Continuous Pre - and Post - Catalyst Hydrocarbon and Nitrogen Compounds-Monitoring of various DeNOx Reactions by twin CI-Mass Spectrometry

Oral Presentation at SAE 2000 World Congress, March 6-9, 2000 Cobo Center Detroit, Michigan, USA

J. Villinger*, W. Federer, S. Praun
* Corresponding Author

Abstract

Today’s concepts of dynamic emission control in lean operating engine demand a rapid monitoring of all relevant molecular components, their concentrations and therefore in pre and post catalyst exhaust gas. Storage capacities and breakthrough characteristics of catalysts, reaction rates, response times and interference levels of NO sensors are studied no more in stationary gas distributions but must be evaluated under transient conditions. On the basis of V&F AIRSENSE MS technology a twin CI-MS system enables the simultaneous and synchronous monitoring of relevant gaseous components with dynamic capabilities from 0,1 ppm to 5000 ppm and a high time resolution.

Introduction

Rate and quantity of NO formation in the internal combustion process is largely dependent on temperatures, pressures, the thermal fuel stability and the concentration of CO₂, H₂O, O₂, N₂ during the compression and combustion stroke of the engine. While fuel and EGR conditions may be optimized, the driving conditions influence pressures and temperatures in the cylinder and hence the formation of NO. All DeNOx concepts for road vehicles can not be based on equilibrium stoichiometry like fuel air ratios but must follow the NO-formation in all-different load settings and transient conditions.

For this reason a fast multicomponent monitoring technique is needed. FTIR-instruments show their limits in gas response times and lower detection levels, predominantly in diluted gases CVS applications. Mass spectrometer systems allow very fast response and detection times at high sensitivity and low detection levels. With the use of refined ionization techniques for the gases, the V&F CIMS technology has been used in the catalytic research as well as in quality control field since 1988 in some 65 units worldwide. The new field of high dynamic reaction studies forced the development of the “TWIN CIMS”, today’s fastest multicomponent monitoring system for exhaust gas emission matrices.
The CIMS Technology – Instrumentation

The technology and the main features of the V&F Twin-CIMS can be described as follows. The detection principle of the instrument is the analysis of the molecular weight of the substances. Sample gas is introduced to a high vacuum chamber and transformed into ions that are subsequently mass selected by electromagnetic fields and counted in a particle detector (figure 1 shows one branch of the whole system).

As different molecules may carry the identical molecular weight, like e.g. N₂ and CO or formaldehyde and NO or CO₂ and N₂O, the instrument uses different ionization levels (i.e. different primary ion beams) to distinguish between mass identical molecules. Every molecule has an individual energy that is necessary to remove an electron and thus convert the molecule into an ion. An additional separation effect is gained through the formation of defined fragment ions. The interaction of the ion beam with the gas sample results in well-defined product ions. A krypton ion beam with 13.9 eV energy, for instance, separates the mass identical molecules N₂ (14.2 eV) and CO (13.7 eV). The mass identity of methanol CH₃OH and oxygen O₂ on mass 32 is solved by ionization with xenon (12.2 eV) that generates an O₂⁻ ion on mass 32 and a CH₃O⁺ ion on mass 31. Larger hydrocarbons, for example, need ionization energies in the range of 10 eV created by a mercury ion beam.

The method of ionization by different energy levels allows a multiple use of the mass scale and to see molecules from different perspectives (table 1).
Tab. 1 General technical data of the analyzer

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Gas response time:</td>
<td>$T_{90} = 30 \text{ msec}$</td>
</tr>
<tr>
<td>Gas transfer temperature:</td>
<td>$60° - 210 °C$</td>
</tr>
</tbody>
</table>
| Measurement cycle / Detection level (ref.: benzene) | $1 \text{ msec} \quad 0,5 \text{ ppm} \quad 10 \text{ msec} \quad 0,05 \text{ ppm}$
|                        | $5 \text{ sec} \quad 0,05 \text{ ppb}$                          |
| Dynamic range:         | $1:10^4$                                         |
| Operation              | Selection of up to 40 channels per set from application orientated control library scripts |

Application 1

Nitrogen Traps

Simply, a nitrogen trap oxidizes NO to NO$_2$ and will store some amount of NO$_2$ on its surface. A NOx sensor positioned post catalyst may signal the breakthrough of NO$_x$ to the FI computer. As a result one or several hydrocarbon spikes may be created either by a rich injection or a post injection in the case for CDI and GDI engine concepts and are emitted to the exhaust gas stream. This support of hydrogen and hydrocarbons to the nitrogen trap initiates the discharge and conversion of NO$_2$ into N$_2$ and water.

As no chemical reaction goes one channel and one way only, as soon as more then two compounds are present, care has to be taken in the overall control of the system to avoid unwanted side reactions (figure 2 and 3).
Fig. 2 Postcatalytical reactions of selected compounds

Fig. 3 DeNOx-HC side reactions
In a flow reactor study the typical feed gas, representing a lean engine concept was run over a catalyst.

