18} IOS SBF USED IN DISCHARGE SEDIMENT TOXICITY TESTING

Mud weight of SBF discharged with cuttings (pounds per gallon)	Reference C_{16}–C_{18} IOs SBF (pounds per gallon)	Reference C_{16}–C_{18} IOs SBF synthetic to water ratio (%)
8.5–11	9.0	75/25
>11–14	11.5	80/20
>14	14.5	85/15
Plastic Viscosity (PV), centipoise (cP)	12–30	
Yield Point (YP), pounds/100 sq. ft	10–20	
10-second gel, pounds/100 sq. ft	8–15	
10-minute gel, pounds/100 sq. ft	12–30	
Electrical stability, V	>300	

[66 FR 6901, Jan. 22, 2001, as amended at 77 FR 29845, May 18, 2012]

Subpart B [Reserved]

Subpart C—Onshore Subcategory

§ 435.30 Applicability; description of the onshore subcategory.

The provisions of this subpart are applicable to those facilities engaged in the production, field exploration, drilling, well completion and well treatment in the oil and gas extraction industry which are located landward of the inner boundary of the territorial seas as defined in 40 CFR 125.1(gg) and which are not included within subpart D, E, or F, *Provided, however*, That the applicability of this subpart to (a) facilities in existence on April 13, 1979 or thereafter engaged in the production, field exploration, drilling, well completion and well treatment in the oil and gas extraction industry which are located on land and which would have been considered ''coastal'' as defined under the interim final regulations for this industry (40 CFR 435.41, 41 FR 44942, October 13, 1976) or which are (b)

located in the Santa Maria Basin of California is suspended.

(Secs. 301, 304(b) and 501 of the Clean Water Act as amended, 33 U.S.C. 1251 *et seq.*)

[44 FR 22075, Apr. 13, 1979, as amended at 47 FR 31555, July 21, 1982]

§ 435.31 Specialized definitions.

For the purpose of this subpart:

(a) The general definitions, abbreviations, and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

§ 435.32 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

Except as provided in §§ 125.30 through 125.32, any existing point source subject to this subpart shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT): there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment (*i.e.*, produced water, drilling muds, drill cuttings, and produced sand).

[60 FR 33966, June 29, 1995]

§ 435.33 Pretreatment standards for existing sources (PSES).

(a) *PSES for wastewater from unconventional oil and gas extraction.* Except as provided in 40 CFR 403.7 and 403.13, any existing source subject to this section, must achieve the following pretreatment standards for existing sources (PSES).

(1) There shall be no discharge of wastewater pollutants associated with production, field exploration, drilling, well completion, or well treatment for unconventional oil and gas extraction (including, but not limited to, drilling muds, drill cuttings, produced sand, produced water) into publicly owned treatment works.

(2) For the purposes of this section,

(i) *Unconventional oil and gas* means crude oil and natural gas produced by a well drilled into a shale and/or tight formation (including, but not limited to, shale gas, shale oil, tight gas, tight oil).

(ii) *Drill cuttings* means the particles generated by drilling into subsurface geologic formations and carried out from the wellbore with the drilling fluid.

(iii) *Drilling mud* means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure.

(iv) *Produced sand* means the slurried particles used in hydraulic fracturing, the accumulated formation sands, and scales particles generated during production. Produced sand also includes desander discharge from the produced water waste stream, and blowdown of the water phase from the produced water treating system.

(v) *Produced water* means the fluid brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and includes, where present, formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

(3) *Compliance deadline for existing sources.* Existing sources discharging into publicly owned treatment works on or between April 7, 2015 and June 28, 2016, shall comply with the PSES by August 29, 2019. All other existing sources shall comply by August 29, 2016.

(b) *PSES for Wastewater from Conventional Oil and Gas Extraction.* [Reserved]

[81 FR 41857, June 28, 2016, as amended at 81 FR 88127, Dec. 7, 2016]

§ 435.34 Pretreatment standards for new sources (PSNS).

(a) *PSNS for wastewater from unconventional oil and gas extraction.* Except as provided in 40 CFR 403.7 and 403.13, any new source with discharges subject to this section must achieve the following pretreatment standards for new sources (PSNS).

(1) There shall be no discharge of wastewater pollutants associated with production, field exploration, drilling, well completion, or well treatment for unconventional oil and gas extraction (including, but not limited to, drilling muds, drill cuttings, produced sand,

produced water) into publicly owned treatment works.

(2) For the purposes of this section, the definitions of unconventional oil and gas, drill cuttings, drilling muds, produced sand, and produced water are as specified in § 435.33(b)(2)(i) through (v).

(b) *PSNS for Wastewater from Conventional Oil and Gas Extraction.* [Reserved]

[81 FR 41857, June 28, 2016]

Subpart D—Coastal Subcategory

SOURCE: 61 FR 66125, Dec. 16, 1996, unless otherwise noted.

§ 435.40 Applicability; description of the coastal subcategory.

