

Optimized Supercritical Fluid Chromatographic Instrumentation for the Analysis of Petroleum Fractions

Bruce E. Richter*, Brian A. Jones, and Nathan L. Porter

Sensar/Larson-Davis, 1652 W. 820 N., Provo, UT 84601

Abstract

The performance of a supercritical fluid chromatograph (SFC) for the analysis of petroleum fractions, specifically diesel and jet fuels, is reported. The SFC instrument passes the requirements of ASTM Method 5186-96 for accuracy, linearity, and repeatability following the proper adjustment of detector gas flows and detector temperature. Up to a sixfold improvement in the precision (measured as relative standard deviation) is seen when the pressure transducer is temperature-controlled independent of the laboratory air temperature.

Introduction

The separation of petroleum fractions into the individual hydrocarbon groups can be difficult because of the need to separate a large number of very similar molecules. Many techniques have been investigated and used with varying levels of success. A commonly used method is fluorescence indicator adsorption (FIA) (1). FIA has been widely used but suffers from precision and boiling point limitations, particularly for diesel fuels. Nuclear magnetic resonance and mass spectrometry have been used to provide structural information and aromatic content in diesel fuels (2). Neither of these techniques is routinely used for hydrocarbon group analysis because of high initial capital costs and operational complexities. High-performance liquid chromatography (HPLC) is another alternative to FIA because of its speed and resolution capability (3,4), but HPLC lacks a sensitive and universal detector that can be used for the general analysis of petroleum fractions.

Supercritical fluid chromatography (SFC) with flame ionization detection (FID) has been shown to work well for hydrocarbon group analysis (5-7). In fact, the American Society of Testing and Materials (ASTM) has accepted the use of SFC for the determination of aromatic content of jet and diesel fuels (8). Very little work has been reported in recent years on the use of SFC for hydrocarbon group analyses. Li et al. (9) published a paper on the use of packed capillary columns for group-type separation of

diesel fuels. More recently, M'Hamdi et al. (10) discussed the characteristics of a commercial SFC system and the use of a column switching approach to improve the separation of the aromatic fractions when using SFC with carbon dioxide.

This paper is a report on our development and evaluation of new SFC instrumentation for the analysis of petroleum fractions. The effect of detector gas flow rates and detector temperature on mass accuracy and linearity was investigated. After careful study, it was determined that retention time reproducibility is greatly enhanced by controlling the temperature of the pressure transducer on the pump.

Experimental

Instrumentation

A prototype of a Sensar Series 3000 chromatograph (Sensar/Larson-Davis, Provo, UT) was used for all experimentation. The syringe pump had a 10-mL volume and was cooled to approximately -10°C using a thermoelectric chip. The pump was configured to refill after each run or whenever its volume was less than 1 mL. We found that a single refill of the pump provided for runs of more than an hour with the 1-mm i.d. packed columns used for this study. The oven was a GC-type oven with a cavity large enough to house several columns and switching valves. The FID was optimized for use in microcolumn separations such as capillary GC. The FID had a very short flame jet length (1.1 cm) that made it very suitable for use in SFC. The oven was outfitted with a Valco (Houston, TX) valve for injection. The internal loop had a volume of 0.5 μL . Data collection and manipulation were performed using EZChrom Elite chromatography data collection software from Scientific Software (San Ramon, CA). The carbon dioxide was SFC grade from Scott Specialty Gases (Plumsteadville, PA).

Columns and chromatographic conditions

The columns were packed in-house using established slurry packing methods. The stainless steel columns were either 50 or 75 cm \times 1-mm i.d. (in-house) and packed with 5- μm silica (60- \AA pore size, YMC, Wilmington, NC). The oven was maintained at 40°C ,

* Author to whom correspondence should be addressed.

and the pump was maintained at 200 atm. The post-column restrictor was an 8 to 15-cm length of 15- μ m i.d. fused-silica tubing (Polymicro Technologies, Phoenix, AZ). The restrictor was connected directly to the outlet of the packed columns using polymeric ferrules and stainless steel nuts (Upchurch Scientific, Oak Harbor, WA) to reduce dead volume. The outlet end of the restrictor was placed 1 mm from the tip of the flame jet in the FID.

Test solutions and samples

Test solutions were prepared using hexadecane, toluene, tetralin (1,2,3,4-tetrahydronaphthalene), and naphthalene (Aldrich Chemicals, Milwaukee, WI) in the mass ratios 75:20:3:2. This test solution was injected neat without any dilution. Samples of diesel or jet fuels were obtained from local suppliers and were analyzed either neat or diluted with hexadecane to check linearity.

