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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



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Health and Environmental Sciences Department

API PUBLICATION NUMBER 4611

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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

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

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.

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

"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).

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 $\geq 30,000$ 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.

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.

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

	Extractables in Drilling Muds ^a mg/kg	PAH in Mineral Oils ^b % Wt.	C_{25} - C_{30} in Diesel Oils ^b % Wt.
N	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

^a (Weintritt, 1989)

^b (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.

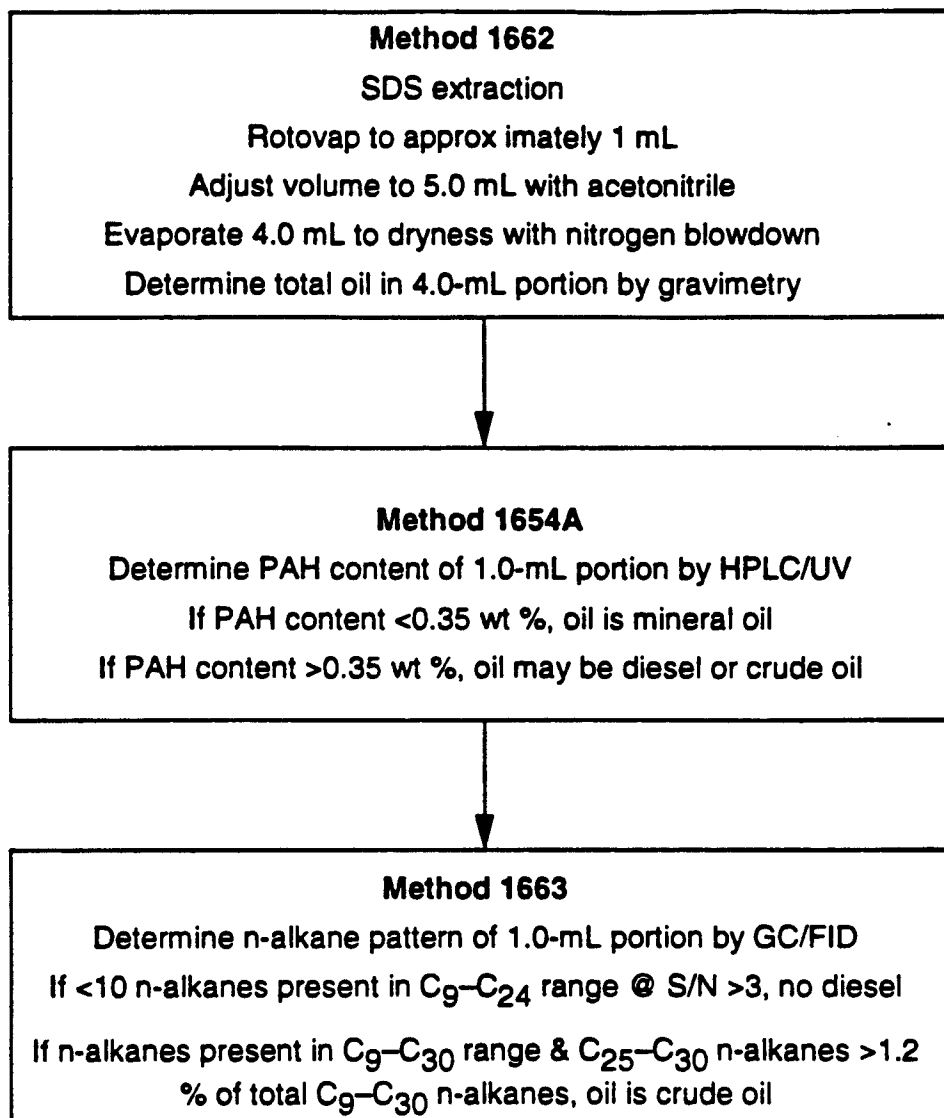


Figure 1. Tiered Analysis by Methods 1662, 1654A, and 1663 (EPA, 1992)

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 n-alkanes 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.

Table 2. Interlaboratory study plan of methods 1662, 1654A, and 1663
Six Laboratory Participants + One Sample Prep Lab

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

^a IPR is Initial Precision & Recovery

^b 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 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.

Table 3. Initial precision and recovery results

LABORATORY	A	B	C	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 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 ₂₅ -C ₃₀)						
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	B	C	D	E	F
% RECOVERY						
Found	88.	75.	80.	72.	64.	96.
Acceptance	----- (47% - 149%) -----					
% RELATIVE S.D.						
Found	9.	13.	10.	22.	12.	4.
Acceptance	----- (34%) -----					

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

LABORATORY	A	B	C	D	E	F
% RECOVERY						
Found	111.	86.	109.	77.	78.	99.
Acceptance	----- (67% - 156%) -----					
% RELATIVE S.D.						
Found	3.	5.	1.	10.	11.	1.
Acceptance	----- (44%) -----					

Table 6. Initial precision & recovery results (Method 1663 - mg/ml C₂₅-C₃₀)

LABORATORY	A	B	C	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.

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

LABORATORY	A	B	C	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 ₂₅ -C ₃₀						
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

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.

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.

