Parts per billion

Measurement of nitrogen compounds in exhaust gas

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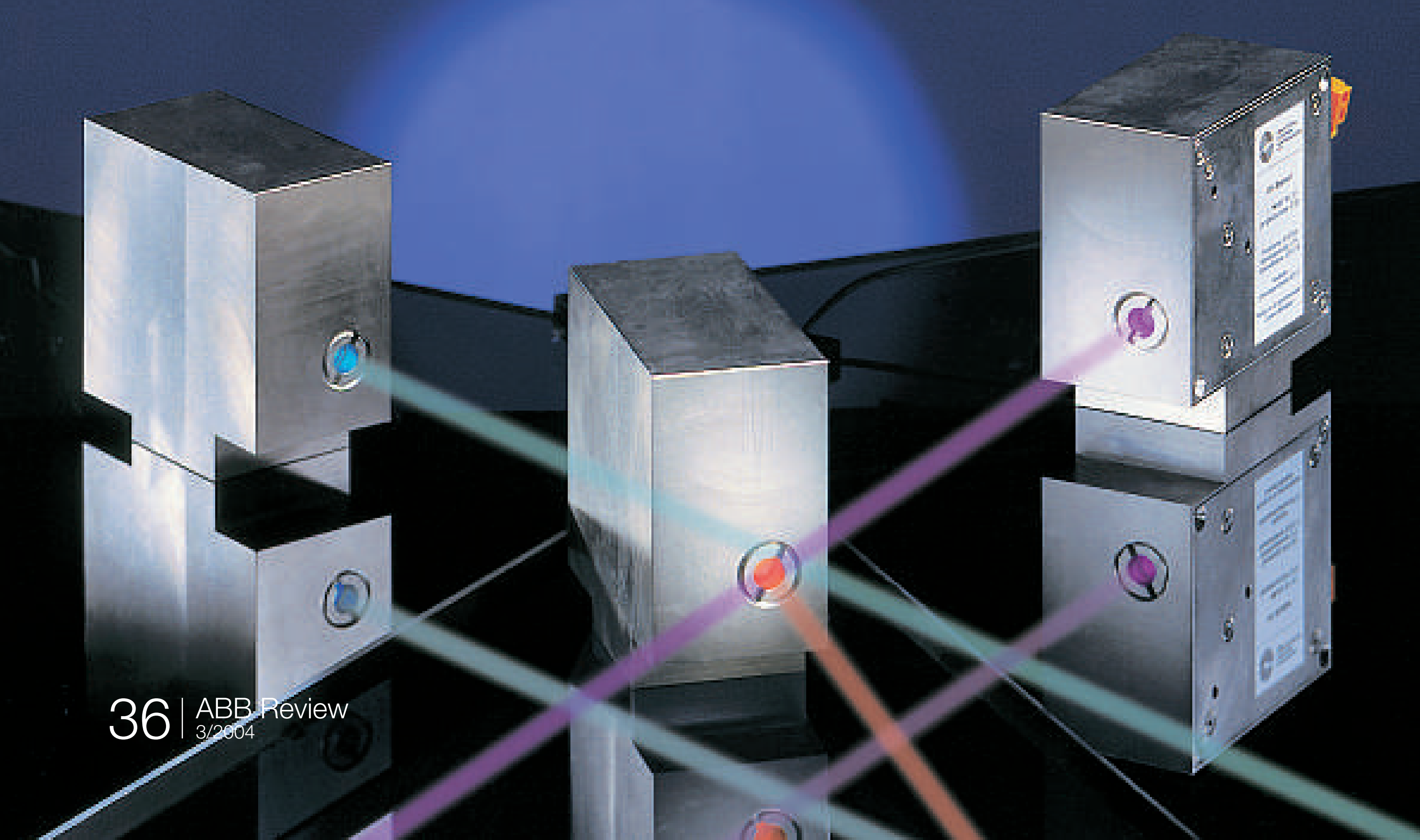
Environmental standards and technological advances continue to cut emission levels from combustion applications such as transportation and power generation. The lowering of pollutant concentrations in exhaust gas is increasing demands on measurement technology.

