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High-temperature Simulated Distillation Applications in Petroleum Characterization

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Simulated distillation (SimDist) is a gas chromatography (GC) technique which separates individual hydrocarbon components in the order of their boiling points, and is used to simulate the time-consuming laboratory-scale physical distillation procedure known as true boiling point (TBP) distillation. The separation is accomplished with a nonpolar chromatography column using a gas chromatograph equipped with an oven and injector that can be temperature programmed. A flame ionization detector (FID) is used for detection and measurement of the hydrocarbon analytes. The result of SimDist analysis provides a quantitative percent mass yield as a function of boiling point of the hydrocarbon components of the sample. The chromatographic elution times of the hydrocarbons are calibrated to the atmospheric equivalent boiling point (AEBP) of the paraffins reference material. The SimDist method ASTM (American Society for Testing and Materials) D2887 covers the boiling range 55–538 °C (100–1000 °F) which covers the n*-alkanes (*n*-paraffins) of chain length about C_5–C_{44}. The high-temperature simulated distillation (HTSD) method covers the boiling range 36–750 °C (97–1382 °F) which covers the* n*-alkane range of about C_5–C_{120}. A key difference between ASTM D2887 and HTSD is the ability of the latter technique to handle residue-containing samples (i.e. material boiling > 538 °C, 1000 °F). SimDist and laboratory-scale physical distillation procedures are routinely used for determining boiling ranges of petroleum crude oils and refined products, which include crude oil bottoms and residue processing characterization. The boiling point with yield profile data of these materials are used in operational decisions made by refinery engineers to improve product yields and product quality. Data from SimDists are valuable for computer modeling of refining processes for improvements in design and process optimization. Precise yield correlations between HTSD and crude assay distillation (methods ASTM D2892 and D5236) have allowed HTSD to be successfully used in place of physical distillation procedures. This has given the refiner the ability to rapidly evaluate crude oils for selection of those with economic advantages and more favorable refining margins. SimDist methods are becoming more widely used in environmental applications. HTSD is useful for characterizing hydrocarbons which can be present as soil and water contaminants; for example, to map and follow hydrocarbon removal processes.*

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1 INTRODUCTION

SimDist is a GC technique which separates individual hydrocarbon components in the order of their boiling points, and is used to simulate time-consuming laboratory-scale physical distillation procedures. The separation is accomplished with a chromatography column coated with a nonpolar (hydrocarbon-like), stationary phase, and uses a gas chromatograph equipped with an oven and injector which can be temperature programmed. A FID is used for detection and measurement of the hydrocarbon analytes. The SimDist analysis result provides a quantitative percent mass yield as a function of boiling point of the hydrocarbon components of the sample being analyzed. The chromatographic elution times of the hydrocarbon components are calibrated to the AEBP of the *n*-alkane as described in a method from the ASTM(1) by using *n*-alkane (*n*-paraffin) reference material. In the SimDist method ASTM D2887,(1) the *n*-alkane calibration reference covers the boiling range 55–538 °C (100–1000 °F) which covers the *n*-alkanes with a chain length of about C_5–C_{44}. In the HTSD method, the *n*-alkane calibration reference (a hydrogenated polyolefin wax, polywax 655) covers the boiling range 36–750 °C (97–1382 °F) which covers the *n*-alkanes with a chain length of about C_5–C_{120}. A key difference between ASTM D2887 and HTSD is the ability of HTSD to handle residue-containing samples (i.e. material boiling $>$ 538 °C or 1000 °F).

SimDist and laboratory-scale physical distillation methods are routinely used for determining boiling ranges of petroleum crude oils and refined products. The boiling point with yield profile data of these materials are used in operational decisions made by refinery enginers to improve product yields and product quality. SimDist is valuable for, and can improve results from, computer modeling of refining processes for improvements in design and process optimization. Precise yield correlations between HTSD and crude assay distillation (a procedure which uses methods ASTM D2892(2) and D5236(3)) have allowed HTSD to be successfully used in place of physical distillation procedures. This can result in economic advantages for the refiner in the selection of crude oils, with more favorable refining margins. SimDist methods are also now becoming more widely used in environmental applications; for example, in characterizing hydrocarbons which can be present as soil and water contaminants.

2 HISTORY

SimDist was reported early in the 1960s by Eggertsen et al.(4) and Green et al.(5,6) as a method of simulating the time-consuming laboratory-scale physical distillation "TBP" procedure(7) by using GC. The SimDist technique is based on the fundamental assumption that individual nonpolar hydrocarbon components of a sample elute in the order of their boiling points from a GC column coated with nonpolar (hydrocarbon-like), stationary phase. The elution, or retention, time is dependent upon vapor pressure of the component and its affinity for the stationary phase. This varies with different types of hydrocarbons. For example, aromatic hydrocarbons and cycloalkanes (naphthenes) generally elute earlier than *n*-alkanes having the same boiling points. In SimDist, conditions are selected to give limited column efficiency and resolution unlike other chromatography techniques, which generally aim for highly efficient conditions that achieve high-resolution separation of components. The lower resolution analysis conditions provide distillation data that agree with physical distillation.

SimDist became an ASTM standard method in 1973, with the designation D2887, "Boiling Range Distribution of Petroleum Fractions by GC". The current edition is designated D2887-97. This method covers the determination of the boiling range distribution of petroleum products and fractions having a final boiling point (FBP) of 538 °C (1000 °F) or lower at atmospheric pressure.

HTSD is a relatively recent method which extends ASTM D2887 determination of the boiling range distribution of hydrocarbons to a FBP of about 750 °C (1382 °F). Technological advances in capillary GC columns and stationary phases together with either programmed temperature vaporization (PTV) or on-column injection techniques, provide adequate separation from C_5 to C_{120} normal paraffins and allows the characterization of petroleum products from about 36–750 °C (97–1382 °F). Under the special conditions of HTSD, elution of materials from the GC column occurs at up to 260–316 °C (500–600 °F) below their AEBP. For instance, the elution of C_{110} (AEBP of 735 °C or 1355 °F) occurs at a column temperature of about 427 °C (800 °F). Also under these conditions, little or no evidence of cracking is normally seen in HTSD.

3 COMPARISON OF AMERICAN SOCIETY FOR TESTING AND MATERIALS DISTILLATION AND SIMULATED DISTILLATION METHODS

A summary of ASTM physical distillation and SimDist methods is presented schematically in Figure 1 and discussed in detail below.

