

Comprehensive Report of API Crude Oil Characterization Measurements

API TECHNICAL REPORT 997
FIRST EDITION, AUGUST 2000



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Downstream Segment

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FIRST EDITION, AUGUST 2000

Work Performed For
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ABSTRACT

A consortium of American Petroleum Institute member companies has sponsored a research program consisting of a series of projects on the characterization of crude oils. The goal of this program was to obtain complete sets of assay and thermophysical property data on a few widely varying crude oils to test the basic correlations and models typically used in the design of crude oil refining and related facilities. The crude oils chosen were Alaskan North Slope, Utah Altamont, and San Joaquin Valley. This report provides descriptions of the test procedures, discussions of their accuracy, and a comprehensive compilation of the data for the three crude oils measured under this program. The scope of this report is limited to discussion of the characterization tests and compilation of the data. Although the data were generated to allow for the evaluation of various correlations used for design purposes, such evaluation has been/will be done by API's Technical Data Committee and may be published later. It is important to note, however, that a number of these data have been utilized in the development of correlations that are included in the three most recent revisions of the API Technical Data Book, most notably Chapter 2 (Characterization) and Chapter 3 (Distillation Interconversions).

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<u>Sponsor Company</u>	<u>Years of Sponsorship</u>
Amoco Oil Company	1989 – 98
Chevron Research and Technology	1993 – 98
Fluor Daniel	1989 – 98
M. W. Kellogg	1992 – 98
Mobil Research & Development	1989 – 97
Pennzoil Products	1989 – 98
Phillips Petroleum	1989 – 98
Shell Oil Company	1989 – 97
Sun Refining & Marketing	1989 – 90
Tesoro Petroleum	1989 – 90

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1. INTRODUCTION

The American Petroleum Institute (API), under the sponsorship of several members of the Technical Data Committee, has set up a subscription research program for the characterization of crude oils. The goal of this program was to obtain complete sets of characterization and thermophysical property data on a few widely varying crude oils to test the basic correlations utilized in the design of crude oil refining and related facilities. These correlations have been used regularly in the refining industry even though they are based on an old, incomplete data bank and, in many cases, on strictly pure component hydrocarbon data. Previous API sponsored studies have reported inconsistencies and serious gaps in the existing data. Also, new characterization methods, such as gas chromatographic simulated distillation, are being used without sufficient tie-in with the older methods used to estimate the required design properties. The data gaps and inconsistencies are particularly severe for the higher molecular weight fractions for which **new correlating parameters may be required.**

The crude oils selected by the sponsors were Alaska North Slope (ANS) crude, Utah Altamont (ALT) crude (very paraffinic), and San Joaquin Valley (SJV) crude (very aromatic). The program consisted of several research projects conducted by the National Institute for Petroleum and Energy Research (NIPER) operated by the IIT Research Institute (1983-1993) and BDM Oklahoma (1994-1998). Except for a few tasks that were subcontracted, the experimental work was conducted by NIPER personnel. Results from each of the previous projects in this program have been reported previously (1-12). This final comprehensive report was prepared by former NIPER personnel employed by TRW Petroleum Technologies, after TRW purchased BDM (1998).

1.1 SCOPE

Each crude was distilled into narrow boiling fractions and detailed characterization was performed on the whole crude, narrow boiling fractions, appropriate composites, and residues. The scope of NIPER's involvement in the program was to produce detailed assay and thermophysical property data. Although the rationale for obtaining the data was to evaluate various correlations used for design purposes, such evaluation was beyond the scope of NIPER's involvement. Hence, this final comprehensive report is in large part a collection of data without attempts to develop or evaluate correlations. Such development or evaluation of correlations falls within the purview of the project sponsors.

1.2 REPORT ORGANIZATION

Chapter 1 of the report is the Introduction. Chapter 2 covers distillation and gas chromatographic simulated distillation of the three crude oils and their fractions. Chapter 3 covers general physical properties and Chapter 4 covers chemical properties. Chapters 5 through 10 focus on thermophysical property data with separate chapters on vapor pressure, heat capacity, thermal conductivity, viscosity, gravity, and molecular weight. A brief summary is given in chapter 11. A list of references and the data tables follow Chapter 11.

Each chapter contains a brief description of the method(s) or procedure(s) and a discussion of the accuracy of each as appropriate. Discussion of accuracy generally includes references to the ASTM precision statements in each method. ASTM defines repeatability as the value (r) for which “the difference between successive results obtained by the same operator in the same laboratory with the same apparatus under constant operating conditions on identical test material would, in the long run, exceed only in one case in twenty.” Reproducibility (R) is defined such that “the difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of the test method, exceed the R value only in one case in twenty. ASTM tests performed by NIPER personnel were run according to the latest published methods (13) unless otherwise noted. Tests were generally run in duplicate when practical and when sample quantity permitted. When the results from duplicate runs were outside the ASTM repeatability, **a third run was made and the closest two results averaged**. In addition, standard reference materials were run periodically for most tests depending on availability of suitable standards. Two distillate fractions were run through a number of tests as blind samples as a further quality assurance check. Finally, a second set of vapor pressure measurements on one distillate was made by another laboratory.

The NIPER analytical laboratory has maintained and improved its quality program for many years and received accreditation under the API 1512 Petroleum Test Laboratory Accreditation Program in 1996 becoming the second lab to receive accreditation under that program. Heat capacity and vapor pressure data were provided by NIPER’s Thermodynamics Laboratory, which has a long history and excellent reputation for production of highly accurate and precise data.

2. DISTILLATION AND SIMULATED DISTILLATION

2.1 Distillation

2.1.1 Preparative Crude Oil Distillation

The three crude oils characterized in this program were supplied by the project sponsors. Analyses were performed on both the whole crude and distillation fractions. This section describes the initial crude oil distillations to provide samples for further characterization.

It was necessary to distill a large quantity (80-90 gallons) of crude oil to obtain the quantities of material required for analyses and for distribution to project sponsors and other contractors. Because of the large amount of material to be distilled, the distillations to 950° F were subcontracted to the Pittsburgh Applied Research Center (PARC). Their initial distillation was conducted in a 150 gallon batch still with packed column, timed reflux, and vacuum to approximately 15 mm Hg. This distillation was carried out up to a corrected vapor temperature of 850° F. Bottoms from the 150 gallon still were charged to 10-liter Sarnia stills with no column packing, no reflux, and with vacuum to about 0.6 mm Hg. This distillation was terminated at a corrected vapor temperature of 950° F.

Results of these distillations are summarized in Table 1. Yields were determined in weight percent and then converted to volume percent using the specific gravities included in Table 1.

Production of the higher boiling cuts was performed at NIPER via short path distillation on a 6-inch Pope still. There were three passes through the short path still: 1) to produce a nominal 950-1050° F distillate and >1050° F resid, 2) to produce a nominal 1050-1150° F distillate and >1150° F resid, and 3) to produce a nominal 1150-1250° F distillate and >1250° F resid. Actual weights and recoveries from each pass are summarized in Table 2 and volume percent yields on a whole crude basis are summarized in Table 1 along with the data provided by PARC.

In addition to the individual cuts shown in Table 1 composites of certain wider boiling range cuts were made by back blending appropriate individual cuts in proportion to their weight percent yields in the distillations. The following composites were made:

450-650° F
>650° F resid
650-950° F
950-1250° F

Including the whole crude and the four composites, 20 different samples from ANS and ALT crudes and 19 samples from SJV crude were measured in this program.

Precision of the distillations is dependent upon the distillation equipment and the care taken in performing the distillation. Important equipment parameters include proper column packing, temperature and pressure sensor locations and calibration, and distillation rate to avoid column flooding. Comparison of the preparative scale distillation results with the ASTM D 2892 and ASTM D 1160 results in Tables 4 and 7, respectively, can give some indication of the precision or at least consistency between the distillations. Also for comparison, simulated distillation data by ASTM D 5307 are included with the comparison data shown in Table 3. In general, the data agree reasonably well considering the different methods involved and the interpolations needed to obtain the directly comparable data. In particular, the preparative distillation data and the ASTM D 2892 data for the ANS crude showed very good agreement.

2.1.2 Analytical Crude Oil Distillation

In addition to the preparative distillations described above, each whole crude was also distilled by ASTM D 2892, Distillation of Crude Petroleum (15-Theoretical Plate Column). Results for these distillations are reported in Table 4. Repeatability for this method is under statistical review by ASTM. Reproducibility is 1.2% for both mass and volume percent for distillation at atmospheric pressure and 1.4 and 1.5%, respectively, for distillation under vacuum. No statement of bias is made for this method since there is no accepted reference material suitable for determination of bias.

