

# Perform automated distillations with fast gas chromatography

Using this analytical technique can increase productivity

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Distillation has been used to determine petroleum boiling ranges from the earliest days of oil recovery and processing. Knowing material composition in terms of its carbon distribution or boiling range enables the hydrocarbon processing industry (HPI) to evaluate quality or establish processing schemes for further upgrade. Conventional distillation is still used to determine boiling range and it generally fits three American Society of Testing and Materials (ASTM) methods.

**Distillation methods.** The ASTM D-86 “Standard Method for Distillation of Petroleum Products” is of single-plate efficiency and has been known as an Engler distillation for many years. It is executed at atmospheric pressure and consequently is limited to samples of higher volatility such as gasolines through middle distillates including kerosines, turbine fuels and light gasoils.

ASTM D-1160 “Standard Method for Distillation of Petroleum Products at Reduced Pressure” is also of single-plate efficiency. It is run at reduced pressure and is limited to nonvolatile samples that may decompose if distilled at atmospheric pressure. Typical samples tested, but not limited to, are heavy distillates, lube stocks and crude oils. The method requires accurate control of the still pressure to construct a distillation curve relating volume recovered and boiling point at the controlled pressure.

ASTM D-2892 “Standard Method for Distillation of Crude Petroleum by 15-Theoretical Plate Column” is operated at reduced pressure and a 5:1 reflux ratio. It is

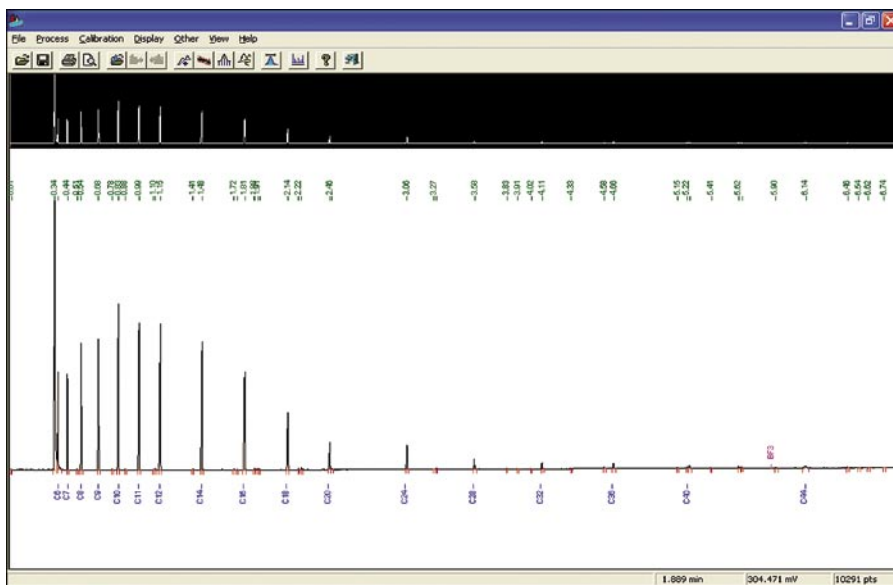


FIG. 1 Boiling point calibration blend C<sub>6</sub>–C<sub>44</sub>.

also referred to as a 15/5 true boiling point (TBP). The samples are approximately the same as D-1160. This method provides data to construct a distillation curve and recovers a liquefied gas fraction, distillate fractions and a residuum from standardized conditions. The fractions may be analyzed to determine yields in volume and mass fractions.

Each method has a unique fit to a boiling range and to operating conditions specific to that distillation. To some extent, all the methods have benefited from automation by reducing the amount of direct operator involvement during testing. However, this has not reduced analysis time and one defi-

ciency common to all is the time required to complete a distillation. A D-86 test for gasoline may require 20 min. under automated control. A D-1160 reduced pressure test may require 1 hr or longer to completely distill the sample. The D-2892 crude distillation may take many hours for a similar sample and crude assays can take 24 hr to complete.

A shared problem is that the stills are made of glass components requiring cleanup between analyses. Extra flasks and pots are always used to expedite setup, but at some point it must be cleaned. Glassware is expensive and nondisposable. The mechanical cleaning process uses solvents

## PROCESS AND LABORATORY ANALYZERS

and, in some cases, automated glassware washers, increasing analysis cost. Apparatus cleanup and reassembly adds considerably to the test cycle time. In many facilities, multiple stills are used to increase productivity which proportionally increases staffing. Even with advancements in automatic distillation equipment, the process is labor intensive and slow.

