



THE DETERMINATION OF OLEFIN CONTENT IN GASOLINE BY SUPERCRITICAL FLUID CHROMATOGRAPHY (SFC)

INTRODUCTION

Various methods have traditionally been used to determine olefin content in gasoline with the most widely used being fluorescence indicator adsorption (FIA). FIA employs a long silica column typically about four feet in length. Gasoline is mixed with fluorescent indicator dyes and the mixture is passed through the column. Separation of olefinic, aromatic and saturate compounds is observed under UV light. The quantitation is dependent on the accuracy of the observation of the fluorescent bands. Consequently the method is not only tedious, but also subject to operator bias. Another analysis that is frequently used is the PIONA method that is based on GC and GC/MS. These methods depend on the complete separation of hydrocarbons in gasoline followed by summation of the peaks corresponding to the olefins. The presence of closely related compounds and the large number of possible compounds dictate that the highest resolution chromatography be coupled with the highest resolution mass spectrometer available. For example, typical low-cost tabletop GC/MS systems do not have adequate resolution for complete separation of all the components. Consequently, the cost of instrumentation as well as the operator sophistication required precludes the use of this technique in most refinery laboratories. As a result, FIA is preferred to this method and is used at the refineries.

In this note we describe an alternative method using supercritical fluid chromatography to obtain a class type separation for the determination of olefins in gasoline. Since it has become an official ASTM (American Society for Testing and Materials) method, ASTM D6550, the popularity has increased due to ease of use and accuracy. In addition, the California Air Resources Board (CARB) mandated as of January 1, 2002 that all gasolines being sold or refined in the state of California must be analyzed by ASTM D6550 to determine the olefin content.

METHOD OVERVIEW

ASTM D6550 uses supercritical carbon dioxide as the mobile phase along with two six-port switching valves to achieve the desired group type separation. The switching valves are needed to connect a silica column and silver loaded silica column in series and to direct the eluent flow between the two columns. The sample first passes through the silica column to separate the saturate and olefin from the aromatic and polar compounds. While the aromatic and polar species are retained on the silica column, the olefinic and saturate compounds pass through to the silver-

loaded silica column where the olefinic species are trapped and the saturates continue through to the detector. The valves are then actuated so that the silica column is in the backflush mode to remove the polar and aromatic compounds. This is followed by returning the valves to their original position and forward flushing the silver-loaded column to remove any remaining saturates. At this point the olefinic species are the only compounds still retained, and the valves are actuated to backflush them from the silver-loaded column to the detector. Switching times are determined by analysis of standard solutions and an external calibration curve is created to determine the olefin content in gasolines.

EXPERIMENTAL

Instrumentation: All chromatographic analyses were performed with a Selerity Technologies' Series 3000 SFC equipped with two six-port switching valves and a flame ionization detector.

Columns: A 50-cm X 1-mm ID silica gel and a 5-cm X 1-mm silver-loaded silica column were used and obtained from Selerity Technologies (Salt Lake City, UT, USA).

Oven temperature at 75°C, Flame ionization detector temperature at 400°C.

Reagent and Samples: HPLC grade hexane and toluene used for timing solutions were obtained from Aldrich Chemical Co. (Milwaukee, WI, USA). ASTM round robin samples were obtained from Spectrum Quality Standards (Houston, TX, USA). All of the gases used were obtained from Airgas (Salt Lake City, UT, USA). SFC grade carbon dioxide was used for the carrier gas and technical grade helium was used to actuate the injection and switching valves.

RESULTS

A typical chromatogram of gasoline obtained from this method on the Selerity Technologies' Series 3000 SFC is shown in Figure 1. The chromatogram shows a class-type separation of the three components found in gasoline: saturates, aromatics, and olefins. Table 1 specifies the conditions used during this analysis and Table 2 shows the results obtained from the Series 3000 SFC that was submitted to the ASTM round-robin for method D6550 acceptance. The data is from two different laboratories and is compared with the average of all of the participants (6 laboratories) in the study. As you can see the results obtained from the Series 3000 are well within the accepted tolerances of the round-robin.



CONCLUSION

The Series 3000 SFC with switching valve option provides results that are within the range expected for a chromatographic method. With the consistent results obtained, the Series 3000 is preferred to the traditional FIA method and provides an economical and accurate alternative to GC and GC/MS methods.

