Exhaust Gas Emission Analysis

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**Exhaust Gas**

Exhaust gas or flue gas is emitted as a result of the combustion of fuels such as natural gas, gasoline/petrol, biodiesel blends, diesel fuel, fuel oil or coal. According to the type of engine, it is discharged into the atmosphere through an exhaust pipe, flue gas stack or propelling nozzle. It is a major component of *motor vehicle emissions* which can also include:

- Crankcase blow-by
- Evaporation of unused gasoline

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Emission measurement

- It is important to measure the emission concentration to test the engine performance and meet emission legislations
- Regulated emissions – CO, HC, PM, NOx
- Unregulated emissions – Formaldehyde, SO₂, CO₂, CH₄, Benzene, Aldehydes
- Different methods are used to measure different gases present in engine exhaust
- Commonly used methods for emission measurement -
  - Non-dispersive Infrared – For CO and CO₂ measurement
  - Flame Ionization Detector – For HC measurement
  - Chemiluminescence Analyzer – For NOx measurement
  - Smoke meter (Opacimeter) – Smoke measurement
  - Partial and full flow systems for particulate measurement

Non-Dispersive Infrared Spectroscopy
Non-Dispersive Infrared Spectroscopy

1. Non-Dispersive Infra-Red (NDIR) detectors are the industry standard method of measuring the concentration of carbon oxides (CO & CO₂).
2. Each constituent gas in a sample will absorb some infra red at a particular frequency.
3. By shining an infra-red beam through a sample cell (containing CO or CO₂), and measuring the amount of infra-red absorbed by the sample at the necessary wavelength, a NDIR detector is able to measure the volumetric concentration of CO or CO₂ in the sample.

• A chopper wheel mounted in front of the detector continually corrects the offset and gain of the analyser, and allows a single sampling head to measure the concentrations of two different gases.
Non-Dispersive Infrared Spectroscopy

- A non-dispersive infrared sensor (or NDIR sensor) is a simple spectroscopic sensor often used as a gas detector. It is non-dispersive in the sense of optical dispersion since the infrared energy is allowed to pass through the atmospheric sampling chamber without deformation.
- The main components of an NDIR sensor are:
  - an infrared source (lamp)
  - a sample chamber or light tube
  - a light filter and
  - an infrared detector.
- The IR light is directed through the sample chamber towards the detector.
- In parallel there is another chamber with an enclosed reference gas, typically nitrogen.
- The gas in the sample chamber causes absorption of specific wavelengths according to the Beer–Lambert law, and the attenuation of these wavelengths is measured by the detector to determine the gas concentration.
- The detector has an optical filter in front of it that eliminates all light except the wavelength that the selected gas molecules can absorb.

Non-Dispersive Infrared Spectroscopy

- Used for measurement of CO and CO₂.
- IR radiations of characteristic absorption spectrum are absorbed by gases.
- Transmittance of particular gas is given by Beer's Law:

\[ \tau = \exp(-raL) \]

where,

- \( r \) = gas density
- \( a \) = absorptivity
- \( L \) = path length
Infrared Transmittance Spectra

Tailpipe CO and CO2 at 2000rpm

Figure 5-8 CO and CO2 infrared transmittance spectra.

Figure 5-8 CO and CO2 infrared transmittance spectra.

Tailpipe CO and CO2 at 2000rpm

Fuel NDIR analyzer for CO:CO2
2.0 litre port fuel injected gasoline engine with new catalyst
2000RPM, 90Nm steady state, changing AFR

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Working of NDIR System

- Sample cells and detector cells are filled with gas to be measured
- Reference cells are filled with air
- IR radiations are absorbed in sample cells thus less IR to detector cells
- This leads to differential pressure in detector cells
- Differential pressure is measured and related to gas concentration
- The movement of diaphragm is calibrated by passing gases of known composition through sample cell

NDIR system for CO and CO₂ Measurement
Requirements for accurate measurement

- Windows needs to be transparent to infrared (quartz and mica)
- Minimization of fouling of windows

Fouling is caused by

- Particulates
- Condensation of water vapors and high molecular weight HC

Fouling can be minimized by

- Heating the sample lines and analyzer
- Cooling and removing the condensate then warming the sample to ambient temperature
Flame Ionization Detector

- A flame ionization detector (FID) is an instrument that measures the concentration of organic species in a gas stream. It is frequently used as a detector in gas chromatography. Standalone FIDs can also be used in applications such as landfill gas monitoring, fugitive emissions monitoring and internal combustion engine emissions measurement.
• The flame ionisation detector (FID) is the automotive emissions industry standard method of measuring hydrocarbon (HC) concentration.
• The sample gas is introduced into a hydrogen flame inside the FID.
• Any hydrocarbons in the sample will produce ions when they are burnt.
• Ions are detected using a metal collector which is biased with a high DC voltage.
• The current across this collector is thus proportional to the rate of ionisation which in turn depends upon the concentration of HC in the sample gas.
• The ionisation process is very rapid, so the slow time response of conventional FIDs is mainly due to sample handling.
• A typical slow analyser might have a response time of 1-2 seconds.
• The Cambustion HFR fast response FID analyzers use conventional detection principles and a unique patented sampling system to give millisecond response times.

