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HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT

API PUBLICATION NUMBER 4611

**APRIL 1995** 

Interlaboratory Study of EPA Methods 1662, 1654A, and 1663 for the Determination of Diesel, Mineral and Crude Oils in Drilling Muds from Offshore Oil and Gas Industry Discharges





American Petroleum Institute



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# Interlaboratory Study of EPA Methods 1662, 1654A, and 1663 for the Determination of Diesel, Mineral and Crude Oils in Drilling Muds from Offshore Oil and Gas Industry Discharges

Health and Environmental Sciences Department

**API PUBLICATION NUMBER 4611** 

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**APRIL** 1994





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### ACKNOWLEDGMENTS

The following participants in this work are recognized for their contributions of time and expertise during the course of this study:

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#### ABSTRACT

The effluent limitation guidelines being promulgated by the United States Environmental Protection Agency (EPA) for the offshore oil and gas industry include the prohibition of the discharge of diesel oil in drilling muds and drill cuttings from offshore oil and gas platforms. Analytical test procedures have been developed by the EPA to allow monitoring for diesel oil in drilling fluids whenever necessary to ensure compliance with the regulation. In the development of these analytical techniques, the EPA and the Technology/Diesel Analysis Work Group of the American Petroleum Institute (API) conducted studies to evaluate various extraction and analytical measurement techniques for reliable determination of diesel, mineral, and crude oils in drilling muds. The resulting Method 1662 (Soxhlet/Dean-Stark Extraction and Gravimetry for Total Extractable Material in Drilling Mud), Method 1654A (HPLC/UV for Polynuclear Aromatic Hydrocarbons Content of Oil), and Method 1663 (GC/FID for differentiation of Diesel and Crude Oil).

This report describes the methods and presents the results of the interlaboratory validation study of the methods. The large volume of raw data of this interlaboratory study, which includes calibration documentation, chromatograms, and EPA report forms are not included in this report, but are available in retrievable record from the American Petroleum Institute, Washington, D.C.



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#### EXECUTIVE SUMMARY

This report presents the results of the interlaboratory validation study of EPA Methods 1662, 1654A, and 1663, which was conducted with participation from the U.S. Environmental Protection Agency (EPA) and the American Petroleum Institute (API). The report discusses the development work conducted by EPA and API which resulted in these EPA methods, the interlaboratory validation study, and the method revisions required as a result of the validation study. Although this report shows that the methods developed were not perfect in their initial application, it is believed that the minor modifications to the methods as discussed later in this report will result in the reliable determination of diesel oil in drilling mud.

#### DEVELOPMENT OF EPA METHODS 1662, 1654A, AND 1663

EPA Methods 1662, 1654A, and 1663 are analytical test procedures, which have been issued by the EPA, to allow monitoring for diesel oil in drilling fluids whenever necessary to ensure regulatory compliance to the EPA Effluent Limitation Guidelines for the Offshore Oil and Gas Industry. The regulation includes a ban on the discharge of diesel oil in drilling muds and drill cuttings.

The methods were developed from work conducted by the EPA and the API Technology/Diesel Analysis Work Group. Various extraction methods were evaluated, and analytical measurement techniques were tested for the measurement of diesel oil. Because of the potential presence of mineral oil and/or crude oil in drilling muds, the analysis requires diesel oil to be distinguished from mineral oil and crude oil. Since no single analytical technique was found adequate, this method development effort has resulted in a tiered analysis approach for determining diesel oil in drilling muds using Methods 1662, 1654A, and 1663. With this approach, the analytical method required is guided by the results and decision criteria at each tier in the procedure.

Method 1662 for Total Extractable Material in Drilling Mud uses a Soxhlet/Dean-Stark (SDS) extractor to remove oil from the drilling mud for weighing and further analysis. Method 1654A for Polynuclear Aromatic Hydrocarbons (PAH) Content of Oil measures the PAH content of the extracted oil by high performance liquid chromatography with

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ultraviolet detection (HPLC/UV). If the PAH content is less than 0.35 weight percent, the oil is mineral oil. If the PAH content is equal to or greater than 0.35 weight percent, the oil is diesel oil or crude oil. Method 1663 for Differentiation of Diesel and Crude Oil uses gas chromatography with flame ionization detection (GC-FID) to measure the presence and distribution of hydrocarbons in the extracted oil. The presence of n-alkanes in the  $C_9-C_{24}$  range indicates the presence of diesel or crude oil. The oil is crude oil if the  $C_{25}-C_{30}$  n-alkane content is greater than 1.2 percent of the total  $C_9-C_{30}$  n-alkane content.

#### THE INTERLABORATORY STUDY OF THE METHODS

The interlaboratory study included six analytical laboratories. An additional laboratory prepared and shipped the round-robin samples to the participants. A seawater/lignosulfonate drilling fluid was used to prepare hot-rolled drilling mud samples, which were spiked with either mineral oil, diesel oil, or crude oil. Mud samples containing each type of oil were received by the participants for analysis. The EPA Sample Control Center for this study was DynCorp-Viar.

#### **RESULTS AND CONCLUSIONS**

All the participants in this interlaboratory study were able to carry out the analytical test procedures, once certain procedural problems, discussed in detail in this report, were addressed and corrected through the EPA Sample Control Center.

The initial precision and recovery QA acceptance criteria for each method were met by all laboratory participants. However, the analytical results for the oil spiked drilling mud samples showed measureable interlaboratory variabilities.

The mean and range of recovery values for extractables by Method 1662 was 70 (18 - 153) percent for the mineral oil spiked mud, 83 (29 - 200) percent for the diesel oil spiked mud, and 66 (24 - 82) percent for the crude oil spiked mud.

Four of six laboratories correctly identified the oil in the mineral oil spiked mud to be mineral oil on the basis of PAH content by Method 1654A. Of the two laboratories which reported the higher PAH contents, one of these reported 0.38 percent, which is

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essentially at the criteria concentration (0.35 percent) of the method. The diesel oil spiked mud samples showed higher PAH contents than mineral oil spiked mud samples in every case. The mean interlaboratory value was 3.4 percent PAH for the diesel oil spiked samples. Five of the six laboratories reported PAH in oil values greater than 0.35 percent for diesel oil spiked samples. These laboratories would thus have correctly identified the oil in this mud as diesel oil (or crude oil). The sixth laboratory reported a value of 0.32 percent PAH, which is also essentially at the 0.35 percent criteria concentration of the method.

Four laboratories reported greater than 1.2 percent weight  $C_{25}$ - $C_{30}$  n-alkane concentrations by Method 1663 for the crude oil spiked samples. In these four of six cases, Method 1663 would have differentiated diesel oil and crude oil. Two of the six laboratories, however, would not have differentiated diesel oil and crude oil. In these two cases, the analytical data obtained may have been due to excess dilutions of the sample and/or insufficient instrument sensitivity settings. All laboratories reported less than 1.2 percent values for the mineral oil and diesel oil spiked samples. Low recovery of extractables by Method 1662 did not correlate with or result in low PAH recovery by Method 1654A, or low  $C_{25}$ - $C_{30}$  percent n-alkanes by Method 1663.

Editorial corrections, laboratory procedure instructions, and method detection limit clarifications, as discussed in this report, need to be made in the methods revisions. EPA Sample Control Center has reported that methods corrections will be incorporated in the revised version of these EPA methods.

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# Section 1 INTRODUCTION

Diesel oil in drilling fluids (muds) and drill cuttings cannot be discharged from offshore oil and gas platforms. The diesel oil prohibition is part of the effluent limitation guidelines for the offshore oil and gas industry being promulgated by the U.S. Environmental Protection Agency (EPA) [58 FR 12454-12512]. In support of the final rule, EPA has issued a compendium of analytical methods for the determination of diesel, mineral, and crude oils in offshore oil and gas industry discharges (EPA, 1992). The analytical test procedures were developed to allow monitoring for diesel oil in drilling fluids whenever necessary to ensure compliance with the regulation.

Initially, Method 1651 (Retort, Gravimetry, and GC-FID) was developed for diesel monitoring and proposed as part of the 40 CFR Part 435 rule [56 FR 10664-10715]. This method uses a retort apparatus to thermally extract oil from drilling mud. The oil in the extract is weighed and then further analyzed by gas chromatography with flame ionization detection (GC-FID). Diesel oil identification is done by comparing the pattern of GC peaks in the oil with the pattern produced by a diesel oil reference.

The American Petroleum Institute (API) and its member companies criticized Method 1651 because the method is not definitive for diesel, since it can show potential interferences from mineral oil and crude oil. Mineral oil is an allowed lubricity additive for drilling fluids, which may be discharged in drilling muds as long as the discharge passes the sheen test and toxicity limits are met. Crude oil arising from the oil bearing formation can have hydrocarbons which interfere in the same boiling range used in Method 1651 to identify diesel hydrocarbons. Other objections to Method 1651 were that the retort apparatus used in the method is not sufficiently reproducible to serve as an analytical extraction technique, and the device can produce analytical artifacts with some types of muds.

For a number of years, EPA and API have been investigating methods for determination of diesel oil in drilling muds and drill cuttings. What initially appeared to be a simple problem of selecting the appropriate method for the determination of

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"diesel oil" turned out to be a very formidable problem that involved developing multiple methods in order to distinguish diesel oil from mineral oil and crude oil.

The problem of distinguishing differences between oils comes about because of the great variety of diesel, mineral, and crude oils. In many instances, these oils contain common components in overlapping concentrations making a simple absolute test for diesel oil virtually impossible. Techniques such as ultraviolet (UV) spectrometry and gas chromatography combined with mass spectrometry (GC/MS) were tested initially in attempts to determine the qualitative differences between oils. Unfortunately, the concentrations of the specific components measured by these techniques are either so similar that differences cannot be distinguished (e.g. mineral and diesel oil by UV spectroscopy) or the components are so low and highly variable in concentration that reliable measurements cannot be made (e.g., the PAH by GC/MS).

After working on this problem for several years, and with the cooperation of many members of the API Technology/Diesel Analysis Work Group, the API and the EPA were able to characterize diesel, mineral, and crude oils from multiple sources in the industry. The distribution and total amounts of the UV absorbing components of the oils were characterized by High Performance Liquid Chromatography with Ultraviolet Detection (HPLC/UV), and the distribution and concentrations of the components detectable by flame ionization detection were characterized by GC/FID. A study of these distributions finally yielded differences between the various oil types which could be determined by using the hierarchy of tiered tests employed in the interlaboratory study presented in this report.

In developing the tiered analytical procedure for diesel oil in drilling muds, the EPA and the API Technology/Diesel Analysis Work Group conducted studies to evaluate various alternative extraction and analytical measurement techniques for diesel, mineral, and crude oils in drilling muds (Raia, 1992; Benjamin, 1992; Weintritt, 1989). This work has resulted in Method 1662 (Soxhlet/Dean-Stark Extraction and Gravimetry for Total Extractable Material in Drilling Mud), Method 1654A (HPLC/UV for Polynuclear Aromatic Hydrocarbons Content of Oil), and Method 1663 (GC/FID for differentiation of Diesel and Crude Oil).

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The member companies of the API Technology/Diesel Analysis Work Group and individuals working under the auspices of API and the EPA are to be commended for their perseverance in resolution of the technical challenges presented by what started out as a task seeking a simple means to reliably measure diesel oil. Although this report shows that the methods developed were not perfect in their initial application in this interlaboratory study, it is believed that the minor modifications to the methods as discussed in this report will result in the reliable determination of diesel oil in drilling mud.

