GHOST Measurement Procedure Standardisations

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# Preface

The standardisations of the observational measurement procedures have been done with the aim of trying to wrangle and digest the scope and of the information provided across all the different in-situ publicly reporting data networks.

Ultimately the goal of capturing all this information in an ordered manner is to provide a huge store of information that provides insight on the quality of observations, and also allow potential biases reported in the observations to be captured and flagged.

# Conceptual Design

For the purpose of standardising the measurement methods, a database containing all the possible measuring instruments by measurement method has been constructed.

Almost all measuring instruments come with an instrumental manual written by the instrument manufacturer that gives information pertaining to the quality of the measuring instrument in measuring specific parameters. These manuals give information such as lower/upper limits of detection, flow rates, precision, accuracy, zero drift, etc. All of this information is captured in standardised variables, named with a preceding ‘documented\_’ string.

This ‘documented’ information however is just applicable for the out of the box, measurement experts in the lab may have optimised the measurement methodology to provide better (or worse!) limits of detections, etc… They sometimes give this information enclosed with the reported data. This ‘documented’ information can therefore be thought as template information, with updated more accurate information provided by the data reporters. All of this reported information is captured in standardised variables, named with a preceding ‘reported\_’ string.

In the majority of cases, a single instrument is responsible for the sampling, filtering and measurement of a specific parameter (notably for measuring for gas-phase species). However in some instances there are multiple stages involved in the measurement procedure, for example, the passive chemical/physical trapping of a particular parameter followed by spectrophotometric analysis at a later date.

The standardisations here therefore needs to be general enough to capture information pertaining to multiple stages of measurement procedures. Therefore all information is separated out between 3 distinct categories: **Primary Sampling**, **Sample Preparation** and **Measurement**.

The **primary sampling** category exists for cases when the sampling is separate from the measuring instrument/method, for example, low volume samplers which filter for specifically-sized aerosols and then are measured by manual gravimetry. Information regarding primary sampling instruments is maintained separately to that for measuring instruments.

**Sample preparation** refers to all processes which affect the ultimate measurement of the specific parameter between primary sampling and the point of measurement, e.g these can be primary measurement methods applied before the ultimate the ultimate measurement of a species.

The **measurement** category refers to all information regarding the ultimate measurement of a parameter. In the majority of cases, the sampling/preparation and measurement is undertaken all by 1 contained instrument.

# Definition Syntax

Some key standardisations are here outlined here:

## Sampling Type

***The “sampling type” refers to the type of sampling used by the primary sampling instrument measurement instrument,, or is the sample preparation phase).***

**continuous:** air is drawn in continuously, with a consistent flow rate.

**injection:** instrument is injected with limited quantities of air.

**continuous injection**: instrument is periodically injected with limited quantities of air.

**passive:** air is not drawn in, rather the air sampled is the ambient air which interacts which measurement apparatus.

**remote:** instrument does not actively sample air, but uses advanced optical techniques to measure parameters in air over long distances.

**manual:** no instrument is used to determine measured values, they are determined manually (e.g. this applies for some colorimetric methods where measured values are derived manually via the colour of reagent after reaction with a compound of interest).

## Sample Preparation

***The “sample preparation” refers to all preparations made before the ultimate measurement of sample.***

***\*These can be multiple in number.***

**flask:** sample was collected/stored in measurement flasks/canisters before analysis.

**preconcentration:** sample was preconcentrated before analysis. This refers to the process of concentrating a sample before analysis, so that trace components won't be overlooked. This is done typically through absorption of the sample onto a cooled, sorbent-packed trap before thermal desorption to transfer very quickly the sample to the analytical system. Can be more than 1 trap, with different adsorbents.

filter: air was passed through a filtering system before analysis, selectively retaining compound(s) of interest.

**filter pack**: sample was collected in a filter pack, selectively retaining compound(s) of interest.

**denuder**: air was passed through a denuder before analysis to selectively retain compound(s) of interest (a denuder is cylindrical or annular conduit or tube internally coated with a reagent that selectively reacts with a stable flow of gas).

**sorbent tube:** sample was passed through a sorbent tube to trap and retain the compound(s) of interest.

**reagent reaction**: sample reacted with a liquid/solid chemical reagent before measurement.

## Measurement Method

***The “measurement method” refers to the method utilised in the ultimate measurement of a parameter.***

**ultraviolet photometry:** Operates on the principle that a specific species efficiently absorbs light at a known wavelength in the UV range. This is the case for ozone, at 253.65nm.

The degree to which the UV light is absorbed by a specific species is directly related to the species concentration as described by the Beer-Lambert Law (I/Io = e−KLC; K = molecular absorption coefficient at STP (308 cm-1 atm-1 for O3), L = optical path length of cell, C = species concentration , I = light intensity of sample gas, Io = light intensity of sample without measured species (reference gas) ).

Typical measurement operation for ozone:

1. Ambient air is continuously drawn through the analyser by a vacuum pump.

2. Sample is split into two flow paths. One path incorporates a scrubber which selectively removes ozone, while the other path does not.

3. Both flow paths are connected to a solenoid valve, which switches at a fixed interval to allow either the sample gas stream (I), or the scrubbed, reference gas stream (Io), to flow through a quartz tube (cell) of accurately known length.

4. Typically a mercury vapour lamp at one end of the quartz cell produces a monochromatic beam of ultraviolet light at 254 nm. A vacuum diode at the opposite end of the cell measures the intensity of transmitted light (I/Io).

5. The intensities of 254 nm UV light transmitted through the sample (I) and ozone-free reference gas streams (Io) are related to the concentration (C) of ozone in the sample gas stream according to the Beer-Lambert Law.

6. The analyzer’s microprocessor calculates the absolute concentration in molecules cm-3, and is then converted to a mixing ratio using in-instrument measured sample temperature and pressure.

Known interferences: Gaseous hydrocarbons with strong absorption at 254 nm, such as aromatic hydrocarbons (i.e., benzene and substituted benzene rings).

**visible photometry:** Operates on the principle that a specific species efficiently absorbs light at a known wavelength in the visible range. This is the case for NO2, at 405nm.

The degree to which the visible light is absorbed by a specific species is directly related to the species concentration as described by the Beer-Lambert Law (C = 1/Lσ \* ln(Io/I) ; σ = absorption cross section (6.06×10-19 cm2 molec-1 for NO2 at 405nm), L = optical path length of cell, C = species concentration , I = light intensity of sample gas, Io = light intensity of sample without measured species (reference gas) ).

Typical measurement operation for NO2 (and indirectly NO):

1. Ambient air is continuously drawn through the instrument by a vacuum pump.

2. An NO2 scrubber valve alternately bypasses and sends the sample air through a heated NO2 scrubber to remove all NO2 in the sample.

3. The NO2-scrubbed/unscrubbed air alternately passes through the optical cell (of known length) and the cell flow meter. Alternate switching of the NO2 scrubber valve once every 5 seconds allows the measurement of a light intensity in the absence of NO2 and presence of NO2.

4. A light-emitting diode (LED) emits a monochromatic beam of light at 405nm. A photodiode at the other end of the cell measures the intensity of transmitted light (I/Io).

5. The intensities of 254 nm light transmitted through the sample (I) and NO2-free reference gas streams (Io) are related to the concentration (C) of ozone in the sample gas stream according to the Beer-Lambert Law.

6. The analyser's microprocessor calculates the absolute concentration in molecules cm-3, and is then converted to a mixing ratio using in-instrument measured sample temperature and pressure.

7. NO is measured indirectly by bypassing the NO2 scrubber and measuring the light intensity while adding (I) or not adding (Io) ozone to convert NO to NO2 according to the well-known reaction: NO + O3 → NO2 + O2

Known interferences: Water vapour, small particles (< 5 um)

**ethylene chemiluminescence:** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of ozone with ethylene, leading to an excited molecule. The return to a fundamental electronic state of the excited molecules is made by luminous radiation in a specific spectrum, which can be measured. The concentration of sample ozone is directly proportional to the intensity of light emitted. The broadband emission is detected using a photomultiplier tube (at 440 nm for ethylene + ozone).

Known interferences: water vapour

**eosin-Y chemiluminescence:** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of ozone with eosin-Y, leading to an excited molecule. The return to a fundamental electronic state of the excited molecules is made by luminous radiation in a specific spectrum, which can be measured. The concentration of sample ozone is directly proportional to the intensity of light emitted. The broadband emission is detected using a photomultiplier tube (at ~560 nm for eosin-Y + ozone).

Known interferences: water vapour

**rhodamine B chemiluminescence:** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of ozone with rhodamine B, leading to an excited molecule. The return to a fundamental electronic state of the excited molecules is made by luminous radiation in a specific spectrum, which can be measured. The concentration of sample ozone is directly proportional to the intensity of light emitted. The broadband emission is detected using a photomultiplier tube (at ~580 nm for rhodamine B + ozone).

Known interferences: water vapour

**chemiluminescence (internal molybdenum converter):** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of NO with ozone (NO+O3 --> NO2\*+O2).

The return to a fundamental electronic state of the excited NO2\* molecules is made by luminous radiation in a 600-3000 nm spectrum (NO2\* --> NO2 + hv), which can be measured.

This method is designed specifically to directly measure NO directly (and NOx/NO2 indirectly). O3 can also be measured by inverting the measurement technique (using canister of NO for reaction).

Typical measurement operation for NO (and NOx/NO2 indirectly):

1. Sample air is drawn into the reaction cell via two separate (alternating) paths; the NO and NOx channels.

2. NO in the first path (NO channel) reacts with ozone (from ozone generator) according to the following reaction: NO+O3 --> NO2\*+O2.

