We're Going Global

GASOLINE COMPOSITION BY ASTM D1319 FIA

The three major types of hydrocarbons in gasoline are saturates, olefins, and aromatics. They may be identified and quantified by running **ASTM D1319** (EI IP156) Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption commonly called **FIA**.

Why do we need to test FIA?

Olefins in gasoline can contribute to photochemical reactions in the atmosphere which result in the formation of photochemical smog in susceptible urban areas. Olefins are reactive and are easily oxidized and polymerized to form gums and varnishes. Olefins do not occur naturally in crude oil but are formed during refining.

Aromatics in gasoline have an effect on the combustion quality of the fuel and an increased amount of aromatics can have a negative impact on vehicle emissions.

There are several methods available for the measurement of olefin and aromatic content but the EPA has prescribed that ASTM D1319 be used to quantify the olefin content in Reformulated Gasoline (RFG). ASTM D1319 may also be correlated to determine Aromatics in RFG gasoline.

The determination of the total volume % of saturates, olefins, and aromatics in petroleum fractions is also important in characterizing the quality of gasoline blending components and feeds for catalytic reforming processes. ASTM D1319 can also be used to measure the quality of other fuels, such as specified in ASTM D1655 Aviation Turbine Fuels.

ASTM D1319 FIA Test Method Summary

This test was developed in the early 1940s. A 0.75 mL of sample of the fuel to be tested is introduced into a special glass adsorption column tightly packed with activated silica gel. The top of the column is packed with a small layer of the silica gel containing a mixture of fluorescent dyes. Alcohol is added to desorb the sample down the column. Air pressure is applied to move the sample down the column.

The aromatics, olefins, saturates and dyes are separated in accordance with their adsorption affinities to the activated silica gel. By measuring the separation of each dye, the relative proportions of saturates, olefins and aromatics can be determined. The volume percentage of each hydrocarbon type is calculated from the length of each zone in the column.

