Designation: D 4007 – 81 (Reapproved 1995)ε1

An American National Standard

Designation: Manual of Petroleum Measurement Standards Chapter 10.3 (MPMS)

Designation: IP 359/82

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)[1]

This standard is issued under the fixed designation D 4007; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This test method has been approved by the sponsoring committees and accepted by the Cooperating Societies in accordance with established procedures. This method was issued as a joint ASTM-API-IP standard in 1981.

ε[1] NOTE—Editorial changes were made throughout in September 1995.

1. Scope

1.1 This test method describes the laboratory determination of water and sediment in crude oils by means of the centrifuge procedure. This centrifuge method for determining water and sediment in crude oils is not entirely satisfactory. The amount of water detected is almost always lower than the actual water content. When a highly accurate value is required, the revised procedures for water by distillation (Test Method D 4006 (Note 1)) and sediment by extraction (Test Method D 473) must be used.

NOTE 1—Test Method D 4006 has been determined to be the preferred and most accurate method for the determination of water.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see 6.1 and 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 95 Test Method for Water in Petroleum Products and Bituminous Materials by Distillation[2]

D 96 Test Methods for Water and Sediment in Crude Oil by Centrifuge Method (Field Procedure)[2]

D 362 Specification for Industrial Grade Toluene[3]

D 473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method[2]

D 665 Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water[2]

D 1796 Test Method for Water and Sediment in Fuel Oils by the Centrifuge Method (Laboratory Procedure)[2]

D 4006 Test Method for Water in Crude Oil by Distillation[4]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[4]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[4]

2.2 *API Standards:*

MPMS8 "Sampling Petroleum and Petroleum Products"[5]

2.3 *IP Standard:*

Specification for Toluole[6]

3. Summary of Test Method

3.1 Equal volumes of crude oil and water saturated toluene are placed into a cone-shaped centrifuge tube. After centrifugation, the volume of the higher gravity water and sediment layer at the bottom of the tube is read.

4. Significance and Use

4.1 The water and sediment content of crude oil is significant because it can cause corrosion of equipment and problems in processing. A determination of water and sediment content is

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D 02.02 on Static Petroleum Measurement.

Current edition approved March 27, 1981. Published May 1981.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 06.03.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] Available from the American Petroleum Institute, 1220 L St., N.W., Washington, DC 20005.

[6] Available from the Institute of Petroleum, 61 New Cavendish St., London, W.I., England.

required to measure accurately net volumes of actual oil in sales, taxation, exchanges, and custody transfers.

5. Apparatus

5.1 *Centrifuge*:

5.1.1 A centrifuge capable of spinning two or more filled cone-shaped, 203-mm (8-in.) centrifuge tubes at a speed that can be controlled to give a relative centrifugal force (rcf) of a minimum of 600 at the tip of the tubes shall be used.

5.1.2 The revolving head, trunnion rings, and trunnion cups, including the cushions, shall be soundly constructed to withstand the maximum centrifugal force capable of being delivered by the power source. The trunnion cups and cushions shall firmly support the tubes when the centrifuge is in motion. The centrifuge shall be enclosed by a metal shield or case strong enough to eliminate danger if any breakage occurs.

5.1.3 The centrifuge shall be heated and should be controlled thermostatically to avoid unsafe conditions. It should be capable of maintaining the sample temperature during the entire run at 60 ± 3°C (140 ± 5°F).

5.1.4 Electric powered and heated centrifuges must meet all safety requirements for use in hazardous areas.

5.1.5 Calculate the speed of the rotating head in revolutions per minute (r/min) as follows:

$$\text{r/min} = 1335\sqrt{\text{rcf}/d} \quad (1)$$

where:

rcf = relative centrifugal force and

d = diameter of swing measured between tips of opposite tubes when in rotating position, mm, or

$$\text{rpm} = 265\sqrt{\text{rcf}/d} \quad (2)$$

where:

rcf = relative centrifugal force and

d = diameter of swing measured between tips of opposite tubes when in rotating position, in.