Results and Discussion

Investigation of detector gas flow rates

There are two key issues with any FID that is to be used for the analysis of petroleum fractions by SFC. The first issue pertains to the detector accuracy test as defined in Method 5186-96. The second issue pertains to the stability of the flame in the FID with respect to high column flow rates.

For the detector to pass the accuracy test, the measured response factors of each component in the test mixture must be within $\pm 10\%$ of the theoretical response factors. In other words, the area percent of each component obtained from the chromatographic analysis of the test mixture must be within $\pm 10\%$ of the actual mass percent of the solution. We have found that the best way to attain the required results is through adjustment of the detector gas flows and the detector temperature. Table I shows the results of testing the detector gas flows (the table does not include all collected data). As Table I shows, the flow rates required to pass the accuracy test (90 mL/min H_2 and 600 mL/min air) are considerably higher than flow rates used for gas chromatography (GC) (typically 30 mL/min H_2 and 350 mL/min air). The area percent of the naphthalene (Table I) did not fall within the $\pm 10\%$ window until the flow rates were increased to the higher values (90 mL/min H_2 and 600 mL/min air). The data also indicate that increasing the detector gases above these values does not change the results. In addition, we found that the use of nitrogen as make-up gas at flow rates from 1 to 15 mL/min did not alter the area percent assay. The response factors for these compounds are different than those reported in GC literature, probably attributable

to the presence of CO_2 at high flow rates and the high flow rates of the detector gases required to ensure the flame remains ignited during operation.

With the detector gases at optimized flow rates, experiments were performed to determine the highest column flow rate that could be introduced into the FID without extinguishing the flame. For these experiments, a short piece (8 cm) of 15- μ m i.d. fused-silica tubing was used as the restrictor. The pump pressure was programmed to slowly increase from 1000 to 6000 psi. It was found that a column flow as high as 285 mL/min (expanded gas flow) could be introduced into the FID without extinguishing the

Table I. Effect of Detector Flow Rate on Area Percent Assay*

Flow rates (mL/min)		Hexadecane	Toluene	Tetralin	Naphthalene
H_2	air				
40	400	74.1	20.4	3.22	2.23
55	500	74.5	20.0	3.19	2.25
60	500	74.7	19.9	3.17	2.22
75	550	75.1	19.6	3.13	2.20
90	600	75.2	19.5	3.10	2.18
90	700	75.4	19.3	3.10	2.18
100	700	75.3	19.4	3.10	2.18

* Detector temperature was 350°C. Mass percentages of standards were 74.97% for hexadecane, 19.99% for toluene, 3.04% for tetralin, and 2.00% for naphthalene.

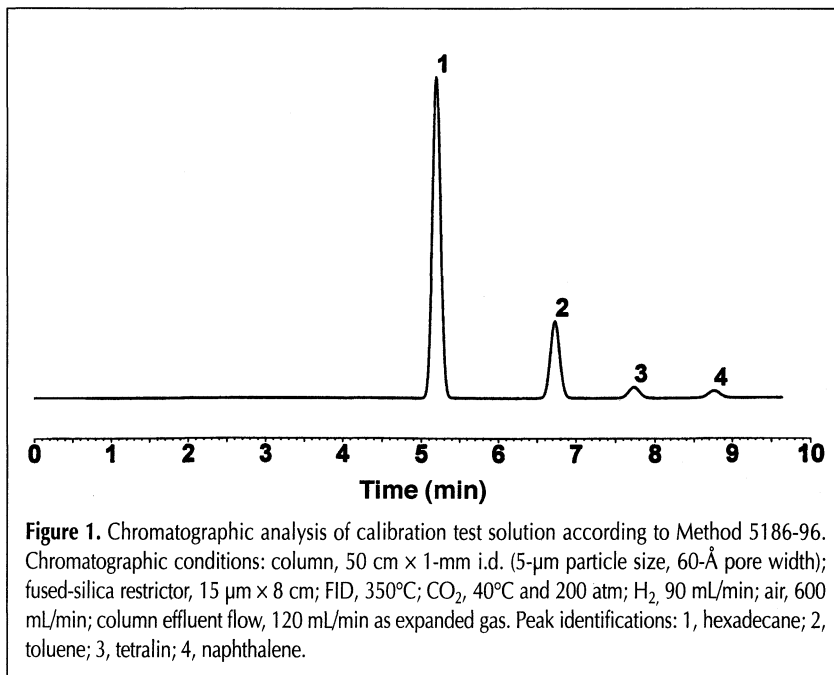


Table II. Effect of Detector Temperature on Area Percent Assay*

Detector temperature (°C)	Hexadecane	Toluene	Tetralin	Naphthalene
350	75.2	19.5	3.11	2.18
400	75.7	19.2	3.03	2.13
450	75.8	19.2	2.97	2.09

