

THE DETECTION AND MONITORING OF OZONE IN INDUSTRIAL ENVIRONMENTS

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The recent consensus of biomedical opinion indicates a downward adjustment of TLV for ozone. A reappraisal of the sort of levels which occur in industrial environments is made and the techniques for their monitoring examined. A method based on the absorption by ozone of U.V. radiation has proved to be the most useful method tried.

INTRODUCTION

Ozone, due to its Victorian association with invigorating health effects, has long been underestimated as a potential industrial hazard. As pointed out by King (1972), the recommended figure of 1.0 part of ozone per million parts of air (p.p.m.) as the threshold limit value (TLV) in 1943 has been steadily reduced in the light of biomedical investigation to 0.2 p.p.m. in 1960 and down further to 0.1 p.p.m. in 1963 and recently a new figure of 0.04 p.p.m. (Jones et al. 1970) has been suggested, although the U.S. National Academy of Science has suggested 0.02 p.p.m. for prolonged exposure.

Industrially ozone is usually a by-product, of high voltage sources, arc discharges, X-ray equipment, ultra-violet lamps and arc welding equipment, but in processes involving bleaching of oils, waxes, textiles, drying of varnishes and printing ink, deodorising and sterilisation of water and air, ozone is deliberately produced and utilised.

Thus, reassessment of ozone as a potential hazard in the processes mentioned should be made from the point of view of a decreased T.L.V.

In the atmosphere, the background levels of ozone are produced by solar radiation, the probable reactions are given by Chapman (1930) as:

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In the stratospheric region, ozone acts as a biological shield preventing radiation in the wavelength range 2000 - 2900 Å from reaching earth. In the stratosphere the concentration can be as high as 0.03 p.p.m. (5). At ground level, in severe photochemical smog conditions, ozone concentrations as high as 0.1 p.p.m. have been encountered. This latter concentration can lead to serious health effects over a long period, as illustrated by the experience in Los Angeles.

This toxicity of ozone has been well studied and documented and is worth underlining. It is exacerbated by the ability of ozone to anaesthetize the nasal receptors and so prolonged exposure becomes increasingly dangerous as does a slow build up in concentration as the people exposed become unaware of the distinctive smell which denotes its presence. This is probably partly the reason for the success of ozone as a deodoriser.

In the short term, exposure to low concentrations of ozone of about 0.05 p.p.m. for one hour, may result in dryness of the mouth, throat irritation, coughing and headaches (Henschler et al. 1960).

In the long term the main effects are:

- 1) Radiomimetic. It has been found that ozone can cause many of the symptoms of radiation damage in body tissue.
- 2) Secondary infection. Ozone acts as a deep lung irritant and reduces body resistance to disease.

It can be deduced that the toxicity of ozone outweighs the benefits derived from it. There is, therefore, an obvious need for a careful monitoring of ozone level produced in industries and environments at very low levels compared to other industrial pollutants such as carbon monoxide and hydrogen sulphide.

In this study, different methods for determining and monitoring ozone were examined in relation to their applicabilities in certain environments.

EXPERIMENTAL

The main techniques examined were:

1) The Classical KI Wet Chemical Method

This was used as the main calibration standard. The method employs either neutral or alkaline aqueous KI solution as the reagent. The sample to be analysed is passed through

the KI solution and the amount of the resulting iodine liberated after acidification of the test solution is measured spectroscopically. This method can give high specificity and accuracy but may involve long operational time and is not portable or rapid.

2) The Draeger Toxic Gas Detection Method

This method involves bleaching of an indigo dye by O₃ and the extent of bleaching is proportional to the amount of ozone present. The sample is drawn through the dye and metered by a hand pump, hence the amount of ozone in the sample can be evaluated.

This technique is attractive as the apparatus involved is very portable and simple to operate. Due to its simplicity it can be used when an immediate order of magnitude indication is required. The limitations are mainly long integration times for small concentrations; it cannot be used for a continuous monitoring measurement.

