

# Simulated Distillation Methods for Petroleum Fractions with Minimal Residue in the Boiling Range of 35–700°C

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## Abstract

This article describes improvements to the standard methods in simulated distillation achieved by using columns of high stability. Details of the influence of analytical parameters on acceptability of results (precision and bias) and optimization of procedure to obtain a procedure compatible with routine analyses are reported.

## Introduction

Simulated distillation (SD) is a gas chromatography (GC) technique used for over 20 years to characterize petroleum fractions. Improvements to the GC columns now allow evaluation up to a final boiling point of 720°C. Several methods have been standardized or are in the process of being standardized, such as American Society of Testing and Materials ASTM D2887 (1), ASTM D5307 (2), and ASTM D3710 (3). Utilization of these standardized methods raises several problems in routine analysis, such as choosing of operating conditions and stationary phase (standard methods indicate only some possibilities), obtaining a good overlap between the different methods, defining a procedure (calibration, blank, quantitation, etc.) compatible with automation and reproducibility of the method, and processing data to ensure good results without manual control. Many papers describe the optimization of analytical parameters (4–6), column lifetime, and varied retention time (7–8). Stability of the baseline is most important, enabling reduction of the frequency of calibration runs, blanks, and quality control samples (4).

The purpose of this work is to define the criteria for simulated distillation needed to implement a routine and automatic method: the choice of low-bleed stationary phases to achieve agreement with true boiling point (TBP) results, repeatability of retention times, frequency of the calibration and blank, and defining tests of acquisition and calculation for data processing. New columns with cladded metal (stainless steel and A aluminum) and dimethylpolysiloxane or methylcarboranepoly-siloxane as a stationary phase were tested. These columns are highly thermostable. From these tests two methods have been

established; the first corresponding to the conventional SD (CSD) for samples with a boiling range extended to 650°C; and the second corresponding to the high temperature SD (HTSD) for samples with a boiling point range of 174–700°C. A procedure compatible with routine analysis is described, and the precision of the methods is determined.

## Experimental

All of the development work was carried out using a Hewlett-Packard 5890 or a Fisons 8000 GC equipped with a constant flow rate of carrier gas and a cooled on-column injector. Capillary

**Table I. Operating Conditions for CSD and HTSD Methods**

	CSD Method	HTSD Method	
		cladded steel column	cladded aluminum column
Initial oven temperature	35°C	35°C	35°C
Initial hold	1 min	1 min	1 min
Program <sub>1</sub>	10°C/min	10°C/min	15°C/min
Final <sub>1</sub>	390°C	150°C	420°C
Program <sub>2</sub>		5°C/min	
Final <sub>2</sub>		410 °C/min	
Final hold	14 min	60 min	20 min
Initial injector temperature*	80°C	180°C	180°C
Program	50°C/min	20°C/min	20°C/min
Final	390°C	420°C	420°C
Final hold	45 min	35 min	35 min
Detector temperature	400 °C	420 °C	420 °C
Carrier gas	helium	helium	helium
Constant flow	10 mL/min	10 mL/min	10 mL/min
Injection size	0.5–1 mL	1–2 mL	1–2 mL
Sample dilution in CS2	30 volume %	5 g/L	5 g/L
Slice rate	2 Hz	1 Hz	1 Hz

\* Applies only to HP 5890.

columns were megabore type (530- $\mu\text{m}$  i.d.). For each method, two columns were tested. For the CSD method, a Chrompack 10-m HT-SimDist CB column (0.5  $\mu\text{m}$  dimethylsiloxane, deactivated metal) and a Restek 15-m MXT-1 column (0.5 mm dimethylsiloxane, steel-clad) were tested. For the HTSD method, a Chrompack 5-m HT-SimDist CB column (0.15 mm dimethylsiloxane, deactivated metal) and an SGE 12-m HT-5 column (0.15 mm methylcarboranopolysiloxane, clad aluminum) were tested. The operating conditions for CSD and HTSD are given in Table I.

TBP distillations were performed according to the ASTM D2892 method.

