



Investigation of SVOC nanoparticle emission from light duty diesel engine using GC×GC-ToF-MS

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- Introduction
- Research Objectives
- Experimental Setup
- Test Procedure
- Results and Discussion
- Conclusions

Introduction

- SVOC(Semi volatile organic compounds) are a major component of diesel emissions
- SVOC vaporise and are oxidised, forming a greater mass of SOA(Secondary organic aerosol)
- SVOC partitioning between the gas and aerosol phases under ambient conditions, contributes uncertainties to SOA formation
- Stringent emission legislation on light duty vehicle emission at cold start transient condition and scarce research of SVOC quantification in this field

Research Objectives

Research Objectives



- To quantify specific SVOCs in diesel exhaust particulate matter
- To investigate a large hump in the chromatogram referred to as Unresolved Complex Mixture (UCM) by GCXGC-TOF (time of flight)-MS(Mass spectrum)technology
 - Interpretation for alkane, alkyl-cyclohexane and PAH species
 - SVOC quantification comparison between warm start and cold start
 - Oil fraction contribution to engine particulate emission
 - Soft ionization-14ev source(original 70ev) application for detailed isomers analysis

Experimental Setup

The Capability of Cold Cell Transient Facility



The Engine:

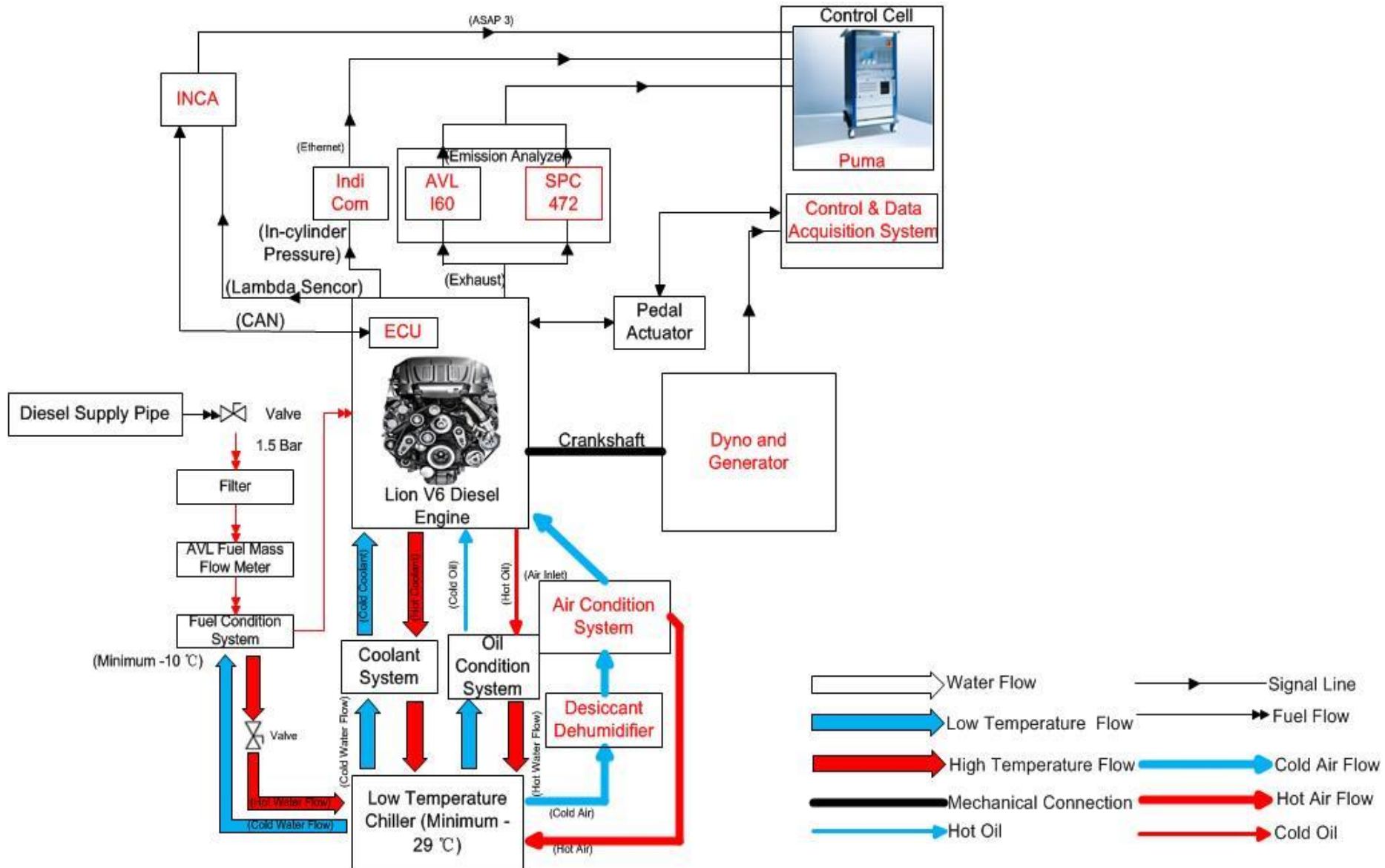
Commercially used six cylinder common rail turbo charged diesel engine



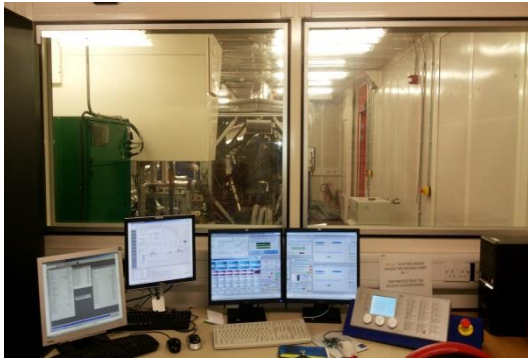
Type of the engine	Jaguar V6 3.0L Diesel
Bore	81.0 mm
Stroke	90.0 mm
Displacement volume	2993 cm ³
Maximum torque	600 Nm @ 2000 rpm
Maximum power	199.1 kW @ 4000 rpm
Compression ratio	16.1:1
Connecting rod length	160.0 mm

- NEDC transient cycle test at cold start and warm start condition
- Diesel (zero sulphur), synthetic oil (5W-30)
- Sample collected after DOC aftertreatment device

