

Fast Hydrocarbon and Sulfur Simulated Distillation Using the Agilent Low Thermal Mass (LTM) System on the 7890A GC and 355 Sulfur Chemiluminescence Detector

Application Note

Hydrocarbon Processing

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Abstract

A fast multielement simulated distillation method (SimDis) based on Low Thermal Mass (LTM) column technology is described. The LTM system technology using resistive heating allows rapid temperature programming with extremely fast column cool-down. Significantly shortened analytical cycle times as compared to conventional air bath GC ovens are achieved. The method combines hydrocarbon SimDis with an FID with sulfur SimDis using the Agilent 355 sulfur chemiluminescence detector (SCD) in a series configuration. The results show that the LTM method produces a run time for both hydrocarbon and sulfur boiling point distribution at least six times shorter than the conventional ASTM D2887 procedure [1]. The results agree with the specification in ASTM D2887 for the reference gas oil checkout sample.



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Introduction

Sulfur and carbon simulated distillation provide meaningful information to optimize refining processes and demonstrate compliance with petroleum product specifications. To meet the increasing needs for greater productivity, a fast sulfur and carbon SimDis method was developed using LTM technology. LTM technology was developed by RVM Scientific and acquired by Agilent Technologies in 2008 [2]. The Agilent 7890A system is designed to work with the LTM column module components to heat and cool the column very efficiently to significantly shorten analytical cycle times as compared to conventional air bath GC oven techniques involving much higher thermal mass. Aside from selectivity, temperature programming is an extremely useful feature of gas chromatography. When appropriate column dimensions and flow rates are chosen, high program rates (such as, 200 °C/min) can be used to great advantage. Agilent's method translation software can be useful in this regard [3]. For example, as temperature program rates increase, a corresponding increase in column flow rate should also be considered to achieve more optimal overall system performance. The system (except external power supply) is built into a replacement GC oven door, which is mounted as an add-on to an Agilent 7890A GC. The method described here combines hydrocarbon SimDis with sulfur selective SimDis using an FID and an SCD in series with simultaneous acquisition of both signals.

Experimental

This two-channel SimDis application uses the Agilent 7890A GC configured with a high-temperature programmable temperature vaporizer (HT-PTV) inlet and an SCD mounted in series with an FID by using a special adapter. A 5-inch format LTM column module is used for the analysis. Samples, such as boiling point (BP) calibration C5-C40, polywaxes, and resids, that are too viscous or waxy to sample with a syringe are heated to approximately 80 °C for a few minutes before injection.

The SimDis application software can process one or two channels of signal data (FID and SCD) from the GC ChemStation. The software is based on four modules: Browse, Setup, SimDis, and Report. Each module provides specific functions to rapidly perform multielement SimDis calculations. For example, the Setup module allows you to assign the files to use for BP Calibration, Blank, and QC reference. The detailed GC conditions used are listed in Table 1.

Table 1. Gas Chromatographic Conditions

HT-PTV inlet	
Temperature	350 °C
Split ratio	30:1
Injection volume	0.1 µL
7890/LTM	
Column (LTM)	DB-1 5 m × 320 mm × 1 µm
LTM temperature program	45 to 350 °C at 150 °C/min, hold 1 min (GC oven: 300 °C, held for duration)
Column flow (He)	Ramp pressure: 18 psi to 42 psi at 11.8 psi/min
FID temperatures	350 °C
H ₂ flow	40 mL/min
Air flow	400 mL/min
Make up (N ₂)	40 mL/min
Data rate	5 Hz
SCD	
Burner temperature	800 °C
Vacuum of burner	324 Torr
Vacuum of reaction cell	11.6 Torr
H ₂	40 SCCM
Air	8.3 SCCM
Data rate (AIB)	5 Hz
LTM system	G6578A, bundle for 1-channel 5-inch modules

Processing Two-Channel Data in the SimDis Software

The Agilent SimDis System enables the use of gas chromatography to determine the boiling point range distribution and percent recovery of petroleum fractions. The SimDis software allows for reports to be generated in two ways: automated and manual. Both require the user to first manually set a blank, calibration, and optional QC reference chromatogram. When working with dual channels, the SimDis software requires that each channel be labeled by the detector type rather than the defaults used by the GC ChemStation. Since the SCD operates off the analog input board (AIB), its signal begins with "AIB." For this reason, the Post-Run command macro SCDnamer.mac must be run to rename the signal file. The macro renames the AIB2B.ch channel as SCD1.ch. If the channel name is not corrected, the software will switch the FID and SCD channels during analysis, giving faulty results. The macro code to do this is shown below. It assumes that the AIB is in the rear position (B).