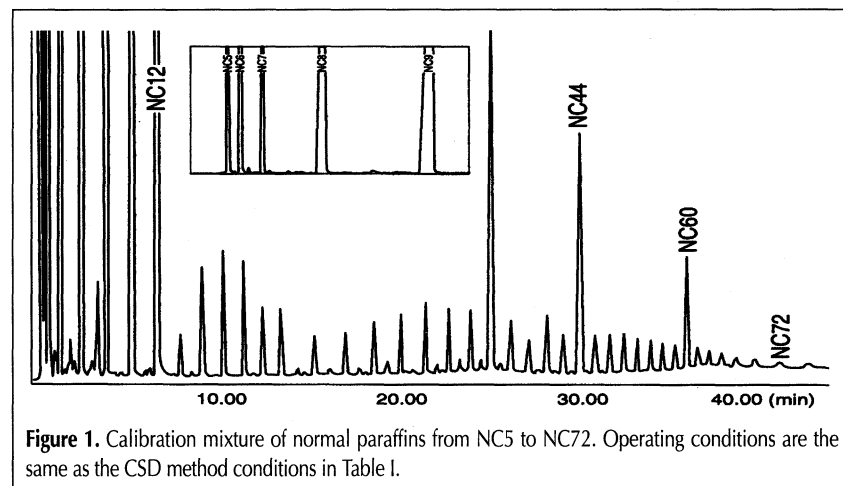


Figure 1. Calibration mixture of normal paraffins from NC5 to NC72. Operating conditions are the same as the CSD method conditions in Table I.

Table II. Bias (in  $^{\circ}\text{C}$ ) between CSD and TBP

Concentration (%)	Sample 1*			Sample 2†			Sample 3‡		
	CSD	TBP	Bias	CSD	TBP	Bias	CSD	TBP	Bias
10	197	192	5	237	233	4	187	184	3
30	233	230	3	278	274	4	222	217	5
50	269	264	5	310	306	4	251	246	5
70	307	304	3	338	334	4	281	280	1
90	360	356	4	372	368	4	326	325	1

\* Sample 1: hydrotreated gasoil with 2% aromatics.

† Sample 2: hydrodemetallation gasoil with 50% aromatics.

‡ Sample 3: light cycle oil with 75% aromatics.

Table III. Bias (in  $^{\circ}\text{C}$ ) between HTSD and TBP

Concentration (%)	DAO 1*			DAO 2†			VD‡			AR§		
	HTSD	TBP	Bias	HTSD	TBP	Bias	HTSD	TBP	Bias	HTSD	TBP	Bias
10	537	546	-9	410	415	-5	388	401	-13	401	414	-13
20	553	559	-6	476	482	-6	413	424	-11	427	436	-9
30	565	568	-3	529	527	2	435	444	-9	450	458	-8
40	575	576	-1				457	466	-9	476	482	-6
50							482	490	-8	507	511	-4
60							510	514	-4	542	547	-5
70							542	542	0			

\* Desasphalted oil 1: 45% saturates, 49.7% aromatics, 5.8% resins, 0% asphaltenes.

† Desasphalted oil 2: 8.5% saturates, 35% aromatics, 34% resins, 14.5% asphaltenes.

‡ Vacuum distillate: 31.2% saturates, 53.3% aromatics, 15.5% resins, 0.2% asphaltenes.

§ Atmospheric residue: 59% saturates, 19% aromatics, 19.5% resins, 2.5% asphaltenes.

Calculations were performed using Chromdis SD software developed by IFP and JMBS (JMBS-France). This software carries out tests on baseline stability and the acquisition slices (sample and blank) and calculates the boiling range distribution.

## Results and discussion

### Operating conditions

#### Selection of the stationary phase

In SD, the elution and separation of compounds are evaluated using three criteria: separation of the boiling point calibration mixture, elution or non-complete elution of the sample, and elution of compounds versus their boiling points. Since it is necessary in SD to calibrate the dependence of retention time on boiling point by a mixture of normal alkanes, the separation of these compounds is an important parameter. Film thickness is the most important parameter that determines the range of boiling point for a CSD method. The selection of the film thickness is a compromise between the separation of light components and the elution of the last paraffins at the final temperature of the column (compatible with a low column bleed). For new clad metal columns, a film thickness of 0.5  $\mu\text{m}$  allows separation of the normal paraffins C5 and C6 (resolution greater than 1.2 at 35 $^{\circ}\text{C}$  and 10 mL/min) and elution of the normal paraffin C72 at an oven temperature of 390 $^{\circ}\text{C}$ . With these performances, the scope of the CSD method can be extended to a final boiling point of 650 $^{\circ}\text{C}$ . Figure 1 shows the chromatogram of a mixture of C5–C72 normal paraffins. For the HTSD method, it is necessary to decrease the film thickness to 0.10–0.15  $\mu\text{m}$  in order to elute the normal paraffin C100.

Column performance is affected by non-eluting residues. The problem can be resolved by installing a precolumn with a back-flush (9). Baseline reproducibility is improved, but the precolumn needs regular replacement to maintain good performance.

The SD methods developed in this work are applicable only to samples that are completely eluted. In this case, heavy samples with asphaltenes were desasphalted, and the method will therefore not apply to crude oils with asphaltenes because of the loss of light components during removal of asphaltenes.