Schematic of Cold Engine Transient Test Facility



Cold Engine Transient Test Facility



Control Room



Engine test cell



Utilities Room



Fast FID



Fast NOx



DMS 500

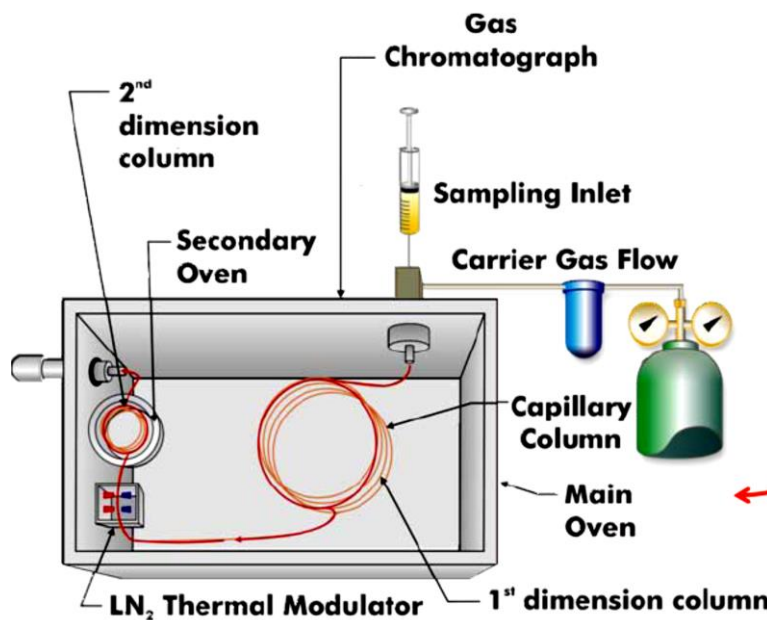


SPC 472

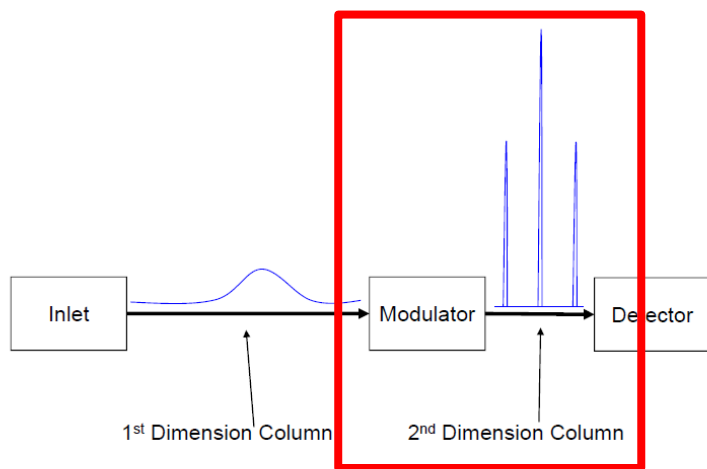
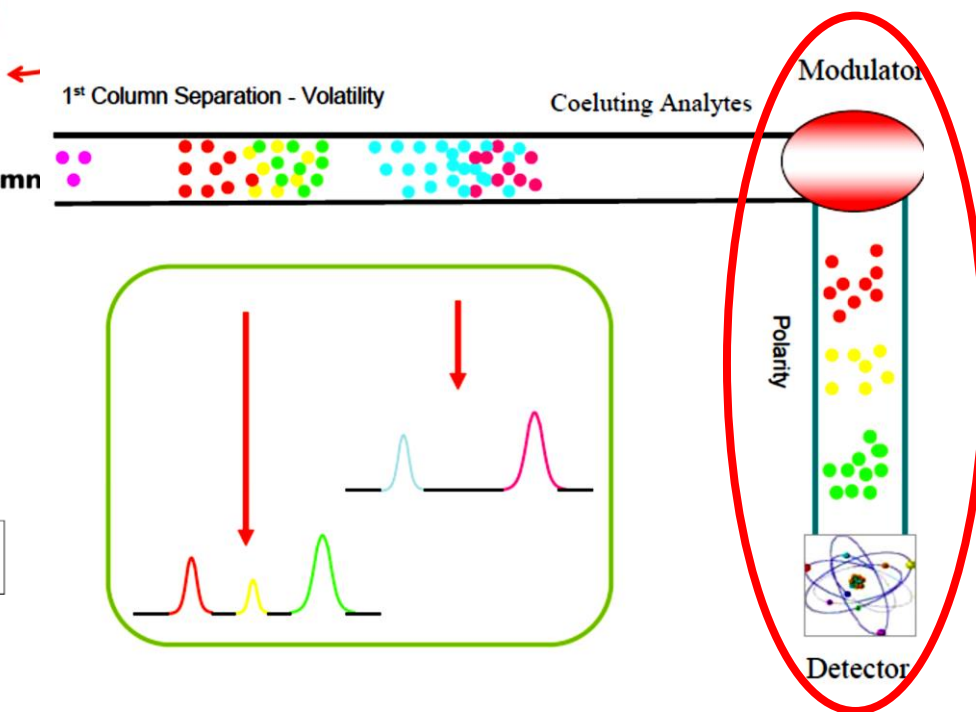


AMA i60

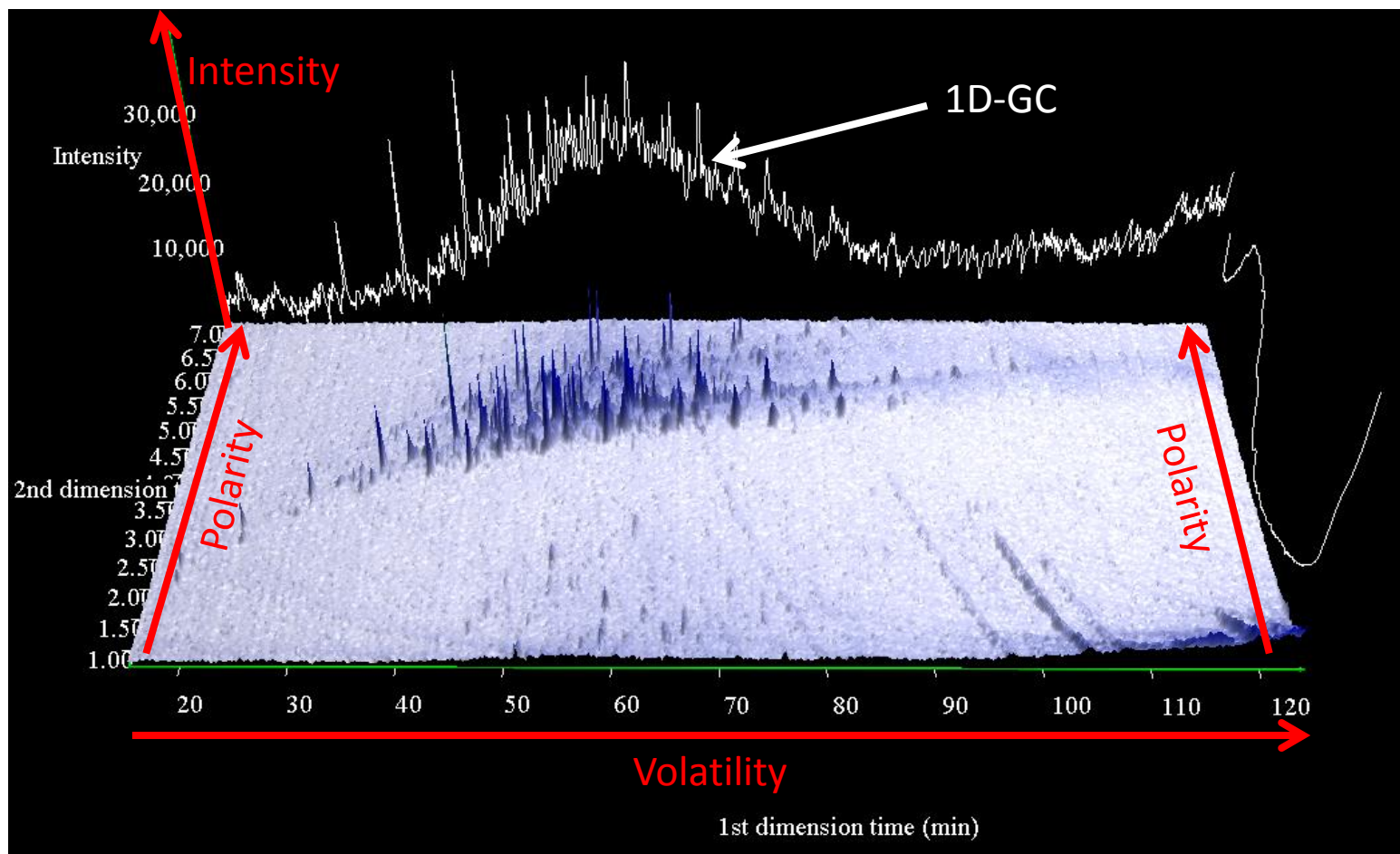
GC×GC Technology



The **modulator** traps and releases sequential components from the 1st column (**volatility**) effluent and injects it into the 2nd column (**polarity**) for further separation