3. The excited NO2 molecules quickly returns to the ground state, releasing the excess energy. This release takes the form of a quantum of light (hv). The distribution of wavelengths for these quanta range between 600 and 3000 nm, with a peak at about 1200 nm (NO2\* --> NO2 +hv (1200nm))

4. Luminescence from the reaction is detected using a photomultiplier tube (PMT). Photons enter the PMT and strike a negatively charged photo cathode causing it to emit electrons. These electrons are accelerated by an applied high voltage and multiplied through a sequence of similar acceleration steps (dynodes) until a useable current signal is generated. The more light present (in this case photons given off by the chemiluminescent reaction described above), the more current is produced. Therefore the more NO present in the reaction cell the more current is produced by the PMT.

5. Before entering the PMT, light is passed through a high-pass optical filter only transparent to wavelengths of light above 645nm. The narrowness of this band of sensitivity allows avoids the potential of extraneous light and radiation that might interfere with the measurement (e.g. some oxides of sulfur can also be chemiluminescent emitters when in contact with O3 but give off light at much shorter wavelengths (usually around 260nm to 480nm)).

6. All things being constant (temperature, pressure, amount of ozone present, etc.), the relationship between the amount of NO present in the reaction cell and the amount of light emitted from the reaction is very linear. If more NO is present, more IR light is produced.

7. In addition, sometimes the excited NO2 collides with other gaseous molecules in the reaction cell chamber or even the molecules of the reaction cell walls and transfers its excess energy to this collision partner (represented by M) without emitting any light at all. In fact, by far the largest portion of the excited NO2 returns to the ground state this way, leaving only a few percent yield of usable chemiluminescence (NO2\* + M --> NO2 + M). The probability of a collision between the NO2\* molecule and a collision partner M increases proportionally with the reaction cell pressure. This non-radiating collision with the NO2\* molecules is usually referred to as third body quenching. Even under the best conditions only about 20% of the NO2 that is formed by the key chemiluminescence reaction is in the excited state. In order to maximize chemiluminescence, the reaction cell is maintained at reduced pressure (thereby reducing the amount of available collision partners) and is supplied with a large, constant excess of ozone (about 3000-5000 ppm) from the internal ozone generator.

8. The second path (NOx channel) travels through a delay loop and a heated molybdenum converter (at 315degC). The heated molybdenum reacts with NO2 in the sample gas and produces a NO gas and a variety of molybdenum. (xNO2 + yMo --> xNO + MyOz (at 315degC)).

9. Once the NO2 in the sample gas has been converted to NO, it is routed to the reaction cell where it undergoes the chemiluminescence reaction and is measured by the PMT.

10. By converting the NO2 in the sample gas into NO, the analyser indirectly measures total NOx content of the sample gas (i.e. the NO present + the converted NO2 present).

11. By switching the sample gas stream in and out of the molybdenum converter every 6 - 10 seconds, the analyser is able to quasi-continuously measure both the NO and the total NOx content.

12. The NO2 concentration is not directly measured but calculated by subtracting the known NO content of the sample gas from the known NOx content.

Known interferences: Water vapour (above 20 ppmv), 3rd body quenching (CO2, SOx), other NOy species converted to NO by molybdenum converter (PAN, ethyl nitrate, ethyl nitrite, HONO, HNO3, methyl nitrate, n-propyl nitrate, n-butyl nitrate, nitrocresol, NH3), other species undergoing chemiluminescence with O3 (SOx).

*\*Not accepted QA type for NO/NOx due to bias in measuring NO2, due to molybdenum converters.*

**chemiluminescence (external molybdenum converter):** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of NO with ozone (NO+O3 --> NO2\*+O2).

The return to a fundamental electronic state of the excited NO2\* molecules is made by luminous radiation in a 600-3000 nm spectrum (NO2\* --> NO2 + hv), which can be measured.

This method is designed specifically to directly measure NO (and NOy indirectly).

Typical measurement operation for NO (and NOy indirectly)

1. Sample air is drawn into the reaction cell via two separate (alternating) paths; the NO and NOy channels.

2. NO in the first path (NO channel) reacts with ozone (from ozone generator) according to the following reaction: NO+O3 --> NO2\*+O2.

3. The excited NO2 molecules quickly returns to the ground state, releasing the excess energy. This release takes the form of a quantum of light (hv). The distribution of wavelengths for these quanta range between 600 and 3000 nm, with a peak at about 1200 nm (NO2\* --> NO2 +hv (1200nm))

4. Luminescence from the reaction is detected using a photomultiplier tube (PMT). Photons enter the PMT and strike a negatively charged photo cathode causing it to emit electrons. These electrons are accelerated by an applied high voltage and multiplied through a sequence of similar acceleration steps (dynodes) until a useable current signal is generated. The more light present (in this case photons given off by the chemiluminescent reaction described above), the more current is produced. Therefore the more NO present in the reaction cell the more current is produced by the PMT.

5. Before entering the PMT, light is passed through a high-pass optical filter only transparent to wavelengths of light above 645nm. The narrowness of this band of sensitivity allows avoids the potential of extraneous light and radiation that might interfere with the measurement (e.g. some oxides of sulfur can also be chemiluminescent emitters when in contact with O3 but give off light at much shorter wavelengths (usually around 260nm to 480nm)).

6. All things being constant (temperature, pressure, amount of ozone present, etc.), the relationship between the amount of NO present in the reaction cell and the amount of light emitted from the reaction is very linear. If more NO is present, more IR light is produced.

7. In addition, sometimes the excited NO2 collides with other gaseous molecules in the reaction cell chamber or even the molecules of the reaction cell walls and transfers its excess energy to this collision partner (represented by M) without emitting any light at all. In fact, by far the largest portion of the excited NO2 returns to the ground state this way, leaving only a few percent yield of usable chemiluminescence (NO2\* + M --> NO2 + M). The probability of a collision between the NO2\* molecule and a collision partner M increases proportionally with the reaction cell pressure. This non-radiating collision with the NO2\* molecules is usually referred to as third body quenching. Even under the best conditions only about 20% of the NO2 that is formed by the key chemiluminescence reaction is in the excited state. In order to maximize chemiluminescence, the reaction cell is maintained at reduced pressure (thereby reducing the amount of available collision partners) and is supplied with a large, constant excess of ozone (about 3000-5000 ppm) from the internal ozone generator.

8. The second path (NOy channel) before entering the instrument enters an externally mounted heated molybdenum converter (at 315degC), with less than 10cm tubing between the converter and sample entry. The heated molybdenum reacts with NOy in the sample gas and produces a NO gas and a variety of molybdenum (3NOy + Mo --> 3NO + MoO3 (at 315degC)). Minimising the transit time and surface contact area between the sample inlet and converter enables the conversion of labile components of NOy.

9. Once the NOy in the sample gas has been converted to NO, it is routed to the reaction cell where it undergoes the chemiluminescence reaction and is measured by the PMT.

10. By converting the NOy in the sample gas into NO, the analyser indirectly measures total NOy content of the sample gas (i.e. the NO present + the converted NO2 present).

11. By switching the sample gas stream in and out of the molybdenum converter every 6 - 10 seconds, the analyser is able to quasi-continuously measure both the NO and the total NOy content.

Known interferences: Water vapour (above 20 ppmv), 3rd body quenching (CO2, SOx), other species undergoing chemiluminescence with O3 (SOx).

**chemiluminescence (internal photolytic converter):** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of NO with ozone (NO+O3 --> NO2\*+O2).

The return to a fundamental electronic state of the excited NO2\* molecules is made by luminous radiation in a 600-3000 nm spectrum (NO2\* --> NO2 + hv), which can be measured.

This method is designed specifically to directly measure NO (and NOx/NO2 indirectly).

Typical measurement operation for NO (and NOx/NO2 indirectly):

1. Sample air is drawn into the reaction cell via two separate (alternating) paths; the NO and NOx channels.

2. NO in the first path (NO channel) reacts with ozone (from ozone generator) according to the following reaction: NO+O3 --> NO2\*+O2.

3. The excited NO2 molecules quickly returns to the ground state, releasing the excess energy. This release takes the form of a quantum of light (hv). The distribution of wavelengths for these quanta range between 600 and 3000 nm, with a peak at about 1200 nm (NO2\* --> NO2 +hv (1200nm))

4. Luminescence from the reaction is detected using a photomultiplier tube (PMT). Photons enter the PMT and strike a negatively charged photo cathode causing it to emit electrons. These electrons are accelerated by an applied high voltage and multiplied through a sequence of similar acceleration steps (dynodes) until a useable current signal is generated. The more light present (in this case photons given off by the chemiluminescent reaction described above), the more current is produced. Therefore the more NO present in the reaction cell the more current is produced by the PMT.

5. Before entering the PMT, light is passed through a high-pass optical filter only transparent to wavelengths of light above 645nm. The narrowness of this band of sensitivity allows avoids the potential of extraneous light and radiation that might interfere with the measurement (e.g. some oxides of sulfur can also be chemiluminescent emitters when in contact with O3 but give off light at much shorter wavelengths (usually around 260nm to 480nm)).

6. All things being constant (temperature, pressure, amount of ozone present, etc.), the relationship between the amount of NO present in the reaction cell and the amount of light emitted from the reaction is very linear. If more NO is present, more IR light is produced.