Figure 3 shows the upload of the trap in lean periods, when the oxygen signal is high and the small discharge periods under the rich conditions. See figure 4 for the average concentrations found.

During the rich conditions we find as side reaction products high concentrations of NH₃, also small amounts of N₂O are formed and emitted.

The accurate knowledge of time, the rate of increase, and the maximum of the concentrations of side reaction are key numbers for the catalytic engineers for development and optimization of their products.

The CIMS technology, allowing the determination of a compounds concentration in 100 msec at a lower detection level of 1 ppm, currently represents the fastest multicomponent monitoring technique on the market. This however is true for molecular setups falling in the same ionization level setting. For many automotive emissions monitoring works such setups are established. The dynamic research on nitrogen traps needs a very mixed ionization setup.

**Operating conditions on CIMS and TWIN -CIMS instruments**

Considering all reasonable demands for a nitrogen trap monitoring system, including desulfuration and even N₂ detection in argon driven flow reactors, are to be seen in table 2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>range [Vol %]</th>
<th>Energy in MS</th>
<th>detection time [msec]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>10</td>
<td>ME</td>
<td>50</td>
</tr>
<tr>
<td>CO₂</td>
<td>14</td>
<td>HE</td>
<td>30</td>
</tr>
<tr>
<td>H₂O</td>
<td>12</td>
<td>ME</td>
<td>30</td>
</tr>
<tr>
<td>CO</td>
<td>5</td>
<td>HE</td>
<td>200</td>
</tr>
<tr>
<td>CH₄</td>
<td>0,2</td>
<td>ME</td>
<td>100</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0,2</td>
<td>LE</td>
<td>100</td>
</tr>
<tr>
<td>NO</td>
<td>0,05</td>
<td>LE</td>
<td>100</td>
</tr>
<tr>
<td>NO₂</td>
<td>0,01</td>
<td>LE hi</td>
<td>100</td>
</tr>
<tr>
<td>HNO₂</td>
<td>20 ppm</td>
<td>ME</td>
<td>100</td>
</tr>
<tr>
<td>N₂O</td>
<td>200 ppm</td>
<td>ME</td>
<td>150</td>
</tr>
<tr>
<td>NH₃</td>
<td>0,2</td>
<td>LE</td>
<td>100</td>
</tr>
<tr>
<td>H₂S</td>
<td>50 ppm</td>
<td>LE</td>
<td>100</td>
</tr>
<tr>
<td>COS</td>
<td>20 ppm</td>
<td>ME</td>
<td>50</td>
</tr>
<tr>
<td>SO₂</td>
<td>50 ppm</td>
<td>ME</td>
<td>100</td>
</tr>
<tr>
<td>N₂</td>
<td>0,5</td>
<td>LE hi</td>
<td>200</td>
</tr>
</tbody>
</table>

Leaving out the N₂ monitoring, we need a time resolved quantitative knowledge of 14 molecular species to make catalytic design engineers happy. If all molecules of the above list were to be measured under one ionization level we could approach cycle
times of less the one second. The need for changing the ionization energy, results in applying different primary source gases and thereby primary ionization beams. Switching times from one gas to the next are between 200 and 600 msec in the mass spectrometer and do bring up the overall cycle time in the CIMS to 2.8 sec for this operation setup.

Currently all our users do run subsequences of the setup like NO, NO₂, NH₃, H₂S with cycles of 3 Hz, or SO₂, H₂S, NO₂, NH₃, O₂ with 2 Hz and must add together the information. This can be done when the catalyst system operates reproducibly. In some applications the overall operation costs become so high, that the TWIN-CIMS is needed.

Figure 4 shows the high time resolution of the Twin MS system that can explain how the individual reactions are started in time in the lean to rich transition. Here the first side reaction is the formation of N₂O. It may be caused by a steep temperature increase on the catalyst surface. The exothermal hydrogen oxidation does release this heat which may cause a decomposition of the NO₂ complex on the catalyst back to NO, thereby degassing a small NO burst into the exhaust. Only when all the oxygen and oxygenated species are burned, the NH₃ is formed on the catalyst.

![DeNOx Dynamic](image)

Fig. 4 High time resolution of the Twin MS in DeNOx dynamic reactions
Formation of HNO₂ in Diesel exhaust

Engines with inadequate hydrocarbon discharge systems may suffer further emission. Low load conditions are accompanied by low exhaust gas temperatures causing the NOx sensor to fail. In oxidation catalyst the NO from the combustion process is oxidized to NO₂ under temperatures below 420 °C. When no reduction medium like hydrogen, hydrocarbons or ammonia is present at the catalyst, NO and NO₂ will leave the catalyst. Ratios up to 12/1 NO₂/NO are measured in the tailpipe emissions.

