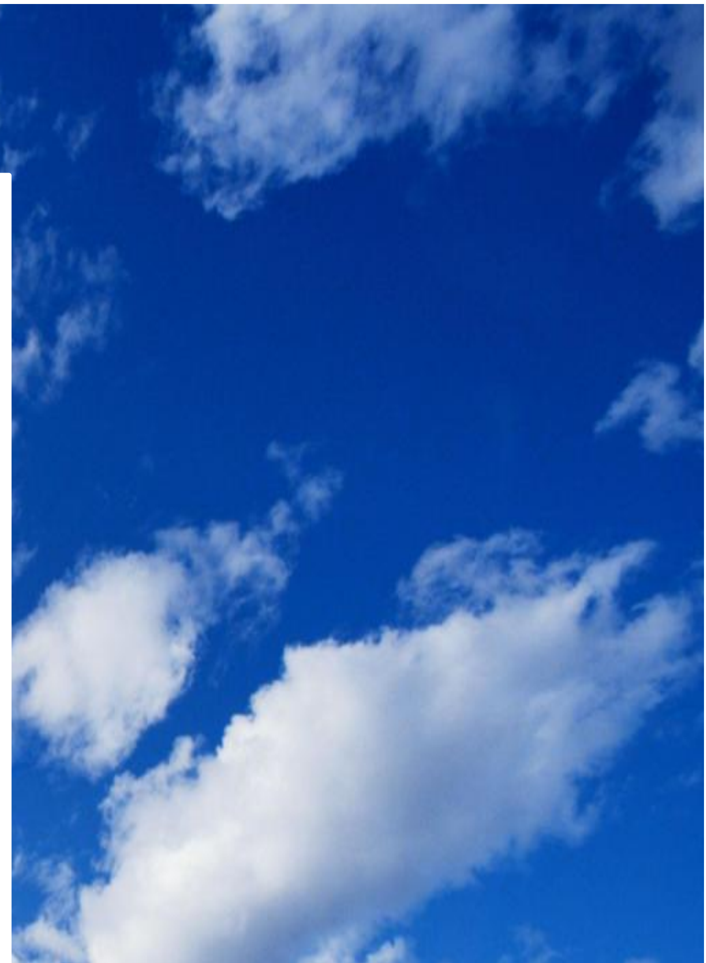
# SULPHUR DIOXIDE ($SO_2$) INSTRUMENTS



Sulphur dioxide is a critical pollutant causing health risks and needs to be monitored using specialized instrumentation.

South African Weather Service

# What is Sulphur Dioxide

Sulphur Dioxide or $SO_2$ is a colorless, non-flammable gas. Once released into the atmosphere, $SO_2$ is converted to other compounds, predominantly Sulphates which is an important precursor of secondary particulate matter. The principle man-made source of $SO_2$ is in waste gas produced by burning fossil fuels (e.g., coal, heavy fuels) and biomass which contain Sulphur. $SO_2$ is produced naturally by volcanic activity.

**Definition**
Sulphur dioxide is the chemical compound with the formula $SO_2$.

It is a toxic gas responsible for the smell of burnt matches. It is released naturally by volcanic activity and is produced as a by-product of copper extraction and the burning of fossil fuels contaminated with sulfur compounds.

The chemical composition of Sulphur Dioxide is written as $SO_2$ which tells us that this gas consists of one Sulphur molecule and two Oxygen molecules.

$$S + O_2 \longrightarrow SO_2$$

$SO_2$ is a bent molecule with $C_{2v}$ symmetry point group. A valence bond theory approach considering just *s* and *p* orbitals would describe the bonding in terms of resonance between two resonance structures.

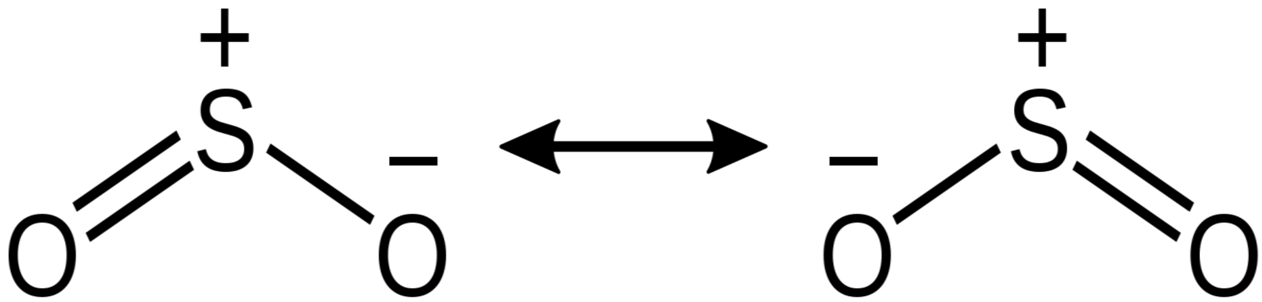


Figure 4.1: Representation of the two resonance structures of $SO_2$.

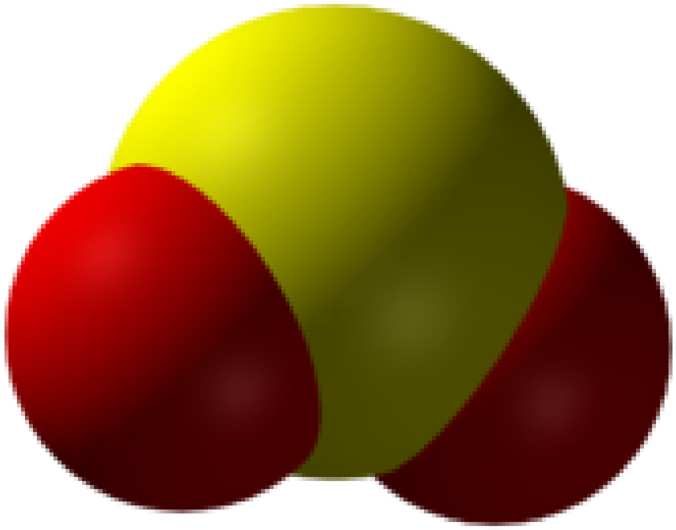


Figure 4.2: 3D representation of the chemical composition of $SO_2$.

# How do we measure $SO_2$

The measurement of Sulphur Dioxide ($SO_2$) in air is based on Fluorescence Spectroscopy principles.

**Definition**
Fluorescence spectroscopy (also known as fluorimetry or spectrofluorometry) is a type of electromagnetic spectroscopy that analyzes fluorescence from a sample. It involves using a beam of light, usually ultraviolet light, that excites the electrons in molecules of certain compounds and causes them to emit light.

To enable us to measure trace levels of $SO_2$ in ambient air we also make use of the principles of fluorescence spectroscopy 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.
- Source that can emit ultraviolet light.
- Measuring chamber for the fluorescence to take place without interference.
- Sensor that can measure the fluorescence.

Although several different type of $SO_2$ 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 $SO_2$ in ambient air. To understand the principle of fluorescence spectroscopy we first need to look at how ultraviolet light affects the $SO_2$ molecules.

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

Light is measured by its wavelength (in nanometers) 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.

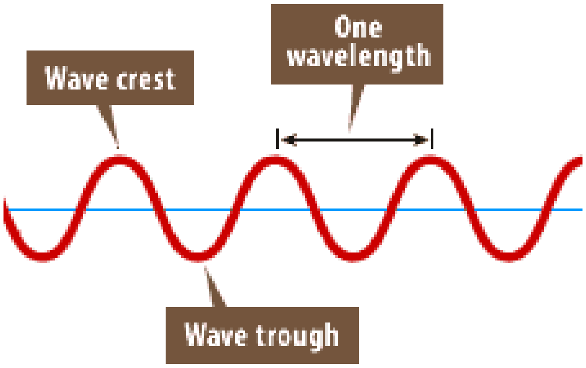



Figure 4.3: Light is measured in wavelength or frequency.

**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.

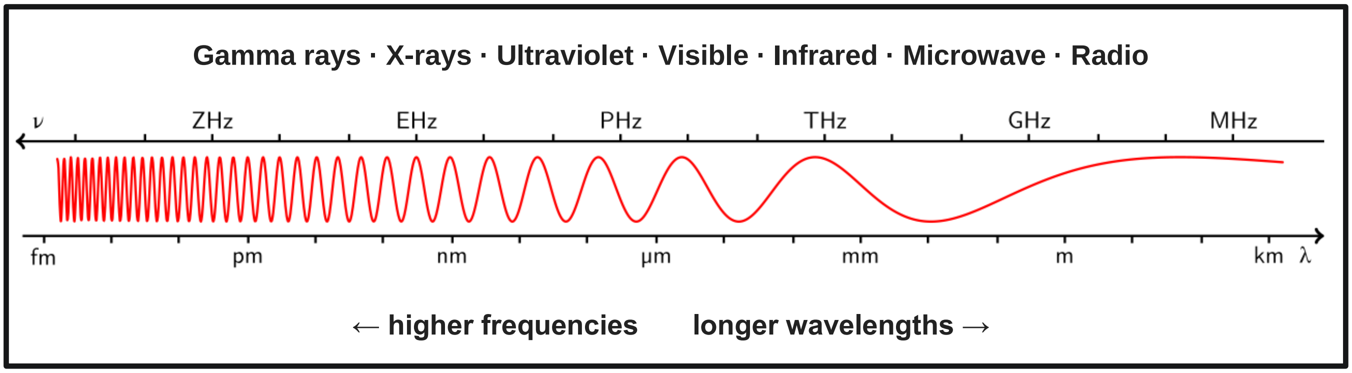



Figure 4.4: The full electromagnetic spectrum.

