

Module III: Air Pollution Monitoring & Control

Pollution Sources: Stationary & Mobile emission Sources. Monitoring & Control of air pollutants using high volume sampler, cyclone separators, wet scrubbers, electrostatic precipitators, etc. automobile emission control.

Sources of pollutants:

Stationary Emission Source

Point sources: Large, stationary sources of emissions that have specific locations and release pollutants in quantities above an emission threshold are known as.

Area sources: facilities whose individual emissions do not qualify them as point sources

Major source: has the potential to emit, pollutants over a major source threshold

Minor source: emits less pollutant than the major source threshold.

Emission point: smokestacks, storage tanks, equipment leaks, process wastewater handling/treatment area, loading and unloading facilities

Process vent: Distillation columns and oxidation vents.

[Discuss about what are the gases emitted by these sources]

Mobile sources:

Transportation

Mobile sources include both on road vehicles and off road equipments

Highway Vehicles: Gasoline and diesel powered automobiles, buses and trucks.

Marine Vessels: Commercial, military and recreational.

Aircraft and Railroads

Paved and Unpaved Roads

Off-Road Equipment: Gasoline and diesel powered lawn and garden equipment, industrial and recreational engines

[Discuss about what are the gases emitted by these sources]

Natural Sources:

Volcanos, plant metabolism, lightning, soil microbes, soil, rock etc.

[note: A brief discussion should be needed about the pollutants which are emitted by coal fired plants, industry (oil , gas, coal), metal ore smelting, power plants, petroleum refineries, transportations.]

Automobile emission control:

The main pollutants in automobile emission are CO, NO_x, and hydrocarbon (HC) along with some particulates. When one of the pollutants in internal combustion engines is subjected to

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control measure, the amount of the others affected at the same time. In four stroke internal combustion engine the most important factor is the air to fuel ratio.

[note: The students are already familiar with four stroke engine and how it works in the first semester engineering chemistry, we are giving a brief, the main components of the four stroke engine, not in detail. But we should show them the diagram of the four strokes.]

The conventional Otto cycle engine: Four stroke internal combustion engines contains-

- I. **Intake stroke:** The descending piston draws in a mixture of fuel and air through the open intake valve.
- II. **Compression stroke:** the raising of piston compresses the air/fuel mixture in the cylinder against the now closed intake and exhaust valve. As the piston approaches the top of the compression stroke, the spark plug fires, igniting the mixture.
- III. **Power stroke:** in the power stroke, the burning mixture expands and forces the piston down which turns crankshaft and delivers power to drive the train.
- IV. **Exhaust stroke:** in exhaust stroke, the exhaust valve opens and the raising piston forces the combustion products out of the cylinder through the exhaust system and into the air. [this is the exhaust system, which need to be control to minimise the emission of the pollutants]

In diesel engine operates with a similar cycle, but they compress fuel more during the compression stroke which makes the cylinder so hot that they ignite of their own accord without needing a spark plug.

[Diagram of the four strokes of internal combustion engines should be here]

[Note: Before going to the exhaust control system to minimise the emission of pollutants from automobiles, we need to discuss about air/fuel ratio in the intake stroke of the internal combustion engine]

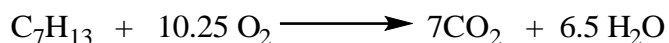
Air to fuel ratio and lean/rich fuel:

The single most important factor in determining emissions from a four stroke internal combustion engine is the ratio of air to fuel in the mixtures as it enters the cylinder during the intake stroke.

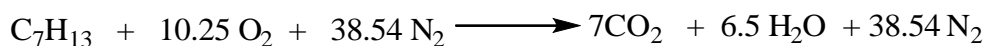
To analyse that mixture ration and its impact on emission, let us begin with the stoichiometry of the gasoline combustion. Modern gasolines are blend of various hydrocarbons, an average formulation can be represented as C_7H_{13} .

