

# SIMS 500 - Rapid Low Energy Secondary Ion Mass Spectrometer for In-Line Analysis of Gaseous Compounds - Technology and Applications in Automotive Emission Testing

J. Villinger, W. Federer, R. Resch,  
M. Lubich, W. Sejkora, A. Dornauer  
V&F Analysetechnik

## ABSTRACT

A new multichannel gas analyzer based on ion - neutral interaction principles is introduced. This gas phase secondary ion mass spectrometer using several well defined energy levels for the ionization process quantitatively analyzes gas mixtures without the use of preselection techniques.

A high sensitivity for many compounds together with high cycle rates allows dynamic studies of gaseous emission in the low and sub ppm range.

Transient studies of inorganic compounds like NO, NH<sub>3</sub>, H<sub>2</sub>S, COS and SO<sub>2</sub> in catalytic converter systems and differential hydrocarbon analyses of C<sub>1</sub> to C<sub>8</sub> prove the versatility of the instrument.

## INTRODUCTION

For any engineer, in-line time resolved emission measurements represent a far higher information level than off-line integral data on the process under study. Automotive emission testing is more and more focused to transient and non-equilibrium conditions of energy-converter systems as they are the major cause for today's gaseous emissions of vehicles.

Combining the analytical speed of a mass spectrometer system with a new sensitive and characteristic ionization mechanism for the sample gas, has results in a creating powerful tool for the engineer.

The use of an ion beam in forming secondary ions from sample molecules differs significantly from standard techniques. The charge transfer from the ion to the molecule generates reproducible images depending on the internal energy of the ion beam.

Thus, possible interferences of isobaric molecules ( identical molecular weight ) can often be resolved by different ionization levels and allow the multiple use of the same mass number for different molecules. Ethan, formaldehyde and nitricoxide carry the same molecular weight, but can be separated by use of different ion beams.

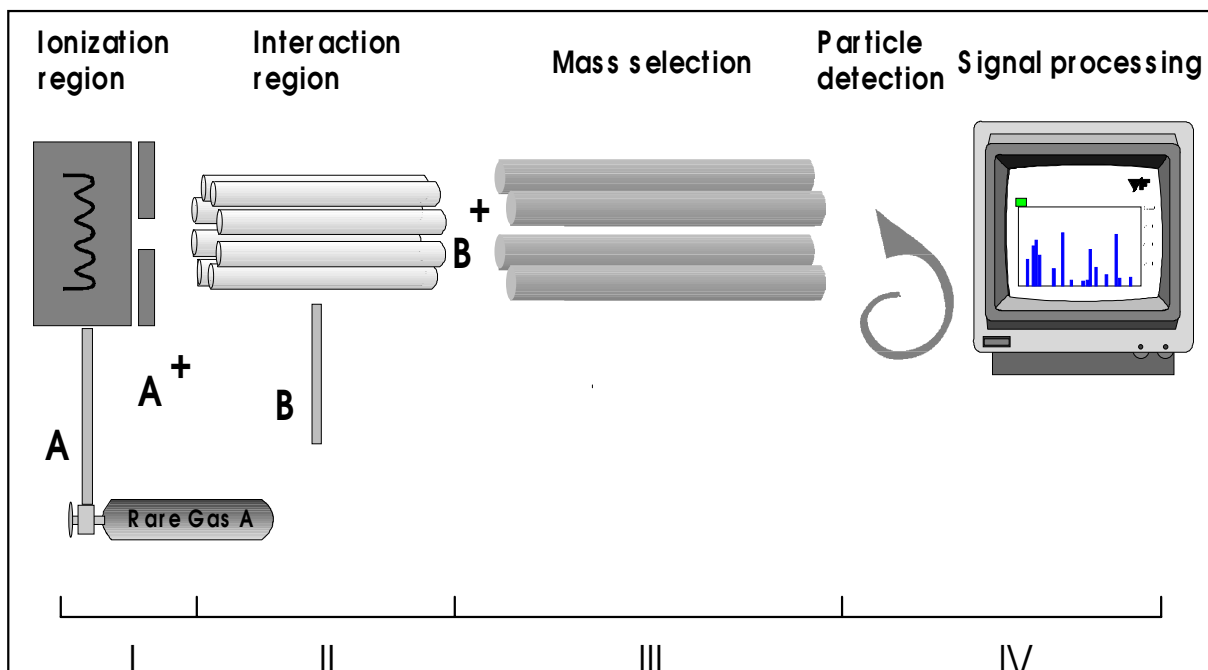
## TECHNOLOGY

Every mass selective device like magnetic sector fields, time of flight analyzers or electromagnetic separators like quadrupoles operate on charged species only.

The ionization process determines the mass where a molecule appears in the analyzer. Commonly, the ionization is done by fast electrons bombarding the gas, thereby generating not only parent ions, but also daughter ions, and even doubly charged ions of the molecule. As many molecules fragment into very similar patterns, gas analysis of mixtures becomes extremely difficult.

Electron impact ionization is ( somewhat simplified ) proceeding through a momentum transfer of the electron's motion onto the molecule. In this fast collision process energies between zero and the kinetic energy of the transferred to the molecule and produce - in case of polyatomic molecules - various fragment ions.

On the other hand, a well defined beam carries a sharp internal energy level ( the ionization potential ). The interaction of an ion beam with neutral molecules gives defined ion products. Depending on the total energy of the system ion - molecule, the charge transfer results in parent or daughter ions.