3) The Ultra Violet Spectrophotometric Method

The method utilises the ultra violet absorption of ozone, assuming the Beer-Lambert law, i.e. amount of u.v. absorbed is proportional to the concentration of ozone.

This method can give high accuracy and sensitivity (0.001 p.p.m.) if care is taken. The equipment can be made portable and can have short sampling times. The main drawback lies in possible interference by other substances in the sample, e.g. smoke and dust, which might scatter or absorb at the same wavelength.

4) The Chemiluminescent Method

This is the standard technique recommended by the Environmental Protection Agency (E.P.A.), and it employs a reaction which emits. The light emitted is proportional to the reactant concentration.

This method is thus highly specific and is also sensitive (1 p.p.b.) and accurate. It has short sampling times and therefore can be used for continuous monitoring. The main drawbacks are high cost and complexity.

PROCEDURES

1) Classical KI Method

The ozone sample was bubbled through an alkaline solution of potassium iodide and the amount of iodine liberated, after acidification, was determined, from the absorption of light at 352 um (ASTM D 1609-60) by the triiodide ions (I⁺³).

2) Draeger Method (Draeger Normalair Ltd)

The sample was drawn through a fixed amount of silica gel

impregnated with an indigo dye, contained in a long thin glass tube, by a hand pump. This hand pump also metered the sample passing through the reagent, one stroke of the hand pump is equivalent to 100 c.c. of sample. The extent of bleaching of the dye by ozone indicates the concentration of ozone and this was read off from the integral seals.

3) Ultra Violet Absorption

The instrument used in these studies was a DASIBI model 1003 AH with a sampling time of 22 seconds. The sample flow rate was set at 2 l/min and the sampling probe was fixed at different sampling points in order to get steady readings. The concentrations were displayed digitally on the front panel meter.

4) Chemiluminescence

The chemiluminescence equipment was constructed in the laboratory (Visanuvimol, 1973) and used ethylene as the other reactant. The sampling flow rate was 1 l/min and the ethylene flow rate 1 l/hr. The two reactants were introduced into a reaction cell which was well shielded from external illumination. The light emitted by the reaction was monitored by the photo-multiplier, whose output could be digitised and recorded on paper tape for averaging.

RESULTS AND DISCUSSION

1) Production of Ozone in High Voltage Test Areas

High voltages (20 kv - 30 kv) involved in the production and testing of high power transformers are a potential source of ozone and a field study of methods of detection and measurement of ozone in their vicinity was attempted.

The case studied involved insulation testing of a heavy transformer. The testing site was situated in an open area where other work was also carried out. The ventilation was merely convective roof type and the movement of air in the testing site was undetectably low.

The operation involved the connecting of cables to terminals inside the cable box of the transformer and raising the voltage of the transformer to about 30 kv. This was sustained for a few minutes before turning off and immediately disconnecting the cables from the terminals.

At the end of the high voltage testing, it was found that a strong ozone odour was very noticeable. The presence of ozone was confirmed by using the Draeger method. This method was initially used because of its portability and suitability for this preliminary investigation. The Draeger method gave the following results:

Inside the cable box	0.3 p.p.m.
5 feet from cable box	0.0 "

From the calibration, graph 1, of concentrations found by Draeger v.s. that found by the Classical KI method it can be seen that the Draeger consistently gives about a third of that concentration given by the KI method. From this graph the concentration of ozone inside the cable box if measured by the KI method would be as high as 0.9 p.p.m. (9 times greater than the TLV).

This investigation confirmed the production and the hazardous levels of ozone in high voltage environments. A recommendation forwarded was an installation of a local ventilation above the cable box in order to remove the ozone produced.

2) Production of Ozone by Ultra Violet Sources

In the College Audio Visual department a high intensity Xenon lamp projector was suspected of producing high levels of ozone and investigation of this type of source was undertaken. In this study two different methods for the detection and measurement of ozone were compared; these were the Draeger Toxic Gas Detection and chemiluminescent methods, the latter calibrated against the classical KI method.