This report will discuss these methods and the results of the interlaboratory validation study of the methods, which has been conducted by EPA and the API.

# Section 2 METHOD DEVELOPMENT AND DISCUSSION

# DRILLING MUD DISCHARGE MONITORING FOR OIL AND TOXICITY The discharge of drilling muds from offshore platforms requires environmental compliance monitoring for oil and toxicity. Regulatory requirements are:

- no free oil can be present, as measured by the static sheen test (the visual sheen test is allowed in EPA Region VI);
- a toxicity limitation in the suspended particulate phase of the mud to mysids as measured by the 96-h LC50 >= 30,000 ppm;
- no diesel can be present as documented by the well inventory record, and
- verified by confirmatory analytical testing when required.

For confirmatory analysis of diesel, EPA Methods 1662, 1654A, and 1663 are used in a tiered analysis approach as discussed below.

# DEVELOPMENT OF EPA METHODS 1662, 1654A, AND 1663

In the development of Methods 1662, 1654A, and 1663, work conducted by EPA and the API Technology/Diesel Analysis Work Group was aimed at obtaining a good alternative extraction procedure to the retort, and a measurement finish that would allow diesel to be distinguished from mineral oil and crude oil.

The extraction techniques evaluated in addition to the retort were:

- Soxhlet/Dean-Stark (SDS);
- sonication with acetone/methylene chloride (1:1 V/V); and
- supercritical fluid extraction (SFE) with carbon dioxide.

Laboratory prepared hot-rolled muds were spiked at two concentration levels of diesel. One level was at 0.2% and the other at 2.0%. Similarly, other mud samples were spiked with mineral oil and with crude. Based on the recovery data from these extraction studies, SDS was selected as the best extraction procedure for diesel in drilling muds [Raia, 1992]. SFE gave lower recoveries for diesel than did the other techniques tested in this study. This may have been due in part to problems caused from the relatively high water contents of drilling muds.

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In the analytical measurement of diesel in drilling muds, definitive techniques are required that allow diesel to be distinguished from interferences caused by the potential presence of mineral oil and/or crude oil. Diesel oil is known to generally contain higher concentrations of polynuclear aromatic hydrocarbons (PAHs) than does mineral oil. Further, the alkane hydrocarbons in diesel are generally in the boiling range of  $C_{10}$ - $C_{24}$ , while in crude oils, the alkane hydrocarbons generally range lower than  $C_{10}$  and extend beyond  $C_{24}$ . These distinguishing characteristics, PAH content and alkane boiling range, were the basis of selecting High Performance Liquid Chromatography with Ultraviolet Detection (HPLC/UV) for measuring PAHs, and GC-FID for determining n-alkane boiling point profiles.

A study was then made to quantify the PAH contents and n-alkane distributions in diesel, mineral, and crude oils (Benjamin, 1992). Retort results for drilling muds from offshore drilling sites were surveyed to determine levels of total extractable material in drilling muds (Weintritt, 1989). The results are summarized in Table 1. These data provided PAH concentration levels that could be used to distinguish diesel oil from mineral oil, and n-alkane distributions that could be used to differentiate diesel oil from crude oil. The survey also provided an indication of background concentration levels of extractable material in drilling muds to which diesel had never been added. This information provided the basis for how the tiered analysis approach is employed, using PAH content and n-alkane distributions, to determine diesel oil in drilling muds.

20	30		
	Extractables in Drilling Muds <sup>a</sup> mg/kg	PAH in Mineral Oils⁵ % Wt.	C <sub>25</sub> -C <sub>30</sub> in Diesel Oils⁵ % Wt.
Ν	14	9	10
Mean	1267.0	0.1590	0.45
S.D.	748.0	0.0935	0.39
Mean + 2SD	2764.0	0.3459	1.22

Table 1. Survey of extractables in drilling muds, PAH in mineral oils, and  $C_{25}$ - $C_{30}$  in diesel oils

<sup>a</sup> (Weintritt, 1989)

<sup>b</sup> (Benjamin, 1992)

### DIFFERENTIATION OF DIESEL, MINERAL, AND CRUDE OILS BY EPA METHODS 1662, 1654A, AND 1663

The tiered analysis approach employing EPA Methods 1662, 1654A, and 1663 to determine the presence of diesel oil in drilling muds is shown in Figure 1. With this approach, the analytical method required is guided by the results and decision criteria at each tier in the procedure.



Figure 1. Tiered Analysis by Methods 1662, 1654A, and 1663 (EPA, 1992)

Method 1662 uses a Soxhlet/Dean-Stark (SDS) extractor to remove oil from the drilling mud. The total oil in the extract can be measured by weighing a measured portion of the extract. The other portion of the extract is used in Methods 1654A and 1663.

The PAH content of the extracted oil is measured as phenanthrene by HPLC/UV in Method 1654A. If the PAH content is less than 0.35 weight percent, the oil is mineral oil. If the PAH content is equal to or greater than 0.35 weight percent, the oil is diesel oil or crude oil.

Method 1663 uses GC-FID to measure the presence and distribution of hydrocarbons in the extracted oil. The presence of n-alkanes in the  $C_9$ - $C_{24}$  range indicates the presence of diesel or crude oil. If less than 10 n-alkanes are present in the  $C_9$ - $C_{24}$ range (at a signal-to-noise ratio of 3 or greater for each n-alkane), diesel oil is not present. If 10 or more n-alkanes are present in the  $C_9$ - $C_{24}$  range, the percentage of nalkanes in the  $C_{25}$ - $C_{30}$  range are used to determine if the oil is crude oil. The oil is crude oil if the  $C_{25}$ - $C_{30}$  n-alkane content is greater than 1.2 percent of the total  $C_9$ - $C_{30}$ n-alkane content.

#### Section 3

#### INTERLABORATORY STUDY OF METHODS 1662, 1654A, AND 1663

The interlaboratory round-robin test of methods 1662, 1654A, and 1663, has been conducted by EPA and the API Technology/Diesel Analysis Work Group. DyneCorp Viar (Alexandria, Virginia) served as sample control center for the study.

#### INTERLABORATORY TEST DESIGN

The interlaboratory test design included six analytical laboratories; three were EPA contract laboratories, and three were API contract laboratories. One additional laboratory, Weintritt Consulting Services (Lafayette, Louisiana), prepared and distributed the drilling mud samples for testing.

The three EPA contract laboratories were Analytical Technologies, Inc. (Fort Collins, Colorado), Commonwealth Technology, Inc. (Lexington, Kentucky), and Pacific Analytical, Inc. (Carlsbad, California). The three API contract laboratories were Core Laboratories (Houston, Texas), Southern Petroleum Laboratories (Scott, Louisiana), and MI Drilling Fluids Co. (Houston, Texas). These laboratories were respectively designated as A, B, C, D, E, and F for this interlaboratory study.

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EPA Method	1662 Extractable Oil % Wt.	1654A PAH in Oil % Wt.	1663 C <sub>25</sub> -C <sub>30</sub> % Wt.	1663 Diesel mg/ML
Sample ID		Number of S	Samples	
IPR *	4X	4X	4X	4X
Blank (1662)	1X	1X	1X	1X
Blank (1654A) or (1663)	1X	1X	1X	1X
OPR <sup>b</sup>	1X	1X	1X	1X
Mud + Diesel	2X	2X	2X	2X
Mud + Mineral	2X	2X	2X	2X
Mud + Crude	2X	2X	2X	2X

Table 2.	Interlaboratory study plan of methods 1662, 1654A, and 1	663
	Six Laboratory Participants + One Sample Prep Lab	

<sup>a</sup> IPR is Initial Precision & Recovery

<sup>b</sup> OPR is Ongoing Precision & Recovery

The interlaboratory study plan is shown in Table 2. The laboratory participants received three drilling mud samples. One sample was spiked with diesel oil, another with mineral oil, and the other with crude oil. The laboratories were instructed to report initial and ongoing precision and recovery quality assurance (QA) results for each method as specified. Each of the mud samples was analyzed in duplicate. Chromatograms and calibration data were submitted with the reported test results.

#### PREPARATION OF DRILLING MUD SAMPLES

The drilling mud samples were prepared and spiked with oils as described in Appendix A in the letter of February 26, 1993 from Weintritt Consulting Services to Mr. Dan Caudle, Conoco, Inc. Thirty barrels of a 12 lb/gal seawater/lignosulfonate drilling fluid was prepared and tested according to API recommended practices. The prepared drilling fluid was used to prepare hot-rolled drilling mud samples containing 0.3 percent volume of oil. Eight samples (one pint each) were prepared to contain mineral oil (Conoco LVT 200); eight samples (one pint each) contained diesel oil, and another eight samples (one pint each) contained or contained diesel oil, and another eight samples (one pint each) contained crude oil (Conoco, Lafayette). One sample of the drilling mud contained no added oil. A recommended procedure was provided to each laboratory for sampling the spiked drilling muds from the containers. The labs receiving the samples were not informed of the oil concentrations or type of oils present. The sample numbers and corresponding laboratory assignments are given in Appendix A.

### INITIAL PRECISION AND RECOVERY QA RESULTS

The initial precision and recovery results are summarized in Tables 3 through 6. All participating laboratories were able to meet the initial precision and recovery QA acceptance criteria for the methods (Table 5). Laboratory E reported that losses of analyte in Method 1654A occurred in the procedure where the sample extracts are concentrated to eliminate chromatographic interference caused by the toluene solvent.

The ongoing precision and recovery QA criteria were met by all participating laboratories, except for laboratory E, which did not report this data with their results. Laboratory F showed 111 percent recovery for Method 1663, which has an acceptance criteria specification of 78-110 percent.

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	Table 3.	Initial	precision	and	recovery	results
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LABORATORY	A	В	С	D	E	F			
1662 (% Wt. Extract.)									
SPIKE	0.25	0.20	0.25	0.25	0.25	0.25			
MEAN	0.22	0.15	0.20	0.18	0.16	0.24			
S.D.	0.02	0.02	0.02	0.04	0.02	0.01			
1654A (mg/ml PAI	1654A (mg/ml PAH)								
SPIKE	1.25	1.25	1.25	1.25	1.25	1.26			
MEAN	1.39	1.07	1.36	0.96	0.98	1.25			
S.D.	0.04	0.05	0.01	0.10	0.10	0.01			
1663 (mg/ml C <sub>25</sub> -C	1663 (mg/ml C <sub>25</sub> -C <sub>30</sub> )								
SPIKE	1.25	1.25	1.25	1.25	1.25	1.26			
MEAN	1.24	1.13	1.20	1.16	1.11	1.24			
S.D.	0.02	0.12	0.22	0.14	0.03	0.09			

### Table 4. Initial precision & recovery results (Method 1662 - % Wt.)

LABORATORY	A	В	С	D	E	F	
% RECOVERY							
Found	88.	75.	80.	72.	64.	96.	
Acceptance	(47% - 149%)						
% RELATIVE S.	% RELATIVE S.D.						
Found	9.	13.	10.	22.	12.	4.	
Acceptance							

### Table 5. Initial precision & recovery results (Method 1654A - mg/ml PAH)

LABORATORY	A	В	С	D	E	F		
% RECOVERY								
Found	111.	86.	109.	77.	78.	99.		
Acceptance	(67% - 156%)							
% RELATIVE S.C	% RELATIVE S.D.							
Found	3.	5.	1.	10.	11.	1.		
Acceptance								

# Table 6. Initial precision & recovery results (Method 1663 - mg/ml C<sub>25</sub>-C<sub>30</sub>)

LABORATORY	A	В	С	D	E	F		
% RECOVERY								
Found	99.	90.	96.	93.	89.	98.		
Acceptance		(80% - 108%)						
% RELATIVE S.D.								
Found	2.	11.	18.	12.	3.	7.		
Acceptance	(18%)							

#### **RESULTS FOR OIL SPIKED DRILLING MUD SAMPLES**

The interlaboratory results for the oil spiked drilling mud samples are summarized in Tables 7 through 10 and Figures 2 through 4. The results summary provided by the sample control center (DynCorp Viar) is given in Appendix B. The results given in Table 7 are mean values and show measureable interlaboratory variabilities. Tables 8, 9, and 10 show duplicate results for spiked drilling muds according to Methods 1662, 1654A, and 1663, respectively.