GC×GC Technology – An example



Test Procedure

Test Procedure



- Average instantaneous results are taken from 3 repeat tests for ambient transient condition
- Oil and fuel are controlled by the main control unit(all with over 90 °C for warm start and 25 °C \pm 3°C for cold start)
- Ventilation system preset temperature and humidity of the room were 23 \pm 2°C and 51 \pm 2% respectively
- Partial flow sampling system-SPC472
 - Dilution Air Temperature <52 °C
 - HEPA connected in compressed air inlet
 - Cyclone separator <2.5 μ m equipped



AVL SPC472



Results and Discussions

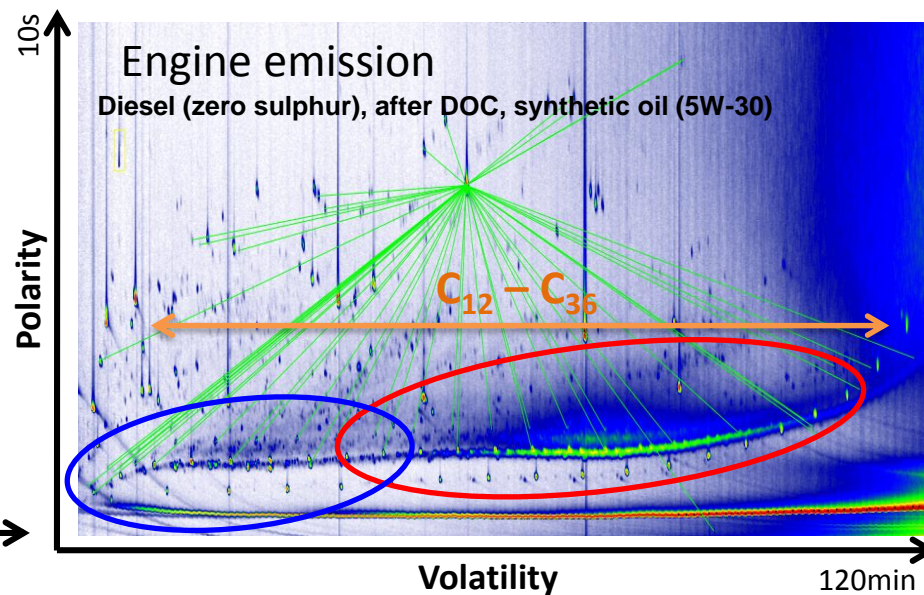
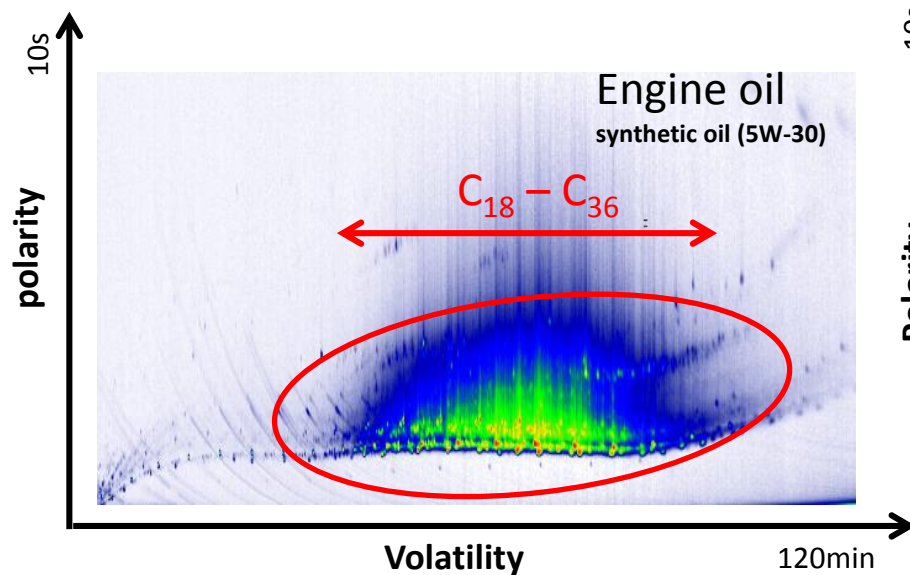
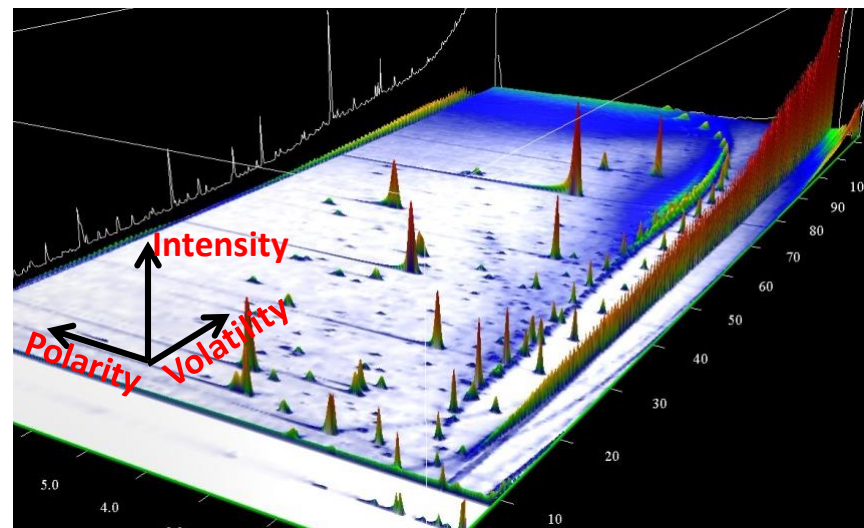
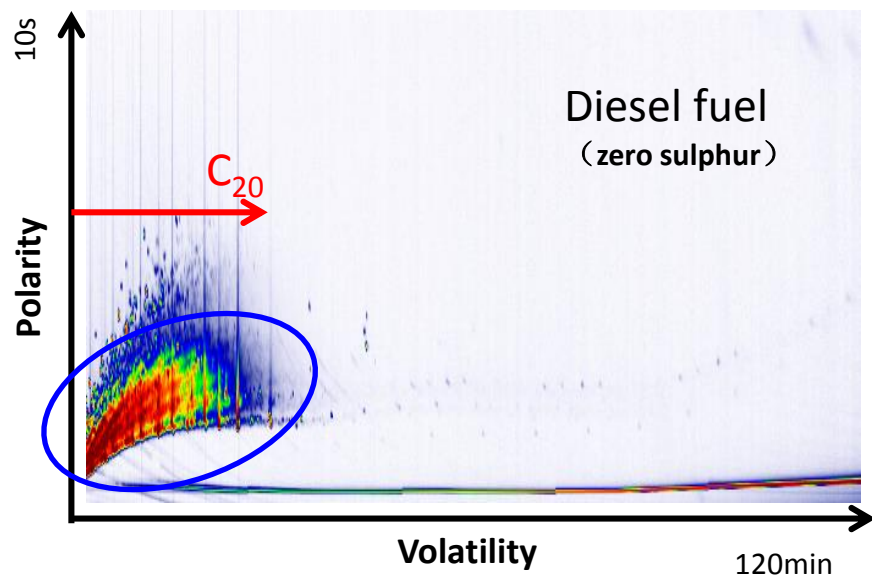
Results and Discussions