The provisions of this subpart are applicable to those facilities engaged in field exploration, drilling, well production, and well treatment in the oil and gas industry in areas defined as ''coastal.'' The term ''coastal'' shall mean:

(a) Any location in or on a water of the United States landward of the inner boundary of the territorial seas; or

(b)(1) Any location landward from the inner boundary of the territorial seas and bounded on the inland side by the line defined by the inner boundary of the territorial seas eastward of the point defined by 89°45′ West Longitude and 29°46′ North Latitude and continuing as follows west of that point:

Direction to west longitude	Direction to north latitude
West, 89°48′	North, 29°50′.
West, 90°12′	North, 30°06′.
West, 90°20′	South, 29°35′.
West, 90°35′	South, 29°30′.
West, 90°43′	South, 29°25′.
West, 90°57′	North, 29°32′.
West, 91°02′	North, 29°40′.
West, 91°14′	South, 29°32′.
West, 91°27′	North, 29°37′.
West, 91°33′	North, 29°46′.
West, 91°46′	North, 29°50′.
West, 91°50′	North, 29°55′.
West, 91°56′	South, 29°50′.
West, 92°10′	South, 29°44′.
West, 92°55′	North, 29°46′.
West, 93°15′	North, 30°14′.
West, 93°49′	South, 30°07′.
West, 94°03′	South, 30°03′.
West, 94°10′	South, 30°00′.
West, 94°20′	South, 29°53′.
West, 95°00′	South, 29°35′.
West, 95°13′	South, 29°28′.
East, 95°08′	South, 29°15′.
West, 95°11′	South, 29°08′.
West, 95°22′	South, 28°56′.
West, 95°30′	South, 28°55′.
West, 95°33′	South, 28°49′.
West, 95°40′	South, 28°47′.
West, 96°42′	South, 28°41′.
East, 96°40′	South, 28°28′.
West, 96°54′	South, 28°20′.
West, 97°03′	South, 28°13′.
West, 97°15′	South, 27°58′.
West, 97°40′	South, 27°45′.
West, 97°46′	South, 27°28′.
West, 97°51′	South, 27°22′.
East, 97°46′	South, 27°14′.
East, 97°30′	South, 26°30′.
East, 97°26′	South, 26°11′.

(2) East to 97°19′ West Longitude and Southward to the U.S.-Mexican border.

§ 435.41 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

(b) *Average of daily values for 30 consecutive days* means the average of the daily values obtained during any 30 consecutive day period.

(c) *Base fluid* means the continuous phase or suspending medium of a drilling fluid formulation.

(d) *Base fluid retained on cuttings* as applied to BAT effluent limitations and NSPS refers to the ''Determination of the Amount of Non-Aqueous Drilling Fluid (NAF) Base Fluid from Drill Cuttings by a Retort Chamber (Derived from API Recommended Practice 13B–2)'', EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

(e) *Biodegradation rate* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the ''Protocol for the Determination of Degradation of Non Aqueous Base Fluids in a Marine Closed Bottle Biodegradation Test System: Modified ISO 11734:1995,'' EPA Method 1647, supplemented with ''Procedure for Mixing Base Fluids With Sediments,'' EPA Method 1646. Both EPA Method 1646 and 1647 are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–

11–004. See paragraph (mm) of this section.

(f) *Cook Inlet* refers to coastal locations north of the line between Cape Douglas on the West and Port Chatham on the east.

(g) *Daily values* as applied to produced water effluent limitations and NSPS means the daily measurements used to assess compliance with the maximum for any one day.

(h) *Deck drainage* means any waste resulting from deck washings, spillage, rainwater, and runoff from gutters and drains including drip pans and work areas within facilities subject to this subpart.

(i) *Development facility* means any fixed or mobile structure subject to this subpart that is engaged in the drilling of productive wells.

(j) *Dewatering effluent* means wastewater from drilling fluids and drill cuttings dewatering activities (including but not limited to reserve pits or other tanks or vessels, and chemical or mechanical treatment occurring during the drilling solids separation/recycle/disposal process).

(k) *Diesel oil* refers to the grade of distillate fuel oil, as specified in the American Society for Testing and Materials Standard Specification for Diesel Fuel Oils D975–91, that is typically used as the continuous phase in conventional oil-based drilling fluids. This incorporation by reference was approved by the Director of the Federal Register in accordance with 5 U.S.C. 552(a) and 1 CFR part 51. Copies may be obtained from the American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428. Copies may be inspected at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*. A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460.

(l) *Domestic waste* means the materials discharged from sinks, showers, laundries, safety showers, eye-wash stations, hand-wash stations, fish cleaning stations, and galleys located within facilities subject to this subpart.

(m) *Drill cuttings* means the particles generated by drilling into subsurface geologic formations and carried out from the wellbore with the drilling fluid. Examples of drill cuttings include small pieces of rock varying in size and texture from fine silt to gravel. Drill cuttings are generally generated from solids control equipment and settle out and accumulate in quiescent areas in the solids control equipment or other equipment processing drilling fluid (*i.e.*, accumulated solids).