The suspected source was situated in a room of about 15 feet x 25 feet x 10 feet high. There were two sources of ventilation available in the room, these were a general and a forced ventilation. When the forced ventilation was turned off the air movement in the room was undetectably low, but when turned on air circulation could be felt in the area around the suspected ozone source.

When the forced ventilation was turned off, ozone could be smelt a few feet away from the projector only minutes after start up. Ozone was, however, undetectable at this point when the forced ventilation was switched on.

The measurements by the methods mentioned above confirmed the existence of ozone and indicated the concentrations as follows:

Forced Ventilation off:

	DTGD	Chemiluminescent
Projector exhaust	Ca. 0.05 p.p.m.	Ca. 0.04 p.p.m.
1 ft away from projector	-(smell)	-(smell)

Forced Ventilation on:

Projector exhaust	Ca. 0.03 p.p.m.	Ca. 0.03 p.p.m.
1 ft away from projector	-	-

The investigation carried out illustrated the source of ozone, confirmed its existence and indicated the levels of the concentrations encountered. The investigation also showed the

importance of the ventilation system. The recommendation forwarded was that the forced ventilation should always be used when the projector was in operation, and if greater safety was required, an extractor should be situated directly above the projector.

3) Ozone from an Air Deodoriser

The ozone concentrations from a domestic deodoriser employing a high voltage capacitor as an ozone source were measured using the three methods. These were the Classical KI, Draeger and U.V. methods.

The measurements were made in an enclosure of about 800 l. in volume, having no ventilation. The atmosphere was sampled at 2 l/min. and the sampling point was 2 feet away from one side of and at the same level as the source. The three methods were carried out at or corrected to the same point in time.

The recorded results were:

Time after starting (min.)	0	10	20	30	40	50
Draeger method, ppm	0.000	0.032	0.04	0.05	0.054	0.058
U.V. method, ppm	0.027	0.110	0.140	0.155	0.160	0.164
K.I. method, ppm	0.000	0.130	0.160	0.185	-	-

Additional measurements were also made by U.V. method in a room of about 80,000 l. with forced air circulation and the results recorded as follows:

Concentrations	Concentrations, p.p.m.
Immediately in front of (touching) the deodoriser	12.0 - 17.0
Immediately in front of the source	0.2 - 0.4

The calibration curve of U.V. against K.I. measurements, shown on graphs, indicates that there is a close agreement between the results of the two methods.

CONCLUSION

In all three cases mentioned there was an ozone level which was in excess of the present TLV. The methods employed were considered from the aspects of reliability, sensitivity, accuracy, practicability, ease and cost of operation.

The classical KI method has a low cost of operation and a maximum sensitivity of about 0.00062 mg/ml KI solution (Thorp

1940). The ease of operation, accuracy and reliability depend somewhat on the operator but are sufficient for a reference technique.

The Draeger method provides a good indication of ozone but usually two or three times too low, at least at very low levels. It is a low cost, useful and simple method. The whole apparatus is small and light in weight, making it ideal for hand held operation.

The chemiluminescent method possesses a high degree of accuracy. With the use of high gain photomultiplier tube, very high sensitivity (~ 0.001 p.p.m.) is obtainable. The apparatus is, however, expensive. The system is complicated, and in general only semi-portable.

The u.v. apparatus used again had a high sensitivity (~ 0.001 p.p.m.) and accuracy (if no interference). It was very simple to operate, but in dusty atmospheres precautions should be taken to avoid interference effects. It was compact and semi-portable.

In conclusion, the results obtained in the cases studied indicate that:

- 1) Ozone was produced in high voltage operation, at levels several times higher than the TLV. Reducing the hazard by using local ventilation is essential.
- 2) High intensity Xenon and Mercury lamps used in a projector produced ozone at significant levels ($\sqrt{ }$ threshold of smell, 0.008-0.02 p.p.m.). The accumulated concentration could be reduced by the use of forced ventilation.
- 3) The concentrations of ozone measured immediately in front of domestic deodorisers were between 12 and 16 times higher than the TLV.

