

Mass spectrometric analysis of heavy and base oils

Master's thesis

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11.2.2018

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B1. Abstract

Base oil production from crude oil has become more complex as demanded product properties, yield objective and field competition have increased interest in research towards high viscosity index (VI) base oils. Conventional lubricant grade base oil enjoyed biggest market share until 2000-2004 but now high VHVI product demands have introduced also novel production methods for heavy-type base oils such as Fischer-Tropsch method based gas-to-liquid (GTL) and poly-internal-olefin (PIO) base oils. In this MSc, different mass spectrometric methods for heavy and base oils were compared and in-house field ionization method was characterized and method validation was begun. Base oil mass analytics uses mainly Fourier transformation ion cyclotron resonance (FT-ICR) and sector mass analyzers with soft ionization methods as well as novel ambient ionization (AI) methods. While heaviest asphaltene compounds require resolutions that are achievable only by FT-ICR instruments majority of petroleum studies including quantitative fraction studies can be done with more cost-efficient and operator-friendly sector and Orbitrap instruments. Novel AI methods are arguably fastest expanding area of mass spectrometry and provide interesting field to follow also for petroleum analysis.

B2. Yhteenveto

Perusöljyjen vaaditut ominaisuudet, saanto tavoitteet ja kilpailu alalla ovat kasvaneet muuttaen perusöljy teollisuuden tuotannon monimutkaisemmaksi ja haastavammaksi lisäten tutkimuksen vaatimuksia kohti korkean viskositeetin perusöljyjä. Tavanomaiset perusöljyt ovat olleet hallitsevassa markkina-asemassa vuoteen 2000-2004 asti, mutta nykyään korkean viskositeetin vaatimukset ovat tuoneet uusia tuotantomenetelmiä, kuten Fischer-Tropsch synteesiin perustuva gas-to-liquid (GTL) tai poly-internal-olefin (PIO) öljyjä. Pro Gradu työn kirjallisessa osassa esitettiin ja vertailtiin massaspektrometrisia menetelmiä perusöljyjen ja raskaiden öljyjen tutkimiseen. Työn kokeellisessa osassa yrityksen sisäinen kenttäionisaatio (FI) menetelmä karakterisoitiin ja validointi aloitettiin. Massa-analysointina perusöljyanalytiikka käyttää yleisesti Fourier muunnosta hyödyntäviä ioni syklotroniresistanssi- (FT-ICR) tai sektori -analysointoreja yhdessä pehmeiden, sekä AI ionisaatiomenetelmien kanssa. Raskaimpien asfalteenien mittauksen tarvitessa vielä FT-ICR analysointia, valtaosa tutkimuksesta voidaan tehdä kustannustehokkaammalla ja käyttäjäystävällisemmällä sektorianalysointorilla ja enenemissä määrin myös Orbitrap analysointorilla. Nopeimmin kasvava ionisaatiomenetelmäalue on AI menetelmät, jotka pyrkivät ionisoimaan näytteen ilman ylimääräistä esikäsittelyä. AI menetelmistä useilla pystytään mittaamaan perusöljyn tapaisia yhdisteitä ja AI menetelmät tarjoavat mielenkiintoisen alueen seurata petrolikemian analyysimenetelmien kannalta.

C. Foreword

This Master's thesis studies were done in 2015-2016 in Neste's R&D in Kilpilahti industrial area of Porvoo in collaboration with Neste Oyj. It is a combination of literature review and empirical research for actual use. Literature review was done to compare different mass spectrometric methods and their suitability for heavy and base oil products. Experimental research was done to empirically characterize and update inhouse Neste Method no.430 (**NM430**). NM430 is important in-house group-type analysis based on different fractions that is used for qualitative and quantitative composition analysis of high viscosity index base oil -type samples with varying viscosities.

Literature review relies on published research, literature and in-house material. NM430 has importance in Neste oil trade and hence parts of research are confidential. Thesis was supervised by Elina Kalenius, Academy research fellow in Jyväskylä university and Elias Ikonen, researcher at Neste Oyj.

I would like firstly to acknowledge my supervisors Elina Kalenius for her time, input and persistence; Elias Ikonen for hours of mentoring, enthusiasm and vertiginous insight in mass spectrometry; Jyrki Viidanoja for firm and unyielding professional knowledge, insight and experience on method validations and characterizations; Tiina Laaksonen for committing to this thesis midway; Jin Chunfen for her time, tutoring and help in work that without this work would have not been possible. Also, I would like to acknowledge everyone at Neste R&D chemistry group for warm working atmosphere and great team spirit that provided unforgettable research project. Last but not least I would like to thank you my family and friends.

E. Used abbreviations

Abbreviations	
AI	Ambient ionization
APCI	Atmospheric pressure chemical ionization
API	American Petroleum Institute
APPI	Atmospheric pressure photo-ionization
ASP	Average structure parameters
ASTM	American Society for Testing Materials
B	Electromagnetic analyzer
CI	Chemical ionization
CMRP	Condensed multiring paraffins
CMSBO	Chemically modified soy bean oil
DBE	Double bond equivalent
DFS	Dual focusing system
DIP	Direct injection probe
DOSY	Diffusion ordered spectroscopy
EDS	Energy disperetive X-ray specroscopy
EHC	Emitter heating current
ESA	Electrostatic analyzer
ESBO	Epoxized soybean oil
ESI	Electrospray ionization
FAB	Fast atom bombardment
FAME	Fatty acid methyl esters
FBP	Final boiling point
FCC	Cracking unit; Fluid catalytic cracking
FD	Field desorption
FI	Field ionization
FID	Flame ionization detector
F-T	Fischer-Tropsch process
FT-ICR	Fourier transformation ion cyclotron resonance
FT-IR	Fourier transformation infra-red spectroscopy
GC	gas chromatograph
GLP	Good laboratory practice
GTL	Gas-to-Liquid products
H/C	hydrogen to carbon relation
HDS	Hydrodesulphurization
HPLC	high performance liquid chromatography
HRMS	High resolution mass spectrometry
HTGC	High temperature gas chromatography
ILSAC	International Lubricants Standardization and Approval Commitee
LC	liquid chromatograph
LDI	laser desorption ionization
LIAD	Laser induced acoustic ionization
LIFDI	Liquid injection field desorption ionization
LOD	Limit of detection
LOQ	Limit of qualitication
MALDI	Matrix assisted laser desorption ionization
NM430	Neste Method no. 430

NMR	Nuclear magnetic resonance
OIP	Oil in place
PAH	Polyaromatic hydrocarbons
PAO	Poly-alpha-olefins
PIO	Poly-internal-olefin
PONA	Paraffins, olefins, naphthenes and aromatics fractions
PTFE	polytetrafluoroethylene (Teflon)
RSD	Relative standard deviation
SAE	Society of Auto-motive Engineers
SARA	Saturates, aromatics, resins, asphaltenes fractions
SD	Standard deviation
SIMDIS	Simulated distillation
SEC	Size exclusion chromatography
SEM	Scanning electron microscope
SFS	Saybolt Furol Seconds (Viscosity measures)
SIM	Select ion monitoring
SNO compounds	Sulphur, nitrogen and oxygen containing compounds
SS	Spot-size on SEM
TAN	Total acid number
TBN	Total base number
TCC	Thermofor catalytic cracking (Cracking unit)
TCD	thermal conductivity detector
TIC	Total ion current
TLC	Thin layer chromatography
TOF	Time of flight
UCBO	Unconventional base oils
USGS	United States Geological Survey
UV-VIS	ultraviolet-visible light spectroscopy
WD	Working distance on SEM
VGO	Vacuum gas oil
VHVI	Very high viscosity index
VI	Viscosity index
VO	Vegetable oils
VRC	Vacuum reduced crude
XVHI	Extra high viscosity Index

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1 Introduction to theory part

“My formula for success is rise early, work late, and strike oil.”

-J. Paul Getty¹

Oil is major commodity as largest primary energy source in all energy consumption and reason for political petrol-aggression. Oil produces energy by combustion and it is precursor in many chemicals, plastics and lubricates. According to George E. Totten from ASTM international, first written uses of oils are already from 4000 B.C. near Euphrates river banks, now known as Iraq. There asphalt was used for waterproofing items as pottery and baths.² Today uses are rather different as around 96 % of passenger cars have either diesel or gasoline engine in EU.³ Interesting side plot is that years 1899 and 1900 were top years for electric cars as they were sold and used more than any other car types.⁴ Historically base oils were unwanted by-product and waste but now they are widely used and priced manufactured product.

Petroleum is broadly studied with mass spectrometry as it is unique method to study even complex samples while other methods as infrared (IR) and Nuclear magnetic resonance (NMR) spectroscopy and physical measurements can give only average information of structure, functional groups and characteristics of studied oil sample.

Base oils are most probably more studied than published data might suggest. Possibly as there is just little interest for industries to publish their research for competitors. Also petroleomics are a niche market for mass spectrometer vendors and there might be less interest to develop methods further for petroleum analytics than commercially more valuable markets.

With arising interest in eco-friendliness, one of environmental concerns is lubricant oil biodegradation. Mineral and synthetic lubricant oils are rarely biodegradable and show toxic behavior in aquatic environments. Green alternatives have shown steady increase also in lubrication markets. Bio-based lubricant oils include vegetable oils and chemically modified vegetable oils such as canola oil and chemically modified soy bean oil. Canola oil has shown some promising properties for automobile lubrication.⁵ Still bio-based lubricant oils have under 1% market share of all lubricants market.⁶

Ecological consensus along with Renewable Energy Sources (RES)-directive drives petroleum industries towards less polluting and renewable energy sources and petrol based materials, as vehicle fuels and lubricants. These include bio-plastics and renewable oil products that can be chemically identical to crude oil counterparts (such as NeXTBTL products from Neste Oyj) or totally different products such as fatty acids methyl esters (FAMES) and alcohols. 2015 United Nations Climate Change Conference CMP21 and Paris agreement requires profound changes in vehicles in use either by exploitation of electric vehicles or changing fuel form fossil based to renewable. Possible processes to produce bio-based fuels are i.e. pyrolysis, Fischer-Tropsch –synthesis and refining pine oil byproduct. Prices of biofuels are still high i.e. Fatty acid methyl ester (FAME) ton costs around 800 dollars in 2016.⁷ It is arguable that this trend pushes also research focus for petroleum based lubricants and their alternatives.

This Master's thesis discusses base and heavy oils and their mass spectrometric measurements. Base oils are part of heavy oils distilled from crude oil and they are used mainly in lubrication applications. Heavy oils in some definitions includes also asphaltenes and vacuum distillation residue, but these are less discussed here as the topic is already broad. Mass spectrometric measurement methods are narrowed to methods with viable use in petroleum analysis with emphasis in nonpolar base and lubricant oils. Also their suitability to quantitative base oil measurements is addressed. Practicality of different methods as alternatives for current Neste method are also viewed.

Methods used in oil refining and especially in base oils and their competitive and complementary products (i.e. bio-based and synthetic lubricants) are generally displayed for better general view. However chromatographic techniques (i.e. GC, LC and HPLC) and fractioning used in base oil analytics are not covered in depth within this topic. Other oil products as gasolines, kerosenes and asphaltenes are on less importance.

2 Crude oil and oil refining

Term *petroleum* is sometimes used as synonym for crude oil but normally petroleum refers also to gaseous and solid hydrocarbon formations. Crude oil is liquid hydrocarbon mixture that is found beneath earth's surface in geological foundations. Crude oil consists of liquid and dissolved gaseous hydrocarbons, but the line between gaseous, liquid and solid is not unambiguous in extreme pressures and temperatures i.e. many normally gaseous hydrocarbons are liquid or they are dissolved in liquid phase under high pressure. Oil volume is typically reported as barrels (bbl) where 1 barrel equals to 159 liters.⁸

More modern oil use is believed to have begun by refining paraffin from crude oil by James Young in 1847. By 1851 the first oil well and refinery was built by E.W. Binney & CO for manufacturing paraffin wax.⁹ Kerosene and paraffin wax production was main goal of refineries of 1860s and 1870s while many other oil fractions valuable today were thought as unwanted by-product.¹⁰ Major oil fields were discovered during rest of the 19th century and by 1950 oil hunt had sifted to sea where first drilling platform was built in Gulf of Mexico in 1947.

By 1860 crude oil production was under 400 000 barrels annually in US. Oil production over ten folded with 4 million barrels each year by 1869 and in 21th century oil production is measured in billions of barrels annually. Oil drilling has come quite far since E.W. Binney & CO's drilling times. Earlier oil wells were done with hammering, but this was replaced by rotating drilling in the beginning of 20th century. Today around 3-12 millions of barrels are produced each day as production quantities depend on number of factors i.e. oil price, economical state and political motives.¹¹

This chapter introduces current consensus of oil origin, basics of oil drilling and refining crude oil to base and lubricant oils, chemical composition and physical properties of oil products and different analytical methods to study petroleum compounds.

2.1 Crude oil origin

Current consensus is that crude oil originates from biomaterial and is therefore called **biogenic**. Contrarily Kolesnikov¹² and Kutcherov¹³ with their colleagues found that some hydrocarbons can be formed also from non-biogenic origin and therefor their and similar theories are called **abiogenic** theories. Abiogenic theory is partly supported by NASA finding vast quantities of crude oil like abiogenic liquid hydrocarbon mixture in Saturn's moon Titan observed with Cassini spacecraft.¹⁴ Still majority of Earth's oil reservoirs are determined to be biogenic while few are still under studies.⁸

In biogenic theory crude oil is formed in so called hydrocarbon traps where large quantities of biomaterial are buried under sedimentary rock for long periods of time in high temperature and pressure with anaerobic conditions. Proteins, carbohydrates and biopolymers begin to break down in process called anaerobic digestion with optimal temperatures of 50-150 °C. Optimal depth depends on temperature and few other factors, but deeper than 5 km biomaterial tends to form mainly gaseous products.⁸ Products can then condense to polymers and inorganic material begins to form mineral components. This results in kerogen and bitumen rich sedimentary material such as oil shale. Smallest of these polymers are humic and fulmic acids. By time biomaterial starts to lose oxygen, nitrogen and sulfur alongside with other functional groups.¹⁵

Kerogen can then go through process called **catagenesis** where organic kerogens form shorter hydrocarbons. Similar event is used in industrial cracking process. Catagenesis is more efficient in higher pressure and temperature and therefore deeper oils are typically lighter. Liquid flow happens mainly in porous surrounding in secondary migration and after that oil and gas flows towards pressure minimum until movement stops in barrier.⁸

According to OPEC biggest oil deposits are in Venezuela (24,9%), Saudi Arabia (22,1%) and Iran (13,1%).¹⁶ Proved reserves size of 15 biggest oil deposit countries in 2014 was around 1 514 billion barrels.¹⁷ Reporting reserve size is not as straight forward because many factors play role in measuring oil deposit size and as David Morehouse found out, they tend to go through so called **reserves growth**, where oil deposits are measured bigger by time.¹⁸ There are many reasons for this i.e. one is that extraction methods get more efficient and different oil deposits are now considered to be available like oil shales.

All oil in one place is addressed as Oil in Place (OIP) and from this a certain amount can be recovered according to recovery factor of used technology. All oil sites are not economically recoverable and many factors together are used in assisting oil deposit size. Possible oil deposits can be plotted out by age composition, geological history and oil critical factors. These factors rule out heartlands where sediment formations are all negative for oil deposits and this is the reason why i.e. in Finland it is highly unlikely to strike oil. Also all mountain ranges and places with intense heat or bedrock movement are negative factors for oil formation.⁸

Most of oceanic crust can be ruled out as around 70 % of ocean floor is covered in few hundred meters thick unconsolidated or semi consolidated sediments that are negative for oil formations as seen in figure 1 of estimated undiscovered oil deposits and tectonic plate boundaries. This explains why it is unlikely to find oil within oceanic crust.⁸ Around 650 billion barrels of oil and 778 billion barrels of oil equivalent is estimated to be undiscovered according to United States Geological Survey (USGS).¹⁹ Map of estimated sites can be seen on figure 1 and table of quantities can be seen in table 1.

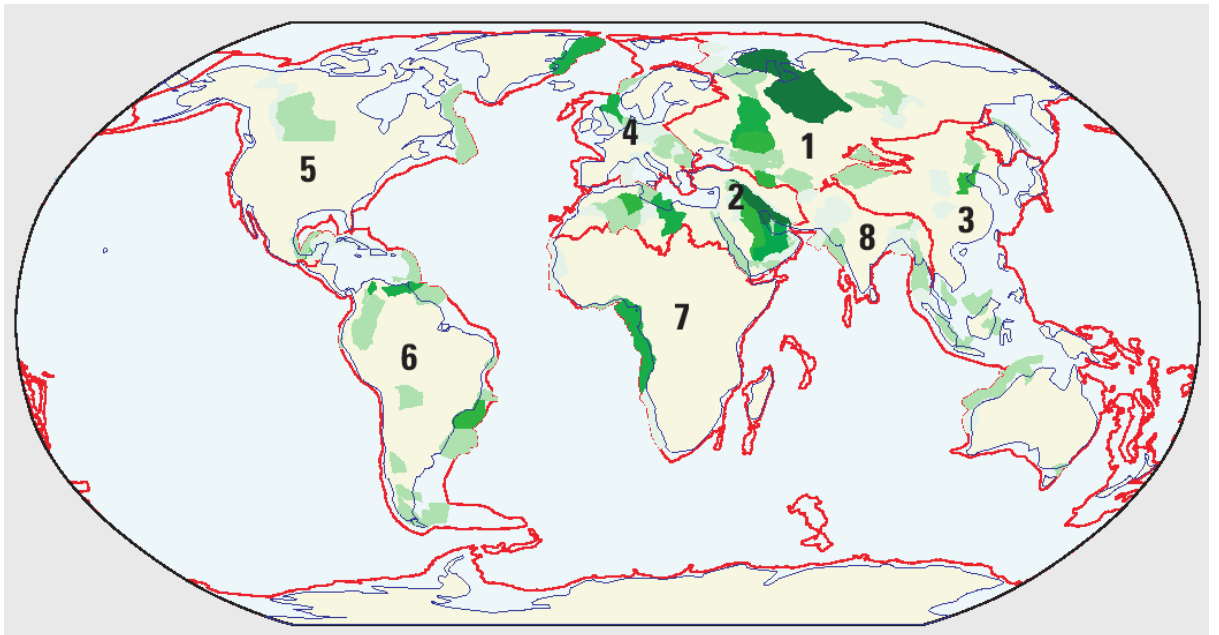


Figure 1. Cumulative production and estimated undiscovered oil deposits. Red outlines continental crust from oceanic crust. Figure from USGS world Petroleum Assessment 2000.¹⁹

Table 1. Estimated volumes of undiscovered oil according to figure 1. Table from USGS world Petroleum Assessment 2000¹⁹

Region	Oil (billion barrels)	Percent of world total	Natural gas (billion barrels of oil equivalent)	Natural gas (trillion cubic feet)	Percent of world total
1: Former Soviet Union	116	17,9	269	1611	34,5
2: Middle East and North Africa	230	35,4	228	1370	29,3
3: Asia-Pacific	30	4,6	63	379	8,1
4: Europe	22	3,4	52	312	6,7
5: North America	70	10,9	26	155	3,3
6: Central and South America	105	16,2	81	487	10,4
7: Sub-Saharan Africa and Antarctica	72	11,0	39	235	5,0
8: South Asia	4	0,6	20	120	2,6
Total	649		778	4469	

Most of possible oil locations are offshore and near continental crust and oceanic crust borders. Today large interest is in unconventional oil deposits such as shale oil, shale gas and coal-bed methane that were previously quite disregarded but could play important role in future oil market. For example Estonia is over self-sufficient in energy production and is one of the biggest shale oil exporting countries according to World Energy Council,²⁰ but mainly because of this, Estonia is in the top 10 when comparing the biggest ecological footprints of different nations in all world.²¹

2.2 Crude oil composition

Crude oil is highly complex mixture of hydrocarbons and impurities and one of the most complex samples known. Hydrocarbons range from small, simple and volatile molecules to large, nonvolatile compounds. As directional magnitude of complexity Cristine A. Hugley *et al.*²² found over 11 000 compositionally distinct components made up from hydrocarbons with heteroatoms (O, N, S) in single ESI-FTICR mass spectrum of crude oil adding up to only 10 % of all petroleum molecules. Hydrocarbons in oils can be divided and classified in numerous ways but here most useful will be dividing them by hydrocarbon compositions. Hydrocarbons in crude oil are divided into three groups: paraffins, naphthenes and aromatics.

Paraffins and iso-paraffins (also known as **aliphatic** hydrocarbons) are linear or branched. **Naphthenes** are hydrocarbons with cycloalkane ring structures and **aromatics** are benzene ring derivatives. Different environment produces different type of crude oil

as mentioned in chapter 2.1 resulting in that crude oil can have certain composition of paraffins, aromatics and naphthenes. Easy presentation of this is composition triangle where each class is at end of triangle as seen in figure 2.

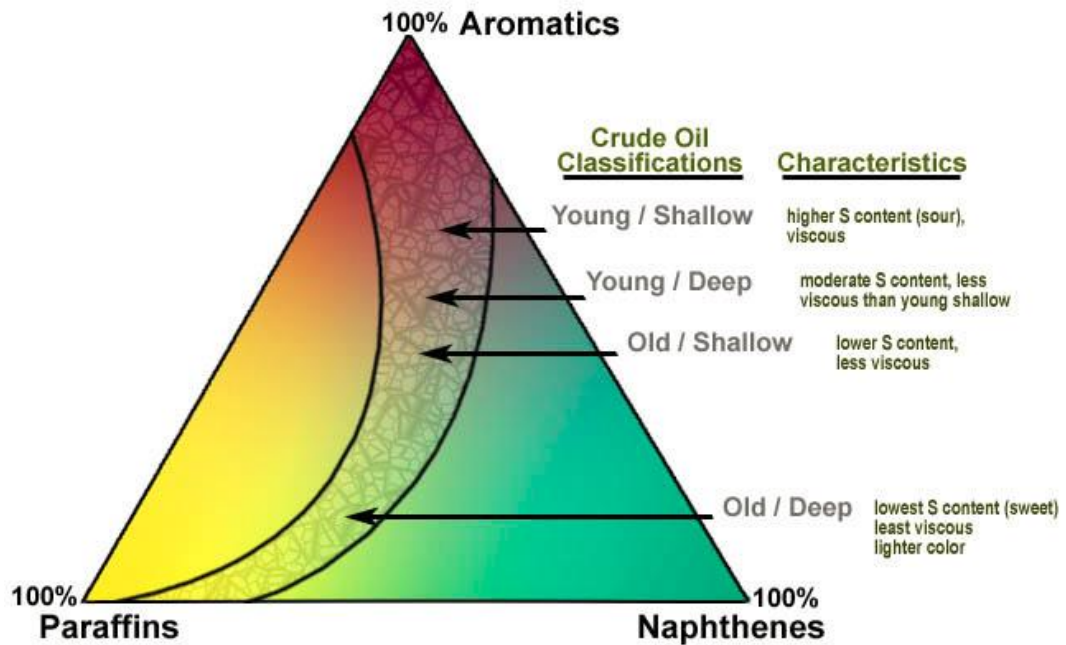


Figure 2. Crude oil composition triangle.²³ Shaded area represents typical crude oil compositions. Sulfur content tends to lower when oil is more paraffinic than aromatic. and very little of high naphthenic crude oil exists

Crude oil normally has no **olefins** (alkenes, compounds with double bonds) but they are readily produced in oil refining and olefins are used as a chemical marker that oil has been refined. Aromatics with fused rings are called **Poly-aromatic hydrocarbons (PAHs)**, this class includes also toxic and mutagenic compounds that have gained some media attention.²⁴ Chemically different crude oil fractions are displayed in figure 3.