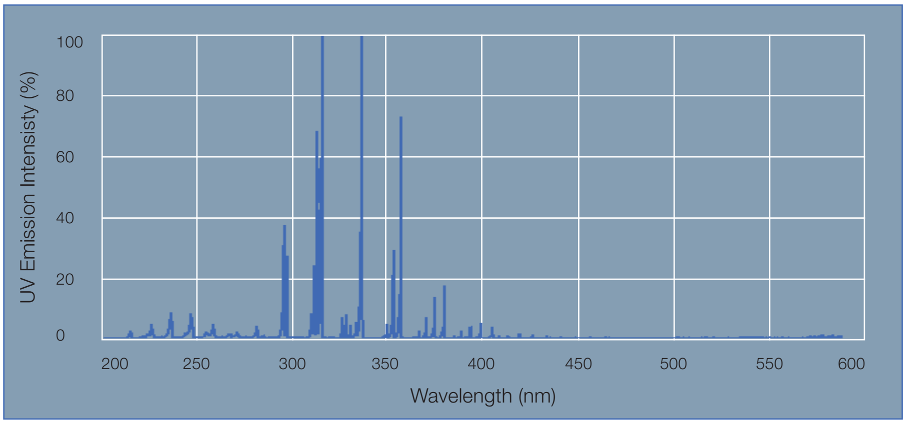
Measurement of pollutants is required for monitoring and adjusting pollutant reduction systems. Such measurement equipment must be reliable and low maintenance. Continuous gas analyzers from ABB show how innovative approaches permit industrial metrology to achieve higher sensitivity – now measured in parts per billion!



Just as the semiconductor industry is achieving increasingly higher levels of integration, analysis technology is advancing into lower measurement ranges. In analogy to Moore's Law of the semiconductor industry, measurement resolution for emission gas monitoring has halved at an impressive regularity of every 2 to 3 years.

Typical measuring ranges		
Measuring component	Smallest range	Largest range
NO	0…25 ppm	0…500 ppm
NO_2	0…40 ppm	0…500 ppm
NH_3	0…25 ppm	0…500 ppm

1 Emission spectrum of EDL (electrodelss light source). The radiation is produced by exciting N_2 and O_2 in a high frequency field.



Measurement data and processes

The automotive industry has reduced nitrogen oxide pollution levels by progress in engine technology. Oxidating catalytic converters (oxicat) provide further emission reductions.

For larger applications, ranging from diesel engines for trucks to gas fired power plants, these methods are insufficient. In California for example, NO emission from gas-fired plants may not exceed 5 ppm. DeNOx catalytic converters based on the SCR (selective catalytic reduction) permit the fulfillment of these requirements 2.

Such converters rely on dosing with urea or ammonia to remove NO.

Schematic reaction:
$NO + NH_3 \rightarrow H_2O + N_2$

To provide the correct doses, accurate knowledge of NO, NO_2 and NH_3 concentrations in the exhaust gas are a prerequisite. The process relies on sensitive measurement equipment.

In the automotive industry, measurements are performed either in a laboratory test setup or on a moving test vehicle. In a power plant, the measurement must be performed directly in the chimney flue.

Detection by resonance

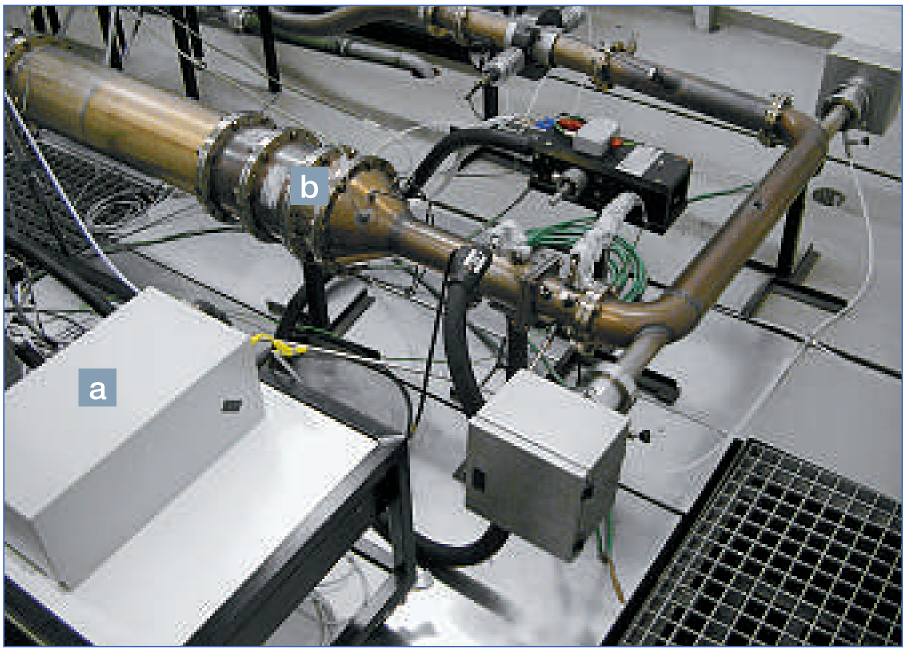
Limas11 HW of the AO2000 gas analyzer series detects the presence of very small concentrations of NO gas in a sample by analyzing the absorption resonance of the gas to specific light frequencies. Resonance spectroscopy is a unique approach in the field of UV photometers. Whereas the principle may sound straightforward in theory, the practical realization of such a setup requires greater sophistication. Noise from such sources as impurities in the apparatus and variations in the light must be taken into account.

