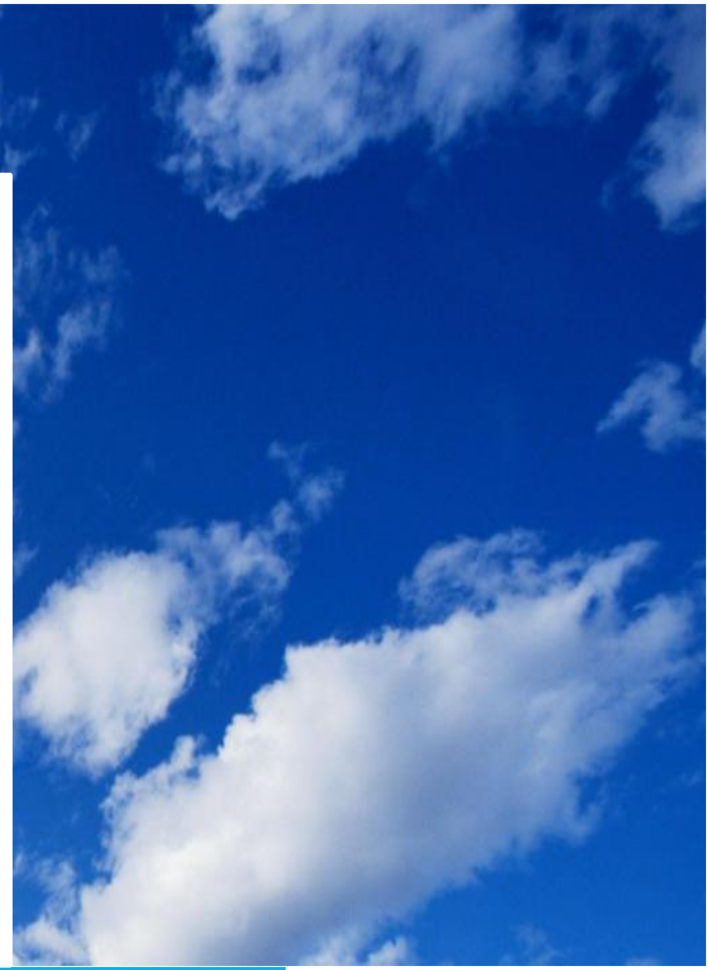
NITROGEN OXIDES (NO_X) INSTRUMENTS



Nitrogen Oxides is the sum of Nitric Oxide and Nitrogen Dioxide which are critical pollutants causing health risks and these need to be monitored using specialized instrumentation.

South African Weather Service

What is Nitrogen Oxides

Nitrogen Oxides or NO_x is a generic term for the nitrogen oxides that are most relevant for air pollution, namely Nitric Oxide (NO) and Nitrogen Dioxide (NO_2). These gases contribute to the formation of smog and acid rain, as well as affecting the tropospheric ozone. NO_x gases are usually produced from the reaction among Nitrogen and Oxygen during combustion of fuels especially at high temperatures, such as in car engines. In areas of high motor vehicle traffic, for instance in large cities, the Nitrogen Oxides emitted can be a significant source of air pollution. NO_x gases are also produced naturally by lightning.

Definition
Nitrogen Oxides is any of several oxides of nitrogen most of which are produced in combustion and are considered to be atmospheric pollutants: such as Nitric Oxide (NO), Nitrogen Dioxide (NO_2) and Nitrous Oxide (N_2O).

In atmospheric chemistry and when measuring air pollution using a Nitrogen Oxides (NO_X) instrument we measure two of these pollutants and the sum of them.

$$NO + NO_2 = NO_X$$

Definition

Nitric Oxide (NO) is a colorless poisonous gas formed by oxidation of nitrogen or ammonia that is present in the atmosphere. Nitric oxide forms in combustion systems and can be generated by lightning in thunderstorms. In mammals, including humans, nitric oxide is a signaling molecule in many physiological and pathological processes

The chemical composition of Nitric Oxide is written as NO which tells us that this gas consists of one Nitrogen molecule and one Oxygen molecule. Nitric Oxide is a free radical, for example it has an unpaired electron.

Figure 5.1: Representation of the two skeletal structures of NO.

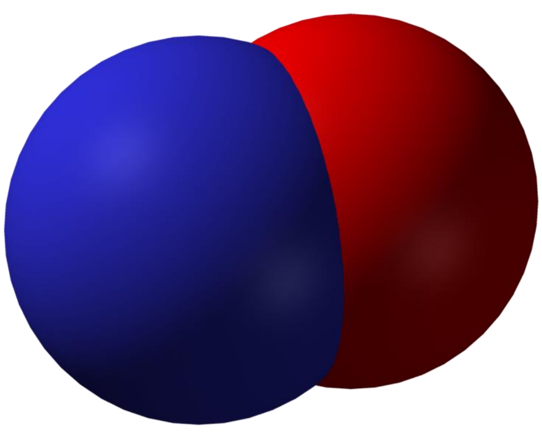


Figure 5.2: 3D representation of the chemical composition of NO.

Definition

Nitrogen Dioxide (NO_2) is a toxic reddish brown gas that is a strong oxidizing agent, is produced by combustion (as of fossil fuels), and is an atmospheric pollutant (as in smog). It is one of several nitrogen oxides. NO_2 is an intermediate in the industrial synthesis of nitric acid, millions of tons of which are produced each year for use primarily in the production of fertilizers.

The chemical composition of Nitrogen Dioxide is written as NO_2 which tells us that this gas consists of one Nitrogen molecule and two Oxygen molecules. Nitrogen dioxide is a paramagnetic, bent molecule with C_2v point group symmetry.

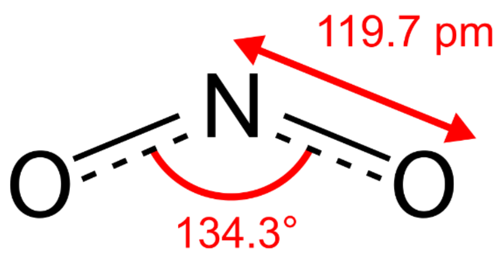


Figure 5.3: Representation of the two skeletal structures of NO_2.

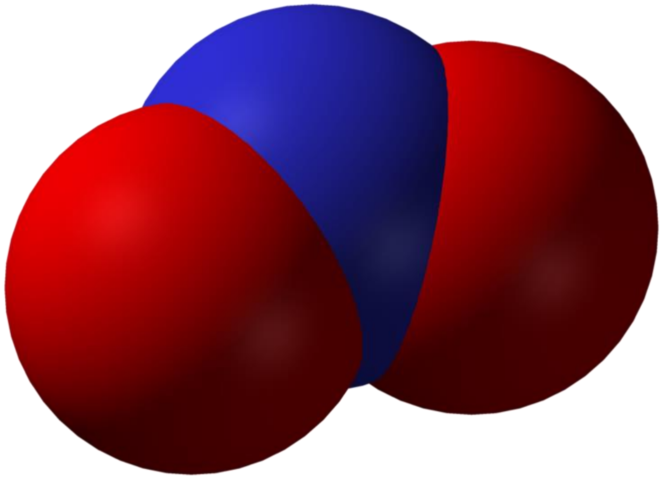


Figure 5.4: 3D representation of the chemical composition of NO_2.

How do we measure NO, NO_2 and NO_x

The measurement of the Oxides of Nitrogen is performed by gas phase Chemiluminescence which is the production of light from a chemical reaction.

Definition
Chemiluminescence (also chemoluminescence) is the emission of light (luminescence), as the result of a chemical reaction that takes place.

To enable us to measure trace levels of NO, NO_2 and NO_x in ambient air we also make use of the principles of chemiluminescence and certain components are required inside an instrument to do so. These basic components include:

- Electrical circuits to power the sensors and other circuits.
- Electronic circuits to measure voltages from sensors and circuits.
- Processor that can perform calculations and display data.
- Measuring chamber for the chemiluminescence to take place without interference.
- Sensor that can measure the chemiluminescence (light being emitted).
- Source that can create ozone (O_3) which is required for the chemical reaction that needs to take place.

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

*LIGHT

Although several different type of NO_x analysers are available on the market and they are all manufactured by different suppliers most instruments make use of the same basic components and principle to measure NO_x in ambient air. To understand the principle of chemiluminescence we first need to look at how we can measure the chemiluminescence reaction.

What is Ultraviolet and Infrared light and how do we measure it?

Light is measured by its wavelength (in nanometers or micrometers) or frequency (in Hertz). One wavelength equals the distance between two successive wave crests or troughs. Frequency (Hertz) equals the number of waves that passes a given point per second.

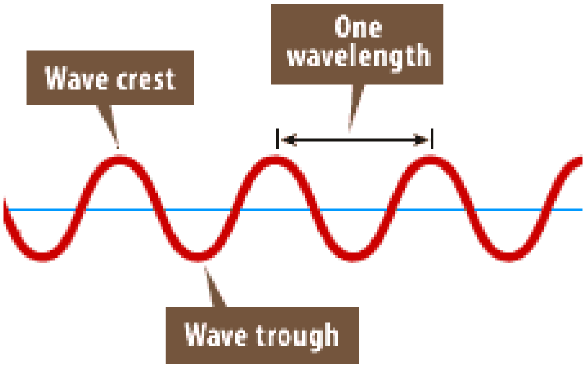


Figure 5.5: Light is measured in wavelength or frequency.

Definition
In physics, the wavelength is the spatial period of a periodic wave—the distance over which the wave's shape repeats.

Definition
Frequency is the number of occurrences of a repeating event per unit of time. It is also referred to as temporal frequency, which emphasizes the contrast to spatial frequency and angular frequency.

