Technical Note

Diatomic Nitrogen Interference on total Nitrogen analysis by Oxidative Combustion and Chemiluminescence Detection

- Diatomic Nitrogen (N_2) Interference
- Importance of high purity system gasses
- Importance of leak tight system

Keywords: ElemeNtS, **Nitrogen, Chemiluminescence, Interference**

INTRODUCTION

In this technical note we will discuss the influence of Diatomic Nitrogen (N_2) to the total Nitrogen response of a Chemiluminescence detector as used in the ElemeNtS. Diatomic Nitrogen might be introduced into the Elements system due to impurities in the system gasses (Argon/Helium or Oxygen), or air leaks in the flow path.

Oxygen (O_2) and nitrogen (N_2) do not react at ambient temperatures. But at high temperatures, they undergo an endothermic reaction producing various oxides of nitrogen. Such temperatures arise, for example, inside an internal combustion engine or during the combustion of a mixture of air/oxygen and fuel, and naturally in a lightning flash.

Thermal NO_x refers to NO_x formed through high temperature oxidation of the diatomic nitrogen found in combustion air. The formation rate is primarily a function of temperature and the residence time of nitrogen at that temperature. At high temperatures, usually above 1600 °C (2900 °F), molecular nitrogen (N_2) and oxygen (O_2) in the combustion air disassociate into their atomic states and participate in a series of reactions.

The three principal reactions (the extended Zel'dovich mechanism) producing thermal NOx are:

$N_2 + O \rightarrow NO + N$

$N + O_2 \rightarrow NO + O$

$N + OH \rightarrow NO + H$

At default furnace temperature (950 °C/1050 °C), the reaction between oxygen (O_2) and nitrogen (N_2) doesn't take place at a significant rate. However, when a sample is injected (the sample acts as a fuel) into the oxygen rich combustion zone, the temperature at the combustion zone rise above 1600 °C. As a result, during injection the present N_2 reacts with O_2 to form NO.

MEASURING PRINCIPLE

A sample of a liquid petroleum hydrocarbons is directly injected, by a fully automated liquid where the nitrogen bound components (and partly diatom sampler, into a high temperature, dual temperature zone combustion tube ic nitrogen gas) are vaporized and combusted. The released nitrogen is oxidized to nitrogen oxide (NO) in an oxygen rich atmosphere.

$$R - N + O_2 \xrightarrow{1050°C} CO_2 + NO + H_2O$$

A stream of inert gas (helium or argon) is taking the reaction products, after removal of the produced water vapor, into a reaction chamber. Here, under reduced pressure (using a build-in vacuum pump) the NO molecules are converted to excited NO_2^* by adding Ozone and emitting light (chemiluminescence) while it relaxes to a stable state.

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

EXPERIMENTAL CONDITIONS

Tests are executed on a vertical ElemeNtS TS/TN configuration. The Accura connector at the back of the instrument (which normally only serves as a loop for the helium/argon flow) is modified with a T-piece connector. With an additional external Mass Flow Controller we are able to add Instrument air at a controlled rate trough the T-Piece to the helium/argon flow.

The air flow is consecutively added to the Carrier gas in ascending order from 1 to 10 ml/min. Air contains ~78% N_2

