Application Note: 10074

Simulated Distillation of Petroleum Products (ASTM D2887) by GC in less than two minutes

Riccardo Facchetti, Andrea Cadoppi – Thermo Electron Corporation, Milan, Italy

Key Words

- SimDist
- ASTM D2887
- 80 Seconds Analysis

Introduction

Simulated distillation is a GC method used to characterize petroleum fractions and products, since it permits the quick determination of their boiling range distribution. Samples are analyzed on a non polar chromatographic column that separates the hydrocarbons in order of their boiling points. These are correlated with the retention times, through a calibration curve obtained by running under the same conditions a known mixture of hydrocarbons, usually n-alkanes, covering the boiling range expected in the sample. Results are reported as a correlation between the boiling points and the percentages of the sample eluted from the column.

The determination of the boiling range distribution of petroleum fractions by conventional GC is a rapid analytical tool, which is widely used to replace conventional distillation methods for control of refining operations and specification testing.

New Technology

The huge demand of samples to be analyzed every day by labs in the petrochemical industry requires an increased speed of analysis.

An impressive gain in analysis speed compared to the conventional GC procedure is obtained through Ultra Fast Gas Chromatography. Ultra Fast GC implies the use of short (2-10m) narrow bore capillaries and temperature programming conditions usually faster than 2°C/s. This leads to peak widths in the 50-200ms range. The analysis times are in the range of 1 minute or even less.

Programming rates in the range 2-20°C/s are not achievable with conventional GC ovens but only through direct resistive heating of the capillary columns.

The new technology developed by Thermo Electron Corporation is based on the Ultra Fast GC system, that is a dedicated configuration of Trace GC.

Figure 1: UFM.

The system incorporates an ultra fast column module UFM (Figure 1) consisting in a fused silica column coiled along with a heating element and a temperature sensor such to insure the direct resistive heating of the capillary column. The assembly is held in an easy to handle metal cage. This permits to achieve temperature programming rates up to 20°C/s, or even more, and to reach high temperatures of 370°C. Being placed inside the oven of a conventional Trace GC (see Figure 2), the Ultra Fast Module cools down fast (around 1 minute from 350°C to 40°C) by automatically activating the oven fan at the end of the temperature programming period or final isothermal run. Capillary columns with a broad range of lengths and diameters can be incorporated in the Module. The column module inlet is installed on the split-splitless injector and the outlet on a Fast FID.

Figure 2: Trace GC with UFM.

Tests and Results

Simulated Distillation of ASTM D2887 Reference Oil was performed by Ultra Fast GC. To take advantage of the high heating rates of the Direct Resistive Heating module a RTX-1 column, 5m long, 0.32 mm i.d., 0.1 mm film thickness was used.

The column temperature was programmed from 40 °C (12 sec) to 350 °C (18 sec) at a heating rate of 5 °C/sec. The initial isotherm was needed to achieve the correct elution of the hydrocarbons with lower boiling points.

The injector was used in split mode. The injector temperature was set at 280 °C while the detector (fast FID) heating block temperature was set at 350 °C.

The ability of the system to achieve excellent repeatability on retention times and peak areas and on Simulated Distillation results has been investigated.

A repeatability test has been performed injecting a calibration mixture of n-alkanes C6-C44.

Thermo ELECTRON CORPORATION

In Figure 3 a calibration chromatogram is presented.

The results reported in Table 1 point out the excellent performances of the system in terms of repeatability of retention times and peak areas.

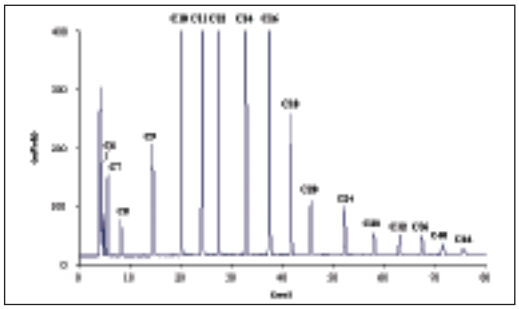

Figure 3: Calibration Chromatogram.

	RET. TIME (SEC)	RT ST. DEV (SEC)	AREA ST DEV%
C6	4.58	0.04	1.65
C7	5.64	0.04	1.09
C8	8.33	0.05	0.95
C9	14.5	0.04	0.89
C10	20.13	0.01	0.97
C11	24.22	0.02	1.04
C12	27.47	0.02	1.08
C14	32.87	0.02	1.17
C16	37.51	0.02	1.30
C18	41.73	0.01	1.33
C20	45.58	0.01	1.36
C24	52.27	0.01	1.59
C28	57.98	0.01	1.61
C32	63.00	0.01	1.40
C36	67.42	0.03	1.27
C40	71.54	0.03	1.37
C44	75.53	0.03	1.36

Table 1: Repeatability test results. Data are based on 10 consecutive injections.