**Method automation.** Gas chromatographs (GCs) were first commercialized in 1955. New detector technology, capillary column introduction and temperature programmed separations advanced chromatographic science and made practical applications possible.

In 1964, work describing the first sound application of GC distillation determining TPB was published.<sup>1</sup> It is based on the linear relationship between chromatographic retention volume for compounds in a homologous series and its TBP. Specific separation conditions are required, ensuring the relationship's validity. The study demonstrated the effectiveness for determining distillation curves from chromatographic data. To distinguish this process from those less efficient, it was labeled "simulated distillation" (SD) and is now the industry-established term for GC distillation.

Early users fumbled with low-performance GCs and the inability to digitally integrate data. SD of complex hydrocarbon liquids produced chromatograms far too intricate for any area measurement technique being used at that time. Once the disc integrator was introduced, its recordable pen made area measurements possible.

Data reduction was laborious and error prone. However, the distillation data was in TBP form and recovered material was presented in 1% increments, if desired. SD extended the boiling range beyond all conventional stills to approximately 1,000°F with a complete distribution. Instrument sensitivity produced smooth curves for easier data interpretation and accurate cut point information for a full distillation.

Sample cracking was no longer a problem. Upon injection and vaporization, the sample undergoes a great change in partial pressure, causing column behavior to mimic a reduced pressure still with high theoretical efficiency. This condition is maintained throughout the elution period and is equivalent to a D-2892 TBP distillation.

The GC approach is straightforward. A non-polar liquid phase is required to ensure compounds in a homologous series elute in boiling point order and is adequately valid

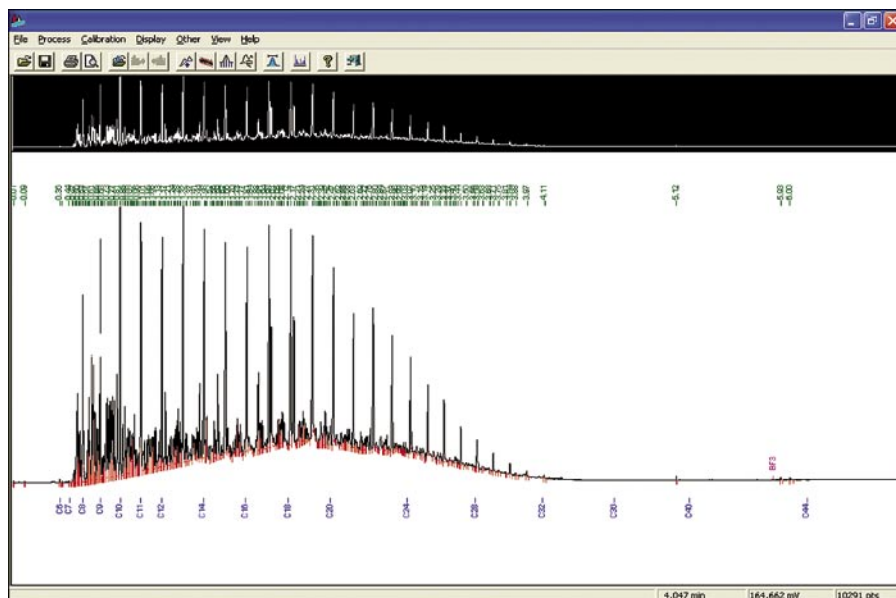


FIG. 2 ASTM reference gasoil.