LABORATORY	A	В	С	D	E	F			
% Wt. Extract.									
M + Mineral	0.18	0.26	0.05	0.03	0.09	0.10			
M + Diesel	0.14	0.17	0.34	0.05	0.07	0.08			
M + Crude	0.14	0.13	0.14	0.04	0.12	0.10			
% Wt. PAH									
M + Mineral	0.18	2.65	0.12	0.38	0.07	0.21			
M + Diesel	2.70	3.80	0.32	2.74	7.13	3.68			
M + Crude	1.16	5.40	0.23	1.78	0.15	1.53			
% Wt. C <sub>25</sub> -C <sub>30</sub>									
M + Mineral	<1.0	<1.0	<1.2	<1.0	0.09	<1.0			
M + Diesel	<1.0	<1.0	<1.2	0.6	0.24	<1.0			
M + Crude	1.53	<1.0	<1.2	7.5	7.10	6.1			

Table 7. Results for spiked drilling mud samples (Methods 1662, 1654A, and 1663)

### Method 1662

The percent weight extractables data by Method 1662 (Table 7) should be comparable to the nominal spike concentration of 0.17 percent weight oil which was added to each mud (0.3 percent volume of oil in the 12 lb/gal mud preparation).

The percent recovery of extractable oil obtained by Method 1662 is shown graphically for each laboratory in Figure 2. The mean and range of recovery values for each mud was 70 (18 - 153) percent for the mineral oil spiked mud, 83 (29 - 200) percent for the diesel oil spiked mud, and 66 (24 - 82) percent for the crude oil spiked mud. Several of the laboratories showed relatively low recovery results. Laboratory C however showed too high recovery (200 percent) for the diesel spiked mud. Some participants commented that they experienced problems with the Soxhlet/Dean-Stark extractor frit being clogged with mud particles. This caused slow percolation of toluene through the sample and long extraction times.

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The acceptance criteria given in Method 1662 for matrix spike recovery is 35 - 59 percent. If this same level of recovery acceptance were applied to the spiked mud samples results, the acceptance criteria would be met for each sample by laboratories A, B, E, and F. Laboratories C and D would not meet the acceptance criteria. Laboratory A results were close to the true nominal oil values. This laboratory has had prior experience with the procedures of the method, since it had performed analyses in the development phases of the methods.

Method 1662 (% Wt. Extractable Material in Drilling Mud)						
	M + 1	<i>lineral</i>	M + Diesel		M + Crude	
Run #	1	2	1	2	1	2
(RPD Acceptance = 34%)						
LABORATORY						
А	0.16	0.19	0.13	0.15	0.15	0.12
В	0.24	0.27	0.17	0.17	0.14	0.12
C	0.02	0.09	0.36	0.33	0.06	0.23
D	0.03	0.03	0.04	0.05	0.04	0.04
E	0.10	0.08	0.06	0.08	0.12	0.11
F	0.09	0.11	0.08	0.09 0.07	0.11	0.11 0.08





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#### Method 1654A

The results for PAH in oil by Method 1654A are given in Table 7 and shown graphically in Figure 3. The decision criteria used in the tiered analysis procedure (Figure 1) specifies that oil extracted from the drilling mud by Method 1662 is mineral oil, if the PAH content in the oil by Method 1654A is less than 0.35 percent weight. Otherwise, the extracted oil may be diesel or crude oil.

The mineral oil spiked muds showed less than 0.35 percent PAH by four of six laboratories. Two laboratories, B and D, reported PAH contents of 2.65 percent and 0.38 percent, respectively. Four of the six laboratories would thus have clearly and correctly identified the oil in this mud to be mineral oil. Laboratories B and D would have false positively identified the oil as diesel oil or crude oil. Duplicate PAH values by Laboratory D for the mineral oil spiked mud were 0.20 and 0.56 percent, which were outside the precision criteria of the method. Repeat analyses of this sample should thus have been performed. In an environmental monitoring situation, false positives for diesel oil would likely be further scrutinized with repeat analyses for verification.

The diesel oil spiked mud samples showed higher PAH contents than mineral oil spiked mud samples in every case. The mean interlaboratory value was 3.3 percent PAH for the diesel oil spiked samples. Five of six laboratories reported PAH in oil values greater than 0.35 percent for diesel spiked samples. Laboratory C reported 0.32 percent, a value which was essentially at the criteria concentration of the method. These laboratories thus would have correctly identified the oil in this mud to be diesel oil (or crude oil).

For the crude oil spiked muds, four of the six laboratories reported greater than 0.35 percent PAH in oil values. In these cases, the crude oil would be correctly identified as "not mineral oil," and Method 1663 would then be used to determine that the oil is not diesel oil. Laboratories C and E reported 0.23 percent PAH and 0.15 percent PAH, respectively for these mud samples. These two laboratories would thus have incorrectly identified the crude oil in this mud sample as mineral oil, but no error in diesel oil identification would have been made.

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An important observation is that low recovery of extractables by Method 1662 did not correlate with or result in low PAH recovery by Method 1654A. That is, PAH contents greater than the 0.35 percent decision criteria were correctly found for diesel spiked muds, even when low recoveries for extractables in these muds were obtained by Method 1662.

		Method 1	654A (% Wt. P.	AH in Oil)		
	M + Mineral		M + Diesel		M + Crude	
Run #	1	2	1	2	1	2
		(RPD	Acceptance =	44%)	•	
LABORATO	RY					
A	0.20	0.17	2.85	2.54	1.09	1.24
В	2.9	2.4	3.9	3.7	4.9	5.8
С	0.03	0.22	0.36	0.29	0.35	0.11
D	0.20	0.56	2.86	2.61	1.78	1.77
E	0.07	0.07	7.71	6.55	0.12	0.18
F	0.25	0.17	5.26	3.10 2.68	1.36	1.34 1.90

Table 9. Duplicate results of spiked drilling muds (Method 1654A)





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### Method 1663

Results by GC-FID with Method 1663 are given in Table 7 and shown graphically in Figure 4. All laboratories reported less than 1.2 percent weight  $C_{25}$ - $C_{30}$  n-alkane concentrations for the mineral oil and diesel oil spiked samples. The 1.2 percent concentration level for  $C_{25}$ - $C_{30}$  n-alkanes is the decision criteria used in the tiered analysis procedure to differentiate diesel oil and crude oil (Figure 1.). The interlaboratory mean value and range for laboratories A, D, E, and F was 5.6 (1.5 - 6.1) percent  $C_{25}$ - $C_{30}$  n-alkanes for the crude oil spiked samples. Laboratories B and C reported less than 1.2 percent n-alkanes for these samples.

Again, an important observation is that low recovery of extractables by Method 1662 did not correlate with or result in low  $C_{25}$ - $C_{30}$  percent n-alkanes by Method 1663. That is,  $C_{25}$ - $C_{30}$  n-alkanes concentrations greater than the 1.2 percent decision criteria were correctly found for crude oil spiked muds, even when low recoveries for extractables in these muds were obtained by Method 1662.

Method 1663 (% Wt. C <sub>25</sub> -C <sub>30</sub> )							
	M + Mineral		M + I	M + Diesel		M + Crude	
Run #	11	2	1	2	1	2	
(RPD Acceptance = 16%)							
LABORATORY							
A	<1.00	<1.00	<1.00	<1.00	1.57	1.51	
В	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	
С	<1.20	<1.20	<1.20	<1.20	<1.20	<1.20	
D	<1.00	<1.00	0.60	0.60	8.50	6.50	
E	<1.00	<1.00	<1.00	<1.00	6.80	7.30	
F	<1.00	<1.00	<1.00	<1.00	3.70	3.70 11.0	

 Table 10.
 Duplicate results of spiked drilling muds (Method 1663)

#### **Duplicates Results**

Duplicate values data and QA acceptance criteria for the spiked drilling mud samples are given for each method in Tables 7 through 10, respectively. Precision of duplicates data was in the acceptable range for most analyses. Results which were outside duplicate precision criteria were as follows: laboratory C data (by Method 1662 and Method 1654A) for the mineral oil and crude oil spiked muds; laboratory D



Figure 4.  $C_{25}$ - $C_{30}$  in Oil by Method 1663 (%  $nC_{25}$ - $nC_{30}/C_9$ - $C_{30}$  n-Alkanes)

data (by Method 1654A) for the mineral oil spiked mud, and crude oil spiked mud (by Method 1663); laboratory F data (by Method 1654A) for the diesel oil spiked mud, and crude oil spiked mud (by Method 1663).

### COMMENTS OFFERED BY STUDY PARTICIPANTS

Narrative comments concerning the methods were reported by the laboratory participants with their results. These comments are given in Appendix C. During the course of the study some laboratory problems were encountered with the methods procedures, as written, which required method modifications and correction. Solvent incompatibilities among Methods 1662, 1654A, and 1663, required a more thorough solvent exchange procedure with acetonitrile to assure that large amounts of toluene do not interfere in the measurement of PAHs. A solvent change from hexane to methylene chloride was required so that standards are miscible in acetonitrile in

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Method 1663. A memorandum of March 4, 1993 (also given in Appendix C.) was issued by the EPA Sample Control Center (DynCorp-Viar) to all study participants addressing the technical issues requiring correction, so that the interlaboratory study could be completed. Errata sheets for Method 1662, 1654A, and 1663 were included in the memorandum. The EPA Sample Control Center reported in the memorandum that the corrections will be incorporated into an updated version of these EPA methods.

Another procedure issue raised by some of the study participants concerned the slow percolation of toluene through the sample in the Soxhlet/Dean-Stark extraction of Method 1662. In this case, the method may be improved by clarifying the written procedure to instruct that the mixture of mud sample and quartz sand is to be placed on top of 50 gram of quartz sand in a cellulose thimble for the extraction.

Editorial corrections in Method 1654A include changing a reference in Equation 3 from "Section 11.5.5 of Method 1662" to "Section 10.5.5 of Method 1662." Table 1 of Method 1654A requires units corrections from "mg/ml" to "ug/ml" for PAH in diesel oil, and a label clarification concerning "Diesel oil in Mud Extract" or "PAH in Mud Extract." The detection limit of 0.76 percent weight shown in the Table is not appropriate for the 0.35 percent weight decision criteria used in the tiered analysis procedure. The 1/5 factor in Equation 3 should be changed to 1/4.