! SCDNamer call this as a post run command when an SCD is installed

! it renames the dual channel AIB2B.ch to SCD1.ch to allow simdis to properly calibrate

NAME SCDNamer

! This macro renames the SCD files named as AIB2B.ch to SCD1.ch
if filestat(mode,dadatapath\$+dadatfile\$+"\AIB2B.CH")=1

```
rename dadatapath$+dadatfile$+"\AIB2B.ch",dadatapath$+dadatfile$+"\SCD1.ch"
```

```
print "File Renamed"
```

```
else
```

```
print "No AIB2B File found"
```

```
endif
```

```
RETURN
```

```
ENDMACRO
```

Under the Setup tab of SimDis, select the default chromatograms to be used for the calculation. All desired solvent masking should be done here. The calibration run should have major carbon peaks identified; this can be done with an imported calibration table from ChemStation or manually in SimDis. The QC reference should have concentrations and dilution factors entered. Now enter the SimDis pane and set the parameters to be used. Do not include the solvent peak in the calculations and account for the baseline and noise using a zeroing method. In order to get proper percent recovery values make sure Normalize to 100% is not selected and a proper dilution factor is entered. Set the settings as default. For

automation, enter ChemStation and select SimDis > Setup > Use SimDis Defaults under Data Analysis and select a report to generate after each run. For manual operation, select the desired chromatogram under the Report pane in SimDis and enter the report pane to view and print results.

Results and Discussion

The LTM column module employs a unique direct resistive heating technology using ceramic-insulated heating wire where contact with the capillary column is maximized. This is packaged in a very low mass assembly. Accurate and precise temperature sensing is possible by incorporating the temperature sensor with the capillary GC column. This technology greatly reduces GC analytical cycle times, addressing demands for greater productivity. The result for the D2887 reference gas oil (RGO) shows that the run time using LTM is less than 2.5 minutes, or about six times faster compared to conventional ASTM D2887 procedures. The SimDis results agree with the specifications of ASTM D2887 with excellent repeatability (see Table 2). The upper chromatogram in Figure 1 shows the D2887 RGO analysis by conventional air bath GC oven and the lower chromatogram shows RGO by LTM GC. The run time is about 2.5 minutes and 15 minutes for LTM and conventional air bath GC, respectively.