5.2 *Centrifuge Tubes*—Each centrifuge tube shall be a 203-mm (8-in.) cone-shaped tube, conforming to dimensions given in Fig. 1 and made of thoroughly annealed glass. The graduations, numbered as shown in Fig. 1, shall be clear and distinct, and the mouth shall be constricted in shape for closure with a cork. Scale error tolerances and the smallest graduations between various calibration marks are given in Table 1 and apply to calibrations made with air-free water at 20°C (68°F), when reading the bottom of the shaded meniscus.

5.3 *Bath*—The bath shall be either a solid metal block bath or a liquid bath of sufficient depth for immersing the centrifuge tube in the vertical position to the 100-mL mark. Means shall be provided for maintaining the temperature at 60 ± 3°C (140 ± 5°F).

NOTE 2—By contractual agreement 49 ± 3°C (120 ± 5°F) may be used.

6. Solvent

6.1 *Toluene* (**Warning**—See Note 3.) conforming to Specification D 362 or to the IP Specification for Toluole.

NOTE 3—**Warning:** Flammable.

6.1.1 Typical characteristics for this material are

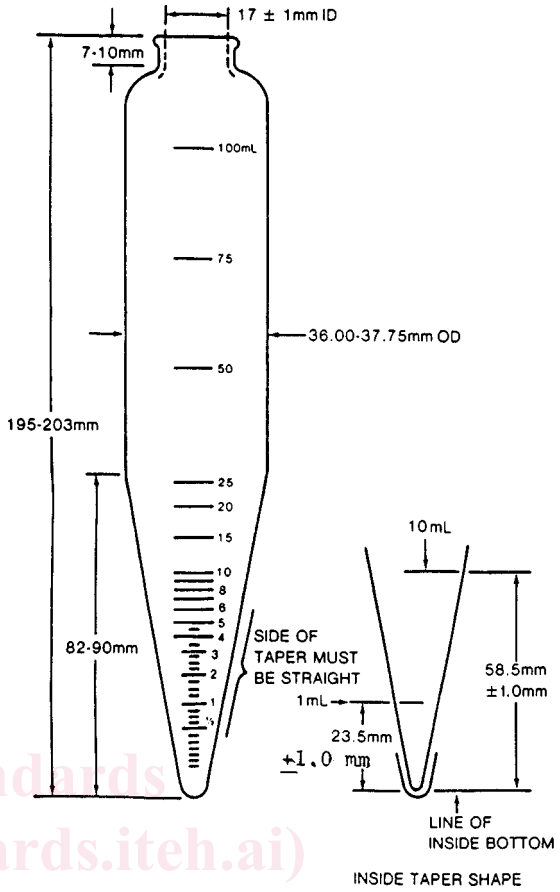

FIG. 1 Eight-Inch (203-mm) Centrifuge Tube

TABLE 1 Centrifuge Tube Calibration Tolerances for 8-in. (203-mm) Tube

Range, mm	Subdivision, mm	Volume Tolerance, mm
0 to 0.1	0.05	±0.02
Above 0.1 to 0.3	0.05	±0.03
Above 0.3 to 0.5	0.05	±0.05
Above 0.5 to 1.0	0.10	±0.05
Above 1.0 to 2.0	0.10	±0.10
Above 2.0 to 3.0	0.20	±0.10
Above 3.0 to 5.0	0.5	±0.20
Above 5.0 to 10	1.0	±0.50
Above 10 to 25	5.0	±1.00
Above 25 to 100	25.0	±1.00

Molecular weight	92.14
Color (APHA)	10
Boiling range (initial to dry point)[A]	2.0°C (36°F)
Residue after evaporation	0.001 %
Substances darkened by H_2SO_4	passes ACS test
Sulfur compounds (as S)	0.003 %

[A] Recorded boiling point 110.6°C

6.1.2 The solvent shall be water-saturated at 60 ± 3°C (140 ± 5°F) (see Note 2) but shall be free of suspended water. See Annex A1 for the solvent-water saturation procedure.

