# CLASS COMPOSITION OF LIQUID FUELS BY LIQUID CHROMATOGRAPHY

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Liquid fuels are complex mixtures of hydrocarbons, obtained from the distillation of petroleum products.

A simple, rapid estimation of combustion character of a fuel can be made if the amount of aliphatic, aromatic, and di aromatic hydrocarbons can be determined.

Most saturated aliphatics in the heptane-decane range have heats of combustion of 1200-1300 k cal/mole and require about 45 cubic feet of air per cubic foot of organic vapor for complete combustion. The unsaturated aliphatics have heats of combustion about 10% less than the corresponding saturate member and require about 40 cubic feet of air per cubic foot of organic vapor for complete combustion. Mono aromatic compounds have heats of combustion of 750 k cal/mole and require about 35 cubic feet of air per cubic foot of organic vapor for complete combustion. The naphthanic compounds have heats of combustion of 1500 k cal/mole and require some 60 cubic feet of air per cubic foot of organic vapor for complete combustion. Bi phenyl compounds have heats of combustion of 1800-1900 k cal/mole and require some 75 feet of air per cubic foot of organic vapor for complete combustion.

Thus, if the amount of saturated aliphatic, aromatic, and di aromatic hydrocarbons are known, estimation of the heat of combustion and air requirements of a fuel can be made. It must be remembered, however, that in most combustion processes the amount of air is fixed because of draft. Knowing the availability of air for the combustion, and that required by the fuel, allow estimates to be made as to whether the combustion will be complete or not.

The information on the class composition of a liquid fuel can be obtained in less than 12 minutes using Waters' technology.

## SCOPE

This method describes a procedure for the determination of the aliphatic, aromatic, naphthanic, and bi phenyl compounds in petroleum fractions that distill below 600°F. Samples should be depentanized if they contain any of the following -- $C_3$ or lighter hydrocarbons; more than 5% $C_4$ hydrocarbons; more than 10% $C_4$ and $C_5$ hydrocarbons.

## OUTLINE OF METHOD

The sample, 2λ, is introduced by means of a microliter syringe into a high pressure, high speed liquid chromatograph.

The hydrocarbons are retained according to their sorption affinities into aliphatic, aromatic, naphthanic, and bi phenyl compounds.

The detector is a low volume differential refractometer that displays the mass of material eluting from the end of the column. The response of the detector is dependent upon the index of refraction difference between the solute and the solvent.

With this method a semi skilled technician can perform a separation in twelve minutes.

The recorder gives a permanent display of the separation. No additions have to be made to the sample and colored or fluorescing compounds will not interfere.

The separation can be done in the laboratory without any special precautions.

Once equilibrium has been established during initial start up, the equipment is ready for use at any time.

## APPARATUS

The separation has been achieved on a Waters' ALC model 201 under the following conditions:

Column: PORASIL T - 4 ft. x 2.3 mm I.D.

Solvent: n-heptane - J. T. Baker - Baker Grade M 955
boiling range 98-99°C

Flow rate: 1.0 ml/min.

Pressure drop: 550 psig

Attenuator setting: 8X

Sample volume: 2.0λ

Chart speed: 12 in/hr

Septum material: Buna-N

Retention volumes:

| | |
|---|---|
| saturated aliphatic<br>unsaturated aliphatic<br>cyclo aliphatic | 4.92 mls |
| aromatics | 6.59 mls |
| naphthanic | 8.17 mls |
| bi phenyls | 9.15 mls |

## APPLICATIONS

Chromatograms are attached displaying the separation of a standard misture and four different liquid fuels. The standard is a misture of n-octane, benzene, 2-methyl naphthalene and ρ-methyl biphenyl. The samples are a jet fuel, #2 fuel oil, two #6 fuel oil, and bunker C fuel.

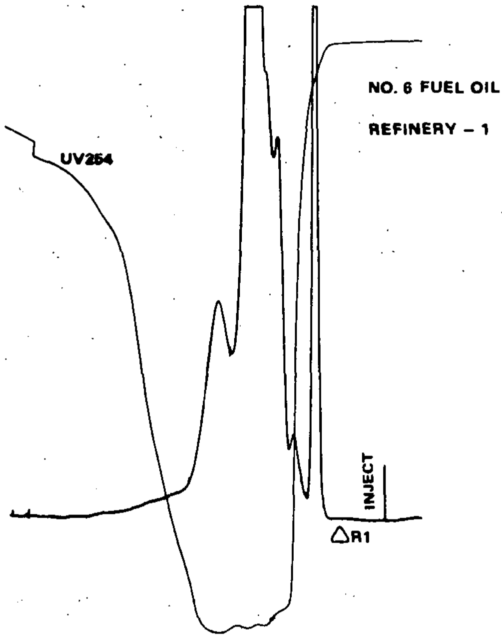
Note the difference of composition between the two #6 fuel oils from the different refineries.