Considering the toxicity of ozone, much lower levels of ozone should be tolerated in processes where it is essential, but non-essential uses, such as deodorising, should be discouraged.

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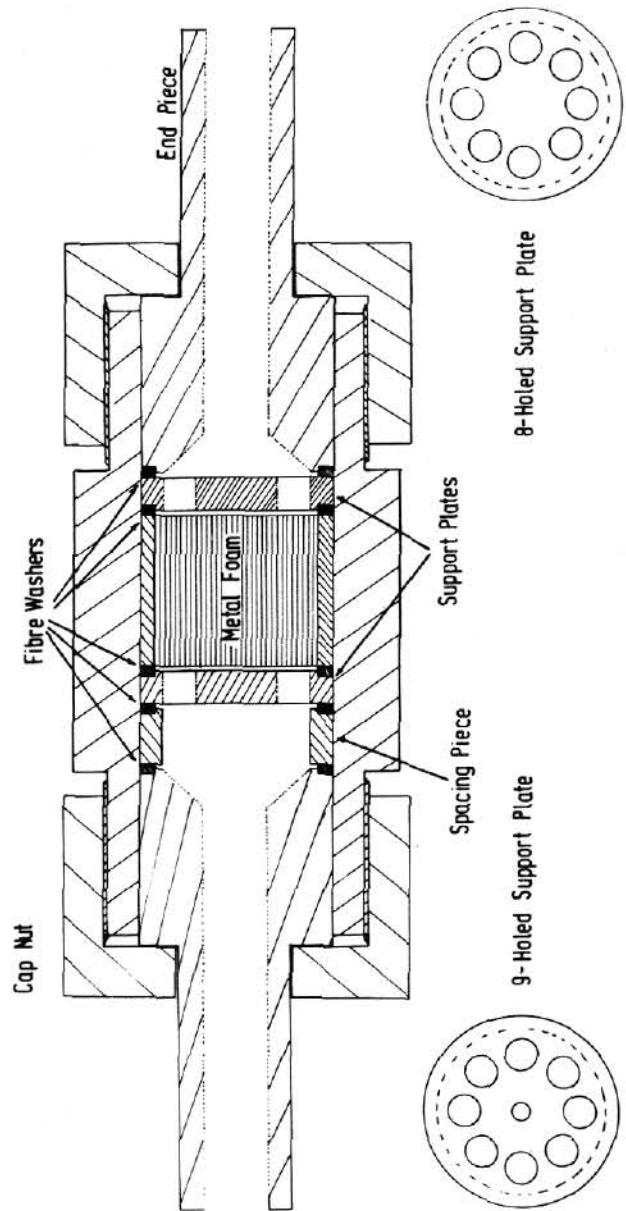