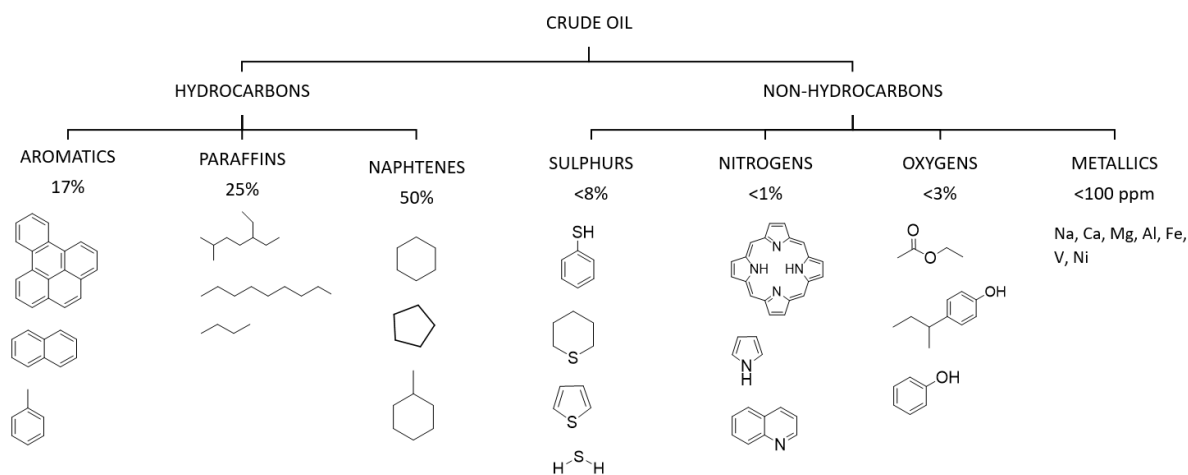


Figure 3. Typical chemical composition of crude oil with molecule examples. Metals are typically as inorganic salts, organometallic compounds or with porphyrin.²⁵

Typical crude oil heteroatoms include oxygen, nitrogen, sulfur and metal impurities with sulfur being most abundant. Nonmetals are typically addressed as **SNO-compounds** and their concentration is limited in environmental and commercial agreements and they also cause problems on refining. Removal of SNO-compounds is essential but also expensive as sulfur and oxygen compounds cause corrosion in production and refinery equipment also their combustion derivatives (SO_2 , NO_x) can react with water resulting in acid rains, and nitrogen compounds in fuels and lubricants along form gums and precipitates within time of storage. Few practical methods exist in removal of them and currently most used method is catalytic hydrotreatment.²⁶

With sour crude oils, sulfur may have to be extracted already before shipping as its compounds are corrosive and highly toxic. Sulfur can be extracted from crude oil with process called hydrodesulphurization (HDS) which uses catalyst to remove excess sulfur. Heteroatoms make up polar components of crude oils and heavy distillates generally contain more aromatic and heteroatomic compounds than lighter counterparts.⁸

Along paraffin-naphthenic-aromatic composition divisions are **SARA** and **PONA**. SARA- fractioning means to divide crude oil composition to saturates-aromatics-resins-asphaltenes, there are also few different methods to measure SARA which needs to be accounted when comparing results. PONA stands for paraffins-olefins-naphthenes-aromatics. PONA is widely used for intermediate products such as fluid catalytic cracking products to determine quality of naphtha.²⁷

Majority of crude oil hydrocarbons are under 400 Da.²⁸ Small polar compounds in oil are called **resins** and they are responsible for oil adhesion. Resins are typically heterocyclic hydrocarbons, phenols, acids, monoaromatic steroid and alcohols. Larger and in some literature only polar²⁸ components are called **asphaltenes** where name is resulting from their asphalt- like properties. High viscosity oils with detrimental amount of heteroatoms with high molecular weight are typically addressed as **bitumen** but there are some variations to its characterization. It is typically contains paraffins, aromatics, polar compounds and asphaltenes as an emulsion and it is either process residue or very heavy crude such as Athabasca bitumen.¹⁵

Asphaltene size is still quite unknown and mean molecular weight ranges over 2 orders of magnitude for similar samples as mass spectrometry with electrospray ionization, field desorption and chemical ionization MS methods predict average weight to be around 500-1000 Da while fast atom bombardment and plasma desorption mass spectrometry as well as size exclusion chromatography shows intense peaks over range 10 000 to $> 10^6$ Da.²⁹ Asphaltenes are defined by solubility classification (i.e. toluene solutions of asphaltenes, n-heptane solutions of asphaltenes etc.) Asphaltenes are not dissolved in petroleum but they are dispersed as colloids and they tend to aggregate at low concentrations for instance at 150 mg/l in toluene produces already nanoaggregates.¹⁵

Asphaltenes have been studied quite intensively but still rather little is known about their molecular composition. Polar cyclic compound have low concentration in crude oil, but they are persistent in environment and tends to concentrate.²⁸ Asphaltenes acts as geochemical markers and they yield valuable information from oil origin and they are used as chemical marker to distinguish oil spill origin and owner. Asphaltene study is predicted to increase as unconventional oil resources include more asphaltenes (up to 15 %) than conventional resources.²⁹

Easy and relatively robust method to evaluate crude oil is API-gravity measurement. API-gravity reflects how heavy or light crude oil or oil products are and it gives directional information of chemical composition and crude oil price. Scale is fixed to water so that oils with API-gravity higher than 10 floats on water and less than 10 sinks. Crude oil rating according to viscosity and API-gravity range can be seen in table 2.

Table 2. Crude oil rating according to API-gravity range, viscosity and sample oil reserves³⁰

Crude oils	Sample oil reserves	Viscosity (centipoise)	Range with familiar substances	Typical API gravity range
Tar and Bitumen	Alberta, Canada-Peace River	10 ⁸ -10 ⁶	Window putty to vegetable shortening	6-10
Extra-Heavy Oil	Venezuela-Boscan	10 ⁵ - 10 ⁴	Peanut butter to tomato ketchup	10-12
Heavy oil	California-Kern River	10 ³	Molasses to honey	14-22
Intermediate Oil	Saudi Arabia, Arab Heavy	100	Maple syrup to corn oil	25-30
Light Oil	UK-Brent	10-1	water	31-40
Ultra-Light Oil	Texas Shale Oil-Eagle Ford	0,1	Nail polish remover	+41

API-gravity correlates highly with viscosity of crude oil that is fundamental oil and product property and API-gravity can be considered inverse measurement of density and even though it is dimensionless it is normally expressed in degrees. API-gravity is affected by ratio of different hydrocarbon groups and sulfur content. API-gravity is also temperature dependent and that needs to be corrected for the calculation. API-gravity can be calculated from SG (specific gravity) as follows

$$API\ gravity = 141.5 / (SG - 131.5) \quad (1)$$

Exact measuring temperatures, needed corrections and density adjusting can be found on American Society of Testing and Materials (ASTM)-literature.³¹ API-gravity is measured with hydrometer apparatus that consists of ballast, float and stem. API-gravity reading is taken at graduated stem where hydrometer floats in liquid surface. Measurement principle with hydrometer can be seen in figure 4.

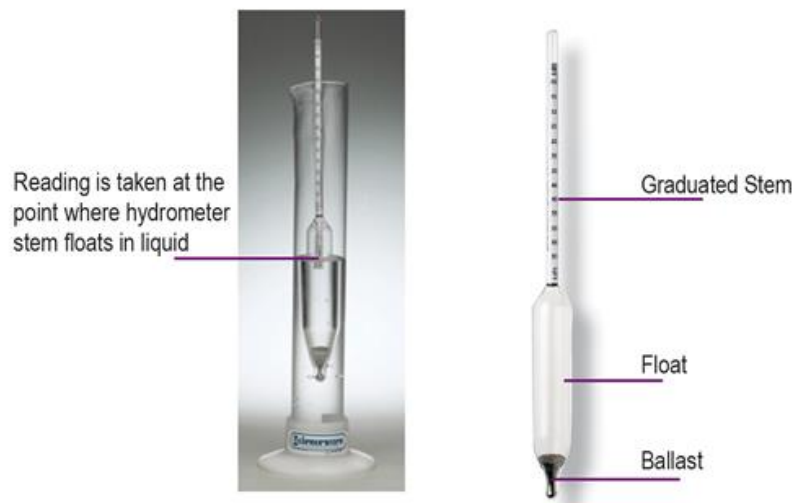


Figure 4. Hydrometer used in measuring API gravity.³²

Crude oil is typically valued based on three factors: its origin (i.e. Brent and Arab Light), API-gravity and sulfur content that is also called sweetness and sourness. As discussed in chapter 2.1 crude oil composition depends on place of origin and formation time.⁸

2.3 Oil refining

Refining aims either to decrease levels of unwanted compounds and contaminants or to modify compounds to more desirable and valuable products. Refining starts from crude oil and results in number of petrochemical products. Oil refineries are normally planned and tuned for specific type of oil feed (ie. high sulfurous) and have according process steps as some processes cannot be used with certain feeds.³³

2.3.1 Refining crude oil

Fundamental process in crude oil refining is **fraction distillation** that partially separates light low boiling compounds from high boiling heavy compounds with continuous distillation. Gaseous products are condensed in condenser and distillate products goes to receivers. Lighter distillates are typically more valuable than heavy distillates. Yield can be increased when distillation is done in two parts, first in atmospheric pressure and resulting bottom fraction again in high vacuum fraction distillation column. Further and common processes include **desalting** where excess salt is washed out with water and **desulfurization** where sulfur is extracted alongside cracking units.³⁴

In fraction distillation oil is distilled in colon with spacers inside it where biggest pressure and temperature is at bottom of the colon, spacers are used to provide equilibrium stages with different pressures and temperatures for wanted distillate product as seen in figure 5. Effectivity is improved with reflux, where a part of distillate is recycled back to column. Refluxing improves the purity but also adds price as less oil can be distilled in same time.³³

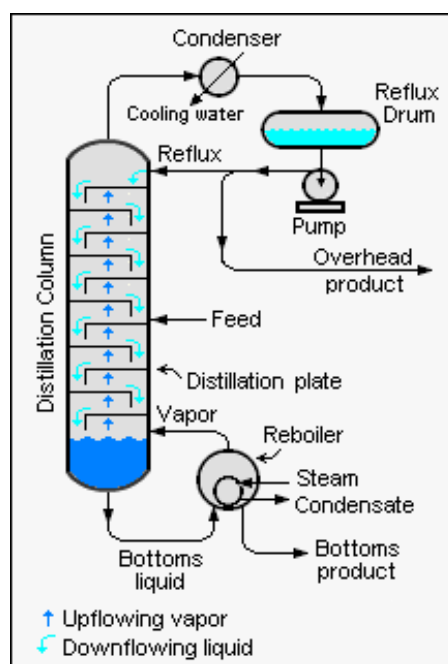


Figure 5. Basic principle of fraction distillation column with reflux flow. Image is property of Milton Beychok.

Cracking and **hydrocracking** transforms catalytically heavy oils into more valuable lighter fractions. One example of cracking methods is called **fluid catalytic cracking** (FCC) where the units are either stacked or side by side. Each design is under a license which needs to be bought for use from example ExxonMobil and Shell.³⁴ Hydrocracking, is typically used if hydrogen to carbon ratio (H/C-ratio) is relatively low and it is used alongside catalytic cracking. Where normal cracking is used for chemically smaller and simpler molecules to retain olefins in example gasoline. Hydrocracking is used for bigger and more complex molecules e.g. aromatic cyclic oils and coker distillates but there is little selectivity as cracking affects all molecules. **Hydrogenation** of double bonds happens after cracking and it also reduces impurities that reacts with hydrogen.³⁴ Simplified cracking process of linear paraffin can be seen on figure 6.

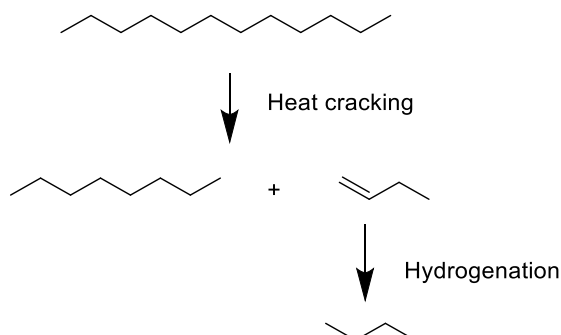


Figure 6. Cracking process with linear paraffins.³⁴

Bottom oil, also known as **Vacuum gas oil** (abr. VGO) or **Vacuum reduced crude**, (abr. VRC) is residues from distillation and has large portion of impurities and low H/C -ratio. There are few options to what to do with VRC and process depends from many factors as company, sulfur content, used type of crude oil and economics. VRC cannot normally be cracked as it has many catalytic poisons and low H/C-ratio results in deactivation of catalysts relatively fast.³⁴

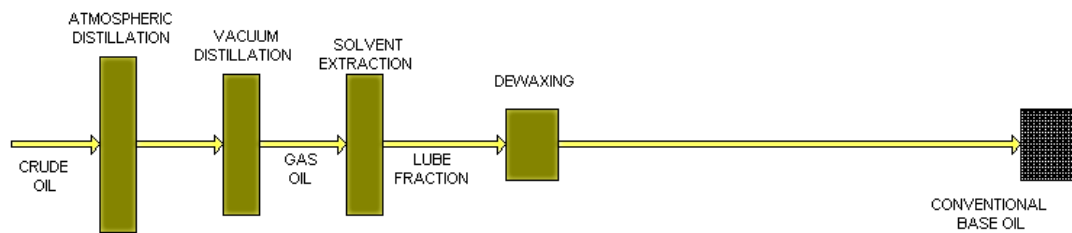
An option for problematic bottom oil is to coke it. Bottom oil is coked into solid coke while light part of it is recovered. **Coking** is done on high temperature (1095-1260 °C) and it has few alternatives like delayed coking, flexicoking and fluid coking. VRC can be sold also as refined bitumen or it can be hydroprocessed and solvent extracted where up to two thirds can be used as feed for cracking processes.³⁴

2.3.2 Refining processes towards lubricants and base oils.

Mineral or petroleum based lubricant oils are heavy fractions from crude oil fraction distillates. They are specified as typically chemically modified mineral oils with high **viscosity index (VI)** where most desired molecules are highly branched paraffins and small-ringed cyclic paraffins. VI is represented normally using API and SAE classifications that are discussed in chapter 3.1. Heavy distillate fractions go through number of refining processes depending on wanted product. Common processes include deasphalting to remove heavy fractions, solvent refining or hydrogen refining to remove aromatics and heteroaromatic compounds, solvent or catalytic dewaxing is used remove linear paraffins (waxes) that would crystallize in low temperatures and lastly hydrogen finishing or clay treatment to remove trace impurities. Yield and quality of a base stock is dependent on the quality of crude oil and efficiency of different operations with decreasing yield after every process.⁶

There are two general processing pipelines to produce base oils from crude distillates: **solvent refining** and **hydrotreating** where simplified process diagram can be seen in figure 7. Solvent refining extracts wanted compounds from feed and hydrotreating chemically transforms other compounds to more valuable products and is less constrained by feed concentrations.³⁵

SOLVENT REFINING



HYDROTREATING

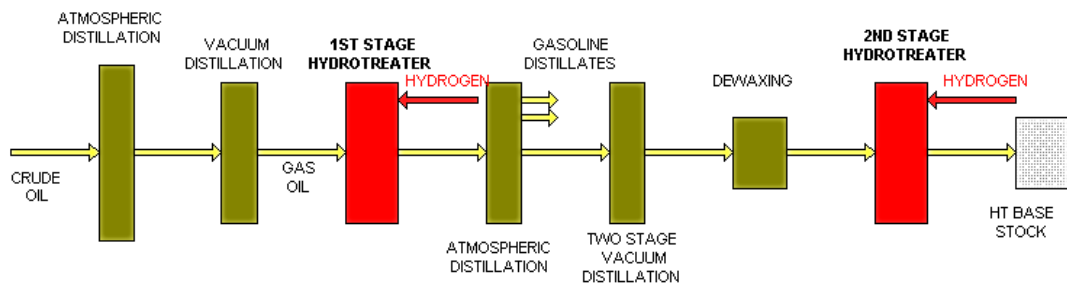


Figure 7. Solvent refining and hydrotreating flow diagrams.³⁶

Solvent refining is simpler and cheaper but has low yield which drops exponentially when pursuing high VI compounds. Hydrotreating is more complex and expensive method but it has higher yield and can produce high VI compounds in different scale when compared to solvent refining. Solvent refining separates unwanted aromatics and heteroaromatic compounds leaving desired product, but it has several limitations, most notably yield drops highly when pursuing higher VI components as there are just small part of them in feed.⁶

Hydrotreating and hydrocracking transforms ring structures into more desirable components and it involves following typical steps: extraction of sulfur and nitrogen in desulfurization and denitrogenation followed by double bond saturations, ring separations and openings and lastly side chain hydrocracking and hydroisomerization. These steps are visualized in figure 8. Valuable high VI (API III class including VHVI/UCBO, XVHI more discussed in chapter 3) base oils are mainly attained with hydrocracking.⁶

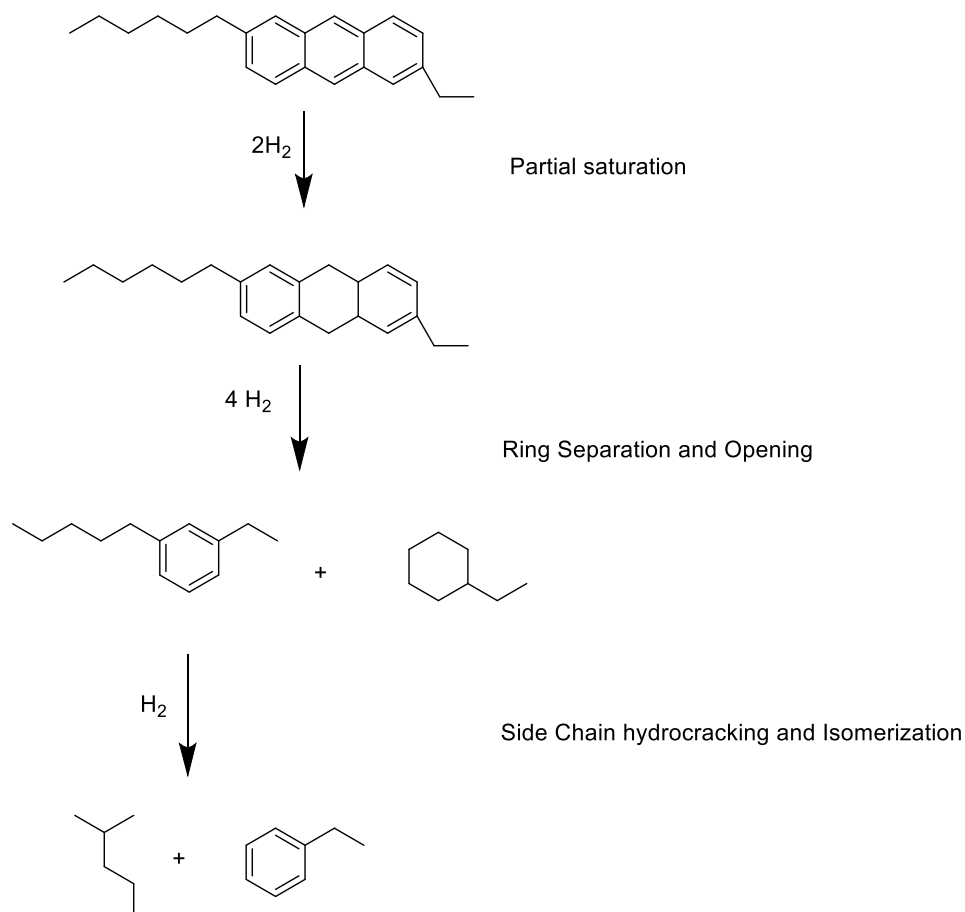


Figure 8. Example of hydrocracking heavy -type molecules in oil.^{6,34}

Currently hydrotreating is becoming more common and with different feeds even +140 VI range can be achieved. Attained VI range is highly affected by feed wax content where under 30 % wax VGO produce 100-127 VI oils in API groups II and III and over 70 % wax feeds produce 140-144 VI products. Different feeds require partially different processes.⁶ Iso-paraffins are valuable compounds in high VI base oils as viscosity index increases with iso-paraffin content as seen on figure 9.

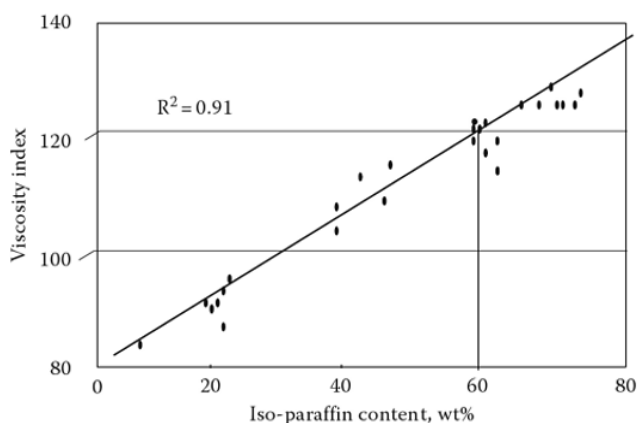


Figure 9. VI as a function of iso-paraffin content with coefficient of determination.⁶

Likewise, unwanted compounds such as linear alkanes and condensed multi-ring or polynaphthenes (i.e. tetra-, penta- and hexa-naphthenes) decrease VI. condensed multiring paraffin content lowers VI as seen in figure 10.

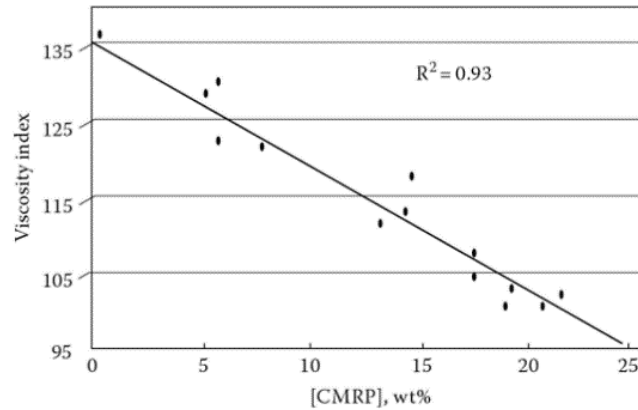


Figure 10. VI as a function of poly-naphthene content (here as condensed multiring paraffin content, CMRP) with coefficient of determination.⁶

Hydrotreating process is compromise between VI and yield where yield drops exponentially when VI is increased. VI can be controlled with operational conditions i.e. with hydrocracking temperature. API category, production method and composition comparison can be seen in table 3.⁶

Table 3. Chemical compositions of different API category and refining processed base oils⁶

Base Stock	A	B	C	D	E	F	G
API Category	I	I	II	II	II	II+	III
Processing	Solvent Refined	Solvent Refined	Hydrocracked	Hydrocracked	Severely Hydrocracked	Severely Hydrocracked	Severely Hydrocracked
Dewaxing	Solvent	Solvent	Solvent	Iso	Solvent	Iso-	Iso-
HRMS, m-%							
Alkenes (n- and isoparaffins)	25,7	29,0	23,7	30,2	32,6	51,4	76,1
Mono-cycloparaffins	20,8	25,0	30,8	30,5	34,2	24,4	14,7
Poly-cycloparaffins	27,9	31,7	39,1	35,3	32,9	23,9	9,2
Aromatics	24,9	14,2	6,4	4,0	0,6	0,3	0,0
Thiophenes	0,7	0,1	0,0	0,0	0,0	0,0	0,0
Paraffins+ mono-cycloparaffins	46,5	54,0	54,5	60,7	66,7	75,8	90,8

Processing method greatly affects attained VI and hydrocarbon types. Alkanes (n- and iso-paraffins) portion grow with API category while aromatic portion dismisses. Mono-cycloparaffins and poly-cycloparaffins content depends with processing method.

2.4 Analytical methods for petroleum products

Here are expressed and shortly described typical and widespread chemical analysis methods used with petroleum products and side streams. Basic and bulk properties (i.e. functional groups and H/C ratios) can be measured with spectroscopic, chromatographic, X-ray based and NMR methods but these cannot distinguish individual elemental compositions on molecular level as does mass spectrometry that is further addressed in chapter 4. Highly used methods are chromatographic, mainly gas chromatographic (GC) and its derivatives that can be connected to MS for further analysis.²² Considered methods include spectroscopic (UV-VIS, IR, Raman), NMR (¹H, ¹³C) and Chromatographic (GC, HTGC, GCxGC, HPLC, TLC) methods which are introduced.

2.4.1 Optical spectroscopy

Spectroscopy is valuable tool in detecting basic properties of base oil samples and it is also usable in primary analysis of unknown type oil based samples. Applicable spectroscopy methods are IR that can be used to identify functional groups and hydrogen bonding in mixture and also structural parameters such as paraffinic, aromatic and naphthenic character of hydrocarbons.

Fourier transform IR (FT-IR) can be used for quantitative analysis of functional groups even with solid hydrocarbons. In study of B. Wilt and W. Welch³⁷ asphaltene content determination of crude oil could be determined with FT-IR quantitatively with 0.95 % coefficient of determination (r^2). Their predicted asphaltene content and actual asphaltene content that was used for calibration can be seen on figure 11.

