# Determination of Aromatics in Jet and Diesel Fuels by Supercritical Fluid Chromatography with Flame Ionization Detection (SFC-FID): A Quantitative Study

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## Abstract

**The fluorescent indicator adsorption (FIA) method is the most commonly used industry method for the determination of total aromatics in light fuels. Alternative methods using supercritical fluid chromatography coupled with flame ionization detection (SFC-FID) have been proposed. Quantitative studies are performed on aromatics in jet and diesel fuel, using standard blends derived from gasoline, jet, and diesel fuels to determine the accuracy of SFC methods. The goal is to develop a simple method for use in a rapid, automated routine. To this end, a single column, one mobile phase under constant density, and no temperature programming or valve switching is used.**

## Introduction

The most common industry method for the determination of total aromatics in light fuels is the fluorescent indicator adsorption (FIA) method (1). There is significant world wide interest in developing alternative methods because of the precision and boiling point limitations of the FIA method, particularly for diesel fuels. Nuclear magnetic resonance (NMR) and mass spectrometry (MS) have been used to provide detailed structural information and aromaticity content in diesel fuels (2). However, these techniques are not generally used in routine analysis because of the high initial capital expenditure and the requirement of highly skilled operators. Liquid chromatography (LC) has been used extensively in the analysis of hydrocarbon group type (3,4). Generally, aromatic hydrocarbons are readily separated by LC methods in a short analysis time, but these methods lack a universal quantitative mass detector. The usefulness of the UV and refractive index (RI) detectors is limited because of the lack of uniform response to the various isomers and compound classes found in petroleum streams. Elaborate calibration schemes have been developed but these calibration procedures are usually time consuming. A dielectric constant detector, which has been proven to have a more constant response to most hydrocarbons, has recently been reported to have

been used with good success (5). However, our experience with the use of the dielectric constant detector is somewhat negative because of its temperamental behavior.

Recently, supercritical fluid chromatography with flame ionization detection (SFC-FID) has emerged as a technique which has solved the need for a hydrocarbon universal mass detector. When supercritical $CO_2$ is used as the mobile phase, the conventional FID may be used successfully for hydrocarbon analysis. Generally, the flame ionization detector has a uniform response for hydrocarbons. A number of papers have appeared in the literature on the analysis of light distillates by SFC. Norris and Rowdon (6) described the use of SFC for saturate, olefin, and aromatic analysis by employing a series of LC columns. Campbell et al. (7) described a more successful saturate, olefin, and aromatic hydrocarbon analysis. Temperature programming was employed to elute the aromatics. Fuhr et al. (8) described the determination of aromatics in heating oils and diesel fuels. More recently, Lee et al. (9) described an SFC method for the determination of aromatics in diesel fuels and compared the results to the time consuming FIA method routinely employed in the petroleum industry. The SFC method described by Lee et al. required extensive sample dilution in order to operate in the linear region of the flame ionization detector. Although standard blends were prepared, no quantitative results were presented to describe the full quantitative aspect of the method.

In this paper, a detailed quantitative study is described for the determination of aromatics in jet and diesel fuels by SFC. Data are presented on standard blends derived from gasoline, jet, and diesel fuels. The nonlinearity of the flame ionization detector described by Lee et al. was significantly improved by employing air as the FID makeup gas. The determination of naphthalenes in jet fuels is also discussed. Our goal in the development of the SFC method for total aromatics is simplicity to ensure its usefulness as a rapid, automated routine method. As a result, a single column, a single mobile phase under constant density condition, and no temperature programming or valve switching is employed.

## Experimental

*Instrumentation.* A Lee Scientific 501B supercritical fluid chromatograph equipped with a 175-mL syringe pump, a 0.1-$\mu$L

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Valco injection valve, a Hewlett-Packard 5890 oven, and an H-P flame ionization detector was employed. Both the pump and the injection valve were cooled to 10°C by a Brinkman Lauda RM-6 circulating water bath (VWR Scientific). The carbon dioxide mobile phase (C. I. G. grade, 99.99% pure) was obtained from Matheson Gas. Additional purification of the $CO_2$ was obtained with an inline scrubber filled with activated alumina.

The analysis was performed on a 25-cm × 2.0-mm i.d. column packed with 5-$\mu$m Chromegasphere SI-60 silica (ES Industries). The column oven was held isothermally at 30°C and the pump pressure maintained at a constant 115 atmospheres.

The postcolumn restrictor was constructed from a 25-cm length of 20-$\mu$m i.d. fused-silica tubing (Polymicro Tech) connected directly to the column exit to minimize dead volume, and inserted approximately 5 mm below the FID flame. Flame air and hydrogen flows were 300 and 60 mL/min, respectively. Air at 15 mL/min was used as the FID makeup gas. The FID was operated at 350°C.

