Yield Correlations Between Crude Assay Distillation

And High Temperature Simulated Distillation (HTSD)

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Paper 51b

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Summary

The ability to rapidly and accurately evaluate the variability of distillation yield curves of opportunistic crudes and crudes from currently producing fields has increasingly important economic considerations in refining margins. Recent advances in the analytical laboratory using gas chromatography techniques have allowed the method of *High Temperature Simulated Distillation* (HTSD) to be successfully used in place of the laboratory method of *Crude Assay* Distillation (ASTM D2892 and D5236). This paper presents a brief description of the HTSD analysis (including detailed precision data) and the HTSD yield curve *correlations* to Crude Assay distillations for a variety of crudes. By knowing the statistical significance of the HTSD data generated and the correlation to existing crude assay, marginal values of various crudes can be derived and the economics evaluated.

In this study, approximately 100 crudes were analyzed by Crude Assay Distillation and HTSD. To allow a meaningful comparison of the yield curves obtained by Crude Assay Distillation and HTSD, the crudes were grouped into light, intermediate, and heavy categories by API gravity. The yield curves are compared at 10 distillation cutpoints. At each cutpoint, the average percent weight (%weight) differences between Crude Assay Distillation and HTSD are summarized for each API Gravity grouping. In addition, the estimated precision of the correlation between Crude Assay Distillation and HTSD at each distillation cutpoint is presented.

Crude Assay Distillation

ASTM Standard Test Method D2892 for the Distillation of Crude Petroleum defines the methodology for Crude Assay Distillation. The method uses a 15 plate column operating under a reflux ratio of 5:1. This is known as TBP or True Boiling Point. The distillation is usually started at ambient pressure (760mm Hg) and then switched to vacuum conditions (from 100 and then to 5 mm Hg) to extend the method to about 650°F Atmospheric Equivalent Boiling Point (AEBP). At this point the remaining charge is transferred to a vacuum potstill method (ASTM D5236) where the distillation continues at 0.5mm Hg, thus allowing an AEBP limit of about 1000-1050°F. Conversion tables for the vacuum conditions to AEBP are included in the method.

Although the Crude Assay Distillation (D2892 and D5236) method provides only an estimate of the yields of the fractions of various boiling ranges, the results (when properly and skillfully obtained) are of great importance for the *characterization and commercial trading of crudes*.

Several areas that contribute to the variance of the D2892 method include:

1.) Column hold up
2.) Conversion to AEBP from various vacuum settings
3.) Cracking Limits on the maximum distilling temperature are different for different types of crudes.
4.) Pressure drops across the column.

HTSD Methodology

High Temperature Simulated Distillation[1] (HTSD) is basically an extension of ASTM method D2887 for the boiling range distribution of hydrocarbons by gas chromatography (GC). ***(Figure1).*** The analysis is calibrated by correlating the C5 to C120 n-paraffins elution time to their Atmospheric Equivalent Boiling Point (AEBP) as described in API Project 44. ***(Figure 2).***

A key difference however between HTSD and D2887 is the ability of HTSD to handle *residue containing* samples. (i.e. 1000°F+) The range of applications[2] for HTSD includes: Crude Oil Characterization, Cat Crack feed and product, CFH feed and product, Hydrotreater feed and products, Atmospheric Residue, Vacuum Gas Oils[3], Deasphalted Oils, and Vacuum Tower Bottoms (pitch).

Under the special conditions of HTSD, elution of materials from the GC column occurs at *up to 500-600°F below their AEBP*. For instance, the elution of C_{110} (AEBP of 1351°F) occurs at about 800°F column temperature. Also under these conditions, little or no evidence of cracking is normally seen in HTSD.

HTSD Precision

The Quality Control (QC) and Quality Assurance (QA) procedures in the lab to assure the integrity of HTSD must be followed rigorously to ensure statistically meaningful results.[1] The initial QC involved the analysis of a reference oil ***(Figure 3)*** that has been physically distilled by ASTM D2892 (TBP). This material (with FBP<1000°F) is used to calibrate the HTSD system as an external standard for all % recovery calculations. In addition, the HTSD analysis results are compared to the physical weight distribution data from the true boiling point (TBP) distillation. The statistical error of the difference between HTSD data versus TBP is then reported. ***(Table 1).***

For HTSD analysis of crudes, a *full, wide boiling range (naphtha and residue containing) petroleum sample* is routinely analyzed for QA. The typical HTSD report for a full range petroleum sample is shown in ***Table 2***. The HTSD cutpoint statistics for this full range hydrocarbon are summarized below for 500+ determinations:

HTSD Cutpoint	%Weight	Std. Dev.
360°F	12.7	0.3
480°F	19.6	0.3
650°F	28.9	0.3
1000°F	73.0	0.5
1351°F	98.4	0.9

Grouping of Crudes by API Gravity

For the purpose of this study approximately 100 Crudes were analyzed by Crude Assay Distillation and HTSD and grouped into the following three categories based on API Gravity (density).

Crude Type	API Gravity	# 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

The crudes included in this study have a widely varying content of pitch of Pitch, Sulfur, Nickel, Vanadium, Conradison Carbon or Microcarbon Residue, and Asphaltene.

Comparison of Crude Assay and HTSD

The comparisons of the yield curves (expressed in %weight) of Crude Assay (ASTM D2892) to HTSD are presented for five typical crudes spanning the range of light, intermediate, and heavy API gravities. ***(Figures 4, 5, 6, 7, & 8).*** Each crude is compared at the following ten distillation cutpoints:

Cutpoint Number	Cutpoint Temperature °F
1	68
2	155
3	265
4	350
5	400
6	500
7	600
8	750
9	900
10	1000

In the next series of comparisons, the % weight at each of the ten cutpoints as determined by HTSD was subtracted from the % weight from Crude Assay Distillation. The average differences for all the crudes in each of the three API categories are shown in ***Figures 9, 10, & 11***. In addition, these figures also show the estimated standard deviation of the differences in the yields of Assay (D2298) minus HTSD.

Conclusions

About one hundred crudes ranging in API gravity from light to intermediate to heavy were analyzed. The comparison of the distillation yield curves (% weight) as determined by Crude Assay Distillation (ASTM D2892 and D5236) and by HTSD shows good overall agreement. In general, the difference observed at each cutpoint is < +/-2 % weight ***(Figure 12).*** However, an exception is the cutpoint region from 750°F for light and intermediate crudes and the region from 750-900°F for heavy crudes. The 750°F cutpoint is the first cutpoint following the crossover from ASTM D2892 (TBP-15 plate) to D5236 (Vacuum Potstill, 1 plate) conditions. This change in distillation conditions is thought to contribute most of the difference when compared to HTSD, which has no pressure-related crossover effects.

The precision of HTSD cutpoints up to 1000°F is better than 0.5%wt. The estimated precision of the correlation between Crude Assay Distillation and HTSD yield at each cutpoint result in a standard deviations of <2% weight except at the crossover point at 750°F ***(Figure 13).***

The future opportunities of Crude Characterization by HTSD include:

1.) Tighter precision than conventional lab distillation.
2.) Faster turnaround and less expense than laboratory physical distillation.
3.) Valuable business tool for evaluating new crudes and confirming crude quality before purchase.
4.) Ensuring crude product integrity during transportation and delivery.

References:

1.) D.C. Villalanti, D. Janson, P. Colle, "Hydrocarbon Characterization by High Temperature Simulated Distillation (HTSD)," Session 4b , AIChE Spring Meeting, Houston, TX., March 19-23, 1995.

2.) S.W. Golden, D.C. Villalanti, G.R. Martin, "Feed Characterization and Deepcut Vacuum Columns: Simulation and Design, Impact of High Temperature Simulated Distillation", Session 47a, AIChE Spring Meeting, Atlanta, GA., April 18-20, 1994

3.) S.W. Golden, S. Craft, D.C. Villalanti, "Refinery analytical techniques optimize unit performance", Hydrocarbon Processing, November 1995.

