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AUTOMATED SIMULATED DISTILLATION BY GAS CHROMATOGRAPHY

PERFORMANCE TEST FOR PETROLEUM PRODUCT CONTROL

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SUMMARY

Experimental conditions of simulated distillation (SD) have been standardized for the boiling range control of products from various process plants, mainly devoted to heavy petroleum feedstock conversion. One injection port of a gas chromatograph, provided with an automatic sampler, was replaced with a special device (temperature-programmed injection and high-temperature back-flushed pre-column). Dexsil 300 GC was chosen as the stationary phase for its good performance with highly aromatic samples. A Fortran post-run computer program was developed to increase the reliability of the results. Many comparisons of SD results with those of classical ASTM distillation tests were made and their respective performances were critically examined.

INTRODUCTION

Simulated distillation (SD) by gas chromatography (GC) has been used extensively for petroleum samples since about 1965. Butler¹ reviewed all work prior to 1976, including correlations with classical distillation tests. Improvements in gas chromatograph performance by use of microprocessors and the development of powerful laboratory automation systems have led to increased quality of the results and have extended the field of SD applications to non-virgin petroleum products, even if they contain undistillable fractions. An ASTM method has been proposed² for SD of wide-boiling-range samples with evaluation of the non-eluted fraction by a dual run, one with the sample and another after addition of known amounts of four *n*-alkanes. The high column temperature needed for distillation information up to 538°C (1000°F) and column contamination by heavier products lead to a baseline drift of the GC signal, which is not easily corrected. For coal-derived liquids, Southern *et al.*³ developed a baseline correction method, but used a vacuum thermogravimetric method to calculate the residue above 538°C. In recent investigations, short, coated Pyrex capillary columns were heated to 420°C and connected to an on-column injector. Luke and Ray⁴ achieved a final boiling point of 650°C and Trestianu *et al.*⁵ eluted hydrocarbon fractions up to a final boiling point of 800°C. The residue is

determined by means of an internal standard, which is not easy for heavy, viscous materials.

This paper describes an automated routine SD method, capable of analysing on the same apparatus wide-boiling-range samples or distillation cuts from thermal and catalytic conversion processes for various heavy petroleum feedstocks, which takes into account all the main critical parameters. The choice of the stationary phase (Dexsil 300) (preferred to all silicone gums), used in our laboratory for more than 10 years and tested by other French petroleum laboratories⁶, is highlighted by the problem of calibrating retention time (RT) *versus* boiling point (BP) for highly aromatic compounds with an *n*-alkane mixture. The versatility of the gas chromatograph, modified by a special device described elsewhere⁷, is demonstrated by the application of SD to various samples. A special computer program that has been developed in our Institute is described for the most critical parameters of the method, *viz.*, baseline drift correction, tests of integration to determine significant area values at the end of the analysis and quantitative methods for samples leaving a residue. Analytical procedures are given for automation of SD with a GC automatic sampler. Comparisons with several standardized distillation tests⁸⁻¹⁰ up to 550°C are given and discussed for typical petroleum samples.

EXPERIMENTAL

Equipment for simulated distillation

The gas chromatograph was a Model 5880A from Hewlett-Packard (HP) (Palo Alto, CA, U.S.A.) provided with two injectors for 1/8-in. packed columns and only one flame ionization detector. One injection port was a temperature-programmed injector connected to a short pre-column that could be back-flushed by a pneumatic commutation system, actuated by the chromatograph processor. Details have been published previously⁷. The injector design and flow scheme are available from Analytical Controls (Delft, The Netherlands). An HP Model 7671 A automatic sampler could be connected to either of the injection ports. It was controlled by the chromatograph processor in a procedure for a sampling sequence. For data acquisition and SD classical integration by slices, an HP 3350 A laboratory automation system was used. A FORTRAN post-run program was developed by our laboratory, to improve *n*-alkane calibration, tests of convergence between sample signal and memorised base line and evaluation of the residue at 575°C, if necessary.

Equipment for distillation tests

SD results were compared with three types of distillation tests. The first, called TBP (true boiling point), was an actual fractionation with an efficient column (with either plates or packing) and a reflux device. The second was a controlled evaporation without reflux, having an efficiency of about one theoretical plate. The third was a continuous evaporation under considerably reduced pressures and at high temperatures on a falling thin film. TBP distillation tests were carried out according to ASTM Method D2892-78⁸ with an automatic apparatus (Minidist, Gecil, Lyon, France). For manual tests, the ASTM Method recommendations were observed, but our column was more efficient (30 plates instead of 15) and the reflux ratio was higher (10 instead of 5). These methods give information up to 400°C AET (atmosphere equiv-

alent temperature). To reach higher temperatures, no column is used but instead, a short, hollow tube and an even lower pressure.