For complete combustion in oxygen,

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In air N_2 is present, 3.76 mol of N_2 accompanying in every mole of oxygen. Thus $10.25 \times 3.76 = 38.54$ moles of N_2 can be placed each side of the reaction which will give-



Where any oxidation of N_2 to nitrogen oxides has been neglected.

Stoichiometric Air to fuel ratio:

1 mol of $\text{C}_7\text{H}_{13} = 97 \text{ g}$

10.25 mol of $\text{O}_2 = 328 \text{ g}$

38.54 mol of $\text{N}_2 = 1079 \text{ g}$

Considering air to be made up only oxygen and nitrogen, the air fuel ratio needed for complete oxidation of gasoline is = air/ fuel =14.5

Stoichiometric ratio of gasoline is 14.5

Air fuel ratio >14.5 – Lean fuel

Air fuel ratio <14.5 – Rich fuel

If the actual air/fuel mixture has less air than what the stoichiometric ratio, indicates is necessary for complete combustion, the mixture is said to be rich fuel.

If more air is provided than what is necessary, the mixture is then said to be lean.

[Note: a brief discussion about the pollutants emitted by motor vehicles indicating the role of lean and rich fuel mixture.]

[Effect of air/fuel ration on emission, power and fuel economy should be discussed by describing a figure of the relation among air/fuel ration, emissions, power and fuel economy]

Exhaust system control:

During the exhaust stroke of an internal combustion engine, combustion gases are pushed through the manifold and out the tailpipe. It is the exhaust system that most of the control of automobiles emission now occurs.

Commonly used system for the treatment of exhaust gases are-

- (i) Thermal reactor
- (ii) Exhaust gas recirculation system
- (iii) Catalytic converter

[A brief discussion about thermal reactor and exhaust gas recirculation system for the control of automobile emission should be discussed in the class.]

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Earlier two way catalytic converter are used to control the HC and CO pollutant, but as NO_x has also immense effect on the atmosphere, a three way catalytic converter needed where one can control all the three important pollutants.

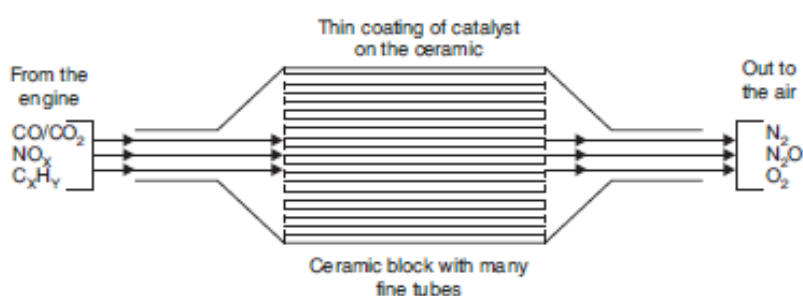
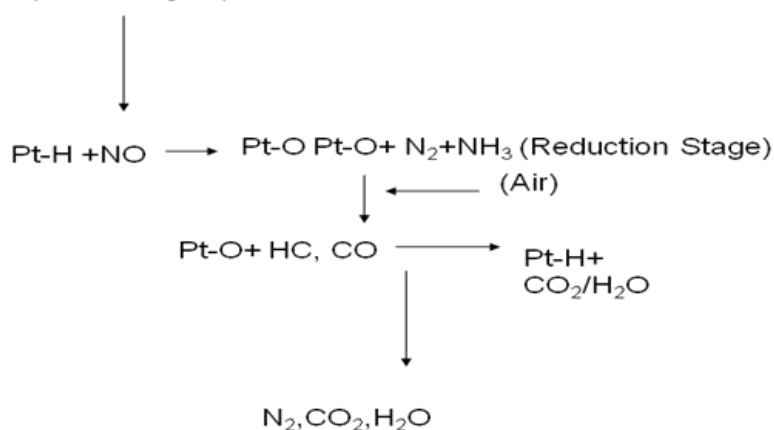
Three way catalytic converter: A three way catalytic converter is able to oxidise hydrocarbons and CO to H₂O and CO₂ while reducing NO_x to N₂ all in the same bed of catalyst. It is very effective in controlling emissions near stoichiometric conditions where the engine performance and efficiency are greatest.