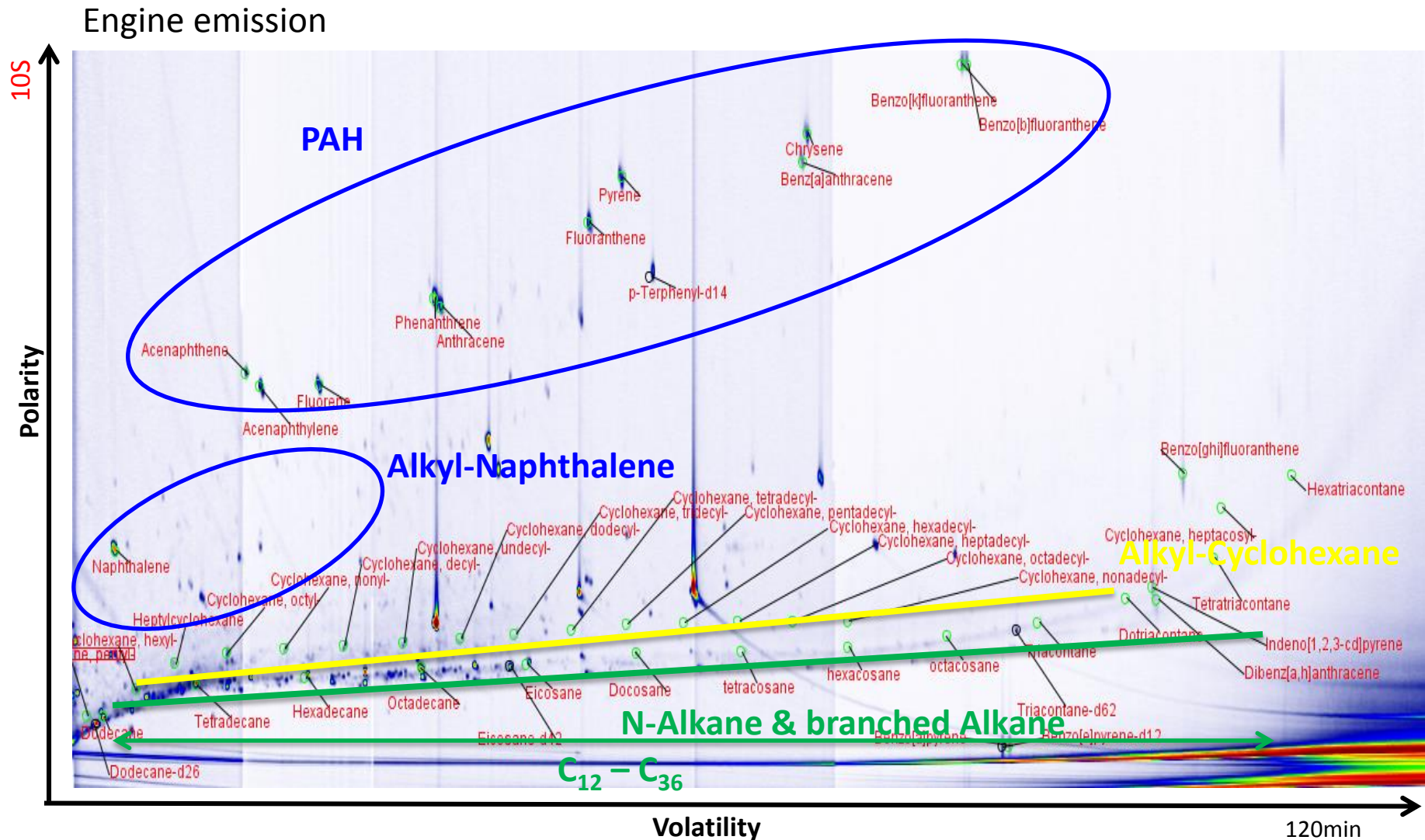
Section 1 - Chromatography interpretation for engine emission, oil and diesel fuel