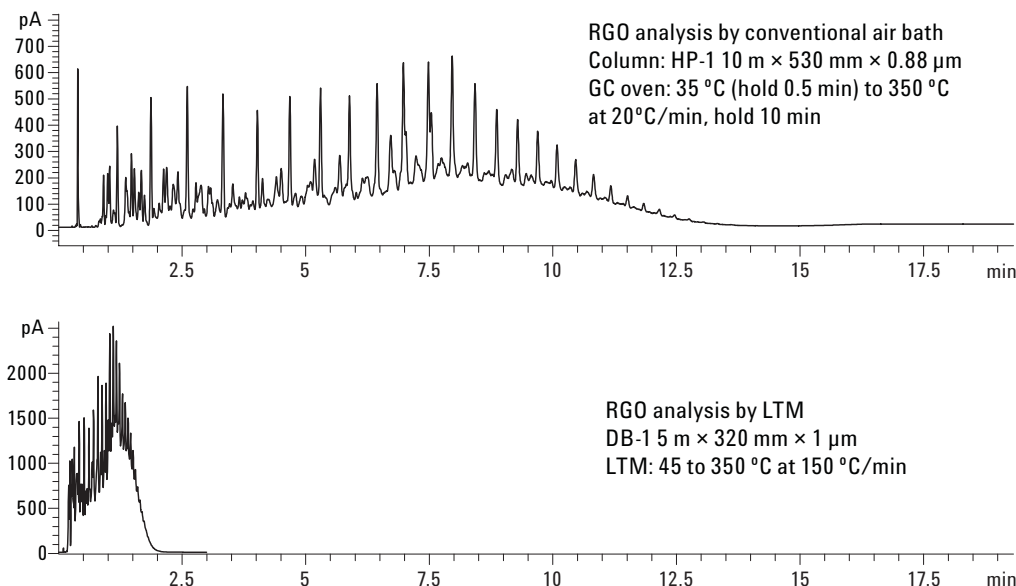


Figure 1. Comparison of RGO analysis by LTM and air bath GC ovens.

Table 2. RGO SimDis Results with the LTM System

	ASTM D2887 Values			Observed Value										Average	Difference	RSD%
	BP, °C	Allowable difference		1	2	3	4	5	6	7	8	9	10			
IBP	115	7.6		112	113	112	113	112	113	112	113	112	113	112.5	2.5	0.47
10%	176	4.1		173	174	173	174	173	174	173	174	173	174	173.5	2.5	0.30
20%	224	4.9		220	220	220	220	220	220	220	220	220	220	220	4	0.00
30%	259	4.7		254	255	255	255	255	255	255	255	255	255	254.9	4.1	0.12
40%	289	4.3		285	286	285	287	285	286	285	286	286	286	285.7	3.3	0.24
50%	312	4.3		309	310	309	310	309	309	309	309	309	309	309.2	2.8	0.14
60%	332	4.3		329	330	329	330	329	330	329	329	329	329	329.3	2.7	0.15
70%	354	4.3		350	352	351	352	351	352	351	352	351	352	351.4	2.6	0.20
80%	378	4.3		375	376	375	377	375	376	375	376	375	376	375.6	2.4	0.19
90%	407	4.3		404	405	405	406	404	406	404	405	404	405	404.8	2.2	0.19
FBP	475	11.8		474	475	475	476	475	476	475	475	475	475	475.1	-0.1	0.12

A mixture of C5 through C40 n-alkanes with known boiling points which are used for establishing the correlation between RT (min) and BP (°C) can be separated in less than 2.5 minutes with repeatability in retention time better than 0.1 percent relative standard deviation (RSD). Table 3 shows

RT stability with RSD of approximately 0.02 to 0.15 percent (C40) using a rapid temperature program of 150 °C/min ramped from 45 to 350 °C. These results indicate a lack of cold spots and temperature nonuniformity in the LTM column module. Figure 2 is an overlay of five consecutive runs of the C5 to C40 calibration mixture.