NO as well as NO₂ are reactive species, NO will oxidize at ambient temperatures with oxygen to NO₂.

\[
\begin{align*}
\text{NO + NO₂ + H₂O} & \rightarrow \text{2HONO} \quad (1) \\
2\text{NO₂ + H₂O} & \rightarrow \text{HONO + HNO₃} \quad (2)
\end{align*}
\]

Reaction (1) a three body reaction forming HNO₂ along the surface of the exhaust system under the catalytic help of soot under gas temperatures below 220 °C is believed to be the major source of HNO₂ [Lee and Schwartz 1981]. Reaction (2) has been suggested to explain the observation of the formation of the gasphase HNO₂ in environmental chambers in the dark when both NO₂ and H₂O are present [Sakamaki et. al., 1983, Pitts et al, 1984]. HNO₃ could not be detected with their experimental methods and was assumed to remain adsorbed at the chamber surface. So the assumption 2 remains speculative.

We could not detect HNO₃ with our technique. The gas inlet pressure reduction system to the mass spectrometer is constructed in stainless steel and heated up to 250 °C for low adsorption times of the gases and leads to rapid decomposition of HNO₃ into NO₂ which was present in the exhaust gases.

As a source for the demonstration of HNO₂ emissions a standard MAN bus for public transport equipped with oxidation catalyst was chosen. The start from the bus stop where low temperature conditions assure in reality, was simulated through acceleration under brakes.

Tailpipe gas was transferred to the mass spectrometer in a heated gas line. Figure 5 shows the concentrations of NO₂ on the left scale and HNO₂ and benzene (as reference) on the right scale.
Fig. 5  Nitrogen side reactions in a MAN-bus

**Application 2**

**NH3 or Urea as reducing agent for DeNOx - the alternative solution.**

NH3 is a very strong reducing agent, develops a good gasphase at moderate temperatures and has as strong inertia against auto oxidation. Of all possible NH3 sources, compressed NH3 and dry or liquid urea are at present in development. Urea is introduced in the exhaust stream pre catalyst and decomposes thermally to NH3 and HNCO (isocyanic acid). Isocyanic acid reacts readily with water vapor in a three-body reaction to generate another NH3 molecule and CO2.
H₂NCONH₂
↓ heat
H₂O
HNCO + NH₃
↓ H₂O
CO₂ + 2NH₃

Introducing another nitrogen containing molecule as NH₃ into the DeNOx reaction sequence opens speculations to unwanted gaseous byproducts, like high NO₂-formation or autooxidation of NH₃ into NO, together with unwanted NH₃ degassing from the catalyst and creating high NH₃ tailpipe emissions. Recent developments during the past years reached extremely high conversion rates for NOx under stationary conditions and also NH₃ blowby under transient conditions was reduced to very low levels.

The proof or disproof of the speculations described above was possible with applying the V&F CIMS technology to the experimental method of “isotopic labelling” one or more of the compounds involved in the reactions (figure 6 and 7).

“Isotopic labelling” a gaseous compound for clarifying a reaction pathway is “the” classic identification method and always involves a mass spectrometer as the detection device. Isotopic labelled compounds still have the same chemical characteristic but appear on different molecular weights in a mass spectrometer detection system.

In flow reactor systems, buffered with Argon instead of N₂, it was shown that under normal operating conditions the reduction of NOx with NH₃ ends to 99,5 % in N₂ and H₂O. However under unfavorable conditions N₂O was formed up to 40 % as an unwanted byproduct.

When ¹⁵NH₃ is used in the reduction reaction with ¹⁴NOx nitrogen is formed thereof mass 29 (¹⁴N¹⁵N) must appear, instead of the common nitrogen mass 28.

N₂O as a sequence can be formed from a) NO or NO₂ only, from b) NH₃ only or c) from the N₂ reduction product.

In case a, we must see a mass 44, in case b we must see a mass 46 and in case c we must see a mass 45. As a fact, the experiment shows the formation of the mass 45, so N₂O is formed from the reaction product N₂. According to the N₂O formation the N₂ signal drops. The N₂ molecule formed from NO₂ and NH₃ is left in a vibrationally exited state and due to the high catalytic temperature the relaxation of the N₂ modes to the ground state is slow. Exited N₂ molecules have much lower reaction barriers against oxidation steps when colliding with oxygenated species.

However: Theoretical chemists still allow a further source of the N₂O formation. This source is the rapid decomposition of the activated reaction complex NH₃N₂O before the N₂ molecule is formed.
Fig. 6 Isotope labelled DeNOx reaction

Fig. 7 Temperature dependence of DeNOx reactions with Isotope labelled $^{15}$NH$_3$
Conclusion

Uploading a catalyst with a gaseous compound until its breakthrough may vary from 0.05 sec to 20 minutes depending on its capacity in number of moles at given temperature and its age and condition. Dynamically discharging catalysts by feed gas composition variations are in the range of 1 to 40 seconds. Slopes, curvatures, peak maxima and time integrals of the concentration curves of compounds represent important data understanding reaction types and pathways to the catalytic design engineer. The TWIN-CIMS technology offers sample rates from 10 msec/compound for 10 ppm on to 200 msec/compound for 0.1 ppm, independent in type and ionization energy of the compound.