# ENGINE EXHAUST EMISSION CONTROL

### SI/CI ENGINE EMISSIONS

- Unburned Hydro Carbons
- Carbon monoxide
- Oxides of nitrogen
- Oxides of sulphur and
- Particulates including smoke

# FORMATION OF NOX

The chemical mechanism of NO x formation during combustion obeys hundreds of elementary chemical reactions.

Depending on the temperature range, stoichiometric ratio and type of nitrous species present in the combustion zone the oxides of nitrogen formation mechanism changes.

# MAJOR SOURCES OF NO<sub>X</sub> FORMATION DURING COMBUSTION

- Air nitrogen (N₂)
  - Thermal NO<sub>x</sub>
  - Prompt NO<sub>x</sub>

- Fuel nitrogen (N<sub>F</sub>)
  - Fuel NO<sub>x</sub>

## THERMAL NO<sub>x</sub>

Thermal NO x refers to NO x formed through high temperature oxidation of the diatomic nitrogen found in combustion air.

- The formation rate is primarily a function of temperature and the residence time of nitrogen at that temperature.
- At high temperatures, usually above 1700K molecular nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) in the combustion air disassociate into their atomic states and participate in a series of reactions.

## THERMAL NO<sub>x</sub>

- It is necessary to limit residence time to control NO<sub>x</sub> formation, which favours very short combustor designs.
- Thermal NO<sub>x</sub> production also increases with the square root of operating pressure.
- The formation of thermal NO x is given by extended Zeldovich mechanism.

$$N_2 + O \rightarrow NO + N$$
 $N + O_2 \rightarrow NO + O$ 
 $N + OH \rightarrow NO + H$ 

The above three reactions are reversible reactions.

# PROMPT NO<sub>x</sub>

Prompt NO<sub>x</sub> can be a major source on formation of NO<sub>x</sub> at low-temperature combustion of oxygenated fuels such as biodiesel.

- Radicals such as C, CH, and CH<sub>2</sub> fragments derived from fuel reacts with the atmospheric nitrogen at low temperature when compared to thermal NO<sub>x</sub>.
- This results in the formation of fixed species of nitrogen such as NH (nitrogen monohydride), HCN (hydrogen cyanide), H<sub>2</sub>CN (dihydrogen cyanide) and CN- (cyano radical).

# FUEL NO<sub>x</sub>

This type of NO<sub>x</sub> is produced when nitrogen-bearing fuels such as certain coals and oil are used as fuel.

During combustion, the nitrogen bound in the fuel is released as a free radical and ultimately forms free N<sub>2</sub>, or NO.

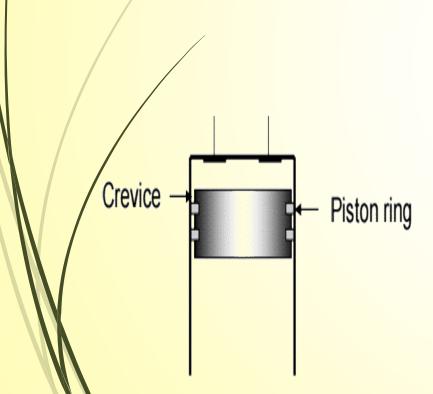
Fuel NO x can contribute as much as 50% of total emissions when combusting oil and as much as 80% when combusting coal.

- Hydrocarbon emissions result from the presence of unburned fuel in the engine exhaust.
- About 9% of the fuel supplied to the engine is not burned during the normal combustion phase of the expansion stroke.
- Only 2% ends up in the exhaust the rest is consumed during the other three strokes.
- As a consequence hydrocarbon emissions cause a decrease in the thermal efficiency, as well as being an air pollutant.

There are six primary mechanisms believed to be responsible for hydrocarbon emissions:

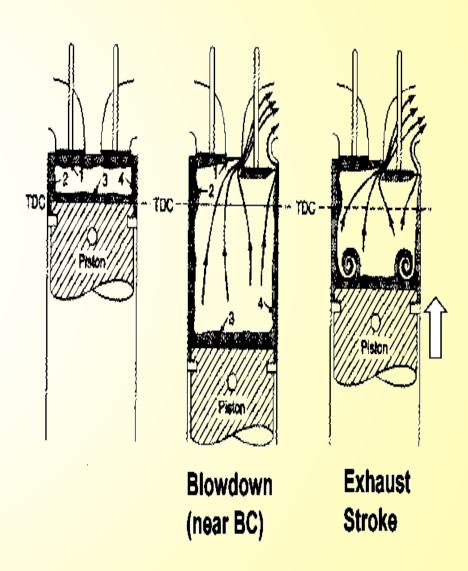
/	Source	% fuel escaping normal combustion	% HC emissions
	Crevices	5.2	38
	Oil layers	1.0	16
	Deposits	1.0	16
	Liquid fuel	1.2	20
	Flame quench	0.5	5
	Exhaust valve leakage	0.1	5
	Total	9.0	100

- Crevices these are narrow regions in the combustion chamber into which the flame cannot propagate because it is smaller than the quenching distance.
- Crevices are located around the piston, head gasket, spark plug and valve seats and represent about 1 to 2% of the clearance volume.
- The crevice around the piston is by far the largest, during compression the fuel air mixture is forced into the crevice (density higher than cylinder gas since gas is cooler near walls) and released during expansion.



- Oil layers Since the piston ring is not 100% effective in preventing oil migration into the cylinder above the piston, an oil layer exists within the combustion chamber that traps fuel.
- Deposits Carbon deposits build up on the valves, cylinder and piston crown. These deposits are porous with pore sizes smaller than the quenching distance so trapped fuel cannot burn.
- <u>Liquid fuel</u> For some fuel injection systems there is a possibility that liquid fuel is introduced into the cylinder past an open intake valve.
- The less volatile fuel constituents may not vaporize (especially during engine warm-up) and be absorbed by the crevices or carbon deposits.

- Flame quenching It has been shown that the flame does not burn completely to the internal surfaces, the flame extinguishes at a small but finite distance from the wall.
- When the exhaust valve opens the large rush of gas escaping the cylinder drags with it some of the hydrocarbons released from the crevices, oil layer and deposits.
- During the exhaust stroke the piston rolls the hydrocarbons distributed along the walls into a large vortex that ultimately becomes large enough that a portion of it is exhausted.



#### CARBON MONOXIDE EMISSION FORMATION

- Carbon monoxide remains in the exhaust if the oxidation of CO to CO2 is not complete.
- This is because carbon monoxide is an intermediate product in the combustion process.
- Generally this is due to lack of sufficient oxygen.
- The emission levels of CO from gasoline engine are highly dependent on A/F ratio.
- The amount of CO released reduces as the mixture is made leaner.
- Better carburetion and fuel distribution are key to low CO emission in addition to operating the engine at increased airfuel ratio.