Light is measured at different wavelengths in nanometres, the electromagnetic spectrum for light is the available range of light that we can measure, the spectrum starts at a wavelength of 200 nM up to 20 µM. Ultraviolet light which is used for fluorescence spectroscopy and which helps us to measure $SO_2$ starts from 200 nM up to 400 nM, the visible light spectrum (VIS) that we see as colors is from 400 nM up to 700 nM. The next range of light is near infrared (NIR) which is measured from 700 nM up to 2 µM and the last spectrum of light is infrared light (IR) which is measured from 2 µM up to 20 µM.

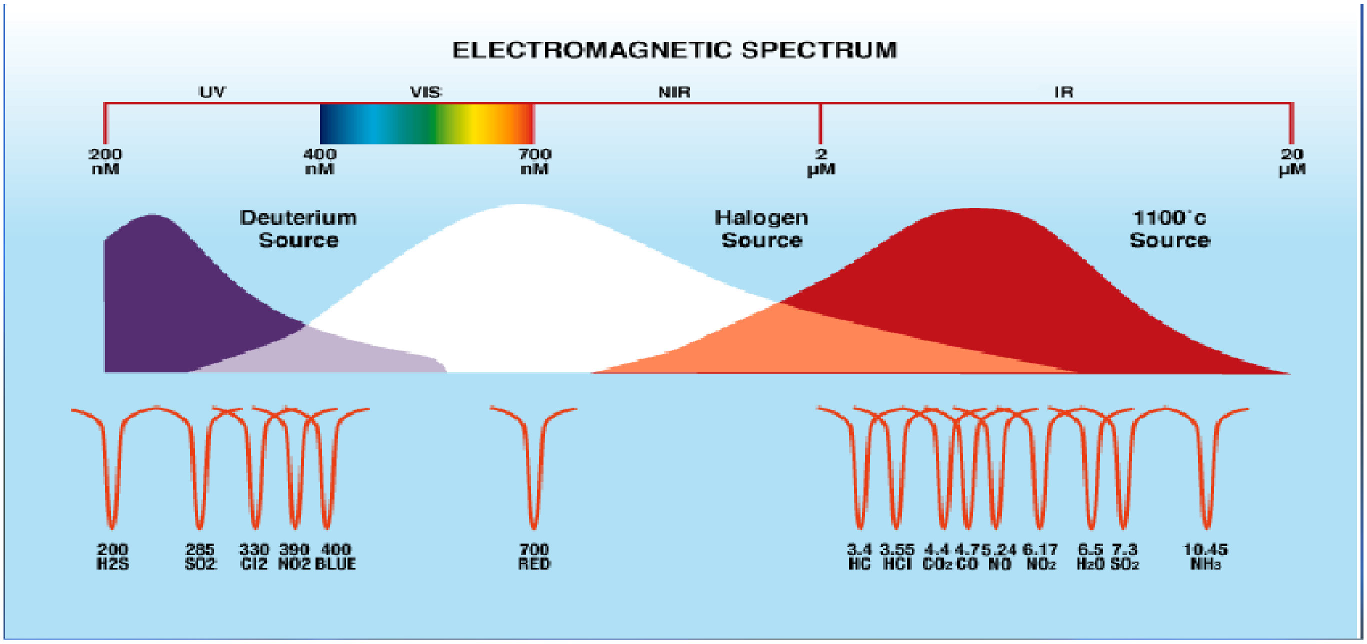



Figure 4.6: The electromagnetic spectrum of light.

# Operation principles of $SO_2$ instruments

Fluorescence spectroscopy in $SO_2$ measurement is the excitation of $SO_2$ molecules by using ultraviolet light. When ultraviolet light at a wavelength of 214 nm is absorbed by an $SO_2$ molecule that molecule is excited by the ultraviolet rays and emits light at a different wavelength of 330 nm and this wavelength of light is measured by a detector.

The detector that is used in $SO_2$ analysers 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 fluorescence and a small current is produced, this current is then amplified by the PMT and the voltage produced can be measured by the microprocessor.

Figure 4.7: Photo multiplier tubes (PMT).

In order to make sure that only a specific wavelength of light is introduced to the sample of $SO_2$ we make us of optic filters. The UV light emits a broad range of UV rays and are normally made from Mercury or Zinc. The 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. This type of optical filter is called a band pass filter.

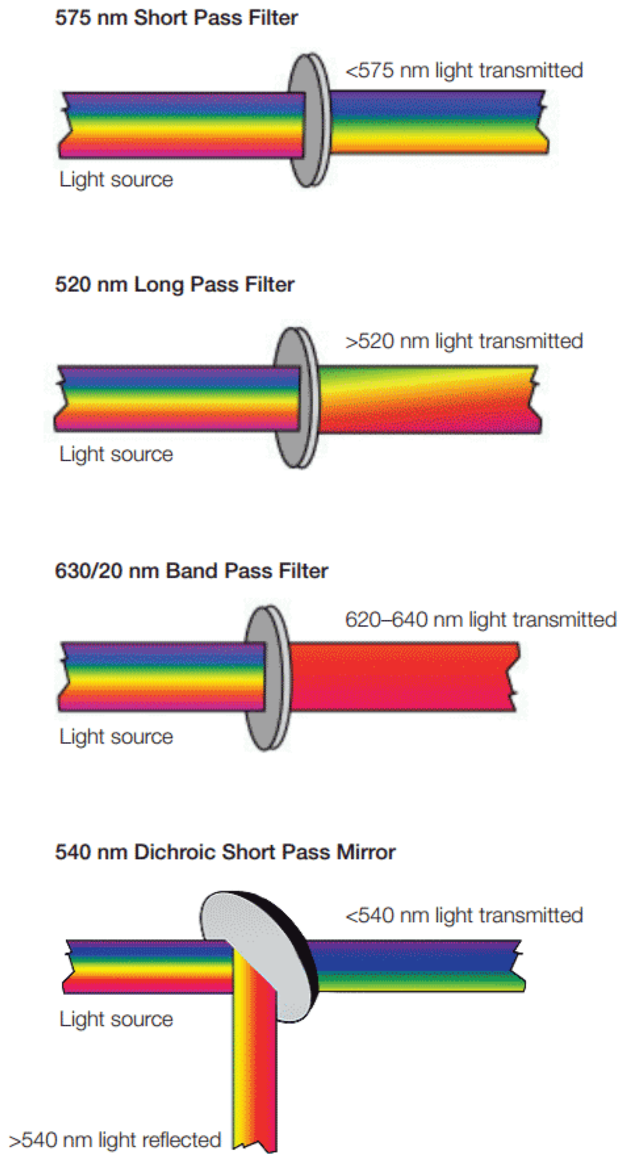



Figure 4.8: Different types of optical filters.

Taking all of the above information into consideration we can measure $SO_2$ particles in air.

1. The light source emits uv-light which is used to excite the particles in the sample but we only want to excite $SO_2$ particles.
2. We make use of a band pass filter which will only allow uv-light with a wavelength of 214nm to pass through.
3. The $SO_2$ particles that are present in the sample is excited by the 214nm uv-light that is absorbed by the particle.
4. The $SO_2$ particles that absorbed the uv-light now emits light at a new wavelength which is 330nm.
5. To measure only the new wavelength of 330nm a second band pass optical filter is installed which will only allow 330nm to pass through.
6. The PMT now can measure the correct wavelength of 330nm and also the frequency of this wavelength and provide a measured value to the user.