3.1 Physical Distillation Methods

Laboratory-scale physical distillation methods are routinely used by petroleum refineries for determining

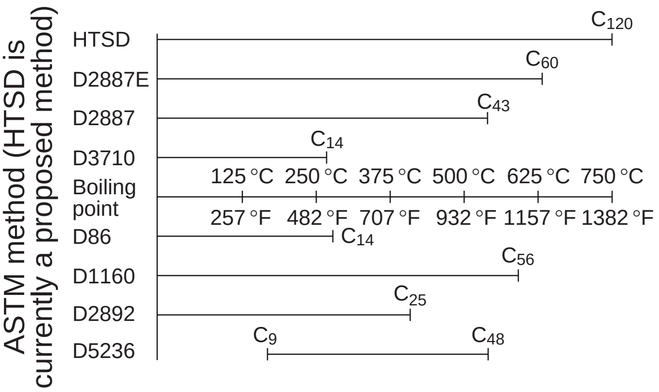


Figure 1 Summary of ASTM physical and simulated distillation.

the boiling ranges of crude oils and their products. ASTM D86[8] has been used as a quality control (QC) test since the 1920s. This method is a one-plate distillation that covers the range of materials boiling up to about 254 °C (490 °F). ASTM D1160[9] is a similar method but is conducted at reduced pressure and covers the determination of the range of boiling points for petroleum products that can be partially or completely vaporized at a maximum liquid temperature of 400 °C (752 °F). This temperature corresponds to an atmospheric equivalent (vapour) temperature of about 600 °C when run under 1 mmHg (the lowest pressure permitted). Petroleum products and fractions in this range may decompose if distilled at atmospheric pressure. ASTM D2892[2] is used for samples with a wide boiling range such as crude petroleum up to a final cut temperature of 400 °C (752 °F) atmospheric equivalent temperature (AET). The method can also be applied to any petroleum mixtures except liquified petroleum gases, very light naphthas, and fractions having initial boiling points (IBPs) above 400 °C. This test method uses a fractionating column having an efficiency of 14–18 theoretical plates operated at a reflux ratio of 5 : 1 for the production of liquefied gas, distillate fractions, and residuum. The method provides for the determination of yields of material as both mass and volume. A graph of temperature versus mass-percent distilled can be produced, and this distillation curve corresponds to a laboratory technique which is defined at 15/5 (15 theoretical plate, 5 : 1 reflux ratio) or TBP. ASTM D5236[3] is for distillation of heavy hydrocarbon mixtures such as heavy crude oils, petroleum distillates, residues, and synthetic mixtures with IBPs greater than 150 °C (300 °F). This method provides for the determination of standard distillation curves to the highest AET possible by conventional distillation. The maximum achievable temperature up to 565 °C (1050 °F) AET is dependent upon the heat tolerance of the charge.

3.2 Simulated Distillation Methods

SimDist methods which have been adopted as ASTM test methods are D2887,[1] D3710,[10] and D5307.[11] Method D2887-97 covers the determination by GC of the boiling range distribution of petroleum products and fractions having a FBP of 538 °C (1000 °F) or lower at atmospheric pressure. Method D3710-95 covers the determination by GC of the boiling range distribution of gasoline and gasoline components with a FBP 260 °C (500 °F) or lower. D5307-97 is for the determination by GC of boiling range distribution of crude petroleum through 538 °C (1000 °F), with material boiling above 538 °C being reported as residue.

HTSD by GC, which is currently under ASTM Committee D-2 proposed development status, is an extension of ASTM method D2887 for application to petroleum products and fractions, and materials containing higher boiling range materials above 538 °C (1000 °F). This method is used for determining the boiling point distribution of petroleum products and fractions in the range up to about 732 °C (1350 °F) at atmospheric pressure, and reports material boiling higher than this as material boiling >732 °C (1350 °F). The method is applicable to a wide range of fully eluting and noncompletely eluting materials, which include petroleum crude oil, cat crack feed and product, hydrotreater feed and products, atmospheric residue, vacuum gas oils, deasphalted oils, and vacuum tower bottoms (pitch).

4 METHODOLOGY

By the proper choice of GC conditions and equipment in HTSD, separation in the boiling range from C_5 to C_{120} *n*-alkanes is carried out routinely. To accomplish the goal of eluting heavy materials up to the equivalent of C_{120}, a thin film of column nonpolar stationary phase is used. The film thickness varies from 0.05–0.15 m, which, with a 0.53 mm internal diameter (ID) capillary column results in a phase ratio (volume of the column vs the volume of the stationary phase) high enough to permit the elution of materials from the column at temperatures up to 260–316 °C (500–600 °F) below their AEBP.

GC instrumentation for HTSD is typically equipped with a PTV injector and FID. The analysis is carried out with a relatively short capillary column about 5 m length, 0.53 mm ID, and 0.05–0.15 µm film thickness. The temperature conditions of the column oven and injector are set initially at either near ambient or sub-ambient (−20 °C) and then programmed at a specified linear rate to a final temperature of about 430 °C. Sub-ambient initial conditions are generally required to cover a wide boiling range of samples. Helium carrier gas is used. The detector signal is recorded as area slices (time intervals) for consecutive increasing retention times. SimDist software is used for data acquisition and results calculations.

4.1 Sample Preparation

A consequence of the conditions necessary for HTSD is a limited concentration capacity of the column due to the small amount of stationary phase. This requires appropriate dilution of the standards and samples (usually in carbon disulfide). Liquid hydrocarbon samples such as petroleum crude oils, gas oils, and solid or semi-solid residue materials, such as vacuum tower bottoms and asphaltic materials, are typically prepared at a concentration of about 2 mass percent in the solvent. Environmental samples such as oil-contaminated soils and waters are generally prepared at higher concentrations on the order of about 50 mass percent solvent to sample to improve sensitivity.

4.2 High-temperature Simulated Distillation Analysis

Because of the highly inert conditions of high-purity fused silica and special treated metal GC columns, the gentle injection techniques, and the short time at maximum temperature, little or no evidence of cracking is normally seen in HTSD. Because of the column breakdown (bleed) during the final portion of an HTSD analysis and the need to dilute the sample to approximately 1–2%, a blank GC run using only the solvent is recorded in the data system. This solvent blank is then subtracted from all subsequent GC runs in the analysis sequence of calibration, QC, and samples (Figure 2). This blank subtraction accomplishes

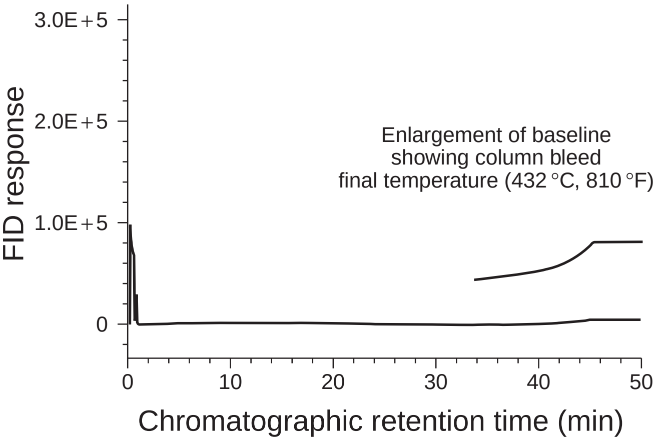
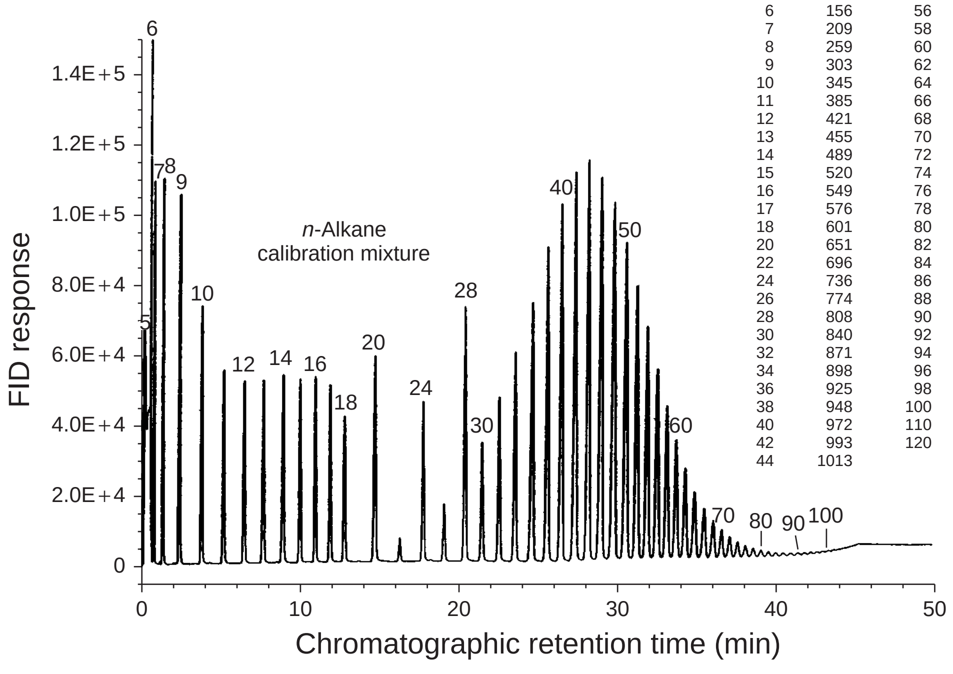