2.1.3 Distillation of Fractions

Individual cuts or composites from the preparative distillation were distilled by various methods. Fractions were distilled on a 15-theoretical plate column by ASTM D 2892. This distillation procedure, which was carried out with an automated apparatus, was not designed for distillation of narrow range cuts and control of the distillations proved to be exceedingly difficult. Repeatability would be expected to be considerably higher than that published in the method. Results are summarized in Table 5.

ASTM D 86, Distillation of Petroleum Products, which is a simple atmospheric pressure distillation, was applied to cuts boiling below 750° F. Cuts from 650-750° F were run by both ASTM D 86 and ASTM D 1160 at the request of the project sponsors although these cuts are

outside the scope of ASTM D 86. Thus, the ASTM D 86 precision and bias statements do not apply to the 650-750° F distillate cut data. Data for distillations of seven individual cuts and the 450-650° F composite are provided in Table 6 using an automated method. Repeatability for distillation of group 1 (gasoline range) materials is 7° F for the initial boiling point (IBP) and 8° F for the final boiling point (FBP) with values for intermediate temperatures a function of the slope of temperature versus volume percent distilled. Repeatability for group 4 (diesel/kerosine range) is 6.3° F for both IBP and FBP with intermediate values a function of slope. A much more extensive discussion is given in ASTM D 86 (13). No statement of bias is made for this method.

Higher boiling fractions and composites were distilled by ASTM D 1160, Distillation of Petroleum Products at Reduced Pressures. The distillations were conducted at either 10 mm Hg (650-750° F, 750-850° F, 850-950° F, 650-950° F composite, and >650° F resid) or 1 mm Hg (850-950° F, 950-1050° F, and >650° F resid). Data for the 10 mm and 1 mm Hg distillations are provided in Tables 7 and 8, respectively. Both the vapor temperatures and atmospheric equivalent temperatures are provided. Repeatability is again a complicated function of the slope of temperature versus volume percent distilled. For distillations conducted at 10 mm Hg, repeatability ranges between 3.4 and 11.7° F atmospheric equivalent temperature for volume recovered between 5 and 90 volume percent. For distillations conducted at 1 mm Hg, repeatability ranges between 4.3 and 10.3° F. Repeatabilities for IBP and FBP at 10 mm Hg are 27 and 12.8° F, respectively. For distillation at 1 mm Hg, the corresponding repeatabilities are 30.6 and 5.9° F, respectively. No statement of bias is made due to lack of a suitable reference material.

2.2 Simulated Distillation by Gas Chromatography

2.2.1 Boiling Range Distribution of Whole Crude by ASTM D 5307 (P 167)

The boiling range distribution of the whole crude oils was determined by the proposed ASTM P 167 which was subsequently approved and published in 1992 as ASTM D 5307, Boiling Range Distribution of Crude Petroleum by Gas Chromatography (GC). The method is applicable to whole crude oils that can be dissolved in a solvent for introduction by means of a microsyringe. The crude oil is normally diluted in carbon disulfide and injected into a GC column that separates hydrocarbons in boiling point order. Boiling points are assigned to the time axis by comparison to a calibration curve obtained under the same chromatographic conditions by running a mixture of n-paraffins of known boiling point through a temperature of 1000° F. The amount of material boiling above 1000° F is estimated from a second run of the sample

containing an internal standard. Repeatability varies with percent eluted off the column ranging from 6.7° F for the IBP to 37.3° F for 90% off. No bias can be determined as the boiling range distribution can only be defined in terms of a test method. A more detailed description of precision is given in the method (13). The simulated distillation data are provided in Table 9.

2.2.2 Boiling Range Distribution of <500° F Fractions by ASTM D 3710

The IBP-320° F, 320-450° F, and 450-500° F fractions were analyzed by ASTM D 3710, Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography. This method is applicable to petroleum products and fractions with a final boiling point below 500° F. A GC column is employed under conditions that allow determination of isopentane and lighter saturates discretely. The time axis is calibrated using a known mixture of hydrocarbons covering the boiling range expected in the sample. Repeatability is a function of the volume percent recovered and the rate of change in temperature with percent recovered (dT/dV). Values for IBP and FBP are 2° F and 6° F, respectively. Values for 20 to 95 percent recovered range from 2° F to 19° F depending on dT/dV . A more complete description and a table are given in the method (13). Bias cannot be determined as there is no acceptable reference material for the method. Results are presented in Table 10.

2.2.3 Boiling Range Distribution of Fractions by ASTM D 2887

All distillate fractions and composites boiling between 320 and 850° F (7 distillate fractions and 1 composite) were analyzed by ASTM D 2887, Boiling Range Distribution of Petroleum Fractions by Gas Chromatography. This method is applicable to petroleum products with a final boiling point of 1000° F or lower. Repeatability for IBP by this method is 0.11 (X-32) where X is the average of two results in °F. Repeatability for 10-40% off is 1.4° F; for 50-90% off, r is 1.8° F; and for FBP, r is 5.8° F. Results are presented in Table 11.

2.2.4 Boiling Range Distribution of High Boiling Fractions and Resids by ASTM D 5307 and High Temperature Simulated Distillation

Three methods were used to determine boiling range distributions for the high boiling fractions and resids from the three crudes. The first, ASTM D 5307, has been discussed earlier. The second is a variation of the ASTM proposed high temperature method "Boiling Range Distribution of Heavy Petroleum Fractions by Gas Chromatography" that is analogous to ASTM D 2887. This method uses a high temperature GC and column to elute material boiling below

1350° F. An internal standard is not used, and complete sample elution by 1350° F is assumed. The third is the ASTM proposed high temperature method in a variation that uses an internal standard. This method is applicable to materials with an initial boiling point of at least 600° F, since elution of the internal standard (typically C₁₄ and C₁₆ *n*-paraffins) must be complete before the sample elution begins. Reproducibility and repeatability data on the two proposed methods are not available and bias has not been determined due to lack of an accepted reference material. Data for the fractions and resids from the three crudes are listed in Table 12. Most samples were run by the proposed high temperature method using an internal standard. Samples run by the proposed method without an internal standard and one sample run by ASTM D 5307 are indicated by footnotes.

3. GENERAL PHYSICAL PROPERTY CHARACTERIZATION DATA

3.1 Cloud Point

Cloud points were determined for all fractions distilling between 320 and 550° F by ASTM D 2500, Cloud Point of Petroleum Products. This method is applicable to petroleum products that are transparent in layers of 40 mm thickness, and with cloud points below 120° F. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid that is cooled at a specified rate. The repeatability for this test is 3.6° F. Reproducibility is 7.2° F. The procedure has no bias as the value of cloud point can be defined only in terms of a test method. Results are listed in Table 13.

3.2 Pour Point

Pour points on the whole crude and all distillate fractions above 450° F were determined by ASTM D 97, Pour Point for Petroleum Products. This method is applicable to any petroleum product. The pour point is the lowest temperature at which the sample shows movement after first being heated and then cooled at a specified rate and examined at 5° F intervals. Repeatability for this method is 5° F. Reproducibility is 10° F. No bias statement can be made since there are no criteria for measuring bias for the test-product combinations in the method. Results are provided in Table 13. Pour point determinations on samples of the 850-950° F distillates from ANS and ALT crude oils that were submitted with sample numbers without specific sample information (blind) were identical with the original sample determinations. A later repeat determination on the 1150-1250° F distillate from ANS crude deviated by 10° F from the original determination. This deviation is within the reproducibility limits of the method.

3.3 Freeze Point

Freeze points were determined for fractions distilling between 320 and 550° F by ASTM D 2386, Freezing Point of Aviation Fuels. This method is applicable to aviation turbine fuels and aviation gasolines, although the precision data were determined using only aviation turbine fuels. The method involves cooling the fuel until solid hydrocarbon crystals appear, and then noting the temperature at which the crystals disappear as the temperature is allowed to rise. The repeatability of the method is 1.4° F. Reproducibility is 4.1° F. Bias could not be established since no liquid hydrocarbon mixtures of known freezing point that simulate aviation fuels could be found. Results are listed in Table 13.