*Preparation of standard blends.* To verify the accuracy of the SFC method a number of reference standards of known aromatic concentrations were prepared. The jet fuel saturate composite was obtained by removing the aromatics according to ASTM D1019, *Olefinic Plus Aromatic Hydrocarbons in Petroleum Distillates* (10). The composition of jet fuel aromatics was approximated by adding a mixture of dimethylnaphthalenes (Aldrich Chemical) to a 160°C plus cut of an aromatic rich gasoline reformate. This 160°C plus fraction contained mostly alkylbenzenes and naphthalenes. The small amount of saturates present in the reformate was determined by a PNA analyzer (11). Saturate and aromatic fractions of diesel fuels were obtained by silica gel preparative LC. The saturate and aromatic fractions were blended back in various concentrations by weight to obtain mixtures approximating the composition of fuels.

*Sample preparation prior to SFC analysis.* All samples were diluted 1:1 with carbon disulfide prior to analysis to facilitate introduction into the liquid sampling valve.

## Results and Discussion

*SFC optimization.* The restrictor position in the FID is important to prevent splitting of the saturates peak. This is especially evident in samples with a high normal paraffin content. The restrictor is located as close as possible to the flame to minimize peak splitting. If the restrictor is closer than the 5 mm we used, the base line becomes noisy and the flame is often blown out. The absence of peak splitting is verified by injecting a high boiling normal paraffin ($nC_{22}$) diluted 1:1 in $CS_2$.

Initially, accurate quantitation of the standard jet and diesel fuel blends could not be achieved due to a nonlinear response of the detector as illustrated in Figure 1A. Further dilution of the samples with carbon disulfide did not improve the results. Addition of air as makeup gas (about 15 mL/min) removed this nonlinearity as shown in Figure 1B. Premixing the air with the hydrogen in this manner probably improved the burning characteristics of the FID flame.

*Jet fuel analysis.* A chromatogram of a typical jet fuel separation is shown in Figure 2. Jet fuels are base-line resolved into nonaromatics and 1- and 2-ring aromatics on the silica gel column. Good resolution is obtained between the 1- and 2-ring aromatics. Further work is in progress to confirm the identity of the 1-ring and 2-ring clusters. Table I summarizes the analysis

of the standard jet fuel blends containing known aromatic concentrations. The agreement with actual values is excellent, with only slight bias of 1-2% relative standard deviation (RSD), which may be because of a slight difference in the saturate and aromatic responses. The precision at the 50 wt % aromatic level is approximately 1% RSD. Table II demonstrates that SFC provides excellent results for 2-ring aromatics (naphthalenes) spiked into jet fuel-derived saturated hydrocarbons. Therefore, for jet fuels, SFC may be used for the determination of total saturates, total 1-ring, and total 2-ring aromatic hydrocarbons.

*Diesel fuel analysis.* An SFC chromatogram of a diesel fuel separation is shown in Figure 3. The separation between the saturates and the aromatics is not complete and the aromatic ring separation is not as distinct as in the case with jet fuels.
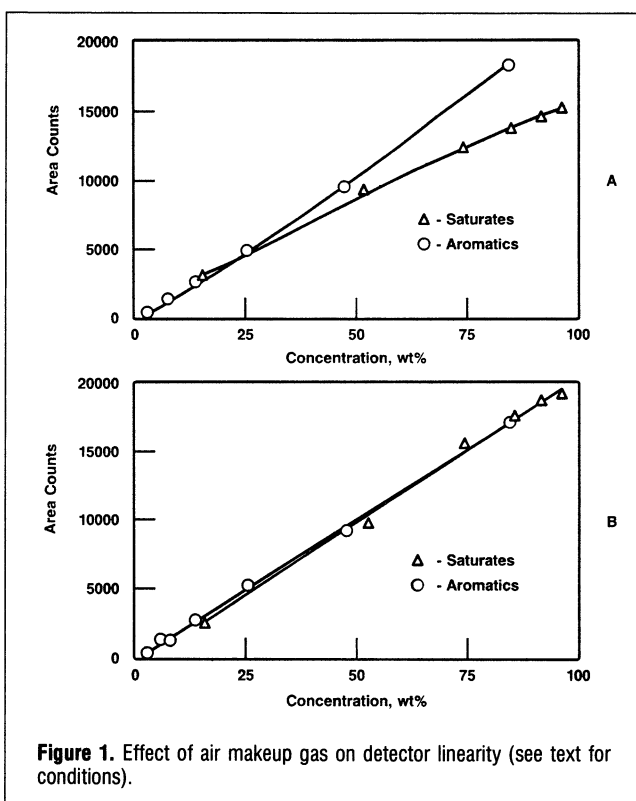