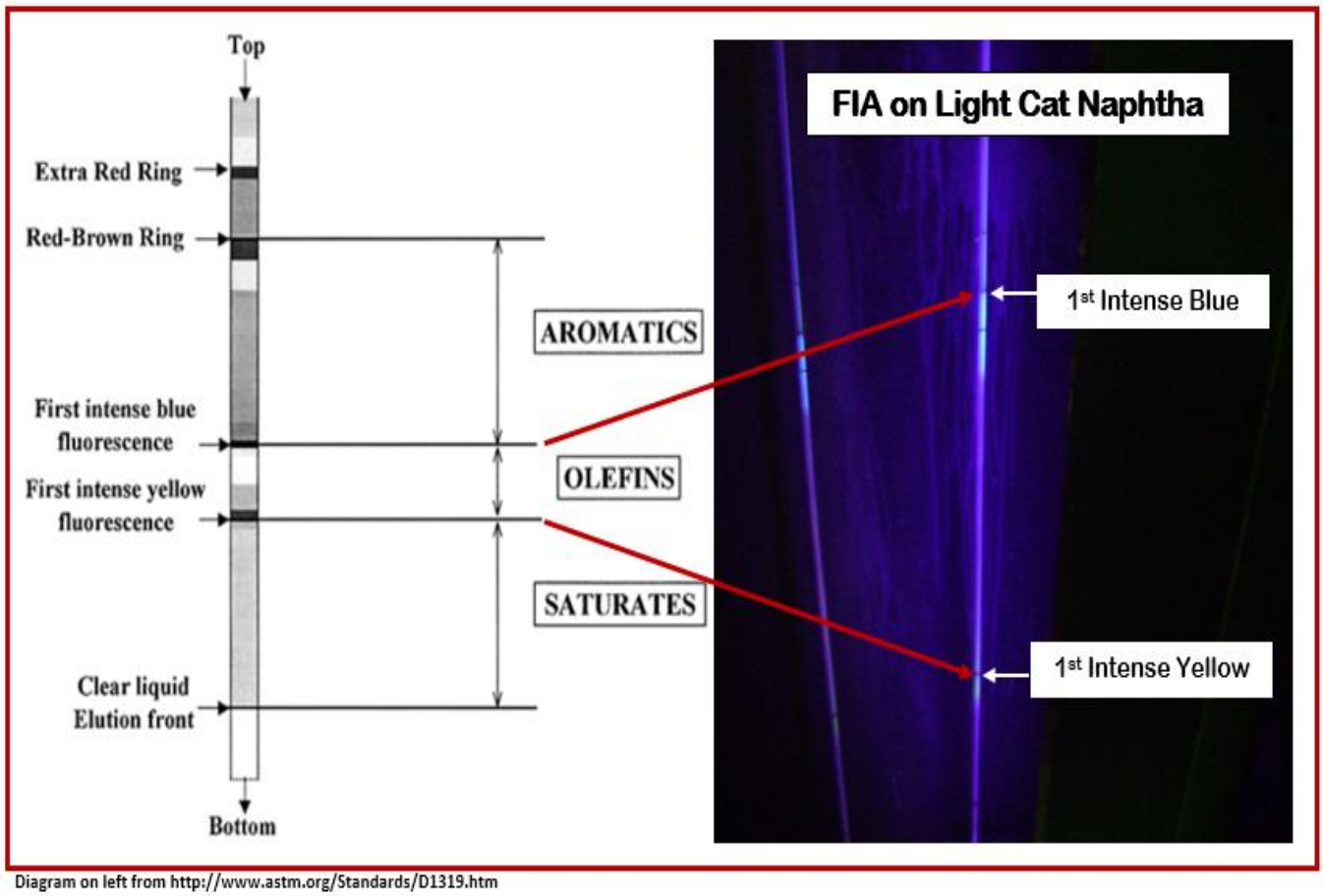


Diagram on left from http://www.astm.org/Standards/D1319.htm

The fluorescent dyes are separated selectively, with the hydrocarbon types, and make the boundaries of the aromatic (blue band), olefin (yellow band), and saturate (clear front end) visible under ultraviolet light.

The saturates separate and move down the column first because they have less of an affinity for the silica gel than olefins and aromatics.