6.2 *Demulsifier*—A demulsifier should be used to promote the separation of water from the sample and to prevent its clinging to the walls of the centrifuge tube. The recommended stock solution is 25 % demulsifier to 75 % toluene. For some crude oils a different ratio of demulsifier to toluene may be required. Demulsifiers used in the concentration and quantity

recommended will not add to the water and sediment volume determined. The solution must be stored in a dark bottle that is tightly closed.

7. Sampling

7.1 Sampling is defined as all steps required to obtain an aliquot of the contents of any pipe, tank, or other system and to place the sample into the laboratory test container.

7.2 Only representative samples obtained as specified in the API MPMS, Chapter 8 (or Practice D 4057 and Practice D 4177), shall be used for this test method.

8. Procedure

8.1 Fill each of two centrifuge tubes (5.2) to the 50-mL mark with sample directly from the sample container. Then, with a pipet, add 50 mL of toluene, which has been water saturated at 60°C (140°F) or 49°C (120°F) (see Note 2). Read the top of the meniscus at both the 50 and 100-mL marks. Add 0.2 mL of demulsifier solution (6.2) to each tube, using a 0.2-mL pipet. An automatic pipettor may be used. Stopper the tube tightly and invert the tubes ten times to ensure that the oil and solvent are uniformly mixed.

8.2 In the case where the crude oil is very viscous and mixing of the solvent with the oil would be difficult, the solvent may be added to the centrifuge tube first to facilitate mixing. Care must be taken in order not to fill the centrifuge tube past the 100-mL mark with the sample.

8.3 Loosen the stoppers slightly and immerse the tubes to the 100-mL mark for at least 15 min in the bath maintained at 60 ± 3°C (140 ± 5°F) (see Note 2). Secure the stoppers and again invert the tubes ten times to ensure uniform mixing of oil and solvent. *The vapor pressure at 60°C (140°F) is approximately double that at 40°C (104°F).*

8.4 Place the tubes in the trunnion cups on opposite sides of the centrifuge to establish a balanced condition. Retighten the corks and spin for 10 min at a minimum relative centrifugal force of 600 calculated from the equation given in 5.1.5.

8.5 Immediately after the centrifuge comes to rest following the spin, read and record the combined volume of water and sediment at the bottom of each tube to the nearest 0.05 mL from 0.1 to 1-mL graduations and to the nearest 0.1-mL above 1-mL graduations. Below 0.1 mL, estimate to the nearest 0.025 mL (refer to Fig. 2). Return the tubes without agitation to the centrifuge and spin for another 10 min at the same rate.

8.6 Repeat this operation until the combined volume of water and sediment remains constant for two consecutive readings. In general, not more than two spinnings are required.

8.7 The temperature of the sample during the entire centrifuging procedure should be maintained at 60 ± 3°C (140 ± 5°F) (see Note 2).

8.8 To avoid the danger of tubes breaking in the cups, care must be taken that the tubes are bedded onto the bottom cushion so that no part of the tube is in contact with the rim of the cup.

9. Calculation

9.1 Record the final volume of water and sediment in each tube. If the difference between the two readings is greater than one subdivision on the centrifuge tube (see Table 1) or 0.025 mL for readings of 0.10 mL and below, the readings are inadmissible and the determination shall be repeated.

9.2 Express the sum of the two admissible readings as the percent by volume of water and sediment; report the results as shown in Table 2.

10. Precision

10.1 The precision of this method, as obtained by statistical examination of interlaboratory test results in the range from 0.01 to 1.0 %, is described in 10.1.1 and 10.1.2.

10.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty:

From 0.0 % to 0.3 % water, see Fig. 3.

From 0.3 % to 1.0 % water, repeatability is constant at 0.12.

10.1.2 *Reproducibility*—The difference between two single and independent test results obtained by different operators working in different laboratories on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty:

From 0.0 % to 0.3 % water, see Fig. 3.

From 0.3 % to 1.0 % water, reproducibility is constant at 0.28.