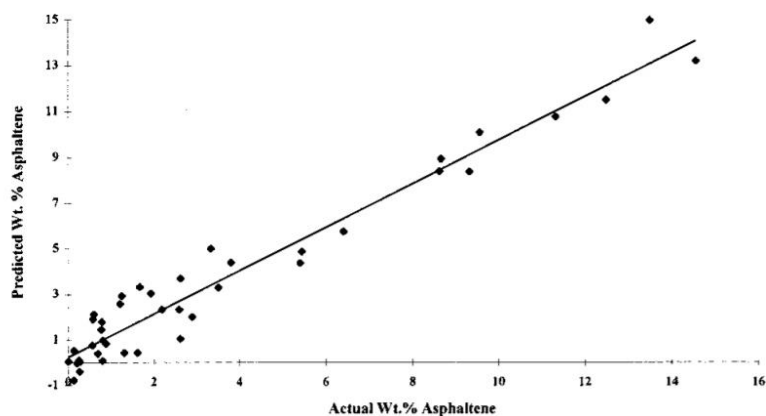


Figure 11. Predicted and actual asphaltene content in tested crude oil sample in 1998 study by B. Wilt and W. Welch.³⁷

In addition, Raman spectroscopy can be used to analyze aromatic and olefinic compounds in hydrocarbon mixtures and it does not need a sample preparation but with heavy samples spectroscopy data is more qualitative than quantitative.³⁸

2.4.2 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy (NMR) can measure compounds with odd number nuclei isotopes. Hydrogen and carbon have corresponding ^1H and ^{13}C isotopes that can be used for hydrocarbon analysis. NMR detects different average chemical structures and compositions in petroleum samples.

In base oils, all protons are attached to carbon and their shift is narrow (within 0-2ppm) rendering ^1H NMR next to useless in oil analytics. ^{13}C is more meaningful and it can be used in some length with base oils. Typically, NMR has difficulties to measure mixtures and complex compounds and this makes component analysis of pure NMR quite unusable with lubricant oils. More promising NMR method is diffusion-ordered spectroscopy (DOSY) and other suitable NMR measures include average structure parameters (ASP's i.e. average carbon chain length or branched hydrocarbons.) and 2D tests (as HSQC/HMQC/HETCOR, HMBC).³⁹

2.4.3 Chromatography

Chromatographic techniques play important role in analysis of oils including lubricants and it is extremely efficient when combined with mass spectrometry. In chromatographic techniques sample fractions are separated with mobile phase and stationary (immobile) phase based on their chemical and physical properties i.e. molecular size, polarity etc. Sample is dissolved within mobile phase and with its different adhesion to stationary phase leads to separation of components. Chromatographic methods with oil products include gas and liquid mobile phases.

Gas chromatography (GC) is used to analyze oil components that can be vaporized without decomposition. GC uses carrier gas as mobile phase and stationary phase is inside lining of glass or metal tube called column and it can be layer of liquid or polymer. GC detectors include destructive type flame ionization detector (FID) or mass spectrometry

(MS) or nondestructive thermal conductivity detector (TCD). GC analysis of petroleum and TLC analysis of VGO widely uses SARA (Saturates, Aromatics, Resins, Asphaltenes) fractioning expressed in figure 12.

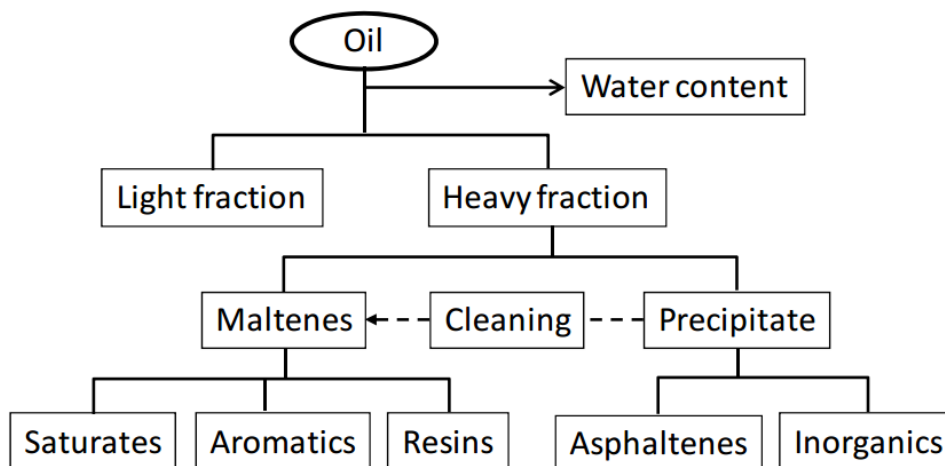


Figure 11. Oil SARA fraction method used with GC measurements.⁴⁰

Asphaltenes are hardest oil fraction to measure with GC as they have high boiling point. Some success has been with high temperature GC (HTGC) with short (5 m) glass capillary by M. Subramanian et al.⁴¹ HTGC with simulated distillation (SD or SIMDIS) can manage samples with boiling point up to around 540 °C. Higher boiling ranges can be covered with short, capillary columns up to final boiling point (FBP) of 800 °C with column temperature of 430 °C.⁴²

Comprehensive two-dimensional gas chromatography (GCxGC or 2D-GC) extends conventional GC's usability with new dimension when both polar and non-polar columns can be used to separate sample composition. Generated raster file can be patched with computer software to GCxGC chromatogram. GCxGC benefits in petroleum analysis that include: Structured chromatograms, better separation, larger capacity and higher sensitivity, but also suffers from peak tailing from cooling cryogenic modulator and big file sizes of measurements.⁴⁰ GCxGC-MS can be used to separate and analyze even highly complex samples beyond normal GC-MS capabilities. Example of GCxGC from Seeley *et al.*⁴³ studies of different biodiesels and petroleum diesel can be seen in figure 13.

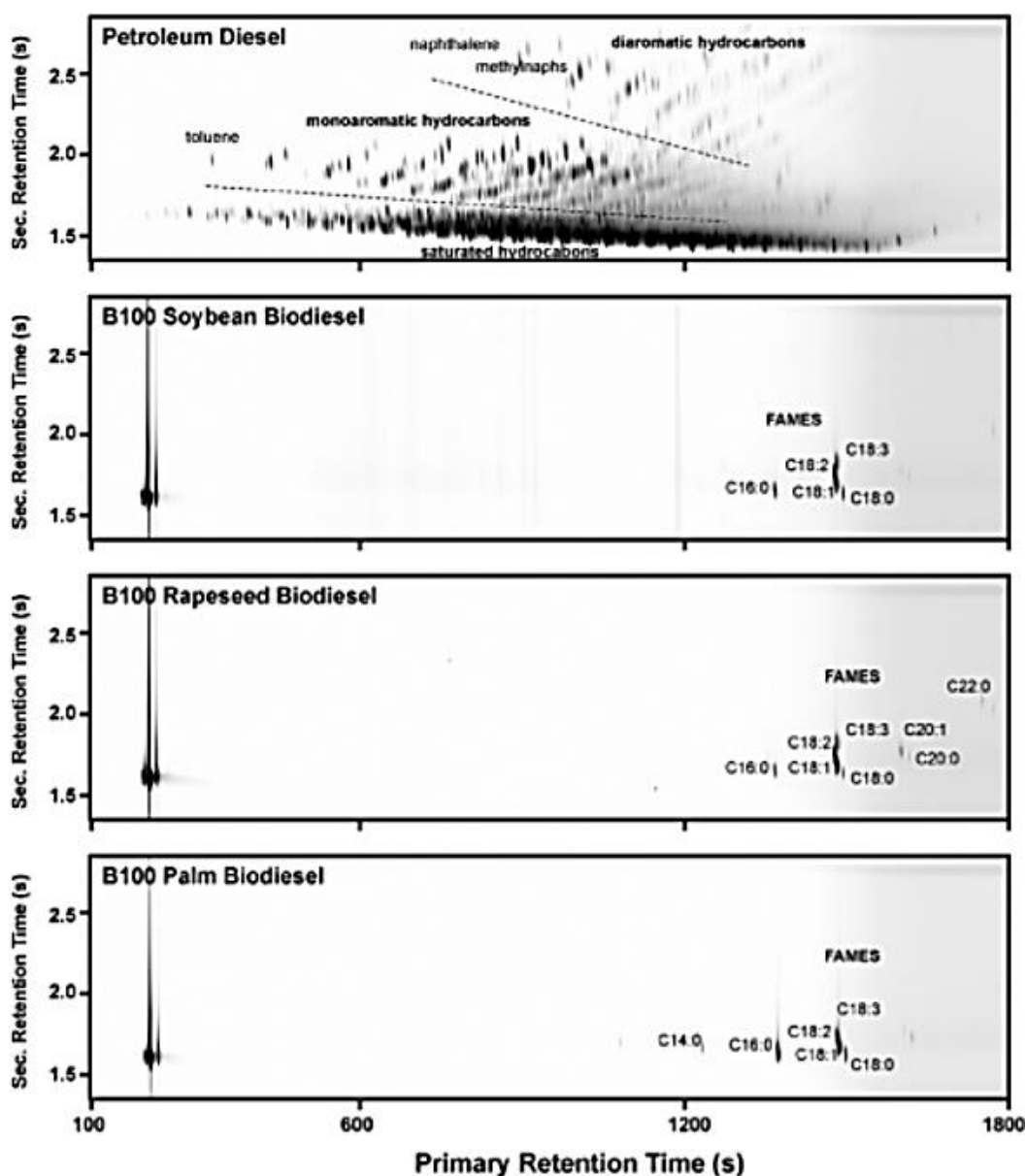


Figure 13. GCxGC high level signal amplified chromatograms from Seeley et al. studies of pure petroleum diesel and 3 types of pure biodiesel.⁴³

Chromatography with liquid phase includes open-column liquid chromatography, high performance liquid chromatography (HPLC), thin layer chromatography (TLC) and size exclusion chromatography (SEC).⁴⁴ LC is most used in analysis of crude oil with 80 % heavy oil fraction that needs temperatures higher than 350 °C to vaporize. These are more efficiently analyzed with HPLC than GC. HPLC enables to study whole sample if it is soluble in suitable organic solvent.⁴² TLC is able to analyze non-volatile products but it is more qualitative than quantitative analyzing method.³⁸

3 Lubrication, lubricants and base oils

Lubricants are used to reduce friction and wear of one or more surfaces in different applications. Study of lubrications and overall interacting surfaces in motion belongs in field of **Tribology**. Classical example of friction regimes is Stribeck curve which plots friction coefficient with different lubrication parameters.⁴⁵

Fundamental properties of lubricants are optimal lubrication film so that this film should be thick enough to ensure moving parts apart with enough lubrication in wanted use and environment, but also thin enough to minimize additional drag according to Stribeck curve. Lubricant should have suitable behavior within temperature range and also be chemically and physically quite inert in used applications i.e. they should not boil, freeze or combust in use. They should also carry away excess heat, contaminant and debris. Important environmental property is temperature as lubricants behave differently in different temperatures.

Most lubricants lose viscosity with increased temperature and cold conditions limits certain type of lubricants due to crystallization of oil wax components. Temperature depended lubricant properties include VI and pour point. There are lubricants in all physical phases but liquid lubricants and especially petroleum based products are most used. Lubricants can also be emulsions or water solutions used i.e. in drilling but this thesis addresses mainly petroleum based lubrication in automotive and engine uses.⁶ Typical lubrication oil is made up of base oil and additives. Typical lubricating oil contains about 90 % of base oil and 10 % of additives. Additives include metal detergents, viscosity modifiers, anti-foaming agents, pour point depressants etc.⁴⁶

Historically adding lubrication between surfaces to reduce friction dates at least to 17th century as residues of plant and animal oils are found from chariot axles and big stones. In late 18th century mineral oils started to gain popularity along factory bloom. Synthetic base oils (including PAO's and ester lubricants) emerged in 1950s for extreme conditions mainly for warfare as mineral oil tended to solidify that time because of their high wax content, but synthetic oil could be used in subzero conditions on eastern and northern fronts also in winter times. Within 1950's and 1960's synthetic oils got more popularity as they could be also used in high temperature uses, as in aviation engines and metal work.

By 1970's synthetic oils were available for public use in automobiles and hydrocracking and hydrotreating were introduced as alternatives for solvent dewaxing adding crude oil flexibility.^{6,46} Today lubricant oils are complex and tailored for specific needs and eco-friendliness are key develop directions. New-type lubricants include PIO's and GTL.⁶

In following sub-chapters basic use and important properties (viscosity, viscosity index, TAN and TBN) are reviewed. Lubricant types based on origin are also viewed (petroleum based, synthetic and bio-based). Main emphasis is in petroleum based automotive lubricants but bio-based, synthetic and other phase lubricants are also introduced.

3.1 Viscosity and classification of lubricants

Viscosity is one of the most important features in lubricant and base oils. It is expressed as resistance to deformation or so-called inner friction of flowing liquids under shear or tensile stress so that less viscous fluids flow more freely. There are different kinds of viscosities such as dynamic, kinematic and bulk viscosity. Dynamic viscosity (η) expresses relationship with Newtonian fluids between shearing stress (F/A) to the rate of deformation (du/dy) and it is also addressed as absolute viscosity.⁴⁷

$$\eta = \frac{F/A}{du/dy} \quad (1)$$

SI unit of dynamic viscosity is Pascal seconds (Pa s), but more used unit is Poise (P) where 10 P equals to one Pa s. Kinematic viscosity is measure of viscosity under gravity and it is expressed by dynamic viscosity to density.⁴⁷

$$\nu = \frac{\eta}{\rho} \quad (2)$$

SI unit of kinematic viscosity is square meters per second (m^2/s) but more used unit is stokes (St) and centistokes (cSt). Bulk viscosity is present in compressible fluids that are not under shear stress but have internal friction when in compression or expansion. There are some other non-SI-unit based viscosity measures and grades used in lubricant and base oils such as Saybolt universal second (SUS), Saybolt Furol seconds (SFS), SAE and API.⁴⁷

Viscosity of oil keeps thick enough lubrication layer between surfaces preventing them from touching but also thin enough to reduce additional drag according to Stribeck curve. Viscosity is not constant with changing conditions as it depends from temperature and pressure. Temperature dependence is measured with VI. VI represents relationship with viscosity and temperature and it is calculated by ASTM standards in 40 °C and 100 °C. All hydrocarbon oils decrease in viscosity with increasing temperature. Generally higher VI is favored as they maintain greater part of their viscosity in higher temperatures as seen in table 4 where compared base oils had originally 4 cSt viscosity.³¹

Table 4. Comparison of different 4 cSt base oils.⁶

Parameter	Test Method	PAO	100N	100N	100NLP	VHVI	VHVI	VHVI
SAE		IV	I	I	I	III	III	III
KV at 100 °C, cSt	ASTM D445	3,84	3,81	4,06	4,02	3,75	5,2	3,98
KV at 40 °C, cSt	ASTM D445	16,7	18,6	20,2	20,1	16,2	NR	16,61
KV at -40 °C, cSt	ASTM D 445	2390	Solid	Solid	Solid	Solid	Solid	Solid
VI	ASTM D 2270	124	89	98	94	121	127	141
Pour point, °C	ASTM D 97	-72	-15	-12	-15	-27	-18	-38*
Flash point, °C	ASTM D 92	213	200	212	197	206	210	225

*Probably pour point depressed

** Volatility at 250 °C after 1h, alternative is ASTM D5800

VI is affected and it can be modified by base oil composition. Paraffinic saturates increase VI while aromatics, naphthenes and impurities (mainly sulfur) decrease VI as discussed in chapter 2.3. VI can be modified after base oil production with additives which are widely used in multi-grade oils. These include polymers that can be thought as polymer coils which are tangled in cold and expand in high temperature increasing viscosity and reverting out temperature effect on viscosity. Typical viscosity classifications include SAE, API, ILSAC and ASTM from which SAE and API are discussed in oncoming chapters. Classifications and grades include number of tables that are desired to be excluded from this thesis as they are easily findable from common literature and they add little informational value to basic theory.⁶

Some base oils are still in SUS units and they can be divided into four different classes: low (90-150N), medium (200-250N), heavy (500-600N) and bright stock (very heavy) as expressed on Chevron Information Bulletin 13.⁴⁸ Additional letters are also used to address oil type such is N that stands for neutral and SN for solvent neutral.

SAE defines oil grade i.e. viscosity characteristics and engine can be built to certain viscosity grade lubricant oil. API groups define oil type i.e. what oil composes of and how it has been manufactured. Also API standards have minimum requirements in lubrication, heat capacity and cooling efficiency and they have certificates for lubricants meeting specific requirements (example API-TA).⁶

Other important properties of oils are **pour point**, **TAN** and **TBN**. Pour point is the lowest temperature where oil will flow under standardized test conditions and it is relevant when lubrication is used in cold conditions. Normally lubrication oils have pour point of -40 to 0 °C. There are different pour points i.e. viscosity pour point and wax pour point. **Total acid number** (TAN) measures increase of oil oxidation and also increased concentration of corrosive acidic compounds and **Total base number** (TBN) represents reserve acid neutralization capability of the oil. TAN and TBN cross themselves over time when oil is used for long period of time.

3.1.1 SAE

Society of Auto-motive Engineers (SAE) is U.S. based standardization organization with emphasis in transport industries. SAE has widely used SAE J 300 and SAE J 306 standards that classifies automotive engine lubricant oils in to 12 groups (0W, 5W, 10W, 15W, 20W, 25W, 20, 30, 40, 50, 60) where W stands for winter. Groups have different requirements in different temperature. There is also similar classification for automotive gear lubricant viscosity grades (70W, 75W, 80W, 85W, 80, 85, 90, 110, 140, 190 and 250). There are different requirements for different temperatures, in example for high temperature requirements are as follows: minimum kinematic viscosity at 100 °C, high temperature maximum kinematic viscosity at 100 °C and high shear rate viscosity at 150 °C. All requirements can be found in SAE publications.⁶

SAE classified lubricants can be divided into **monograde** or **multi-grade**. Monograde fulfills one SAE viscosity standard where multi-grade needs to fulfill two standards in different conditions i.e. 15W/40 oil meets 15W standard in cold climate and 40 -standard in normal operation temperature. Currently majority of automotive oils are multi-grade – type where properties are achieved with additives such as VI-modifier while monograde uses are seasonal or restricted use (crude example being lawn mower) and applications that are sensitive to VI-modifiers.⁶

3.1.2 API lubricant grades

API lubricant grades (also known as stock categories) are widely used in petroleum industry and it include five classes with some additional remarks. API groups are I, II, III, IV and V, they are determined from viscosity index and manufacturing processes need to obtain certain viscosity type (API 1509 Appendix E). Groups I, II, and III are for petroleum based base oils and some with “+” in addition for specific qualities. IV is for PAO type oils (synthetic) and V is for all the rest (including synthetic and bio-based). Different API groups, corresponding VI, composition and manufacturing methods are arranged in table 5.⁴⁶

Table 5. API groups and corresponding viscosity indexes (VI), composition and manufacturing methods⁶

API grade	VI	Composition	Manufacturing type
I	80-120	Saturates <90 % and/or sulfur >0.03 %. (Aromatics >10 %)	Solvent extraction, catalytic dewaxing, hydrofinishing processes.
I+	103-108	Saturates <90 % and/or sulfur >0.03 %	Typical base oils are 150SN (Solvent neutral), 500SN, 150BS (brightstock)
II	80-120	Saturates > 90 % and sulfur < 0.03 %	Hydrocracking and solvent or catalytic dewaxing processes.
II+	113-119	Saturates > 90 % and sulfur < 0.03 %	Virtually all hydrocarbons are saturated which increases antioxidation properties.
III	>120	Saturates > 90 %, sulfur < 0.03 %	Manufactured further from base oils with isohydromerization
III+	>140	Saturates > 90 %, sulfur < 0.03 %	
IV (PAOs)	-	Poly-alpha-olefins	alpha-olefin polymerization
V (Other)	-	i.e. Esters, Modified vegetable oils	varies

For more detailed chemical composition with API grades, see table 3. API III class base oils are also known as very high viscosity index (VHVI) oils or unconventional base oils (UCBO) by different manufacturers. Oils with VI over 140 are also known as extra high viscosity index (XHVI) oils.

3.2 Types of lubricants

Lubricants can be divided by number of ways by their physical phase (solid, liquid), lubrication properties, origin, use etc. Here expressed division is based on their origin: crude oil based mineral lubricant oils, synthetically made lubricant oils and bio-based lubricant oils. Other lubricants are shortly expressed but not reviewed further. Division is still quite artificial as many synthetic lubricant base oils originate from petroleum products and petroleum is also considered biogenic. Because of this synthetic oil are specified here to mean base oils from other sources than crude oil.

Synthetic and mineral oil differences are quite shallow as conversion of VGO to high grade API III oils modifies chemically over 80 % of its components and in some literature highly modified mineral oil (API grade III) is addressed as fully synthetic.⁶ There is exponentially larger number of lubricants in all uses combined i.e. industrial, aviation and marine. Used oil is normally selected based on use and price. Synthetics have some benefits when compared to petroleum based oils, but not all factors are better. Important notice is also the price as rare and far refined oils are more expensive than basic oils as seen in table 6.

Table 6. Western European List Prices for Lubricant Base oils, March 2004⁶

Fluid	List price (\$/ton)	Relative price to Group I
Group I base oils	370	1.0
Group III (VHVI) base oils	600-700	1.6-1.9
Group III+ (XHVI) base oils	900-1000	2.4-2.7
PAO	1400-1500	3.8-4.1
Polyalkylene glycols	2300-3500	6.0-6.6
Polybutenes	950-1750	2.6-4.7
Diesters	2300-3500	6.2-9.5
Polyol esters	3000-4000	8.1-10.8
Phosphate esters	3750-5250	10.1-14.8
Alkyl benzenes	1350-1450	3.6-3.9

Current interest is in biodegradability and ultra-high performance products i.e. alkylated aromatics and especially alkylated naphthalenes as they have outstanding thermos-oxidative and hydrolytic stability with good VI.⁴⁹

3.2.1 Mineral lubricant oil

Petroleum based lubricant oils have carbon number typically within C₁₅-C₄₀.²⁸ They are manufactured from high boiling crude oil fractions that are either solvent refined or hydroprocessed as discussed in chapter 2.3. Chemical composition depends highly from feed and processing history and base stocks are composed of thousands of different chemical components and their isomers unlike synthetic stocks that contain just few chemically different molecules.²²

Mineral lubricant oils can be grouped in similar categories as crude oil: paraffins (including n-paraffins and iso-paraffins), naphthenes (most commonly cycloparaffins and dicycloparaffins, but polycycloparaffins with 3, 4, 5 and higher saturated rings can be present in smaller concentrations). Mineral based lubricant oils are graded with API grades as discussed in chapter 3.1⁶ Chemical and physical comparison of same class (150N) base oil with different API groups can be seen in table 7.

Table 7. Comparison of 150N Base oil API groups I, II, III, and IV⁶

API Group	I	II	III	IV
Processing	Solvent refined	Lube Hydro cracking	VHVI	Synthetic PAO
Physical characteristics				
KV at 100 °C, cSt	30,1	29,6	32,5	31,3
KV at 40 °C, cSt	5,1	5,1	6,0	5,9
VI	95	99	133	135
Pour point, °C	-12	-12	-15	-60
Flash point, °C	216	222	234	240
CCS, viscosity at -20 °C, cP	2100	2000	1230	900
NOACK**, % loss	17,0	16,5	7,8	7,0
Chemical characteristics				
Sulphur, ppm	5800	300	<10	<10
Nitrogen, ppm	12	4	<1	<1
Composition, wt-%				
Paraffins	27,6	33,4	55,5	100,0
Aromatics	22,5	3,5	0,8	0,0
1-ring naphthenes	20,8	30,2	20,4	0,0
2-ring naphthenes	25,9	17,2	12,1	0,0
3-ring naphthenes	2,9	9,3	9,1	0,0
4-ring naphthenes	0,3	5,1	2,1	0,0
5-ring naphthenes	0,0	1,1	0,0	0,0

It is evident that higher API group presents higher VI, lower pour point and higher flashpoint. These physical qualities are result of chemical composition. With higher API group heteroatom concentration and aromatic fraction decreases while paraffin fraction increases. For example, extra high VI III- API category contains over 90 % of paraffins and only trace amounts of aromatics.⁴⁶

Solvent refining produces mainly low VI base oils (API I and API II classes) and Hydroprocessing with isomerization produces high VI base oils (API III including VHVI and XVHI base oils). Trend in lubricant base oils is increase of high VI (API III including VHVI and XVHI) products and decrease of low VI oils (mainly API I class). In 2004 first time API II and III class oil production capacity surpassed the production capacity of API I oils with clear trend as seen in figure 14.

