General Article

Ozone: A Pollutant and a Protector Gas

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Abstract

The natural balance of ozone in the stratosphere is due to continuous formation of ozone from oxygen and dissociation of it into oxygen in presence UV radiation. Amount of ozone can be determined by colorimetric method. It is poisonous gas near the earth surface in biosphere and protective shield in stratosphere. Depletion of ozone layer and formation of hole in it is due to reaction of CFCS, NO_x, OH, H_2O with ozone in stratosphere. Direct entrance of UV -B in the biosphere causes skin cancer, cataract, blindness, suppression of immune system degradation of plastics, reduction of food, vegetable & fish production and then alters the overall ecosystem. Protector ozone layer can be saved by replacing CFCS by HCFCS, by reducing supersonic flight & nuclear explosions, by refilling ozone in depleted area and by conducting public awareness about importance of ozone layer.

Keywords: Pollutants, stratosphere, CFCS, colorimeter, skin cancer.

Introduction

Ozone, the O_3 form of oxygen, is harmful for living beings in lower layer of atmosphere near the earth's surface (biosphere). It forms a distinct protective layer in the upper atmosphere. Most of the atmospheric ozone is found in stratosphere (11-50 km from earth surface) at altitude between 15 to 35 km. In this region its concentration is 10 ppm and near the ground surface it is found in trace amount and this blue pungent gas acts as highly pollutant. It forms only 10^{-5} % of the entire atmosphere. The highest concentration of ozone occurs at altitude from 26 to 28 km in the tropics and from 12 to 20 km towards the poles. O_3 concentration is more near the

poles than at the equator & more abundant in winter than in summer. The ozone layer was discovered in 1913 by the French physicists Charles Fabry and Henri Buisson. The ozone layer has the capacity to absorb almost 97-99% of the harmful UV radiations that Sun emit and which can produce long term devastating effects on humans beings as well as plants and animals.

In nature, there is a continuous formation of ozone from oxygen in presence of UV radiation through natural atmospheric process and they are also being destroyed naturally. UV radiation of shorter wave length coming from sun breaks oxygen molecule into oxygen atoms and these atomic oxygen combines with molecular oxygen to form ozone **(Ambasht, 2005**).

$O_2 + UV (l < 220\ nm) \longrightarrow O + O$

$O_2 + O \longrightarrow O_3$

Or $2O_2 + UV \longrightarrow O_3 + O$

Ozone is itself a very reactive and occasionally accepts atomic oxygen transforming both into molecular oxygen.

$O_3 + O \quad 2O_2$

UV radiation at wavelength longer than 242 nm can't be absorbed by O_2 it is absorbed by O_3 causing molecule to split into one atom & one molecule of oxygen.

$O_3 + UV (l > 310\ nm) \longrightarrow O_2 + O$

$O_3 + O \longrightarrow O_2 + O_2$

Hence, *ozone is constantly created by solar radiation photolysis on earth's atmosphere & is constantly removed by reaction with UV radiation of longer wavelength.* Ozone is easily destroyed by nitrogen, hydrogen and chlorine containing compounds (H_2O, NO, HO, CFCS) found in nature as well as released by various kinds of human activities.

Ozone layer in the stratosphere absorbs solar UV-B (280-320 nm) which is most harmful part of the ultraviolet. Ozone blanket totally absorbs highly harmful UV-B (280-320 nm), nearly totally absorbs harmful UV-C (200-280nm) and passes harmless longest wave length UV-A (320-400 nm). Thus it acts as protector gas for plants, animals by absorbing harmful UV radiation in stratosphere and as pollutant around the ground level (troposphere). Exposure of harmful UV-B radiation causes mutation, skin cancer, cataract, adverse effect on animals and plants.

Data and Methods

Ozone is a important reactive oxidant in air. Now a days, ozone in the atmosphere is recording by the satellite. Experimentally, it can be analyzed by physical as well as chemical methods. The average concentration in air is < 0.08 ppm. It can be determined by redox titration, coulometer, colorimeter (spectrophotometric method), UV absorption, 1R absorption & chemilumicence methods.

Theory

The simplest method involving iodine is colorimetry which involves liberation of iodine in following manner.

$$O_3 + 3KI + H_2O \longrightarrow KI_3 + 2KOH + O_2$$

Materials: Equipments and reagents

- Absorbing solution: 1% Kl+0.1M phosphate buffer (P^H=6.8)
- lodine stock solution 0.05N
- Working Solution: Diluted 5ml of 0.5 stock solution to 100 ml.
- Standard solution of iodine.
- SO2 absorber
- Chromic oxide as a scrubber during reaction.
- Spectrophotometer/colorimeter.

Method

A 10 ml of absorbing solution is put in the midget impinger. Air is passed at the flow rate of 0.5 –3 L minute^{-1} for 15 minutes. The total volume of air passed is measured. The temperature and pressure is also measured. The absorbing solution was transferred to 10 ml volumetric flask. The absorbance of colored solution was measured at 352 nm on spectrometer within 30 minutes. A standard calibration curve is prepared from stock solution of iodine.