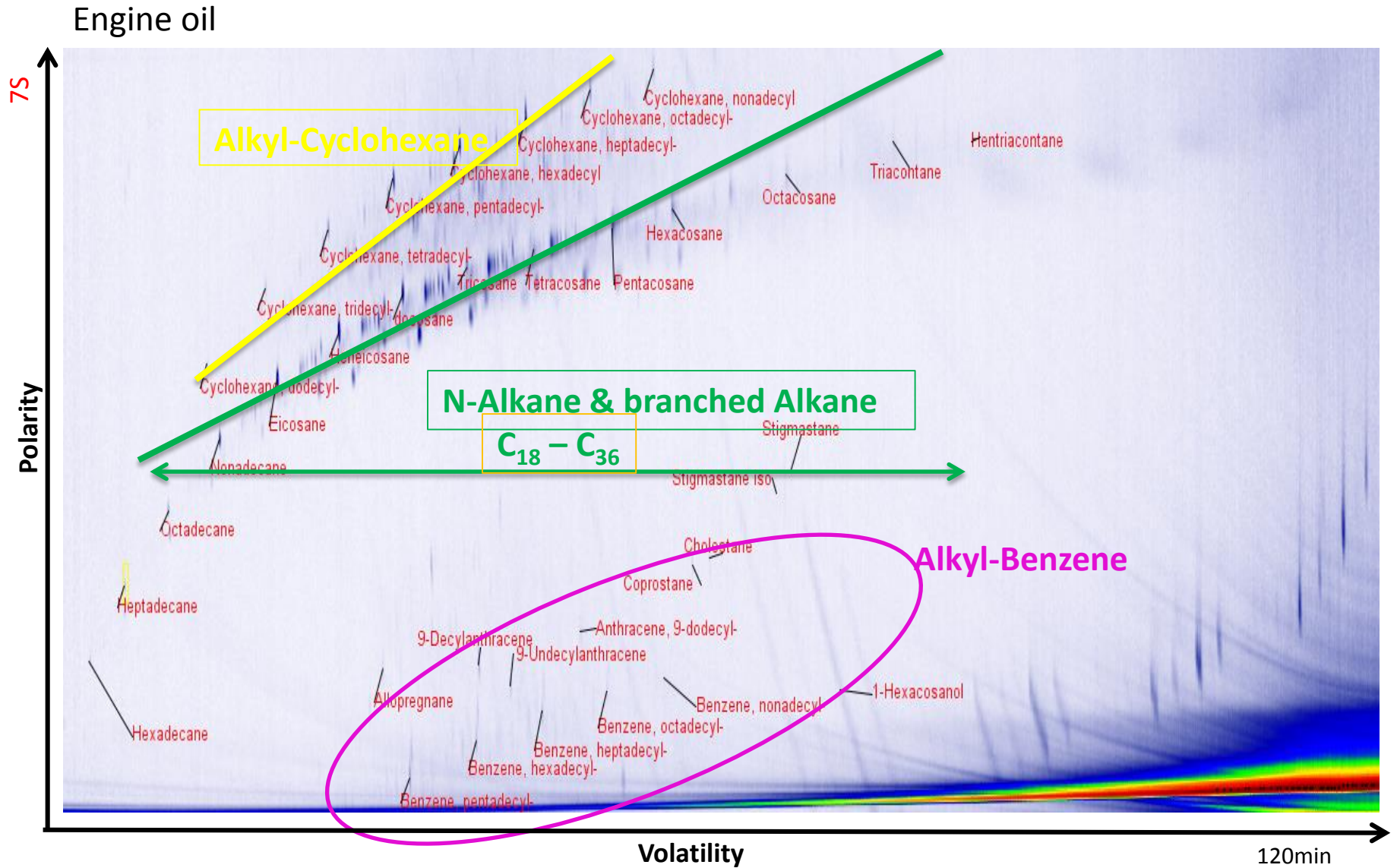


Fuel and Engine oil fraction contributed to engine emission

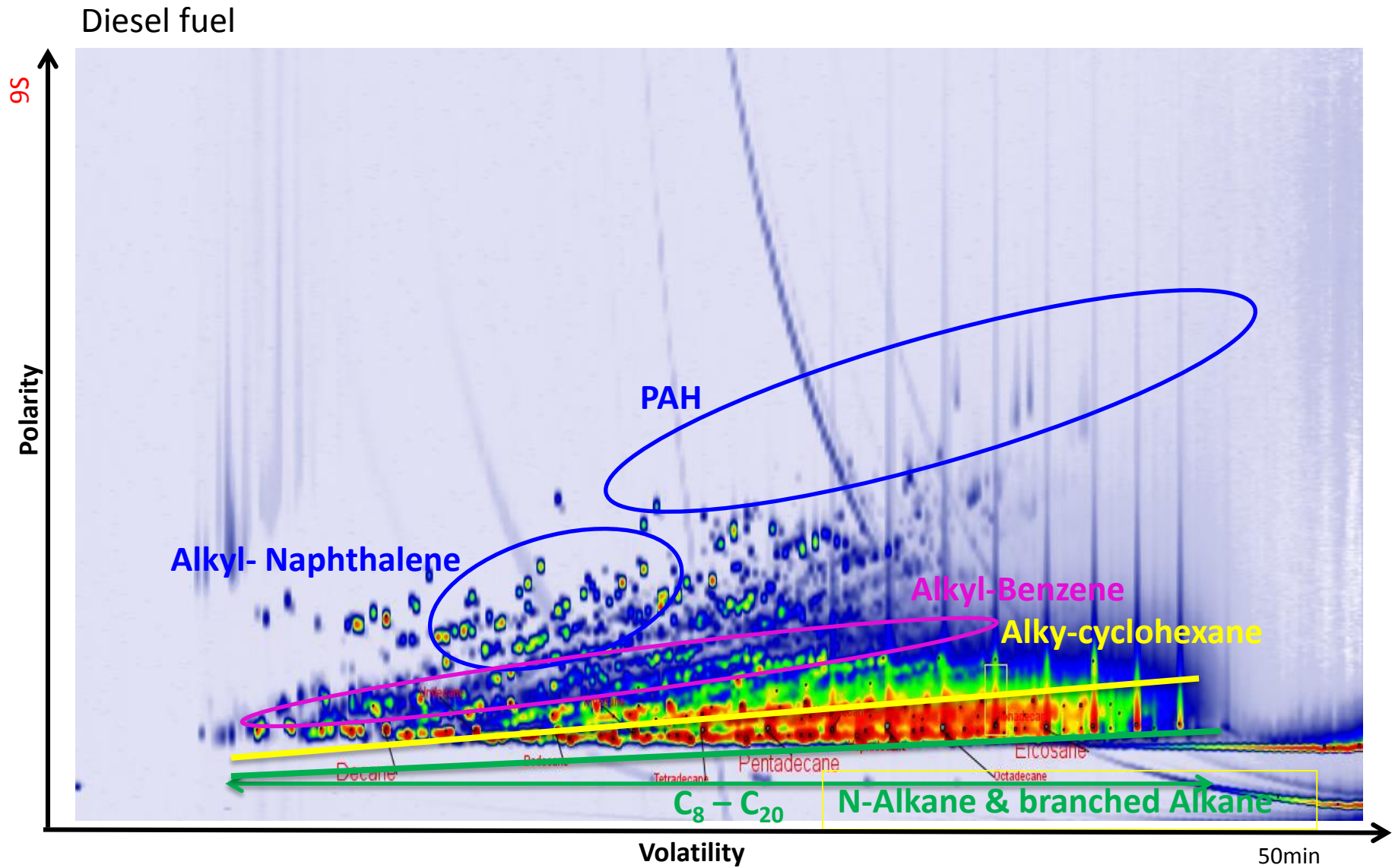


Chromatography of engine emission





Chromatography of diesel fuel



Major components of diesel fuel, engine oil and engine emission



Classes and groups	Engine oil
N-Alkane	C18-C36
Alky-Cyclohexane	C18-C25
BTEX family	Toluene family
	Ethylbenzene family
	Xylene family

Classes and groups	Diesel fuel
N-Alkane	C8-C20
Alky-Cyclohexane	C12-C17
BTEX family	Toluene family
	Ethylbenzene family
	Xylene family
PAH	Naphthalene
	Acenaphthene
	Phenanthrene

Classes and groups	Engine Emission
N-Alkane	C12-C36
Alky-Cyclohexane	C13-C26
PAH	Napthalene
	Acenaphthene
	Fluorene
	Anthracene
	Fluoranthene
	Pyrene
	Benz[a]anthracene
	Chrysene
	Benzo[b] fluoranthene
	Benzo[k] fluoranthene
	Benzo[a] fluoranthene
	Dibenzo[a,h] anthracene
	Benzo[ghi] perylene
	Indeno[1,2,3-cd] pyrene