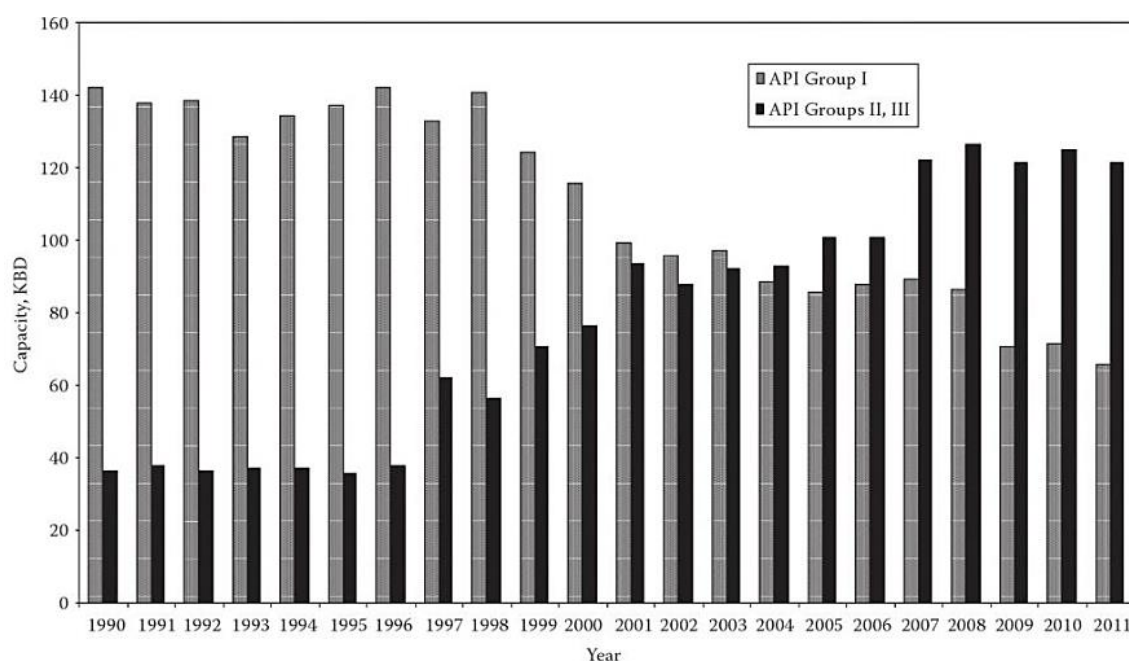


Figure 12. API I and API II & III capacities of north America 1990-2012.⁶

Refineries have significant investments in hydroprocessing technologies and several breakthroughs in catalyst development and utilization has been made to maximize feed flexibility and VI retention.⁴⁶ As reminder of chapter 2.5 Isomerized and saturated paraffins are preferred and as they have higher VI and lower pour point. High upside in hydroprocessing is that it can be used to upgrade lower quality into high value high VI base oils. Mineral oil quality is related to portion of paraffins and monocycloparaffins. Chemical difference between synthetic PAO (up to 100 % isomerized paraffins) and cheaper API grade III is getting smaller.⁶

3.2.2 Synthetic lubricant oils

Synthetic lubricant oils are chemically produced and they cannot be extracted from crude oil. Synthetic lubricants are classified in API categories IV and V where PAO is in API grade IV and everything else is in API grade V. Synthetics were used mainly as niche-product as they had some properties superior to mineral based lubricants i.e. pour point and VI but today synthetic oils market share is great and difference between PAO and API III is getting smaller.⁵⁰ Different synthetic oil types can be seen in table 8.

Table 8. Examples of different synthetic lubricant types

Synthetic type	Example
Pure hydrocarbons	PAO, PIO, alkyl cyclopentanes, alkylated aromatics
Oxygen containing hydrocarbons	Polyalkylene glycols, carboxylic acid esters, polyphenyl ethers and polymethacrylates
Oxygen and phosphorus containing hydrocarbons	Phosphoric acid esters
Silicon and oxygen containing hydrocarbons	Silicone oils, siloxanes and silicate esters
Fluorine and oxygen containing hydrocarbons	Polyfluoroalkyl ethers
Fluorine and chlorine containing carbons-compounds	Chlorofluorocarbons and chlorotrifluoroethylenes

Quantitatively most important synthetic lubricants are PAO, esters and PAO/ester-blends as seen in table 9. In addition, many synthetics especially different esters are used as additives on base stocks because of their superior lubricity compared to typical base stocks.⁶

Table 9. Pathmaster Marketing estimated consumptions (tons) consumptions of synthetic Base oils in western Europe between years 1990-2002 ⁶

Year	1990	1996	1998	2000	2001	2002
Synthetic type (tons)						
PAO	45	90	125	190	220	220
Esters	45	55	90	110	120	125
Polyisobutenes	22	28	38	46	50	52
Polyalkylene glycols*	15	18	23	25	25	26
Phosphate esters	4	4	5	5	5	5
Alkyl benzenes	8	9	11	11	11	11
Others	6	8	9	10	11	11
Total (tons)	145	212	301	397	442	450

*PAG content only.

Most important synthetic lubricant in volume is **poly-alpha-olefins** (PAO) which are practically saturated olefin oligomers that can be categorized as paraffins. PAO was first presented by Gulf Oil Company and later Chevron acquired it. Today PAO includes catalytic oligomerization products of linear olefins with six to ten carbon atoms. PAO's are produced in two-step reaction sequence from linear alpha-olefins. First step is oligomer mixture production with catalyst (typically BF_3) with protic co-catalyst with hydroxide group ROH (such as water or alcohol). Alpha-olefins produce alpha-olefin dimers, trimers, tetramers etc.^{6,50} Second step after washing away catalysts is hydrogenation of unsaturated oligomer and distillation of unreacted or unwanted monomers. Hydrogenation is typically performed with metal catalyst (i.e. palladium/alumina). Viscosity of product depends on used catalyst and higher viscosity (40 and 100 cSt) PAO are produced with different catalysts such as TiCl_4 or alkyl halides.^{6,50}

Other synthetic hydrocarbon-type stocks are poly-internal-olefins (PIO), GTL and esters. PIO is produced in similar manner than PAO's but n-olefins are used as feedstock instead of alpha-olefins.⁵⁰ Lubricant suitability of PIO is still being studied.⁶ Gas-to-Liquid (GTL) uses Fischer-Tropsch (F-T) synthesis wax as feed and it is capable to produce high grade fuels, chemicals and lubricating products from natural gas or similar less expensive feed and this has gained merit for GTL. GTL and other F-T based oils are close in compositional comparison to PAOs and high VI API III+ mineral oils.⁶

Esters are produced with classical reversible Fischer esterification between alcohol and acid. Typical lubricant esters include carboxyl acid based esters, diesters and polyol esters but these represent only minute part of all ester production. Bio-based esters typically have quite poor thermo-oxidative stability as unsaturated fatty acids oxidize even at room temperature. Because of the number of possible different esters, they provide almost limitless structural and performance possibilities.⁶

3.2.3 Bio-based lubricant oils and modified bio-lubricants

Biodegradable lubricant fluids have shown steady growth in last decade. Bio-based lubricant oils normally defined as agricultural materials and their derivatives, such as animal fat, vegetable oils (VO) and chemically modified VOs. These can be considered "green" as they are renewable, possess high levels of biodegradability, low aquatic

toxicity and do not accumulate on the environment. First new age bio-lubricant oil was used in 1996 when canola oil was used to pursue ecofriendly alternatives for vehicle lubricants and now many lubricant oil vendors have developed products that use fully or partially animal or plant based oils. ⁶

Chemically bio-based lubricants generally mean compounds with long carbon chains with carboxylic acid- or ester groups such as triglycerides and fatty acids. Short triglycerides or fatty acid chains are water soluble, but as chain length increases the water solubility decreases. Linear (saturated) chains have also high melting point and are mainly solids in room temperature limiting their use. Most of VO compositions are triacylglycerols and other oils include free fatty acids, sterols, diglycerols etc. Vegetable oils normally include high portion of unsaturated fats. Polyunsaturated fatty acids have double bonds in multiple sites up to typical maximum of six. Lipid peroxidation readily rises while degree of unsaturation increases. Double bonds can also be *trans*-bonds and these *trans*-fats increase thermal stability but has little impact on melting point.⁶

Vegetable oils have in some applications (as in rolling, cutting and drawing) some better properties compared to conventional oils including superior lubricity, good anticorrosion, better viscosity-temperature characteristics and low evaporation loss. Vegetable oils are bad in cold environment as they have poor low-temperature fluidity and they have low thermo-oxidative and hydrolytic stability. Highly unsaturated fats are also vulnerable to rancidification.⁶

VO's can be genetically or chemically altered to improve cold environment properties and oxidative stability together with additives, diluents or functional fluids. Most of chemically modified biodegradable VO's are esters but these are more expensive than common VO's or mineral based lubricants. Most common VO is soybean oil and it is the cheapest easily available VO worldwide while other VO include canola, rapeseed, sunflower, peanuts etc. Different chemical functional groups depending on VO feed can be altered. Common functional sites are double bonds that can be epoxidized with acids or hydrogen peroxide to produce epoxidized VO's i.e. epoxidized soybean oil (ESBO) that is potential chemical product precursor with many materials as it's epoxy site can be easily functionalized. ESBO based diester derivatives, chemically modified soybean oil (CMSBO), have good oxidative stability and low-temperature properties in lubricant use compared to mineral based lubricants.⁵¹

3.2.4 Other lubricants

Other lubricants include non-liquid lubricants, i.e. solid lubricants as graphite, metal alloys, polytetrafluoroethylene (PTFE or brand name Teflon) and molybdenum disulfide; gaseous lubricants such as air cushions or air bearings; and phase mixtures, emulsions and solutions.

Solid or dry lubricants are typically used in high temperature uses when liquid and oil based lubricates cannot be selected. Main solid lubricants are molybdenum disulfide and graphite where lubricating properties can be explained by layered structure with weak forces between layers as with graphite, but consensus has shifted once graphene was noticed to lose its lubricative properties in space. Some non-lamellar structures express good lubricating properties as well such as soft metals, metal alloys and some oxides. Recent development in solid lubricants are micro-porous polymeric lubricants (MPL) where polymer structure contains small pores that can be filled even over 50 m-% with lubricant. Polymer structure can absorb or release oil when needed.^{52,53}

Gaseous lubricants have lowest viscosity known and contrary to liquid lubricants their viscosity increases with temperature. Gaseous lubricants include air, nitrogen, helium and oxygen. They can be used in ultra-high and ultra-low temperature uses such as aerodynamic and aerostatic bearings, but their viscosity limits carrying capacity to much smaller than with liquid or solid lubricants.⁵²

Phase mixtures and emulsions contain many components possibly in different phases i.e. water-in-oil emulsions and refrigerant-lubricant mixtures. They are typically used as compromise for both source material qualities. Water-in-oil mixtures contain water emulsified in oil as fire-resistant hydraulic fluids and it trades lubrication compared to pure oil to fire-resistivity. Refrigerators and air-conditioning systems use refrigerant-lubricant mixtures that are strongly asymmetric and can contain complex phase behavior such as open and closed miscibility gaps, liquid-liquid-vapor equilibrium and density inversions.⁵⁴

4 MS methods for base and heavy oil samples

Mass spectrometry is one of the most important analysis tools in petroleomics even as oil samples are tedious to measure with mass spectrometer. Mass spectrometry gives information of elemental compositions of individual molecules and it can be coupled with other important analytical instruments, such as chromatography discussed in chapter 2.4.3. Using chromatographic separation methods with increasingly heavier oil samples with heteroatoms becomes harder and more practical method is to use high resolution mass spectrometry with direct insertion or infusion.

Difficulties with base and heavy oils are result from nonpolar and highly complex samples in quite large mass range including isobaric ions with close m/z values already without fragmentation (i.e. ^{13}C versus ^{12}CH (4.5 mDa), ^{13}CH versus ^{12}CD (2.9 mDa), and H_2 versus D (1.5 mDa)). Oils also have low vapor pressure and thus high boiling point for atmospheric pressure ionization techniques where nonvolatile and thermally labile samples are problematic and petroleum products suffer from fragmentation even with soft ionization methods.

Base oil sample properties require soft and suitable ionizing method with high enough resolution in mass analyzer to distinguish peaks from another and short enough flight/pass time for sample not to fragment. Challenging petroleum samples can be argued as benchmark of mass spectrometry method performance in some cases.²² For perspective, positive ESI-MS spectrum consisting of only polar components of crude oil (10 % of all molecules)¹⁵ with mass range between 200 and 800 m/z can be seen in figure 15.

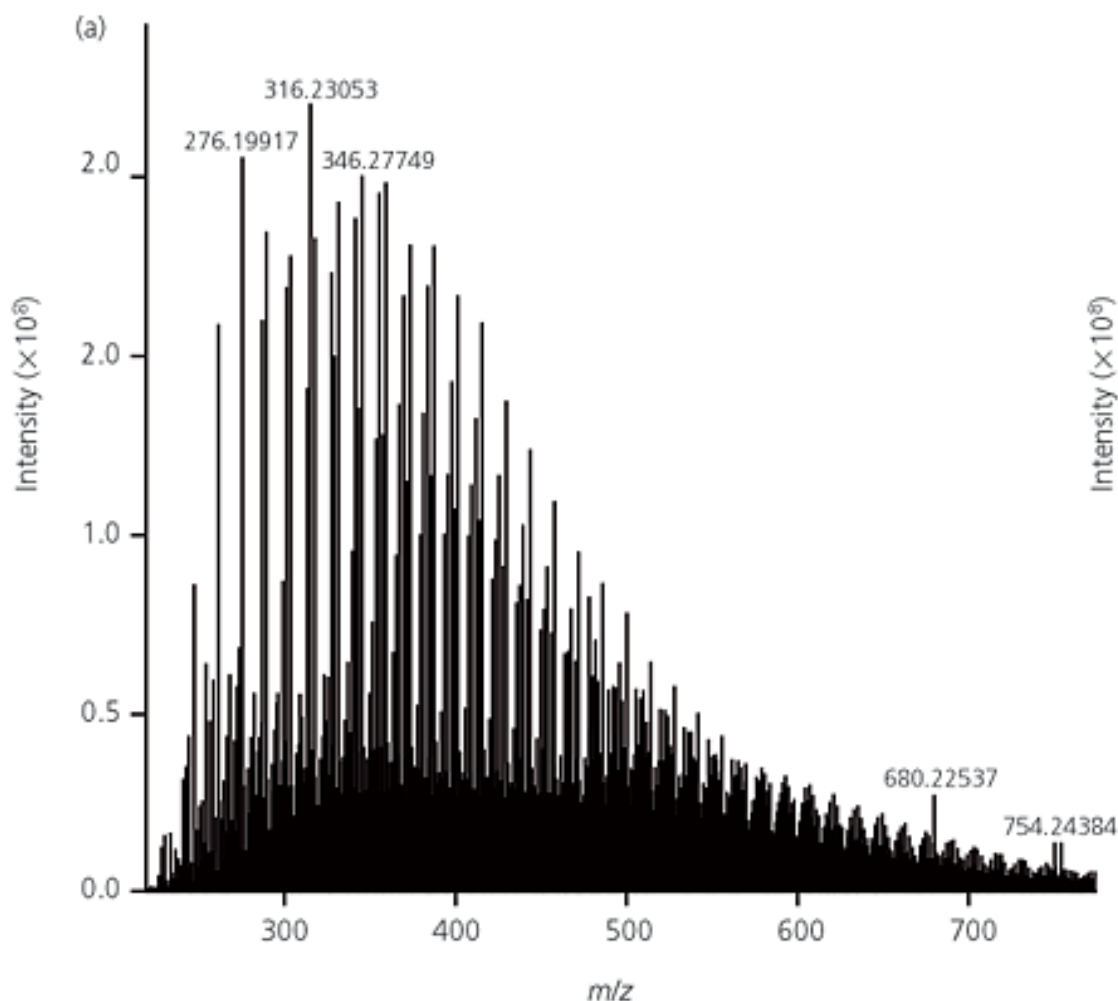


Figure 13. ESI spectrum in positive ionization mode of crude oil.⁵⁵

In 2007 there was yet no robust MS method to characterize molecular mass distributions or chemical structures broadly of petroleum derived products above ~ 400 - 450 Da according to Alan A. Herods *et al.*⁵⁶ overview. Different ionization methods with mass analyzer can be used to attain different chemical information of petroleum samples with over 450 Da mass range. Oil sample results can be further analyzed dividing mass peaks to different groups and categories based on homologous series.

High resolution mass spectrometry (HRMS) can assign ions from solvent processed base oils (API group I) into 38 hydrocarbon groups: Paraffins (n- and iso-), monocycloparaffins, noncondensed polycycloparaffins, condensed polycycloparaffins, aromatic types (16 classes) having between 1 and 7 condensed aromatic or saturated rings, aromatic types (16 classes) containing sulfur and aromatic types (3 classes) containing oxygen. API group I base stocks have wider range of base stock components including thiophenes and aromatics than those that are present in Group II and III base stocks.⁶

Other coping methods to ease complex petroleum analysis is highly exploited graphical comparison of Kendrick mass defect versus Kendrick mass plots, 2D or 3D van Krevelen analysis (H/C ratio vs O/C ration or N/C ratio or S/C) and isoabundance-contoured plots of DBE and carbon numbers. Kendrick mass sets chosen fragment (typically CH₂) to integer value in Da. For example, CH₂ is given value of 14 Da instead of IUPAC value of 14.01565. IUPAC value mass defect versus nominal mass would give visually skewed plot when compared to one with Kendrick's masses. Example of petroleum Kendrick plot can be seen on figure 16.^{57,58}

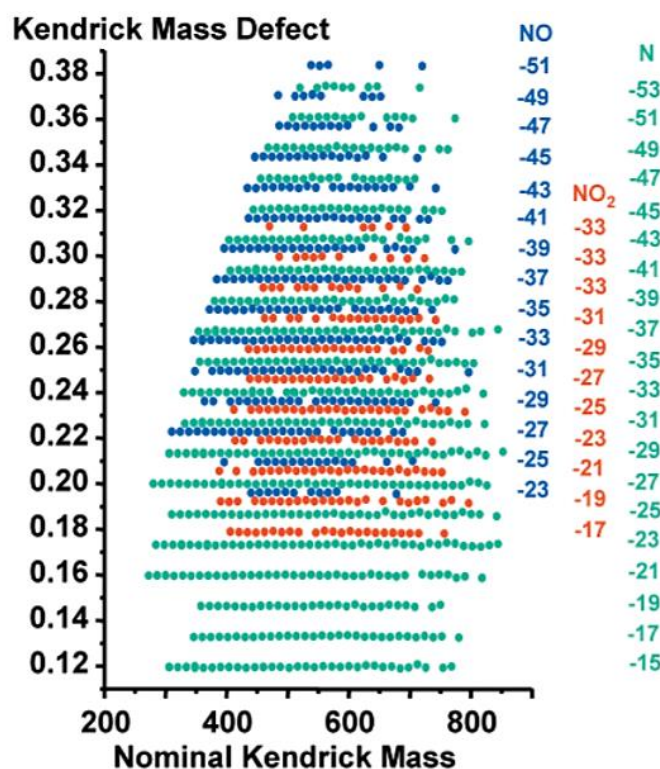


Figure 16. Kendrick mass defect versus nominal Kendrick mass.⁵⁸

Kendrick mass plot gives faster visual evaluation of different compound classes (e.g. NO) and different types of hydrocarbons differ in mass defect and distribution of CH₂ groups than purely statistical data would give.⁵⁸

In this chapter mass spectrometry is generally introduced and common petroleum ionization methods and analyzers are discussed. Methods capable to analyze nonpolar samples are emphasized but also some widespread methods capable to analyze polar samples are presented in small extent. Object is not to list all ionization methods and analyzers as only small portion are suitable with petroleum based samples. Different ionization methods are discussed in chapter 4.2 and different analyzers in chapter 4.3.

4.1 Mass spectrometry

Mass spectrometer (MS) distinguishes different ions based on their different mass-to-charge ratio (m/z) by secondary measurement methods such as flight time, flight path or resonance frequency. Sample molecules are first ionized in ion source and then ions are separated by mass analyzer. Lastly ions are detected with ion detector together with computer data system. Overview of MS magnet sector instrument can be seen in figure 17. There are many kinds of ionization techniques for different kinds of samples and number of different analyzers that separate ions based on their masses.⁵⁹

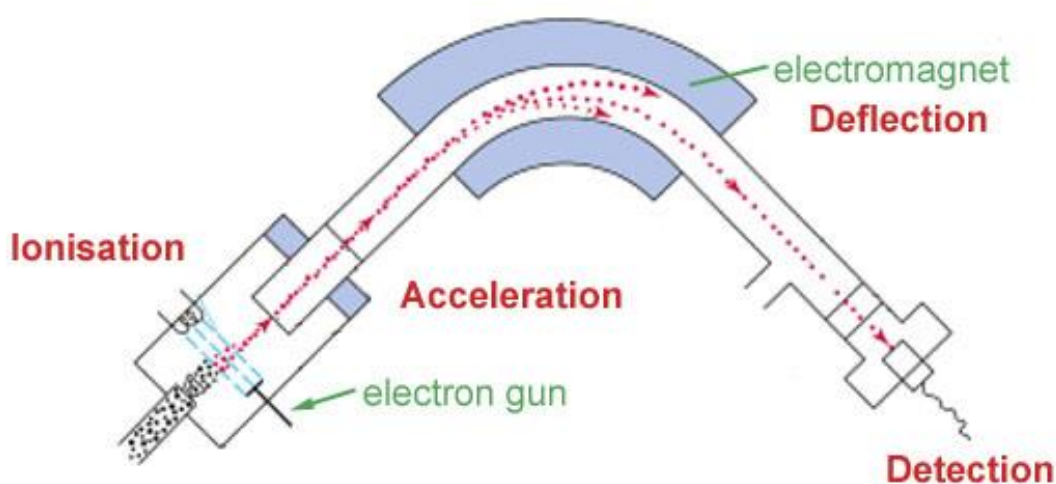


Figure 14. Basic principle of MS instrument with EI ion source and sector analyzer.⁶⁰

Modern MS is sensitive, rapid and informative analytical tool that can be used both in quantitative and qualitative measurements from pure compounds and isotopes to extremely heavy and complex mixtures in all phases. MS methods are able deal down to 10^{-15} - 10^{-21} M analyte concentrations and when this is compared to Avogadro's number ($6.022 \cdot 10^{23}$) we can see that these methods get closer to absolute limit of analysis in sensitivity.⁶¹

There are considerable number of different assemblies of ionization methods, mass analyzers and detectors. Few of many examples of mass spectrometry uses are protein sequencing and characterization, drug discovery by determining drug structures, metabolites and disease biomarkers; genomics by determining oligonucleotide sequences; environmental testing to analyze water purity or food quality as well as in geology to carbon dating and petroleum composition.⁶²

MS can be combined with number of different analytical methods into so-called hyphenated or hybrid techniques. For example, GC-MS stands for gas-chromatograph connected to MS and UPLC-ESI-Q-TOF-MS consists of mass spectrometer where there is first UPLC that is Waters corporation trademarked high performance liquid chromatograph and similar methods by other competing enterprises have abbreviated as UHPLC. This is followed by ESI which is sample ionization method by electrospray ionization, Q stands for quadrupole that can be used either analyzer or collision chamber and TOF is analyzer method where different ions are separated by their time of flight.

According to Stuart M. Press's article⁶³ in Spectroscopy from year 2013, MS demand trend has been ascendant as more mass spectrometers are sold each year. MS focus has been on clinical analysis sector that is the strongest industrial driver of demand for mass spectrometers and LC-MS add up to 50% of all spectrometer demand in 2012 as seen in figure 18.

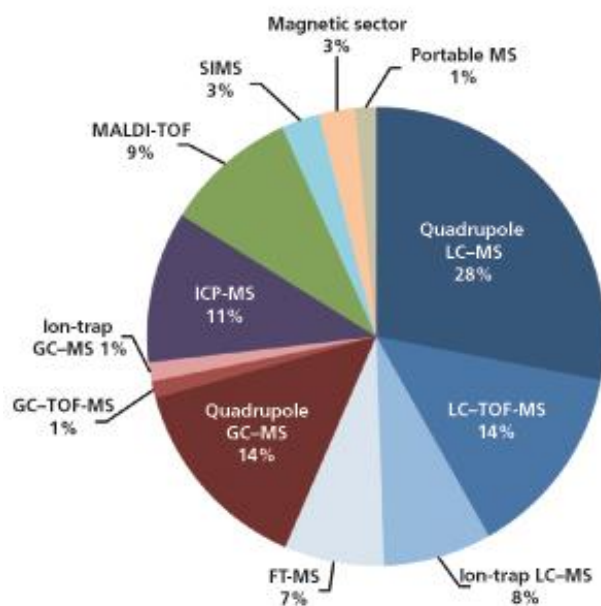


Figure 15. Worldwide demand for Mass spectrometric methods in 2012.⁶³

There are only few mass spectrometer manufacturers even when considering risen demand for MS equipment. There is still steep entry barrier mainly due to design, manufacture, marketing and support complexity. Major vendors and their market shares have remained fairly consistent during the past decade but competitive landscape has shifted considerably. One of the most recent trends include Thermo's Orbitraps increased popularity as mass analyzer but has little available market share data.⁶³

4.2 Ionization methods

Ionization method is tool ionize sample molecule for mass analyzer and different ionization methods can be used with heavy oil samples depending on studied properties together certain mass analyzers. No one ionization method is optimal for total spectrum of oil samples and therefore different portions of crude oil and oil products are ionized with different ionization methods, i.e. polar components can be ionized steadily with ESI, volatile nonpolar components with FD and heaviest asphaltenes with LDI based ambient ionization methods i.e. Matrix assisted laser desorption ionization (MALDI) and two step laser ionization (L^2MS).