3.4 Refractive Index

Refractive indexes for the distillates boiling below 650° F were measured by ASTM D 1218, Refractive Index and Refractive Dispersion of Hydrocarbon Liquids using the sodium D line and at 20° C. Measurements for the higher boiling distillates (>650° F) were made by ASTM D 1747, Refractive Index of Viscous Materials. These measurements were also made with the sodium D line but at 80° C. ASTM D 1218 is applicable to transparent and light-colored hydrocarbon liquids that have refractive indexes in the range from 1.33 to 1.50, and at temperatures from 20 to 30° C. The method involves measuring the refractive index by the critical angle method with a Bausch & Lomb Precision Refractometer using monochromatic light. Prior to measurement of samples, a calibration was obtained with certified liquid standards (n-hexadecane, trans-decahydronaphthalene, and 1-methylnaphthalene). Repeatability and reproducibility are 0.00006 and bias is expected to be no more than 0.00006. ASTM D 1747 is applicable to transparent and light-colored viscous hydrocarbon liquids and melted solids which have a refractive index in the range between 1.33 and 1.60, and at temperatures from 80 to 100° C. In other respects, the method is similar to ASTM D 1218. Repeatability for successive results from this method is 0.00007. Reproducibility is 0.0006. Bias is under study by the ASTM subcommittee. Refractive index results are summarized in Table 13. Results obtained for the 850-950° F blind samples were well within the reproducibility of 0.0006 as compared to those obtained from the original samples.

3.5 Flash Point

Flash points were determined by ASTM D 93, Flash Point by Pensky-Martens Closed Cup Tester. The basic procedure (Method A) was used. This method is applicable to petroleum

products with flash points in the range from 40 to 360° C, including fuel oils, lube oils, liquids with suspensions of solids, liquids that tend to form a surface film under test conditions, and other liquids with viscosities of 5.5 cSt or more at 40° C. Repeatability of Procedure A is given by the relationship: $r = 0.035X$ where X is the average of two measurements in °C. Bias was not determined since there is no accepted reference material suitable for determination of bias. Results are listed in Table 13. The flash point determined on the ANS blind sample was identical to the original determination. Variation for the ALT flash points (220.5° C versus 220° C) was well within the repeatability (7.7° C). A later repeat determination of the flash point for the 850-950° F distillate from SJV crude deviated from the average of the two determinations by 4.0° C, which is within the repeatability (7.6° C)

3.6 Aniline Point

Aniline points were run by Method A of ASTM D 611, Aniline Point and Mixed Aniline Point of Petroleum Products and Hydrocarbon Solvents. Method A is applicable to clear samples or to samples not darker than No. 6.5 ASTM color, as determined by Test Method ASTM D 1500, having an initial boiling point above room temperature and where the aniline point is below the bubble point and above the solidification point of the aniline-sample mixture. The method involves mixing specified volumes of aniline and sample, or aniline and sample plus *n*-heptane, in a tube while heating at a controlled rate until the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which two phases separate is recorded as the aniline point, or mixed aniline point. Repeatability for aniline point and mixed aniline point in the method is 0.3° F for clear and light colored samples. Reproducibility is 0.9° F. A statement of bias is under development by the ASTM subcommittee. Results are provided in Table 13.

3.7 Smoke Point

Smoke points were run by ASTM D 1322, Smoke Point of Kerosine and Aviation Turbine Fuel. Smoke point is defined as the maximum height in millimeters, of a smokeless flame of fuel burned in a wick-fed lamp of specified design. The method involves burning the sample in an enclosed wick-fed lamp that is calibrated daily against pure hydrocarbon blends of known smoke point. The maximum height of flame attained without smoking is determined to the nearest 0.5 mm. Repeatability is 2 mm. Reproducibility is 3 mm. Bias cannot be determined since the value of the smoke point can only be defined in terms of a test method. Results are listed in Table 13.

3.8 Reid Vapor Pressure

The Reid vapor pressure of the whole crude was determined by ASTM D 5191, Vapor Pressure of Petroleum Products (Mini Method). This method, which uses automated total vapor pressure instruments, is suitable for testing samples with boiling points above 32° F that exert a vapor pressure between 1 and 18.6 psi at 100° F at a vapor-to-liquid ratio of 4:1. A known volume of chilled, air-saturated sample is introduced into an evacuated temperature controlled chamber that has a total volume of 5 times the volume of the injected sample. The test sample is allowed to reach thermal equilibrium at the test temperature of 100° F and the total pressure is measured with a pressure transducer sensor and indicator. The total pressure is then converted to a dry vapor pressure equivalent (DVPE) through use of a correlation equation. Previous interlaboratory studies with gasoline samples have shown no bias between the DVPE value and Reid vapor pressure measured by ASTM D 323. The repeatability of total pressure in method ASTM D 5191 is given by $0.00807(DVPE + 18.0 \text{ psi})$. Absolute bias cannot be determined for lack of a suitable reference material. Relative bias studies resulted in the correlation between total vapor pressure and DVPE. The Reid vapor pressures of the three crude oils are listed in Table 13.

3.9 Octane Numbers

Research and motor octane numbers were run by ASTM D 2699, Knock Characteristics of Motor Fuels by the Research Method, and ASTM D 2700, Knock Characteristics of Motor and Aviation Fuels by the Motor Method, respectively. These analyses were subcontracted to Phillips Petroleum Co. Results are included in Table 13. The research octane is applicable to motor gasolines intended for use in spark-ignition engines. The motor octane method is applicable to motor and aviation gasolines intended for use in spark ignition engines. In both methods the knocking tendency of the fuel is determined by comparison with the knocking tendencies for blends of ASTM reference fuels of known octane numbers under standard operating conditions in a single cylinder engine.

Precision data are not available for the range of octane numbers measured for these samples. Repeatability of the research method for gasolines with an average research octane number (RON) level of 90 is 0.2 RON. Reproducibility is 0.7 RON at the same level. For the motor method, repeatability for gasolines with average motor octane number (MON) level of 85 is 0.3 MON. Reproducibility for gasolines with average MON of 80.0 is 1.2 MON.

3.10 Water

Water contents of the three crudes were determined by ASTM D 4928, Water in Crude Oils by Coulometric Karl Fischer Titration. The method applies to crude oils with water content between 0.02 and 5 wt. %. Mercaptans and sulfides interfere at concentrations exceeding 500 ppm sulfur. A thoroughly homogenized aliquot of the crude oil is injected into the titration vessel of a Karl Fischer apparatus and titrated with iodine that is generated coulometrically at the anode. The end-point is determined when excess iodine is detected by an electrometric end-point detector. One mole of iodine reacts with one mole of water, and thus the quantity of water is proportional to the total integrated current according to Faraday's Law. Repeatability for a sample varies from 0.003 at 0.02 wt. % to 0.12 at 5.0 wt. % according to the relationship: $r = 0.040X^{2/3}$, where X is the sample mean from 0.005 to 5 wt. %. Reproducibility is $0.105X^{2/3}$. Determinations of samples with known quantities of added water showed no differences between observed and expected values. Water content results are summarized in Table 13.

3.11 Sediment

Sediment in the whole crudes was determined by ASTM D 473, Sediment in Crude Oils and Fuel Oils by the Extraction Method, in which the crude oil sample is extracted with refluxing toluene. Repeatability is given by the relationship: $r = 0.017 + 0.255X$, where X is the average result in percent. Reproducibility is given by $R = 0.033 + 0.255X$. Sediment results are summarized in Table 13.

4. CHEMICAL ANALYSIS DATA

4.1 Detailed Hydrocarbon Analysis

Detailed component analyses were performed on the whole crudes, the IBP-165° F, and the 165-320° F fractions. The method used and related methods are widely employed in the petroleum industry for detailed component analysis. These methods are often modifications and extensions of ASTM D 5134, Detailed Analysis of Petroleum Naphthas through *n*-Nonane by Capillary Gas Chromatography. When applied to a whole crude, an internal standard is used to provide concentrations on a whole crude basis. Repeatability of these methods may be similar to that of D 5134. Repeatability and reproducibility values for a number of individual compounds are given in Table 3 of ASTM D 5134. Some examples of repeatability are *n*-Butane ($r = 0.091X^{0.85}$), Benzene ($r = 0.037X^{0.67}$), and *n*-Nonane ($r = 0.017X$). Bias cannot be determined

since there is no accepted reference material suitable for determining bias. Results of the detailed hydrocarbon analyses are provided in Table 14. The first page for each sample in the table provides the total concentration for each compound class (paraffins, isoparaffins, etc.) and the concentration of each carbon number in each compound class. The following pages provide the concentrations of each identified compound in chromatographic order.