Results and Discussions

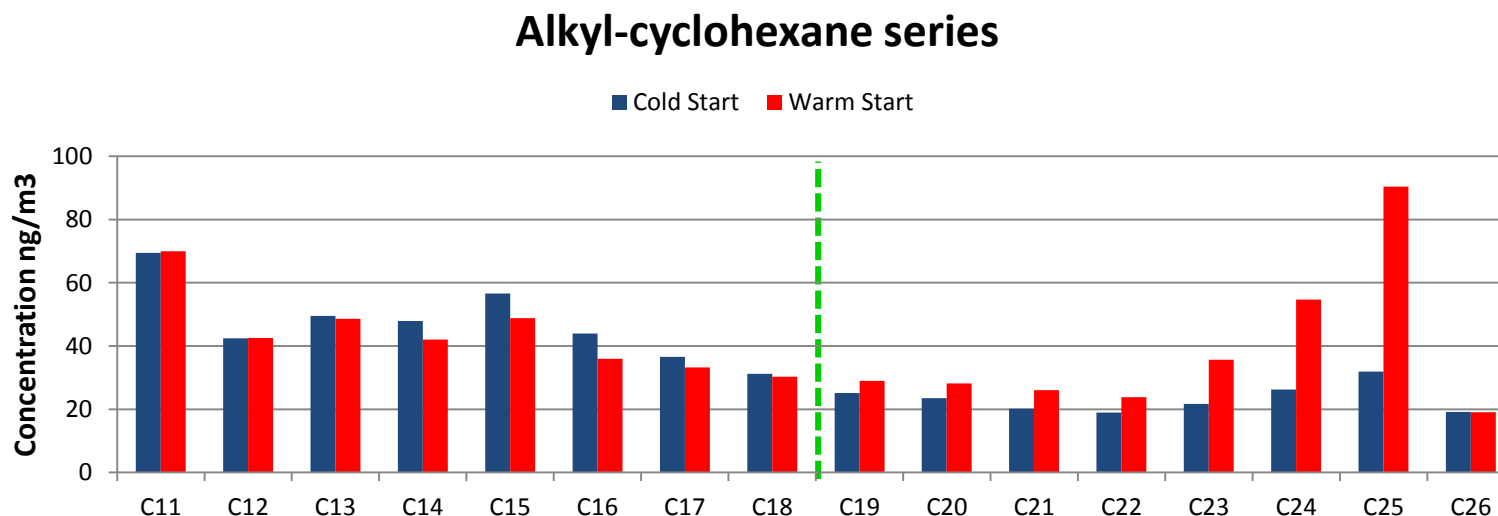
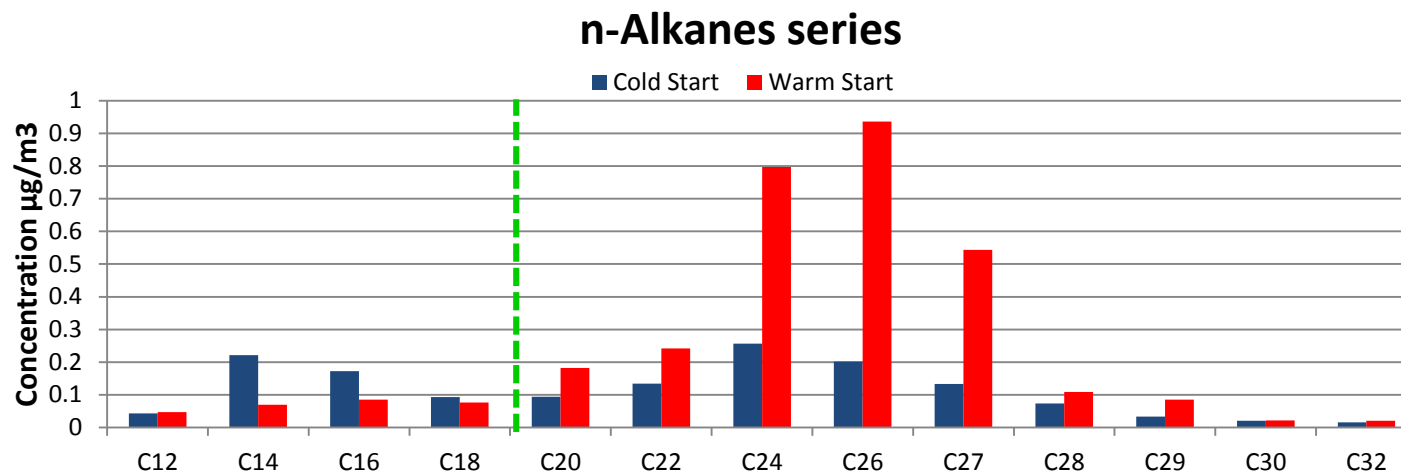


Section 2 -Quantification of n-Alkane, Alkyl-Cyclohexane & PAH



Particulates(n-Alkane & Alkyl-Cyclohexane)

- (1) Diesel (zero sulphur), after DOC, synthetic oil (5W-30), **NEDC, cold start**
(2) Diesel (zero sulphur), after DOC, synthetic oil (5W-30), **NEDC, warm start**

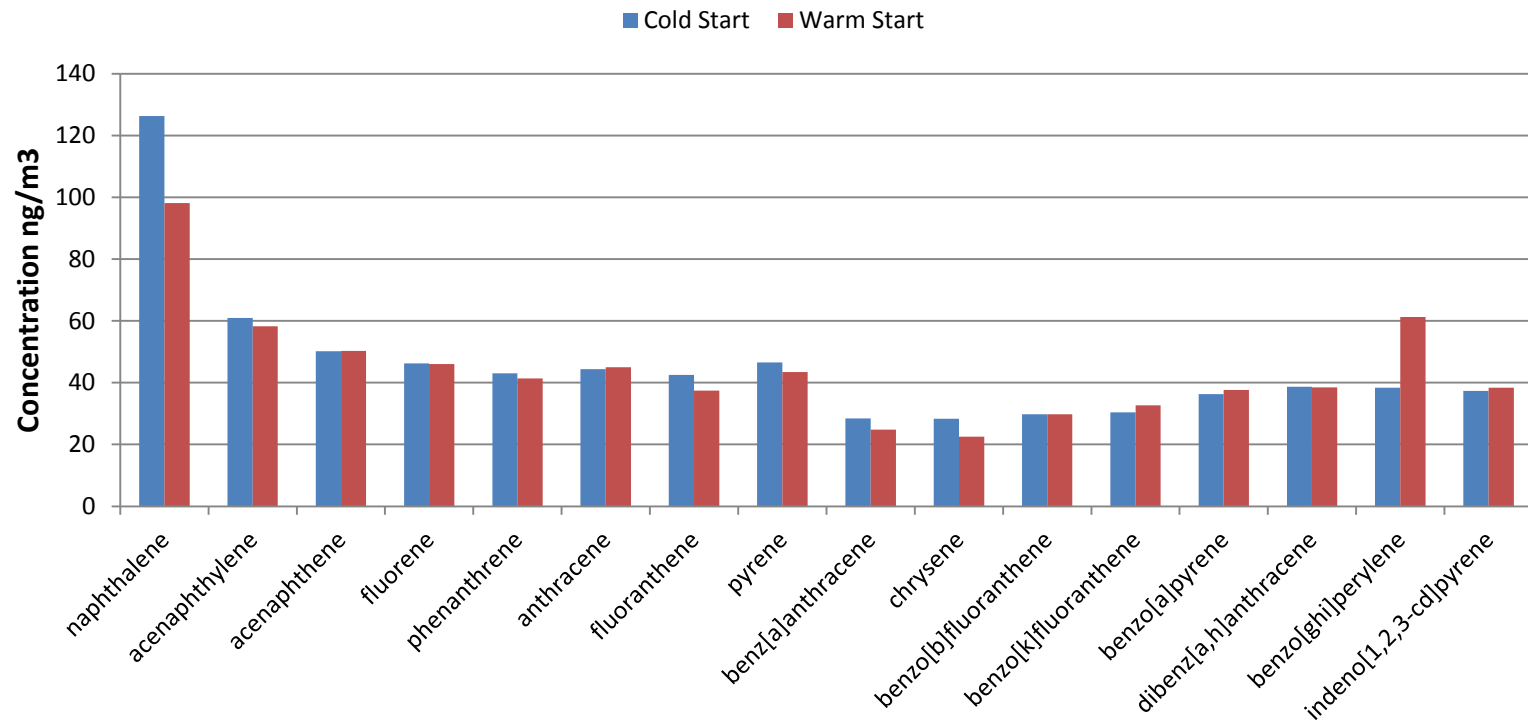


Particulates (PAH)



- (1) Diesel (zero sulphur), after DOC, synthetic oil (5W-30), **NEDC, cold start**
- (2) Diesel (zero sulphur), after DOC, synthetic oil (5W-30), **NEDC, warm start**