Figure 2 Analysis of carbon disulfide solvent blank by using HTSD.



Boiling points of *n*-alkanes (ASTM method D2887-97[(1)])

Carbon number	BP (°F)	Carbon number	BP (°F)
1	–258.7	46	1033
2	–127.5	48	1051
3	–44	50	1067
4	32	52	1083
5	97	54	1096
6	156	56	1112
7	209	58	1126
8	259	60	1139
9	303	62	1152
10	345	64	1164
11	385	66	1175
12	421	68	1186
13	455	70	1197
14	489	72	1207
15	520	74	1216
16	549	76	1227
17	576	78	1238
18	601	80	1247
20	651	82	1258
22	696	84	1267
24	736	86	1276
26	774	88	1283
28	808	90	1292
30	840	92	1299
32	871	94	1306
34	898	96	1314
36	925	98	1321
38	948	100	1328
40	972	110	1355
42	993	120	1382
44	1013		

Figure 3 Analysis of C_5–C_{110} *n*-alkane calibration reference mixture by using HTSD.

two important goals: (1) it removes the signal present for the solvent, which occurs just following the start of the analysis near the determination of any light end material present; and (2) the column bleed is compensated. The assumption during this process is that the solvent blank and the column bleed profiles are constant during the calibration and sample analysis. It is the HTSD operator's duty to verify this criteria for statistically meaningful results.

4.3 Calibration

The HTSD calibration involves the analysis of (1) *n*-alkane calibration reference (hydrogenated polyolefin wax, polywax 655 which covers the boiling range C_5-C_{120}) as shown in Figure 3, and (2) a reference oil that has been physically distilled by methods ASTM D2892 and D5236, as shown in Figure 4.

The polywax is used to calibrate chromatography elution times of the hydrocarbon components to the AEBP of the paraffin. The physically distilled reference oil is used as an external standard to calibrate the chromatography system for all sample percent recovery calculations. In addition, the HTSD analysis results found for the reference oil are compared to the mass distribution data known from physical distillation of the reference oil, and the statistical error of the difference between HTSD data versus actual boiling point data is reported (Table 1).

4.4 Determination of Hydrocarbon Yield as a Function of Boiling Point

The HTSD analysis result gives a chromatogram of detector signal response as a function of chromatography retention time, and a tabulated report of boiling point distribution of hydrocarbon yield at specific boiling cut-points in cumulative percent mass of sample (Figure 5, and Table 2). The report shows percent mass of material recovered in the analysis, IBP, FBP, and whether material boiling at higher than 732 °C (1350 °F) is present. The IBP is the temperature (corresponding to the retention time) at which a cumulative yield is equal to 0.5% of the total sample. The FBP is the temperature (corresponding to the retention time) at which a cumulative yield is equal to 99.5% of the total sample. The HTSD result can also be expressed in a carbon number distribution format which gives a graphical plot and tabulated report of yield at each *n*-alkane carbon number in incremental and cumulative percent mass (Figure 6).

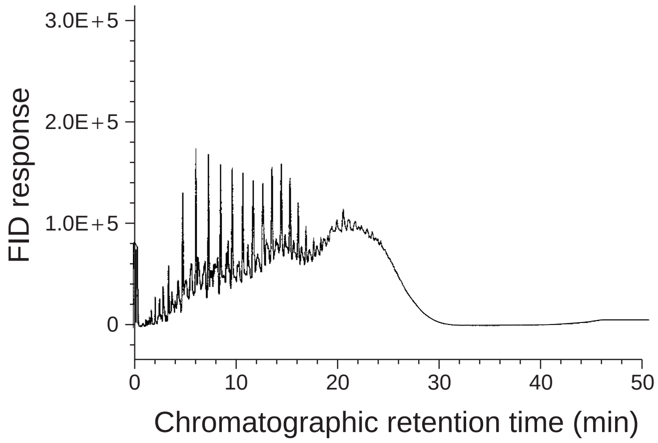


Figure 4 Analysis of ASTM D2892 and D5236 physically distilled reference oil by using HTSD.

Table 1 Results for reference oil obtained using HTSD and two ASTM methods (D2892 and D5236)

Percent area	BP (°F) (ASTM D2892 and D5236)	BP (°F) found (HTSD)	Squared difference (max. acceptance is 139)
10	448	446	4
20	529	526	9
30	603	600	9
40	658	656	4
50	716	715	1
60	777	776	1
70	826	824	4
80	873	871	4
90	923	921	4
		Total:	40

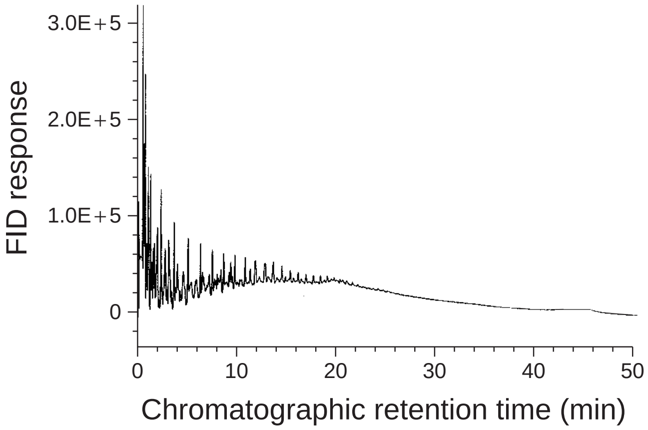


Figure 5 Analysis of Gulf of Mexico crude oil sample by using HTSD.