Finely divided Pt used as a catalyst (Pd and Rh can also be used) which reduces NO_x to N₂ (NH₃) and oxidise HC and CO to CO₂ and H₂O.

Pb free gasoline is used as Pb poisoned the Pt catalyst and thereby reduces the catalytic activity of the catalyst.

Catalytic Converter for treating Auto-emissions

HC, CO, NO (From engine)



Octane number and Knocking:

[Discussion about octane number and knocking (Octane rating, enhancer of octane rating, and factors of knocking) should be in brief as it is already discussed in engineering chemistry, in first semester]

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Particulates

Volcanic eruptions, wind and dust storms, salt spray etc. are natural sources of particulate constituents of the atmosphere. Burning of coal, oil, wood, gaseous fuels; Industrial processes; Smelting and mining operations; fly-ash emissions from power plants, burning of coal refuse and agricultural refuse are man-made activities which release considerable tonnage of particulate matter in atmosphere. Particulate matter has large surface areas hence they provide excellent sites for absorption of various organic and inorganic species. They also scatter light and reduce visibility. The typical particulate air pollutants their sources and effects are summarized below in;

Particulate	Sources	Effects
Dust	Asbestos and cement factories	Causes respiratory and allergic diseases
Smoke	In complete oxidation of fuels in automobiles	Causes skin diseases
Lead dust	lead batteries and automobile exhausts	Causes lead poisoning

Particulate matter can be removed from industrial gaseous effluents with the help of following devices; cyclone collectors, electrostatic precipitators, wet scrubbers and settling chambers.

Control of particulate matter:

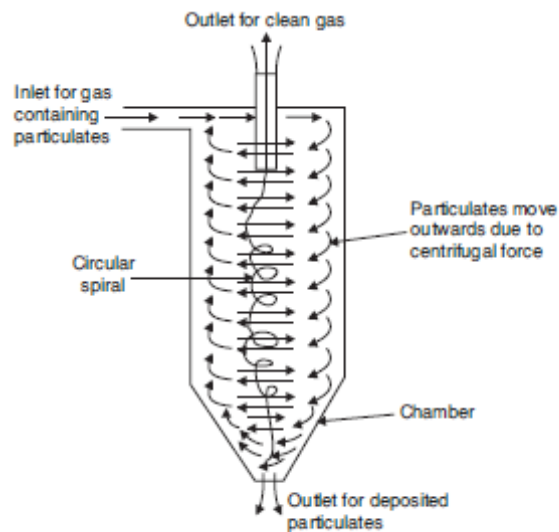
The control techniques of particulate matters depends on the particle size, concentration, corrosivity, toxicity, volumetric flow collection efficiency, allowable pressure drops and cost. For relatively large particles cyclone collector/ separator is used whereas for small particulates baghouse filter or electrostatic precipitators are used.

Cyclone separator:

The general principle of inertia separation is that the particulate-laden gas is forced to change direction. As gas changes direction, the inertia of the particles causes them to continue in the original direction and be separated from the gas stream. The walls of the cyclone narrow toward the bottom of the unit, allowing the particles to be collected in a hopper. The cleaner air leaves the cyclone through the top of the chamber, flowing upward in a spiral vortex, formed within a downward moving spiral. Cyclones are efficient in removing large particles

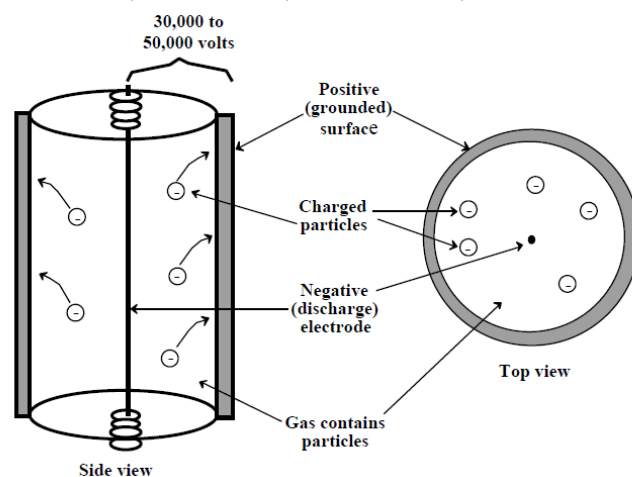
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but are not as efficient with smaller particles. For this reason, they are used with other particulate control devices.