One way to divide ionization methods is ion source operation pressure: Conventional ionization techniques operate in high vacuum (EI, CI, MALDI, FAB/LSIMS, FI/FD) from which EI, CI and FI/FD uses also high temperatures. Atmospheric pressure ionization methods include ESI, APCI, APPI, APLI and AP-MALDI.

Newest and probably most fast progressing MS ionization field is ambient ionization (AI) techniques. Ambient ionization methods are methods that can ionize samples *in situ* (i.e. pharmaceutical testing and explosive residues). Some examples of AI include spray based, chemical ionization based and also acoustic, but as Huanwen Chen⁶⁴ pointed out there are “over 25 different ambient surface desorption/post-ionization methods for the analysis of medium to low volatility compounds have been described in the literature in the last few years.” There is just no rationality to address all of them here.

Progression and possible non-polar sample capability of many methods makes AI really interesting field to follow also from petroleomics point of view as they propose novel petroleum ionization methods. Many of them display same types of limitations as conventional ionization methods that they are based on. For example, spray based methods are less adequate to ionize nonpolar samples as is ESI. AI techniques have yet very little literature on petroleum products and are therefore less expressed here.

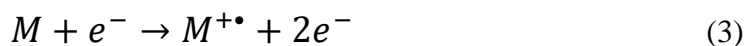
Suitable ionization methods are capable to ionize nonpolar hydrocarbons of wanted size without excess fragmentation. Sample elemental compositions sets requirements for mass analyzer to distinguish different close m/z or isobaric ions.

According to A. Marshall and R. Rodgers⁶⁵ from 2008 suitable soft ionization methods for non-polar petrochemicals are APPI and FD with possible opportunities with L²DI and LIAD. On same direction was T. Schaub⁶⁶ in 2005 proposing also low voltage EI, CI, LDI (laser desorption ionization), APCI, MALDI and FI. Also Kenttämä Labs from Purdue University has developed petroleum ionization methods such as LIAD and APCI.⁶⁷ R. Rodgers and A. McKenna wrote exhaustive review²⁷ of petroleum analysis in 2011 discussing many new advancements on broad scale including compared ionization methods.

ESI and ESI based AI's are largely used to study polar petroleum products but reactive DESI is used to study petroleum products.²⁷ Some other ionization methods have been used for small petroleum studies but these are not addressed further as no additional information of them is published to date.

4.2.1 EI

Electron ionization (EI, or formerly Electron Impact ionization) uses high energy electrons, typically 70 eV, to ionize sample. Electrons are detached by thermionic emission from filament and they are accelerated towards collector plate with electric field. Evaporated sample is flown between filament and collector. High energy electrons from filament ionize some of the sample molecules when enough energy is transferred and electron can be expelled from bonding or nonbonding electron from sample molecules but no actual electron **impact** happens.⁵⁹



Producing predominantly positive radical ions as molecular ions. Typically 10-20 eV is transferred to molecule and approximately 10 eV is enough to ionize most organic molecule and excess energy leads to fragmentation.⁵⁹ Excess energy transferred to sample molecule from electron can produce radical cations, carbocation fragments and different ion pair formations by numerous different methods. Overview of EI ion source can be seen in figure 19.

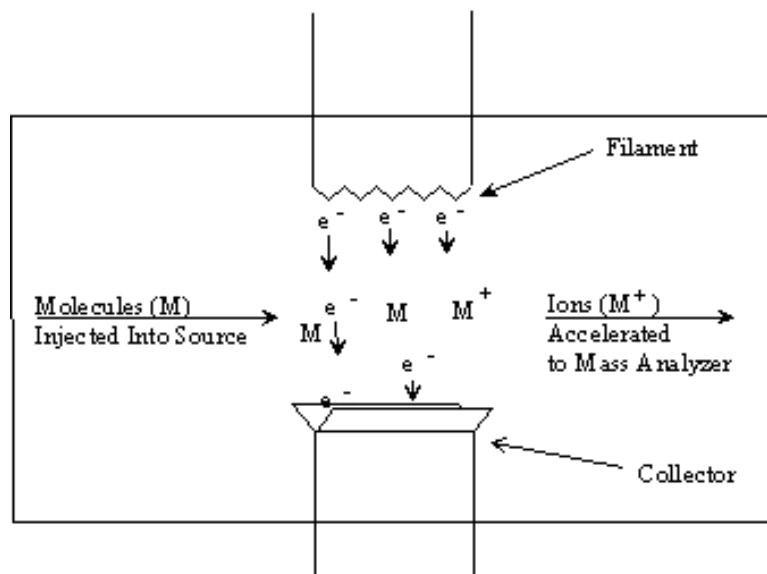


Figure 19. Basic principle of electron ionization.⁶⁸

EI is classical and hard ionization method because it carries large amount of energy to sample which produces more fragmentation. This fragmentation and produced fragmentation pattern can however be used as information of molecule structure as different isomers fragment differently. Number of fragmentation patterns are included in commercial libraries that can be compared to sample results. A drawback is that fragmentation lowers molecular ion abundance and makes spectra more complex. Hydrocarbons demonstrate fragment pattern where CH_2 is repeatedly lost as seen in figure 20.

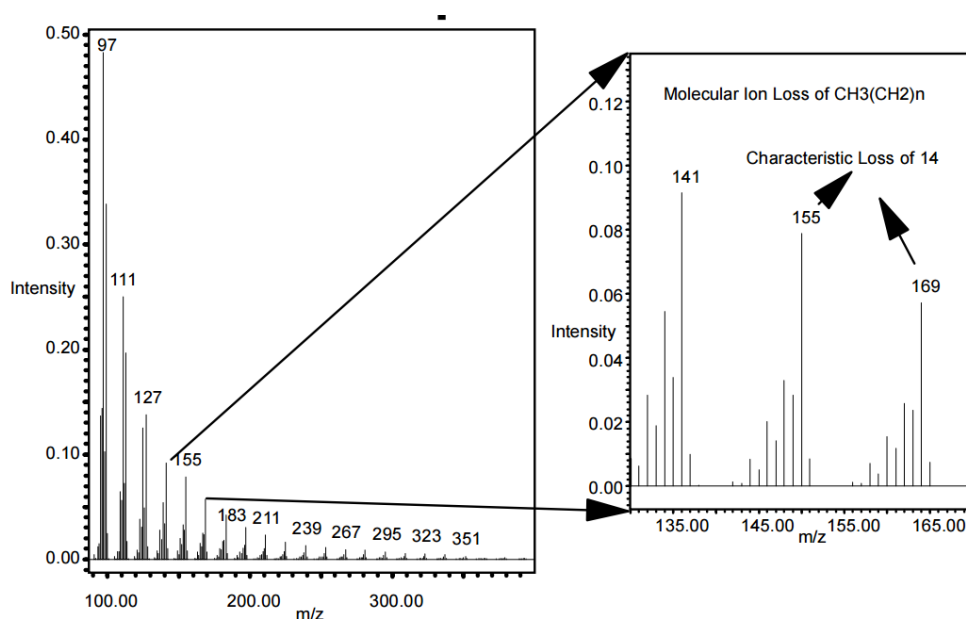


Figure 20. EI fragmentation spectrum of crude oil sample showing CH_2 - pattern.⁶⁹

EI in petroleum analysis can be used to ionize sample type, but the problem with base oils and lubricants that EI ionization causes fragmentation among base oils complexity. High fragmentation makes EI quite unsuitable for already highly complex base oil analysis and molecular ions of big molecules and small quantities cannot be steadily ionized as mass range is limited to approx. 1000 Da.⁶⁹ According to Alexander B. Fialkov *et al.*⁷⁰ conventional EI with mass analyzer is poor at measuring other than minor components in petroleum products as petroleum spectra typically exhibits dominant low mass fragments and the spectra are quite similar to each other.

One useful method of petroleum EI analysis is low voltage EI expressed already in 1988 by Thomas Azcel and C.S Hsu⁷¹ where EI uses 10-18 eV instead of 70 eV to reduce excess fragmentation. This is supported with study by Jinmei Fu⁷² that demonstrated that low voltage EI coupled with FT-ICR is viable method that can be used to study even moderately heavy oil fractions and VGOs. Other EI ionization option to reduce fragmentation is Cold-EI discussed in chapter 4.1.2

One important use of EI with petroleum products is EI usability to oil spill identification with standard ASTM D5739: “Oil spill Identification by Gas Chromatography and Positive Electron Impact Low Resolution Mass Spectrometry”. This ASTM standard is from 1995 and it was updated in 2013.²⁸ This application of EI is important even in Finland where it has large border with Baltic Sea which traffics high quantities of crude oil and oil products. Fingerprinting and identification of oil spill reduce historical “mystery spills” as oil origin can be identified based on chapter 2.4.

4.2.2 Cold- EI

Cold-EI, also known as supersonic GC/MS is developed by Aviv Analytical LTD and its Director Aviv Amirav.⁷³ Cold-EI is based on conventional EI, but it uses ultra-low sample temperatures before ionization reducing fragmentation. GC effluent is expanded with makeup gas through small nozzle. This results in supersonic expansion and molecular beam formation that reduces rotational and vibrational energies of sample molecules within the beam. Temperature drops from transfer line temperature (up to 350 °C) to even -253 °C and excess carrier gas is skimmed off as seen in figure 21.

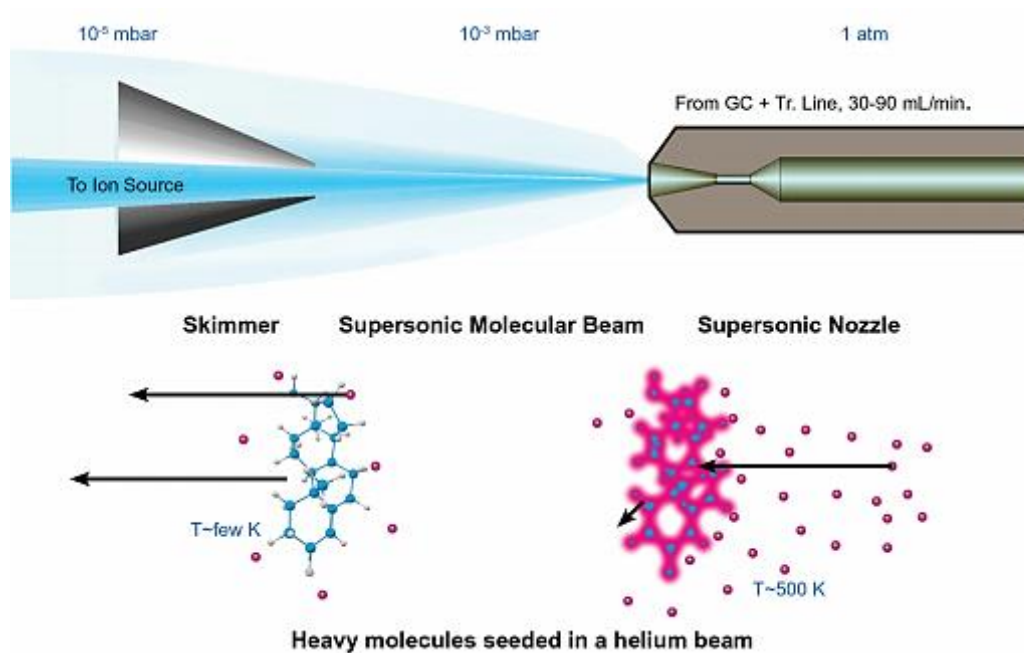


Figure 21. Basic principle of Cold-EI ion source.⁷⁴

According to PerkinElmer Application note⁷⁴, Cold-EI limits fragmentation but it does not fully eliminate all of it and different fragmentation patterns can still be used for spectral library searches. Represented studied molecules were both linear up to n-heptacosane (C_{70}) as well as branched squalane where all relative molecular ion peak intensities were enhanced.

Generally larger molecules have exponentially greater relative molecular ion enhancement with Cold-EI when enhancement factor and carbon number is plotted. Comparison of EI and Cold-EI can be seen with n-Dotriacontane spectra in figure 22.

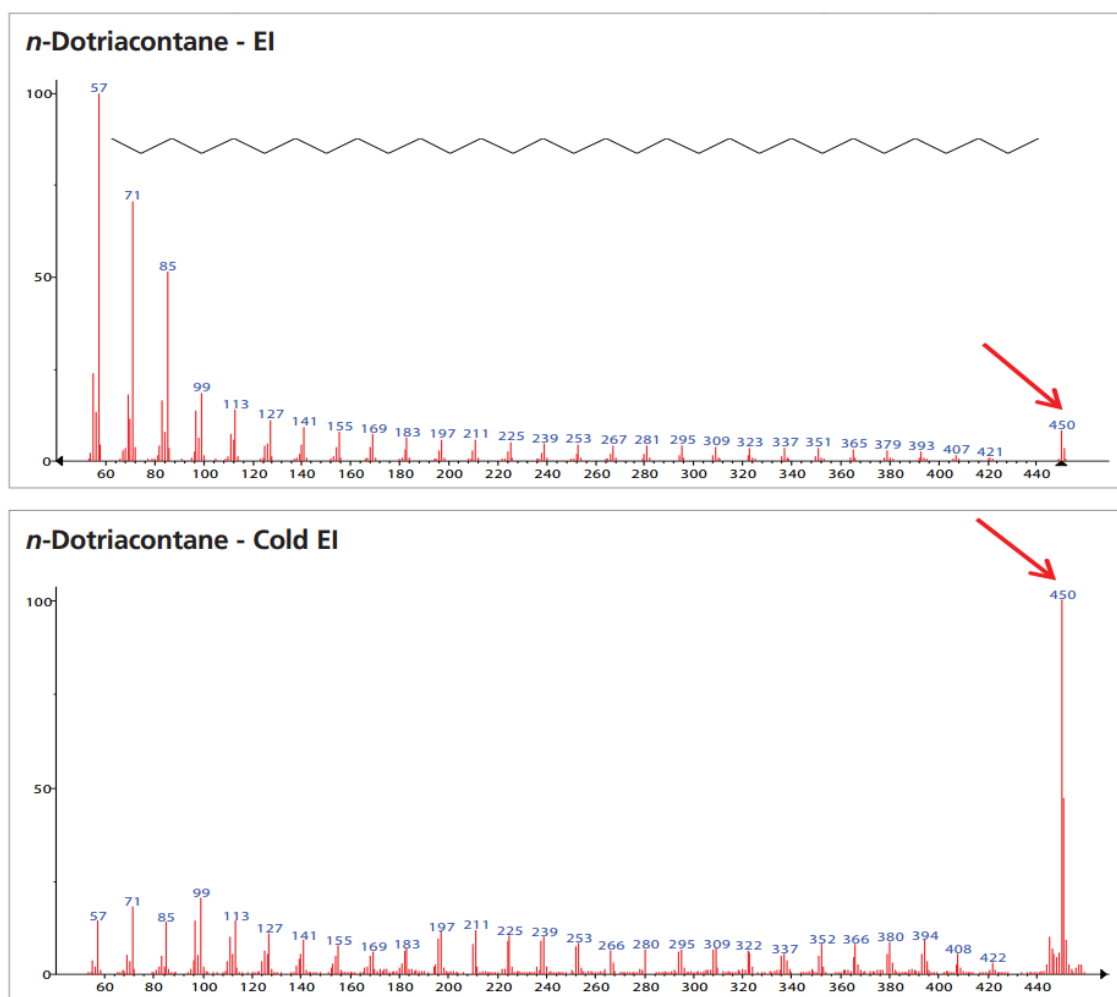


Figure 22. Comparison of EI and Cold-EI mass spectrum of n-Dotriacontane.⁷⁴

Cold-EI is more suitable for heavy and base oil analysis than common EI and major MS-vendors have suitable analyzer and even applications with Cold-EI for example PerkinElmer AxION®iQT™ GC/MS/MS mass spectrometer making Cold-EI more serviceable when compared to other MS market niche products.

Downsides of Cold-EI are that cooled molecules can reheat via reflected and scattered helium atoms near skimmer. Furthermore as Aviv Amirav *et al.*⁷⁵ pointed in their publication, desired molecular ions can go through undesirable collision-induced dissociation in similar manner as in tandem mass spectrometry and magnitude of dissociated molecules can be significant for labile hydrocarbon ions as in petroleum and base oil samples.

Cold-EI can be enhanced in some measurements using low voltage ionization in EI as in Aviv Amirav *et al* research first in 1995⁷⁶ and further in 2015⁷⁵ where they developed combination of low voltage (18 eV) and cold-EI. Since 1995 vibrational cooling has been improved and Cold-EI was combined with advanced commercial GC/MS. They also modified Cold-EI parameters such as nozzle-skimmer distance and helium pressure to reduce greatly unwanted collision-induced dissociation. This ionization method was determined as soft cold-EI.

Petroleum samples have been studied broadly by Cold-EI since 1995 when first Cold-EI and Soft Cold-EI utilizing analysis of hydrocarbons was published by S. Dagan and A. Amirav. They studied successfully straight alkanes from C₁₈ to C₄₀ as well as branched squalane, heteroatomic methylstearate, clorohexadecane, 1-bromohexadecane and dioctylphtalate.⁷⁶

Alexander B. Fialkov along with Aviv Amirav and Alexander Gordin in 2008 analyzed petroleum fuels (diesel fuel and kerosene) by “three ion method” and engine and transformer oils with fast (1-2 s) sampling without separation for oil and fuel fingerprinting. GC-MS is extensively used in areas of oil fingerprinting especially within range of biomarkers and used Cold-EI broadens GC-MS usability exponentially as identification could be done in ~2 s.⁷⁰

Reducing ionization voltage below 18 eV resulted in marginally increased molecular ion abundance but ionization yield dropped steeply. Soft-Cold-EI was utilized successfully in measuring squalene molecular ion with good intensity compared to 70 eV Cold-EI or conventional EI. Effect of Cold-EI and Soft-Cold-EI can be seen in figure 23.⁷⁵

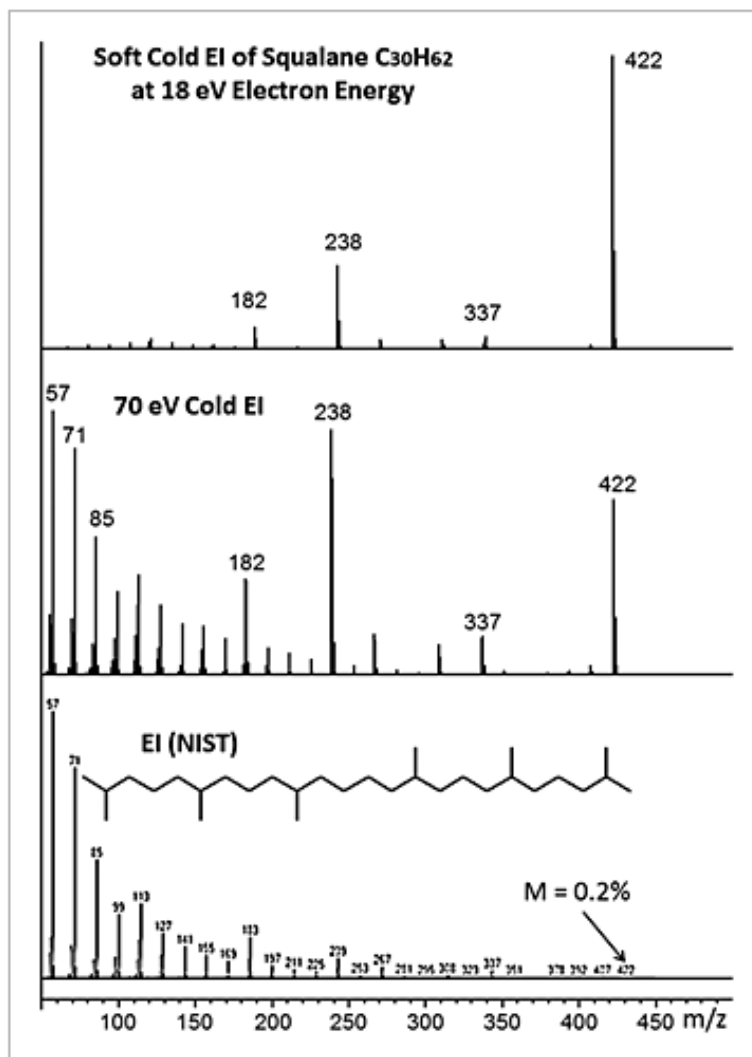


Figure 23. Comparison of Soft-Cold-EI, Cold-EI and EI of squalene.⁷⁵

Cold-EI has also been used successfully in JP8 jet fuel analysis together with Pulsed Flow Modulation GCxGC-MS by U. Keshet, *et al.*⁷⁷ Pulsed Flow Modulation GCxGC-MS is two dimensional GCxGC-modulator that does not consume cryogenic gases thus limiting operation costs. This method was hyphenated as PMF-GCxGC-MS and it was further developed and commercialized by Aviv Analytical LTD.

Cold-EI shows promising results from petroleum products and base oil MS measurements especially together with low voltage EI rendering it as soft ionization method. Cold-EI and Soft-Cold-EI combines gas chromatography methods and mass spectrometric methods fluently together enabling novel petroleum related methods. Both Cold-EI and Soft-Cold-EI are relatively new methods and there is still relatively little independent research done with it to evaluate its suitability further.

4.2.3 APCI

Atmospheric Pressure Chemical Ionization (APCI) is atmospheric pressure ionization method related to chemical ionization. APCI utilizes ionization of gaseous sample in normal atmospheric pressure via APCI probe and corona discharge needle. It is based on two consecutive ionizations, first ionization happens when gas reagent such as methane or ammonia is ionized with electrons in high voltage corona discharge and second ionization happens when this ionized reagent gas ionizes sample vapor with example proton transfer, proton abstraction, adduct formation or charge exchange.⁵⁹ With non-polar samples, discharge-based ionization methods typically occurs by charge transfer and hydride-abstraction ionization pathways.⁷⁸ Overview of APCI ion source can be seen in figure 24.

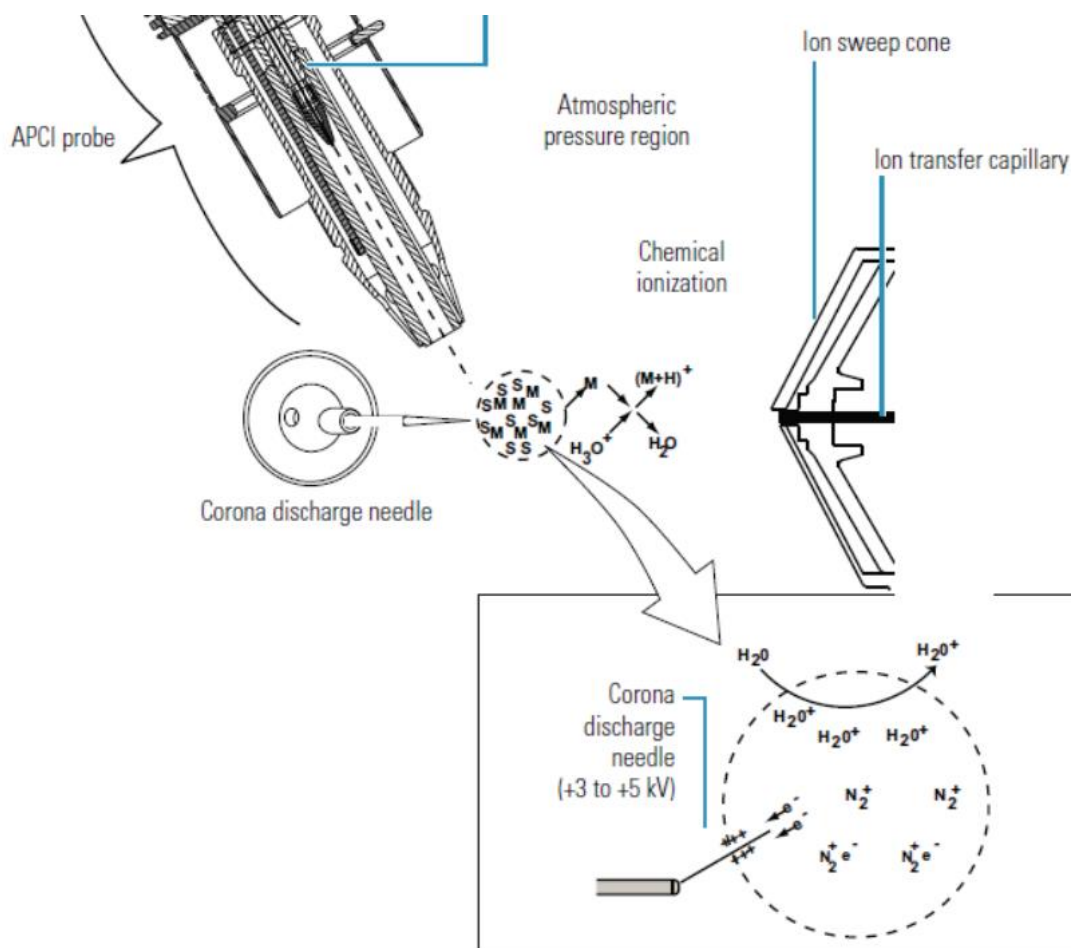


Figure 24. Overview of APCI ion source. Property of Thermo-Scientific.⁷⁹

APCI can be considered as soft ionization method and results in simpler spectrum than energetic ionization methods such as EI but many possible ionization routes result in multiple molecular ions. Ionization routes depend largely from used reagent making spectra possibly highly complex.