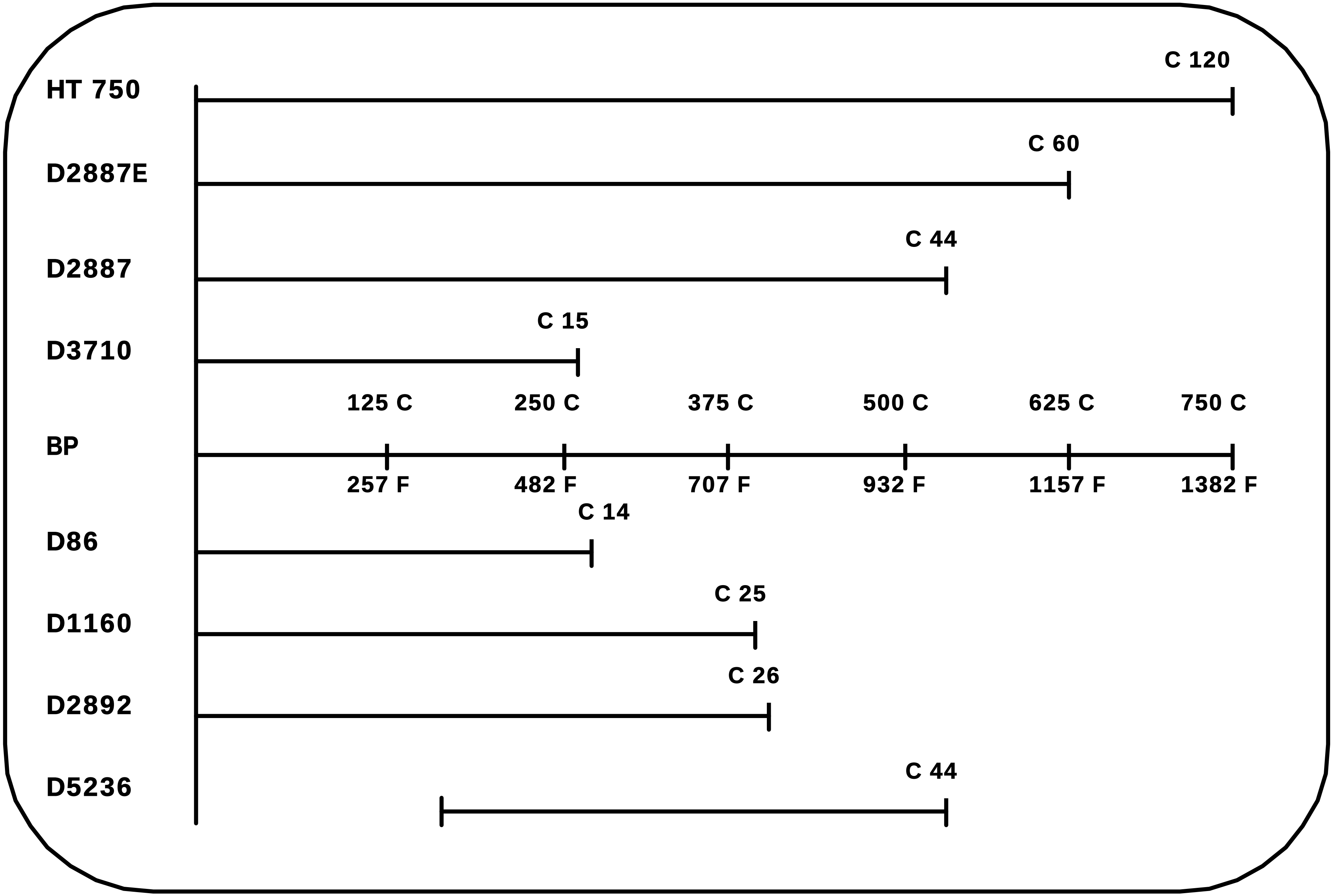
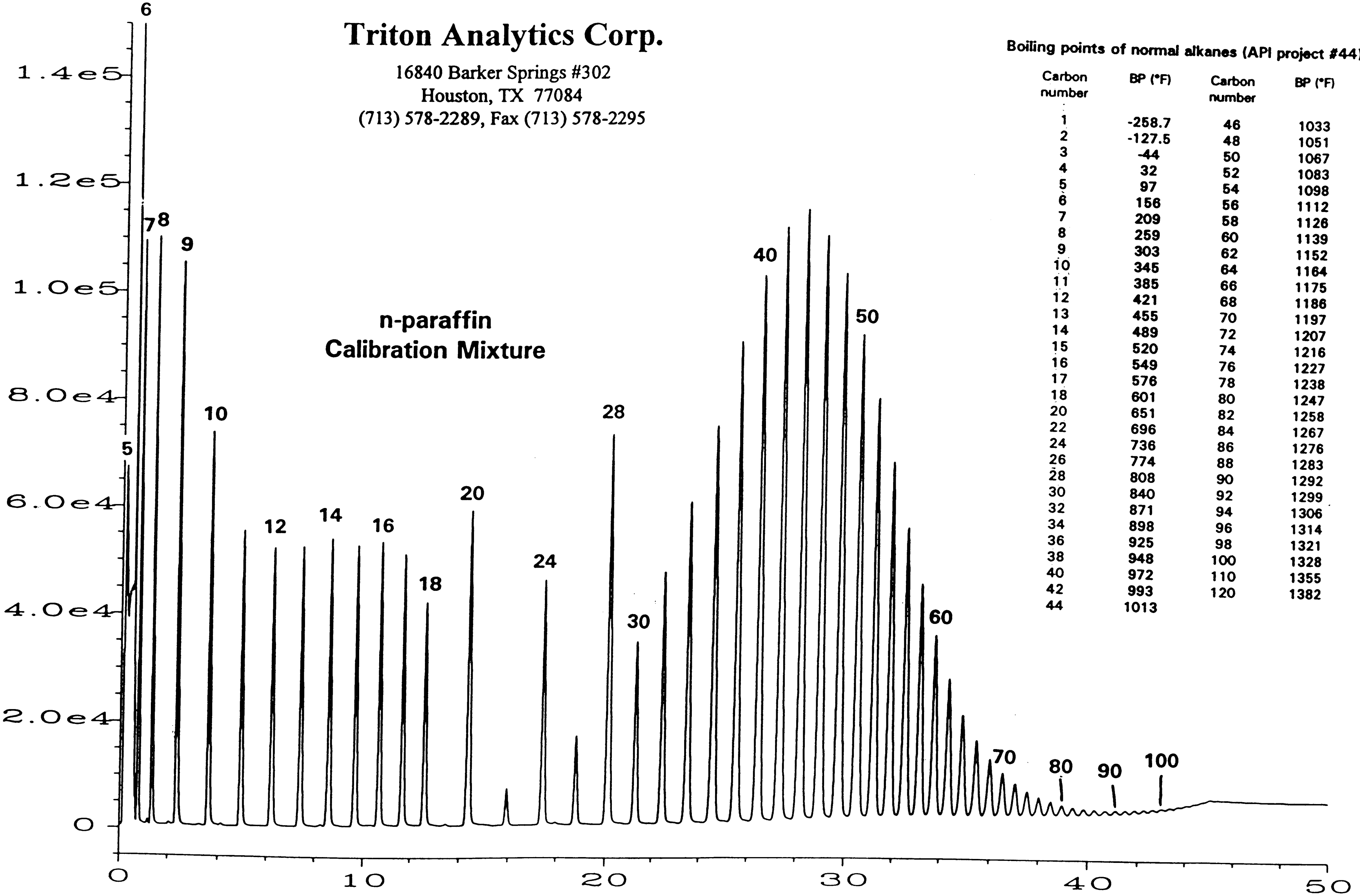


Figure 1 Summary of ASTM Physical and Simulated Distillation



Boiling points of normal alkanes (API project #44)

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	1098
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 2 C_5-C_{110} n-Paraffin HTSD Calibration

Triton Analytics Corp.

