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Résumé — **Amélioration des méthodes de distillation simulée par chromatographie en phase gazeuse pour l'analyse de routine** — La distillation simulée (DS) par chromatographie en phase gazeuse (CPG) est une technique qui remplace avantageusement les méthodes traditionnelles de distillation pour un rapide contrôle des produits pétroliers. Si le principe est simple (séparation des constituants en fonction de leur point d'ébullition par la colonne chromatographique), la mise en œuvre est moins facile. Le premier problème concerne le choix de la phase stationnaire pour obtenir un bon accord avec la courbe de la distillation réelle ; le second est la stabilité de cette phase à la température maximale utilisée. Il y a beaucoup de paramètres interdépendants relatifs à ces deux problèmes. Si plusieurs méthodes ont été standardisées, leurs applications présentent des difficultés en analyse de routine : nécessité de choisir des conditions opératoires (les méthodes indiquent seulement des possibilités), de définir une procédure (calibration, blanc, quantification, etc.) compatible avec la reproductibilité de la methode et son automatisation, et d'assurer un traitement des données donnant des résultats corrects.

L'arrivée ces dernières années de colonnes métalliques très stables a permis un meilleur contrôle des paramètres expérimentaux. Avec ces colonnes, le point final d'ébullition déterminé par les méthodes a été étendu et des procédures ont été définies pour utiliser ces méthodes de routine. Les résultats de DS sont en bon accord avec la distillation physique. Une automatisation de ces méthodes est devenue possible en développant un logiciel qui effectue le traitement des données brutes, le calcul de la courbe de distillation et le contrôle de tous les paramètres définis dans la procédure.

Mots-clés : distillation simulée.

Abstract — ***Improvement of Simulated Distillation Methods by Gas Chromatography in Routine Analysis*** — *Simulated distillation (SD) by gas chromatography (GC) is a technique which advantageously replaces traditional distillation methods for rapid checking of petroleum products yields. If the principle is simple (separation of the components according to their boiling point by the GC column) the implementation is less obvious. The first problem concerns the choice of the stationary phase to obtain good agreement with the real distillation curves; the second is the stability of this phase at the maximum temperatures used. There are many interdependent parameters involved in these two problems. Although several methods have been standardized their applications give rise to a number of difficulties in routine use: need to choose operating conditions (standard methods indicate only some possibilities), determination of the procedure (calibration, blank, quantification, etc.) compatible with automation and reproducibility of the method, data processing to assure a good result.*

The arrival in the last few years of very stable metal capillary columns have provided better control of the experimental parameters. With these columns the determined final boiling point of SD methods has been extended and some procedures have been defined to use these methods in routine analysis. Results of SD are in good agreement with the physical distillation. An automation of these methods has become feasible by developing a software which carries out the raw data processing, the calculation of the SD curve and controls all parameters of the defined procedure.

Keywords: simulated distillation.

INTRODUCTION

Distillation is the most used method for determining the boiling range of petroleum products, but the conventional methods of distillation are very time consuming: characterization of a crude oil by the true boiling point (TBP) method requires several days and several liters of products. In 1960's some authors [1, 2] proposed to use the separation by gas chromatography to simulate the TBP. The concept, called simulated distillation (SD) is based upon the assumption that the components of the sample are eluted from the column in order of their boiling point. Using a mixture of normal paraffins with known boiling points, the correspondence between the retention times and boiling points can be established and then the weight % versus boiling point curve can be constructed. Since that time SD has become a major analytical tool for the characterization of petroleum products in research and refinery laboratories. Many works and articles have been published and several methods were developed and standardized. At the present time, essentially four methods are used in laboratories.

SD methods using packed columns were originally developed for gasoline: ASTM D3710 [3] and middle distillates: ASTM D2887 [4]. These methods assumed 100% sample elution. When samples contain heavy fractions, these fractions are not fully eluted from columns. Evaluation of the eluted fractions can be carried out with an internal standard. With this technique a method has been standardized: ASTM D5307 [5] to determine the boiling point range of the crude oils up to 538 °C. But in this method, column is affected by non-eluting residue and its use in routine analysis is not easy.

