An Investigation of Hydrocarbon Flames using Probe Sampling and GC/MS

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ABSTRACT

Fundamental operation of the Gas Chromatographer/Mass Spectrometer (GC/MS) is discussed. Differences between detection methods are discussed and specific analysis issues are considered. Experimental results by analyzing two conventional jet fuels (Jet-A and JP-8) and a synthetic jet fuel (S-8) are presented and compared. Gas Chromatography/Mass Spectrometry is used to qualify the components of each fuel. Several batches of S-8 from two sources, NASA and AFRL, are analyzed and compared. Strong similarities between the batches are observed, although key differences indicate they are not from the same batch. Results of S-8 fuel analysis are further compared to those obtained by NIST. While good agreement is seen, variations in injection and Gas Chromatography programs are noted to yield discrepancies. Results common to all fuel types show interesting patterns in the peak distribution. Components are eluted in order of increasing molecular weight and isomers of components of the same molecular weight are eluted together. Normal alkanes are the last of each molecular weight group to be eluted. Finally, aromatics follow a similar trend as alkanes, but do not match the molecular weight of the alkane group with which they elute.

FUNDAMENTAL OPERATION OF GC/MS:

Gas Chromatography (GC):
−Sample is injected into column
−Column separates sample mixtures by slowing the flow of mixture components at different rates
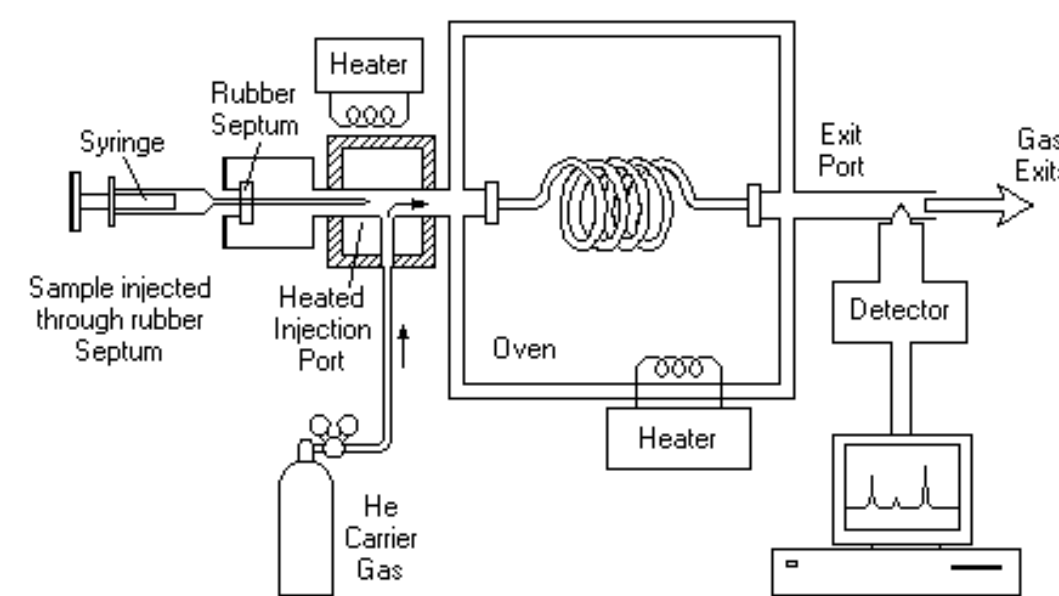−As components elute from the column, they are sent through a detector

Figure 1 – Fundamental parts of a Gas Chromatograph
Image Courtesy: Department of Chemistry, McMaster University, Ontario, Canada[1]