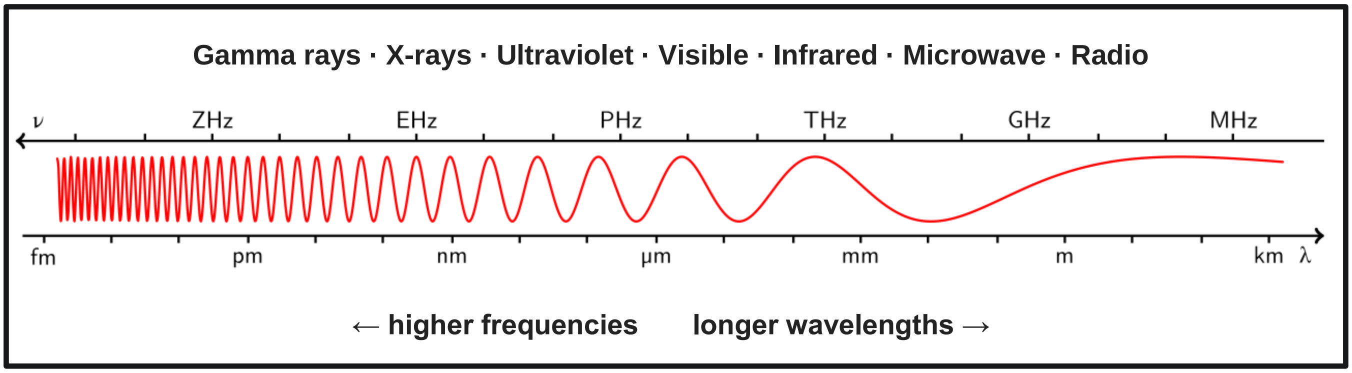


Figure 5.6: The full electromagnetic spectrum.

Light is measured at different wavelengths but usually in nanometres, the electromagnetic spectrum for light is the available range of light that we can measure, the light spectrum starts at a wavelength of 200 nM up to 20 µM. The quantum of light that is released during the chemiluminescence reaction of a NO molecule and an O3 molecule helps us to measure the concentration of the NO, this distribution of wavelength ranges from 600 nm to 3000 nm with a peak at about 1200 nm. Thus the optical measurement in a NO_X analyser is performed in the visible light spectrum but also the infrared spectrum which ranges from near infrared (NIR) which is measured from 700 nM up to 2 µM and infrared spectrum of light is infrared light (IR) which is measured from 2 µM up to 20 µM.

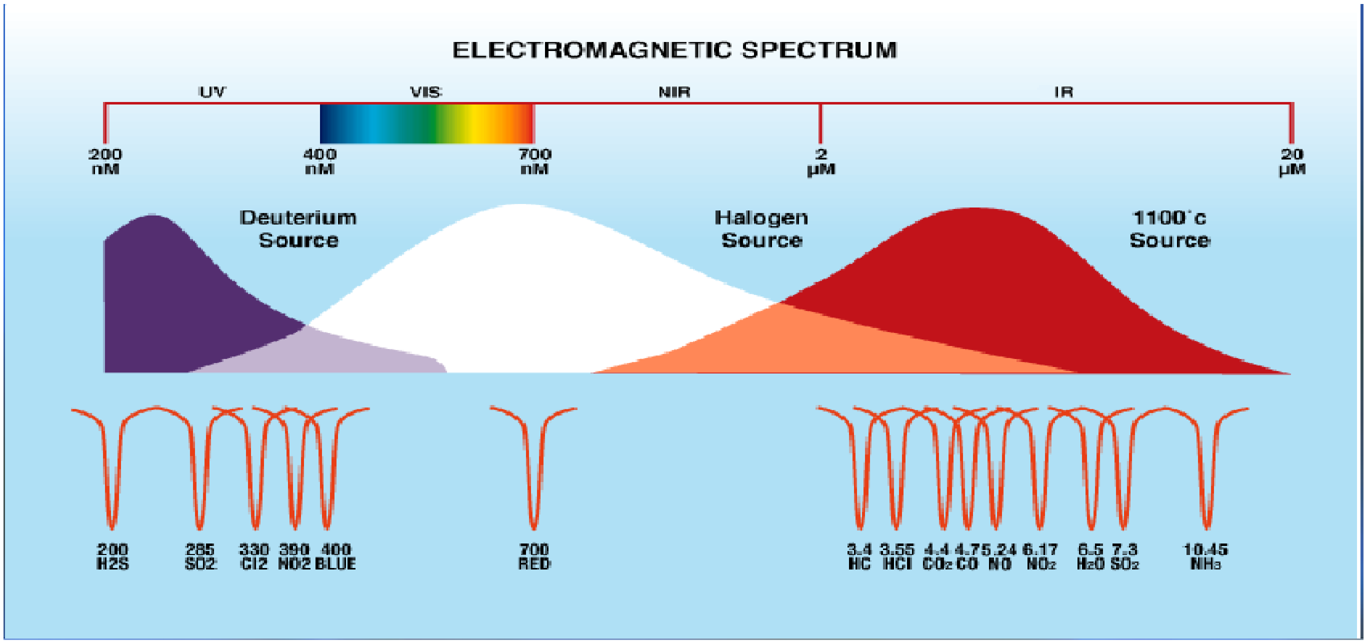


Figure 5.7: The electromagnetic spectrum of light.

Operation principles of NO_X instruments

Chemiluminescence in NO measurement is the quantum of light that is produced when a chemical reaction takes place between a NO molecule and an O3 molecule. During the first step of this chemical reaction one NO molecule collides with one O3 molecule and chemically react to form one oxygen molecule (O_2) and one Nitrogen Dioxide (NO_2) molecule. The NO_2 molecules that are formed during this reaction retain excess energy due to the collision and exists in an exited state, where one of the electrons of the NO_2 molecule resides in a higher energy state (denoted by the asterisk in the following equation.

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

*LIGHT

The second step occurs because the laws of thermodynamics require that systems seek the lowest stable energy state available, therefore the exited NO_2 molecule quickly returns to its ground state releasing the excess energy in a form of quantum of light.

The detector/sensor that is used in NO_X analysers to measure the concentration of NO is called a photo multiplier tube (PMT) which is a detector in a glass vacuum tube that is extremely sensitive to light. The PMT is used to detect very low light caused by the chemiluminescence reaction and a small current is produced, this current is then amplified by the PMT and the voltage produced can be measured by the microprocessor. The measurement of NO is directly proportionate to the amount of NO molecules that is inside the measuring chamber given that sufficient O3 molecules are also available for the chemical reaction to take place.

Figure 5.8: Photo multiplier tubes (PMT).

To ensure that there is no interference from other chemical reactions that can also take place when reacting with O3 for instance some oxides of sulfurs also creates a chemiluminescence reaction when reacting with O3 (usually at much lower wavelengths of around 260 nm to 480 nm). In order to make sure that only a specific wavelength of light is allowed to reach the PMT we make us of an optic filter. An optic filter can selectively transmit only light with a specific wavelength while the rest of the wavelength range is blocked out, by doing this only the specified wavelength of light is allowed through this filter. For the measurement of NO we require an optic filter that will only allow wavelengths of 645 nm and above through and block the other wavelengths, this type of optical filter is called a long pass filter or high pass filter.

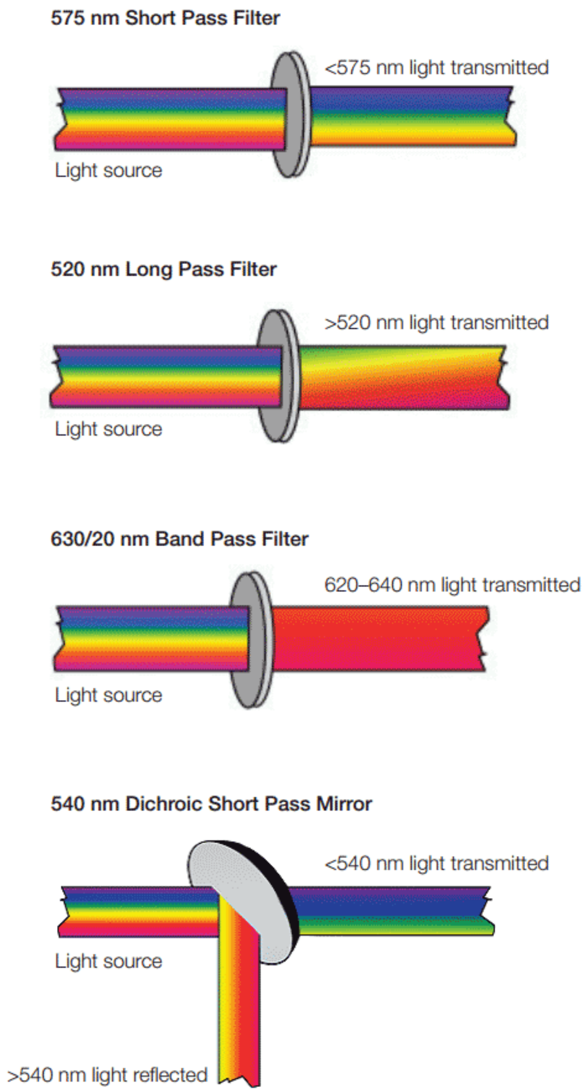


Figure 5.9: Different types of optical filters.

Taking all of the above information into consideration we can measure NO particles in air.

1. The NO molecule reacts with an O3 molecule and a chemiluminescence reaction takes place emitting photons (light).
2. To measure only the light emitted with a wavelength of 650 nm and above the high pass filter is installed between the PMT and the measurement chamber.
3. The PMT now can measure the correct wavelength of 650 nm and above and also the frequency of this wavelength and provide a measured value to the system.