#### Section 4

#### CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are made from this interlaboratory study of EPA Methods 1662, 1654A, and 1663:

- All the laboratory participants in this study were able to carry out the analytical test procedures, once the procedural problems, which were discussed in the above Section and Appendix C of this report, were addressed, corrected, and communicated by the EPA Sample Control Center to the laboratory participants.
- All laboratory participants were able to meet the initial precision and recovery QA acceptance criteria for the methods. Laboratory E reported that losses of analyte occurred in the procedure where the sample extracts are concentrated to eliminate chromatographic interference caused by the toluene solvent.
- The analytical results for the oil spiked drilling mud samples showed measurable interlaboratory variabilities.
- The mean and range of recovery values by Method 1662 for each mud was 70 (18 - 153) percent for the mineral oil spiked mud, 83 (29 - 200) percent for the diesel oil spiked mud, and 66 (24 - 82) percent for the crude oil spiked mud.
- The mineral oil spiked muds showed less than 0.35 percent PAH by Method 1654A by all laboratories except B and D, which reported 2.65 and 0.38 percent, respectively. Four of the six laboratories would thus have correctly identified the oil in this mud to be mineral oil. The duplicate PAH values by Laboratory D for this mud sample were 0.20 and 0.56 percent, which were outside the precision criteria of the method. Repeat analyses of this sample should thus have been performed.
- The diesel oil spiked mud samples showed higher PAH contents than mineral oil spiked mud samples in every case. The mean interlaboratory value was 3.3 percent PAH for the diesel oil spiked samples. Five of six laboratories reported PAH in oil values greater than 0.35 percent for diesel oil spiked samples. These laboratories would thus have correctly identified the oil in this mud as diesel oil (or crude oil). A value of 0.32 percent, which is essentially at the criteria concentration of the method, was reported by the sixth laboratory.
- Four of six laboratories reported greater than 1.2 percent weight C<sub>25</sub>-C<sub>30</sub> n-alkane concentrations by Method 1663 for the crude oil spiked samples. The interlaboratory mean value and range for laboratories A, D, E, F was 5.6

(1.5 - 6.1) percent. Laboratories B and C would not have differentiated diesel oil and crude oil by Method 1663. All laboratories reported less than 1.2 percent values for the mineral oil and diesel oil spiked samples.

- Low recovery of extractables by Method 1662 did not correlate with or result in low PAH recovery by Method 1654A, or low C<sub>25</sub>-C<sub>30</sub> percent n-alkanes by Method 1663. That is, PAH contents greater than the 0.35 percent decision criteria were correctly found for diesel spiked muds, even when low recoveries for extractables in these muds were obtained by Method 1662. Likewise, C<sub>25</sub>-C<sub>30</sub> n-alkanes concentrations greater than the 1.2 percent decision criteria were correctly found for crude oil spiked muds, even when low recoveries for extractables in these muds were obtained by Method 1662.
- Additional editorial corrections, laboratory procedure instructions, and method detection limit clarifications, as discussed in the above Section and Appendix C of this report, need to be made in the methods revisions.
- EPA Sample Control Center has reported that method corrections will be incorporated into an updated version of these EPA methods.

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#### REFERENCE LIST

40 CFR Part 435 (58 FR 12454-12512, No. 41, March 4, 1993).

EPA. 1992. Methods for the Determination of Diesel, Mineral, and Crude Oils in Offshore Oil and Gas Industry Discharges, EPA-821-R-92-008.

Raia, J.C. 1992. *Results of the API Study of Extraction and Analysis Procedures for the Determination of Diesel Oil in Drilling Muds*. Final Report, American Petroleum Institute, Offshore Guidelines Steering Committee, Technology Work Group, Report Prepared by Shell Development Company, Houston, Texas, April 8, 1992.

Benjamin, Ronald. 1992. *Polycyclic Aromatic Hydrocarbon and Normal Alkane Distributions in Diesel, Crude, and Mineral Oils: A Comparative Study*, Volumes 1 and 2, American Petroleum Institute, Technology Work Group, Offshore Effluent Guidelines Task Force, Report Prepared by Core Laboratories, Lafayette, LA, January 10, 1992.

Weintritt, D.J. 1989. *The Analysis of Drilling Fluids and Cuttings from 14 Offshore Drilling Sites*. Final Report, Weintritt Testing Laboratories, March 31, 1989.

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### APPENDIX A

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# PREPARATION OF DRILLING MUDS MEMORANDUM

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APR 2 0 1993



February 26, 1993

**Business Confidential** 

Dr. Dan Caudle Conoco, Inc. P.O.Box 2197 Houston, TX 77252

Subject: Report on the preparation and composition of drilling muds for validation of Methods 1662, 1654A, and 1663.

Dear Dan:

As per letters of 12/15/92 and 02/02/93 from Ms. Alexis Steen, American Petroleum Institute, thirty barrels of a 12 lb/gal seawater/ lignosulfonate drilling fluid was prepared and tested according to API recommended practices.

Composition:

Seawater	288.2	CC
Bentonite	40	g
Spersene	6	ģ
Drispac Reg	1	ģ
Caustic Soda	1-2	ġ
Barite	130	ġ
Rev Dust	40	ġ

The prepared drilling fluid was used to prepare hot-rolled drilling mud samples in the minimum quantities and containing the oils at the concentrations listed below:

<u>Ouantity</u>	<u>Dil Added</u>	<u>Concentration Added</u>		
1 x 1 pt	No added oil	0		
8 x 1 pt	Mineral Oil (Conoco LVT 200)	0.2 - 0.3 percent		
8 x 1 pt	Diesel Oil	0.2 - 0.3 percent		
8 x 1 pt	Crude Oil (Conoco, Lafayette)	0.2 - 0.3 percent		

The individual mud samples were contained in glass 500 mL bottles w/Teflon lined lids and refrigerated from the time of hotrolling. The samples were then packaged with blue ice in styrofoam containers within boxes and shipped Priority Overnight via Federal Express to the laboratories designated by API and EPA. Six sets of samples were shipped to the testing laboratories and two sets kept as backup. (It was originally intended that eight

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February 26, 1993 Dr. Dan Caudle

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sets of samples be tested; however, EPA Sample Control Center designated only three labs in addition to the three selected by API.) As requested by Sample Control Center, a 1 mL diesel standard was sent with each set of samples. The sample numbers given each sample were those designated by Sample Control Center. The samples were shipped February 17, 1993, and, according to Sample Control, received in good condition.

To laboratories performing analyses we recommend the following procedure:

- 1. Warm the sample up to room temperature.
- 2. Drop in a bar magnet and place the drilling fluid sample on a magnetic stirrer. Apply enough power to generate a vortex but not enough to trap air. Stir for 5 minutes.
- 3. While in <u>gentle agitation</u> on the magnetic stirrer, withdraw the volume required for the test with a disposable syringe.
- 4. Proceed with the protocol as instructed in EPA Bulletin

#### DISCUSSION OF MUD PREPARATION AND OUALITY CONTROL

Mud properties at time 0.3 volume % hydrocarbon contaminant was mixed into each eight sample lot was as follows:

Density, lb/gal	12.0
Plastic Viscosity, cp	50
Yield Point, 1b/100 ft <sup>3</sup>	32
Gel Strength, 1b/100 ft <sup>2</sup>	5/2
DH	10.5

The concentration of oil added was kept in the high range of the suggested 0.2 - 0.3 percent in order to get a more accurate reading on the 50 ml retort.

A consistent mixing and sampling routine was used to assure that each lot of samples was of uniform composition.

Ten (10) barrels (350 ml ea) containing 0.3 vol % oil was continuously stirred in a Nalgene beaker with a slow speed stirrer (to minimize air entrapment, partitioning of immiscible liquids or settling of barite).

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February 26, 1993 Dr. Dan Caudle

A number of 100 ml aliquots was removed from the beaker while the drilling mud was continuously stirred and evenly distributed in the eight (8) sample bottles. This was repeated until about 300 ml of homogeneous sample was collected in each container.

A 50 ml retort with the receiver calibrated to 0.1 ml was used before and after the samples were transferred to bottles prior to shipment to verify consistency in mud composition and oil content. Results were as follow:

VOLUME & OIL From Single		
0.0	-	
0.3	0.3	
0.3	0.3	
0.3	0.3	
	VOLUME <u>From 10 bbl Batch</u> 0.0 0.3 0.3 0.3 0.3	

Sincerely,

Don Wein

Donald J. Weintritt President

cc: Ms. Alexis Steen, API

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SAMPLE NUMBER AND LABORATORY ASSIGNMENTS



## Sample Number and Corresponding Laboratory Assignments for the Offshore Oil and Gas Methods 1662, 1654A, and 1663 Validation Study-Episode 4461

Sample number range:	23697-23721			
Lab Name	Blank	Mineral	Diesel	Crude
Core	23697	23698	23706	23714
Southern Petr.		23699	23707	23715
MI Drilling		23700	23708	23716
Analytical Tech.		23701	23709	23717
Commonwealth		23702	23710	23718
Pacific		23703	23711	23719
No Lab <sup>*</sup>		23704	23712	23720
No Lab <sup>*</sup>		23705	23713	23721

\*These aliquots with no laboratory assignments will serve as back up samples.

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# EPA ANALYTICAL SERVICES REQUEST FORM

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U.S. ENVIRONMENTAL PROTECTION AGENCY EAD Sample Control Center P. O. Box 1407 - Alexandria, VA 22313 Phone: 703/557-5040 - FTS/557-5040

SAS Number 1214 Episode 4461

SECTION 1 Special Analytical Services Analytical Services Request

A. EPA Client: HQ OST-EAD

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B. Project Officer or Designate: Bill Telliard

C. Telephone Number: 202/260-5131

D. Date of Request: December 21, 1992

E. Study Name: Draft Methods 1662, 1654A, and 1663 Validation Study

The analytical data provided under this Special Analytical Service (SAS) will be used by the EPA to develop industrial discharge regulations which govern the disposal of specified compounds from industrial sources. The contracted laboratory's strict adherence to the required analytical methods and quality control procedures is essential to assure data validity for this use. The contracted laboratory shall adhere to the Quality Assurance/Quality Control (QA/QC) measures prescribed in this solicitation package, and shall otherwise employ accepted good laboratory practices in all aspects of contract performance.

- 1. General description of analytical service requested: Tiered analysis of sludge samples for various oil content parameters by Draft Methods 1662, 1654A and 1663.
- 2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
  - Approximately three (3) sludge samples to be homogenized and analyzed for various oil content parameters by Draft Method 1662, Draft Method 1654A, and Draft Method 1663. Analyzes will be conducted in a tiered format in the following order: Method 1662, followed by Method 1654A, followed by Method 1663.

The goal of this study is to obtain results for all three samples from at least three or four laboratories. Therefore, it is anticipated that three or four bid lots of three samples will be awarded.

Attachment 1 contains the homogenization procedure for the mud samples. Attachment 2 provides the general instruction for and order of the tiered analyses. Draft Methods 1662, 1654A, and 1663 are included in Appendix B of the attached SOW.

NOTE: EACH OF THE THREE SAMPLES MUST BE ANALYZED IN DUPLICATE.

NOTE: Laboratories who have not completed Draft Method 1662, Draft Method 1654A, or Draft Method 1663 analysis for EAD during the past year must satisfactorily analyze four (4) IPR samples <u>prior to analysis of field samples</u>. The data for these IPR analyses must be <u>faxed to SCC</u> at (703) 684-0610 upon completion. IPR data shall also be submitted with the data package. These IPR samples are non-billable.

 Purpose of analysis (specify whether CWA (Guideline development, review or NPDES compliance monitoring), Superfund (enforcement or remedial action), RCRA, etc.): CWA Offshore Oil and Gas Industry Study.