**FIGURE 1 : Schematic Setup of the Analyzer**

Figure 1 shows the schematic setup of the analyzing system. A pressure controlled gas inlet system feeds a flow of 1.5 cm<sup>3</sup>/min S.T.P. of e.g. Xenon gas to a primary source chamber ( section I ).

By electron impact ionization, a several microamp Xe<sup>+</sup> beam is formed and guided to a high frequency octopole field. The electromagnetic field in the octopole allows low translational energies as it focuses the ions against their tendency to separate by the electrostatic force of their own charges.

In section II, sample gas is introduced to a gas cell via an absolute pressure controlled pressure reduction system. The condition in the gas cell is kept at a level where only single collisions between incoming ions and sample gas molecules may occur. This situation is essential in order to avoid the formation of complex ion species due to secondary ion molecule reactions. As the primary ion beam A<sup>+</sup> is crossing the cell, sample gas ions B<sup>+</sup> are formed according to

$$[B^+] = [A^+] (1 - e^{-[B]kt}) \quad (1)$$

where [B] is the neutral density of sample molecules, k is the reaction rate constant between A<sup>+</sup> and B and t is the residual time of the ions in the cell. The reaction rate constant is related to the atomic reaction cross section  $\sigma$  via

$$k = \{v \sigma (v)\} \quad (2)$$

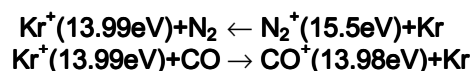
For the molecule charge transfer reactions,  $\sigma$  is determined by the polarizability and permanent

dipole moment of the sample gas molecules and is nearly independent of the relative velocity of the collision partners within several electronvolts of energy. The independence of  $\sigma$  of velocity is a major difference to electron impact ionization where  $\sigma$  is a strong function of the relative velocity.

As the polarizability of molecules with more than four atoms changes slowly with molecule size, the ionization efficiency and consequently the sensitivity of the instrument becomes very uniform.

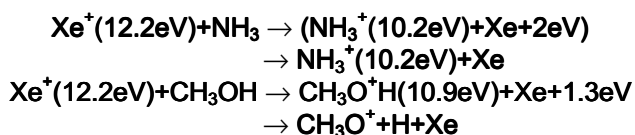
Generally, all sample gas molecules with an ionization potential lower than the incoming ion beam will be ionized. However, the excess degrees of freedom or bond rupture of the molecular ion.