TAC SIMDIS #4 High temperature **2**

Sample name	: AC REF 165A	Instrument	: 1
Method name	: C:\HPCHEM\1\METHODS\ht750c.M	Vial	: 95
Sample type	: Ref 25650.100	Injection	: 1
Sequence name	: 1125B.S	Seq. line	: 4
Operator	: LAG	Sample (g)	: 0.1925
Acquired on	: 11/25/96 7:30:24 PM	Solvent (g)	: 9.7462
Processed on	: 2/10/97 9:05:37 AM	ISTD (g)	: 0.0000
Data File	: 1125B\095F0401.D\FID1A.CH		

Chromatogram:

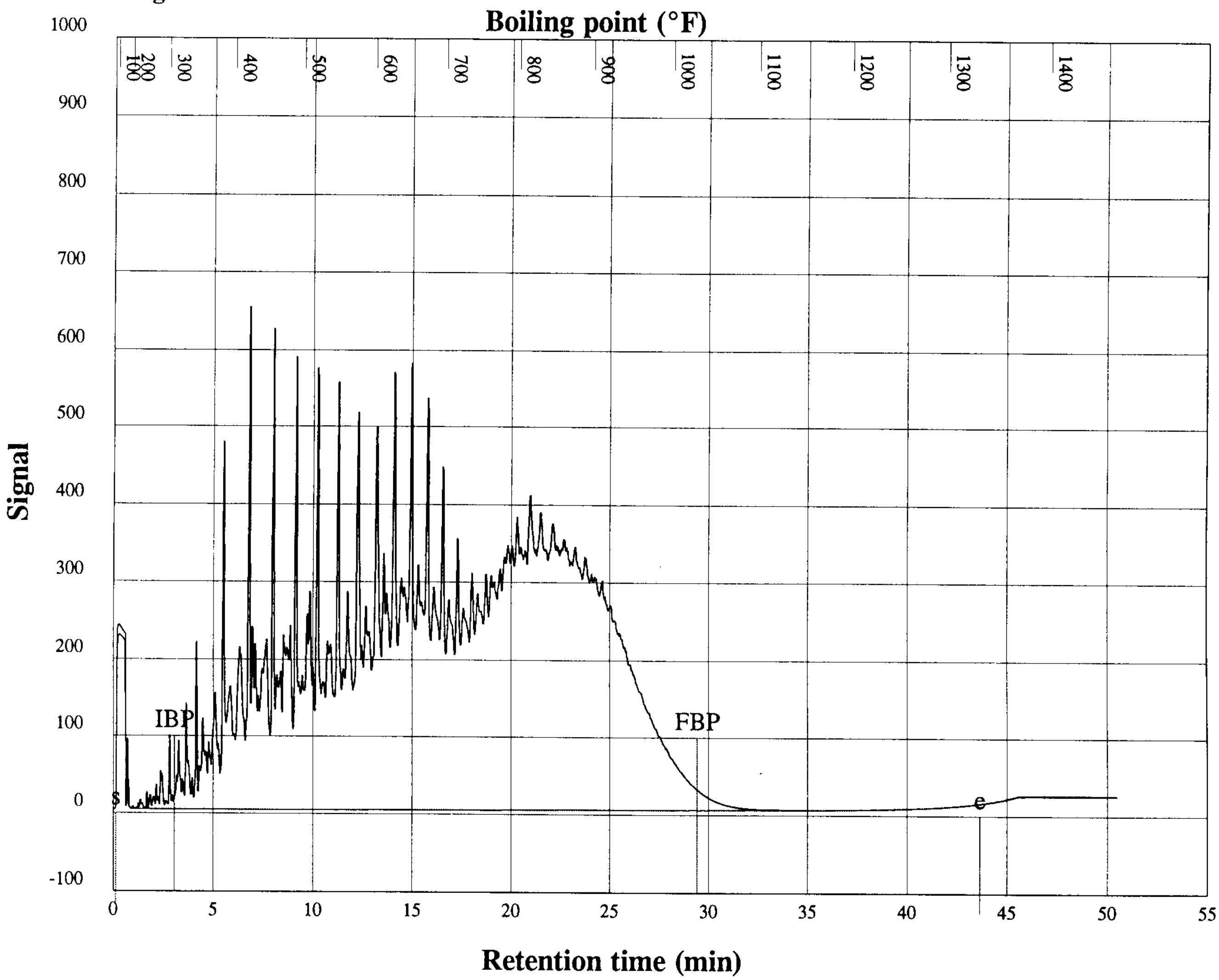


FIGURE 3 D2892 Physically Distilled Reference Oil by HTSD

Triton Analytics Corp.

TAC SIMDIS #4 High temperature **1**

Sample name	: AC REF 165A	Instrument	: 1
Method name	: C:\HPCHEM\1\METHODS\ht750c.M	Vial	: 95
Sample type	: Ref 25650.100	Injection	: 1
Sequence name	: 1125B.S	Seq. line	: 4
Operator	: LAG	Sample (g)	: 0.1925
Acquired on	: 11/25/96 7:30:24 PM	Solvent (g)	: 9.7462
Processed on	: 2/10/97 9:05:37 AM	ISTD (g)	: 0.0000
Data File	: 1125B\095F0401.D\FID1A.CH	Start Elution	: 0.13
Blank used	: 1125B\085F0301.D\FID1A.CH corrected	End Elution	: 43.66
BP Calibrant	: 1125B\090F0201.D\FID1A.CH	Found recovery	: 99.0%
Last Reference	: 1125B\095F0401.D\FID1A.CH On spec.	Used recovery	: 100.0%
Cal. method	: External Standard Method	Response	: 1.0916e-008

Reference sample results:

	Target values	Determined values		Squared diff
Mass%	BP (°F)	BP (°F)	dBP (°F)	
10	448	447	-1	1
20	529	529	0	0
30	603	602	-1	1
40	658	657	-1	1
50	716	717	1	1
60	777	777	0	0
70	826	824	-2	4
80	873	871	-2	4
90	923	922	-1	1
Maximum squared deviation : 140				13