(1) *Wet drill cuttings* means the unaltered drill cuttings and adhering drilling fluid and formation oil carried out from the wellbore with the drilling fluid.

(2) *Dry drill cuttings* means the residue remaining in the retort vessel after completing the retort procedure specified in EPA Method 1674, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

(n) *Drilling fluid* means the circulating fluid (mud) used in the rotary drilling of wells to clean and condition the hole and to counterbalance formation pressure. Classes of drilling fluids are:

(1) *Water-based drilling fluid* means the continuous phase and suspending medium for solids is a water-miscible fluid, regardless of the presence of oil.

(2) *Non-aqueous drilling fluid* means the continuous phase and suspending medium for solids is a water-immiscible fluid, such as oleaginous materials (e.g., mineral oil, enhanced mineral oil, paraffinic oil, C_{16}–C_{18} internal olefins, and C_8–C_{16} fatty acid/2-ethylhexyl esters).

(i) *Oil-based* means the continuous phase of the drilling fluid consists of diesel oil, mineral oil, or some other oil, but contains no synthetic material or enhanced mineral oil.

(ii) *Enhanced mineral oil-based* means the continuous phase of the drilling fluid is enhanced mineral oil.

(iii) *Synthetic-based* means the continuous phase of the drilling fluid is a synthetic material or a combination of synthetic materials.

(o) *Enhanced mineral oil* as applied to enhanced mineral oil-based drilling fluid means a petroleum distillate which has been highly purified and is distinguished from diesel oil and conventional mineral oil in having a lower polycyclic aromatic hydrocarbon (PAH) content. Typically, conventional mineral oils have a PAH content on the order of 0.35 weight percent expressed as phenanthrene, whereas enhanced mineral oils typically have a PAH content of 0.001 or lower weight percent PAH expressed as phenanthrene.

(p) *Exploratory facility* means any fixed or mobile structure subject to this subpart that is engaged in the drilling of wells to determine the nature of potential hydrocarbon reservoirs.

(q) *Formation oil* means the oil from a producing formation which is detected in the drilling fluid, as determined by the GC/MS compliance assurance method, EPA Method 1655, when the drilling fluid is analyzed before being shipped offshore, and as determined by the RPE method, EPA Method 1670, when the drilling fluid is analyzed at the offshore point of discharge. The GC/MS compliance assurance method and the RPE method approved for use with this part are published as appendices to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section. Detection of formation oil by the RPE method may be confirmed by the GC/MS compliance assurance method, and the results of the GC/MS compliance assurance method shall supersede those of the RPE method.

(r) *Garbage* means all kinds of victual, domestic, and operational waste, excluding fresh fish and parts thereof, generated during the normal operation of coastal oil and gas facility and liable to be disposed of continuously or periodically, except dishwater, graywater, and those substances that are defined or listed in other Annexes to MARPOL 73/78. A copy of MARPOL may be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460.

(s) *M9IM* means those offshore facilities continuously manned by nine (9) or fewer persons or only intermittently manned by any number of persons.

(t) *M10* means those offshore facilities continuously manned by ten (10) or more persons.

(u) *Maximum* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the maximum concentration allowed as measured in any single sample of the barite for determination of cadmium and mercury content.

(v) *Maximum for any one day* as applied to BPT, BCT and BAT effluent limitations and NSPS for oil and grease in produced water means the maximum concentration allowed as measured by the average of four grab samples collected over a 24-hour period that are analyzed separately. Alternatively, for BAT and NSPS the maximum concentration allowed may be determined on the basis of physical composition of the four grab samples prior to a single analysis.

(w) *Minimum* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings means the minimum 96-hour LC_{50}. value allowed as measured in any single sample of the discharged waste stream. *Minimum* as applied to BPT and BCT effluent limitations and NSPS for sanitary wastes means the minimum concentration value allowed as measured in any single sample of the discharged waste stream.

(x)(1) *New source* means any facility or activity of this subcategory that meets the definition of ''new source'' under 40 CFR 122.2 and meets the criteria for determination of new sources under 40 CFR 122.29(b) applied consistently with all of the following definitions:

(i) *Water area* as used in ''site'' in 40 CFR 122.29 and 122.2 means the water area and water body floor beneath any exploratory, development, or production facility where such facility is conducting its exploratory, development or production activities.

(ii) *Significant site preparation work* as used in 40 CFR 122.29 means the process of surveying, clearing or preparing an area of the water body floor for the purpose of constructing or placing a development or production facility on or over the site.

(2) ''New Source'' does not include facilities covered by an existing NPDES permit immediately prior to the effective date of these guidelines pending EPA issuance of a new source NPDES permit.

(y) *No discharge of free oil* means that waste streams may not be discharged that contain free oil as evidenced by the monitoring method specified for that particular stream, e.g., deck drainage or miscellaneous discharges cannot be discharged when they would cause a film or sheen upon or discoloration of the surface of the receiving water; drilling fluids or cuttings may not be discharged when they fail EPA Method 1617 (Static Sheen Test), which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

(z) Parameters that are regulated in this subpart and listed with approved methods of analysis in Table 1B at 40 CFR 136.3 are defined as follows:

(1) *Cadmium* means total cadmium.