PAH series

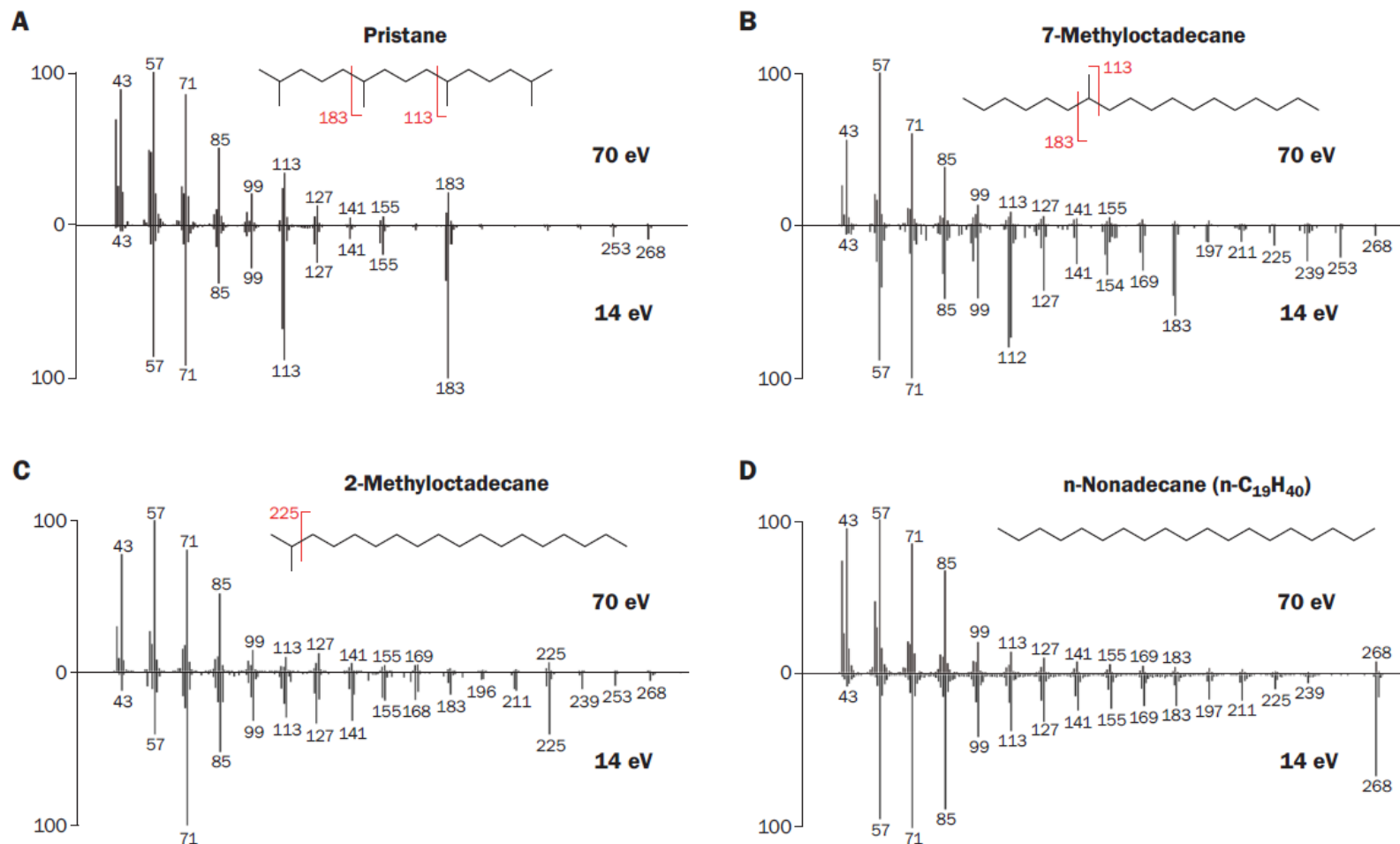


Results and Discussions



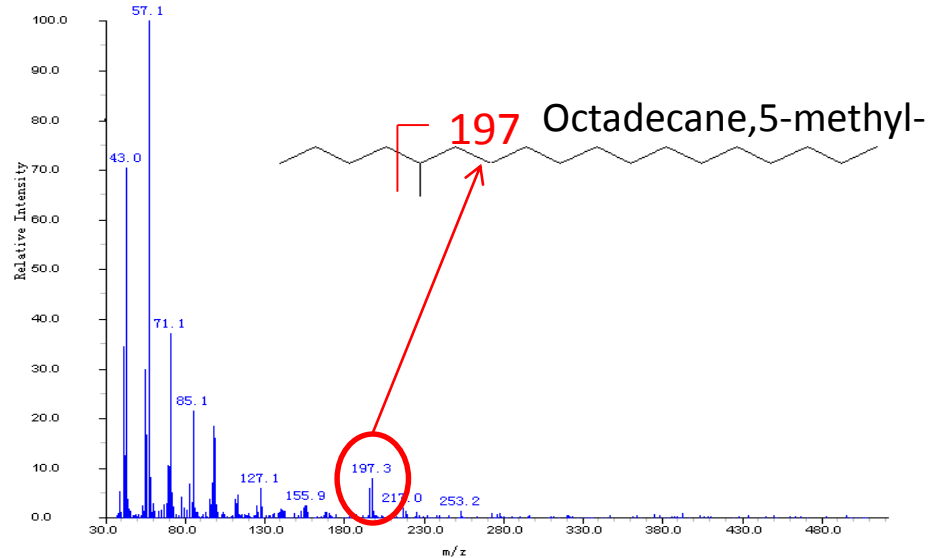
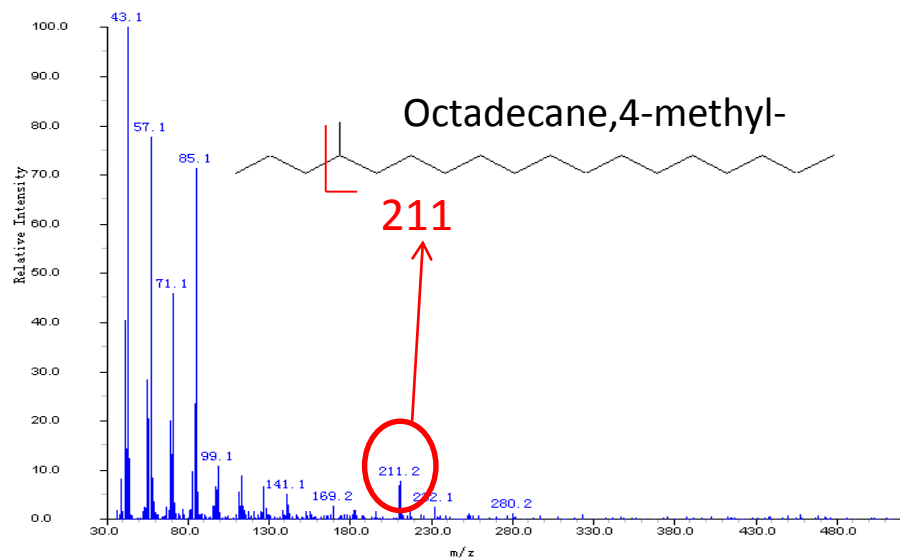
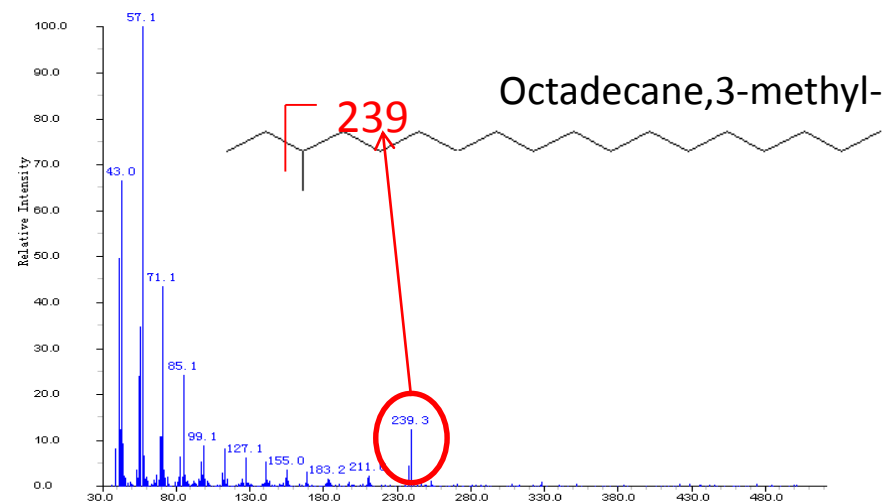
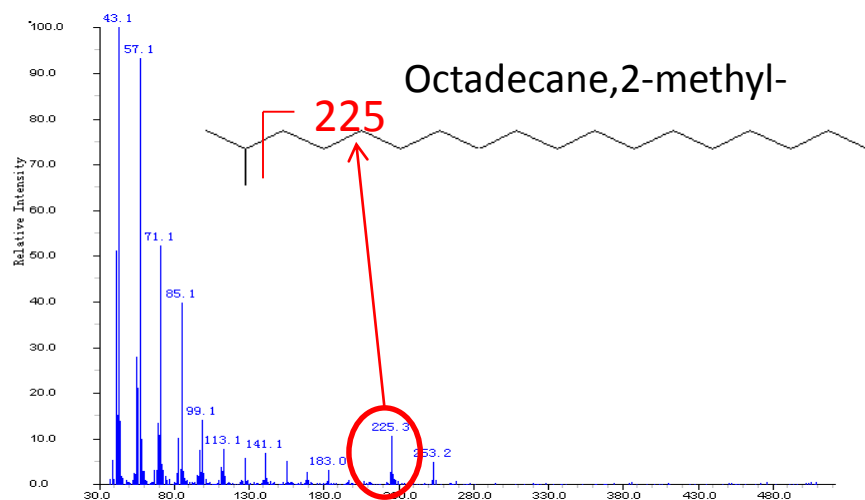
Section3 - Improved detection with soft ionization source