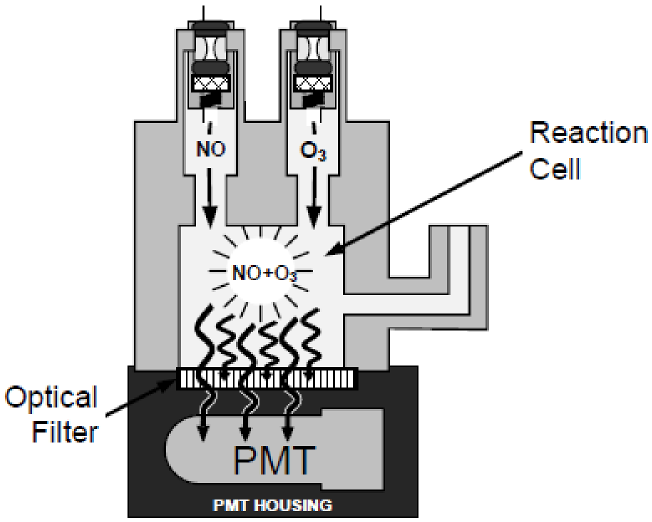


Figure 5.10: Example of the operation principle of NO_X analysers.

It is important to take note that only NO gas can be measured by using the effect of chemiluminescence inside a NO_X analyser.

The NO_X analyser used for ambient air monitoring is however capable for providing three measurements simultaneously which include NO, NO_2 and NO_X. The measurement of NO_X is the sum of NO and NO_2 so the only other part of the equation that needs to be measured is the NO_2 in the sample.

In order to measure the concentration of NO_2 and subsequently calculate the NO_X concentration the instrument periodically switches between different gas streams, the NO stream and NO_2 stream. To enable this the sample that enters the instrument is split into two streams when entering the instrument, this is done so that the same sample can be analysed separately. The first part of the sample enters the measuring chamber and reacts with the O_3 in the chamber and chemiluminescence takes place. The second part of the sample enters a delay loop giving the first part of the sample enough time to react with the O_3 before also entering the measuring chamber. To enable us to measure the NO_2 sample this sample needs to be changed to an NO sample to use the effect of chemiluminescence, this can be done by using a converter.

The Molycon converter is used to convert the NO_2 molecules in the second sample to an only NO sample, by doing this the second sample that contains NO and NO_2 molecules can be measured inside the same instrument at a later time (roughly switching between sample streams every 6 seconds). The Molycon converter is filled with Molybdenum chips and heated up to 320 ^{o}C which converts all NO_2 molecules to NO molecules, this means that the original concentration of NO that has already been measured is also part of this sample but the NO_2 gas that was present in this sample has been converted to NO molecules as well so this sample will be the same concentration or a higher concentration as the sample that was measured first.

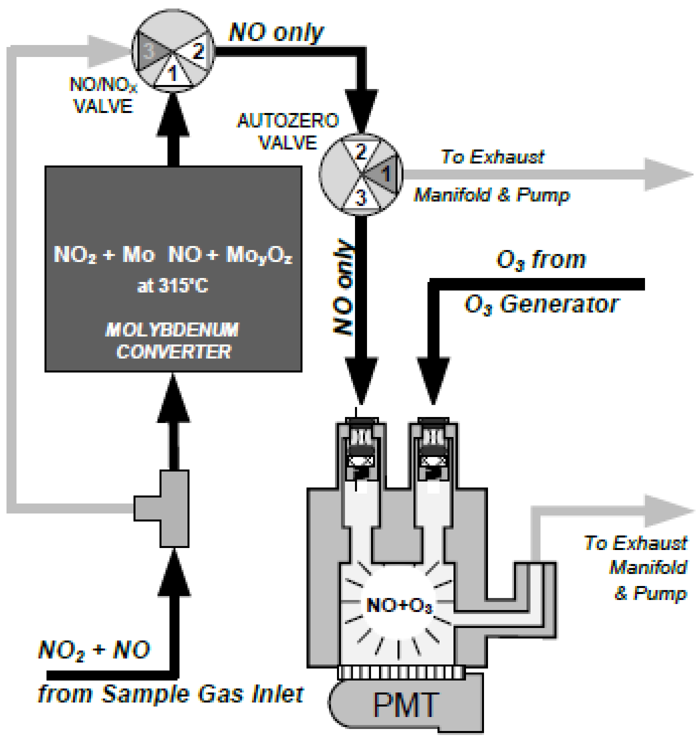


Figure 5.11: NO_2 to NO conversion inside NO_X analysers.

By converting the NO_2 molecules to NO molecules in the second part of the sample, the total NO_x can be measured in the second part of the sample ($NO + NO_2$(converted to NO) $= NO_X$). Finally the NO_2 is not directly measured but calculated by subtracting the first NO sample from the total NO_X sample ($NO_2 = NO_X - NO$).

Examples of NO_X instruments

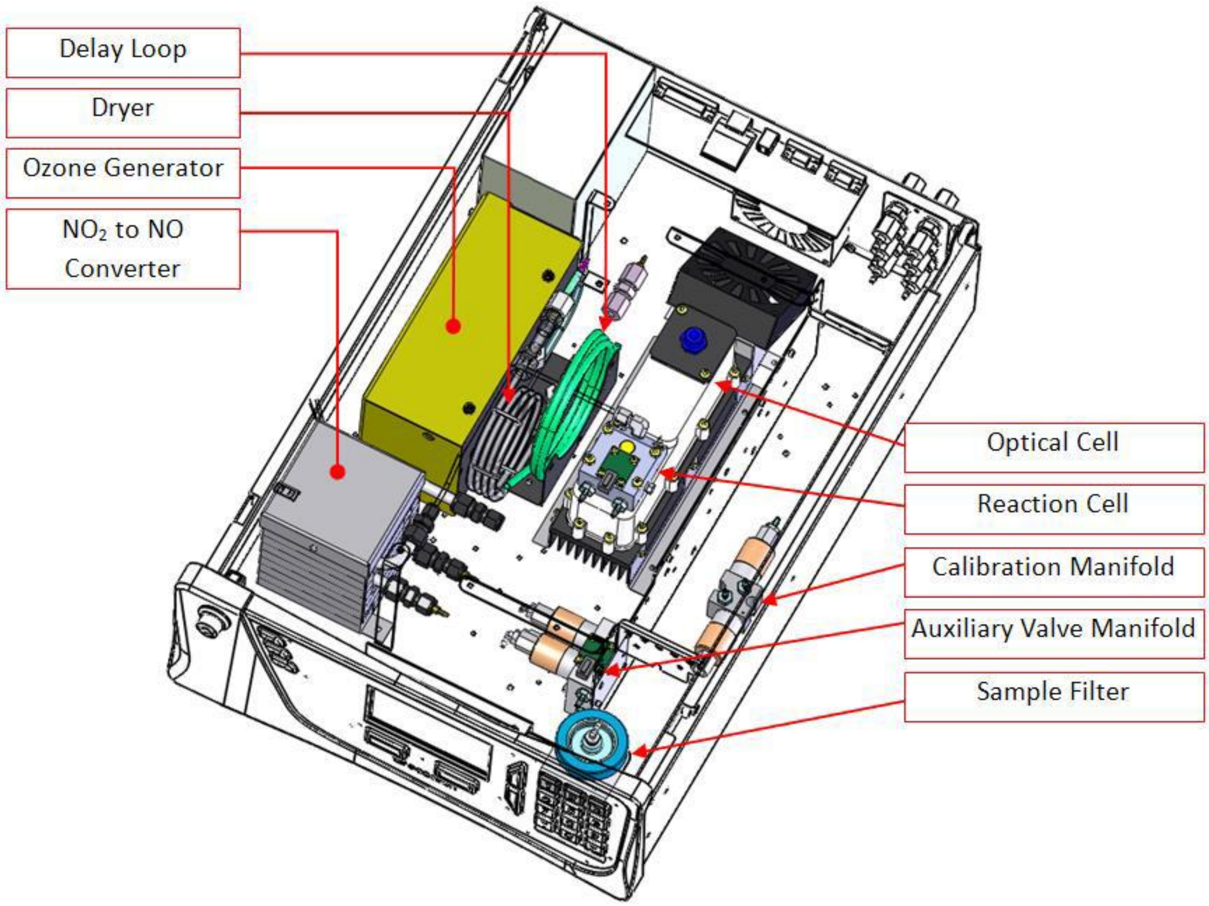


Figure 5.12: Example of the Ecotech Serinus 40 NO_X analyser.