(2) *Chlorine* means total residual chlorine.

(3) *Mercury* means total mercury.

(4) *Oil and Grease* means total recoverable oil and grease.

(aa) *Produced sand* means the slurried particles used in hydraulic fracturing, the accumulated formation sands and scales particles generated during production. Produced sand also includes desander discharge from the produced water waste stream, and blowdown of the water phase from the produced water treating system.

(bb) *Produced water* means the water (brine) brought up from the hydrocarbon-bearing strata during the extraction of oil and gas, and can include formation water, injection water, and any chemicals added downhole or during the oil/water separation process.

(cc) *Production facility* means any fixed or mobile structure subject to this subpart that is either engaged in well completion or used for active recovery of hydrocarbons from producing formations. It includes facilities that are engaged in hydrocarbon fluids separation even if located separately from wellheads.

(dd) *Sanitary waste* means the human body waste discharged from toilets and urinals located within facilities subject to this subpart.

(ee) *SPP toxicity* as applied to BAT effluent limitations and NSPS for drilling fluids and drill cuttings refers to the bioassay test procedure, ''Suspended Particulate Phase (SPP) Toxicity Test,'' presented in EPA Method 1619, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

(ff) *Static sheen test* means the standard test procedure that has been developed for this industrial subcategory for the purpose of demonstrating compliance with the requirement of no discharge of free oil. The methodology for performing the static sheen test is presented in EPA Method 1617, which is published as an appendix to Subpart A of this part and in ''Analytic Methods for the Oil and Gas Extraction Point Source Category,'' EPA–821–R–11–004. See paragraph (mm) of this section.

(gg) *Stock barite* means the barite that was used to formulate a drilling fluid.

(hh) *Synthetic material* as applied to synthetic-based drilling fluid means material produced by the reaction of specific purified chemical feedstock, as opposed to the traditional base fluids such as diesel and mineral oil which are derived from crude oil solely through physical separation processes. Physical separation processes include fractionation and distillation and/or minor chemical reactions such as cracking and hydro processing. Since they are synthesized by the reaction of purified compounds, synthetic materials suitable for use in drilling fluids are typically free of polycyclic aromatic hydrocarbons (PAH's) but are sometimes found to contain levels of PAH up to 0.001 weight percent PAH expressed as phenanthrene. Internal olefins and vegetable esters are two examples of synthetic materials suitable for use by the oil and gas extraction industry in formulating drilling fluids. Internal olefins are synthesized from the isomerization of purified straight-chain (linear) hydrocarbons such as

C_{16}–C_{18} linear alpha olefins. C_{16}–C_{18} linear alpha olefins are unsaturated hydrocarbons with the carbon to carbon double bond in the terminal position. Internal olefins are typically formed from heating linear alpha olefins with a catalyst. The feed material for synthetic linear alpha olefins is typically purified ethylene. Vegetable esters are synthesized from the acid-catalyzed esterification of vegetable fatty acids with various alcohols. EPA listed these two branches of synthetic fluid base materials to provide examples, and EPA does not mean to exclude other synthetic materials that are either in current use or may be used in the future. A synthetic-based drilling fluid may include a combination of synthetic materials.

(ii) *Well completion fluids* means salt solutions, weighted brines, polymers, and various additives used to prevent damage to the well bore during operations which prepare the drilled well for hydrocarbon production.

(jj) *Well treatment fluids* means any fluid used to restore or improve productivity by chemically or physically altering hydrocarbon-bearing strata after a well has been drilled.

(kk) *Workover fluids* means salt solutions, weighted brines, polymers, or other specialty additives used in a producing well to allow for maintenance, repair or abandonment procedures.

(ll) *96-hour LC_5.* means the concentration (parts per million) or percent of the suspended particulate phase (SPP) from a sample that is lethal to 50 percent of the test organisms exposed to that concentration of the SPP after 96 hours of constant exposure.

(mm) *Analytic Methods for the Oil and Gas Extraction Point Source Category* is the EPA document, EPA–821–R–11–004, that compiles analytic methods for this category. Copies may be inspected at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202–741–6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*. A copy may also be inspected at EPA's Water Docket, 1200 Pennsylvania Ave. NW., Washington, DC 20460. This method may be obtained at *http://water.epa.gov/scitech/methods/cwa/index.cfm*.

[61 FR 66125, Dec. 16, 1996; 62 FR 1681, Jan. 13, 1997, as amended at 66 FR 6914, Jan. 22, 2001; 69 FR 18803, Apr. 9, 2004; 77 FR 29845, May 18, 2012]

§ 435.42 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT).