Mass spectrum signal output improvement with soft ionization source(14ev)

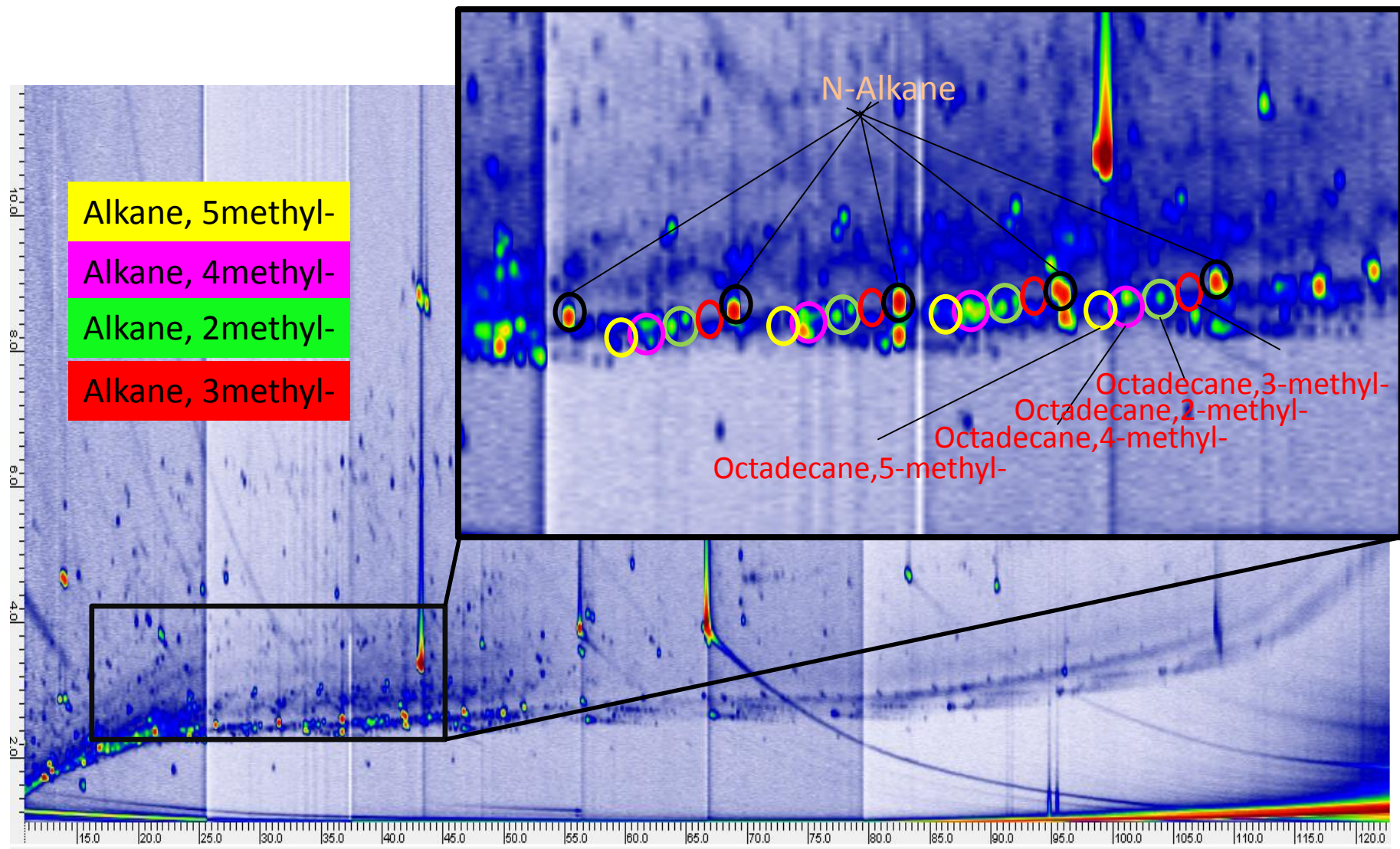


From MARKES International

Example of Isomeric-Alkane analysis by mass spectrum characteristic



Isomeric Alkane distribution order for engine emission



Conclusion

Conclusion



- The SVOC from the diesel engine was observed to contain predominantly **alkanes, alkyl-cyclohexanes, PAH** and various aromatic compounds
- Poor combustion conditions** result in **higher amounts of light SVOC** released during cold start (**Results may be underestimated** since **gas phase** at this range have not been fully sampled and further tests will be conducted with **gas absorption** tube sampling)
- The **heavy SVOC components** were emitted during warm start with more complete combustion and the **Engine oil fraction** was observed to contribute significantly to this emission
- Using a **soft ionization** technique **di-, tri-, tetra- and penta-** substituted aliphatics were positively identified and can be quantified



Thank you for your kind attention!