Topic: Analytical methods for measuring air pollutants

1. Introduction

1.1. Air Pollutants

Air pollution basically considered substances which changes the qualitative composition of air in relation to the average composition. It is involvement of a substance in the air that can have adverse effects on humans and the ecosystem. The substance can be solid particles, liquid droplets, or gases. They can be of natural or man-made. The pollutants are primarily produced from physical processes. But some pollutants are not emitted directly, they appear when primary pollutants react or interact with each other. Some examples of air pollutant are carbon monoxide gas, sulfur dioxide that can be released form vehicles or from factories.

1.2. Measurement of concentration of air pollutants

A great number of technologies and instruments both for sampling and determination of the concentration levels of different components of air pollution are used. These include chromatography, infrared spectroscopy, fluornetry, spectrophotometry and atomic absorption spectroscopy. The pollutants which results in air pollution are predominantly released from industries. Determination of concentration of pollutant is important to analyze the extent of pollution in any particular area and it also help to recover a good environment by accepting several control measures. The concentration of air pollutants is high in urban area as compared to rural areas because the urban areas are nearer to industries.

1.3. Advantages of measurement of air pollutants

The use of appropriate methods and analytical techniques in practices for air studied provide information necessary for estimation of qualitative composition of pollutants. It helps in Study of processes in the atmosphere and interaction range of particular pollutants. It also help in estimating the exposure rate and accumulation of pollutants to living organisms.

2. Toxic gaseous pollutants

There are many different sources that contribute to air pollution, which negatively affect public health and the environment. Toxic gaseous pollutants are one of them and contribute to air pollution in majority. They are basically emitted from automobiles industries, power plants and factories. The analytical methods can be used for the measurement of air pollutants. Among the common gaseous pollutants, the most general are sulfur dioxide, hydrogen sulfide, oxides of nitrogen, hydrogen fluoride, chlorine, hydrogen chloride, hydrogen cyanide, ammonia, carbon monoxide and ozone. For monitoring CO, CO2, NO2 and SO2, instruments based on spectroscopic techniques mainly infrared and paramagnetic properties are frequently used. For low concentration of NOX and SO2 a chemi-luminescent method can be applied. Also fully extractive systems can be sometimes used especially when the air sample contains components which are easily soluble in water.

2.1 Sulfur dioxide as a pollutant

Sulfur dioxide may be considered to be the most important air pollutant. It has very high corrosion rates, plant damage and general toxic effects. The determination of low concentrations of sulfur dioxide is a challenge, the problem associated with its determination is sampling of these pollutants. Sulfur dioxide is stable in the atmosphere for 2-4 days. The concentration of sulfur dioxide can be determined. When the air sample is bubbled through a aqueous dilute solution of sodium tetrachloromercurate (II), $Na_2[HgCl_4]$, containing sulfamic acid. It destroys any nitrogen oxides present in the air. In the whole procedure sulfur dioxide present in the air sample reacts with tetrachloromercurate (II) and it get converted into nonvolatile complex sodium dichorosulfitomercurate (II), $Na_2[HgCl_2(SO_3)]$. The following reaction will take place:

$$Na_2[HgCl_4] + SO_2 + H_2O \rightarrow Na_2[HgCl_2(SO_3)] + 2HCl$$

After the formation of complex a mixture of p-rosaniline dye, formaldehyde and phosphoric acid is added and p-rosaline sulfitomercurate is formed. It results in the liberation of sulfur dioxide from sodium dichlorosulfitomercurate (II) complex and help to maintain the pH of the reaction at 1and can combine with heavy metal ions along with sulfur dioxide in the environment. The concentration of sulfur dioxide in the atmosphere is directly proportional to the concentration of p-rosaline methylsulfonic acid which can be determined calorimetrically.

2.2 Nitrogen dioxide

Contaminated air which contains nitrogen dioxide is bubbled through a solution of sodium hydroxide. This results in the conversion of nitrogen dioxide into sodium nitrate and sodium nitrite.

$$2NO_2 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O$$

The product is then passed to a mixture of hydrogen peroxide, sulfanilic acid, hydrochloric acid and N(1-naphthyl)-ethylenediamine dihydrochloride. The sodium nitrite so formed is then diazotizes with sulfanilic acid and the diazonium salt couples with N-(1-naphthyl)-ethylenediamine dihydrochloride. The concentration of nitrogen dioxide can be determined by Lambert-Beer's law by determining the concentration of coupled compound.