In 1980's, *IFP* [6, 7] developed a method for samples containing non-distillable fractions by using a pre-column with a backflush to eliminate the heavy fractions from the analytical column. SD was determined up to 575 °C with an internal standard. Precolumn was connected to a temperature programmed injector.

In 1985's, some authors [8, 9] introduced the wide bore capillary columns to characterize heavy fractions: capillary columns have the advantage to elute much higher boiling point compounds than packed columns. To operate at temperatures as high as possible, a dedicated chromatographic system was developed with pyrex glass capillaries instead of fused silica capillaries because polyimide clad has a maximum operating temperature limit of approximately 370 °C.

Normal paraffin with 120 carbons (boiling point 720 °C) was eluted with a short glass column and a final oven temperature of 430 °C. Heavy distillates, lubricating oils, deasphalted residues were fully eluted from the columns. It was the first time that an information on the boiling range distribution was given on these samples. High temperature SD (HTSD) was born. But this method was not easy to use due to the important bleeding of the column at the final temperature providing a high baseline drift and variation of retention times with time.

Over the last 12 years, the use of capillary columns has become widespread [10-15]. ASTM D2887 has been up dated with these columns and a new precision determined better than with packed columns. But most laboratories practising this method have some difficulties to achieve the precision in routine analysis. The first problem is the definition of the analysis sequence calibration-blank-samples: after how many samples injections is it necessary to run calibration and blank? The response depends on the reproducibility of baseline drift and retention times. The second problem concerns the raw data processing to determine the initial and final boiling point: there is no standardized algorithm to calculate the start and the end of the sample elution.

Recently, capillary columns with highly stable thin film and aluminium or stainless steel coating have been introduced. Use of these columns for 2 years in *IFP* showed a lower and stable bleeding with a consistency in column manufacturing, providing better control of the experimental parameters. Definition of a reproducible procedure compatible with routine analysis and the precision of the standard method has become feasible. In addition the final determined boiling point of different methods has been also extended.

The purpose of this paper is to describe the three SD methods developed by *IFP* with these new columns and their utilization in routine analysis:

– CSD method (conventional SD): for carbon number distribution of C_5 to C_{72} (35-650 °C);
– HTSD method (high temperature SD): for carbon number distribution of C_{10} to C_{100} (174-720 °C);
– RSD method (residual SD): for carbon number distribution of C_5 to C_{60} (35-615 °C) on samples containing non distillable fractions (asphaltenes) by using the column of the CSD method with a precolumn.

1 EXPERIMENTAL

1.1 GC Apparatus

All of the development work was carried out using Hewlett-Packard 5890 or Fisons 8000 gas chromatographs equipped with a constant-flow rate of carrier gas, a flame ionisation detector and a cooled on-column injector for CSD and HTSD method and a temperature-programmed packed injector connected to a short precolumn that could be back-flushed for RSD method.

1.2 GC Methods

1.2.1 CSD Method

Distributions of boiling point for carbon number from C_5 to C_{72} were obtained using a Chrompack HT SimDist CB (10 m · 0.53 mm i.d., 0.5 mm) deactivated metal capillary column and a Restek, MXT-1 (15 m · 0.53 mm i.d., 0.5 mm) steel clad capillary column. The initial oven temperature was 35 °C and was held for 1 min. Then, the temperature was increased to 390 °C at a rate of 10 °C/min. and was held at 390 °C for 14 min. Carrier gas (helium) flow rate was kept constant at 10 ml/min. Detector temperature was 400 °C.

1.2.2 HTSD Method

Distributions of boiling point for carbon number from C_{10} to C_{100} were obtained using a Chrompack, HT-SimDist CB (5 m · 0.53 mm, 0.15 mm), deactivated metal capillary column and SGE, HT-5 (12 m · 0.53 mm, 0.15 mm), aluminum clad capillary column. For Chrompack column the initial oven temperature was 35 °C (1 min). The temperature was increased to 150 °C at a rate of 10 °C/min, then to 410 °C at a rate of 20 °C/min and was held at 410 °C for 35 min. For SGE column the initial oven temperature was 35 °C (1 min). The temperature was increased to 420 °C (20 min) at a rate of 15 °C/min. Carrier gas flow rate for the two columns was kept constant at 10 ml/min and the detector temperature was 420 °C.