Front channel ON specification

TABLE 1 HTSD vs ASTM D2892 Results for Reference Oil

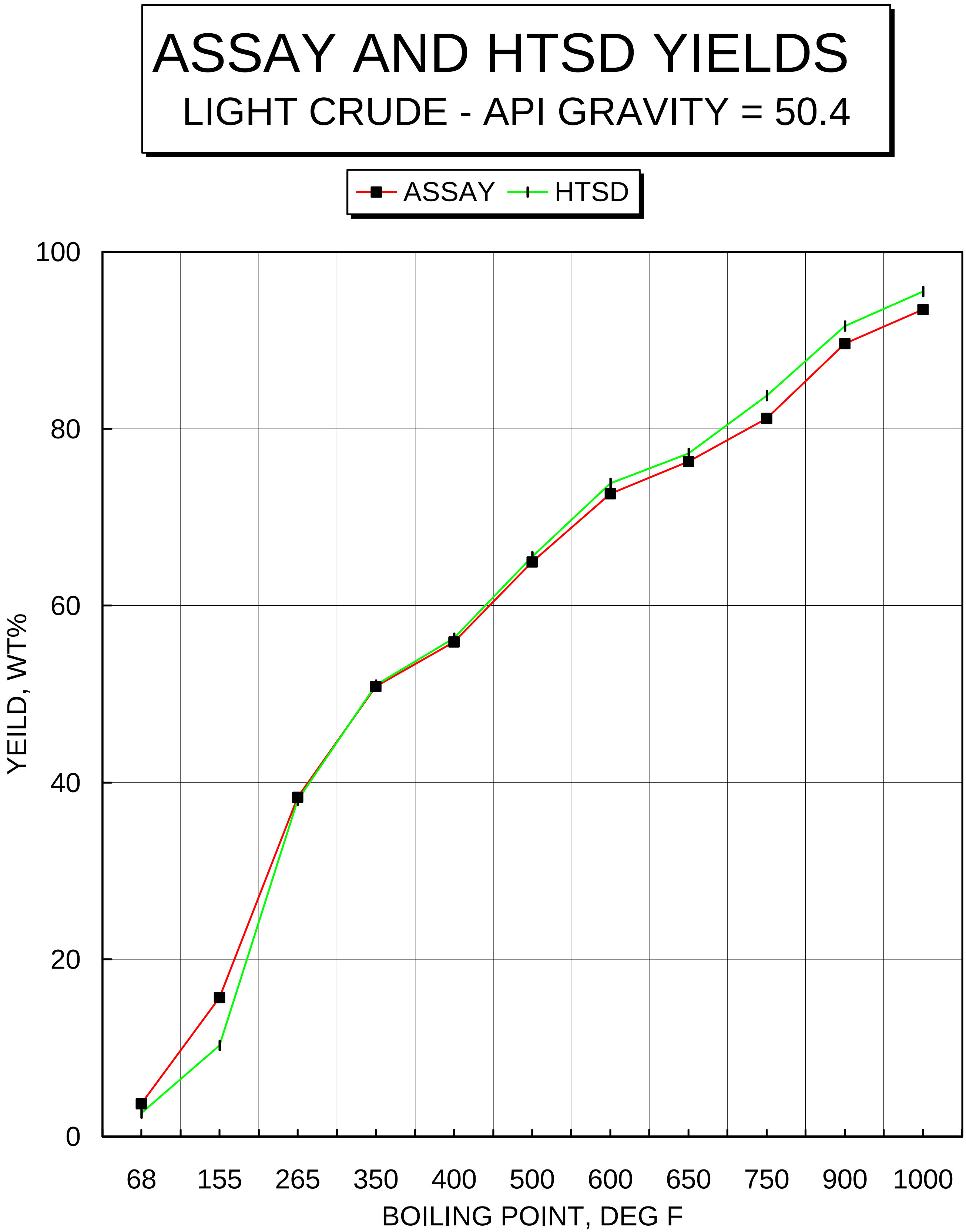
Sample name	: Full Range Cr	Instrument	: 1
Method name	: C:\HPCHEM\1\METHODS\ht750c.M	Vial	: 1
Sample type	: Sample Cryo	Injection	: 1
Sequence name	: 1125B.S	Seq. line	: 5
Operator	: LAG	Sample (g)	: 0.1996
Acquired on	: 11/25/96 8:33:30 PM	Solvent (g)	: 9.7899
Processed on	: 2/10/97 9:05:50 AM	ISTD (g)	: 0.0000
Data File	: 1125B\001F0501.D\FID1A.CH	Start Elution	: 0.08
Blank used	: 1125B\085F0301.D\FID1A.CH	End Elution	: 44.67S
BP Calibrant	: 1125B\090F0201.D\FID1A.CH	Found recovery	: 99.9%
Last Reference	: 1125B\095F0401.D\FID1A.CH On spec.	Used recovery	: 99.5%
Cal. method	: External Standard Method		

Boiling point distribution:

Mass%	BP(°F)	Mass%	BP(°F)	Mass%	BP(°F)	Mass%	BP(°F)	Mass%	BP(°F)
IBP	154	21	522	42	775	63	925	84	1095
1	168	22	544	43	783	64	931	85	1105
2	193	23	562	44	790	65	939	86	1116
3	218	24	580	45	797	66	946	87	1127
4	234	25	599	46	804	67	953	88	1139
5	244	26	615	47	811	68	961	89	1151
6	270	27	630	48	818	69	968	90	1164
7	278	28	647	49	825	70	976	91	1176
8	290	29	659	50	832	71	983	92	1190
9	315	30	672	51	840	72	991	93	1205
10	328	31	682	52	846	73	999	94	1221
11	344	32	693	53	854	74	1007	95	1240
12	358	33	701	54	861	75	1015	96	1261
13	378	34	711	55	868	76	1023	97	1282
14	391	35	719	56	875	77	1032	98	1306
15	407	36	728	57	882	78	1041	99	1334
16	424	37	737	58	889	79	1049		
17	440	38	745	59	896	80	1058		
18	459	39	753	60	903	81	1067		
19	481	40	760	61	910	82	1077		
20	501	41	768	62	917	83	1087		

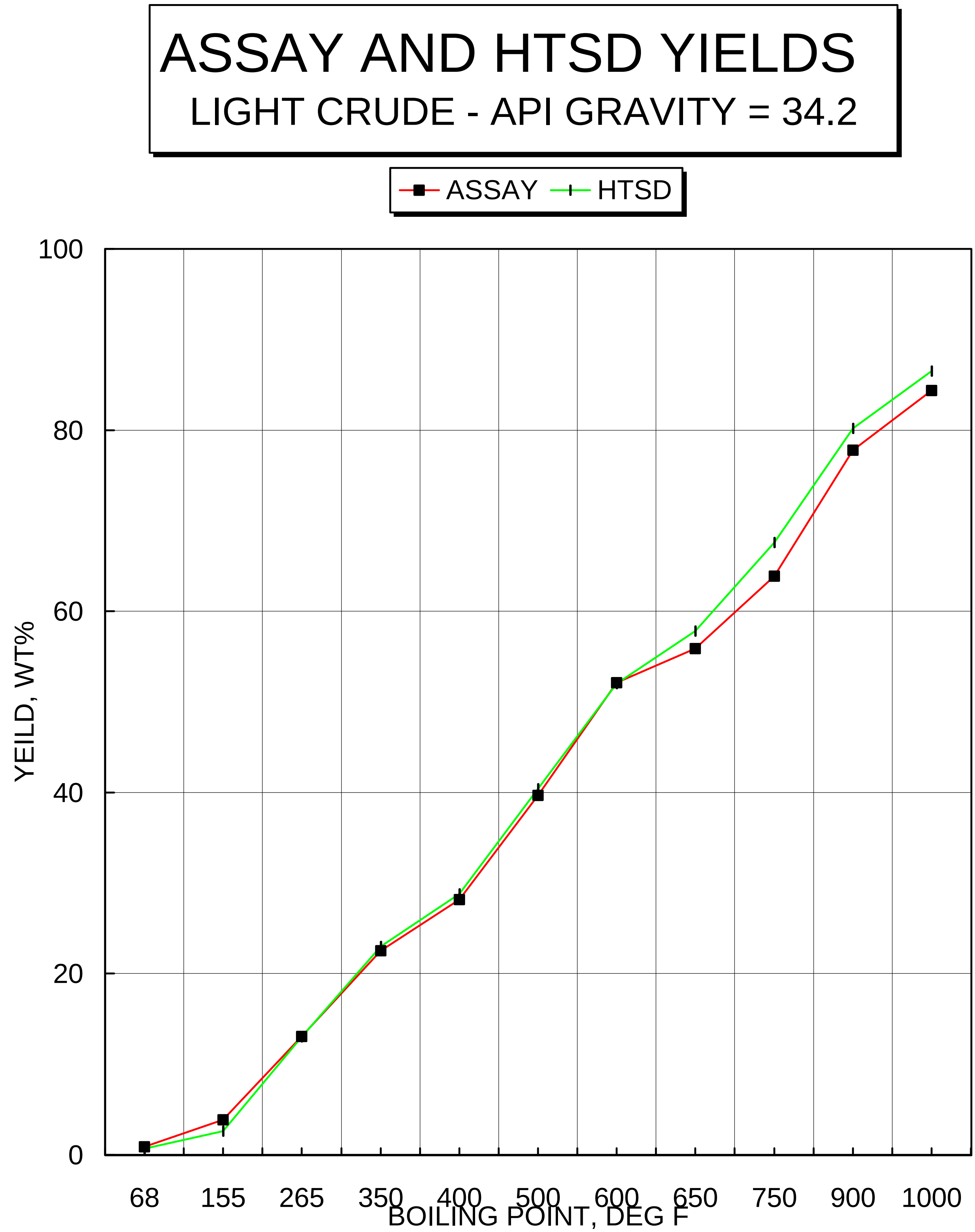
TABLE 2 Typical HTSD Report for Full Range Naphtha and Residue containing Sample