7. In addition, sometimes the excited NO2 collides with other gaseous molecules in the reaction cell chamber or even the molecules of the reaction cell walls and transfers its excess energy to this collision partner (represented by M) without emitting any light at all. In fact, by far the largest portion of the excited NO2 returns to the ground state this way, leaving only a few percent yield of usable chemiluminescence (NO2\* + M --> NO2 + M). The probability of a collision between the NO2\* molecule and a collision partner M increases proportionally with the reaction cell pressure. This non-radiating collision with the NO2\* molecules is usually referred to as third body quenching. Even under the best conditions only about 20% of the NO2 that is formed by the key chemiluminescence reaction is in the excited state. In order to maximize chemiluminescence, the reaction cell is maintained at reduced pressure (thereby reducing the amount of available collision partners) and is supplied with a large, constant excess of ozone (about 3000-5000 ppm) from the internal ozone generator.

8. The second path (NOx channel) travels through a delay loop and a photolytic converter. As the sample gas passes through the converter chamber it is exposed to blue light at specific wavelengths (350-420 nm) from a photolytic light source (blue LEDs, metal halide). This selectively converts NO2 to NO with negligible radiant heating or interference from other gases (NO2 +hv (350-420nm) --> NO + O).

9. Once the NO2 in the sample gas has been converted to NO, it is routed to the reaction cell where it undergoes the chemiluminescence reaction and is measured by the PMT.

10. By converting the NO2 in the sample gas into NO, the analyser indirectly measures total NOx content of the sample gas (i.e. the NO present + the converted NO2 present).

11. By switching the sample gas stream in and out of the photolytic converter every 6 - 10 seconds, the analyser is able to quasi-continuously measure both the NO and the total NOx content.

12. The NO2 concentration is not directly measured but calculated by subtracting the known NO content of the sample gas from the known NOx content.

Known interferences: Water vapour (above 20 ppmv), 3rd body quenching (CO2, SOx), thermal decomposition of PAN to NO2 within the photolysis cell

**chemiluminescence (internal molybdenum and quartz converters):** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of NO with ozone (NO+O3 --> NO2\*+O2).

The return to a fundamental electronic state of the excited NO2\* molecules is made by luminous radiation in a 600-3000 nm spectrum (NO2\* --> NO2 + hv), which can be measured.

This method is designed specifically to directly measure NO (and NH3/NOx/NO2 indirectly).

Typical measurement operation for NO (and NH3/NOx/NO2 indirectly)

1. Sample air is drawn into the reaction cell via three separate (alternating) paths; the NO, TNx and NOx channels.

2. NO in the first path (NO channel) reacts with ozone (from ozone generator) according to the following reaction: NO+O3 --> NO2\*+O2.

3. The excited NO2 molecules quickly returns to the ground state, releasing the excess energy. This release takes the form of a quantum of light (hv). The distribution of wavelengths for these quanta range between 600 and 3000 nm, with a peak at about 1200 nm (NO2\* --> NO2 +hv (1200nm))

4. Luminescence from the reaction is detected using a photomultiplier tube (PMT). Photons enter the PMT and strike a negatively charged photo cathode causing it to emit electrons. These electrons are accelerated by an applied high voltage and multiplied through a sequence of similar acceleration steps (dynodes) until a useable current signal is generated. The more light present (in this case photons given off by the chemiluminescent reaction described above), the more current is produced. Therefore the more NO present in the reaction cell the more current is produced by the PMT.

5. Before entering the PMT, light is passed through a high-pass optical filter only transparent to wavelengths of light above 645nm. The narrowness of this band of sensitivity allows avoids the potential of extraneous light and radiation that might interfere with the measurement (e.g. some oxides of sulfur can also be chemiluminescent emitters when in contact with O3 but give off light at much shorter wavelengths (usually around 260nm to 480nm)).

6. All things being constant (temperature, pressure, amount of ozone present, etc.), the relationship between the amount of NO present in the reaction cell and the amount of light emitted from the reaction is very linear. If more NO is present, more IR light is produced.

7. In addition, sometimes the excited NO2 collides with other gaseous molecules in the reaction cell chamber or even the molecules of the reaction cell walls and transfers its excess energy to this collision partner (represented by M) without emitting any light at all. In fact, by far the largest portion of the excited NO2 returns to the ground state this way, leaving only a few percent yield of usable chemiluminescence (NO2\* + M --> NO2 + M). The probability of a collision between the NO2\* molecule and a collision partner M increases proportionally with the reaction cell pressure. This non-radiating collision with the NO2\* molecules is usually referred to as third body quenching. Even under the best conditions only about 20% of the NO2 that is formed by the key chemiluminescence reaction is in the excited state. In order to maximize chemiluminescence, the reaction cell is maintained at reduced pressure (thereby reducing the amount of available collision partners) and is supplied with a large, constant excess of ozone (about 3000-5000 ppm) from the internal ozone generator.

8. In the second path (TNx channel), sample air is passed through an internal heated quartz converter (at 750 degC). The heated quartz reacts with NH3 and NO2 in the sample gas and produces a NO gas (4NH3 + 5O2 --> 4NO + 6H2O).

9. Once the NO2 and NH3 in the sample gas has been converted to NO, it is routed to the reaction cell where it undergoes the chemiluminescence reaction and is measured by the PMT.

10. By converting the NO2 and NH3 in the sample gas into NO, the analyser indirectly measures total TNx content of the sample gas.

11. The third path (NOx channel) travels through a delay loop and a heated molybdenum converter (at 315degC). The heated molybdenum reacts with NO2 in the sample gas and produces a NO gas and a variety of molybdenum. (xNO2 + yMo --> xNO + MyOz (at 315degC)).

12. Once the NO2 in the sample gas has been converted to NO, it is routed to the reaction cell where it undergoes the chemiluminescence reaction and is measured by the PMT.

13. By converting the NO2 in the sample gas into NO, the analyser measures total NOx content of the sample gas (i.e. the NO present + the converted NO2 present).

14. By switching the sample gas stream between the 3 streams frequently, the analyser is able to quasi-continuously measure both the NO, the total NOx content and TNx.

15. NO2 is indirectly calculated by subtracting the known NO content of the sample gas from the known NOx content.

16. NH3 is indirectly calculated by subtracting the known NOx content of the sample gas from the known TNx content.

Known interferences: Water vapour (above 20 ppmv), 3rd body quenching (CO2, SOx), other NOy species converted to NO by molybdenum converter (PAN, ethyl nitrate, ethyl nitrite, HONO, HNO3, methyl nitrate, n-propyl nitrate, n-butyl nitrate, nitrocresol, NH3), other species undergoing chemiluminescence with O3 (SOx).

*\*Not accepted QA type for NO/NOx due to bias in measuring NO2, due to molybdenum converters.*

**chemiluminescence (internal molybdenum converter and external stainless steel converter):** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of NO with ozone (NO+O3 --> NO2\*+O2).

The return to a fundamental electronic state of the excited NO2\* molecules is made by luminous radiation in a 600-3000 nm spectrum (NO2\* --> NO2 + hv), which can be measured.

This method is designed specifically to directly measure NO (and NH3/NOx/NO2 indirectly).

Typical measurement operation for NO (and NH3/NOx/NO2 indirectly)

1. Sample air is drawn into the reaction cell via three separate (alternating) paths; the NO, TNx and NOx channels.

2. NO in the first path (NO channel) reacts with ozone (from ozone generator) according to the following reaction: NO+O3 --> NO2\*+O2.

3. The excited NO2 molecules quickly returns to the ground state, releasing the excess energy. This release takes the form of a quantum of light (hv). The distribution of wavelengths for these quanta range between 600 and 3000 nm, with a peak at about 1200 nm (NO2\* --> NO2 +hv (1200nm))

4. Luminescence from the reaction is detected using a photomultiplier tube (PMT). Photons enter the PMT and strike a negatively charged photo cathode causing it to emit electrons. These electrons are accelerated by an applied high voltage and multiplied through a sequence of similar acceleration steps (dynodes) until a useable current signal is generated. The more light present (in this case photons given off by the chemiluminescent reaction described above), the more current is produced. Therefore the more NO present in the reaction cell the more current is produced by the PMT.

5. Before entering the PMT, light is passed through a high-pass optical filter only transparent to wavelengths of light above 645nm. The narrowness of this band of sensitivity allows avoids the potential of extraneous light and radiation that might interfere with the measurement (e.g. some oxides of sulfur can also be chemiluminescent emitters when in contact with O3 but give off light at much shorter wavelengths (usually around 260nm to 480nm)).

6. All things being constant (temperature, pressure, amount of ozone present, etc.), the relationship between the amount of NO present in the reaction cell and the amount of light emitted from the reaction is very linear. If more NO is present, more IR light is produced.

7. In addition, sometimes the excited NO2 collides with other gaseous molecules in the reaction cell chamber or even the molecules of the reaction cell walls and transfers its excess energy to this collision partner (represented by M) without emitting any light at all. In fact, by far the largest portion of the excited NO2 returns to the ground state this way, leaving only a few percent yield of usable chemiluminescence (NO2\* + M --> NO2 + M). The probability of a collision between the NO2\* molecule and a collision partner M increases proportionally with the reaction cell pressure. This non-radiating collision with the NO2\* molecules is usually referred to as third body quenching. Even under the best conditions only about 20% of the NO2 that is formed by the key chemiluminescence reaction is in the excited state. In order to maximize chemiluminescence, the reaction cell is maintained at reduced pressure (thereby reducing the amount of available collision partners) and is supplied with a large, constant excess of ozone (about 3000-5000 ppm) from the internal ozone generator.