Light source

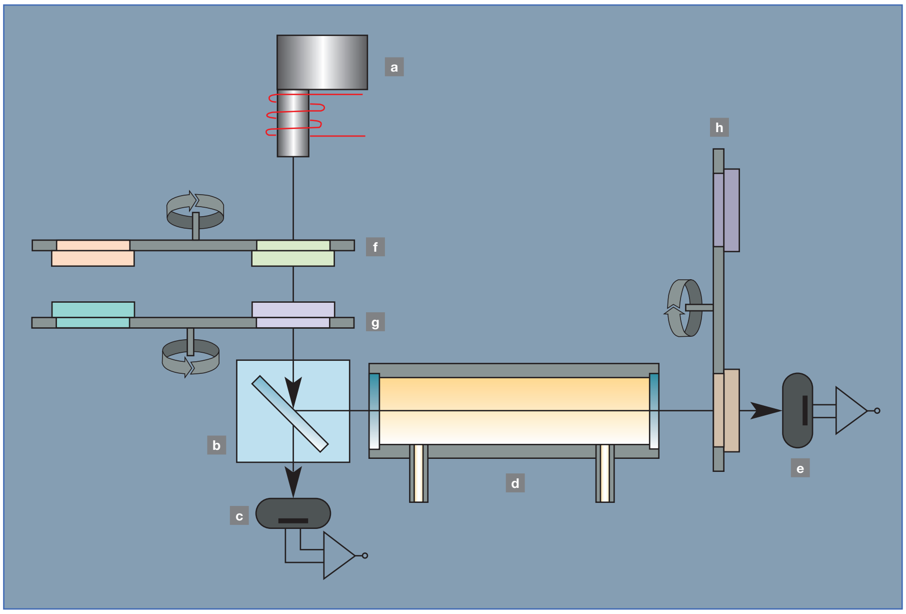
The light is produced in an electrodeless (EDL) source: A high frequency field generates plasma from a mixture of N_2 and O_2 in a quartz bulb. Excited NO* is formed which, on reverting to its ground state, emits ultra-violet radiation with the characteristic spectrum of NO (oscillation and rotation transitions) 1.