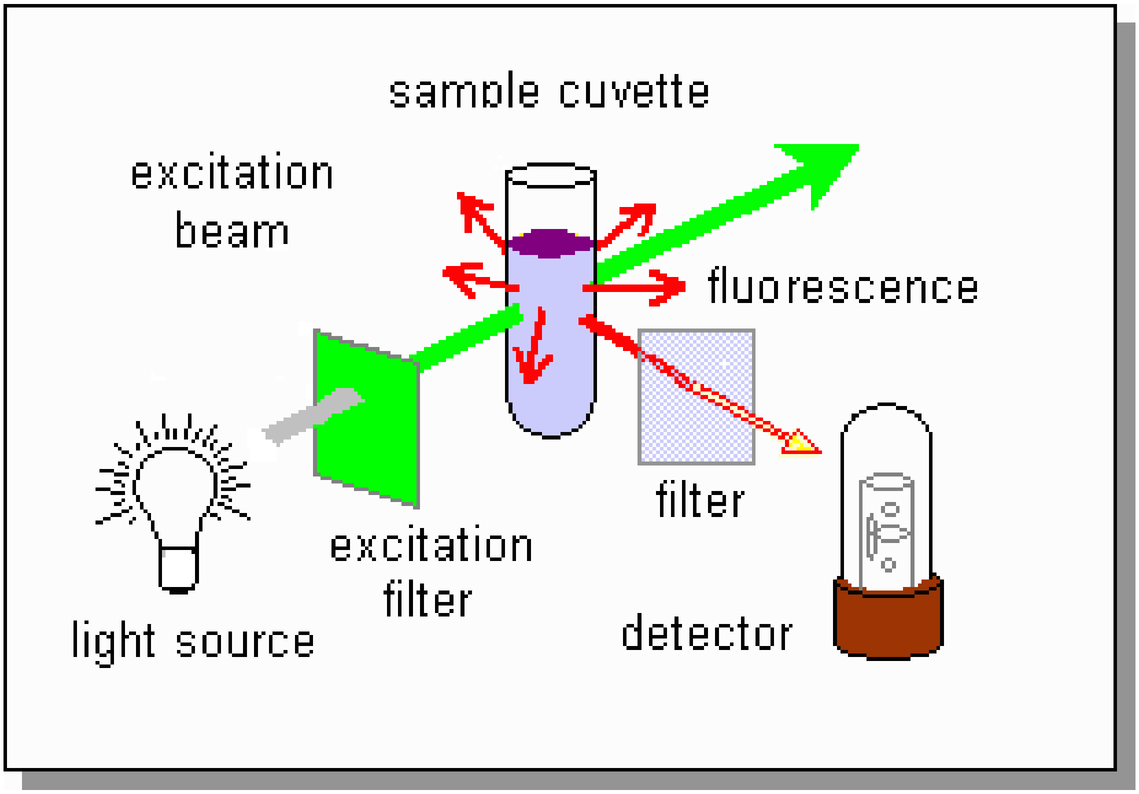



Figure 4.9: Operation principle of $SO_2$ analysers.

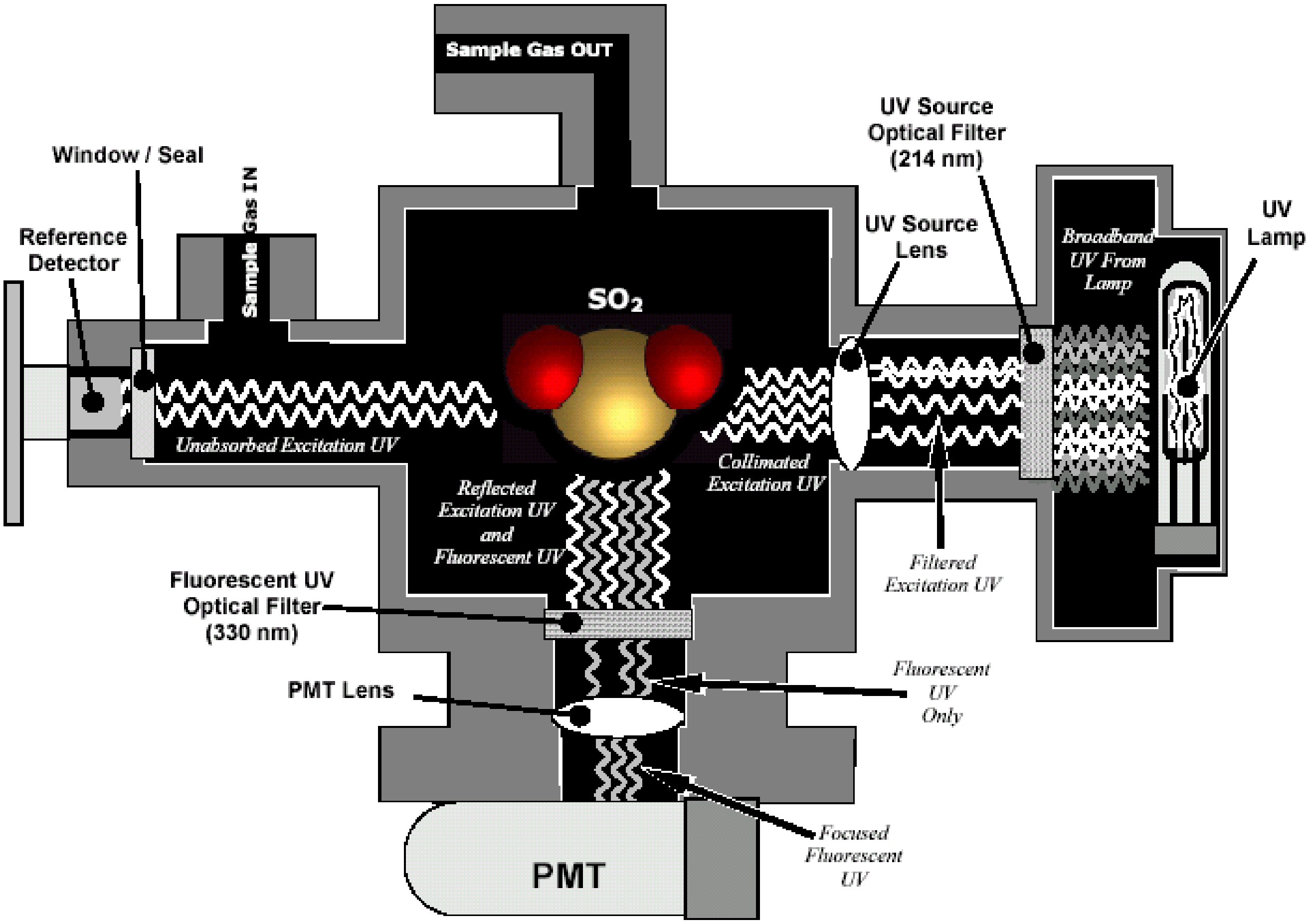



Figure 4.10: Example of the operation principle of $SO_2$ analysers.

The example above is a typical setup of an $SO_2$ analyser, all the previously mentioned components can be seen such as the uv-lamp, the two optical filters and the PMT that measures the frequency or concentration of $SO_2$ particles in the sample.

Also indicated in figure 4.10 is the additional components used to assist the main measurement components in ensuring accurate measurements. Lenses are used to concentrate the uv-light, one is used after the first optical filter (214nm) and one is used after the second optical filter (330nm). Both these lenses ensure the light beam is concentrated and can be measured with accuracy. On the opposite side of the uv-lamp is also a reference detector that measures the light intensity from the uv-lamp, by measuring the intensity the optimality of the uv-lamp can be checked.

# Examples of $SO_2$ instruments

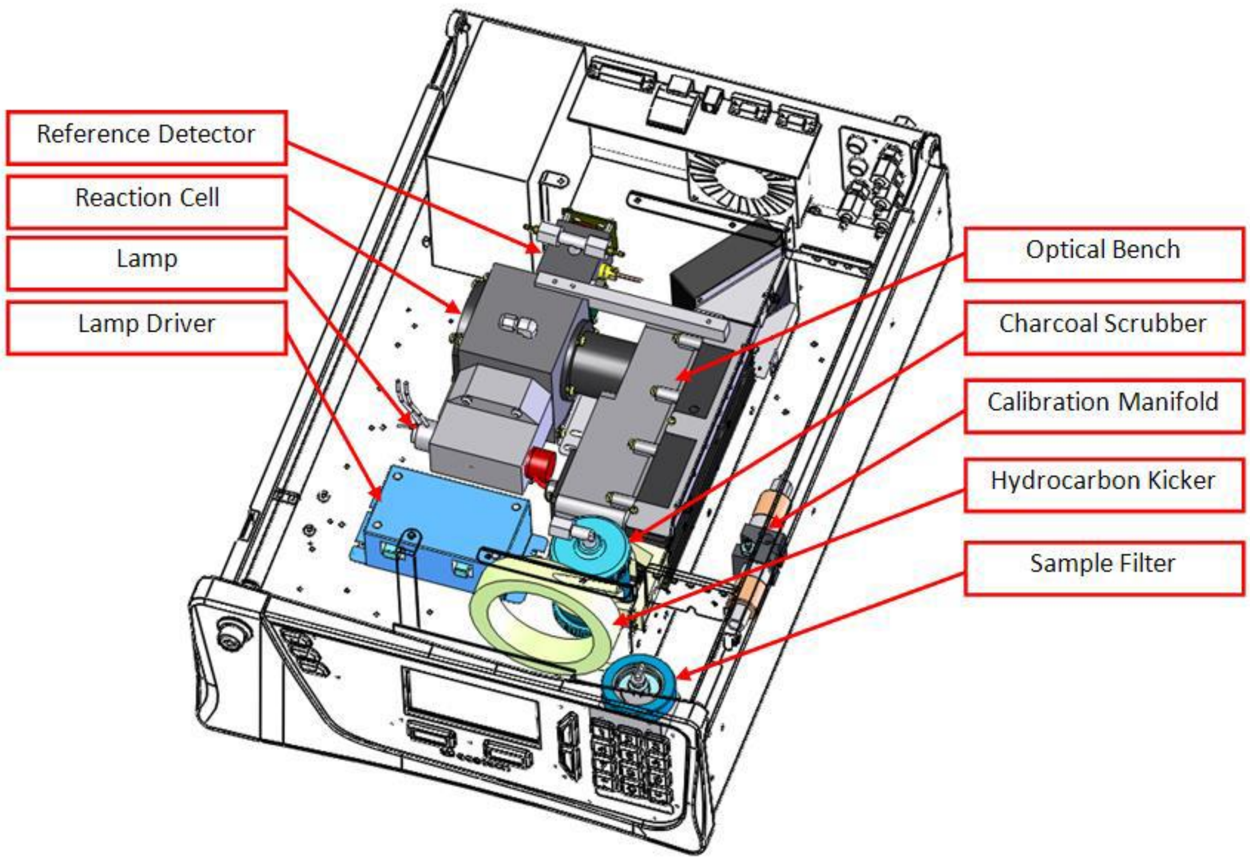



Figure 4.11: Example of the Ecotech Serinus 50 $SO_2$ analyser.