Except as provided in 40 CFR 125.30–125.32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

BPT EFFLUENT LIMITATIONS—OIL AND GREASE

[In milligrams per liter]

Pollutant parameter waste source	Maximum for any 1 day	Average of values for 30 consecutive days shall not exceed	Residual chlorine minimum for any 1 day
Produced water	72	48	NA
Deck drainage	(1)	(1)	NA
Water-based:			
Drilling fluids	(1)	(1)	NA
Drill Cuttings	(1)	(1)	NA
Non-aqueous:			
Drilling fluids	No discharge	No discharge	NA
Drill Cuttings	(1)	(1)	NA
Well treatment, workover, and completion fluids	(1)	(1)	NA
Sanitary:			
M10	NA	NA	[2] 1
M9IM[3]	NA	NA	NA
Domestic[3]	NA	NA	NA
Produced sand	Zero discharge	Zero discharge	NA

[1] No discharge of free oil. See § 435.41(y).
[2] Minimum of 1 mg/l and maintained as close to this concentration as possible.

[3] There shall be no floating solids as a result of the discharge of these wastes.

[61 FR 66125, Dec. 16, 1996, as amended at 66 FR 6916, Jan. 22, 2001; 77 FR 29846, May 18, 2012]

§ 435.43 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT).

Except as provided in 40 CFR 125.30–125.32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best available technology economically achievable (BAT):

BAT EFFLUENT LIMITATIONS

Stream	Pollutant parameter	BAT effluent limitations
Produced Water:		
(A) All coastal areas except Cook Inlet	.....	No discharge.
(B) Cook Inlet	Oil & Grease	The maximum for any one day shall not exceed 42 mg/l, and the 30-day average shall not exceed 29 mg/l.
Drilling Fluids, Drill Cuttings, and Dewatering Effluent: [1]		
(A) All coastal areas except Cook Inlet	.....	No discharge.
(B) Cook Inlet:.		
Water-based drilling fluids, drill cuttings, and dewatering effluent.	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test [4] shall be 3% by volume.
	Free oil	No discharge. [2]
	Diesel oil	No discharge.
	Mercury	1 mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.
Non-aqueous drilling fluids and dewatering effluent.	.....	No discharge.
Drill cuttings associated with non-aqueous drilling fluids.	.....	No discharge. [5]
Well Treatment, Workover and Completion Fluids:		
(A) All coastal areas except Cook Inlet	.....	No discharge.
(B) Cook Inlet	Oil & Grease	The maximum for any one day shall not exceed 42 mg/l, and the 30-day average shall not exceed 29 mg/l.
Produced Sand	.....	No discharge.
Deck Drainage	Free Oil [3]	No discharge.
Domestic Waste	Foam	No discharge.

[1] BAT limitations for dewatering effluent are applicable prospectively, BAT limitations in this rule are not applicable to discharges of dewatering effluent from reserve pits which as of the effective date of this rule no longer receive drilling fluids and drill cuttings. Limitations on such discharges shall be determined by the NPDES permit issuing authority.

[2] As determined by the static sheen test. See § 435.41(ff).

[3] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[4] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.41(ee).

[5] When Cook Inlet operators cannot comply with this no discharge requirement due to technical limitations (*see* appendix 1 of subpart D of this part), Cook Inlet operators shall meet the same stock limitations (C_{16}-C_{18} internal olefin) and discharge limitations for drill cuttings associated with non-aqueous drilling fluids for operators in Offshore waters (*see* § 435.13) in order to discharge drill cuttings associated with non-aqueous drilling fluids.

[61 FR 66125, Dec. 16, 1996; 62 FR 1681, Jan. 13, 1997, as amended at 66 FR 6917, Jan. 22, 2001; 77 FR 29846, May 18, 2012]

§ 435.44 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT).

Except as provided in 40 CFR 125.30–125.32, any existing point source subject to this subpart must achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best conventional pollutant control technology (BCT):

BCT EFFLUENT LIMITATIONS

Stream	Pollutant parameter	BCT effluent limitations
Produced Water (all facilities)	Oil & Grease	The maximum for any one day shall not exceed 72 mg/l and the 30-day average shall not exceed 48 mg/l.
Drilling Fluids and Drill Cuttings and Dewatering Effluent: [1]		
All facilities except Cook Inlet		No discharge.
Cook Inlet:.		
Water-based drilling fluids, drill cuttings, and dewatering effluent.	Free Oil	No discharge. [2]
Non-aqueous drilling fluids and dewatering effluent.		No discharge.
Drill cuttings associated with non-aqueous drilling fluids.	Free Oil	No discharge. [2]
Well Treatment, Workover and Completion Fluids.	Free Oil	No discharge. [2]
Produced Sand		No discharge.
Deck Drainage	Free Oil	No discharge. [3]
Sanitary Waste:		
Sanitary M10	Residual Chlorine	Minimum of 1 mg/l maintained as close to this concentration as possible.
Sanitary M91M	Floating Solids	No discharge.
Domestic Waste	Floating Solids and garbage	No discharge of Floating Solids or garbage.