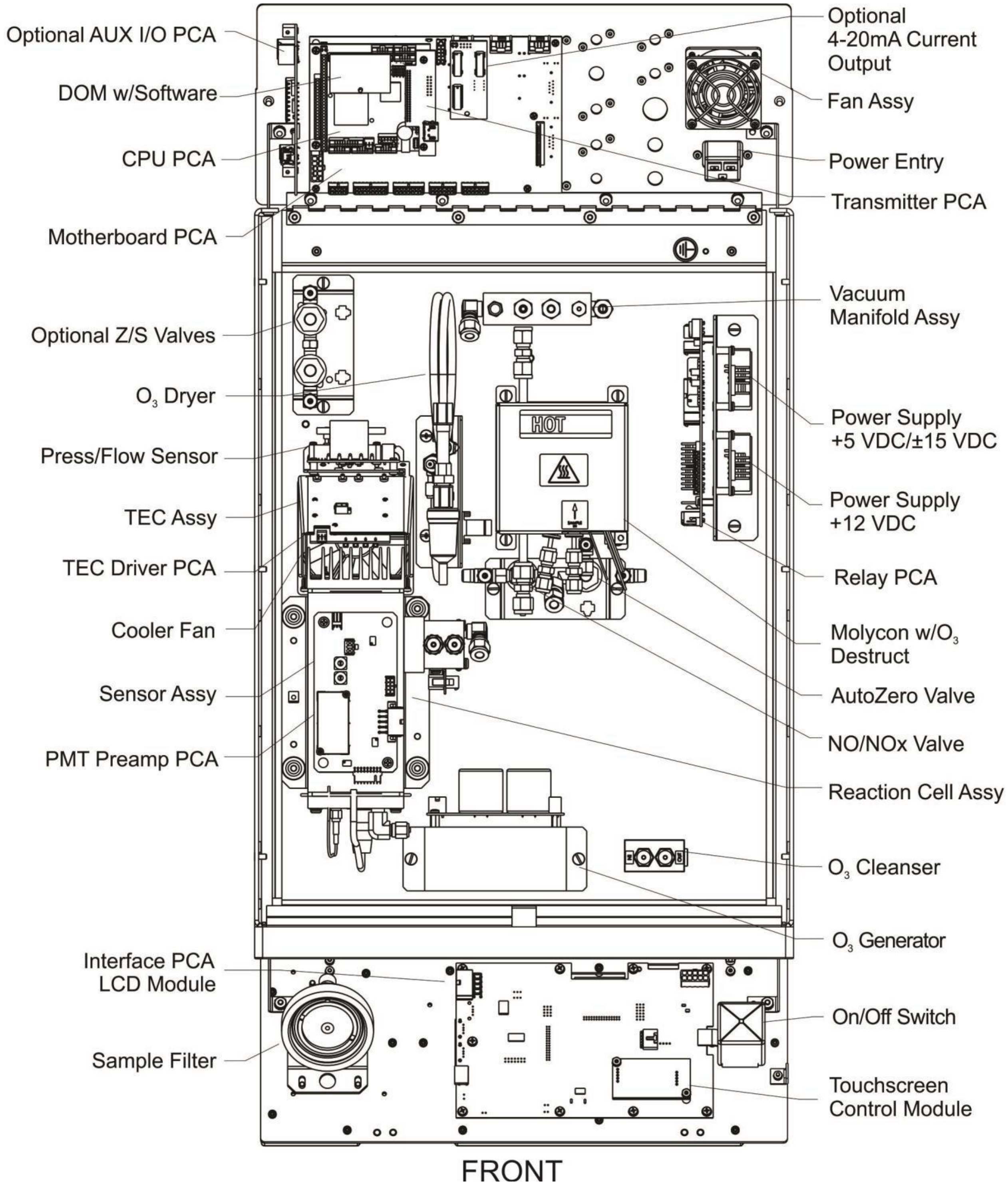


Figure 5.13: Example of API Teledyne T300 NO_X analyser.

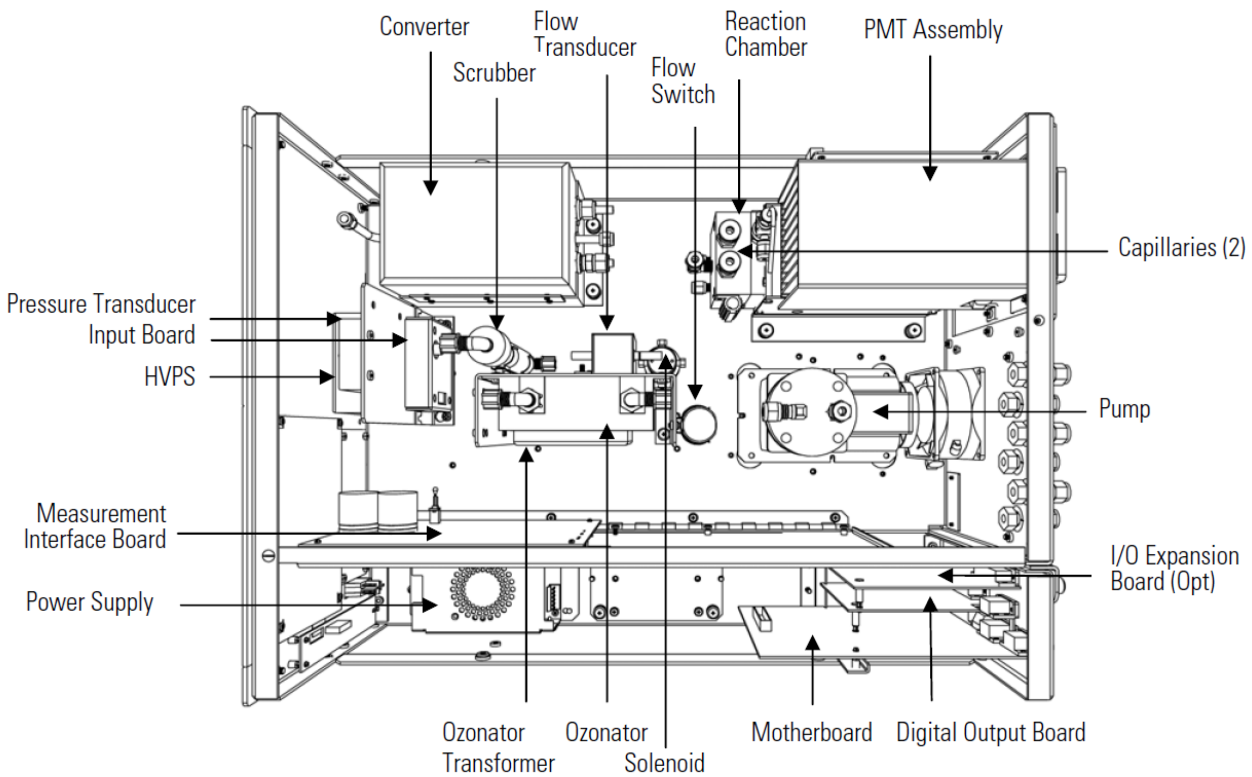


Figure 5.14: Example of Thermo Scientific NO_X analyser.

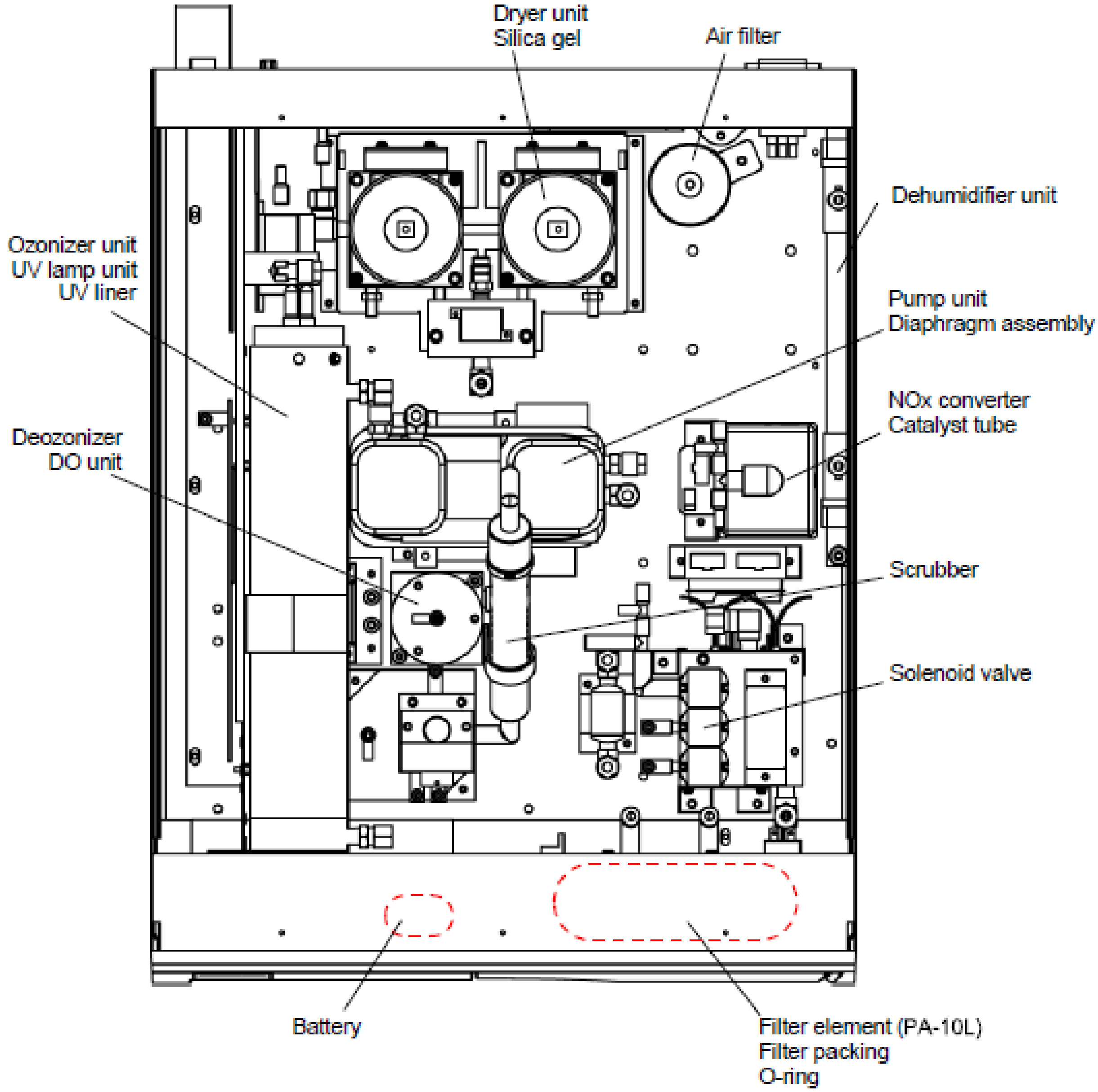
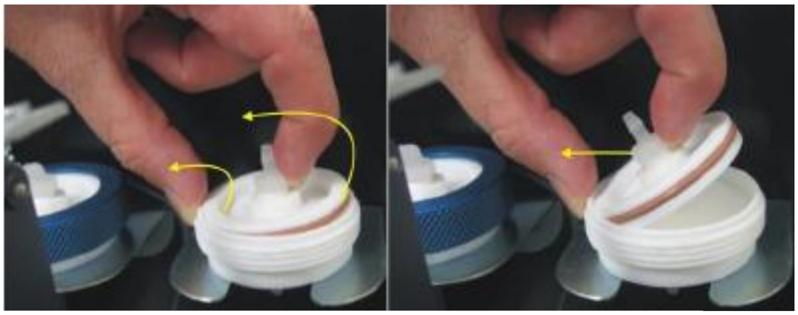