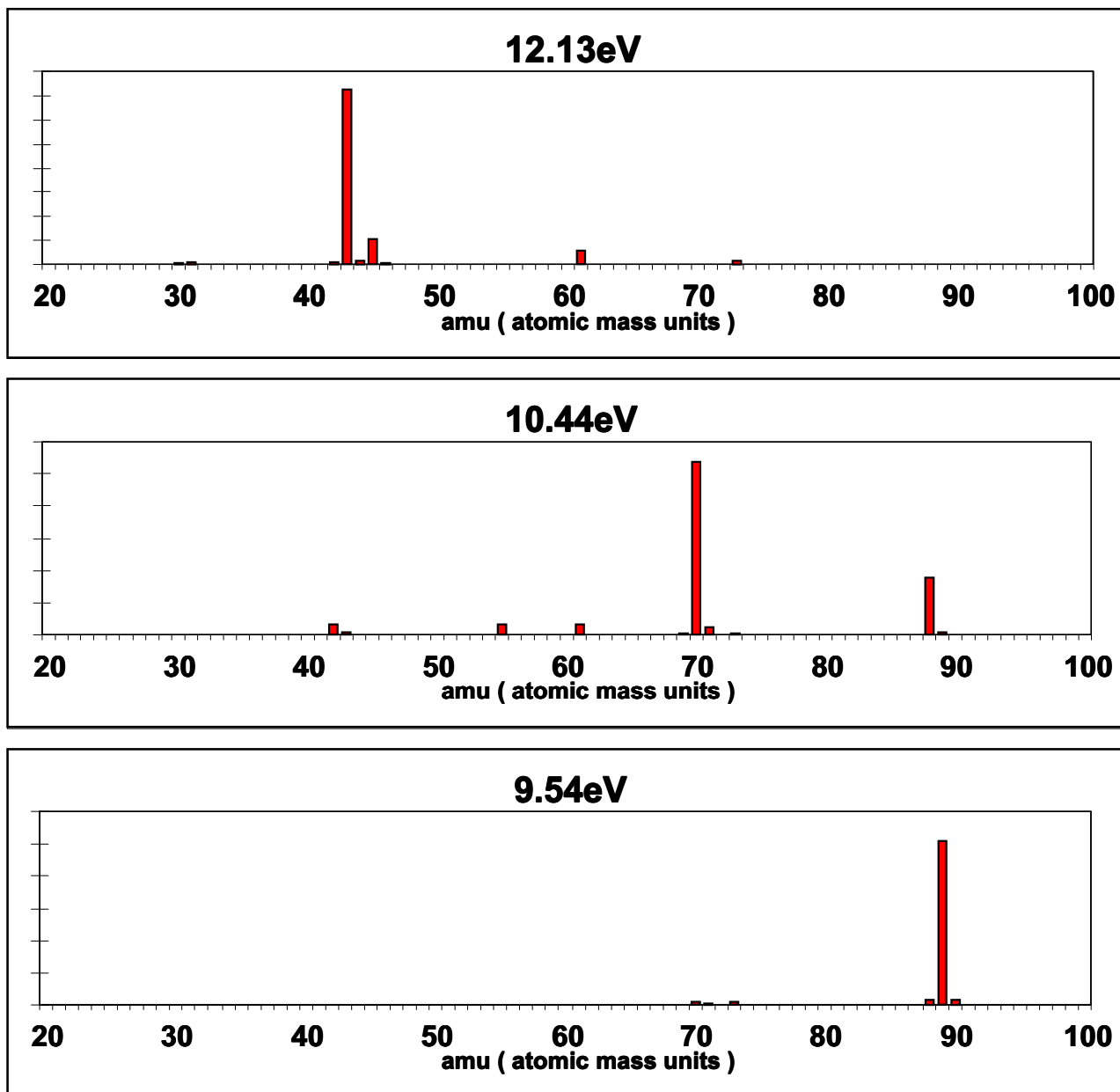
The reaction system



demonstrates the separation of mass identical ( isobaric ) molecules by the ionization process. As the ionization potential of nitrogen is higher than the krypton ions, no ionization occurs and carbonmonoxide can be on the mass 28.

The system





**FIGURE 2 : Molecule Spectra of  $C_4H_8O_2$  for different ionization energies**

shows how excess energy of the collision ( the difference of ionization potential of the reaction partners ) either populates internal vibrational levels as in the Xe-ammonia system, or leads to bond rupture and loss of a hydrogen atom as in case of the Xe-methanol system.

**Figure 2** shows mass spectra of a fragile molecule ionized with three different ion beams. All secondary formed sample gas ions are trapped again in the high frequency octopole field.

Mass selection takes place in a 200 mm long quadrupole rod system ( section III ). Here,

superposition of RF and DC fields produce stable and unstable trajectories of the ions according to their charge to mass ratio. Since ions in unstable trajectories hit the rod system or shielded housing of the quadrupole mass filter where they lose their charge, only ions in stable trajectories can be detected.

A sensitive secondary electron multiplier detects the transmitted ions and generates electric pulses strong enough for fast counting system.

**OPERATION:**

All electrical and mechanical components of the instrument are controlled via computer programs. Operation of the instrument is basically done in two modes:

- A) uncalibrated search of molecular species present in the gas matrix under study.
- B) calibrated measurements of concentration levels of different molecules.

For well established automotive applications mode B is used. A defined number of molecules are chosen from control libraries, calibrated and their concentrations shown on screen, stored on files or presented as zero to ten volts output voltage.

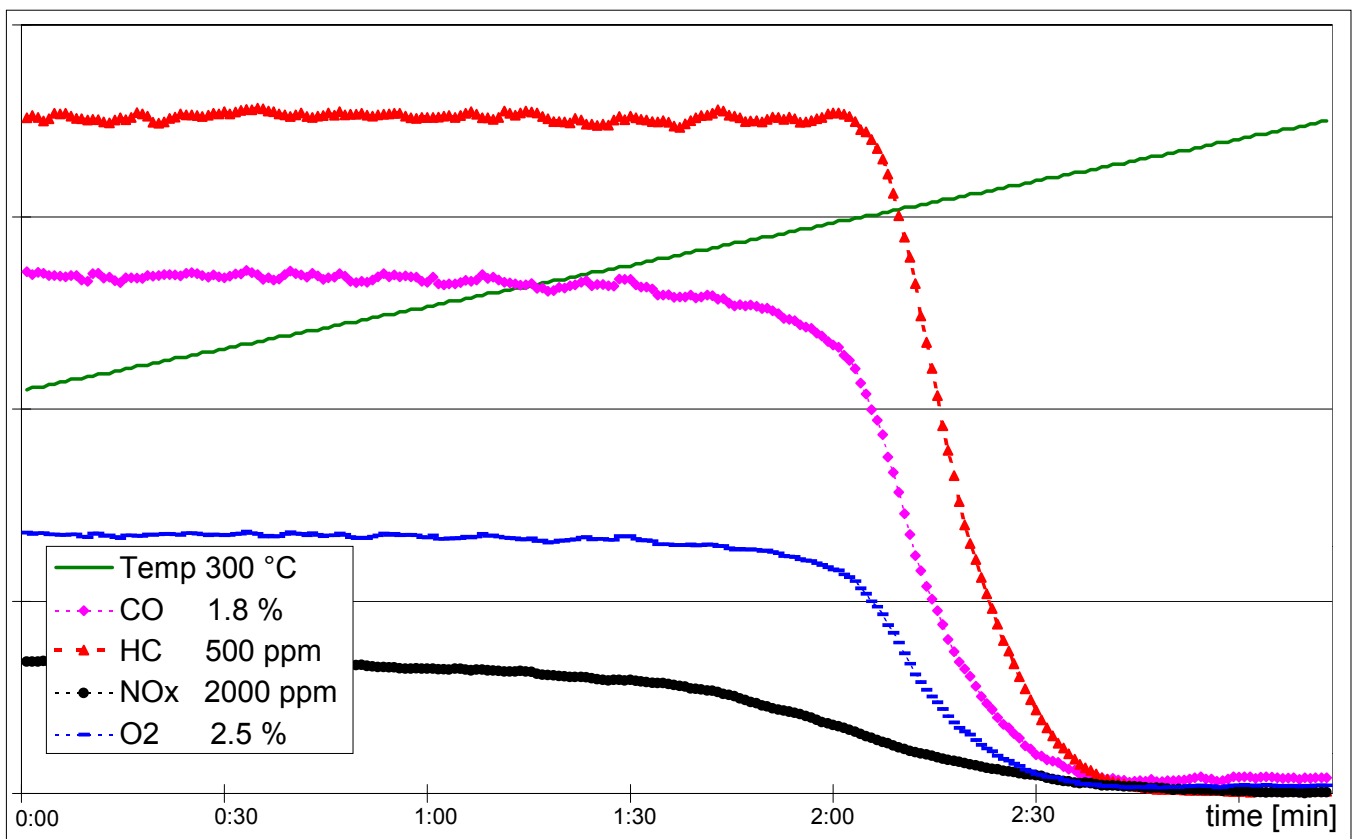
The control libraries define ionizer gas, operating pressure in the gas cell, measurement speed,

sensitivity, accuracy and interference compensation ( if an Interference is present in the gas matrix ).

