Experiences in semivolatile (SVOC) emission measurements at VTT

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SVOC definition

- SVOCs are sufficiently volatile to be in vapor form at the temperature of engine-out exhaust, but condensable under atmospheric conditions.

- Most SVOC molecules have at least 14 carbon atoms and boiling points 240-400 °C. SVOCs may contain PAHs, dioxins and nitro-PAHs (US EPA 40 CFR 1065.1103–1111). Analysed SVOC species are typically PAHs or n-alkanes, but majority of SVOC mass is challenging to identify.

- SVOC concentrations depend on the gas particle partitioning of the emissions, which vary depending on concentration and saturation pressure, other constituents of exhaust gas and sampling parameters.
SVOC definition

- SVOC emissions from cars are not well-known.

- Exhaust emission measurements cover:
  - THC (<C12), which is measured using FID
  - Particulate matter (PM) associated primary organic aerosol (POA).

  **Exhaust emission measurements do no cover SVOCs**, although regulatory test conditions favor condensing of the lightest SVOCs (or IVOCs) in PM.

- Note: SVOCs potentially form secondary organic aerosol (SOA).
Organic emission profiles (Lu et al. 2018)

- Lu et al. classified
  - IVOCs C12 to C22
  - SVOCs C23 to C32
  - LVOCs C33 to C36 (respective to n-alkanes)

- Volatility basis set (VBS) framework lumps organics into logarithmically spaced bins of saturation concentrations (C*) at 298 K. Designed for C12 and larger.

Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions

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Volatility distribution a) gasoline b) diesel. Red dashed line = the particle fraction.
SVOC measurements at VTT

- In 90’s at VTT, SVOCs were collected using PUF material for PAH analyses and Ames tests
  - Demanding, expensive pre-purification of PUF material
  - Filter face velocity and temperature affect the SVOC/PAH emissions

- SVOC sampling (US §1065.1103-1065.1111) with XAD–2 resin with or without PUF plugs.

- XAD and Empore materials were tested in late 90’s at VTT, and Empore materials again in 2015.
SVOC measurements at VTT in 2015

VOCs
- e.g. CO, THC
- C1-C8 hydrocarbons, e.g. methane, acetylene, benzene, toluene, ethyl benzene, xylenes
- C1-C6 carbonyls e.g. formaldehyde, acetaldehyde, hexanal

PM sampling
- e.g. PTFE filters

SVOC sampling
- e.g. Empore disks (or Tenax tube etc.)

PM Quartz filter sampling

Raw exhaust

VOCs
- e.g. CO, THC
- C1-C8 hydrocarbons, e.g. methane, acetylene, benzene, toluene, ethyl benzene, xylenes
- C1-C6 carbonyls e.g. formaldehyde, acetaldehyde, hexanal

PAH compounds e.g. benz[a]pyrene

Mutagenicity e.g. Ames test

Oxidative potential e.g. DTT

Anions e.g. sulphates

Particle characterization, many dilution systems, mass and number size classification, thermodenuder for volatility analysis, access to SMPS, SEM and TEM.

Task Force on Emission Inventories and Projections, May 13-15, 2019, Thessaloniki
Details of sampling

Diluted exhaust
17.5 L/min

Filter TX-40
o.d. 47 mm
Anions

Empore SDB-XS
o.d. 47 mm
PAH, Ames, DTT

Diluted exhaust
200-1500 L/min

Fluoropore 3.0 μm FSLW
2 x o.d. 142 mm
PAH, Ames, DTT

Dil. exhaust 0.1 L/min
TenaxTA-CarbopakB
FMI analysis

PM

SVOC
Empore sampling

- Empore disks are developed for water and air sampling (e.g. for PAH analysis).

- At VTT, Empore disks were tested for SVOC sampling in late 90’s.
  - Two types of Empore disks a) nonpolar C18 (activated) and b) slightly polar SDB
  - Results with both Empore types gave comparable results with PUF sampling,
  - Extraction of heavy PAHs from Empore was more challenging than from PUF.

- In 2015 testing, Empore SDB-XC disks (poly(styrenedivinylbenzene) copolymer) were used for SVOC sampling. Similar Empore products as in 90’s were not available.
VOCs in 2015 measurements

- Methane emission highest from NGV/CNG and FFV/E85.
- BTEX aromatics highest from FFV/E85 and gasoline.
- Note ethene emission from FFV/E85.

VOCs: ~15 E6 diesel, ~150 mg/km gasoline, ~700 mg/km FFV/E85, ~100 mg/km NGV/CNG

Ref. Aakko-Saksa et al. TAP 2019 presentation
SVOC emissions

- Higher SVOC than PM emissions for all cars tested. Very high SVOC emission for Euro 6 diesel car. Chemical composition was not analysed (except PAHs).