Distillation tests were performed according to ASTM Methods D86-78 (IP 123, NF M 07002)⁹ at atmospheric pressure for gasolines and gas oils and Method D1160-77¹⁰ at reduced pressures for heavier compounds. Results are given in volume percent; distillation data can be obtained up to 400°C by Method D86 and up to 550°C (AET) by Method D1160. Our results were generally obtained by manual operation, except for some D1160 results, which were obtained by the Minidist accessory. Molecular distillation (short-path distillation) tests were performed with laboratory-constructed apparatus. Distillation information could be obtained up to 700°C AET. A description of the apparatus and some of our results have been given in a previous paper¹¹.

Normalization of the simulated distillation procedure

SD computer program. The SD program was developed on the HP 3350 A for a post-run FORTRAN program. A general flow-chart is shown in Fig. 1. The acquisition rate was 0.5 s and the slice width was 2 s.

Base-line drift correction. Our first SD computer, developed before 1972, used only a linear correction for baseline drift. Because Dexsil columns show very little bleeding⁶, this simple correction, applied to sample chromatographic signals, has allowed us to obtain good results for samples without residues. As the capability of

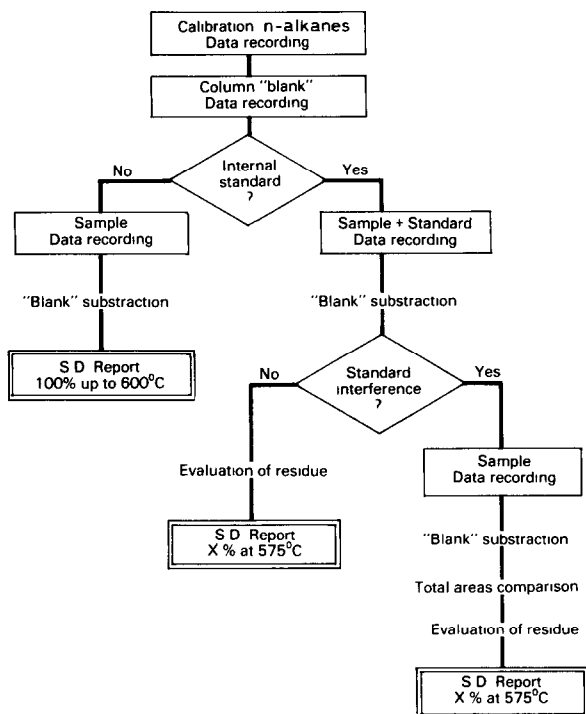


Fig. 1. Flow-chart of SD program.

computers increased around 1978, the correction of sample signals by subtraction of baseline drift signal became easy. This important modification was introduced for our 3354 HP data system in 1983 and has recently been transferred to the new HP 3350A data system. The analysis offset at the start of integration is performed from the mean values during the first 10 s. The offset signals of the sample and column blank are brought into coincidence by translation of the blank signal. The end of significant integration is detected by a convergence test of sample and blank signals, applied after the last peak detection with two alternatives: (1) corrected slices become lower than a limiting value (determined by preliminary tests); or (2) corrected slices maintain the same value for three intervals. This is useful for heavy samples, where the baseline does not return to the "blank" signal.

n-Alkane calibration. The calibration table (RT vs. BP) was established with 32 *n*-alkanes (maximum number) chosen between C₁ (-164°C) and C₇₀ (+647°C); the operator needs to give only the carbon number and the retention time of the peak corresponding to each *n*-alkane. This method permits convenient adjustment of the calibration graph if the chromatographic temperature conditions are modified.

Internal standard calibration. The internal standard was a mixture of C₁₄, C₁₅ and C₁₆ *n*-alkanes. If these alkanes do not interfere with any compound in the sample, one run is sufficient, and calculation of the total theoretical area is simple. If there is interference, this determination requires two analyses (Fig. 1). Calculations are performed with the same equation as in a proposed ASTM method for crude oils², taking into account differences in injection between the two analytical runs. A test has been added to reject the result if the total areas in the two analyses differ by more than 10%.

Analysis sequence. The various samples, calibration mixture, sample, sample plus internal standard and solvent are labelled by different codes in the entering sequence, as defined by the operator. Hence, they are recognized by the program and properly used.