5 QUALITY CONTROL AND INSTRUMENT PERFORMANCE

5.1 Statistical Analysis of Quality Control Samples

QC and quality assurance (QA) procedures adopted for HTSD are rigorously followed to assure the integrity

Table 2 Tabulated report of results from HTSD analysis of a Gulf of Mexico crude oil

Simdis HT 750 analyzer

Data file name:	C:\HPCHEM\1\DATA\0920A\003F0701.D		
Instrument:	1	Vial:	3
Operator:	Triton Analyt.	Injection:	1
Acquired on:	20 Sep 94, 06:29 PM	Seq. line:	7
Processed on:	21 Sep 94, 11:40 AM		
Sample name:	Gulf of Mexico Crude	Sample amt:	0.0969
Method name:	MHC30.MTH	ISTD amt:	0.0000
Calculation based on:	ESTD	Weight CS2:	4.9479
Sequence name:	0920A Cryogenic sequence		
Blank used:	C:\HPCHEM\1\DATA\0920A\085F0201.D		
Calibration used:	C:\HPCHEM\1\DATA\0920A\090F0301.D		
Reference used:	C:\HPCHEM\1\DATA\0920A\095F0401.D		
Recovery (%):	96.7 found		
Response factor:	1.308E-10		
IBP:	104 (°F)		
FBP:	>1351 (°F)		
End elution after:	44.3 min		

Analysis results: %weight versus boiling point

%	BP (°F)	%	BP (°F)	%	BP (°F)	%	BP (°F)
1	140	25	468	49	687	73	921
2	163	26	478	50	696	74	932
3	191	27	489	51	705	75	943
4	209	28	497	52	715	76	955
5	227	29	507	53	724	77	968
6	240	30	515	54	734	78	981
7	260	31	524	55	743	79	994
8	272	32	535	56	753	80	1007
9	285	33	544	57	762	81	1022
10	298	34	553	58	771	82	1037
11	310	35	563	59	780	83	1052
12	320	36	572	60	789	84	1067
13	331	37	579	61	798	85	1085
14	346	38	588	62	807	86	1099
15	355	39	597	63	816	87	1116
16	370	40	605	64	826	88	1134
17	382	41	614	65	836	89	1152
18	392	42	624	66	846	90	1172
19	405	43	632	67	856	91	1192
20	416	44	641	68	867	92	1214
21	426	45	651	69	877	93	1241
22	436	46	660	70	887	94	1269
23	447	47	669	71	898	95	1298
24	457	48	677	72	909	96	1328

Analysis results: table of cutpoints

BP (°F)	%	BP (°F)	%	BP (°F)	%	BP (°F)	%
150	1.2	375	16.6	650	44.9	1100	86.1
220	4.7	500	28.3	1000	79.4	1200	91.3

of HTSD and statistically meaningful results. The QC includes the initial analysis for calibration of the reference oil that has been physically distilled by methods ASTM D2892 and D5236. As discussed in section 4.3 above, the HTSD yield with boiling point results for the reference oil are compared to the physical distillation mass distribution data, and the statistical error of the difference between HTSD data and the data by physical distillation is calculated and compared with acceptance limits established for the HTSD method.

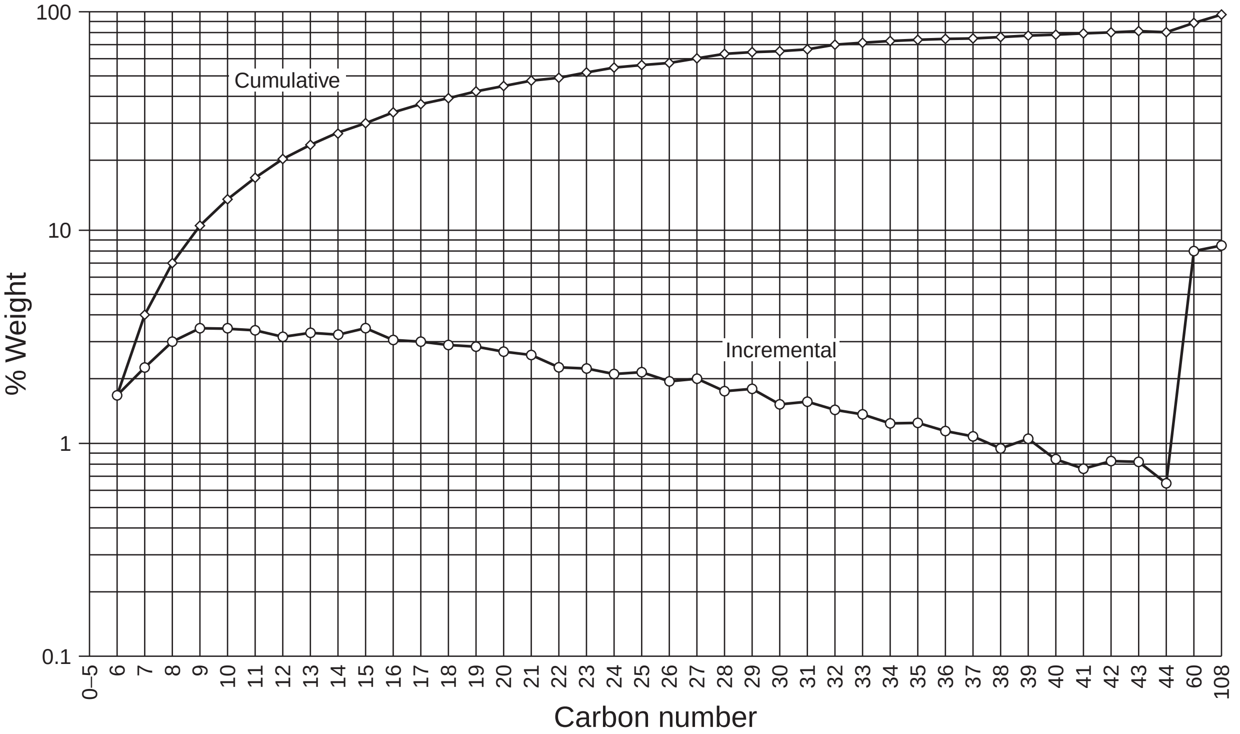


Figure 6 *n*-Alkane carbon number distribution from HTSD analysis of Gulf of Mexico crude oil sample.

Statistical analysis of QC samples is done with materials such as:

- a blend of physically distilled gas oils,
- lube feed stocks,
- hydrotreated residue,
- crude oils of different specific gravity (for example, California crudes and Gulf of Mexico crudes).

For each (QC) sample, the mean and standard deviation (SD) of the temperature vs percent yield is tracked over time. Using an X-type control chart, any excursions beyond ±2 or 3 SD limits will signal an out of control range method (Figures 7 and 8). Appropriate maintenance and corrective action is triggered before a sample analysis is reported.

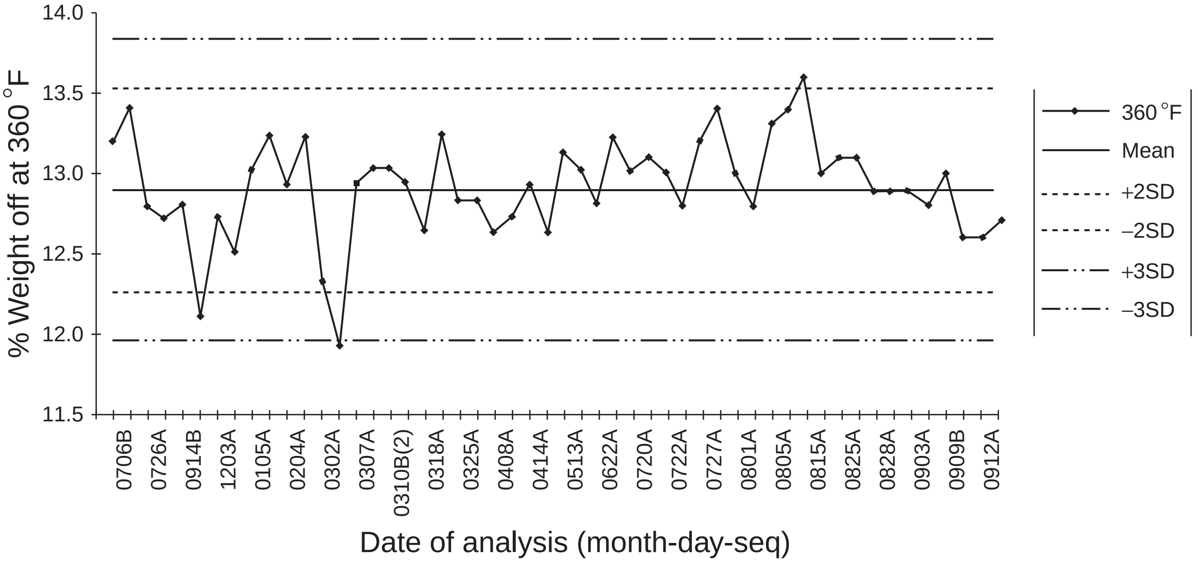


Figure 7 QC X-chart for full range (naphtha and residue-containing) sample (% off at 360 °F) by using HTSD.