[1] BCT limitations for dewatering effluent are applicable prospectively. BCT limitations in this rule are not applicable to discharges of dewatering effluent from reserve pits which as of the effective date of this rule no longer receive drilling fluids and drill cuttings. Limitations on such discharges shall be determined by the NPDES permit issuing authority.
[2] As determined by the static sheen test. See § 435.41(ff).
[3] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[61 FR 66125, Dec. 16, 1996; 62 FR 1682, Jan. 13, 1997, as amended at 66 FR 6917, Jan. 22, 2001; 77 FR 29846, May 18, 2012]

§ 435.45 Standards of performance for new sources (NSPS).

Any new source subject to this subpart must achieve the following new source performance standards (NSPS):

NSPS EFFLUENT LIMITATIONS

Stream	Pollutant parameter	NSPS effluent limitations
Produced Water:		
(A) All coastal areas except Cook Inlet		No discharge.
(B) Cook Inlet	Oil & Grease	The maximum for any one day shall not exceed 42 mg/l, and the 30-day average shall not exceed 29 mg/l.
Drilling Fluids, Drill Cuttings, and Dewatering Effluent: [1]		
(A) All coastal areas except Cook Inlet		No discharge.
(B) Cook Inlet:.		
Water-based drilling fluids, drill cuttings, and dewatering effluent.	SPP Toxicity	Minimum 96-hour LC_{50}. of the SPP Toxicity Test [4] shall be 3% by volume.
	Free oil	No discharge. [2]
	Diesel oil	No discharge.
	Mercury	1 mg/kg dry weight maximum in the stock barite.
	Cadmium	3 mg/kg dry weight maximum in the stock barite.

NSPS EFFLUENT LIMITATIONS—Continued

Stream	Pollutant parameter	NSPS effluent limitations
Non-aqueous drilling fluids and dewatering effluent.	.....	No discharge.
Drill cuttings associated with non-aqueous drilling fluids.	.....	No discharge.[5]
Well Treatment, Workover and Completion Fluids:		
(A) All coastal areas except Cook Inlet	.....	No discharge.
(B) Cook Inlet	Oil & Grease	The maximum for any one day shall not exceed 42 mg/l, and the 30-day average shall not exceed 29 mg/l.
Produced Sand	.....	No discharge.
Deck Drainage	Free Oil[3]	No discharge.
Sanitary Waste		
Sanitary M10	Residual Chlorine	Minimum of 1 mg/l and maintained as close to this concentration as possible.
Sanitary M9IM	Floating Solids	No discharge.
Domestic Waste	Floating Solids, Garbage and Foam.	No discharge of floating solids or garbage or foam.

[1] NSPS limitations for dewatering effluent are applicable prospectively. NSPS limitations in this rule are not applicable to discharges of dewatering effluent from reserve pits which as of the effective date of this rule no longer receive drilling fluids and drill cuttings. Limitations on such discharges shall be determined by the NPDES permit issuing authority.

[2] As determined by the static sheen test. See § 435.41(ff).

[3] As determined by the presence of a film or sheen upon or a discoloration of the surface of the receiving water (visual sheen).

[4] As determined by the suspended particulate phase (SPP) toxicity test. See § 435.41(ee).

[5] When Cook Inlet operators cannot comply with this no discharge requirement due to technical limitations (*see* appendix 1 of subpart D of this part), Cook Inlet operators shall meet the same stock limitations (C_{16}–C_{18} internal olefin) and discharge limitations for drill cuttings associated with non-aqueous drilling fluids for operators in Offshore waters (*see* § 435.15) in order to discharge drill cuttings associated with non-aqueous drilling fluids.

[61 FR 66125, Dec. 16, 1996; 62 FR 1682, Jan. 13, 1997, as amended at 66 FR 6918, Jan. 22, 2001; 77 FR 29846, May 18, 2012]

§ 435.46 Pretreatment standards of performance for existing sources (PSES).

Except as provided in 40 CFR 403.7 and 403.13, any existing source with discharges subject to this subpart that introduces pollutants into a publicly owned treatment works must comply with 40 CFR part 403 and achieve the following pretreatment standards for existing sources (PSES).

PSES EFFLUENT LIMITATIONS

Stream	Pollutant parameter	PSES effluent limitations
Produced Water	.....	No discharge.
Drilling Fluids and Drill Cuttings Well Treatment.		
Workover and Completion Fluids.	.....	No discharge.
Produced Sand	.....	No discharge.
Deck Drainage	.....	No discharge.

§ 435.47 Pretreatment standards of performance for new sources (PSNS).

Except as provided in 40 CFR 403.7 and 403.13, any new source with discharges subject to this subpart that introduces pollutants into a publicly owned treatment works must comply with 40 CFR part 403 and achieve the following pretreatment standards for new sources (PSNS).

PSNS EFFLUENT LIMITATIONS

Stream	Pollutant parameter	PSNS effluent limitations
Produced Water (all facilities).	.....	No discharge.
Drilling fluids and Drill Cuttings.	.....	No discharge.
Well Treatment, Workover and Completion Fluids.	.....	No discharge.
Produced Sand	.....	No discharge.
Deck Drainage	.....	No discharge.