#### **DIESEL ENGINE SMOKE EMISSION**

- Engine exhaust smoke is a visible indicator of the combustion process in the engine.
- Smoke indicates that the combustion is incomplete.
- Smoke in diesel engine can be divided into following three categories:
  - Blue Smoke
  - White Smoke
  - Black Smoke

#### **DIESEL ENGINE SMOKE EMISSION**

#### Blue smoke:

It results from the burning of engine lubricating oil that reaches combustion chamber due to worn piston rings, cylinder liners and valve guides.

#### White or cold smoke:

- It is made up of droplets of unburnt or partially burnt fuel droplets and is usually associated with the engine running at less than normal operating temperature after starting, long period of idling, operating under very light load, operating with leaking injectors and water leakage in combustion chamber.
- This smoke normally fades away as engine is warmed up and brought to normal stage.

#### **DIESEL ENGINE SMOKE EMISSION**

- Black or hot smoke:
  - It consists of unburnt carbon particles (0.5 1 microns in diameter) and other solid products of combustion.
  - This smoke appears after engine is warmed up and is accelerating or pulling under load.

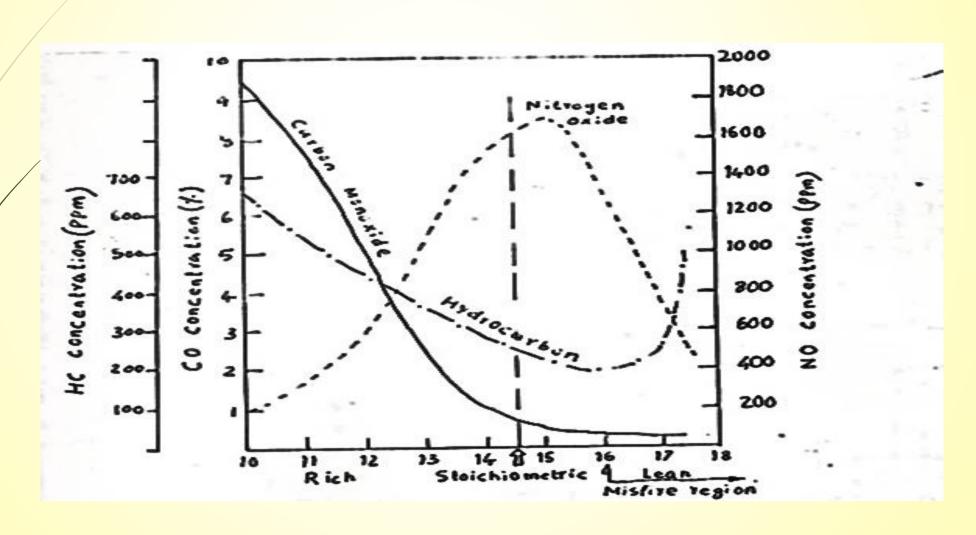
#### FORMATION OF SMOKE IN DIESEL ENGINES

- The main cause of smoke formation is known to be inadequate mixing of fuel and air.
- Smoke is formed when the local temperature is high enough to decompose fuel in a region where there is insufficient oxygen to burn the carbon that is formed.
- The formation of over-rich fuel air mixtures either generally or in localized regions will result in smoke.
- Large amounts of carbons will be formed during the early stage of combustion.
- This carbon appears as smoke if there is insufficient air, if there is insufficient mixing or if local temperatures fall below the carbon reaction temperatures (approximately 100 °C) before the mixing occurs.

#### PARTICULATES EMISSION

- Particulate matter comes from hydrocarbons, lead additives and sulphur dioxide.
- If lead is used with the fuel to control combustion almost 70% of the lead is airborne with the exhaust gasses.
- In that 30% of the particulates rapidly settle to the ground while remaining remains in the atmosphere.
- Particulates when inhaled or taken along with food leads to respiratory problems and other infections.
- Particulates when settle on the ground they spoil the nature of the object on which they are settling.

# SI ENGINE EMISSIONS WITH RESPECT TO AIR FUEL RATIO



- NO<sub>x</sub> is decreased by
- (I) Decreasing the combustion chamber temperature

  The combustion chamber temperature can be decreased by
  - 1. Decreasing compression ratio
  - 2. Retarding spark timing
  - 3. Decreasing charge temperature
  - 4. Decreasing engine speed
  - 5. Decreasing inlet charge pressure
  - 6. Exhaust gas recirculation
  - 7. Increasing humidity

NO<sub>x</sub> is decreased by

(II) By decreasing oxygen available in the flame front

The amount of oxygen available in the chamber can be controlled by

- 1. Rich mixture
- 2. Stratified charge engine
- 3. Divided combustion chamber

Hydrocarbon emission can be decreased by

- 1. Decreasing the compression ratio
- 2. Retarding the spark
- 3. Increasing charge temperature
- 4. Increasing coolant temperature
- 5. Insulating exhaust manifold
- 6. Increasing engine speed
- 7. Lean mixture

CO can be decreased by

- 1. Lean air fuel ratio
- 2. Adding oxygen in the exhaust
- 3. Increasing coolant temperature

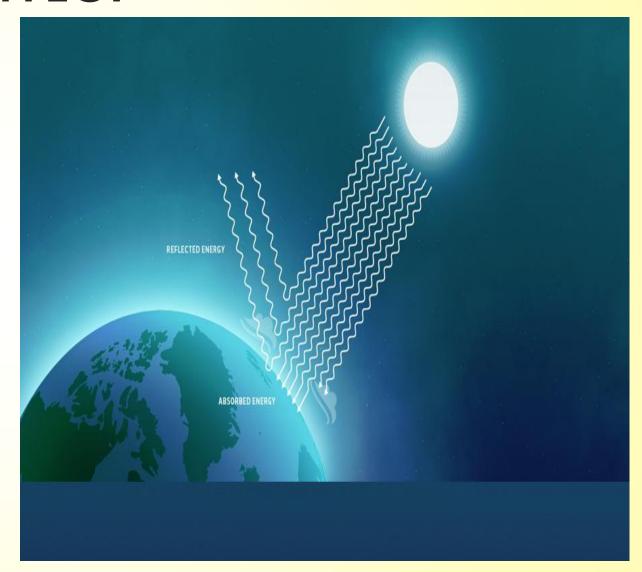
- The greenhouse effect is a process caused by greenhouse gases, which occur naturally in the atmosphere.
- This process plays a crucial role in warming the Earth's surface, making it habitable.