Calculation

The corrected sample of volume of air of 760 mm & 25^{o}C is

$$O_3 \text{ ppm} = \frac{\mu L \text{ of } O_3 \text{ from calibration curve}}{\frac{\mu g \text{ of } O_3 \text{ from calibration curve}}{m^3 \text{ of sample of air passed}} \text{ in litre}}$$

$$O_3 \text{ mg m}^{-3} =$$

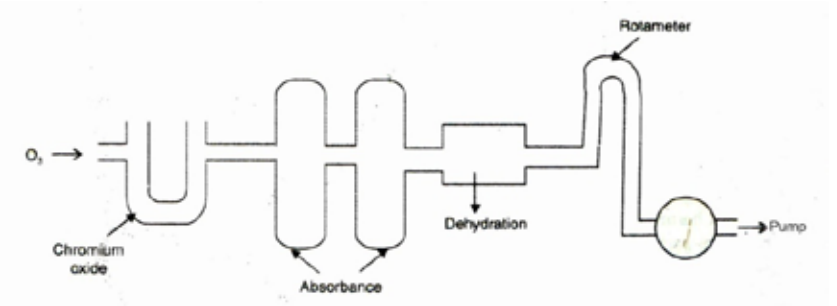

Fig: Assembly for ozone analysis

Results and Discussion

Ozone as a pollutant In the troposphere at higher concentration, O_3 is toxic gases pollutant (If O_3 > 0.1 ppm or 0.002 $\times 10^{-5}$ μμ g m^{-3}). It is formed by silent electric discharge in air or by the interaction of O_2 with UV rays or during welding or from high voltage electric discharge.

Its pollution causes in headache, irritation of eyes and respiratory tracts of human being, headache and coughing. Exposure of 50 ppm of O_3 for several hours will lead to mortality due to pulmonary Oedema (accumulation of liquid in the lungs). Young animals & human are more susceptible to these toxic effects than older subjects **(DE, 2010**).

- O_3 pollution inhibits and reduces the enzymes activity. SH group on enzyme are oxidized by O_3.
- Ozone reacts with olefins to form pollutant chemical adehyde & free radical (Sindhu, 1998).

  $CH_3CH = CH_2 + O_3 \longrightarrow CH_3CHOO + HCHO$

  or $CH_3CHOO + HCOO$
- Dry eye disease is associated with higher ozone & lower humidity.
- Ozone acts as pollutant gas in biosphere. Its pollution causes foliar injury, damages plasma membranes, affect photosynthesis.
- In the USA, Ozone pollution is responsible for about 3 billion dollars annual loss in crop productivity (**Mac Kenzie and El - Ashry, 1989)**.

Effect of ozone pollution on crop plants like soybean, wheat, cotton, maize, tobacco, potato tubers were studied with increasing O_3 concentration crop yield decreases.

Ozone as a protector gas

Ozone is constantly created by short wave length solar radiation photolysis of oxygen on stratosphere and formed a layer (blanket). This ozone layer absorbs harmful UV radiation coming from the Sun and protects the man, animals and plants in biosphere. In stratosphere about 90% of the total ozone is concentrated between 15 to 35 km zone. UV radiation is of smaller wavelengths than of visible light and range from 200 to 400 nm. The 200-280 nm range is called UV-C, 280–320nm is called UV-B and 320-400nm wavelength radiation is called UV-A. Among these, the most dangerous UV-B is strongly absorbed by ozone layer, UV-C is also absorbed by other atmospheric components and UV-A passes through ozone layer but reflected by oxygen and nitrogen back to the space. So, there is a natural mechanism of protection of biosphere against the hazards of UV rays.

Depletion of Ozone Layer

Protective ozone layer in the stratosphere is depleting day by day due to natural process and human activities. CCl_4, CFC_s, CH_4, nitrogen oxides gases, hydroxyl free radical are mainly responsible for depletion of ozone layer.

I. Chlorofluorocarbons ($CFCl_3$, CF_2Cl_2, CF_3Cl etc. $CHClF_2$, CCl_2F –$CClF_2$, $CClF_2$–$ClIF_2$, $CClF_2$– CF_3, CF_2BrCl, CF_3Br, $C_2F_4Br_2$ etc.) are non-toxic, non-inflammable and stable low boiling, less viscous compound. These are used in refrigerators, air conditioners, spray cans, industrial solvents, fire fighting materials. In small amount these are also present in fast food packing materials, plastics, foams, sterilizing agents, cleaning agents, degreasing agents. These slowly move to the stratosphere by random diffusion and release chlorine in presence of UV radiation. This chlorine depletes ozone layer. One molecule of CFC is capable of destroying one lakh O_3 molecules in the stratosphere (**De, 2010)**.

$CFCl_3 + UV$	$Cl + CFCl_2$
$CCl_2F_2 + UV$	$Cl + CClF_2$
$O_3 + Cl$	$ClO + O_2$
$O_3 + ClO$	$2O_2 + Cl$
$ClO + O$	$O_2 + Cl$

Similar catalytic action of breaking ozone into oxygen is also preferred by bromine. Region wise share consumption of CFCS in 1986 was 31% by USA and Canada, 30% by Western Europe, 14% by Eastern Europe, 12% by Japan, 1% by Australia and New Zeland while the rest of the world contributed 12%

II. N_2O produced by biological denitrification very slowly reaches the stratosphere where it gets oxidized into NO which catalyses ozone dissociation.