APPENDIX 1 TO SUBPART D OF PART 435—PROCEDURE FOR DETERMINING WHEN COASTAL COOK INLET OPERATORS QUALIFY FOR AN EXEMPTION FROM THE ZERO DISCHARGE REQUIREMENT FOR EMO-CUTTINGS AND SBF-CUTTINGS IN COASTAL COOK INLET, ALASKA

1.0 SCOPE AND APPLICATION

This appendix is to be used to determine whether a Cook Inlet, Alaska, operator in Coastal waters (Coastal Cook Inlet operator) qualifies for the exemption to the zero discharge requirement established by 40 CFR 435.43 and 435.45 for drill cuttings associated with the following non-aqueous drilling fluids: enhanced mineral oil based drilling fluids (EMO-cuttings) and synthetic-based drilling fluids (SBF-cuttings). Coastal Cook Inlet operators are prohibited from discharging oil-based drilling fluids. This appendix is intended to define those situations under which technical limitations preclude Coastal Cook Inlet operators from complying with the zero discharge requirement for EMO-cuttings and SBF-cuttings. Coastal Cook Inlet operators that qualify for this exemption may be authorized to discharge EMO-cuttings and SBF-cuttings subject to the limitations applicable to operators in Offshore waters (*see* subpart A of this part).

2.0 METHOD

2.1 Any Coastal Cook Inlet operator must achieve the zero discharge limit for EMO-cuttings and SBF-cuttings unless it successfully demonstrates that technical limitations prevent it from being able to dispose of its EMO-cuttings or SBF-cuttings through on-site annular disposal, injection into a Class II underground injection control (UIC) well, or onshore land application.

2.2 To successfully demonstrate that technical limitations prevent it from being able to dispose of its EMO-cuttings or SBF-cuttings through on-site annular disposal, a Coastal Cook Inlet operator must show that it has been unable to establish formation injection in nearby wells that were initially considered for annular or dedicated disposal of EMO-cuttings or SBF-cuttings or prove to the satisfaction of the Alaska Oil and Gas Conservation Commission (AOGCC) that the EMO-cuttings or SBF-cuttings will be confined to the formation disposal interval. This demonstration must include:

a. Documentation, including engineering analysis, that shows (1) an inability to establish formation injection (e.g., formation is too tight), (2) an inability to confine EMO-cuttings or SBF-cuttings in disposal formation (e.g., no confining zone or adequate barrier to confine wastes in formation), or (3) the occurrence of high risk emergency (e.g., mechanical failure of well, loss of ability to inject that risks loss of well which would cause significant economic harm or create a substantial risk to safety); and

b. A risk analysis of alternative disposal options, including environmental assessment, human health and safety, and economic impact, that shows discharge as the lowest risk option.

2.3 To successfully demonstrate that technical limitations prevent it from being able to dispose of its EMO-cuttings or SBF-cuttings through injection into a Class II UIC well, a Coastal Cook Inlet operator must show that it has been unable to establish injection into a Class II UIC well or prove to the satisfaction of the Alaska Oil and Gas Conservation Commission (AOGCC) that the EMO-cuttings or SBF-cuttings will be confined to the formation disposal interval. This demonstration must include:

a. Documentation, including engineering analysis, that shows the inability to confine EMO-cuttings or SBF-cuttings in a Class II UIC well (e.g., no confining zone or adequate barrier to confine wastes in formation);

b. Documentation demonstrating that no Class II UIC well is accessible (e.g., operator does not own, competitor will not allow injection); and

c. A risk analysis of alternative disposal option, including environmental assessment, human health and safety, and economic impact, that shows discharge as the lowest risk option.

2.4 To successfully demonstrate that technical limitations prevent it from being able to dispose of its EMO-cuttings or SBF-cuttings through land application, a Coastal Cook Inlet operator must show that it has been unable to handle drilling waste or dispose of EMO-cuttings or SBF-cuttings at an appropriate land disposal site. This demonstration must include:

a. Documentation of site restrictions that preclude land application (e.g., no land disposal sites available);

b. Documentation of the platform's lack of capacity for adequate storage of EMO-cuttings or SBF-cuttings (e.g., limited storage or room for cuttings transfer); or

c. Documentation of inability to transfer EMO-cuttings or SBF-cuttings from platform to land for disposal (e.g., extremely low tides, high wave action).

3.0 PROCEDURE

3.1 Except as described in Section 3.2 of this appendix, a Coastal Cook Inlet operator believing that it qualifies for the exemption to the zero discharge requirement for EMO-cuttings or SBF-cuttings must apply for and obtain an individual NPDES permit prior to discharging EMO-cuttings or SBF-cuttings to waters of the United States.