Some molecules do not immediately achieve their ground state but fall to an

2 DeNox process for lorry engine
a) Limas 11analyzer
b) SCR catalyst

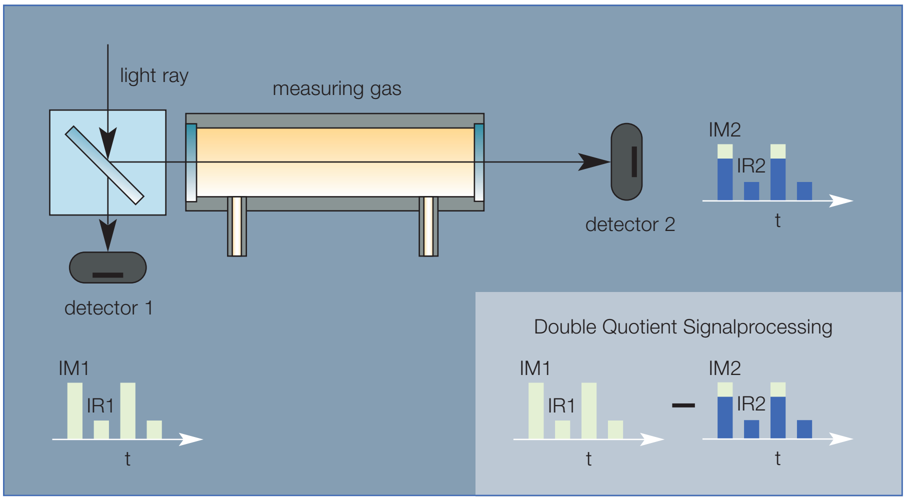


3 Diagram showing the functioning of Limas11 HW.



Light is emitted at a. The beam is spilt at b, with one part being passed through the measuring gas in d. Detectors c and e compare the radiation intensity before and after passing through the measuring gas. The filter-wheel at f constantly switches between measurement and reference radiation. The filter-wheels at f and g constantly switch between measurement and reference radiation. The filter-wheel h is for calibration purposes.

4 The intensities of measurement radiation (IM1) and reference radiation (IR1) before passing through the test gas are compared with the same intensities after passing through the gas (IM2 and IR2).



The measurement radiation is affected by absorption and attenuation whereas the reference radiation is affected only by absorption. A double quotient calculation permits the separation of the two effects. The concentration of the measuring gas is derived from the result.

excited state. As shall be explained later, Limas11 HW uses the radiation from this transition as reference radiation.

Resonant absorption

The light beam from the EDL source 3a is split into two beams using a semi-transparent mirror 3b. One of these beams is directly captured by the first detector 3c and the other is directed through a cell containing the measuring gas 3d. If the measuring gas contains traces of NO, it marks its presence by absorbing some of the radiation.

On leaving the measuring cell, the beam is captured by another detector 3e. Comparison of this measurement with that of the first detector compensates for changes of the light intensity, caused by the EDL light source or temperature effects of the filters. This is, however, not sufficient for achieving the required accuracy. Resonant absorption by NO cannot be distinguished from the effects of attenuation of the beam on its passage through the gas and glass, or the influence of contamination.

For an accurate indication of resonant absorption, the attenuation must be taken into account. This is where the reference radiation is used.

Reference radiation

Reference radiation is used to distinguish absorption from attenuation. It is emitted by NO* in the plasma and occupies the same frequency band as the measurement radiation but is not subject to resonant absorption by NO in its ground state. It is, however, subject to the same attenuation and can be used to quantify this.

By comparing the intensity drop of the measurement radiation on passing through the measuring gas with that of the reference radiation, the effects of attenuation and absorption can be separated.

A filter-wheel is placed between the light source and the first detector 3f. Different filters permit the passage of either the total radiation (measurement plus reference radiation) or only the reference radiation.

The resonant absorption for the measurement radiation is extracted using double quotient signal processing 4.

This method makes the measurement very tolerant towards impurities: The measurement cell can accumulate dirt without this effecting the result of the measurement. In an extreme situation, measurement remains possible with the cell half full of water.

The setup of the filter wheel is innovative: A classical filter-wheel is powered by a constant-speed motor. As the windows themselves are small, the light pulses are applied to the test gas during only a short part of the total measurement cycle. Limas11 HW uses a stepped motor which permits pulses to be applied during a considerably longer part of the cycle 5. This mechanism increases the signal to noise ratio by a factor of 2 to 3.

Measuring cell design

Further sensitivity is added to the measurement through the design of the measuring cell. Instead of the usual arrangement with the gas entering at one end and exiting at the other, the cell of Limas11 HW has a central inlet with outlets at the outer ends 6. The advantage of this arrangement is that soot and dirt particles collide with the wall opposite the inlet where they are adsorbed. Coating of the windows of the measurement cell by this dirt and soot is greatly reduced. This is especially important for small measurement ranges.