Fig 2 - FLASH-BACK ARRESTOR ASSEMBLY

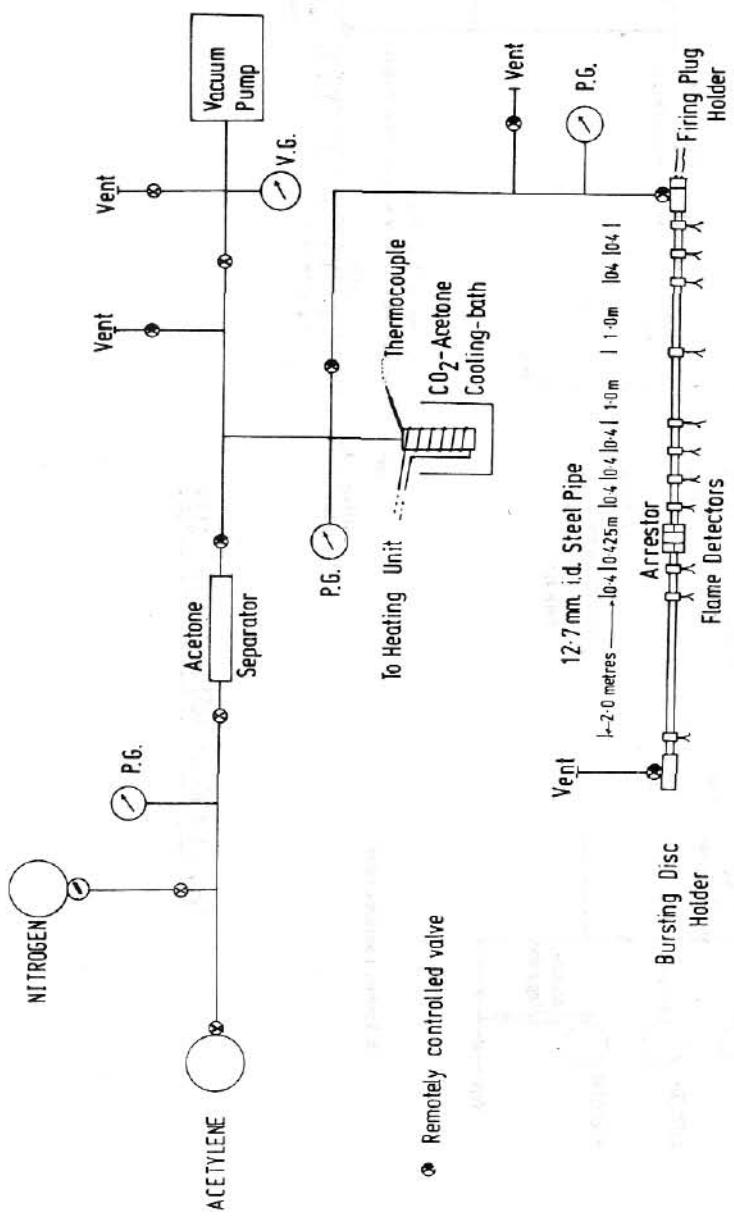


Fig.3.- STATIC HIGH PRESSURE ACETYLENE FIRING SYSTEM

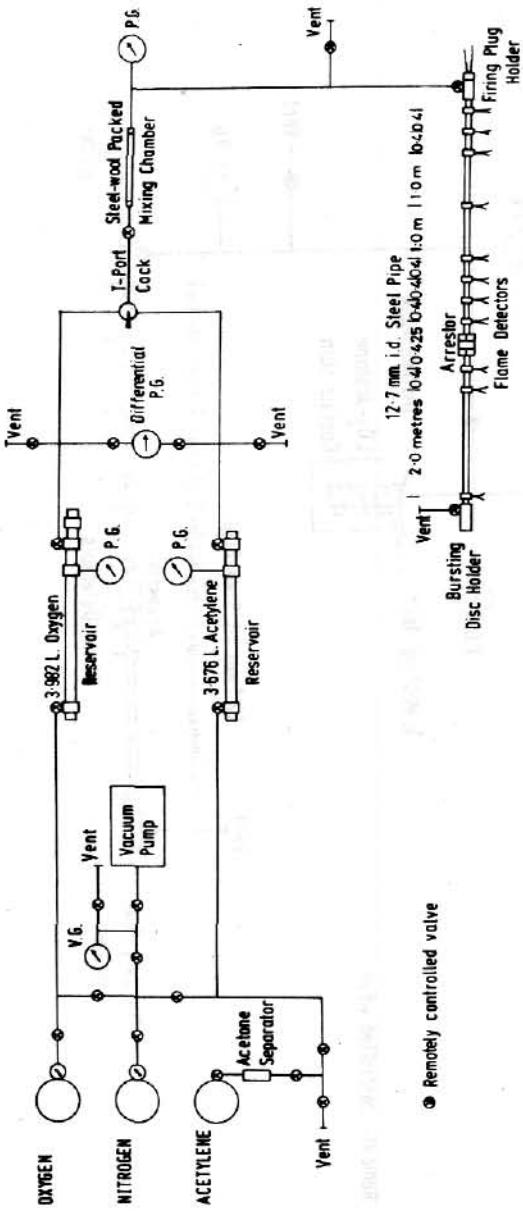