Choice of the stationary phase

The ASTM methods for gasoline¹², petroleum fractions¹³, heavy oil products² and most published methods use silicone gums (OV-1, OV-101 or UCW-98) as stationary phases for packed columns. Recent publications on capillary columns used for SD show the same tendency^{4,5,14,15}. Another type of polymer (polycarborane-siloxane) called Dexsil, which is non-polar and very stable at high temperatures, appeared around 1972 and was applied to many heavy products¹⁶. This phase was used extensively by our laboratory for SD. Our previous published papers^{6,7} have shown that it is the most stable phase at high temperature (380°C), permitting work with only one column, without a bleed compensation column, and that it is even less polar than UCW-98.

The major problems in the calibration of the BP scale using *n*-alkane retention times are encountered in the analysis of highly aromatic samples, because aromatic compounds give a different calibration graph. Table I shows the difference observed between the aromatics BP (AET) calculated from their retention times with *n*-alkane calibration and those given in physical constants tables, on two columns, OV-101 and Dexsil-300; values for UCW-98 were measured by the ASTM D2887 method¹³. Except for light aromatic compounds, Dexsil 300 appears to remain the best sta-

TABLE I
 DIFFERENCE (Δ) OF AROMATIC BP WITH *n*-ALKANE CALIBRATION ($^{\circ}$ C)

Compound	True BP	Dexsil 300		OV-101		UCW-98	
		Calc. BP	Δ^*	Calc. BP	Δ^*	Calc. BP	Δ^*
Benzene	80	—		86	+6		+4
Toluene	110	—		120	+10		+2
<i>m</i> -Xylene	139	156	+17	145	+6		0
1,3,4-Trimethylbenzene	165	176	+11	160	-5		
1,2,4,5-Tetramethylbenzene	197	206	+9	196	-1		
Tetralin	207	—		203	-4		
Naphthalene	218	224	+6	212	-6		-11
Diphenyl	256	254	-2	244	-12		
2,3-Dimethylnaphthalene	268	272	+4	254	-14		
Acenaphthene	279	283	+4	262	-17		
Dibenzothiophene	332	328	-4	305	-27		-32
Phenanthrene	339	335	-4	—	—	304	-34
Anthracene	340	336	-4	312	-28	—	-35
Pyrene	393	380	-13	356	-37	347	-48
Benzofluorene	413	392	-21	368	-45		
Triphenylene**	424	416	-8			352	-72
Benzophenanthrene**	425	405	-20				
Chrysene**	447	422	-25			387	-60
Benzo[a]pyrene**	478	454	-24				
Picene**	520	484	-36				
Coronene**	525	522	-3				

* Δ = calculated value—reference table value.

** Values from previous work⁶.

tionary phase. The support used to prepare the packing is less important, but Chromosorb G (Johns-Manville, Denver, CO, U.S.A.) continues to be used because of its physical properties. It is a relative dense, hard material with a low surface area (0.5 m²/g). Thus, with only 2 wt.-% of stationary phase, the support is almost completely covered; this eliminates adsorption or degradation phenomena and allows low column retention.

Analytical procedures

Equipment. Recommendations for column conditioning to minimize baseline drift and control the efficiency required have been given elsewhere⁶. For wide-BP range samples⁷, the experimental conditions are as follows: (a) pre-column (0.2 m \times 1/8 in. I.D.) and column (1.5 m \times 1/8 in. I.D.) located in the same oven are packed with 2 wt.-% Dexsil 300 on Chromosorb G; initial temperature, 60 $^{\circ}$ C, held for 1 min, then programmed to 380 $^{\circ}$ C at 16 $^{\circ}$ C/min and kept at this value for 10 min; (b) injection device connected to an automatic sampler delivering 1 μ l; the temperature of the injector is programmed from 200 $^{\circ}$ C (30 s) to 380 $^{\circ}$ C in 12 min; (c) flame ionization detector kept at 400 $^{\circ}$ C; (d) carrier gas, helium, at a flow-rate of 2.4 l/h and head pressure 5 bar. With these conditions, the analysis cycle time is about 60 min, but the duration of integration is only 25 min for SD results up to 575 $^{\circ}$ C. They

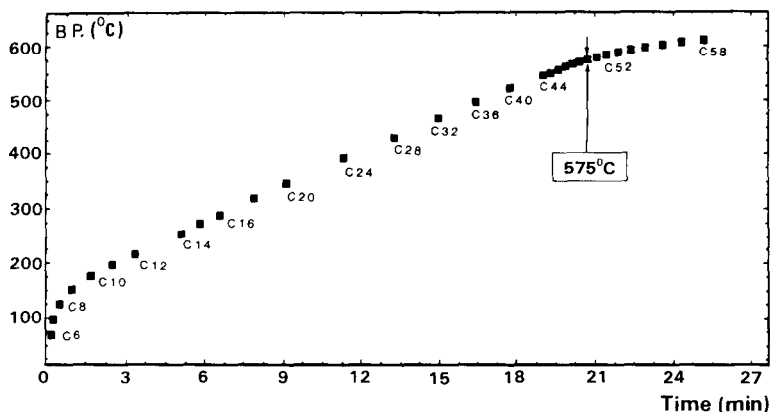


Fig. 2. Calibration graph with *n*-alkanes on Dexsil 300. For conditions, see text.

