Measurement Principle of the chemiluminescence method (ECO PHYSICS CLD 822 CM hr)

The chemiluminescence method offers the best results whenever the difficult analysis of the tiny molecule NO in gases is required. Chemiluminescence method allows to detect extremely low concentrations of NO, being not only fast but also very sensitive and NO specific.
The reaction scheme of NO and O_3 by chemiluminescence is as follows:

NO	+	O_3	$\longrightarrow$	NO_2	+	O_2	[1]
NO	+	O_3	$\longrightarrow$	NO_2^*	+	O_2	[2]
NO_2^*			$\longrightarrow$	NO_2	+	hv	[3]
NO_2^*	+	M	$\longrightarrow$	NO_2	+	M	[4]

The radiation emission is in the wavelength between 600 and 3000 nm with an intensity maximum at approximately 1200nm. This chemiluminescence signal is detected photo-electrically. When O_3 is present in excess the signal is proportional to the NO concentration of the sample gas. By far the largest portion of the NO_2^* returns to ground state without radiation emission, due to collisions with other molecules (M) [4]. In order to enhance the light yield the pressure in the reaction chamber is reduced.
Quenching is an unwanted phenomenon, and the extent to which it occurs depends on the character of the colliding molecule M. For instance water (H_2O) and carbon dioxide (CO_2) quench NO chemiluminescence more effectively than nitrogen (N_2) and oxygen (O_2).
In order to measure NO_2 in the sample gas, it has first to be converted into NO. To accomplish this chemical reduction the sample gas is passed through a Converter heated to more than 300 °C (Converter M, Fig.2). If the Converter contains for example carbon as reducing agent, the following reaction takes place:

NO_2	+	C	$\longrightarrow$	NO	+	CO	[5]

Modern Converters contain metallic active material, which allows better selectivity of NO_2. Since sample gas normally contains both NO and NO_2, it is possible to measure the sum [NO] + [NO_2] = [NO_x] in the Converter channel. Using a catalytic Converter C (Fig.2) that also converts amines to NO and a selective Converter M that only converts NO_2, the difference [NO_{xAmine}] - [NO_x] can be interpreted under certain conditions as the ammonia [NH_3] concentration.

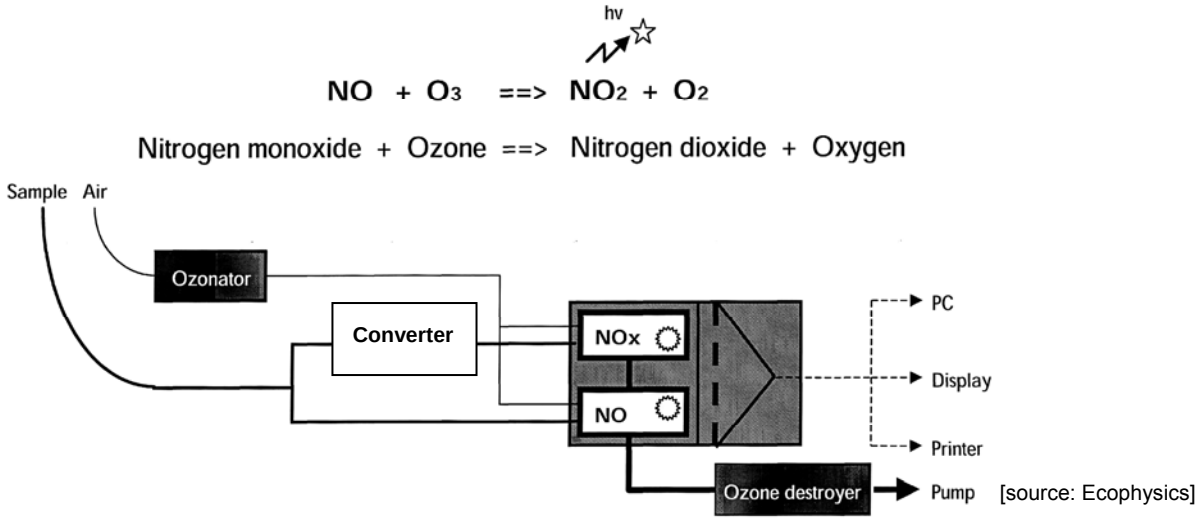


Figure 1: Components of a Nitrogen Oxides Analyzer (Chemiluminecence Detection CLD)