4.2 Hydrocarbon Types by Mass Spectrometry

Hydrocarbon type analyses were run on distillate fractions and composites distilling between 450 and 650° F by the mass spectrometric method of Richard M. Teeter (14). A type analysis does not yield information on individual components in a mixture, but rather it does supply information on the relative amounts of classes or types of compounds. Thus, the Teeter method determines the relative amounts of eight types of saturate hydrocarbons (zero through seven rings), ten types of aromatic hydrocarbons, and four types of sulfur-containing aromatic compounds. Although the type analysis does not yield results of high accuracy, the results can be very useful in comparisons to determine trends and in correlations with processing parameters, product quality, or any other property that is related to or determined by composition. The method is limited to low-olefin, petroleum distillate fractions in the boiling range 350 to 1050° F which contain less than 5% oxygen, nitrogen, or sulfur compounds. Only the 22 compound types listed in the method are determined; all others are ignored. Other factors that can produce erroneous results are large amounts of a single compound, any other unusual distribution of compounds, or thermally unstable components. The mass spectral resolution required for the method is 5,000 (10% valley definition). The main advantage over the standard ASTM methods that apply to fractions in the same boiling range is the absence of need for prior separation of the samples.

Another advantage for the Teeter method over ASTM Method D 2425 for middle distillates (or diesel fuels) is the determination of more compound types (up to 22 compared to 11 for ASTM D 2425). In particular, the determination of thiophenic types by the Teeter method could be a very important advantage for some samples in view of the forthcoming more stringent control of the level of sulfur species in gasoline and other petroleum products (the ASTM method determines only hydrocarbon types). For higher boiling samples in the gas-oil range, the combination of ASTM D 2786 (7 saturate and 1 aromatic types) and ASTM D 3239 (18 aromatic hydrocarbon and 3 aromatic sulfur-containing types) does determine more compound types than the Teeter method, but requires the prior separation and analysis of two samples. Overall, the precision and accuracy of the Teeter and various ASTM methods are comparable. A summary of

the analytical results for a sample used for QA/QC purposes in our laboratory and in a client's laboratory (using a different mass spectrometric method [modified Robinson method similar to ASTM D 2425] and instrument [CEC 21-103]) are shown below:

Compound Type	Teeter Method on Our MS-50	Client's 21-103 data
Paraffins	16.01 ± 0.29	16.91 ± 0.43
Naphthenes	14.55 ± 0.47	16.06 ± 0.46
Aromatics	69.40 ± 0.56	67.03 ± 0.55

The error limits listed are plus or minus one standard deviation. The agreement between the results from the two methods is quite good, especially considering that the data were acquired by different operators using different methods and different instruments located in different laboratories. Results for the Teeter analysis are provided in Table 15.

4.3 Aromatic Carbon by Nuclear Magnetic Resonance Spectroscopy

Aromatic carbon contents of three fractions and one composite were determined using carbon-13 nuclear magnetic resonance (NMR) spectrometry. Results are listed in Table 16. The aromaticity, f_a , is defined as the mole fraction of aromatic carbons in the sample, and is obtained by finding the ratio of the aromatic carbon signal integral to the total carbon signal integral from the NMR spectrum. The fastest procedure is to obtain the proton NMR spectrum of the sample, which is inherently quantitative. However, the underlying carbon structure of the sample must be inferred from the proton spectrum using some assumptions based on the nature of the sample, so the resulting aromaticity is subject to some uncertainty.

Because of the variable interaction of the carbon-13 nuclear spin with those of the attached protons during proton decoupling (nuclear Overhauser effect, NOE) and the long spin-lattice relaxation times of non-protonated carbons, care must be exercised to obtain quantitative carbon-13 NMR spectra. Gated decoupling is used where the proton decoupling field is applied only during signal acquisition and not during the longer delay between successive pulses to avoid the variable NOE. A long delay between successive pulses is used to allow complete relaxation of the different carbon types in the sample between pulses to achieve quantitative results. Because of the low isotopic ratio of carbon-13 in the sample, many successive signals must be added to achieve adequate signal/noise ratios, leading to long experiment times. The experiment can be

shortened by adding a relaxation agent, such as chromium acetylacetonate, to the sample solution. This can shorten the time by a factor of four or more.

From the quantitative carbon-13 NMR spectrum, the integral of the aromatic carbon signal (105-160 ppm from TMS) and the total carbon-13 integral are obtained to calculate the aromaticity. If the sample contains olefinic material or water, the signals from olefinic carbon-13 are located in the same region as the aromatic carbon-13 signals and can lead to a larger value for the aromaticity. The proton spectrum usually will reveal whether there is significant olefinic material present in the sample, so the wise procedure is to do both experiments even though petroleum crude oils generally contain no olefinic material.

The aromatic carbon content method is essentially Procedure C of ASTM D 5292 which was approved and published by ASTM in 1993. Repeatability of ASTM D 5292 is given by the relationship: $r = 0.59X^{1/3}$ where X is the aromatic content determined in the method. Reproducibility is given by $R = 1.37X^{1/3}$. No bias was found for single pure hydrocarbons or a known mixture of pure aromatic compounds. Bias cannot be determined for typical petroleum fractions since there is no suitable accepted reference method available.

4.4 Elemental Analyses

Elemental analyses are provided in Table 17. Carbon, hydrogen and nitrogen were determined by Method B of ASTM D 5291, Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants, using a Perkin-Elmer 240C instrument. The sample is combusted to carbon dioxide, water, and nitrogen oxides. Oxygen is removed and the nitrogen oxides are reduced to nitrogen. The gases are separated on a column before quantitative determination. Good repeatability is typically obtained for carbon and hydrogen via this method but the nitrogen values are of questionable value. Repeatabilities published with the method are $r = 0.0072(X+48.48)$ for carbon in the range 75 to 87 wt. %, $r = 0.1162X^{0.5}$ for hydrogen in the range 9 to 16 wt. %, and $r = 0.1670$ for nitrogen in the range 0.75 to 2.5 wt. %, where X is the average wt. % value determined for each element, respectively. Reproducibilities are $R = 0.018(X+48.48)$, $R = 0.2314(X^{0.5})$, and $R = 0.4456$ for carbon, hydrogen, and nitrogen, respectively. Bias could not be determined for lack of a suitable petroleum based reference material.

Carbon contents for the two blind samples (850-950° F ANS and ALT distillates), were well within the repeatability ($r = 0.96$ wt. %) for the method as compared to the original samples. In

like manner, the hydrogen contents were well within the repeatabilities for the two crude oil distillates ($r = 0.4$ wt. % for ANS, $r = 0.45$ wt. % for ALT). The nitrogen values repeated well, but both were outside the applicable range of the method.

Nitrogen values determined by chemiluminescence (ASTM D 4629 and ASTM D 5762 with a modification (15)), which are also reported in Table 17, are much more reliable. Method ASTM D 4629, Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection, is applicable to liquid hydrocarbons boiling in the range from approximately 122° F to 752° F, with viscosities between about 0.2 to 10 cSt at room temperature, and with total nitrogen contents from 0.3 to 100 mg/kg. In this method, the sample is injected into an inert gas stream, vaporized, and carried into a high temperature zone where oxygen is introduced to convert organic and bound nitrogen into nitric oxide. The nitric oxide is reacted with ozone to produce electronically excited nitrogen dioxide. The light emitted as the excited molecules decay is detected by a photomultiplier tube and the resulting signal is related to nitrogen content of the sample. Precision is given by $r = 0.15X^{0.54}$, where X is the average of two test results. Reproducibility is given by $R = 0.85X^{0.54}$. Bias for the method has not been determined. In the modified method ASTM D 5762, the neat sample is introduced into the instrument in the sample boat instead of a diluted sample. Results obtained with the modified method were essentially the same as those obtained by sample dilution before injection by syringe. Precision is expected to be comparable also. Repeatability for ASTM D 5762 is given by the relationship: $r = 0.099X$, where X is the average of two test results in $\mu\text{g/g}$. Reproducibility is given by $R = 0.291X$. Results for a NIST Standard Reference Material showed no significant bias. Nitrogen content of the ANS blind sample by modified ASTM D 5762 was identical to the original sample and was thus well within the repeatability ($r = 0.025$ wt. %). Deviation of the two results for the ALT 850-950° F distillate was 0.002 as compared to 0.002 for reproducibility.