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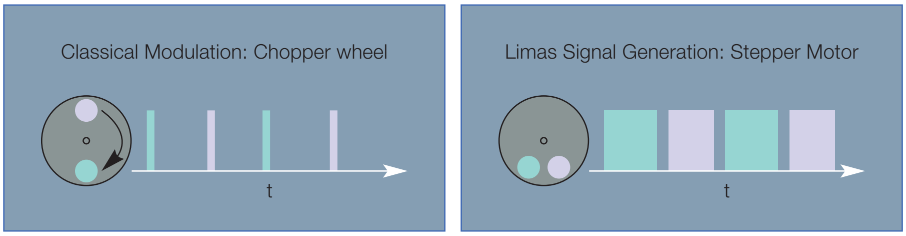
Safety

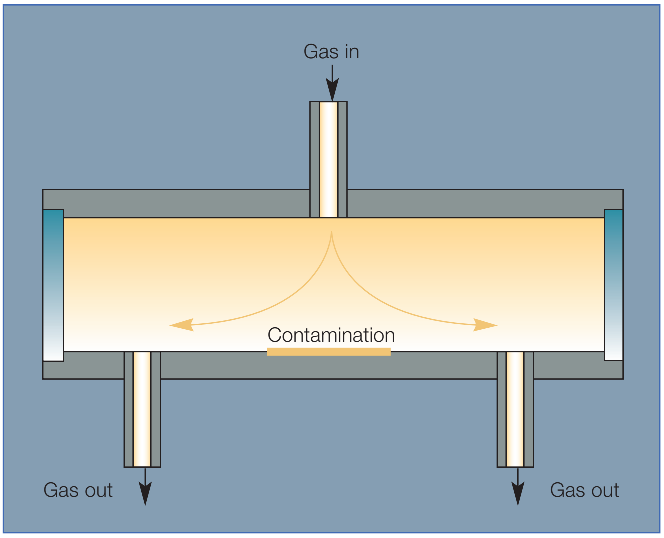
The cell has a gas purging arrangement. Purge gas is passed through chambers adjoining the cell windows 7. Leaks in the window gaskets or a breakage of the glass are quickly detected through monitoring of the purge gas. The purging arrangement also ensures that any leaked test gas is removed safely.

This approach uses standard components and replaces elaborate constructive measures such as separate enclosures for optics and electronics (to prevent gas from contaminating the air within the setup and so affecting results). Flammable, corrosive or toxic gases can be safely measured with a simple setup.

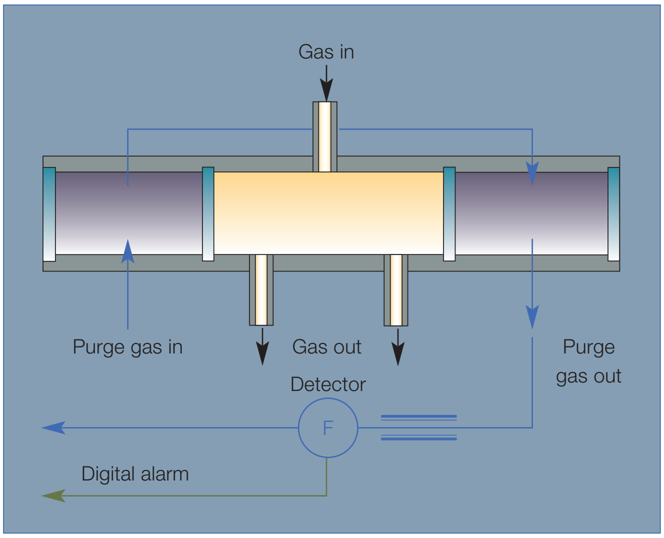
5 A classical filter wheel is rotated at constant speed; the measurement and reference phases only account for a small part of the test cycle. Replacing the constant speed motor by a stepper motor extends these phases. This increases the signal to noise ratio by a factor of 2 to 3.