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- 4. Estimated date(s) of collection: Samples have already been collected and will be shipped to the laboratory upon award.
- Estimated date(s) and method of shipment: Samples will be sent via overnight air. A Saturday delivery is
  possible for this Episode. Laboratory personnel must be available to receive Saturday deliveries.
- 6. Number of days analysis and data required after laboratory receipt of samples: 30 day data turnaround from receipt of last sample at lab. Lab must adhere to analytical holding times as stated in the methods.
- 7. Analytical protocol required (attach copy if other than a protocol currently used in this program):
  - o Procedure for Homogenization of Muds (Attachment 1)
  - Figure 1-Differentiation of Diesel, Mineral, and Crude Oil by SDS Extraction, HPLC/UV, and GC/FID using Methods 1662, 1654A, and 1663, respectively (Attachment 2)
  - Draft Method 1662-Total Extractable Material in Drilling Mud by SDS Extraction and Gravimetry (Appendix B of the attached SOW)
  - Draft Method 1654A-PAH Content of Oil by HPLC/UV (Appendix B of the attached SOW)
  - Draft Method 1663-Differentiation of Diesel and Crude Oil by GC/FID (Appendix B of the attached SOW)
- Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):
  - ALL SAMPLES MUST BE PREPARED USING THE HOMOGENIZATION PROCEDURE FOR MUDS, WHICH IS PROVIDED AS ATTACHMENT 1.
  - SAMPLES MUST BE ANALYZED FOLLOWING THE TIERED ORDER AND INSTRUCTIONS PRESENTED IN ATTACHMENT 2.
  - EACH OF THE SAMPLES MUST BE ANALYZED IN DUPLICATE. THE LAB MUST REPORT A SEPARATE VALUE FOR EACH OF THE DUPLICATE ANALYSES FOR EACH OF THE METHODS.
- Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:
  - Laboratories must submit data on the Reporting Forms included in the attached SOW.
  - Laboratories must submit summary data in electronic format in a DBase or ASCII text format. SCC will provide a diskette with the appropriate format to the laboratory upon award.
  - Laboratory must report a separate value for each of the duplicate analyses for each of the methods.
  - a) A narrative that details any problems with or deviations from the referenced methods and reports problems associated with the analysis of specific samples. The narrative should also provide comments on the method(s) performance on various analytes and matrices. In the event of a failure of a particular sample the narrative should offer reasons and/or recommendations.
  - b) A list of samples received vs. those analyzed, and a run chronology.
  - c) Summary reports of all sample and QA/QC analyses.

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- d) Raw data chromatograms, quantitation reports, strip charts, etc.
- e) Three summary data packages and one raw data package. Data packages must be paginated.
- 10. Other (use additional sheets or attach supplementary information, as needed):
- 11. Name of sampling/shipping contact:

Phone:

12. Data Requirements

Parameter

**Detection Limit** 

Precision Desired (+/- or Concentration)

Per referenced methods and Item 8 above.

Note: The calculations performed by the laboratory in generating sample data must be able to be reproduced by a 3rd party from the data package.

13. QC Requirements

The following minimum QC requirements are to be met for the analyses of the parameters listed in Item 7 (in addition to any QC described in the methods EXCEPT for the analysis of Matrix Spikes):

- <u>Initial Precision and Recovery</u> samples shall be analyzed prior to the analysis of field samples. QA/QC limits are stated in the methods.
- Ongoing Precision and Recovery samples shall be extracted and concentrated with each batch of samples. A batch is comprised of samples started through the extraction and concentration process at the same time, to a maximum of ten samples. QA/QC limits are stated in the methods.
- <u>Duplicate analyses</u> are required for ALL samples. QA/QC limits are stated in the methods.
- <u>Method Blanks</u> are required at a frequency of one per ten samples. The laboratory is required to use a reference matrix for this analysis. The QA/QC limits are stated in the methods. NOTE: A METHOD BLANK MUST BE RUN WITH THE IPR SAMPLES.
- Instrument Calibration shall be confirmed through the use of Initial and Continuing Calibration Verification Standards. The QA/QC limits are stated in the methods.
- NOTE: Matrix spikes are NOT required.

All other QC (except matrix spikes) listed in the methods must be performed.

Note: QC samples are not billable under this program. All data are subject to final technical review and acceptance by Viar and the EAD EPA Project Officer

14. Action Required if Limits are Exceeded

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Contact Carrie Ruswell immediately at 703/519-1385.

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ATTACHMENT 1

#### Homogenization of Drilling Muds 28 October 1992 Draft

- 1. Scope and Application: This procedure is for homogenization of drilling mud samples received by the laboratory. During shipment and storage, drilling mud samples may stratify. These samples must therefore be homogenized before an aliquot is taken for analysis.
- 2. Receipt of Drilling Mud Samples: Mud samples may be received in pint jars, cosmetic jars, mayonnaise jars, Mason jars, or other forms of sample containers. Mud samples are to be refrigerated until the time of the analysis. At that time, the samples are brought to room temperature before homogenization.

#### 3. Apparatus:

- 3.1 Sterling Multi-products Model 93 Multi-mixer or Hamilton Beach Model 936-2 (or equivalent), operable to 2000 rpm, with disk mixing blade.
- 3.2 Variac or equivalent for controlling the speed of the mixer.
- 4. Homogenization

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- 4.1 Bring the sample to room temperature.
- 4.2 Shake the bottle for 1 2 minutes to mix the layers.
- 4.3 Remove the lid and, using a spoon or spatula, scrape all mud from the underside of the lid and add to the sample container.
- 4.4 If there is insufficient room in the sample container to operate the homogenizer without the mud overflowing the container, proceed as follows:
  - 4.4.1 Using a spoon, spatula, or by pouring, remove a sufficient amount (but no more than half) of the sample from the sample container to allow homogenization of the remaining sample. Place the portion removed in a jar large enough to allow homogenization of the entire sample.
  - 4.4.2 Homogenize the portion remaining in the original sample container per steps 4.5 4.6.
  - 4.4.3 Transfer the remaining sample from the original container to the larger container, scraping the sides with the spoon or spatula to transfer all of the mud to the larger container.
  - 4.4.4 Homogenize the total sample in the larger container per steps 4.5 4.6.
- 4.5 Insert the mixing blade into the mud to a depth approximately one inch from the bottom.
- 4.6 Slowly increase the speed until 2000 rpm is reached. Mix for approximately five minutes at 2000 rpm. Turn mixer off and remove from the mud.

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4.7 Immediately remove the aliquot required for testing.

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# ATTACHMENT 2

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METHOD 1662

SDS EXTRACTION

ROTOVAP TO APPROX 1 mL

ADJUST VOLUME TO 5.0 mL WITH ACETONITRILE

SPLIT 1.0 mL FOR HPLC/UV & GCFID

EVAPORATE 4.0 mL TO DRYNESS WITH NITROGEN BLOWDOWN

DETERMINE TOTAL OIL IN 4.0 mL PORTION BY GRAVIMETRY

METHOD 1654A

DETERMINE PAH CONTENT OF 1.0 mL PORTION BY HPLC/UV

IF PAH CONTENT <0.35 WT \$, OIL IS MINERAL OIL

IF PAH CONTENT >0.35 WT \$, OIL MAY BE DIESEL OR CRUDE

METHOD 1663

DETERMINE N-ALKANE PATTERN OF 1.0 mL PORTION BY GC/FID IF <10 N-ALKANES PRESENT IN C9 - C24 RANGE & S/N >5, NO DIESEL IF N-ALKANES PRESENT IN C9 - C30 RANGE & C25 - C30 N-ALKANES >1.2 % OF TOTAL C9 - C30 N-ALKANES, OIL IS CRUDE OIL

Figure 1 - Differentiation of Diesel, Mineral, and Crude Oil by SDS Extraction, HPLC/UV, and GC/FID Using Methods 1662, 1654A, and 1663, Respectively

ot for Resale

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API LAB SELECTION MEMORANDUM

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American Petroleum Institute 1220 L Street, Northwest Washington, D.C. 20005

Alexis E. Steen, M.S. Senior Environmental Scientist (202) 682-8339

December 15, 1992

Earlene Broussard Weintritt Consulting Services 305 Guidry Road Lafayette, LA 70503-5603

Dear Ms. Broussard:

API has three laboratories that will be participating in the EPA interlaboratory validation study of Methods 1662, 1654A, and 1663 on drilling muds containing oils. The addresses and contact names for the three laboratories are below:

- 1. Lawrence Scott CORE Laboratories, Inc. 8210 Mosley Road Houston, TX 77075 713-943-9776
- 2. Ronald Benjamin Southern Petroleum Laboratory 500 Ambassador Caffery Parkway Scott, LA 70583-8544 318-984-2374
- 3. Marc Churan M-I Drilling Fluids Company 5950 North Course Drive Houston, TX 77072 713-561-1507

EPA will be selecting up to five participating laboratories for a total of eight organizations to which drilling mud samples will be shipped. EPA's contractor, VIAR, is coordinating the EPA laboratory selections. You will be contacted soon by Ms. Carrie Buswell/VIAR (703-519-1385) regarding the status of the validation study logistics.

An equal opportunity employer

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Letter to Earlene Broussard

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December 15, 1992

As we discussed last week, VIAR hopes to have the EPA laboratories selected by 11 December (at the earliest). Ms. Buswell indicated that VIAR is also designing a new data reporting form which will include laboratory QA/QC information. Please provide me a copy of any Weintritt correspondence with VIAR, and contact me should there be any questions.

Happy Holidays.

Sincerely,

alice Stem

Alexis Steen

CC:

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J. Shaw/API J. Ray/Shell J. Raia/Shell D. Caudle/Conoco C. Buswell/VIAR

Diesel Oil in Drilling Muds Round-Robin Contract File

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EPA INTERLABORATORY STUDY REQUEST MEMORANDUM

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OCT 5 .992

WATER

Mr Dan Caudle Conoco Inc PO Box 2197 Houston TX 77252

Dear Mr Caudle

EPA requests the assistance of the Offshore Operators Committee (OOC) of the American Petroleum Institute (API) in the preparation and distribution of drilling mud samples and in providing industry laboratories or laboratories under contract to API or its member companies for an interlaboratory study for validation of EPA Methods 1662, 1654A, and 1663.

#### Drilling Mud Samples

Please prepare hot-rolled drilling mud samples in the minimum quantities and containing the oils at the concentrations listed in the table below:

2	uar	nt:	ity	Oil added	Concentration added
1	X	1	pt	No added oil	0
8	X	1	pt	Mineral oil	0.2 - 0.3 percent
8	x	1	pt	Diesel oil	0.2 - 0.3 percent
8	X	1	pt	Crude oil	0.2 - 0.3 percent

The exact concentration in the 0.2 - 0.3 percent range is to be selected by the OOC and kept confidential until the study is completed. The individual mud samples should be contained in glass 500 mL bottles with Teflon lined lids and should be refrigerated from the time of rolling. Care should be taken to assure that the samples are as uniform as possible. The bottles should be ready for shipment by November 1, 1992.

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#### Laboratories

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Please make a minimum of three laboratories available for the inter-laboratory study. EPA estimates that each laboratory will need to make a minimum of 10 analytical runs, four for an initial precision and recovery (IFR) study to demonstrate proficiency with the methods, and a duplicate pair of analytical runs for each of three mud samples. EPA estimates the cost of the analytical runs at \$600.00. Additional quality control (QC) runs may be necessary but are included in EPA's estimate.

Details of the inter-laboratory study will become available near the end of October, 1992.

If you have questions concerning this request, please call me at 202-260-7134.