8. In the second path (TNx channel), sample air is first drawn through an externally mounted heated stainless steel converter (at 750 degC). The heated stainless steel reacts with NH3 and NO2 in the sample gas and produces a NO gas (4NH3 + 5O2 --> 4NO + 6H2O).

9. Once the NO2 and NH3 in the sample gas has been converted to NO, it is routed to the reaction cell where it undergoes the chemiluminescence reaction and is measured by the PMT.

10. By converting the NO2 and NH3 in the sample gas into NO, the analyser indirectly measures total TNx content of the sample gas.

11. The third path (NOx channel) travels through a delay loop and a heated molybdenum converter (at 315degC). The heated molybdenum reacts with NO2 in the sample gas and produces a NO gas and a variety of molybdenum. (xNO2 + yMo --> xNO + MyOz (at 315degC)).

12. Once the NO2 in the sample gas has been converted to NO, it is routed to the reaction cell where it undergoes the chemiluminescence reaction and is measured by the PMT.

13. By converting the NO2 in the sample gas into NO, the analyser measures total NOx content of the sample gas (i.e. the NO present + the converted NO2 present).

14. By switching the sample gas stream between the 3 streams frequently, the analyser is able to quasi-continuously measure both the NO, the total NOx content and TNx.

15. NO2 is indirectly calculated by subtracting the known NO content of the sample gas from the known NOx content.

16. NH3 is indirectly calculated by subtracting the known NOx content of the sample gas from the known TNx content.

Known interferences: Water vapour (above 20 ppmv), 3rd body quenching (CO2, SOx), other NOy species converted to NO by molybdenum converter (PAN, ethyl nitrate, ethyl nitrite, HONO, HNO3, methyl nitrate, n-propyl nitrate, n-butyl nitrate, nitrocresol, NH3), other species undergoing chemiluminescence with O3 (SOx).

*\*Not accepted QA type for NO/NOx due to bias in measuring NO2, due to molybdenum converters.*

**sulphur chemiluminescence - gas chromatography:** Chemiluminescence is the emission of light (luminescence), as the result of a chemical reaction. Chemiluminescence occurs as a result of the reaction of SO and ozone (SO+O3 --> SO2\*+O2).

The return to a fundamental electronic state of the excited SO2\* molecules is made by luminous radiation in a specific spectrum (SO2\* --> SO2 + hv), which can be measured (by a photomultiplier tube).

The concentration of sample total sulphur is directly proportional to the intensity of light emitted.

This method can be mixed with gas chromatography (GC) to allow to determination of specific sulphur compounds (i.e. SO2). The gas sample is passed through a GC column before being ultimately measured by the photomultiplier detector.

Gas chromatography (GC) is a method used for separating and analysing compounds that can be vaporized without decomposition. A sample solution is injected into a instrument, entering a gas stream which transports the sample (mobile phase) into a separation tube known as the "column".

The mobile phase is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. Helium remains the most commonly used carrier gas in about 90% of instruments although hydrogen is preferred for improved separations. The column consists of a microscopic layer of liquid or polymer on an inert solid support a microscopic layer of liquid or polymer on an inert solid support (stationary phase), inside a piece of glass or metal tubing, placed inside a piece of glass or metal tubing.

Once inside the column, the gaseous compounds being analysed interact with the walls of the column coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound.  The comparison of retention times is what gives GC its analytical usefulness. If greater separation of compounds is required, multiple distinct columns can be used for this purpose.

**flame photometric detection (FPD):** Many elements give characteristic emission when burned in flame. Absorption of energy from the flame allows a ground state atom or molecule to reach an excited state. The atom/molecule may return to the ground state through emission of light (luminescence), which can be subsequently measured (by a photomultiplier tube). This process is a chemiluminescent process (where luminescence occurs as the result of a chemical reaction).

The concentration of the sample gas is directly proportional to the intensity of light emitted. This method has been applied for the measurement of sulphur containing species (i.e. SO2).

For specific measurement of solely SO2, the sample gas must be scrubbed of other sulphur species prior to measurement, and the photomultiplier detector measures emission centred near 394nm.

Known interferences: Other sulphur compounds

**flame ionisation detection (FID):** This method is based on the principle of the generation of an electrical current that is proportional to the rate of ion formation, dependent on the concentrations of species in the sample gas.

The method is typically the standard detection method for hydrocarbons, however the method is also sensitive to almost all compounds, mostly combustible ones.

There are, however, a few compounds to which the method has very little, if any, sensitivity, including: O2, N2, SO2, NO, N2O, NO2, NH3, CO, CO2, and H2O.

Typical measurement operation for hydrocarbons:

1. The sample gas is introduced into a hydrogen flame inside the flame ionisation detector.

2. Any hydrocarbons in the sample will produce ions when they are burnt.

3. Ions are detected using a metal collector which is biased with a high DC voltage.

4. The current across this collector is thus proportional to the rate of ionisation which in turn depends upon the concentration of hydrocarbons in the sample gas.

Known interferences: Method is non-specific for different gases in the sample.

**Conductimetry:** Involves the absorption of a specific gas species in deionized water, to produce an acid, which can be detected by a conductivity cell. Through the use of the deionized water reagent, measurements are susceptible to interferences from CO2, salt aerosols, acid mists and basic gases.  Addition of hydrogen peroxide to the deionized water minimises interference (through reduced solubility of CO2 within the water).

This method been used extensively to measure SO2.

Known interferences: Any gas that can form or remove ions (NO2, NH3, HCl, Cl2 are the worst known interferants).

**second derivative spectroscopy:** Derivative spectroscopy involves plotting the first, second or higher order derivatives of a spectrum with respect to wavelength.

Usually this is obtained by a microprocessor connected in series with a spectrophotometer, which computes the derivative with respect to time as the spectrum is scanned at constant speed.

The "true" wavelength derivative is linearly related to the time derivative recorded, the magnitude of which is directly affected by scanning speed and spectral band width.

#The derivative process provides two general advantages: first, an effective enhancement of resolution, which can be useful to separate two or more components with overlapping spectra; second, a discrimination in favour of the sharpest features of a spectrum, used to eliminate interferences by broad band constituents. However, this process results in a decrease in the signal to noise ratio. Both advantages and disadvantages increase with the derivative order. Generally, the second derivative is more useful than the first ones.

***\*****Not QA accepted measurement techniques for NO or NO2 due to dominance of other more accurate techniques in measuring these species*

**coulometry:** Measures the current necessary to maintain a low concentration of halide and halogen at equilibrium. Typical coulometric methods use solutions of potassium bromide (halide) and bromine (halogen) in dilute sulphuric acid. The concentration of bromine is measured as a voltage between an indicator electrode and a bromide reference electrode.

When the measured species is present, the bromine concentration is decreased through reaction. A feedback system then compensates by generator bromine at a generator electrode. The current required to regenerate the bromine is directly proportional to the concentration of the measured species.

The method is extremely sensitive to interference through reaction with other undesired species (typically NO, NO2, O3, sulphur species, Cl2). Other species are typically removed through pre-filters. This method been used to measure NO2 and SO2.

Known interferences: Reaction with other gases, typically: NO, NO2, O3, sulphur species, Cl2.

**\****Not QA accepted measurement techniques for NO2 or NOx due to dominance of other more accurate techniques in measuring these species*

Polarography: An electrochemical technique where the cell current is measured as a function of time and as a function of the potential between the indicator and reference electrodes.

The working electrode is a dropping mercury (or other liquid conductor) electrode and unstirred solutions are used.

The potential is varied using pulses of linearly increasing amplitude (one pulse during each drop lifetime) and the current is sampled before and after each voltage pulse.

*\*Not QA accepted measurement techniques for NO or NO2 due to dominance of other more accurate techniques in measuring these species.*

**ultraviolet fluorescence:** Fluorescence is the emission of light (luminescence) by a substance that has absorbed light or other electromagnetic radiation (excitation). In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation.

Ultraviolet fluorescence specifically refers to the process of a species being excited by ultraviolet light (10nm to 400nm) (species + hv (UV) --> species\*). The return to a fundamental electronic state of the excited species is made by luminous radiation on a longer wavelength spectrum (species\* --> species + hv). SO2 is efficiently excited to an excited state (SO2\*) by UV light between 190 nm-230 nm, subsequently fluorescing light at approximately 330nm (SO2\* --> SO2 +hv(330nm)), which can be measured.

Typical measurement operation for SO2:

1. The sample is drawn into the sample bulkhead (typically the sample flows through a hydrocarbon “kicker,” which removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall).

2. The sample then flows into the measurement cell, where pulsating UV light from a light source (typically mercury or zinc vapour lamp) between 190nm-230nm excites the SO2 molecules by the reaction: SO2 + hv (190nm-230nm) --> SO2\* . A vacuum diode, UV detector that converts UV light to a DC current is used to measure the intensity of the excitation UV source lamp.

3. Typically a band pass filter limits the wavelength of the UV source light to approximately 214 nm, and therefore the excitation reaction becomes: SO2 + hv (214nm) --> SO2\*

4. The amount SO2 converted to SO2\* in the sample chamber is dependent on the average intensity of the UV light (Ia) and not its peak intensity because the intensity of UV light is not constant in every part of the sample chamber. Some of the photons are absorbed by the SO2 as the light travels through the sample gas. The equation for defining the average intensity of the UV light (Ia) is: Ia = I0 [1 − exp(− ax(SO2))], Where: I0 = Intensity of the excitation UV light, a = The absorption coefficient of SO2 (a constant), SO2 = Concentration of SO2 in the sample chamber, x = The distance between the UV source and the SO2 molecule(s) being affected (path length).