FIGURE 4



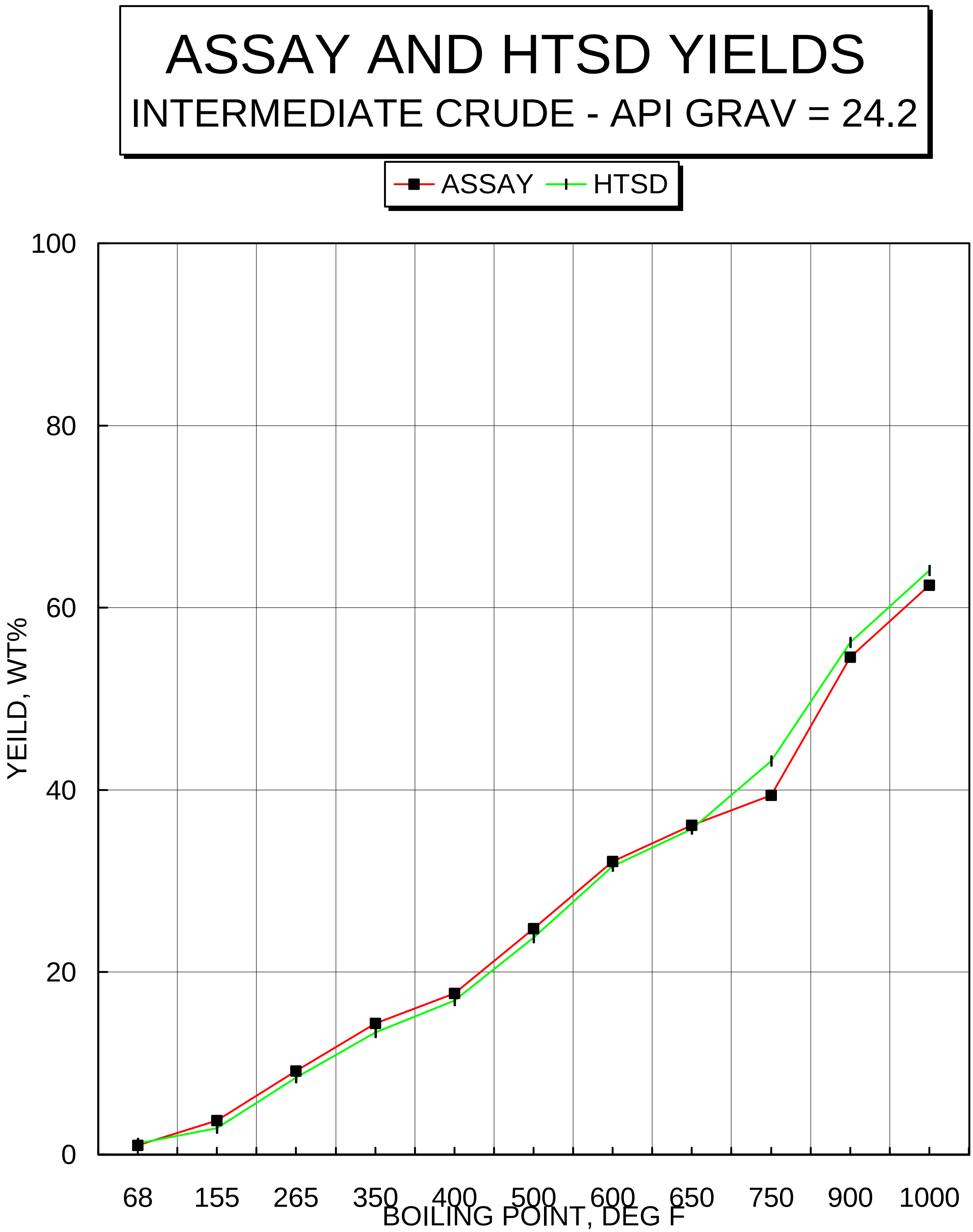
ASSAY AND HTSD YIELDS
LIGHT CRUDE - API GRAVITY = 50.4
ASSAY
HTSD
100
80
60
40
20
0
YEILD, WT%
68
155
265
350
400
500
600
650
750
900
1000
BOILING POINT, DEG F

FIGURE 5



ASSAY AND HTSD YIELDS
LIGHT CRUDE - API GRAVITY = 34.2
ASSAY
HTSD
100
80
60
40
20
0
YEILD, WT%
68
155
265
350
400
500
600
650
750
900
1000
BOILING POINT, DEG F

FIGURE 6



ASSAY AND HTSD YIELDS
INTERMEDIATE CRUDE - API GRAV = 24.2
ASSAY
HTSD
100
80
60
40
20
0
YEILD, WT%
68
155
265
350
400
500
600
650
750
900
1000
BOILING POINT, DEG F

FIGURE 7

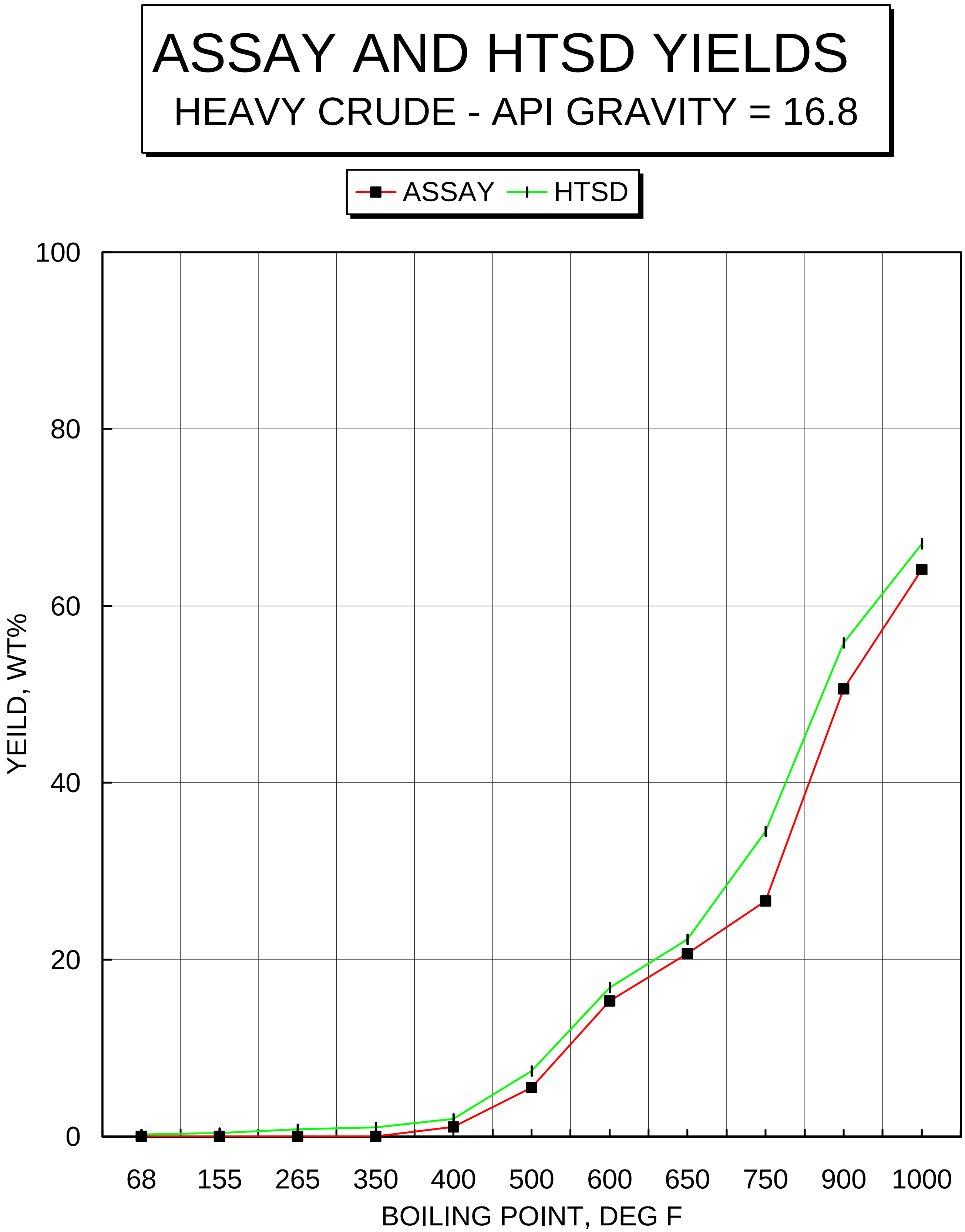

ASSAY AND HTSD YIELDS
HEAVY CRUDE - API GRAVITY = 16.8
ASSAY
HTSD
100
80
60
40
20
0
YEILD, WT%
68
155
265
350
400
500
600
650
750
900
1000
BOILING POINT, DEG F