Electrostatic precipitators:

An ESP is a particle control device that uses electrical forces to move the particles out of the flowing gas stream and onto collector plates. The ESP places electrical charges on the particles, causing them to be attracted to oppositely charged metal plates located in the precipitator. The particles are removed from the plates by "rapping" and collected in a hopper located below the unit. The removal efficiencies for ESPs are highly variable; however, for very small particles alone, the removal efficiency is about 99 percent. Electrostatic precipitators are not only used in utility applications but also other industries (for other exhaust gas particles) such as cement (dust), pulp & paper (salt cake & lime dust), petrochemicals (sulfuric acid mist), and steel (dust & fumes).

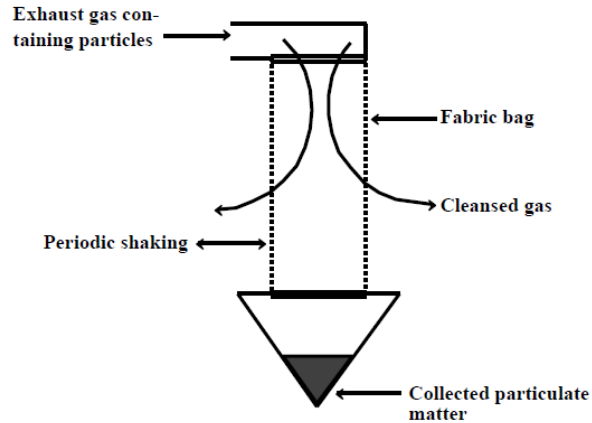


Baghouse filter:

Fabric filters, or baghouses, remove dust from a gas stream by passing the stream through a porous fabric. The fabric filter is efficient at removing fine particles and can exceed efficiencies of 99 percent in most applications. The selection of the fiber material and fabric construction is important to baghouse performance. The fiber material from which the fabric

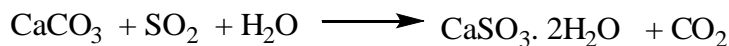
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is made must have adequate strength characteristics at the maximum gas temperature expected and adequate chemical compatibility with both the gas and the collected dust. One disadvantage of the fabric filter is that high-temperature gases often have to be cooled before contacting the filter medium.

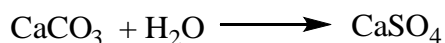
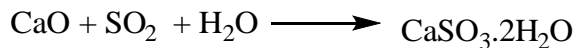


Wet scrubbers:

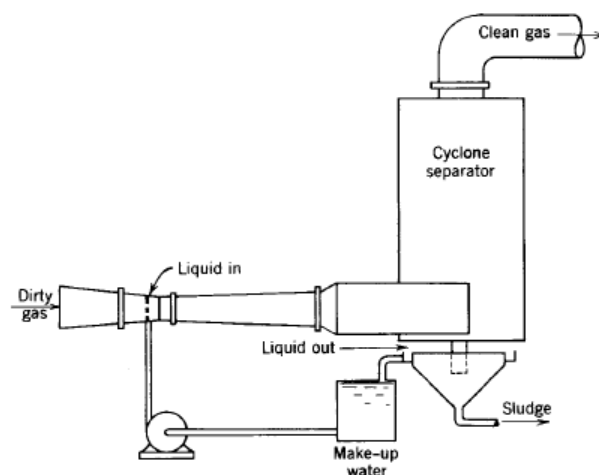
It is used to control and remove flue gases as precipitators. Finely pulverised limestone is mixed with water to create slurry that is sprayed into the flue gases. The flue gas, SO_2 is absorbed by the slurry producing a CaSO_3 or CaSO_4 precipitate. The precipitator is removed from the scrubbers as sludge.



