Size distribution and PAH content of particulates emitted by DI and IDI Diesel engines
Particulate Matter Size Distribution And Associated PAH Content
From Indirect And Direct Injection Diesel Engines

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This study presents part of the results we obtained on particulate matter size distribution and associated PAH content of indirect and direct injection Diesel engines. It is included in a large framework which consist in evaluating contribution of vehicle emission to global atmospheric aerosols.

Testing conditions:

Vehicles were tested on a roller test bench, equipped with dilution tunnel and constant volume sampling: a Peugeot 405, 1.9 litres engine, with indirect injection and a Peugeot 406, 2 litres engine, with direct injection.

Two driving cycles were used: MVEG, which is a well-known European driving cycle, and HYZEM which is an urban cycle, based on statistical studies of real traffic conditions in cities. This is a shorter cycle, with strong accelerations and decelerations.

The same test fuel was used for both vehicles: a reference fuel from PSA, with 485 ± 5 ppm of sulphur content. And particulate matter was collected by regulated sampling (47 mm Pallflex T60A20 filters), and using a special device in order to study size distribution (SDI 2000).

Analysis apparatus

A SDI 2000 (Diffusional and Inertial Spectrometer) was used. It allows to collect particles as a function of their size. This device was developed in the CEA Saclay in France (by Dr D.Boulaud). The coarse particulate fraction (0.4 - 10 µm) is collected by an height stages Andersen impactor, and the fine one (8 nm - 0.4 µm) by a six stages diffusion battery. Results on particulate mass are treated by a software in order to correct and obtain right granulometric distributions. It is easy to understand that, due to the size separation of particles, the duration of collection was 3 times more important with SDI than regulated sampling.

After being collected, particle mass was measured with a micrometrical balance, after stabilisation of filters under controlled conditions (temperature and hygrometry).

For particle analysis, we used an Accelerated Solvent Extractor with methylene chloride. A clean-up phase allows to separate PAH from others compounds, which could add background during GC/MS analysis. We worked with internal standards, and 16 PAH from EPA were under focus.

Validation of analytical method

In order to validate our method, we have measured certified soot from the National Institute for Standard and Technology (sample 1650a) included in the Standard Reference Material program. The graph 1 shows the results for 11 PAHs, with high concentrations on the left, and low concentrations on the right. We can show that certified data are recovered within experimental uncertainties, and conclude that our measurement is in agreement with certified data.

![Graph 1: comparison between experimental and certified data for 11 PAHs measured on soot NIST 1650a (left: high conc.; right: low conc.)](image)

In the second part of this validation, we did a round robin test with four other laboratories. A Diesel indirect injection powered vehicle was driven on a MVEG cycle. Analysis provided by the working group were compared for different emission ranges. And results were homogeneous. Once again, the analytical method was validated.

Results

Two driving cycles were compared. The graph 2 shows the results for the direct injection engine (406 HDi).

Concerning total PM, there is no significant difference between the sampling devices for MVEG cycle. We can see only one little difference for HYZEM cycle, but not really significant. If we compare driving cycles, MVEG emissions are lower than HYZEM emissions. It could be related to the higher SOF content of HYZEM

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emissions (31% for HYZEM, 12% for MVEG). The same behaviour is observed for 405 IDi.

A difference can be seen for total PAH emissions (graph 3). Indeed, PAH concentrations are higher for SDI than for regulated sampling, which could be due to condensation or adsorption phenomena. Just remember that duration of particle collection were 3 times more important with SDI.

Graph 2: comparison between SDI and regulated sampling for total PM emission (µg/km) from 406 HDi, in MVEG and HYZEM cycles

Graph 3: comparison between SDI and regulated sampling for total PAH emission (µg/g) from 406 HDi, in MVEG and HYZEM cycles

Now if we look at PM emissions (graph 4), we can see that MVEG emissions are 40% lower for 406 HDi. This difference is not observed with HYZEM cycle. Also, MVEG cycle leads to lower particle emission comparing to HYZEM. Ratios between coarse and fine particles are not significantly different for each cycle and each vehicle.

Graph 4: PM emissions (µg/km) from IDi and HDi engines for MVEG and HYZEM driving cycles

Previous differences are not observed with PAH emissions (graph 5). Because of high standard deviations, we can not differentiate neither the two cycles nor the two vehicles. Particles are collected in 14 size classes. As we add classes to compare coarse and fine fractions, we add uncertainties too.

Graph 5: total PAH emissions (µg/g) from IDi and HDi engines for MVEG and HYZEM driving cycles

As we can see in graph 6, both pyrene and chrysene have same distribution, with a main mode at 0.2 µm, and two others at 1.0 and 7.0 µm. Same behaviour is observed for HYZEM cycle. However, the distribution of 405 IDi are different and depend on PAH molecular weight. These distributions could be a part of a fingerprint of these emissions.

Graph 6: PAH distribution for pyrene and chrysene, from 406 HDi in MVEG cycle

Conclusion - On going work

In conclusion, we can say that our analytical method is suitable whatever the engine. We have shown that PM emission decrease with direct injection engine. We have found the same order of magnitude for PAH emission. There is only one problem with SDI for PAH emissions, because we didn’t recover same results than with regulated sampling.