APCI is more efficient than CI because in atmospheric pressure there is higher collision frequency, better ionization efficiency and it is softer than CI due collisional cooling where ions collide softly with gas atoms decreasing internal energy. Downside is that APCI can produce different ions from same compound that can be hard to distinguish from others, moisture and sample vaporization can be problematic and reagents are selective in some extent. Like other atmospheric pressure ionization methods, APCI can be coupled with prior separation methods such as LC or GC and it is therefore popular with trace analysis and pharmacological studies.⁵⁹

One of first promising petroleum APCI studies were conducted successfully by Suzanne E. Bell⁸⁰ in 1994. Bell studied ion mobility and ionization pathways of alkanes, alkenes and cycloalkanes with APCI, CI-MS and IMS. Bell concluded that APCI ionization of alkanes favored hydride abstraction over proton transfer pathways resulting in $[M-1]^+$ and $[M-3]^+$ ion formations as proposed for cyclohexane on figure 25.

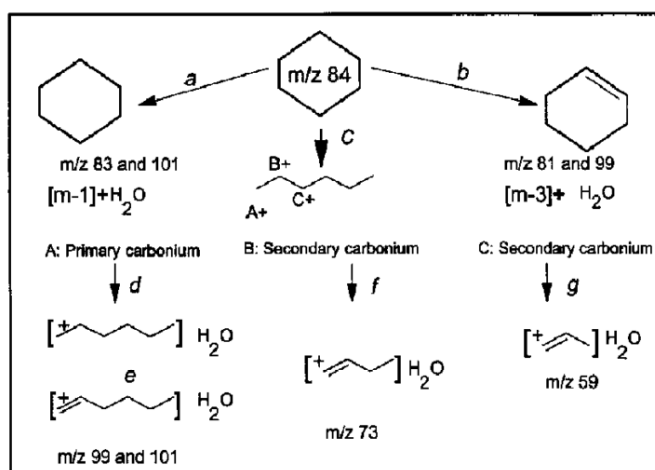


Figure 25. Proposed APCI-MS ionization of cyclohexane on E. Bell's studies in 1994.⁸⁰

Results were utilizable further but there were some problems with excess fragmentation of molecular ions.⁸⁰ Further studies showed that high molecular weight alkanes can be ionized intact by using ligated-metal ion chemistry by cationization methods for example

with silver cations by Grace *et al.*⁸¹ in 2005 and Roithova *et al.*⁸² in 2007, or by transition metals (Fe, Co and Ni) by Jackson *et al.*⁸³ already in 1986.

N. Hourani and N. Kuhnert⁸⁴ studied ionization of pure model compounds and motor oil samples with APCI in 2012. Their approach was to optimize APCI-TOF-MS in positive ionization mode specifically for hard to ionize compounds. They managed to ionize all model compounds without any additives and without fragmentation.⁸⁴ Same research group in the same year developed APCI method for nonpolar compounds further. They developed and tested novel direct-infusion APCI method for heavy hydrocarbon analysis. This was reported to produce mainly $[M-H]^+$ ions between C_{10} and C_{40} under nitrogen gas source from light shredder waste. This study was successful in measuring model molecule mixtures and real life shredder waste samples effectively, but quantification was problematic as few alkanes did not respond effectively in additional experiments with APCI-TOF-MS and it is yet to be applicable for routine analysis of waste samples due to high investment and instrument costs.⁸⁵

APCI-MS has been used to study petroleum products and lubricants in some extent and it has been found useful with oil samples in Purdue University with linear quadrupole ion trap (LQIT) and FT-ICR analyzer. For example APCI was used with $CIMn(H_2O)^+$ and laser-induced acoustic desorption (LIAD) in study by Kenttämäa *et al.*^{86,87} LIAD is further discussed in chapter 4.2.7.

C. Jin *et al.*⁸⁸ compared APCI-MS and FI-MS for analysis of large saturated hydrocarbons. APCI was combined with LQIT and FI with double focusing sector (DFS) analyzer. Hydrocarbon class distributions were measured from lubricant base oils and APCI was found to yield average molecular weights and distributions over three lubricant base oils. APCI-MS measurement reproducibility was found to be substantially better while paraffinic content and carbon chain length increase with viscosity was similar.⁸⁸ This suggests that APCI might overtake popular FI-MS in heavy petroleum analysis. APCI with LQIT was also used by Gao *et al.*⁸⁹ who studied wide range of saturated and unsaturated hydrocarbons with HPLC/APCI. By using pentane, hexane and cyclohexane as solvent/reagent they were able to measure linear and branched alkanes with low fragmentation.

Direct analysis in real time (DART)-MS utilizes penning ionization and was used to evaluate PAH measurements and crude oil analysis by Rummel *et al.*⁹⁰ in 2010. They used a custom-build DART coupled with FT-ICR for NIST Heavy Sweet crude oil samples that could be measured for long times and resulted in both radical and protonated molecular PAH ions. This method was limited to relatively low boiling components.^{27,90}

Recent interesting new ionization methods include atmospheric solid analysis probe (ASAP) and its GC combined ensemble APGC by C. Wu *et al.*⁷⁸ in 2015. ASAP and APGC were able to measure paraffins, isoparaffins, and alkylbenzenes standards with high expectation that it could also be suitable for heavy non-saturate petroleum fractions.

4.2.4 APPI

Atmospheric Pressure Photo-Ionization (APPI) is soft ionization method that uses 10.0 eV and 10.6 eV photons from krypton discharge lamp to ionize compounds with ionization energies under photon ionization energy. This selectively ionizes suitable sample molecules but not typical solvents and gases. APPI ionization efficiency can be increased by dopant such as toluene that acts by proton transfer reactions and results in even electron ions i.e. $[M+H]^+$.

APPI has been combined with FT-ICR for few reasons: APPI ionizes broader range of compound classes and its spectra contains remarkably more peaks than in spectra measured using ESI-MS. Secondly APPI generates radical cations $[M]^+$ that can further abstract proton from abundant solvent to form $[M+H]^+$ ions from same molecule, making it necessary to resolve $[M]^+$ with ^{13}C from $[M+H]^+$ with ^{12}C that have mass difference of only 4.5 mDa.^{65,91} Basic principle can be seen in figure 26.

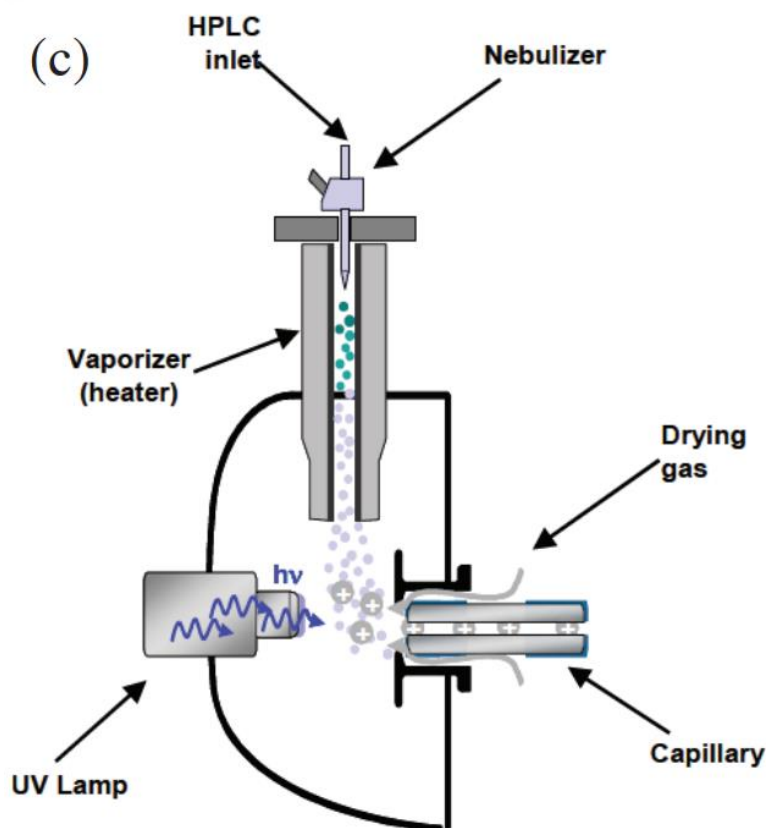


Figure 26. Basic operation principle of APPI ion source.⁷⁹

Suitability of APPI with wanted sample depends on ionization energy rather than proton affinity as with ESI and APCI. APPI can ionize wide range of polarities and it is tolerant to matrix components of HPLC additives.

Current petroleum related research using APPI is related to environment and biotic samples and tracking organic pollutant levels such as PAH's. APPI has even greater sensitivity than more commonly used ESI with unconjugated steroids in Yamamoto *et al.*⁹² research. They were able to measure them in level of ng/L from water samples.

Pengxiang Yang *et al.*⁷⁹ found that APPI was most suitable ionization method when compared with ESI and APCI with mass analyzer to measure petroleum sample in their brief comparison in collaboration with Thermo Scientific. APPI was complementary with ESI and APCI where ESI could ionize polar and light samples, APCI polar and part of nonpolar with medium weight samples and APPI mostly nonpolar and heavy samples as seen in figure 27.

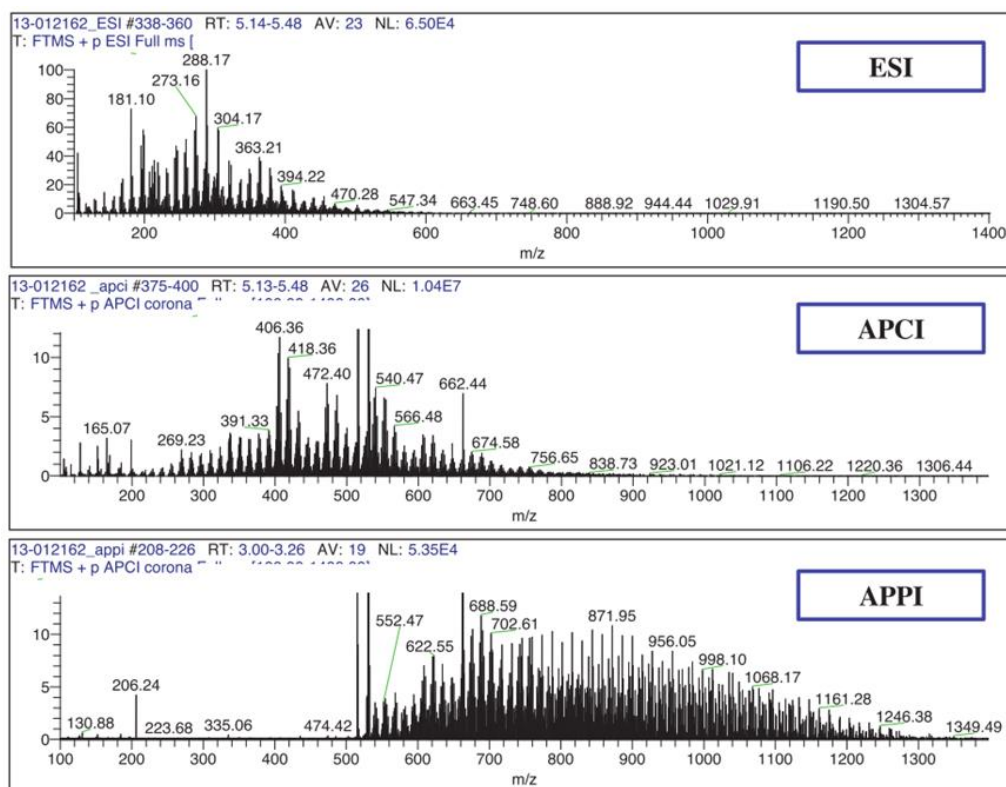


Figure 27. Comparison of ESI, APCI and APPI spectra of same petroleum sample.⁷⁹

Another direction of Petroleum analysis was with APPI-DART-MS that was used for motor oil analysis by B. Musselman⁹³ in collaboration with Ionsense in 2012. They found that APPI-DART was able to detect many compound classes that normal DART was not able in both unused such as tricyclic terpanes, cholestanes, monochromatic steranes and diahopanes, and used motor oils such as naphthalenes, fluorenes, biphenyl and pyrenes.

J. Purcell⁹¹ from Florida State University studied APPI-FT-ICR for Petroleum analysis as Dissertation in 2007. Emphasis was in complex petroleum samples as industries have shifted towards more complex crude oils with higher sulfur contents. APPI was useful with low-polarity and non-polar samples but it typically needed a dopant such as toluene as proton donor and toluene radical cation as electron acceptor. Dissertation covered nine topics of APPI petroleum research.

Purcell along C. Hendrickson, A. Rodgers and A. Marshall⁹⁴ further studied dopant role in proton transfer in APPI in 2007. They also deduced what types of petroleum molecules produce typically negative or positive ions as their formation happens simultaneously with APPI. Downside of APPI-MS is high mass load with flow rates from 50 to 200 $\mu\text{L}/\text{min}$ which increases ion source and mass analyzer contamination.

Novel petroleum applications of APPI techniques are microchip APPI mass spectrometers (μ APPI-MS) presented by Kauppila *et al.*⁹⁵ in 2004. Microchip APPI uses significantly lower mass load and flow rates (0.05 to 10 μ L/min) reducing ion source and analyzer contamination. μ APPI-MS has been used to study PAHs, petroleum, steroids, polychlorinated biphenyls and illicit drugs with high sensitivity and quantitative performance.⁹⁶

Petroleum analysis with μ APPI-MS were done by Haapala *et al.*⁹⁶ at University of Helsinki in 2009. μ APPI was able to produce 60 % of signal response compared with conventional APPI when considering that μ APPI used 2 μ L/min and conventional APPI 50 μ L/min flow rate that equals to 15-fold higher sensitivity and μ APPI efficiently evaporated even high molecular weight components. Replacing cheap microchip with sample would eliminate typical MS carry-over effects.⁹⁶

4.2.5 ESI

Electrospray ionization (ESI) is widely used soft ionization method with little fragmentation to study polar samples. In ESI the sample is first dissolved in volatile solvent and this is fed through small and charged spray needle inside ion source. This spray needle produces Taylor cone towards opposing plate with opposing charge and a jet of charged liquid droplets accelerate in electric field. From ESI droplets solvent evaporates and charge concentrates until Rayleigh limit is attained and droplet emits sample ions. Sketch of ionization procedure can be seen in figure 28. ESI is sensitive, well studied and robust atmospheric pressure ionization method that causes minor fragmentation and is compatible with LC and GC inlets. This addition soft ionization, suitability to labile and polar compounds with relatively low maintenance and acquisition costs has made ESI one of the widely-used ionization methods.⁵⁹

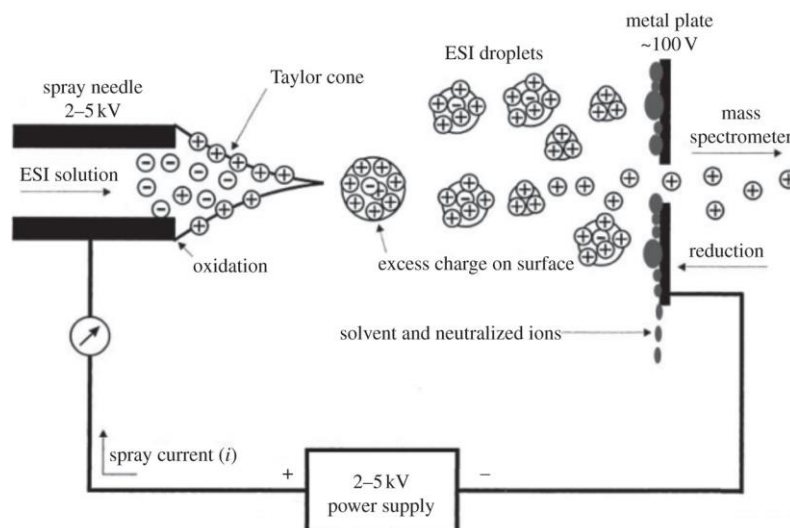


Figure 28. Basic principle of ESI ionization.⁹⁷

ESI does not work well with purely nonpolar samples such as base oils and lubricants and it suffers from multiply charged ions making results more complex. ESI is still widely used in petroleum studies as most troublesome and complex compounds are polar. Typically and routinely ESI has been used to characterize crude oil parts (i.e. elemental composition and naphthenic acid extraction).^{98,99} According to Quan Shi¹⁰⁰ ESI is mainly used to determine compositional characteristics from petroleum distillates, crude oils and bitumens. Petroleum ESI-MS research typically studies heteroatom compounds containing nitrogen, oxygen, sulfur and metals.

Christine A. Hughey *et al.*¹⁰¹ determined elemental composition of processed and unprocessed Diesel fuel with ESI-FT-ICR-MS in 2001. They were able to effectively analyze nitrogen containing pyridine homologues that hinders removal of heteroatoms and destabilizes products under storage. In history elemental composition analysis was done cumbersome with complex and inefficient separation schemes before ESI-MS method but this research provides alternative measurement methods for future.

H. Müller and J. Andersson¹⁰² studied high weight sulfur containing polyaromatics (PASHs) with ESI-FTICR-MS before and after partial hydrodesulfurication (HDS) process in 2005. PASHs are present in high boiling residues that are mostly waste that could be used as energy source if sulfur and other heteroatomic compounds could be removed. They concluded that PASH could be effectively detected using ESI-FTICR-MS, partial HDS removed effectively PASH compounds with one S atom but compounds with more sulphur were mainly unaffected requiring other separation processes.

Geoffrey Klein *et al.*¹⁰³ studied hydrotreatment-resistant heteroatoms in crude oils with ESI-FT-ICR-MS in 2006. They compared hydrotreated and untreated distillation fractions to improve understanding of hydrotreating mechanisms as hydrodenitrogenation is primary process to remove nitrogen. This mechanism remains partly unknown. These compounds are typically NSO-containing and problematic as they are present in large quantities in heavy crude oils. Nitrogen containing compounds tend to produce coke at surface of the catalyst used in hydrotreatment resulting in complete or partial deactivation. They found out that hydrotreatment-resistant compounds typically contained one nitrogen atom as pyridinic and pyrrolic benzologs. Compounds with more than one heteroatoms were partially removed and compounds with both oxygen and sulfur were fully removed and ESI-FT-IR-MS was successful in measuring compounds in sample.

Geoffrey Klein *et al.*¹⁰⁴ also studied asphaltenes deposit to its crude oil counterpart for geographically different crude oils with ESI-FT-ICR MS in 2006. ESI was selected as it can be used in complex sample matrix without pre-chromatographic separation. Negative-ion electrospray was selected as studied asphaltenes are acidic. Crude oil deposits contained higher aromatic character and higher heteroatomic character compared to their crude oil counterpart in detail.

In line with analysis equipment downscaling and miniaturized method attractiveness, Matthias Wilm and Matthias Mann¹⁰⁵ developed novel electrospray with structural modification of conventional ESI to attain under 25 nl/min flow rate introduced as micro-ESI (often also as nano-ESI). Nano-ESI can spray purely aqueous solutions and hydrophilic compounds without organic dopants or chemical stabilization. Nano-ESI was developed further by A. Schmitd *et al.*¹⁰⁶ who studied different flow rate effects and borderline between conventional ESI and nano-ESI. S. Kim *et al.*⁵⁷ studied closely related Chip-based micro-ESI with FT-ICR-MS with petroleum samples. This was used to study and benchmark in-house automated method with high reproducibility was attained with heteroatom class distributions, DBE and carbon number determination as result. Overall advancements in nano-ESI are more suited in pharmacological and protein analysis than in petroleomics.

ESI-based ambient ionization methods are also widely used in petroleum analysis. For example, petroleum fuels (gasoline, biodiesel and petrol diesel blends) have been analyzed for typification, adulteration or quality control with easy ambient sonic-spray

ionization (EASI)-MS by R. Alberici *et al.*¹⁰⁷ in 2010 by analyzing natural and artificial markers. Study suggests EASI-MS as attractive method for fast, single shot characterization and quality control of fuels in general as measurement requires little to no preparation and pre-separation steps.

Peter A. Eckert *et al.*¹⁰⁸ also studied polar components of liquid crude petroleum using nanospray-DESI in 2012. They used three different solvents (acetonitrile/toluene, acetonitrile/water, methanol/water) where acetonitrile/toluene is commonly used with petroleum analysis. This study showed that acetonitrile/toluene solvent produced typical electrospray-like spectra but acetonitrile/water and methanol/water solvents produced completely different spectra that together with literature data suggest that these selectively extract water-soluble components. This could be used to rapid characterization of water soluble components of petroleum samples that are still somewhat cumbersome to measure.

Pure hydrocarbons can also be analyzed by DESI as expressed by Chunping Wu *et al.*¹⁰⁹ in their study of saturated hydrocarbons via electrical discharge with DESI in 2014. This reactive DESI targets nonpolar abundant alkanes by electrical discharge and derivation agent, resulting oxidation products. These particular products are easily detected and measured by ion trap or Orbitrap and quantitative measurements can be performed as well. This method is so far limited to low boiling petroleum products and their samples as seen in figure 29 where signal response of each alkane was calculated as the sum of all oxidation and dehydrogenation peaks. Signals were not observed for C_5H_{12} to $C_{13}H_{28}$.²⁷

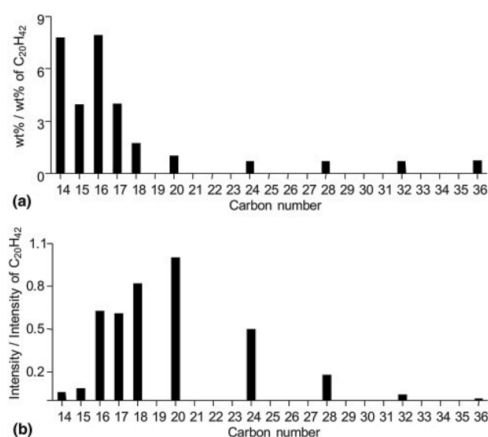


Figure 29. a) Wt-% of alkanes relative to wt-% n-eicosane in an alkane standard. b) Signal response of different alkanes relative to n-eicosane, derived from mass spectrum.¹⁰⁹

Alongside reactive DESI, the problem of nonpolar fractions with ESI has been studied by L. Jincheng *et al.*¹¹⁰ who published research in 2016 of ESI-MS measurements of aromatic compounds with HCOONH₄ as ionization promoter. This method has potential to ionize full spectrum of oil polarities but needs additional research.

Downside of majority of ESI methods (excluding reactive DESI) is that they are incapable to measure majority (90 %) of oil composing from nonpolar hydrocarbons, but according to Marshall and Rodgers⁶⁵ majority of problems with pollutants, catalytic poisons, deposit formation during production, and highest boiling fractions with lowest value are due to polar components that can be efficiently measured with ESI-MS. ESI is still highly used to study petroleum products and new ambient ionization methods bring new measuring capabilities to it as with ionization promoters and reactive DESI.

4.2.6 FI/FD/LIFDI

Field ionization -and field desorption (FI and FD) are one of the first classic ionization methods studied already in 1960s by H. D. Beckey and finally published in 1969.¹¹¹⁻¹¹⁴ Both FI and FD are based on quantum tunneling of sample molecules electrons from gaseous samples within high potential electric field producing mainly M⁺ and [M+H]⁺ ions. High enough electric field is gained with high potential difference with sharp edges in ion source i.e. razor blades or needles, but currently mainly from emitter wire where there are number of small and sharp carbon needles as seen in figure 30.