For absolute accuracy of measured values of  $\pm 5\%$  calibration of components is done by sensitivity cross correlations to a single calibration molecule. This is done by entering the known concentration of the component into the program once in respect to the calibration marker molecule. For higher accuracy, individual component calibration has to be done daily.

### SULPHUR KINETICS ON CATALYTIC CONVERTERS:

Historically in automotive emission monitoring the SIMS - technology was first applied to catalytic converter studies at the BMW car test abs in the year 1988 ( Carlowitz ). Light Off - tests demand a fast, synchronaeous responding analyzing system.

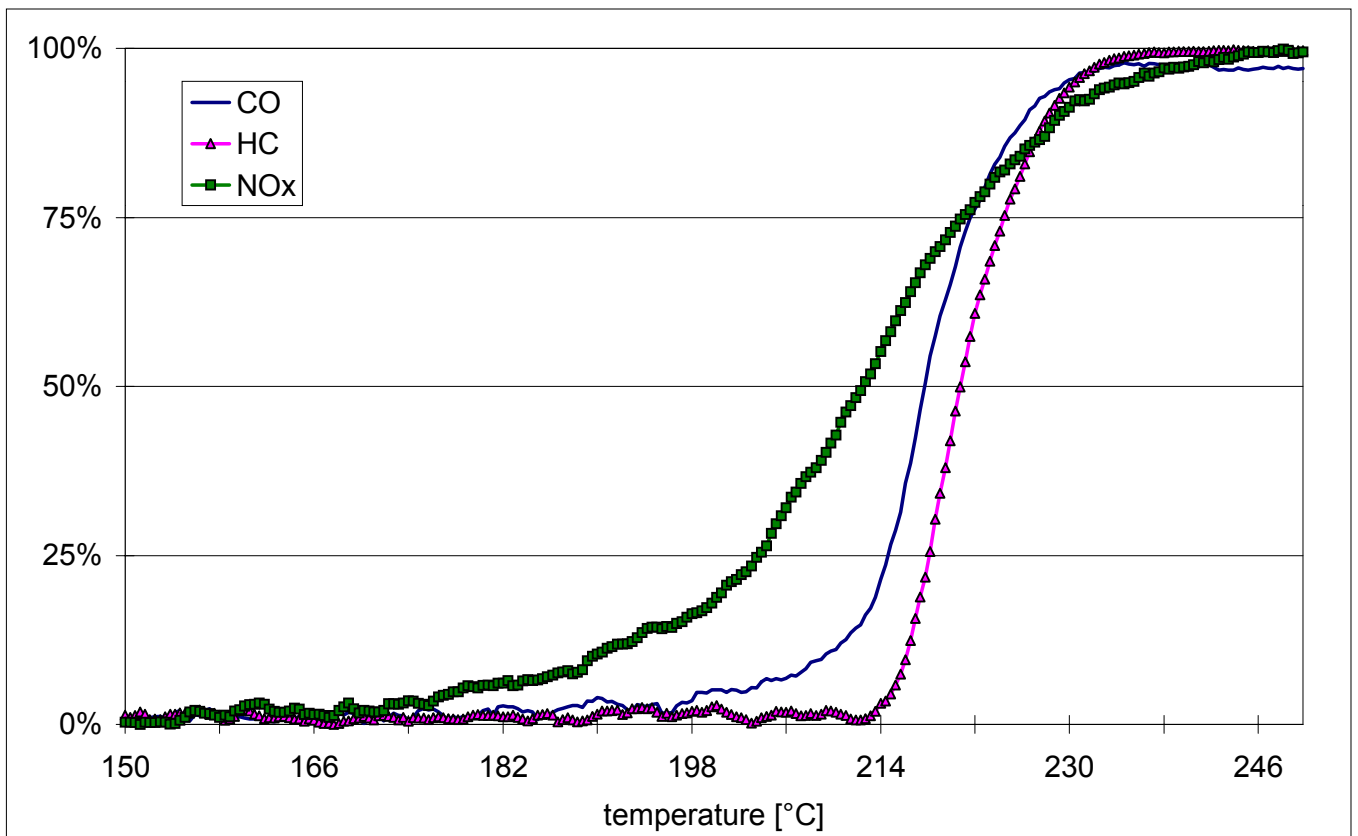


**FIGURE 3 : LIGHT OFF TEST**

At a heating rate of  $100\text{ }^{\circ}\text{C}$  per minute a cycle rate of  $2\text{ sec}^{-1}$  for the compounds NO, CO, HC and  $\text{O}_2$  must be realized to follow the conversion rate curve. **Figure 3** shows the concentrations of the different

compounds after the converter and additionally the converter temperature as a function of time.

Hydrocarbon concentration falls off in a rate of  $15\text{ ppm/sec}$  and Carbonmonoxide  $700\text{ ppm/sec}$  as the converter lights off.