**Figure 1.** Effect of air makeup gas on detector linearity (see text for conditions).
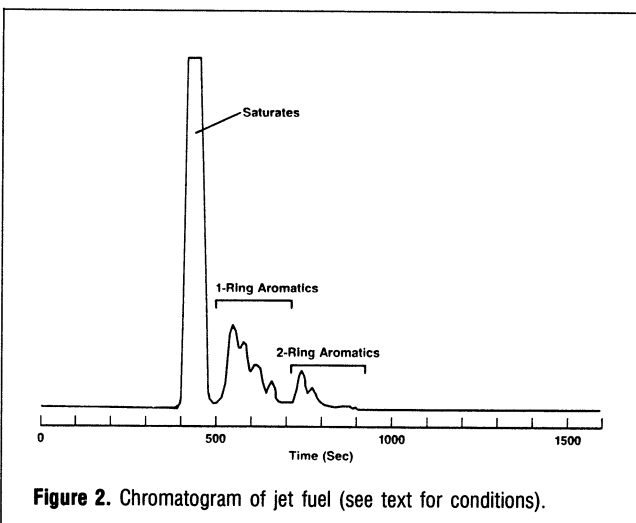


**Figure 2.** Chromatogram of jet fuel (see text for conditions).

The data from the standard diesel fuel blends containing a known aromatic concentration is summarized in Table III and Figure 4. These blends were prepared from aromatics and saturates derived from actual diesel fuels by preparative LC. The present SFC method is accurate to approximately 10% aromatics. Below 10% aromatics, incomplete separation of the saturates and aromatics components causes the measured aromatic content to be higher than actual values. The relative error becomes progressively larger as the aromatic concentrations decrease. For example, the estimated absolute error at the 5% aromatic level is approximately ± 1 wt % aromatics. The precision at the 11–50 wt % aromatic level is approximately 1% RSD (Table V). Further work to improve this resolution is in progress.

Table IV compares the SFC weight percent results to those obtained by preparative LC for a number of diesel fuels. LC is not generally applicable to diesel fuels because the solvent

### Table I. SFC Analysis of Jet Fuel Blends

| Jet blend sample | Actual aromatics (wt%) | SFC aromatics (wt%) | Relative difference |
|---|---|---|---|
| 1 | 50.81 | 51.3 | +0.9% |
| 2 | 42.03 | 42.4 | +0.9% |
| 3 | 32.87 | 33.3 | +1.3% |
| 4 | 26.83 | 27.3 | +1.8% |
| 5 | 21.53 | 21.9 | +1.7% |
| 6 | 18.90 | 19.4 | +2.6% |
| 7 | 15.29 | 15.8 | +3.3% |
| 8 | 11.40 | 11.6 | +1.8% |
| 9 | 6.84 | 7.0 | +2.3% |

### Table II. SFC Naphthalene Results for Jet Fuel Blends

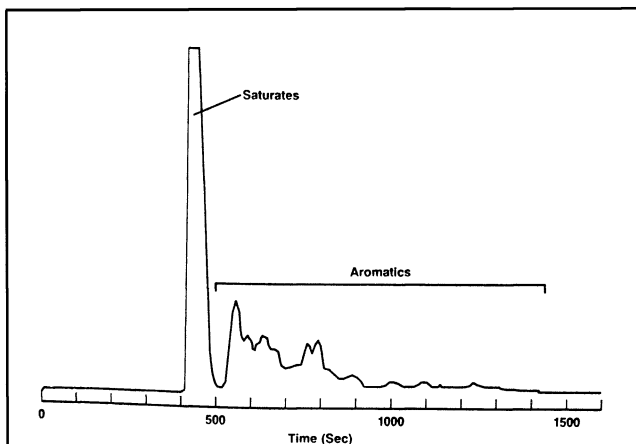| Jet blend sample | Actual naphthalenes (wt%) | SFC naphthalenes (wt%) |
|---|---|---|
| 1 | 0.4 | 0.4 |
| 2 | 0.8 | 0.8 |
| 3 | 1.2 | 1.2 |
| 4 | 1.5 | 1.6 |
| 5 | 1.8 | 1.7 |
| 6 | 2.2 | 2.4 |
| 7 | 2.8 | 2.7 |
| 8 | 3.7 | 3.7 |
| 9 | 4.5 | 4.3 |



Figure 3. Chromatogram of diesel fuel (see text for conditions).