Flame Ionization Detector

- For measurement of Hydrocarbons
- FID ionizes the HC molecules and counts the number of C atoms based on current produced in process
- HC molecules are measured in ppm of C (or ppm of no. of C atoms in reference)
- FID consists of –
  - Burner
  - Ion collector assembly
  - Current Amplifier
Working Principle of FID

- Sample is mixed with H₂ in burner assembly and mixture is burned in diffusion flames
- HC molecules get ionized (pure H₂-air does not ionize)
- Ions are collected by ion collector by the influence of applied electric field between them
- Thus small current is produced between collector plates
- This current is amplified and output current becomes a measure of HC molecules

- Usually hydrogen-helium (40:60) is used as fuel for burner
- Calibrated with Propane or Methane mixtures of Nitrogen
- Samples are heated to a temperature of 191°C to avoid condensation of heavy hydrocarbons
Advantages and Disadvantages of FID

Flame ionization detectors are used very widely in gas chromatography because of a number of advantages:

- **Cost:** Flame ionization detectors are relatively inexpensive to acquire and operate.
- **Low maintenance requirements:** Apart from cleaning or replacing the FID jet, these detectors require no maintenance.
- **Rugged construction:** FIDs are relatively resistant to misuse.
- **Linearity and detection ranges:** FIDs can measure organic substance concentration at very low and very high levels, having a linear response of $10^6$.

Disadvantages:

- Flame ionization detectors cannot detect inorganic substances.
- In some systems, CO and CO$_2$ can be detected in the FID using a methanizer, which is a bed of Ni catalyst that reduces CO and CO$_2$ to methane, which can be in turn detected by the FID.
Emission measurements

- Methane is measured using
  - Gas chromatographic method (GC)
  - Non-methane cutter method (NMC)

- GC Method
  - Molecular sieve Porapak column is used to separate the sample into
    i. CH₄-air –CO
    ii. NMHC-CO₂-H₂O
  - Molecular sieve separates methane from air and CO
  - Further sample is passed to FID
  - Thus Methane content gets measured

- Non-Methane Cutter (NMC)
  - All HC except methane are oxidized to CO₂ and water on catalyst
  - Gas sample is passed through NMC and only CH₄ gets detected by HFID

Chemiluminescence Analyzer – For NOₓ measurement
Chemiluminescence

Chemiluminescence is the production of light from a chemical reaction. Two chemicals react to form an excited (high-energy) intermediate, which breaks down releasing some of its energy as photons of light to reach its ground state.

Chemiluminescence Analyzer – For NO\textsubscript{x} measurement

- A chemi-luminescence detector (CLD) is the industry standard method of measuring nitric oxide (NO) concentration.
- The reaction between NO and O\textsubscript{3} (ozone) emits light.
- This reaction is the basis for the CLD in which the photons produced are detected by a photo multiplier tube (PMT).
- The CLD output voltage is proportional to NO concentration.
- The light-producing reaction is very rapid so careful sample handling is important in a very rapid response instrument.
- It uses a unique sampling system coupled with miniaturised CLD technology to give millisecond response times.
- It has two remote sampling heads controlled by a Main Control Unit and is capable of simultaneous sampling in two locations.
When NO and ozone (O\(_3\)) react a small fraction (about 10% at 26.7° C) of excited NO\(_2\) molecules is produced as per the following reactions:

\[
NO + O_3 \leftrightarrow NO_2^* + O_2
\]

\[
NO_2^* \rightarrow NO_2 + hv
\]

As the excited molecules of NO\(_2\) decay to ground state, light in the wavelength region 0.6-3.0 µm is emitted. The quantity of excited NO\(_2\) produced is fixed at a given reaction temperature and the intensity of light produced during decay of excited NO\(_2\) is proportional to the concentration of NO in the sample. Following reactions:
Chemiluminescence Analyzer - Working

- The sample containing NO flows to a reactor where it reacts with ozone produced from oxygen in ‘ozonator’.
- In the reactor NO is converted to NO₂.
- A photomultiplier tube detects the light emitted by the excited NO₂.
- The signal is then amplified and fed to recorder or indicating equipment.
- For the measurement of nitrogen oxides (NOx), NO₂ in the sample is first converted to NO by heating in a NO₂-to-NO converter prior to its introduction into the reactor.
- At 315º C, about 90 percent of NO₂ is converted to NO. The total concentration of NOx in the sample is thus, measured as NO.
- When the sample is introduced in the reactor bypassing the NO₂-to-NO converter, concentration of NO alone is determined.
- The difference between the two measurements provides the concentration of NO₂ in the sample. The response of the instrument is linear with NO concentration.
- The technique is very sensitive and can detect up to 10⁻³ ppm of NOx. The output signal is proportional to the product of sample flow rate and NO concentration. As the method is flow sensitive an accurate flow control is necessary.
- The calibration and operation are done at the same flow rate and reactor temperature.