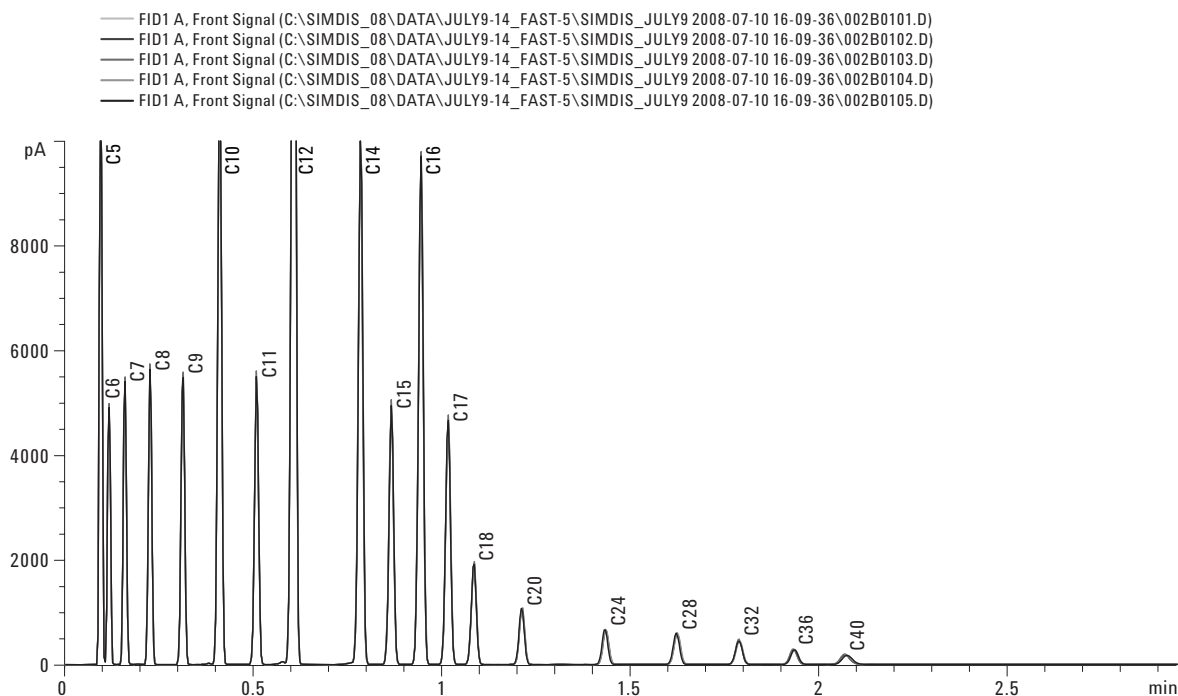


Figure 2. Overlays of five consecutive runs of the C5 to C40 calibration mixture. Chromatographic overlay shows outstanding repeatability. LTM: 45 to 350 °C at 150 °C/min.

Table3. Retention Time Repeatability of C5 to C40 Calibration Mixture (n = 5)

	1	2	3	4	5	Average	SD	RSD%
C5	0.09766	0.09760	0.09766	0.09763	0.09764	0.09764	2.33E-05	0.024
C6	0.11999	0.11992	0.11994	0.11989	0.11993	0.11994	3.67E-05	0.031
C7	0.16285	0.16274	0.16270	0.16263	0.16270	0.16272	8.07E-05	0.050
C8	0.23072	0.23051	0.23045	0.23036	0.23045	0.23050	0.000135	0.059
C9	0.31908	0.31883	0.31877	0.31867	0.31874	0.31882	0.000158	0.049
C10	0.41803	0.41775	0.41779	0.41777	0.41780	0.41783	0.000117	0.028
C11	0.51730	0.51707	0.51711	0.51716	0.51719	0.51717	8.61E-05	0.017
C12	0.61713	0.61688	0.61723	0.61716	0.61721	0.61712	0.000138	0.022
C14	0.79706	0.79676	0.79746	0.79707	0.79733	0.79714	0.000271	0.034
C15	0.87963	0.87964	0.88004	0.87985	0.88009	0.87985	0.000216	0.025
C16	0.95952	0.95940	0.95986	0.95941	0.95966	0.95957	0.000192	0.020
C17	1.03290	1.03263	1.03314	1.03279	1.03257	1.03281	0.000225	0.022
C18	1.10255	1.10190	1.10250	1.10236	1.10201	1.10226	0.00029	0.026
C20	1.23235	1.23131	1.23203	1.23151	1.23060	1.23156	0.000676	0.055
C24	1.45819	1.45721	1.45683	1.45772	1.45470	1.45693	0.001348	0.093
C28	1.65011	1.64884	1.64878	1.65001	1.64698	1.64895	0.001261	0.076
C32	1.81666	1.81587	1.81535	1.81739	1.81562	1.81618	0.000834	0.046
C36	1.96355	1.96259	1.96200	1.96611	1.96522	1.96389	0.001738	0.088
C40	2.10071	2.10110	2.10021	2.10619	2.10665	2.10297	0.003168	0.151

This work combines hydrocarbon SimDis with sulfur selective SimDis using an SCD mounted over the FID for simultaneous dual detector acquisition. In this configuration, about 20% of the FID exhaust gases enter the SCD burner, reducing sensitivity to 1/5 observed in an SCD-only configuration. This series configuration provides more than enough sensitivity for SimDis. A sample with known sulfur concentration is used as a QC reference (external reference sample) to calibrate

response factors (RFs) for the sulfur channel needed for calculation of total sulfur. Sulfur linearity of the LTM method was checked by injecting the standard mixture at different concentration levels, ranging from 100 to 1,500 ng/ μ L (ppm). The calibration curve is displayed in Figure 3, giving a correlation coefficient above 0.999.