TABLE 1 :

CHROMATOGRAPHIC CONDITIONS

Mobile phase: Carbon dioxide, at 220 atm
 Oven Temperature: 75 °C
 FID: 400 °C

FIGURE 1 :
 CHROMATOGRAPHIC RESULTS OF GASOLINE SEPARATED INTO ITS COMPONENTS:
 SATURATES, AROMATICS, AND OLEFINS.

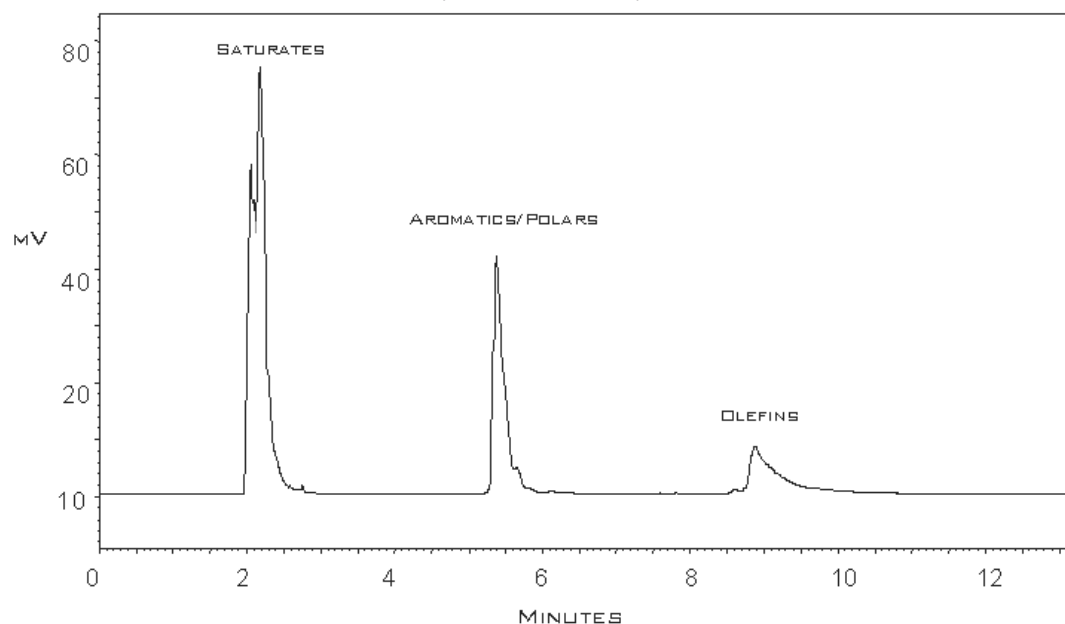


TABLE 2:

RESULTS OBTAINED FROM THE SERIES 3000 SFC COMPARED TO THE ASTM ROUND-ROBIN AVERAGE

| Series 3000 Runs | Sample Number | | | | | | | | | | | | | | |
|------------------|---------------|-----|------|------|-----|-----|------|-----|------|------|-----|------|------|------|------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| System 1 Run 1 | 7.0 | 1.3 | 17.8 | 11.0 | 1.4 | 3.0 | 9.8 | 4.8 | 13.6 | 12.1 | 6.4 | 21.2 | 13.6 | 25.7 | 11.8 |
| System 1 Run 2 | 7.1 | 1.3 | 17.8 | 10.9 | 1.4 | 3.2 | 10.3 | 4.8 | 14.4 | 12.2 | 6.5 | 20.9 | 13.8 | 26.9 | 11.0 |
| System 2 Run 1 | 6.7 | 0.9 | 19.0 | 10.5 | 1.1 | 2.4 | 9.4 | 4.1 | 13.6 | 12.0 | 6.1 | 20.3 | 14.3 | 27.5 | 11.7 |
| System 2 Run 2 | 6.7 | 0.8 | 19.2 | 10.5 | 1.1 | 2.4 | 9.4 | 4.1 | 13.7 | 12.0 | 6.1 | 20.2 | 14.3 | 27.5 | 11.6 |
| RR Average* | 6.8 | 1.2 | 18.3 | 10.5 | 1.3 | 2.7 | 9.1 | 4.1 | 13.0 | 11.5 | 6.0 | 19.3 | 13.5 | 25.9 | 11.1 |

* "ROUND-ROBIN AVERAGE" REPRESENTS AVERAGE OF DATA FROM ALL ROUND-ROBIN PARTICIPANTS.