The olefins have less of an affinity for the silica gel than aromatics and move down the column before the aromatics.

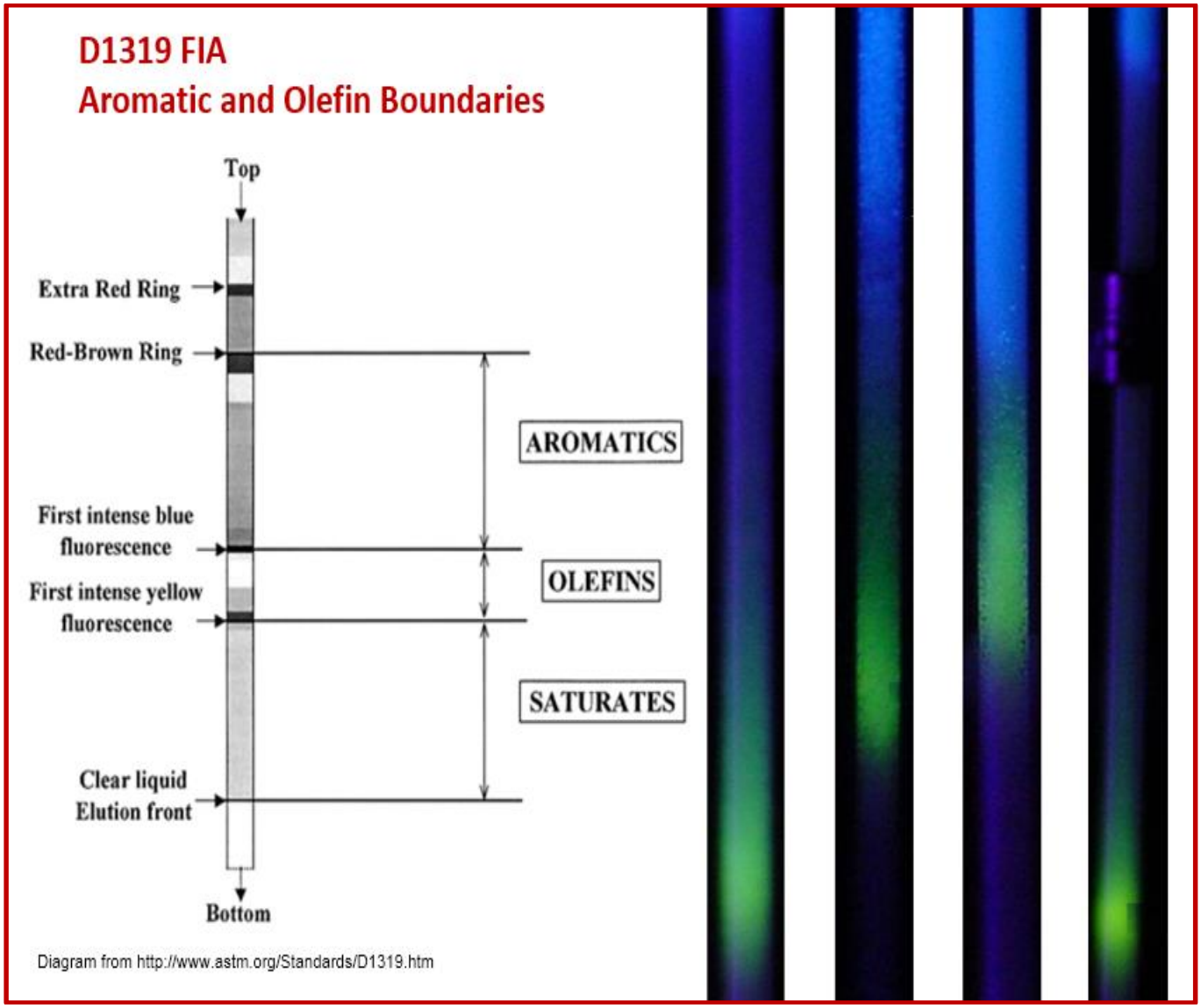
The dye mixture contains three different components, one which has an affinity for silica gel which is greater than the saturates but less than the olefins. This dye (yellow band) marks the interface between the saturates molecules and the olefins as it moves through the column.