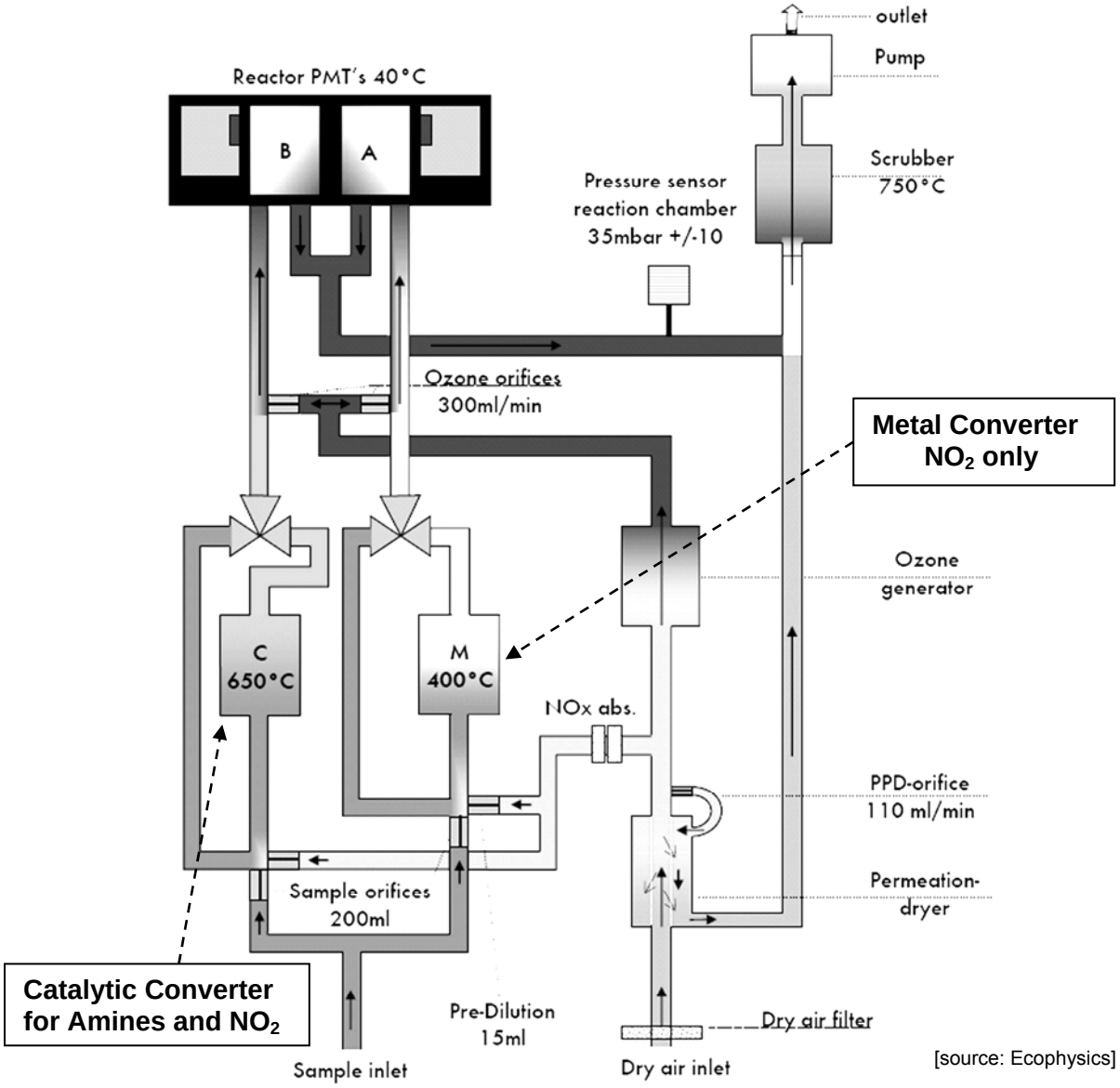
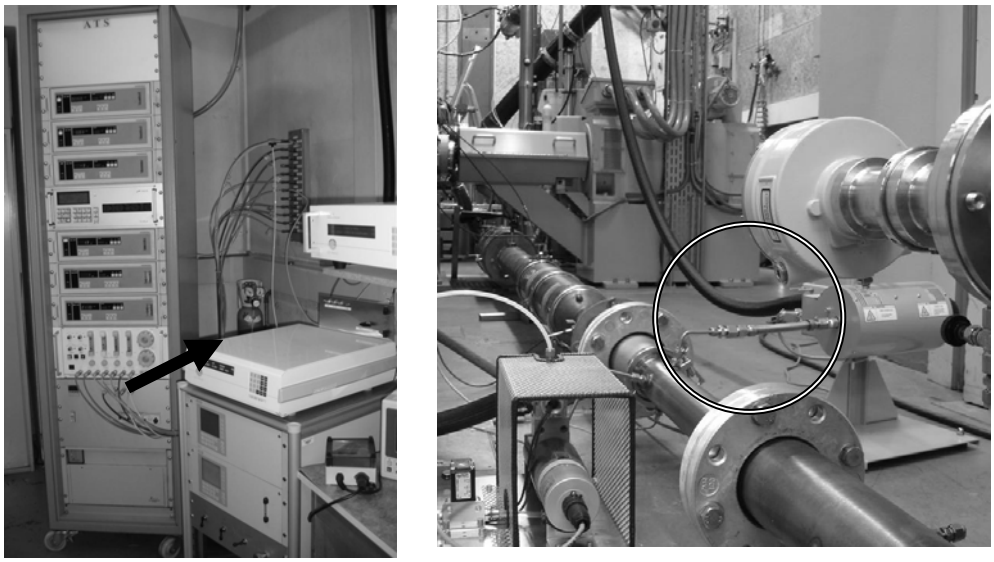


Figure 2: Two converter analyzer for NO_xAmine, NO_x, NO_2 and NH_3



[source: AFHB]

Figure 3: CLD analyzer (arrow) and sampling line (circle) at the test stand