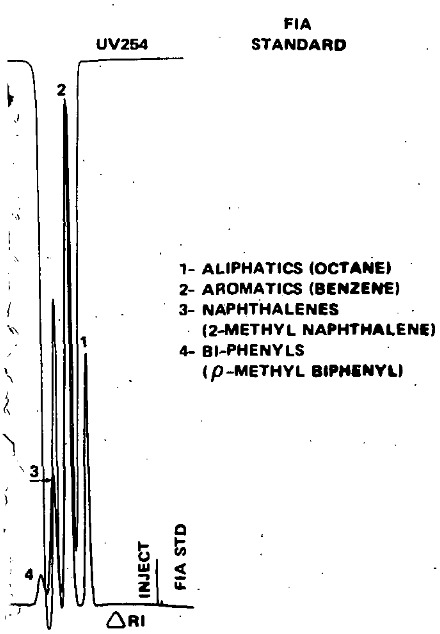
The chromatographic evidence confirms what is known about these fuels, as you go from the jet fuel through #2-#6 fuel oil to the bunker C the amount of condensed aromatics increase.

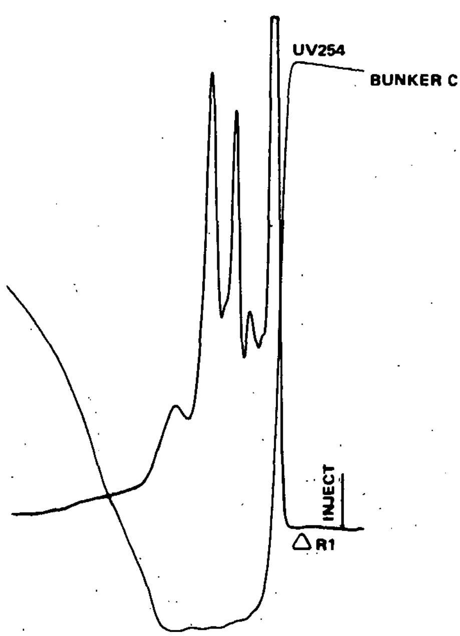
Thus, by determining composition of a fuel and knowing the air required for complete combustion, the draft requirement of a combustion process could be adjusted.

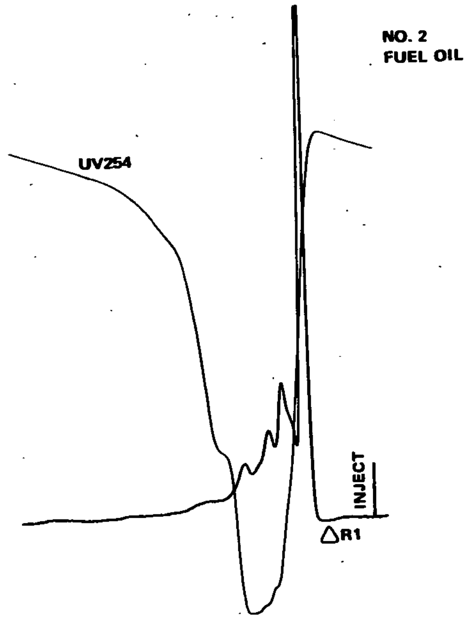
Reproducibility of the method, as determined from ten runs of the #2 fuel oil, is -

| | |
|---|---|
| aliphatics | ±0.80% |
| aromatics | ±1.40% |
| naphthalenic | ±1.18% |
| bi phenyl | ±1.80% |

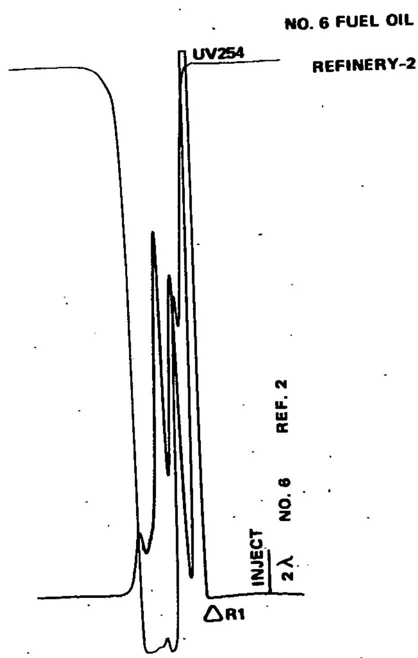

NO. 6 FUEL OIL
REFINERY – 1
UV254
INJECT
△R1


FIA
STANDARD
UV254
1
2
3
4
INJECT
FIA STD
△RI
1- ALIPHATICS (OCTANE)
2- AROMATICS (BENZENE)
3- NAPHTHALENES
(2-METHYL NAPHTHALENE)
4- BI-PHENYLS
(ρ-METHYL BIPHENYL)


UV254
BUNKER C
INJECT
△R1


NO. 2
FUEL OIL
UV254
INJECT
ΔR1


UV254
JET FUEL
A-1
INJECT
JET A-1
ΔRI


NO. 6 FUEL OIL
UV254
REFINERY-2
REF. 2
NO. 6
INJECT
2λ
ΔR1