appear to be convenient for almost all samples, except light cuts. For these cuts the programming rate must be decreased to 8°C/min. Under the temperature conditions given in the text, the calibration of BP vs. RT is linear for *n*-alkanes between C₉ and C₅₂ (see Fig. 2). For samples with a BP range of 150–400°C the column can be connected for normal or modified injection without heating the injector or back-flushing the pre-column.

Before any sample series is run, it is necessary to check the baseline drift by a run with a solvent injection (generally carbon disulphide) and also the column efficiency, *R*, which must be between 1.5 and 2 and is given by:

$$R = \frac{d_2 - d_1}{w_2 + w_1}$$

where *d*₁ and *d*₂ are the retention times of C₂₈ and C₂₉ *n*-alkanes and *w*₁ and *w*₂ are the widths at half-height of the corresponding peaks. For heavy-compound analysis, special care must be taken to obtain a quantitative flame ionization detection (FID) response by analysing a test sample or mixture of petroleum cuts.

Sample preparation. To allow the use of the automatic GC sampler, the samples must be fluid and free from insoluble material. Therefore, all samples coming from conversion units are generally diluted with carbon disulphide (1:1, v/v). This solvent shows good efficiency and a very small FID response; it burns without strong corrosive effects, in contrast to dichloromethane. Moreover, addition of an internal standard becomes easier, and total amount of hydrocarbon sample injected is smaller. For cracking conversion products, dilution avoids precipitation. The internal standard is a mixture of three *n*-alkanes (C₁₄–C₁₆) in about equal proportions. Used only for compounds leaving a residue at 600°C, this calibration mixture is added to the sample at a concentration of 3–4 wt.-%. For very heavy and viscous materials, dilution of *n*-alkanes added to the sample will take several hours. For light and fluid samples, the dilution step can be avoided.

Description of the automatic analysis sequence. Because the entire SD operation has been automated, regular controls are required and new information obtained must be entered in the SD computer program automatically:

(1) *n*-Alkane calibration is performed every week.

(2) The column blank (baseline drift) is recorded after six sample injections for heavy compounds; for others, this is done every 24 h.

(3) For samples leaving a residue and having an initial boiling point higher than 300°C, *i.e.*, containing not even small concentrations of hydrocarbons lighter than the standard mixture (*n*-C₁₄-C₁₆), only one injection is required, and the classical method of calculation with an internal standard is applied.

(4) For very wide BP range samples leaving a residue, two runs are necessary; in the first, the sample (diluted with carbon disulphide) is injected and in the second one, sample + standard *n*-alkane mixture (diluted with carbon disulphide) is injected. Because carbon disulphide is a light solvent, evaporation can occur accidentally even in screw-capped bottles; therefore, if total integrated areas of the two injections differ by more than 10%, the sample preparation has to be repeated.

The SD determination of these products is more critical than that of the others. Our experience has grown by collaboration with an analytical working group from ELF and Total in a French project for the evaluation of heavy petroleum cuts (AS-VAHL). This group proposed its SD method at the ASTM meeting in 1983.

RESULTS AND DISCUSSION

Influence of BP calibration mixture on SD results

The tendency of non-polar silicone stationary phases (OV-1, UCW-98) to allow aromatics to be eluted before aliphatic compounds with the same boiling point is clearly shown in Table I; it has been described previously in ASTM 2887¹³ and by Southern *et al.*³. Differences in BP (AET) values for aromatics calculated from SD *n*-alkane calibration and those given by physical tables have been interpreted¹³⁻¹⁵ on the basis of BP pressure conversion charts from reduced to atmospheric pressure, which are different for aromatic and saturated compounds. Southern *et al.*³ proposed a correction of the calculated BP which took into account sample aromaticity, determined by ¹³C NMR spectroscopy. Even if the conversion charts affect the SD results, the different silicone gum selectivity for *n*-alkanes and polycyclic aromatics seems to be the more important factor. Definitely, for Dexsil 300 stationary phase this effect is much less, especially for highly condensed aromatics.