Mass Spectrometry (MS):
−"Source" ionizes components eluted from the column
−Ions are directed into an electrical field created by voltages applied to conductive rods
−Ions of particular mass to charge ratio have stable paths through the rods and reach the detector
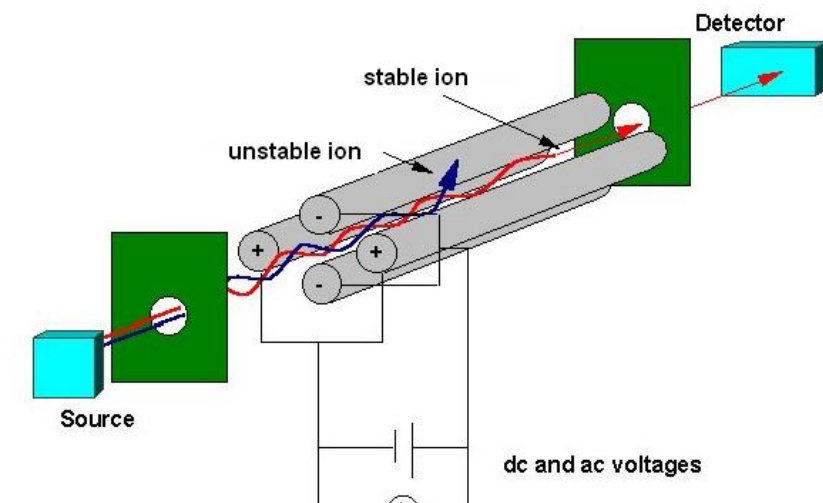−Varying the electrical field allows particular ions through

Figure 2 – Fundamental parts of a Quadrupole Mass Spectrometer, the kind used on this project.
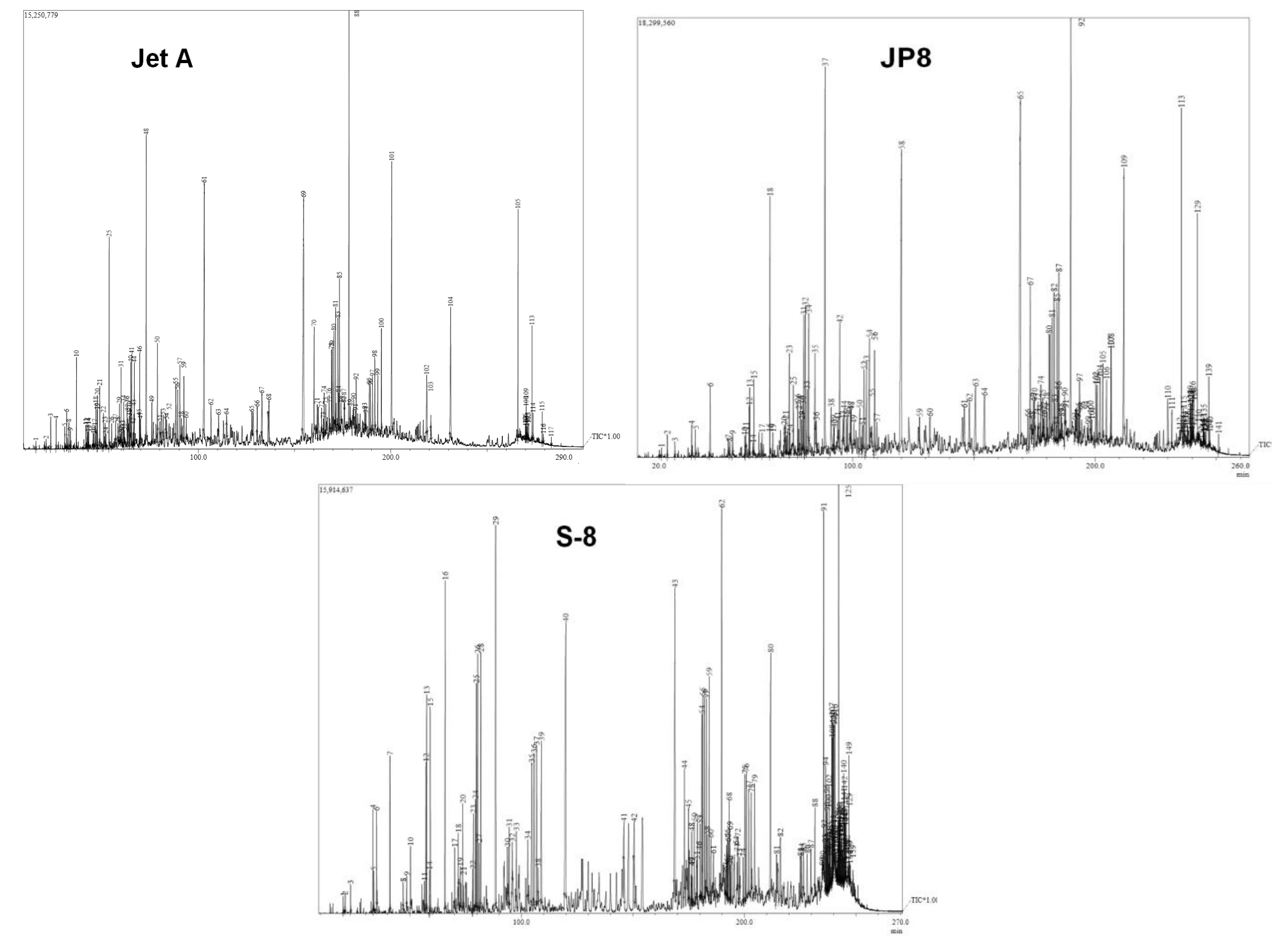**Image Courtesy: Department of Chemistry, University of Adelaide, Australia[2]**