Sulfur values, including results by three different methods, are also reported in Table 17. Sulfur contents were determined for the whole crude and its fractions through 950° F by ASTM D 4294, Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence (XRF) Spectrometry. ASTM D 1552, Sulfur in Petroleum Products (High-Temperature/Infrared (IR) Method), was used for sulfur determination on the >650° F samples. This method is more accurate than the XRF method for heavy samples. For the fractions containing trace sulfur levels, the microcoulometric method, ASTM D 3120, Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry, is more appropriate.

The XRF method is applicable to a wide range of samples with concentrations in the range from 0.0150 to 5.00 wt. % sulfur. In this method, the sample is placed in the beam emitted from an X-ray source and the resultant excited characteristic X radiation is measured. The accumulated count is compared to counts obtained previously from calibration samples to obtain sulfur concentration in wt. %. Repeatability for this ASTM method is given by the relationship: $r = 0.02894(X+0.1691)$ where X is the sulfur concentration in wt. %. Reproducibility is given by $R = 0.1215(X+0.05555)$. Bias was determined in a study of eight NIST reference materials with sulfur contents ranging from 0.0146 to 3.02 wt. %. Six samples showed small positive biases and two showed negative biases. Only one value, -0.0119 for the reference standard containing 0.381 wt. % sulfur, was considered to be significant. From the data in Table 17, the sulfur contents for the regular and blind 850-950° F ANS samples are identical. Values for the corresponding ALT samples deviated by 0.004 wt. % and thus the difference is well within the repeatability (0.006).

The high temperature method, ASTM D 1552, with resistance furnace and IR detection was used. The method is applicable to samples boiling above 177° C (350° F) and containing not less than 0.06 wt. % sulfur. Since only about 97% of sulfur is converted to sulfur dioxide after combustion at 2500° F, a calibration factor determined from standards is required. Repeatability for two test results from the procedure with IR detection used in this work varies from 0.04 for sulfur contents from 0.0 to 0.5 wt. %, 0.09 for sulfur contents from 1.0 to 2.0 wt. %, and 0.16 for sulfur contents from 4.0 to 5.0 wt. %. Corresponding reproducibility values are 0.13, 0.27, and 0.49, respectively. Although bias in the method is still under study, no statistically significant bias was found between the iodate and IR detector procedures. One sulfur analysis by this method was repeated at a later time. The difference of 0.11 wt. % between the two determinations for the 650-950° F composite SJV samples (1.19 and 1.30 wt. %) is considerably less than the reproducibility (0.27 wt. %).

Comparisons of values for samples analyzed by both the XRF and high temperature methods can also shed light on the accuracy of the analyses. Values for the 650-750° F (1.312 and 1.33), 750-850° F (1.210 and 1.22), 850-950° F (1.213 and 1.21), and 650-950° F composite (1.234 and 1.19 wt. %) SJV samples by ASTM D 4294 (XRF) and ASTM D 1552 (IR) methods, respectively, show excellent agreement, with the differences observed being within the repeatabilities of both methods.

The microcoulometric method, ASTM D 3120, is applicable to light liquid hydrocarbons boiling in the range from 26 to 274° C (80 to 525° F) with sulfur contents from 3.0 to 100 ppm by

weight, or to higher sulfur contents with appropriate dilution. In this method, a liquid sample is injected into a combustion tube maintained at about 800° C having a flowing stream of 80% oxygen and 20% inert gas. The sulfur dioxide produced flows into a titration cell where it reacts with triiodide ion in the electrolyte. The triiodide consumed is coulometrically replaced and the total current required is a measure of the sulfur present in the sample injected. Repeatability of the method is 28% of the average value determined. Reproducibility is 38% of the average value. Bias is not available due to lack of a suitable accepted reference material. Method ASTM D 3120 was applied to the 165-320° F and 320-450° F distillates from all three crude oils. No repeat runs were made but XRF data were obtained on these samples also. Agreement between the values from the two methods for the SJV distillates was quite good and well within the repeatability of method ASTM D 3120. Results for the two distillates from ANS and ALT crude oils agree reasonably well considering three of the four values determined by XRF are outside the range of applicability.

4.5 Carbon Residue

Carbon Residue was determined by ASTM D 524, Ramsbottom Carbon Residue of Petroleum Products or by ASTM D 4530, Determination of Carbon Residue (Micro method). In the Ramsbottom method, a weighed sample in a special glass bulb having a capillary opening is placed in a metal furnace maintained at approximately 550° C. The volatile material is evaporated with or without decomposition and the heavier material undergoes cracking and coking reactions. After a specified heating period, the bulb is removed, cooled in a desiccator, and reweighed. The weight of the residue is expressed as a percentage of the original sample weight. Repeatability is given by a complex relationship expressed as a curve on a log/log plot of r versus average Ramsbottom Carbon Residue. Values of r vary from 0.02 wt. % for a residue value of 0.04 wt. %, to 2 wt. % for a residue value of 20 wt. %. Corresponding values for reproducibility are 0.026 and 3 wt. %, respectively. No bias was given for the method since the test is empirical. Comparison of results from the ANS and ALT blind sample with the original 850-950° F distillate results show one pair of results within repeatability (ALT) and one outside the reproducibility (ANS, $R = 0.06$, values 0.24 and 0.32 wt. %).

In the Micro Carbon Residue method, a weighed sample is placed in a glass vial and heated to 500° C under a nitrogen atmosphere in a controlled manner for a specific time. As the sample undergoes coking reactions, volatiles are swept away by the nitrogen. The carbonaceous-type residue remaining is reported as a percent of the original sample. Repeatability is given by the relationship: $r = 0.0770X^{2/3}$ where X is the percent micro carbon residue. Reproducibility is

given by $R = 0.2451X^{2/3}$. No bias was reported for this method as the wt. % of carbon residue can be defined only in terms of the test method. Carbon residue results are listed in Table 18. The difference between determinations of Micro Carbon residue by ASTM D 4530 on the original and blind ANS 850-950° F distillate was 0.05 wt. % (0.36 - 0.31). This difference was well within the reproducibility (0.12 wt. %).

5. EBULLIOMETRIC VAPOR PRESSURE MEASUREMENTS

Prior to the ebulliometric vapor pressure measurements each fraction was carefully outgassed (degassed) on a vacuum line using freeze, pump, thaw cycles. Three cycles were used to remove dissolved air. Liquid nitrogen was used in the outgassing to prevent the loss of light ends. The outgassing procedure was undertaken to prevent thermal oxidation of the sample by small amounts of dissolved oxygen during the subsequent high-temperature vapor pressure measurements.

The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Institute for Standards and Technology (NIST). All temperature measurements were made in terms of the ITS-90 (16,17) and subsequently converted to °F. Measurements of electric resistance and potential difference were made in terms of standards traceable to calibrations at NIST. Vapor pressures were determined in Pascals. Values reported in mm Hg were derived using the conversion factor 1 mm Hg = 133.322 Pa.

The vapor pressure measurements were made using twin comparative ebulliometry, wherein both the boiling and condensation temperatures are measured, and the pressure in the system is determined by comparison with standards. The ebulliometer is a one-stage total reflux boiler designed to minimize superheating of the boiling liquid. The essential features of the ebulliometric equipment and procedures for vapor-pressure measurements are described in the literature (18, 19, 20). The ASTM Standard Test Method E 1719-97 gives details of the methodology for ebulliometry (boiling temperature only). The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure under a common helium atmosphere. In the pressure region from 25 to 270 kPa, water was used as the standard, and the pressures were derived using the internationally accepted equation of state for ordinary water revised to ITS-90 (21). In the pressure region from 2 to 25 kPa, decane was used as the standard. Pressures were calculated on ITS-90 for those measurements using the equation:

$$\ln(p/\text{kPa}) = 7.73165 + (1/T_r)\{-9.98917(1-T_r) + 5.28411(1-T_r)^{1.5} - 6.51326(1-T_r)^{2.5} - 2.68400(1-T_r)^5\}, \quad (1)$$

where $T_r = T/(617.650 \text{ K})$ and T denotes the condensation temperature for the decane.