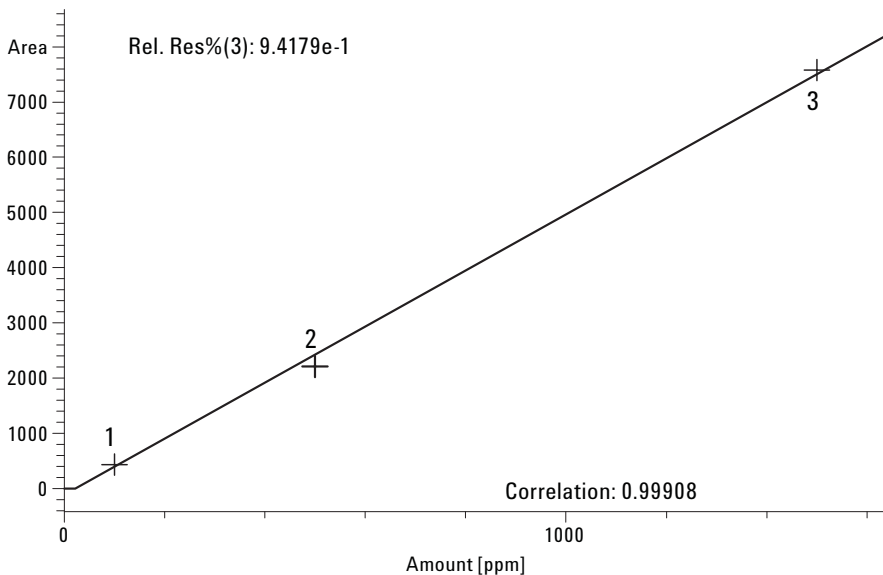


Figure 3. Linearity of sulfur with the SCD and LTM system.

A high-sulfur light cycle oil (LCO) sample was analyzed. Data were processed for hydrocarbon and sulfur simulated distillation, yielding excellent repeatability as shown in Table 4. The RSD is less than 0.4 percent for hydrocarbon and 0.5 percent

except that of FBP for sulfur. The average total sulfur is 260.8 ppm with an RSD of 4.83 percent. Figure 4 shows the chromatograms for sulfur (top) and carbon (bottom).