FIGURE 8

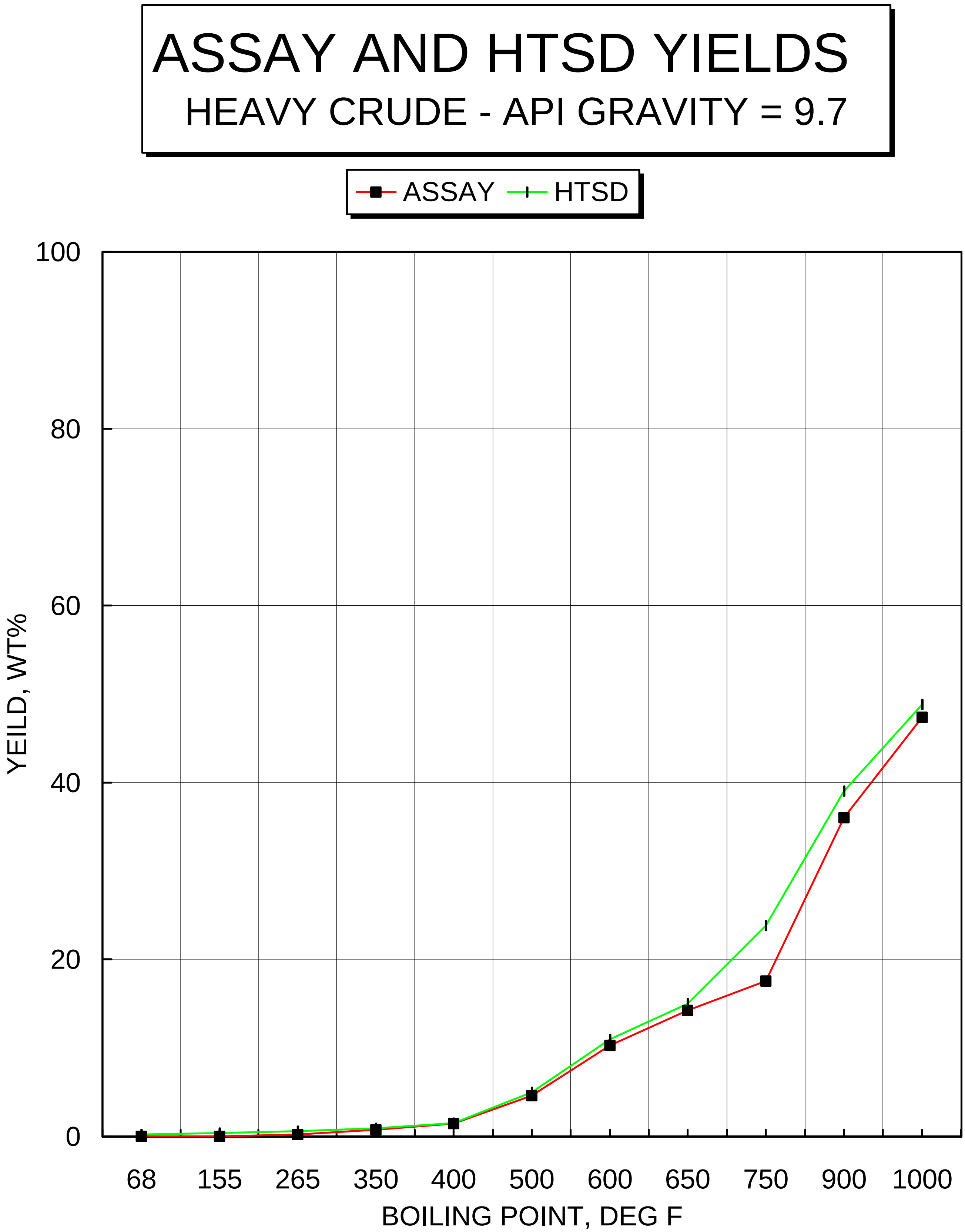
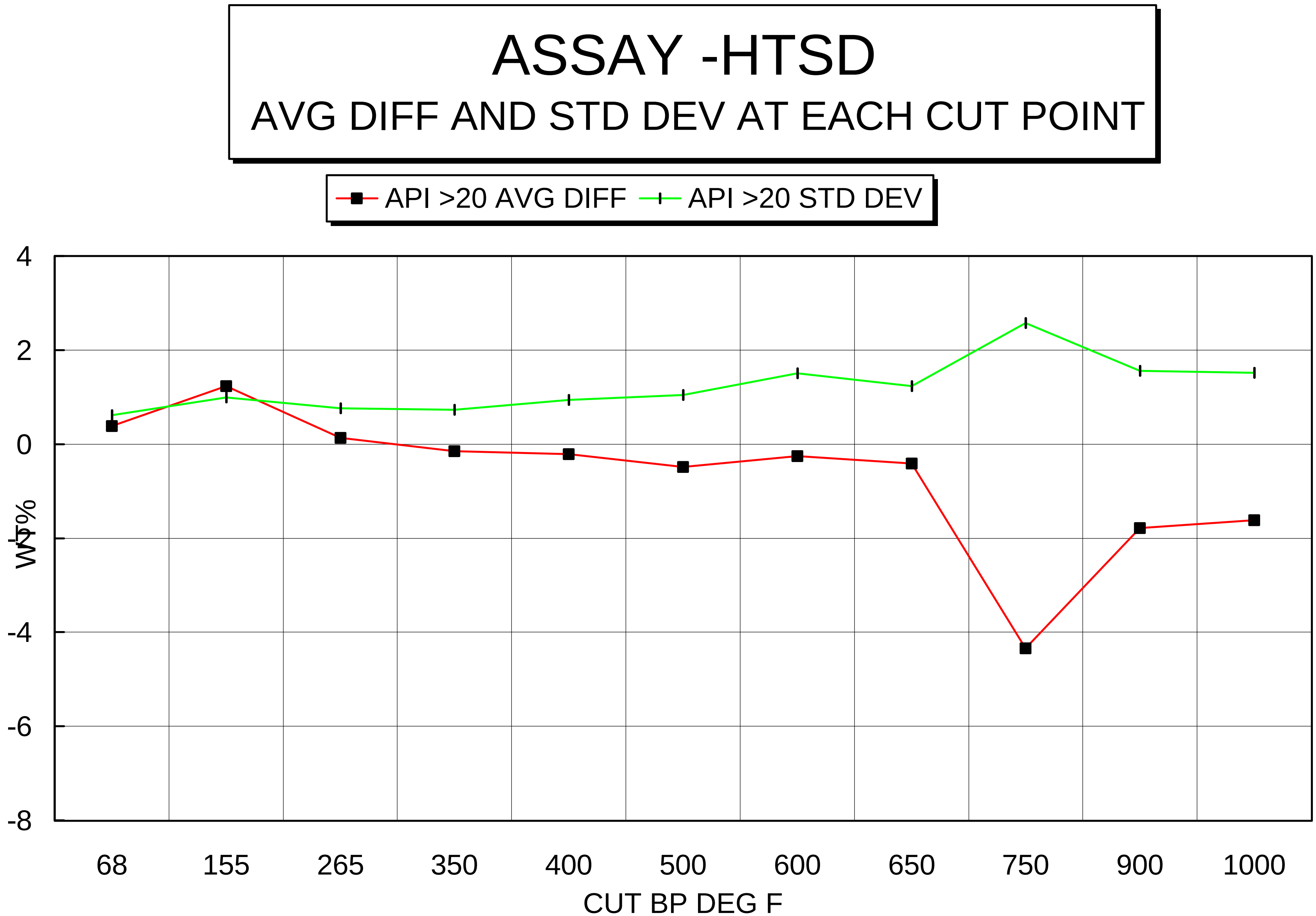
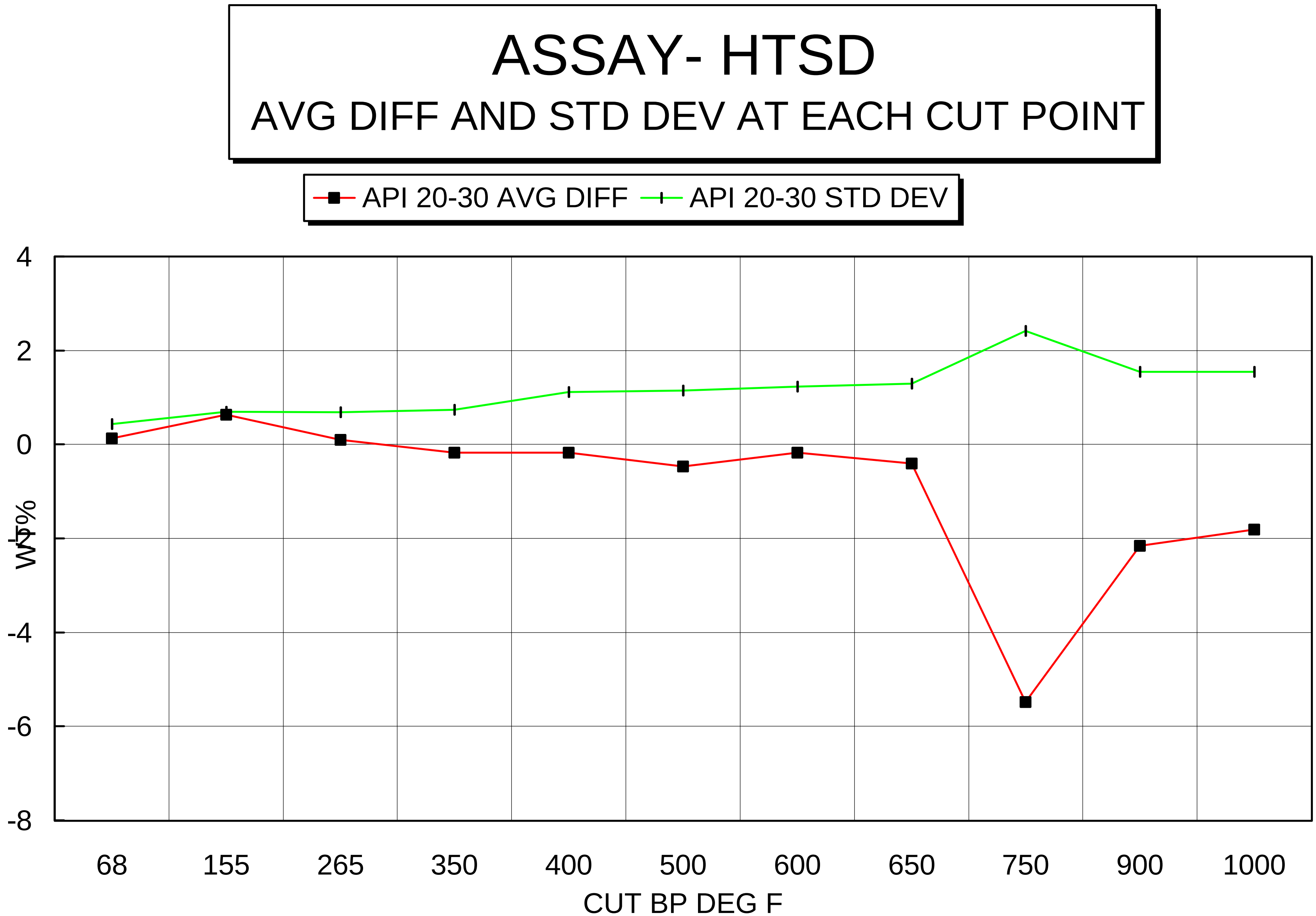