5. SO2\* then fluoresces light at a longer (lower energy) wavelength centred at 330nm: SO2\* --> SO2 + hv (330nm).

6. The amount of detectable UV given off by the decay of the SO2\* is affected by the rate at which this reaction occurs (k). F = k(SO2\*), Where: F = the amount of fluorescent light given off, k = The rate at which the SO2\* decays into SO2, SO2\* = Amount of excited-state SO2 in the sample chamber. Therefore: (SO2\*) -kf --> SO2 + hv (330nm)

7. The function (k) is affected by the temperature of the gas. The warmer the gas, the faster the individual molecules decay back into their ground state and the more photons of UV light are given off per unit of time. Given that the absorption rate of SO2 (a) is constant, the amount of fluorescence (F) is a result of: a) The amount of SO2\* created which is affected by the variable factors: concentration of SO2; intensity of UV light (I0); path length of the UV light(x) and b) The amount of fluorescent light created which is affected by the variable factors: the amount of SO2\* present and the rate of decay (k) which changes based on the temperature of the gas.

8. When and the intensity of the light (I0) is known; path length of excited light is short (x); the temperature of the gas is known and compensated for so that the rate of SO2\*decay is constant (k). and; no interfering conditions are present (such as interfering gases or stray light); the amount of fluorescent light emitted (F) is directly related to the concentration of the SO2 in the Sample Chamber.

9. A Photo Multiplier Tube (PMT) detects the UV given off by the SO2\* decay (330 nm) and outputs an analog signal. Several focusing lenses and optical filters ensure that both the PMT and source lamp vacuum diode are exposed to an optimum amount of only the right wavelengths of UV. To further assure that the PMT only detects light given off by decaying SO2\* the pathway of the excitation UV and field of view of the PMT are perpendicular to each other and the inside surfaces of the sample chamber are coated with a layer of black teflon that absorbs stray light.

10. The net result of the careful instrumental precision is any variation in UV fluorescence can be directly attributed to changes in the concentration of SO2 in the sample gas.

Known interferences: 3rd body quenching (NO, CO2, O2, H2O), light pollution, UV absorption by ozone, other species undergoing ultraviolet fluorescence (poly-nuclear aromatics, NO).

**thermal reduction - ultraviolet fluorescence:** Indirect method for the measurement of sulphate (SO4--) through the conversion of SO4-- to SO2 by thermal reduction, which is then measured by ultraviolet fluorescence.

The sulphate is converted by drawing a continuous stream of sample across a hot reactive surface that reduces sulphate particles in the sample stream to sulfur dioxide gas.  The concentrations of sulphate in the ambient air are then quantified by comparing the signal produced when aerosol-laden sample is drawn directly into the converter to a background signal that is produced when the sample stream is run through a high-efficiency particulate aerosol filter that removes the sulfate before conversion. The difference in signal between the filtered and unfiltered sample can be attributed to sulfur dioxide that is formed from sulfate particles in the unfiltered sample stream. By routinely switching between the filtered and unfiltered sample streams, the instrument readings can be continuously adjusted or corrected for changes in background signal that might be produced by traces of SO2 or other interfering gases.

This frequent adjustment for changes in background signal improves the system stability, which in turn improves the limit of detection.

**laser-Induced fluorescence (LIF):** Fluorescence is the emission of light (luminescence) by a substance that has absorbed light or other electromagnetic radiation (excitation). In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation.

Laser-induced fluorescence (LIF) is a method where fluorescence is induced by an atom or molecule being excited  by the absorption of laser light.

The emission light is detected using a photomutiplier tube. The amount of a species present in the sample is proportional to the intensity of the emission light of a specific wavelength and quantification is possible by using calibration data.

The LIF method has been used mostly in the measurement of hydroxyl and hydroperoxyl radicals, but is also used for measurement of NO/NO2.

Known Interferences: Laser power modulation (laser excitation could generate OH radicals biasing the measurement). 3rd body quenching.

**vacuum ultraviolet resonance fluorescence (VUF):** Fluorescence is the emission of light (luminescence) by a substance that has absorbed light or other electromagnetic radiation (excitation). In most cases, the emitted light has a longer wavelength, and therefore lower energy, than the absorbed radiation.

Vacuum Ultraviolet Resonance Fluorescence is a method where a reasonance lamp excited by reasonance fluorescence discharge (in combiantion with an optical filter) produces photons in the ultraviolet which react with a sample gas, inducing fluorescence in the vacuum ultraviolet (UV radiaion 10nm-200nm), subsequently detected by a photomultiplier tube.

This method can be employed for CO, with the reasonance lamp emitting UV light between 145nm-151nm, with fluorescence occurring between 160nm-190nm.

Known interferences: Water vapour, drifts in lamp intensity, continuum raman scattering by O2.

**cavity ringdown spectroscopy (CRDS):** Based on absorption spectroscopy, Cavity Ringdown Spectroscopy works by attuning light rays to the unique molecular fingerprint of the sample species. By measuring the time it takes the light to fade or "ring-down", you receive an accurate molecular count in milliseconds. The time of light decay, in essence, provides an exact, non-invasive, and rapid means to detect contaminants in the air, in gases, and even in the breath. The method is typically employed to measure CO and other greenhouse gases (e.g CO2, CH4, H2O).

Typical measurement operation:

1. A Continuous Wave (CW) diode laser emits a directed beam of light energy through an ultra-high reflective mirror into the absorption cell (cavity).

2. The light reflects back and forth between two ultra-high reflective mirrors multiple times, up to a total path length of 100 kilometers.

3. Once the photodiode detector “sees” a preset level of light energy, the light source is shuttered or diverted from the cavity.

4. On each successive pass, a small amount of light or ring-down signal emits through the second mirror and is sensed by the light detector.

5. Once the light "rings down", the detector achieves a point of zero light energy in milliseconds, and the measurement is complete.

6. The computer-controlled system tunes the laser off the absorption peak for the sample species to determine the τ empty value, equivalent to a zero baseline correction. It tunes back to the absorption peak to determine the τ value, dependent on the sample species concentration.

7. The concentration of the sample species is directly calculated using Beer’s Law. The measured value constitutes an absolute measurement and is unaffected by losses outside the ring-down cavity.

Known interferences: Water vapour, CO2 and particulates.

**cavity attenuated phase shift spectroscopy (CAPS):** Operates on the principle that a specific species efficiently absorbs light at a known wavelength. This is the case for NO2, at 450nm. The degree to which the light is absorbed by a specific species is directly related to the species concentration as described by the Beer-Lambert Law (A = εLC; A = Absorbance (mol litres-1), ε = Molar absorptivity (litres mol-1 cm-1), L = mean optical path length of cell, C = species concentration). Emitted light in an optical cell is reflected back and forth between two mirrors, building intensity and running a very long path length. The long path length extends the “time” or “life” of the photon, thus providing ample time to measure absorbance when a species is present. The method is typically employed for direct measurement of NO2.

Typical measurement operation for NO2:

1. The sample is drawn into the sample bulkhead, before being passed into the measurement cell.

2. Light is emitted from a blue ultraviolet (UV) light emitting diode (LED) centered at 450 nm (a prominent absorption band for NO2).

3. The measurement cell contains high reflectivity mirrors located at either end to provide an extensive optical path length. The optical cell resides in a temperature controlled oven. The oven raises the ambient temperature of the sample gas to 45 degrees Celsius. This mitigates the formation of moisture on the surfaces of the mirrors while also minimiSing changes in the absorption coefficient due to temperature fluctuations.

4. The CAPS method is unique in that it applies the fundamental optical absorption law in the frequency domain, rather than using relative changes in light intensity as the primary signal.

5. UV light from the modulating high intensity LED enters a near confocal optical cell through the rear of mirror A. The intensity of the light, as observed by a vacuum photodiode detector, which is also modulating at a slightly different frequency, located behind Mirror B, builds exponentially in the cell while the LED is ON. The opposite is true when the LED is OFF. Because both mirrors are highly reflective at 450 nm, a prominent absorption band for NO2, the light takes a considerable amount of time to plateau in the absence of the absorbing gas.

6. When NO2 is present, the mean path length traveled by the light is significantly reduced. This has two effects on the observed intensity as measured by the detector: a) The light plateau intensity level is lower, b) The light intensity plateaus sooner. Thus, an observed phase shift from the modulating LED is detected. The phase shift is largest when measuring zero air and decreases when NO2 is present.

7. Both the LED and the Detector are modulated ON and OFF such that the observed signal has a much lower frequency, equal to the difference between the modulated frequencies and is referred to as a beat frequency. The system hardware and software take advantage of this, as it makes it easier to post process the signal using a microcontroller. The technique is known as heterodyning.

8. The instrument translates the phase shift from the presence of absorbing gas into a concentration measurement. Typical absorption techniques of other analysers take a reference and measure value of the light intensity “level” in order to derive concentration and compensate for source drift. Using the CAPS technique the amount of phase shift remains constant for a given concentration, even if the LED drifts over time. The measurement approach offers many advantages over traditional chemiluminescence analysers, such as faster response (single gas stream), lower noise at span and more importantly greater specificity.