2.3 Carbon monoxide

Carbon monoxide has a characteristic infrared absorption near 4.6 μm. The absorption of infrared radiation by the CO molecule therefore can be used to measure CO concentration in the presence of other gases. It is based on the fact that carbon monoxide possesses a dipole moment which absorbs infrared radiation.

2.3.1 Non-dispersive infrared analyzer

The non-dispersive infrared analyzer is made up of having a sample cell in which sample of polluted air can be kept and a reference cell containing pure air. The infrared beam from a source is reflected by choppers alternately through the sample cell and the reference cell. The intensity of the beam emerging from sample cell is decreased since carbon monoxide absorbs IR radiation. The beam is then strike a detector containing carbon monoxide and a movable diaphragm. The carbon monoxide in the detector absorbs infrared radiation and becomes hot and the portion of the detector which faces the sample cell receiving lower intensity of infrared radiation is less hot. The diaphragm moves from low temperature portion to high temperature. The distension of diaphragm is proportional to the difference in intensity of infrared radiation, which is then proportional to the amount of carbon monoxide present in contaminated air

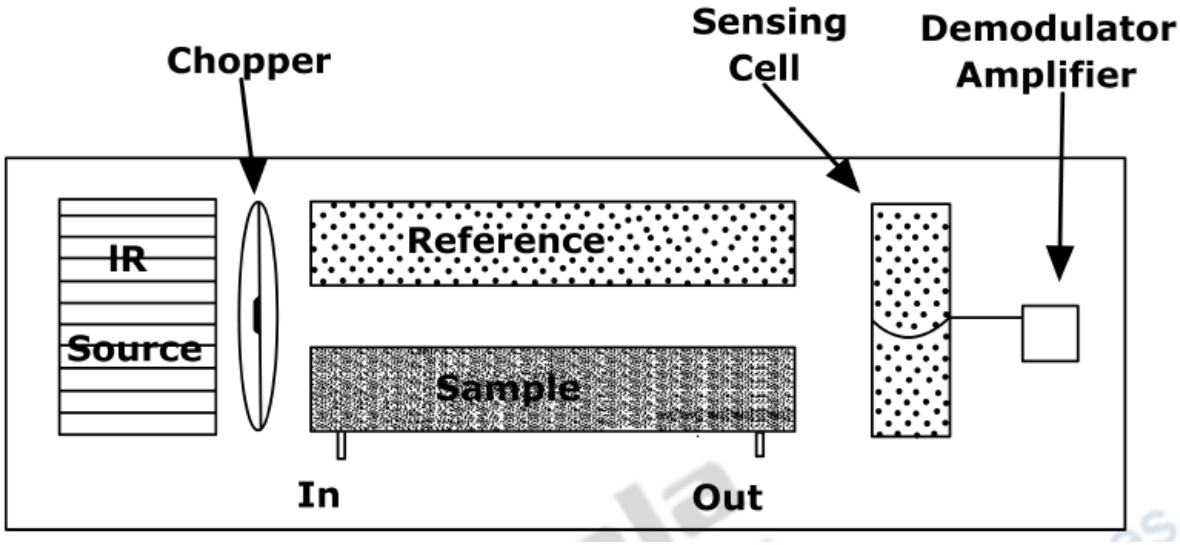


Figure: A nondispersive infrared analyser

Non-dispersive infrared systems have several advantages. They are not sensitive to flow rate, they require no wet chemicals, they are reasonably independent of ambient air temperature changes, they are sensitive over wide concentration ranges and these systems may be operated by nontechnical personnel.

2.3.2 Resonance Fluorescence

Resonance fluorescence of CO in the vacuum ultraviolet has been used for a highly sensitive instrument. In this technique atmospheric CO absorbs radiation in the range of 150-nm from a radio frequency discharge lamp, and fluorescence from the excited CO is detected by a photomultiplier tube. The lamp generates plasma in a continuous flow of CO2 in argon. The pressure in the fluorescence chamber must be maintained between 7 and 9 bar to balance interference from oxygen and CO signal. Permeation tubes can also be used for preparing standard mixtures of such pollutant gases as sulfur dioxide and nitrogen dioxide. In the permeation tube techniques, a sample of the pure gas under pressure is allowed to diffuse through a calibrated partition at a defined rate into a diluents gas stream to give a standard sample of known composition. Another possible way to liberate known amounts of CO into a diluent gas is by thermal decomposition of nickel tetracarbonyl [$Ni(CO)_4$].