3.2 Discharges occurring as the result a high risk emergency (e.g., mechanical failure

of well, loss of ability to inject that risks loss of well which would cause significant economic harm or safety) may be authorized by a general NPDES permit provided that:

a. The Coastal Cook Inlet operator satisfactorily demonstrates to EPA Region 10 the fulfillment of the other exemption requirements described in Section 2.0 of this appendix, or

b. The general permit allows for high risk emergency discharges and provides Reporting Requirements to EPA Region 10 immediately upon commencing discharge.

[66 FR 6918, Jan. 22, 2001]

Subpart E—Agricultural and Wildlife Water Use Subcategory

§ 435.50 Applicability; description of the beneficial use subcategory.

The provisions of this subpart are applicable to those onshore facilities located in the continental United States and west of the 98th meridian for which the produced water has a use in agriculture or wildlife propagation when discharged into navigable waters. These facilities are engaged in the production, drilling, well completion, and well treatment in the oil and gas extraction industry.

§ 435.51 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations, and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

(b) The term ''onshore'' shall mean all land areas landward of the territorial seas as defined in 40 CFR 125.1(gg).

(c) The term ''use in agricultural or wildlife propagation'' means that the produced water is of good enough quality to be used for wildlife or livestock watering or other agricultural uses and that the produced water is actually put to such use during periods of discharge.

§ 435.52 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

Except as provided in §§ 125.30 through 125.32, any existing point source subject to this subpart shall achieve the following effluent limitations representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available (BPT):

(a) There shall be no discharge of waste pollutants into navigable waters from any source (other than produced water) associated with production, field exploration, drilling, well completion, or well treatment (*i.e.*, drilling muds, drill cuttings, and produced sands).

(b) Produced water discharges shall not exceed the following daily maximum limitation:

Effluent characteristics	Effluent limitation (mg/l)
Oil and Grease	35.

[44 FR 22075, Apr. 13, 1979, as amended at 60 FR 33967, June 29, 1995]

Subpart F—Stripper Subcategory

§ 435.60 Applicability; description of the stripper subcategory.

The provisions of this subpart are applicable to those onshore facilities which produce 10 barrels per well per calendar day or less of crude oil and which are operating at the maximum feasible rate of production and in accordance with recognized conservation practices. These facilities are engaged in production, and well treatment in the oil and gas extraction industry.

§ 435.61 Specialized definitions.

For the purpose of this subpart:

(a) Except as provided below, the general definitions, abbreviations, and methods of analysis set forth in 40 CFR part 401 shall apply to this subpart.

(b) The term ''onshore'' shall mean all land areas landward of the inner boundary of the territorial seas as defined in 40 CFR 125.1(gg).

(c) The term ''well'' shall means crude oil producing wells and shall not include gas wells or wells injecting water for disposal or for enchanced recovery of oil or gas.

(d) The term ''gas well'' shall mean any well which produces natural gas in a ratio to the petroleum liquids produced greater than 15,000 cubic feet of gas per 1 barrel (42 gallons) of petroleum liquids.

Subpart G—General Provisions

§ 435.70 Applicability.

(a) *Purpose.* This subpart is intended to prevent oil and gas facilities, for which effluent limitations guidelines and standards, new source performance standards, or pretreatment standards have been promulgated under this part, from circumventing the effluent limitations guidelines and standards applicable to those facilities by moving effluent produced in one subcategory to another subcategory for disposal under less stringent requirements than intended by this part.

(b) *Applicability.* The effluent limitations and standards applicable to an oil and gas facility shall be determined as follows:

(1) An Oil and Gas facility, operator, or its agent or contractor may move its wastewaters from a facility located in one subcategory to another subcategory for treatment and return it to a location covered by the original subcategory for disposal. In such case, the effluent limitations guidelines, new source performance standards, or pretreatment standards for the original subcategory apply.

(2) An Oil and Gas facility, operator, or its agent or contractor may move its wastewaters from a facility located in one subcategory to another subcategory for disposal or treatment and disposal, provided:

(i) If an Oil and Gas facility, operator or its agent or contractor moves wastewaters from a wellhead located in one subcategory to another subcategory where oil and gas facilities are governed by less stringent effluent limitations guidelines, new source performance standards, or pretreatment standards, the more stringent effluent limitations guidelines, new source performance standards, or pretreatment standards applicable to the subcategory where the wellhead is located shall apply.

(ii) If an Oil and Gas facility, operator or its agent moves effluent from a wellhead located in one subcategory to another subcategory where oil and gas facilities are governed by more stringent effluent limitations guidelines, new source performance standards, or pretreatment standards, the more stringent effluent limitations guidelines, new source performance standards, or pretreatment standards applicable at the point of discharge shall apply.

[61 FR 66129, Dec. 16, 1996]

Subpart H—Coalbed Methane Subcategory [Reserved]

PART 436—MINERAL MINING AND PROCESSING POINT SOURCE CATEGORY

Subpart A—Dimension Stone Subcategory [Reserved]

Subpart B—Crushed Stone Subcategory

Sec.

Subpart C—Construction Sand and Gravel Subcategory

Subpart D—Industrial Sand Subcategory

Subpart E—Gypsum Subcategory