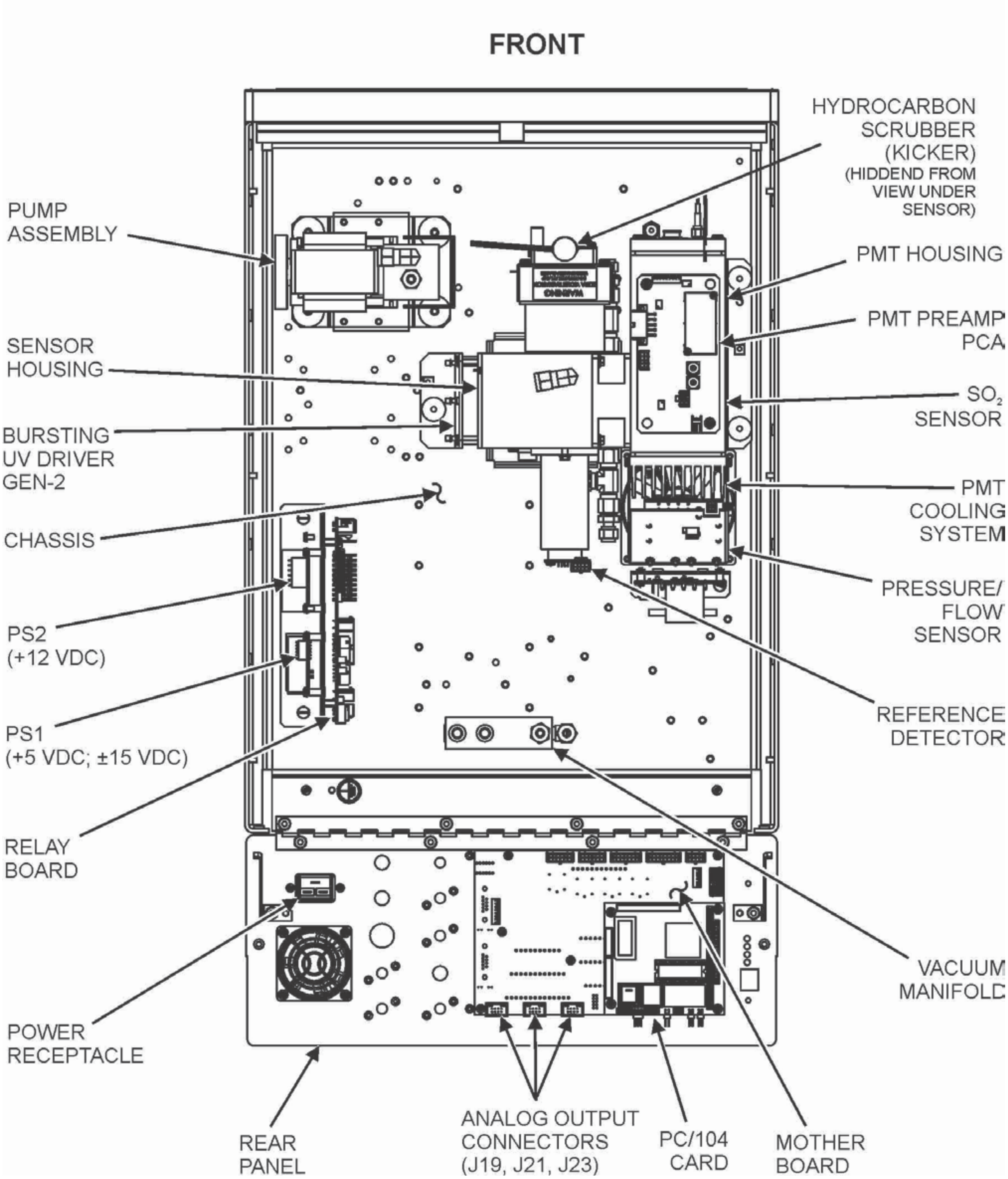



Figure 4.12: Example of API Teledyne T400 $SO_2$ analyser.

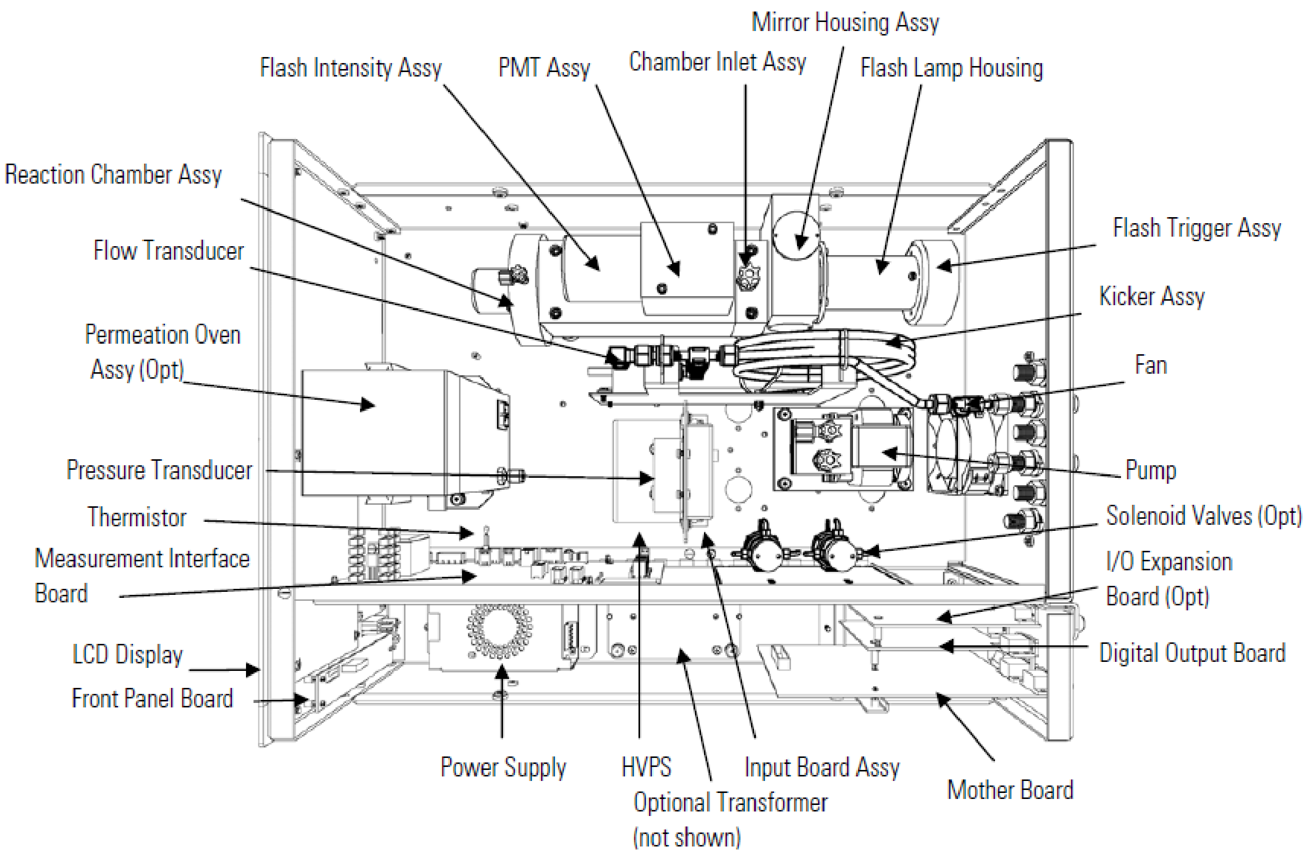



Figure 4.13: Example of Thermo Scientific $SO_2$ analyser.