11. Keywords

11.1 centrifuge; centrifuge tube; crude oil; laboratory procedure; sampling; sediment and water; solvent

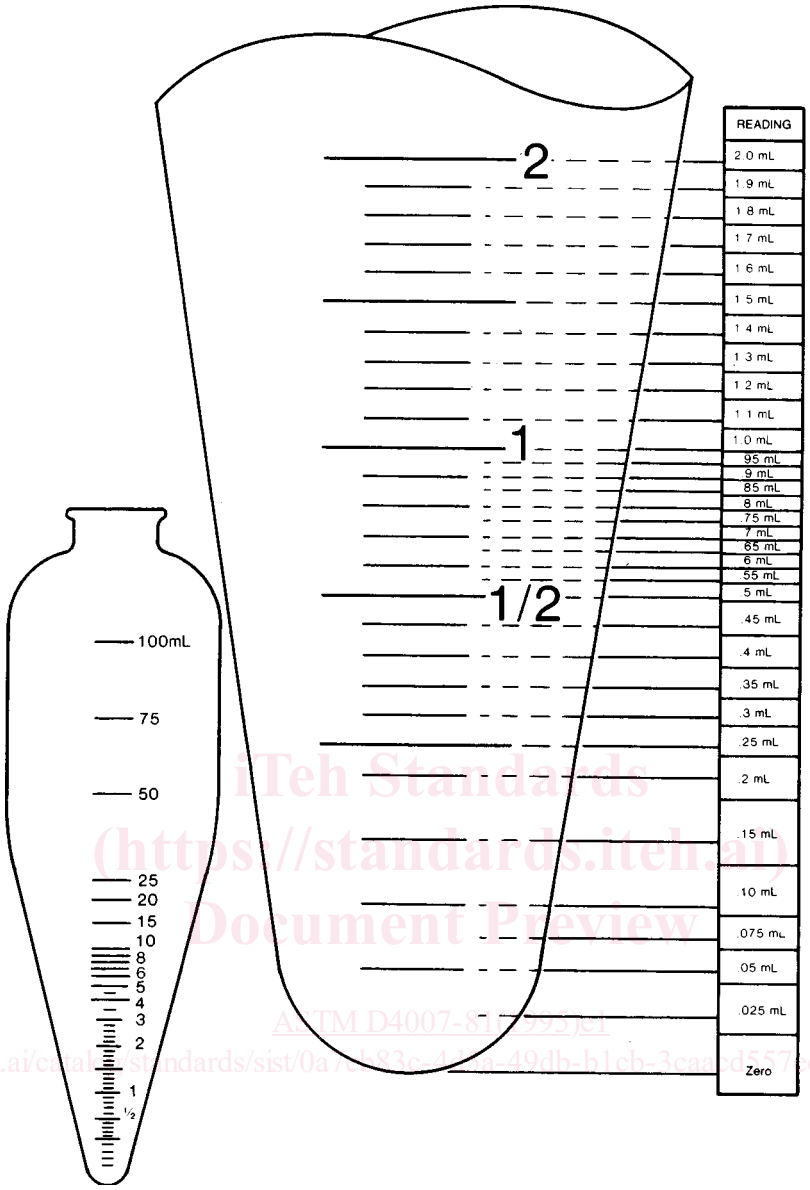

FIG. 2 Procedure for Reading Water and Sediment When Using an ASTM 100-mm Cone-Shaped Centrifuge Tube

TABLE 2 Expression of Results, mm[A]

Tube 1	Tube 2	Total Percent Water and Sediment
No visible water and sediment	No visible water and sediment	—
No visible water and sediment	0.025	0.025
0.025	0.025	0.05
0.025	0.05	0.075
0.05	0.05	0.10
0.05	0.075	0.125
0.075	0.075	0.15
0.075	0.10	0.175
0.10	0.10	0.20
0.10	0.15	0.25

[A] For volumetric tolerances, see Table 1.