However, Table I shows also that this tendency is reversed for light alkylben-

TABLE II

SD ON NAPHTHA SAMPLE (18% AROMATICS CONTENT) (WEIGHT-% VERSUS BP IN °C)

Weight-%	BP (°C)	
	Stationary phase	
	Dexsil 300	OV-101
5	89	91
20	124	123
50	154	153
80	187	182
95	201	195
98	205	198

TABLE III

SD ON LCO SAMPLE (78% AROMATICS CONTENT) (WEIGHT-% VERSUS BP IN °C)

Weight-%	BP (°C)			
	Stationary phase			
	Dexsil 300		OV-101	
	<i>n</i> -Alkane calibration	Aromatic calibration	<i>n</i> -Alkane calibration	Aromatic calibration
0	168*	154*	159*	159*
5	200	192	193	196
10	221	219	212	218
30	244	239	234	245
50	256	255	248	262
70	272	272	263	279
90	295	300	285	307
95	303	308	294	319
98	312	319	303	329
100	323**	332**	314**	344**

* Initial BP.

** Final BP.

zene compounds (boiling point < 150°C). This effect will not influence the SD results for petroleum cuts (except alkylbenzene products) because their concentrations are low; this phenomenon may be induced by the low column temperature for the elution of these light aromatics; up to 100°C, the viscosity of Dexsil remains high. To em-

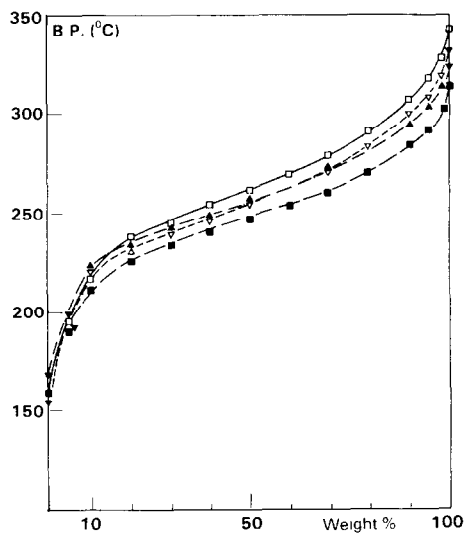


Fig. 3. SD curves for a highly aromatic oil. On Dexsil 300: calibration with (\blacktriangle) *n*-alkanes and (∇) polycyclic aromatics. On OV-101: calibration with (\blacksquare) *n*-alkanes and (\square) polycyclic aromatics. For operating conditions, see text.

phasize the effect of aromaticity on SD results, two typical mean BP petroleum samples were analysed on OV-101 and Dexsil columns with the conditions given in the text. Table II gives the two sets of results for a naphtha cut and Table III for a light cracking oil (LCO).

The differences in the SD results for Dexsil and OV-101 columns are not very great for naphtha containing 18% of aromatics, of which 16% are alkylbenzene compounds. For the LCO sample, the SD results are significantly different over the entire percentage range. Its total aromatic content is 75% with a distribution, obtained by mass spectrometry, of 14% alkylbenzenes, 30% indans and tetralins, 20% naphthalenes and 11% more highly condensed aromatics. Consequently, an aromatic calibration was carried out for this LCO sample on the two columns with the aromatic compounds detailed in Table I. The differences between the two systems of calibration (*n*-alkanes, aromatics) are much smaller on the Dexsil than on the OV-101 column. The SD curves obtained on this sample are reproduced in Fig. 3.

For heavier fractions, with a higher condensed aromatics content, SD results obtained on the OV-101 column with the two calibration mixtures become too different. Therefore, for heavier fractions, Dexsil 300 was always used with the *n*-alkane calibration.

Reliability of automated SD method

The reliability is related to adequacy of the apparatus, column stability and computer program efficiency. The use of a temperature-programmed injector has allowed good transfer of the sample to the pre-column, without flash effects caused by light compounds (BP < 150°C, solvent or hydrocarbons); details have been given

TABLE IV

REPEATABILITY OF SD RESULTS FOR VARIOUS SAMPLES

x = arithmetic mean value; σ = standard deviation; *n* = number of determinations.

Weight-%	Lubricating oil		Vacuum gas		Viscoreduction product (<i>C</i> ₅ +)		Crude oil residue	
	<i>x</i> (°C) (<i>n</i> = 4)	σ	<i>x</i> (°C) (<i>n</i> = 11)	σ	<i>x</i> (°C) (<i>n</i> = 8)	σ	<i>x</i> (°C) (<i>n</i> = 13)	σ
0	139*	3.8	357*	0.75	170*	1.31	339*	1.26
10	236	1.0	388	0.41	287	2.17	383	0.64
20	290	0.5	412	0.44	358	1.92	414	0.76
30	334	1.0	432	0.72	406	2.05	445	0.97
40	363	1.1	451	0.77	445	2.13	475	1.22
50	381	0.6	468	0.75	480	2.70	510	1.71
60	397	0.6	487	0.56	520	3.72	549	2.80
70	412	1.0	507	0.86				
80	427	0.5	528	0.98				
90	445	0.5	552	1.03				
95	458	0	566	1.07				
100	506**	1.2	—	—				

* Initial BP.

