

OZONE : Health Hazards and Precautionary Measures

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INTRODUCTION

1. This guidance note contains information on the principal hazards to health from ozone and on potential sources of exposure. General advice on precautionary measures, control techniques and legal requirements is given.
2. Ozone, O₃, is a toxic gas possessing a distinctive odour and is a normal constituent of the earth's atmosphere. Ozone is produced deliberately for a variety of industrial purposes and is also produced naturally from oxygen whenever ultra-violet radiation or electrical discharges occur, e.g. at high altitudes or by the action of lightning. Such natural occurrence is unlikely to produce concentrations hazardous to man.
3. Because of its strong tendency to decompose and to release oxygen, ozone is extremely reactive and is a powerful oxidising agent which reacts explosively with oil and grease. Nevertheless it can be used with safety in industry. For example, since it readily oxidises organic matter, it is used as a bactericide and algacide.
4. Ozone itself is a distinctly blue coloured gas (bp – 111.9°C) and is about one and a half times heavier than air (density 2.144g/l). Ozone is used as "ozonised air", a colourless gas produced when ozone is generated from part of the oxygen in air (see para 13). Ozone cannot be stored or transported in vessels because it decomposes spontaneously in the presence of oxidisable impurities, humidity and solid surfaces. The rate of decomposition increases with temperature.
5. Background concentrations in our immediate atmosphere vary as a function of season, weather conditions, altitude and humidity.

EFFECTS OF OZONE

6. Low concentrations of ozone have a significant effect upon textiles, fabrics, organic dyes, metals, plastics and paints and cause the characteristic cracking of stressed rubber,

commonly called "weathering". A few substances, however, are resistant to the oxidising effect of ozone and these include glass and some stainless steels.

7. The acute toxicity of ozone to man has long been recognised and is well documented¹⁻⁸. The symptomatic and clinical effects of ozone at various concentrations are summarised in Table 1. Ozone is irritant to mucous membranes of eyes and respirator tract, and high concentrations can cause pulmonary oedema.
8. It is possible that there are secondary sites of reaction to ozone characterised by a defect in oxygen dissociation from oxyhaemoglobin in the tissues. Even at an exposure level of 0.1ppm ozone, premature ageing may result in man if exposure is sufficiently prolonged.

EXPOSURE LIMITS

9. The Health and Safety at work etc Act 1974 requires every employer to ensure, so far as is reasonably practicable, the health of all his employees and others who may be affected by the work he undertakes. The Act also places duties in respect of health and safety matters on the self-employed. The Factories Act 1961 requires factory occupiers to take all practicable measures to protect employed persons against inhalation of fume. The general policy adopted by the Health and Safety Executive is that exposure to hazardous substances should be kept at low as is reasonably practicable and in any case exposure should be kept within published standards by the application of engineering controls or other suitable control techniques. The Health and Safety Executive publishes, in guidance notes in the RH series, information on exposure limits applied in the UK.
10. The recommended exposure limit for ozone is 0.1ppm (0.2mg/m³) calculated as an 8-hour time-weighted average concentration. There is also a short-term exposure limit for ozone of 0.3ppm (0.6mg/m³) calculated as a 15-minute time-weighted average concentration.

SOURCES OF EXPOSURE

11. Ozone is made using ultra-violet radiation or electrical discharge either intentionally for the purpose of a specific process or incidentally to a

process. It is an unstable substance but its rate of decomposition varies widely according to temperature and humidity. A given ozone output yielding a faint trace of ozone in a workroom atmosphere on a humid day may create an undesirable concentration on a dry day.

INTENTIONAL PRODUCTION

12. Ozone is usually produced intentionally by silent electrical discharge in air. Alternative means of production such as bombardment of air with ultra-violet or ionising radiation, or electrolysis of cooled sulphuric acid, are uncommon in practice.

13. There are basically three types of ozone generator in use, working at:

- (a) Atmospheric pressure – typically a box through which material to be treated with ozone is passed, and in which a silent electrical discharge is initiated through the air by means of metal electrodes. This system is often used for surface treatment of plastic film.
- (b) Reduced pressure – found in swimming pool disinfection plants whereby dried air is drawn through glass tubes across which a silent electrical discharge is struck. The reduced pressure is generated by a sidestream from the circulating pool water forming a venturi vacuum.
- (c) Positive pressure – found in potable water treatment plants and throughout industry generally. Dried air is blown through glass tubes across which a silent electrical discharge is struck and this ozonised air emerges at positive pressure.

14. The processes for which ozone is produced are outlined below.

SURFACE TREATMENT

15. Various industries which manufacture or use plastic packaging in its various forms use ozone to pre-treat the plastic surface immediately before printing.