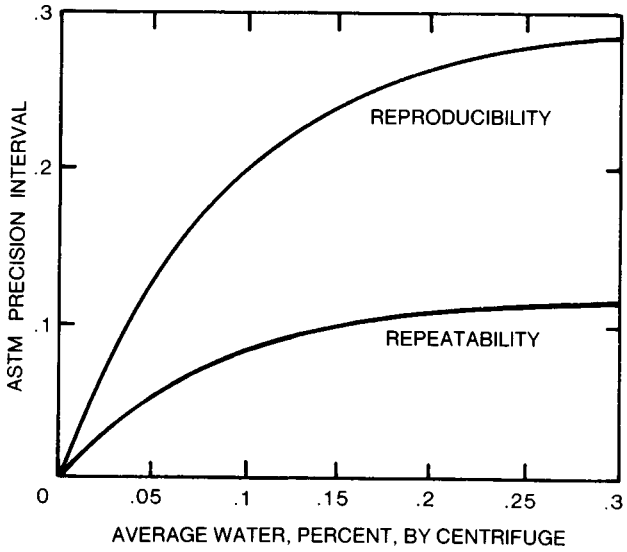

FIG. 3 Basic Sediment and Water Precision

ANNEXES

(Mandatory Information)

A1. PROCEDURE TO WATER-SATURATE TOLUENE

A1.1 Scope

A1.1.1 This method is satisfactory for the water saturation of toluene to be used for determination of water and sediment in crude oils by the centrifuge method.

A1.2 Significance

A1.2.1 Fig. A1.1 shows that water is soluble in toluene to a significant extent. The percent of water that will dissolve increases as the temperature is increased from about 0.03 % at 21°C (70°F) to about 0.17 % at 70°C (158°F). Toluene, as normally supplied, is relatively dry and if used in an as-received condition, will dissolve a portion of or even all of any water present in a crude oil sample. This would reduce the

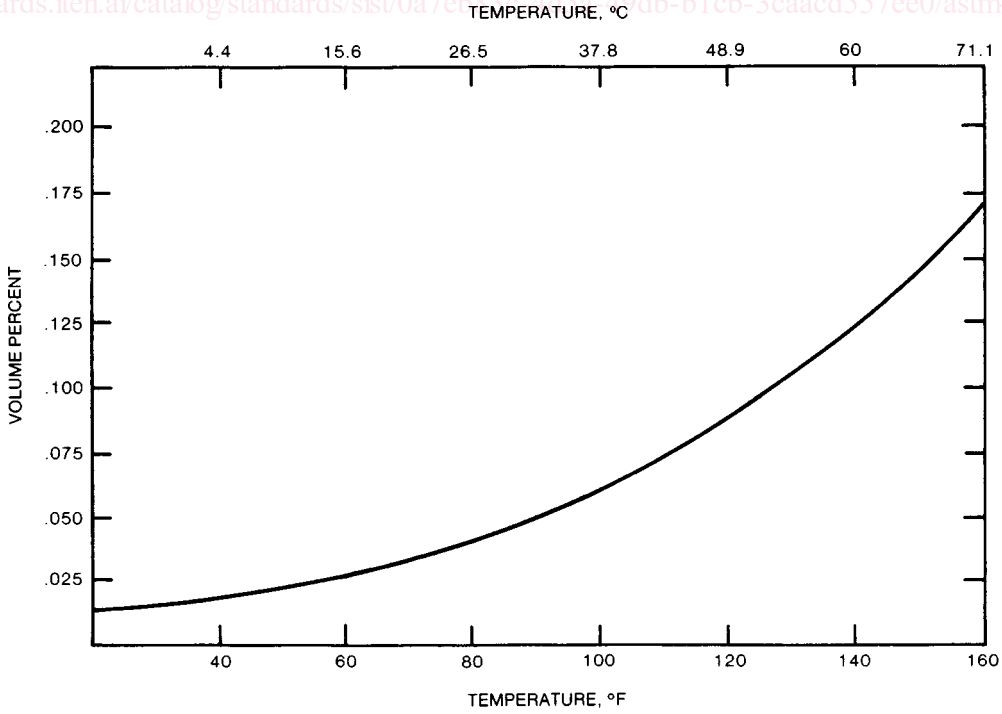

FIG. A1.1 Solubility of Water in Toluene

apparent sediment and water level in the crude sample. To determine water and sediment accurately by centrifuge on a crude oil sample, the toluene must first be saturated at the centrifuge test temperature.

