Tracer Study to assess the effect of lubrication oil and fuel on catalyst aging for different combustion techniques, oil and fuel types


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Introduction

The aging of catalytic converters for exhaust gas after-treatment in internal combustion engines by both chemical and thermal processes is relevant for both environmental and economic reasons. While several mechanisms have been investigated, the sources, which emit elements responsible for poisoning and accelerated catalyst aging, are often not clear and not easily to quantify. Therefore, the catalyst aging project at Empa was initiated to investigate whether and which extent catalyst specific poisoning elements, e.g. phosphorus or sulphur originate from the employed lubrication oil or the used fuel types.

The project aims to understand the mechanisms of possible impacts of the different fuel or oil sources on the catalyst conversion efficiency. The major goal of the project is the investigation of the oil- and fuel-induced aging of catalysts in petrol-, biofuel- and natural gas vehicles. Therefore, four nearly identical passenger cars, operated with different fuel types: i.e. natural gas CNG, gasoline E0 and biofuel blends E5 and E85 are investigated in test stand experiments as well as in long-term on-road experiments compared to get information on long-term influence of the different fuel types.

Moreover, for the CNG vehicles which are suspected to show accelerated catalyst aging in comparison to other fuel types, two lubrication oil types (low saps and high saps) are compared for two identical CNG vehicles operated under similar conditions but with two different lubrication oils.

Additionally simulation chamber experiments were carried out get more information on the mechanism of catalyst aging and the influence on the conversion rate for exhaust gas emissions.

The project consists from three parts and aims to answer the following research questions:

Part 1: Tracer experiments

1. Investigation of the Influence of the fuel and the lubrication oil type on the elemental composition of the emission
2. Identification of the origination of possible catalyst poisoning elements from the different possible sources
3. Identification of possible transport paths
4. Quantification of oil contribution based on calculations of tracers
Part 2: Simulation chamber experiments

1. Investigation of pollutant-induced catalyst aging and the underlying destruction mechanism (e.g. the influence of phosphorous poisoning on the conversion efficiency of CH₄)
2. Influence of different catalyst poisoning types on the conversion rate of relevant exhaust gas components like methane, NOₓ, CO

Part 3: On-road long-term influence of oil and fuel type on the catalyst efficiency (2 years test for 40000 km)

1. On-road tests of pollutant-induced catalyst aging in long-term experiments over 40000 km for 2 years
2. Investigation of pollutant-induced catalyst aging and the underlying destruction mechanism in long-term vehicle experiments
3. Long-term-influence of low- and high-saps oil types on the catalyst aging and efficiency for CNG vehicles
4. Influence of different catalyst poisoning types on the conversion rate of methane, NOₓ, CO, etc. in long-term vehicle experiments

Experimental Setup

For the project parts 1 (Tracer Study) and 3 (Long-term Influence), Euro IV conform vehicles, identically in construction, were operated with the fuel types CNG, gasoline E0 and the two biofuel blends E5 and E85. Two further identical CNG vehicles were operated with low SAPS and high SAPS lubrication oil to study the influence of oil additive packages on a potential accelerated catalyst aging. Table 1 gives an overview of the employed vehicles and the used operation conditions for the tests.

Table 1: Vehicles (Euro IV conform) and operation conditions for the experiments of the tracer and the long-term behaviour project parts.

<table>
<thead>
<tr>
<th>Vehicle type</th>
<th>Fuel type</th>
<th>Lubrication oils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ford Focus 1.8L SW</td>
<td>E0: standard conform gasoline (SN EN 228)</td>
<td>Ford WSS M2C 913-A</td>
</tr>
<tr>
<td>Ford Focus 1.8L SW</td>
<td>E5: 5% ethanol reference fuel (SN EN 228)</td>
<td>Ford WSS M2C 913-A</td>
</tr>
<tr>
<td>Ford Focus 1.8L SW</td>
<td>E85: 85% ethanol (analysis every 2'000 km)</td>
<td>Ford WSS M2C 913-A</td>
</tr>
<tr>
<td>Ford Focus 1.8L SW</td>
<td>CNG: Swiss CNG petrol station quality</td>
<td>Ford WSS M2C 913-A</td>
</tr>
<tr>
<td>VW Touran 2.0L</td>
<td>CNG: Swiss CNG petrol station quality</td>
<td>VW 502 00</td>
</tr>
<tr>
<td>VW Touran 2.0L</td>
<td>CNG: Swiss CNG petrol station quality</td>
<td>VW 504 00 (low SAPS)</td>
</tr>
</tbody>
</table>
**Part 1: Tracer experiments**