Metals and PAH distributions could provide fingerprint of vehicle emissions. Also, atmospheric samples analysis of airborne particulate matter in different urban sites is on progress. Finally, all results will be submitted to statistical data analysis to evaluate the contribution of vehicle emissions to atmospheric aerosols.

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Summary

Testing conditions
vehicle
analysis apparatus

Method validation
NIST 1650a
Round Robin Test

Results

Conclusion - Future work
PM size distribution and PAH content

Testing Conditions

Roller test bench (CVS)

1.  
   405  1.9 L  Diesel Indirect Injection (XUD9A)

2.  
   406  2.0 L  Diesel Direct Injection (DW10 ATED)
   HDi - common rail

MVEG driving cycle 11 km, 20 min
HYZEM (urban cycle) 2.9 km, 9 min

3.  Same Test Fuel: reference fuel PSA (S = 485 ± 5 ppm)

Regulated sampling (47mm T60A20 filters)
Size distribution (SDI 2000)
PM size distribution and PAH content

- Particle sampling (SDI 2000)
  - Particle weighing
    - filter stabilisation
    - micrometrical balance
  - Particle analysis
    - Accelerated Solvent Extraction (CH$_2$Cl$_2$)
    - Clean-up phase
    - GC/MS with Internal standards
    - 16 EPA PAHs under focus
PM size distribution and PAH content

16 EPA PAHs

- NAPH (128 g/mol)
- ACY (152)
- ACE (152)
- FLUO (166)
- PHEN (178)
- ANTH (178)
- FLRT (202)
- PYR (202)
- B(a)A (228)
- CHRYS (228)
- B(b)F (252)
- B(k)F (252)
- B(a)P (252)
- IND(1,2,3-cd)P (276)
- B(ghi)P (276)
- dB(ah)A (278)

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PM size distribution and PAH content

Analysis validation

NIST 1650a (Diesel certified soot)

Certified data are « recovered » within experimental uncertainties

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PM size distribution and PAH content

Analysis validation  ➔  Round Robin Test

Diesel vehicle, MVEG cycle, 5 laboratories

B(a)P = Benzo(a)Pyrene

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Mean of all laboratories with standard deviation

Homogeneous results

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PM size distribution and PAH content

- **Apparatus evaluation**  
  **SDI 2000 vs Regulated Sampling**

**PM emission : 406 HDi**

**SOF :**  
MVEG = 12 ± 4 %  
HYZEM = 31 ± 7 %

- no significant difference / sampling apparatus
- MVEG < HYZEM
- SOF → HYZEM ≈ 2 × MVEG
PM size distribution and PAH content

- **Apparatus evaluation**
  - **SDI 2000** vs **Regulated Sampling**
  - **Total PAH (µg/g)**
    - MVEG
    - HYZEM

- **PAH**
  - Regulated: RSD ≈ 30\%
  - SDI > Regulated → Pb (condensation, adsorption)

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PM size distribution and PAH content

**PM emissions (g/km)**

<table>
<thead>
<tr>
<th>405 IDi</th>
<th>VS</th>
<th>406 HDi</th>
</tr>
</thead>
<tbody>
<tr>
<td>MVEG</td>
<td>HYZEM</td>
<td>MVEG</td>
</tr>
<tr>
<td>emission (g/km)</td>
<td>PM&lt;sub&gt;0.4&lt;/sub&gt;</td>
<td>emission (g/km)</td>
</tr>
<tr>
<td>0.000</td>
<td>0.040</td>
<td>0.000</td>
</tr>
<tr>
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<td>0.080</td>
<td>0.040</td>
</tr>
<tr>
<td>0.060</td>
<td>0.100</td>
<td>0.060</td>
</tr>
<tr>
<td>0.080</td>
<td>0.120</td>
<td>0.080</td>
</tr>
</tbody>
</table>

**Conclusion**

- HDi < IDi → -40%
- MVEG < HYZEM
- 40% < PM<sub>0.4</sub> / PM<sub>tot</sub> < 60%

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PM size distribution and PAH content

- PAH emissions (µg/g)

405 IDi vs 406 HDi

Conclusion

- HDi ≈ IDi
- MVEG ≈ HYZEM
- PM_{0.4} ≈ PM_{10-0.4}

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PM size distribution and PAH content

**PAH distribution : 406 HDi MVEG**

- **Pyrene**
  - Main mode : 0.2 µm
  - Others : 1.0 µm
  - 7.0 µm

- **Chrysene**
  - All PAHs
  - Same distributions

  **HYZEM** : Same behaviour

**Fingerprint of HDi emission ?**

- **405 IDi**
  - **Low MW**
    - 0.2 µm (main)
    - 5.5 µm
  - **High MW**
    - 0.1 µm (main)
    - 1.5 µm

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PM size distribution and PAH content

<table>
<thead>
<tr>
<th>Conclusions</th>
<th>405 IDi</th>
<th>406 HDi</th>
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</thead>
<tbody>
<tr>
<td>- Analytical method suitable?</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>- PM regulated emissions</td>
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<td>- 40 %</td>
</tr>
<tr>
<td>- Total PAH emissions</td>
<td>=</td>
<td>=</td>
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<tr>
<td>- SDI: questionable for total PAH / regulated sampling</td>
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PAH distributions ➔ Fingerprint of vehicle emissions

On going work

- Metals distributions
- Atmospheric samples
- DataBase analysis

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