2.4 Methane (greenhouse gas)

It is an open path infrared detector and can scan a wide area. It is used for detecting gas leaks from a distance therefore it is widely used to inspect areas such as processing plants, storage tanks over-head rack mounted piping and compressor stations. In the whole process firstly the laser light beam is projected on a target. A fraction of beam is scattered from the target surface and returned to the source. The light which is returned is then collected and focused onto a detector. The presence of methane in the air is detected by the returned light and the reading for this is displayed in ppm-m in meter.

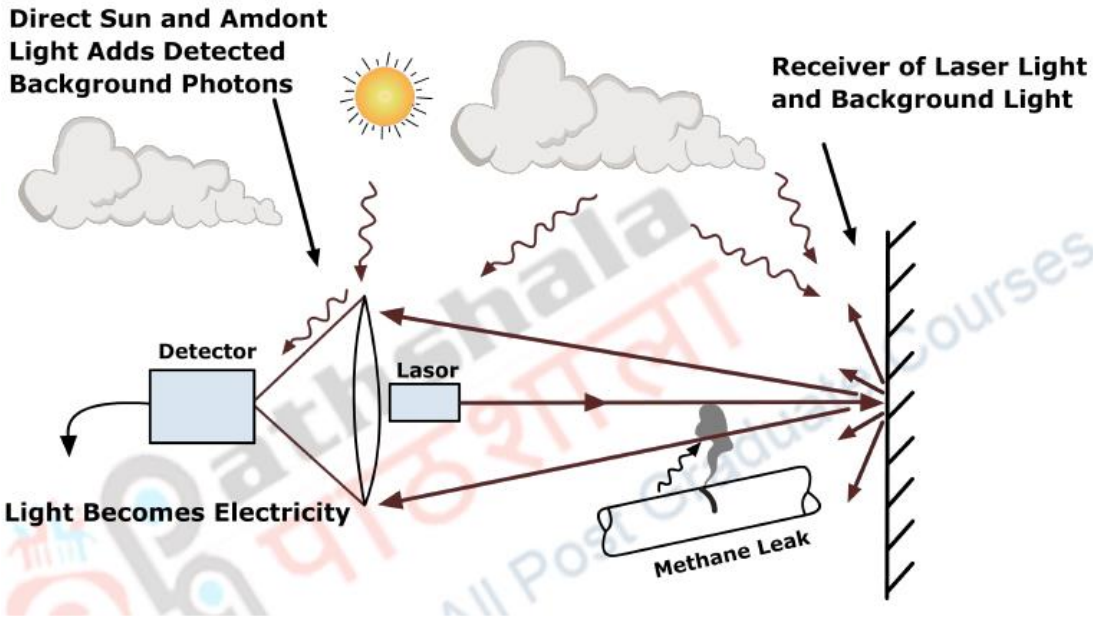


Figure: Remote laser detection

3. Suspended matter and photochemical smog

3.1 Analysis of suspended matter

In order to determine the extent of air pollution by particulates one of the most widely accepted method is to determine the amount of dust that settle from atmosphere or that is washed from the air by rain fall. The determination of dust fall is made gravimetrically on samples that have been collected for a given period of time. A perforated polished aluminum box containing a polyethylene cup is used for collecting dust. In areas where wind velocity is high the inside of the polyethylene container is coated with grease the dust sticks to the grease and is not lost by wind action. In very cold places a volatile antifreeze like isopropanol is added to the dust collector so as to avoid the freezing of rain water.

The aluminum box is placed in an open place. This treatment eliminates any moisture which may have adhered to the collector. The polyethylene cup is then heated for 1 hour and the weight of the particulate in the container is determined.

$$X = a/\pi b^2$$

Where a is the weight of the dust in milligrams and b is the radius of the container