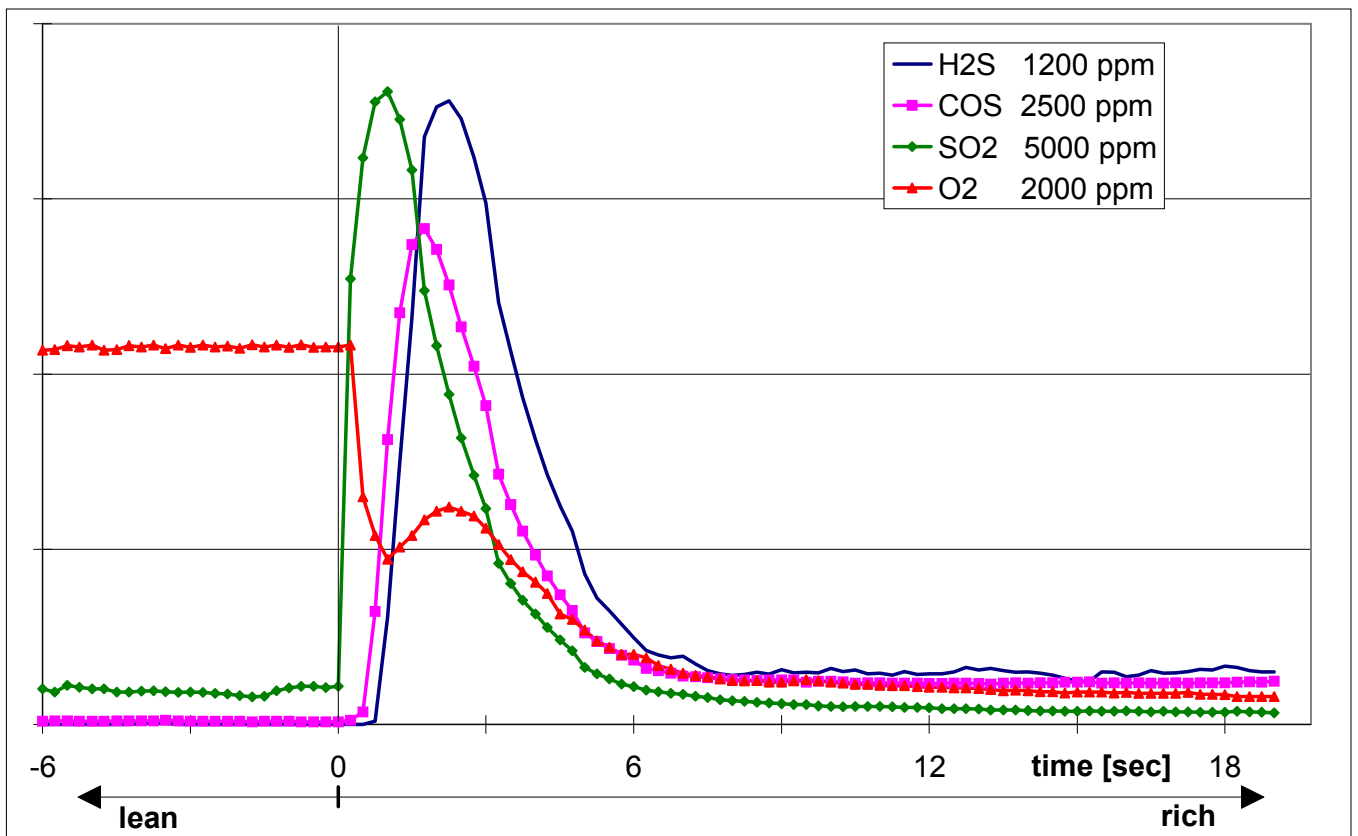
**FIGURE 4 : CONVERSION RATE IN THE LIGHT OFF TEST**

**Figure 4** shows the conversion rate via temperature calculated from the data in **Figure 3**.

A striking effect of engine - converter systems is  $H_2S$  emission under non equilibrium conditions as acceleration periods of the engine. **Figure 5** shows the concentration of gaseous sulphur emission together with  $O_2$  after the converter as a function of time in a lean to rich transition.

Residual sulphur in the fuel is oxidized to  $SO_2$  in the combustion chamber under normal working

conditions of the engine.  $SO_2$  can be stored in significant amounts as a sulfate on the catalytic converter's surface. In combustion conditions with  $\lambda$  less than 0.9 the reducing atmosphere of the engine's exhaust gas contains enough hydrogen, carbonmonoxide and unsaturated hydrocarbon residuals to convert the sulphur into gaseous sulphur emissions.



**FIGURE 5 : LEAN TO RICH TRANSITION**

At the moment of the  $\lambda$  transition the temperature of the converter is rising instantly by the oxidizing action of the oxygen on the converter, thus desorbing  $\text{SO}_2$  at the first strong emission from the converter. As the oxygen level decreases on the converter of half oxidized state of sulphur - carbonmonoxisulfide - is formed and released as gaseous compound. When the oxygen drops to zero,  $\text{H}_2\text{S}$  becomes the main gaseous sulphur emission.

### **AROMATIC HYDROCARBON EMISSION**

Amongst various hydrocarbon species present in the engine's exhaust the group of aromatic hydrocarbons ranging from benzene, toluene, xylene and higher substituted rings is becoming increasingly important in NMHC monitoring.