However, human-generated greenhouse gas emissions upset the natural balance and lead to increased warmth.

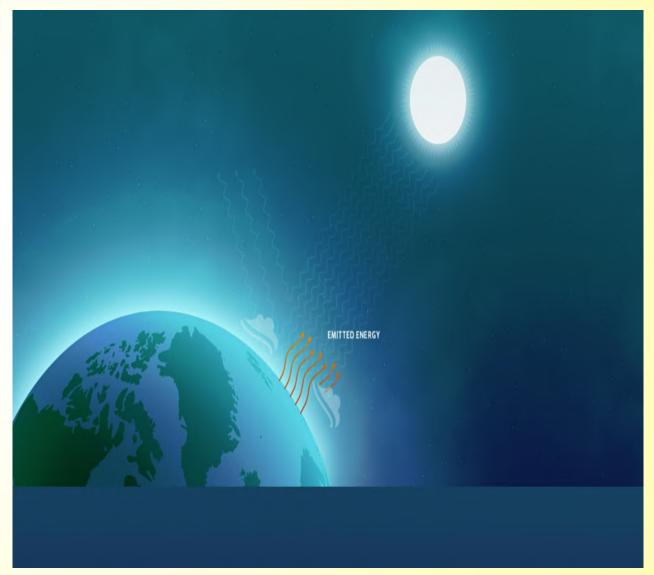
The following are the green house gases and their constituents

- Water Vapour (36–70%)
- Carbon dioxide (9–26%)
- Methane (4–9%)
- Ozone (3–7%)

- The Sun emits energy that is transmitted to Earth.
- The Sun is very hot, the energy is emitted in high-energy short wavelengths that penetrate the Earth's atmosphere.
- About 30% of the Sun's energy is reflected directly back into space by the atmosphere, clouds, and surface of the Earth.

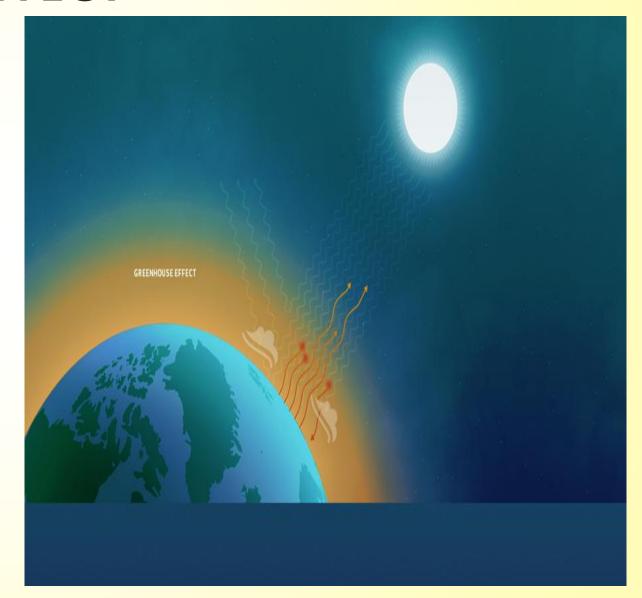


- The rest of the Sun's energy is absorbed into the Earth's system.
- Because the Earth is cooler than the Sun, the energy is emitted in the form of infrared radiation, at wavelengths longer than the incoming solar energy.



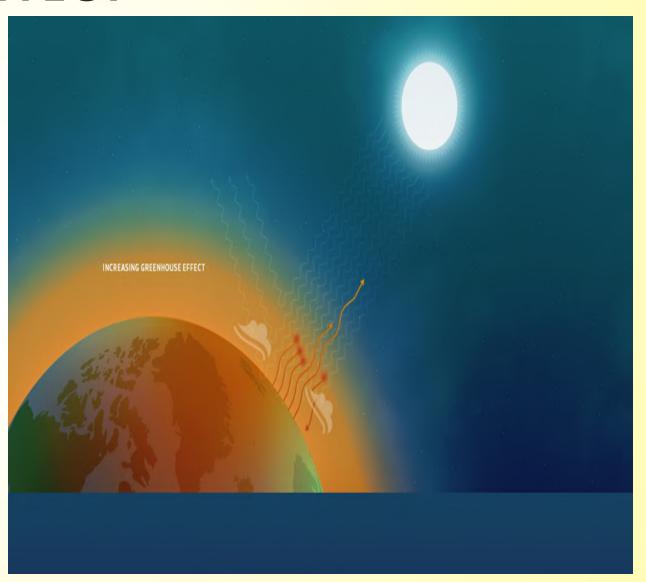
Greenhouse gases in the atmosphere absorb much of the long-wave energy emitted from the Earth's surface, preventing it from immediately escaping from the Earth's system.

■ The greenhouse gases then re-emit this energy in all directions, warming the Earth's surface and lower atmosphere.



The atmospheric concentration of green house gases has increased over the past two centuries, largely due to human-generated carbon dioxide emissions from burning fossil fuels.

This change causes Earth's surface temperature to increase.



- The exhaust gases from an engine contain harmful substances such as oxides of nitrogen (NO x), carbon monoxide (CO) and Hydrocarbons (HC).
- These substances produce extreme environment hazards.
- A 3-way catalytic converters convert these harmful substances to less harmful nitrogen (N<sub>2</sub>), carbon-di-oxide (CO<sub>2</sub>) and water (H<sub>2</sub>O).

A three-way catalytic converter makes use of two catalysts to convert harmful gases to harmless gases.

- Reduction Catalyst and
- Oxidation Catalyst
- The reduction catalyst is made of platinum and rhodium
- The oxidation catalyst is made of platinum and palladium.
- Both the catalysts have a ceramic honeycomb structure.

#### Stage 1 – Reduction Catalyst

- The exhaust gases are first sent over the reduction catalyst (which is made of platinum and rhodium).
- It converts oxides of nitrogen  $(NO_x)$  to nitrogen  $(N_2)$  and oxygen  $(O_2)$ .
- The following reactions take place when the exhaust gases pass over the reduction catalyst.

$$2NO \rightarrow N_2 + O_2$$

$$2NO_2 \rightarrow N_2 + 2O_2$$

#### **Stage 1 – Reduction Catalyst**

The reduction catalyst simply rips off nitrogen and oxygen from the oxides of nitrogen.

The nitrogen and oxygen are harmless gases while oxides of nitrogen are really harmful to the environment.