Sometime, lime is also used instead of limestone in the slurry.



Lime is more expensive than limestone and SO_2 removal efficiency upto 95%



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High volume samplers:

High volume sampler is used for the collection of atmospheric particulate material. Filtration is the most common technique for sampling particulate matter. Although there are varieties of filter material used for the filtration, in high volume sampler glass fibres is used which efficiency is upto 99% of particles with 0.8 micron diameter. High volume of air samples are used to pump large volume of air upto 2000 cubic meter at a rate of about 1.7 cubic meter / min. Depending upon the particle size, one should use very small glass fibre for the efficient collection.

Analysis of gaseous pollutants:

The common techniques for the analysis of gaseous pollutants are in the table below:

Pollutant	Measurement Methods
SO ₂	Ultraviolet pulsed fluorescence, flame photometry, coulometric; dilution or permeation tube calibrators
CO	Nondispersive infrared tank gas and dilution calibration, gas filter correlation
O ₃	Gas-phase chemiluminescence ultraviolet (UV) spectrometry; ozone UV generators and UV spectrometer or gas-phase titration (GPT) calibrators
NO ₂	Chemiluminescence; permeation or GPT calibration
Lead	High-volume sampler and atomic absorption analysis
PM ₁₀ ^a	Tapered-element oscillating microbalance, automated beta gauge
PM _{2.5}	Twenty-four-hour filter sampling
TSPs ^b	High-volume sampler and weight determination
Sulfates, nitrates	High-volume sampler and chemical analysis—deposit dissolved and analyzed colorimetrically
Hydrocarbons	Flame ionization and gas chromatography ^c ; calibration with methane tank gas
Asbestos and other fibrous aerosols	Induced oscillation/optical scattering, microscope, and electron microscope
Biologic aerosols	Impaction (Petri dish), incubated 24 hr and microbial colonies counted

^a 10 μ m or small particle.

^b Total suspended particulates. type, size, and composition are important.

^c Not generally required to measure these if O₃ is measured

Nitrogen Oxide

Chemiluminescence Analyzer:

Nitric oxide (NO) is measured by the gas-phase chemiluminescent reaction between nitric oxide and ozone. This technique is also used to determine nitrogen dioxide (NO₂) by catalytically reducing NO₂ in the sample air to a quantitative amount of NO. Sample air is drawn through a capillary into a chamber held at 25 in. Hg vacuum. Ozone produced by

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electrical discharge in oxygen is also introduced into the chamber. The luminescence resulting from the reaction between NO and ozone is detected by a temperature-stabilized photomultiplier tube and wavelength filter. An automatic valving system periodically diverts the sample air through a heated activated-carbon catalyst bed to convert NO₂ to NO before it enters the reaction chamber. The sample measured from the converter is called NO_x. Since it contains the original NO plus NO produced from the NO₂ conversion, the differences between the sequential NO_x and NO readings are reported as NO_x. Primary dynamic calibrations are performed with gas-phase titration using ozone and nitric oxide standards and with NO₂ permeation tubes.

Carbon Monoxide

Infrared (IR) Analyzer:

This method utilizes dual beam photometers with detection accomplished by means of parallel absorption chambers or cells that are separated by a movable diaphragm. The IR energy passes into each chamber—one containing the sample with CO, the other containing the reference gas. The reference gas heats up more than the ambient air sample with CO since CO absorbs more of the IR energy. This results in higher temperature and, hence, the volume-pressure in the reference chamber that is transmitted to the separating diaphragm designed to provide an electrical output to measure the CO concentration. However, it is necessary to remove water vapor interference as the humidity in ambient air absorbed by IR energy can introduce a significant error in CO readings. In one instrument (the EPA reference method), the interference due to water vapor is eliminated by first passing one portion of the ambient air sample through a catalytic converter where CO is converted to CO₂ prior to entry into the reference chamber. The other half of the air sample containing CO passes directly into the sample chamber. This procedure cancels out the effect of moisture since both gas streams are identical except for the presence of CO.³⁷ Carbon monoxide is also measured by gas-phase correlation.

