

Determination of Ozone in the Atmosphere

1. SCOPE

The method is simple, sensitive and specific for the determination of ozone in air. It responds only to ozone and is not affected by other oxidizing or reducing agents.

2. FIELD OF APPLICATION

The method is useful for the determination of ozone in the ambient or polluted air. Ozone can be monitored continuously when this method is used in combination with a formaldehyde monitor. This method has proved to be very useful for determining low concentrations of ozone in ozonized air produced in laboratories where the air used is not very pure.

3. PRINCIPLE OF THE METHOD, REACTIONS AND SPECIFICITIES

The method presented here is based on the reaction of ozone with 4-allyl-2-methoxy phenol (eugenol). Ozone preferentially attacks the olefinic bond in allyl group and releases an equivalent amount for formaldehyde. The resultant formaldehyde is collected in distilled water and determined by a slight modification of West-Gaeke method for sulfur dioxide (9.1).

4. REAGENTS AND MATERIALS

Para-rosaniline hydrochloride (Fisher Scientific Co., Catalog No. 42500). Mercuric chloride, sodium chloride, sodium hydroxide, potassium iodide, sulfamic acid and standard formaldehyde solution (1,000mg/l).

4.1 *Sodium tetrachloromercurate II solution*

This solution was prepared by dissolving 13.6g of mercuric chloride and 5.8g of sodium chloride per liter of distilled water.

4.2 *Sodium dichloro-sulfite mercurate II solution*

Dissolve 0.25g of sodium sulfite in 50ml of sodium tetrachloromercurate II solution. (This reagent is unstable and should not be used over 24hrs).

4.3 *Para-rosaniline reagent*

Prepared by dissolving 0.16g of para-rosaniline hydrochloride in 24ml of concentrated HCl, then diluting to 100ml with distilled water.

4.4 *Alkaline iodide solution*

Ten grams of KI and 40g of NaOH were dissolved per liter of water.

4.5 *Acidifying reagent*

Five g of sulfamic acid were dissolved in 100ml of water, then 84ml of 85% phosphoric acid were added and the mixture was made up to 200ml.

4.6 *Preparation of ozonized air*

The ozonized air used in laboratory was produced by passing pre-purified air through a brown glass aspirator bottle of 5 liter capacity in which a germicidal lamp (4W Germicidal Lamp, G.E. 024511) was fixed. The mouth of the bottle was sealed with a cork through which the leads of the lamp and an outlet tube were passed as shown in Figure 1. Initially, the lamp was kept on for a week so that it could generate enough ozone to react with any of the organic matter that might be present in the aspirator. After this equilibration, the lamp was turned on every morning at least an hour before any samples were ozonized. An ozone concentration of 0.5 to 10ppm was obtained as desired by controlling the flow of air through the aspirator. Lower concentrations, down to 0.05ppm, were obtained by partially covering the lamp with aluminum foil and keeping it on for ten days to equilibrate for any possible reaction of ozone with aluminum foil.

4.7 *Purification of eugenol*

Eugenol as well as all other l-alkenes tried were found to contain formaldehyde as impurity. This may be due to the exposure of the compounds to atmospheric ozone. Each compound was purified just before use, by passing it over 3in column of pure dry sodium sulfite crystals.

4.8 *Apparatus*

Gas samplers (described by Wartburg, Pate and Lodge, 1969), midget impingers (MSA Catalog No. 46984); air flow meters (Fisher and Porter Co., Catalog No. 450-015); Dyna-vac pump (Cole-Parmer, Catalog No. 7064); Beckman D.B. Spectrophotometer.

5. SAMPLING AND SAMPLES

The sampling equipment was set up as shown in Figure 1. The gas samples shown were obtained from the National Center for Atmospheric Research, Boulder, Colorado. Midget impingers were also tried and found to be satisfactory. Two sampling bubblers were used in series. One was used as an impinger in which air containing ozone was impinged upon the surface of eugenol placed in the container; the second, containing 10ml of distilled water, was used as an absorber for formaldehyde. Air in the first impinger was passed through an orifice of 1mm diameter at a rate of 2l/m. The jet velocity has been estimated to be 44m/sec. With 1ml of eugenol in the tube, the spacing tip and the surface of the eugenol was 5mm. In the second bubbler the orifice may be replaced by a frit which must be completely immersed in the water for absorbing the formaldehyde (Page 229).

6. PROCEDURES

6.1 Determination of formaldehyde

Two reliable methods are available for the determination of formaldehyde: (1) The method developed by Lyles et al. (9.1), and (2) By the use of chromotropic acid (9.2). The chromotropic acid method was tried, but some vapors of eugenol were carried into the air along with the formaldehyde formed and interfered with the determination of formaldehyde. Moreover, the sampling solution used in the latter method (0.1% chromotropic acid in concentrated sulfuric acid) is certainly not a desirable one to work with. The method of Lyles et al., which is based on the reverse of the West-Gaeke method for sulfur dioxide, has been found to be simple, reliable, and satisfactory for the determination of formaldehyde formed by the ozonolysis of eugenol. To ten milliliters of aqueous solution of formaldehyde, add one milliliter of sodium dichloro-sulfito-mercurate II solution and mix thoroughly. Add one milliliter of para-rosaniline solution, mix and allow to stand for 20min. Determine absorbance at 560mm, and by the use of standard calibration curve determine the total amount of formaldehyde in 10ml of sampling solution.