#### Stage 2 – Oxidation Catalyst

- Exhaust gases that are free of oxides of nitrogen (NO<sub>x</sub>) are then sent over the oxidation catalyst (made of platinum and palladium).
- The oxidation catalyst coverts carbon-monoxide (CO) and hydrocarbons (HC) in the gases into carbon-di-oxide (CO<sub>2</sub>) and water (H<sub>2</sub>O).
- The following reactions takes place when the exhaust gases pass over the oxidation catalyst:

$$2CO + O_2 \rightarrow 2CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O$$

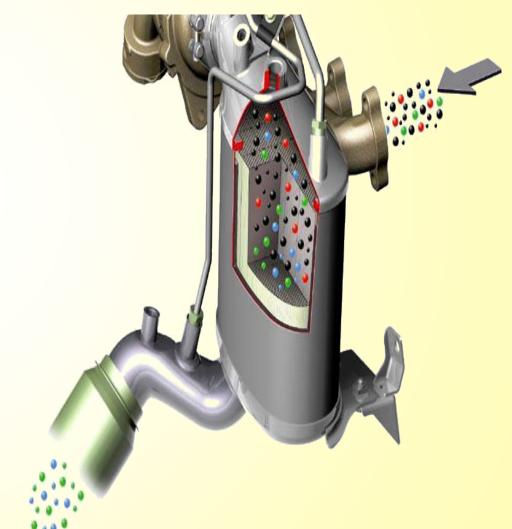
- For efficient working of a three way catalytic converter the air fuel ratio must be maintained at stoichiometric air fuel ratio (14.7:1).
- A catalytic converter will start working only when the exhaust gases reaches the temperature of 250°C.
- When the fuel contains lead as an additive, it will poison the catalyst.

# DIESEL PARTICULATE FILTER (PARTICULATE TRAP)

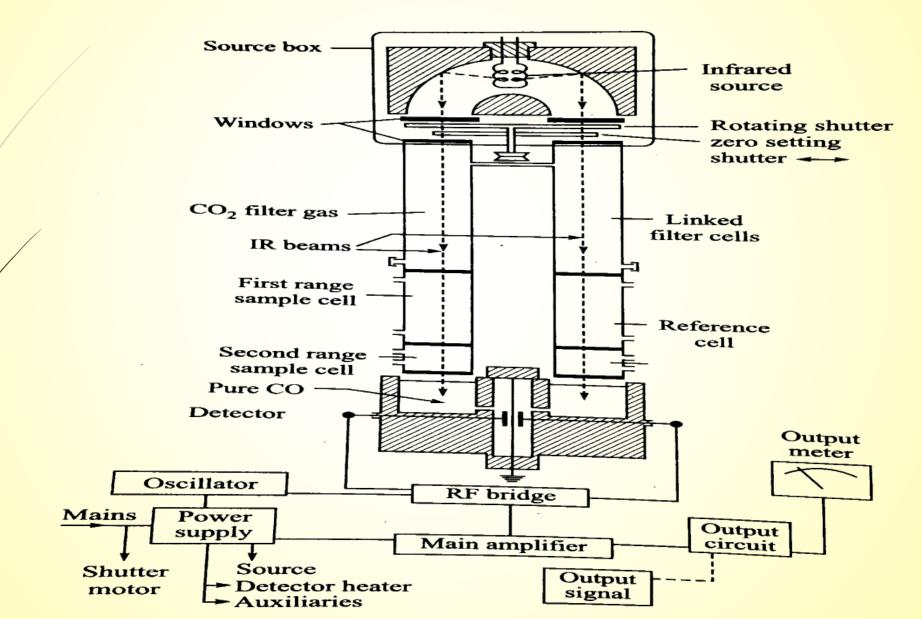
- A diesel particulate filter (or DPF) is a device designed to remove diesel particulate matter or soot from the exhaust gas of a diesel engine.
- The diesel particulate filters usually remove 85% or more of the soot and under certain conditions can attain soot removal efficiencies of close to 100%.
- Some filters are single-use, intended for disposal and replacement once it is full of accumulated ash.

# DIESEL PARTICULATE FILTER (PARTICULATE TRAP)

- The others type is designed to burn off the accumulated particulate either passively through the use of a catalyst or by active means such as a fuel burner which heats the filter to soot combustion temperatures.
- when the filter is full the sensor elevates exhaust temperature or lets in high amounts of NO x to oxidize the accumulated particulate matters.

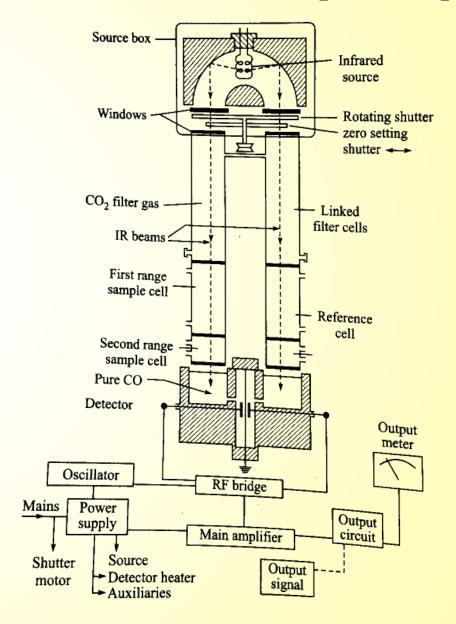


- The NDIR analyser is used to measure the concentration of carbon dioxide and carbon monoxide.
- This device is based on the principle that the infrared energy of particular wavelength, peculiar to a certain gas will be absorbed by the gas.
- The infrared energy of other wavelengths will be transmitted by that gas.
- The carbon dioxide will absorb the infrared wavelength band of 4 to 4.5 (µm) microns.
- The carbon monoxide will absorb the infrared wavelength band of 4.5 to 5 (µm) microns.

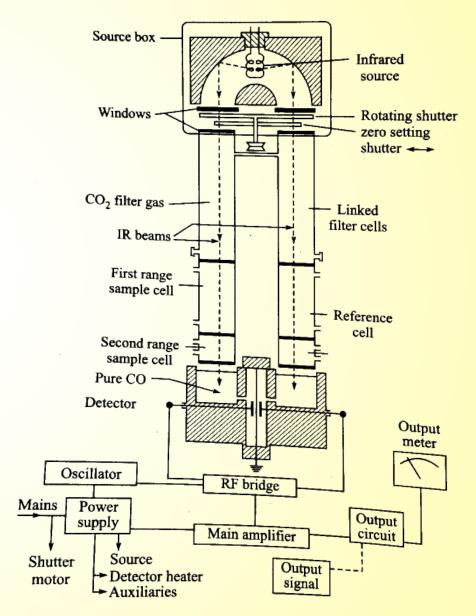


A wideband infrared radiation source consist of a heated wire, which is placed in a quartz tube mounted in the source block.