$N_2O + O \rightarrow 2NO$

$O_3 + NO \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

III. Oxides of nitrogen as exhaust of supersonic jet, automobiles, chimneys, nuclear explosion, lighting, volcano activities and present in free states in nature also deplete ozone layer.

$N_2 + O_2 \rightarrow 2NO$

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

IV. Hydroxyl free radical present in atmosphere & obtained by oxidation of CH_4 also catalyze usually above 40 km height.

$CH_4 + O \rightarrow CH_3 + OH$

$O_3 + OH \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

All these breaking down systems are end up in forming HCl & HNO_3.

V. The presence of water vapor and species such as OH in the stratosphere lowers the amount of ozone.

$O_3 + OH \rightarrow HO_2 + O_2$

$O_3 + OH \rightarrow 2O_2 + H$

$H_2O + UV \rightarrow H + OH$

$H_2O + UV \rightarrow H_2 + O$

$O_3 + HO_2 \rightarrow OH + O_2 + O_2$

Hence, H_2O acts as pollutant in stratosphere.

Due to the reaction of CFCS, NO_x, CH_4, OH with ozone in stratosphere ozone layer is going to depleting day by day. Ozone hole (depleted region) was first observed in October, 1980 by the NASA (National Auronautic & Space Administration). The overall reduction in ozone

layer is almost 8 percent. To save the ozone layer Kyoto protocol (1986), Mont real protocol (1987), London conference (1990), Bali (Indonesia 2008) summit etc. has been overcome.

On September 25, 2010, the average size of ozone hole was 22 million square Kilometers. The recorded size of hole in 2000 & 2006 was 29 million square kilometers, in 2015 (September- October) it was 25.6 million square kilometer as recorded by NASA & minimum concentration of ozone was 101 Dobson unit (DU). According to NASA atmospheric scientist Paul Newman, there are still plenty of ozone depleting chlorine and bromine compounds present in the stratosphere. Moreover, the lower atmosphere was colder than in previous years, which creates favourable conditions for ozone depleting chemical reactions.

Harmful effect of ozone hole formation

After ozone layer depletion and formation of ozone hole, the harmful UV ray (specially UV-B directly enters into the biosphere causes harmful effect on plants, animals and man.

- Direct exposure of UV-B radiation causes skin cancer (non-melanoma skin cancer). On depleting the ozone layer by 1% skin cancer increases by 6%.
- UV-B damage to eyes particularly cataract and blindness (**UNEP, 1993)**. 1% decreasing in ozone cataract & blindness patients increase by 100000 to 150,000. In cold region snow blindness is of course more due to UV-C radiation.
- UV-B exposure causes suppression of body's immune system which results vast variety of other infectious disease.
- Two thirds of about 300 crops tested species are found to be UV-B sensitive (**UNEP, 1993**). Pease, bean, melons, mustard & cabbage are most sensitive while the quality of varieties of potato, tomato, sugar beet and soybean are reduced. In most of the plants rate of photosynthesis decrease & then the biomass due to UV-B (**Teramura et. al. 1991**).
- In marine ecosystem, UV-B alters the food chain and ecosystem functions. Plankton, fish larva, Shrimps, phytoplankton are adversely affected by UV-B. CO_2 sink capacity decreases,

- UV-B exposure degrades the plastics used in construction.
- UV-B penetration causes global warming.

Protection of Ozone layer

Biosphere protecting ozone layer in the stratosphere can be saved from its depletion and exposure of harmful UV-B can be reduced by using proper precautions.

- By replacing CFCS by less harmful hydrochlorofluorocarbons (HCFCS) & methyl cyclohexane. In long term plan, ozone depleting substances must be completely phase out.
- By reducing the flight of high altitude supersonic jet and nuclear explosions which exhaust NO_x gases.
- By installing the solar powered Ozonator (matching to produce Ozone) in stratosphere by balloons to plug the ozone holes.
- By encouraging the development of products, technologies and initiatives that reap in co-benefits in climate change and energy efficiency.
- By improving the commercial refrigeration and by replacing halons in fire protection.
- By conducting the foster domestic and internal partnership to protect the ozone layer.
- By conducting the public awareness about ozone, ozone layer depletion and its harmful effect.

Conclusion

Ozone acts as pollutant in the biosphere and as protector gas in the stratosphere. Harmful UV-B entering through the depleted ozone layer (ozone hole) is damaging the health of mankind, reducing the food, vegetable & fish production, altering the ecosystem function & balance and causing huge monetary losses. From this realization, therefore, massive global efforts have to be initiated. The problem is global. Rich and poor men alike are being affected with least concern for geographical boundaries. Therefore, all nations have to join in the common endeavour of conservation of ozone and prevention of UV-B enhancement.

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