7. CALCULATIONS

Convert the volume of air sampled to the volume at standard conditions of 25°C, 760mm Hg:

$$V_R = V \times \frac{P}{760} \times \frac{298}{(t + 273)}$$

- V_R = volume of air at 25°C and 1 atmosphere.
 V = volume of air sampled, liters.
 P = barometric pressure, mm Hg.
 t = temperature of air sampled, °C.

Ordinarily, the correction for pressure is slight and may be neglected.

If we assume 1:1 stoichiometry for the 1% neutral buffered KI method (10.6) for ozone, the following expression should be used for determining ozone concentrations:

$$\text{ppm ozone} = \frac{\mu\text{g HCHO found} \times 224}{30 \times \text{volume of air sampled (liters)}} \times 1.54$$

8. STOICHIOMETRY OF THE REACTION

Ozone concentration in an air containing about 2ppm of ozone was determined by the formaldehyde method, the neutral iodide method and the alkaline iodide method. The same ozonized air under exactly similar conditions was used in all three determinations. The following results were obtained:

<i>Method Used</i>	<i>Ozone Concentration (ppm)</i>
Neutral iodide	2.3
Alkaline iodide	1.55
Eugenol-formaldehyde	1.50

A recent report on stoichiometry of iodide method, by Boyd et al. (9.4), provided evidence that the alkaline iodide method to yield one iodine molecule for every one molecule of ozone absorbed and that the neutral iodide method actually yields 1.54 molecules of iodine for every one molecule of ozone absorbed. On the contrary, the results obtained by Kopczynski and Bufalini (9.5) show that in neutral iodide method one mole of iodine is released per mole of ozone. Results of this study are in complete agreement with the alkaline iodide method (9.6). Because of unavailability of standard ozone concentrations it is difficult to decide as to which method yields true results. Obviously, a standard method of generating known concentration of ozone is badly needed.

8.1 Determinations of ozone at different concentration levels

Ozone was determined in several samples of air containing ozone in the range of 0.05 to 2.0ppm. Each concentration level was determined three times by alkaline iodide method as well as by eugenol-formaldehyde. Results are given in Table I.

TABLE 1

Comparative study of eugenol-formaldehyde method and alkaline iodide method.

Ozone concentration (ppm)*	
Alkaline iodide method	Eugenol-formaldehyde method
0.045	0.050
0.11	0.10
0.18	0.17
0.25	0.25
0.99	0.92
1.20	1.15
1.50	1.45
1.90	1.80

*Results tabulated are averages of three samples.

The eugenol-formaldehyde method yields comparable results to those obtained by alkaline iodide method of Byers and Saltzman (9.6), at all concentrations with the range of 0.05 to 2ppm ozone concentration. Since ozone is not likely to exist in concentrations higher than 2.0ppm in ordinary atmospheres, higher concentrations were not studied. A few higher concentrations, in the range of 2-5ppm of ozone, were determined by eugenol-formaldehyde method, but no comparison was made with iodide method.

8.2 Sensitivity of the method

The sensitivity of the method is exactly the same as that for formaldehyde method of Lyles et al. (9.1), since each molecule of ozone yields proportional amounts of formaldehyde. Ozone concentration of 0.02ppm can be easily determined by sampling the air for 40 minutes at a rate of two liters per minute.

8.3 Selectivity of the method

The eugenol-formaldehyde method described seems to be specific for ozone; only formaldehyde will interfere. Simultaneous determination of formaldehyde must be carried out and the concentration of formaldehyde must be subtracted from the concentration of ozone obtained.

Since formaldehyde can be determined with the same technique by removing the first impinges, this would present no difficulty whatsoever. Interference effects of hydrogen peroxide (3%) and peracetic acid were studied by spraying the two solutions into the air being sampled. Neither

hydrogen peroxide nor peracetic acid gave any formaldehyde when reacted with eugenol. Sulfur dioxide and other reducing agents present in the air do not interfere.

8.4 Field studies

The method is now being tested for on-site determinations of ozone. Preliminary studies indicate that the method would be quite suitable for field studies (9.7). Any formaldehyde monitoring equipment can be easily adopted for monitoring ozone. A midget impinger containing 1ml of eugenol is all that need be connected to the equipment to convert it to an ozone monitor.

9. REFERENCES

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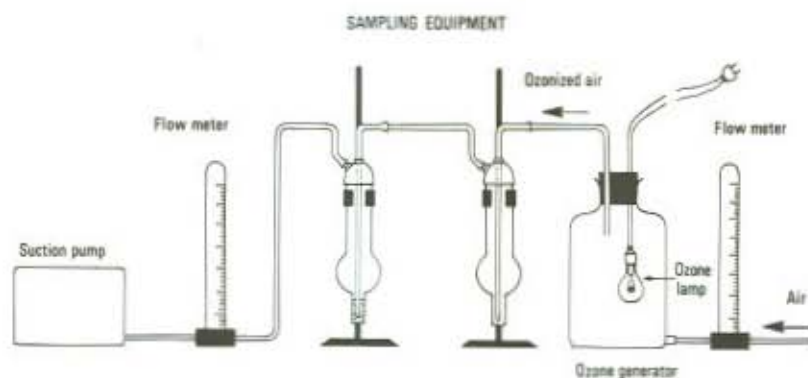


Fig. 1