1.2.3 RSD Method

Distributions of boiling point for carbon number from C_5 to C_{60} were obtained using the same capillary column as for CSD method. The precolumn was a packed column (20 cm · 1/8 inches) with Dexsil 300 at 2% on Chromosorb G. The initial oven temperature was 35 °C. It was increased to 390 °C at a rate of 16 °C/min and was held at 390 °C for 42 min. Carrier gas flow rate was kept constant at 13 ml/min. Detector temperature was 400 °C. Evaluating residues boiling above 615 °C was carried out with addition of an internal standard (mixture of normal paraffins C_{14}, C_{15}, C_{16}). If these paraffins do not interfere with any compound in the sample, one run is sufficient. If there is interference, this determination requires two analyses and calculations are performed with the same equation as in ASTM method for crude oil.

1.3 Raw Data Processing

Raw data processing is an important step before calculation of the boiling range distribution. Two major problems have an effect on the precision of results: subtraction of the baseline drift and determination of the start and the end elution times. Standard methods give only guidance on the processing. From *IFP* experience over 20 years, these problems require in first, a control of the quality of the area slices.

1.3.1 Acquisition Validity Tests

Some thresholds must be defined to evaluate the first slices stability, the level of negative slices, the offset between the blank and the sample. Moreover, the level of the last area slice of the sample must be tested and should not overcome a defined value.

1.3.2 Treatment of the Baseline

Three different 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 start and the end baseline values of the sample run. The second baseline 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.

1.3.3 Determination of the Start and the End Elution Times

This determination is very important for the precision of the initial and final boiling points. The best way is to determine the difference between two consecutive slices after the solvent elution for the start elution time and from the end of the analysis for the end elution time. This difference is compared to the total area of the sample to define a level of change corresponding to the the start and the end of elution time.

1.4 Calculations

The weight % versus boiling point were calculated by using the algorithm defined in the ASTM methods. This calculation and determination of the parameters described above (acquisition validity tests, treatment of the base line, start and end of elution times) were performed with the

software Chromdis, developed by *IFP* and *JMBS* (Grenoble, France). A general flow chart of raw data processing and calculations for the 3 SD methods is shown in Figure 1.

Several types of results can be obtained from the calculations. The standard report gives for each eluted % the corresponding temperature (in °C or °F); 0.5% is reported as the initial boiling point of the sample and 99.5% is reported as final boiling point. An eluted % can be reported for a fixed temperature: this result allows to determine the conversion for an effluent of refining process. From these data, the distillation curve is plotted. Figure 2 shows the mean screen of the software, giving the chromatogram of the sample and the blank, the calibration curve, the result and the distillation curve.

1.5 Analytical Procedure

On-column injection requires a dilution of the samples. Carbon disulfide is used as solvent for its small response to the detector. Dilution ratio depends on the methods. Before any sample serie, it is necessary to check baseline drift by a run with the solvent using for sample dilution.