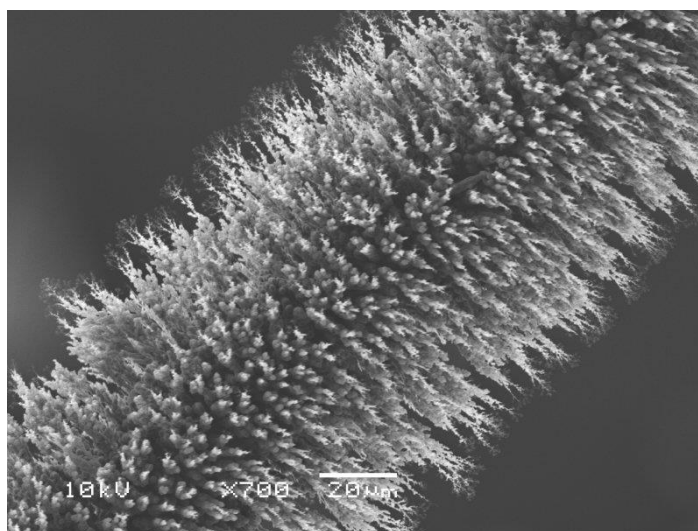


Figure 30. Carbon whisker emitter produced by Linden. Figure is property of Linden CMS.¹¹⁵

FI and FD are capable of ionizing wide range of samples including both polar and non-polar and difference with FI and FD is rather small as both ionize sample with same mechanism. Difference is that FI ionizes gaseous samples introduced from near emitter and FD liquid samples loaded straight to emitter. Today other ionization methods have surpassed FI and FD in many fields, but FI and FD are still significant ionization methods in petroleum analysis. FI and FD can ionize nonpolar hydrocarbons with little fragmentation and produce intense M^{+} ions without need for matrix or reagents.¹¹⁶

First uses of FI and FD in heavy petroleum analytics was in 1968 by W.L. Mead¹¹⁷ who studied petroleum based waxes with FI-MS sporting razorblade. So far FI and FD has been widely used with crude oil and different petroleum fractions including diesel, lubricating oils, VRC etc.^{118,119} FI and FD are up to date most successful ionization techniques for saturated hydrocarbons.⁸⁷ Downside to FI and FD methods in petroleum analytics is that they suffer from laborious measurements with small ionization efficiency, bad reproducibility of ionization efficiency, sensitivity dependency of sample carbon number and structure, and with low resolution isobaric ions, DBEs with n and $n+7$ i.e. nonane and naphthalene that both have nominal masses of 128 are not distinguished. Problem with isobaric ions can be avoided by separating sample into aliphatic and aromatic fractions.^{118,120}

T. Ogawa¹¹⁸ in 2005 optimized measurement conditions for diesel fuel measurements with FI-MS connected with GC. First reservoir and ion source temperature was optimized, secondly emitter current, cathode voltage and ion focusing mode was optimized and influence of these parameters can be seen on figure 31.

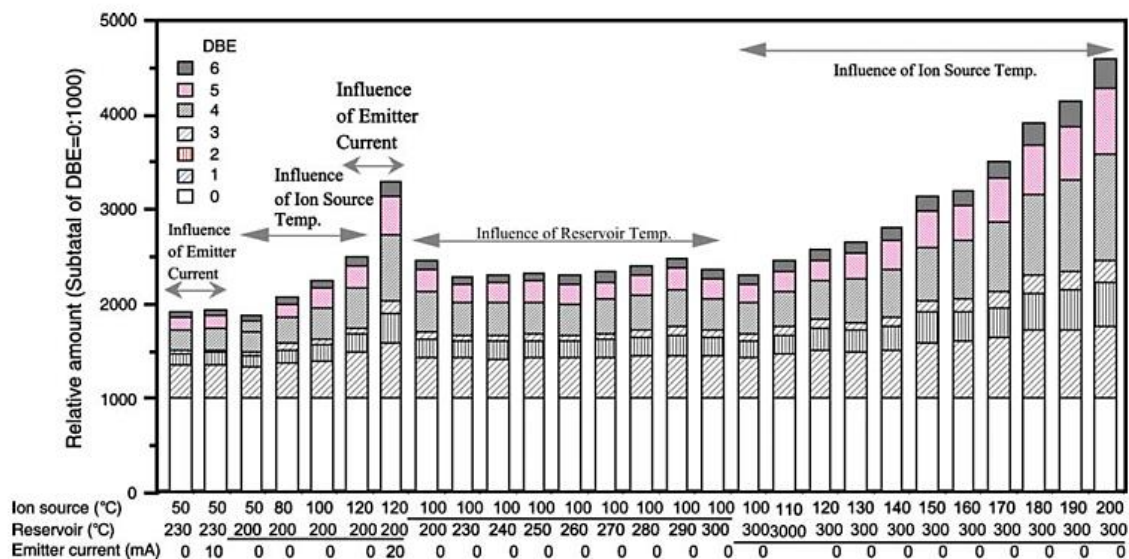


Figure 31. Influence of tested parameters (ion source temperature, reservoir temperature and emitter current) to DBE distributions in study by T. Owaga.¹¹⁸

FI uses about 30 times more sample than EI and reservoir was evacuated sufficiently (over 10min). Some memory background was found to affect reproducibility and it was suppressed by 30-40mA emitter heating current during reservoir evacuation. As a result, variation coefficient was less than 5,1% for sum intensities of each DBE.¹¹⁸

FI methods are suitable on volatile samples under vacuum. Use of vacuum with sample introduction limits light samples as volatile samples evaporate already before measurement. Volatility also sets upper mass limit to m/z 1200-1500.⁵⁶ As discussed in chapter 4.2.3, Chunfen Jin *et al.*⁸⁸ found APCI methods more reliable in quantitative measurements of heavy petroleum based base oils.

New application field for FI and FD is liquid injection field desorption ionization (LIFDI) that was developed by Bernhart Linden.^{121,122} LIFDI methods have opportunity to measure air and moisture sensitive compounds i.e. neutral metal complexes with silica inlet without breaking gas atmosphere or vacuum. LIFDI could be compatible with autosamplers speeding up FI-MS and FD-MS measurements considerably and freeing operator time as no pressure pumping is required as it is with conventional FI-MS and FD-MS measurements where sample has to be loaded with each measurement.

Potential FI and FD would require more study but it is hard to believe that revolutionary FI and FD applications would be revealed in near future as the method is old but less popular reducing manufacturer's interest in FI and FD development. Possible and interesting direction of FI/FD based ionization methods in petroleum studies could be ultralow –voltage field ionization discharge from whiskered silicon nanowires studied by Ramin Banan Sadeghian and M. Saif Islam. So far ultralow-voltage FI has not been applied to petroleum samples.¹²³

4.2.7 LDI

Laser desorption ionization methods (LDIs) are soft ionization methods that produce molecular ions with powerful laser. First sample is desorbed with powerful laser and next desorbed sample is ionized by protonation or deprotonation in gaseous phase. Ionization can be enhanced using different matrixes or surfaces as in Surface/Matrix Assisted Laser desorption ionization (SALDI/MALDI) and Material enhanced laser desorption ionization (MELDI). Other LDI based important ion petroleum analysis methods include Laser Induced acoustic ionization (LIAD). LDIs are usually used in combination of TOF due to pulsing nature of the techniques.

LDI, MALDI and SEC, are mainly used as the only viable methods with heavy portions of petroleum i.e. asphaltenes, kerogens, coal-derived tars. Problems with LDI based ionization methods are heavy aggregates and small fragments with power needed to ionize petroleum samples, matrix resulting in complex results with high resolution requirements in mass analyzer and in overall LDI cannot produce reliable data from petroleum products for quantitative research.^{56,124} MALDI Matrix molecules result in difficulties such as background signals and spectral interferences that limit LDI usability to molecules heavier than m/z 700.¹²⁵ Newest advances with LDI includes Two-step laser (L^2MS) and matrix free MELDI. L^2MS includes two-colored lasers in which first vaporizes sample and second ionizes vaporized sample that could overcome disadvantages of conventional laser desorption ionization.²⁹ Matrix free MELDI especially with carbon nanomaterials i.e. diamond-like carbon, C_{60} fullerenes are excellent energy-absorbing materials lowering m/z limit of LDI method.¹²⁵

Currently highest mass range including asphaltenes is acquired with MALDI. Ultra-heavy petroleum products such as vacuum residues and coal tar pitch show highest molecular sizes attained from petroleum mass spectrometric measurements and these are attained using MALDI in combination of thin layer chromatography (TLC).¹²⁶ MALDI-MS with TLC can reach up to 40 000- 60 000 Da.¹²⁷

There is some controversy in molecular weight distribution of asphaltenes depending on method used. ESI, FD and CI mass spectrometric measurements; fluorescence based diffusion measurements, and electron microscopy results suggest asphaltene weight distribution to be 500-1000 Da while fast atom bombardment (FAB), plasma desorption measurements and size exclusion chromatography suggest distribution to tail far beyond 10 000 Da. Pomerantz *et al.*²⁹ studied petroleum asphaltenes molecular-mass distributions with L²MS to clarify asphaltene molecular weight distribution. Results support hypothesis that >1000 Da are mainly caused by aggregation. Results are reported to be in accordance with other MS methods used and L²MS has shown to successfully measure quantities of n-heptane asphaltenes.

LIAD is acoustic desorption method pioneered by H. Kenttämää in Purdue University.^{27,128,129} LIAD uses focused IR laser that hits metal foil and forms thermal and acoustic waves. Acoustic waves propagate to other side of thin metal foil from where sample is desorbed as neutral molecules and can be ionized either by EI or CI and it can be coupled successfully with FT-ICR.^{67,128} Kenttämää *et al.*⁸⁶ used the cyclopentadienyl cobalt radical cation (CpCo⁺) as ionizing agent in analysis of various hydrocarbon samples with LIAD-FT-ICR-MS. Same research group later switched to less aggressive aquachloromanganese(II) cation [ClMn(H₂O)⁺] that resulted in exclusive adduct ion [adduct+H₂O]⁺. Major advance was combining APCI with LIAD that enabled evaporation and ionization of both polar and non-polar samples resulting mainly in molecular ions with little fragmentation with carbondisulfide (CS₂) as reagent.

LIAD-FT-ICR has been used by Crawford *et al.*¹²⁸ in petroleum distillate analysis. Low energy EI (10 eV) was found to be better than conventional (70 eV) as it resulted in much simpler mass spectra with less fragmentation. Low energy EI however suffers from low yields and saturated hydrocarbons with high ionization energy (IE>10 eV) are poorly ionized. Pinkston *et al.*¹³⁰ studied asphaltenes and asphaltene model compounds using LIAD-FT-ICR with 70 eV EI ionization. Asphaltene molecular weight distribution was

about 350-1050 Da that correlates to many asphaltene studies. LIAD-FT-ICR with CI ionization by $[\text{ClMn}(\text{H}_2\text{O})]^+$ has been used to study base oil fractions by Duan *et al.*⁸⁷ Method was found to be promising even as quantitative method for base oil analysis.

Petroleum measurements with matrix including LDI methods are partially controversial as when compared to other data by asphaltenes. LDI methods have abnormally big molecular weights ($>10\,000$ Da) that are not found with other ionization methods including L²DI and LIAD. This has been explained by parameter settings, arguing that predominant heavy type asphaltenes with high energy laser pulse are present only because high enough laser energy can desorb high molecular weight compounds or that these compounds result from aggregation.¹³¹

4.3 Mass analyzers

While different ionization methods are just different means to an end to attain gas-phased ions the mass analyzer is responsible of distinguishing different ions. Mass analyzer together with detector system and computer produce mass spectra.

Mass analyzer distinguishes different ions based on their mass-to-charge (m/z) values after ionization rather than pure ion mass. There are seven general types of mass analyzers from which four are suitable with complex and heavy petroleum samples: Time of Flight Mass Analyzers (TOF), Magnetic Sector Mass Analyzers, Electrostatic Sector Mass Analyzers, Fourier Transform Ion Cyclotron Resonance (FT-ICR) analyzers and Orbitrap analyzers. Quadrupole and ion traps have too low resolution to be used in crude, lubricant and base oil analysis on their own but are shortly described with ion traps (i.e. LQIT) that have important applications in petroleum analysis. In addition, hybrid instruments also use combination of these to improve operation i.e. Dual Focusing Sector (DFS) instruments that use both magnetic and electrostatic sectors and QTOF that uses quadrupole along with TOF.⁵⁹

One manner of dividing mass analyzers is on their operation as follows: scanning type analyzers, trapped ion mass analyzers and TOF analyzers. Scan time means analyzing speed that mass analyzer takes to scan one particular mass range (u/s) Scanning type analyzers are quadrupole and sector instruments where mass range is scanned by ramping either magnet field or electric field so that only ions with certain m/z values are passed to

detector. Trapped ion mass analyzers include ICR, Orbitrap and quadrupole ion trap where ions are trapped in space by electric and magnetic fields (Penning trap), static and oscillating electric fields (Paul trap) or by orbital motion around coaxial central electrode wire (Kingdon trap) and m/z is determined from cyclotron frequency of the ions. TOF includes linear or reflector TOF analyzers that both differentiate ions based on their flight time with same energy. Another divination method would be to consider ion sampling of different mass analyzers: Ion traps, TOF, FT-ICR and Orbitrap are so called pulsed while sector and quadrupole mass analyzers can be considered continuous.⁵⁹

Important performance parameters as presented by E. Hoffmann⁵⁹ include: **mass range limit** that presents upper limit of m/z range, **scan speed** that presents mass range described above, **transmission** presents the ratio of how many ionized sample ions reach detector from mass analyzer, **accuracy** that describes difference between measured m/z and theoretical m/z and lastly **resolution**. Resolution or resolving power indicates mass analyzers capability to distinguish ions with close m/z values but how it is defined differences between literature. One of these is proposed by Marshall and it states that two peaks are resolved if the valley intensity between those peaks is below 10% with sector and FT-ICR instruments and 50% with quadrupoles, ion traps and TOF of the smaller peak. Resolution in this definition is the ratio of mass per resolved mass difference. Resolution can be distinguished with one peak by peak width by intensity fraction (typically 50%) and this is addressed as full width half maximum resolution (FWHM). These two different resolution definitions relate when peak intensities are equal, then full width resolution at X % equals to resolution at 2X % for the valley. To answer question “how much resolution is enough? ” is not a simple question and as A. Marshall *et al.*¹³² noted, resolution rarely is linear with m/z and when two peaks have remarkably different intensity, resolution requirement is bigger.

No mass analyzer is superior on all aspects and different analyzers differ from each other by parameters including accuracy, resolution, mass range, scan speed, measurement speed, maintenance requirements and price. Selected mass analyzer is typically compromise from different factors and wanted parameters such as intended sample type and budget. Not all mass analyzers are compatible with all ionization methods.

4.3.1 FT-ICR

Fourier transformation ion cyclotron resonance (FT-ICR) mass analyzers presents highest resolution and sensitivity currently achieved and this makes it especially important in heavy petroleomics and samples with close doublets. Ions in FT-ICR analyzer cells (typically penning traps) are excited in constant magnetic field with radio frequency (RF) or pulsed electric field perpendicular to magnetic field that leads ions in circular motion. Excited ions induce a charge in receiver plates and this is measured as image current as interferogram time-domain spectrum of sine waves of all measured ions simultaneously and mass spectrum is acquired by Fourier transformation. Another important advantage is that all ions are measured at the same time shortening measurement time considerably. Basic operation principle can be seen in figure 32.

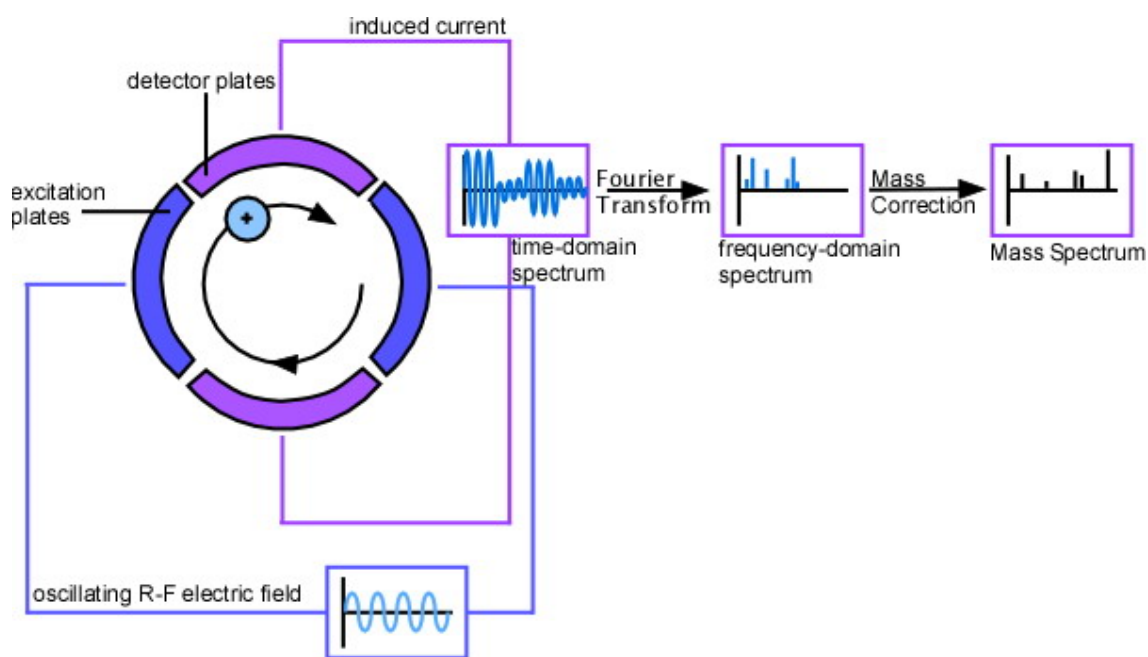


Figure 32. Basic principle of FT-ICR mass analyzer. Property of Nicole James.¹³³

Resolution with FT-ICR-MS can be increased by increasing either magnetic field or measuring time. Applying high magnetic fields from superconductors took FT-ICR greatly forward and today superconducting electric magnets can reach magnetic fields over 10 Tesla. FT-ICR has currently the highest broadband resolving power and mass accuracy to date because superconducting magnetic field is more stable than RF-signal and **Fellget's Advantage** shortly states that multiplex measurements have weaker signal to noise ratio than simple direct measurements.¹³⁴ FT-ICR downside is its laborious operation and price compared to other mass analyzers limiting FT-ICR to just minor part of mass spectrometry laboratories.

Long time FT-ICR was the only tools capable to differentiate isobaric ions within heavy oils including heteroatoms in such samples as asphaltenes, coal pitch tars and other heavy refinery side streams but currently Orbitrap has enough resolution for these studies as well. FT-ICR and Orbitrap are also practical with ionization methods that produce molecular ions from hydrocarbons with close doubles (i.e. APPI: M^+ with C_{13} and $M+H^+$ ESI: multiply charged ions).⁶⁵ FT-ICR is especially used with asphaltene analysis with different ionization methods as LIAD¹³⁰, ESI^{124,135}, FD⁶⁵, APPI^{65,135}, APCI¹³⁵, LDI¹³⁵ and MALDI¹³⁵. FT-ICR is also used to study hydrotreatment resistant portions (i.e.VRC) of petroleum with ESI²⁶, aromatic compounds in different refinery streams with FD¹³⁶ and also base oil fractions with LIAD or CI.⁸⁷

FT-ICR still has big resolution advantage to all other mass analyzers but this gap is getting narrower mainly with Orbitrap. FT-ICR downside is its high acquisition and operation price and required know-how.

4.3.2 Orbitrap

Orbitrap is one of the most recent analyzer that resembles FT-ICR in operation with ion trap -like properties reported first in 2000 and introduced in 2005 by Thermo Fisher Scientific. It is based on similar orbital trapping as in Kingdon ion trap but has been further developed with many features, such as Fourier transform after current detection as in FT-ICR. Structurally Orbitrap mass analyzer has outer electrode shaped as barrel and second electrode inside shaped as a spindle. Applied DC voltage causes electrons to oscillate on z-plane while circling inner electrode. Basic operation principle can be seen on figure 33.

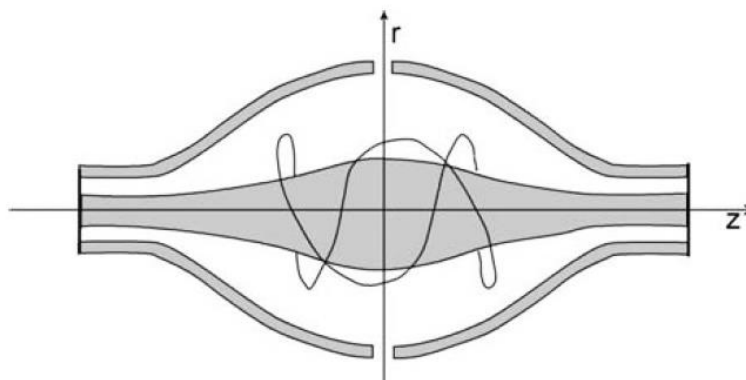


Figure 33. Basic operation principle of Orbitrap mass analyzer according to ⁵⁹

It would be safe to say that current Orbitrap resolving power equals roughly to that of FT-ICR a decade ago. Orbitraps recent popularity has lot to do with its fast development and fundamentally cheaper acquisition and use expenses than that of FT-ICR. Latest Orbitraps can reach 450 000 FWHM at m/z 200 with mass accuracy of < 3 ppm.¹³⁷

Use of LC and UHPLC coupled with HRMS (FT-ICRS, TOF or Orbitrap) has gained more interest because of advantages in both targeted and nontargeted analysis, retrospective analysis, higher selectivity with lower sample preparation and sample optimization. Orbitraps properties make it along TOF arguably most used mass analyzer coupled LC and UHPLC techniques today and it is used for example in trace analysis of complex matrix i.e. forensics studies, pesticides and environmental analysis and its resolution comes closer to that of FT-ICR.¹³⁷

LTQ Orbitrap XL has already been used to study biomass pyrolysates, petroleum distillates and natural organic matter. Pomeranz *et al.*¹³⁸ studied Orbitrap as cheaper alternative for FT-ICR for petroleum studies with high resolution ($m/\Delta m$) of 200 000 at m/z 500. Study suggests That Orbitrap with ESI can identify dominant components and produce accurate fingerprint of nonvolatile and polar fractions of crude oil and it could be applied to other ionization methods as well.

P. Yang *et al.*⁷⁹ along with Thermo Scientific studied different ionization methods with Orbitrap used in petroleum analysis (APPI, APCI, ESI) by direct injection method. This publication suggests that APPI would be most suitable ionization method with Orbitrap to study petroleum fractions overall as it could ionize both nonpolar and polar fractions that could not be done with APCI or ESI alone as can be seen in figure 27 of chapter 4.2.4.

E. Smith and Y. Lee¹³⁹ studied bio-oils from fast pyrolysis of biomass by LDI using Orbitrap as mass analyzer in 2010. These bio-oils can be refined to biofuels but they differ from petroleum and particularly their non-volatile compound compositions are still not well known. Orbitrap or other ion trap was practical when measuring oxidation products from reactive DESI as in Wu *et al.*^{27,109} research in 2010.

4.3.3 TOF

Time of flight (TOF) instruments are popular and widely used mass analyzers featuring next to unlimited mass range and good resolution. TOF has also high scan speed compared to other mass analyzers capable of differentiating petroleum ions as was seen in table 10. TOF instruments measure sample m/z values by their flight time where expelled ion packages from ion source are accelerated with equal kinetic energy by electric field between electrodes. After acceleration ions go through field free region in flight tube until they hit detector. Lighter ions have higher speed and hit detector before heavier ions as seen in figure 34.

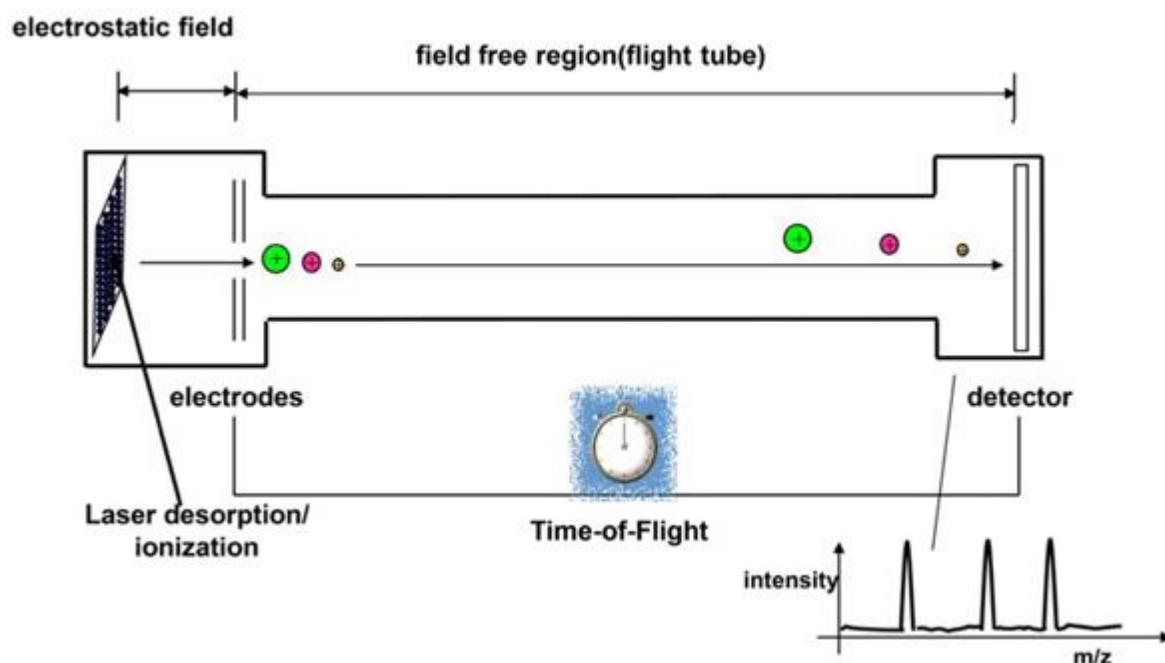


Figure 34. Basic principle of TOF mass analyzer shown with LDI ionization.¹⁴⁰

There are two kinds of TOF instruments in use that differ from flight tube composition: linear flight tubes and reflectors. Older instruments use linear flight tubes that have high mass range but also low resolution and these are physically big. Reflector-type TOF instruments reflect ions with electromagnetic fields and are more compact, have higher resolution and higher usability but also lower mass range.⁵⁹

TOF instruments are versatile and widely used mass analyzers that are cheaper, smaller and easier to operate than FT-ICR and sector instruments. One of the most prominent feature is high mass range that can be used when studying heavy samples i.e. asphaltenes with methods such as MALDI and other laser desorption ionization methods.²⁷

TOF is also used to study petroleum products and other hydrocarbons with carbon number between C_6 - C_{44} by EI and low-voltage EI. Also low voltage EI in combination with TOF could be used to study also aromatic compositions in petroleum and coal liquid.¹¹⁶ Polar fractions of petroleum are typically ionized with ESI and this can be used in combination with TOF if resolution is sufficient for sample type.