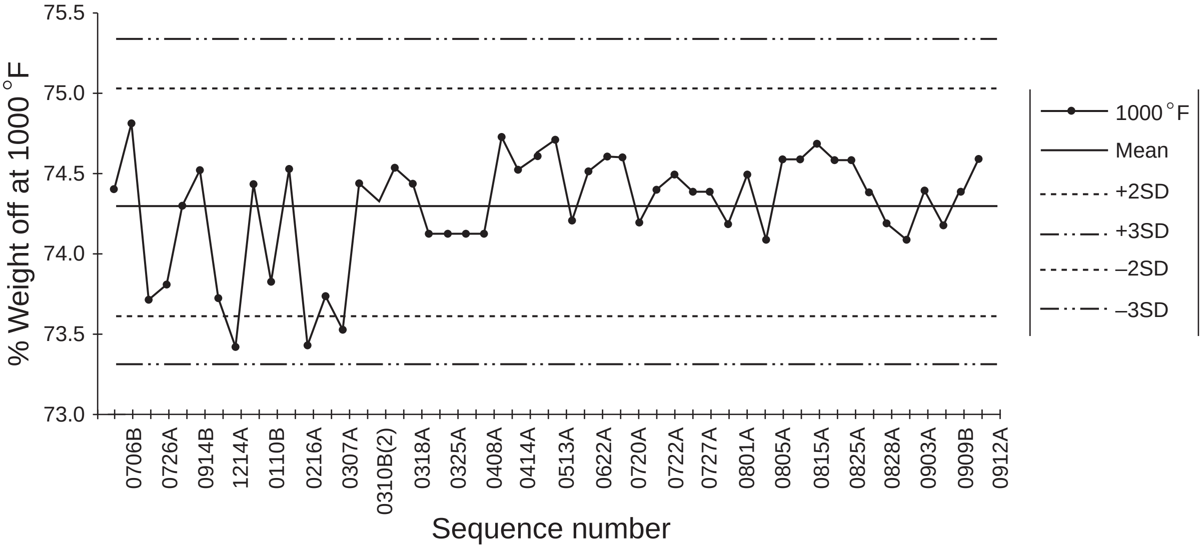


Figure 8 QC X-chart for full range (naphtha and residue-containing) sample (% off at 1000 °F or pitch yield) by using HTSD.

5.2 Instrument Performance and Maintenance

Careful operator evaluation of the system performance is a condition for accurate HTSD data. Visual inspection of the *n*-alkane calibration reference is useful in evaluating system performance. Chromatographic peak shape symmetry of the *n*-alkanes and changes in their retention times can give an indication of the condition of the chromatography column and also the GC injector liner. The solvent blank analysis is also important in monitoring any shifts in baseline during the analysis.

Performance is affected by variables such as loss of the stationary phase at high temperatures (i.e. resulting in loss of film thickness and sample capacity) and the unavoidable build-up from residue containing samples of nonvolatile materials, such as metals, and asphaltenes in the injector and the column. Corrective action often involves replacing the GC injector liner, cutting off a short length of the column at the inlet, or replacing the column with a new one.

5.3 Interlaboratory "Round-robin" Test Results

Since HTSD is currently under ASTM proposed method status, methodologies that are followed in conducting this analysis vary. Users of the technique generally follow a manufacturer's recommended practices for their particular instrumentation. Interlaboratory "round-robin" testing of HTSD draft methods and ruggedness studies for reproducibility are under investigation by ASTM Committee D-2 Study Group and internally by petroleum refining companies that use the technique. The data in Table 3 (provided by Royal Dutch/Shell Laboratories) show interlaboratory round-robin results for five different crude oils by six laboratories. The percent mass of hydrocarbon yield with temperature are given for each crude type and laboratory. Statistical analysis of the data shows the averages, SDs, relative SDs, and the overall average SDs for the HTSD analyses. As shown, precision is best at the cut point yields of 20%, 50%, and 70%, and is lower near the beginning and end cut points of 10% and 90%. The relative SDs of the total percent recoveries of material in the range <720 °C (corresponding to the boiling point of *n*-alkane C_{100}) ranged from about 1% to 5% for the different crude oils tested.

6 PETROLEUM REFINING APPLICATIONS

Distillation is the primary separation process used in crude-oil refining. Although the refinery unit has some nonideality that is not seen in laboratory-scale distillation, laboratory distillation is valuable in simulating the actual plant process. Laboratory analysis data on refinery process streams are often relied on as part of evaluation of unit performance. Process improvement and optimization decisions can be made with the help of laboratory test results that relate to plant occurrences.

6.1 Atmospheric Crude Distillates

Most atmospheric crude units produce atmospheric gas oil (AGO) product for hydrocracker or fluidized catalytic cracker (FCC) feed. A well-designed and proper operating unit will produce AGO with only barely detectable levels of metals present. Generally no volatile metals are found in AGO. Some units, however, produce AGO with relatively high levels of undesirable metals, such as