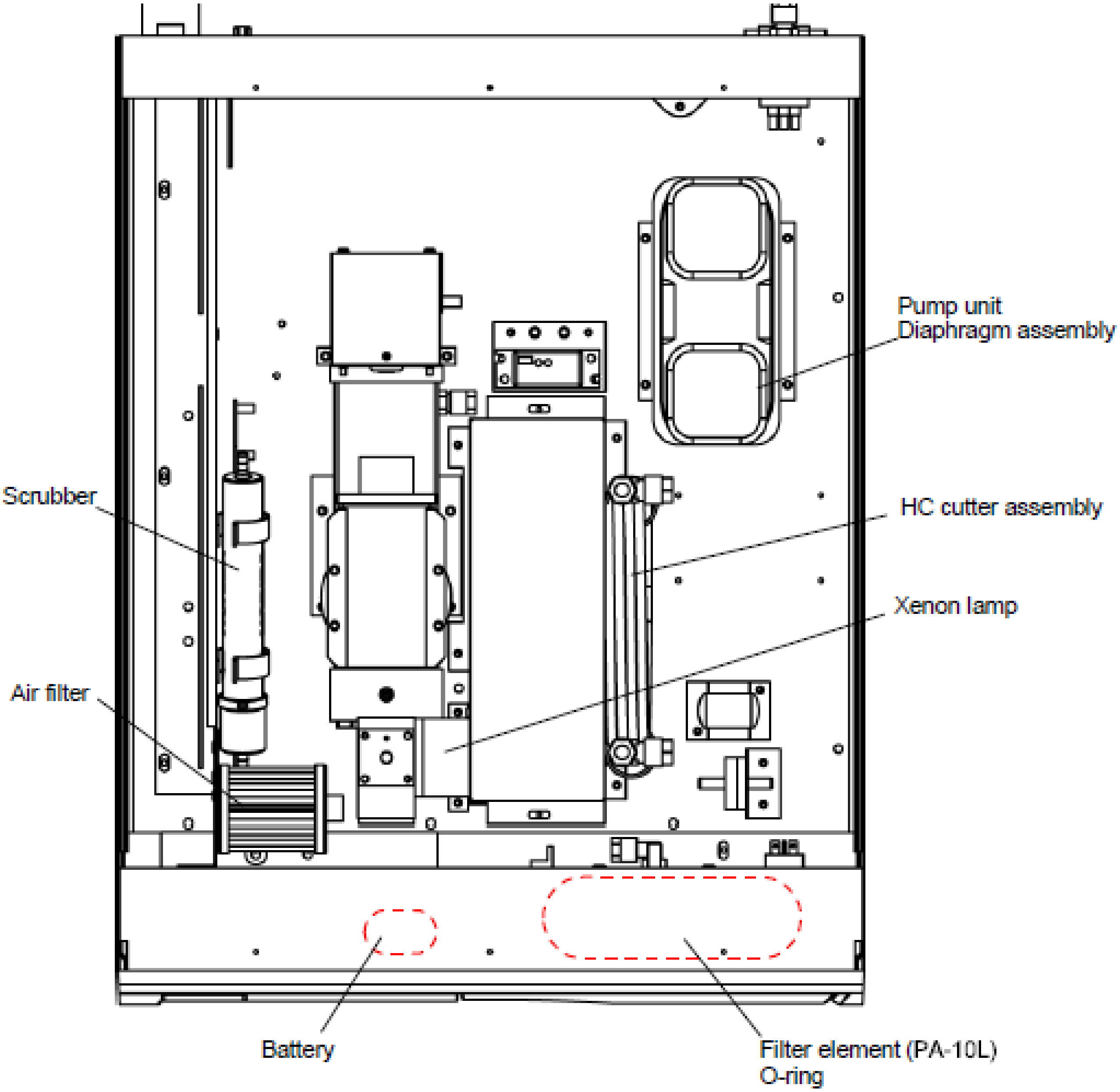
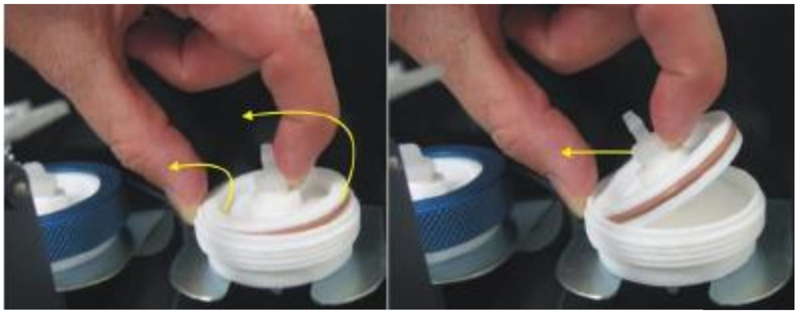


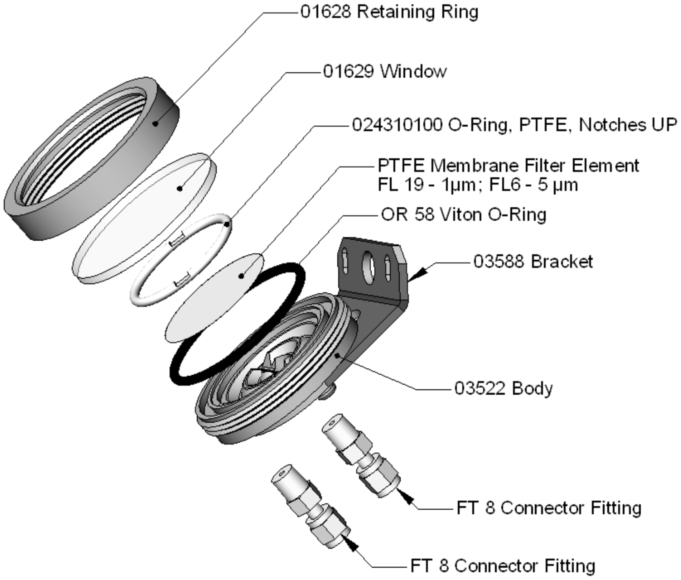

Figure 4.14: Example of Horiba APSA370 $SO_2$ analyser.

# Internal components of $SO_2$ instruments

From the above examples several different internal components of the $SO_2$ 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 4.15: Examples of particulate filters used in an $SO_2$ 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.

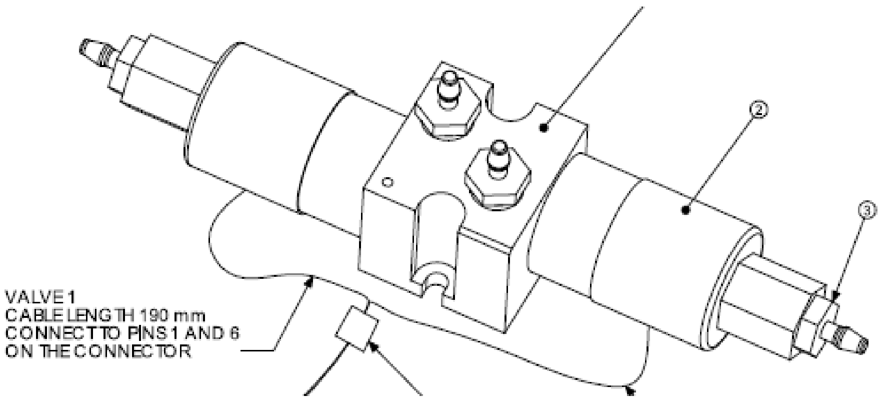
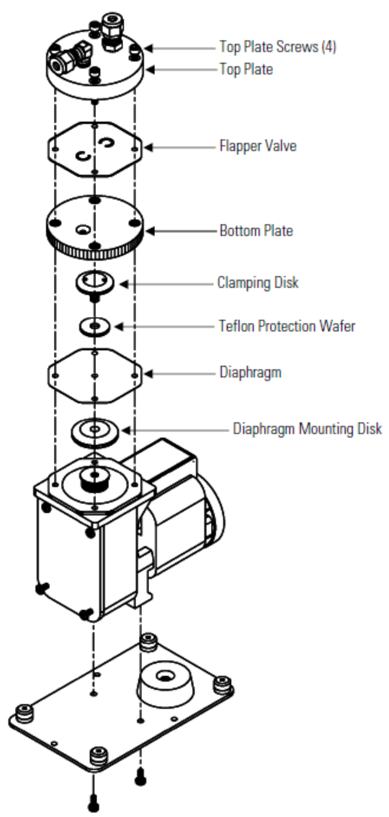



Figure 4.16: Example of valve block used in an $SO_2$ analyser.

## 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 4.17: Example of a pump used to draw air through an $SO_2$ analyser.

# Hydrocarbon kicker

**Definition**
A hydrocarbon is an organic chemical compound composed exclusively of hydrogen and carbon atoms. Hydrocarbons are naturally-occurring compounds and form the basis of crude oil, natural gas, coal, and other important energy sources.

Hydrocarbons are naturally-occurring and can influence the measurement of $SO_2$ particles. To ensure an accurate measurement of $SO_2$ the Hydrocarbons must be removed from the sample before entering the reaction chamber, a Hydrocarbon kicker is used to perform this task.