ELECTRICAL DISCHARGES

16. Ozone is generally produced around high voltage equipment and by electrical discharges in specific processes e.g.

- (a) Arc welding – reactive metals such as aluminium and titanium, and also stainless steel are arc welded in an inert shield of argon or carbon dioxide. The intense radiation from the arc produces significant quantities of ozone.

- (b) Static eliminators are often used in industry to remove static electricity from recently moulded plastic articles, and continuous use of them in a poorly ventilated room could lead to the build-up of an irritating level of ozone above the recommended exposure limit. The main factor which determines the amount of ozone produced is the voltage across the collector plates; the higher the voltage the more ozone is produced.

- (c) Electrostatic precipitators are used to remove dust and some airborne contaminants from the air and they produce ozone also. More ozone is produced if there are rough or sharp edges on, for example, new metal parts since intense local voltage gradients are produced.

VENTILATION

17. Areas into which ozone may escape must be equipped with adequate ventilation and extraction facilities. In ozone plant rooms, it is recommended that ten changes of room air per hour be achieved to enable dangerous accumulations of gas to be dispersed within a few minutes.

18. Ozone should be prevented from entering the workroom air by the use of exhaust appliances placed close to the source of emission. The ozone may then be passed through appropriate filters before discharge to a safe place in the open air. In the case of ozonators operating under negative pressure, the process acts as its own exhaust ventilator. In the case of atmospheric pressure ozonators, effective local exhaust ventilation is necessary because the ozonators are not enclosed. Cinema projection lamps should present no ozone hazard provided adequate mechanical exhaust ventilation is fitted to the lamp housing and the exhausted air is vented to a safe place. Many processes incidentally producing ozone (e.g. welding, ultra-violet curing inks) will have some ventilation provided to deal with other problems from process.

SAFE SYSTEMS OF WORK

19. In order to ensure that plant and processes are properly operated and controlled to minimise risk to health, satisfactory safe systems of work need to be established and maintained by means of appropriate training and supervision.

20. All people operating ozone plant should be given full training in all aspects of the operation of the ozonator and associated equipment and should be trained in emergency and first aid procedures. Emergency action plans should be prepared for all sites where ozone is generated deliberately in potentially hazardous quantities.

21. Special care may be required when opening sealed plant for maintenance purposes. Guidance Note GS5¹⁰ should be consulted for detailed advice on permit-to-work systems and precautions on entry into confined spaces.

22. Work on ozone plant should only be undertaken by a person specifically authorised to do the work. Such a person should be trained and be competent to do the work in a safe manner. When carrying out repairs or maintenance work on an ozonator, the ozonator transformer must be isolated and locked off, and a permit to work must be issued, to avoid risks from ozone and from electrical hazard.

23. The cleaning materials used for cleaning ozone units and pipework must be free from oil or grease.

24. In the event of an ozone leak a plant restart should not be attempted until the source of leakage has been investigated and rectified. Leak detection by nose is not satisfactory because even slight leaks cause the sense of smell to be numbed and lead to the false conclusion that a leak no longer exists.

25. Appropriate warning signs indicating the presence of a potential toxic gas hazard should be displayed on ozone plant access doors or in passageways leading to the plant room.

MONITORING

26. Ozone detectors may be used to provide audible and visual warnings of ozone leaks. Such alarm signals may be used to initiate emergency procedures, or to automatically turn on plant room ventilation and shut down the ozonator. Ozone-in-air monitors are essential in plant rooms where ozonators and associated equipment operate under positive pressure, because of the greater risk of ozone leakage outward. The monitors in such situations should actuate automatic ozonator shut down at 0.3ppm ozone or less, while actuating warning alarms at 0.1ppm or less.

27. Minor ozone leaks can be detected and located by means of moist starch/potassium iodide paper which turns blue on exposure to ozone.

28. It is essential to carry out regular testing and calibration of all sensor equipment used.

EXHAUST EMISSION

29. Process gas venting to atmosphere should pass through an ozone destructor device or be released in such a way as to present no hazard. A destructor is a catalyst filter or other device which causes ozone to decompose in a controlled manner to oxygen. Provided the discharge point allows adequate dilution a destructor device may

not be necessary. If a catalyst bed, for example activated carbon, is used as an ozone destructor it is possible that the bed could become exhausted during a period of operation and this should be borne in mind when arranging maintenance schedules.

30. Deflection weather caps are not recommended for discharge stacks since these hinder dispersal. Vertical discharge stacks are recommended with a discharge velocity of 15-20m/s to aid dispersal and avoid re-circulation into buildings. Stacks and extraction vents should be carefully sited so that they do not feed fresh air ventilation intakes.