Table 3 HTSD interlaboratory round-robin results for crude oils

Crude oil and laboratory	Yield at temperature (°C)					%<720 °C (<1328 °F)	% >720 °C (>1328 °F)
	10%	20%	50%	70%	90%		
Arabian Light							
−Lab A	118	179	348	472	653	94.4	5.6
−Lab B	127	185	351	474	660	93.2	6.8
−Lab C	125	182	352	479	680	94.1	5.9
−Lab D	156	174	332	443	592	94.7	5.3
−Lab E	112	167	330	443	589	95.3	4.7
−Lab F	117	175	331	443	589	93.9	6.1
Average	125.8	177.0	340.7	459.0	627.2	94.3	5.7
SD	15.8	6.4	10.7	17.7	41.7	0.7	0.7
% Relative SD	12.5	3.6	3.1	3.9	6.6	0.8	12.5
RAS Burden Medium							
−Lab A	149	236	442	575	ND	87.6	12.4
−Lab B	152	240	446	576	ND	85.7	14.3
−Lab C	149	236	444	582	ND	86.4	13.6
−Lab D	103	195	388	504	647	89	11
−Lab E	138	229	432	558	ND	89	11
−Lab F	153	236	435	559	744	89.2	10.8
Average	140.7	228.7	431.2	559.0	695.5	87.8	12.2
SD	19.2	16.9	21.8	28.6	68.6	1.5	1.5
% Relative SD	13.7	7.4	5.1	5.1	9.9	1.7	12.3
Sahara Blend Extra Light							
−Lab A	87	129	255	357	526	97.2	2.8
−Lab B	99	142	274	387	645	91.6	8.4
−Lab C	103	134	255	354	508	103	0
−Lab D	83	130	253	350	504	102	0
−Lab E	99	133	254	351	499	106	0
−Lab F	101	140	258	353	498	99.2	0.8
Average	95.3	134.7	258.2	358.7	530.0	99.8	2.0
SD	8.2	5.3	7.9	14.1	57.2	5.1	3.3
% Relative SD	8.6	3.9	3.1	3.9	10.8	5.1	165.9
Summatran Light Waxy							
−Lab A	157	235	402	497	686	92.6	7.4
−Lab B	172	248	415	526	ND	88.4	11.6
−Lab C	158	235	398	486	658	95.8	4.2
−Lab D	130	213	389	480	654	95.6	4.4
−Lab E	162	236	402	490	666	95.4	4.6
−Lab F	167	237	399	485	653	96.7	3.3
Average	157.7	234.0	400.8	494.0	663.4	94.1	5.9
SD	14.7	11.4	8.4	16.7	13.6	3.1	3.1
% Relative SD	9.3	4.9	2.1	3.4	2.1	3.3	52.5
Alba Heavy							
−Lab A	255	309	451	559	705	91.8	8.2
−Lab B	258	315	466	581	ND	85.9	14.1
−Lab C	252	305	444	544	687	95.5	4.5
−Lab D	250	305	446	550	697	93.8	6.2
−Lab E	254	308	447	536	687	95	5
−Lab F	248	302	437	532	664	97.4	2.6
Average	252.8	307.3	448.5	550.3	688.0	93.2	6.8
SD	3.6	4.5	9.7	17.9	15.4	4.0	4.0
% Relative SD	1.4	1.5	2.2	3.2	2.2	4.3	59.8
Overall avg SD	12.3	8.9	11.7	19.0	39.3	2.9	2.5

30 ppm mass nickel plus vanadium caused from entrained residue.(12) An example of estimating an entrainment level is to fractionate AGO by ASTM D5236 into two cuts containing the first 95 volume percent and final 5 volume percent. HTSD results, along with results from metals analysis methods, can then be used to help quantify the residue entrainment.

6.2 Crude Vacuum Distillates

Crude vacuum column units produce heavy distillate for downstream processing in an FCC or hydrotreater. Knowing the feedstock distillation curve slope and incremental gas oil contaminants is valuable for optimizing production of heavy vacuum gas oil (HVGO). Understanding contaminant distribution and HVGO product quality is important. For many crudes, high amounts of volatile metals and residue can lead to downstream catalyst poisoning. Laboratory analysis data is important for measuring HVGO yields and quality at different cut points and to determine feedstock contaminant distributions for predictive design work. Distillation curve data for vacuum column feedstocks are obtained in the laboratory by using various distillation techniques such as column distillation, short-path distillation, and SimDist by GC.(12) Column distillation includes spinning-band distillation, batch distillation (ASTM D5236), and continuous-flash vaporization. Physical distillation methods result in overlap between cuts and resultant inaccuracy in the contaminant distribution curve. HTSD analysis of each cut allows the contaminant curve to be corrected for overlap. An example of this application of HTSD is shown in Figure 9. In another example as shown in Figure 10, HTSD was used to characterize seven laboratory preparative high vacuum distillation fractions at 25 °F cut points. The HTSD result can determine both the median boiling point of each fraction and also the preparative distillation efficiency or dispersion. With the boiling range of the preparative fraction precisely defined by HTSD and data concerning the properties, obtained by conducting other analyses on the preparative fractions such as density, asphaltenes, Conrad Carbon, and metals, useful vacuum tower optimization models for specific feeds and specific catalyst poisons can be developed.

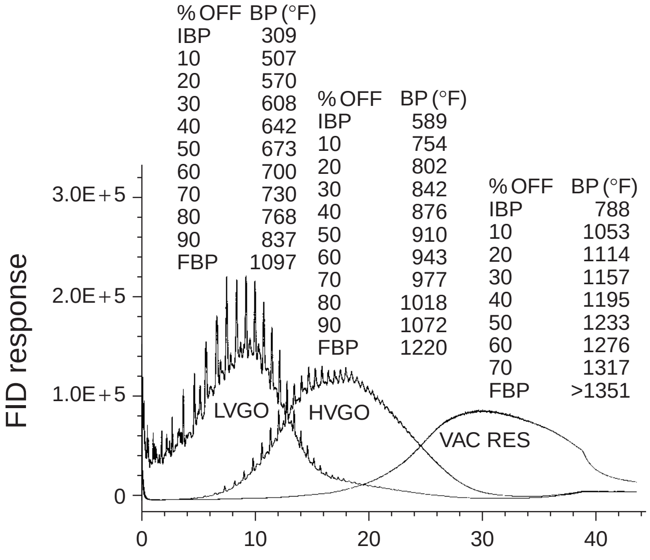


Figure 9 Analysis to characterize refinery vacuum tower products by using HTSD.

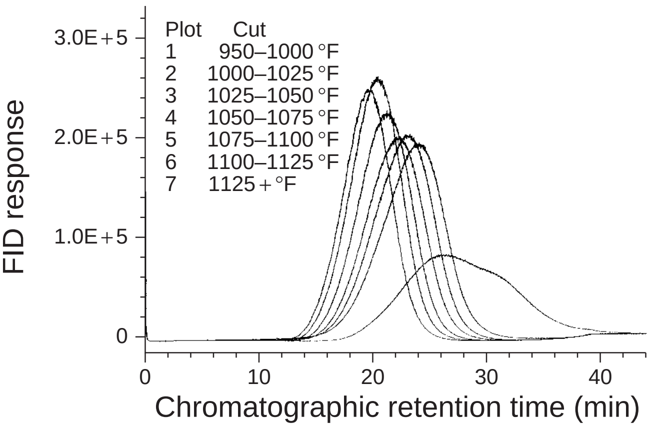


Figure 10 Analysis to characterize preparative physical distillation cuts by using HTSD.

6.3 Resid Processing Characterization

Crude oil bottoms present challenges to refiners who need to effectively convert them into useful products. Among the many "bottom of the barrel" processes available, solvent deasphalting is predominantly used to recover high-value deasphalted gas oil (DAO) from petroleum resid. DAO is excellent feedstock for lube oil, fluid catalytic cracking, and hydrocracking. The residuum oil supercritical extraction (ROSE™) process licensed by Kellogg Brown & Root is a state-of-the-art solvent extraction process widely used in the industry today.(13) HTSD is a useful tool for characterizing hydrocarbons by using boiling point profiles of fractions from the resid solvent extraction process.

The HTSD data presented in Figure 11 and in Table 4 show the chromatograms and percent mass yield as a function of boiling point for sample fractions from a ROSE™ process.(14) In this study, propane was used to extract the deasphalted oil fraction from the petroleum residue.