* Detector flows were 90 mL/min for H_2 and 600 mL/min for air. Mass percentages of standards were 74.97% for hexadecane, 19.99% for toluene, 3.04% for tetralin, and 2.00% for naphthalene.

flame. This means that it is possible to introduce the entire column effluent from a 2-mm-i.d. packed column for Method 5186-96 without the need to split some of the column flow to waste. When using a 1-mm-i.d. column, it is possible to operate at high column flow rates to get shorter analysis times. Figure 1 shows a chromatogram of the calibration standard with a column flow rate of approximately 120 mL/min expanded gas flow. The separation was complete in less than 10 min, and the resolution requirements of the method were met. For the chromatogram shown in Figure 1, the resolution between hexade-

cane and toluene was 7.5, the resolution between toluene and tetralin was 4.1, and the resolution between tetralin and naphthalene was 3.5. The method requires a resolution of at least 4 between hexadecane and toluene and at least 2 between toluene and tetralin and between tetralin and naphthalene.

Investigation of detector temperature

Based on personal experience in the laboratory, it was known that adjusting the detector temperature could also have an effect on the detector accuracy. Table II demonstrates that raising the temperature of the FID can change the results. The requirements of Method 5186-96 are met when the FID is at 350°C, but the average relative error between the observed values and the true mass percent is less when the detector is at 450°C (2.3% at 350°C and 0.54% at 450°C). Even though there was less relative error at 450°C than at 350°C, we chose to operate the FID at 350°C for the remainder of the testing because of operator convenience considerations.

Linearity of response

To pass the linearity portion of Method 5186-96, two dilutions (50 and 25 mass percent) of a diesel motor fuel were prepared in hexadecane. The pure diesel and the two dilutions were analyzed under the conditions specified in the method. The results of the analyses of the dilutions were used to predict the aromatic content of the original diesel sample. The predicted value must agree with the assay results within the repeatability limits stated in the method in order for the detector to pass the linearity test.

In this case, a diesel that had approximately 30% total aromatic content was chosen. From the results from the dilutions, 32.26% aromatics was predicted; the actual assay of the diesel was 32.29% total aromatics. That was well within the repeatability limits of 0.4 mass percent as specified by the method. The detector passed the linearity performance requirements with the optimized detector conditions (350°C, 90 mL/min H₂, 600 mL/min air).

Performance with fuel samples

Once the detector accuracy and linearity were determined, the performance of the system was investigated using actual fuel samples to evaluate the repeatability obtained. Table III shows the tabulated results from the analyses of two diesel samples and two jet fuels. The acceptable repeatability window was calculated from Method 5186-96 and is given there only for total aromatic and polyaromatic content. The method states that the range between successive runs must fall within the repeatability window to pass the precision test. The RSD values are shown only as a point of reference. The ranges of the

Table III. Repeatability Comparison for Fuel Analyses

	Average (n = 3)	RSD (%)	Range	Acceptable repeatability window
Diesel fuel A				
Saturates	67.7	0.15	0.20	NA*
Monoaromatics	25.1	0.05	0.11	NA
Polyaromatics	7.19	0.03	0.08	0.22
Total aromatics	32.3	0.08	0.20	0.36
Diesel fuel B				
Saturates	65.3	0.10	0.14	NA
Monoaromatics	28.1	0.19	0.13	NA
Polyaromatics	6.58	0.0	0.0	0.22
Total aromatics	34.7	0.16	0.13	0.36
Jet fuel A				
Saturates	83.7	0.08	0.14	NA
Monoaromatics	14.3	0.11	0.04	NA
Polyaromatics	2.05	2.7	0.12	0.18
Total aromatics	16.4	0.35	0.14	0.30
Jet fuel B				
Saturates	77.4	0.07	0.11	NA
Monoaromatics	19.9	0.15	0.07	NA
Polyaromatics	2.75	1.8	0.11	0.19
Total aromatics	22.6	0.20	0.11	0.33

* NA, not applicable.