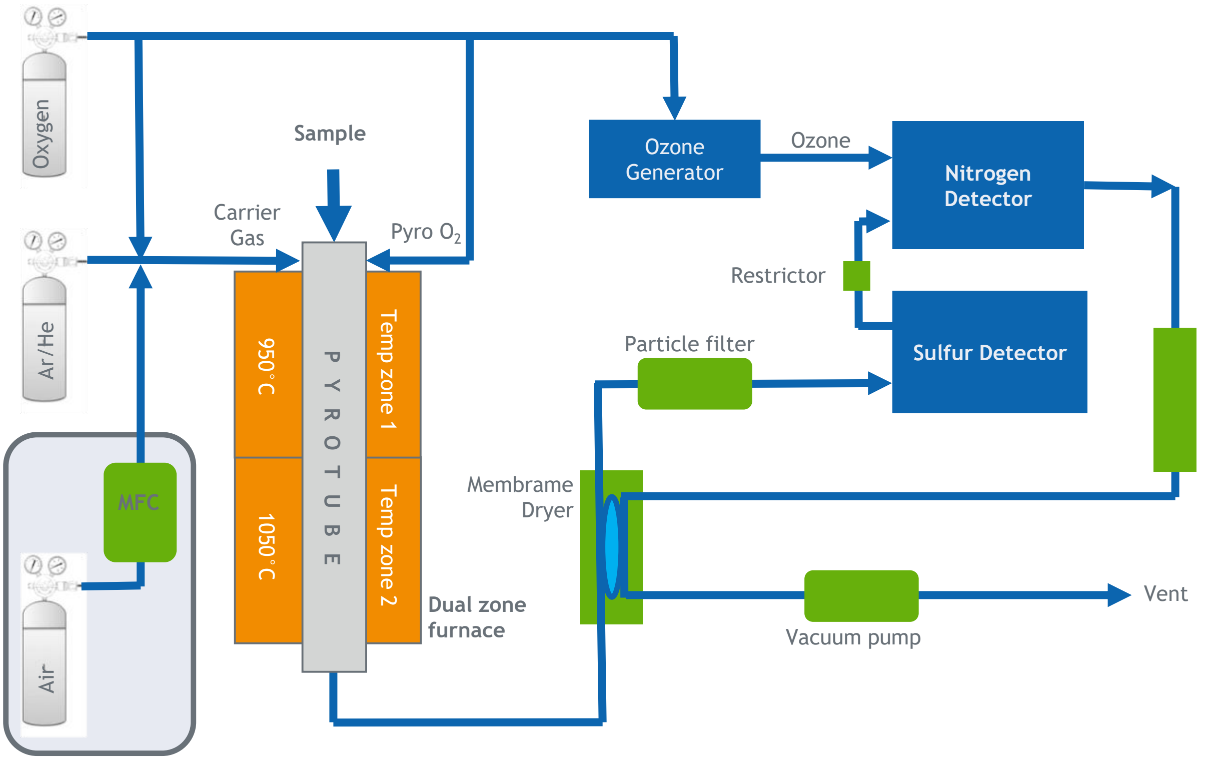
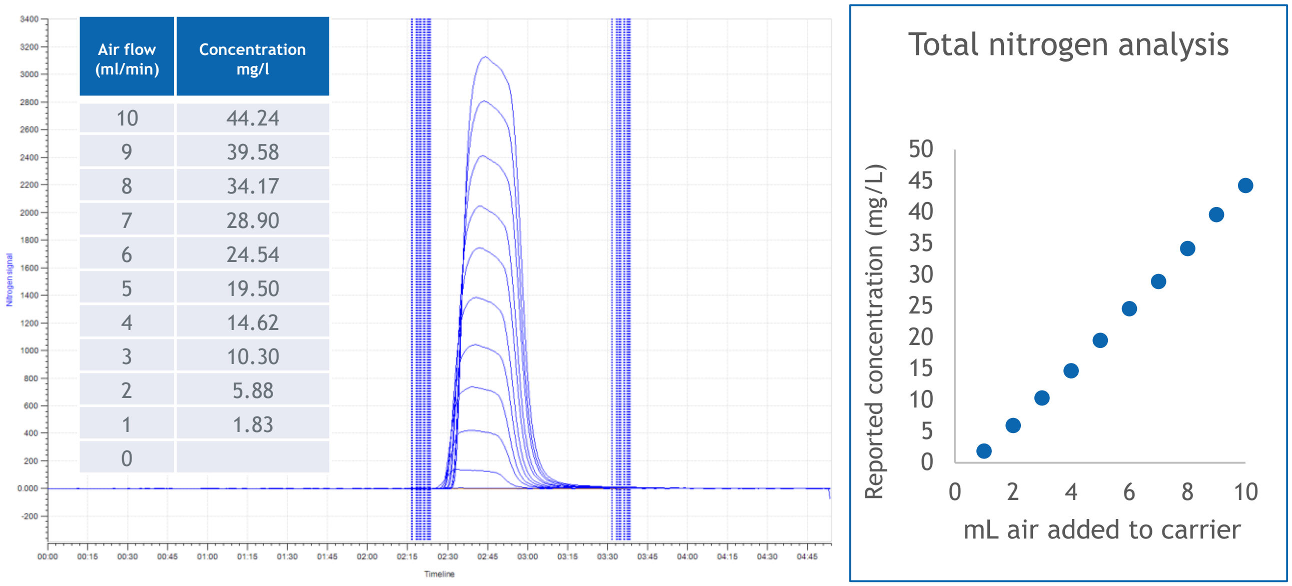


Figure 2: Adding a controlled air flow for additional N_2

RESULTS

A blank (Toluene) sample is injected by the 749 automatic liquid sampler. For each analysis, the air flow is consecutively added to the Carrier gas in ascending order from 0 to 10 ml/min (incremental steps of 1 ml/min). An overlay is created of the various amounts of air (N_2) added to the carrier gas. During the injection of a blank (Toluene) sample, a clear increase in baseline is visible caused by the amount of N_2 added. This proves that a leak in the flowpath of the supply gasses result in a “false positive” response of the nitrogen chemiluminescence detector.



Air flow (ml/min)	Concentration mg/l
10	44.24
9	39.58
8	34.17
7	28.90
6	24.54
5	19.50
4	14.62
3	10.30
2	5.88
1	1.83
0	

Figure 3: Overlay of different amounts of air (N_2) added to the carrier gas, and the response during sample injection.

CONCLUSION

This technical note describes the influence of diatomic Nitrogen (N_2) to the total Nitrogen response of a Chemiluminescence detector. When a sample is injected (the sample acts as a fuel) into the oxygen rich combustion zone, the temperature at the combustion zone rise above 1600 °C. As a result, during injection the present N_2 reacts with O_2 to form NO, which gives a positive response on the chemiluminescence detector. Therefore, it is extremely important that the supply gasses are of high quality (grade 5.0) and the supply lines are leak tight (no air introduction). It is advised to perform an automatic vacuum and pressure test, which is integrated in the ElemeNtS system, on a regular basis.

Antek's lab instruments provide reliable, precise elemental analysis for total nitrogen and sulfur, speciated nitrogen and sulfur, fluoride, chloride, and bromide. Antek products are recognized by global regulating bodies, leading scientific research institutions, and process laboratories as the instrument of choice for selective multi-element detection.