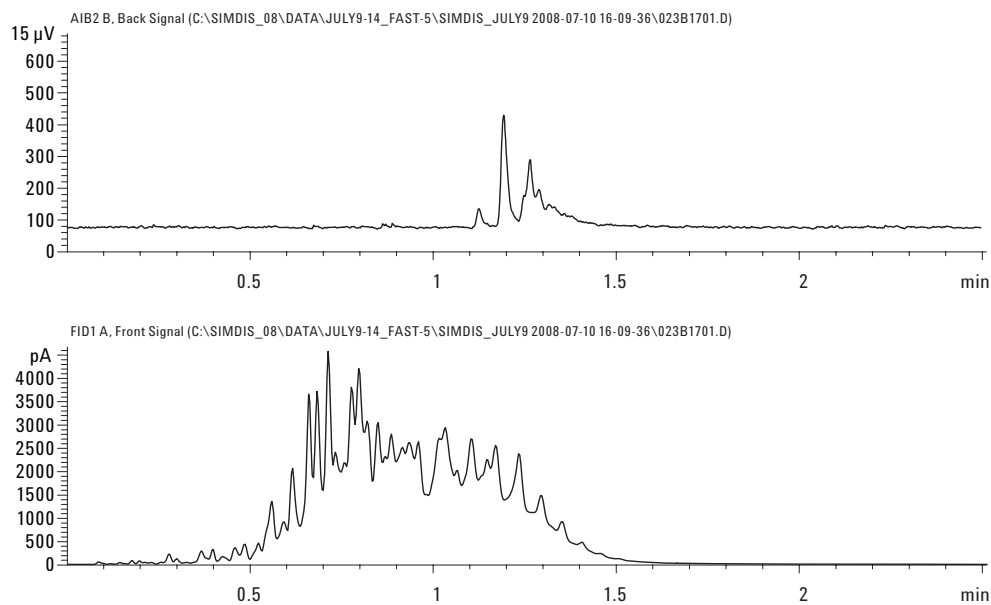


Figure 4. Chromatograms for sulfur and carbon. Sulfur top chromatogram.

Table 4. Hydrocarbon and Sulfur SimDis Results for Light Cycle Oil

Hydrocarbon SimDis												
	BP, °C										Average	RSD%
IBP	139	140	139	140	140	139	140	139	140	139	139.5	0.38
10%	222	223	222	223	223	222	223	222	224	223	222.7	0.30
20%	235	236	235	236	236	235	236	235	236	235	235.5	0.22
30%	249	250	249	250	250	249	250	249	250	249	249.5	0.21
40%	262	262	262	262	262	262	262	262	262	262	262.0	0.00
50%	276	277	277	277	277	277	277	276	277	277	276.8	0.15
60%	293	294	293	294	294	293	294	293	294	293	293.5	0.18
70%	308	309	308	309	309	308	309	308	309	308	308.5	0.17
80%	326	326	326	326	327	326	326	326	326	326	326.1	0.10
90%	347	347	347	347	347	347	347	347	347	347	347.0	0.00
FBP	411	411	411	412	413	412	412	412	412	412	411.8	0.15
Sulfur SimDis												
	BP, °C											
IBP	319	320	318	319	320	319	318	319	319	318	318.9	0.22
10%	334	334	334	334	334	334	334	334	334	334	334.0	0.00
20%	335	335	335	335	336	335	335	335	335	335	335.1	0.09
30%	337	337	337	337	337	337	337	337	337	337	337.0	0.00
40%	341	340	343	341	340	345	344	342	341	342	341.9	0.50
50%	349	349	349	349	349	350	349	349	349	349	349.1	0.09
60%	352	351	352	351	352	352	351	352	351	352	351.6	0.14
70%	355	354	355	355	355	355	355	355	355	355	354.9	0.08
80%	361	358	360	360	359	360	360	359	359	360	359.6	0.22
90%	368	365	367	367	366	369	368	367	367	367	367.1	0.30
FBP	399	384	385	386	383	407	392	384	395	395	391.0	2.05
Total sulfur (ppm)	260	237	255	262	252	281	273	254	263	273	260.8	4.83

Conclusions

A fast dual detector (FID and SCD in series) simulated distillation method using an LTM system on the 7890A GC provides a cycle time improvement over conventional systems of about 6X.

The SimDis result for ASTM D2887 RGO shows that the LTM system is equivalent to that of air-bath GCs. Results agree with the RGO specification of ASTM D2887 with RSDs of 0.12 to 0.47 percent across the reported percent off range. Wide boiling range hydrocarbons (C5 to C40 BP calibration mixtures) also show very good RT stability with RSD of 0.02 to 0.15 percent using a rapid column module temperature program of 150 °C /min ramped from 45 to 350 °C and sample injection using the HT-PTV. Sulfur linearity of the LTM/SCD system reveals an excellent correlation coefficient, above 0.999. SimDis of a high sulfur LCO sample shows an RSD of less than 0.4 percent for hydrocarbon and 0.5 percent except that of FBP for sulfur. The average total sulfur is 260.8 ppm, with an RSD of 4.83 percent.

References

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- 2 "Agilent Low Thermal Mass (LTM) System for Gas Chromatography," Agilent Technologies publication 5989-8711EN, June 2008
- 3 Method Translation Software. Download from Agilent.com:
<http://www.agilent.com/chem/mts>

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