Table 8. Duplicate Results of spiked drilling muds (Method 1662)

Method 1662 (% Wt. Extractable Material in Drilling Mud)						
	M + Mineral		M + Diesel		M + Crude	
Run #	1	2	1	2	1	2
(RPD Acceptance = 34%)						
LABORATORY						
A	0.16	0.19	0.13	0.15	0.15	0.12
B	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

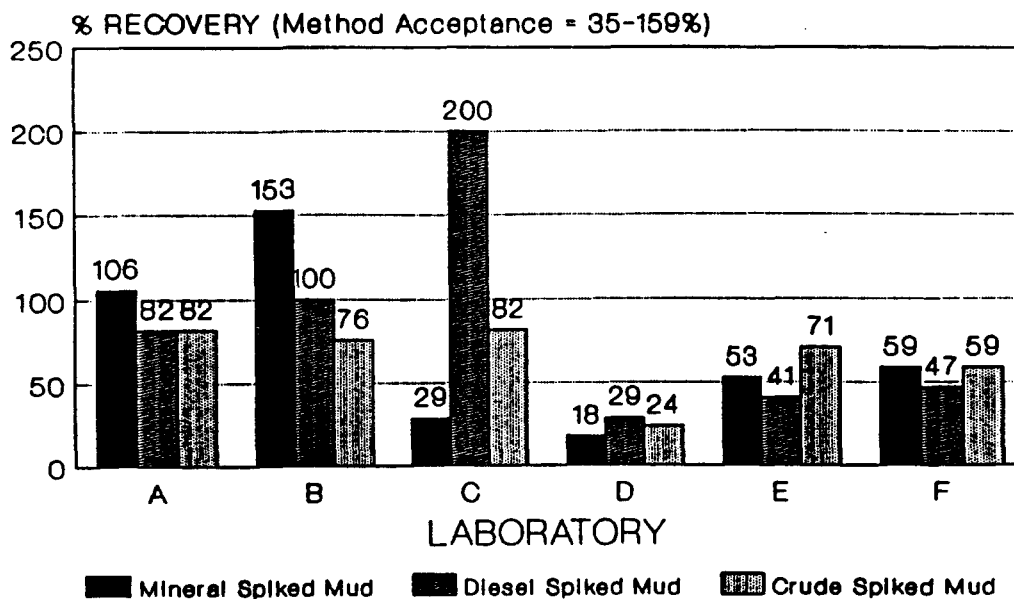


Figure 2. Recovery Results Method 1662
Percent Extractable Oil in Spiked Mud
(Oil Added at 0.3% Volume)

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.

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.

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

Method 1654A (% Wt. PAH in Oil)						
	M + Mineral		M + Diesel		M + Crude	
Run #	1	2	1	2	1	2
(RPD Acceptance = 44%)						
LABORATORY						
A	0.20	0.17	2.85	2.54	1.09	1.24
B	2.9	2.4	3.9	3.7	4.9	5.8
C	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

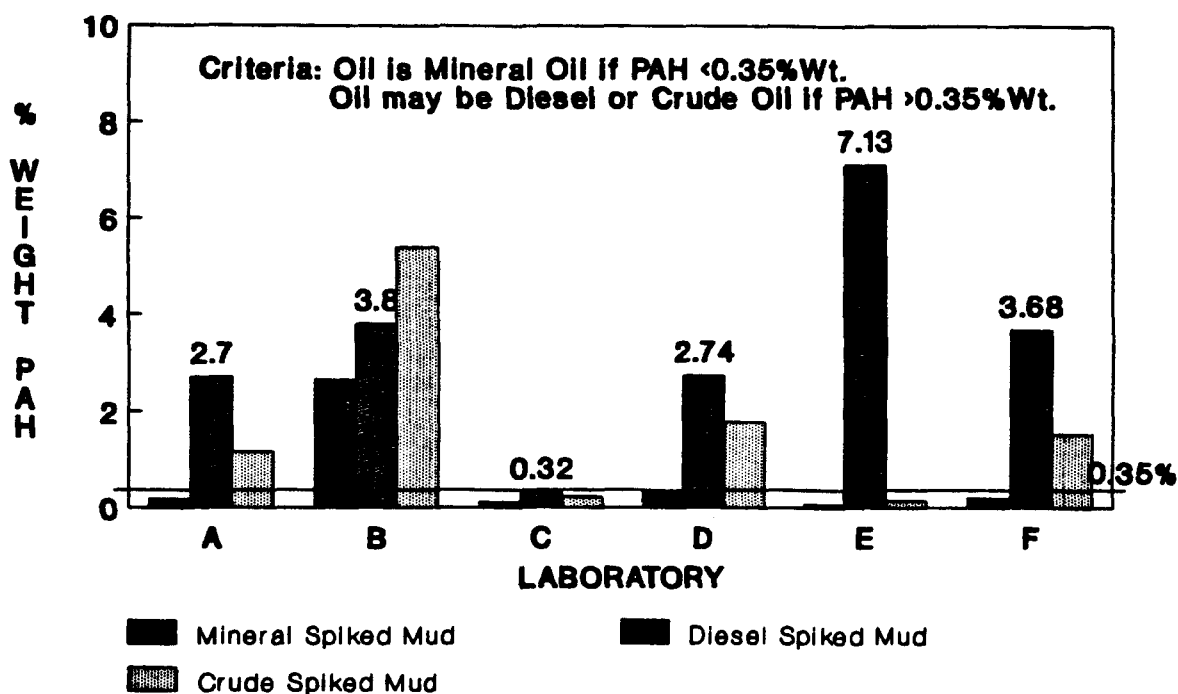


Figure 3. PAH in Oil by Method 1654A
(% Wt. PAH in Oil Extracted from Mud)
(Oil Added at 0.3% Volume)

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.

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

Method 1663 (% Wt. C_{25} - C_{30})						
	M + Mineral		M + Diesel		M + Crude	
Run #	1	2	1	2	1	2
(RPD Acceptance = 16%)						
LABORATORY						
A	<1.00	<1.00	<1.00	<1.00	1.57	1.51
B	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
C	<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

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