The source identification study includes experiments with stable tracers on a vehicle test stand. With the exception of the CNG, all fuels were spiked with bismuth Bi (10 ppm) each, and the oils of all cars were spiked with 50 ppm indium In as tracers. The vehicle test stand experiments were carried out under steady state conditions at three constant speeds, i.e. 50 km/h, 80 km/h and 120 km/h. To evaluate the emission situation in different parts of the engine, samples were taken at 3 distinct sampling points in the engine; in the intake air, at the engine out and after the catalytic converter. The sampling was carried out using a washing bottle assembly with subsequent backup filter. Later elemental analysis of the adsorption solution allowed assumptions on origins of the contamination (source identification) as well as information on the distribution at different points in the engine and an assessment of the deposition rates on the catalyst.

Samples were taken at 3 distinct measuring points in the engine: air inlet (MP1), engine out (MP3), after catalyst (MP4). Due to technical reasons the realization of the also planned point MP 2 was not possible. The following graph shows the measuring points in detail:

**Figure 1:** Sampling points for tracer experiments

The sampling equipment consisted from a 3 bottle wash bottle assembly and a subsequent backup filter. The adsorption solution was a 1:1 mixture from a 6 % nitric acid HNO₃ and 6 % hydroperoxide H₂O₂. All chemicals used were in high purity quality grades. The average adsorption efficiency was determined for wash-bottle 1 at 73 % and for the 2-wash-bottle-system+backup-filter at 91.5 %. Figure 2 shows a principle of the sampling set-up, figure 3 presents a photo of the wash bottle assembly.
**Figure 2:** Principle of the sampling set-up

**Figure 3:** Photograph of the wash bottle assembly
All adsorption solutions from the wash bottles were analyzed in double determinations using plasma mass spectrometry (ICP-MS). The backup filters were digested microwave-assistant using an acid mixture and subsequently also analyzed by ICP-MS.

Results and Discussion

An important prerequisite for an appropriate sampling are sufficient blank levels for the sampling. Therefore, field blanks were taking during sampling. Table 2 summarizes the results of the field blanks and the calculated achievable detection limits for the sampling with the above described wash bottle assembly.

Table 2: Field blanks and detection limits for the tracer experiments

<table>
<thead>
<tr>
<th></th>
<th>Bi</th>
<th>In</th>
<th>P</th>
<th>S</th>
<th>Ca</th>
<th>Zn</th>
<th>Fe</th>
<th>Mg</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
<td>µg/L</td>
</tr>
<tr>
<td>DL (analysis)</td>
<td>0.001</td>
<td>0.001</td>
<td>0.05</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>Fieldblank 1 A</td>
<td>0.007</td>
<td>0.006</td>
<td>-0.2</td>
<td>213</td>
<td>154</td>
<td>7.4</td>
<td>2.3</td>
<td>17.4</td>
</tr>
<tr>
<td>Fieldblank 1 B</td>
<td>0.025</td>
<td>0.112</td>
<td>0.9</td>
<td>24</td>
<td>34</td>
<td>8.7</td>
<td>4.1</td>
<td>13.7</td>
</tr>
<tr>
<td>Fieldblank 2 A</td>
<td>0.014</td>
<td>0.006</td>
<td>-0.9</td>
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<td>78</td>
<td>4.7</td>
<td>4.2</td>
<td>8.5</td>
</tr>
<tr>
<td>Fieldblank 2 B</td>
<td>0.010</td>
<td>0.005</td>
<td>-0.8</td>
<td>-28</td>
<td>53</td>
<td>11.5</td>
<td>1.0</td>
<td>6.6</td>
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<tr>
<td>Fieldblank 3 A</td>
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<td>Fieldblank 3 B</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fieldblank 4 A</td>
<td>0.015</td>
<td>&lt;DL</td>
<td>1.5</td>
<td>&lt;DL</td>
<td>109</td>
<td>1.5</td>
<td>1.6</td>
<td>5.5</td>
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<tr>
<td>Fieldblank 4 B</td>
<td>0.008</td>
<td>&lt;DL</td>
<td>0.1</td>
<td>&lt;DL</td>
<td>27</td>
<td>0.7</td>
<td>0.7</td>
<td>6.8</td>
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<tr>
<td>Fieldblank 5 A</td>
<td>&lt;DL</td>
<td>&gt;DL</td>
<td>0.8</td>
<td>24</td>
<td>132</td>
<td>7.3</td>
<td>5.5</td>
<td>12.2</td>
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<tr>
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<td>0.9</td>
<td>23</td>
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<td>3.8</td>
<td>9.7</td>
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<tr>
<td>Fieldblank 6 A</td>
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<td>&lt;DL</td>
<td>1.8</td>
<td>22</td>
<td>54</td>
<td>6.6</td>
<td>1.9</td>
<td>20.2</td>
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<tr>
<td>Fieldblank 6 B</td>
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<td>&lt;DL</td>
<td>1.9</td>
<td>21</td>
<td>109</td>
<td>6.7</td>
<td>2.0</td>
<td>15.3</td>
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<tr>
<td>Fieldblank 7 A</td>
<td>&lt;DL</td>
<td>0.001</td>
<td>1.1</td>
<td>20</td>
<td>136</td>
<td>4.7</td>
<td>1.7</td>
<td>9.7</td>
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<tr>
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<td>&lt;DL</td>
<td>2.3</td>
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<td>&lt;DL</td>
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<td>51</td>
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<td>1.8</td>
<td>18.4</td>
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<tr>
<td>Fieldblank 8 B</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>1.2</td>
<td>54</td>
<td>40</td>
<td>5.5</td>
<td>1.7</td>
<td>13.9</td>
</tr>
</tbody>
</table>