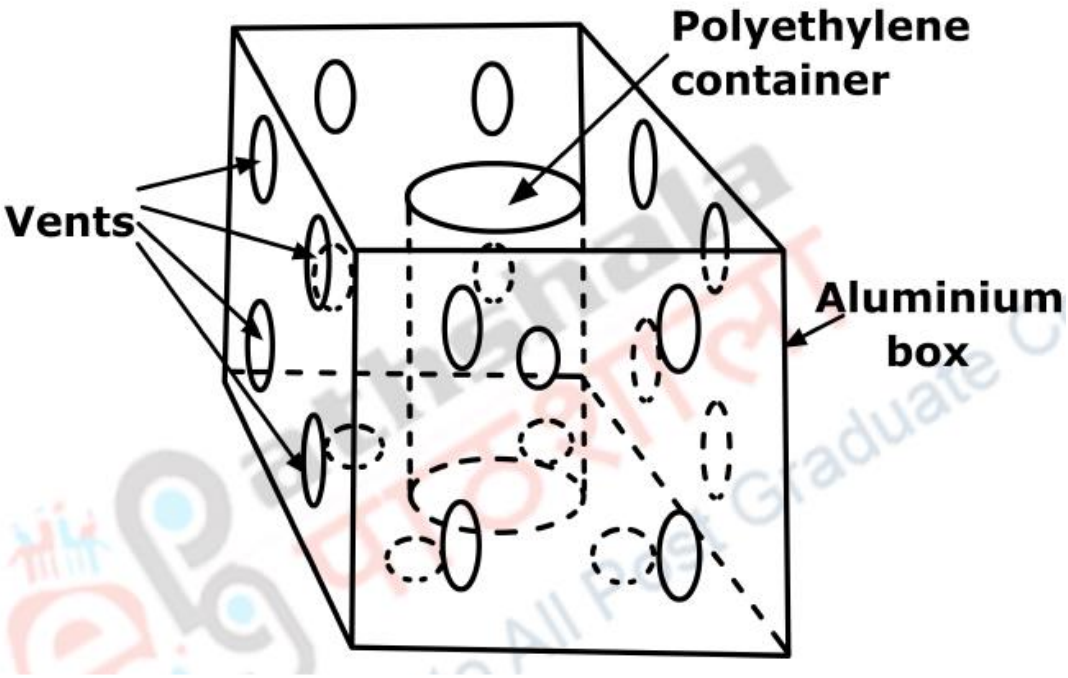


Figure: Gravimetric estimation of dustfall

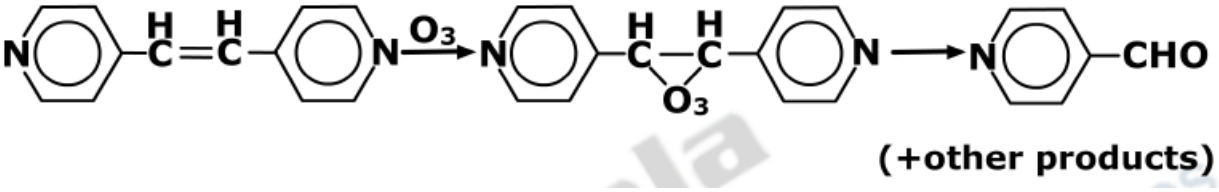
In order to collect the total dust collected in the polythene container is washed with a jet of hot, distilled water the washings are qualitatively filtered in an evaporating dish. Water is evaporated from the filtrate by heating the sample is dried by further heating the dried sample is then washed. And the amount of water insoluble dust is calculated as follow

$$Y = a-c$$

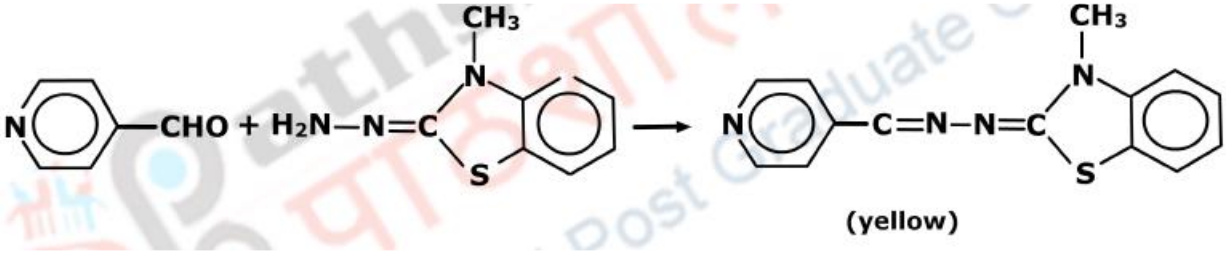
Where c is the weight of soluble particulates.