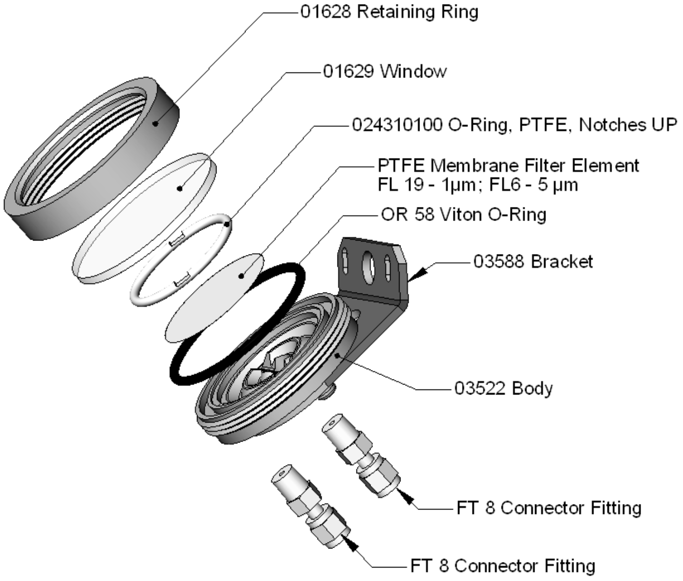
Figure 5.15: Example of Horiba APNA370 NO_X analyser.

Internal components of NO_X instruments

From the above examples several different internal components of the NO_X instruments are shown, these internal components are used to ensure that the sample is delivered to the reaction chamber and that any impurities is scrubbed from the sample. Some of the internal components are discussed in further detail below.

Particulate filter





- All instruments will have a particulate filter. The filter is used to prevent contamination of the internal components of the instrument.
- Contamination of the filter can result in degrading of the instrument performance, including
  - Slow response time (Lower flow)
  - Erroneous readings (Cell contamination)
  - Temperature drift

Figure 5.16: Examples of particulate filters used in an NO_X analyser.

Valve block (Manifold)

During sampling or calibration of the instrument the flow of air needs to be redirected for a specific mode of operation. Valve blocks fitted with small electronic valves are used to control the flow of air as indicated by the user. The valve block can also be referred to as the zero/span/sample control block.

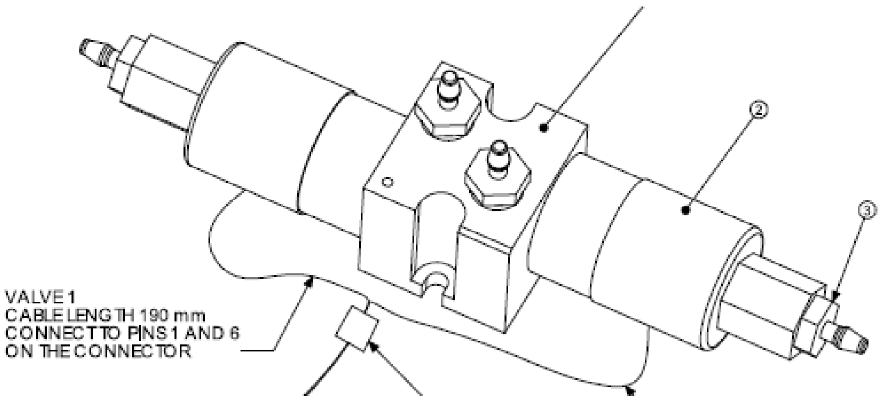
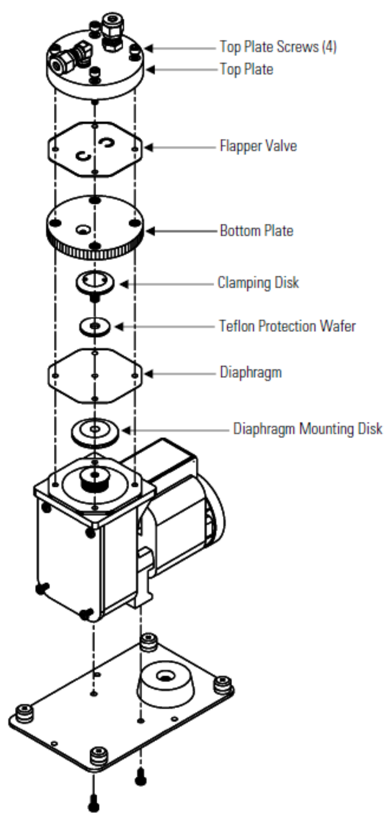


Figure 5.17: Example of valve block used in an NO_X analyser.

Pump



- All instruments require a source of flow to provide a sample to the reaction chamber. For this purpose a pump is used to draw a sample through the instrument.
- A pump can either be built into the instrument or be external and connected to the exhaust port.
- All gas instrument pumps are diaphragm pumps. Meaning a small piston pushes against a diaphragm creating a vacuum thus generating suction.

Figure 5.18: Example of a pump used to draw air through an NO_X analyser.

Ozone (O_3 generator)

Definition
a colourless unstable toxic gas with a pungent odour and powerful oxidizing properties, formed from oxygen by electrical discharges or ultraviolet light. It differs from normal oxygen (O_2) in having three atoms in its molecule (O_3).

Ozone molecules are naturally-occurring in air due to the sun's uv rays that reacts with O_2 molecules. However inside a NO_X instrument we need to create O_3 to react with NO molecules to create the chemiluminescence effect. To ensure an accurate measurement of NO we require a sufficient amount of O_3 to react with the NO sample. This can be done by using an Ozone generator, there are two ways used to create Ozone from O_2 molecules. The first is using uv-light or a uv-lamp to create O_3 and the second way is using an electrical discharge like a electric coil to create O_3.

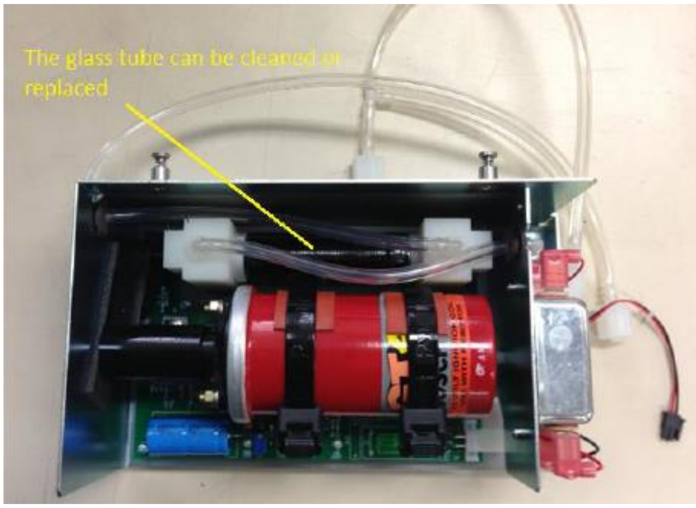
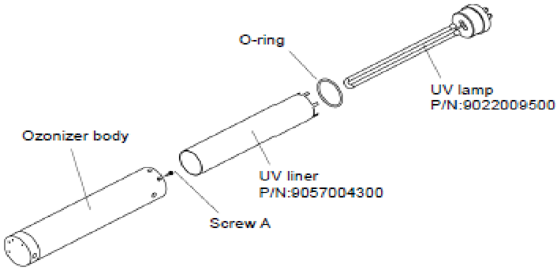


Figure 5.19: Example of an Ozone generator used in a NO_X analyser.



- Ozone is formed from O_2 molecules by using a uv-lamp or an electrical discharge.

Figure 5.20: Operation of an Ozone generator.

Dryer

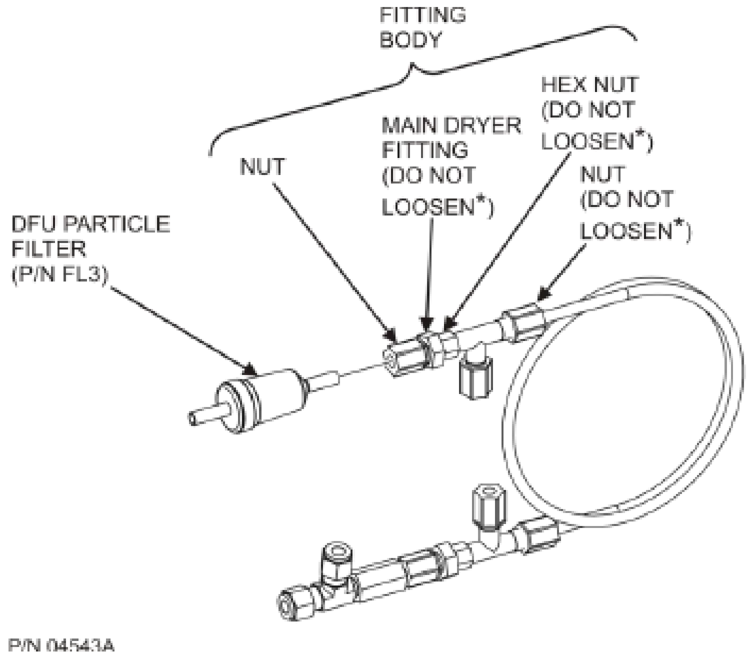


Figure 5.21: Example of a dryer used in a NO_X analyser.