4.3.4 Sector instruments

Sector instruments are oldest model of mass analyzers that use magnetic (B) or electrostatic sector (ESA) to deflect ions flight path. Magnetic sector filters mass range and electrostatic sector focuses kinetic energy differences. Sector instruments can be used either by ramping magnetic sector or ramping applied electric field together with acceleration voltage. Basic operation principle can be seen in figure 35.

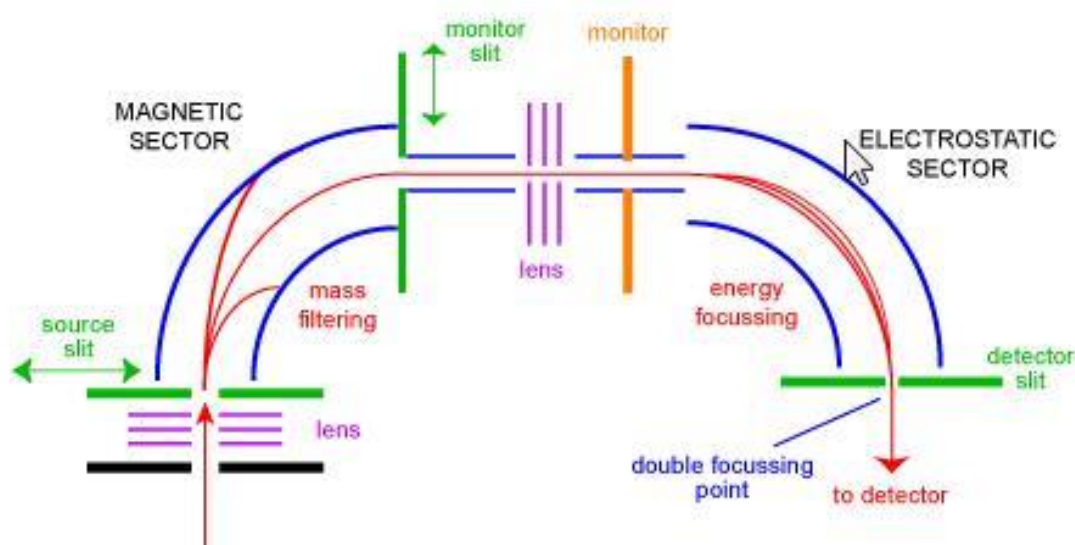


Figure 35. Basic operation principle of sector instrument with both magnetic and electrostatic sector.¹⁴¹

Sector instruments are practical with petroleum analysis and widely used. One possible drawback with sector instrument is scan time. Sector instruments take some time depending on used parameters to scan wanted mass range mainly because sector hysteresis that can result in inconsistent results when using pulsing ionization method (such as MALDI). Petroleum samples measured using pulsing ionization methods could affect reliability of results. Sector instruments have adequate resolution for many

petroleum studies and it is considerably smaller, cheaper and easier to operate and maintain than FT-ICR.

Sector instruments are most usable with pure hydrocarbon petroleum samples not including heteroatomic compounds such as distillate products and base oils and group analysis. For example, sector instrument with FI has been used to study base oil type branched hydrocarbons and saturates with carbon number C₆₇-C₁₀₃ in petroleum samples by J. Gross *et al.*¹⁴² in 2001 as well as with model compounds by on-line liquid chromatography-field ionization mass spectrometry by Z. Liang and C.S. Hsu¹⁴³ in 1998 and with C. Jin⁸⁸ in 2016. Other lubricant related studies are multi-element analyses with laser ablation inductively coupled plasma (LA-ICP) -MS using sector mass analyzer in ng/g range by N. Vorapalawut *et al.*¹⁴⁴ in 2010. LA-ICP MS provides effective ways to study problematic wear metals that appear in used lubricating oils and result in operation problems.

4.3.5 Quadrupole analyzers and ion traps

Quadrupole mass filters and ion traps use electrodes with oscillating electric fields to filter wanted ions where resonant ions pass quadrupoles while non-resonant ions are deflected out. Quadrupole mass analyzers are efficient as tandem MS instruments and they can be used either in full scan mode or select ion monitoring (SIM). SIM offers better sensitivity and quantitation but measures just certain m/z signal. 2D and 3D ion traps use same operation principle as quadrupole mass analyzers and are therefore combined here. Basic operation principle of quadrupole instrument can be seen in figure 36.

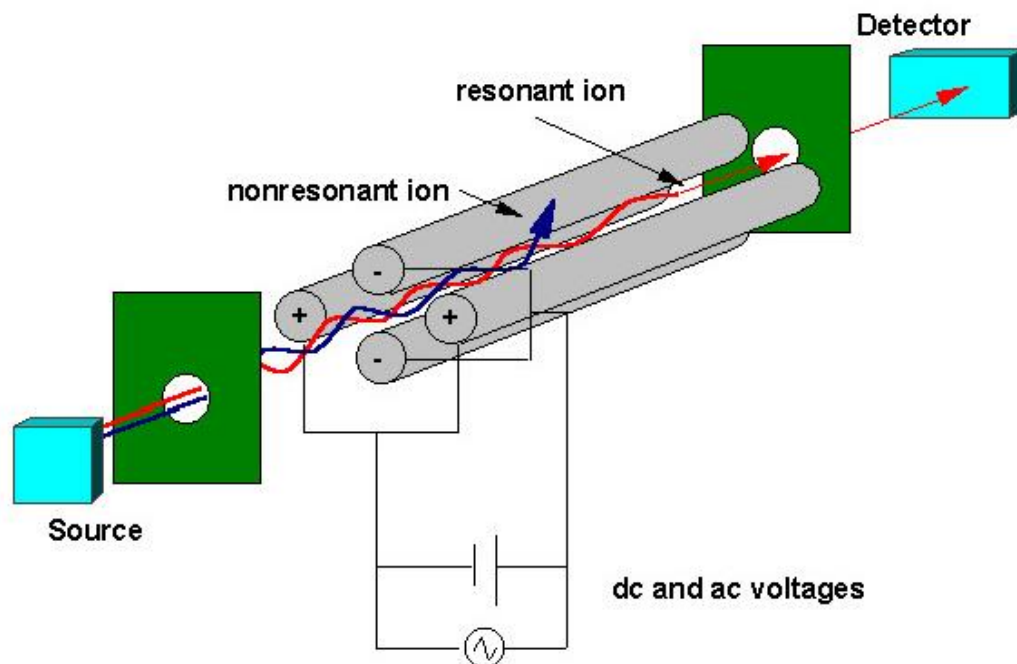


Figure 36. Basic operation principle of quadrupole instruments. In practice round metal rods are replaced by poles with precise hyperbolic surfaces.¹⁴¹

Quadrupoles are little use as analyzers in heavy petroleum products because they have insufficient resolution to separate isobaric ions but they are readily used with lighter petroleum products (i.e. gaseous products, benzene and diesel) analysis coupled with GC. Highest resolutions to date have been by M. Amad and R. Houk. They reflected ions multiple times through quadrupole and attained impressive resolution (FWHM) of 22 000 at m/z 28 but this has quite limited usability.¹⁴⁵

Ion traps are used to select and trap certain ions especially in tandem mass spectrometry. Ion traps are typically Penning traps that use electric and magnetic fields, Kingdon traps where ions circulate centroid in static electric field with no potential minimum or Paul traps that use static and oscillating electric fields to trap ions in space. Ion traps are commonly divided in 2D or 3D ion traps where example of 3D ion trap is Paul ion trap as ions can be trapped in all three dimensions while 2D traps are linear. Common 2D ion trap type is for example quadrupole ion trap.⁵⁹ Basic structure of Paul ion trap can be seen on figure 37.

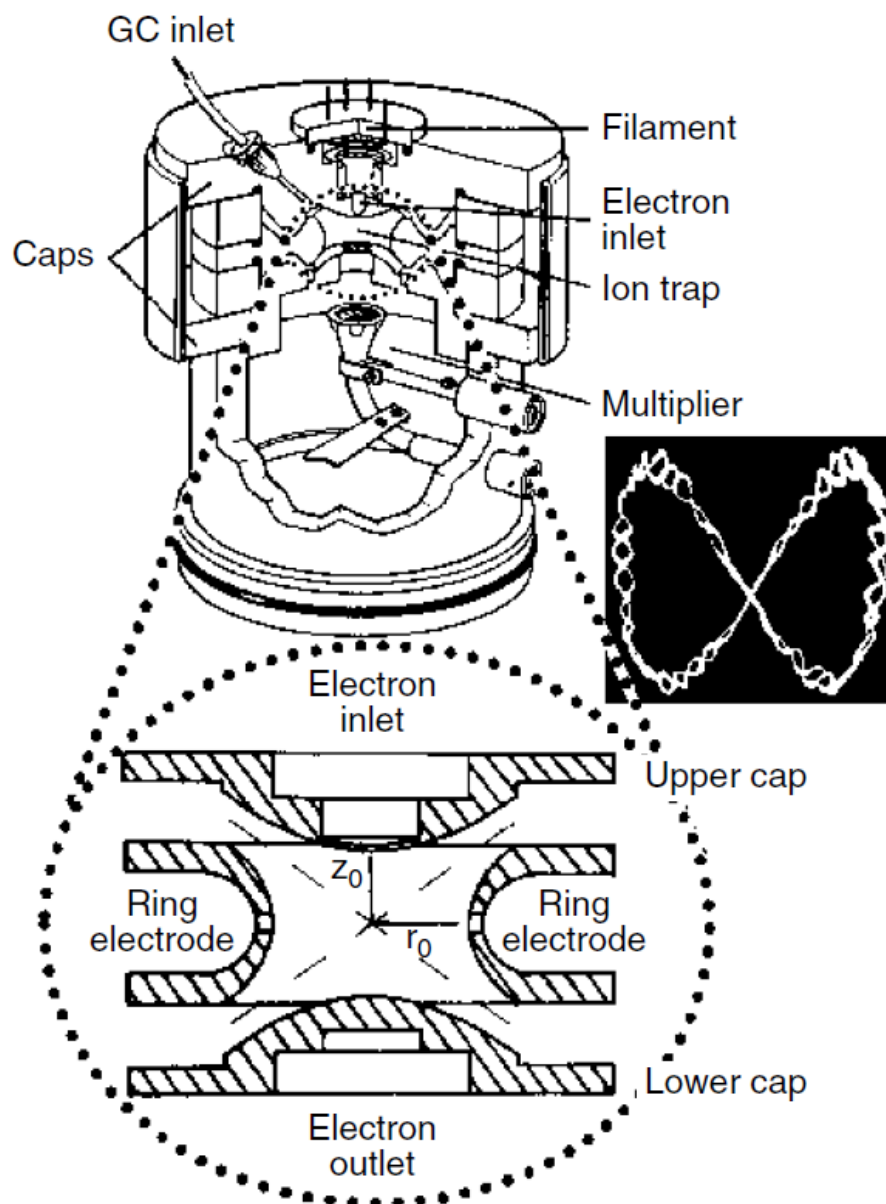


Figure 37. Basic structure of ion trap MS with detailed schematic of ion trap and ion motion.⁵⁹

Miniature mass spectrometers sometimes use rarer cylindrical ion trap.¹⁴⁶ Ion traps are used to trap ions or as mass analyzers with same operation principle as FT-ICR by oscillating frequency and Fourier transformation. Other uses for ion traps are quantum computation and information processing typically with Penning type ion trap. Basic sketch of 2D quadrupole ion trap was seen in figure 36.

4.3.6 Evaluation of MS methods for base oil type petroleum products

Deciding most suitable method and device assembly is not straightforward and there are few suggested features to consider when evaluating most suitable combination of ionization method and mass analyzer. First there is sample type that importantly includes molecular weight range, sample phase and polarity. These are greatly affected with feed and processing history in heavy petroleum samples and problematic compounds in processes and products are arguably heaviest polar petroleum compounds. Secondly extent of sample diversity should be evaluated i.e. range of different sample types intended to be measured. Ionization methods as APPI and FI have wider range of use but ionization methods such as APCI or EI have quite limited upper mass range for heaviest petroleum samples. Similar difference persists with mass analyzers where. Orbitrap can be considered more flexible mass analyzer with heavy petroleum samples than quadrupole allowing versatile experiments measured with same mass analyzer. Lastly available resources should to be assessed including personnel capabilities, budget and use environment. FT-ICR features highest resolving power but it binds most resources as being the most expensive mass analyzer to purchase and maintain and requires relatively trained personnel for operation. High resolving power can be achieved also with Orbitrap that features approximately as good resolution that FT-ICR did decade ago but it is significantly cheaper and easier to use. TOF and sector instruments can be used in certain petroleum analysis

Suitable ionization methods for non-polar base oil based on before discussed research are EI, FI/FD/LIFDI, LDIs, LIAD, APCI and APPI. These ionization methods have been used for long and there are plenty of research literature available. Promising ionization methods based on rather narrow available research material are: Reactive DESI, low voltage and cold-EI, low voltage FI and laser desorption ionization methods. Comparison of different ionization methods for heavy and nonpolar petroleum samples are collected into table 10.

Table 10. Sample types measured with different ionization methods with discussion and evaluated disadvantages

Ionization method	Sample types and references.	Discussion of suitability
EI	-	High fragmentation limits mass range significantly with all EI based ionization methods
Soft- EI	Petroleum heavy fractions; ⁷² Petroleum fuels ^{70,77}	Fragmentation is not prominent, but results still in complex spectra. Significant ion dissociation with labile hydrocarbons
Cold-EI	linear alkanes up to C ₇₀ ; ⁷⁴ JP8 Jet fuel. ⁷⁷	Molecular ion enhanced when compared to normal EI.
Soft-Cold-EI	Linear alkanes (C ₁₂ -C ₄₀); ⁷⁶ Squalane, C ₂₄ H ₅₀ ⁷⁵	Soft-Cold EI retains molecular ion reproducibly. Fragmentation even smaller than with soft or cold EI alone.
APCI	Alkanes, alkenes and cycloalkanes; ⁸⁰ C ₁₈ -C ₄₀ ; ⁸¹ Simple alkanes(C ₂ -C ₆); ^{82,83} Lubricant base oils; ⁸⁸ Nonvolatile and nonpolar hydrocarbons; ⁸⁴ Alkanes between C ₁₀ -C ₄₀ ⁸⁵	More suited to non-polar samples than ESI but less than APPI. Thermal degradation and fragmentation are problems. Limited suitability with labile and heavy samples due to the vaporization process.
APCI/LIAD	Base oil fractions; ⁸⁷ Saturated and unsaturated hydrocarbons; ⁸⁹ Petroleum heavy fractions; ¹⁴⁷ Aromatic, aliphatic, saturated and unsaturated hydrocarbons ⁸⁶	As only small portion of sample is desorbed in LIAD this could have negative affect on sensitivity and reproducibility of these methods.
DART ASAP or APGC	Polycyclic aromatic hydrocarbons ⁹³ paraffins, isoparaffins, and alkylbenzenes ⁷⁸	Fragmentation could be a problem with quantitative petroleum samples. Possibility of ramping vaporization temperature is similar to methods with FI
APPI	Petroleum oil; ⁷⁹ SARA fractions of crude oil; ⁹¹ Canadian Athabasca bitumen middle distillate ⁹⁴	Isobaric ions require high resolution. More suited for nonpolar samples than APCI and ESI. Can quantitatively measure polar fractions and nonpolar fractions simultaneously. Too high ionization potential can be a problem with certain samples and may require dopant and low ionization efficiency ⁵⁹
APPI-DART	Motor oil ⁹³	APPI-DART enhances, but there is little research on its suitability with heavy petroleum samples.
μAPPI	Petroleum ⁹⁶	Higher efficiency with sample load, lower when comparing overall results. more for research
ESI	Polar fractions of crude oil NSO compounds, naphthenic acid extraction; ^{98,99,101,104,148} PASH compounds of VCR; ¹⁰² nonpolar aromatic compounds ¹¹⁰	Generally suitable for polar samples. Limited suitability for nonpolar samples with HCOONH ₄ as ionization promoter
Nano-ESI	Heavy petroleum intermediates and products ⁵⁷	Nonpolar samples, mainly for automated measurement and miniature equipment study
EASI	Petroleum fuels ¹⁰⁷	polar samples, requires only little sample preparation
DESI	Saturated hydrocarbons ¹⁰⁹	Exceptional ESI method where also nonpolar molecules can be ionized. Other methods are still better.
FI/FD	LIFDI FT-ICR with sewing machine oil. ¹²²	
FI	Petroleum based waxes; ¹¹⁷ Diesel fuel; ¹¹⁸ Broad range of nonpolar hydrocarbons; ¹¹⁹ Base oils; ⁸⁸ Heavy hydrocarbons ⁵⁶	Much petroleum studies already from 1960-1970. laborious measurement
low V-FI	Gaseous samples ¹²³	Ultralow voltage FI has been presented that can bypass many of the problems with conventional FI but this has not been tested with heavy petroleum like hydrocarbons.
FD	FD TOF ¹⁴⁷	
LDI	Pitch and petroleum vacuum residue ¹²⁶	Aggregation and fragmentation if mass above 500 Da ⁵⁹
L ² DI	Asphaltenes; ²⁹ Asphaltene molecule distributions ¹³¹	Aggregation
MALDI	Coal-tar pitch ¹²⁷	Well suited to heaviest samples. Aggregation, low shot-by-shot reproducibility, sample preparation requirements ⁵⁹
LIAD	LIAD/CIMn- (H ₂ O) ⁺ CI with base oils; ⁸⁷ APCI-LIAD with saturated heavy petroleum products and intermediates; ¹²⁹ Petroleum distillates; ¹²⁸ LIAD/EI with asphaltenes and asphaltene model compounds ¹³⁰	LIAD/EI perhaps one of the rare studies where high mass molecular ions were detected from complex petroleum sample without significant fragmentation.

Comparing methods as a table gives overall view but is slightly superficial as suitability depends on multiple other factors starting from sample type, complexity, polarity, impurities and possible additional coupled methods as chromatography or additional MS.

In addition to expressed table, following limitations are good to consider with expressed ionization methods: EI/CI/APCI require thermal evaporation and this possibly results in thermal degradation limiting heavy molecular weight samples.¹²⁸ EI and its derivatives all feature fragmentation on some level that can either be used in structure research but in base oil research is an issue. ESI is used for polar components mainly and petroleum includes approx. 10% of these polar molecules that are the most troublesome fractions, so their research is well justified. Rare studies are made with ESI ionizing also nonpolar samples, but there is no foreseeable applicability with it to complex and heavy nonpolar samples.

ESI and MALDI also feature preferential ionization of acidic and basic compounds and nonpolar molecular ions are normally not detected.⁶⁷ MALDI as well as many other LDI methods suffer from sample aggregation when measuring heavy petroleum samples.¹²⁴ APPI is more prone to produce isobaric ions that require considerably more resolution attained only with FT-ICR or Orbitrap mass analyzer. Isobaric ions are also sample dependent and can exist with other ionization methods as well. FI/FD methods suffer from laborious measurement practice and reproducibility could be an issue. Field ionization and desorption methods are most suited to quantitative measurements of base oil fractions and research with it is largely done with sector instrument or FT-ICR. FI could be coupled with chromatography to manage laborious measurement, but this might result in new problems in reproducibility with constant sample amount between different sample viscosities.

As recapitulation, not all mass analyzers and ionization methods are comparable and fitness including multiple parameters hardly is a line from bad to good. Suitable mass analyzers for heavy petroleum samples have properties that can be compared including accuracy, resolution, price and mass limit. These are collected alongside advantages and disadvantages to table 11.

Table 11. Typical performance parameters of different mass analyzers for comparison^{59,137,149,150}

Mass analyzer	FT-ICR	Orbitrap	Quadrupole	Sector	TOF	
Mass limit	30 000	50 000	4000	20 000	>1 000 000 10 000	Linear Reflector
Resolution	>1 000 000	450 000	<4000	100 000	5 000 80 000	Linear Reflector
Accuracy	<1 ppm	<3 ppm	100 ppm	<5 ppm	<5 ppm <50 ppm	Linear Reflector
Ion sampling	Pulsed	Pulsed	Continuous	Continuous	Pulsed	
price	\$\$\$\$	\$\$\$	\$\$	\$\$\$	\$\$	
Advantages	High resolution, well suited for tandem mass spectrometry	High resolution, well suited for tandem mass spectrometry	Small size, low cost, tolerant of high pressure, well suited for electrospray	Capable of high resolution, capable of exact mass, medium mass range, can be reliable	Highest mass range, very fast scan speed, low cost, well suited with pulsed ionization method (i.e. MALDI)	
Disadvantages	High vacuum required, low temperature required, expensive, massive size	High vacuum required, low aptitude with low and very low energy ions	Mass range limited to about 3 000 m/z, poor adaptability with pulsed ionization methods (i.e. MALDI)	Not tolerant of high pressures, Expensive, massive size, relatively low scanning	Low resolution linear but suitable with reflector TOF reflector TOF has limited m/z range	

It needs to be highlighted that given performance values are directional as some differences were noted while assembling table. Some possible reasons are: temporal differences as methods go forward relatively fast (i.e. Orbitrap), there might be some different definitions of values as is with resolution (discussed in chapter 4.3) and values can be dependent in example with resolution and accuracy; low resolution mass analyzers do not have high accuracy.

Suitable mass analyzers with heavy and nonpolar base oil type samples are FT-ICR, Orbitrap and sector instruments. FT-ICR was the most versatile mass analyzer suited in quantitative and qualitative petroleum research but it is limited by operation expenses and its performance is rivaled by Orbitrap. Sector instrument are still viable option also with moderately heavy samples but they lack resolution with heaviest samples and there are no immediate future advancements in sight with sector instruments. Quadrupole and ion traps are commonly used with GC for light petroleum samples but they have inadequate resolution to be used as mass analyzers with heavy samples as is also the case of TOF. Instead they play important role in MS/MS (tandem) and collision chambers research.

5 Summary

Petroleum industry is going through change as product performance demand increases, environmental concerns impacts processes and materials and margin of profit varies as oil price sways. Preferred properties of demanded lubrication products are high viscosity index, low degradation in use but biodegradable with low environmental impact. Especially once niche products have today increasingly higher demands such as VHVI, bio based lubricants such as ESBO and high-performance synthetics such as PAO, PIO and GTL. On contrary crude oil feed becomes complex and heavier as easy and light crude oils are largely depleted. Changes in petroleum industries have impacted base oil production to shift from low VI products (API I and API II) to higher VI products (API II+, API III). Processes have changed from solvent refining to hydrotreating and more complex feeds such as waxes and heavy fractions of VRC are used stretching feed continuously further.

Increased demands for heavy and base oils require additional expenses in research and development of both new processes and analysis methods. While chromatography and NMR unveil valuable typical and averaged information of petroleum samples, mass spectrometry still is the only method capable of producing information of individual molecule compositions. Widely used ionization methods with heavy petroleum fractions and products are electrospray ionization with polar components; matrix assisted laser desorption ionization and other laser desorption ionizations with heavy asphaltene studies; and FI, FD, APPI, LIAD and APCI with nonpolar components. Promising ionization methods for nonpolar petroleum MS methods are APCI/LIAD, Cold-EI, low voltage EI, Reactive DESI, APPI, and low voltage FI. It should be noted that commonly used methods such as FD and ESI have been used and further developed for decades while arising methods such as LIAD-APCI and reactive DESI have just emerged and are under further development.

Resolution and sensitivity limits suitable mass analyzers as complex samples and isobaric ions require enough resolving power. Most suitable mass analyzer for heavy petroleum research with highest resolution is FT-ICR where operational and acquisition costs limit its usability and newly emerging Orbitrap. Other common and suitable mass analyzers are sector instruments, TOF and ion traps (such as LQIT).

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