Smoke opacity meters
smoke opacity meters

- Smoke and smoke opacity meters are instruments measuring the optical properties of diesel exhaust.
- These instruments have been designed to quantify the visible black smoke emission utilizing such physical phenomena as the extinction of a light beam by scattering and absorption.
- In general, smoke and opacity meters are much simpler (some of them very simple) and less costly in comparison to most other instruments used for PM measurement.
- They are often used to evaluate smoke emissions in locations outside the laboratory, such as in maintenance shops or in the field.
- In fact, the smoke opacity measurement is the only relatively low-cost and widely available method to measure a PM-related emission parameter in the field.
- For this reason, opacity limits are used in most inspection and maintenance (I&M) or periodic technical inspection (PTI) programs for diesel engines.
- Smoke opacity limits may be also included as auxiliary limits in new engine emission standards.
Smoke opacity meters

- Smoke meters that use light can be broadly classified into two types: a light reflecting type that measures smoke concentration based on changes in the reflectivity when light is shown on PM collected on a filter, and a light transmitting type (opacimeter) that measures smoke concentration based on the strength of the absorbed and scattered light when light is shown directly on the exhaust gas.

- The exhaust gas is drawn into the sample cell, and when the gas contains black smoke due to high temperature fuel combustion and blue and white smoke due to unburned oil, unburned fuel and water, the visible light from the light source is attenuated due to absorption and scattering. The concentration of smoke is calculated from the amount of attenuation using the Lambert-Beer equation (Equation (1)).

- The result is expressed as an opacity $N$ (%) given by Equation (2), or a light absorption coefficient $k$ (m$^{-1}$) given by Equation (3).

$$I = I_0 \cdot e^{-kL} = I_0 \cdot (1 - N/100)$$  \hspace{1cm} (1)

$$N = (1-I/I_0) \cdot 100$$  \hspace{1cm} (2)

$$k = -1/L \cdot \ln(1-N/100)$$  \hspace{1cm} (3)

$I_0$ : Light intensity when there is no smoke
$I$ : Light intensity when smoke exists
$L$ : Cell length (m)
Before the exhaust gas and its components can be measured, it has to be sampled from the exhaust system. The sampling system acts as an important interface between the exhaust and measurement systems. Its role is to pre-condition the sample to meet the requirements of the particular measurement instruments—such as temperature, concentration, or the presence of moisture and volatiles—while preventing or at least minimizing physical and/or chemical changes of the measured species. Most measurement instruments are designed to operate close to ambient temperature.

Dilution—which is also an effective means to obtain the required temperature reduction—is the preferred method in most exhaust gas measurements. Dilution may be also required to lower the concentrations to match the ranges of the instruments used or exhaust gas has to be cooled to an adequate level.
Dilution Tunnel

- **Raw Gas Sampling.** In spite of what has been said above, undiluted or raw gas sampling is also a common technique because of the relative simplicity of the sampling system. However, because of the high concentration of moisture, particulates, and high temperature, it is not an easy task to obtain reproducible and reliable results. While allowed for some regulatory applications, it is mainly used for non-regulatory and/or field testing.

- *Instruments such as smoke meters or opacity meters can handle the high concentrations of undiluted exhaust constituents and can be operated at elevated temperatures to avoid condensation. These instruments can therefore be used with an undiluted sample. Opacity meters, however, run into problems with the detection limit for modern low emission engines.*

- **Isokinetic Sampling.** When taking a sample from a gas flow (diluted or raw), ideally the flow velocity in the sampling line should be the same as in the flow, a condition referred to as isokinetic sampling. Otherwise, aerodynamic effects may lead to a depletion or an enrichment of coarse particles in the sampling line. The importance of this effect increases with increasing particle size. For the size range of interest in diesel emissions, errors due to non-isokinetic sampling are usually negligible.

### Dilution Tunnel

The dilution tunnels are of two types:

- Partial flow
- Full flow dilution tunnel

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*Image of a dilution tunnel diagram*
Partial Flow Dilution Tunnel

- In the partial-flow system, only a small part of the exhaust stream is diluted.
- To withdraw a true representative of the exhaust gas the following systems have been developed; Isokinetic sampling systems, Flow controlled systems with concentration measurement, and Flow controlled systems with flow measurement.

Full Flow Dilution Tunnel
Full flow dilution tunnel

- In the full flow system, entire exhaust of the engine/vehicle is diluted with the filtered room air. The full flow system is quite large in size and expensive. For small engines/vehicles only the primary dilution tunnel is used. For the large engines to provide the desired dilution ratio, the gas is diluted again in the secondary dilution tunnel.

- The sample is withdrawn for measurements from the secondary dilution tunnel in the large engines. The dilution ratio is maintained around 10:1. The temperature of the diluted exhaust gases at the primary filter is maintained at 325º K or less by a heat exchanger.

- After thorough mixing of exhaust and air in the dilution tunnel, a constant flow rate sample is extracted that is filtered through a Teflon coated glass fibre filter. The mass of particulate is determined by weighing the particulate mass collected on the filter.

- A reference filter is used to determine the particulate mass in the dilution air for correction of PM measurement for the background PM. The filter papers are conditioned before and after filtration to prevent condensation of any moisture or deposition of foreign particulate matter from atmosphere.

Dilution Tunnel
Dilution Tunnel

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Thanks