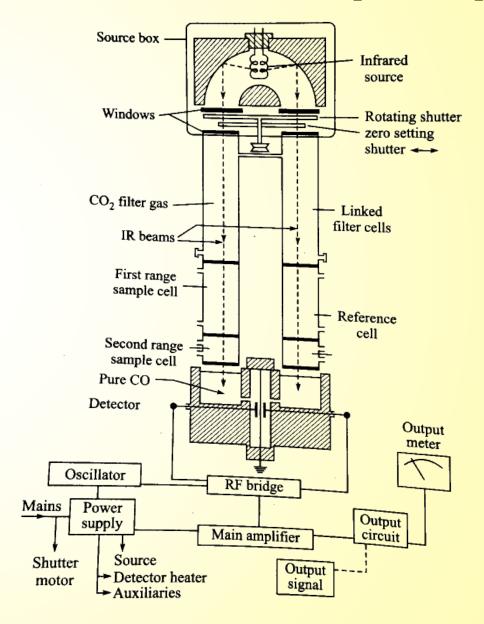
Radiation from the source is reflected within the mounting block and passes out of a symmetrical pair of rectangular apertures as two parallel beams into two separate cells – a sample cell and a reference cell.



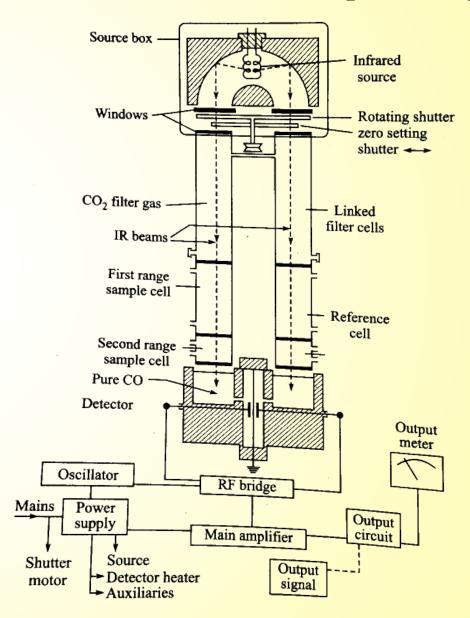
- These cells are internally highly polished and gold plated to ensure high transmission of radiation.
- After passing through these cells the infrared radiation is received in two separate detector cells, which are full of the gas whose concentration is to be measured.
- The two detector cells contain equal amount of this gas and are separated by a flexible diaphragm.



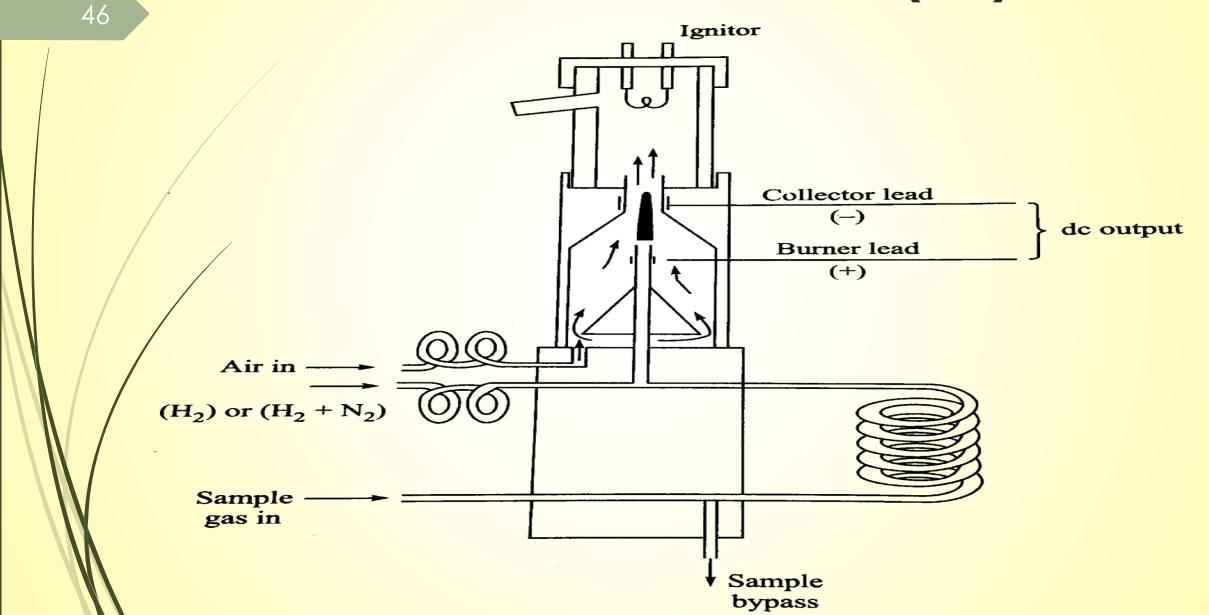
- The sample cell is a flow through tube that receives a continuous stream of mixture of gases to be analysed.
- When the particular gas to be measured is present in the sample, it absorbs the infrared radiation at its characteristic wavelength.
- The percent of radiation absorbed is proportional to the molecular concentration of the component of the interest in the sample.



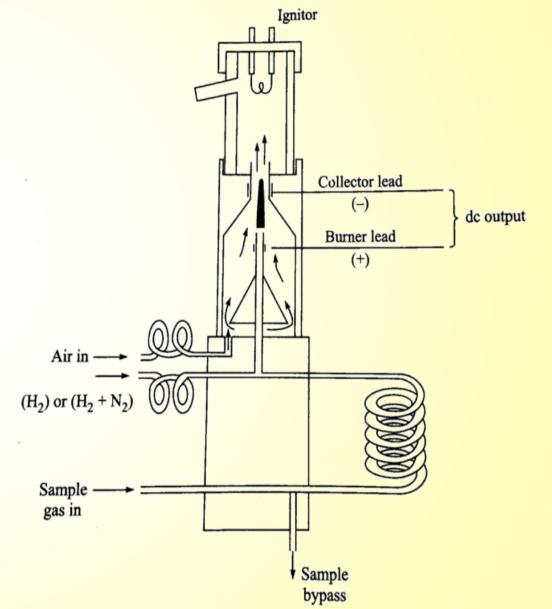
- The reference cell consist of inert gases usually Nitrogen.
- No radiant energy is absorbed in the reference cell, the corresponding chamber in the detector is heated more and its pressure becomes higher than the other chamber.
- This pressure differential causes the diaphragm to move and vary the capacitance.
- The variation of capacitance is proportional to the concentration of species of interest in the sample cell.