Other Common Detection Methods:
−Flame Ionization Detector
−Specializes in quantifying organic hydrocarbons
−Thermal Conductivity Detector
−Specializes in detecting non-hydrocarbons

Advantages of GC/MS:
−GC specializes in separating mixtures into components
−MS specializes in identifying individual compounds
−The combination provides a "best of both worlds" approach.

References:
1: http://www.chemistry.mcmaster.ca/~chem2oa3/labmanual_2002-03/2oa3_exp2.html
2:http://www.chemistry.adelaide.edu.au/external/soc-rel/content/quadrupo.htm

SAMPLE CHROMATOGRAMS OF JET FUELS:

Figures 3,4,5 – Mass Spectrographs for Jet A, JP-8 and S-8 Jet fuels. Note the large number of peaks for all three cases

Separation Method Details:
−Column:
−5 meter tuning column (5% diphenyl / 95% dimethyl polysiloxane, 1.0 μm film thickness)
−100 meter column (100% dimethyl polysiloxane, 0.5 μm film thickness)
−Optimized for hydrocarbon seperation
−Temperature is controlled by the GC. A specific program is chosen, ramping the temperature from 60°C to 250°C over the course of approximately 3 hours.
−Holds are placed at temperatures in the middle of the program to optimize separation of intermediate compounds
−Large number of components and heavy components necessitate long programs with high temperatures for this length column
−Temperature programs are largely empirically chosen

Data Analysis Method:
−Computer data system collects output mass spectra from the MS
−Peaks are integrated by program "GCMSSolutions"
−Compounds are identified by their mass spectra by looking up the spectra in an NIST database

RESULTS OF MS ANALYSIS OF JET FUELS:

Name	Jet A	JP8	S-8
# of Peaks Identified	117	141	149
Primary Species:	Dodecane	Decane	Octane
	Hexadecane	Dodecane	Nonane (5)
	Decane	Tridecane	Decane (3)
	Octane	Cyclohexane	Undecane (2)
	Cyclohexane	Benzene	Dodecane (1)
	Benzene	Benzene Isomers	Tridecane (4)
	Benzene Isomers	Non-Hydrocarbon Additives	Tetradecane (6)

Table 1 - Components identified in Jet Fuels. Numbers in parenthesis indicate ranking in area percent of that compound's peak. Note the absence aromatic molecules from the synthetic fuel, S-8