Fig. 4. - STATIC OXY-ACETYLENE FIRING SYSTEM

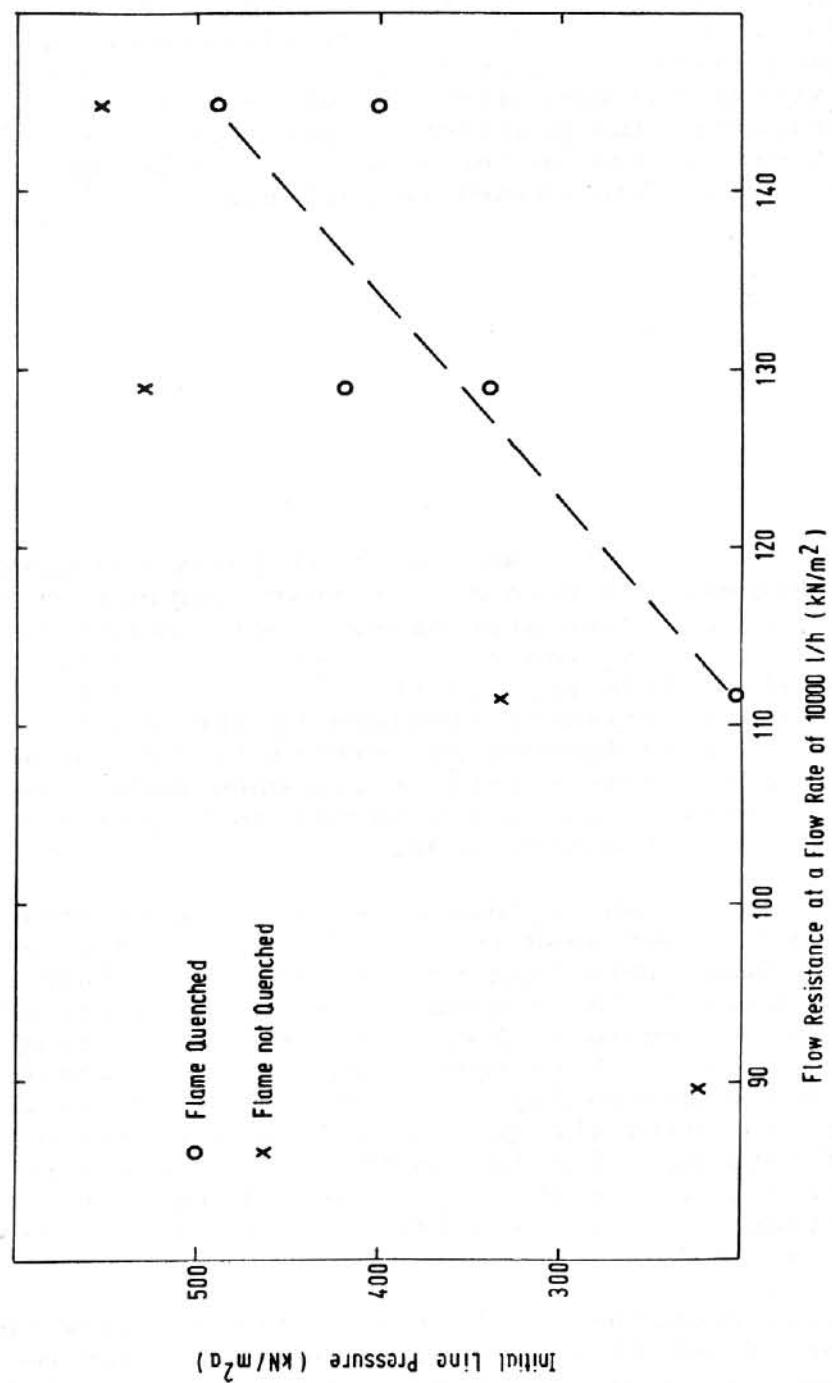


Fig.5.-RELATION BETWEEN QUENCHING EFFICIENCY AND FLOW RESISTANCE FOR A 50mm CORE