To simulate a true distillation, it is essential that the elution order of the compounds corresponds to the order of their boiling points. With non-polar stationary phases, the boiling points of non-alkylated aromatics (di- and poly-) calculated from their retention times with an *n*-alkane

calibration show a bias compared with those given in tables of physical constants. The stationary phase that gives the smallest bias is a polycarboranesiloxane (Dexsil) (9), but this phase cannot be cross-linked. However, because many petroleum sample aromatics are highly alkylated with chains of different lengths, the most stable stationary phases that give a lower bias compared with the TBP are dimethylpolysiloxane and methylcarboranepolysiloxane. Table II gives the bias using CSD for three dif-

ferent gasoils with aromatic contents from 2 to 75%, and Table III gives the bias for four different petroleum cuts using HTSD with dimethylpolysiloxane as stationary phase. The bias is < 5°C for CSD and < 13°C for HSTD.

#### Optimization of operating conditions

Different authors agree on the influence of the operating conditions on the results. Variations in the carrier gas flow, temperature programming, and film thickness of the stationary phase give some bias in the repeatability of the method (less than 2°C) (4,5). The effect of the sample dilution is noticeable for CSD methods when the concentration is lower than 10%. In Table IV, this effect is shown for three different samples. The best agreement with the TBP results is obtained with a concentration above 10% (30% in Tables II and III).

#### Column lifetime

In SD, column lifetime is defined by three parameters: column resolution, baseline drift, and the variation of retention time (RT) of *n*-alkanes. These parameters are interdependent and are affected by the bleed rate of the stationary phase or the deposit of very heavy compounds in the chromatographic system. The standard methods address only column resolution.

Baseline drift can be defined by the ratio of total slices of the blank to total slices of the sample. Baseline drift must be less than 5%. Frequency of calibration depends on the variation of the RTs and has an effect on the precision of the result. A criterion of variation of RT versus the repeatability of the method can be defined; a new calibration must be carried out when variation in RT corresponds to a variation in temperature (°C) greater than 50% of the repeatability. The lifetime of commercial clad metal columns with these defined parameters can vary slightly. For CSD, the lifetime is greater than 500 oven cycles. In HTSD, the lifetime is about 150 oven cycles.

#### Frequency of calibration runs and blanks

Using the defined criterion of variation of RT, the frequency for the CSD method is about one blank after 5–7 samples and a calibration after 20–25 samples. For the HTSD method, the frequency is about one blank after 4–5 samples and a calibration after 10 samples. These frequencies allow the development of a procedure compatible with a routine analysis.

#### Quantitation

A basic instrumental requirement is constant detector response and minimal injection discrimination over the range of boiling points covered by the method. This parameter is verified by a weighed mixture containing three cuts of crude

**Table IV. Effect of Sample Dilution: Bias (in °C) between 30, 10, and 2%**

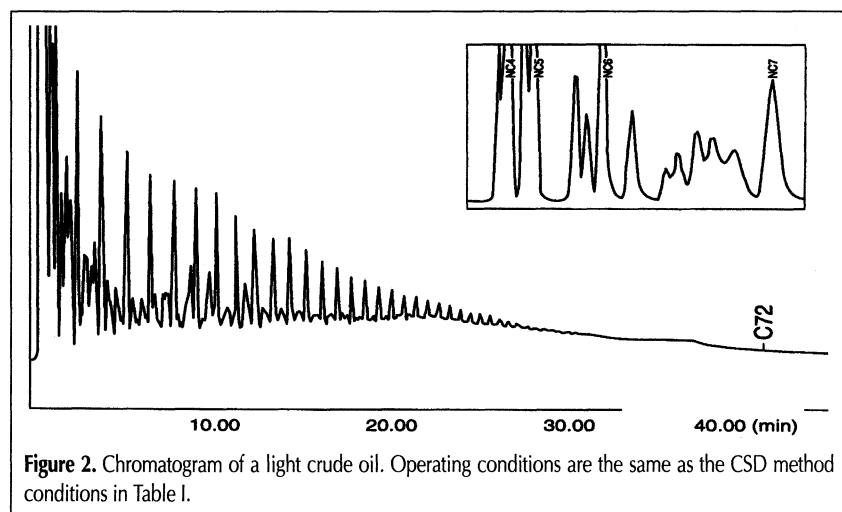
Concentration (%)	Sample 1*		Sample 2†		Sample 3‡	
	Bias 30/10 (°C)	Bias 30/2 (°C)	Bias 30/10 (°C)	Bias 30/2 (°C)	Bias 30/10 (°C)	Bias 30/2 (°C)
10	2	2	1	2	1	2
50	2	2	2	4	2	4
90	2	4	2	5	2	5

\* Sample 1: hydrotreated gasoil with 2% aromatics.  
† Sample 2: hydrodemetallation gasoil with 50% aromatics.  
‡ Sample 3: light cycle oil with 75% aromatics.