Sim Dis Analysis										
% Off	Deg F	% Off	Deg F	% Off	Deg F	% Off	Deg F	% Off	Deg F	% Off
IBP	238.5									
1	244.8	21	432.9	41	550.8	61	630.1	81	709.9	
2	259.5	22	441.4	42	556.1	62	633.8	82	714.5	
3	270.4	23	448.6	43	561.3	63	638.4	83	718.4	
4	278.6	24	455.0	44	565.5	64	642.8	84	723.0	
5	287.4	25	460.3	45	570.3	65	647.1	85	728.4	
6	296.7	26	468.8	46	574.2	66	650.7	86	733.9	
7	306.5	27	476.5	47	577.0	67	653.6	87	738.5	
8	316.3	28	482.1	48	580.0	68	657.0	88	743.9	
9	324.3	29	487.1	49	584.4	69	661.4	89	750.2	
10	333.9	30	491.2	50	589.0	70	665.7	90	755.9	
11	344.3	31	498.1	51	593.4	71	669.9	91	761.7	
12	352.3	32	505.3	52	597.9	72	673.4	92	768.9	
13	361.8	33	510.6	53	601.0	73	676.6	93	775.5	
14	374.0	34	515.9	54	603.8	74	680.4	94	783.3	
15	384.1	35	519.8	55	606.9	75	684.9	95	791.7	
16	390.4	36	524.3	56	611.0	76	689.2	96	801.3	
17	400.0	37	530.9	57	615.3	77	693.2	97	812.3	
18	410.4	38	536.7	58	619.8	78	696.8	98	826.7	
19	419.4	39	542.5	59	624.1	79	700.4	99	847.2	
20	425.0	40	547.2	60	627.2	80	705.0	FBP	863.2	

FIG. 3 ASTM reference gasoil report.

for all hydrocarbons. Research and field experience has shown that a short column of low efficiency produces the best fit to TBP.

**The 1970s.** When digitized integrators were introduced, a great improvement in area measurement was achieved. Coupled with early parallel developments in electronic calculators and computers, the chore of summarizing large data sets was reduced from hours to minutes. Data accuracy improved and became relatively error-free. SD use rapidly grew in the HPI and eventually was proposed for study by the ASTM.

Its attributes were obvious to users:

- A very small sample is required, about 1 microliter

- Much faster distillation time, less than 1 hr (a small percentage of the conventional distillation time required for D-2892)

- Better defined initial and final boiling points

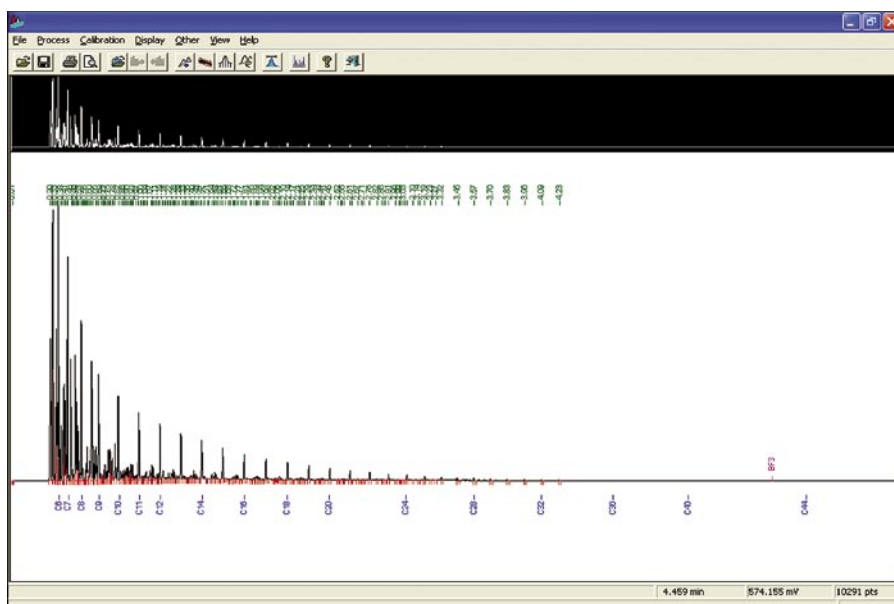
- Total sample accounted for
- No glassware cleanup.

Liquid automatic samplers, introduced by GC suppliers, made the process completely automated. In 1972, ASTM published the first standard method for the "Boiling Point Distribution of Petroleum Fractions by Gas Chromatography," D-2887. Continued GC development has resulted in performance and reliability improvements.

**The 1980s and beyond.** Computer technology has enhanced features and available post-processing software for aiding the analyst in terms of automation, productivity and data management. The chromatography approach has stood the test of time—over 30 years without significant change.