** Final BP.

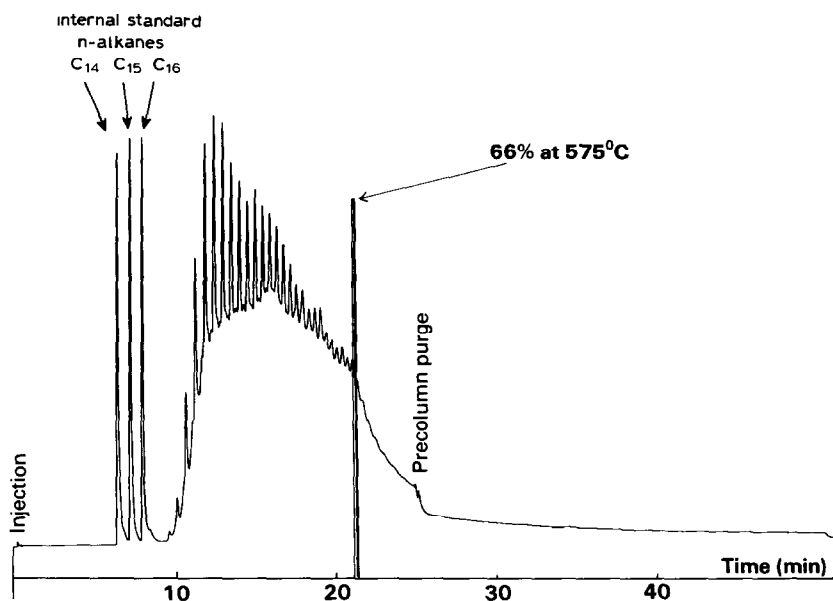


Fig. 4. Chromatogram of petroleum residue with internal standard mixture.

previously⁷. This injection mode improved the results for samples containing light-cut (> 20%) and heavy products; with a normal injector, the light compounds content was always in excess for synthetic mixtures. The use of a pre-column back-flushed pneumatically after transfer of hydrocarbons up to C₅₆ (BP 600°C) to the main column avoids contamination and gives an end signal with a greater slope. The pre-column lifetime is at least 2 weeks for high-residue samples and the column lifetime is more than 3 months in continuous operation.

The repeatability of SD results appears to be of the same order for samples with or without residues, even if interference of the internal standard mixture (*n*-C₁₄-C₁₆) with sample components requires two runs per sample. For vacuum gas oils (370-536°C), addition of an internal standard is not necessary. Published results⁶ have shown very good repeatability and reproducibility between four laboratories; one set of results on a Safaniya sample is reported in Table IV for eleven analyses. A determination on a lubricating oil sample is also reported for four analyses.

With high-BP residues, the addition of an internal standard is necessary for evaluating residues boiling above 575°C, which is the upper limit reached up to now in routine analysis. As the initial BP is above 300°C in most instances, the internal standard mixture does not interfere with the sample and the analysis can be performed in one run; Table IV shows the results for a petroleum residue of BP > 400°C with thirteen analyses. The chromatogram is reproduced in Fig. 4. For crude oils or raw heavy-product conversion samples, two runs are necessary to evaluate residues of BP > 575°C because of interference with internal standard mixture. In Table IV results are given for one product of a viscoreduction test (> 150°C) from eight analyses. From all the results collected in Table IV, it appears that the most reproducible SD results are obtained when the entire sample is eluted from the column, even if

TABLE V
COMPARISON OF SD AND TBP RESULTS

Temperature (°C)	Weight-%									
	Crude oils				Conversion products					
	Kuwait		Boscan		Thermal process			Catalytic process		
	SD	TBP	SD	TBP	SD	Raw data	Corrected data	SD	TBP	
								Manual	Auto	
100	7	6.5						4.5	5	5.4
150					2.1	1.3	2.0			
200	21	21.0	4.0	4.9				22.5	22.5	23.8
250								52.0	51.2	52.2
300	35.5	36.0	12.8	14.2						
350					23.0	23.0	23.0			
400	50.0	50.0	23.7	24.3				79.0	76.5	79.9
500	64.5	63.5	38.5	39.9						
550	70.6				61.4	51.0	65.9			
575			47.1	46.3						

the sample contains light hydrocarbons. With the standard deviation observed for lubricating oil and vacuum gas oil samples, the repeatability is good and the confidence interval appears to be 2°C or less; this interval is equal to σt , where σ is the standard deviation and t a statistical factor. For 95% probability and ten measurements, this factor is around 2. For samples with residues, results obtained by use of an internal standard in one or two runs (if the sample contains light fractions) still show good reliability. For a crude oil residue, SD is obtained in one run, because the internal standard does not interfere with the sample. The observed repeatability decreases slightly with increasing temperature; the confidence interval increases from 2°C to *ca.* 5°C at 550°C. For samples such as viscoreduction products, which require two analyses, the repeatability decreases slightly, and the confidence interval increases to *ca.* 7°C.