The dryer inside a NO_X analyser is used to ensure dry air scrubbed from any moisture and hydrocarbons is supplied to the Ozone generator for generating O_3 from the O_2 supplied by the dryer. This is done by using the principle of reverse flow osmosis to remove any moisture and hydrocarbons from the air that needs to enter the Ozone generator.

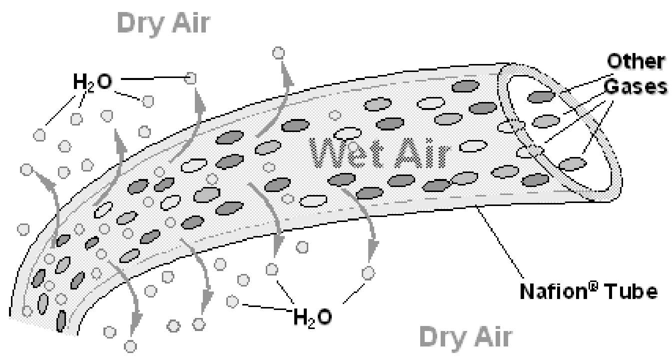


Figure 5.22: Operating principle of a dryer used in a NO_X analyser.

Reaction Cell

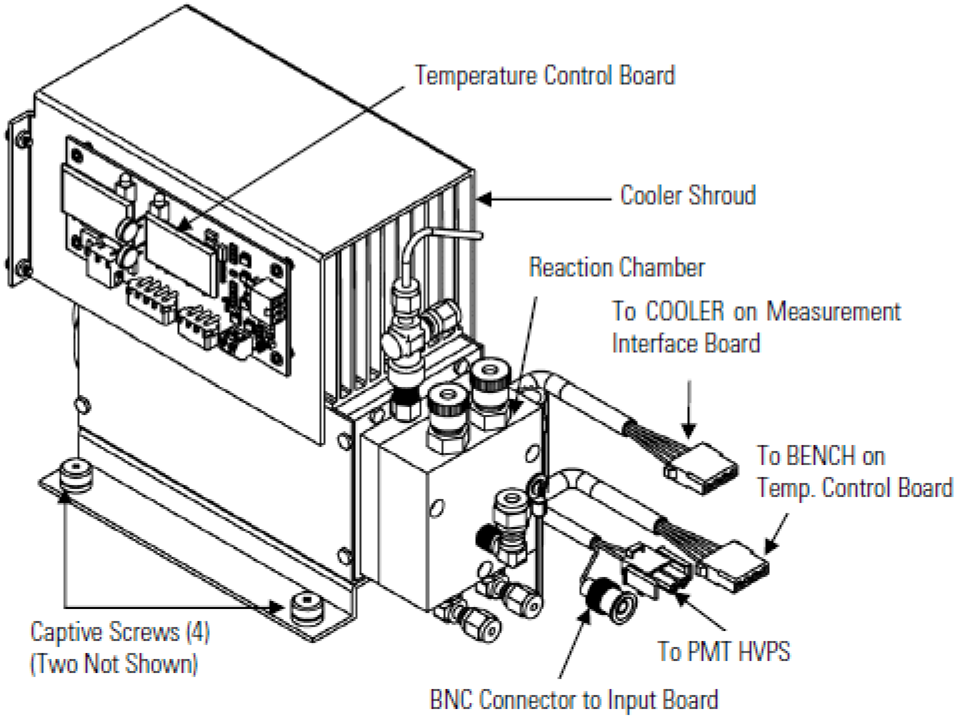


Figure 5.23: Example of the reaction cell on a NO_X analyser.

The reaction cell is where the chemiluminescence effect takes place and where the measurement of both samples are performed, the reaction cell is usually made up of six main components:

1. Reaction Chamber
2. Optical filter
3. Photomultiplier Tube (PMT)
4. PMT Cooler
5. PMT High Voltage Supply
6. Valve manifold block

Reaction chamber

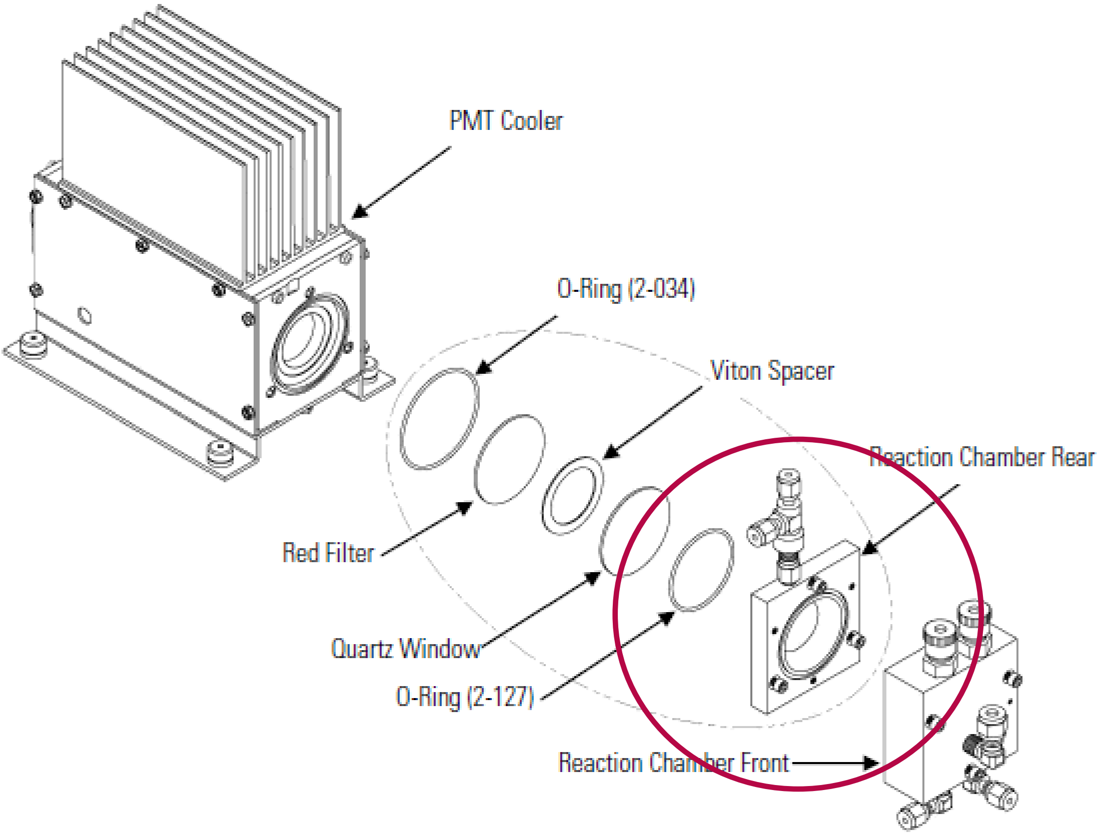


Figure 5.24: Example of the reaction chamber on a NO_X analyser.

This is the sample chamber where NO gas molecules reacts with the O_3 gas molecules inside the chamber, this reaction forms NO_2 gas in an excited state and light is emitted at a wavelength of above 650 nm which can then be measured by the PMT.

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

*LIGHT

Optical filters

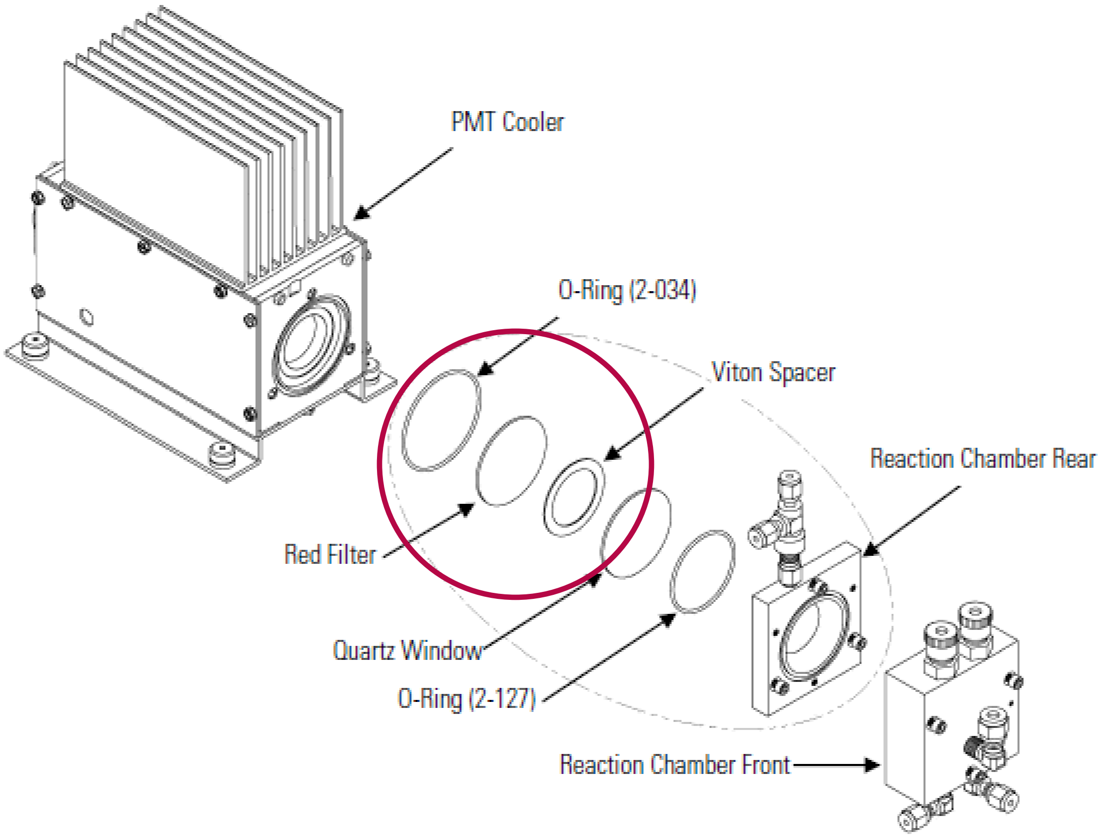


Figure 5.25: Example of the optical filters on a NO_X analyser.