Known interferences: direct spectral interference with photochemically produced 1,2-dicarbonyl species (e.g., glyoxal, methylglyoxal)

**differential optical absorption spectroscopy (DOAS):** The basic principle used in Differential optical absorption spectroscopy (DOAS) is absorption spectroscopy. DOAS allows the quantitative determination of multiple atmospheric trace gas concentrations by recording and evaluating the characteristic absorption structures (lines or bands) of the trace gas molecules along an absorption path of known length in the open atmosphere, following the Beer-Lambert law (I = Io e−KLC; K = molecular absorption coefficient at STP, L = optical path length of cell, C = species concentration , I = light intensity of sample gas, Io = light intensity of sample without measured species (reference gas) ).

The wavelength of light where a distinct absorption peak occurs is determined for analyte. A wavelength on either side of the absorption peak is next determined. The intensity of a light source at wavelength is measured and then the intensity is measured again after the light passes through the analyte. The difference of the intensities is proportional to the concentration to the analyte.

DOAS is a long path measuring technique. Measurements can be made in an optical pathway from 1 to 10 kilometers. The method measures the average concentration of a species along the path length, not for any single molecule. In the real atmosphere, multiple effects contribute to the overall attenuation of the light. In particular, aerosols and clouds scatter light and thereby reduce the intensity of the direct beam while increasing intensities measured in other directions. Also, there rarely is only one absorber relevant at a given wavelength and this also needs to be accounted for.

The solution to this problem lies in the use of measurements at several wavelengths. Each molecule has a characteristic absorption spectrum (its spectral fingerprint) and therefore, simultaneous measurements at different wavelengths enable the separation of the contributions of the different absorbers. This is what DOAS does.

Scattering by aerosols also needs accounting for. Their extinction cross-sections can be approximated by power laws (λ\*\*-4 for Rayleigh scattering and λ\*\*-1..0 for Mie scattering), the coefficients of which can be determined in the fit. The basic principle behind the separation of aerosol extinction and trace gas absorption is that the latter are identified using those parts of their absorption cross-sections that vary rapidly with wavelength.

The more slowly varying parts of the absorption can not be separated from extinction by aerosols which is why the absorption cross-sections are often high pass filtered before use in a DOAS retrieval.

In addition to their effect on the spectral distribution of the intensity measured, aerosols can also have a significant impact on the light path of scattered light. This has to be modelled explicitly when computing the airmass factors for the light path correction.

The DOAS technique is characterised by the following:

(a) measuring the transmitted light intensity over a relatively (compared to the width of an absorption band) broad spectral interval;

(b) high‐pass filtering of the spectra to obtain a differential absorption signal and eliminating broad‐band extinction processes such as Rayleigh and Mie scattering (RS and MS);

(c) quantitative determination of trace column densities by matching the observed spectral signatures to prerecorded (reference) spectra by, for instance, least‐squares methods.

DOAS instruments are often divided into two main groups: passive and active ones. The active DOAS system such as longpath(LP)-systems and cavity-enhanced(CE) DOAS systems have their own light-source, whereas passive ones use the sun as their light source, e.g. MAX(Multi-axial)-DOAS. Also the moon can be used for night-time DOAS measurements, but here usually direct light measurements need to be done instead of scattered light measurements as it is the case for passive DOAS systems such as the MAX-DOAS.

Typical measurement operation:

1. The positioning of the emitter and the receiver define the monitoring path. The light source in the emitter is a high-pressure xenon lamp. This type of light source radiates an almost smooth spectrum ranging from approximately 200 nm up to 500 nm, and from about 1200 to 3000 nm. Within these ranges a number of gaseous substances show specific absorption spectra. The lamp spectrum is however not perfectly smooth, but the remaining "hills" in the spectral output are being taken care of in the evaluation.

2. The emitted light beam is directed towards the receiver, and on its way the intensity is affected by scattering and absorption in molecules and particles.

3. To ascertain the initial intensity (Io) of the light source across the path, there are typically two approaches: (a) Use of measurements at different light paths. If it is possible to take two measurements with the same initial intensity but at different light path lengths L, the dependence on the initial intensity cancels if one looks at the ratio of the two measurements. This approach is e.g. used in zenith-sky DOAS, where a measurement at low sun (long light path through the atmosphere) is analysed with a measurement taken at high sun (short light path). (b) Use of measurements at different wavelengths. In this approach, one exploits the fact that many molecules have structured spectra and light at different wavelengths experiences different absorption strengths. If the initial intensity does not vary with wavelength, one can look at the ratio of two measurements at different wavelengths to remove the dependence on Io. This approach is often used in long-path measurements which employ a lamp. It also is one reason to call this method differential as changes in absorption are used.

4. From the receiver the captured light is led via an opto-fibre to the analyser. The function of the fibre is only to avoid exposing the opto-analyser to dust, high humidity, temperature variations, etc.

5. When the light reaches the analyser, it enters a spectrometer. Inside the spectrometer, a grating refracts the light into its wavelength components. The refracted light is then projected onto a rapid scanning slit in front of a photo-multiplier detector or an infrared sensitive diode, where a selected part of the spectrum is detected. The scanning slit device makes it possible to record all wavelengths separately.

6. As the grating is moveable, any chosen part of the spectrum can be detected. The wavelength window can thus be optimised for a certain component, with respect to parameters such as sensitivity and interfering pollutants. Approximately 100 scans per second are recorded.

7. The current from the detector is converted into digital signals by a 12 bit analogue-to-digital converter, and the signal is stored and accumulated in a multi-channel register. The detected spectrum is typically 40 nm wide in the UV range and approximately twice as wide in the IR range. Each scan is digitised into 1000 points.

8. Each pollutant is monitored during a time period entered by the operator. When the data accumulation is finished, the evaluation process is started. At the same time the next data accumulation period starts.

Known interferences: Interference by miscellaneous atmospheric constituents. Heavy rain and fog, and even high humidity. Atmospheric turbulence, such as that from thermal-induced effects, can distort reflections. Anything that interrupts the path of the laser will cause some interference (i.e., animals, cars, planes, etc.).

**electrochemical membrane diffusion:** Methodology developed specifically for measurement of NH3: <https://www.sciencedirect.com/science/article/pii/S0003267003012650?via%3Dihub>

Gas is sampled in a sampler comprising two opposite channels separated by a gas permeable, water repellent polypropylene membrane. Subsequently, the acid sample solution is pumped into a selector where an alkaline solution is added to ionize all sampled ambient acid gasses, resulting in an enhanced selectivity.

In the selector, the ammonia can diffuse through a second membrane into a purified water stream where an electrolyte conductivity sensor quantifies the resulting ammonium concentration. The realized system is shown to be selective enough not to be influenced by normal ambient carbon dioxide concentrations.

Experiments with a gas flow of 3 ml/min, containing ammonia concentrations ranging from 9.8 to 0.3 ppm in a nitrogen carrier flow, into a 15 μl/min sample solution flow and finally into a 5 μl/min purified water stream have been carried out and show that the system is sensitive to ammonia concentration below 1 ppmv.

Known interferences: CO2

**photoacoustic spectroscopy:** Gaseous samples are continuously drawn through a measurement cell, where they are interrogated spectroscopically with the output radiation of a carbon dioxide/tunable quantum cascade laser.

This is used in conjunction with a highly sensitive acoustic detector to measure trace gas concentrations. Laser tuning is accomplished using proprietary algorithms that do not require the use of a spectrometer or other wavelength measurement device.  The laser is tuned to a known gaseous absorption line and passed through a cell containing the gas sample. If the trace gas species is present, the gas sample will be slightly heated. This heating can be measured very accurately and linearly by microphones in the cell and the amplitude of the electrical signal from the microphones correlate with the trace gas concentration.

If there is no trace gas present, there will be no signal from the microphone. This is, therefore, the highly desirable "zero-background measurement".

Traditional spectroscopic methods measure the total power of the laser beam with and without a sample in the path. For very weak attenuations that result from trace gas concentrations, this process requires taking the difference of two large numbers, each with a finite uncertainty, to compute a small real number. This complication is avoided using this method.

This method has been used to measure NH3.

**non-dispersive infrared absorption (luft):** Operates on the principle that a specific species efficiently absorbs IR light at a known wavelength in the IR range. This is the case for CO, at 4.7um.

The degree to which the IR light is absorbed by a specific species is directly related to the species concentration as described by the Beer-Lambert Law (I/Io = e−KLC; K = molecular absorption coefficient at STP, L = optical path length of cell, C = species concentration , I = light intensity of sample gas, Io = light intensity of sample without measured species (reference gas) ).

Typical measurement operation for CO:

1. The sample is drawn into the through the sample bulkhead

2. IR radiation from a IR source (at 4.7 um) is passed through a rotating shutter creating a series of pulses.

3. These pulses are split simultaneously into 2 measurement cells. One cell contains the sample gas, termed the sample stream (I), and cell contains a non-absorbing gas at the specific wavelength (i.e N2), termed the reference stream (Io).

4. Both the pulses then exit the cells and fall on a IR photo-detector.

5. The intensities of 4.7 um light transmitted through the sample (I) and CO-free reference beams (Io) are related to the concentration (C) of CO in the sample gas stream according to the Beer-Lambert Law.

6. The analyser’s microprocessor calculates the absolute concentration in molecules cm-3, and is then converted to a mixing ratio using in-instrument measured sample temperature and pressure.

Known Interferences:

Water vapour and CO2

**non-dispersive infrared absorption (gas-filter correlation):** Operates on the principle that a specific species efficiently absorbs IR light at a known wavelength in the IR range. This is the case for CO, at 4.7um. The degree to which the IR light is absorbed by a specific species is directly related to the species concentration as described by the Beer-Lambert Law (I/Io = e−KLC; K = molecular absorption coefficient at STP, L = optical path length of cell, C = species concentration , I = light intensity of sample gas, Io = light intensity of sample without measured species (reference gas) ).