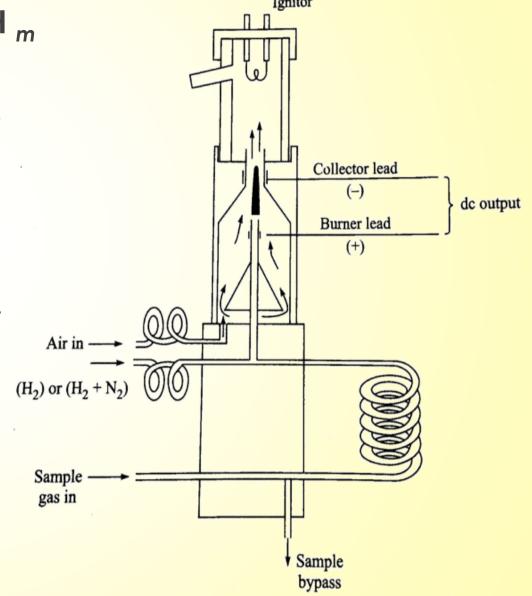
- The FID is used to measure Unburned Hydrocarbon emission in the exhaust gases.
- It is based on the principle that pure hydrogen air flames produces very little ionization, but if a few hydrocarbon molecules are introduced the flame produces a large amount of ionization.
- The amount of ionization is proportional to the number of carbon atoms present in the hydrocarbon molecules.



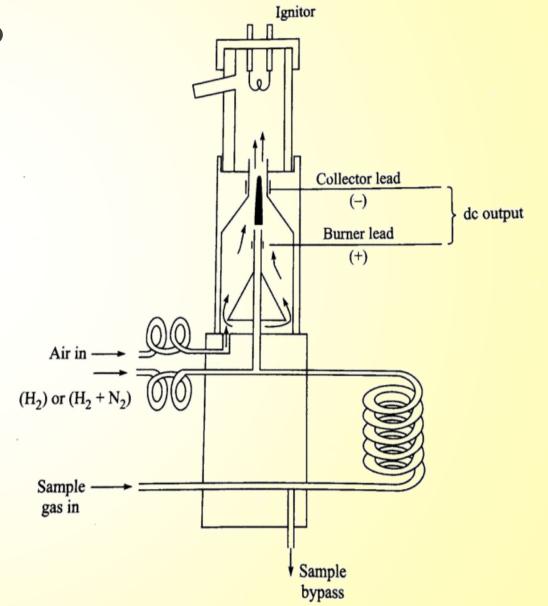
- It consist of a burner assembly, an ignitor, an ion collector and electric circuitry.
- The burner consist of a central capillary tube.
- Hydrogen, or a mixture of hydrogen and nitrogen, enters one leg of the capillary tube.
- The sample gas enters from the other leg of the capillary tube.
- The length and bore of the capillary tubes are selected to control the flow rate.

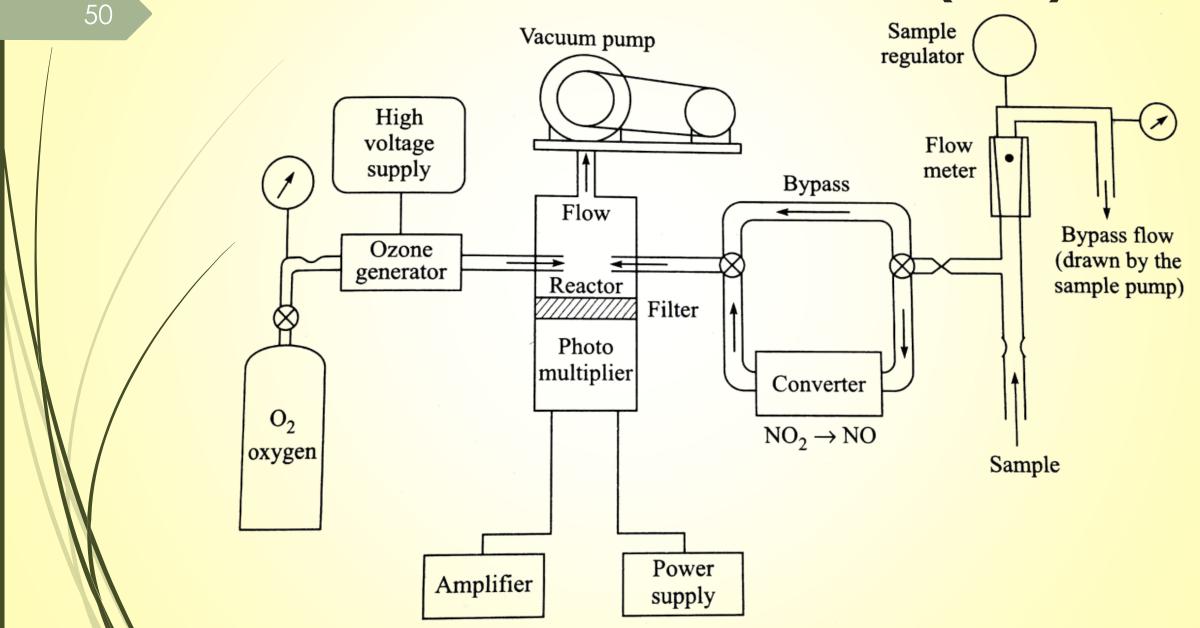


- The mixture of H<sub>2</sub> N<sub>2</sub> C<sub>n</sub> H<sub>m</sub> then flows up the burner tube.
- The air required for combustion is introduced from around the capillary tube.
- The combustible mixture formed in the mixing chamber is ignited by a hot wire at top of the burner assembly.
- An electrostatic field is produced in the vicinity of the flame by an electric polarizing battery.



- This causes the electrons to go to the burner jet and positive ions go to the collector.
- The flow of ions to collector and flow of electrons to the burner complete the electric circuit.
- The dc signal produced is proportional to the number of ions formed and the number of ions is proportional to the number of carbon atoms in the flame.