HTSD has proven valuable for characterizing yield at defined temperatures for heavy feeds and products in the development of technology for upgrading crude and heavy oils. For example, the chromatograms shown

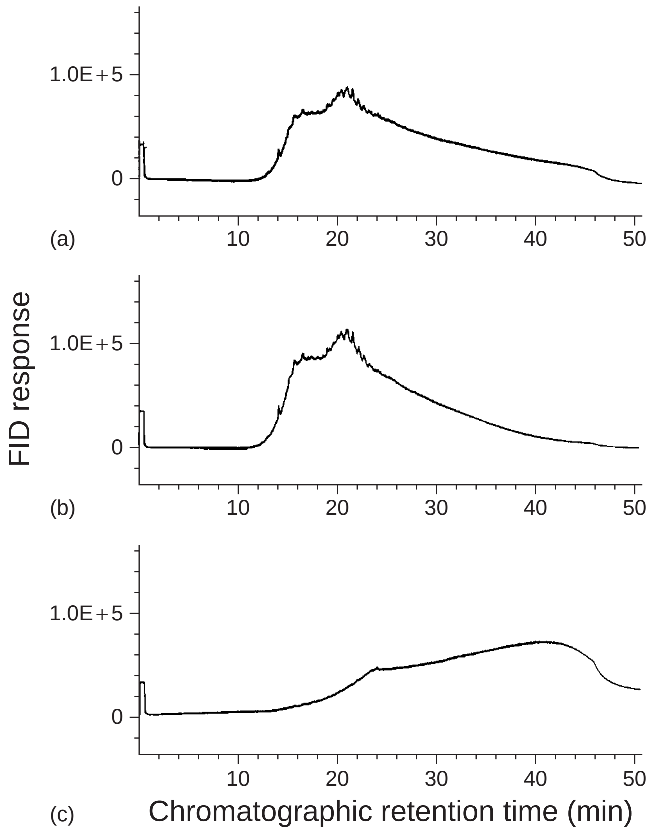


Figure 11 Analysis for resid (a), DAO (b), and asphaltene (c) from the ROSE™ process by using HTSD.

Table 4 HTSD yield (% weight) as a function of boiling point for fractions from the (ROSE™) process

Sample	IBP (°C)	371 °C (700 °F) % wt	482 °C (900 °F) % wt	538 °C (1000 °F) % wt	Recovery at 733 °C (1351 °F) % wt
Resid	317	10.4	46.8	61.6	96.4
Deasphalted oil	314	13.2	57.9	74.0	100
Asphaltene	361	0.7	11.6	22.6	82.6

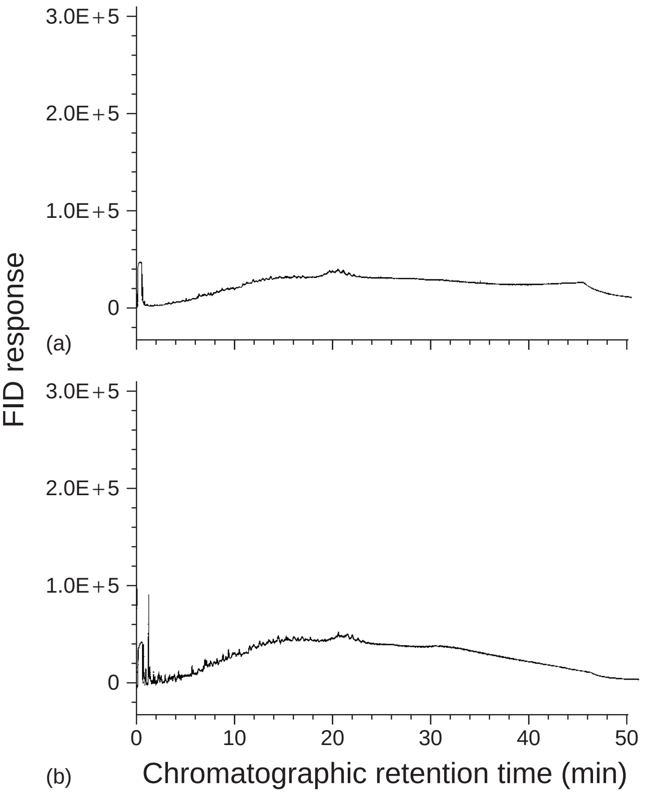


Figure 12 Analysis for feed (a) and product (b) from the Exxon FLEXCOR T process by using HTSD.

Table 5 HTSD yield (% weight) as a function of boiling point for process feed and product samples from the FLEXCOR T process

Sample	IBP (°C)	249 °C (480 °F) % wt	371 °C (700 °F) % wt	538 °C (1000 °F) % wt	Recovery at 733 °C (1351 °F) % wt
Feed	172	4.1	38.4	47.8	80.1
Product	236	7.2	47.0	56.8	85.1

in Figure 12 along with the data in Table 5 illustrate HTSD results for process feed and product samples from the FLEXCOR T process. This is a proprietary Exxon process to upgrade crude and heavy oils with a high naphthenic acid (i.e. total acid number (TAN)) content. The process reduces TAN (reportedly by about 90%) and as a result reduces the corrosivity of crudes and heavy oils caused by TAN in downstream refineries. The process provides moderate resid conversion under low severity operating conditions. While HTSD for this application is not for detection or measurement of TAN removal, HTSD is valuable for characterizing the reduction in the amount of resid and the increase of liquid yield at defined temperatures.

7 CRUDE OIL CHARACTERIZATION

7.1 Yield Correlations between Crude Assay Distillation and High-temperature Simulated Distillation

The crude assay distillation procedure is defined by the methodologies of ASTM Methods D2892 and D5236. The procedure first uses a 15-plate column operating under a reflux ratio of 5 : 1 (D2892) which, as discussed in section 3.1, is known as TBP distillation. The distillation is usually started at ambient pressure (760 mmHg) and then switched to vacuum conditions (for example, from 100 mmHg and then to 2 mmHg minimum) to extend the method to about 343 °C (650 °F) AEBP. At this point the remaining charge is transferred to a vacuum potstill method (D5236) where the distillation is continued at lower pressure (0.3 and 0.1 mmHg minimum allowed) thus allowing for an AEBP limit of about 538–565 °C (1000–1050 °F). Conversion tables for the vacuum conditions to AEBP are included in the methods.

Although the crude assay distillation (D2892 and D5236) procedure provides only an estimate of the yields of the products of various boiling ranges, the results (when properly and skillfully obtained) are of great importance for the characterization and commercial trading of crudes. However, several areas that can contribute to data variability of the crude assay distillation procedure include:

- the use of two different consecutive distillation methods with widely different characteristics such as efficiency, column hold-up and pressure drop across the column;
- inaccuracies in pressure and temperature readings and the subsequent conversion to AEBP;
- maximum attainable temperatures (AEBP) and cracking limits (maximum liquid temperature tolerance) are different for different types of crudes.

This grouping represented a good range of crudes with widely varying content of pitch, sulfur, nickel, vanadium, oxygen, Conradison Carbon or microcarbon residue, and asphaltene.

The comparisons of the yield curves (expressed in mass percent) of crude assay (ASTM D2892 and D5236) to HTSD were presented for five typical crudes spanning the range of light, intermediate, and heavy API gravities. Each crude was compared at eleven distillation cutpoints (°F): 68, 155, 265, 350, 400, 500, 600, 700, 800, 900, 1000. In another series of comparisons, the percent mass at each of the eleven cutpoints as determined by HTSD was subtracted from the percent mass from crude assay (D2892 and D5236).

The HTSD analysis results of crudes have been compared to crude assay distillation results in a study reported by Villalanti et al.$^{(15)}$ About 100 crudes ranging in API gravity from light to heavy were analyzed. In that study the crudes were grouped into three categories (Table 6) based on API gravity. API gravity is a function of relative density (specific gravity) that is widely used in the petroleum industry. The API value [(141.5/specific gravity 60/60 °F) −131.5 min] requires no statement temperature because it is included in the definition of the measurement; API gravity values decrease as density increases and range from 0 (equivalent to density 1.076) to 100 (equivalent to density 0.6112).