The methodology also applies the gas-filter correlation technique. This is applied as water vapour and CO2 absorb light at 4.7 um as well as CO, and ensures measurements are specific for CO.

Typical measurement operation for CO:

1. The sample is drawn into the through the sample bulkhead

2. IR radiation from a IR source (at 4.7 um) is passed through a multi-pass cell length with sample gas. The sample cell uses mirrors at each end to reflect the IR beam back and forth through the sample gas a number of times. The total length that the reflected light travels is directly related to the intended sensitivity of the instrument. The lower the concentrations the instrument is designed to detect, the longer the light path must be in order to create detectable levels of attenuation.

A gas-filter correlation wheel is combined with this system. This wheel contains three parts to increase measurement accuracy: CO, N2 and the mask:  The CO window contains saturation (40 %) of CO which acts as a reference beam – absorbing a known amount of light. The N2 window, containing 100 % N2, does not absorb IR at 4.7 um at all and is used during normal CO measurement. The mask totally blocks the light source and is used to determine background signals, the strength of other signals relative to each other and the background.

3. The IR source is passed through the rotating filter wheel before entering the multi-pass cell:  When the light beam is intercepted by the CO portion of the wheel, the carbon monoxide, which is at relatively high concentration, absorbs all wavelengths that are co-specific, creating and emanating light beam that is “CO blind”. This “optically scrubbed” portion of the beam is designated the Reference beam (Io). The nitrogen-intercepted portion of the beam, which is “CO sensitive”, is designated the sample beam (I). In the absence of CO no attenuation of the Io and I portion of the beam will occur. Species other than CO will cause an equal attenuation of both I and Io portions of the beam. If CO is present in the air being sampled, then the beam portion generated by the CO side of the wheel will experience no attenuation, but the beam portion generated by the N2 portion of the wheel will be attenuated to the degree dictated by the level of CO concentration. When the light beam is intercepted by the mask, this is labelled the "dark portion". This provides a zero light reference point to compensate for the "dark current" of the detector.

4. A band pass filter is fitted on the exit of the sample cell, allowing only 4.7 um wavelength light to pass.

5. The infrared radiation then exits the optical cell and falls on an IR photo-detector.

6. The intensities of 4.7 um light transmitted through the sample (I) and CO-free reference beams (Io) are related to the concentration (C) of CO in the sample gas stream according to the Beer-Lambert Law.

7. The analyser's microprocessor records the imbalance between the I and Io beams portions and performs a data linearisation, calculating the absolute concentration in molecules cm-3, and is then converted to a mixing ratio using in-instrument measured sample temperature and pressure.

Known Interferences:

Water vapour and CO2

**non-dispersive infrared absorption (cross-flow modulation):**

**dual isotope fluorescence:**

**gas chromatography - electron capture detection (GC-ECD):**

**gas chromatography - flame ionisation detection (GC-FID):**

**gas chromatography - dual flame ionisation detection (GC-DualFID):**

**gas chromatography - fourier transform infrared spectroscopy (GC-FTIR):**

**gas chromatography - mass spectrometry (GC-MS):**

**gas chromatography - direct temperature resolved mass spectrometry (GC-DTMS) :**

**gas chromatography - mass spectrometry - flame ionisation detection**

**(GC-MS-FID):**

**gas chromatography - fourier transform infrared spectroscopy - mass**

**spectrometry (GC-FTIR-MS):**

**gas chromatography - unknown detection (GC-?):**

**proton transfer reaction - mass spectrometry (PTR-MS):**

**colorimetry:** Colorimetry fundamentally refers to the determination of species concentrations based on the colour of a solution.

Intrinsically, this is based on Beer-Lambert's law, according to which the absorption of light transmitted through the medium is directly proportional to the medium concentration. However, the way this colour is extrapolated to give a concentration, adds complexity to the definition of this method.

In the most basic of senses the colour can be analysed manually, with the concentration directly extrapolated through a colour chart, or given through the length of colour stain on a glass tube from reagent reaction. The determination can be done in a more specific, automated fashion through the use of colorimeters.

In a colorimeter, a beam of light with a specific wavelength is passed through a solution via a series of lenses, which navigate the colored light to the measuring device.

#This analyses the color compared to an existing standard. A microprocessor then calculates the absorbance or percent transmittance.

If the concentration of the solution is greater, more light will be absorbed, which can be identified by measuring the difference between the amount of light at its origin and that after passing the solution.

Colorimeters are usually portable and use LED light sources and color filters. As a result, they operate at fixed wavelengths and can only accommodate tests that incorporate those wavelengths.

Unless additional information is given, make assumption colorimetry method uses instrumental injection of sample species, following chemical reaction with a reagent.

**spectrophotometry:** Spectrophotometry is also based on Beer-Lambert's law, where the absorption of light transmitted through the medium is directly proportional to the medium concentration.

A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the color, or more specifically, the wavelength of light.

Spectrophotometers are usually bench top instruments and use light sources that can produce a range of wavelengths, use monochromators to select for a desired wavelength. As a result, spectrophotometers can be used for a broad range of tests.

The distinction between spectrophotometry and colorimetry is not always clear.

Colorimeters and spectrophotometers both measure sample absorbance to determine analyte concentrations.

The main distinction is that a spectrophotometer can be set to measure % transmittance or absorbance over a wide range of wavelengths, whereas a colorimeter determines absorbance at specific, visible, wavelengths.

Unless additional information is given, make assumption spectrophotometry method uses instrumental injection of sample species, following chemical reaction with a reagent.

**ion chromatography:** Ion chromatography (or ion-exchange chromatography) is a chromatography process that separates ions and polar molecules based on their affinity to the ion exchanger.

It works on almost any kind of charged molecule—including large proteins, small nucleotides, and amino acids. However, ion chromatography must be done in conditions that are one unit away from the isoelectric point of a protein.

The two types of ion chromatography are anion-exchange and cation-exchange.

Cation-exchange chromatography is used when the molecule of interest is positively charged. The molecule is positively charged because the pH for chromatography is less than the pI. In this type of chromatography, the stationary phase is negatively charged and positively charged molecules are loaded to be attracted to it.

Anion-exchange chromatography is when the stationary phase is positively charged and negatively charged molecules (meaning that pH for chromatography is greater than the pI) are loaded to be attracted to it.

Typical Operation:

1. A sample of the mixture to be analyzed (analyte) is injected into a carrier fluid (the eluent).

2. The combination is passed through a column containing a stationary fixed material (adsorbent).

3. Compounds contained in the analyte are then partitioned between the stationary adsorbent and the moving eluent/analyte mixture.

4. Different dissolved materials adhere to the adsorbent with different forces. The ones that adhere strongly are moved through the adsorbent more slowly as the eluent flows over them. As the eluent flows through the column the components of the analyte will move down the column at different speeds and therefore separate from one another.

5. A detector is used to analyze the output at the end of the column. There are various detectors, typically they use an electrical conductivity detector.

6. Each time analyte molecules/ions emerge from the chromatography column the detector generates a measurable signal which is usually printed out as a peak on the chromatogram.

7. A suppressor is used to reduce the background conductance of the eluent and at the same time enhance the conductance of the sample ions.

**\****Not QA accepted measurement techniques for NO/NO2/NOx due to dominance of other more accurate techniques in measuring these species.*

**Titration:** Titration is a common laboratory method of quantitative chemical analysis that is used to determine the concentration of an identified analyte. Since volume measurements play a key role in titration, it is also known as volumetric analysis.

A reagent, called the titrant or titrator is prepared as a standard solution. A known concentration and volume of titrant reacts with a solution of analyte or titrand to determine concentration. The volume of titrant reacted is called titration volume. Titration can be also done automatically, in a continuous process.

Typical measurement operation:

1. A typical titration begins with a beaker or Erlenmeyer flask containing a very precise volume of the analyte and a small amount of indicator (such as phenolphthalein) placed underneath a calibrated burette or chemistry pipetting syringe containing the titrant.

2. Small volumes of the titrant are then added to the analyte and indicator until the indicator changes color in reaction to the titrant saturation threshold, reflecting arrival at the endpoint of the titration.

3. Depending on the endpoint desired, single drops or less than a single drop of the titrant can make the difference between a permanent and temporary change in the indicator.

4. When the endpoint of the reaction is reached, the volume of reactant consumed is measured and used to calculate the concentration of analyte by: Ca = Ct\*Vt\*M / Va  ;where Ca is the concentration of the analyte, typically in molarity; Ct is the concentration of the titrant, typically in molarity; Vt is the volume of the titrant used, typically in liters; M is the mole ratio of the analyte and reactant from the balanced chemical equation; and Va is the volume of the analyte used, typically in liters.

Unless additional information is given, make assumption titration uses instrumental injection of sample species, following chemical reaction with a reagent.

**aerosol mass spectrometry (AMS):** This method is a variation of the Mass Spectrometry method to analyse gas-phase species, specific for aerosols.

In Aerosol Mass Spectrometry, aerosol particles are – together with a small fraction (10−7) of a carrier gas – directed onto the tungsten vaporizer, typically heated to a temperature of 550–600 ◦C.

Non-refractory material flash-vaporises, and the emerging vapor is electron-impact-ionised (70 eV) for subsequent analysis with a quadrupole or a time-of-flight mass spectrometer. In addition to the measurement of the aerosol beam (“beam-open” mass spectrum), also the instrument background is measured with the aerosol beam blocked (“beam-closed” mass spectrum).