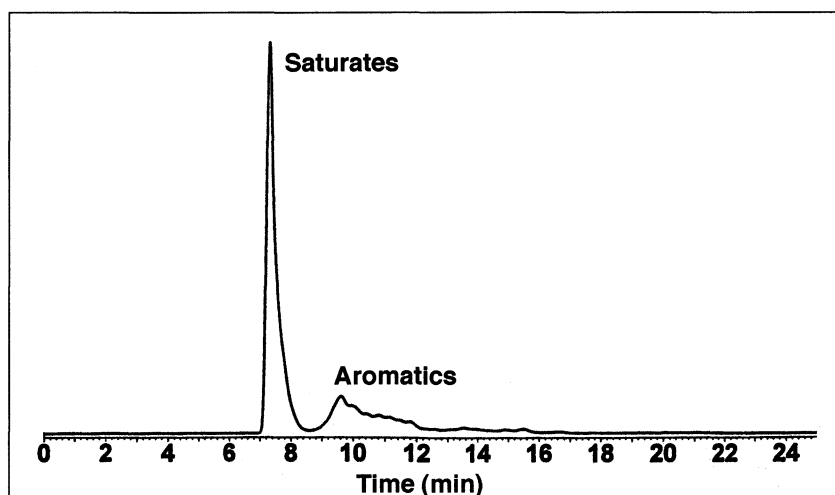


Figure 2. Chromatogram of diesel fuel sample A. Chromatographic conditions: column, 75 cm × 1-mm i.d. (5- μ m particles, 60- Å pore width); fused-silica restrictor, 15 μ m × 12 cm; FID, 350°C; CO₂, 40°C and 200 atm; H₂, 90 mL/min; air, 600 mL/min; column effluent flow, 120 mL/min as expanded gas.

experimental data are being compared to the acceptable repeatability window as defined in Method 5186-96. As can be seen, the system also complies with the precision requirements as specified in the method. Figures 2 and 3 show chromatograms of a diesel fuel and jet fuel sample, respectively, and are typical of the results obtained for these samples when using the optimized operating conditions.

Effect of temperature-controlled transducer

The output of pressure transducers that are routinely used in chromatography can be effected by the temperature of the air in which they function. This does not present significant problems when using conventional HPLC, because the pumps are most often operated in a flow-control rather than pressure-control

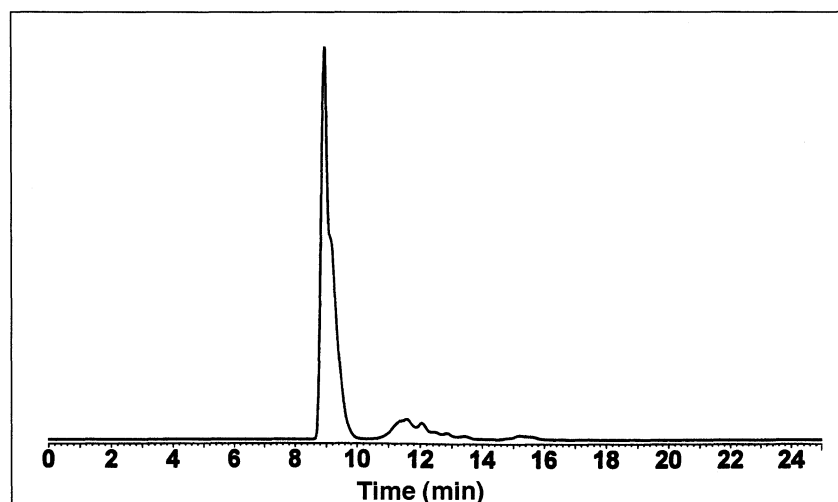


Figure 3. Chromatogram of jet fuel sample A. Chromatographic conditions: column, 75 cm \times 1-mm i.d. (5- μ m particles, 60- Å pore width); fused-silica restrictor, 15 μ m \times 12 cm; FID, 350°C; CO₂, 40°C and 200 atm; H₂, 90 mL/min; air, 600 mL/min; column effluent flow, 120 mL/min as expanded gas.

mode. Changing the pressure transducer output can be problematic for chromatography involving a pressure control mode, especially SFC. When the pressure of the supercritical fluid changes, the solvent strength of the mobile phase changes, which in turn causes the retention times of the analytes to shift. If isobaric analyses are performed using SFC and the temperature of the laboratory air changes several degrees, then poor retention time reproducibilities will result.

To perform the analysis specified in Method 5186-96, a standard solution is run to obtain retention time windows and cut-off points for the grouping of compound classes. That is how the total mono- and polyaromatic content is obtained. Once this is established, several samples are analyzed before another calibration standard is run. Changes in room temperature can give rise to poor assay reproducibility, because compound retention times are shifting but the cut-off point times are set values in the data collection method and do not change unless another calibration standard is run. We believed that controlling the temperature of the transducer independent from the laboratory air could enhance the overall reproducibility.