Injection sequences of the different samples (calibration mixture, sample, sample with internal standard, solvent) were established in accordance with the respect of the defined parameters above. For quality control, a test sample is running one time a week.
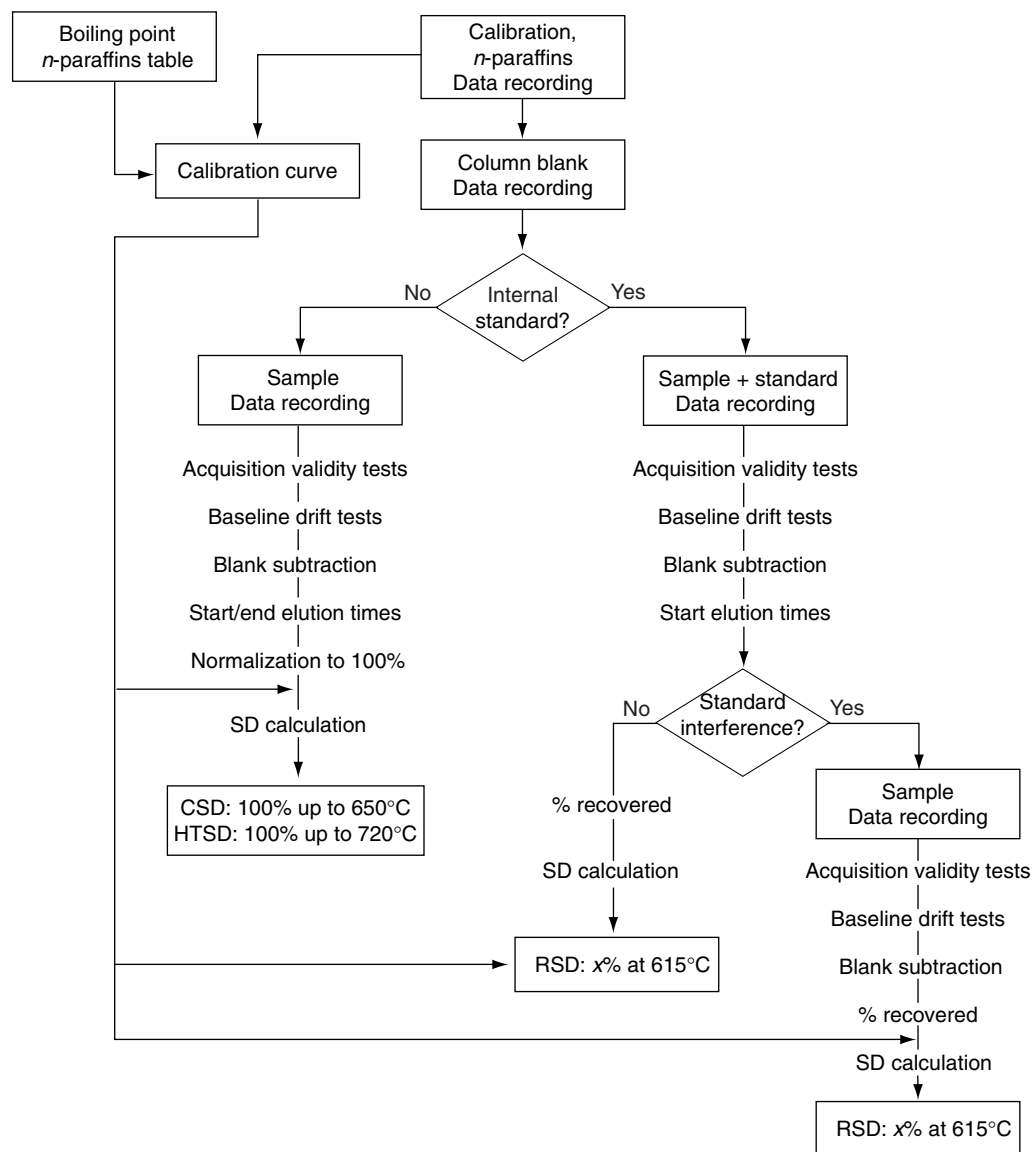

Figure 1

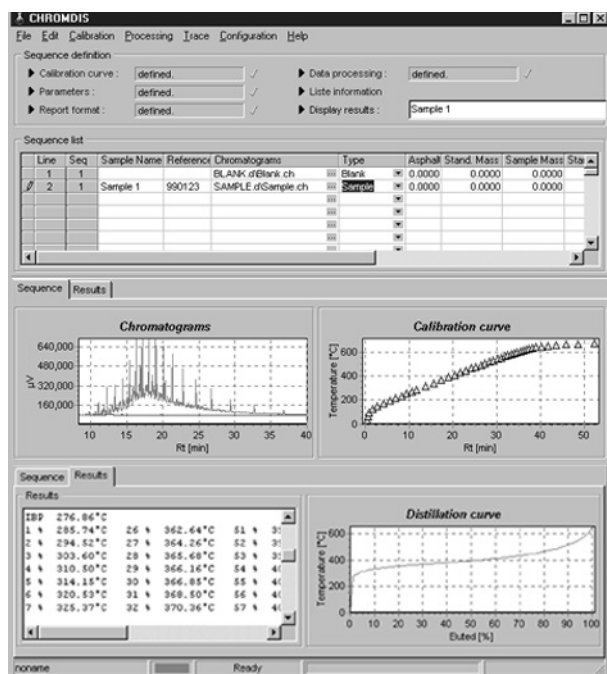General flow chart of raw data processing and calculations for the 3 SD methods.

Figure 2

Mean screen of the software, giving the chromatogram of the sample and the blank, the calibration curve, the result and the distillation curve.