The particle contribution is calculated from the difference of both measurements (“difference” spectrum), assuming that all particle components vaporize quickly compared to the beam-open–beam-closed cycle length.

For calculation of mass concentrations of species from the difference spectrum, each individual m/z is associated with one or several of these species.

For the standard analysis of the unit mass resolution spectra, these associations are listed in the “frag table”, which needs to be adapted for special measurement situations by the user.

Measurements with the high-resolution time-of-flight AMS (HR-ToF-AMS) allow the quantification of individual signals in the spectra with certain elemental composition.

#For measurements of the continental or urban background aerosol the assumptions behind this procedure are typically well met and the AMS provides robust quantitative information on the sub-micron aerosol composition.

However, under certain conditions, e.g., when measuring close to anthropogenic sources or in the marine environment, the limitations of these assumptions are sometimes reached and the standard analysis could result in misinterpretation of the mass spectra.

The method can be performed online (sampling ambient air) or offline (through injection). It is assumed unless otherwise stated that instrumental sampling is done via injection.

**gravimetry:** An air pump draws ambient air at a constant flow rate into a specially shaped inlet where particulate matter is separated into size fractions.

#Particulate matter is then collected on a filter. Each filter is weighed before and after use, to determine the net mass gain due to collected matter.

#The total volume of air filtered is known from the constant air flow, and the difference in filter weights is used to calculate the particulate matter concentration in micrograms per cubic meter (μg/m3) of air.

Known Interferences:

-Particulate matter may be lost during filter handling and weighing procedures, especially if filter is exposed to warming.

-Gaseous species may contaminate filters.

-Humidity and absorbed water may be difficult to control both during operations and when handling filters.

-Removing filters and transporting to a lab for analysis may affect results.

-Meteorological conditions may affect flow rate.

**tapered element oscillating microbalance - gravimetry:** The TEOM - Gravimetric method essentially involves a  true “gravimetric” instrument that draws (then heats) ambient air through a filter at constant flow rate, continuously weighing the filter and calculating near real-time mass concentrations of particulate matter

#The weighing principle used in the tapered element oscillating microbalance (TEOM) TEOM mass transducer is similar to that of a laboratory microbalance in that the mass change detected by the sensor is the result of the measurement of a change in a parameter (in this case, frequency) that is directly coupled via a physical law (or from first principles).

#Typical operation:

#1. Air is drawn through a tapered glass element with a filter attached.

#2. The element oscillates according to a characteristic frequency, that decreases as mass accumulates on the attached filter.

#3. Measurement of the change in frequency converts to measurement of the accumulated mass.

**tapered element oscillating microbalance - filter dynamics measurement**

**system - gravimetry:** The Filter Dynamics Measurement System (FDMS) is a hybrid of the TEOM system which is able to measure the semi-volatile fraction of airborne particulate matter.

#This can be important in the study of primary and secondary PM and to ensure there are no losses of these semi volatile fractions due to sampling conditions.

**beta-attenuation:** Beta particles (electrons with energies in the 0.01 to 0.1 MeV range) are attenuated according to an approximate exponential function when they pass through particulate deposits on a filter tape.

Automated samplers (analyzers) use a continuous filter tape, first measuring the attenuation by the unexposed tape, and then measuring the attenuation after the tape has passed through the ambient air flow.

#The attenuation measurement converts to a measure of the mass on the filter, so that the filters do not require later laboratory analysis for the mass variable. For some devices, the beta particle source is 14C.

Known Interferences:

-Particulate matter may be lost due to filter tape advance and vibration, especially if filter is exposed to warming.

-Gaseous species may contaminate filters.

-Humidity and absorbed water may be difficult to control during operations.

-Meteorological conditions may affect flow rate.

-Although on-site real-time mass measurement offers significant improvements over the filter removal and laboratory analysis process, the beta emission and detection process present additional on-site maintenance requirements.

**Impaction:** Impaction is a methodology employed for the measurement of particulate matter where some information on the particle size distribution is desired

An impactor has two co-linear plates; one acts as a collection surface for the particles, the other one has small nozzle or nozzles in it to control the flow velocity.

#The sample flow is first led through the nozzles to achieve a certain, exact flow velocity. After the sample passes through the nozzles it is turned sharply in front of the collection plate in which case particles larger than stage cut diameter cannot follow the flow stream lines but are impacted onto the collection plate. Particles smaller that the stage cut diameter continue to the following impactor stages where they are further size classified and collected. By changing the dimensions in each impactor stage, different sized particles can be collected on different impactor stages. Typically there are stage cut points of 10, 2.5 and 1.0 µm.

Before the measurement a collection substrate is placed on each of the impactor stages and this substrate is weighed before and after the measurement to determine particle size distribution. Depending on the used substrate material, a chemical composition of the collected particles may also be determined after the sample collection.

Typically PM10 impactor particles >1.0 µm are collected on 25 mm substrates and particles <1.0 µm are collected on a 47 mm filter. Different material substrates and filters can be used in the impactor depending on the used particle analysis method.

**nephelometry:** This method uses the light scattered by tiny particles (nephelometry) to determine the particulate matter concentration in the ambient air directly and continuously.

A highly sensitive scattered light sensor lies at the heart of the applied measuring method. The light emitted by an intensity stabilized laser diode illuminates a measuring space defined by the optical path.

The light scattered by all the aerosol particles inside this measuring space is captured by a semiconductor photodetector positioned at an angle of 90°. After amplification, the outcome of this measurement is made available as a voltage signal. The signal is directly proportional to the mass concentration of the aerosol in the measuring space.

The physical principles governing light scattering determine that aerosol particles whose diameter approximately corresponds to the applied wavelength scatter the light most efficiently in relation to mass. In other words, they are the prevailing contributor to the photometer output signal. For this reason the output signal of a dispersion photodetector deployed outdoors is dominated by the PM2.5 fraction.

Simple dispersion photometry is thus subject to limitations for the measurement of the PM10 concentration because the complementary coarse fraction PM2.5 to PM10 contributes substantially less to the output signal in relation to mass and is therefore under-represented in the measurement.

**beta-attenuation - nephelometry:** Hybrid of beta-attenuation and nephelometry methods enhancing the overall performance. Has accuracy of the beta-attenuation method with high time resolution of a nephelometer. See: https://www3.epa.gov/ttnamti1/files/2006conference/goohssharp.pdf

**optical particle counter:** An optical particle counter (OPC) relies on a focused light beam and ambient/forward particle scattering. Using a long optical path, the scattered light can be separated from the main optical beam, detected and counted.

Since the energy of the scattered light is very small compared to the original light field, this kind of OPC usually needs a high power laser input, a set of optics to focus the light field, and sensitive light detecting equipment to capture the signal.

This makes traditional OPCs relatively large and expensive.

**thermal-optical analysis (TOA):** Thermal-optical analysis (TOA) has been widely used to separate carbonaceous aerosols from ambient and source samples into two components, organic and elemental carbon.

This method uses volatility to separate groups of carbon, and laser monitoring to correct for the transformation of non-absorbing carbon into pyrolytic carbon that absorbs light.

Thermal analysis has been used to classify carbonaceous aerosols in both ambient and source samples into light-absorbing carbon (LAC) and organic carbon (OC). Because thermal analysis does not yield a true value of LAC, the refractory component it measures takes a different name: elemental carbon (EC). (This has no relationship to a chemist’s definition of “elemental.”)

Thermal methods rely on the assumption that organic carbon is volatile, and the strongly light absorbing carbon is stable or refractory at elevated temperatures.

#It assumes that LAC in a sample is unchanged until exposed to both elevated temperatures and an oxidant, so that carbon driven off at low temperatures or in the absence of oxygen must be OC.

Ideally, TOA would be a separation-and-detection technique similar to chromatography, but failures of separation have hampered its interpretation. Some OC undergoes pyrolysis or charring in the absence of oxygen, forming pyrolyzed carbon (“charring”) instead of volatilizing (Huntzicker et al., 1982).

For that reason, the sample is also monitored optically. The sample usually becomes blacker as charring occurs in an inert atmosphere, and the blackness decreases as the pyrolyzed carbon burns later in the analysis.  This change is detected by monitoring either transmittance or reflectance (sometimes both). When the filter’s transmittance or reflectance returns to the original value, it is assumed that the remaining material is EC.

This point is colloquially termed the OC/EC split and the combined analysis is known as thermal-optical analysis (TOA). Investigations of the thermal-optical method have examined “round-robin” tests of different protocols, or sequences of temperature and analysis environments (e.g., Cadle et al., 1990; Countess et al., 1990; Schmid et al., 2001).

Studies have provided the differences between OC/EC split produced by various temperature programs (e.g., Chow et al., 2001; Subrama- nian et al., 2006), and quantification of positive and negative artifacts (e.g., Cadle et al., 1983; Huebert and Charlson, 1996;Kirchstetter et al., 2001).

Some examples of successful results have been agreement on measurement of total carbon (Schmid et al., 2001) and reproducible measurements of EC and OC from careful and consistent application of thermal programs (Schauer et al., 2003).

A wide variety of temperature programs has been used in TOA, often with differing results (Schmid et al., 2001; Watson et al., 2005). The combination of temperature program and optical analysis best suited to analyzing different types of samples is still a subject of debate. Many papers have pointed out challenges in interpreting TOA results (Cadle et al., 1983; Reid et al., 1998; Chow et al., 2001; Conny et al., 2003; Subramanian et al., 2006), and the method has both detractors and supporters.

**unknown:** measurement method is unknown.