In the following 4 graphs selected results of the tracer experiments are presented. The data are given vehicle wise. The sampling points are named as MP1 (air inlet), MP3 (engine out), and MP4 (after catalyst) according to the positions given in figure 1. The different tests for the 3 driven steady state conditions at 50 km/h, 80 km/h and 120 km/h are marked with the different symbols given here:

- ♦ 50 km/h
- ★ 80 km/h
- ▲ 120 km/h
**Table 3:** Fuel consumption L/100 km

<table>
<thead>
<tr>
<th>at km/h</th>
<th>E0</th>
<th>E5</th>
<th>E85</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>4.1</td>
<td>4.3</td>
<td>5.7</td>
</tr>
<tr>
<td>80</td>
<td>4.5</td>
<td>4.7</td>
<td>6.2</td>
</tr>
<tr>
<td>120</td>
<td>6.8</td>
<td>7.0</td>
<td>9.2</td>
</tr>
</tbody>
</table>

**Figure 4:** Bi (fuel tracer) for the vehicles operated with E0, E5, E85

**Figure 5:** Comparison of In (oil tracer) for the CNG vehicles
Figure 4 shows the results of the fuel tracer bismuth Bi for the experiments for the vehicles operated with E0, E5, and E85. It can clearly be observed that the highest concentration is usually found for the sampling point MP3 which represents the position engine out before the catalyst. The different vehicles and speeds give different Bi concentrations which clearly correlate with the fuel consumption, which is presented in table 3 as fuel consumption in L/100 km.

Figure 5 depicts the comparison of Indium In, the oil tracer for the three different CNG vehicles. The determined concentration levels for In are quite low, which is consistent to the low concentration levels of 50 ppm for the oil tracer in the lubrication oil only and the low oil consumption during the test durations of 30 minutes for each steady state condition only.
However, it is clearly visible, that the VW Touran shown a larger emission for the In than the Ford CNG vehicle. Anyway, since the data often range close to the detection limits, for future experiments longer measuring times or higher oil tracer contents should be used.

Two of the most prominent catalyst poisoning elements are sulphur S and phosphorus P. Figure 6 gives the results for phosphorus P for the vehicles operated with E0, E5, E85 and figure 7 shows the comparison of the sulphur S results for the three CNG vehicles. As expected also for these elements the sampling position MP 3 (engine out) shows usually the highest element concentrations compared to MP1 (inlet air) and MP4 (after catalyst). For the two Touran CNG vehicles higher phosphorus P emissions where determined than for the Ford vehicles operated by CNG, E0, E5 und E85. This is probably caused by a higher oil consumption of the Touran models. Similarly, the CNG vehicles tend to higher sulphur S emissions, whereas again the Touran models showed higher emission rates than the Ford model operated with CNG. However, since the project is at the beginning, the observed phenomenon is still under investigation.