ASSAY AND HTSD YIELDS
HEAVY CRUDE - API GRAVITY = 9.7
ASSAY
HTSD
100
80
60
40
20
0
YEILD, WT%
68
155
265
350
400
500
600
650
750
900
1000
BOILING POINT, DEG F

FIGURE 9



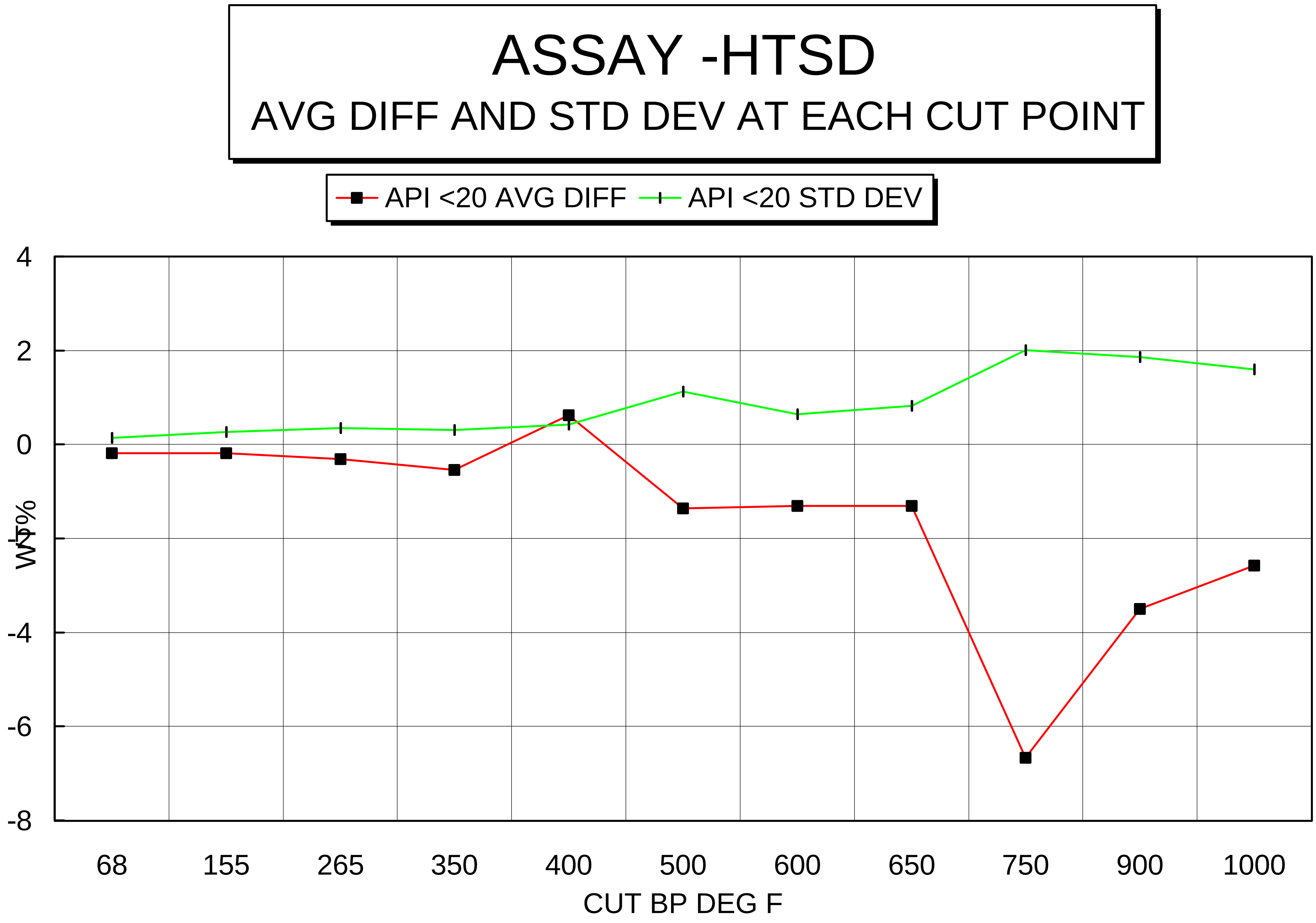
CRUDES GROUPED BY API GRAVITIES

FIGURE 10