31. The control of ozone input to a process is crucial since excess ozone can lead to high levels of vented ozone.

32. Activated carbon filters must under no circumstances be exposed to ozone concentrations higher than 20g/m³ since the reaction may become auto-accelerated and lead to an explosion. The automatic shutdown is a safeguard against this risk.

FIRST AID

33. If a person is overcome by ozone, the following precautions should be adopted:

- (a) Remove the patient to a warm uncontaminated atmosphere and loosen tight clothing at the neck and waist.
- (b) Keep the patient at rest.
- (c) If the patient has difficulty in breathing, oxygen may be administered provided that a suitable apparatus and a trained operator are available.
- (d) If breathing is weak or has ceased, artificial respiration should be started. The mouth-to-mouth or mouth-to-nose methods are preferred.
- (e) Seek medical aid.

34. Ozone poisoning should be treated symptomatically. This may include bed rest, analgesics to relieve pain, and antibiotics as may be prescribed by a medical practitioner.

SAMPLING AND ANALYTICAL METHODS

35. Sampling strategies to monitor the extent of exposure to ozone or to assess compliance with exposure limits should be carefully planned and the advice of an occupational hygienist may prove useful. Short-term sampling may be used to identify peak exposures and to assist in the prevention of acute gassing incidents. It may not be valid, however, to use the results of such sampling for the determination of time-weighted average long-term exposures. Personal atmospheric sampling is to be

recommended when assessing the actual pattern and duration of exposure. (Further information is contained in Health and Safety Executive guidance notes on Exposure Limits).

36. The traditional method of determining ozone in air may be used¹² but continuous ozone monitors are now available which use a variety of techniques including onemiluminescence, ultra-violet photometry and electro-onemical cells. Relatively inexpensive gas detector tubes are also available. These are ideal for spot check, provided that interfering gases, such as oxidising agents, are known to be absent.

STATUTORY REQUIREMENTS

37. The general duties of employers, the self-employed, manufacturers, suppliers and of employees at work are contained in the Health and Safety at Work etc Act 1974. Other relevant statutory provisions include the Factories Act 1961, the Offices, Shops and a Railway Premises Act 1963 and the various regulations and orders made under these Acts. The following is a brief summary of the principal requirements with regard to potential ozone health risks:

(a) Health and Safety at work etc Act 1974

- s.2 & 3 general duties of employers and the self-employed
- s.6 general duties of manufacturers
- s.7 general duties of employees

(b) Factories Act 1961

- s.4 provision of ventilation
- s.30 dangerous fumes
- s.63 removal of dust of fumes

(c) Offices, Shops and Railway Premises Act 1963

- s.7 provision of ventilation

(d) The Shipbuilding and Ship-Repairing Regulations 1960 – Regulation 53

The Iron & Steel Foundries Regulations 1953 – Regulation 7

The Non-Ferrous Metals (Smelting and Founding) Regulations 1962 – Regulation 11

The Electricity (Factories Act) Special Regulations 1944

The Notification of Accidents and Dangerous Occurrences Regulations 1980

The Health and Safety (First Aid) Regulations 1981.

Table 1 Effects of ozone

Concentration ppm	Description of effects
0.003-0.01	Threshold of odour perception by average person in clean air.
0.02-0.04	Representative average total oxidant concentrations in major US cities in 1964. Approx. 95% of oxidants is ozone.
0.1	<i>Recommended exposure limit.</i> Eye, nose and throat irritation often experienced.
0.2-0.5	Reduced dark adaptation and alteration of extra-ocular muscle balance occurs after several hours' exposure.
0.5	Nausea and headache sometimes occurs. Extended exposure can cause pulmonary oedema and enhance susceptibility to respiratory infections (both bacterial and viral).
1.0	10 minutes exposure typically reduces desaturation rate of oxyhaemoglobin to 50%.
1-2	Chronic exposure (one year for 6 hours per day) at this level has resulted in bronchiolitis and bronchitis in animals. 2 hour exposure can cause headache, chest pain and dryness of respiratory tract and a reported 20% reduction in timed vital capacity of the lung.
1.5-2	Exposure for 2 hours typically results in cough, substernal pain and excessive sputum.
5-25	Experimentation showed that 3 hour exposure at 12ppm was lethal for rats and 25ppm was lethal for guinea pigs. Humans (welders) exposed to 9ppm developed pulmonary oedema. Their chest X-rays were normal in 2-3 weeks, but 9 months later they still exhibited fatigue and exertional dyspnoea (laboured respiration).
50	30 minute exposure may be fatal.

FURTHER INFORMATION

This Guidance Note is produced by the Health and Safety Executive. Further advice on this or any other publications produced by the Executive is obtainable from St High's House, Stanley Precinct, Bootle, Merseyside L20 3QY, or from Area Offices of the HSE.