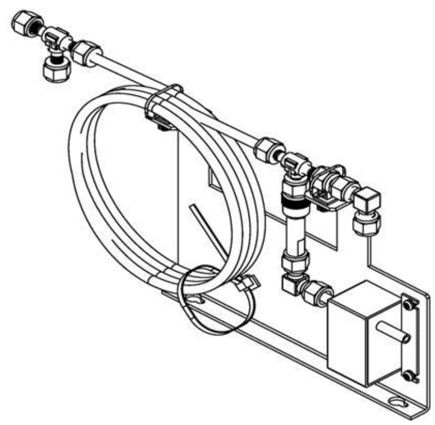
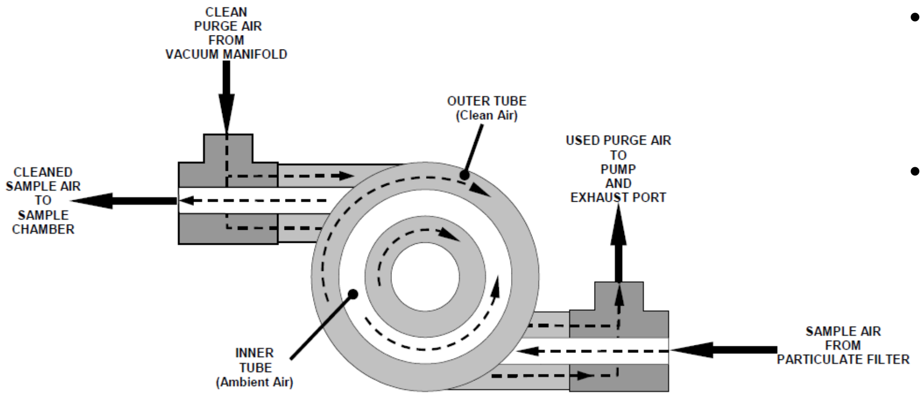


Figure 4.18: Example of a Hydrocarbon kicker used in an $SO_2$ analyser.




- Removes interfering hydrocarbons from the sample air.
- Achieved by counter current exchange, where air with a lower concentration of hydrocarbons moves in an opposite direction to air with a higher concentration.

Figure 4.19: Operation of a Hydrocarbon kicker.

## Reaction Cell

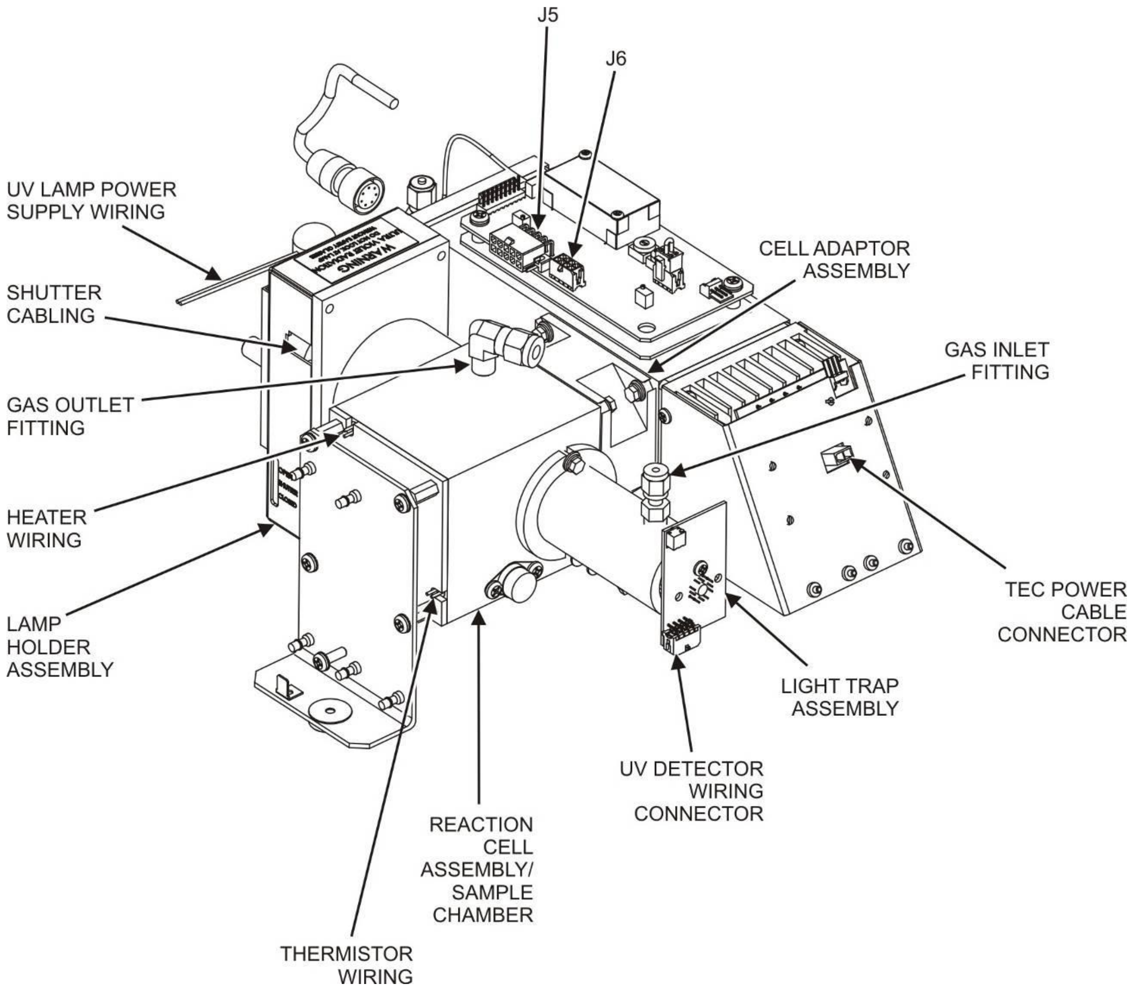



Figure 4.20: Example of the reaction cell on an $SO_2$ analyser.

The reaction cell is where the fluorescence spectroscopy takes place and where the measurement of the sample is performed, the reaction cell is usually made up of six main components:

1. Reaction Chamber
2. Optical filters
3. UV Source
4. UV Reference Detector
5. Photomultiplier Tube (PMT)
6. PMT Cooler
7. PMT High Voltage Supply

## Reaction chamber

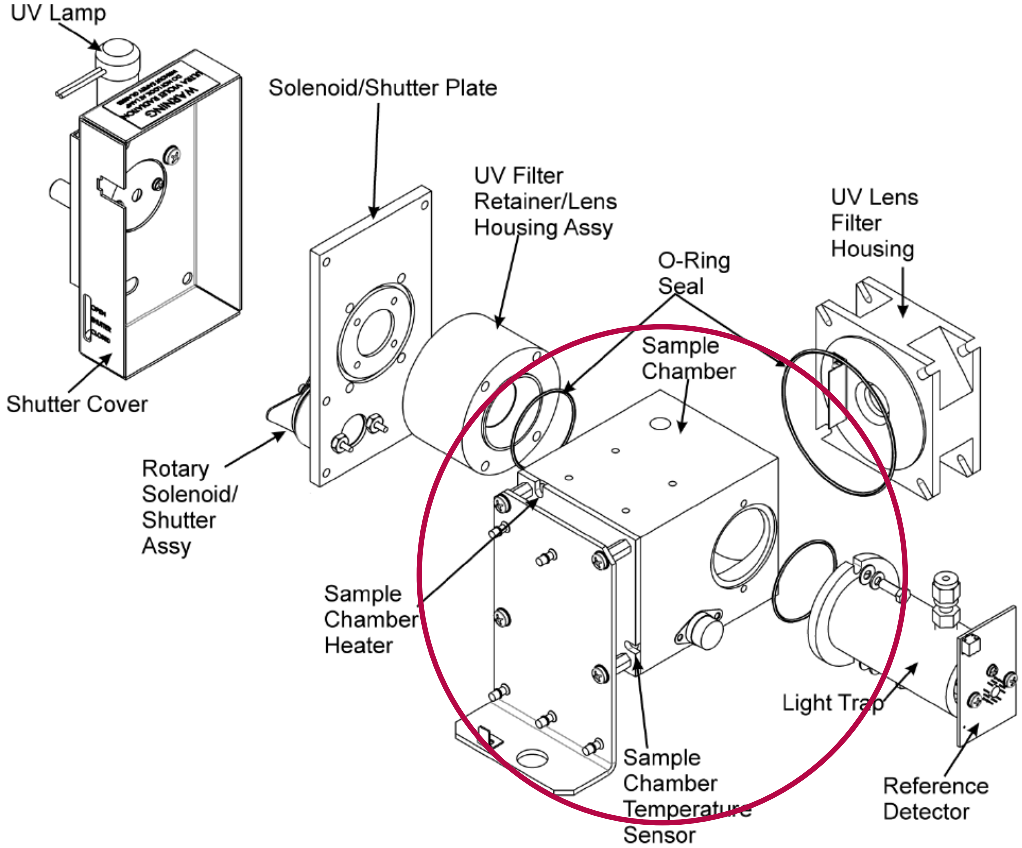



Figure 4.21: Example of the reaction chamber on an $SO_2$ analyser.