Feeney and Huber¹⁷ observed much higher standard deviations ($\sigma \approx 7$ at 520°C) for a sample requiring two analyses.

Comparisons with distillation tests

Some fundamental aspects of chromatographic separations used for SD application must be recalled:

(1) sample fractionation on the GC column is carried out at a low partial pressure;

(2) the resolving power of the GC column is good even at the highest temperatures, as successive *n*-alkane peaks are resolved up to around C₄₂, *i.e.*, with differences in BP of less than 10°C;

(3) because in gas chromatography there is a continuous equilibrium, comparison of SD results with distillation tests has some physical meaning if a significant

TABLE VI
COMPARISON OF SD AND ASTM D1160 RESULTS

Weight-%	Temperature (°C)						
	Crude oil residue			Conversion products			
	SD	D1160		Sample A		Sample B	
		Manual	Auto	SD	D1160	SD	D1160
IBP	267	260	284	215	230	212	
5	354		361	292	301	372	
10	386	400	394	368	361	445	
20	424	430	428	468	455	501	
30	453	461	451	527	525	536	
40	480	483	479	570	544 (560)*	565	
50	510	509	508				
60	542	Cracking	539				

* Corrected value (see text).

efficiency is achieved in distillation and a pseudo-equilibrium ensured by refluxing in the distillation column.

This is the case for TBP distillation⁸ or molecular distillation (MD)^{11,14,18}. Moreover, the results can be expressed in weight-%, as in SD. Unfortunately, these methods are time consuming (2 days or more) and require large sample volumes (>2l). Therefore, product specification control is still made by ASTM tests D86 at atmospheric pressure and D1160 under reduced pressure. In the two methods, results are given in volume-%; the extensive use of these methods justifies all the correlation experiments with SD results.

Comparisons of SD and TBP tests

The ASTM TBP method gives distillation fractions up to 400°C (AET). For

TABLE VII
COMPARISON OF SD AND ASTM D86 RESULTS

Weight-%	Temperature (°C)							
	Aromatic oil		Fractions of conversion products					
	SD	D86	Sample 1			Sample 2		
			SD	D86*	D86	SD	D86*	D86
10	221	230	174	218	179	165	214	155
30	244	241	249	260	248	264	273	256
50	256	249	290	288	281	309	307	294
70	272	259	259	314	309	339	323	315
90	295	274	370	350	351	364	340	332

* These values are given by HP computer correlation from SD results.

higher BP cuts, evaporation under vacuum or molecular distillation is used. In Table V results are given for two types of samples, total crude oils and heavy petroleum fraction conversion products.

The results appear good for crude oils, either light (*e.g.*, Kuwait, 31.4° API) or heavy (*e.g.*, Boscan, 10.7° API). For conversion products, the comparison is generally good up to about 500°C. For higher BP some differences could occur, distillation fractionation always giving the smaller value; it seems that the high residue viscosity does not allow total recovery of the fraction expected at the temperature observed in the distillation head. SD control up to 575°C of the last isolated fraction and of the residue allows the correction of the fractionation data, by recalculation of the weight-% actually eluted at the fractionation temperature observed. Automated TBP distillation apparatus with continuous vacuum control increases the agreement between SD and TBP results up to 400°C.

Comparison of SD and ASTM D1160 results

For comparison, it is necessary to use weight-% in SD and volume-% in the D1160 method. As shown in Table VI, the hypothesis seems reasonable and the agreement between the two methods is generally good up to 500°C. Vacuum control automation improves the repeatability of the method D1160 and increases the agreement with the SD results. Whereas for crude oil residues the results are in good agreement, this is not always so for conversion products; often the D1160 test gives a distillate content greater than that calculated from SD. The effect is the opposite of that observed for TBP. In SD control of distillate and residues from the D1160 test, material seems to be swept off at the end of D1160 test, because the flask heating has to be greatly increased. Indeed, SD control of the distillate shows that the final BP is much higher than the assumed BP, the residue contribution being small at the corresponding temperature. Thus, for Sample A, the distillate final BP is higher than 600°C and at 570°C 96.2% is eluted, whereas only 11% of the residue is eluted. Thus, 544°C is not representative of 40% eluted, and 560°C is the corrected value.