- SVOCs were collected after PM filters using Empore disks. Back-up filter of PM sampling captures some SVOCs, but not substantially.

Sum of PM, SVOC and THC mass emissions are surprisingly similar for different cars.

Ref. Aakko-Saksa et al. TAP 2019 presentation
PAHs in SVOCs and in PM

- Sum of 16 PAHs high in SVOCs when compared with PM.

- Sum of 7 PAHs at the same level in PM and SVOCs for Euro 6.

- High PAH emissions from gasoline car and FFV/E85.
Secondary organic aerosol (SOA)

In 2015 measurements, SOA formation decreased as ethanol content of the fuel increased and aromatics content decreased.

BTEX compounds had a large impact on SOA formation. Also Nordin et al. (2013) found C6–C9 aromatics as SOA precursors.

SVOCs as SOA formers?
Organic fraction of POA could also give valuable information
EC/OC analysis

- The thermal-optical technique based on the evolution of carbon species in different temperatures.
- Temperature and gas atmosphere adjusted while monitoring a laser signal reflectance or transmission through the sample matrix.

Heating in steps up to 550–900 °C in inert He to remove OC. The organics may be pyrolysed (PC) inducing decrease in the laser signal. Oxygen introduced and temperature elevated step-wise. Carbon oxidised to CO$_2$, converted to methane and detected by FID. PC formed compensated by determining the point (split) when the laser signal achieves its original value.
Simulated distillation

- PM extracted with DCM and analysed with GC.
- Distillation range of PM SOF in sample was 250-500 °C.
Fuel/lube

The fuel/lube analysis was used in 90’s, which part of PM SOF originates from the lube oil and which part from the fuel. Fuel/lube analysis was carried out with GC / solid injection method by Neste using standard chromatograms of lube oil and 10 % distillation residue of the fuel. For gasoline particulates it is assumed that compounds other than those found in the boiling area of the lube standard originate from the fuel.

Aakko-Saksa et al., EU PARFIN project report.
Thank you
References


- Roslund, P. et al. (2014) ‘Unregulated emissions from Euro 5 emission level cars (VTT-R-04308-14)’.

Introduction

- New renewable and alternative transport fuels are introduced, and engine and exhaust aftertreatment technologies develop. Valid and comparable data is needed both on the direct and indirect effects of these new technologies.
- Real-world emissions are increasingly important (transient driving, cold temperatures), particularly unregulated emissions that are less studied than regulated emissions.
- Goal was to investigate emissions from Euro 5/6 cars (Euro 2 as reference), i.a. methane, aromatics, aldehydes, nitrogen dioxide, nitrous oxide, ammonia, semivolatile organic compound (SVOC), PAH, mutagenicity and oxidative potential. Test temperature -7 °C.
PAH in SVOC
# Priority PAHs

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- No. of rings/aromatic rings
- Collins et al. (1998)
An example of driving cycle

The NEDC driving cycle
Particle characterization
- Several dilution systems: full flow and partial flow tunnels, ejectors and porous tube diluters.
- Mass size classification: DLPI, DGI, virtual impactors (PM 2.5, PM1).
- Real-time number size classification by ELPIs (>8 nm).
- Thermodener for volatility analysis of size fractions.
- Access to SMPS and to electron microscopes (SEM, TEM).

Semivolatiles
- Extraction with toluene or DCM
- Extraction with IPA
- Anions (Electrophoresis)
  - Sulphate
  - Nitrate
  - Phosphate
  - Fluoride
  - Oxalate
  - Acetate
  - Bromide
  - Chloride

PAH compounds (GC/MS)
- Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]-anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a, h]anthracene, benzo[g,h,i]perylene, indeno [1,2,3-cd]pyrene.

DCM exchange to DMSO

Mutagenicity test
- TA98±S9
- TA98NR±S9

Oxidative potential
- DTT assay

Extraction/ methanol

Extraction/ IPA

Carbonyl compounds (HPLC)
- Formaldehyde, acetaldehyde, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butyraldehyde, benzaldehyde, Valeraldehyde, methylaldehyde, hexanal

C1-C8 hydrocarbons (Gas chromatograph)
- Methane, ethane, ethene, propane, propene, acetylene, i-butene, 1,3-butaadiene, benzene, toluene, ethyl benzene, m-, p-, o-xylene

Particulate matter

Exhaust dilution

Solid particle number (BCPC)

Filter sampling

Quartz filter sampling

EC/OC

Multi-component, real-time gases (FTIR)
- e.g. NH3, NO2, alcohols

Regulated gaseous
- CO/CO2 (NDIR)
- THC (HFD)
- NOx (CLD)

Raw exhaust

Tedar bags

Extracted

18/05/2019   VTT – beyond the obvious