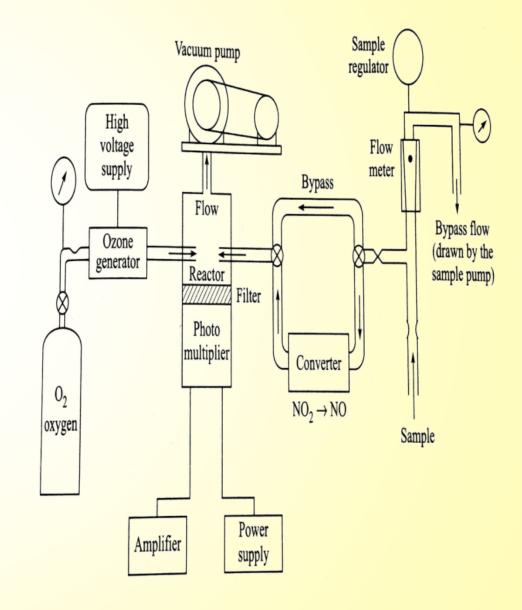


- The CLA measures the nitric oxide (NO) concentrations.
- This technique is based on the principle that NO reacts with ozone (O<sub>3</sub>) to give some NO<sub>2</sub> in an electrically excited state.
- These excited molecules on decaying to ground state emit red light (photons) in the wave length region from 0.6µm to 3µm.

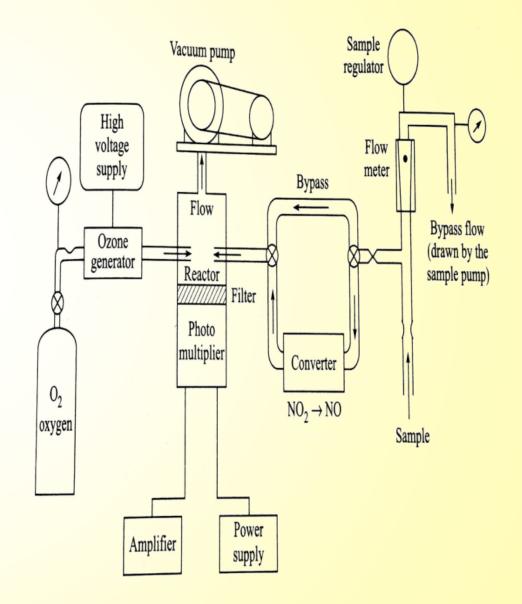
$$\frac{\mathsf{NO} + \mathsf{O}_3}{\mathsf{NO}_2^*} \to \mathsf{NO}_2^* + \mathsf{O}_2$$

$$\frac{\mathsf{NO}_2^*}{\mathsf{NO}_2^*} \to \mathsf{NO}_2 + \mathsf{hv}$$

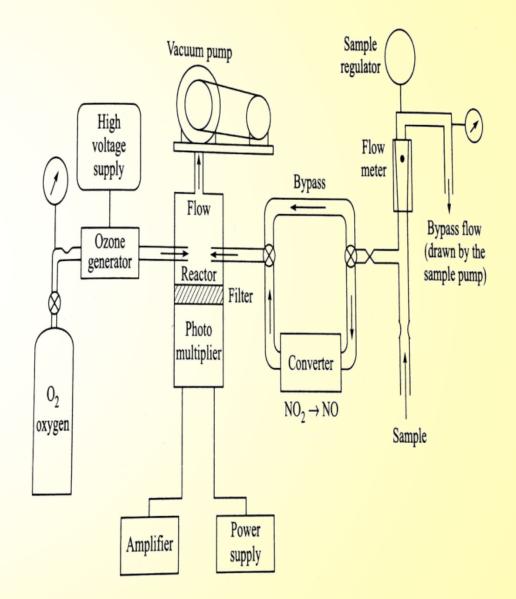
H - Plank's constant, v - Photon



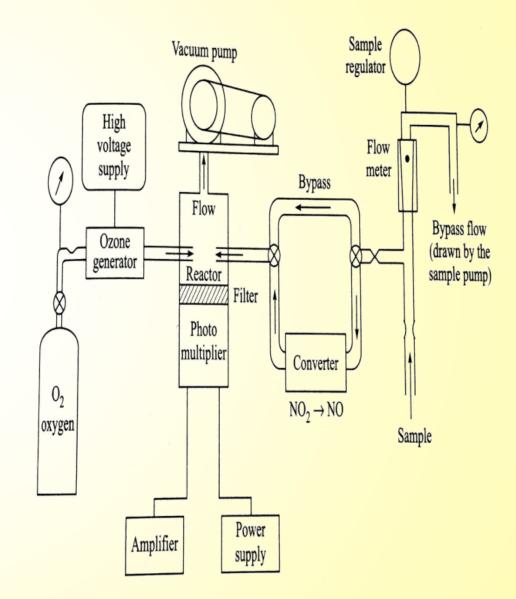
- The oxides of nitrogen (NO<sub>x</sub>) from the engine exhaust comprise mainly the combination of nitric oxide (NO) and nitrous oxide (NO<sub>2</sub>).
- by converting any exhaust NO<sub>2</sub> to NO in a thermo catalytic converter before supplying the exhaust gas to the analyser, the value of total nitrogen oxides (NO<sub>x</sub>) can be obtained.



- The vacuum pump controls the pressure in the reaction chamber and draws ozone and the exhaust sample.
- The ozone is produced by an electric discharge in oxygen at low pressure.
- The converter converts the NO<sub>2</sub> into NO
- In this device an arrangement is made by using a bypass line, so that it may be possible to measure only the NO concentration or NO+NO 2 concentration in the exhaust.

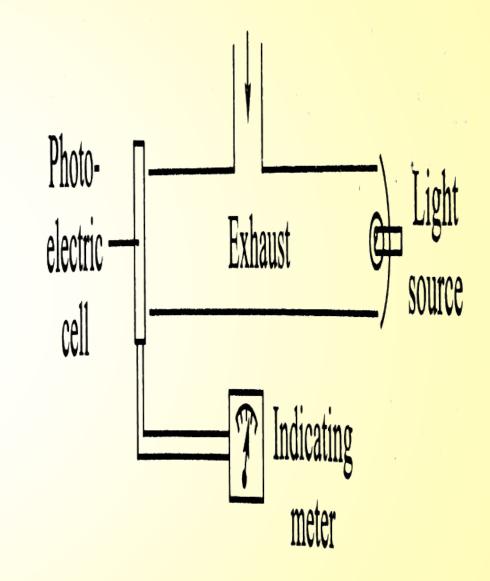


- A mixture of exhaust gas and ozone enters into the reaction chamber.
- In the chamber the gas mixture is heated at a temperature of 600°C.
- When heated the mixture produces some electronically excited molecules of NO2.
- This on decaying emits light, which is detected accurately by a photomultiplier.
- The this signal is then amplified and fed into a recorder.