3.2 Analysis of constituents of photochemical smog

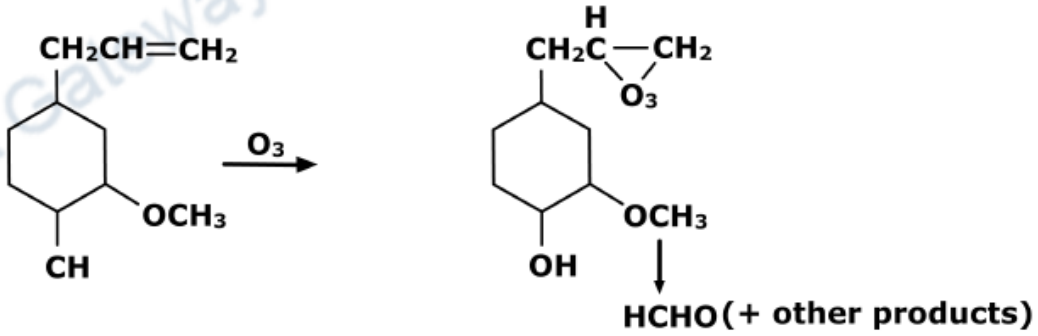
The main constituents of photochemical smog originate from automobile exhaust. The main constituent of smog is the oxides of nitrogen, nitric oxide and nitrogen dioxide. The formation of smog initiates with the photolysis of nitrogen dioxide and the oxygen released from this reaction most of the time reacts with molecular oxygen to form ozone. Therefore, the intensity of photochemical smog can be determined by measuring the concentration of ozone. For determining the concentration of ozone, polluted air is bubbled through and acidified solution of potassium iodide. The reaction results in the formation of triiodide ions whose concentration is then can be determined spectrophotometrically. A most significant contribution to the analytical chemistry of ozone is the ozonolysis reaction for determining ozone in air. 4,4-dimethoxystilbene as the reagent; the resulting ozonide reaction product cleaves to form anisaldehyde which can then be determine by colorimetric reaction. The reaction can be modified by using 1,2-di(4-pyridyl)ethylene as the reagent. And the following reaction will take place.

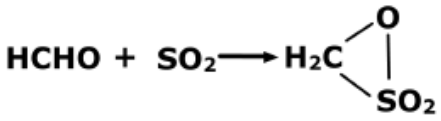


The pyridine-4-aldehyde produced is then determined by a simple spectrophotometric method.



There is also a rapid, reliable and specific method for ozone determination. In this method also the final product is determined spectrophotomertically but by using p-rosaniline hydrochloride.





4. Determination of other pollutants

Some other pollutants such as chlorine, ammonia and hydrogen cyanide can be determined by Infrared spectroscopy. The organic pollutant collected and concentrated from air can be determined by freeze out techniques. Gas chromatography is a great method to study the organic pollutant. The analytical measurement of inorganic particulate pollutants is also equally important. The atomic absorption spectroscopy is used for the evaluation of metal concentration. The method has great advantages of selectivity, sensitivity and modification of this approach by introducing a dithizone extraction step to concentrate and stabilize the metals before atomization and determination by atomic absorption spectroscopy, In this method ethyl propionate is used as a solvent as it is free from any hazard to environment. The use of mixed ligands causes the extraction of metals into ethyl propionate which can be extended to include most of the metals. The inorganic pollutants which includes arsenic, beryllium, cadmium, cobalt, lead nickel, silver and zinc can be concentrated and stabilized through complexion with a dithizone–oxime acetylacetone mixture followed by extraction into ethyl propionate and the determined by atomic absorption spectroscopy.

5. Summary

- The air pollutants are primarily produced from physical processes. But some pollutants are not emitted directly, they appear when primary pollutants react or interact with each other.

- Determination of concentration of pollutant is important to analyze the extent of pollution in any particular area.
- Toxic gaseous pollutants are one of them and contribute to air pollution in majority. They are basically emitted from automobiles industries, power plants and factories.
- The analytical methods for measuring concentration of air pollutants include chromatography, infrared spectroscopy, fluorornetry, spectrophotometry and atomic absorption spectroscopy.
- The most dominated air pollutants are oxides of sulfur, nitrogen and carbon.
- Photochemical smog, suspended matter and greenhouse gases are also contributed to air pollution.
- Some other pollutants such as chlorine, ammonia and hydrogen cyanide can be determined by Infrared spectroscopy.

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Note: Figures and reactions are copied from internet.
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