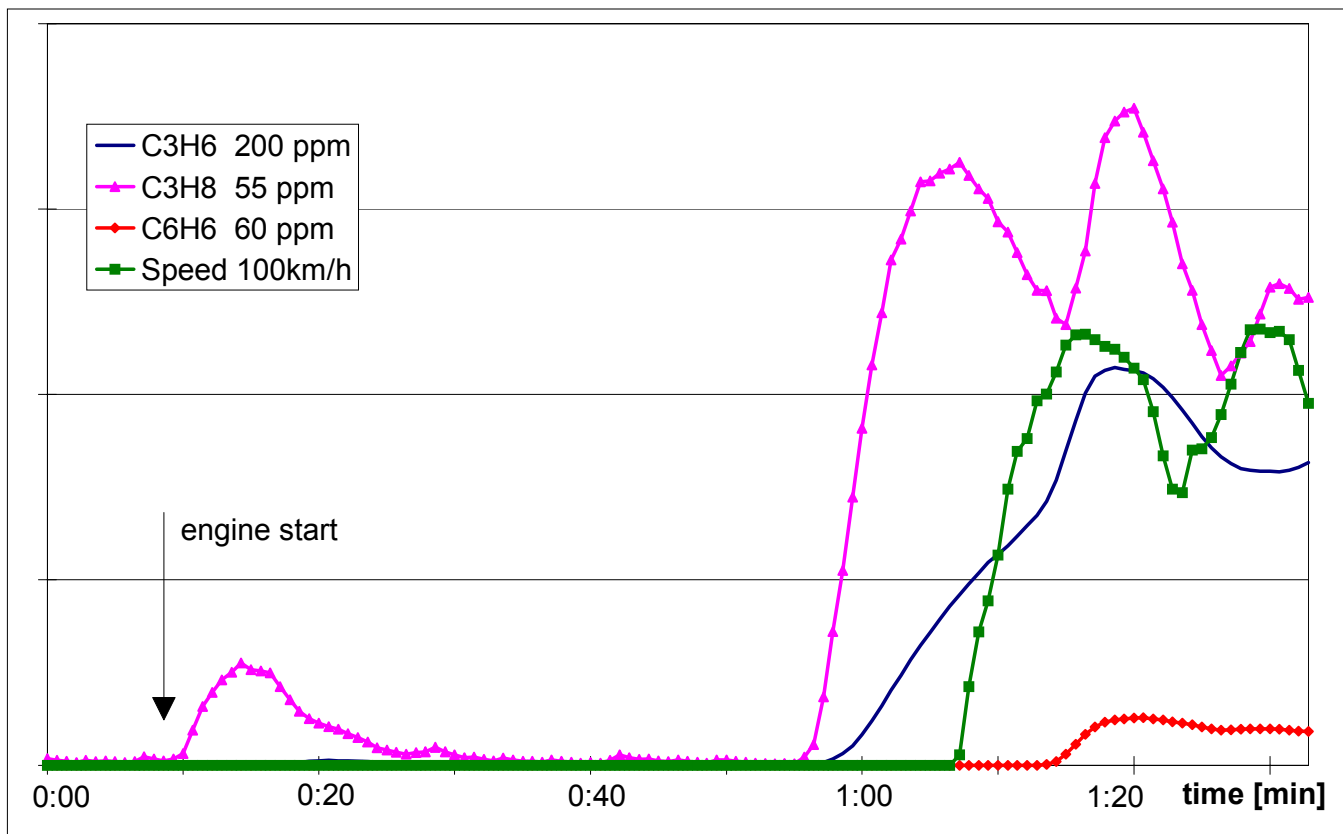
Their high ozon formation potential in the atmosphere's chemistry as well as their toxic and in

case of benzene carcinogenic potential results in drastic emission restrictions.

However, the easiest way to substitute lead as antiknock compound is to add more aromatic compounds to today's fuels. European high octane rated fuels contain up to 30% of toluene.

Although benzene is present only in a small amount in fuel it is formed by demethylation steps out of higher aromatics in the combustion chamber. Even under standard driving conditions several hundred ppm of benzene are found in the raw exhaust of the engine.

Benzene is physically active by its electron resonant energy, yet chemically more stable against neutral-neutral reactions compared to other hydrocarbons present in automotive exhaust. Therefore, benzene shows strong adsorption onto cold catalytic surfaces and a slower reactivity against oxidation by the operating catalyst.



