



# Hydrocarbons and fuels analyses with the supersonic gas chromatography mass spectrometry—The novel concept of isomer abundance analysis

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## ABSTRACT

Hydrocarbon analysis with standard GC–MS is confronted by the limited range of volatile compounds amenable for analysis and by the similarity of electron ionization mass spectra for many compounds which show weak or no molecular ions for heavy hydrocarbons. The use of GC–MS with supersonic molecular beams (Supersonic GC–MS) significantly extends the range of heavy hydrocarbons that can be analyzed, and provides trustworthy enhanced molecular ion to all hydrocarbons. In addition, unique isomer mass spectral features are obtained in the ionization of vibrationally cold hydrocarbons. The availability of molecular ions for all hydrocarbons results in the ability to obtain unique chromatographic isomer distribution patterns that can serve as a new method for fuel characterization and identification. Examples of the applicability and use of this novel isomer abundance analysis (IAA) method to diesel fuel, kerosene and oil analyses are shown. It is suggested that in similarity to the “three ions method” for identification purposes, three isomer abundance patterns can serve for fuel characterization. The applications of the Supersonic GC–MS for engine motor oil analysis and transformer oil analysis are also demonstrated and discussed, including the capability to achieve fast 1–2 s sampling without separation for oil and fuel fingerprinting. The relatively fast analysis of biodiesel is described, demonstrating the provision of molecular ions to heavy triglycerides. Isomer abundance analysis with the Supersonic GC–MS could find broad range of applications including petrochemicals and fuel analysis, arson analysis, environmental oil/fuel spill analysis, fuel adulteration analysis and motor oil analysis.

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## 1. Introduction

Hydrocarbon analysis by gas chromatography mass spectrometry (GC–MS) is of vital importance to a broad range of applications and its importance is greater than commonly perceived. Petrochemicals and fuels are obviously the most important type of hydrocarbon mixtures which require characterization and analysis in almost all the steps of fuel preparation. However, currently the relative use of GC–MS in comparison with GC with flame ionization detector (FID) is significantly lower than in other areas of GC. The main reason for this is that GC–MS often gives only little more information than GC–FID for hydrocarbons since the electron ionization (EI) mass spectra of all the heavy saturated hydrocarbons are practically the same, as they suffer from the lack of molecular ions and share similar dominant low mass fragments. Furthermore, these hydrocarbons are not easily amenable for chemical ionization and are incompatible with electrospray LC–MS or even with UV detection of HPLC. On the other hand GC–FID can typically detect much

less volatile (much bigger) hydrocarbons than GC–MS. Thus, the main tools in the arsenal of analytical chemistry are weak when it comes to hydrocarbon analysis.

We note that hydrocarbon analysis encompasses several additional important areas such as arson analysis, transformer oil analysis, pharmaceutical and perfume oil analysis, environmental oil/fuel spill analysis, fuel adulteration analysis and motor oil analysis particularly in engines and vehicle exhausts. The subject of fuel, such as diesel fuel characterization and identification is of particular importance for forensic arson investigations, environmental forensic and in the exploration of fuel adulteration.

GC–MS is extensively used in areas of oil fingerprinting, particularly with a range of biomarkers [1,2] and in arson residue investigations [3]. However, GC–MS is mostly used for the detection of minor components in fuels, such as aromatic and polycyclic aromatic hydrocarbons (PAH) and their derivatives, and “biomarkers” (especially, for oil analysis), while providing only general information about the major fuel components namely alkane distributions. The main reason for this strategy as described above is that the EI mass spectra of all the heavy hydrocarbons are very similar, practically the same, and are void of fuel characterization information. Biomarkers are detected through parent ions such

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as  $m/z = 191$  for terpanes and  $m/z = 217, 218$  for steranes, and they provide relatively complex extracted ion chromatograms. In addition, the range of hydrocarbons amenable for GC–MS analysis is limited to 450–500 a.m.u. [4] and these authors [4] claim that “currently above the 450–500 a.m.u. range no single method is unambiguously capable of indicating molecular mass distributions or chemical structure features in complex fuel-derived mixtures”. In order to better resolve complex hydrocarbons and fuel mixtures comprehensive two-dimensional GC  $\times$  GC [5,6] and GC  $\times$  GC–MS [7] was used and FTICR–MS was applied [8,9]. However, the analysis and characterization of large hydrocarbon mixtures via its majority constituents is still challenging [10] yet very important for its combustion, lubrication and other physical and chemical properties.

In the last decade we developed and explored the performance capabilities of a new type of GC–MS, based on the use of a supersonic molecular beam (SMB) (named by us as Supersonic GC–MS). Supersonic GC–MS is based on the use of an SMB for interfacing the GC to the MS [11–20] and as a medium for electron ionization of sample compounds while they are vibrationally cold in the SMB [11,13,17,21,22]. SMBs are characterized by intra-molecular vibrational super-cooling, unidirectional molecular motion with controlled hyperthermal kinetic energy (1–20 eV), mass focusing similar to that in a jet separator, and capability to handle a very broad range of column flow rates from standard 1 mL/min (or lower) up to 90 mL/min [11,12,17].