The precision in the temperature measurements for the ebulliometric vapor-pressure studies was 0.001 K. Uncertainties in the pressures are adequately described by:

$$\sigma(p) = (0.001) \{ (dp_{(\text{ref})}/dT)^2 + (dp_{(x)}/dT)^2 \}^{1/2} \quad (2)$$

where $p_{(\text{ref})}$ is the vapor pressure of the reference substance and $p_{(x)}$ is the vapor pressure of the sample under study.

Table 19 lists the vapor pressure measurements made on each of the fractions. The temperatures are in °F and the pressures in mm Hg. In table 19, T_{cond} is the condensation temperature for the corresponding pressure, p . T_{boil} is the temperature of the boiling liquid for the corresponding pressure and $\Delta T = T_{\text{boil}} - T_{\text{cond}}$. $\sigma(p)$ gives the precision of the measurements when a pure component sample is refluxed in the ebulliometer. For a pure component sample, ΔT usually averages less than 0.03° F. **Temperatures listed for the vapor pressure data are defined in terms of the ebulliometer system and do not correspond exactly with similar terms used in engineering practice. However, the condensation temperature should be within a few degrees of what is referred to in engineering terms as the bubble point.**

Vapor pressure measurements on the 600–650° F SJV distillate were also conducted by Wiltec Research Company. Table 19A gives the vapor pressure data from 144° C (292° F) to 330° C (627° F). The measured vapor pressure data was also correlated by the Antoine equation. The correlated pressures and the percent deviations between the two pressures are listed in the table also.

The vapor pressure data from Wiltec agreed very well with that measured by NIPER. For comparison, the NIPER data and the combined data were also correlated by the Antoine equation, $\ln P(\text{mm Hg}) = A - B/(T(\text{K}) - 93.)$. The following values were found for A , B , R^2 for the correlation, and the average % deviation between calculated and measured pressures:

Data Set	A	B	R^2	Ave. % Dev. P
Wiltec	16.631	5186.4	0.9999	1.39
NIPER	16.659	5192.4	0.9999	0.78
Combined	16.645	5190.2	0.9999	1.33

The precision of the NIPER data as indicated by the average % deviation of 0.78% was very good.

6. TWO-PHASE HEAT CAPACITY AND PSEUDO-CRITICAL TEMPERATURE MEASUREMENTS

Several fractions of the ANS, ALT, and SJV crudes were selected for heat capacity measurements. The samples were carefully outgassed (degassed) on a vacuum line using freeze, pump, thaw cycles. Three cycles were used for each sample to remove dissolved air. Liquid nitrogen was used in the outgassing to prevent the loss of "light ends." The outgassing procedure was undertaken to prevent thermal oxidation of the samples during the subsequent high-temperature heat-capacity measurements.

Values of the heat capacity are reported in units of Btu/(lb °F). They were measured in units of J/(gK) and converted by multiplying by the factor 0.2390056. Temperature measurements were made in terms of the IPTS-68(22) or ITS = 90(16) and were subsequently converted to °F. Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards (NBS).

Differential-scanning calorimetric measurements were made with a Perkin-Elmer DSC II which was fitted with a glove box to exclude air from the head. The calorimeter head was flushed with dry nitrogen. A Perkin-Elmer Intercooler II "freon" refrigeration unit was used to remove energy from the calorimetric head.

The samples were confined in high-pressure cells fabricated at NIPER.(23) The cells were made from 17-4 PH chromium nickel stainless steel (AISI#630), and had an internal volume of approximately 0.05 cm³. The cells were sealed with gold gaskets in the form of washers. The internal volumes of the cells were determined from the masses of water held by the cells after they were immersed and sealed in distilled water. The heights of the cells were determined after sealing to correct the volumes for compression of the gold gaskets. It was practical to work with the cells filled in the range of 0.5 to 1.5 times the critical density. In that range, the saturation temperatures are typically within 20 K (36° F) of the critical temperature.

Oxygen is known to be a promoter for the formation of free radicals leading to sample decomposition at high temperatures. Therefore, care was used to exclude oxygen from both the samples and the cells. All cells were sealed in an atmosphere of dry nitrogen.

All measurements of the two-phase heat capacities (liquid plus vapor) were determined with a stepwise heating method described by Mraw and Naas.(24) Measurements were made in 20-K (36° F) increments at a heating rate of 5 K•min⁻¹. An integrating voltmeter was used to give an almost continuous integration of the imbalance signal from the d.s.c. A computer was programmed to step through the heat-equilibration-heat cycles, collect the imbalance signals from the voltmeter, and monitor the temperature from the d.s.c.

The temperature scale of the d.s.c. was calibrated before each set of heat-capacity measurements by measurement of the melting temperatures of NIST Standard Reference Materials (SRM's) indium (429.78 K), tin (505.06 K), and lead (600.65 K). The energy scale was assumed to be dependent upon temperature, scanning rate, and the gain settings for the instrument. Imbalance signals were calibrated with sapphire using published heat-capacity values.(25)

None of the three heat capacities – heat capacity at constant volume (C_v), heat capacity at constant pressure (C_p), or heat capacity at saturated pressure (C_{sat}) — can be directly measured conveniently for a liquid along its saturation line. The third heat capacity, C_{sat} , is the most closely related to experiment, and could, in principle, be measured directly in a calorimeter whose volume was adjusted to be that of the saturated liquid at each temperature. This would, however, be difficult to realize experimentally. In practice the measurement is of the heat capacity at constant total volume of a liquid in equilibrium with a small amount of its vapor. The difference between the measured (liquid + vapor) heat capacities and C_{sat} is small at low vapor pressures ($p < 0.1$ MPa), but becomes significant as the vapor pressure increases. This difference was first discussed as a problem of practical importance when heat capacities were required in the refrigeration industry for compounds such as liquid ammonia, carbon dioxide, and methyl chloride. Osborne and van Dusen(26) and Babcock(27) gave full analyses of the heat capacity in the two-phase system and derived C_p and C_{sat} . Hoge(28) gave a clearer and more concise description, but he derived C_{sat} only.

Details of the theoretical background for the determination of heat capacities at vapor-saturation pressure, C_{sat} , with results obtained with a d.s.c. have been described previously(29). Although the theoretical analysis was derived assuming the substance in the d.s.c. cell was a pure compound, unpublished research at NIPER has shown it can be applied successfully to narrow-

boiling fractions provided the boiling range of the fractions is 50° F or less. In this research the absence of vapor pressure measurements over a sufficient range of pressures (approximately 10 to 270 kPa), and density measurements over a range of temperature, precluded the derivation of C_{sat} values for each fraction.

The experimental two-phase heat capacities C_X^{II} for the selected fractions are listed in Table 20. As noted above, the absence of both vapor pressure measurements and density as a function of temperature precluded calculation of C_{sat} values for either fraction. To partially compensate for the missing data the fractions were studied with about 20 mg of sample in the cells to minimize the vaporization correction, thereby more closely approximating C_{sat} .

7. THERMAL CONDUCTIVITY

Thermal conductivity measurements by ASTM D 2717, Thermal Conductivity of Liquids, at three temperatures (40, 100 and 150° C) were carried out by Phoenix Chemical Laboratory, Inc. Data for fractions between 320 to 950° F are listed in Table 21. The method is applicable to nonmetallic liquids that are: 1) chemically compatible with borosilicate glass and platinum; 2) moderately transparent or absorbent to infrared radiation; and 3) have a vapor pressure less than 200 mm Hg at the temperature of the test. Materials with vapor pressures up to 50 psia can be tested in an appropriate pressurized cell. The thermal conductivity is determined by measurement of the temperature gradient produced across the liquid sample by a known amount of energy introduced into the cell by electrically heating the platinum element. The cell is constructed according to precise specifications given in the test method. Precision and bias have not been determined due to lack of sufficient volunteers for a cooperative laboratory study. A preliminary estimate of repeatability is 10% of the average of two results by the same operator.

8. VISCOSITY

Viscosities were run by ASTM D 445, Kinematic Viscosity of Transparent and Opaque Liquids and by modified ASTM D 4741, Measuring Viscosity at High Temperature and High Shear Rate by Tapered-Plug Viscometer, using a Haake viscometer. Method ASTM D 445 is applicable to transparent and opaque liquid petroleum products with viscosities in the range 0.2 to 300,000 cSt at all temperatures. In the method, time is measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible head and at a

closely controlled and known temperature. The kinematic viscosity is the product of the measured flow time and the calibration constant of the viscometer.