This is the sample chamber where the uv-light at 214nm fluoresces the $SO_2$ gas inside the chamber, the $SO_2$ gas is then excited and emits a new wavelength of 330nm which can then be measured by the PMT.

$$SO_2 + uv_{214nm} \rightarrow SO_2^*$$

$$SO_2^* = \text{Excited } SO_2 = SO_{2\ (UV330nm)}$$

## Optical filters

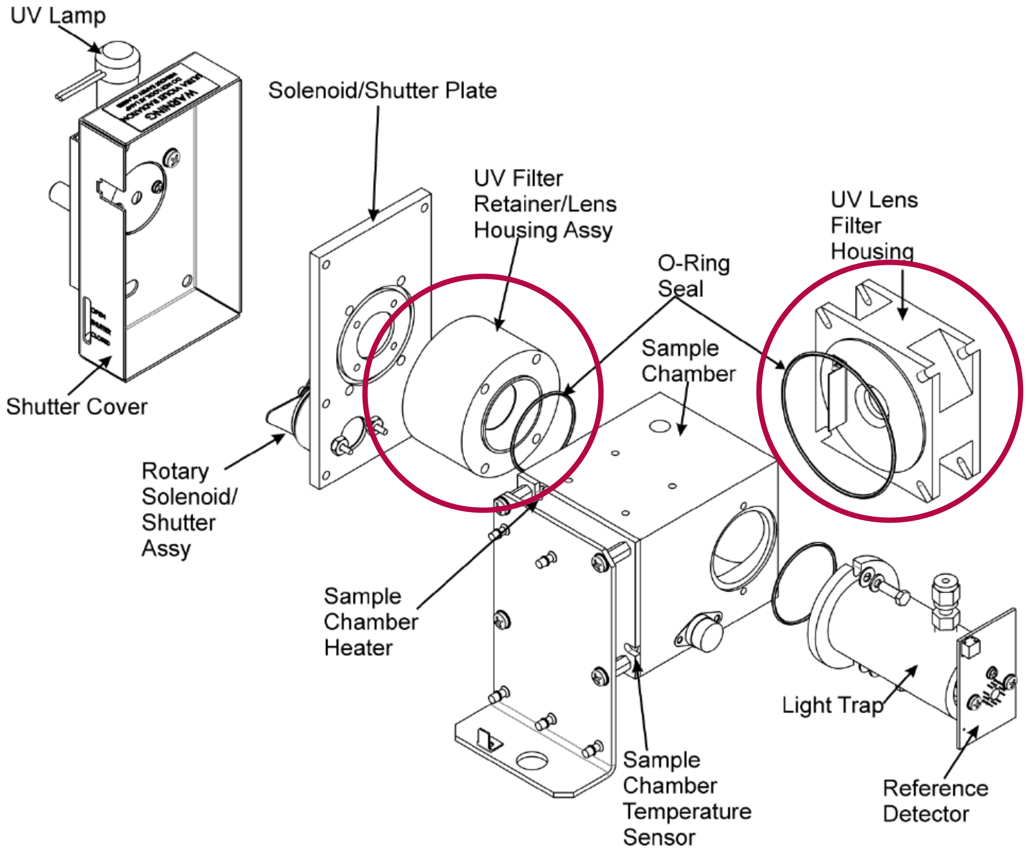



Figure 4.22: Example of the optical filters on an $SO_2$ analyser.

The optical filters are used to filter out the undesired wavelengths of uv-light inside the chamber. The uv-light entering the sample chamber is limited to 214nm and the uv-light that can exit the sample chamber is limited to 330nm. Lenses are used in conjunction with the optical filters to focus uv-light inside the chamber.

## Light source (uv-lamp)

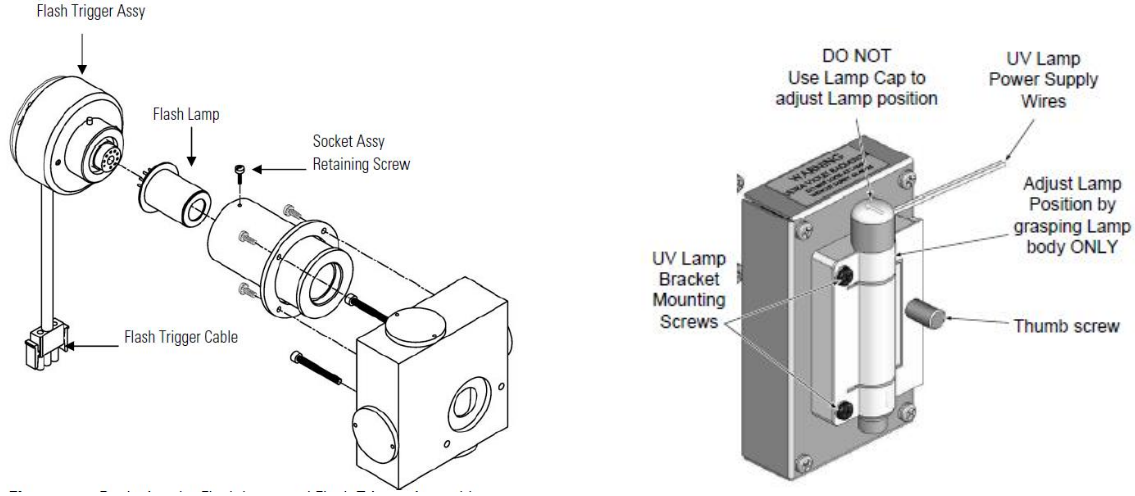


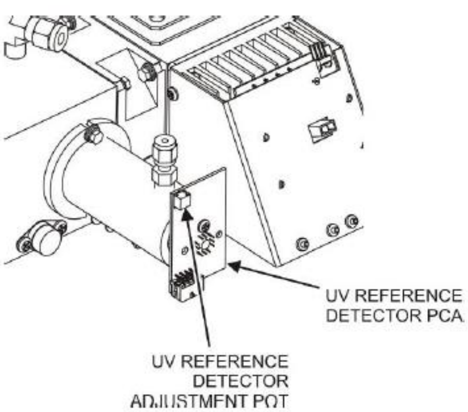

Figure 4.23: Example of the uv-lamp sources used in an $SO_2$ analyser.

The light source is either a zinc or mercury lamp which emits uv radiation over a broad range. Gas instruments usually either make use of one of two types of uv-sources:

- UV Lamp
- UV Flasher

Lamp position: the lamp output is not even across the length of the lamp. During testing the lamp can be adjusted for optimal operation, the lamp may also be adjusted when the lamp intensity

## UV reference detector




The UV reference detector monitors the intensity of the UV radiation.

The detector is used for measurement accuracy during zero checks and also the effectiveness of the lamp and if replacement is required.

The detector is also used to adjust the uv-lamp for optimal operation.

Figure 4.24: Example of the uv-lamp detector used in an $SO_2$ analyser.

## Photomultiplier tube (PMT)

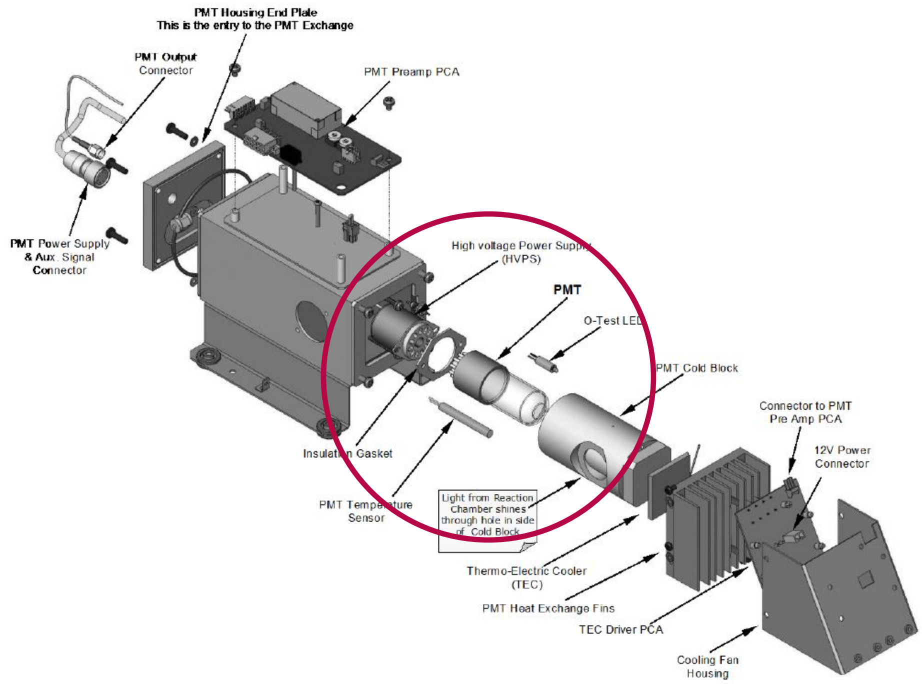
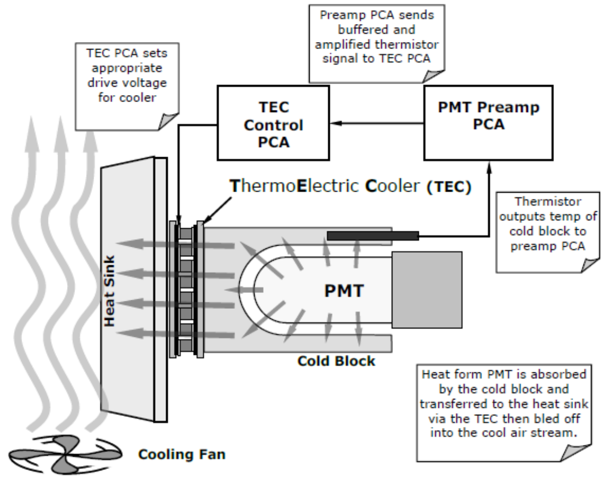



Figure 4.25: Example of the PMT used in an $SO_2$ analyser.