GC–MS with supersonic molecular beams (Supersonic GC–MS) can significantly improve hydrocarbon analysis through five of its main beneficial features of: (a) enhanced molecular ion that is practically always observed [13,21] even for very large hydrocarbons [11]; (b) tailing free fast ion source response time regardless

of sample volatility; (c) extended range of low volatility compounds amenable for analysis [11,19]. This extended range is mostly attributed to the ability to use high column flow rates which result in lower elution temperatures and the use of a scattering-free fly-through ion source [11,19]; (d) enhanced isomer mass spectral information; and (e) compatibility with easy to use pulsed flow modulation comprehensive GC  $\times$  GC–MS with SMB [23,24].

In this paper we present our results in hydrocarbon mixtures analysis with the Supersonic GC–MS and in the development of a novel method of isomer abundance analysis for improved fuel characterization.

## 2. Experimental—the Supersonic GC–MS system

Experiments were performed with our older Supersonic GC–MS system that is based on a modified Agilent 6890 GC+5972 MS [17–19] and mostly with our recently developed Supersonic GC–MS that is based on the modification of a Varian 1200 GC–MS which we named 1200-SMB [11]. In the Supersonic GC–MS (such as the 1200-SMB) the column output is mixed with helium make-up gas ( $\sim 90$  mL/min total), and flows to the supersonic nozzle through a heated and temperature controlled transfer line. The helium flow can be mixed (via the opening of one valve) with perfluorotributylamine (PFTBA) for periodic system tuning and calibration, or with methanol vapor for inducing cluster chemical ionization [25,26]. The sample compounds seeded in helium expand from a 100  $\mu$ m diameter supersonic nozzle into a nozzle vacuum chamber that is differentially pumped by a Varian Navigator 301 turbo molecular pump (Varian Inc., Torino, Italy) with 250 L/s pumping speed. The helium pressure at this vacuum chamber is about  $6 \times 10^{-3}$  mbar.

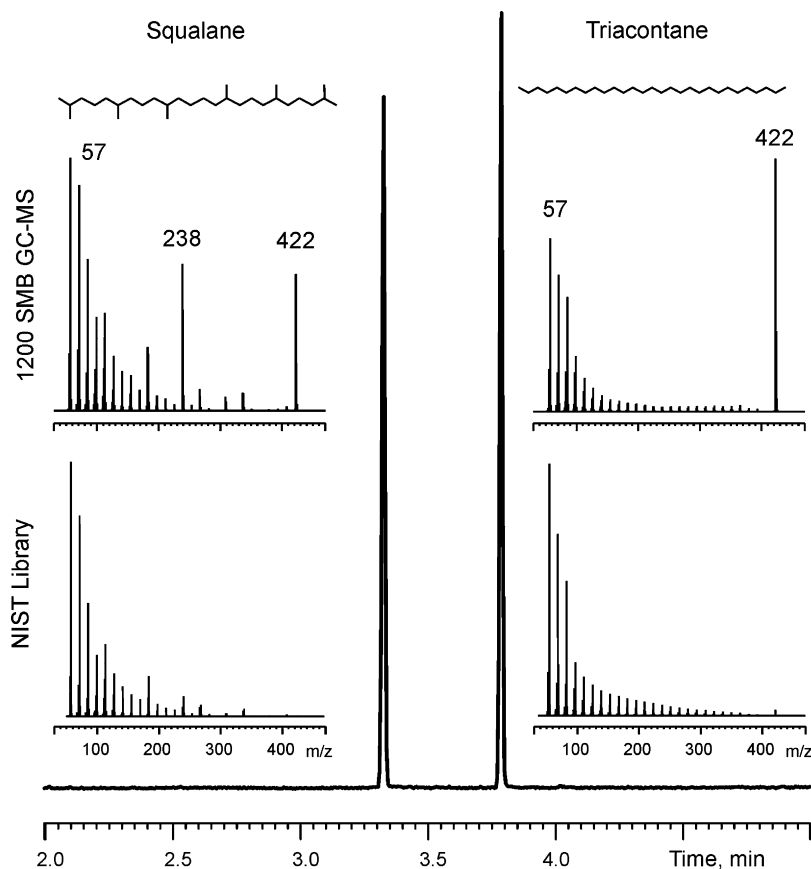


Fig. 1. Total ion mass chromatogram of a mixture of *n*-C<sub>30</sub>H<sub>62</sub> and squalane with the 1200-SMB together with their cold EI mass spectra in the insets.

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