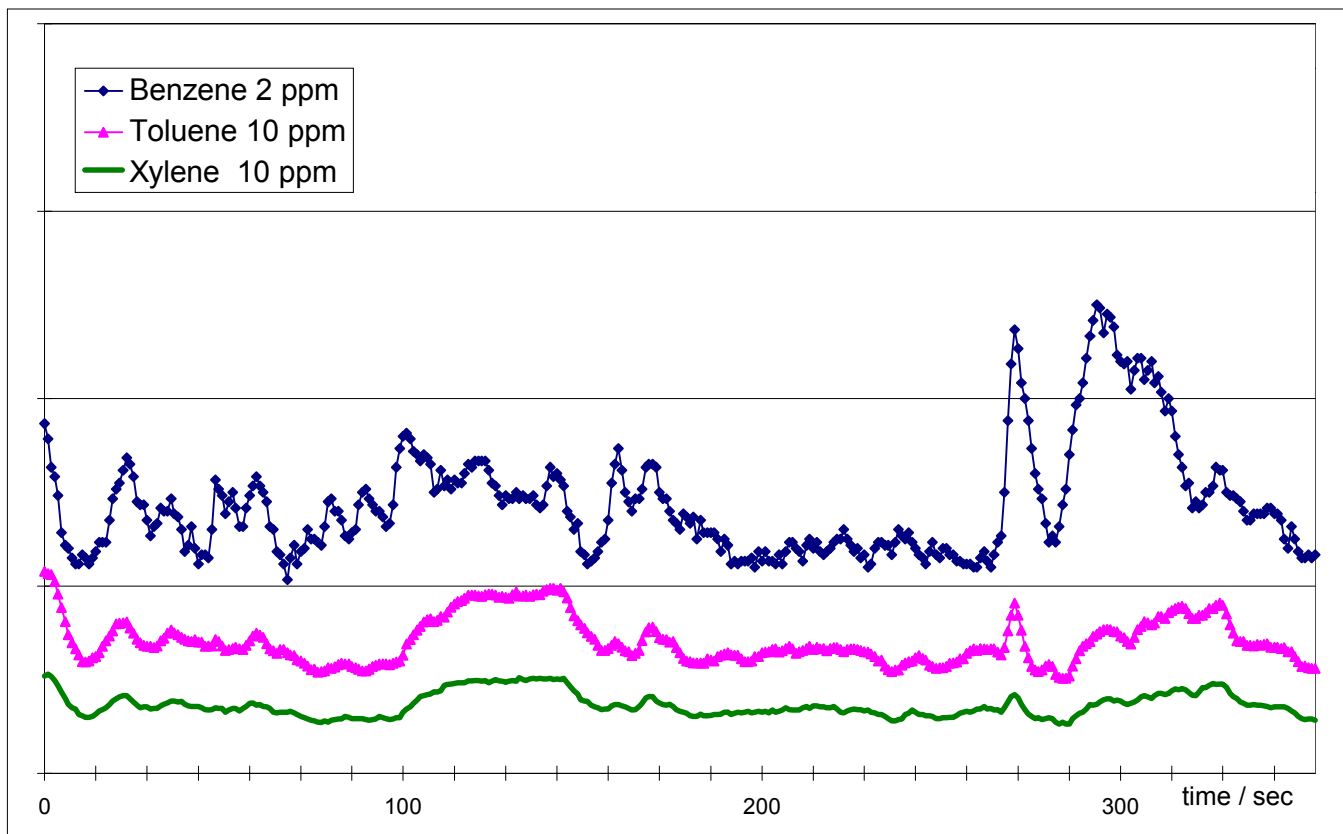
**FIGURE 6 : AROMATIC COMPOUNDS IN A COLD CATALYTIC CONVERTER**

The strong adaptive effect of aromatic compounds especially benzene, can be seen in **Figure 6**. In the first minute of a cold start some selected hydrocarbons are monitored with time resolution of 600 msec. After firing up the engine it was left in idle for approximately one minute. We observe that saturated hydrocarbons appear immediately after start with methane as strongest emission. Seconds later, double bonded hydrocarbons like C<sub>2</sub>H<sub>4</sub> or C<sub>3</sub>H<sub>6</sub> and triple bonded compounds like C<sub>2</sub>H<sub>2</sub> appear in the exhaust gas.

Only very much later, benzene and higher aromatics are observed ( for graphical reasons only a

few selected compounds are shown in the figure ). The first acceleration ( indicated by "speed" ) results in a very strong desorption of aromatic stored on the converter's surface by the action of their long ranging electric forces.

This figure looks very different for a warm start and there are also low temperature synthesized hydrocarbon products that only appear within a small temperature range of the catalyst. Some of these compounds produce the distinct smell of a cold exhaust.