### Table III. SFC Analysis of Diesel Fuel Blends

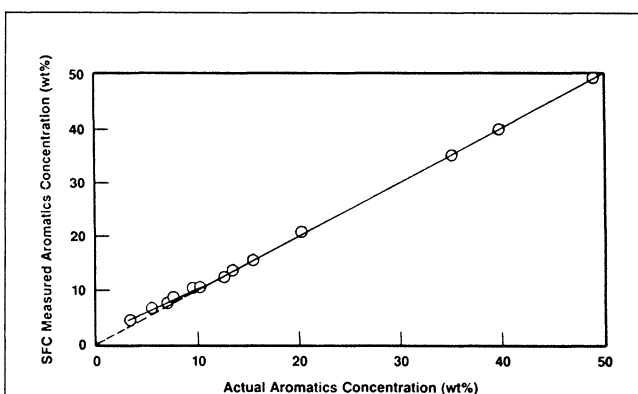| Diesel blend sample | Actual (wt%) | SFC (wt%) | Relative difference |
|---|---|---|---|
| 1 | 49.19 | 48.5 | +1.4 |
| 2 | 39.86 | 39.3 | +1.4 |
| 3 | 35.24 | 34.8 | +1.2 |
| 4 | 20.40 | 20.5 | +0.5 |
| 5 | 15.57 | 15.4 | −1.1 |
| 6 | 13.71 | 13.7 | 0.0 |
| 7 | 12.75 | 12.5 | −2.0 |
| 8 | 10.43 | 10.5 | +0.7 |
| 9 | 9.81 | 10.3 | +5.0 |
| 10 | 7.91 | 8.7 | +10.0 |
| 11 | 7.27 | 7.8 | +7.3 |
| 12 | 5.60 | 6.8 | +21.4 |
| 13 | 3.56 | 4.8 | +34.8 |



Figure 4. Plot of SFC results versus the actual for diesel fuel blends; (a) 10–50 wt% aromatics, slope = 0.98, $r$ = 0.99995, (b) 3–10 wt% aromatics, slope = 0.82, $r$ = 0.9965.

### Table IV. Comparison of SFC with Preparative LC for Diesel Fuels

| Diesel fuel sample | Duplicate LC (wt%) | Average LC (wt%) | SFC (wt%) | Relative difference |
|---|---|---|---|---|
| 1 | 28.4 32.2 | 30.3 | 31.1 | +2.6% |
| 2 | 27.9 26.6 | 27.2 | 27.7 | +1.8% |
| 3 | 30.2 28.3 | 29.2 | 30.9 | +5.8% |
| 4 | 22.2 24.3 | 23.2 | 23.8 | +2.6% |
| 5 | 32.9 32.5 | 32.7 | 33.1 | +1.2% |
| 6 | 32.8 34.7 | 33.8 | 33.5 | −0.9% |
| 7 | 30.3 31.1 | 30.7 | 30.2 | −1.6% |
| 8 | 27.6 30.0 | 28.8 | 28.9 | +0.3% |
| 9 | 32.5 34.4 | 33.4 | 30.0 | −10.2% |
| 10 | 13.0 14.2 | 13.6 | 12.6 | −7.4% |

evaporation step causes a significant loss of the highly volatile 200°C minus components. The results presented in Table IV are for diesel fuels with less than 10% of the sample boiling below 200°C, at which temperature loss of the sample during the solvent removal step is minimized. There is an excellent comparison between the LC and SFC results. Table V summarizes the short term (17 day) repeatability of the SFC method. Excellent precision is obtained.

## Conclusion

SFC provides an accurate and precise method for determination of aromatics in jet (> 1% aromatics) and diesel fuels (> 10% aromatics). Work is in progress to improve the saturate and aromatic separations and to extend the method for diesel fuels to aromatics levels below 10 wt %.

| Table V. SFC Repeatability | | | | |
|---|---|---|---|---|
| Day | Diesel 1 (wt%) | Diesel 2 (wt%) | Jet 1 (wt%) | Jet 2 (wt%) |
| 1 | 48.1 | 11.4 | 24.0 | 5.1 |
| 3 | 48.8 | 11.4 | 24.3 | 5.0 |
| 4 | 48.7 | 11.2 | 24.5 | 4.9 |
| 5 | 48.8 | 11.4 | 24.2 | 4.8 |
| 8 | 48.7 | 11.5 | 24.5 | 5.0 |
| 9 | 48.7 | 11.5 | 24.4 | 4.9 |
| 10 | 48.8 | 11.5 | 24.4 | 5.0 |
| 11 | 48.2 | 11.4 | 24.4 | 5.2 |
| 15 | 48.8 | 11.2 | 24.1 | 5.0 |
| 17 | 48.2 | 11.3 | 24.2 | 4.8 |
| Average | 48.5 | 11.4 | 24.3 | 5.0 |
| S.D. | 0.3 | 0.1 | 0.2 | 0.1 |
| R.S.D. | 0.6% | 1.0% | 0.7% | 2.6% |

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