The PMT can detect trace amounts of light and is used to detects the amount of light caused by the excited $SO_2$ particles. The detection of light creates a small voltage which can then be used as a direct measurement of $SO_2$ 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 4.26: Example of the PMT cooler used in an $SO_2$ analyser.

# Flow of an $SO_2$ particle inside the instrument

With the knowledge of the principles of operation and all the internal components used inside an $SO_2$ analyser we can piece together the flow of how a $SO_2$ particle is measured.

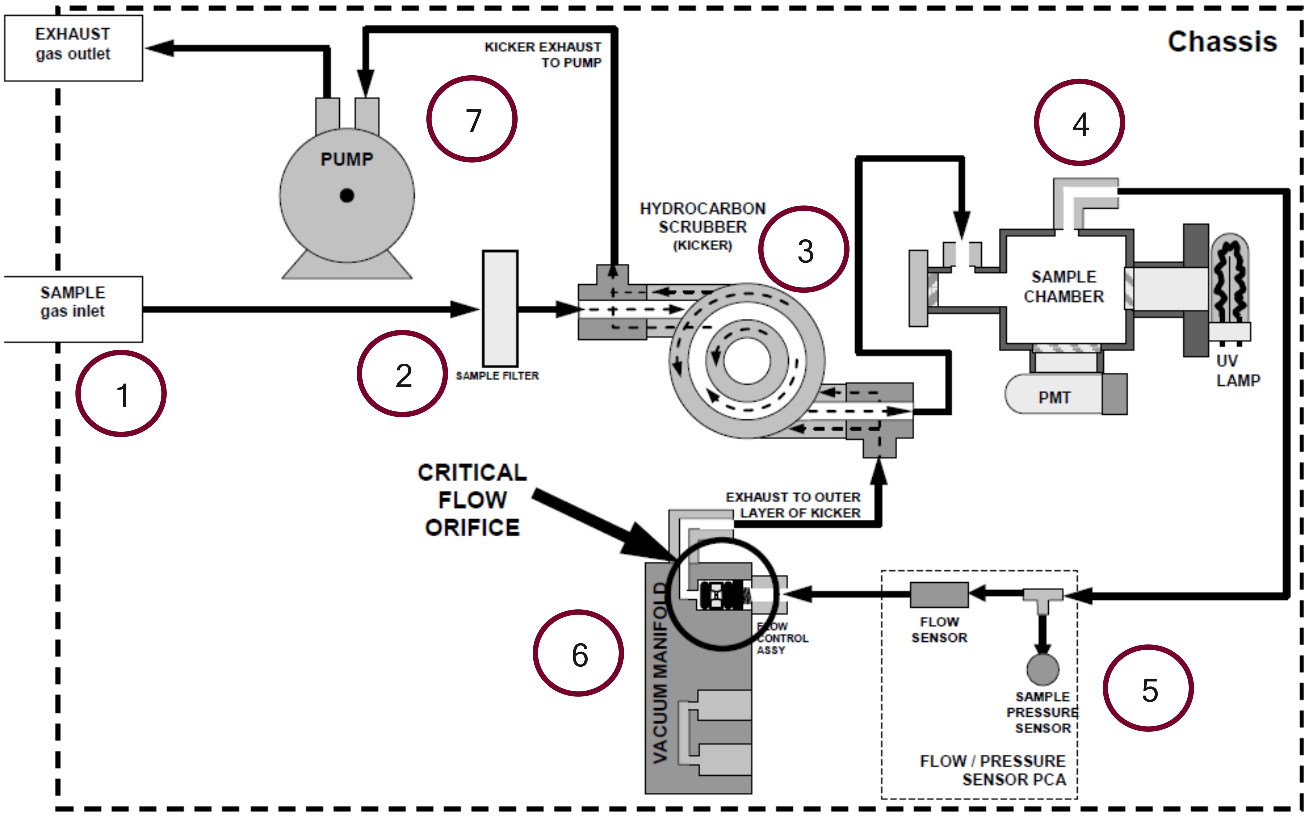



Figure 4.27: Flow process inside an $SO_2$ analyser.

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 will next pass through the Hydrocarbon kicker to further eliminate any unwanted interferences that can negatively affect the measurement of $SO_2$.

4. The sample now enters the reaction cell where the $SO_2$ particles can react with the uv-light created by the uv source. The uv-light with a wavelength of 214nm react with the $SO_2$ particles and exites the particles to emit a new wavelength of 330nm. This light is focused onto the PMT that measures the amount of exited uv-light and the small voltages created by the PMT can now be used to calculate the amount of $SO_2$ present in the sample.

5. The sample can now exit the reaction cell and passes through a flow sensor or pressure sensor to measure the flow of air through the instrument.

6. The next step can sometimes also be introduced between steps 2 and 3, the critical orifice inside the manifold is used to allow the correct amount of air to pass through the instrument.

7. 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 Hydrocarbon kicker and finally exiting the instrument via the pump or exhaust outlet.

# Maintenance of $SO_2$ 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 4.1 provides a schedule of the maintenance and likely repairs that can be performed on an $SO_2$ 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 |
| UV Source | Replace | 6-Monthly if required |
| Pump | Rebuild Head | If flow drops below instrument operational norms |
| Pneumatics | Clean | Annually if required |
| Reaction Cell | Clean | Annually if required |

Table 4.1: Maintenance and repair schedule.

From table 4.1 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 4.15.

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.

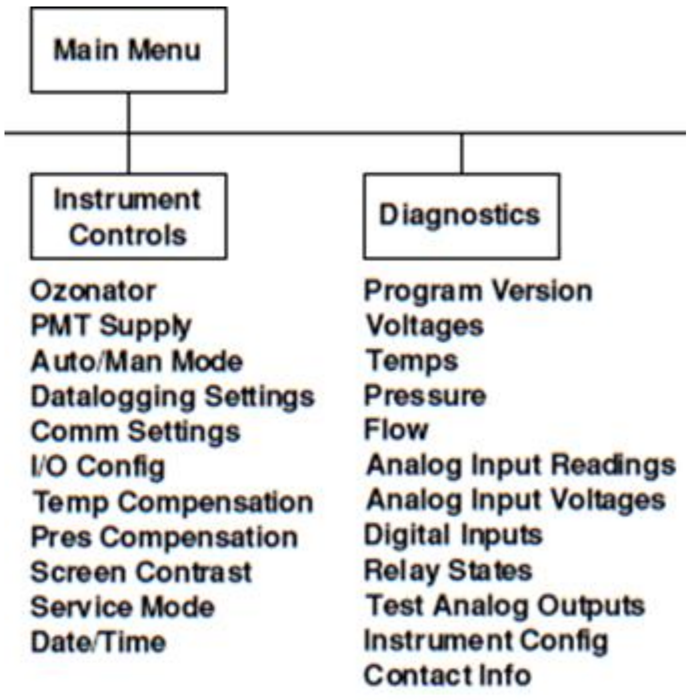



Figure 4.28: Example of instrument menu to check system diagnostics.

| SO$_2$ API Analyser | | | |
|---|---|---|---|
| Manufacturer | API | Station Name: | |
| Model Number | M100 E/ T100 SO2 | Operator Name: | |
| Serial Number | 2984 | Date: | |

**Diagnostics check sheet**

| SO$_2$ Parameters | Nominal value / range (1) | Observed (2) | Value 1=2 (Y/N) | Deviation |
|---|---|---|---|---|
| Range (ppb) | 0 – 500 ppb | 0-500 | | |
| Stability | 0.02 - 2 | 0.07 | | |
| Sample Pressure IN-HG-A | ~2" < Ambient | 23.5 | | |
| Sample Flow (cc/min) | 650 ± 10% | 611.7 | | |
| PMT (Zero Mode) mV | -20 – 150 | | | |
| PMT (Span Mode) mV | 0 – 5000 | | | |
| PMT (NORM Mode) mV | 0 – 5000 | 1.1 | | |
| UV Lamp mV | 900 – 4800 | 10038 | | |
| Str Light | <100 /Zero Air | | | |
| Lamp Ratio mV | 30 – 120% | 24.8 | | |
| Dark PMT mV | -50 - 200 | 8.2 | | |
| Slope | 1 ± 0.3 | 1.015 | | |
| Offset mV | -250 | 0.077 | | |
| HVPS V | 400 - 900 | 539 | | |
| Rcell Temp | 50 ± 1 °C | 50.0 | | |
| Box Temp | Ambient + ~ 5 °C | 30.0 | | |
| PMT Temp | 7 ± 2 °C | 8.4 | | |
| IZS Temp | 50 ± 1 °C | — | | |

Figure 4.29: Example of instrument diagnostics that were recorded.