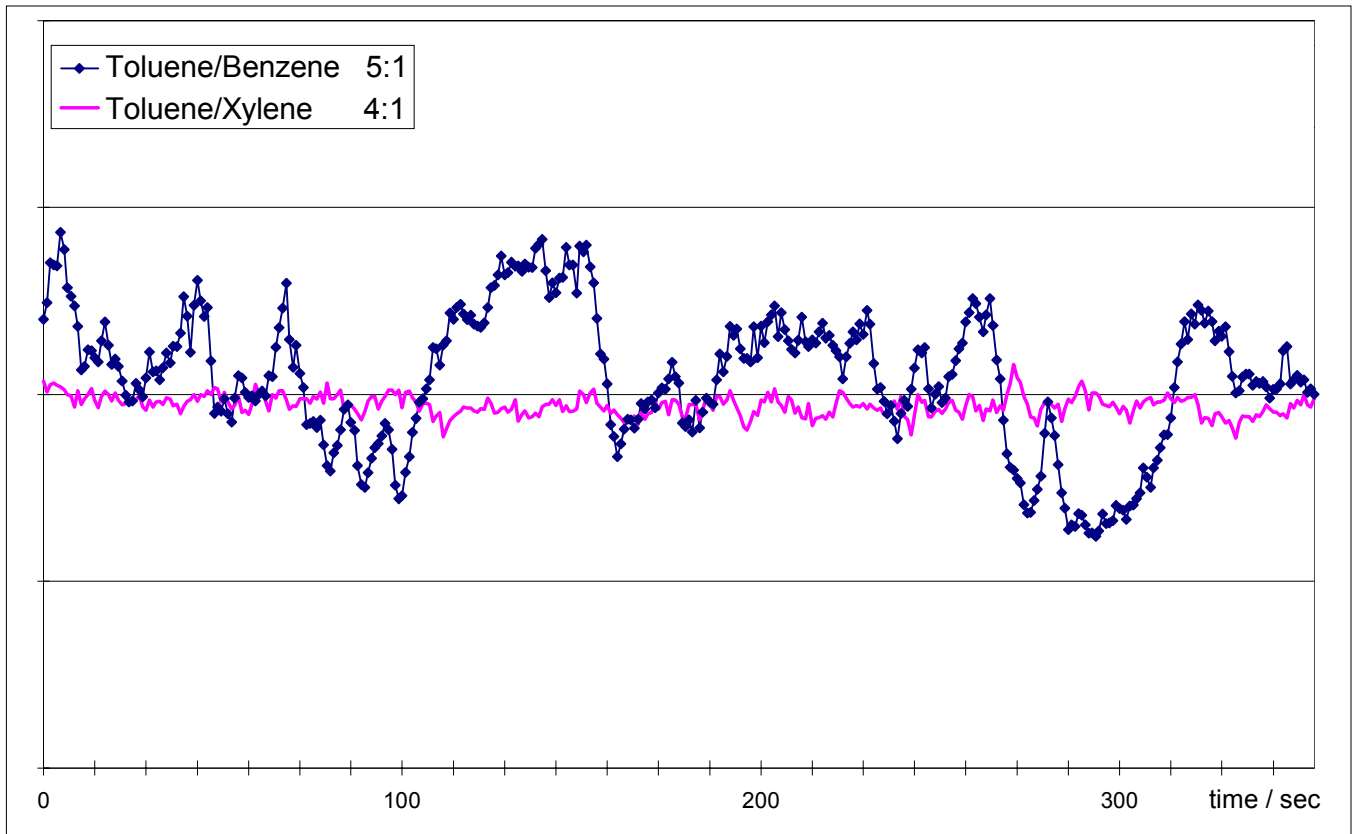
**FIGURE 7 : FORMATION OF BENZENE**

The formation of benzene in the combustion process can be seen in **Figure 7**.

The picture shows measurements of benzene, toluene and xylene taken within an FTP 75 cycle. Measurement time was 200 msec per compound and the instrument follows the concentrations in the low ppm range with high time resolution.

The signal strength was 6000 pulses per ppm and second on the detector for each compound. Background noise generated by impurities in the inlet system and vacuum chamber was 120 pulses per second. Thus the signal - noise ratio was 1200 to 24 for benzene for a 200 msec measurement cycle.



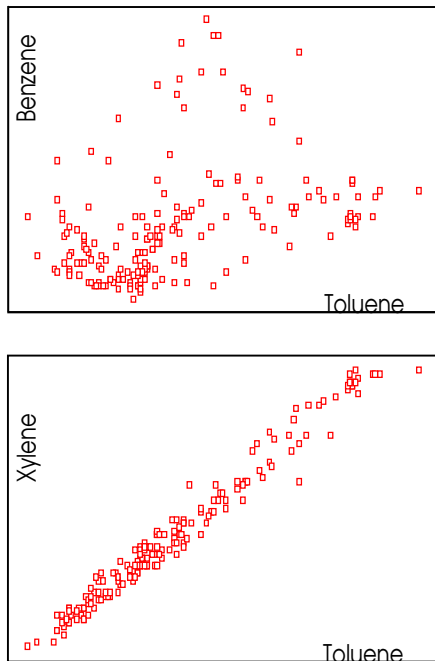


**FIGURE 8 : CONCENTRATION RATIO**

If we form the ratio of the concentration of toluene to benzene and toluene to xylene respectively ( **Figure 8** ), we realize that the ratio toluene to xylene is constant ( within the statistical errors of the measurement ) whereas the ratio toluene to benzene varies as the operating conditions of the engine vary during the test. This fact tells us two important facts:

- A) benzene is generated in the combustion chamber.
- B) toluene and xylene represent absolutely unburned fuel and are so-called "zero order hydrocarbons emissions".

In contrast to common chemical considerations that 3-methyl-benzene can be formed to xylene or toluene and that xylene can be formed to toluene in the combustion chamber, the measurement dynamics of this instrument shows that within the operating range of FTP test cycles these theoretically possible reactions are absolutely negligible and higher aromatics above benzene represent unburned fuel.



**FIGURE 9 : CORRELATION PLOTTINGS OF BENZENE, TOLUENE AND XYLENE IN THE FTP TEST**

Correlation diagrams plotted from the data files represented in **Figure 7** give an additional perspective of this fact (**Figure 9**). The positive correlation of benzene to toluene concentrations are coupled through a complicated function. Toluene and xylene however correlate in a simple and linear behavior. They are either oxidized and burnt or they appear in a fixed ratio in the exhaust.

## CONCLUSION:

Mass spectrometers are amongst LASER detection systems the fastest and amongst particle detectors the most sensitive monitors available today. Gas particles travelling with an average speed of 500 to 1000 m/sec at room temperature don't go long distances at atmospheric pressure conditions as their collision rate of approximately  $10^{12}$  per  $\text{sec}^{-1}$  slows down their net motion. However, the same gas particles travel 20 cm within 50  $\mu\text{sec}$  when they don't experience collisions as in the high vacuum chamber. Ions driven by electromagnetic fields travel several meters within a few microseconds.

Together with the above described ionization technique to resolve gas mixtures with no or low interference problems, the SIMS 500 is a sensitive and time resolving multichannel analyzer system. Not only inorganic and organic gaseous compounds can be measured down to low ppm levels, the speed of resolution allows new insights to the complex thermodynamic system of an engine and catalytic converter.