A non-polar column and temperature programming are still basic requirements for an SD test. The introduction of capillary columns in fused silica—and recently, metal—has improved column life and offered the analyst more choices in matching a particular sample to a boiling range. However, packed columns are still in common use, especially for high-volatility samples such as gasoline. The high-phase loading enables propane to be separated with lower use of cryogenic fluids for cooling. Considerable cost savings can be obtained with high sample throughput, especially by commercial laboratories.

Another column adaptation is using narrow-bore capillary columns having between



**FIG. 4** Light crude oil.

**TABLE 1. Retention time precision for calibration blend**

	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>24</sub>	C <sub>28</sub>	C <sub>32</sub>	C <sub>36</sub>	C <sub>40</sub>	C <sub>44</sub>
RT average	0.37	0.44	0.54	0.68	0.83	0.99	1.15	1.47	1.8	2.13	2.46	3.05	3.58	4.1	4.65	5.23	6.13
Standard deviation	.005	.004	.003	.004	.003	.003	.000	.004	.003	.004	.005	.004	.005	.005	.005	.007	.007
Relative standard deviation, %	0.33	0.39	0.42	0.41	0.33	0.27	0.22	0.18	0.18	0.16	0.15	0.13	0.12	0.11	0.09	0.1	0.1

**TABLE 2. Retention time precision for reference gasoil, C<sub>7</sub>–C<sub>32</sub>**

	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>24</sub>	C <sub>28</sub>	C <sub>32</sub>
RT average	0.43	0.54	0.67	0.83	0.99	1.15	1.47	1.80	2.13	2.45	3.04	3.57	4.10
Standard deviation	.005	.003	.003	.004	.004	.000	.005	.006	.015	.005	.006	.012	.004
Relative standard deviation, %	1.152	0.613	0.613	0.452	0.379	0.000	0.339	0.325	0.684	0.187	0.197	0.348	0.100

**TABLE 3. Light crude**

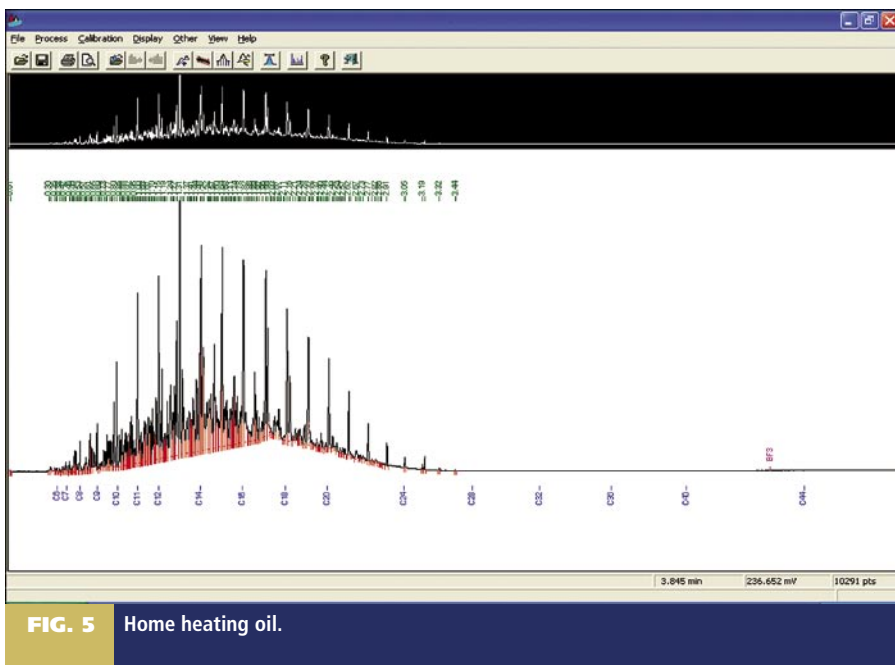
	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>24</sub>	C <sub>28</sub>	C <sub>32</sub>
RT average	0.38	0.44	0.54	0.68	0.83	0.99	1.15	1.47	1.80	2.13	2.46	3.05	3.58	4.10
Standard deviation	.002	.004	.005	.003	.002	.003	.000	.002	.002	.004	.001	.005	.004	.003
Relative standard deviation, %	0.555	0.853	0.844	0.408	0.241	0.335	0.000	0.136	0.111	0.204	0.040	0.156	0.105	0.081