The optical filters are used to filter out the undesired wavelengths of light inside the chamber so that only the correct wavelength reaches the PMT. The red filter referred to is a high pass filter that only allows wavelengths above 650 nm to pass through to the PMT for measurement.

Photomultiplier tube (PMT)

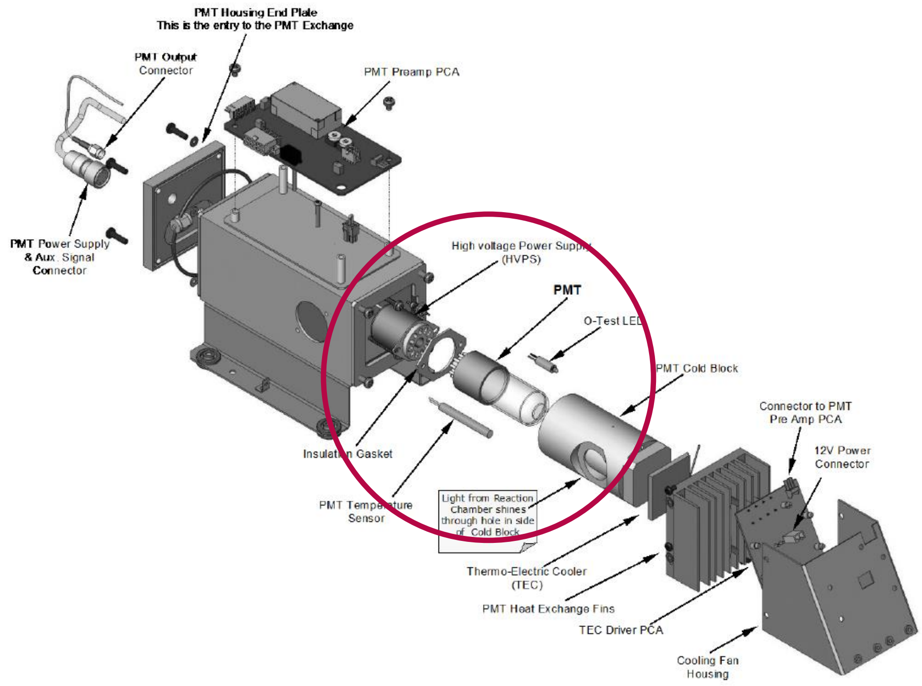
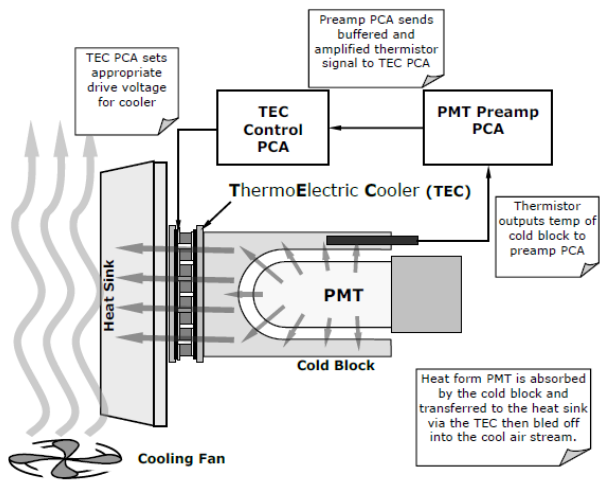


Figure 5.26: Example of the PMT used in a NO_X analyser.

The PMT can detect trace amounts of light and is used to detect the amount of light caused by the excited NO_2 particles. The detection of light creates a small voltage which can then be used as a direct measurement of NO in the cell.

PMT cooler



The PMT functions optimally at a low temperature of 10ºC - 13ºC. Due to the electronics involved that creates heat inside the instrument a cooler must be used to ensure that the PMT is operated at a constant temperature of between 10ºC - 13ºC.

To assist with cooling the PMT a heatsink and cooling fan is used in conjunction with the thermoelectric cooler.

Figure 5.27: Example of the PMT cooler used in a NO_X analyser.

Molybdenum Converter (Molycon)

The Molybdenum converter is used to convert any NO_2 into NO by using high temperatures (320^{O}C) and a catalyst called Molybdenum chips. This is done to convert all NO_2 molecules to NO molecules as the NO_X analyser can only measure NO by using the effect of chemiluminescence.

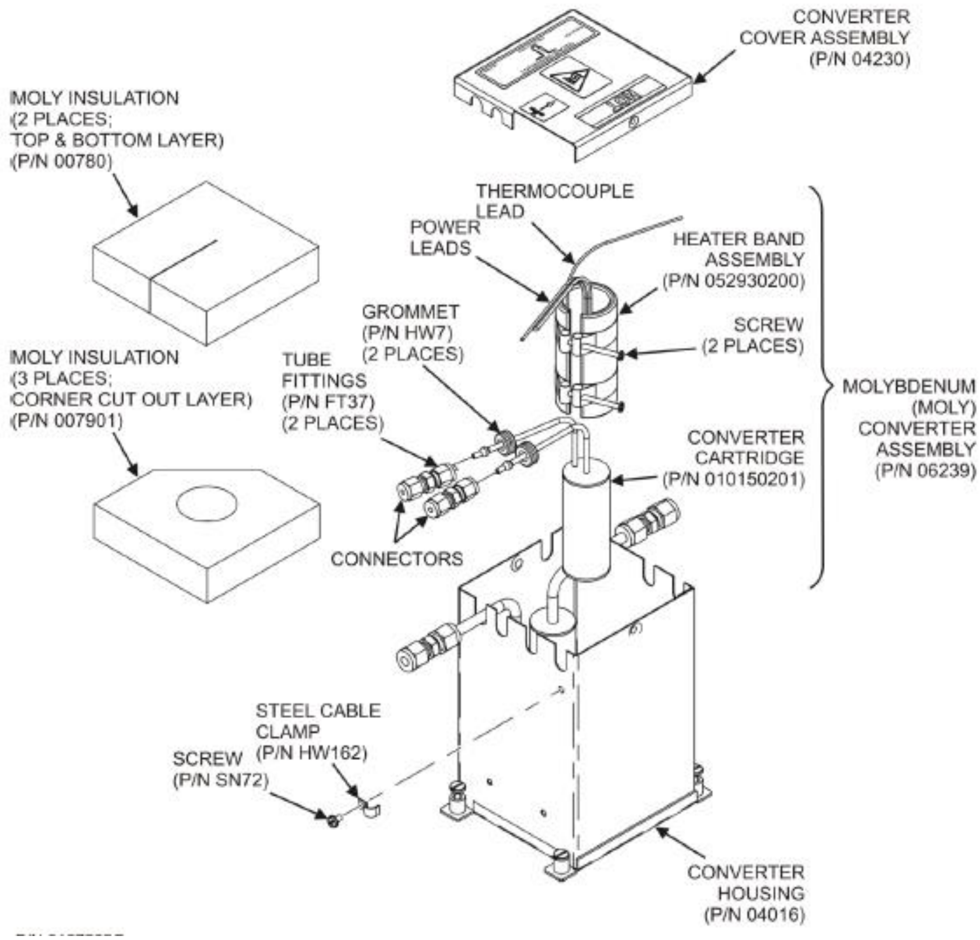


Figure 5.28: Example of the Molycon used in a NO_X analyser.

The Molycon must be effective in converting all NO_2 molecules into NO molecules thus the converter efficiency is checked during quarterly calibrations to ensure the effectiveness of the converter. The Molycon converter must have an efficiency of 96% or higher, if the efficiency is below 96% the converter material must be replaced or a new converter must be installed.

Flow of a NO_X molecule inside the instrument

With the knowledge of the principles of operation and all the internal components used inside an NO_X analyser we can piece together the flow of how a NO molecule is measured.