The other in fuels or oils present elements such as calcium Ca, zinc Zn, manganese Mg, or iron Fe where also determined but the monitoring is challenging because these elements are omnipresent and can originate from various sources. Moreover, these elements are already present in relatively high concentrations in inlet air. However, the project is ongoing. The here presented data show the first experiments of the first project for the tracer experiments only. Further data can be presented in the near future.

Acknowledgements:

The authors are grateful to VSS, EV, SVGW, and Bafu for finance; Umicore for providing model catalysts; as well as Motorex and Exxonmobil for the preparation of the tracer-doped oils.

References:

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The aging of catalytic converters for exhaust gas after-treatment in internal combustion engines by both chemical and thermal processes is relevant for both environmental and economic reasons. While several mechanisms have been investigated, the sources, which are responsible for catalyst aging, are often not clear and not easily quantifiable. More specifically, we investigated whether catalyst poisoning, e.g. by phosphorus, sulphur or other ingredients has its source in employed lubrication oil or fuel and how the impact of the deposition influences the conversion behaviour. With this aim, four nearly identical passenger cars, operated with different fuels: i.e. CNG, gasoline and gasoline E0 and biofuel blends E5 and E85 were investigated. With the exception of the CNG, all fuels were spiked with Bi (10 ppm) each, and the oils of all cars were spiked with 50 ppm in as tracers. The vehicles were driven at constant speed (50 / 80 / 120 km/h) and samples were taken at 3 distinct sampling points in the engine; in the intake air, at the engine out and after the catalytic converter. The analysis of the metals then allowed conclusions with respect of the contamination source and distribution.

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**Project Goals**

Oil- and fuel-induced aging of catalysts in petrol-, biofuel- and natural gas vehicles

**Part 1: Tracer experiments**
1. Influence of fuel / lube oil type on elemental composition of emission and contribution
2. Identification of possible transport paths
3. Quantification of oil contribution based on calculations of tracers

**Part 2: Simulation chamber experiments**
1. Investigation of pollutant-induced catalyst aging and the destruction mechanism (P poisoning - CH4+O2)
2. Influence of different catalyst poisoning types on the conversion rate of methane, NOx, CO

**Part 3: Long-term influence**
1. Investigation of pollutant-induced catalyst aging and the destruction mechanism
2. Influence of different catalyst poisoning types on the conversion rate of methane, NOx, CO

**Vehicles, fuels, lube oils**

<table>
<thead>
<tr>
<th>Vehicles (Euro IV conform)</th>
<th>4x Ford Focus 1.8L SW</th>
<th>2x VW Touran 2.0L</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0 Oil 1</td>
<td>CNG Oil 2</td>
<td>CNG Oil 3</td>
</tr>
<tr>
<td>E5 Oil 1</td>
<td>CNG Oil 3</td>
<td>CNG Oil 1</td>
</tr>
<tr>
<td>E85 Oil 1</td>
<td>CNG Oil 2</td>
<td>CNG Oil 3</td>
</tr>
<tr>
<td>CNG Oil 1</td>
<td>CNG Oil 3</td>
<td>CNG Oil 2</td>
</tr>
</tbody>
</table>

**Lubrication oils**

- Oil 1: Ford WSS M2C 913-A
- Oil 2: VW 502 00
- Oil 3: VW 504 00 (low SAPS)

**Fuels**

- E0: standard conform gasoline (SN EN 228)
- E5: 5% ethanol gasoline (SN EN 228)
- E85: 85% ethanol (analysis every 2'000 km)
- CNG: swiss CNG petrol station quality

**Tracers**

- fuel: 10 ppm Bi (E0, E5, E85)
- oil: 50 ppm in (all oils)

**Test conditions for tracer experiments:**

steady state driving at 50, 80 and 120 km/h
3 measuring points: air inlet, engine out, after catalyst

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**Literature**


**Acknowledgements:**

VSS, EV, SVGW, Bafu for finance; Umicore for model catalysts; Motores and Exxonmobil for oil mixing with tracers;