Method ASTM D 4741 was modified to cover determination of the dynamic viscosity of oils using a Haake Rotovisco RV 12/RV 100 with the PK 100 cone and plate sensor system. Samples were run according to the Haake manual. The viscosity of a sample is given by the measured shear stress divided by the preset shear rate.

Kinematic viscosity measurements were made at a total of eight temperatures (0, 25, 40, 70, 100, 125, 150, and 175° C) with viscosities of all samples up to 950° F being made at two or more temperatures. Viscosities (in centistokes) are reported in Table 22. Dynamic viscosity (in centipoise) was measured on four fractions boiling above 950° F at four temperatures (70, 100, 125, and 150° C) by Haake viscometer. These dynamic viscosities were subsequently converted to kinematic viscosities by the following equation:

$$\text{kinematic viscosity} = \text{dynamic viscosity} / \text{density}$$

at the same temperature used for measuring the viscosity. Data are also shown in Table 22.

Precision for viscosity by ASTM D 445 is given for a number of petroleum fractions and products at a number of temperatures. Data appropriate for the fractions in this study are the following. Repeatability for ASTM D 445 viscosity of base oils at 104 and 212° F is 0.0011X, where X is the average of results being compared. Corresponding reproducibility is 0.0065X. For residual fuel oils at 176 and 212° F, repeatability for this method is 0.013 (X+8). Corresponding reproducibility is 0.04 (X+8). For gas oils, repeatability for measurement at 104° F is 0.0043 (X+1). Corresponding reproducibility is 0.0082 (X+1). Repeatability and reproducibility for petroleum wax at 212° F are 0.0141X^{1.2} and 0.0366X^{1.2}, respectively. No statement of bias was made in the method.

Repeatability for ASTM D 4741 was 2.8 % of the mean of two test measurements being compared. Reproducibility was 5.0 % of the mean. Both were based on a 12 laboratory study of 12 ASTM engine oils in the range from 2.4 to 4.8 centipoise. No statement of bias could be made since all determinations are relative to the calibration fluid. Repeatability of test results using the Haake instrument is comparable to that of ASTM D 4741 according to the Haake manual.

Repeat measurements of kinematic viscosity by ASTM D 445 were made on several samples. Comparing precision data with the sample data is difficult as the sample type/temperatures for

the precision data do not match the sample/temperature combinations for the ANS, ALT, and SJV data. With one exception, the data from the ANS and ALT 850-950° F distillate blind samples were well within the repeatability for gas oils at 104° F, although the measurements were made at 158, 180, 212, and 257° F. The exception was data for the ALT fraction measured at 158° F which were outside the repeatability (0.048) and reproducibility (0.09). Comparing this very waxy crude sample with repeatability and reproducibility for petroleum wax at 212° F shows the data are well within the reproducibility (0.60). Repeat runs for the SJV 450-650° F composite sample gave 6.747 and 6.750 cSt at 104° F; and 3.131 and 3.087 cSt at 158° F. The data at 104° F were within the repeatability ($r = 0.007$), but the data at 158° F were outside the reproducibility ($R = 0.022$), both using the precision data for gas oils at 104° F. Repeat runs for the ALT 650-950° F composite at 158° F (6.362/6.198) and 212° F (3.644/3.733) were outside the repeatability and reproducibility for gas oils, but were within the reproducibility and repeatability for petroleum wax ($R = 0.332$ and $r = 0.068$), respectively. The repeat run at 257° F (2.602/2.598) was well within the repeatability value for gas oils at 104° F (0.015) or petroleum wax at 212° F (0.044).

9. GRAVITY

Specific gravities and API gravities for the whole crude oils, their fractions, and resids are presented in Table 23. Specific gravities for the crude and fractions through 950° F were measured by ASTM D 4052, Density and Relative Density of Liquids by Digital Density Meter, when feasible. The API gravities were calculated from the specific gravities at 60/60° F. Specific gravities for the >650° F and >950° F resids and higher boiling fractions were determined by pycnometer, ASTM D 70, Specific Gravity of Semi-solid Bituminous Materials; or by hydrometer, ASTM D 1298, Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method, with the results corrected to 60° F and then recorrected to other temperatures by ASTM D 1250 using Volume X, Background, Development, and Implementation Procedures as needed.

ASTM Method D 4052 is applicable to petroleum distillates and viscous oils that can be handled in a normal manner as liquids at test temperatures between 60 and 95° F and that have vapor pressures below 600 mm Hg and viscosities below about 15,000 cSt at the test temperature. In this method about 0.7 mL of sample is injected into an oscillating sample tube and the change in oscillation frequency caused by the change in mass of the tube is used along with calibration data to determine the density of the sample. Specific gravity is calculated by dividing by the density of water at the same temperature. Repeatability for tests conducted at 60 and 68° F with samples

in the range 0.68 to 0.97 g/mL was determined to be 0.0001. Reproducibility was 0.0005 g/mL. A study of four standard reference oils certified by pycnometry with densities ranging from 0.747 to 0.927 g/mL at 20° C and viscosities between 1 and 5,000 centipoise (also at 68° F) indicated that this method can be biased by up to 0.0006 g/mL.

ASTM Method D 1298 is applicable to crude petroleum, petroleum products, and mixtures of petroleum and nonpetroleum products normally handled as liquids, and having a Reid vapor pressure of 26 psi or less. Density, relative density (specific gravity), or API gravity is determined using a glass hydrometer at a temperature convenient for the sample. Density values are converted to 15° C, and specific gravity and API gravity to 60° F, by means of international standard tables. Repeatability for transparent, nonviscous samples measured in the temperature range 29 to 76° F is 0.0005 for density and specific gravity (0.1 for API gravity in temperature range 42 to 78° F). Reproducibility is 0.0012 and 0.3, respectively. For opaque samples, repeatability for measurements in the same temperature ranges is 0.0006 for density and specific gravity and 0.2 for API. Reproducibility is 0.0015 and 0.5, respectively.

ASTM Method D 70 is applicable to viscous, semi-solid bituminous materials. The method is gravimetric using a pycnometer of known volume. Repeatability at 60° F is 0.003 and reproducibility is 0.007.

Agreement between repeated specific gravity determinations by ASTM D 4052 is mixed although much of the comparison data is within or near the repeatability of 0.0001. For example, the original and repeat values for specific gravity of the 550-600° F fraction from SJV crude at 60° F were 0.8914 and 0.8913, respectively. A similar comparison for the ANS 750-850° F fraction with values of 0.9296 and 0.9303 was close to the reproducibility of 0.0005. Three determinations on the SJV 750-850° F fraction (0.9604, 0.9627, and 0.9625) showed good agreement between the latter two values, but not between the first and the latter two.

Agreement between specific gravity data determined by PARC (method unspecified) and those determined by NIPER on the same fractions was also mixed with some data being identical (0.8633 for the ANS 500-550° F fraction) and some data showing relatively large differences (0.9548 and 0.9437 for the ANS 850-950° F fraction, respectively). Most of the comparative data showed reasonable agreement with over half being within the reproducibility for the method.

Agreement between repeated specific gravity determinations by ASTM D 1298 at 60° F was mixed as well. Values for the original and blind ALT 850-950° F samples was within the repeatability of 0.0005 (0.8409 and 0.8405, respectively). Three runs of the ALT 750-850° F fraction showed fair agreement between the latter two, but not between the first and either of the latter two (0.8338, 0.8275, and 0.8264, respectively). This discrepancy may be due to difficulties in running waxy samples by this hydrometer method.

Agreement between results on the same samples at the same temperature but by different methods was mixed also.

10. MOLECULAR WEIGHT

Molecular weight for the 320-450° F fraction was subcontracted to Core Laboratories for determination by freezing point depression. Repeatability is given by $r = 0.03X$, where X is the average molecular weights. No value for reproducibility was available. Molecular weights for all higher boiling fractions were determined by ASTM D 2503, Molecular Weight (Relative Molecular Mass) of Hydrocarbons by Thermoelectric Measurement of Vapor Pressure using a Wescan Model 232A Molecular Weight Apparatus. This method is applicable to petroleum fractions with initial boiling point above 430° F and with molecular weights up to 3000, although precision has not been established above 800. A weighed portion of the sample is dissolved in a known quantity of a suitable solvent. A drop of the solution and a drop of the solvent are suspended, side by side, on separate thermistors in a closed chamber saturated with solvent vapor. Solvent condenses on the sample drop since the vapor pressure of the solution is lower than that of the solvent. This causes a temperature difference between the two drops. The resultant change in temperature is measured and used to determine the molecular weight of the sample by reference to a previously prepared calibration curve. Repeatability is 5 g/mol for molecular weights in the range 245 to 399, 12 in the range 400 to 599, and 30 in the range 600 to 800. Reproducibilities for the three ranges are 14, 32, and 94 g/mol, respectively. Molecular weight data are listed in Table 24.