Sincerely

W A Telliard, Chief Analytical Methods Staff Engineering and Analysis Division (WH-552)

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## APPENDIX B

## **RESULTS SUMMARY BY DYNCORP-VIAR**

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## RESULTS FOR EPISODE 4461 - INTERLABORATORY STUDY OF METHODS 1662, 16542, AND 1663

Sample	% Solids	Method 1662 Extractable Material	Method 1654A PAH Content	Method 1663 % C25-C30 n-alkanes	
23701 (mineral)	43	0.16 %wt	<b>0.20 %</b> wt	ND	
23701D	44	0.19 %wt	0.17 %wt	ND	
23709 (diesel)	44	0.13 %wt	2.85 %wt	ND	
23709D	44	0.15 %wt	2.54 %wt	ND	
23717 (crude)	43	0.15 %wt	1.09 %wt	1.57	
23717D	43	0.12 %wt	1.24 %wt	1.51	
Blank		< 0.1 %wt	< 0.01 %wt*	ND	

ANALYTICAL TECHNOLOGIES, INC.

\*The laboratory did not report a detection limit. The detection limit reported is the Method 1654A MDL.

ND = Not detected.

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## RESULTS FOR EPISODE 4461 - INTERLABORATORY STUDY OF METHODS 1662, 1654a, AND 1663

#### COMMONWEALTH TECHNOLOGIES, INC.

Sample	% Solids_	Method 1662 Extractable Material	Method 1654A PAH Content	Method 1663 % C25-C30 n-alkanes
23702 (mineral)	<b>9</b> 6	0.24 %wt	2.9 %wt	ND
23702D	78	0.27 %wt	2.4 %wt	ND
23710 (diesel)	98	0.17 %wt	3.9 <b>%</b> wt	ND
23710D	<b>8</b> 6	0.17 %wt	3.7 %wt	ND
23718 (crude)	95	0.14 %wt	4.9 %wt	ND
23718D	98	0.12 %wt	5.8 %wt	ND
Blank		< 0.1 %wt*	< 0.01 %wt*	ND

"The laboratory did not report detection limits. The limits reported are those that are listed in the respective methods.

ND = Not detected.

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#### RESULTS FOR EPISODE 4461 - INTERLABORATORY STUDY OF METHODS 1662, 1654a, AND 1663

### PACIFIC ANALYTICAL, INC.

Sample	% Solids	Method 1662 Extractable Material	Method 1654A PAH Content	Method 1663 % C25-C30 n-alkanes	_
23703 (mineral)	47	0.021 %wt*	0.03 %wt	ND	
23703D		0.087 %wt*	0.22 %wt	ND	
23711 (diesel)	46	0.36 %wt	0.36 %wt	ND	
23711D		0.33 <b>%</b> wt	0.29 %wt	ND	
23719 (crude)	43	0.064 %wt*	0.35 %wt	ND	
23719D		0.23 %wt	0.11 %wt	ND	
Blank		< 0.01 %wt**	< 0.01 %wt	ND	

\*Values reported are below the Method 1662 MDL of 0.1 %wt.

\*\*This laboratory reported detection limit is different from the Method 1662 method detection limit of 0.1 %wt.

ND = Not detected.

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### RESULTS FOR EPISODE 4461 - INTERLABORATORY STUDY OF METHODS 1662, 1654a, AND 1663

### CORE LABORATORIES, TEXAS

Sample	% Solids	Method 1662 Extractable Material	Method 1654A PAH Content	Method 1663 % C25-C30 n-alkanes
23697 (field bland	67.1 «)	0.016 %wt*	0.63 %wt	ND
23697D	<del>6</del> 6.8	0.017 %wt*	0.60 %wt	ND
23698 (mineral)	68.5	0.027 %wt*	0.20 %wt	ND
23698D	67	0.029 %wt*	0.56 %wt	ND
23706 (diesel)	<b>6</b> 6.1	0.045 %wt*	2.86 %wt	0.6
23706D	<b>6</b> 6.5	0.054 %wt*	2.61 %wt	0.6
23714 (crude)	65.2	0.039 %wt*	1.78 %wt	8.5
23714D	65.9	0.043 %wt*	1.77 %wt	6.5
Blank	100	< 0.1 %wt**	< 0.01 %wt	ND

\*Values reported are below the Method 1662 MDL of 0.1 %wt.

\*\*The laboratory did not report a detection limit. The limit reported is the Method 1662 MDL. ND = Not detected.

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### RESULTS FOR EPISODE 4461 - INTERLABORATORY STUDY OF METHODS 1662, 1654a, AND 1663

### SOUTHERN PETROLEUM LABS

	% Solids	Method 1662 Extractable Material	Method 1654A PAH Content	Method 1663 % C25-C30 n-alkanes	
23699 (mineral)	53.3	0.0975 %wt*	0.070 %wt	0.13	
23699D	48.5	0.0763 %wt*	0.070 %wt	0.05	
23707 (diesel)	<b>55</b> .6	0.0616 %wt*	7.71 <b>%</b> wt	0.27	
23707D	51.1	0.0825 %wt*	6.55 %wt	0.22	
23715 (crude)	45.7	0.118 %wt	0.125 %wt	6.8	
23715D	42.8	0.111 %wt	0.184 %wt	7.3	

\*Values reported are below the Method 1662 MDL of 0.1 %wt.

## RESULTS FOR EPISODE 4461 - INTERLABORATORY STUDY OF METHODS 1662, 16542, AND 1663

### MI DRILLING FLUIDS CO.

Sample	% Solids	Method 1662 Extractable Material	Method 1654A PAH Content	Method 1663 % C25-C30 n-alkanes
23700 (mineral)	<b>50</b> .7	0.094 %wt*	0.249 %wt	ND
23700D	51.2	0.107 %wt	0.169 %wt	ND
23708 (diesel)	49.1	0.076 %wt*	5.262 %wt	ND
23708D	49.6	0.089 %wt*	3.096 %wt	ND
23708D	48.2	0.069 %wt*	2.677 %wt	ND
23716 (crude)	49.9	0.108 %wt	1.358 %wt	3.71
23716D	49.8	0.107 %wt	1.341 %wt	11.0
23716D	47.9	0.076 %wt	1.904 %wt	3.70

\*Values reported are below the Method 1662 MDL of 0.1 % wt.

ND = Not detected.

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# APPENDIX C

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## NARRATIVE COMMENTS BY LAB PARTICIPANTS

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#### SAS 1214 Narrative Comments

METHOD 1662

No problems were encountered. Results were calculated using Equation 5 in Method 1662. Since 1 ml of the extract was removed for HPLC and GC analysis, the results were multiplied by 1.25.

#### METHOD 1654A

Blanks showed responses in the PAH retention time window. The responses were relatively low compared to the responses observed for the samples. The blank responses were subtracted from the sample responses when calculating the results.

The following equation was used to calculate results (the equation is not the same as Equation 3 in Method 1654A) :

% PAH in oil = 0.1 [Ve\*Cp/Wr]

where: Ve = volume of extract evaporated in Method 1662 (ml). For these samples Ve = 4.

Cp = Concentration of PAH measured (ug/ml)

Wr = weight of oil in concentration tube from Method 1662(mg).

Calculations are shown on the raw data peak integration reports for each sample.

Sample 23717 contained a significant concentration of unresolved constituents which made quantitation of PAH difficult. The unresolved constituents caused the signal to be elevated at the end of the analysis (signal did not return to original baseline). Since the signal did not return the original baseline, integration of the PAH responses was not clearly defined.

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METHOD 1663

Calculation of the percent C25-C30 n-alkanes were performed using Equation 3.

The internal standard solution used in the analysis of these samples was different than the solution described in Sec. 6.2.1.3. The internal standard solution contained 200 ug/ml of 1,3,5trichlorobenzene dissolved in acetonitrile.

An additional standard was included in the analytical sequence (identified as a diesel range organic standard) which contained the following n-alkanes: C-10,12,14,16,18,20,22,24,26,28. The standard was used to clearly define retention time windows for the n-alkanes.

Sample 23717 was analyzed at two levels of dilution (undiluted and 1:10). The 1:10 dilution results gave responses well above the detection limit for n-alkanes up to C-25. The undiluted extract results revealed C-26 and C-27 peaks which were not detectable in the 1:10 dilution. The undiluted extract results were used for calculations.

C-4

COMMONWEALTH TECHNOLOGY, INC. Environmental and Network Resources Consulting and Amelysical Services

Kentucky Offices
 Lexington
 Louisville

February 25, 1993

TO: Carrie Buswell SCC 300 N. Lee Street Alexandria, VA 22314

\*\*\* VIA FACSIMILE\*\*\*

5C FROM: Shih-Ling Chang

RE: Method 1663 and 1654

1. We believe that there is an error in the quantity of TCB needed for the analysis. We agree that the concentration of normal hydrocarbon recommended (Table 1 in the method and summary table below) but not that of the Internal Standard. The split/splitiess injector is not the issue since two sets of chemicals are introduced simultaneously. If one is higher than our expectation, the other one should be proportionally so, too.

	Concentration of Soluti	Concentration of Solutions for GC Injection	
	Normal Hydrocarbon	Int. Std. (TCB)	int Std./Std.
Method 1662,	10-200 ng/µL	50 <i>µgiµ</i> L	~ 250
CTI Proposal	10-200 ng/µL	100 ng/µL	~ 1

- Hexane is not miscible with acetonitrile at a Hexane/ACN of 10;1 ratio as required by 6.2.3 of method 1663 we believe that the diesel components will be pulled into the hexane layer. However, we fell the method need to address this insolubility and indicate that the hexane layer is to be used for analysis.
- 3. Method 1654: Diesel oil is not very soluble in acetonitrile. We have two fold difficulties:
  - a. The standard of diesel oil at 1.25 mg/mL (Table 2) is not soluble in acetonitrile.
  - b. The addition of toluene is needed to keep diesel in acatonitrile of the sample extract. However, the presence of diesel causes a significant UV background - need advice in the aspect.

I will be in touch with you concerning these issues. Thank you very much.

LABORATORY DIVISION	Ĝ	(606) 276- Fax: (606) 278-
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EPA-SAS No Episode No Sample No CTI Sample No	Date Analyst
Regarding: Method 1654A	Lec. 1992 EL.
Problem Description: $\underline{Typp qraph}$ $\underline{DP.35}$ $\underline{Fo}3$ , $Wr$ $\underline{1662}$ $\underline{9Table 1, P.37}$ $\underline{P}$ Corrective Action Taken: 	<u>ic errors</u> : <u>Here wit 11.5.5 of</u> method <u>AH wits should be upfor</u> 

mit.500 Skiełew. 50/11/02

C-6

PACIFIC ANALYTICAL, INC. 6349 PASED DEL LAGO CARLSBAD, CALIFORNIA 92009

NARRATIVE FOR SAS 1214

Samples:	23703 *	23711	23719
	23703 dup	23711 dup	23719 dus

1. All comments in narrative for IPR samples apply and are not restated in this narrative. IPR narrative is attached.

2. Samples consisted of a suspension of solids and oil in water. The samples were tan colored and grain size was very fine similar to clay. Droplets of what appeared to be oil were visible in the viscous mud.

3. Samples were extracted using method 1662. The mechanical means of homogenizing the samples was used as specified in the method. The duplicate analysis of sample 23711 indicated that the homogenization produced two similar samples. The large RPD values of the measurements for samples 23703 and 23719 indicated that the droplets of oil were not dispersed evenly by the mixing and stirring of these samples. IPR and DPR values were within specifications for these samples.