2 RESULTS AND DISCUSSION

2.1 Choice of the Stationary Phase of the Column

To simulate a distillation, it is essential that the order of elution corresponds to the order of boiling points. With non-polar stationary phases, the boiling points of non-alkylated aromatics (di- and poly-) calculated from their retention times with *n*-alkane calibration show a bias with those given in physical constant tables [7]. For these compounds, the stationary phase which gives the smaller bias is a polycarboranesiloxane (Dexsil) but this phase cannot be chemically bonded. Film coated columns are not used in SD because their have a lower maximum operating temperature and a high bleed.

However, the bonded phases, dimethylpolysiloxane and carboranemethylpolysiloxane (HT5), the most stable stationary phases, give a bias between SD and TBP within the precision of the SD methods. These results can be explained because in the petroleum samples, aromatics are alkylated with chains of different lengths which decreased their polarity. Table 1 gives the bias in CSD for three different gasoils with aromatic contents from 2% to 75% and Table 2 gives the bias in HTSD for four different petroleum cuts with dimethylpolysiloxane as stationary phase. The bias

is smaller than 5 °C for CSD and smaller than 13 °C for HTSD. For HTSD results the bias is always negative due to, perhaps, a phase ratio for the column more higher than for CSD columns.

TABLE 1

Bias in °C between CSD and TBP

%	1			2			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

Type of samples: 1: hydrotreated gasoil with 2% of aromatics; 2: hydrodemetallation gasoil with 50% of aromatics; 3: light cycle oil with 75% of aromatics.

TABLE 2

Bias in °C between HTSD and TBP

%	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			

Type of samples: DAO 1, desasphalted oil 1: saturates: 45%, aromatics: 49.7%, resines: 5.8%. DAO 2, desasphalted oil 2: saturates: 8.5%, aromatics: 35%, resines: 34%. VD, vaccum distillate: saturates: 31.2%, aromatics: 53.3%, resines: 15.5%, asphaltenes: 0.2%. AR, atmospheric residue: saturates: 59%, aromatics: 19%, resines: 19.5%, asphaltenes: 2.5%.

2.2 Stationary Phase Film Thickness

As in SD it is necessary 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 defining the range of boiling point determined. It is a compromise between the separation of light components and the elution of the last paraffins at a final temperature of the column compatible with a low bleeding. For CSD method with new metallic clad columns, a film thickness of 0.5 μm

allows separation of the normal paraffins C_5 and C_6 (resolution > 1.2 at 35 °C and 10 ml/min) and elution of the normal paraffin C_{72} at 390 °C. With these performances the scope of the CSD method can be extended to a final boiling point of 650 °C. Figure 3 shows the chromatogram of a mixture of normal paraffins C_5-C_{72}. For HTSD method, it is necessary to decrease the film thickness to 0.10-0.15 μm to elute the normal paraffin C_{100}. In this case, the separation of light paraffins is not good and the method does not apply with samples containing light components below the normal paraffin C_{10}. Figure 4 shows the chromatogram of a mixture of normal paraffins C_{10} - C_{100}.

2.3 Optimization of Operating Conditions

Different authors agree concerning the influence of the operating conditions on the results. Variations of the carrier gas flow and temperature programming of the stationary phase give some bias corresponding to the repeatability of the method: less than 2 °C. The effect of the sample dilution rate by carbon disulphide is noticeable, for CSD method, when the sample concentration is lower than 10%. The best agreement with the TBP results is obtained with a concentration upper than 10%.

2.4 Column Lifetime

Column lifetime depends on three parameters: column resolution, baseline drift and variation of retention time (Rt) of n-alkanes. These parameters are interdependent and correspond to the bleeding of stationary phase or the deposit

of very heavy compounds. Only column resolution is defined in the standard methods.

A baseline drift can be defined from the chromatogram by the ratio: total area slices of the blank/total slices of the sample. This ratio must be less than 5% for CSD method and 15% for HTSD method. Frequency of calibration depends on the variation of the retention times 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 Rt variation corresponds to a variation of 1 °C. Lifetime of commercial metallic clad columns with these defined parameters can slightly vary. With CSD and RSD methods lifetime is greater than 500 oven cycles. With HTSD method, lifetime is about 150 oven cycles.