**Table V. Bias (in °C) between CSD and HTSD**

Concentration (%)	Sample 1*			Sample 2†			Sample 3‡		
	HTSD	CSD	Bias	HTSD	CSD	Bias	HTSD	CSD	Bias
1	475.9	453.1	22.8	218.3	195.4	22.9	338.2	331.5	6.7
5	516.9	512.1	4.8	263.3	257.4	5.9	373	371	2
10	532.5	528.5	4.0	298.2	295.3	2.9	399.5	400.6	1.1
20	541.2	5538	3.2	322.4	320.5	1.9	422.3	423.9	-1.6
30	551	547.8	3.2	348.3	347.1	1.2	444.2	446.6	-2.4
40	559.1	556.2	2.9	375.1	374.6	0.5	464	466.7	-2.7
50	566.1	563.4	2.7	404.2	403.6	0.6	484.1	486.3	-2.2
60	573	569.8	3.2	431.9	433.7	-1.8	503.9	506	-2.1
70	579.7	576.2	3.5	462.9	466.1	-3.2	524.5	527.3	-2.8
80	586.8	584.1	2.7	500.5	502.9	-2.4	548.1	551.4	-3.3
90	596.5	593.5	3	544.7	548.2	-3.5	576.9	580.7	-3.8
99.5	647.3	628.2	19.1	628.2	629.3	-1.1	639	639.7	-0.7

\* Sample 1: hydrotreated gasoil with 2% aromatics.  
† Sample 2: hydrodemetallation gasoil with 50% aromatics.  
‡ Sample 3: light cycle oil with 75% aromatics.



**Figure 2.** Chromatogram of a light crude oil. Operating conditions are the same as the CSD method conditions in Table I.

oil with no overlapping zone between these cuts. The results must differ by less than 3% from the known concentration of these three cuts.

### Raw data processing

#### *Treatment of the baseline*

Three different software methods are generally used for baseline compensation: slice-by-slice subtraction of a stored baseline, slice-by-slice subtraction after an adjustment of the starting sample baseline with the stored baseline, and reshaping a stored baseline to match the initial and final baseline values of the sample run. The latter compensation procedure works well when the samples are completely eluted from the column. Adjustment of the baseline must be determined on the average first slices before the start of solvent elution.

#### *Determination of the start and the end elution times*

Determination of the initial and final elution times of the sample is important to the precision of the initial and final boiling points. To obtain elution times, it is best to determine the difference between two consecutive slices after the solvent elution (initial elution time) and after the end of the analysis (final elution time). This difference is compared to the total area of the sample to define a level of change corresponding to the start and end of elution time.

#### *Acquisition Validity Tests*

Quality of the acquisition slices must be controlled before baseline compensation and determination of the initial and final elution times. These tests concern the stability of the first slices (sample and blank) and negative slices and the offset and value of the last slice for the sample.

### Standard methods and routine analysis

#### *Overlap between conventional and high temperature simulated distillation method*

Generally, SD methods cannot be used accurately over the entire boiling point range with a sample (e.g., crude oil or conversion effluent) containing both light and heavy compounds. A number of laboratories analyze crude oils with a single SD method; however, the lack of resolution, the solvent coelution in the C4–C6 region, and column overload reduce the accuracy of the simulated distillation. A more accurate approach is to prepare fractionated distillation yielding two cuts of the sample and then apply the CSD and HTSD methods on the light and heavy fraction, respectively. In this case, the overlap between the two methods is very important. Table V gives the bias (in °C) between

CSD and HTSD methods with three different samples using a boiling range compatible with the two methods.

#### *Precision*

The repeatability has been estimated from IFP laboratories for the extended CSD method. The values are given in the Table VI with the values of ASTM D2887.

#### *Advantages of the extended CSD method*

With the extended CSD method up to 650°C, samples with a FBP of 650°C that were previously analyzed by the HTSD method can now be analyzed with better precision by the CSD method, especially for initial boiling point and FBP determination. Moreover, for routine use, this method is easier and more practicable (frequency of calibration, blanks, etc.). The majority of conversion effluents (FCC, hydrocracking, hydrotreatment, etc.) and light crude oils can now be analyzed directly without distillation. As an example, Figure 2 shows the chromatogram of a light crude oil using the CSD method.

## Conclusion

By selecting the most stable columns that give a good agreement with the TBP distillation, several improvements to SD methods have been realized, such as the reduction of the column bleed with stable baselines, reduction of the number of calibration runs and blanks, and extension of the FBP for the CSD method. With these improvements, and by fixing parameters for column stability and tests for raw data processing, it is possible to obtain a procedure compatible with routine analysis. Automation of this analysis can be carried out using data processing software which controls all parameters of the method.

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	% Recovered	
	Extended CSD	ASTM D2887
IBP	3	6
5–95	1	2.5
FBP	3	5