A second dye component has an affinity for the silica gel somewhere between that of the olefins and aromatics and this blue band marks the olefin-aromatic boundary.

A third dye component (red-brown band) falls between the aromatics and the isopropyl alcohol use as the solvent, marking the final boundary.

First Intense Blue – First Intense Yellow?

It takes a highly trained and skilled chemist or technician to run a FIA. Please see the four FIA tubes on the right in the picture below. What do you see as the most intense blue or yellow? And bear in mind when you are marking the tubes the sample is moving. You must be quick and decisive in your determination.



ASTM D1319 Adsorption Columns - Analyzer Sections

Standard Wall (left) **Precision Bore (right)**

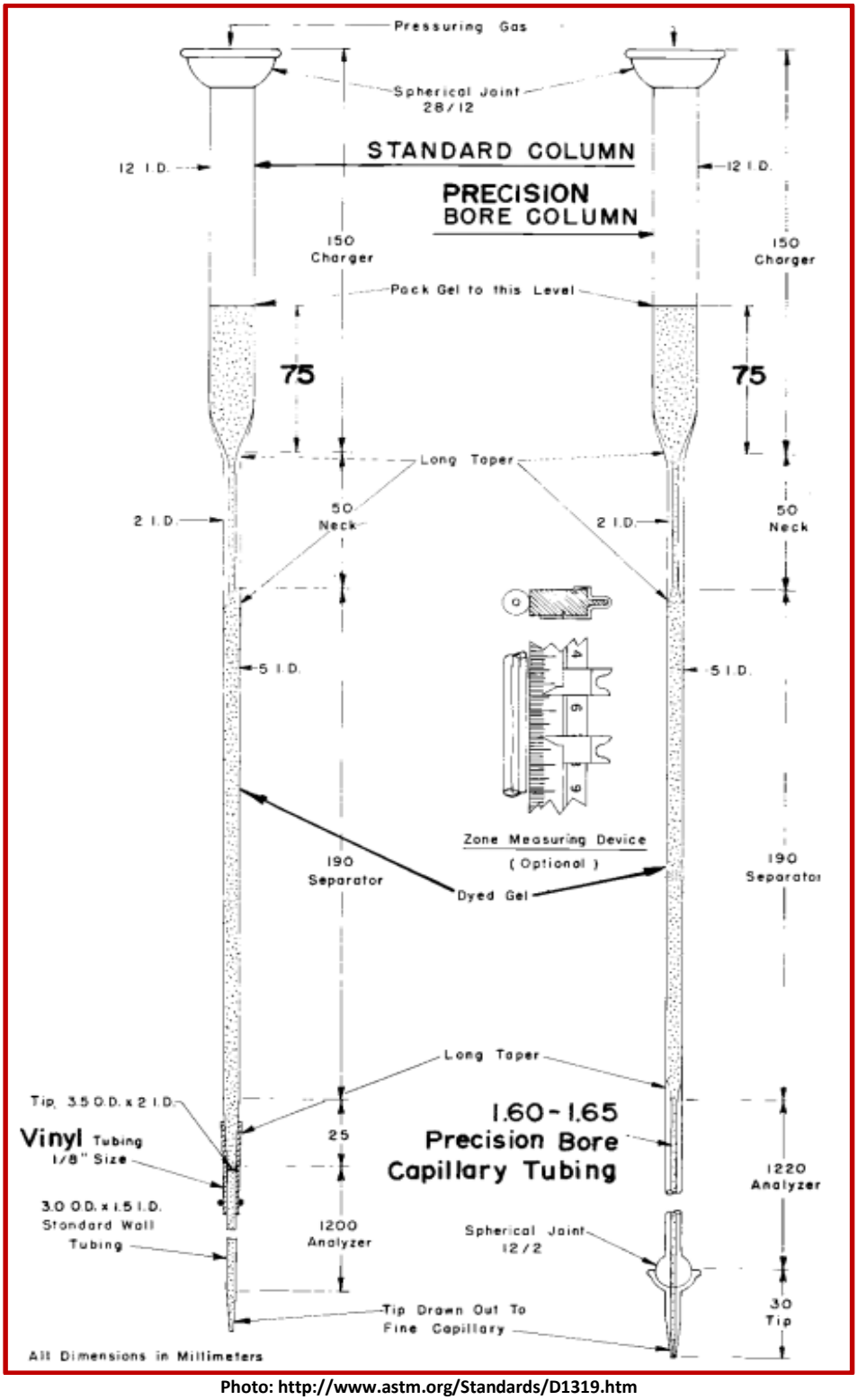


Photo: http://www.astm.org/Standards/D1319.htm

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RFG Regulations and Olefin Content by ASTM D1319

Code of Federal Regulations

The electronic code of federal regulations can be found at: http://www.ecfr.gov/

Title 40: Protection of Environment
Chapter I - ENVIRONMENTAL PROTECTION AGENCY
Subchapter C - AIR PROGRAMS
PART 80—REGULATION OF FUELS AND FUEL ADDITIVES
Subpart D—Reformulated Gasoline
40 CFR Ch. I (7–1–10 Edition)

§80.46 Measurement of reformulated gasoline and conventional gasoline fuel parameters.

(b) Olefins. Olefin content must be determined by use of the following methods:

(1) Through December 31, 2015, olefin content must be determined using ASTM D1319. Beginning January 1, 2016, the olefin content of gasoline must be determined by a test method approved under §80.47.

(2) Through December 31, 2015, any refiner or importer may determine olefin content using ASTM D6550 for purposes of meeting any testing requirements involving olefin content, provided that the refiner or importer test result is correlated with the method specified in paragraph (b) (1) of this section on a site-specific basis, in order to achieve an unbiased prediction of the result in volume percent, for the method specified in paragraph (b) (1) of this section.

Other ASTM Test Methods for Hydrocarbon Composition of Gasoline

ASTM D6550

Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography

This test method compares favorably with Test Method D1319 (FIA) for the determination of total olefins in motor gasolines. It does not require any sample preparation, has a comparatively short analysis time of about 10 min, and is readily automated. Alternative methods for determination of olefins in gasoline include Test Methods D6839 and D6296.

ASTM D6839

Hydrocarbon Types, Oxygenated Compounds, and Benzene in Spark Ignition Engine Fuels by Gas Chromatography

This test method covers the quantitative determination of saturates, olefins, aromatics, and oxygenates in spark-ignition engine fuels by multidimensional gas chromatography. Each hydrocarbon type can be reported either by carbon number or as a total.

ASTM D6296

Total Olefins in Spark-ignition Engine Fuels by Multidimensional Gas Chromatography

The fast total olefins (FTO) system analyzes streams with concentrations of 0.2%-35% olefins. This GC system determines C4 - C10 olefins in all finished motor gasolines, straight naphthas and FCC naphthas. It reports in weight % and liquid volume % and a full analysis takes just 20 minutes. The FTO analysis exceeds the repeatability capabilities of ASTM D 1319 (the Fluorescent Indicator Absorption-FIA-method) and incorporates ASTM D 6296 - Total Olefins in Spark-Ignition Engine Fuels by Multi-Dimensional GC.

ASTM D6730

Standard Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by 100–Meter Capillary (with Precolumn) High-Resolution Gas Chromatography

The ASTM D 6730 method is a Gas Chromotography method for the detailed hydrocarbon analysis (DHA) of gasolines.

ASTM D5443

Standard Test Method for Paraffin, Naphthene, and Aromatic Hydrocarbon Type Analysis in Petroleum Distillates through 200 °C by Multi-Dimensional Gas Chromatography

This test method covers the determination of paraffins, naphthenes, and aromatics by carbon number in low olefinic hydrocarbon streams having final boiling points of 200 °C or less. If olefin content is >5% D5443 is not applicable.