Table 6 Crude type, based on API gravity

Crude type	API gravity	Number of crudes	API range
Light	>30	49	30.1–52.3
Intermediate	20–30	27	20.5–30.0
Heavy	<20	8	9.7–19.5

Table 7 HTSD cutpoint data for a QA sample

HTSD cutpoint (°F)	% Mass	SD
360	12.7	0.3
480	19.6	0.3
650	28.9	0.3
1000	73.0	0.5
1351	98.4	0.9

The QA sample for the HTSD analysis was a full range (naphtha and residue containing) petroleum sample. The HTSD cutpoint statistics determined for the QA sample for more than 500 determinations were as given in Table 7.

The comparison of the distillation yield curves (percent mass) as determined by crude assay and by HTSD showed good agreement. In general, the difference was better than ±2% mass over the cutpoint range of IBP to 538 °C (1000 °F) (Figure 13). The only exception to this is the region around 399 °C (750 °F). The deviation in this region is caused by the change from high efficiency (15 plates) D2892 distillation to low efficiency (one plate) D5236 distillation. The distillation at this point goes from TBP distillation to non-TBP distillation. This results in a larger deviation for HTSD versus physical distillation at the crossover and beyond, and also introduces a bias between D2892 and D5236 (Figures 13 and 14). The fact that HTSD has no crossover effects is one of its main advantages for modelling and monitoring purposes.

The SD of HTSD at cutpoints up to 538 °C (1000 °F) is better than 0.5%. The estimated precision of the

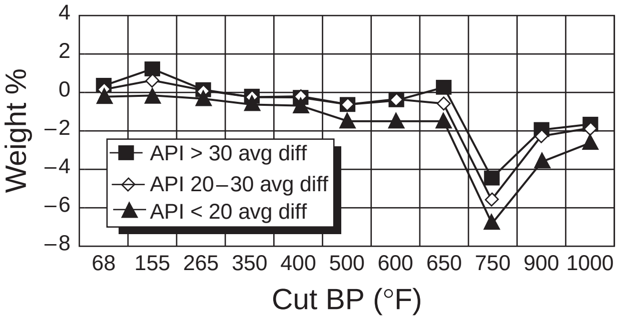


Figure 13 Comparison of physical distillation assay and HTSD as % weight difference in their values at each cut point for crude oils grouped by API gravities.

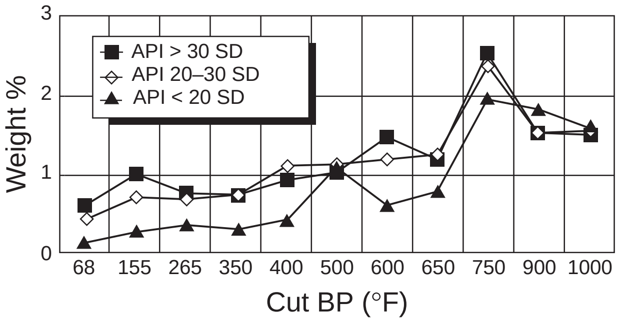


Figure 14 Comparison of physical distillation assay and HTSD as the SD of the difference of their values at each cut point for crude oils grouped by API gravities.

correlation between crude assay distillation and HTSD yield at each cutpoint results in an SD of <2% weight except at the crossover point at 399 °C (750 °F) (Figure 14).

Advantages cited in that study for characterization of crude by HTSD include:

- method precision;
- faster turnaround and less expense than laboratory physical distillation;
- valuable business tool for evaluating new crudes and confirming crude quality before purchase;
- ensuring crude product integrity during transportation and delivery.

7.2 Crude Oil Contaminants

Product integrity must be verified in the course of crude oil trading. Enormous quantities of crude oil are transported and processed daily. Product adulteration can occur whether intentionally or not. A useful application of HTSD is in monitoring product integrity. For example, the blending of pitch (defined as 538 °C+ or 1000 °F+) into crudes has been spotted at concentration levels of about 1.5 percent mass and lower.(16) Advantages of HTSD for this application include speed of analysis, small sample quantity requirement, and extended boiling range of the method.

8 PETROLEUM HYDROCARBONS IN ENVIRONMENTAL SAMPLES

SimDist methods are becoming more widely used in environmental applications. HTSD is useful for characterizing hydrocarbons which can be present as soil and water contaminants; for example, to map and follow hydrocarbon removal processes which may involve biodegradation, thermal, and/or physical separation methods.

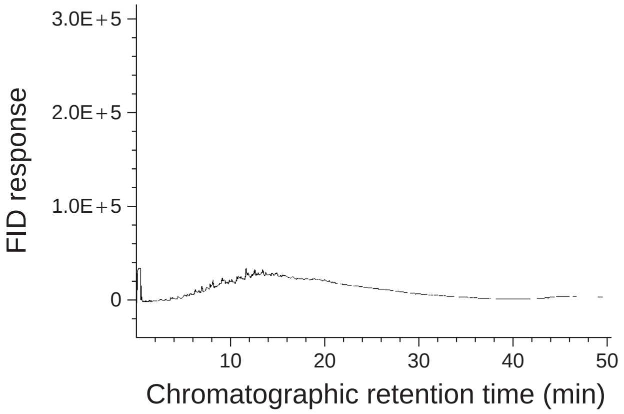


Figure 15 Analysis of environmental soil sample extract by using HTSD.

8.1 Soil Contaminants

An example of a soil extract analysis by HTSD is shown in Figure 15. For analysis the soil is weighed into a small vial and contacted with a weighed amount of solvent such as carbon disulfide, and the extract is analyzed. To improve sensitivity, samples are prepared for analysis at soil to solvent ratios of about 50 percent mass. Other extraction techniques and solvents can also be used. The HTSD result is useful for characterizing the amounts of material over boiling range regions representative of naphtha, gasoline, diesel, and heavier material. The detectable hydrocarbons can be reported on the basis of percent mass of soil as received or on a normalized percent hydrocarbons.

8.2 Oily Waters

In the HTSD analysis of a predominantly aqueous matrix, the sample is weighed into a small vial and shaken with a weighed amount of solvent, such as carbon disulfide, and the extract analyzed. In this case the extract is the bottom layer because carbon disulfide is denser than water. Water to solvent ratios of about 50% mass are used. Other extraction techniques and solvents can also be used. As with soil samples, the HTSD result is useful for characterizing the amounts of petroleum hydrocarbons in the boiling range of naphtha, gasoline, diesel, and heavier material. The detectable hydrocarbons can be reported on basis of percent mass of sample as received or on a normalized percent hydrocarbon basis.

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ABBREVIATIONS AND ACRONYMS

AEBP	Atmospheric Equivalent Boiling Point
AET	Atmospheric Equivalent Temperature
AGO	Atmospheric Gas Oil
ASTM	American Society for Testing and Materials
DAO	Deasphalted Gas Oil
FBP	Final Boiling Point
FCC	Fluidized Catalytic Cracker
FID	Flame Ionization Detector
GC	Gas Chromatography
HTSD	High-temperature Simulated Distillation
HVGO	Heavy Vacuum Gas Oil
IBP	Initial Boiling Point
ID	Internal Diameter
PTV	Programmed Temperature Vaporization
QA	Quality Assurance
QC	Quality Control
ROSE™	Residuum Oil Supercritical Extraction
SD	Standard Deviation
SimDist	Simulated Distillation
TAN	Total Acid Number
TBP	True Boiling Point

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