2.5 Frequency of Calibration Runs and Blanks

With the criteria of variation of Rt defined above, blank and calibration frequency for CSD methods are about one blank after 5-7 samples and one calibration after 20-25 samples. For HTSD method 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.

The procedure for RSD method is more restricting and required a regular replacement of the precolumn. The frequency depends on the quantity of residues in the samples analyzed: between 10 and 20 runs. A new calibration is carried out after each replacement.
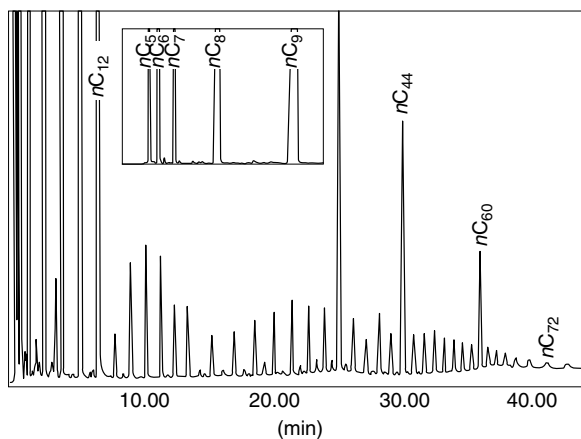

Figure 3

CSD method, calibration mixture of normal paraffins from nC_5 to nC_{72}. Operating conditions: see section 1.2.
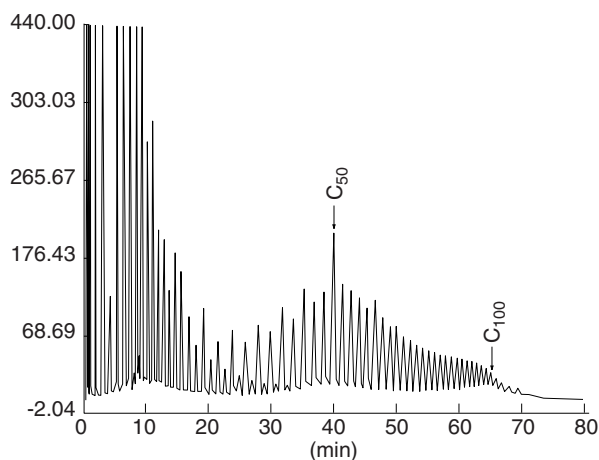

Figure 4

HTSD method, calibration mixture of normal paraffins from nC_{10} to nC_{100}. Operating conditions: see section 1.2.

2.6 Overlap between CSD and HTSD Method

SD methods cannot be used with a sample (crude oil or effluent of conversion process) containing both light compounds and heavy compounds. A preparative distillation giving two cuts must be carried out on the sample to apply the CSD and HTSD methods. In this case, SD results must be similar in the region of overlap between the distillation curves of the cuts. Table 3 gives the bias in °C between CSD and HTSD methods for three different samples (low, medium and high aromatic content) having a boiling range compatible with the two methods. Bias more importants for initial (IBP) and final (FBP) boiling point, up to 23 °C, come from the precision of the HTSD method which is less good for these determinations.

2.7 Overlap between RSD and HTSD Methods

Table 4 gives the comparison between RSD and HTSD Methods on heavy petroleum samples. For HTSD method, samples containing asphaltenes have been deasphalted to be fully eluted from the column, and results have been corrected for asphaltene content to be compared to the results of RSD method (raw samples injected).

2.8 Advantages of the CSD Method

With the CSD method extended up to 650 °C, samples with a final boiling point of 650 °C which were previously analyzed by the HTSD method, can be now analyzed by the CSD method with a better precision especially for IBP and FBP determination. Moreover for routine use, this method is easier and more practicable (frequency of calibration, blank, 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 5 shows the chromatogram of a light crude oil with the CSD method.