Ozone

Chemiluminescence Analyzer:

Ozone is measured by the gas-phase chemiluminescence technique, which utilizes the reaction between ethylene and ozone (O₃). Sample air is drawn into a mixing chamber at a flow rate of 1 L /min where it is mixed with ethylene gas and introduced at a flow rate of 25 cc/min. The luminescence resulting from the reaction of the ethylene with ambient ozone in the air supply is detected by a temperature-stabilized photomultiplier tube. This signal is then amplified and monitored by telemetry and on-site recorders. These ozone instruments contain

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provision for weekly zero and span checks. Primary dynamic calibrations are periodically performed that require standardization against a known, artificially generated ozone atmosphere. Ozone is also measured by UV light instrumentation.

Sulfur dioxide:

West Gaeke Spectrophotometric method:

The modified West-Gaeke spectrophotometric method remains the standard method for the monitoring 0.0005-5 ppm SO₂ in ambient air. SO₂ is collected in a scrubbing solution containing HgCl₄²⁻ (HgCl₂ + KCl), the collection efficiency being around 95%. The solution is allowed to react with HCHO and then with para-rosaniline hydrochloride which form a red-violet dye. The absorbance of the product red-violet dye is measured at 548 nm.

The major interference from NO₂ (> 2 ppm) when present is eliminated by the addition of sulfamic acid H₂NSO₃H. This reagent acts as a reducing agent converting NO₂ to N₂.

Alternative fuels: A brief discussion necessary of the following fuels including advantage and disadvantage of each fuel. [For reference, please go through G. M. Masters]

Cleaner gasoline: Motor vehicle hydrocarbon emission are not only the results of inefficient combustion, but also caused by vaporisation of the fuel itself. To help control of these evaporative emissions, automobiles are equipped with vapour recovery system. Gasoline can be formulated to help reduce tailpipe emission of CO and HC by adding oxygenates that encourage complete combustion, e.g. Ethanol, MTBE. To enhance octane rating replacing TEL, BTX is also used.

A number of alternative gasoline are being investigated as possible fuels for the future. These includes ethanol, methanol, CNG, Hydrogen, electricity etc. The motivation for developing vehicles capable of running on these fuels is a combination of the potential to reduce air pollution and to reduce our demand for petroleum and the negative environment, non-renewable resource depletion and the security issues associated with its use.

[A brief introduction the following fuels is necessary]

Ethanol:

Methanol:

Biodiesel:

Compressed natural gases:

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Electric drive vehicles:

Fuel cell vehicles:

Clean air act and their amendments: (Preventing and reducing air pollution)

The US congress passed clear air act in 1955, 1970, 1977 and 1990 providing federal air pollution regulation to deal with the air pollution problems.

[Here we have to discuss the aim of the clean air act and their amendments to attain the goal.]

Environmental protection agency was established by the amendments in 1970. EPA was required to establish national ambient air quality standards (NAAQS), New source performance standards (NSPS).

NAAQS now exists for six criteria pollutants CO, Pb, NO₂, ground level O₃, SO₂ and two categories of particulate matters. The clean air act requires that the list of six criteria pollutants be reviewed periodically and that standards according to the latest scientific information.

The clean air act amendments 1990: The clean air act amendments of 1990 broadened its scope to include the control of pollutants that effect global problem- stratospheric ozone depletion. Principal changes in the act included the following-

- i. Creation of new acid rain program
- ii. New requirements for nonattainment areas
- iii. Tightened automobile emission standards and new fuel requirements
- iv. New toxic air pollutant control
- v. Phase out schedule for ozone depleting substances

[Discuss about the acid rain program and ozone depleting substances.]