The ASTM Reference Oil was diluted in CS_2. 1 µl was injected in split mode. A chromatogram of ASTM D2887 reference oil is shown in Figure 4, superimposed on the calibration chromatogram.

Such chromatogram is compared with that achieved by conventional GC SimDist procedure. The Ultra Fast GC analysis is 20 times quicker.

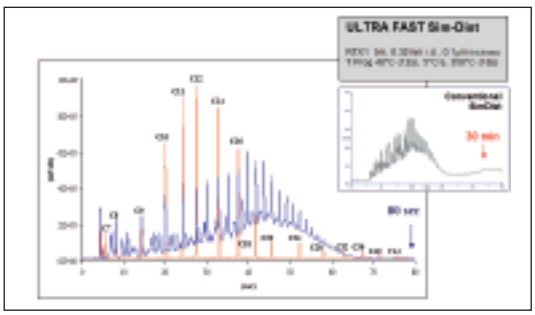

Figure 4: Ultra Fast Simulated Distillation of ASTM D2887 Reference Oil and comparison of the same analysis performed in conventional conditions.

In order to evaluate the precision and the accuracy of the results, various Simdist analyses have been performed.

The software processes the data following the procedure described in the ASTM D2887 [1] method.

Ultra Fast Gas Chromatography, being able to generate peak widths of 100 msec, needs a special software for Simdist analysis, able to operate with very thin slices. The data shown have been obtained using SimdiChrom Software, optimized to operate with slices as narrow as 10 msec.

The boiling points distributions obtained with UFGC SimDist, reported in Table 2 and in Figure 5, show an excellent repeatability, and fit perfectly with the data obtained by using conventional conditions. The data are in good agreement with the ASTM D2887 reference oil boiling range distribution data provided by Supelco.

% OFF	BOILING POINT (°C)		
	REFERENCE DATA	RUN 1	RUN 2
0.5% (IBP)	115	112	112
5%	151	148	147
10%	176	173	175
15%	201	197	198
20%	224	221	220
25%	243	241	240
30%	259	255	256
35%	275	271	272
40%	289	287	288
45%	302	298	299
50%	312	309	308
55%	321	318	318
60%	332	329	330
65%	343	339	340
70%	354	350	352
75%	365	362	363
80%	378	374	376
85%	391	388	387
90%	407	404	404
95%	428	426	425
99.5%	475	474	475

Table 2: Boiling points distribution of ASTM D2887 Reference Oil by Ultra Fast GC SimDist. IBP=Initial Boiling Point - FBP=Final Boiling Point

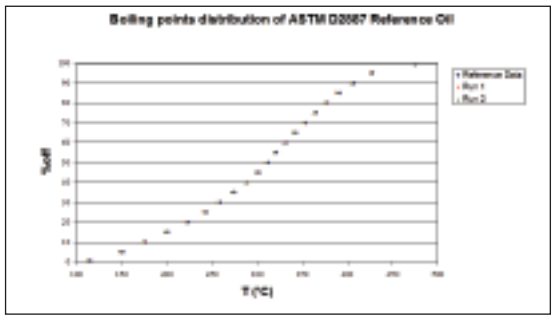

Figure 5

Conclusion

Ultra Fast GC Simulated Distillation of petroleum products can be achieved by using the system developed by Thermo, based on direct resistive heating of the capillary columns.

The analysis can be performed 20 times quicker than in conventional GC without loosing performances in terms of precision and accuracy.

The method complies with ASTM D2887, Standard Test Method for Boiling Range Distribution of Petroleum Fractions By GC.

In addition to these offices, Thermo Electron Corporation maintains a network of representative organizations throughout the world.

Australia
+61 2 9898 1244
Austria
+43 1 333 50340
Belgium
+32 2 482 30 30
Canada
+1 800 532 4752
China
+86 10 5850 3588
France
+33 1 60 92 48 00
Germany
+49 6103 4080
Italy
+39 02 950 591
Japan
+81 45 453 9100
Netherlands
+31 76 587 98 88
Nordic
+46 8 556 468 00
South Africa
+27 11 570 1840
Spain
+34 91 657 4930
Switzerland
+41 61 48784 00
UK
+44 1442 233555
USA
+1 800 532 4752

www.thermo.com

ISO 9001
DNV-CERT-00203-94-AQ

Thermo Electron S.p.A. Milan, Italy is ISO Certified.

AN10074_E 12/04C

Thermo
ELECTRON CORPORATION