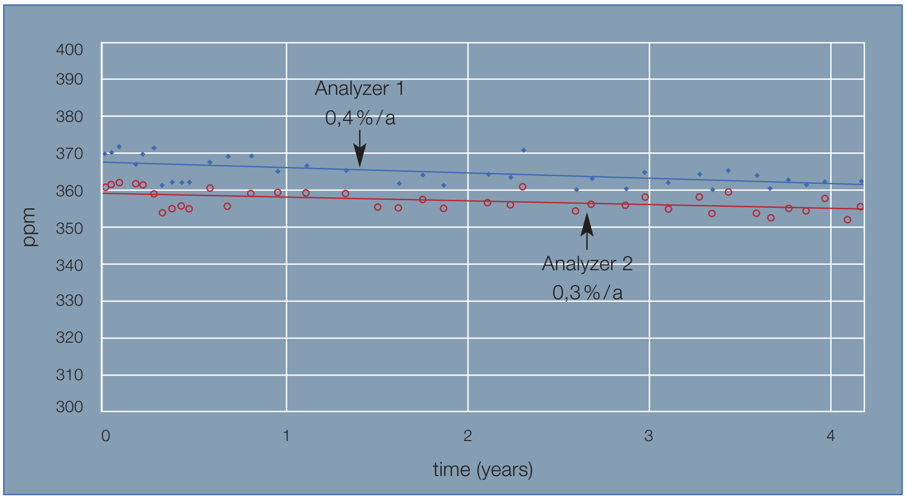
6 Most of the contamination is adsorbed on the wall opposite the cell inlet, keeping the windows relatively clean.



7 Chambers on either side of the test gas are flushed with purge gas. A detector F warns if any test gas leaks into the purge gas, thus improving safety while simplifying the total setup.



8 The long-term measurement stability of a test cell according to TÜV measurements



Calibration

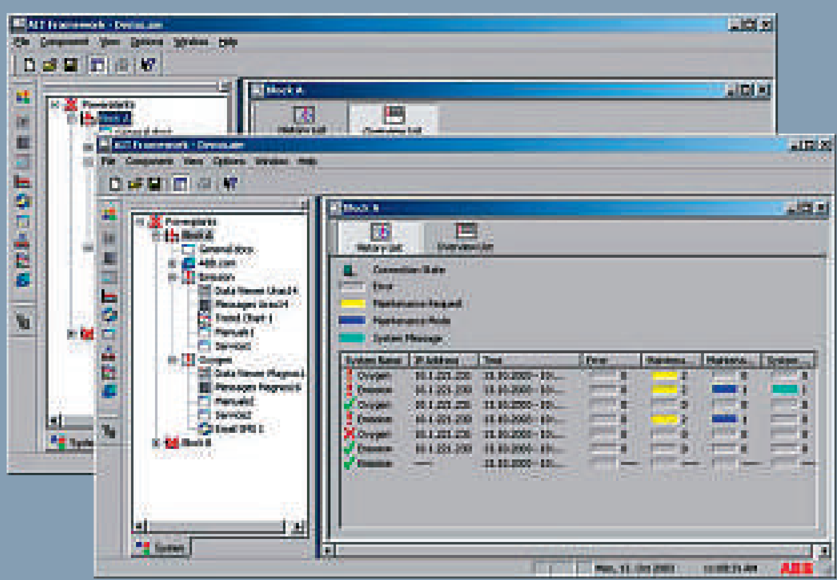
Calibration is performed with a quartz cell containing a measurement component 3h. Calibration is simplified resulting in system and time cost savings.

The remarkable long-term stability of a calibration cell is shown in 8.

Multi-component measurements

The measurement setup can easily be extended for measuring several gases simultaneously. Additional windows can be added to the filter-wheels to cover additional frequencies. For example, in a DeNOx denitrogenation process, NO, NO_2 and NH_3 can all be measured at the same time.

9 Analyze[IT] Explorer permits remote diagnosis and maintenance



Applications

Limas11 HW offers an alternative to established CLD (chemiluminescence) analyzers. Major advantages in comparison to CLD analyzers are:

- No ozonizer / deozonizer: less maintenance
- No high vacuum pump: less maintenance
- No quenching for other measuring components such as H_2O or CO_2: less cross sensitivity

Potential applications for Limas11 HW in the automotive industry 2 include development activities for:

- Vehicle engines
- Larger engines (as used in ships).
- Catalytic converters
- Automotive pollution treatments
- Production of test gas bottles

Combustion plant developers can use it for developing:

- Combustion chambers
- Burners
- Combustion engineering
- Pollution treatments

The equipment can also be used by suppliers of DeNOx plants, gas turbines, gas-fired burners and for stack testing.

Remote maintenance with Analyze[IT] Explorer

Analyze[IT] Explorer 9 makes all available data visible and accessible for remote maintenance on Ethernet TCP/IP networks. Maintenance outlay can be reduced and predictive maintenance raises reliability.

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