Trends in the Chromatograms of Jet Fuels:
−Compounds elute in order of increasing molecular weight
−Compounds with the same molecular weight elute in the following order:
−Multi-methyl isomers
−Mono-methyl isomers
−n-alkanes
−The n-alkane of each weight is the last of that weight to elute. Thus, peaks can be grouped by molecular weight, with the weight of each group increasing by 14
−Cyclic and aromatic molecules follow a similar trend, but do not match the molecular weight of the alkane group with which they elute
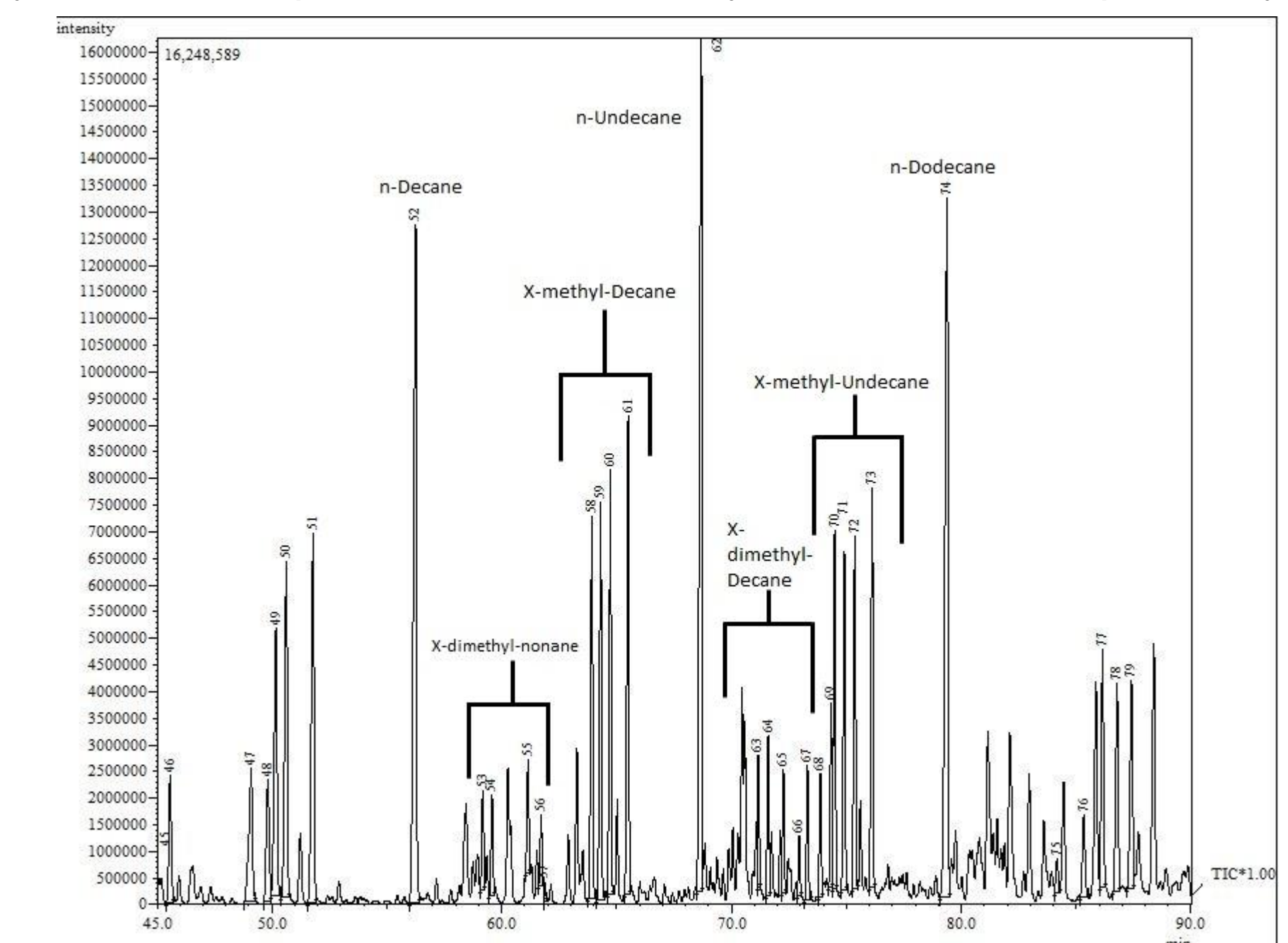−Only saturated aliphatic and aromatic hydrocarbons were positively identified

Figure 6– Portion of S-8 chromatogram, showing features described, such as grouping of isomers and major alkane peaks

Comparison of NASA and Air Force Research Laboratory (AFRL) S-8 Batches:
−Strong similarities exist between the batches
−Many matches for retention time and compound between NASA and AFRL
−More than 2/3 of total identified compounds match (~70 matches/90 identified compounds)
−More stringent peak selection criteria reduce total number of compounds from above (149 peaks to 90 peaks)
−Matches for major compounds are expected because these are the same base fuel
−Small differences indicate that these are different batches of S-8 fuel
−NASA batch is missing lighter components present in AFRL batch
−NASA batch is possibly weighted toward heavier compounds
−Injection method errors may cause bias from one sample run to the next