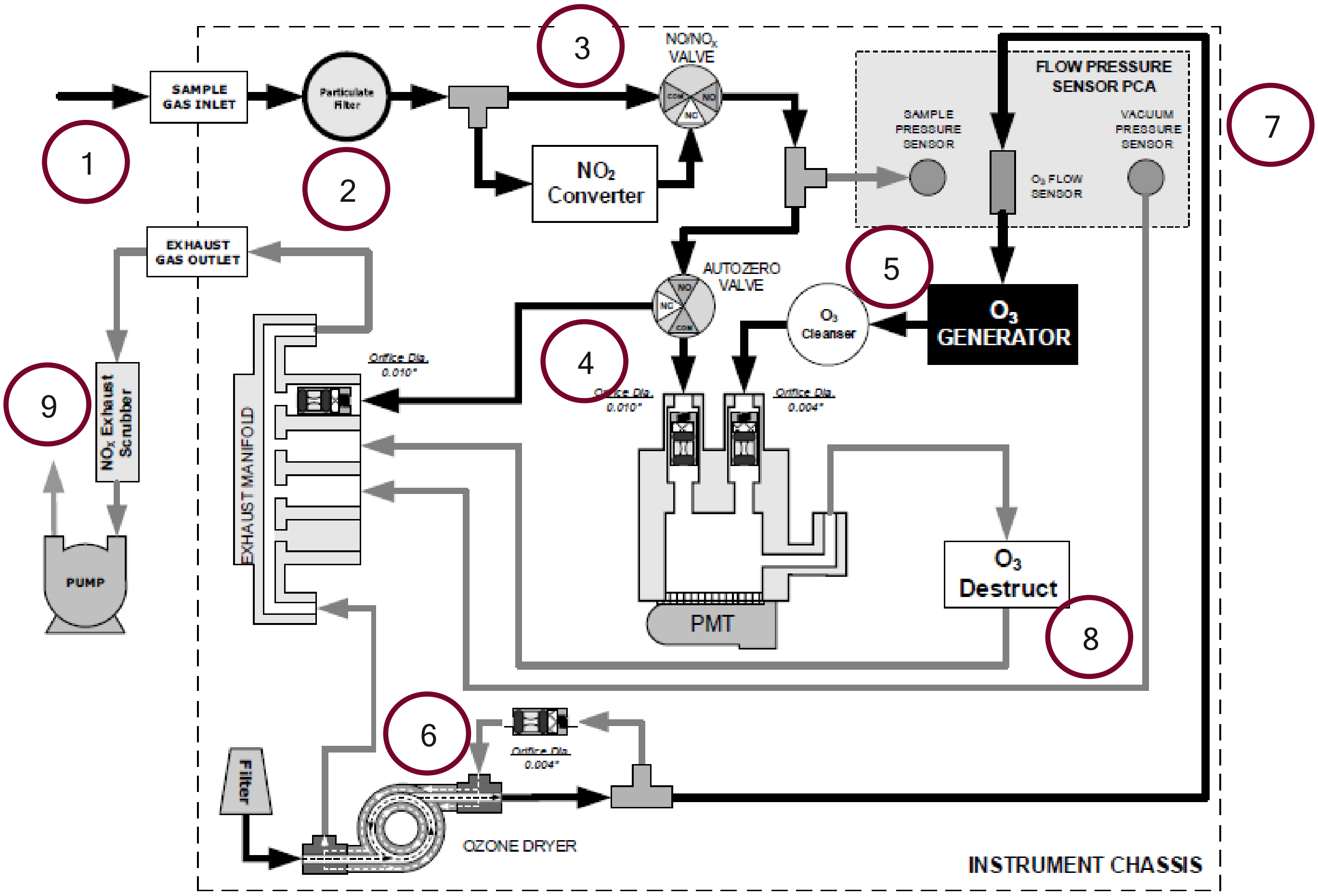


Figure 5.29: Flow process inside a NO_X analyser.

1. The sample enters the sample inlet due to the suction created by the pump on the opposite side of the process. The pump is always the final component in the flow process as the pump needs to create a flow of air through the instrument.

2. Once the sample has entered the inlet the sample filter first removes any small dust particles that can influence or contaminate the operation of the instrument.

3. The sample is split into two sample streams, the first sample stream is the normal NO sample which will go directly to the measurement chamber and the second sample stream will first go through the delay loop and into the Molycon converter to convert all NO_2 to NO and is measured as NO_X.

4. The two sample streams enter the measurement chamber where the NO molecules can react with the O_3 supplied by the O_3 generator. The chemiluminescence effect takes place and the amount of NO molecules can be measured by the PMT. The valve manifold switches and the second sample stream enters the same measurement chamber where the total NO_X can now be measured by measuring the amount of NO molecules that were added to the original amount after converter the NO_2 molecules to NO molecules in that sample. The two measurements from the PMT can now be used to calculate the amount of NO_2 present in the sample.

5. The Ozone generator constantly creates O_3 and supplies the O_3 to the reaction cell to react with any NO molecules in the sample.

6. The Ozone generator is supplied with dry air from the dryer.

7. The system is equipped with flow sensors and pressure sensors to ensure the correct flow of sample through the instrument. It is important to ensure that the flows on the NO_X is correct to ensure enough O_2 reaches the Ozone generator and to ensure the sample that was split in two sample streams are measured at different times inside the measurement chamber.

8. It is important to remember that not all the O_3 that is created by the Ozone generator is used by the sample inside the measuring chamber thus before the sample can exit the instrument the excess O_3 must be destroyed as this can damage the pump and harm the environment. For this a catalyst or Ozone destroyer is used between the exit of the measuring chamber and the suction side of the pump.

9. Finally the sample will exit the instrument by being suction created by the pump and the air that flows in an opposite direction through the dryer and finally exiting the instrument via the pump or exhaust outlet.

Maintenance of NO_X instruments

Ambient air monitoring instruments are specialized equipment and just like a car these instruments require regular checks and maintenance to ensure that it continues to operate and to ensure the accuracy of measurements and reliability of instrumentation. Table 5.1 provides a schedule of the maintenance and likely repairs that can be performed on an NO_X analyser.

Item	Action	Frequency
Particulate Filter	**Change**	**Bi-Weekly or sooner**
Diagnostic Checks	**Evaluate**	**Bi-Weekly**
Zero/Span Checks	**Evaluate**	**Bi-Weekly**
Multi-point calibration	**Calibrate and verify**	**Every 3 months**
Zero Air Scrubber	Replace	6-Monthly
Ozone generator	Replace	Annually if required
Pump	Rebuild Head	If flow drops below instrument operational norms
Pneumatics	Clean	Annually if required
Reaction Cell	Clean	Annually if required

Table 5.1: Maintenance and repair schedule.

From table 5.1 the three most important maintenance items are mentioned first with the most important maintenance item being the changing the particulate filter every two weeks.

The particulate filter ensures that no dust or debris enters the instrument as this can contaminate the lenses, optical filters and sensors which will affect the operation of the instrument. Always make sure to change the operating mode of the instrument or switch of the pump when replacing the particulate filter, this way no fine particulates can enter the instrument while changing out the filter. Refer to figure 5.16.

The second important item to check is the diagnostics of the instrument, these are the parameters of the measurements of internal control systems that are in place to ensure optimal operation of the instrument. Most instruments will display a warning on the screen of the instrument if there are any of the parameters that are not within the specified range but it is also important to check all the parameters every two weeks to ensure there were no major changes in any if the parameters.

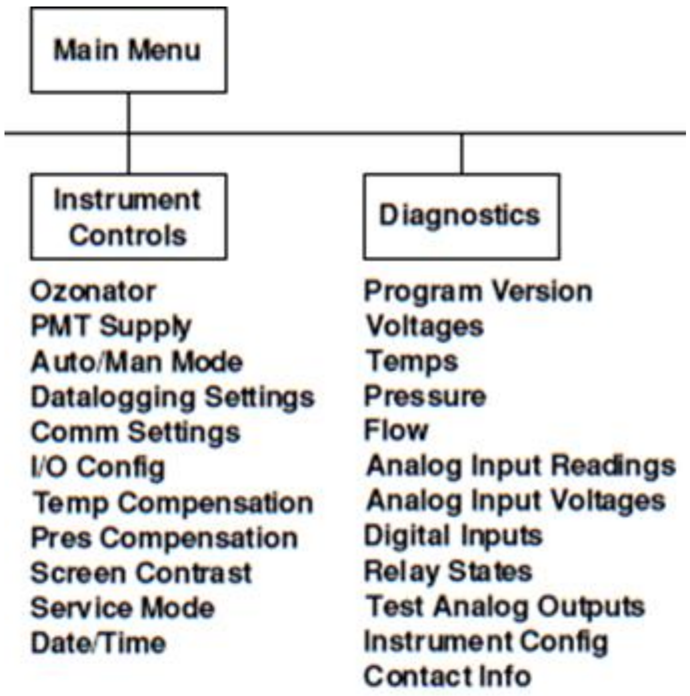


Figure 5.30: Example of instrument menu to check system diagnostics.

NOx Analyser			
Manufacturer	Environment-SA	Station Name	Delmas
Model Number	AC 32 M	Operator	Pieter
Serial Number	04-2481	Date	07/05/2017

Diagnostic Check sheet

NOx Parameter	Nominal value/range(1)	Observed	Updated Values	Deviation
Meas. Chan. Pressure (mbar)	200	195		
Converter Temperature (°C)	340	340		
Converter Autonomy (d)	above 000	0		
Chamber Temperature (°C)	60	60		
PM Temperature (°C)	10	10		
Sample Inlet Pressure (mbar)	current	814		
Internal Temperature (°C)	10 - 55	31		
NO Span Coefficient	current	2.3626		
NOx Span Coefficient	current	2.3843		
NO Offset	current	0.1		
NOx Offset	current	0.2		

Figure 5.31: Example of instrument diagnostics that were recorded.

https://en.wikipedia.org/wiki/Frequency
https://en.wikipedia.org/wiki/Chemiluminescence
https://pubs.rsc.org/en/content/articlelanding/1964/tf/tf9646000359/unauth#!divAbstract
https://en.wikipedia.org/wiki/NOx
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https://www.merriam-webster.com/dictionary/nitrogen%20oxide
https://www.merriam-webster.com/dictionary/nitric%20oxide
https://www.merriam-webster.com/dictionary/nitrogen%20dioxide
API T200 manual
Ecotech Serinus S40 operation manual