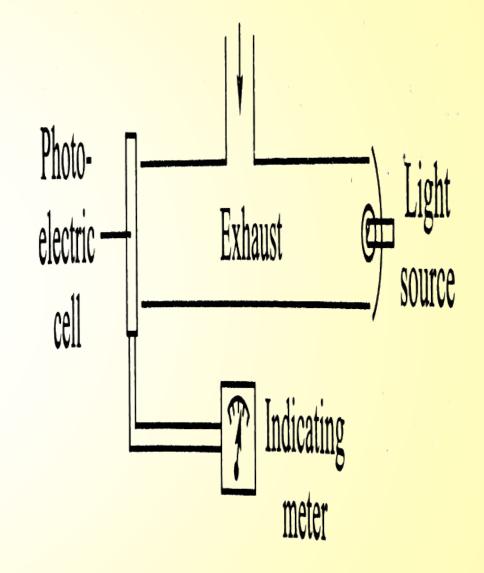
#### HARTRIDGE SMOKE METER

- It based on the principle that the intensity of a light beam is reduced by smoke which is the intensity of smoke.
- The light from a source is passed through a standard length of tube where the exhaust gas sample is continuously supplied from the engine and at other end of the tube the transmitted light is measured by a photo electric cell.
- The photoelectric cell converts the light intensity to an electrical signal.



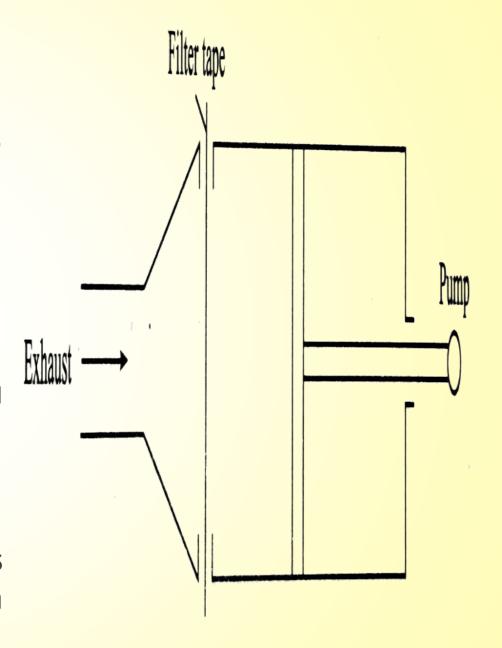
#### HARTRIDGE SMOKE METER

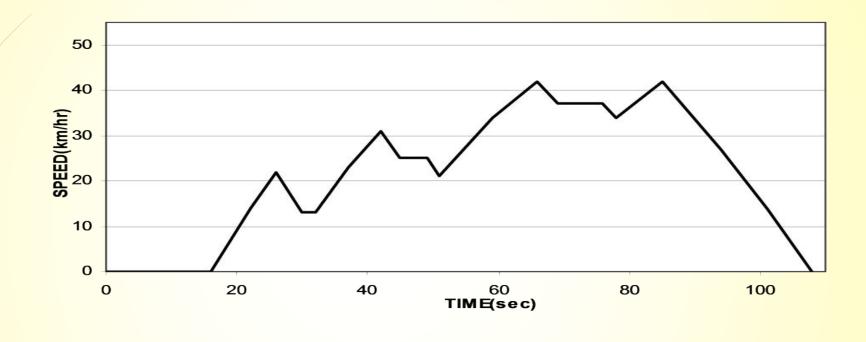
- The intensity of smoke is expressed in the terms of smoke density.
- It is defined as the ratio of electric output from the photoelectric cell when an exhaust sample is passed through the tube to the electric output when clean air is supplied.



#### **BOSCH SMOKE METER**

- It is based on the principle that when a certain quantity of exhaust gas passes through a fixed filter paper, some smoke smudge is obtained on it, which is the measure of smoke intensity.
- A fixed quantity of the exhaust gas from the engine is introduced into a tube, where it passes through a fixed filter paper.
- Depending upon the smoke density, some quantity of smudge is deposited on the filter paper, which can be evaluated optically.





	Time	Distance	Avg. Speed	Max. Speed	Max. accel.	Max Decel	ldle time ratio	Accel. Time ratio	Decel time ratio	Cruise time ratio
	sec	km	km/h	km/h	m/s2	m/s3	%	%	%	%
IDC (6 Cycles)	648	3.948	21.93	42	0.65	0.63	14.81	38.89	34.26	12.04

Standard	Reference	YEAR	Region	
India 2000	Euro 1	2000	Nationwide	
		2001	NCR*, Mumbai, Kolkata, Chennai	
Bharat Stage II	Euro 2	2003.04	NCR*, 13 Cities†	
		2005.04	Nationwide	
Discount Charge III	Euro 3	2005.04	NCR*, 13 Cities†	
Bharat Stage III		2010.04	Nationwide	
Bharat Stage IV	Euro 4	2010.04	NCR*, 13 Cities†	
Bharat Stage V	Euro 5	(to be skipped)		
Bharat Stage VI	Euro 6	2020.04 (proposed)	Entire country	

<sup>\*</sup> National Capital Region (Delhi)† Mumbai, Kolkata, Chennai, Bengaluru, Hyderabad, Ahmedabad, Pune, Surat, Kanpur, Lucknow, Sholapur, Jamshedpur and Agra

Year	Reference	Test	СО	НС	NO <sub>x</sub>	PM
1992	_	ECE R49	17.3–32.6	2.7–3.7	-	_
1996	_	ECE R49	11.20	2.40	14.4	_
2000	Euro I	ECE R49	4.5	1.1	8.0	0.36*
2005†	Euro II	ECE R49	4.0	1.1	7.0	0.15
2010† Eu	Farre III	ESC	2.1	0.66	5.0	0.10
	Euro III	ETC	5.45	0.78	5.0	0.16
2010‡	Euro IV	ESC	1.5	0.46	3.5	0.02
		ETC	4.0	0.55	3.5	0.03

Year	Reference	СО	НС	HC+NO <sub>x</sub>	NO <sub>x</sub>
1991	_	14.3–27.1	2.0-2.9	_	
1996	_	8.68-12.4	_	3.00-4.36	
1998*	-	4.34-6.20	_	1.50-2.18	
2000	Euro 1	2.72-6.90	_	0.97-1.70	
2005†	Euro 2	2.2-5.0	_	0.5–0.7	
2010†	Euro 3	2.3 4.17 5.22	0.20 0.25 0.29	_	0.15 0.18 0.21
<b>2010</b> ‡	Euro 4	1.0 1.81 2.27	0.1 0.13 0.16	_	0.08 0.10 0.11

<sup>\*</sup> for catalytic converter fitted vehicles

† earlier introduction in selected regions