TABLE 3

Bias in °C between CSD and HTSD

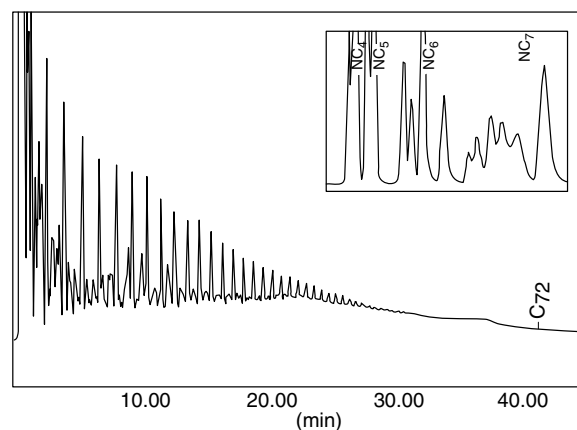| %	1			2			3		
	HTSD	CSD	Bias	HTSD	CSD	Bias	HTSD	CSD	Bias
IBP	475.9	453.1	22.8	218.3	195.4	22.9	338.2	331.5	6.7
5	516.9	512.1	4.8	263.3	257.4	5.9	373	371	2
10	532.5	528.5	4.0	298.2	295.3	2.9	399.5	400.6	1.1
20	541.2	553.8	3.2	322.4	320.5	1.9	422.3	423.9	-1.6
30	551	547.8	3.2	348.3	347.1	1.2	444.2	446.6	-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
FBP	647.3	628.2	19.1	628.2	629.3	-1.1	639	639.7	-0.7

Figure 5

Chromatogram of a light crude oil. Operating conditions, CSD method: see section 1.2.

TABLE 4

Bias in °C between RSD and HTSD

%	Sample 1 Asphaltenes: 24%			Sample 2 Asphaltenes: 11%			Sample 3 Asphaltenes: 0%			Sample 4 Asphaltenes: 0%		
	HTSD	RSD	Bias	HTSD	RSD	Bias	HTSD	RSD	Bias	HTSD	RSD	Bias
IBP	298	285.5	12.5	312.0	306.4	5.4	381	379.2	1.8	435.9	436.0	-0.1
10	390	395.4	-5.4	402.0	408.6	-6.6	537	542.2	-5.2	504.6	511.2	-6.6
20	446	458.8	-13.8	446.0	459.0	-13	553	556.2	-3	539.9	545.0	-5.1
30	495	506.8	-11.8	484.0	494.0	-10	565	566.5	-1.5	568.3	569.7	-1.5
40	554	556.7	-2.7	521	527.6	-6.6	575	575.6	-0.6	592.5	596.8	-4.3
45	582	582.7	-0.7	540	544	-4	580	580	0			
50				562	560.8	1.2	585	585.1	-0.1			
55				583	579.7	3.3	590	591.2	-1.2			

2.9 Precision

Repeatability has been estimated from IFP laboratories for the extended CSD method. Values are given in Table 5 and compared with the data of ASTM D2887. Precision was improved for each recovered %.

TABLE 5

Repeatability in °C compared to ASTM D2887

Recovered %	Extended CSD	ASTM D2887
Initial boiling point (IBP)	3	6
5 to 95	1	2.5
Final boiling point (FBP)	3	5

2.10 Laboratory Productivity

These new columns and new defined parameters described above are used in *IFP* for two years in routine analysis (several thousands analyses a year). With a better stable baseline and consistency in column batches, analytical procedures are more reproducible: less blank runs and calibration runs are needed, column lifetimes are increased, less equipment maintenance is required. Standardization of raw data processing and its controls by the Chromdis, software ensure an automation of these analyses. A specific interface of the software has been developed so that the automatic system can be used by a non specialist, a chromatographist ensuring the follow up of the procedure and the maintenance.

CONCLUSION

Since the first result reports, 30 years ago, the simulated distillation has become a technique very successful in the applications to the control of refinery processes and quality control. Constant improvements have been made for the beginning to obtain more reliable methods. If the most important improvement has been the replacement of packed columns by capillary columns, the last advances, concerning the stability of the columns and the raw data processing, have allowed a better control of SD parameters. With these new more stable columns, the definition of some reproducible

procedures compatible with a routine analysis and with the precision of the standard methods became feasible.

By using these procedures and appropriate control tests for raw data processing, an automation of analyses was carried out with a data processing software which controls all parameters of methods. This automated SD system can operate continuously. Running for two years in our company, these methods have shown their ruggedness The reliability of the SD results as well as the productivity of the laboratories have been greatly increased.

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