Agreement between repeated molecular weight determinations by ASTM D 2503 was reasonably good except for the SJV 500-550° F fraction (228/246), which was outside the reproducibility. The data for the ANS and ALT 850-950° F fractions and blind samples showed excellent agreement as did the freezing point depression molecular weight determinations for the ANS and SJV 320-450° F fractions.

11. SUMMARY

Crude oil characterization and thermophysical property data from the twelve reports issued in the course of the API research program on characterization of crude oils are compiled in this comprehensive report. The goal of the API program was to obtain complete sets of property data on a few widely varying crude oils to test the basic correlations necessary to evaluate a crude oil for design purposes. The crude oils selected by the project sponsors were Alaska North Slope (a typical and important crude for a number of U.S. refineries), Utah Altamont (a very paraffinic crude), and San Joaquin Valley (an aromatic crude). In general, data obtained on the two blind samples and data from repeat runs on samples taken out of cold storage were in good agreement with original data. Reproducibility precision values apply more closely in the comparisons with repeat runs which were made two to four years after the original runs, and often by different operators. The scope of this report is limited to a discussion of the characterization tests and their accuracy, and to a comprehensive compilation of data for the three crudes. The thermodynamics and petroleum test laboratories at NIPER have a long history of producing high quality data and have always taken the utmost care and pride in their work. The vast majority of the data produced in this program are judged to be highly reliable. Nevertheless, every test method has its limitations. Data which are judged to be of particularly high quality, given the limitations of the particular method, are vapor pressure, heat capacity, refractive index, flash point, carbon, hydrogen, nitrogen, sulfur, hydrocarbon types by mass spectrometry, and aromatic carbon by nuclear magnetic resonance spectrometry. Some problems were encountered with the gravity and viscosity data, particularly with the waxy Altamont crude samples.

In addition, the ASTM D 86 distillation data for the 650-750° F distillates, run at the sponsors' request, should not be considered reliable as these distillates are outside the range covered by the method. Similarly, the ASTM D 2892 distillations of the narrow boiling range cuts are not reliable as the method applies to crude oils and the automated equipment is not designed for use on such narrow cuts. Finally, although the data were generated to allow evaluation of various correlations used for design purposes, such evaluation is beyond the scope of this report and have been/will be done by API Technical Data Committee participants.

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Table 1. Preparative Distillation of Alaska North Slope (ANS), Altamont (ALT), and San Joaquin Valley (SJV) Crudes^a

	ANS						ALT		SJV	
	Vapor Temp. ^b °F	Pressure ^b mm Hg	AET ^c °F	Yield wt. %	Yield vol. %	Cumulative Yield vol. %	API Grav.	Spec. Grav.	Yield ^e wt. %	Spec. Grav.
Crude							27.3	0.8911		0.9772
Cut 1	163	740	165	3.0	4.1	4.1	85.6	0.6518	--	--
Cut 2	318	740	320	9.6	11.3	15.4	55.8	0.7555	0.9	0.8081
Cut 3	314	87	450	9.6	10.6	26.0	43.2	0.8100	2.4	0.8529
Cut 4	328	48	500	4.7	4.9	30.9	35.6	0.8468	3.1	0.8735
Cut 5	348	29	550	5.4	5.6	36.5	32.4	0.8633	6.0	0.8849
Cut 6	375	22	600	4.4	4.5	41.0	31.2	0.8697	4.6	0.9106
Cut 7	420	22	650	5.4	5.4	46.5	28.0	0.8871	8.0	0.9340
Cut 8	478	12	750	10.5	10.3	56.8	24.8	0.9053	9.6	0.9490
Cut 9	565	12	850	11.1	10.7	67.4	20.9	0.9285	11.5	0.9600
Cut 10	526 ^d	0.61 ^d	950	6.5	6.1	73.5	16.7	0.9548	17.9	0.9888
Bottoms			>950	28.1	24.7	98.3	8.0	1.0142	31.8	1.0580
Cut 11			1050	4.0				^f 0.9603	4.1	^h 1.0034
Cut 12			1150	5.3				^f 0.9656	3.9	^h 1.0051
Cut 13			1250	5.7				^f 0.9812	5.7	^h 1.0183
>1250 Resid			>1250	12.9				^g 1.0029	17.9	^h 1.0436
Total Loss				1.9					4.4	

^a Distillation to produce cuts 1 through 10 were performed by Pittsburgh Applied Research Center. Fractions 1-9 were obtained with a 150 gallon batch still charged with 90 gallons of crude and fraction 10 was obtained from 10-liter Sarnia stills. Cuts 11 through 13 were prepared by NIPER using short path distillation on a 6-inch Pope still.

^b Data for ANS crude; similar data for ALT and SJV crudes are found in references 2 and 4, respectively.

^c Atmospheric equivalent temperature.

^d Average of 11 Sarnia still runs.

^e First cut made at 320° F due to insufficient material boiling below 165° F.

^f ASTM D 4052 @ 80/80° F.

^g ASTM D 70 @ 180/180° F.

^h ASTM D 70 @ 60/60° F.

Table 2. Short Path Distillation of ANS, ALT, and SJV >950° F Resids: Yields and Recoveries

	ANS		ALT		SJV	
	wt., kg	wt. %	wt., kg	wt. %	wt., kg	wt. %
First Pass (Nominal 950-1050° F)						
Total Charge	43.081		26.14		26.22	
Distillate	6.216	14.4	4.42	16.9	3.40	12.97
Resid	36.859	85.6	21.63	82.8	22.75	86.77
Total Recovered	43.075	99.9	26.05	99.7	26.15	99.74
Second Pass (Nominal 1050-1150° F)						
Total Charge	24.37		21.60		22.41	
Distillate	5.37	22.1	6.03	27.9	3.15	14.06
Resid	18.97	77.9	15.52	71.9	19.25	85.90
Total Recovered	24.34	99.88	21.55	99.8	22.40	99.96
Third Pass (Nominal 1150-1250° F)						
Total Charge	13.63		15.49		15.22	
Distillate	4.19	30.8	6.76	43.6	3.64	23.92
Resid	9.43	69.2	8.72	56.3	11.51	75.62
Total Recovered	13.62	99.93	15.48	99.9	15.15	99.54

Table 3. Comparison of Preparative Distillation Cut Yields with ASTM Distillation and Simulated Distillation Data (wt. %)

Distillation Cut	ANS		ALT		SIV				
	Prep	D 2892 ^a D 1160 ^b	Prep	D 2892 ^a D 1160 ^b	Prep	D 2892 ^a D 1160 ^b D 5307 ^c			
IBP - 165° F	3.0	2.9	3.4	1.2	0.4	0.2	0.0	0.0	0.0
165 - 320° F	9.6	9.7	10.3	8.2	6.7	8.0	0.9	1.0	0.0
320 - 450° F	9.6	9.6	10.3	8.7	8.9	9.1	2.4	2.5	4.3
450 - 500° F	4.7	4.8	4.8	5.9	3.9	4.6	3.1	3.0	3.2
500 - 550° F	5.4	5.0	5.4	4.3	4.3	5.3	6.0	4.0	4.2
550 - 600° F	4.4	4.4	5.0	6.2	5.5	4.8	4.6	4.6	5.0
600 - 650° F	5.4	4.9	5.7	4.4	6.2	6.0	8.0	5.4	5.6
650 - 750° F	10.5	8.2	11.1	9.2	10.6	12.5	9.6	8.2	12.1
750 - 850° F	11.1	12.3	10.9	13.4	16.5	14.0	11.5	16.6	13.5
850 - 950° F	6.5	9.9	9.9	10.4	12.4	10.3	17.9	12.2	11.8
Cumulative Total	70.2	71.7	76.0	71.9	75.4	74.8	64.0	57.5	59.7

^a Data obtained from Table 4 for cuts up to 650° F.

^b Data for >650° F cuts obtained from Table 7 by linear interpolation or extrapolation and conversion to whole crude basis.

^c Data obtained from Table 9 by linear interpolation.