Comparisons of SD and ASTM D86 results

Direct comparisons between SD weight-% and D86 volume-% are not good and the two curves cross at around 50%. The results given in Table VII show that the difference is greater at 90% than at 10%. Calculation of D86 results from SD by a correlation proposed by Hewlett-Packard was applied to two samples. The results became more satisfactory at 90% but were too different at 10%. Therefore, these tests show that correlations of SD with the D86 method will probably remain illusory for general applications, as Butler indicated¹.

CONCLUSION

With a standardized procedure on a modified gas chromatograph provided with a short Dexsil-300 packed column, SD allows the control of the boiling range up to 575°C. At 575°C the reliability of the method is good, but it depends on the sample; giving the best performances (< 2°C) for samples without residues, it increases to *ca.* 4–7°C for samples with residues. The reliability and productivity of SD determinations have been greatly increased in our laboratory, especially for products

leaving an undistillable residue. Its elimination is necessary in order to avoid plugging of the injector and also of the column; back-flushing of the pre-column appears to be the easiest method. Comparisons with TBP distillation are very good up to about 450°C. At higher temperatures, correlations obtained with molecular distillation or evaporation under vacuum are good up to 500°C. While comparisons with the D86 method appear unsatisfactory, comparisons with ASTM D1160 methods are fairly good up to 500°C; beyond that, they are not always reliable.

By means of an automated dedicated gas chromatographic unit and a standardized analytical procedure, SD could become a good alternative to ASTM D1160 and D86 methods for product specifications, but it cannot replace TBP distillation, which is designed to isolate fractions.

REFERENCES

- 1 R. D. Butler, in K. H. Algelt and T. H. Gouw (Editors), *Chromatography in Petroleum Science*, Marcel Dekker, New York 1979, p. 75.
- 2 *ASTM Standards in Chromatography*, ASTM, Philadelphia, PA, 1st ed., 1981, p. 735.
- 3 T. G. Southern, A. Iacchelli, D. Cuthiell and M. L. Selucky, *Anal. Chem.*, 57 (1985) 303.
- 4 L. A. Luke and J. E. Ray, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 193.
- 5 S. Trestianu, G. Ziloli, A. Sironi, C. Saravalle, F. Munari, M. Galli, G. Gaspar, J. M. Collin and J. L. Jovelin, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 771.
- 6 N. Petroff, J. M. Collin, N. Feillens and G. Follain, *Rev. Inst. Fr. Petrol.*, 36 (1981) 467.
- 7 J. P. Durand and N. Petroff, in B. Tissot (Editor), *Characterization of Heavy Petroleum Residues (Proc. Int. Symp., Lyon, June 25-27 1984)*, Technip Ed., Paris, 1984, p. 200.
- 8 *ASTM D2892-78*, ASTM Standards, Philadelphia, PA, 1980, Part 24, p. 813.
- 9 *ASTM D86-78*, ASTM Standards, Philadelphia, PA, 1980, Part 23, p. 8.
- 10 *ASTM D1160-77*, ASTM Standards, Philadelphia, PA, 1980, Part 23, p. 597.
- 11 N. Petroff, in B. Tissot (Editor), *Characterization of Heavy Petroleum Residues (Proc. Int. Symp., Lyon, June 25-27 1984)*, Technip Ed., Paris, 1984, p. 247.
- 12 *ASTM D3710-78*, ASTM Standards, Philadelphia, 1980, Part 25, p. 439.
- 13 *ASTM D2887-78*, ASTM Standards, Philadelphia, 1980, Part 24, p. 788.
- 14 U. Lutz, H. H. Oelert, O. Glinzer, M. Lübke and D. Severin, in B. Tissot (Editor), *Characterization of Heavy Petroleum Residues (Proc. Int. Symp., Lyon, June 25-27 1984)*, Technip Ed., Paris, 1984, p. 242.
- 15 O. Glinzer, *Erdöl Kohle*, 38 (1985) 213.
- 16 *Guide to Stationary Phases for Gas Chromatography*, Analabs, North Haven, CT, 11th ed., 1977.
- 17 M. J. Feeney and L. Huber, in B. Tissot (Editor), *Characterization of Heavy Petroleum Residues (Proc. Int. Symp., Lyon, June 25-27 1984)*, Technip Ed., Paris, 1984, p. 206.
- 18 P. Vercier and M. Mouton, *Analisis*, 10 (1982) 57.