For these experiments, an aluminum block (1 cubic inch) was machined and attached to the pressure transducer. The temperature of the block and the transducer were controlled using a power transistor and an operational amplifier circuit with a temperature sensor connected to the block.

To determine if controlling the temperature of the transducer made a difference, we varied the temperature of the laboratory air from 22 to 29°C as assays of jet and diesel fuel were performed using Method 5186-96. In the first set of experiments, no efforts were made to control the temperature of the transducer. In the second set of experiments, the transducer was controlled at 45°C while the laboratory air temperature varied between 22 and 29°C. Table IV shows that controlling the temperature of the transducer has a large impact on the assay reproducibility when laboratory air is changing temperatures. In all cases, the precision (measured as RSD) of the individual group assay as well as the average RSD for each sample improved when the temperature of the transducer was controlled. Jet fuel sample C showed more than a sixfold improvement in the average RSD with the temperature-controlled transducer in place.

Conclusion

The performance of a SFC instrument in terms of its compliance with ASTM Method 5186-96 for the analysis of diesel and jet fuels was discussed. The effect of detector gas flows and

Table IV. Effect of Controlling the Pressure Transducer Temperature

	RSD (%) without temperature control	RSD (%) with temperature control
Diesel C		
Saturates	0.13	0.08
Monoaromatics	0.33	0.08
Polyaromatics	2.7	0.70
Total aromatics	0.25	0.14
Average	0.86	0.25
Jet fuel C		
Saturates	0.09	0.02
Monoaromatics	0.74	0.28
Polyaromatics	9.6	1.2
Total aromatics	0.48	0.09
Average	2.7	0.40
Jet fuel D		
Saturates	0.12	0.03
Monoaromatics	0.39	0.19
Polyaromatics	6.5	0.92
Total aromatics	0.41	0.09
Average	1.8	0.31

detector temperature was investigated. We found that the FID could be optimized such that it complied with the accuracy, linearity and repeatability requirements of the method. We also found that controlling the temperature of the pump pressure transducer had a major impact on precision. We measured a more than sixfold improvement in the RSD when the laboratory air was allowed to vary between 22 and 29°C and the temperature of the transducer was controlled.

References

1. ASTM D 1319, *Annual book of ASTM standards*, Vol. 17, 1973, p 476.
2. B. Glavincevski and L. Gordner. *An Overview of the Methods of Structural Analysis: Proton NMR and GC-MS of Middle Distillate Aromatic Fractions*. SAE Technical Paper series 852079, SAE, Warrendale, PA, 1985.
3. P.C. Hayes and S.D. Anderson. Quantitative determination of hydrocarbons by structural group type via high-performance liquid chromatography with dielectric constant detection: a review. *J. Chromatogr. Sci.* **26**: 210 (1988).
4. E. Robert, J.J. Beboulene, G. Codet, and D. Enache. High-performance liquid chromatography coupled with capillary gas chromatography. Application to the determination of the aromatics content in middle distillates. *J. Chromatogr.* **683**: 215 (1994).
5. R.M. Campbell and M.L. Lee. Supercritical fluid fractionation of petroleum- and coal-derived mixtures. *Anal. Chem.* **58**: 2247-51 (1986).
6. R.M. Campbell, N.M. Djordjevic, K.E. Markides, and M.L. Lee. Supercritical fluid chromatographic determination of hydrocarbon groups in gasolines and middle distillate fuels. *Anal. Chem.* **60**: 356-62 (1988).
7. F.P. Di Sanzo and R.E. Yoder. Determination of aromatics in jet and diesel fuels by supercritical fluid chromatography with flame ionization detector (SFC-FID): a quantitative study. *J. Chromatogr. Sci.* **29**: 4-7 (1991).
8. ASTM D 5186-96, *Annual book of ASTM standards*, Vol. 6, 1996, p 3.
9. W. Li, A. Malik, M.L. Lee, B.A. Jones, N.L. Porter and B.E. Richter. Group-type separation of diesel fuels using packed capillary column supercritical fluid chromatography. *Anal. Chem.* **67**: 647-54 (1995).
10. R. M'Hamdi, D. Thiébaud, and M. Caude. Packed column SFC of gas oils part I: hydrocarbon group separation using pure carbon dioxide. *J. High Resol. Chromatogr.* **20**: 545-54 (1997).

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