**TABLE 4. Home heating oil**

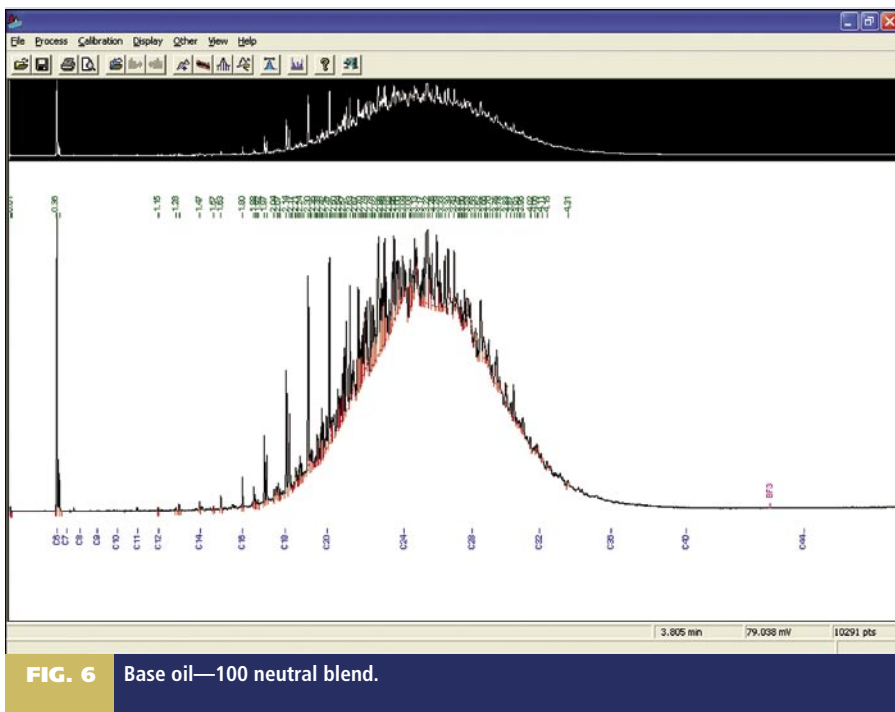
	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>24</sub>
RT average	0.36	0.43	0.54	0.67	0.83	0.99	1.15	1.48	1.79	2.12	2.45	3.05
Standard deviation	.000	.005	.004	.005	.005	.004	.002	.005	.007	.006	.007	.005
Relative standard deviation, %	0.000	1.152	0.753	0.681	0.576	0.379	0.174	0.344	0.398	0.289	0.289	0.164

**TABLE 5. Base oil—100 neutral blend**

	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	C <sub>14</sub>	C <sub>16</sub>	C <sub>18</sub>	C <sub>20</sub>	C <sub>24</sub>	C <sub>28</sub>
RT average	0.82	0.98	1.14	1.47	1.79	2.13	2.45	3.05	3.58
Standard deviation	.000	.000	.000	.006	.005	.004	.009	.005	.007
Relative standard deviation, %	0.000	0.000	0.000	0.440	0.256	0.176	0.347	0.166	0.193



**FIG. 5** Home heating oil.



**FIG. 6** Base oil—100 neutral blend.

0.05 mm and 0.1 mm internal diameters. Efficiencies are high for short lengths and can be used in fast SD (FSD). The narrow bore columns make full-range analyses possible in about 5 to 6 min. GC cool down to the starting temperature is additive and brings the 6.8 min. cycle time to reason. In 30 years, GC run time for a single test has been reduced from 1 hr to 5 min.

**Today's technology.** GC oven temperature control and temperature ramps are

now precise. Maximum oven temperatures are consistent with the latest bonded phases and extend the boiling range even further. Distillation continues to be a base measurement for the HPI assessing quality or performance across the entire hydrocarbon range. GCs offer speed and information not obtainable from conventional equipment.

High throughput is essential in modern laboratories that may have multiple responsibilities to process control, blending and product specification. Productivity

and return on investment are frequently weighed as measures of justification for capital purchases. The huge reliance on distillation has continually shifted the analytical burden from stills to instrumentation. Productivity is now measured in tests/hr and may even be sufficiently fast to effect process control. Fractionating tower control has been managed by SD for many years.