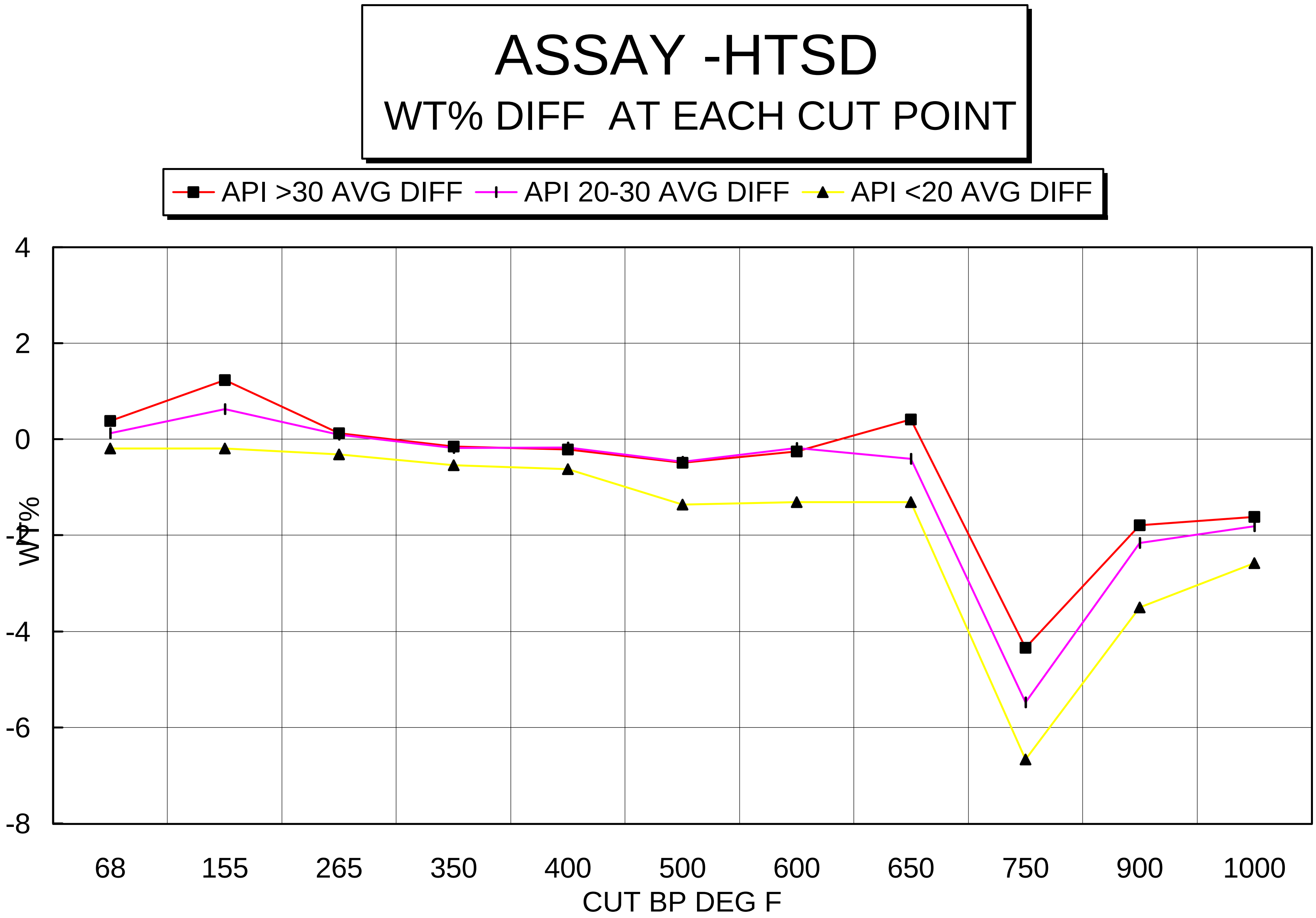
CRUDES GROUPED BY API GRAVITIES

FIGURE 11



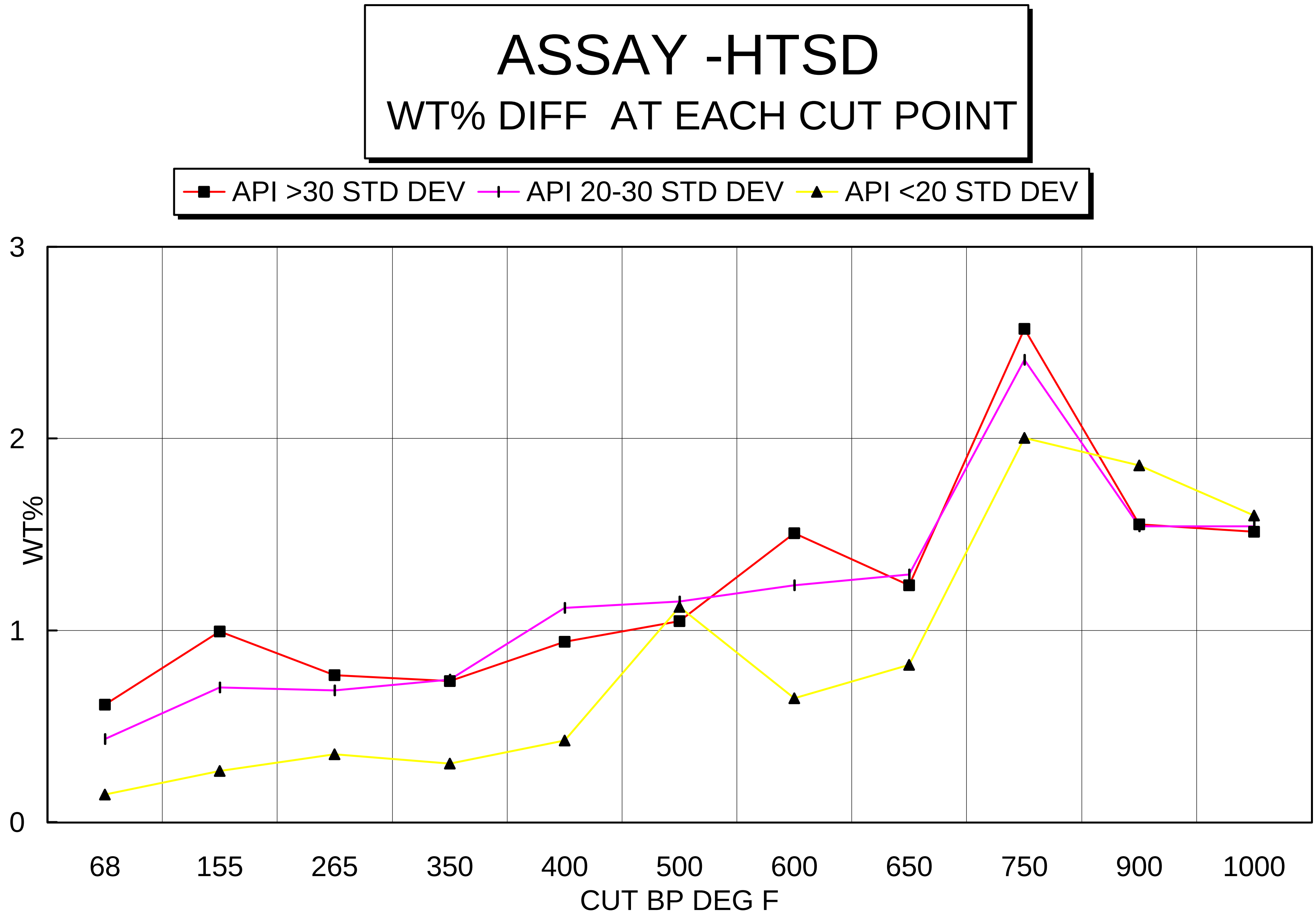
CRUDES GROUPED BY API GRAVITIES

FIGURE 12



CRUDES GROUPED BY API GRAVITIES

FIGURE 13



CRUDES GROUPED BY API GRAVITIES