4. Two Class S weights, 10 mG and 100 mG, were used to check the calibration of the Mettler AE160 balance used to make the measurements for Method 1662. This balance is accurate to 0.1 mG.

5. The results for Method 1663 indicated that two similar sample extracts were produced for sample 23711 by Method 1662. The large RPD value and visual inspection of the chromatograms obtained from the GC/FID analysis of the extracts indicate that the oil content of the duplicate aliquots for 23703 and 23719 were quite different. IPR and DPR values were within specifications for these samples.

6. The results for Method 1654a resulted in good RPD values for all samples. Sample 23711 contained PAHs above 100 uG/Gram. Samples 23703 and 23719 contained only slight traces of PAH's. Detection limits were stated for oil but not for mud. A detection limit of 100 uG/Gram was used for reporting. IPR and OPR values were within specifications for these samples.

7. Calculations for all samples and methods were based on a 25 gram sample. The samples contained 50 to 60 percent moisture. The methods addressed calculations based on oil and not a soil or sludge. Values reported are extract concentration times the final extract volume (including

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splits) divided by the wet sample size. The reported % Solids is from one measurement made on each sample.

8. Method 1663 is not specific about reporting concentrations for diesel so all samples were quantitated in the same way as the IPRs and OPRs.

9. Method 1663, sample 23703 was quantitated, for comparison purposes, as diesel even though there were only 7 peaks in the c10 ... c24 range.

10. Method 1663 day showed several very small peaks in the c25  $\dots$  c30 range which were considered insufficient evidence of crude oil. Expanded chromatograms of the related areas are included.

11. Method 1663: Note that the method does no provide a procedure for identifying the peaks in the c25 .. c30 range as they are not in any standards or check samples.

12. Method 1663: The method is not clear on cetection limit for c25 .. c30 n-alkanes. A value of 1.2% was used.

13. The date of acquisition listed on the raw data is in the British format of Day/Month/Year.

14. The diskette specified in the SAS request to be supplied by SCC for reporting the electronic data has not been received.

Submitted	sy: CS Parson	Date:	20 MAX 93
	C.S.Parsons, Operations	Manager	

# 000002

#### PACIFIC ANALYTICAL. INC.

NARRATIVE FOR SAS 1214 PRECSION AND RECOVERY DATA

METHODS 1654A, 1662; and 1663.

1. Initial Precsion and Recovery (IPP, samples were performed using diesel obtained at a local service station. This is No. 2 diesel. A standard of diesel sent by SCC was broken in route. A replacement has been received and will be used for calibrationfor the samples associated with SAS 1214.

2. Method 1502 was used for sample extraction. The balance used for the gravitametric determination was a Mettler AE160. The balance calibration is verified using 10 gram and 20 gram class S weights. The balance wieghs to an accuracy of 0.0001mG. The requested weights of 10mG and 100mG are being acquired to use on the samples for SAS 1214.

3. Method 1663 was performed using a HP5880 gas chromatograph equiped with a flame photometric detector and a capillary split/splitless injector. The analysis was performed with an initial splitless injection of 0.5 minutes. The linearity of the internal standard at 5000 ppm was verified by analyzing lower concentrations. The internal standard was made up into acetonitrile to spike into the sample extract obtained from the Method 1662 extraction.

4. Method 1654a was performed using an Eldex 9600 tertiary pump. a Spectra Physics autosampler equiped with a 20 uL loop, a Timberline column heater, and an ACS model 750/11 UV-VIS detector with a 254nm filter. The columns used were two 150 x 4.6 mm E18 columns with 300 Angstrom support and a gaurd column.

5. A few problems were noted with Method 1654a when extracts come from Method 1662. The solvent used in method 1662 is toluene. The solvent exchange to acetonitrile leaves varying amounts of toluene in the extract. This shows up in the UV trace at 254nm as a large peakabout 1 minute before naphthalene elutes. This peak is not a problem with pure diesel samples but will pose a problem when trying to integrate the total area of more volatile oils. Integration was performed by projecting the baseline forward under the PAH hump. This resulted in slightly high values in the recovery determined for diesel. The reported average recovery is 109% of the true value. The method limits are 87 to 107 percent. The reported precision is 1 %. The method limit is 10 %.

Date: 28 7.693 ason Submitted by:

C.S. Parsons, Operations Manager

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CORE LABORATORIES

April 5, 1993

Dyncorp Viar Inc. Sample Control Center P. O. Box 1407 Alexandria, Virginia 22313

Attn: William A Telliard

Project: Diesel, Mineral and Crude Oil

Case Narrative

EPA Samples: 23697, 23698, 23706, 23714

Method 1662

The analytical procedure was modified as specified in the errata sheet to eliminate solvent incompatibility between Methods 1662, 1654A and 1663. The diesel sample used for the standard, spikes, OPR and IPR samples was supplied along with the samples.

#### Method 1654A

The analysis was performed as described in the method and errata sheet however some uncertainty was encountered in the reporting requirements. The confusion arises from the fact that several different quantities are calculated and it is unclear which parameters were being requested. These quantities are:

PAH content of the Oil (calculated from phenanthrene response factor and oil recovery.)

Diesel content of the sample (calculated from diesel response factor and sample weight.) Both quantities were reported.

Some problem was also encountered when performing the analysis of method blanks since a small amount of oil was recovered ( less than the acceptable amount) and some UV response was also noted (more than the instrument blank). This led to calculated values for the PAH content of oil greater than 0.5 % and in the range of two of the samples.

------\* \*\*\* \*\* -----





CORE LABORATORIES

Method 1663

The column specified in the method was installed in a chromatograph however it was not possible to achieve the retention times specified in table 3. (A requirement under the note in section 7.1) The chromatographic conditions were set as specified in the method with the exception that it was found to be necessary to go to a final oven temperature of 275 deg. C. in order to elute the C25-C30 hydrocarbons. The resulting resolution was considered sufficient for the analysis and the analysis proceeded using slightly different retention times for the components. Quantitation of the diesel amounts were performed using the internal standard at the concentration specified in the method, however the C25 - C30 peaks amounts in the samples were too close the the detection limit to perform the ratio calculation on the original injections. The split rate was lowered on the GC and the samples reanalyzed. This resulted in an over-range condition on the internal standard (not needed for the ratio calculation) but it did allow for easy integration of the N-paraffin peaks in the C25-C30 range if present.

Larry Scott

Technology Manager

C-11

LAPAYETTE AREA LAR 500 AMBASSADOR CAFFERY PRWY SCDTI LOUISIANA 200 70583 8544 PHONE (318) 237-4775

\*\*\* CASE NARRATIVE \*\*\*

SPL LAB ID NO. X0305103 X0305104 X0305105

EPA EAD EPISODE NO. 4461

Data reported in this study were generated with the following method modifications:

1. Method 1662 - a waterbath controlled at 95 C was used in conjunction with a nitrogen blowdown to evaporate the sample extracts to dryness. This resulted in loss of analyte but precision and recovery measurements met method specified acceptance criteria. A rotary evaporator was not used in the procedure.

1.1. The diesel oil used for QC samples was Laboratory Stock.

2. Method 1654A - Concentration of the sample extract to eliminate interferences caused by toluene in the QC and sample extracts contributed to significant losses of anaylte and therefore low recovery of diesel in the QC samples.

3. Method 1663 - Calculations of percent C25-C30 hydrocarbons used the C10 - C30 range in normalizing the results. The effect on final results is unknown but suspected to be minimal.

SPL, Incorporated

Ron Benjamin Project Manager

C-12
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5950 N COURSE DR P.O BOX 721110 HOUSTON TX 77272 (713) 551-1300 FAX (713) 561-7240

TO: Carrie Buswell

FROM: Marc Churan

COPY TO: Alexis E. Steen Joe Raia // Art Leuterman Roger Bleier DATE: June 24, 1993

SUBJECT: Diesel, Mineral, and Crude Oi in Discharge

The results generated by M-I Drilling Fluids for samples 23700, 23708 and 23716 using Method 1662, Method 1654A, and Method 1663 are summarized in Table I. The required documentation, including HPLC and GC chromatograms, are enclosed with this report. Following the table of results is a narrative and comments sheet.

I apologize for the time it took to get this completed and for any inconvenience it may have caused.

Regards,

Man Clus

Marc Churan Manager, analytical Services



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### NARRATIVE AND COMMENTS

METHOD 1662: Total Extractable Material in Drilling Mud by SDS Extraction and Gravimetry

This lab has only two complete Soxhlet/Dean-Stark Extractors and was limited to running only two extraction at any given time.

Initial extractions using 50 grams of sand in a 25 gram sample (Section 10.1.2) appeared to prevent complete extraction with only a small amount of toluene flowing through the sample after several hours of extraction. Most of the toluene was flowing over the top of the thimble. The wet sample was plugging the frit of the extraction thimble and after 24 hours of extraction the sample still contained water. By adding an additional 40 grams of sand to the sample before extraction the toluene was flowing through the sample and most of the water appeared to have been distilled into the collection receiver. The sample after extraction was mostly wet with toluene but the solids were fairly well cemented together which may have prevented complete extraction.

in section 10.2.2.5 of Method 1662 should the toluene in the Dean-Stark receiver be included in the extract?

The rotary evaporator was operated at approximately 90°C (Section 10.3.1.1). Several samples were lost due to the sample evaporating during the concentration step. The time required for concentration prevented complete monitoring of the evaporation.

Several analyses were done on each sample in an effort to get reproducible results. The reported results are for those analyses that produced similar values.

The diesel oil sample received with the samples was used for all spike recovery analyses.

METHOD 1654A: PAH Content of Oil by HPLC/UV

The only problem was the presence of residual toluene in some samples and the solvent incompatibility which was addressed in the Errata Sheet. The diesel oil and crude oil extracts were not completely soluble in acetonitrile and methylene chloride was required for solubility.

Recovery performance in Table 1 is confusing. Should the recovery be the amount of PAH in diesel or the amount of diesel oil spiked? Also should the units in Table 1 for PAH in diesel oil be mg/mL or  $\mu$ g/mL?

METHOD 1663: Differentiation of Diesel and Crude Oil by GC/FID

This lab used a mass spectrometry detector instead of an FID detector. Our GC/MS was already equipped with the proper column for the analysis and it was more convenient to use our current set up. The recommended temperature programs specified in the method

produced very similar retention times as those in Table 3.

Some samples showed peaks in the C25 to C30 range where as the duplicate analysis did not. This appears to be due to the sample size (amount of oil in the extract) being to low for the smaller peaks to be detected.

Some chromatogram (samples 23700 and 23708) showed C9 to C12 peaks where as duplicate analyses showed no peaks before C12. This would indicate the loss of lighter hydrocarbons during concentration steps.

Section 14.2 in Method 1663 is confusing. To determine the amount of diesel oil should the response factor be that in Section 7.2.2.2 or Section 7.2.3? Also should Equation 4 read "Concentration of oil in sample" or "Concentration of diesel oil in sample"? It is not clear which should be reported. Should the concentration of diesel oil be reported if there are less than ten n-alkane peaks present in the C9 to C24 range?

## COMMENTS:

This test method is to be used to distinguish between diesel, mineral, and crude oil. It does not address the possibility of the synthetic fluids now being used by M-I Drilling Fluids (NOVASOL) and Baroid (Petro-free).