A1.3 Reagents

A1.3.1 *Toluene* conforming to Specification D 362 or to the IP Specification for Toluole.

A1.3.2 *Water*, either distilled or tap water.

A1.4 Apparatus

A1.4.1 *Liquid-Heating Bath* of sufficient depth for immersing a 1-qt or 1-L bottle to its shoulder. Means shall be provided for maintaining the temperature at 60 ± 3°C (140 ± 5°F).

A1.4.2 *Glass Bottle*, 1-qt or 1-L, with screw top.

A1.5 Procedure

A1.5.1 Adjust the heating bath to the temperature at which the centrifuge test is to be run. Maintain the bath temperature to ±3°C (50°F).

A1.5.2 Fill the glass bottle with 700 to 800 mL of toluene. Add 25 mL of water. Screw the cap on the bottle and shake vigorously for 30 s.

A1.5.3 Loosen the cap and place the bottle in the bath for 30 min. Remove the bottle, tighten the cap, and shake cautiously for 30 s.

A1.5.4 Repeat above procedure (A1.5.3) three times. *The vapor pressure of toluene at 60°C (140°F) is approximately twice that at 38°C (100°F).*

A1.5.4.1 Allow the bottle with the water-toluene mixture to sit in the bath 48 h before using. This will ensure complete equilibrium between the toluene and the free water as well as complete saturation at the desired temperature. If it is necessary to use the water-saturated toluene before the 48-h equilibration time has been completed, the solvent must be poured into centrifuge tubes and centrifuged in the same equipment at the same relative centrifuge force and temperature that is used for the centrifuge test. The toluene must be carefully pipetted from the centrifuge tube so that any free water that may be in the bottom of the tube is not disturbed.

A1.5.4.2 Saturation is time- and temperature-dependent. It is recommended that bottles of the toluene-water mixture be kept at test temperature in the bath at all times so that saturated solvent will be available whenever tests are to be run. .

A2. Precautionary Statement

A2.1 Toluene—Precaution **Keep away from heat, sparks, and open flame.**

Vapor harmful.

Toluene is toxic.

Particular care must be taken to avoid breathing the vapor and to protect the eyes.

Keep container closed.

Use with adequate ventilation.

Avoid prolonged or repeated contact with the skin.

APPENDIX

(Nonmandatory Information)

X1. PRECISION AND ACCURACY OF METHODS FOR DETERMINING WATER IN CRUDE OILS

X1.1 Summary

X1.1.1 This round-robin testing program has shown that the distillation method as practiced is somewhat more accurate than the centrifuge method. The average correction for the distillation method is about 0.06, whereas the centrifuge correction is about 0.10. However, this correction is not constant nor does it correlate well with the measured concentration.

X1.1.2 There is a slight improvement in the precision of the distillation method over the present Test Method D 95: 0.08 repeatability versus 0.1 and 0.11 versus 0.2 for reproducibility. These figures are applicable from 0.1 to 1 % water content, the maximum level studied in this program.

X1.1.3 The precision of the centrifuge method is worse than the distillation: repeatability is about 0.12 and the reproducibility 0.28.

X1.2 Introduction

X1.2.1 In view of the economic importance of measuring the water content of crude oils precisely and accurately, a working group of API/ASTM Joint Committee on Static Petroleum Measurement (COSM) undertook the evaluation of two methods for determining water in crudes. A distillation method (Test Method D 95) and a centrifuge method (Test Method D 1796) were evaluated in this program. Both methods were modified slightly in an attempt to improve the precision and accuracy.

X1.3 Experimental

X1.3.1 *Samples*

The following seven crude oils were obtained for this program:

Crude	Source