GC distillation speed is related to heat-up (ramp rate) and cool-down. One without the other impacts the test's cycle and has a negative bearing on lab productivity. Modern GCs have rapid ramp rates and when applied to narrow-bore columns produce an elution period in the area of 5 min. for a full boiling range sample. This time varies depending on actual column length, film thickness and temperature ramp rate. However, cool-down to an equilibrated start temperature may require another 5 min. to 6 min., effectively doubling the GC distillation cycle time.

**The next generation.** A new technology utilizes a radically redesigned double-walled oven. The new oven design, with concentric air exhaust, allows faster oven cooling to reduce injection-to-injection times and also permits near-ambient operation. Fan speeds are automatically adjusted during the heating and cooling periods.

During the heating cycle, relatively slow fan speeds are applied, achieving accurate ramp rates. The cooling cycle has higher fan speeds providing the fastest cooling rates. Cool-down is enhanced by using forced convection air. The air stream path maximizes the convective cooling effect by passing directly over the heated components including the oven insulation. Performance characteristics for this oven are ideally suited to FSD applications.

SD productivity is measured by cycle time— injection-to-injection. The extremely fast cool down and equilibration for this GC sets a new standard for productivity. Fast GC now actually stands for measurable gains in productivity for SD users.

Retention time (RT) repeatability is the variable responsible for good SD. Since the RT to boiling point relationship is the basis for the distribution calculation, precision is paramount. The calibration curve is constructed from the boiling points of normal paraffins and its respective RTs. Samples are compared to this curve based on RT intervals.

Experiments were designed to show RT precision developed in a "fast" operation mode. A typical calibration chromatogram using normal paraffins is shown in Fig. 1.

It should be noted that the rapid elution maintains peak shape without introducing background noise. Table 1 is the data derived from 25 repetitive runs under conditions described in ASTM D-2887. The data shows excellent RT precision. Viewed in isolation and compared with conventional SD precision, the data may seem unimpressive. However, the data is obtained under fast chromatography parameters, causing the elution profile to be recorded over a small fraction of the time required for conventional SD.

Fig. 2 is a chromatogram for an ASTM reference gasoil. The material is highly characterized and has a large consensus data base to support its reference for SD quality control. Table 2 is the data set derived from 25 repetitive runs under the same conditions as the calibration runs. The precision of the RT measurements are again excellent. Fig. 3 is an SD report for gasoil at 1% intervals. Three other samples were analyzed (Figs. 4, 5, 6 and Tables 3, 4, 5) covering a broad range of hydrocarbons.

The RT precision is maintained throughout the carbon range, indicating the precision obtained from the new oven design. The elution profile was 40°C to a maximum of 300°C. Accuracy is demonstrated for the critical SD variable—RT. All the samples, regardless of final boiling point, were eluted in less than 4 min. and exhibited complete recovery. The cycle period (injection-to-injection) is 6.83 min. for the entire experiment.

**Moving forward.** Productivity is greatly improved with the double-walled oven's heat-up precision and cool-down performance. Experimental tests demonstrated RT precision under accelerated chromatographic conditions. The data also clearly shows the precision required to perform FSD. The injection-to-injection cycle time of 6.83 min. creates a new performance standard for SD analyses without using cryogenic cooling. Implementing this technology can enhance communications between the operating unit and laboratory, enabling faster decisions regarding unit operations. **HP**

#### LITERATURE CITED

- <sup>1</sup> Green, L. E., L. J. Schmauch and J. C. Worman, "Simulated distillation by gas chromatography," *Analytical Chemistry*, November 1964, pp. 1512–1516.

**Clarence Wentzel** is the president and one of the founders of Arnel Inc., a PerkinElmer LAS engineering business partner for 15 years. He has more than 35 years of experience in the development and application of analytical instrument technology for the petroleum and petrochemical industries. Mr. Wentzel has been awarded 7 patents in chemical and instrumental analyses and has published and presented numerous papers on analytical methodologies. He has participated in many ASTM development projects as a continuous member since 1972.



**Andrew Tipler** is a senior scientist in the Chromatography Business Unit of PerkinElmer Instruments. He has been with PerkinElmer for 24 years and has been responsible for developing new technologies and applications for the company's GC product line. These technologies include GCs, headspace samplers and thermal desorption systems. Mr. Tipler has been awarded 9 patents for innovations in GC and has presented papers at many international symposia.

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