# DYNCORP-VIAR TECHNICAL ISSUES MEMORANDUM



#### MEMORANDUM

- DATE: March 4, 1993
- TO: All laboratories involved in the Methods 1662, 1654A, and 1663 Interlaboratory Study
- FROM: Carrie Buswell (3)
- SUBJECT: Technical issues

Listed below is a summary of the laboratory problems and issues that have been presented to date during the course of this study, along with the appropriate corrective action procedures. An errata sheet is attached that addresses most of these issues. These corrections will eventually be incorporated into an updated version of the associated methods. Please implement these corrections immediately.

If you have already resolved these issues with your own laboratory specific procedure that is different from the corrective procedures cited below, please contact me at (703) 519-1385. I will need to know the specifics of the procedure to determine if it is acceptable.

If any other problems or technical issues are encountered, please inform me as soon as possible so I can ensure that a resolution is obtained and that all other laboratories involved are notified. Your cooperation is greatly appreciated.

#### Summary of Problems Encountered:

- 1) I had arranged for the samplers to send along a diesel oil standard with the shipment of samples. By the time the samples arrived at the laboratories, however, some of the laboratories had already extracted and analyzed the IPRs using their own diesel oil standard. Rather than require the laboratories to reanalyze the IPRs or recalibrate, they have the option of continuing to use the laboratory standard or they can start over with the diesel standard that was sent with the samples. In either case, they need to use either the laboratory standard or the sampler's standard and remain consistent throughout the study. Laboratories should note in the narrative which standard they used.
- 2) Table 2 of Method 1654A is misleading because it lists diesel oil with the three polynuclear aromatic hydrocarbon compounds used in the calibration standard. Diesel oil is not run with the other three compounds. Rather, a single point calibration is required for the diesel oil, independent of the other three compounds, in order to quantitate and determine the recovery of the diesel oil in the IPKs and OPRs from Method 1662.

Resolution: See the errata sheet under Method 1654A, Table 2.

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 In Method 1662, samples are extracted in toluene, concentrated, and brought up in acetonitrile. An aliquot of this sample is split off and used for Method 1654A and 1663 analysis.

A problem arises during Method 1663 analysis when the internal standard, which is made up in bexane, is mixed with the sample extract, which is in acetonitrile (Section 11.2 of Method 1663). Acetonitrile and hexane are immiscible.

Resolution: To correct this situation, laboratories can make up the Method 1663 internal standard and calibration standard in acetonitrile. Alternatively, they can follow the errate sheet procedure for Method 1663.

4) Some laboratories have claimed that the internal standard concentration in Method 1663 is too high, and that it will overload their column. This concentration is required to ensure that no matter what the concentration of crude, mineral, or diesel oil is, the internal standard will not be obscured.

It should also be noted that <u>Method 1663 specifies the use of a split injection GC</u>, and the concentrations of the standards, etc. in this method cater to this instrumentation. Therefore, if the laboratory is not using a GC analytical system with split injection, the concentration of the internal standard will be too high. In this situation, the laboratory has two options.

- a) Make up the internal standard stock solution (which is now made up in acctonitrile) at a lower concentration.
- b) Make up the internal standard stock solution at the method specified concentration, add to equal volumes of the calibration extract or the sample extract as is specified in Sections 6.2.4 and 11.2, respectively, then dilute the combined solutions to an appropriate concentration before injecting into the GC. It is important that the laboratory treat the internal standard, the sample extract, and the calibration standard identically. Any dilutions that are to be made need to be applied to all solutions <u>after</u> the solutions have been combined.

NOTE: Laboratories may use their discretion when choosing a suitable dilution factor. They must, however, make sure that in all circumstances the internal standard is not obscured by any oil that is in the sample. Otherwise, they will need to reanalyze with the internal standard at a higher concentration. If this means that the internal standard stock solution has to be modified, then new IPRs and OPRs must be run, and the samples will need to be reanalyzed.

5) The diesel oil standard does not go into acetonitrile. The mixture turns cloudy.

Resolution: See the errata sheet for Method 1654A and Method 1663.

Alternatively, toluene can be used in place of methylene chloride for the procedures in the errata sheet for Method 1654A, Section 6.2.1.1.1 and Section 10.3.1. The laboratory must demonstrate, however, that the toluene peak does not interfere with the retention time window that is measured.

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6) Residual toluene remains in the Method 1662 sample extract after it is transferred to acetonitrile. This may interfere with the Method 1654A HPLC UV analysis if the toluene peak overlaps with any peaks within the retention time window that is measured.

Resolution: For practical purposes, it is not possible to remove all of the toluene, but the amount of residual toluene may be diminished by following the procedures in the errata sheet for Method 1662.

- NOTE: The electronic deliverable requirement has been waived. Laboratories only need to send in a hardcopy version of the data.
- cc: Alexis Steen, API Dan Caudie, Conoco Bill Telliard, EPA Dale Rushneck, Interface

## ERRATA SHEET

#### Method 1662

This errata sheet modifies Method 1662 to eliminate the solvent incompatibility between Methods 1662, 1654A, and 1663 by adding a more thorough solvent exchange procedure to assure that large amounts of toluene do not interfere in the determination of polynuclear aromatic hydrocarbons (PAH) in Method 1654A. If Method 1662 is used as a stand alone method to determine the extractable material content of mud, this errata sheet is not necessary.

Change Section 10.4.2 to the following:

10.4.2 Extracts to be used in Method 1654A and Method 1663: Remove 1.00 mL with a volumetric pipette, place in a clean, calibrated K-D concentrator tube, and exchange to acetonitrile per Section 10.6.

Add Section 10.6. and Sections 10.6.1 - 10.6.6 as follows:

10.6 Exchange to acetonitrile

10.6.1 Follow steps 10.5.1 - 10.5.3.

10.6.2 Evaporate to near dryness (final volume approximately 50 uL)

10.6.3 Add 100 uL of methylene chloride and 400 uL of acetonitrile to redissolve the oil.

- 10.6.4 Remove with a Pasteur pipette and place in a 2 3 mL amber vial calibrated to 1.00 mL.
- 10.6.5 Using a syringe and small portions of acetonitrile, rinse the inside surface of the K-D concentrator tube and quantitatively transfer to the vial.
- 10.6.6 Seal and store in the dark at -20° to -10° C. Adjust the final volume to 1.00 mL immediately prior to analysis.

## ERRATA SHEET

### Method 1663

This errate sheet modifies Method 1663 to eliminate the solvent incompatibility between Methods 1662, 1654A, and 1663 by changing the solvent in which standards are made from hexane to methylene chloride, so that the standards are miscible in acetonitrile. If Method 1663 is used as a stand alone method to determine the presence of diesel or crude oil in the absence of Method 1654A, this errate sheet is not necessary.

Change Section 6.1 to the following:

6.1 Methylene chloride: ACS grade or equivalent.

Change Section 6.2.1 and Sections 6.2.1.1 - 6.2.1.3 to the following:

- 6.2.1 Stock solutions: Prepare in methylene chloride for injection into the GC. Observe the safety precautions in Section 4.
  - 6.2.1.1 Diesel oil (62.5 mg/mL): If QC extracts from Method 1662 are to be tested, use the oil that was spiked to produce these extracts. Weigh 6.25 g of diesel oil to three significant figures in a 100-mL ground-glass stoppered volumetric flask and fill to the mark with methylene chloride. After the oil is completely dissolved, transfer the solution to a 150-mL bottle with PTFE-lined cap.
  - 6.2.1.2 Normal hydrocarbons-decane  $(C_{12})$ , hexadecane  $(C_{16})$ , and tetracosane  $(C_{24})$ : Dissolve an appropriate amount of reference material in a suitable solvent. For example, weigh 10.0 mg of decane in a 10-mL volumetric flask and fill to the mark with methylene chloride. After the decane is completely dissolved, transfer the solution to a 15-mL vial with PTFE-lined cap.
  - 6.2.1.3 Internal standard: Dissolve 1.0 g of 1,3,5-trichlorobenzene (TCB, Kodak No. 1801 or equivalent) in 100 mL methylene chloride. After the TCB is completely dissolved, transfer the solution to a 150-mL bottle with PTFE-lined cap. Label with the concentration and date. Mark the level of the meniscus on the bottle to detect solvent loss.

Change Section 6.2.3 to the following:

6.2.3 Precision and recovery standard: Dilute the stock solution of diesel oil (Section 6.2.1.1) to produce a concentration of 1.25 mg/mL in methylene chloride. This standard is used for initial precision and recovery (IPR, Section 8.2) and ongoing precision and recovery (OPR, Section 12.5).

Change Section 10.3.1 to the following:

10.3.1 Weigh 100 mg into a 10-mL volumetric flask and dilute to the mark with methylene chloride to produce a concentration of 10 mg/mL. Stopper and mix thoroughly.

Change Section 10.3.2 to the following:

10.3.2 Using a calibrated 1.0-mL volumetric pipette, withdraw 1.0-mL of the solution created in Section 10.3.1 and place in a 10-mL volumetric flask. Then withdraw an additional 0.25 mL of the solution and add it to the 10-mL volumetric flask (for a total of 1.25 mL). Fill to the mark with methylene chloride to produce a concentration of 1.25 mg/mL (1250 ug/mL). This solution will be near, but not above, the limit of the calibration range and will match the concentration of the QC samples from Method 1662 (assuming 100% recovery).

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## ERRATA SHEET

### Method 1654A

This errate sheet modifies Method 1654A to eliminate the solvent incompatibility between Methods 1662, 1654A, and 1663. If Method 1654A is used as a stand alone method to determine the PAH content of oil that is soluble in acetonitrile, this errate sheet is not necessary.

Change Section 6.2.1 to the following:

6.2.1 Stock solutions: Prepare in methylene chloride or methanol and dilute in accontrile for injection into the HPLC. Observe the safety precautions in Section 4.

Change Section 6.2.1.1 to the following and add Sections 6.2.1.1.1 and 6.2.1.1.2:

- 6.2.1.1 Diesel oil solutions
  - 6.2.1.1.1 Stock solution in methylene chloride (62.5 mg/mL): If QC extracts from Method 1662 are to be tested, use the oil that was spiked in that method. Weigh 6.25 g of diesel oil into a 100-mL ground-glass-stoppered volumetric flask and fill to the mark with methylene chloride.
  - 6.2.1.1.2 Diesel oil calibration solution (1.25 mg/mL): After the oil in the stock solution (Section 6.2.1.1.1) is completely dissolved, remove 1.00 mL and place in a 50 mL volumetric flask. Dilute to the mark with acetonitrile. Mix thoroughly and transfer to a clean 150-mL bottle with PTFE-lined cap.

Change Section 6.2.3 to the following:

6.2.3 Precision and recovery standard: The diesel oil calibration solution (Section 6.2.1.1.2) is used for initial precision and recovery (IPR; Section 8.2) and ongoing precision and recovery (OPR; Section 12.6).

Change Section 7.6.2 to the following:

7.6.2 Determine the calibration factor for diesel oil by dividing the integrated area (Section 7.6.1) by the diesel oil concentration (Section 6.2.1.1.2).

Change Section 10.3.1 to the following:

10.3.1 Weigh 100 mg into a 10-mL volumetric flask and dilute to the mark with methylene chloride to produce a concentration of 10 mg/mL. Stopper and mix thoroughly.

Change Table 2 to the following:

Table 2: Draw a horizontal line between Indeno (1,2,3-cd) pyrene and Diesel oil.

Add a double asterisk to Diesel oil in this table (Diesel oil)

Add a footnote at the bottom of the table as follows:

\*\* Diesel oil is calibrated separately using a single point calibration (Section 7.6).

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